
**Surface chemical analysis — X-ray
photoelectron spectroscopy —
Repeatability and constancy of intensity
scale**

*Analyse chimique des surfaces — Spectroscopie de photoélectrons par
rayons X — Répétabilité et constance de l'échelle d'intensité*

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Contents

Page

Foreword.....	iv
Introduction	v
1 Scope	1
2 Symbols and abbreviations	1
3 Outline of method	2
4 Method for evaluating the repeatability and constancy of the intensity scale.....	2
4.1 Obtaining the reference sample	2
4.2 Mounting the sample	3
4.3 Cleaning the sample	3
4.4 Choosing the spectrometer settings for which intensity stability is to be determined	4
4.5 Operating the instrument.....	5
4.6 Options for initial or subsequent evaluation measurements.....	5
4.7 Measurements for the intensity and repeatability.....	5
4.8 Calculating the peak area intensities, intensity ratios and uncertainties.....	6
4.9 Procedure for the regular evaluation of the constancy of the intensity scale	7
4.10 Next evaluation	7
Annex A (informative) Example of calculations and measurements of the intensity repeatability for a commercial X-ray photoelectron spectrometer using unmonochromated Mg K α X-rays	9
Bibliography	12

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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.

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Introduction

X-ray photoelectron spectroscopy (XPS) 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 binding energies of their core levels with tabulations of those energies for the different elements. Information on the quantities of such elements can be derived from the measured photoelectron 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 XPS 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 X-ray 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 XPS 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 X-ray photoelectron spectrometers with unmonochromated aluminium (Al) or magnesium (Mg) X-rays or monochromated Al X-rays.

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 XPS instruments. This method may be conducted at the same time as the spectrometer energy calibration using ISO 15472 [1].

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Surface chemical analysis — X-ray photoelectron spectroscopy — Repeatability and constancy of intensity scale

1 Scope

This International Standard specifies a method for evaluating the repeatability and constancy of the intensity scale of X-ray photoelectron spectrometers, for general analytical purposes, using unmonochromated Al or Mg X-rays or monochromated Al X-rays. 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 instrument settings that may affect this constancy.

2 Symbols and abbreviations

A_2	average peak area for the Cu 2p _{3/2} peak after removing the Shirley background
A_{2j}	a value contributing to A_2 for the j th measurement in a set of measurements
A_3	average peak area for the Cu 3p peak after removing the Shirley background
A_{3j}	a value contributing to A_3 for the j th measurement in a set of measurements
i	identifier for one of the three parameters P_i
j	index for one of the individual measures of the parameter P_{ij}
P_i	parameter representing the mean value of any of A_2 , A_3 and A_3/A_2
P_{ij}	the j th measure of parameter with average value P_i
$U_{95}(P_i)$	uncertainty in the mean value of P_i , at 95 % confidence level
XPS	X-ray photoelectron spectroscopy
δ	value of the tolerance limit for A_3/A_2 for compliance at 95 % confidence level (set by the analyst)
Δ	energy offset for the instrumental binding energy scale, equal to the measured Cu 2p _{3/2} binding energy value for the maximum intensity at the peak minus 932,7 eV
$\sigma(P_i)$	repeatability standard deviation for the parameter P_i

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 X-ray photoelectron spectrometer using this procedure, it is necessary to obtain and prepare a copper reference foil in order to measure the intensities of the Cu 2p_{3/2} and Cu 3p X-ray photoelectron peaks with the appropriate instrumental settings. These peaks are chosen as they are near the high and low binding-energy limits used in practical analysis. These peaks are well established for this purpose and relevant reference data exist.

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 2p_{3/2} and Cu 3p 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 X-ray source, 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 [2]. However, these response functions may have a complex dependence on energy [3] 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 their ratio of 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 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. For Auger electron spectrometers operated in the “constant $\Delta E/E$ mode” (also known as the constant retardation ratio mode or fixed retardation ratio mode), rates of drift as high as 40 % per year have been measured with major changes occurring after installing a new detector [4]. For XPS instruments operated in the “constant ΔE mode” (also known as the constant analyser energy mode or fixed analyser energy mode), these effects are thought to be weaker. Thus, three 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 three months.

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.

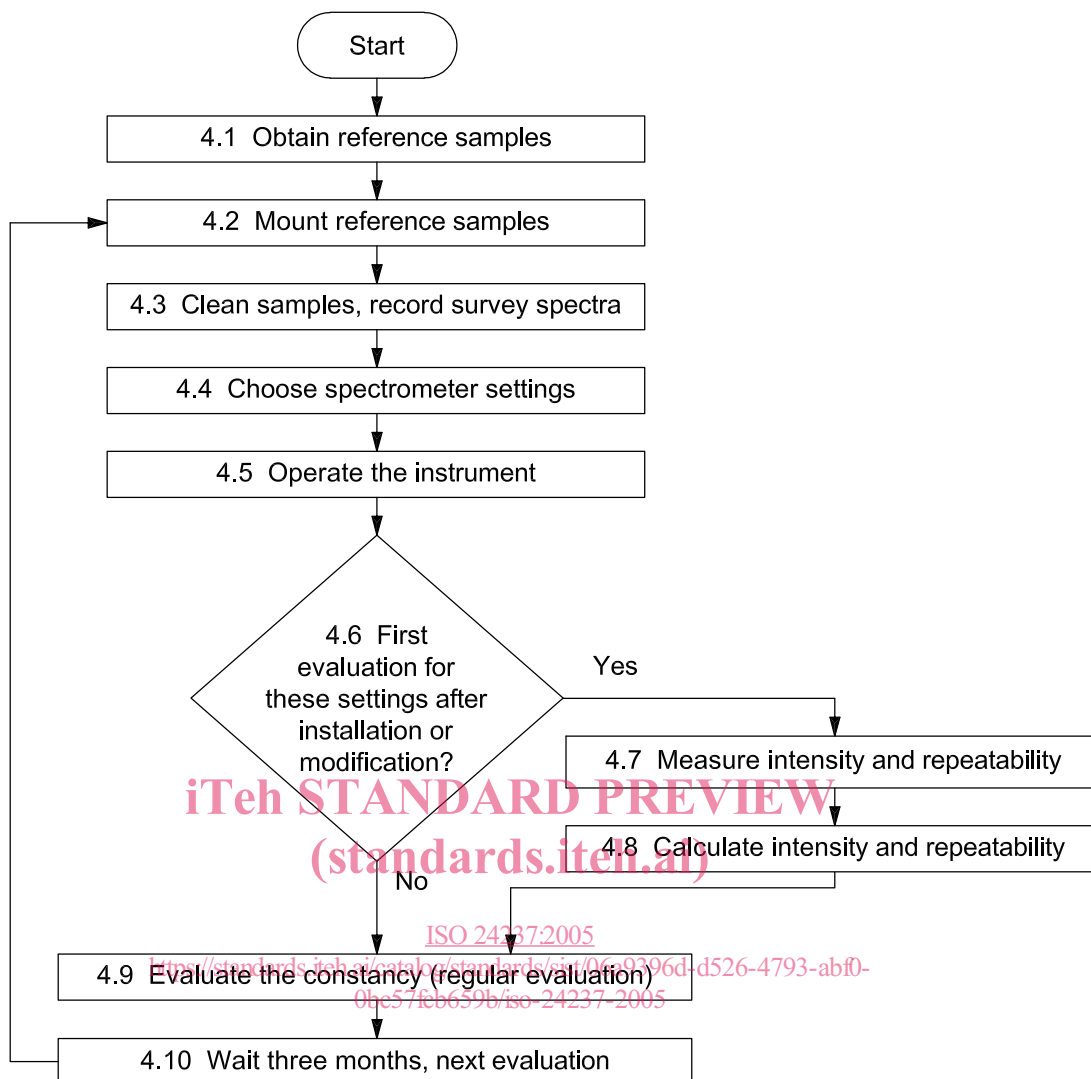


Figure 1 — Flowchart of the sequence of operations of the method
(subclause numbers are given with items for cross-referencing with the body of the text)

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

NOTE 2 Double-sided adhesive tape may lead to contamination, charging or vacuum degradation, particularly over the timescales expected for the use of this International Standard.

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 1s photoelectron 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.

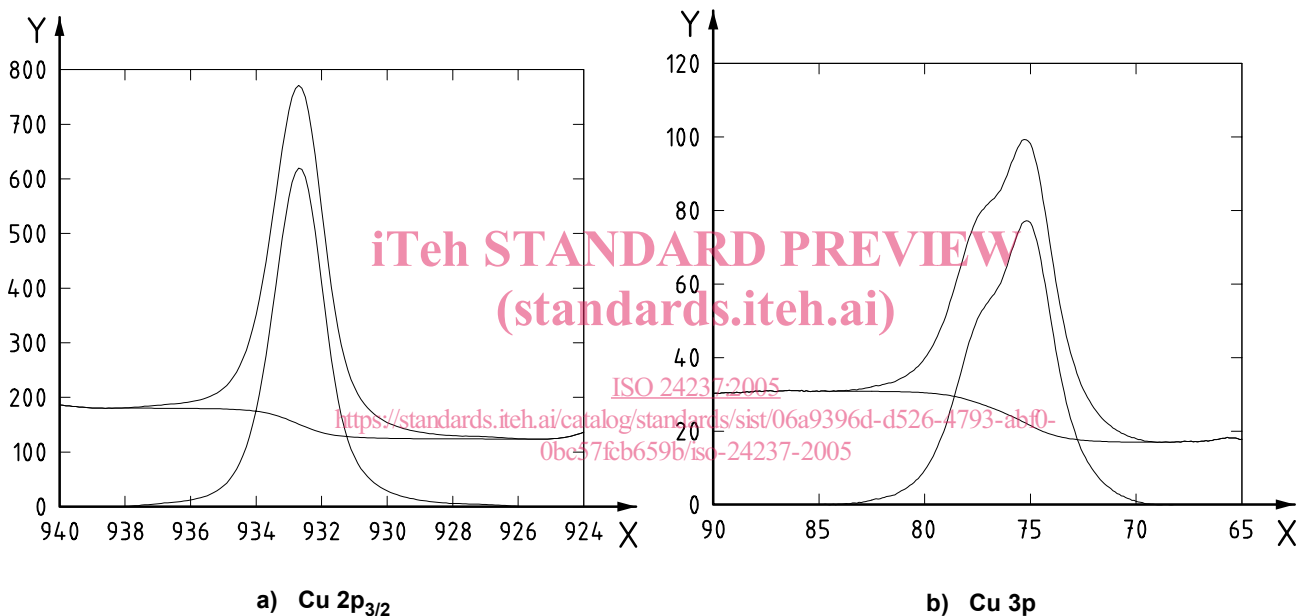
The quality of vacuum necessary here is such that the oxygen and carbon 1s peak heights do not exceed 3 % of the heights of the most intense metal peaks by the time the data acquisition is completed in 4.7 or at the end of the working day (whichever is the earlier).

NOTE 1 Inert-gas ion-sputtering conditions that have been found suitable for cleaning are 1 min of a 30 μ A beam of 5 keV argon ions covering 1 cm² of the sample. These conditions provide a sputtering flux density of 1,8 mC·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 the procedure is required at intervals of three 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 widescan Cu XPS spectra are given in References [5] to [8]. Details of the peaks 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 binding energy (eV)
 Y intensity/1 000 counts

Figure 2 — Example spectra using unmonochromated Al X-rays of a) Cu 2p_{3/2} and b) Cu 3p peaks recorded at 0,1 eV energy intervals (The upper curve in each case is the recorded data. The smooth sigmoidal curve shows the Shirley background and the bottom curve shows the peak after subtraction of the Shirley background.)

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 X-ray source and 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 15472 [1]. 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 15472:2001 [1] in 5.7 when using the copper 2p_{3/2} peak 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^[3] 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 the operation is within the manufacturer's recommended ranges for X-ray power, 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 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 X-ray source for a period, for example 1 h, before making measurements in order to reduce drift and variability.

NOTE 2 Monochromators may need a warm-up time and the X-ray energies transmitted may depend on the ambient temperature or the temperature around the monochromator. Records of these temperatures may help diagnose any problems observed of intensity drift.

NOTE 3 High counting rates^[9] or incorrect detector voltages^[9,10] 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 The sample-positioning procedure may need to be particularly thorough for some spectrometers with monochromated X-ray sources^[11].

4.7.2 Record the Cu 2p_{3/2} and 3p peaks, as shown in Figures 2a) and 2b), respectively, using the settings chosen in 4.4 and 4.5. These spectra shall be recorded over binding-energy ranges of 924 eV to 940 eV and 65 eV to 90 eV, respectively, with an energy increment at or near 0,1 eV and the dwell time at or near 1 s. Do not change any operating conditions between the two spectra except the binding-energy range. If the count level at the Cu 3p peak is less than 100 000, 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 The sample-positioning procedure is critical for obtaining consistent intensities. The positioning procedure should provide confidence that electrons from the Cu sample and only the Cu sample are analysed.

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