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Surface chemical analysis — Auger electron spectroscopy — Repeatability and constancy of intensity scale

Analyse chimique des surfaces — Spectroscopie d'électrons Auger — Répétabilité et constance de l'échelle d'énergie

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Foreword

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ISO 24236 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 measured kinetic energies of emitted Auger electrons with tabulations of those energies for the different elements. Information on the quantities of such elements can be derived from the measured Auger electron intensities. Calculation of the quantities present may then be made using formulae and relative sensitivity factors provided by the spectrometer manufacturer. It is important that the sensitivity factors are appropriate for the instrument and this will generally be the case directly after installation of the equipment or calibration of the instrument intensity/energy response function by an appropriate organization. There are two important instrumental contributions to the uncertainty of AES intensity measurements that are addressed in this International Standard: (i) the repeatability of intensity measurements and (ii) the drift of the intensities with time.

Repeatability is important for analysing the trends and differences between samples that are similar. The instrumental issues that limit the measurement repeatability include the stability of the electron beam source, the settings of the detector, the sensitivity of the instrument to the sample placement, the data acquisition parameters and the data-processing procedure. The drift of the instrument intensity scale will limit the overall accuracy of any quantitative interpretation and arises from such effects as the ageing of components of the structure of the spectrometer, of its electronic supplies and of the detector. In AES instruments, it has been found that, in service, the instrument intensity/energy response function may change as the instrument ages.

This International Standard describes a simple method for determining the repeatability and constancy of the intensity scale of the instrument so that remedial action, such as improving the operating procedure, resetting of the instrument parameters or recalibration of the intensity/energy response function, may be made. This method should, therefore, be conducted at regular intervals and is most useful if the data include a period in which the instrument has been checked to be working correctly by the manufacturer or other appropriate body. This method uses a sample of pure copper (Cu) and is applicable to Auger electron spectrometers with an electron gun with a beam energy of 2 keV or greater.

This method does not address all of the possible defects of instruments since the required tests would be very time-consuming and need both specialist knowledge and equipment. This method is, however, designed to address the basic common problem of repeatability and of drift of the intensity scales of AES instruments. This method may be conducted at the same time as the spectrometer energy calibration using ISO 17973 [1] or ISO 17974 [2].

Surface chemical analysis — Auger electron spectroscopy — Repeatability and constancy of intensity scale

1 Scope

This International Standard specifies a method for evaluating the constancy and repeatability of the intensity scale of Auger electron spectrometers, for general analytical purposes, using an electron gun with a beam energy of 2 keV or greater. It is only applicable to instruments that incorporate an ion gun for sputter cleaning. It is not intended to be a calibration of the intensity/energy response function. That calibration may be made by the instrument manufacturer or other organization. The present procedure provides data to evaluate and confirm the accuracy with which the intensity/energy response function remains constant with instrument usage. Guidance is given on some of the instrumental settings that may affect this constancy.

2 Symbols

H_{L}	average peak-to-peak height of the Cu L_3VV peak in the differential mode
$H_{\mathrm{L}j}$	a value contributing to H_{L} for the jth measurement in a set of measurements
H_{M}	average peak-to-peak height of the Cu $M_{2,3}VV$ peak in the differential mode
$H_{\mathrm{M}j}$	a value contributing to H_{M} for the jth measurement in a set of measurements
i	identifier for one of the five parameters P_i
j	index for one of the individual measurements of the parameter P_{ij}
N_{L}	average maximum intensity at the Cu L_3VV peak in the direct mode
$N_{\mathrm{L}j}$	a value contributing to N_{L} for the jth measurement in a set of measurements
N_{M}	average maximum intensity at the Cu $M_{2,3}VV$ peak in the direct mode
$N_{\mathrm{M}j}$	a value contributing to N_{M} for the jth measurement in a set of measurements
P_i	parameter representing the mean value of any of H_{L}, H_{M}, N_{L}, N_{M} and $H_{\mathrm{L}}/H_{\mathrm{M}}$
P_{ij}	the jth measurement of a parameter with average value P_i
$U_{95}(P_i)$	uncertainty in the mean value of P_i, at 95 % confidence level
W	peak full width at half maximum height
β	analogue system scan rate
δ	value of the tolerance limit for $H_{\mathrm{L}}/H_{\mathrm{M}}$ for compliance at 95 % confidence level (set by the analyst)
$\sigma(P_i)$	repeatability standard deviation for the parameter P_i
τ	analogue detection system time constant

3 Outline of method

Here, the method is outlined so that the detailed procedure, given in Clause 4, may be understood in context. To evaluate an Auger electron spectrometer using this procedure, it is necessary to obtain and prepare a copper reference foil in order to measure the intensities of the Cu $M_{2,3}VV$ and Cu L_3VV Auger electron peaks with the appropriate instrumental settings. These peaks are chosen as they are near the middle and low kinetic-energy limits used in practical analysis. These peaks are well established for this purpose and relevant reference data exist. The low-energy, Cu $M_{2,3}VV$, peak is chosen to be in an energy range where stray magnetic fields can cause unwanted intensity changes and hence serves to monitor this problem.

The initial steps of procuring the sample and setting up the instrument are described from 4.1 to 4.5, as shown in the flowchart of Figure 1, with the relevant subclause headings paraphrased.

From 4.6, a user will move to 4.7 unless there has been a previous determination of the intensity repeatability. In 4.7, measurements are made of the intensities of the Cu $M_{2,3}VV$ and Cu L_3VV peaks in a sequence repeated seven times. These data give the repeatability standard deviations of the peak intensities. These repeatabilities have contributions from the stability of the electron beam intensity, the spectrometer detector and the electronic supplies, from the sensitivity of the measured peak intensity to the sample position and from the statistical noise at the peak. In the method, conditions are defined to ensure that the statistical noise at the measured intensities is relatively small. This is discussed in Annex A. The value of the repeatability standard deviation may depend on the sample-positioning procedure. In 4.7.1, 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 absolute values of the intensities of the two peaks are known for well-defined conditions and so, in principle, these two intensity values could be used to establish part of the spectrometer intensity/energy response function [3]. However, these response functions may have a complex dependence on energy [4] and so a determination of the intensities at two energies is insufficient. In this method, therefore, the scope is limited to evaluating the constancy of the intensity/energy response function as indicated by the constancy of the intensities at these two energies and of the ratio of their intensities, within an uncertainty derived from the measurement repeatability. These determinations are made in 4.7 and the calculation is based on these measurements and performed in 4.8, as shown in the flowchart of Figure 1. Following this, the first of the simpler regular determinations of intensity constancy is made in 4.9.

In practice, the intensity/energy response function of spectrometers may change significantly with instrument use. If this occurs, it may modify quantified results deduced from spectra. In this case, it is important to consider the following actions: (i) improving the sample positioning, (ii) using longer warm-up times, (iii) re-setting the equipment to regain the original response function, (iv) re-determining the relative sensitivity factors used for quantification either experimentally or by calculation, or (v) increasing the stated uncertainty of any quantified results obtained. The choice of action will depend on the requirements and on the rate of drift of the intensity ratios recorded in this procedure. Rates of drift as high as 40 % per year have been measured, with major changes occurring after installing new detectors [5]. Thus, two months after the first of the regular assessments in 4.9, or after any substantive changes have been made to the spectrometer, the procedure from 4.2 to 4.5 is repeated, followed by a regular assessment as described in 4.9, at intervals of two months. Steps 4.7 and 4.8 do not need to be repeated unless a significant change is made to the instrument.

4 Method for evaluating the repeatability and constancy of the intensity scale

4.1 Obtaining the reference sample

A sample of polycrystalline Cu of at least 99,8 % purity shall be used. For convenience, this sample is usually in the form of foil typically measuring 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick.

NOTE If the sample appears to need cleaning, a short dip in 1 % nitric acid may be used with subsequent rinsing in distilled water. If the sample has been stored in the air for more than a few days, the dip in nitric acid will make the sample cleaning, required later in 4.3.1, easier.

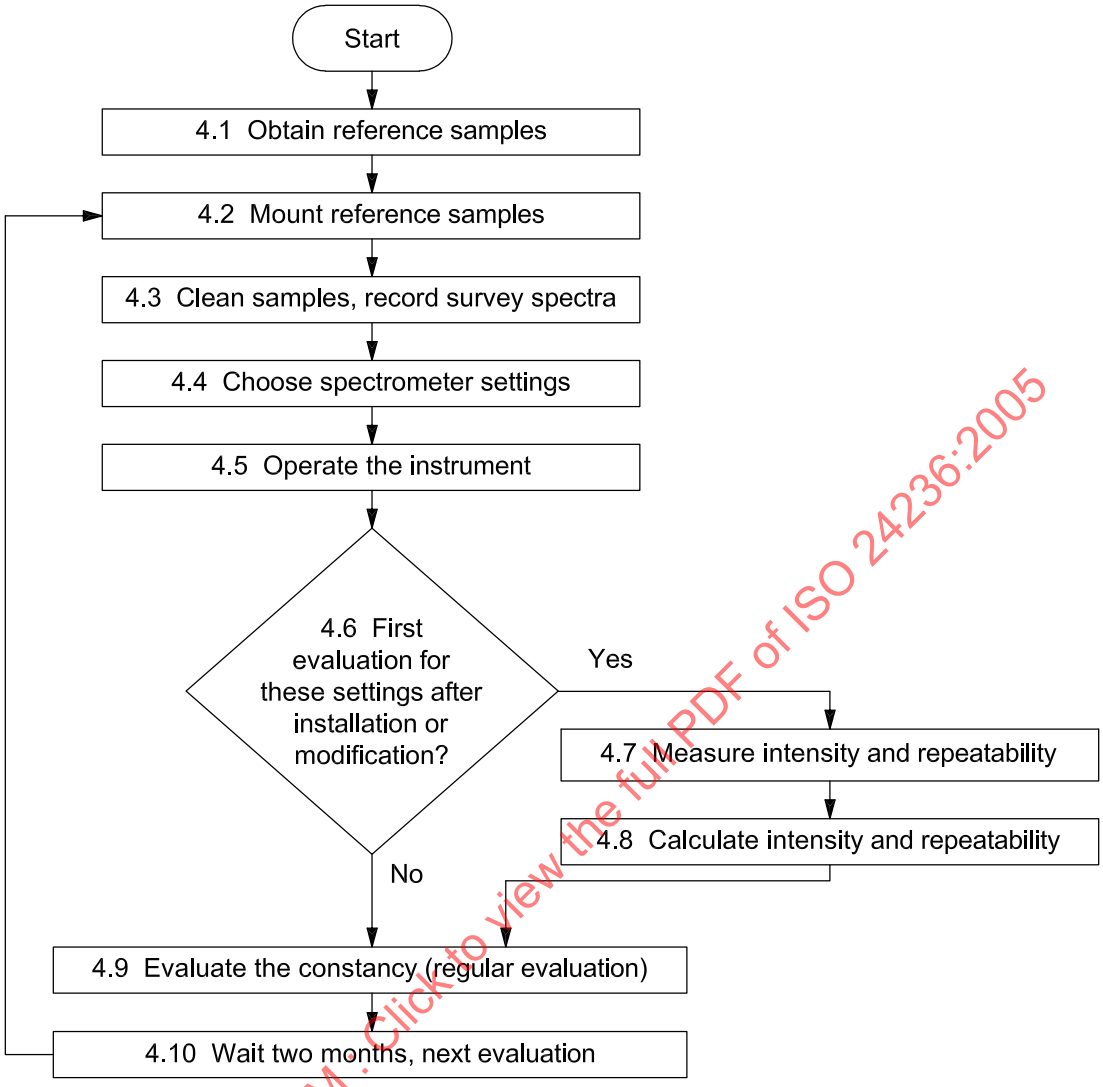


Figure 1 — Flowchart of the sequence of operations of the method
(subclause numbers are given with items for cross-referencing with the body of the text)

4.2 Mounting the sample

Mount the sample on the sample holder using fixing screws, or other metallic means, to ensure electrical contact. Do not use double-sided adhesive tape.

NOTE Repeat measurements of the sample are required at intervals of two months. Mounting the sample so that it may be kept in the vacuum system is a useful convenience.

4.3 Cleaning the sample

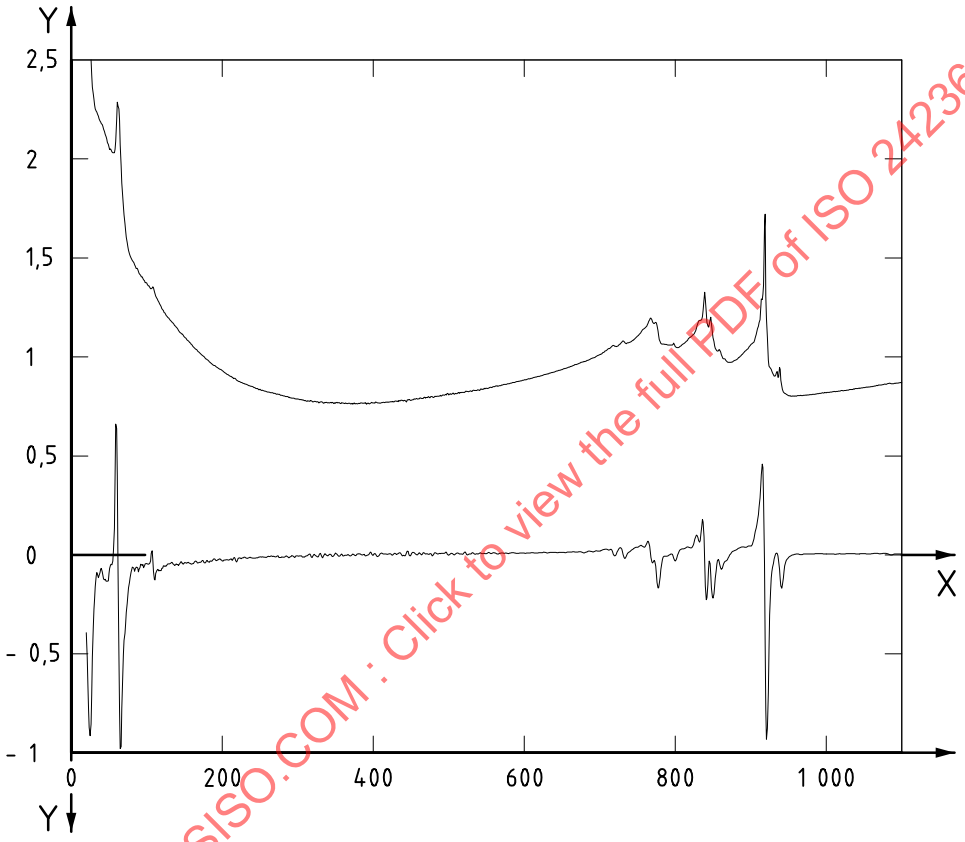
4.3.1 Produce an ultra-high vacuum and clean the sample by ion sputtering to reduce the contamination until the heights of the oxygen and carbon Auger electron peaks are each less than 2 % of the heights of the most intense metal peak in a survey spectrum. Record a survey (widescan) spectrum to ensure that the only significant peaks are those of Cu. Ensure that there are no peaks that are characteristic of the sample holder. The quality of vacuum necessary here is such that the oxygen and carbon peak heights do not exceed 3 % of the heights of the most intense metal peaks by the time the data acquisition is completed in 4.7 or at the end of the working day (whichever is the earlier).

NOTE 1 Inert-gas ion-sputtering conditions that have been found suitable for cleaning are 1 min of a 30 µA beam of 5 keV argon ions covering 1 cm^2 of the sample. These conditions provide a sputtering flux density of 1,8 $mC \cdot cm^{-2}$ that may also be produced by other settings of beam current, time and sputtered area, depending on the equipment available. The flux density and area to be sputtered clean may vary from instrument to instrument.

NOTE 2 A repeat of this procedure is required at intervals of two months. Excessive sputtering may lead to changes in the emitted absolute intensities that may eventually become significant. Do not sputter more than necessary or the sample may become very rough and need to be replaced.

NOTE 3 Example Cu AES spectra are given in Figure 2.

4.3.2 The measurements required for this International Standard should be performed during one working day. If more than one day is required, confirm the cleanness of the Cu at the start of each day's work.



Key

X electron kinetic energy (eV)

Y intensity/10^4

Figure 2 — Widescan (survey) spectra for clean Cu, measured in the constant $\Delta E/E$ mode, with the direct spectrum shown uppermost and the differential spectrum below

4.4 Choosing the spectrometer settings for which intensity stability is to be determined

Choose the spectrometer operating settings for which the intensity stability is to be determined. The method from 4.4 to 4.9 shall be repeated for each combination of spectrometer settings of pass energy, retardation ratio, slits, lens settings, etc., for which assessment of intensity constancy is required.

NOTE 1 Analysts may wish to reserve selected settings for quantitative analysis and then only those settings need assessment. Likewise, for determining chemical state, analysts may wish to select restricted settings for energy calibration using ISO 17974 [2]. If the energy settings for energy calibration and the present assessment can be chosen to be the same, there is a useful reduction in effort in conducting the measurements both here in 4.7 and in ISO 17974:2002 [2] in 6.7 when using the copper sample as described below.

NOTE 2 The designs of spectrometers and their circuits vary and so the intensity/energy response function for one combination of lens settings, slits and pass energy will not necessarily be valid for any other setting of the lens, slits and pass energy. Many spectroscopists make accurate intensity measurements under one optimum set of conditions and then only that set of analyser conditions needs evaluation. Any evaluation made is only valid for the combination of settings used.

NOTE 3 The repeatability of the intensity scale as well as the absolute values of the intensities vary with the combination of settings used. In general, the repeatability will be best when using large slits and lower energy resolution.

4.5 Operating the instrument

Operate the instrument in accordance with the manufacturer's documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that operation is within the manufacturer's recommended ranges for beam current, counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Set the electron beam energy to the energy commonly used for analysis, but not less than 2 keV, and set the beam to raster an area of typically 100 µm by 100 µm on the sample. If the spectrometer only analyses an area smaller than this, set the raster to the value commonly used for analysis (this may be zero). Set the beam current to the maximum value generally required for analysis whilst ensuring that the counting rate is within the manufacturer's recommended range. 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 using this procedure. Make a list of the parameters set and record their values.

NOTE 1 Many manufacturers recommend that the control and high-voltage electronics are switched on for at least 4 h to ensure adequate stability. It may also be necessary to have operated the electron gun for a period, for example 20 min, before making measurements in order to reduce drift and variability.

NOTE 2 High counting rates [6] or incorrect detector voltages [6,7] can cause peak distortions that lead to erroneous peak intensity measurements.

4.6 Options for initial or subsequent evaluation measurements

In order to assess the constancy of the intensity scale of an instrument, the intensity repeatabilities need determination. If these have not been determined, proceed as below. If all of these have been determined for the relevant spectrometer settings through prior use of this procedure and if the instrument has not been modified, undergone significant repair or been moved, proceed directly to 4.9, as shown in the flowchart of Figure 1.

4.7 Measurements for the intensity and repeatability

4.7.1 Set the copper sample at the analytical position with the same angle of emission and procedure as normally used. Record this angle. The sample-positioning procedure shall be that normally used for analysis. The sample-positioning procedure shall follow a documented protocol that takes account of the manufacturer's recommendations. Ensure that the procedure is clear and complete.

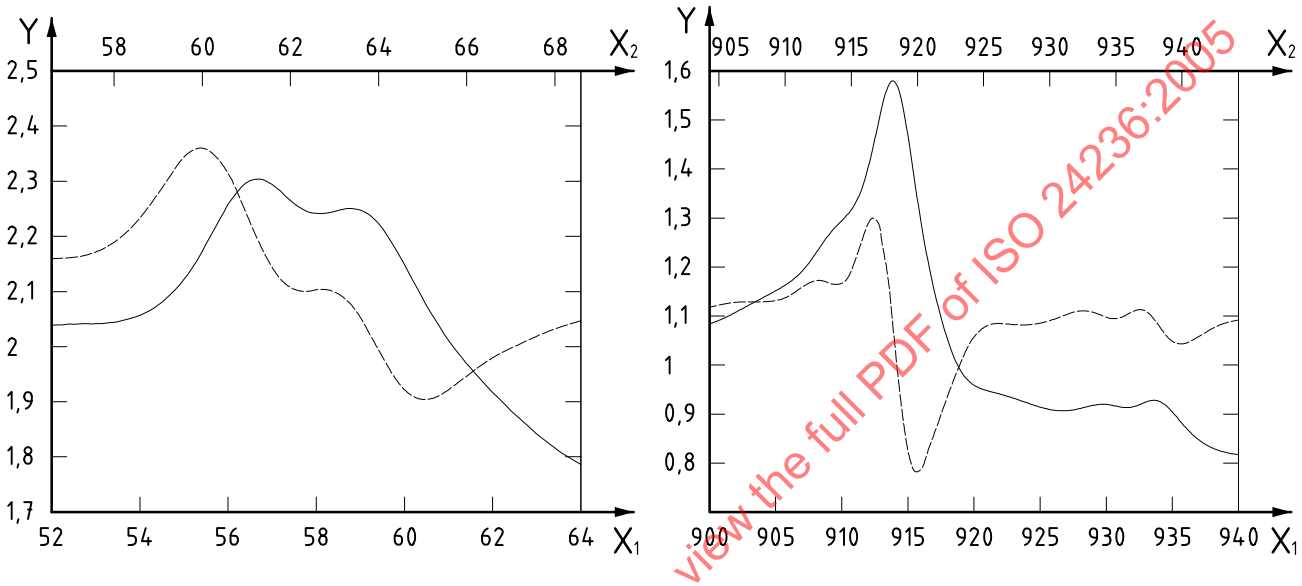
NOTE In spectrometers that have a small analytical area, changes in the sample position may affect the peak intensities more than in other spectrometers. The sample-positioning procedure is then critical for obtaining consistent intensities.

4.7.2 Record the Cu $M_{2,3}VV$ and L_3VV peaks, as shown in Figures 3a) and 3b), respectively, for the direct or differential modes, using the settings chosen in 4.4 and 4.5. Scan the energy ranges shown in Figure 3 and Table 1. If a digital scan is used for the energy scale, set the energy increment at or near 0,1 eV and the dwell time at or near 1 s. If an analogue system is used, set the scan rate, β, at less than $0{,}07 W\tau^{-1}$ eV·s^{-1} where W is the peak full width at half maximum (FWHM) and τ is the detecting amplifier time constant. If the spectrometer only operates in the differential mode, set the differentiating energy to the value usually used or a width as close to 5 eV as possible. Do not change any operating conditions between the spectra except the position on the kinetic-energy scale. Do not reset the beam current, just monitor it if that is possible. If the pulse-counting mode is used and the counts at the Cu $M_{2,3}VV$ peak are less than 1 000 000, better results may be obtained by increasing the dwell time for both peaks. The dwell time finally chosen will be a compromise between the data quality and the duration of the work. Record the parameters set.

NOTE 1 If the pulse-counting mode is used and the instrumental output is in counts per second, the total counts per channel is equal to the counts per channel per second times the time per channel. The time per channel may be chosen to achieve the required number of counts. If the output is in counts per channel per scan and in multi-scanning the output simply averages the results of the scans, the total counts per channel is equal to the average counts per channel times the number of scans. The number of scans may be chosen to achieve the required number of counts.

NOTE 2 The optimum repeatability that can be obtained for different count levels is discussed in Annex A.

NOTE 3 The value of the differentiating energy in systems using the analogue sinusoidal modulation of a spectrometer electrode potential is the modulation energy that, applied to the direct spectrum, would result in an equivalent differential Auger electron spectrum.



a) Cu $M_{2,3}VV$ b) Cu L_3VV

Key

X_1 electron kinetic energy (eV) (vacuum level referenced)

X_2 electron kinetic energy (eV) (Fermi level referenced)

Y intensity/10^4

Figure 3 — Example narrow-scan spectra of a) Cu $M_{2,3}VV$ and b) Cu L_3VV peaks at 0,3 % relative resolution and 0,1 eV energy intervals (continuous line direct mode and dashed line differential mode using a 31-point Savitzky and Golay [6] differential)

(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.)

Table 1 — Kinetic-energy ranges, eV, for measuring the copper peaks

Peak	Kinetic-energy range eV	
	Vacuum level referenced	Fermi level referenced
$M_{2,3}VV$	52 to 64	56,5 to 68,5
L_3VV	900 to 940	904,5 to 944,5
NOTE A spectrometer work function of 4,5 eV is assumed so that vacuum level referenced peaks have energy values 4,5 eV less than Fermi level referenced values.		

4.7.3 Remove the sample from the analytical position and then replace it and repeat 4.7.1. Use the documented sample-positioning procedure. Do not simply return the sample to the same sample holder position unless that is the required procedure. Repeat the sample removal and repositioning with measurements each time until a total of seven spectra for each peak have been recorded.

4.8 Calculating the peak intensities, intensity ratios and uncertainties

4.8.1 If the spectrometer only operates in the differential mode, go to 4.8.3. If it operates in the direct mode, with each of the seven determinations of each peak, j, measure the count rates, N_{Lj} and N_{Mj}, at the maximum intensities of the L_3VV and $M_{2,3}VV$ Auger electron peak regions, respectively. The maximum intensity for the Cu $M_{2,3}VV$ pair of peaks usually occurs for the lower-energy peak as shown in Figure 3a) but, for some spectrometers, may occur for the higher-energy peak. Record which of the two peaks is most intense and use that peak for measuring N_M.

NOTE The data system may present data intensity as counts or counts per second. It may then determine areas by summing the values or by summing the products of the value times the channel interval. Thus, areas may be presented as counts, counts per second, counts eV or counts eV per second. Providing the data are recorded in compliance with 4.7, these differences are unimportant if the units selected are the same for both peaks. Record the dimensions in which the areas are determined.

4.8.2 If the spectral data have been acquired in the direct mode, differentiate them numerically using the data-processing software. Use a differential function with the width usually used or with a width as close to 5 eV as possible and record the differential function chosen and any values used. The differential spectra should now resemble the dashed spectra in Figure 3.

NOTE 1 The differential function width is equal to the energy increment between channels of the kinetic-energy scan times the number of points in the differentiating function.

NOTE 2 Examples of differential spectra are shown dashed in Figure 3 for a 3 eV differentiating function.

NOTE 3 For a Savitzky and Golay cubic/quadratic differential function [8], the function width for 3 eV or 5 eV at 0,1 eV energy intervals should be 31 or 51 points, respectively. Few commercial data-processing systems have this number available and 11 or 31 points may have to be accepted as the upper limit available. The use of 51 points, if available, gives improved data precision. The effect of different differential widths on the repeatability is discussed in Annex A.

4.8.3 With each of the seven measurements, j, for each peak, determine the peak-to-peak heights, H_{Lj} and H_{Mj}, of the L_3VV and $M_{2,3}VV$ Auger electron peaks, respectively.

4.8.4 Review the seven values of each of the peak-to-peak heights for the two peaks and, if the direct mode has been used, the two maximum intensities 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, an inadequate detector voltage or another source of drift. If this appears to be the case, take appropriate action (for example increase the warm-up period) and repeat 4.7.

NOTE An example of drift is given in Figure A.1 in Annex A.

4.8.5 Calculate, for each spectrum, the ratios H_{Lj}/H_{Mj} and, if available, N_{Lj}/N_{Mj}, to give a total of seven values of each of either three or five parameters, P_{ij}, for each of the seven pairs of spectra for the $M_{2,3}VV$ and L_3VV peaks. Here i is the identifier of one of the parameters P_i and j is one of the seven individual measurements of that parameter. For spectra recorded in the differential mode, there are three P_i parameters, H_L, H_M and H_L/H_M. For spectra recorded in the direct mode, there are two additional parameters, N_L and N_M. Calculate, for each of the i parameters, the mean value of P_i and the relative standard deviation, $\sigma(P_i)$, using the equation

$$\left[\sigma\left(P_i\right)\right]^2 = \sum_{j=1}^{7} \frac{(P_{ij} - P_i)^2}{6{P_i}^2} \qquad (1)$$

Record the averages and relative standard deviations for each of the three or five parameters. If any of these relative standard deviations exceeds a value of 3 %, the sample-positioning procedure may need to be reviewed. The relative standard deviations are measures of the repeatability.

NOTE 1 The relative standard deviations of the three or five parameters may depend critically on the sample-positioning procedure.

NOTE 2 A relative standard deviation of 1 % or better for N_L and N_M and 2 % or better for H_L and H_M will be obtainable with most instruments in good working order. Values significantly better than these may require careful selection of the reference sample to have an even texture, small grain size and uniform surface topography. It may also require care in selecting the instrument settings and in stabilization of the electronic supplies. Two examples are provided in Annex A. In one, the relative standard deviation is better than 1 % but, in the other, a low detector voltage setting leads to a deterioration of this value.

4.9 Procedure for the regular evaluation of the constancy of the intensity scale

4.9.1 For the regular assessment of the constancy of the spectrometer intensity scale, either one or two measurements, j, of the $M_{2,3}VV$ and L_3VV peaks shall be made. If two measurements are made, the order shall be $M_{2,3}VV$, L_3VV, $M_{2,3}VV$ and L_3VV, with the sample repositioned using the sample-positioning procedure of 4.7.1 before each pair of measurements. The operating conditions for the spectrometer and the orientation of the sample shall be those chosen and recorded in 4.4, 4.5 and 4.7.

4.9.2 Determine H_L, H_M, H_L/H_M and, if the direct mode is used, also N_L and N_M, as described in 4.8.1, 4.8.3 and 4.8.5. If two measurements have been made of H_L and H_M, determine the average values of each parameter and of the ratio H_L/H_M, and use these values for H_L, H_M and H_L/H_M in the following analysis (and similarly for N_L and N_M, if measured).

4.9.3 The relative uncertainty $U_{95}(P_i)$, at a confidence level of 95 %, for the determinations of the parameters P_i is given by

$$U_{95}(P_i) = 2{,}6\sigma(P_i) \quad \text{for two measurements of the peaks} \tag{2}$$

$$U_{95}(P_i) = 3{,}7\sigma(P_i) \quad \text{for one measurement of the peaks} \tag{3}$$

where $\sigma(P_i)$ has been determined in 4.8.5, using Equation (1). The choice of the number of measurements to use will depend on the requirements for precision in evaluating the constancy of the equipment and the time available to make the measurement.

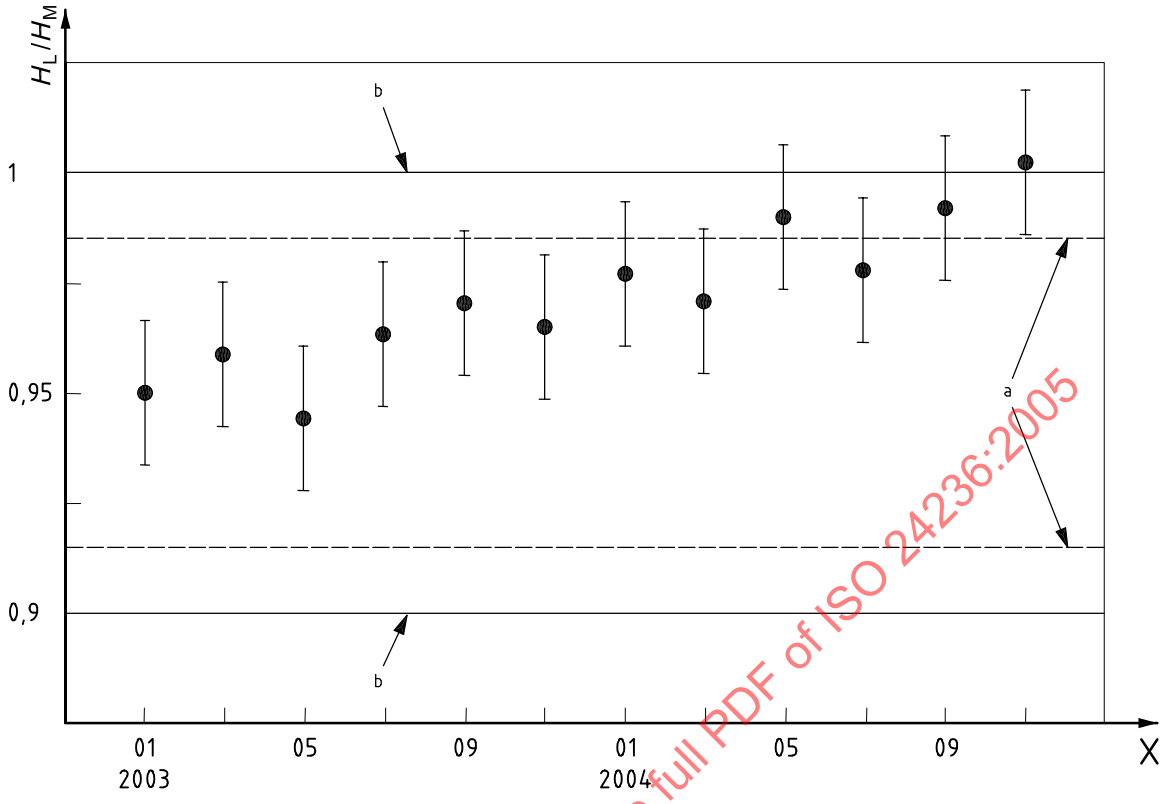
NOTE The derivation of Equations (2) and (3) may be found in References [9] and [10].

4.9.4 Plot a control chart for the ratio H_L/H_M, as illustrated in Figure 4. Define the tolerance limits, $\pm\delta$, based on the constancy required for quantitative analysis, and plot these limits as shown in Figure 4. Add warning limits at $\pm 0{,}7\delta$ and add the confidence limits to the plotted value of H_L/H_M using the value of $U_{95}(H_L/H_M)$ from Equation (2) or (3).

NOTE 1 Typical tolerance limits may be in the range 2 % to 6 % so that, for example, δ in Figure 4 would be in the range 0,019 to 0,057.

NOTE 2 Additional control charts [11,12] for H_L and H_M, separately, help in the diagnosis of changes in the spectrometer. If these two values decrease with time, while the ratio H_L/H_M remains relatively constant, it may be that the detector settings need adjustment. An example illustrating this situation is given in Annex A. Follow the manufacturer's procedures for checking this item. The detector voltage may need to be increased or the discriminator threshold may need to be reduced.

NOTE 3 Additional control charts for N_L and N_M help to diagnose changes in the spectral background arising from internal scattering in the analyser. If N_L or N_M increases whilst H_L/H_M remains unchanged, this scattering may be increasing and affecting the interpretation of the data.



Key

X measurement date (month)
- 01 January
- 05 May
- 09 September

a Warning limits.

b 95 % tolerance limit.

Figure 4 — Schematic control chart [11,12], with tolerance limits set for 5 % drift, to monitor the constancy of the instrumental intensity (The plotted points are values for H_L/H_M that, here, illustrate an instrument that has not been adjusted since the start in January 2003. It is first out of tolerance in May 2004 and action should have been taken, since it passed the warning limit in September 2003. The uncertainties shown for each point, $U_{95}(H_L/H_M)$, are for 95 % confidence where $\sigma(H_L/H_M)$ is 0,6 % and two measurements are made at each determination of the constancy.)

4.10 Next evaluation

Following any significant modification or adjustment to the instrument, or once every two months that the instrument is in use, repeat 4.2 to 4.5 and 4.9, using the same conditions as defined in 4.4, 4.5, 4.7 and 4.8, and add the data to the control chart. If the sum of the value of H_L/H_M and $U_{95}(H_L/H_M)$ reaches the warning limit, the instrument shall be checked and adjusted or the alignment procedure revised so that a new measurement of H_L/H_M, with its associated $U_{95}(H_L/H_M)$, is obtained fully within the acceptance zone. If this is not possible, the tolerance limits, $\pm\delta$, shall be increased, or the intensity scale shall be recalibrated or the sensitivity factors shall be redetermined.

NOTE A procedure for determining sensitivity factors is given in ISO 18118 [13].

Annex A
(informative)

Example of calculations and measurements of the intensity repeatability for a commercial Auger electron spectrometer

A.1 Symbols

A	normalization parameter for Savitzky and Golay smoothing, given by Equation (A.2)
H	peak-to-peak height of a reference peak in the differential mode
m	parameter defining the number of points in a Savitzky and Golay smooth as $2m + 1$
n	count increase per channel in a small energy region
N_0	average counts per channel
S	differential signal given by Equation (A.1)
$\sigma(S)$	standard uncertainty in S
$\sigma(H)$	standard uncertainty in H
$\sigma(H_L)$	standard uncertainty in H_L
$\sigma(H_M)$	standard uncertainty in H_M
$\sigma(H_L/H_M)$	standard uncertainty in H_L/H_M

A.2 Example of calculations and measurements of the intensity repeatability for a commercial Auger electron spectrometer

In this example, spectra acquired for an instrument at a nominal energy resolution of 0,2 % were similar to the data of Figure 3 but were 10 % to 15 % more intense. The Cu $M_{2,3}VV$ and L_3VV peak maximum intensities were 2,55 Mcounts and 1,9 Mcounts, respectively. The measured halfwidths for both peaks were less than those of Figure 3.

Consider first the optimum repeatability where that is limited by the uncertainty arising from the Poissonian counting statistics. For a small region of the spectrum with an average of N_0 counts per channel and with an increase of n counts per channel, a Savitzky and Golay differentiation [8] will give an output signal S where

$$S = n \tag{A.1}$$

This small region could be, for example, the region of maximum slope for the Cu $M_{2,3}VV$ peak at 55 eV to 56 eV in Figure 3a). For the above differentiation, the spectrum is convolved with the Savitzky and Golay coefficients which, for a $2m + 1$ point differential, are $-m/A$, $-(m-1)/A$,…., 0,…., $(m-1)/A$, m/A. Here A is a normalization parameter given by

$$A = \frac{1}{3}m(m+1)(2m+1) \tag{A.2}$$

This calculation is valid for a differential energy width equal to or smaller than the energy interval over which the value of n can be reasonably assumed to be approximately constant. The noise, and hence standard uncertainty associated with this signal S, is given by σ, where, for $n << N_0$,

$$\left[\sigma(S)\right]^2 = \left(\frac{m}{A}\right)^2 N_0 + \left(\frac{m-1}{A}\right)^2 N_0 + \ldots\ldots \left(\frac{m}{A}\right)^2 N_0 \qquad \text{(A.3)}$$

Thus

$$\left[\sigma(S)\right]^2 = \frac{N_0}{A} \qquad \text{(A.4)}$$

and hence

$$\frac{\sigma(S)}{S} = \frac{1}{n}\left(\frac{N_0}{A}\right)^{0,5} \qquad \text{(A.5)}$$

For the Cu $M_{2,3}VV$ and L_3VV peaks, there are both positive and negative slopes either side of the peak that, for the purposes of the present calculation, may be taken to be of equal magnitudes. The maximum positive and negative values of these slopes give the peak-to-peak height H measured here. H is thus approximately twice S. The standard uncertainty, $\sigma(H)$, in H is then given by

$$\frac{\sigma(H)}{H} = \frac{1}{n}\left(\frac{N_0}{2A}\right)^{0,5} \qquad \text{(A.6)}$$

Equations (A.2) and (A.6) show that the relative standard deviation is approximately proportional to $m^{-1,5}$ for small values of m. This result indicates how important it is to use an m value higher than the minimum value of 3. The parameters for one measurement of the Cu $M_{2,3}VV$ and L_3VV peaks in a test in accordance with this International Standard are given in Table A.1. Using these values, the relative standard uncertainties in H_M, H_L and the ratio H_L/H_M, in percent, are calculated from Equation (A.6), for both a 3-point and a 31-point differentiation. These results are shown in Table A.2.

Table A.1 — Measured parameters for the Cu $M_{2,3}VV$ and L_3VV peaks for the uncertainty analysis

Peak	N_0	n
$M_{2,3}VV$	2 340 000	12 000
L_3VV	1 750 000	16 000

Table A.2 — Relative standard uncertainties of the differential amplitudes of the Cu $M_{2,3}VV$ and L_3VV peaks and their ratio for selected m values, calculated using Equation (A.6) and the data of Table A.1, and measured using the procedure described in this International Standard

Peak parameter	Equation (A.6)	Equation (A.6)	Expt (1)	Expt (2)
m	3	31	31	31
A	2	2 480	2 480	2 480
$\sigma(H_M)/H_M$	6,37 %	0,18 %	1,80 %	0,69 %
$\sigma(H_L)/H_L$	4,13 %	0,12 %	0,73 %	0,48 %
$\sigma(H_L/H_M)/(H_L/H_M)$	7,59 %	0,22 %	1,45 %	0,27 %