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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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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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 24236 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 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<sup>[1]</sup> or ISO 17974<sup>[2]</sup>.

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# 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
$H_{Lj}$	a value contributing to $H_L$ for the $j$ th measurement in a set of measurements
$H_M$	average peak-to-peak height of the Cu $M_{2,3VV}$ peak in the differential mode
$H_{Mj}$	a value contributing to $H_M$ for the $j$ th 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
$N_{Lj}$	a value contributing to $N_L$ for the $j$ th measurement in a set of measurements
$N_M$	average maximum intensity at the Cu $M_{2,3VV}$ peak in the direct mode
$N_{Mj}$	a value contributing to $N_M$ for the $j$ th 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 $H_L/H_M$
$P_{ij}$	the $j$ th 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
$\beta$	analogue system scan rate
$\delta$	value of the tolerance limit for $H_L/H_M$ for compliance at 95 % confidence level (set by the analyst)
$\sigma(P_i)$	repeatability standard deviation for the parameter $P_i$
$\tau$	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<sup>[3]</sup>. However, these response functions may have a complex dependence on energy<sup>[4]</sup> 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<sup>[5]</sup>. 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.

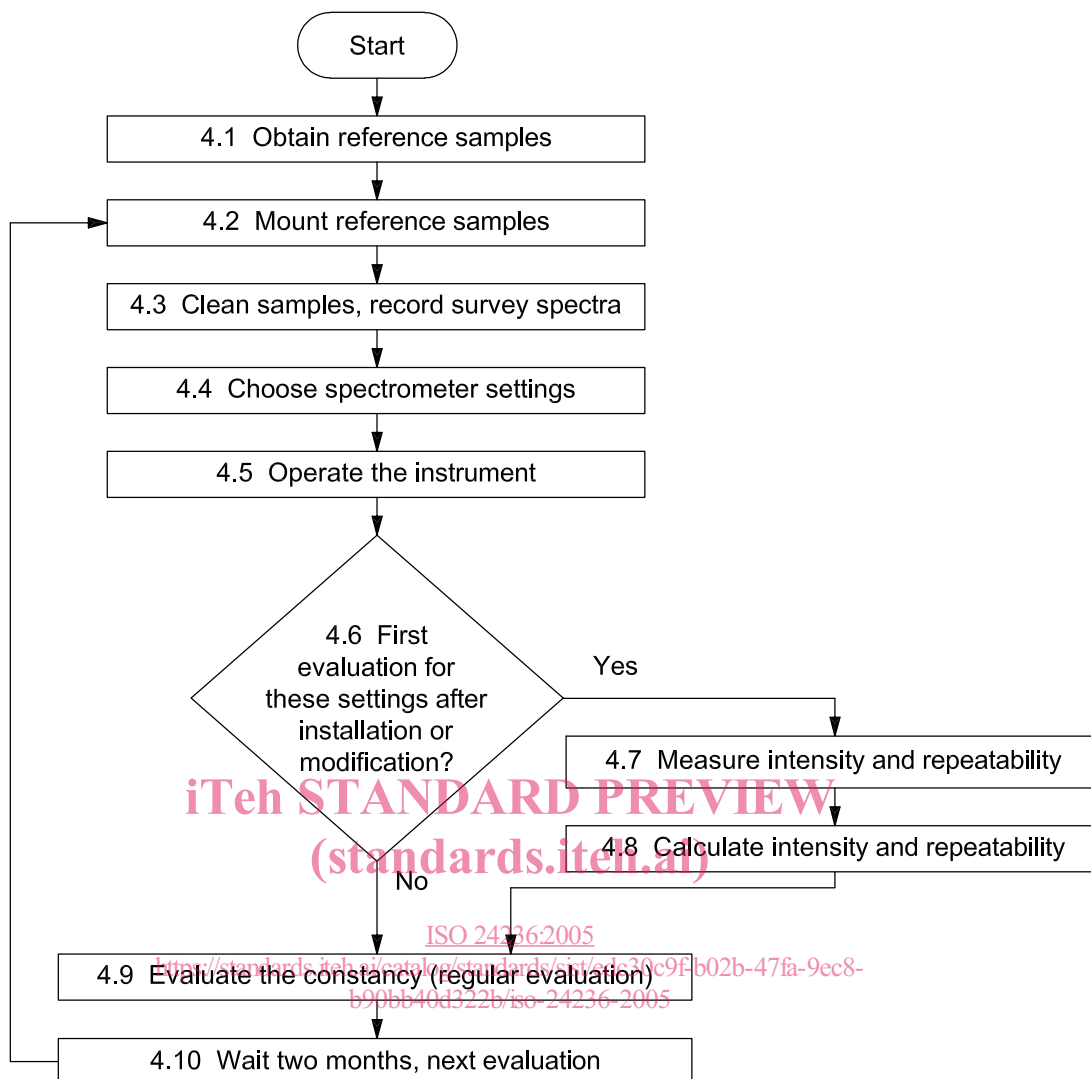
## 4 Method for evaluating the repeatability and constancy of the intensity scale

### 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

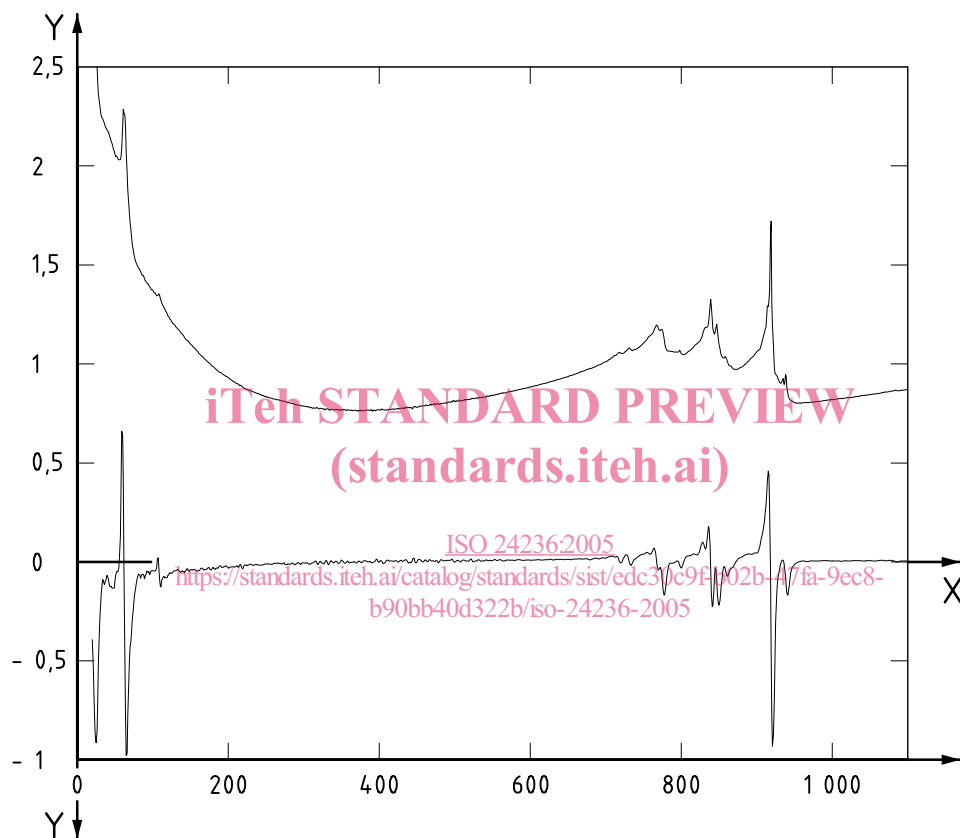
**4.3.1** Produce an ultra-high vacuum and clean the sample by ion sputtering to reduce the contamination until the heights of the oxygen and carbon Auger electron peaks are each less than 2 % of the heights of the most intense metal peak in a survey spectrum. Record a survey (widescan) spectrum to ensure 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  $\mu\text{A}$  beam of 5 keV argon ions covering 1  $\text{cm}^2$  of the sample. These conditions provide a sputtering flux density of 1,8  $\text{mC}\cdot\text{cm}^{-2}$  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<sup>4</sup>

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  $\mu\text{m}$  by 100  $\mu\text{m}$  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<sup>[6]</sup> or incorrect detector voltages<sup>[6,7]</sup> 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,  $\beta$ , at less than  $0,07W\tau^{-1}$  eV·s<sup>-1</sup> where  $W$  is the peak full width at half maximum (FWHM) and  $\tau$  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.