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Surface chemical analysis — X-ray photoelectron spectroscopy — Guidelines for analysis

Analyse chimique des surfaces — Spectroscopie de photoélectrons par rayons X — Lignes directrices pour l'analyse

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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.

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ISO 10810 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. Their chemical states may be determined from shifts in peak positions and other parameters compared with the data for that element in its pure elemental state. Information on the quantities of such elements can be derived from the measured intensities of photoelectron peaks. Calculation of the quantities of the constituent chemical species present in the surface layer studied may then be made using formulae and relative-sensitivity factors provided by the spectrometer manufacturer or locally measured relative-sensitivity factors and appropriate software.

This guidance document is intended to aid the operator of X-ray photoelectron spectrometers to obtain efficient, meaningful analyses from typical samples.

Surface chemical analysis — X-ray photoelectron spectroscopy — Guidelines for analysis

1 Scope

This International Standard is intended to aid the operators of X-ray photoelectron spectrometers in their analysis of typical samples. It takes the operator through the analysis from the handling of the sample and the calibration and setting-up of the spectrometer to the acquisition of wide and narrow scans and also gives advice on quantification and on preparation of the final report.

2 Normative references

The following referenced documents are indispensible for the application of this document. For dated references only the cited edition applies. For undated references, the latest edition of the referenced document (together with any amendments) applies.

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in ISO 18115-1 apply.

4 Symbols and abbreviations

AES	Auger electron spectroscopy
ARXPS	angle-resolved X-ray photoelectron spectroscopy
CCQM	consultative committee for amount of substance
CRM	certified reference material
EAL	effective attenuation length
FAT	fixed analyser transmission
FRR	fixed retard ratio
FWHM	full width at half maximum
IERF	intensity/energy response function
NIST	National Institute of Standards and Technology
NPL	National Physical Laboratory
RM	reference material
RSD	residual standard deviation
S/N	signal-to-noise ratio

XPS X-ray photoelectron spectroscopy

Δ_1 difference between the measured and reference energies for Au $4f_{7/2}$

Δ_4 difference between the measured and reference energies for Cu $2p_{3/2}$

5 Overview of sample analysis

Figure 1 is a flow chart illustrating the analysis of a typical sample by XPS. A preliminary consultation with the supplier of the sample should be used to ensure that the sample is supplied in the form most appropriate for analysis. ISO 18117[2] explains the issues involved with prior handling by the supplier and also gives information on the most suitable container for transportation. In this consideration, the analyst should also identify any particular problems likely to arise. Table 1 provides a list of example problems. Prior to any work, discussions should be held between the analyst and the customer to gain as much information as possible by reviewing what is already known regarding the sample and its history. In addition to the information listed in ISO 18117[2], Table 2 indicates information that will assist in deciding how to conduct the XPS analysis. Following these preliminary discussions, the sample(s) may need to be prepared to allow mounting in the spectrometer and to reduce, where possible, the subsequent analysis time. ISO 18116[1] provides details of how to do this. The analyst will be responsible for the instrument characterization, which will include the calibration state and the overall performance of the XPS instrument. A guide to calibration of the energy scale is given in ISO 15472[14]. Checks for the intensity scale are given in ISO 24237[9] and ISO 21270[18].

Once the specimen has been mounted in the spectrometer and the system pumped down, data acquisition can commence. A wide scan should be obtained first and this then analysed to determine the elements present. ISO 16243[31] provides information on recording and reporting data in XPS. The wide-scan spectrum can provide qualitative and semi-quantitative information regarding composition and the depth distribution of species. This may yield sufficient information to satisfy the customer and the analysis may be terminated. However, in most cases, more data are required and narrow-scan spectra will then be recorded from regions identified in the wide-scan spectrum. Analysis of these narrow-scan spectra will provide chemical-state information, more accurate quantitative information and near-surface depth information. At a later time in the investigation the wide scan should be repeated to determine if there has been degradation (e.g. due to X-ray irradiation or to surface reactions with ambient gases in the vacuum system). Following evaluation of the XPS data, the analyst should produce a report.

Table 1 — Problems likely to arise and related ISO standards

Problem	Example	ISO Standard
Outgassing	Water vapour	ISO 18116
Degradation	Polymers and organics	
Charging	Insulators	ISO 19318[28]
Reduction	Oxides	
Contaminant mobility	Chlorine	
Sample containment	Powders	ISO 18116
Surface topography	Fibres	

Table 2 — Sample information and history

Sample information and history
Thermal
Contamination
Possible composition
Segregation
Surface layer
Homogeneous
Islands

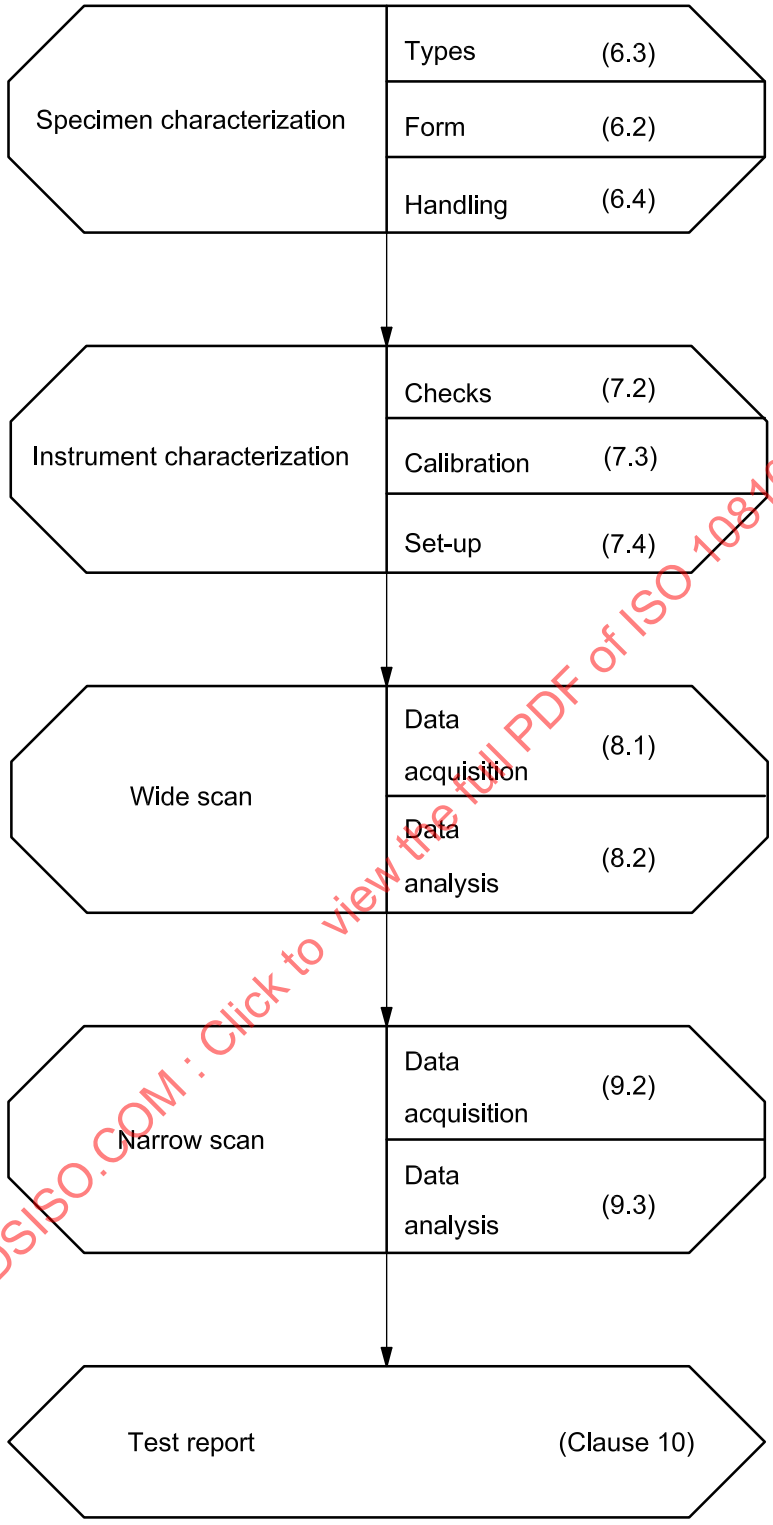


Figure 1 — Flow chart of an XPS analysis
(The numbers in brackets indicate the respective subclauses in this International Standard.)

6 Specimen characterization

6.1 General

The complexity of the interacting factors in XPS analyses arises from the many different forms of specimen materials and the variety of material types that may be encountered as well as from the different XPS experiments that might be required. Table 3 illustrates possible specimen forms, material types, and XPS experiments or issues for further review. The analyst should also be aware that samples can consist of multiple components and phases, and that identification of the components and phases present (and their spatial arrangements) can be an important part of an XPS analysis. A further complication is that non-conducting samples may charge.

Table 3 — Some specimen forms, material types, *in situ* specimen treatments and possible XPS experiments

Specimen forms	Material types	*In situ* specimen treatments	XPS experiments
Adsorbed layers (6.2.3)	Alloy (6.3.2)	Cooling (6.5.2)	Angle-resolved XPS
Amorphous	Biological (6.3.9)	Degradation	Analysis area (small)
Fibres (6.2.8)	Catalyst (6.3.7)	Deposit thin films	Analysis area (large)
Films (6.2.3)	Ceramic (6.3.6)	Expose to high gas pressure (6.5.5)	Depth profile
Interface (6.2.4)	Composite	Fracture (6.5.3)	Imaging
Internal interface (6.2.9)	Glass (6.3.8)	Heating (6.5.2)	Line scan
Liquid	Insulator (6.3.8)	Insert into liquids (6.5.5)	
Multilayered (6.2.4)	Magnetic metal (6.3.5)	Ion bombardment (6.5.4)	
Nano-material	Metal (6.3.2)	Scraping (6.5.3)	
Non-porous (6.2.5)	Non-metal (pure) element		
Pattern system	Polymer (6.3.3)		
Polycrystal	Semiconductor (6.3.4)		
Porous (6.2.6)	Textile		
Powder (6.2.7)			
Residue (6.2.3)			
Segregated layer (6.2.3)			
Single crystal (6.2.2)			
Solid			
Textile (6.2.8)			
Contamination			

6.2 Specimen forms

6.2.1 General

The form of the specimen to be analysed will strongly dictate the kinds of experimental approach that can and need to be employed.

6.2.2 Single crystal

This type of sample should have a flat surface. Quantitative analyses will generally be difficult because of anisotropies in the angular distributions of the photoemitted electrons due to electron diffraction or to forward-focussing effects[3][4]. These anisotropies are nevertheless useful in determining the structural properties of the sample.

6.2.3 Adsorbed or segregated layers, films and residues

It should, in general, be possible to obtain a quantitative analysis and chemical-state information for adsorbed or segregated layers, films and residues[5][6]. If the substrate is a single crystal, however, quantitative analyses will generally be difficult, but the angular distributions of the photoemitted electrons can give useful structural information[3]. Angle-resolved XPS (ARXPS), as described in 9.3.3, will enable the layer thickness to be determined, provided the layer thickness does not exceed around three times the effective attenuation length (EAL) of the substrate peak. This will be of progressively lower accuracy for films above one EAL in thickness.

6.2.4 Interfaces and multilayered samples

Ion sputter depth profiling should permit the depth distribution and thickness of the layers to be determined, together with a semi-quantitative analysis of the layers, as described in 9.3.3.

6.2.5 Non-porous

A quantitative analysis together with chemical-state information can be obtained.

6.2.6 Porous

Only a semi-quantitative analysis may be possible since the sample will have a rough surface.

6.2.7 Powder

Mount the sample by embedding in a suitable matrix. In many cases, indium proves sufficiently soft to be able to accept the powder without particles falling off. Then treat the composite sample as a porous sample but be sure to remember to subtract the indium peaks. Double-sided, carbon-loaded, conductive adhesive tape is also very suitable as a mounting material.

6.2.8 Fibres and textiles

For fibre analysis, the alignment of the fibres relative to the X-ray source may be an important factor. The diameter of the fibre relative to the diameter of the analysis area will also affect the ability to quantify the data. If possible, mount several fibres in a bundle to increase the surface area. However, a quantitative analysis will generally not be possible with many manufacturers' software systems, although some chemical-state information can be obtained. Under certain conditions, it is possible to analyse one monofibre, using a coaxial ion gun to conduct a sputter depth profile or, if there is sufficient spatial resolution in relation to the fibre diameter, ARXPS may be conducted around the circumference.

6.2.9 Internal interface

An internal interface can be analysed using ARXPS, as described in 9.3.3, bearing in mind the depth limit of around three times the EAL discussed in 6.2.3. To analyse a weak or brittle internal interface that occurs at greater depths, it is generally necessary to first expose the interface in the ultra-high vacuum by use of fracture stages, etc. For other internal interfaces, one of the forms of depth profiling described in ISO/TR 15969[21] may prove effective.

6.3 Material types

6.3.1 General

For different materials, there are various consequences for an XPS experiment that may need to be considered. For example, problems may arise when analysing magnetic, radioactive and outgassing samples.

6.3.2 Metals and alloys

With specimens in this category, there should be minimal surface charging, but there may be a surface oxide film together with a high level of carbon contamination. In general, there should be no need for surface treatment prior to analysis. However, in many cases *in situ* ion sputtering is carried out prior to analysis to remove any oxide/contaminant overlayer.

6.3.3 Polymers

It may be difficult to achieve the desired vacuum with this category of sample due to outgassing. During analysis, adventitious carbon and possibly sample charging and sample degradation may occur. The spectra should contain intense peaks from C, O and N, possibly also from F, Cl and S.

6.3.4 Semiconductors

There should be minimal surface charging with these specimens and there should be low levels of carbon contamination. However, expect to see a surface oxide.

6.3.5 Magnetic materials

Take care when handling magnetic materials. First demagnetize them, if possible, and analyse with any magnetic immersion lens switched off. A magnetized sample will affect the performance of a magnetic lens in a way which will depend on the kinetic energy of the electrons being analysed. A magnetized sample may also lead to changes in a measured spectrum that depend on the electron energy. Expect the analysis to be similar to that for metals and alloys.

6.3.6 Ceramics

Sintered or porous ceramics may outgas and it may be difficult to evacuate the chamber to a pressure sufficiently low for XPS analysis. A threshold pressure may be set by the manufacturer to protect the X-ray source or other instrumental items. There may be significant surface charging and one should expect moderate levels of surface carbon contamination.

6.3.7 Catalysts

These samples may behave in a similar way to ceramics, and there may be health and safety considerations when handling.

6.3.8 Glass and insulators

These samples may be analysed but will charge, and the use of an electron flood gun with or without a low-energy positive-ion flood may be necessary to reduce the effect of charging.

6.3.9 Biological

These samples may outgas in the spectrometer and suffer degradation due to either the vacuum environment or the X-ray flux or both.

6.4 Handling and mounting of specimens

Guidelines for the preparation and mounting of specimens for analysis are given in ISO 18116[1] and ISO 18117[2], and general information on specimen handling is also available in two books (see References [5] and [7]).

6.5 Specimen treatments

6.5.1 General

There are many *in situ* treatments available to the analyst to obtain relevant data. Surface layers may be sputtered away using gas and/or liquid-metal ions, but these may, in turn, modify the surface by implanting ions and by preferential sputtering of elements. Motion transfer devices fitted with knives, etc., permit surface layers to be removed without exposing the underlying layer to atmospheric pressure. Heating and cooling stages allow the sample temperature to be modified. Fracture stages allow internal interfaces to be exposed.

6.5.2 Heating and cooling

Many XPS spectrometers are equipped with heating and cooling stages. Cooling is achieved by passing liquid nitrogen through a conducting metal block, although it is rarely possible to reach 77 K and minimum temperatures of 100 K are more realistic, while heating may be achieved by passing a current through a resistive coil, by shining an infra-red lamp onto the sample or by using a hot liquid in the cooling stage.

6.5.3 Scraping and fracture

A fresh surface of a material can be produced either by removing layers from the surface using a sharp implement attached to a transfer device with lateral movement or by cleavage using an impact fracture device at room, or a reduced, temperature. The cooling will enhance the brittleness of many samples.

6.5.4 Ion bombardment for analysing thin films

Ion bombardment is usually with argon ions, although other inert-gas ions, liquid-metal ions (such as gallium) or cluster ions (such as C_{60}^{+}) can be used to remove surface layers from the sample. However, preferential sputtering may result in an analysed surface that is not representative of the original sample.

6.5.5 Exposure to gases and liquids

Chambers with interlocks from the analytical chamber can be used to expose a clean surface prepared as in 6.5.2 to 6.5.4 to high-pressure gases and to liquids over a range of temperatures. The chamber is then evacuated and the sample transferred back to the analytical chamber for analysis. Alternatively, samples may be removed from the system into a pumped transfer module for treatment in other equipment before returning via a similar route.

7 Instrument characterization[8]

7.1 General

X-ray photoelectron spectrometers are not constructed to a standard design, and each instrument will be configured to operate most efficiently in a particular mode. The majority of XPS instruments currently produced will be supplied with an X-ray monochromator. Either by focussing monochromated X-rays or the emitted electrons, a small analysis area may be defined or the sample imaged with selected photoelectrons. However, much excellent work is still conducted with simpler instruments that use broad beams of non-monochromatized X-rays to analyse the sample.

7.2 Instrument checks

7.2.1 System health check[9]

Use of a reference sample of gold, silver and/or copper mounted permanently in the analysis chamber is convenient for checking the system, but it is also advisable to have a sample of a frequently analysed material (e.g. a silicon wafer in a semiconductor laboratory). A spectrum recorded from the reference sample will indicate if the measured energies of the calibrating peaks have drifted. It will also indicate the state of a non-monochromatized X-ray source by showing the presence of ghost peaks from Cu, Mg or Al[10] in the X-ray anode, suggesting it is nearing the end of its life. In addition, it will indicate, by the presence of a high background and increased contamination, that the X-ray window is damaged, and monitoring the intensity of the gold peaks will indicate the efficiency of the X-ray source and the electron detectors. The signal-to-noise (S/N) ratio will vary with energy resolution, spatial resolution and depth resolution. The ultimate performance is not always required, and the analyst may need good repeatability rather than the limits of performance — i.e. good signal levels at modest energy or spatial resolution. The operator should identify the acceptable S/N level for given conditions and regularly monitor the instrument to ensure that this S/N level, or a better level, is maintained.

7.2.2 Mechanical

The sample is mounted on the sample stage, which may have X, Y and Z movements as well as tilt. Proper adjustment of the sample height is crucially important when a focussed monochromatic X-ray source is used.

Tilt needs to be determined accurately from the spectrometer axis as an error of 0,3° in a tilt angle at 60° will result in a 1 % error in the total film thickness. Methods of calibrating emission angles are described by Seah and Spencer[11] (where errors of 2,6° were found in the nominal settings) and by Kim *et al*.[12] and Seah[13]. ARXPS experiments may require the sample to be tilted over an angular range of, typically, 0° to 60° from the surface normal. This may not be possible if the sample is large (e.g. a silicon wafer) and cannot be cut to fit the system.

7.2.3 Sample holder

The sample holder may have facilities for heating and cooling of the sample. The temperature of the sample should be determined by calibration, using a thermocouple or other suitable device. The sample stage may already have a thermocouple attached, but there may be a temperature gradient between the sample surface and the thermocouple position. The temperature measurement should be made with and without the X-ray source and/or ion sputter gun operating, as adventitious heating may influence the measurements.

7.2.4 Vacuum

The vacuum in the analysis chamber can become degraded for various reasons. The pumps may deteriorate (liquid-nitrogen traps not topped up, ion pumps releasing previously pumped gases, etc.), the window on the X-ray source may fail or components may become heated and outgas. During analysis, the sample may degrade due to heating and, during depth profiling, the sample may react with impurities in the sputtering gas. The pressure in the analysis chamber should be continuously monitored and, if an unusual increase in pressure occurs, a mass spectrometer should be used to identify the gas species present in order to determine if they are likely to react with the specimen.

7.3 Instrument calibration

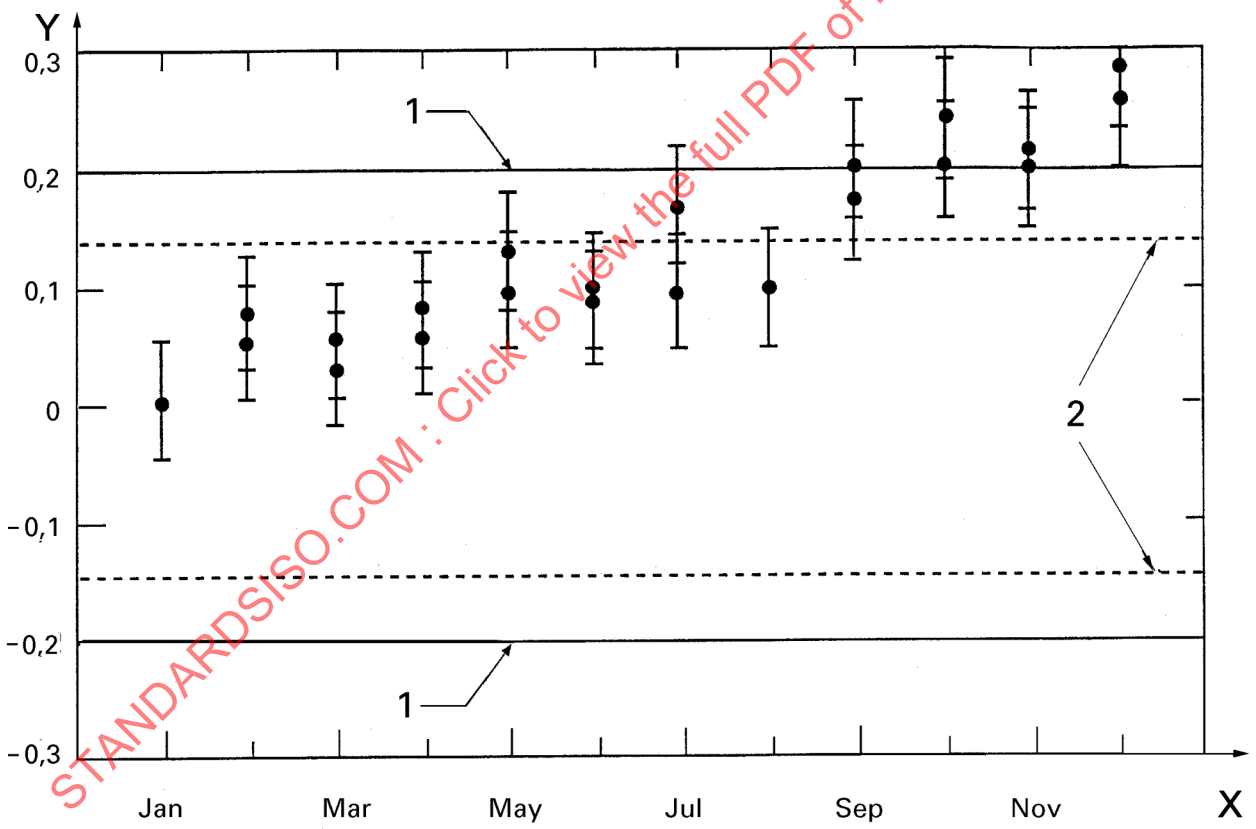
7.3.1 Calibration of binding energy scale

XPS is frequently used for the determination and measurement of chemical shifts of elemental photoelectron and Auger electron lines. Identification of chemical states is based on measurements of peak shifts down to 0,1 eV. It is important that the instrumental binding-energy scale be calibrated to an accuracy of 0,2 eV or better in order for useful comparisons to be made with published or other reference data. ISO 15472[14] describes the method for the accurate calibration of energy scales. This should be used with reference samples of pure gold, silver and copper to enable the calibrations to be made using unmonochromatized Mg

or Al X-rays or monochromatic Al X-rays. It is valid, at the accuracy stated, for binding energies in the range 0 eV to 1 040 eV (users normally extend this to the full energy range available, but note that extrapolating a calibration is significantly more uncertain than interpolating it and so the uncertainty beyond 1 040 eV is unspecified), but is only applicable to instruments fitted with ion guns for specimen cleaning.

Briefly, the method involves ion cleaning of the samples and an initial set of measurements performed once, followed by a second, simpler, set of measurements performed at regular intervals. In the first set of measurements, the binding energies of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks are recorded to obtain the energy scale calibration. In instruments with unmonochromatized X-ray sources, the Cu L_3VV Auger peak energy is measured and, in instruments with a monochromatized Al X-ray source, the Ag $3d_{5/2}$ peak binding energy is recorded to determine the linearity of the energy scale. In subsequent measurements, the binding energies of the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are recorded at regular intervals.

Results of the second set of measurements are generally limited by drift, and the operator should keep records and prepare a control chart to show when tolerance limits have been reached and the instrument needs to be brought back into calibration. A typical control chart is shown in Figure 2, where tolerance limits of ±0,2 eV are indicated. An analyst should select tolerance limits based on the needs of the analytical work and the instrumental capability.



Key

X	calibration date	1	tolerance limits
Y	Δ_1, Δ_4 (eV)	2	warning limits

NOTE The plotted points represent the values Δ_1 and Δ_4, which are the differences between the measured and reference energies for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peak positions that are determined in each calibration check. These are shown to illustrate an instrument that has not been recalibrated since the start in January. It was out of calibration for the first time in July and should have been recalibrated in May, since it has both passed the upper warning limit and reached the recommended four-month time limit given in ISO 15472[14].

Figure 2 — Control chart to monitor the calibration status of an instrument

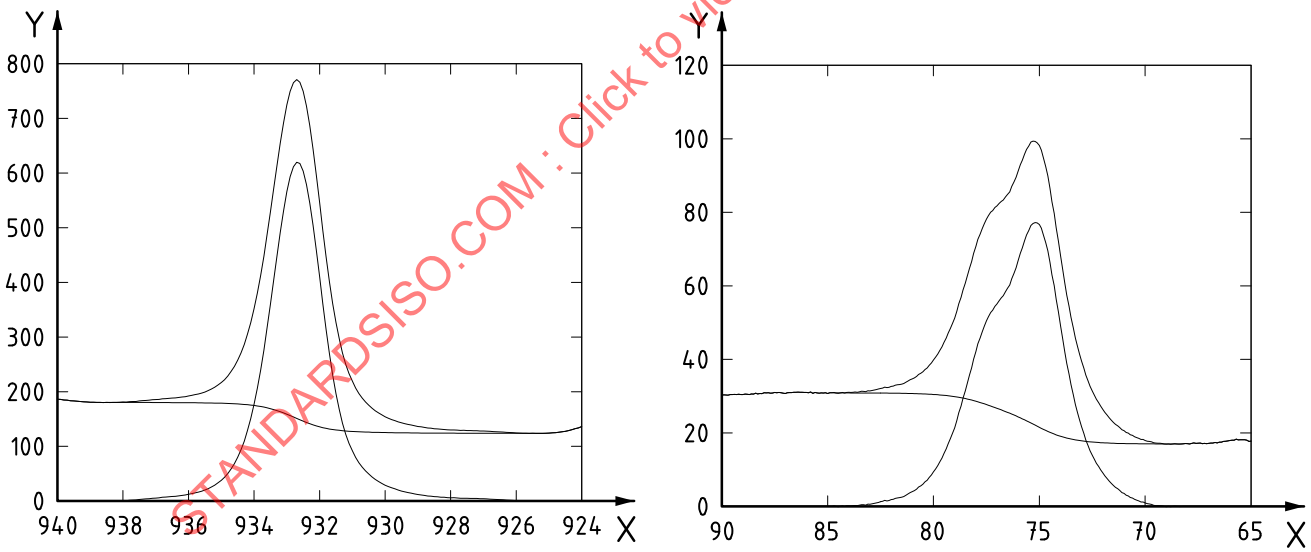
7.3.2 Intensity repeatability and intensity/energy response function (IERF)

The composition of the surface of a sample is determined by recording a spectrum and measuring the intensity of peaks within that spectrum. The composition is then obtained by applying formulae together with sensitivity factors to the selected peak intensities to give a surface composition. It is important that the intensity measurements be repeatable and do not vary significantly between spectra, and that any drift with time be determined. ISO 24237[9] describes a method for determining the repeatability of the intensity over relatively short periods of time (e.g. ten minutes) and the drift in intensity over much longer periods of time (e.g. several months).

The stability of the X-ray source, the detector settings, the sample position and the data-processing methods all contribute to the repeatability. ISO 24237 requires a copper sample and is applicable to unmonochromatic Al and Mg X-ray sources and monochromated Al X-rays. In the method, the copper sample is cleaned using argon ion bombardment, and the Cu $2p_{3/2}$ and Cu 3p peaks (see Figure 3) are measured, in sequence, seven times. These data give the repeatability standard deviations of the peak intensities.

The intensity scale of the instrument may drift with time, which will affect the accuracy of any quantitative measurement. Drift of the instrument scale is caused by factors such as the ageing of the spectrometer components, of electronic supplies and of the detector, and thus the instrument IERF[15] may vary with time[16]. The absolute values of the intensity of the Cu $2p_{3/2}$ and Cu 3p peaks are used to determine the IERF at two energies. This does not define the IERF, but is sufficient to indicate if any changes have occurred.

The intensity repeatability and constancy can be tracked using procedures described in ISO 24237 using Cu. This is essential for consistent quantification. The UK National Physical Laboratory has devised a system for calibrating the IERFs of spectrometers[17], which does this as well as diagnosing sample-to-sample repeatability, ghosts and cross-talk of the unmonochromated twin-anode X-ray sources, internal scattering, etc., automatically.



a) Cu $2p_{3/2}$ b) Cu 3p

Key

X binding energy (eV)

Y intensity/1 000 counts

Figure 3 — 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.)

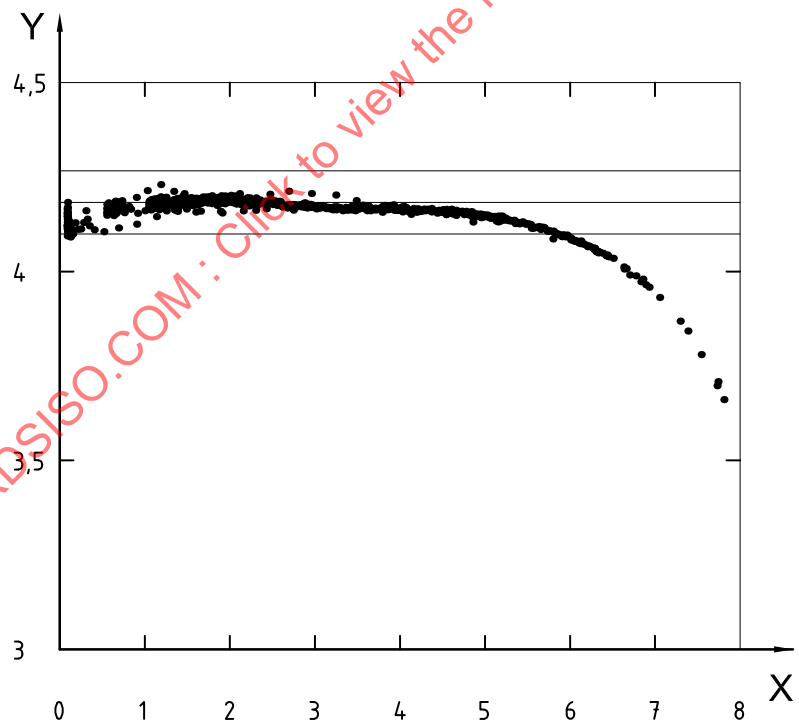
7.3.3 Linearity of intensity scale test

The peak intensities are used, with appropriate correction factors, to determine the surface composition. Non-linearities in the instrument intensity scales can lead to errors in the measured compositions. At sufficiently low count rates (typically less than 1 Mc/s), the intensity scale is generally linear, but it becomes progressively non-linear as the count rate increases.

Two methods for measuring the linearity of the intensity scale are given in ISO 21270[18]. The first method assumes that the spectrometer output is proportional to the X-ray beam flux where the beam flux is capable of being set at 30 or more approximately equal intervals. The second method applies to instruments where the beam flux can only be set at less than 30 (e.g. 2) pre-defined levels.

In the first method, the count rate of the Cu L_3VV Auger peak is determined as a function of the X-ray flux for 30 or more increments in the X-ray flux. The quotient of the count rate and the X-ray flux is plotted against the measured count rate. This plot then allows the linearity range to be determined.

In the second method, a wide-scan spectrum of copper or the stainless-steel sample holder is recorded at a high and a low X-ray flux. A plot of the quotient of the count rates of the two spectra, for each energy channel, versus the count rate for that channel in the high X-ray flux spectrum allows the linearity to be determined. Figure 4 shows an example of such a plot. Three horizontal lines have been drawn, the central one tangential to the average intensity ratio for intensities between 1 Mc/s and 4 Mc/s, and the other two to show limits of the ratio, here ±2,5 %. An analyst should select a tolerance based on the needs of the local work. The example of Figure 4 indicates that the measured intensities deviate from linearity by more than 2,5 % only for count rates greater than 6 Mc/s.



Key

X intensity (Mc/s)

Y intensity ratio

Figure 4 — Ratios of measured intensities, corrected for dead time, at emission currents of the X-ray source of 20 mA and 5 mA, from copper spectra as a function of intensity for the higher emission current, showing the ±2,5 % acceptability limits of divergence from linearity[19]

7.3.4 Lateral resolution

Measurement of the composition as a function of position on the sample surface is a frequent requirement in XPS. The ability of an instrument to determine changes in composition with position is important. The lateral resolution for XPS measurements, defined in ISO 18516[20], depends on the characteristics of either the incident radiation or the lens-analyser-detector system in the spectrometer. ISO 18516 describes methods for determining the lateral resolution which involve measurements of the intensity of a selected XPS spectral feature while a sample with a sharp edge is scanned across the analysis position or a grid is imaged by the spectrometer. The former method is appropriate if the lateral resolution is expected to be larger than 1 µm, while the latter method is recommended if the lateral resolution is expected to be between 20 nm and 5 µm.

7.3.5 Depth resolution[21][22]

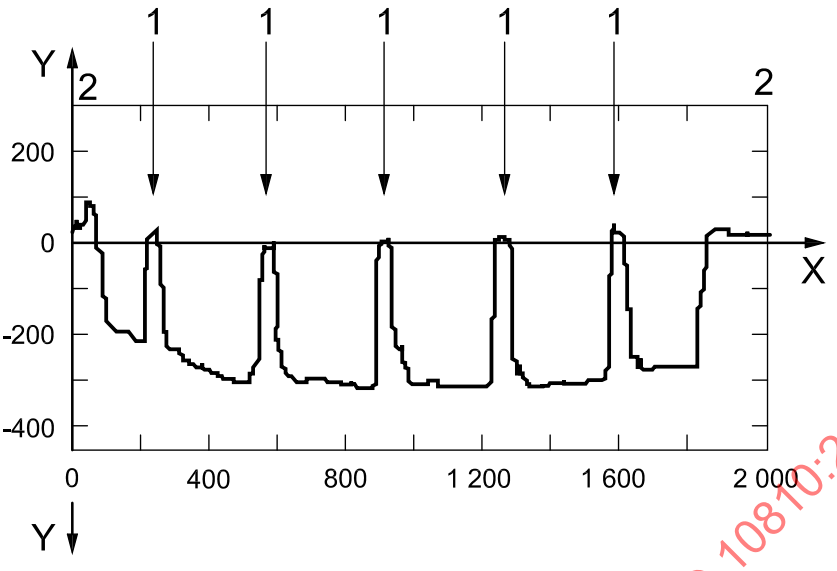
A standard reference material (SRM) is available from NIST[23] which is intended primarily for calibrating sputtered-depth scales and erosion rates in surface analysis of Ni and Cr and which can also be used to determine depth resolution in sputter depth profiling. Its periodic structure, consisting of eight well-defined metal/metal interfaces, can be used to obtain accurate calibration at a number of depths. SRM 2135c is certified for total Cr and total Ni thickness, single-element layer-to-layer uniformity, Ni and Cr bilayer uniformity (periodicity) and single-layer thickness. Certified thickness values, expressed in units of mass/area, are given in the section entitled “Certified Values and Uncertainties” of Reference [23]. This material has been extensively used, particularly in AES and XPS, for adjusting sputtering conditions to attain optimum depth resolution in metal films[24][25]. A different CRM of Ta_2O_5 on Ta is available [BCR-261T[1)]] from IRMM at http://irmm.jrc.ec.europa.eu/html/homepage.htm), which can be used to check the depth resolution at the high level of ~1,7 nm at a depth of 96 nm[26][27] and where the oxide thickness is, again, the item certified.

Analysts need calibrations of sputtered depth and the optimization of sputtering with regard to sample position, angle of incidence, ion type, energy and gas flow rate. They also need the minimum area to be sputtered to be consistent with the depth measurement and depth resolution required. A Faraday cup and a CRM or RM such as Ta_2O_5, SiO_2 or SRM 2135c can be utilized for these measurements.

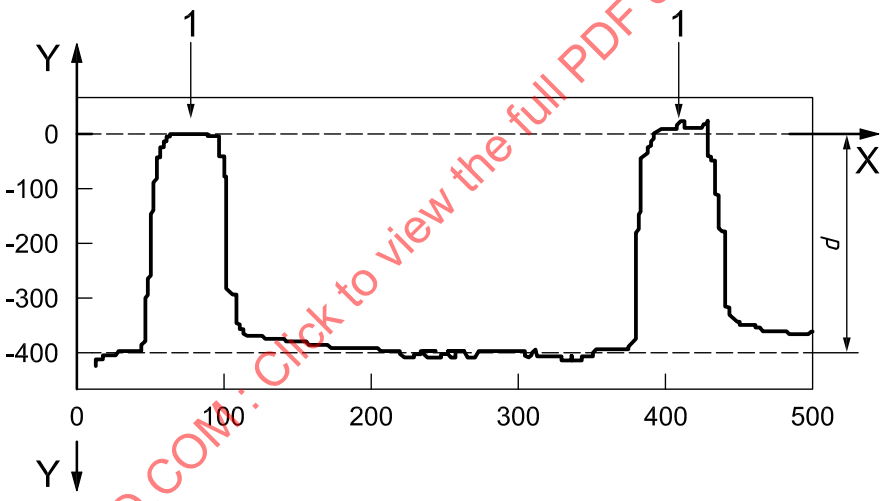
An alternative method for the determination of sputter rate, which is a variant of the mechanical-stylus method, is described in ISO/TR 22335[22]. A copper mesh is placed over the specimen during ion etching and the depth is measured using a mechanical-stylus profiler following etching. Figure 5 shows the topographical profile, as measured with the mechanical stylus, following the ion etching of an aluminium foil with a copper mesh placed over the surface of the aluminium.

Table 4 gives a survey of the different depth-profiling methods.

1) BCR-261T is an example of a suitable CRM available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this reference material.



a) 2 000 µm trace[abc]



b) Higher-magnification trace[d]

Key

X	distance (µm)	1	grid mesh bar positions
Y	depth (nm)	2	foil position

[a] The non-sputtered areas at both edges of the grid mesh shadowed by the aluminium foil and the non-uniformity of the crater are clear.

[b] If the analysis area covers several mesh openings, the average rate is determined as described in ISO/TR 22335[22].

[c] Points 1 and 2 denote the ion-sputtering-shadowed areas due to the mesh bars and the aluminium foil, respectively.

[d] The sputtered depth for the analysed area is determined by averaging the depth at both sides of the mesh opening.

Figure 5 — Examples of stylus profilometer traces after sputtering

Table 4 — Survey of typical applications and uncertainties of the different methods of depth profiling
(taken from ISO/TR 15969[21])

Subclause in ISO/TR 15969:2001	Method/technique	Type of test[a]	Typical application		Uncertainty	
			Depth range (nm)	Material/remarks	nm	%
4.1.2	Stylus	ND	100 to 10 000	Hard	5	1 to 5
	AFM	ND	2 to 700	Hard	2	2
4.1.3	Optical interferometry	ND	200 to 5 000	Polished, reflective	10	0,2 to 5
	Confocal laser	ND	10 to 500 000	Non-transparent	10	2
4.2.2	RM		2 to 500	—	2	2
4.2.3.1	Angle lapping	D	100 to 50 000	Hard	5	1 to 5
	Crater edge	D	20 to 10 000	—	2	1 to 10
	Ball cratering	D	500 to 50 000	Hard, layered structures; thick films	20 (depends on interface roughness)	3 to 7
4.2.3.2	Cross-sectional TEM	D	10 to 1 000	—	0,2	1
	Cross-sectional SEM	D	10 to 300 000	Change in atomic number; contamination problems	5 to 10	2
4.2.3.3	RBS	ND	100 to 30 000	—	5 to 20	5 to 20
4.2.3.4	EPMA and EDS	ND	5 to 1 000	—	2 to 20	5
4.2.3.5	XRF	ND	100 to 100 000	—	10 to 10 000	10
4.2.3.6	GIXRF	ND	1 to 1 000	—	0,1	1
4.2.3.7	Ellipsometry	ND	1 to 5	Non-transparent	0,1 to 1	1
			1 to 10 000	Transparent	0,1 to 1	1
4.2.3.8	Chemical analysis	D	10 to 100 000	—	1 to 10	5 to 10

[a] ND = non-destructive; D = destructive.

7.3.6 Charge correction

Non-conducting samples and conducting samples with a non-conducting surface layer will charge under the X-ray flux resulting in peak shifts relative to the uncharged state. This may cause problems in determining binding energies with the accuracy required for element-state determination and, particularly, for chemical-state determination. There are two methods for dealing with charging. In the first, experimental measures can be taken to minimize the amount of charging (charge control method) while, in the second, corrections for the effects of surface charging can be made following acquisition of spectra (charge correction method). ISO 19318[28] describes methods of charge control and charge correction to be included in reports of XPS measurements.

7.4 Instrument set-up

7.4.1 Optimum settings

There is a trade-off between sensitivity and energy resolution (the highest energy resolution may not be required and a lower energy resolution may give the greater accuracy or precision, depending on requirements). For chemical-state determination, a high energy resolution is needed (e.g. 0,1 eV), but such resolution is not always required for other work. For quantification, a medium energy resolution (e.g. 0,5 eV) is satisfactory, but for detectability a poorer resolution (e.g. >0,5 eV) may be sufficient.

7.4.2 System configuration

The system configuration will be different for different basic types of experiment, such as the survey scan, which will be set for low energy resolution and high sensitivity compared with the narrow scan, when settings for high energy resolution but lower sensitivity will be used. When detecting low concentration levels of elements, an intense X-ray flux will be combined with a low energy resolution to give the highest sensitivity. However, if the sample is likely to degrade, then the lowest X-ray flux must be used. When investigating insulators, where sample charging may be severe, an electron flood gun may be required, and, for samples where an Auger parameter needs to be determined, there is generally the need for bremsstrahlung radiation to be available to ionize the deeper core levels required for the Auger peaks.

8 The wide-scan spectrum

8.1 Data acquisition

8.1.1 General

The wide scan is the first spectrum to be recorded from the sample. It is used to identify all the elements present on the sample surface (except H and He) and to provide an approximate quantification, together with information on sample homogeneity, etc. By acquisition of spectra with multiple sweeps, it can also provide information on sample degradation as a function of time. The steps required in obtaining the wide-scan spectrum are shown in the flow chart in Figure 6. More details can be found in the summary of a workshop held in 2002 to develop recommendations for a future expert system for XPS[29].

8.1.2 Energy resolution

The main task of the survey scan is to detect all peaks in the most time-efficient manner and to minimize the possibly adverse impact of chemical shifts on peak recognition. An energy width (FWHM) for the Ag $3d_{5/2}$ photoelectron peak of <2 eV is recommended.

8.1.3 Energy range, step size and acquisition mode

The range of measured binding energies must be wide enough to include the C_{KLL} Auger peak and other potentially valuable peaks. This range should be 1 150 eV for Mg Kα and 1 350 eV for Al Kα X-rays and should have a sufficient number of steps to obtain peak areas. Software packages such as QUASES (quantitative analysis of surface by electron spectroscopy)[2], developed by Tougaard[30], and other algorithms can then be used to obtain a quantitative analysis. A step size of ~0,4 eV in the fixed analyser transmission (FAT) mode should be used[29]. Multiple scans permit the observation of any drift in peak position and intensity with time. Therefore, use repeat scans to check for drifts or to pass an S/N criterion, terminating at the previously set maximum number of scans, if necessary (see Reference [31]).

8.1.4 Charge correction

Where possible, use the C1s peak from adventitious carbon, assessed using a suitable set of inference rules[32] and set the C1s peak position to reference values of 284,8 eV or 285 eV, but remembering to be consistent and only use one value throughout.

Should the C1s peak not be accessible, then attempt to use the O1s peak, which should be set to 530 eV.

2) QUASES is an example of a suitable software package available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

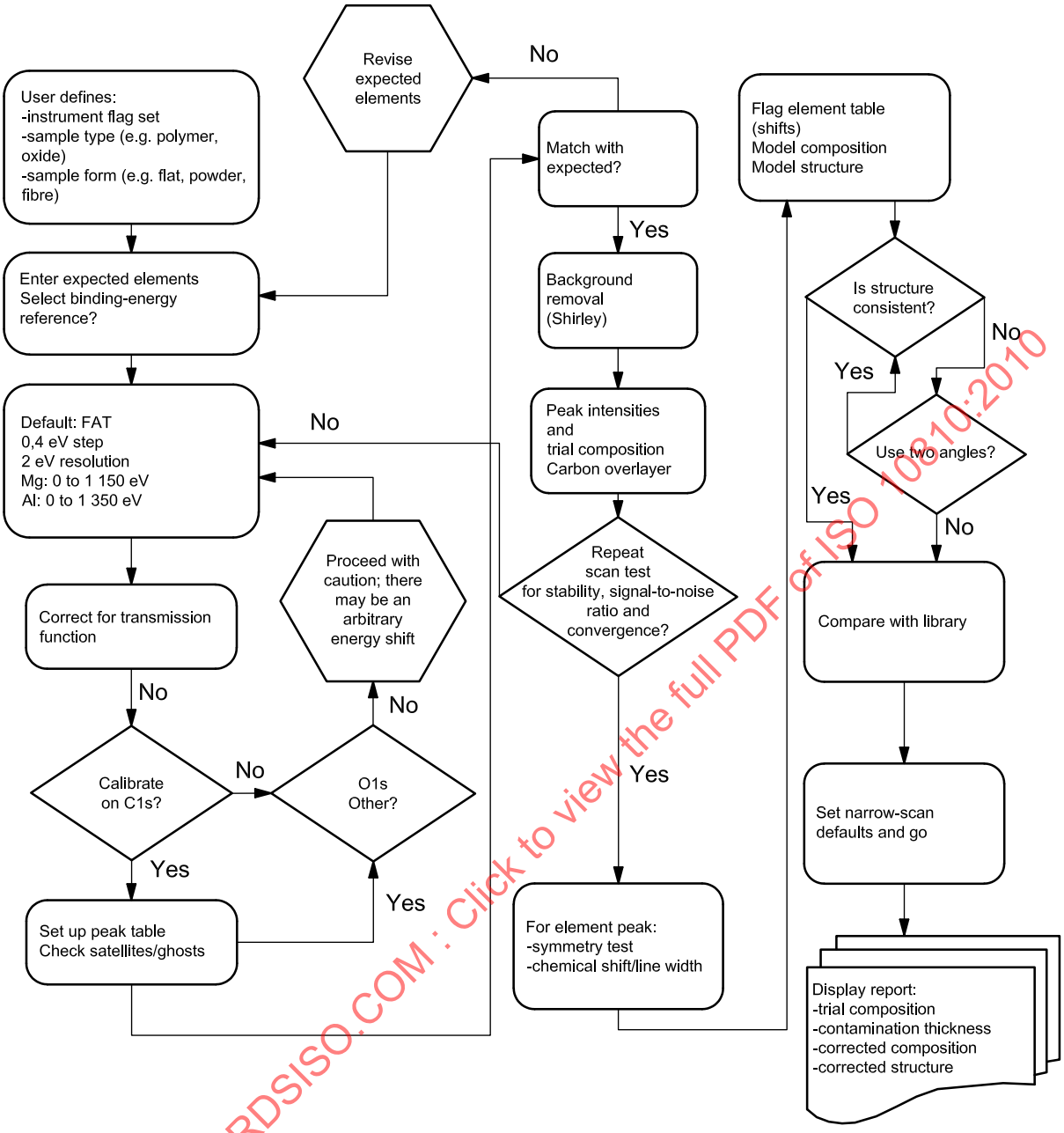


Figure 6 — Steps required to obtain a wide scan

8.2 Data analysis

8.2.1 Peak identification and labelling

Peak identification is most important. It forms the basis for all real-time data processing. All peaks should be labelled and the analyst should do the following:

a) Use pattern recognition. All elements have a number of peaks with specific binding energies and intensities which form an easily recognizable pattern. Identifying these patterns aids peak identification.

b) Include positions of any elements being sought.

c) Note positions of weak peaks due to photoelectrons excited by Cu Lα, O Kα and Mg/Al Kα X-rays from the X-ray source anode. These are peaks excited by X-rays from the second X-ray anode, if present, or from fluorescence X-rays from the window.

8.2.2 Peak intensity

Determine the peak intensity from the peak area after first removing the background. The Shirley[33] background can often be used, but it should be noted that the start and end positions are element-specific. A look-up table is necessary and may be provided with the instrumental software. The Shirley background should revert to a linear background if the background level on the high-binding-energy side of the peak is lower than that on the low-binding-energy side. The operator is referred to two documents: ISO/TR 18392[35] and ISO 20903[34].

8.2.3 Element-specific data

Tabulate all needed data. Such data may include peak positions, peak intensities, photoionization cross-sections or relative-sensitivity factors, EALs, positions of satellite peaks, background type and method of implementation, chemical shifts, peak overlaps, useful Auger peaks, Auger parameters and positions of energy-loss peaks. If peak-fitting or spectrum-fitting was used, record the equations utilized, the binding-energy range over which fits were made, the number of peaks fitted, any constraints in peak parameters, and the results of the fits together with any measures of fit quality and estimates of uncertainties in fit parameters.

8.2.4 Assessment and utilization of peak intensities[34]

Unless there are reasons to believe otherwise (e.g. for analysts who know that their sample consists of a number of layers, each of about 2 nm thickness, as in the semiconductor and magnetic-media applications), produce a table of atomic-percent composition, based on a homogeneous model. Decide, based on the carbon intensity, whether a carbonaceous overlayer is present and, if so, determine its thickness from the peak ratios of the main constituents (high-kinetic-energy peaks from below the overlayer will be relatively more intense than low-kinetic-energy peaks). A rule base developed by Castle[32] for the study of overlayers in corrosion studies may be useful for other applications.

8.2.5 Assessment and utilization of background[35]

The inelastic background shape and intensity relative to a peak gives information on the surface/substrate compositions and distribution of composition with depth (for example, subsurface peaks will have a high background on the low-kinetic-energy side of the peak relative to surface peaks). Where possible, use the Tougaard software[30] (or other suitable simulation software) with the major peaks of all elements as specified by the software producers (for example, it may be necessary to choose peaks that have no other structure within 30 eV of the peak of interest).

8.2.6 Assessment of wide-scan spectrum

Compare the measured wide-scan spectrum with previously measured spectra obtained with the same material (if available) or with spectra in publications and remote spectral libraries to ensure correct identification. It may be helpful to develop standard library formats for spectrum storage to assist in search-and-compare operations.

9 The narrow scan

9.1 General

Following acquisition and analysis of the wide-scan spectrum, regions that require a narrow scan should be identified.

9.2 Data acquisition

9.2.1 Instrument settings

The user should ensure that they are using the appropriate fixed retard ratio (FRR) or fixed analyser transmission (FAT) mode with retard ratio or pass energy and slit settings.

NOTE FRR may have advantages for Auger electron spectroscopy.

The step size should be set so that it is compatible with the anticipated FWHM of the peaks under study in the narrow-scan region (generally at least 10 points per eV).

Protocols for estimating the appropriate acquisition time are given in terms of signal to noise[36] and as a strategy for best practice[37]. The strategy for best practice requires a wide scan or some other primary knowledge to be obtained first in order to determine the dwell times to be used for the subsequent narrow scans.

9.2.2 Choice of region

Always record the C1s and the O1s region, together with regions incorporating the most intense core-level peaks detected on the wide-scan survey spectrum, and, where possible, avoid overlapping peaks.

Should Auger parameters be required for chemical-state information, an Auger peak should be recorded in addition to photoelectron peaks from each element.

9.3 Data analysis

9.3.1 Element identification

Identify elements responsible for photoelectron and Auger electron peaks using published data tabulations[5][6] and XPS handbooks[38][39][40], published spectra[41][42] or the NIST XPS database[43].

9.3.2 Chemical-state identification

9.3.2.1 Methods of identifying chemical state[44]

Consider peak positions, chemical shifts, lineshapes, energy-loss peaks, satellites and the valence-band spectrum. Estimate a rough composition from the measured peak intensities (assuming the sample to be homogeneous). Use a database of chemical shifts of photoelectron lines, Auger electron lines and Auger parameters, as appropriate, to interpret the peak energies. Such a database is available from NIST[43]. Compare the measured spectrum with linear combinations of reference spectra for elements and compounds containing the detected elements, using libraries of spectra or local measurements under the same measurement conditions as used in the analysis (and modifications of the reference spectra where necessary to account for any difference in measurement conditions). The reader is directed to currently available reference spectra[38][39][40][41][42][43][45].

9.3.2.2 Assessment of compositional inhomogeneities in the sample[34]

a) Methods of identifying possible lateral compositional inhomogeneities:

Use imaging XPS, if available, or translate the sample across the analyser field of view.

b) Methods of identifying possible compositional inhomogeneities with depth:

Tilt the sample to obtain XPS data for two widely separated emission angles.

Compare two peak intensities from the same element at widely separated energies, making use of the energy dependence of the electron effective attenuation length.

Observe the background following each peak. The peak with the highest background is usually that of the element deepest in the sample, and that with the lowest background is usually on the surface[46].

NOTE These approaches are useful only if compositional inhomogeneities occur over depths up to the information depth for the measurements[47].

Alternatively, remove surface layers (by sputtering, chemical processes, etc.).

9.3.2.3 Estimation and assessment of trial sample composition

From the measured peak intensities, estimate the composition for an identified phase. Is this estimated composition close to that expected for the sample (e.g. if the bulk composition is "known")? Consider what the estimated composition implies for chemical shifts (of photoelectron lines, Auger lines and Auger parameters), satellites, energy-loss features and the valence-band spectrum. Compare measured spectra with reference spectra for known compounds, where available (the reference spectra may have been measured previously on the same instrument or obtained from handbooks or databases). Is only one compound present?

9.3.2.4 Consideration of possibility of multiple compounds in sample

If multiple compounds are expected or suspected, examine the chemical shifts for various possible stoichiometries and check for the presence of satellites. Compare the measured spectrum with reference data for known compounds, where available (or make measurements locally of suspected compounds). Consider whether the measured spectrum is a linear combination of spectra for expected or suspected compounds (i.e. target factor analysis[48]) and determine the percentages of each phase [although this approach will break down if there are different distributions of phases with position (e.g. depth)]. Consider possible solutions or mixtures of components to produce either a single homogeneous phase (e.g. a polymer blend) or a mixture of phases. Is the measured spectrum a linear combination of spectra for separate phases? This test should be satisfactory unless there is the possibility of surface segregation or some other variation of composition with depth.

9.3.3 Quantification

9.3.3.1 Measurement of peak intensities[34]

a) Intensity measurement for a single peak (single chemical state of an element):

For peak intensity measurements for a series of spectra for similar samples, or for depth profiles where the composition is not varying rapidly with depth, the Shirley background[33][35] can be subtracted in order to determine the area of the "main" peak[34][35]. It is useful to apply the Tougaard algorithms[49][50] as quick checks to determine whether the sample is homogeneous with depth.

b) Intensity measurements for overlapping peaks (multiple chemical states of an element or multiple elements):

Here peak-fits are required using curve-fitting software and analytic functions believed from experience to represent component lineshapes for the local measurement conditions. Be aware of correlated uncertainties in peak parameters derived from fits to overlapping peaks[51][52].

9.3.3.2 Measurement of composition for an identified phase (homogeneous sample)

There are several approaches of varying accuracy.

a) To give an approximate composition:

The instrument will have its own software which will come with built-in sensitivity factors that may be obtained from the average over many samples but will provide a quantification in most cases. An assessment of the problems involved with this approach has been given by Seah and Gilmore[53]. This will be the most convenient method for obtaining a quantification, but may not give the best accuracy.

b) The operator may make use of relative-sensitivity factors for pure elements obtained from published data or from measurements made on pure elements in the spectrometer. The results should give improved accuracy but will be approximate since no corrections have been made for different atomic densities or for matrix effects.

c) To obtain a more accurate composition:

Average matrix relative-sensitivity factors can be used[54][55]. The accuracy of this approach decreases for peaks with kinetic energies less than about 150 eV.

Procedure:

— Measure elemental relative-sensitivity factors for pure elements (e.g. as described in ISO 18118[54]) or check the values supplied with the instrument.

— Compute average matrix relative-sensitivity factors from the product of elemental relative-sensitivity factors and the ratio of specified correction factors for that element and the corresponding correction factors for a hypothetical average matrix with specified material properties.

9.3.3.3 Measurement of composition as a function of depth

Depth information can be obtained in both non-destructive and destructive ways.

Non-destructive depth profiles are obtained by ARXPS or by utilizing the EALs of two peaks from the same element that are widely separated in energy. This has a depth limit as noted in 6.2.3. How the EAL is used (e.g. for measurement of film thickness) is described in two papers by Jablonski and Powell[56][57]. ARXPS can be used to determine element distribution as a function of depth by either tilting the sample relative to the analyser or varying the detection angle of the emerging photoelectrons. Parallel-collection methods, where information is collected simultaneously at different angles, improve the collection efficiency. The use of angle-resolved XPS to determine surface composition has been reviewed by Cumpson[58]. The ARCtick software embodying these concepts is available from the NPL[59]. Accurate layer thickness can be determined when the interfaces are abrupt but the accuracy decreases for broad interfaces. EALs are also used for the determination of the thickness of overlayer films that are thinner than the information depth[47]. NIST has published an EAL database[60] which supplies theoretically derived values of “local” EALs (derived from the slope of the emission depth distribution factor at a specified depth) and “practical” EALs suitable for measurements of overlayer film thickness. The current status of thickness measurements of SiO_2 has been reviewed in CCQM studies[61][62].

Some of the methods are listed below.

a) Non-destructive

— Peak shape analysis using a model for near-surface morphology and a model to correct for inelastic scattering[63][64].

— Angle-resolved XPS. Many algorithms are available (e.g. Cumpson's ARCtick software available from the NPL website) for analysis of data. See Cumpson's review[58] for details and the assumptions made in the analysis. Elastic scattering limits the range of analysis to emission angles smaller than 60° (from the surface normal) unless corrections are made. The appropriate EAL should be used[60]. Nevertheless, it can be difficult to distinguish different possible composition-versus-depth profiles[65].

— Diagnostics:

  — measurements on two lines from the same element at widely separated energies or on the same line for two different incident X-ray energies;

  — excitation energy method[66][67] in which the resulting change in photoelectron energies gives significantly different EALs.

— NIST has software for the simulation of electron spectra for surface analysis (SESSA)[68] that can be used to simulate an XPS spectrum for a multi-layered thin-film sample. The XPS spectrum is simulated for a sample with compositions and film thicknesses believed to be appropriate for the sample of interest. The simulated spectrum is then compared with a measured spectrum, and the film compositions and thicknesses adjusted as needed to obtain maximum consistency between the measured and simulated spectra. The detailed predictions do not, however, always agree with the experimental data[69].

b) Destructive

Depth measurements to depths exceeding a few nanometres require the use of destructive techniques. ISO/TR 15969[21] describes many of these techniques, from ball cratering and taper sectioning to ion sputtering. Table 4 is taken from Annex A of ISO/TR 15969:2001 and is a survey of typical applications and the uncertainties of the different methods. Of these techniques, ball cratering and taper sectioning are treatments generally applied to the sample prior to mounting in the spectrometer, while ion sputtering is the most frequently used *in situ* destructive profiling technique.

Ion sputtering uses either an inert-gas ion (such as argon) or a liquid-metal ion (such as gallium) to remove surface layers from the sample while recording spectra. Ion sputtering will modify the composition of the surface by preferential sputtering of surface atoms and by implanting sputtering ions into the surface. Therefore, it may only be possible to obtain a semi-quantitative measure of composition with depth.

The ion beam incident on the sample surface may be broad and extend over millimetres or may be focussed and rastered over an area to produce the required crater. Ion sputtering combined with XPS produces a signal intensity as a function of sputtering time. The total sputtering time corresponds to a crater depth, and the average sputtering rate is obtained by dividing the crater depth by the sputtering time. Crater depth measurements may be made using a mechanical-stylus method or optical interferometry. Alternatively, a certified reference material or reference material with known layer thickness of Ta_2O_5 on Ta or SiO_2 on Si may be used to calibrate the sputter rate by determining the sputtering time to reach the Ta/Ta_2O_5 or Si/SiO_2 interface. These may be used to optimize the depth resolution and also, with known sputtering-yield data[70][71], to provide a depth scale.

9.3.3.4 Measurement of overlayer-film thickness

Several approaches are useful:

a) Analysis of relative intensities for a substrate and an overlayer peak at a single emission angle.

b) Analysis of relative intensities for a substrate and an overlayer peak at multiple emission angles. For data obtained at emission angles between 0° and 60° (with respect to the surface normal), a single value for the electron EAL can be used[56][57][60][68]. For larger emission angles, the EAL is a strong function of the emission angle.

c) Use of a “correction-factor” function for the depth distribution function[72].

d) Peak shape analysis using models for the near-surface morphology and inelastic scattering[64][73].

e) Comparisons of measured and simulated spectra for a thin-film sample, and iteration of film composition and thickness to obtain maximum consistency of the spectra[68].

f) It may also be possible to derive film thicknesses from analysis of intensities of two lines from the same element with widely different energies or from analysis of intensities of a line for two different incident X-ray energies in which the resulting photoelectron energies are sufficiently different. In both cases, use is made of the dependence of the EAL on electron energy[60].