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Procedure for Measuring the Repeatability of Intensity Scales of X-ray Photoelectron Spectrometers

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ABSTRACT

A procedure is provided for measuring the short and long term repeatabilities for the intensity scales of X-ray photoelectron spectrometers. The procedure is valid for all spectrometers using unmonochromated Al or Mg X-rays or monochromated Al X-rays and can be conducted in instruments equipped with an ion gun for sputter-cleaning. The procedure provides values for the short and long term repeatabilities of the intensity at low and high binding energies as well as the intensity ratio for these energies. This procedure is suitable for those conducting work within ISO 9000 or an Accreditation Scheme as well as those wishing to provide valid analytical measurement. It permits the identification of faults and poor operating procedures to enable users to control and improve their measurement quality.

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CONTENTS

	Page
1 INTRODUCTION	1
2 SCOPE	1
3 SYMBOLS AND ABBREVIATIONS	1
4 PROCEDURE FOR CONFIRMING THE CONSTANCY OF THE INTENSITY SCALE	2
4.1 Obtaining the reference sample	2
4.2 Mounting the sample	2
4.3 Cleaning the sample	2
4.4 Choosing the spectrometer settings for which energy calibration is required	2
4.5 Operating the instrument	3
4.6 Recording data	3
4.7 Determination of the peak area, background and uncertainties	4
4.8 Assessment of the constancy of the intensity scale	5
5 CONCLUSIONS	6
ACKNOWLEDGEMENT	7
REFERENCES	8

1 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 binding energies of their core levels, determined from the measured photoelectron spectra, 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 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 organisation. In modern, complex instruments, it is found that, in service, the instrument intensity/energy response function may change as the instrument ages. This procedure describes a simple method for confirming the constancy and repeatability 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 procedure 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 for confirming the constancy of the intensity scale uses a metallic 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 procedure 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 procedure is, however, designed to address the basic common problem of repeatability and of drift of the intensity scale of XPS instruments.

2 SCOPE

This procedure specifies a method for confirming the constancy and repeatability 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 which 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 organisation. The present procedure provides data to confirm the accuracy with which the intensity/energy response function remains constant with instrument usage. Guidance is given to some of the instrumental settings which may affect this constancy.

3 SYMBOLS AND ABBREVIATIONS

- A_2 peak area for the Cu $2p_{3/2}$ peak after removing the Shirley background
- A_3 peak area for the Cu 3p peak after removing the Shirley background
- B_1 background intensity for the Cu $2p_{3/2}$ peak at the lower binding energy limit given in Table 1
- B_3 background intensity for the Cu 3p peak at the lower binding energy limit given in Table 1
- one of the seven parameters, P

j	one of the seven individual measures of the parameter P_i
P_i	parameter representing any of $A_2, A_3, B_2, B_3, A_3/A_2, A_2/B_2$ and A_3/B_3
P_{ij}	the j th measure of parameter P_i
$\bar{P}$	mean value of the seven measures of P_i
$U_{95}(P)$	uncertainty of the mean value, P , at 95% confidence
δ	value for the tolerance limit for A_3/A_2 for compliance at 95% confidence level (set by the analyst)
σ_i	repeatability standard deviation of the parameter P_i with mean value $\bar{P}_i$

4 PROCEDURE FOR CONFIRMING THE CONSTANCY OF THE INTENSITY SCALE

4.1 OBTAINING THE REFERENCE SAMPLE

For the calibration of X-ray photoelectron spectrometers use a sample of polycrystalline Cu of at least 99.8% purity which, for convenience, is usually in the form of foil typically 10 mm by 10 mm, 0.1 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.

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.

4.3 CLEANING THE SAMPLE

4.3.1 Achieve ultra-high vacuum and clean the sample by ion sputtering to reduce the contamination until the heights of the oxygen and carbon 1s signals 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. The quality of vacuum necessary here is such that the oxygen and carbon 1s peak heights shall not exceed 3% of the heights of the most intense metal peaks by the time you have reached completion of 4.8 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 minute of a 30 μ A beam of 5 keV argon ions covering 1 cm² of the sample.

NOTE 2 Example Cu XPS spectra may be found in references (1) to (4).

4.3.2 Try to conduct all relevant parts of this procedure in one working day. If more than one day is required, confirm the cleanness of the Cu at the start of each day's work.

4.4 CHOOSING THE SPECTROMETER SETTINGS FOR WHICH ENERGY CALIBRATION IS REQUIRED

Choose the spectrometer operating settings for which the energy calibration is required. The calibration procedure from 4.4 to 4.8 shall be repeated for each X-ray source and combination of spectrometer settings of pass energy, retardation ratio, slits, lens settings etc for which confirmation is required.

NOTE The designs of spectrometers and their circuits vary and an intensity/energy response function for one combination of lens settings, slits and pass energy⁵ will not necessarily be valid for any other setting of the lens, slits and pass energies. Many spectroscopists make accurate measurements under one optimum set of conditions and then only that set of analyser conditions needs calibration. Any calibration made is only valid for the combination of settings used.

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 optimisations or checks described by the manufacturer are conducted prior to this calibration. Make a list of parameters that you set and record them.

NOTE 1 Many manufacturers recommend that the control and high voltage electronics are switched on for at least 4 hours before conducting any work where accuracy is important. It may also be necessary to have operated the X-ray anode for a period, for example 1 hour, before making accurate measurements.

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 rates⁶ or incorrect detector voltages^{6,7} can cause peak distortions which lead to erroneous peak intensity measurements.

4.6 RECORDING DATA

4.6.1 Set the Cu sample at the analytical position. Use the manufacturer's or other documented sample positioning procedure. With appropriate settings to give a dwell time initially of 1 second per channel and channel intervals as close to 0.1 eV as practicable, record the regions of the Cu 2p_{3/2} and Cu 3p peaks as shown in Figure 1. Do not change any operating conditions between the spectra except the place on the binding energy scale. If the counts at the Cu 3p peak are less than 100000, better results may be obtained by increasing the dwell time for both peaks. The dwell time finally chosen will be a compromise between high signal intensity and the duration of the work. Record the parameters you set.

NOTE 1 The sample positioning procedure is critical for obtaining good measurements. Ensure that your procedure is clear and complete. The positioning procedure should provide confidence that electrons from the Cu sample and only the Cu sample are analysed.

NOTE 2 Alignment problems can be particularly severe with monochromated X-ray sources⁸

4.6.2 If this is the first time that this procedure is used, remove the sample from the analytical position and then replace it and repeat 4.6.1. 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 measures of each peak have been recorded.

4.7 DETERMINATION OF THE PEAK AREA, BACKGROUND AND UNCERTAINTIES

4.7.1 With each peak subtract a Shirley⁹ background and measure the peak areas. The end points set for the Shirley background are given in Table 1. If, in setting these end points, your data system permits averaging the background over a small energy region, select 3, 4 or 5 points. Record the peak areas A_2 and A_3 for the Cu $2p_{3/2}$ and 3p peaks, respectively, as well as the number of points you use in the end point averaging.

NOTE Your 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 product of the values 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 recording in compliance with 4.6, these differences are unimportant. Record the dimensions in which the areas are determined.

4.7.2 Measure the intensity of the background at the end point of lower binding energy given in Table 1 for the Shirley⁹ background and record the background values B_2 and B_3 for the Cu $2p_{3/2}$ and 3p peaks, where the subscripts 2 and 3 relate to the $2p_{3/2}$ and 3p levels, respectively.

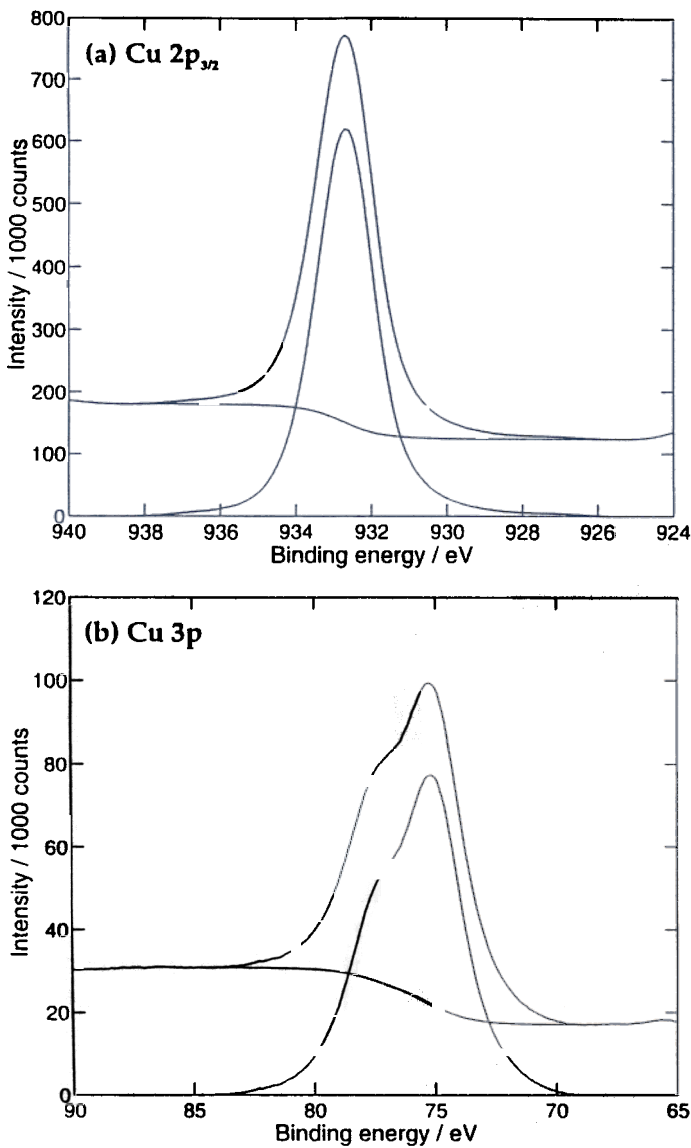


Figure 1 - Example spectra using unmonochromated Al X-rays of (a) Cu $2p_{3/2}$ and (b) Cu 3p peaks. The upper curve in each case is the recorded data, the smooth sigmoidal curve shows the Shirley background and the final curve the peak after subtraction of the Shirley background.

Table 1- Values of the binding energy limits, eV, for the Shirley⁹ background subtraction

Peak	X-ray source		
	unmonochromated Mg	unmonochromated Al	monochromated Al
2p _{3/2}	926.5 and 938.5	925.2 and 938.5	925.2 and 938.5
3p	68.3 and 84.7	68.3 and 84.7	57.6 and 84.7

4.7.3 If this is the first time that this procedure is used you will have seven values of each of the two area and two background parameters. Calculate, for each spectrum the ratios A_3/A_2 , A_2/B_2 and A_3/B_3 to give a total of seven parameters, P_i , for each of the seven pairs of spectra for the 2p_{3/2} and 3p peaks. Here i represents one of the parameters selected (eg A_3/A_2), and j one of the seven individual measures of that parameter. Calculate for each of the i parameters, the mean value $\bar{P}_i$ and the relative standard deviations, σ_i , using the equation:

$$\sigma_i^2 = \sum_{j=1}^7 \frac{(P_{ij} - \bar{P}_i)^2}{6\bar{P}_i^2} \tag{1}$$

Record each of the seven averages and seven relative standard deviations for each parameter. If any of the seven relative standard deviations exceeds a value of 3%, the sample positioning procedure may need to be reviewed.

NOTE The relative standard deviations of the seven parameters may depend critically on sample positioning procedure. In systems with monochromators, for instance, a 10% intensity change may arise from a sample displacement of 0.3 mm from the optimum position⁸.

4.7.4 The relative uncertainty, $U_{95}(P_i)$, of single measures of any of the parameters P_i is given by

$$U_{95}(P_i) = 3.7\sigma_i \tag{2}$$

NOTE The derivation of equation (2) may be found in references (10) and (11).

4.8 ASSESSMENT OF THE CONSTANCY OF THE INTENSITY SCALE

4.8.1 Plot control charts for A_2 , A_3 , B_2 , B_3 the ratios A_3/A_2 , A_2/B_2 and A_3/B_3 , as illustrated in Figure 2. For quantitative analysis it is the ratio A_3/A_2 that is important. Define a percentage limit, $\pm\delta$, for the consistency with which you wish to express quantitative analysis. Plot these control limits for your chosen percentage change for A_3/A_2 on the relevant control chart, as shown in Figure 2. Add warning limits at $\pm0.7\delta$ and add the error bars to the plotted value of A_3/A_2 for the value of $U_{95}(A_3/A_2)$ from equation (2).

4.8.2 Following any significant modification or adjustment to the instrument, or once a month that the instrument is in use repeat 4.1 to 4.7, using the same conditions, 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 adjusted so that a new measurement of A_3/A_2 , with its error bar, is obtained fully within the acceptance zone.

NOTE 1 The control charts^{12,13}, for A_2 and A_3 separately, help you to diagnose changes in the spectrometer. If these two values decrease with time, while the ratio A_3/A_2 remains relatively constant, it may either be that the X-ray anodes are contaminating or that the detector settings need adjustment. Follow the manufacturers procedures for checking these items. The detector voltage may need increasing or the discriminator threshold reducing.

NOTE 2: The control charts for B_2 and B_3 as well as A_2/B_2 and A_3/B_3 help to diagnose changes in the X-ray anode that lead to unwanted X-rays striking the sample (eg cross talk in dual anode systems, oxygen contamination X-rays and copper substrate X-rays) or excess dark current from the detector system. Excess dark current may be caused by a discriminator setting that is too low. Unwanted X-rays may be checked by studying the ghost peaks visible on a gold sample⁵.

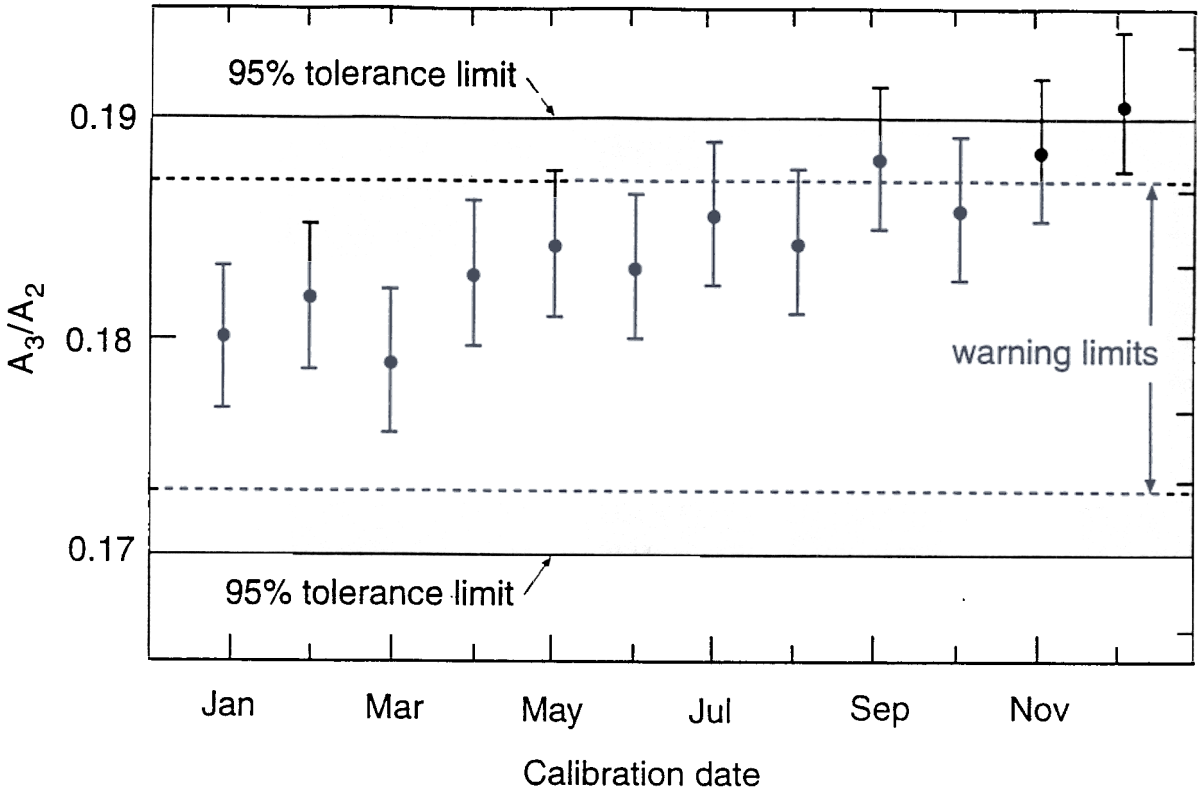


Figure 2 - A schematic control chart^{12,13}, with tolerance limits set for 5,5% drift, to monitor the calibration status of an instrument. The plotted points represent the values for A_3/A_2 , which, here, are shown to illustrate an instrument that has not been adjusted since the start in January. It is first out of calibration in September and should, since it has passed the warning limit, have been recalibrated in May. The uncertainties shown for each point are, $U_{95}(A_3/A_2)$, for 95% confidence where $\sigma(A_3/A_2)$ has a relative value of 0,5%.

5 CONCLUSIONS

A procedure is described, suitable for analysts operating within ISO 9000 or an Accreditation Scheme or those wishing to provide valid analytical measurement. The procedure allows the analyst to define, for their spectrometer, the short and long term repeatabilities for the intensity scale of X-ray photoelectron spectrometers at both low and high binding energies. Both absolute and relative short term repeatabilities are determined. The latter is important for quantitative analysis and should, under normal circumstances be less than 1%. The repeatabilities for the absolute values may exceed this figure but provide data on the quality of the sample alignment procedure being used.

The long term changes in these parameters are monitored and these show directly any faults arising from contamination of the X-ray source and degradation of the electron detector. Plots on control charts with warning limits allow the analyst to provide valid analytical measurements with confidence.

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