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Surface chemical analysis — X-ray photoelectron spectroscopy — Reporting of methods used for charge control and charge correction

Analyse chimique des surfaces — Spectroscopie de photoélectrons — Indication des méthodes mises en œuvre pour le contrôle et la correction de la charge

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO 19318:2004), which has been technically revised.

The main changes compared to the previous edition are as follows:

- Clause 7 has been reorganized and 7.7 (effectiveness of charge control) has been updated;
- Annex A has been updated, in particular A.2.1 (specimen damage), A.2.5.2 (specimen isolation) and A.3.3 (adventitious-hydrocarbon referencing);
- up-to-date bibliographical references have been added throughout the document.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

X-ray photoelectron spectroscopy (XPS) is widely used for the characterization of surfaces of materials. Elements in the test specimen (with the exception of hydrogen and helium) are identified from comparisons of the binding energies of their core levels, determined from measured photoelectron spectra, with tabulations of these binding energies for the various elements. Information on the chemical state of the detected elements can frequently be obtained from small variations (typically between 0,1 eV and 10 eV) of the core-level binding energies from the corresponding values for the pure elements. Reliable determination of chemical shifts often requires that the binding-energy scale of the XPS instrument be calibrated with an uncertainty that could be as small as 0,1 eV.

The surface potential of an insulating specimen will generally change during an XPS measurement due to surface charging, and it is then difficult to determine binding energies with the accuracy needed for elemental identification or chemical-state determination. There are two steps in dealing with this problem:

a) experimental steps can be taken to minimize the amount of surface charging (charge-control methods);

b) corrections for the effects of surface charging can be made after acquisition of the XPS data (charge-correction methods).

Although the build-up of surface charge can complicate analysis in some circumstances, it can be creatively used as a tool to gain information about a specimen.

The amount of induced charge near the surface, its distribution across the specimen surface, and its dependence on experimental conditions are determined by many factors including those associated with the specimen and characteristics of the spectrometer. Charge build-up is a well-studied,[6,7] three-dimensional phenomenon that occurs along the specimen surface and into the material. Charge build-up can also occur at phase boundaries or interface regions within the depth of the specimen that is irradiated by X-rays. Some specimens undergo time-dependent changes in the level of charging because of chemical changes or volatilization induced by photoelectrons and secondary electrons, X-rays, or heating. It is possible that such specimens will never achieve steady-state potentials.

There is no universally applicable method or set of methods for charge control or for charge correction.[8-10] This document specifies the information to be provided to document the method of charge control during data acquisition or the method of charge correction during data analysis, or both. Annex A describes common methods for charge control and charge correction that can be useful for many applications. The particular charge-control method that is chosen in practice depends on the type of specimen (e.g. powder, thin film or thick specimen), the nature of the instrumentation, the size of the specimen, and the extent to which the specimen surface might be modified by a particular procedure.

This document identifies information on methods of charge control or charge correction, or both, to be included in reports of XPS measurements (e.g. from an analyst to a customer or in publications) in order to evaluate, assess and reproduce data on insulating materials and to ensure that measurements on similar materials can be meaningfully compared. It enables published binding energies to be used with confidence by other analysts and will lead to the inclusion of more reliable data in XPS databases.

INTERNATIONAL STANDARD **ISO 19318:2021(E)**

Surface chemical analysis — X-ray photoelectron spectroscopy — Reporting of methods used for charge control and charge correction

1 Scope

This document specifies the minimum amount of information spectroscopy to be reported with the analytical results to describe the methods of charge control and charge correction in measurements of core-level binding energies for insulating specimens by X-ray photoelectron. It also provides methods for charge control and for charge correction in the measurement of binding energies.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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 document, the terms and definitions given in ISO 18115-1 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols and abbreviated terms

BE	binding energy, in eV
BE_{corr}	corrected binding energy, in eV
BE_{meas}	measured binding energy, in eV
$BE_{\mathrm{ref,meas}}$	measured binding energy of a reference material, in eV
BE_{ref}	reference binding energy, in eV
FWHM	full width at half maximum amplitude of a peak in the photoelectron spectrum above the background, in eV
XPS	X-ray photoelectron spectroscopy
Δ_{corr}	correction energy to be added to measured binding energies for charge correction, in eV

5 Apparatus

One or more of the charge-control techniques, also called charge-neutralization techniques, mentioned in Clause A.2 can be employed in most XPS spectrometers. The XPS instrument shall be operated in accordance with the manufacturer's instructions or other documented procedures.

Some of the techniques outlined in Clause A.2 require special apparatus, such as an electron flood gun or a source for evaporative deposition of gold.

Certain specimen-mounting procedures, such as mounting the specimen under a fine metal mesh[11], can enhance electrical contact of the specimen with the specimen holder, or reduce the amount of surface charge build-up. This and other methods of specimen mounting to reduce static charge are described in References [4] and [5].

6 Calibration of binding-energy scale

The binding-energy scale of the X-ray photoelectron spectrometer shall be calibrated using ISO 15472 or another documented method before application of this document.

7 Reporting of information related to charge control

7.1 General

Methods commonly used to control the surface potential and to minimize surface charging are summarized in Clause A.2. Information on the critical specimen and experimental conditions, as specified in 7.2 through 7.7, shall be reported for individual specimens or collections of similar specimens.

7.2 Information about specimen

7.2.1 Specimen form

The form of the specimen shall be reported. The physical nature, source, preparation method and specimen structure can influence charging behaviour.[7]

EXAMPLE 1 Powder.

EXAMPLE 2 Thin film spin-cast on silicon.

EXAMPLE 3 Macroscopic mineral specimen.

7.2.2 Specimen dimensions

The size and shape of a specimen can have a significant effect on the extent of specimen charging. The shape of the specimen shall be reported together with approximate values of the dimensions of the specimen or of any relevant specimen features (e.g. particle diameters).

7.2.3 Specimen mounting methods

Specimen mounting and contact with the specimen holder can significantly impact charging[2-5, 10]. The method by which a specimen is mounted, including information about special methods used to increase conductivity or isolate a specimen from ground, shall be reported.

EXAMPLE 1 Powder specimen pressed into foil, which was attached to a specimen holder using tape.

EXAMPLE 2 1 ml of contaminated liquid deposited on a silicon substrate and dried prior to analysis.

EXAMPLE 3 Specimen held to specimen holder using conductive adhesive tape of a specified type.

EXAMPLE 4 Corroded specimen held on specimen holder by metal screw.

7.2.4 Specimen treatment prior to or during analysis

The specimen treatment prior to or during analysis shall be reported, including any physical or chemical treatment that can affect charging of the specimen during XPS measurements.

EXAMPLE 1 Gold deposition.

EXAMPLE 2 Ar gas implantation from sputter ion source.

NOTE Such treatment of the specimen can modify the surface composition as well as the electrical conductivity, and hence charging, of the surface region.

7.3 Instrument and operating conditions

The instrument operating conditions shall be reported, including details of the:

- particular XPS instrument;
- nature of the X-ray source;
- approximate size of the X-ray beam on the specimen surface;
- analyser pass energy;
- measure of energy resolution such as the FWHM of the silver $3d_{5/2}$ photoelectron line for the selected operating conditions;
- angle between the specimen normal and the X-ray source;
- use or not of a magnetic lens.

7.4 General method for charge control

The particular instrumental component(s) used for charge control shall be identified.

EXAMPLE 1 Electron flood gun.

EXAMPLE 2 Electron flood gun in combination with an ion gun.

EXAMPLE 3 Specimen heating.

EXAMPLE 4 Irradiation with ultraviolet light.

EXAMPLE 5 Vendor XYZ charge neutralization system.[10]

If the components used are not standard for the XPS instrument, information shall be provided on the manufacturer or on the relevant design characteristics.

7.5 Reasons for needing charge control and for choosing the particular method for charge control

The reasons for needing charge control and for choosing a particular method shall be reported.

EXAMPLE 1 The portion of the specimen of interest was isolated from ground. Flood gun electrons were supplied for charge compensation using the standard flood gun for this instrument.

EXAMPLE 2 Experience with similar specimens indicated that differential charging was likely. To obtain good spectra, these specimens were totally isolated from ground. The application of the combined fluxes of a low-energy electron flood gun and a low-energy ion flux produced well-resolved peaks.

EXAMPLE 3 Initial spectra without any charge control showed peak shifting and broadening. Placing a grounded fine grid above the specimen solved these problems without leading to a significant signal due to the grid material. This method is easy to apply and is used routinely in measurements with similar specimens.

7.6 Values of experimental parameters

Values of parameters used to control charge, such as flood gun settings, shall be reported. Information about typical parameters for some charge neutralization systems on modern instruments is provided in Reference [10].

EXAMPLE For the flood gun, the cathode voltage was −5 V (with respect to instrumental ground), the emission current was 20 mA, and the gun cathode was 5 cm from the specimen.

7.7 Information on the effectiveness of the method of charge control

7.7.1 Adequacy of charge control

The adequacy of the charge-control methods for the type of analysis being conducted shall be established. FWHMs and the binding energies (BE_{meas}) of peaks in the measured spectra, after charging effects have been minimized, but before any charge correction has been made, provide one useful method for determining adequacy of the charge-control method. To document the effectiveness of the procedure(s) used to produce appropriate BE and FWHM measurements, it can be useful to have as a comparison a measurement of the FWHM of at least one photoelectron peak of similar chemistry in another specimen that is known to be conductive or for which the method of charge control is believed to be effective.

EXAMPLE 1 The FWHM of the oxidized Si 2p photoline was reduced from 2,4 eV to 1,6 eV by application of a flood gun. The 1,6 eV width is consistent with measurements made on a thin SiO_2 layer on Si.

EXAMPLE 2 The ability to control charge compensation over a wide energy range can be documented by measuring the energy separation between different photoelectron peaks from the same element. The adequacy of such a measurement assumes that there are no complications due to chemical state changes with depth or the presence of second phases.

7.7.2 Damage assessment

It is recommended that specimens be examined for the presence or absence of specimen damage due to sample charging or the impact of the charge neutralization method (see A.2.1) and that the results be recorded. If damage is observed, changes to the charge neutralization parameters can need to be adjusted and the changes recorded.

EXAMPLE Survey scans at the start and end of data collection showed no changes suggestive of intensity of peak structure changes due to damage.

8 Reporting of method(s) used for charge correction and the value of that correction

8.1 General

Many of the methods commonly used for charge correction are summarized in Clause A.3. The critical specimen and experimental parameters in 8.2 and 8.3 shall be reported.

8.2 Approach

The general method for correcting measured binding energies (peak positions) for charging effects shall be specified in sufficient detail so that the method can be reproduced and the effectiveness judged.

8.3 Value of correction energy

Information shall be given on the magnitude of the correction energy (Δ_{corr}) for each spectrum and how this correction energy was determined. The corrected binding energies and values of the reference energies shall be reported.

The correction energy (Δ_{corr}) is determined by taking the difference between the measured binding energy of a reference line ($BE_{ref,meas}$) and an appropriate binding energy value (BE_{ref}) for the reference line (obtained from the literature or other trusted source) using Formula (1):

$$\Delta_{corr} = BE_{ref} - BE_{ref,meas} \qquad (1)$$

The corrected binding energy for another photoelectron peak in the same spectrum (BE_{corr}) can then be found from the sum of the measured binding for that peak (BE_{meas}) and the correction energy:

$$BE_{corr} = BE_{meas} + \Delta_{corr} \qquad (2)$$

NOTE Formulae (1) and (2) apply only when charge compensation has adequately removed differential charging effects.

Annex A
(informative)

Description of methods of charge control and charge correction

A.1 General

This annex describes methods involving charge control, also called charge neutralization (the effort to control or minimize the build-up of charge at a surface or to minimize its effect, or both), as described in Clause A.2; charge correction (the effort to determine a reliable binding energy despite any build-up of charge) as described in Clause A.3; or some combination of the two as described in Clause A.4.

For charge control, peak shape is one of the most important parameters to consider in assessing the effectiveness of a method. Correcting a measured peak-energy position (i.e. binding energy) is accomplished separately using an appropriate charge-correction technique. When both a photoelectron line and a major Auger peak from the same element can be observed, the Auger parameter or the modified Auger parameter, described in Clause A.5, can be used to provide chemical-state information without the need to resort to charge corrections. Although the build-up of charge during XPS is often an unwanted complication, it can also be used to obtain important information about a specimen as noted in A.2.5.2 and A.2.5.3.

The amount and distribution of surface and near-surface charge for a specific experimental system are determined by many factors, including specimen composition, homogeneity, magnitude of bulk and surface conductivities, photoionization cross-section, surface topography, spatial distribution of the exciting X-rays, and availability of neutralizing electrons. Charge build-up occurs along the specimen surface and into the material.[6,7] The presence of particles on or different phases in the specimen surface can result in an uneven distribution of charge across the surface, a phenomenon known as differential charging. Charge build-up can also occur at phase boundaries or interface regions within the specimen that is irradiated by X-rays. Some specimens undergo time-dependent changes in the amount of charging because of chemical and physical changes induced by electrons, X-rays or heat.

There is no single method to overcome all charging problems in all instruments.[8,10] Several new methods were developed in the 1990s, including those that involve electrons, ions or magnetic fields, or both. All methods described in this annex assume that charging is not dependent on the kinetic energy of the signal electrons. It is possible that this will not be the case for some spectrometers or when differential charging occurs as a function of depth into the specimen. As reported in 2000, an inter-laboratory comparison of static-charge stabilization methods for a variety of insulating specimens using referencing to both gold and carbon showed that the standard deviation of the binding-energy measurements from 27 laboratories was, at best, 0,15 eV.[9] The report concluded that the reproducibility was unsatisfactory and that considerable additional work was needed.

A.2 Methods of charge control

A.2.1 Damage caution

Both the build-up of surface charge during XPS[6,10] and the methods that minimize charge accumulation can induce damage in some samples.[10,12] As some of the charge neutralization methods involve charged-particle or photon irradiation or the addition of materials to the surface, the possibility of specimen damage or specimen change from any such irradiations or treatments should be considered and tested by comparing data at different times during data collection.[13,14]

Multiple approaches can be used to check for damage. Some analysts take a rapid survey before and after high resolution scans and examine for differences as an indication of damage. Especially for known or suspected sensitive materials, analysts can take a rapid high-resolution scan of the sensitive species before most of the data collection and compare the initial scan with a similar scan after the majority of data is collected.

Reference [12] demonstrated that standard neutralizer operating conditions can be damaging to particularly sensitive samples, however, it is possible to alter the operation conditions to get effective charge neutralization while minimizing damage.

A.2.2 Electron flood gun[15-18]

Low-energy electron flood guns are frequently used to stabilize the static charging of insulators examined by XPS,[16] in particular when monochromatized X-rays are employed. Optimum operating conditions, for example, filament position, electron energy and electron current, depend upon the orientation of the electron flood gun with respect to the specimen and upon the particular design of the electron flood gun and should, in general, be determined by the user. Low electron energies (usually 10 eV or less) are used to maximize the neutralization effect and reduce the number of electron-bombardment-induced reactions. Currents need to be high enough to be effective, but low enough to avoid specimen damage or unwanted heating. A metal screen placed on or above the specimen can help.[19,20]

A.2.3 Ultraviolet flood lamp[21]

Ultraviolet radiation can produce low-energy electrons (e.g. from the specimen holder) that can be useful in neutralizing specimen charge.

A.2.4 Specimen heating

For a limited number of specimens, heating can increase the electrical conductivity of the specimen, thus decreasing charging.[7] The effects of specimen temperature and possible surface segregation need to be considered.

A.2.5 Electrical connection

A.2.5.1 Grounding and enhanced conduction path

Surrounding insulating materials with a conducting material has been a common approach to minimizing the charge build-up on specimens. This can mean masking a solid specimen with a conducting aperture, grid or foil, or mounting particles on a conducting foil or tape.[7,8]

A.2.5.2 Isolation from ground

For some materials, thin films or mixtures of materials with different electrical properties, non-uniform charge build-up (commonly called differential charging) is frequently observed. In many circumstances differential charging contributes significantly to peak distortion. Approaches to recognizing the presence of differential charge are described in Reference [10]. Differential charging can occur for many types of samples including thin films, materials with many interfaces, and materials with mixed insulating and conducting phases. The presence of a grounded portion of a sample and an insulating portion whose surface potential is influenced or controlled by a charge neutralization system can cause potential gradients in the sample producing complex and distorted XPS spectra.[10] Isolating such specimens from ground can minimize the leading sources of differential charging. Isolation of samples from ground is a recommended procedure for many samples including nanoparticle and polymer powders.[22] This approach allows the charge neutralization system to control sample surface potential[10] and often minimizes spectrum distortion.

Differential charging and multiple near-surface potentials are not bad in all circumstances. For some types of samples this phenomenon can be used to obtain information about the chemistry or composition of conducting or insulating parts of the specimen[23] and a potential gradient across a thin film can provide a source of electrical property information about such films.[24-26]

A.2.5.3 Biasing

Applying a low-voltage bias (−10 V to +10 V or more) to the specimen and observing the changes in the binding energies of various peaks can be used to give information about the electrical contact of a specimen (or parts of a specimen) with the specimen holder. Peaks in an XPS spectrum that shift when the bias is applied are from conducting regions of the specimen. It is possible that other peaks from insulating regions will not shift nearly as much, or at all, and can be interpreted accordingly. This method can sometimes verify that the peaks being used for charge correction (e.g. Au 4f or C 1s) are behaving in the same manner as the peaks of interest from the specimen.[11,21,27] For non-uniform or composite (non-conducting or partially conducting) specimens, a variety of charge shifts can be observed upon biasing. These measurements can provide useful information about the specimen and indicate a need to connect the specimen more carefully to ground or to isolate the specimen from ground. Sometimes, all data for some specimens are collected with a bias applied (see also Clause A.4).

A.2.6 Low-energy ion source

Portions of an insulator surface can be negatively charged, even when some areas exposed to X-rays are charged positively.[10,28] Such effects appear to be particularly important for focused X-ray beam systems, where the X-rays strike only a relatively small portion of the specimen. In these circumstances, the use of a low-energy positive-ion source, in addition to an electron source, can help stabilize (and make more uniform) the surface potential of the specimen.

A.3 Methods of charge correction

A.3.1 General

Because there are many sources of BE shifts in insulating and semiconducting materials, there is no simple way to obtain the “ideal” fundamentally correct BE for each peak in a spectrum in many circumstances. Regardless, with appropriate care, it is usually possible to collect and analyse XPS data on such materials to obtain the desired information. Each of the approaches described in A.3.2 through A.3.7 has advantages and limitations, highlighting the importance of reporting the methods and approaches used.[10]

A.3.2 Differential charging

A variety of methods is often used to determine the amount of binding energy shift due to surface charging. Each of these methods is based on the assumption that differential charging (along the surface or within the specimen) is not present to a significant degree. Approaches to identify the presence of charging and differential charging are described in Reference [10]. If significant differential charging is found to occur or thought to be present, it is possible that it will be necessary to alter the method of charge control.

A.3.3 Adventitious-hydrocarbon referencing [11,15,21,29-33]

Unless specimens are prepared for analysis under carefully controlled atmospheres, the surfaces are usually coated by adventitious carbon and possibly other contaminants from the environment. Once introduced into the spectrometer, further specimen contamination can occur by the adsorption of residual gases, especially in instruments with oil diffusion pumps. These contamination layers are frequently used for charge correction purposes. It is assumed that they accurately reflect the steady-state static charge exhibited by the specimen surface and that they contain an element with a peak of known binding energy. Carbon is most commonly detected in adventitious layers, and photoelectrons from the C 1s transition are often adopted as a reference. However, as described in A.3.3, adventitious C 1s spectra are very useful but often not reliable as an absolute binding energy reference.[10,29,32]

A reference binding energy between 284,6 eV and 285 eV is often used for the C 1s level of this contamination, and the difference between the measured binding energy and the reference value [see Formula (1)] is assumed to be the charge correction to be applied to the measured binding energies for other photoelectron peaks in the spectrum. This reference energy is based on multiple assumptions that the carbon is in the form of a hydrocarbon or graphite, that the carbon binding energy is fully coupled to the sample surface, and that other carbon species either are not present or can be distinguished from this peak.

This method is widely used because of the ubiquitous nature of adventitious carbon and the apparent simplicity of the approach. Observation of the adventitious C 1s peak shape and energy is highly valuable for many purposes, including recognizing the presence of surface charging, optimizing the parameters of charge neutralization, and making a first guess at the extent of needed binding energy corrections.[10] However, there are multiple issues with the assumptions involved in applying this method as an absolute binding energy reference that have been recognized for many decades[29,30] and more recently amplified for studies of adventitious carbon on metal surfaces.[32-34] As reported, there is uncertainty of the true nature of the carbon and the appropriate reference values.[15,29] Although many values reported fall within the range from 284,6 eV to 285,2 eV for the C 1s electrons from hydrocarbon and graphitic carbon, other studies report values significantly outside of that range. Studies of adventitious carbon on metal surfaces showed that the measured binding energy variation can be as much as 2 eV[31]. Other issues contributing to uncertainty include knowing the true nature of the carbon, variability in the coupling of the carbon to the sample surface, thickness dependent variations in the C 1s binding energy, and surface induced alterations of the carbon chemistry on some sample surfaces[10,22,33].

Despite the limitations and uncertainties associated with the use of adventitious carbon for static-charge correction, it is convenient and commonly applied. Carbon referencing, using adventitious carbon along with other carbon signals can be useful for polymers and highly carbonaceous materials where one or more carbon signals have well established binding energies[10,22]. Adventitious carbon can be used as one of several approaches to consistently determining binding energy shifts of a particular sample[10]. If adventitious carbon must to be the primary method used for correction, it is important to recognize the limitations and uncertainties. Often absolute knowledge of binding energies is not as critical as knowing relative positions. To use adventitious carbon as a relative binding energy reference, the reference binding energy (and peak FWHM) should be determined on the user's own spectrometer for specimens with a similar carbon coverage.

A.3.4 Gold deposition[15,16,35-38]

Gold deposition refers to the application of a thin layer (often 0,5 nm to 0,7 nm) of elemental gold to part or all of the surface of an insulator in order to provide a metal calibrant on the specimen surface. This layer can be connected to the spectrometer by mechanical contact with the specimen holder so that both the spectrometer and the layer are at the same electrical potential. It is assumed that the contact between the deposited layer and the surface of the specimen are influenced by the same surface charge and therefore that the specimen binding energies can be referenced to the gold binding energy. In practice, there are many difficulties with this method. Although it is of value in some circumstances (see Clause A.4 and Reference [39]), it is no longer widely used for XPS measurements. In many circumstances, Au forms small islands when deposited on many materials. It has been found that, for gold coverages of less than one monolayer, there can be a reaction with the substrate. In addition to producing changes in the specimen binding energies, such reactions can cause a chemical shift of the Au 4f$_{7/2}$ peak[36,37] that varies with surface coverage, and can result in a binding energy that is different from that expected for the gold metal reference. The influence of such reactions with the gold metal calibrant would be expected to decrease as the gold overlayer thickness increases. However, shifts in the Au 4f$_{7/2}$ peak can occur with changes in the thickness of the deposited material and with changes in its morphology. In addition, it is possible that even thick gold coverages (several monolayers) will not give continuous layers, and differential charging between the gold “islands” and the specimen can occur. In a study examining two approaches to binding energy referencing it was found that gold was useful as a consistent reference, but did not provide absolute accuracy.[39]

A.3.5 Implantation with inert gases[40]

Assumed binding energies of inert gases in solids have been used to measure the amount of charging in insulating specimens when a specimen is implanted with such a gas.[40] However, such implantation can change the chemistry of the specimen and induce binding-energy shifts and even peak splitting in the specimen spectrum. It has also been demonstrated that measured binding energies for an implanted species can vary in different matrices because of varying relaxation effects.[41]

A.3.6 Internal referencing

Sometimes the specimen is of such a nature that a portion of it has spectral lines of known binding energy that can be used as the charge reference.[10,22] This method assumes the invariance of the binding energy of the chosen chemical group in different molecules. The measured peak energy will include the static charge of the specimen. A charge correction, calculated to correct the binding energy of the reference chemical group to the assumed value, can be applied to other measured peaks. If carbon is used, the technique is called internal carbon referencing which can be particularly useful for polymers[22].

A.3.7 Substrate referencing

For work involving thin films on conducting (e.g. metals and non-intrinsic semiconductors) substrates for which the film is thin enough so that peaks from both the substrate and film can be observed, the observed binding energies of the conducting substrate can provide a useful reference for thin insulating overlayers. Substrate referencing can provide consistent and useful information for very similar samples, but consistency of data needs be evaluated and cannot be assumed. Processes such as band-bending[42], interfacial dipole layers, charge accumulation at interfaces leading to dipole electrostatic fields within a layer[10,43], film thickness effects, and possibly interfacial interactions can shift measured binding energies of the thin film relative to the substrate limiting the absolute accuracy of this approach. Interface dipoles, which can be inherent in the sample or induced by electron beam or X-ray exposure, can shift the energies of the material in the overlayer relative to the substrates[13,44]. The strength of the dipole can potentially be assessed from the change of the energy difference between the substrate peaks and the overlayer peaks relative to other samples where the dipoles are not expected to be present.

Substrate referencing is often used without application of charge neutralization methods. However, data can be collected in multiple ways:

i) substrate grounded, no charge neutralization;

ii) substrate grounded and charge neutralization;

iii) substrate isolated from ground but charge neutralization applied.

As shown in References [44], [10], [45] and [46], each of these configurations will produce different experimental results. The presence of inherent X-ray induced charge build-up or electrostatic fields at the substrate-overlayer interface or within the overlayers[10,43] can cause binding energy shifts between the overlayer and substrate. If the binding energy reference used is a core level from the substrate, there can be shifts of the measured binding energies of the species in the overlayers relative to the substrate. In contrast, if adventitious carbon or some other reference binding energy in or on the overlayers is used as the charge reference, the shifts due to electrostatic fields between the substrate and overlayer would be roughly symmetric and reflected by shifts in the BE of the substrate elements of the same magnitude but in the opposite direction. Such shifts can cause measured binding energies to appear at energies that can lead to confusion or misinterpretation if the causes are not recognized.

Mode i) has the advantage or not requiring a charge neutralization system and is useful with the recognition of the possible binding energy shifts. Mode iii), with the sample isolated from ground and charge neutralization, works for many types of thin film samples, but can also include the binding energy shifts between the substrate and overlayer. Based on previous experience and sample type, operators generally have preferences for mode i) or mode iii), recognizing the type of processes the can impact shifts between the substrate and overlayer. Applying charge neutralization to an insulating film on a grounded substrate [mode ii)] often induces a potential gradient across the film.[10,44] Such a gradient can be useful for learning electrical characteristics of a film or layer, but it is not recommended when attempting to use a peak in the substrate as a BE reference for photoelectron peaks in an insulating overlayer.

A.4 Bias referencing[27]

This method involves both charge control and charge correction and it is therefore listed separately, even though the basic elements have been described in Clauses A.2 and A.3. Use is made of a calibrant material introduced onto a specimen surface (as described in Clause A.3) and charge-control methods (Clause A.2) are utilized and optimized for a particular specimen and specific measurement conditions. This technique was developed to deal with observations on some specimens and in some spectrometers that the value of the correction Δ_{corr}, determined with the gold decoration method of charge correction (A.3.4), was not independent of the voltage applied to an electron flood gun. In several cases,[27] it was shown that the energy difference between specimen photoelectron lines and those of gold became independent of the applied flood-gun voltage when the voltage was sufficiently negative (and BE_{meas} moved to lower values). The objective is to adjust the flood-gun voltage so that this energy difference is constant, thereby improving the reliability of Δ_{corr}.

Typically, a small gold dot (with a diameter between 1 mm and 3 mm and with a thickness of about 25 nm) is placed on the specimen surface by vacuum evaporation. XPS spectra of both the gold dot and a representative area of the specimen surface are obtained under the influence of a negative bias (up to approximately 10 V) that can be produced by electrons from a conventional flood gun. The resulting spectra can be referenced to gold by the application of a correction calculated from the difference between the value of $BE_{ref,meas}$ for the Au $4f_{7/2}$ peak under negative bias conditions and the value of BE_{meas} for that same peak when the gold dot is in electrical contact with the spectrometer. In practice, Au $4f_{7/2}$ spectra are usually obtained before and after obtaining XPS data from the specimen in order to monitor system drift. It appears that this method brings about vacuum-level alignment rather than Fermi-level alignment and so it is possible that it will not be independent of the surface work function. [27]

A.5 Auger parameter measurements[47-49]

The Auger parameter is defined as the kinetic energy of the sharpest Auger peak in the spectrum (usually involving core levels) minus the kinetic energy of the most intense photoelectron peak from the same element.[47] (The energy of the ionizing photons must be specified before comparisons can be made between Auger parameter values.) The two measured transitions are equally affected by uniform static charging for most spectrometers. Because the Auger parameter can change with chemical bonding, this charge-independent value provides a different approach for the identification of the chemical state of an element [47,48] when the kinetic energies of both Auger and photoelectron peaks from the same element are available.

The modified Auger parameter is defined as the sum of the Auger parameter and the incident photon energy; alternatively, the modified Auger parameter can be obtained from the sum of the kinetic energy of the sharpest Auger peak in the spectrum and the binding energy of the most intense photoelectron peak from the same element. The modified Auger parameter is independent of photon energy and is often used instead of the Auger parameter to assist in the identification of the chemical state of an element. Some modified Auger parameter data can be found in Reference [50].

Although charging does not modify the Auger parameter in most circumstances, there is a risk that differences in charging as a function of depth, or even differences in the chemical nature of the regions examined as a function of depth, can complicate the measurements if peaks with significantly different mean escape depths are used to obtain the Auger parameter. In such circumstances, reliable interpretation of the measurements will be difficult.