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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

Reference number
ISO 24237:2005(E)

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Foreword

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ISO 24237 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

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].

INTERNATIONAL STANDARD **ISO 24237:2005(E)**

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 jth 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 jth 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 jth 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.

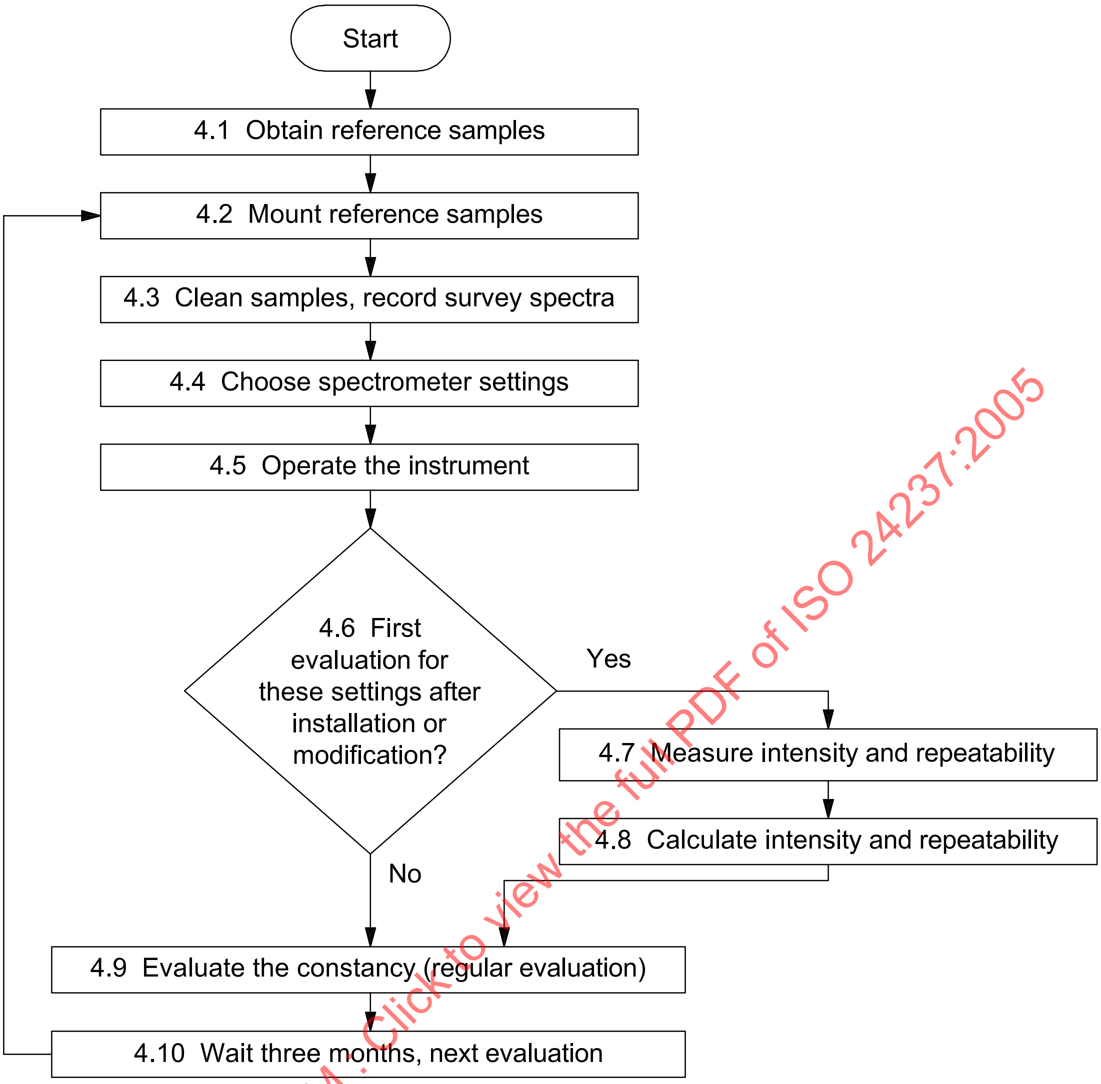


Figure 1 — Flowchart of the sequence of operations of the method
(subclause numbers are given with items for cross-referencing with the body of the text)

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.

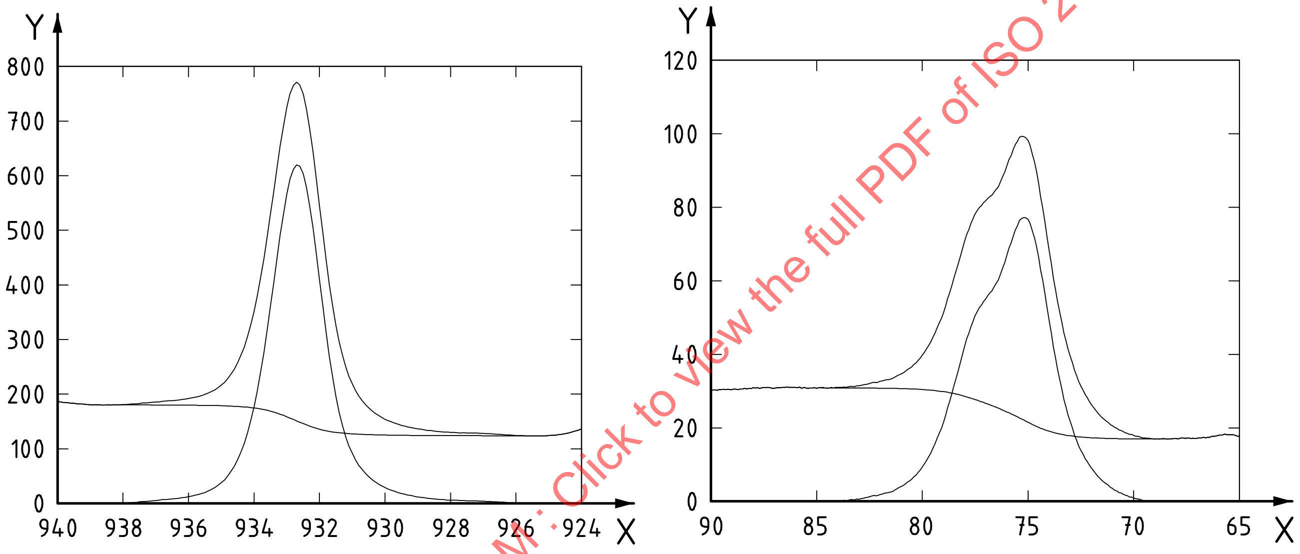
The quality of vacuum necessary here is such that the oxygen and carbon 1s peak heights do not exceed 3 % of the heights of the most intense metal peaks by the time the data acquisition is completed in 4.7 or at the end of the working day (whichever is the earlier).

NOTE 1 Inert-gas ion-sputtering conditions that have been found suitable for cleaning are 1 min of a 30 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·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.



a) Cu 2p$_{3/2}$

b) Cu 3p

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.

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 area intensities, intensity ratios and uncertainties

4.8.1 Confirm that the binding energy of the maximum intensity at the Cu $2p_{3/2}$ peak is in the range 932,7 eV ± 0,1 eV. If it is not, either calculate, to the nearest 0,1 eV, the energy offset to the instrument binding-energy scale, Δ eV, equal to the measured energy minus 932,7 eV, or recalibrate the instrument binding-energy scale using ISO 15472 [1]. Note the action taken and the value, if determined, of Δ.

4.8.2 With each of the seven spectra measured for each peak, determine a Shirley background as indicated in Figure 2, either through curve-fitting an entire measured spectrum or through fits to the regions above and below the peak. Determine and record the peak areas A_{2j} (for each Cu $2p_{3/2}$ spectrum) and A_{3j} (for each Cu 3p spectrum) either through the curve-fitting operation or through subtraction of the Shirley background from the spectrum. The end points to be set for the Shirley background are given in Table 1 for a spectrometer with a binding-energy scale calibrated in accordance with ISO 15472 [1]. If, in 4.8.1, the value of Δ is not zero, add Δ to the values given in Table 1 for use in the instrument. If, in setting these end points, the data system permits averaging the background over a small energy region, select three, four or five points. Record the peak areas A_{2j} and A_{3j} for the Cu $2p_{3/2}$ and 3p peaks, respectively, as well as the number of points used in the end point averaging.

NOTE 1 Details of the Shirley background algorithm are given in Reference [12] and details of the calibration for ISO 15472 [1] are given in Reference [13].

NOTE 2 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.

NOTE 3 The effect of the number of points used for averaging the end points for the Shirley background is discussed in Annex A. There it is shown that this averaging can significantly improve the intensity repeatability.

Table 1 — Values of the binding-energy limits, in eV, for the Shirley background subtraction [11]

Peak	X-ray source		
	Unmonochromated Mg	Unmonochromated Al	Monochromated Al
$2p_{3/2}$	926,4 and 938,4	925,1 and 938,4	925,1 and 938,4
3p	68,2 and 84,6	68,2 and 84,6	67,5 and 84,6

4.8.3 Review the seven values of each of the areas for the two peaks 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.

4.8.4 Calculate, for each spectrum, the ratio A_{3j}/A_{2j} to give a total of three parameters, P_{ij}, for each of the seven pairs of spectra for the $2p_{3/2}$ and 3p peaks. Here i is the identifier of one of the three P_i parameters A_2, A_3 and A_2/A_3 and j is one of the seven individual measurements of that parameter. Calculate, for each of the i parameters, the mean value of P_i and the relative standard deviation, $\sigma(P_i)$, using the equation

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

Record the averages and relative standard deviations for each of the three parameters. If any of the 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 instrument repeatability.

NOTE The relative standard deviations of the three parameters may depend critically on the sample-positioning procedure. In systems with monochromators, for instance, a 10 % intensity change may arise from a sample displacement of 0,3 mm [11].

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 Cu $2p_{3/2}$ and 3p peaks shall be made. If two measurements are made, the order shall be $2p_{3/2}$, 3p, $2p_{3/2}$ and 3p, 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 A_2, A_3 and the ratio A_3/A_2 as described in 4.8.2 and 4.8.4. If two measurements have been made of A_2 and A_3, determine the average values of each parameter and of the ratio A_3/A_2, and use these values for A_2, A_3 and A_3/A_2 in the following analysis.

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

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

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

where $\sigma(P_i)$ has been determined in 4.8.4, 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 [1] and [13].

4.9.4 Plot a control chart for the ratio A_3/A_2, as illustrated in Figure 3. Define the tolerance limits, $\pm\delta$, based on the constancy required for quantitative analysis. Plot these control limits for the chosen percentage change in A_3/A_2 on the relevant control chart, as shown in Figure 3. Add warning limits at $\pm 0{,}7\delta$ and add the confidence limits to the plotted value of A_3/A_2 using the value of $U_{95}(A_3/A_2)$ from Equation (2) or (3).

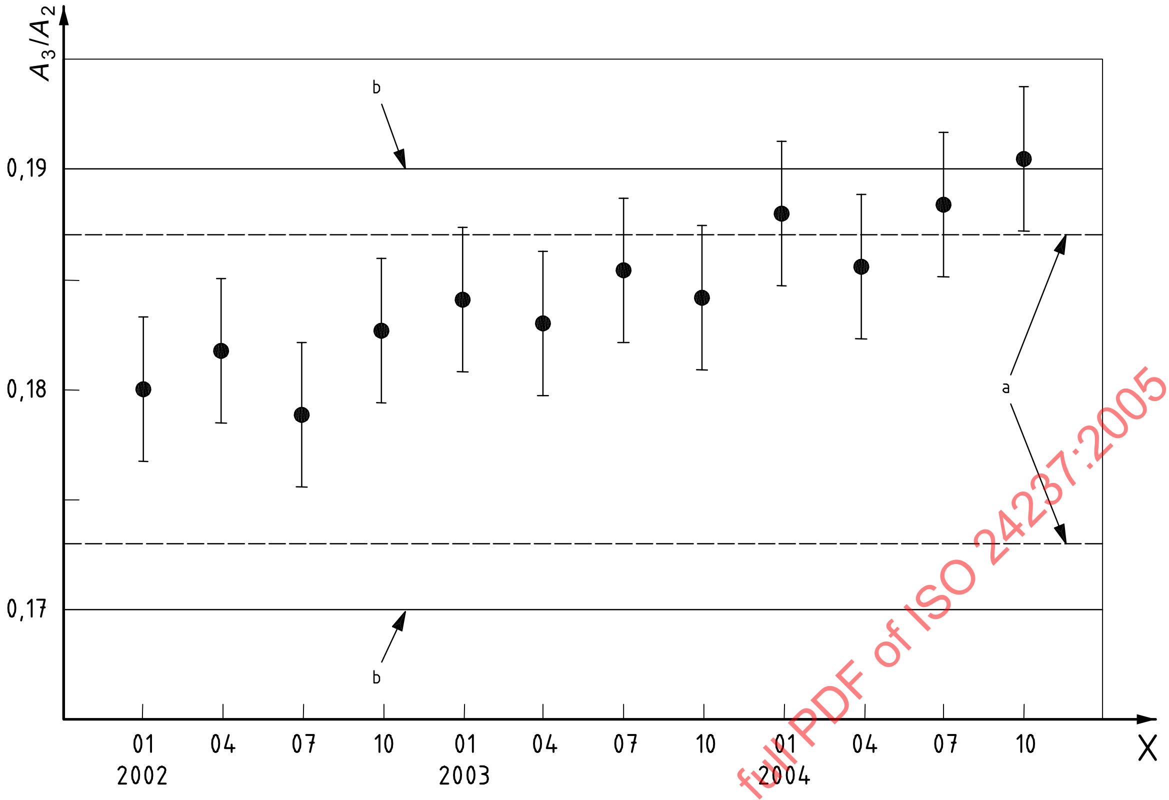
NOTE 1 Typical tolerance limits may be in the range 2 % to 6 % so that, for example, δ in Figure 3 would be in the range 0,004 to 0,012.

NOTE 2 Additional control charts [14,15] for A_2 and A_3, separately, help in the diagnosis of changes in the spectrometer. If these two values decrease with time, while the ratio A_3/A_2 remains relatively constant, it may be either that the X-ray anodes are contaminating or that the detector settings need adjustment. Follow the manufacturer's procedures for checking these items. The detector voltage may need to be increased or the discriminator threshold may need to be reduced.

4.10 Next evaluation

Following any significant modification or adjustment to the instrument, or once every three 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 A_3/A_2 and $U_{95}(A_3/A_2)$ reaches the warning limit, the instrument shall be checked and adjusted or the alignment procedure revised so that a new measurement of A_3/A_2, with its associated $U_{95}(A_3/A_2)$, 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 [16].



Key

X measurement date (month)

01	January
04	April
07	July
10	October

[a] Warning limits.

[b] 95 % tolerance limit.

Figure 3 — Schematic control chart [14,15]**, with tolerance limits set for 6 % drift, to monitor the constancy of the instrumental intensity** (The plotted points are values for A_3/A_2 that, here, illustrate an instrument that has not been adjusted since the start in January 2002. It is first out of tolerance in January 2004 and action should have been taken, since it passed the warning limit in January 2003. The uncertainties shown for each point, $U_{95}(A_3/A_2)$, are for 95 % confidence where $\sigma(A_3/A_2)$ is 0,6 %.)

Annex A
(informative)

Example of calculations and measurements of the intensity repeatability for a commercial X-ray photoelectron spectrometer using unmonochromated Mg Kα X-rays

A.1 Symbols

B	average of B_q and B_r
B_c	number of background counts in channel c
B_q	number of background counts in channel q
B_r	number of background counts in channel r
c	integral channel number, with origin at the start of the scan
N_c	number of counts in channel c
q	lowest channel number that includes the peak of interest
r	highest channel number that includes the peak of interest
t	number of channels over which the background is averaged at each end of the peak range
X	total area of the peak above background
σ	standard uncertainty in X
σ_B	standard uncertainty in the background estimation
$\sigma(X)$	calculated standard uncertainty in X

A.2 Example of calculations and measurements of the intensity repeatability for a commercial X-ray photoelectron spectrometer

In this example, spectra acquired for an instrument at a nominal spectrometer energy resolution of 0,4 eV, analysing an area of 5 mm by 2 mm on the sample surface, were similar to the data of Figure 2. The Cu $2p_{3/2}$ and Cu 3p peak intensities were 1,8 Mcounts and 95 kcounts, respectively. The halfwidths for both peaks were less than those of Figure 2.

Consider first the optimum repeatability where that is limited solely by the uncertainty arising from Poissonian counting statistics. If the peak is defined by number of counts N_c in channels c over the channel range q to r, where the background can be measured as B_c, then the peak area may be written as X where

$$X = \sum_{c=q}^{r} (N_c - B_c) \tag{A.1}$$

Similarly, the standard uncertainty in this measurement, σ, is given by

$$\sigma^2 = \sum_{c=q}^{r} N_c + \sum_{c=q}^{r} B_c \tag{A.2}$$

However, the background B_c is not measured for all of the channels but only for t channels at each end of the peak range. Since the intensities at these ends, B_q and B_r, are approximately the same, the background standard uncertainty, σ_B, is given by

$$\sigma_B^2 = \frac{0{,}5\left(B_q + B_r\right)}{2t} \tag{A.3}$$

The background uncertainty contributions to B_c for each channel in the range $c = q$ to r do not sum randomly in the evaluation of X, i.e. in quadrature as in Equation (A.2), but sum linearly since they are all derived from the same two values, B_q and B_r. Thus

$$\left[\sigma(X)\right]^2 = \sum_{c=q}^{r} N_c + (r-q+1)^2 \frac{(B_q + B_r)}{4t} \tag{A.4}$$

If t were increased to $(r - q + 1)/2$, Equation (A.4) would reduce approximately to Equation (A.2).

Replacing B_q and B_r by their average, B, gives

$$\left[\sigma(X)\right]^2 = \sum_{c=q}^{r} N_c + (r-q+1)^2 \frac{B}{2t} \tag{A.5}$$

Values of the parameters used in this example are shown in Table A.1. This example shows that ΣN_c is approximately $200B$ for the Cu $2p_{3/3}$ peak and approximately $300B$ for the 3p peak. In Equation (A.5), the ΣN_c term is thus less than 1/6 of the second term and contributes less than 8 % to $\sigma(X)$ if

$$t < 6 \tag{A.6}$$

Table A.1 — Measured parameters for the Cu $2p_{3/2}$ and 3p peaks for the uncertainty analysis

Peak	X	B	$r - q + 1$	ΣN_c
$2p_{3/2}$	24 850 000	296 000	121	60 666 000
3p	3 130 000	23 920	165	7 076 800

In general, t will be of the order of 1 to 5 so that, approximately,

$$\sigma(X) = (r-q+1)\left(\frac{B}{2t}\right)^{0{,}5} \tag{A.7}$$

The uncertainty clearly depends rather critically on the chosen value of t. A t value of 11 leads to 3,3 times better uncertainty than a value of 1, irrespective of the absolute signal levels. The calculated relative standard uncertainties for measurements of the Cu $2p_{3/2}$ and 3p peaks for t = 1, 3 and 11 for Equations (A.1) and (A.5) are given in Table A.2. Also given in Table A.2 is the relative standard uncertainty for the measured ratio of the areas of the 3p and $2p_{3/2}$ peaks.