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Surface chemical analysis — X-ray photoelectron spectroscopy — Procedures for assessing the day-to-day performance of an X-ray photoelectron spectrometer

Analyse chimique des surfaces — Spectroscopie de photoélectrons X — Modes opératoires d'évaluation de la performance au jour le jour d'un spectromètre de photoélectrons X

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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 16129 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

Introduction

XPS instruments are complex, and unsatisfactory performance is not always obvious to an operator. It is therefore necessary to provide a test for the correct operation of the system that can be performed regularly and frequently without interfering excessively with the normal work of the laboratory.

A full diagnostic test can require many hours or even days; such a test can be appropriate only when the instrument is known to have a fault that needs to be remedied or following a major maintenance procedure. Data acquired before a problem is uncovered become suspect if the spectrometer has not been routinely tested, leading to a loss of confidence in those data. If a regular check of the instrument is made, changes in performance can be monitored and corrective action taken in good time to ensure that the data supplied are fit-for-purpose. In the event that a serious fault is uncovered, then only the data since the last check can be in doubt and need to be repeated.

The purpose of this document is to provide a user with a procedure which is not excessively time-consuming so that it is capable of being completed on a regular and frequent basis, daily if required. The user will then gain an awareness of the current characteristics of the instrument so that a decision can be made as to whether or not a more complete and time-consuming action is required to return the instrument to a satisfactory level of performance.

This procedure is intended to be applied to an XPS instrument that has been correctly calibrated and aligned in accordance with ISO standards or manufacturer’s instructions. It is designed to highlight aspects of the instrument’s characteristics that differ significantly from those that were measured immediately following the calibration procedure. The procedure does not show how the instrument can be returned to its original state. Instead, it guides the user to possible areas of concern. The procedure provides data that can be used in control charts, allowing trends to be observed and acted upon before data quality deteriorates to an unacceptable level for the needs of the analyst.

Surface chemical analysis — X-ray photoelectron spectroscopy — Procedures for assessing the day-to-day performance of an X-ray photoelectron spectrometer

1 Scope

This International Standard is designed to allow the user to assess, on a regular basis, several key parameters of an X-ray photoelectron spectrometer. It is not intended to provide an exhaustive performance check, but instead provides a rapid set of tests that can be conducted frequently. Aspects of instrument behaviour covered by this International Standard include the vacuum, measurements of spectra of conductive or non-conductive test specimens and the current state of the X-ray source. Other important aspects of the instrument performance (e.g. lateral resolution) fall outside the scope of this International Standard. The standard is intended for use with commercial X-ray photoelectron spectrometers equipped with a monochromated Al Kα X-ray source or with an unmonochromated Al or Mg Kα X-ray source.

2 Terms and definitions

For definitions of the spectroscopy terms used in this International Standard, the reader is referred to ISO 18115-1[10].

The following abbreviations are used:

FWHM	full width at half maximum
PET	poly(ethylene terephthalate)
PTFE	polytetrafluoroethylene
XPS	X-ray photoelectron spectroscopy

3 Initial approach

Most instruments are fitted with a vacuum gauge or gauges. These shall be read frequently and the reasons for large variations understood. A large increase in the pressure can be due to the properties of a test specimen inside the instrument, a fault in the pumping system, an increase in the temperature of the vacuum system or a leak.

Similarly, most instruments have status indicators, either for the system as a whole or for sub-systems or modules. Examples of such indicators include water flow rate, data system communications status and electrical power. These can be visible as part of the instrument hardware itself or on screen through an instrument control (data acquisition) system. Such indicators again shall be carefully monitored, along with any measured values that are reported.

4 Initial instrument calibration, alignment and assessment

Before undertaking the procedure described in the following clauses, it is essential that the instrument be calibrated and aligned to an optimum performance level. This is achieved by following the relevant International Standards (References [5] to [9]) or the manufacturer's instructions. Choose the two settings of the instrument operating conditions that are needed to obtain survey spectra and high-resolution spectra. These should be settings that you regularly use and will be described in Clause 6. Since this is a rapid check, only these two settings are chosen, but these can show faults that are common to all settings. These settings shall always be used in future checks unless they are later found to be less effective than other settings. If the designated settings are changed, data at both the new and old settings shall be recorded at the time of change.

5 Test specimen selection

5.1 General information

Three types of test specimen are required for the full procedure described in this International Standard: a conductive specimen, a non-conductive specimen and a specimen suitable for assessing the quality of the X-ray beam (e.g. X-ray spot size, shape and uniformity). The conductive specimen provides information that the basic energy and intensity calibrations of the instrument are consistent from day to day. When using a non-monochromatic X-ray source having more than one anode material, the survey spectrum shall be examined to check for peaks arising from specimen irradiation from the anode that is not currently being used (this is due to “cross-talk” within the X-ray source). Similarly, when anode coatings wear, X-rays can be emitted from the substrate material, which is often copper. The survey spectrum shall be examined for peaks arising from X-rays produced from the substrate material. When using a magnesium anode, there can be peaks due to radiation from O Kα arising from oxidation of the anode coating. These peaks are often called ghost peaks. Table 1 shows the approximate positions of commonly encountered ghost peaks when acquiring an XPS spectrum from silver using Mg Kα radiation.

Table 1 — Examples of approximate positions, on the binding-energy scale, of frequently encountered ghost peaks in a silver spectrum collected using a magnesium anode

(The photon energy of Mg Kα radiation is 1 253,6 eV)

Radiation giving rise to ghost peaks	**Photon energy** eV	**Possible origin of radiation**	**Peak position on the binding-energy scale** eV
Al Kα	1 486,6	From second anode in a twin anode source	135
O Kα	524,9	From oxide on the surface of the magnesium anode.	1 097
Cu Lα	929,7	From anode substrate	692

The non-conductive specimen is required to confirm that the charge compensation system is operating satisfactorily when non-conducting specimens are being analysed. The nature of the specimen that is required for assessing the X-ray beam depends upon the type of instrument being used. If the analysis position is visible during the normal operation of the instrument, the quality of the focus and the alignment of the X-ray beam from a monochromated source can be assessed using a phosphor specimen. If the analysis position is not visible in normal operation and the instrument is capable of imaging, a uniform (there should be no features visible in an image of the specimen when the instrument is in its optimum condition), conductive specimen can be used; this can be the conductive specimen mentioned above. All specimens used shall be large enough to completely fill the defined analysis region of the spectrometer.

5.2 The conductive specimen

A suitable conductive specimen shall be selected. This should be a material that produces several peaks in the photoelectron spectrum. Preferably, these peaks should be widely spaced in binding energy. The specimen shall be one whose surface can be cleaned easily by sputtering with noble-gas ions.

A pure (≥ 99,8 %) specimen of silver foil is suitable for this measurement and is recommended. If, however, a different material is commonly analysed in the user’s laboratory and conforms to the above criteria, this may be used instead. For convenience, it is assumed here that silver has been selected as the conductive reference material. The same conductive specimen shall be used for all measurements.

5.3 The non-conductive specimen

Non-conductive specimens, and conductive specimens with a non-conductive surface layer, charge under the X-ray flux, resulting in shifts in the peak binding energies relative to the uncharged state.

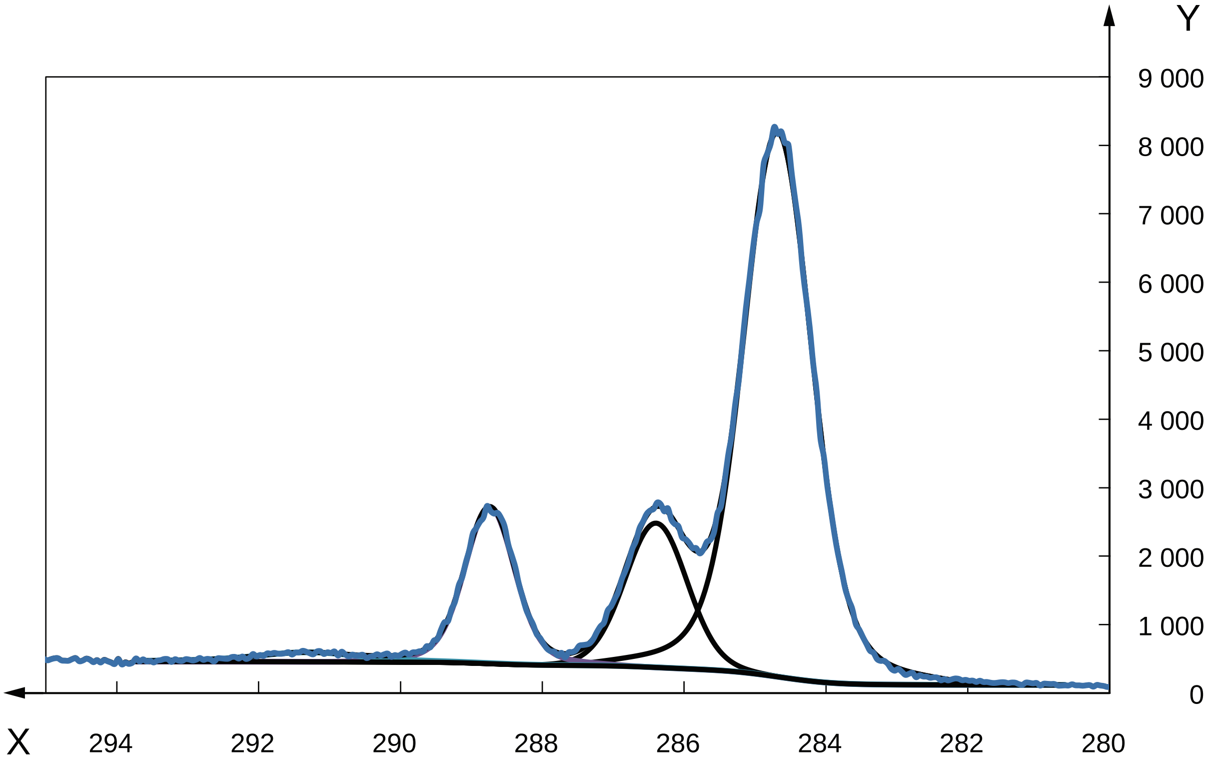
Select a non-conductive material often studied in your laboratory, for which you have a good stock and which is capable of being maintained with a surface in a reproducible state. If you are unsure of a material to use, examples that have been found to be useful for tests of instrumental performance are shown in Table 2. Examples are given with different forms. You might wish to select a specimen with a form similar to that of the specimens most commonly analysed with the instrument. Care shall be taken to select a material which does not exhibit degradation under the X-ray beam during the analysis.

Table 2 — Examples of non-conductive specimens that may be used for this procedure

Material	Form	Cleaning
PET	Sheet or fibre	Not required
Laboratory filter paper	Sheet	Not required

Poly(ethylene terephthalate) (PET) has long been used to evaluate both the energy resolution and the effectiveness of charge control in XPS. It shows a structure of three C 1s peaks together with shake-up intensity. The minimum between the peak at the lowest binding energy and the adjacent peak at a separation of ~1,5 eV is highly sensitive to the combination of the instrumental resolution and the uniformity of the charge correction. The ease of achieving suitable and consistent energy resolution will depend on both the operator and the instrumental capability.

An example of the C 1s spectrum from PET is shown in Figure 1.



Key

X binding energy (eV)

Y number of counts

Figure 1 — Example of a C 1s spectrum from PET

More recently, careful studies on cellulose-based materials (paper) have indicated that these are suitable materials for use in this test (see References [1] and [2]). It has been shown that laboratory filter paper[1] provides reproducible XPS spectra. If using paper, avoid releasing loose fibres into the instrument as they can cause a deterioration in performance.

Alternatively, the specimen can be one with which the user is familiar. It shall be a material that provides a reliably reproducible spectrum with little or no specimen preparation.

5.4 Specimen for assessing the X-ray source

A phosphor specimen is suitable for those instruments that are fitted with a monochromatic X-ray source and in which the analysis position is visible, preferably with a microscope and camera. The phosphor specimen should be as flat and uniform as possible and produce easily visible light under the X-ray bombardment.

Not all phosphor specimens are vacuum-compatible and not all phosphor materials are designed for optimum excitation by X-rays. Ensure that a phosphor specimen of suitable quality is obtained from the supplier of the instrument or from another reputable supplier.[2]

The uniform conductive specimen shall be used if an optical image of the analysis position is not available during the normal operation of the instrument and the instrument is capable of producing X-ray-induced images. The specimen shall be flat and of uniform composition over an area greater than the maximum area that is imaged in the instrument. The silver specimen described in 5.2 would be suitable for this purpose.

6 Collection of reference data

6.1 General information

Once fully calibrated and functioning correctly at the designated settings described in Clause 4, the instrument shall be used to collect a set of reference data. The specimens and the way in which data shall be collected are described in this clause. If the spectrometer is routinely used for conductive specimens, follow the procedure described in 6.2 regularly and that in 6.3 occasionally, whereas for instruments used mainly for insulating specimens follow the procedure described in 6.3 regularly and that in 6.2 occasionally. The interpretation of “regular” and “occasional” depends on the use of the instrument and its behaviour. If data are critical, “regular” might need to be interpreted as daily. For modern instruments used daily in normal use, “regular” may be interpreted as “an interval of one week” and “occasionally” as “a period of one month”, but it must be stressed that the appropriate interval does depend on the instrument and its intended use. Document your reasons for your choice of the intervals. The control charts of Clause 9 will also be useful in determining the frequency at which checks should be made.

All electron optics have an optimum focal point. The specimens shall be at the common focal point of the analyser, the ion gun (if used), the neutralizer (if used) and the X-ray source. If the spectrometer is equipped with an X-ray source whose height above the specimen is adjustable, the X-ray source shall be in the same position for each test.

6.2 Rapid test of the instrument using a conductive specimen

6.2.1 Specimen mounting and pre-treatment

Mount the specimen on an appropriate specimen holder. It is important that the specimen be in good electrical contact with the specimen holder. Place the specimen in the optimum analysis position in the spectrometer.

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1) A suitable type of filter paper is S&S 589 Blue Ribbon Ashless, which can be obtained from Whatman plc, Springfield Mill, James Whatman Way, Maidstone, Kent, ME14 2LE, UK, or one of this company’s international distributors. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

2) Suitable phosphor specimens can be obtained from a number of suppliers, including TMS Vacuum Components, Unit 21 Stirling Road, Castleham Industrial Estate, Hastings, East Sussex, TN38 9NP, UK. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this supplier.

Take care to follow the manufacturer's recommendations for positioning the specimen at the focal point, or use whatever documented procedure is required for analysis. Ensure that all specimen stage parameters (X, Y, Z, rotation and tilt) are correctly set.

If the instrument is fitted with a noble-gas ion gun, the specimen surface shall be cleaned by ion etching, using conditions commonly found to be successful for this purpose and which remove a minimum amount of material. A typical sputtering fluence for cleaning silver is 20 $A \cdot s/m^2$. A typical value for the ion energy is 3 keV. Excessive sputtering leads to significant roughening of the specimen so that it needs frequent replacement.

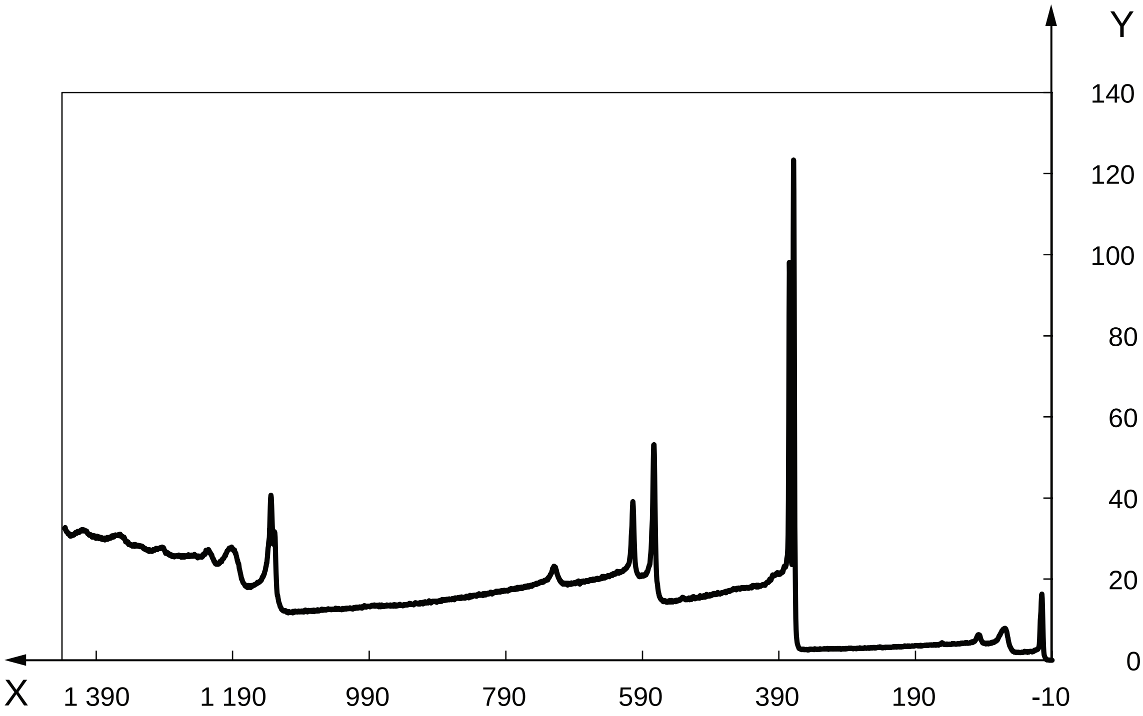
6.2.2 Survey spectrum

A survey or wide-scan spectrum shall be collected over the binding-energy range from −10 eV to a value within 50 eV of the value of the photon energy used to irradiate the specimen (e.g. a binding energy of 1 437 eV for Al Kα X-rays) or to whatever maximum range is available. The analyser shall be operated in the constant analyser energy (CAE) mode. The data shall be collected in energy steps no wider than 0,5 eV. The dwell time at each energy step shall be sufficient to collect at least 10^5 counts in at least one energy channel in an XPS peak. In the case of silver, this will be the Ag $3d_{5/2}$ peak at ~368 eV binding energy. Bear in mind that it is the number of counts that is important here, not the count rate. The acquisition time depends upon the sensitivity of the instrument, so the minimum dwell time per channel is given by 10^5 counts divided by the signal strength in counts per second. On modern instruments, such a spectrum will be collected in a few minutes. Care shall be taken to avoid selecting conditions that would result in count rates that are high enough to induce nonlinearity in the detector.

The pass energy of the analyser used for this spectrum should be the same as that typically used for a survey spectrum. If using monochromatic Al Kα X-rays, it is likely that the pass energy chosen would result in a full width at half-maximum (FWHM) amplitude of between 1,5 eV and 2,5 eV for the Ag $3d_{5/2}$ peak from a clean silver foil. If using non-monochromatic Al or Mg Kα X-rays, it is likely that the pass energy chosen would result in an FWHM of between 1,5 eV and 3,0 eV.

The anode power in the X-ray source should be the same as that typically used for analysis.

Once collected, the spectrum shall be examined, first to ensure that there is a tolerably low level of detectable contamination present on the surface. The presence of a significant quantity of adventitious carbon indicates that the surface is contaminated. The height of the peak due to C 1s should be less than 1 % of the height of the peak due to Ag $3d_{5/2}$. If the carbon peak is too intense, the cleaning procedure shall be repeated and the spectrum collected again. Such a spectrum is shown in Figure 2. In this spectrum, the FWHM of the Ag $3d_{5/2}$ peak is 2,4 eV.



Key

X binding energy (eV)

Y kcounts

Figure 2 — An example of a survey spectrum from a clean silver specimen to be used as a reference
(The spectrum was collected using Al Kα radiaton from an X-ray monochromator)

The survey spectrum shall be examined and the following data recorded to provide reference values for control charts:

a) The number of counts in the channel having the greatest number of counts.

b) The energy position of the channel having the greatest number of counts on the binding-energy scale.

c) The FWHM amplitude of the Ag $3d_{5/2}$ peak.

d) The average number of counts per channel in a background region of the spectrum. For example, the range could be from 450 eV to 460 eV. This range includes the inelastic tail from the Ag 3d peaks and so the background is relatively high, allowing greater precision in the measurement of the number of counts.

e) The total number of counts in all channels in the binding-energy range from –5 eV to –10 eV.

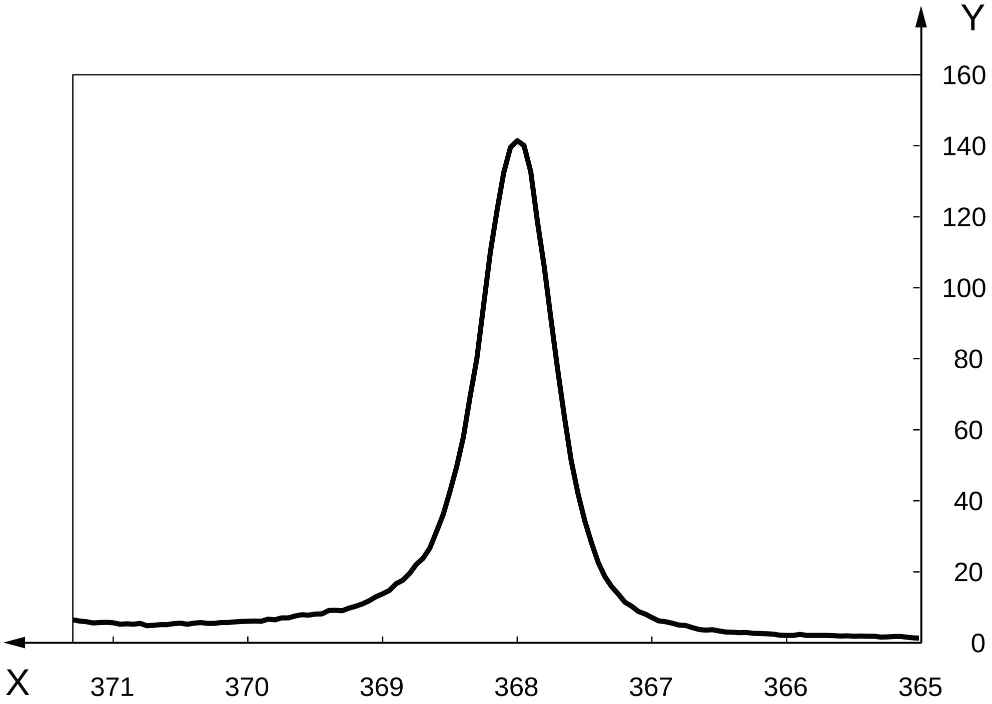
f) The intensity of any ghost peaks present. This is only required if a non-monochromatic X-ray source is being used.

It is not necessary to include the intensity of the C 1s peak in a control chart, but the height of the C 1s peak above its local background shall be noted as it provides a record of the state of the specimen at the time of the measurement.

When measuring the background intensity from a spectrum produced using a non-monochromatic source, care shall be taken to avoid those areas of the spectrum in which ghost or satellite peaks might be present.

6.2.3 High-resolution spectrum

A high-resolution or narrow-scan spectrum shall then be recorded of the Ag $3d_{5/2}$ peak. At a minimum, this spectrum shall be recorded over the binding-energy range from 365 eV to 372 eV. The spectrum shall be collected with an energy step size not larger than 0,05 eV and the dwell time shall be such that there are at least 10^4 counts in the channel containing the greatest number of counts. The acquisition time will depend upon the sensitivity of the instrument, so the minimum dwell time per channel is given by 10^4 counts divided by the signal strength in counts per second. For this spectrum, the pass energy of the analyser should be set to a value normally used by the analyst for the collection of high-resolution spectra. It is anticipated that the FWHM of the Ag $3d_{5/2}$ peak will be in the range 0,55 eV to 0,65 eV if an X-ray monochromator is used and between 0,8 eV to 1,0 eV if a monochromator is not used. Figure 3 shows an example of such a spectrum.



Key

X binding energy (eV)

Y kcounts

Figure 3 — High-resolution Ag $3d_{5/2}$ spectrum from clean silver using Al Kα radiaton from an X-ray monochromator

Once collected, the spectrum shall be examined and the following parameters recorded:

a) The maximum peak height after subtraction of a suitable background (often a Shirley background).

b) The ratio of the intensity of this peak to the intensity of the same peak in the survey spectrum.

c) The peak energy in the binding-energy scale (peak fitting could be used to determine this parameter).

d) The FWHM of the peak above the background chosen.

e) The signal-to-background ratio, defined as the number of counts in the peak maximum divided by the average number of counts in a range of channels remote from the peak. In Figure 3, a suitable range would be those channels between 365,5 eV and 366,5 eV binding energy.

These measurements will be used as reference values in control charts

6.3 Rapid test of the instrument using a non-conductive specimen

6.3.1 Specimen mounting and positioning

Mount and position the specimen in the spectrometer as described for the conductive specimen in 6.2.1. If cleaning with an ion beam is appropriate for the specimen type chosen, sputter the specimen using conditions that have been proved to be effective.

6.3.2 High-resolution spectrum

A high-resolution spectrum shall be recorded over a representative peak in this spectrum. If the specimen is organic in nature, this is likely to be the C 1s peak. The scan range for the spectrum shall be sufficient to include the peaks from all of the chemical states in the material, including any shake-up peaks, if present, and shall allow a background to be fitted. The analyser pass energy should be that customarily used for this type of measurement. It is anticipated that an Ag $3d_{5/2}$ peak from silver foil, if acquired at this pass energy using monochromatic X-rays, would have an FWHM amplitude in the range 0,55 eV to 0,65 eV, or within the range 0,8 eV to 1,0 eV if a monochromator is not used. For the non-conductive specimen, the method normally used for charge compensation or charge control shall be applied when acquiring this spectrum. The operating conditions used in the charge compensation system shall be recorded (e.g. the current and electron energy settings of the flood gun).

The peak-fitting routine normally used shall then be applied to the spectrum. The parameters and constraints used in the fitting routine shall be recorded. The intensity, FWHM amplitude and peak shape parameters, such as the Gauss/Lorentz ratio, shall be recorded for each peak in the fitted spectrum. It is anticipated that these parameters will be readily available from the software used for the peak fitting.

Having acquired the spectrum, the peak intensities, peak widths and peak positions shall be recorded as reference data for a control chart.

6.4 Rapid test of the X-ray source using a phosphor specimen

This subclause applies only when the analysis position is visible to the operator during the normal operation of the instrument. With the phosphor specimen in the normal analysis position and the X-ray source switched on, the visible light emitted by the phosphor shall be observed. If there is a facility for selection of the X-ray spot size, then the largest spot size shall be selected. If there are visible non-uniformities in the spot of emitted light, the phosphor specimen shall be moved in a plane that keeps part of the phosphor specimen at the analysis position while the specimen is being observed. If the observed non-uniformity moves with the specimen, then the non-uniformity is due to the phosphor and shall be neglected. If the non-uniformity remains in the same position, then the cause is likely to be due to some fault in the monochromator (source, anode or crystal).

The size and shape of the spot of emitted radiation shall be noted and, if possible, an image of the spot recorded. The magnification of the image shall also be recorded. If it is possible to change the size of the X-ray spot, a similar image shall be recorded at the minimum X-ray spot size and one intermediate spot size. If the spot of emitted radiation is elliptical, then the orientation of the major and minor axes of the ellipse shall be noted.

6.5 Rapid test of the X-ray source using a uniform conductive specimen

For an instrument without the capability of acquiring an optical image of the specimen at the analysis position, the quality of the X-ray beam shall be assessed by acquiring an image of a uniform conductive specimen. Specimen mounting and pre-treatment for this type of specimen are described in 6.2.1.

The type of image depends upon the spectrometer. The image might be a parallel image acquired from a peak in the XPS spectrum (e.g. Ag $3d_{5/2}$). Alternatively, the image might be an X-ray-induced secondary-electron image on an instrument in which the X-ray beam scanning is possible. In either case, the imaged area shall be the maximum possible for the instrument. The instrumental conditions used to obtain the image shall be recorded.

Once acquired, the image shall be assessed for uniformity. If there are visible non-uniformities in the image, the specimen shall be moved in a plane that keeps part of the specimen at the analysis position and the image acquired again. If the observed non-uniformity moves with the specimen, then the non-uniformity is due to the specimen and shall be neglected. If the non-uniformity remains in the same position on the image, then the cause is likely to be due to some fault in the monochromator (source, anode or crystal) or, in the case an image acquired in the parallel-imaging mode, the imaging detector.

If parallel imaging is used to collect the data and the imaged area is larger than the X-ray spot size, it might be possible to determine and record the size and shape of the spot.

7 Collection of subsequent performance data

The same experimental procedure shall be used to collect subsequent performance data as that used to collect the initial reference data described in Clause 6. The X-ray anode power, spectrum scan range, analyser pass energy, energy step size, and dwell time at each step for acquisition of spectra shall be the same as for the corresponding values used for the reference data set. The data so collected will be referred to as the subsequent performance data.

The performance checks shall be repeated at regular and frequent intervals as described in 6.1. Each set of subsequent performance data shall be compared with the initial reference performance data as described in Clauses 8 and 9. If the subsequent performance data differ significantly from the initial reference performance data for one or more of the parameters listed in Clause 9, the user shall investigate the cause or evaluate the consequences for data collected from other specimens. If the subsequent performance data are consistent with the reference performance data, the subsequent performance data shall be added to the reference performance data. That is, the reference performance data set and the sets of subsequent performance data will become a performance record for the XPS instrument for the time period over which satisfactory performance has been documented.

It is unnecessary to collect a complete set of subsequent performance data on every performance check. The subsequent performance data to be collected will be determined by the type of analysis likely to be undertaken between the times when subsequent performance data are collected. For example, if it is unlikely that data are to be acquired from non-conductive specimens in the analyst’s laboratory, then it is unnecessary to collect subsequent performance data from the non-conductive specimen.

8 Analysis of the performance data

8.1 General information

The simple, rapid measurements described here are capable of yielding a great deal of information about the condition of an XPS instrument and the way in which its condition is changing with time. However, a rapid test is rendered worthless if complex data analysis routines make the process time-consuming.

8.2 Survey spectrum

The parameters listed in 6.2.2 for the survey spectrum shall be entered onto one or more control charts.

If a non-monochromatic X-ray source is used, the survey spectrum shall be examined for the presence of ghost peaks arising from two sources. The first is “cross-talk” which might occur if a dual-anode X-ray source is being used. The ghost spectrum is the XPS spectrum that would be produced by X-rays from the anode that was not selected for collection of the survey spectrum. For example, if a magnesium anode is in use and the second anode is aluminium, the spectrum from pure silver is not expected to have a significant Ag $3d_{5/2}$ peak at approximately 135 eV on the binding-energy scale. If it has, this would indicate cross-talk. Under these conditions, the peak at 135 eV should be less than 5 % of the intensity of the Ag $3d_{5/2}$ peak observed at about 368 eV on the binding-energy scale for X-rays from the magnesium anode. The second possible reason for ghost peaks is that the anode coating is worn and X-rays are emitted from the substrate material. The user shall determine the nature of the substrate from the instrument manufacturer and calculate where, on the binding-energy scale, the peak due to Ag $3d_{5/2}$ would be if Ag is irradiated with X-rays emitted from the substrate material. This region of the spectrum shall be examined for such peaks. A third source of ghost peaks arises from impurities on the anode material. When using a magnesium anode, there might be some magnesium oxide present. This would give rise to O Kα radiation which would produce an Ag $3d^5/_2$ peak in the vicinity of 1 097 eV on the Mg Kα binding-energy scale.

NOTE Examples of ghost spectra are given in Reference [2].

8.3 High-resolution spectrum from the conductive specimen

The parameters listed in 6.2.3 for the high-resolution spectrum from the conductive specimen shall be entered onto one or more control charts.

8.4 High-resolution spectrum from the non-conductive specimen

The parameters listed in 6.3.2 for the high-resolution spectrum from the non-conductive specimen shall be entered onto one or more control charts.

8.5 Images from the phosphor specimen

The images recorded from 7.4 shall be compared with the reference images. Significant changes in the size, shape or uniformity, or the alignment of the major and minor axes, indicate a change in the performance of the monochromator and should be investigated.

8.6 Images from the uniform conductive specimen

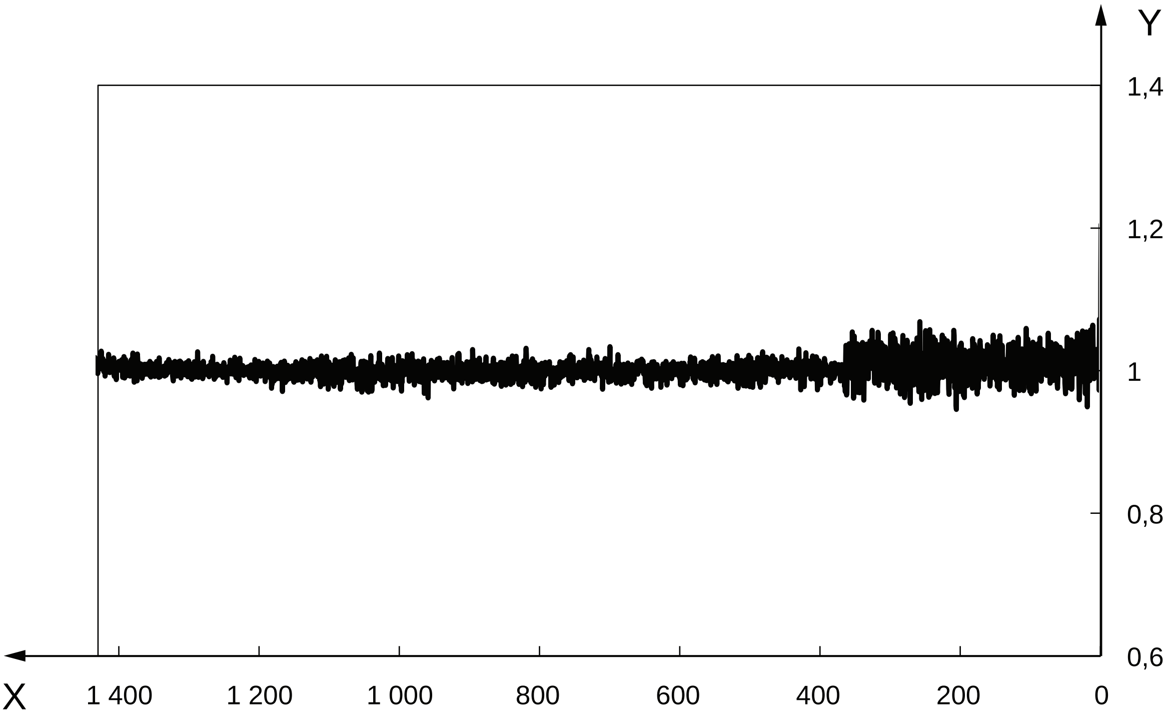
The images recorded from 7.5 shall be compared with the reference images. Significant changes in the uniformity indicate a change in the performance of the monochromator or detector and should be investigated.

8.7 Spectrum ratios

A convenient and sensitive method for determining whether the instrument has changed since the reference data were collected is to calculate the ratio of the subsequent survey spectrum to the reference survey spectrum at each channel on the binding-energy scale. This shall be done if it is convenient with the data analysis software on the XPS instrument or if the data are easily exported to a spreadsheet.

NOTE Examples of ratio spectra and their diagnosis are described in Reference [2].

If the instrument is essentially unchanged since the reference survey spectrum was acquired, the ratio spectrum will have a mean value close to unity but have noise oscillations about that value, as illustrated in Figure 4 for the ratio between a subsequent survey spectrum from silver and the reference survey spectrum. The amplitude of the noise signal will increase at binding energies below that of a significant peak because of the change in the intensity of the background signal. Significant deviations from this type of behaviour should be investigated.



Key

X binding energy (eV)

Y ratio

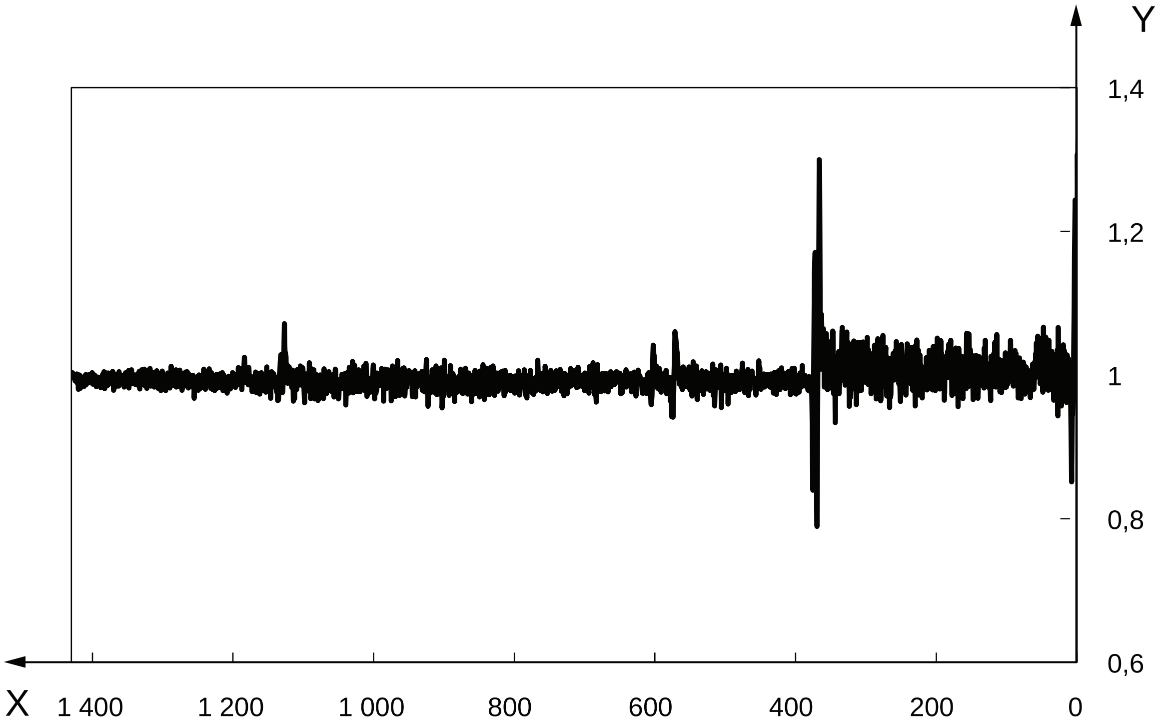
Figure 4 — Ratio of the subsequent survey spectrum to the reference survey spectrum
(In this case, the performance of the instrument was substantially the same during the collection of the subsequent spectrum as it was during the collection of the reference spectrum)

Significant deviations from the behaviour shown in Figure 4, as illustrated in Figures 5 to 7, indicate that the spectrometer characteristics have changed in some way. Table 3 shows how the ratio of survey spectra might change from that shown in Figure 4 for some possible fault conditions. Table 3 also suggests possible causes and remedial actions.

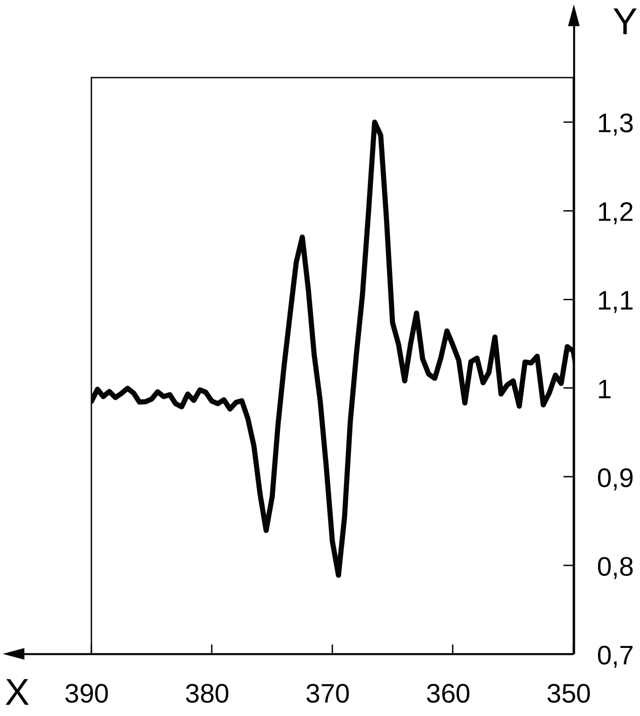
Table 3 — The behaviour of the survey-spectrum ratio under a number of fault conditions, the possible causes and remedial actions that might be necessary

Behaviour of ratio spectrum	Possible fault	Possible causes[a]	Actions	Illustration
Appearance similar to Figure 4, but mean value lower than unity	Uniform loss of sensitivity	X-ray intensity reduced	Check that source emission current is set correctly. Check that emitter to anode voltage is set correctly. For monochromated X-rays, check uniformity of beam using the phosphor. For non-monochromatic X-rays, check position of source (if retractable) and check spectrum for ghost peaks indicating worn anode or increased cross-talk.	
		Detector ageing	Check manufacturer's instructions and increase detector voltage. Do not exceed maximum recommended voltage.	
		Transfer lens transmission reduced	Check positions of lens apertures or irises (if fitted).	
Appearance similar to Figure 4, but a minimum at the main peak energy	The maximum intensity that can be measured is limited	Detector ageing	Check manufacturer's instructions and increase detector voltage. Do not exceed maximum recommended voltage.	
	Increased background signal	The foil in front of a non-monochromated X-ray source is punctured	Replace the foil.	
Positive and negative peaks appearing close to the positions of peaks in the reference spectrum	Peaks in the trial spectrum have shifted relative to those in the reference spectrum	The energy calibration of the instrument has changed.	Follow manufacturer's instructions to recalibrate spectrometer.	Figure 5
	Peak widths in the trial spectrum have changed relative to those in the reference spectrum	The monochromator needs resetting or realignment or an electrical lead has become detached	Check any manufacturer's instructions for optimizing the monochromator or check visually for detached or damaged electrical leads.	Figure 6
A consistently rising or falling trend	The transmission function of the instrument has changed	Mechanical misalignment or spectrometer voltages incorrectly programmed	Check transmission function of instrument.	
Ratio decreases at low kinetic energy (high binding energy)	Compensation for external magnetic fields set incorrectly	Magnetic field in the laboratory has changed due to installation of new equipment or re-routing of power cables	Adjust current in magnetic trim coils (if fitted). Reroute power cables.	Figure 7

[a] This column shows some of the more likely causes; it is not intended to be an exhaustive list. If in doubt about the appropriate course of action to take, contact the instrument manufacturer.



a) Result for whole survey spectrum



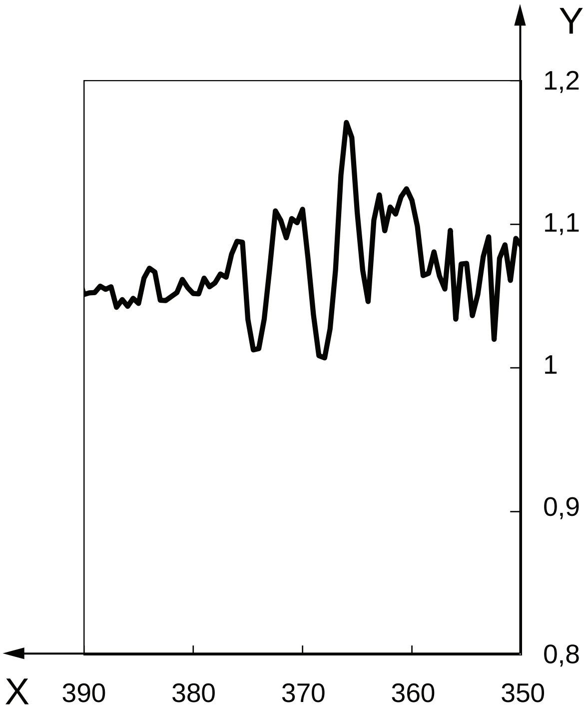
b) Result near the Ag 3d region

Key

X binding energy (eV)

Y ratio

Figure 5 — Ratio of the subsequent survey spectrum to the reference survey spectrum when there is a peak shift of 0,2 eV in the subsequent spectrum

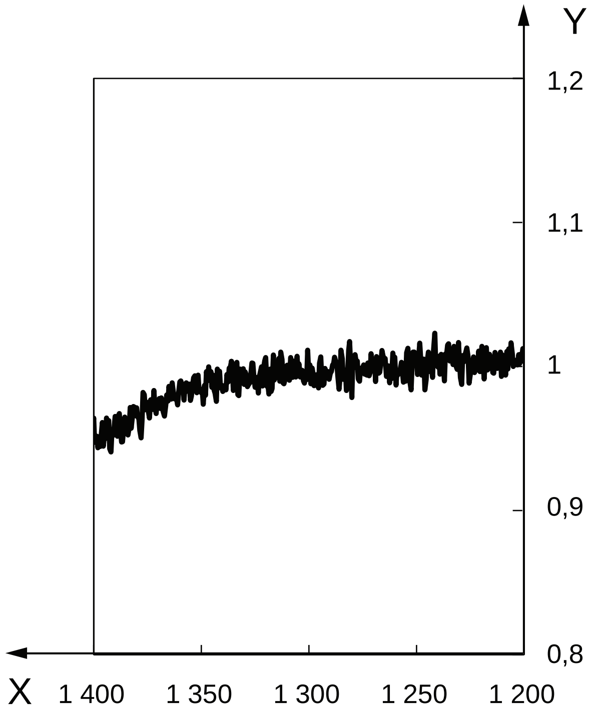


Key

X binding energy (eV)

Y ratio

Figure 6 — Shape of the ratio of the subsequent survey spectrum to the reference survey spectrum in the region close to a peak position when the peak width is greater in the subsequent spectrum than it is in the reference spectrum



Key

X binding energy (eV)

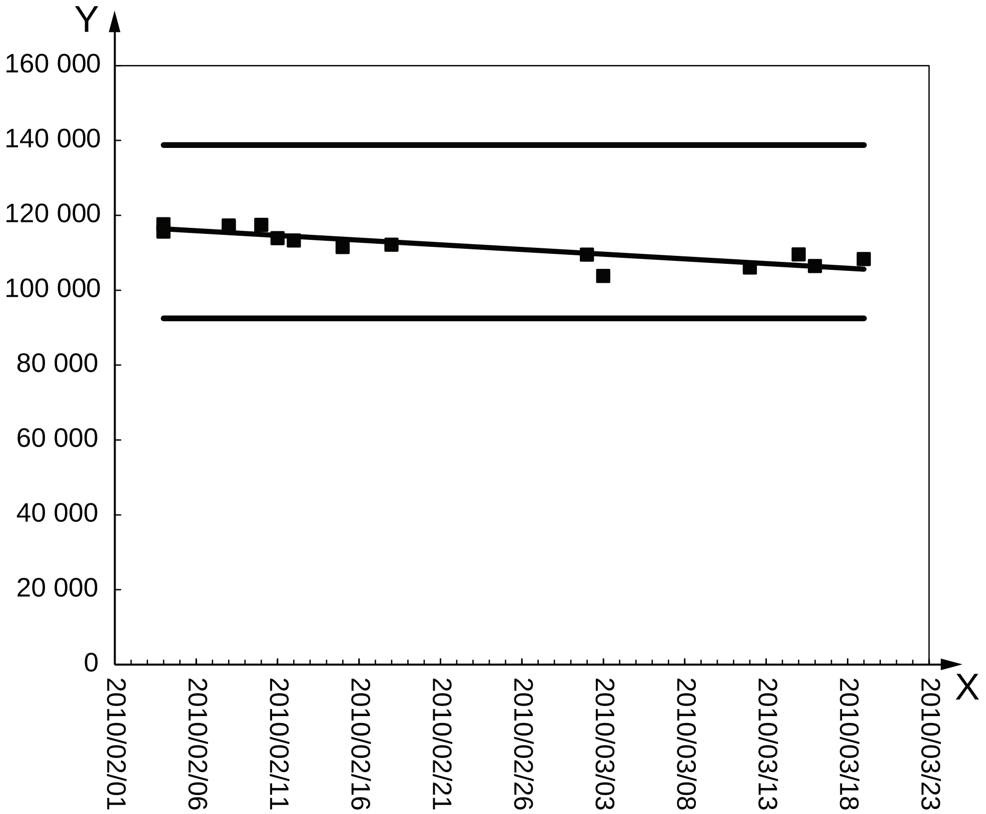
Y ratio

Figure 7 — Ratio of the subsequent survey spectrum to the reference survey spectrum that decreases with decreasing kinetic energy (increasing binding energy)

9 Control charts

Control charts shall be used with the performance data acquired during these measurements. These might reveal long-term trends in the performance of the spectrometer and might allow the user to plan and schedule maintenance activities.

Figure 8 shows an example of a control chart with the number of counts in the Ag $3d_{5/2}$ peak in the survey spectrum as a function of time.



Key

X date

Y peak intensity (number of counts)

Figure 8 — Control chart showing the variation in the number of counts in the Ag 3d$_{5/2}$ peak in the survey spectrum with time. The tolerance limits are also shown

Table 4 shows a list of the control charts that shall be constructed from the performance data obtained by following the procedures described in this International Standard. The actual values obtained from the data set will be dependent upon the instrument, but in all cases the charts will highlight any significant changes in instrument performance. Examples of tolerance limits are given in Table 4, referenced to the initial reference data set. These limits have been found to be useful and are recommended. Other limits may be used and might be more suitable for a particular application or instrument. Reasons for selecting different limits shall be documented.

Table 4 — Examples of tolerance limits for control charts constructed from the performance data obtained by following the procedures described in this International Standard

Parameter	Tolerance limits with respect to reference data set	
	Monochromatic X-rays	**Non-monochromatic X-rays**
Survey spectrum control charts		
Intensity of the Ag $3d_{5/2}$ peak[a]	20 %	20 %
Energy position on the binding-energy scale of the channel having the greatest number of counts (peak position)	±0,5 eV	±1,0 eV
Peak width (FWHM)	±0,5 eV	±0,5 eV
Number of counts in the binding-energy range 450 eV to 460 eV	±20 %	±20 %
Number of counts in the binding-energy range –5 eV to –10 eV	Instrument-dependent[b]	+20 %
High-resolution spectrum control charts (conductive specimen)		
Peak intensity[a]	20 %	20 %
Ratio of the intensity of this peak to the same one in the survey spectrum	10 %	10 %
Peak position	0,2 eV	0,5 eV
Peak width (FWHM)	±0,1 eV	±0,2 eV
Signal-to-background ratio	10 %	10 %
High-resolution spectrum control charts (non-conductive specimen)		
Peak intensity[a]	20 %	20 %
Peak position	0,2 eV	0,5 eV
Peak width (FWHM)	±0,1 eV	0,5 eV

[a] Peak intensity is the height of the peak after the subtraction of a suitable (e.g. Shirley) background.

[b] For an “ideal” instrument the number of counts in this region of the spectrum is expected to be zero. For most actual instruments, there might be some signal due to noise or scattering. The user shall assess the signal in the reference data set and set the action limit at some reasonable value greater than that observed.

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