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Standard Guide to Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy[1]

1. Scope

1.1 This guide acquaints the X-ray photoelectron spectroscopy (XPS) user with the various charge control and charge shift referencing techniques that are and have been used in the acquisition and interpretation of XPS data from surfaces of insulating specimens and provides information needed for reporting the methods used to customers or in the literature.

1.2 This guide is intended to apply to charge control and charge referencing techniques in XPS and is not necessarily applicable to electron-excited systems.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E673 Terminology Relating to Surface Analysis (Withdrawn 2012)[3]

E902 Practice for Checking the Operating Characteristics of X-Ray Photoelectron Spectrometers (Withdrawn 2011)[3]

E1078 Guide for Specimen Preparation and Mounting in Surface Analysis

E1829 Guide for Handling Specimens Prior to Surface Analysis

3. Terminology

3.1 *Definitions*—See Terminology E673 for definitions of terms used in XPS.

3.2 *Symbols:*

BE	Binding energy, in eV
BE_{corr}	Corrected binding energy, in eV
BE_{meas}	Measured binding energy, in eV
BE_{ref}	Reference binding energy, in eV
$BE_{meas, ref}$	Measured Binding energy, in eV, of a reference line
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

4. Overview of Charging Effects

4.1 For insulating specimen surfaces, the emission of photoelectrons following X-ray excitation may result in a temporary (or sometimes persistent) buildup of a positive surface charge caused by the photoelectric effect. Its insulating nature prevents the compensation of the charge buildup by means of electron conduction from the sample holder. This positive surface charge changes the surface potential thereby shifting the measured energies of the photoelectron peaks to higher binding energy. This binding energy shift may reach a nearly steady-state value of between 2 and 5 eV for spectrometers equipped with nonmonochromatic X-ray sources. The surface potential charge and the resulting binding energy shift is, generally, larger for spectrometers equipped with monochromatic X-ray sources because of the, generally, lower flux of low-energy electrons impinging on the specimen surface. This lower flux arises because focused, monochromatic X-ray beams irradiate only a portion of the specimen and not other nearby surfaces (for example, the specimen holder) that are sources of low-energy electrons. The absence of an X-ray window in many monochromatic X-ray sources (or a greater distance of the specimen from the X-ray window) also eliminates another source of low-energy electrons.

4.2 The amount of induced surface charge, its distribution across the specimen surface, and its dependence on experimental conditions are determined by several factors including specimen composition, homogeneity, magnitude of surface conductivity, total photoionization cross-section, surface topography, spatial distribution of the exciting X-rays, and

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

availability of neutralizing electrons. Charge buildup is a well-studied (**1, 2**)[4], three dimensional phenomenon that occurs along the sample surface and into the material. The presence of particles on or different phases in the specimen surface may result in an uneven distribution of charge across the surface, a phenomenon known as differential charging. Charge buildup may also occur at phase boundaries or interface regions within the depth of the sample that is impacted by X-ray radiation.

4.3 Several techniques have been developed for the purpose of controlling charge buildup and the subsequent changes in surface potential in order to obtain meaningful and reproducible data from insulating specimens. These techniques are employed during the data acquisition and are discussed in 7.2.

4.4 Several techniques have been developed for the purpose of correcting the binding energy shifts that result from surface charging. These corrections are performed after the data has been accumulated and are discussed in 7.3.

4.5 The use of the various charge control or charge referencing techniques described in this guide may depend on the available instrument as well as the specimen being analyzed.

4.6 Specimens with non-insulating surfaces are those with a high enough electron conductivity to dynamically compensate the electron loss caused by the photoelectric effect; they neither require control of the surface charge buildup nor charge reference corrections. It is important to distinguish the shifts due to the temporary charge build caused by the photoelectric effect from intrinsic charging effects. Intrinsic effects, such as the accumulation of charge at an interface during film growth, influence the nature of spectra obtained and the BEs measured, but are part of the sample (**3**). It is also possible that the impinging of the X-ray changes the charge distribution by means of volatilization of certain chemical species or the creation or charge centers. Such specimens may never achieve steady-state potentials. Although artifact to the process of measurement, those changes become part of the sample and are not necessarily to be corrected or compensated by the methods described in 7.2 and 7.3.

4.7 Major advances in the ability to control sample charging and to stabilize surface potential were made in the late 1990s including the ability to achieve charge control for small area analysis (**4**). These approaches usually involve the use of electron flood guns and some additional methods (ions or magnetic fields) to control localized surface charge (**5, 6**). As a result of these advances it is now possible to collect high quality reproducible data on many systems. However, these advances do not remove all of the challenges for optimizing the conditions for analysis for complex samples or interpreting the data.

4.8 Although changes in surface potential during XPS analysis and other charging effects are usually viewed as problems to be avoided, such phenomena can be used to extract important information about specimens (**7-9**).

5. Significance and Use

5.1 The acquisition of chemical information from variations in the energy position of peaks in the XPS spectrum is of primary interest in the use of XPS as a surface analytical tool. Surface charging acts to shift spectral peaks independent of their chemical relationship to other elements on the same surface. The desire to eliminate the influence of surface charging on the peak positions and peak shapes has resulted in the development of several empirical methods designed to assist in the interpretation of the XPS peak positions, determine surface chemistry, and allow comparison of spectra of conducting and non-conducting systems of the same element. It is assumed that the spectrometer is generally working properly for non-insulating specimens (see Practice E902).

5.2 Although highly reliable methods have now been developed to stabilize surface potentials during XPS analysis of most materials (**5, 6**), no single method has been developed to deal with surface charging in all circumstances (**10, 11**). For insulators, an appropriate choice of any control or referencing system will depend on the nature of the specimen, the instruments, and the information needed. The appropriate use of charge control and referencing techniques will result in more consistent, reproducible data. Researchers are strongly urged to report both the control and referencing techniques that have been used, the specific peaks and binding energies used as standards (if any), and the criteria applied in determining optimum results so that the appropriate comparisons may be made.

6. Apparatus

6.1 One or more of the charge compensation techniques mentioned in this guide may be employed in virtually any XPS spectrometer.

6.2 Some of the techniques outlined require special accessory apparatus, such as electron flood sources or a source for evaporative deposition.

6.3 Certain specimen mounting procedures, such as mounting the specimen under a fine metal mesh (**12**), can enhance electrical contact of the specimen with the specimen holder, or reduce the amount of surface charge buildup. This and other methods of specimen mounting to reduce static charge are described in detail in Guide E1078 and Guide E1829.

7. Procedures

7.1 The methods described here involve charge control (the effort to control the buildup of charge at a surface or to minimize its effect), charge referencing (the effort to determine a reliable binding energy despite buildup of charge), or some combination of the two. For charge control, peak shape is the most important parameter to consider. A constant and relatively uniformly surface potential provides the conditions needed to obtain reproducible data and optimum peak shape. Correcting the peak position is accomplished separately using an appropriate charge referencing technique. In some circumstances, the Auger parameter can provide chemical information without the need to resort to surface potential corrections.

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[4] The boldface numbers in parentheses refer to a list of references at the end of this standard.

7.2 A variety of different methods is used to either enhance conductivity to minimize charge buildup during XPS analysis or to control the surface potential by other methods. These methods employed to control the surface potential in insulating specimens are listed in Table 1 in approximate order of frequency of use (more frequently used first) and summarized below:

7.2.1 *Methods for Controlling the Sample Surface Potential:*

7.2.1.1 *Electron Flood Gun (**13-16**)*—Use of low-energy electron flood guns to stabilize the surface potential of insulators examined by XPS (**14**), 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 must, in general, be determined by the user. Use low-electron energies (usually 10 eV or less) to maximize the neutralization effect and reduce the number of electron bombardment-induced reactions. A metal screen placed on or above the specimen can help (**17, 18**).

7.2.1.2 *Low Energy Ion Source*—Recent work indicates that portions of an insulator surface can be negatively charged, even when some areas exposed to X-rays are charged positively (**19**). 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, helps stabilize (and make more uniform) the surface potential of the specimen. Several commercial XPS now effectively combine electrons and ions to achieve uniform surface potentials for many types of insulators.

7.2.1.3 *Ultraviolet Flood Lamp (**20**)*—Ultraviolet radiation can also produce low-energy electrons (for example, from the specimen holder) that may be useful in neutralizing specimen charging and stabilizing the surface potential.

7.2.1.4 *Biasing*—Applying a low-voltage bias (-10 to +10 V) to the specimen and observing the changes in the binding energies of various peaks can be used to learn about the electrical contact of a specimen (or parts of a specimen) with the specimen holder. Peaks in the XPS spectrum that shift when the bias is applied are from conducting regions of the specimen. Other peaks from insulating regions may 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 referencing (for example, gold 4f or carbon 1s) are behaving in the same manner as the peaks of interest from the specimen (**12, 20, 21**). For non-uniform or composite (non-conducting or partially conducting) specimens, a variety of charge shifts may be observed upon biasing. This may provide useful information about the sample and indicate a need to more carefully connect the specimen to ground or to isolate the sample from ground. Sometimes all data for some specimens are collected with a bias applied (see also 7.4).

TABLE 1 Methods Used to Stabilize or Control Surface Potential During XPS Analysis

Approach/Method	Section
Controlling the Sample Surface Potential	7.2.1
Electron Flood Gun	7.2.1.1
Low Energy Ion Source	7.2.1.2
Ultraviolet Flood Lamp	7.2.1.3
Biasing	7.2.1.4
Isolation from Ground	7.2.1.5
Minimizing Charge Accumulation	7.2.2
Grounding and Enhanced Conduction Path	7.2.2.1
Specimen Heating	7.2.2.2

7.2.1.5 *Isolation from Ground*—For some materials, or mixtures of materials with different electrical conductivity, differential charging can occur. This phenomenon can be used to obtain information about the sample (**4, 22**) and can sometimes be minimized (and a more uniform sample potential can be achieved) by isolating the specimen from ground. In some circumstances an electron flood gun is more effective in controlling the surface potential when the sample is isolated from ground.

7.2.2 *Methods for Minimizing Charge Accumulation*—These methods attempt to stabilize the surface potential by minimizing the charge buildup or potential change by lowering sample resistance to ground or the spectrometer mount.

7.2.2.1 *Grounding and Enhanced Conduction Path*—Surrounding of insulating materials with a conducting material has been a common approach to minimizing the charge build up on samples. This can mean masking a solid sample with a conducting aperture, grid, or foil or mounting particles on a conducting foil or tape (**2**).

7.2.2.2 *Specimen Heating*—For a limited number of specimens, heating can increase the electrical conductivity of the specimen, thus decreasing charging (**2**).

7.3 *Binding Energy Reference Methods*—A variety of methods (as listed in Table 2 and described below) have been used to determine the amount of binding energy shift resulting from surface charging in insulating specimens. Each of these methods is based on the assumption that differential charging (along the surface or within the sample) is not present to a significant degree. If significant differential charging is found to occur or thought to be present, it may be necessary to alter the method of charge (potential) control.

7.3.1 *Adventitious Carbon Referencing (**12, 13, 20, 23-27**)*—Unless specimens are prepared for analysis under carefully controlled atmospheres, the surface, generally, is coated by adventitious contaminants. 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 can be used for referencing purposes if it is assumed that they truly 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

TABLE 2 Binding Energy Reference Methods

Approach/Method	Section
Adventitious Carbon Referencing	7.3.1
Internal Referencing	7.3.2
Substrate Referencing	7.3.3
Gold Deposition	7.3.4
Implantation with Inert Gases	7.3.5

layers, and photoelectrons from the carbon 1s transition are those most often adopted as a reference.

7.3.1.1 A binding energy of 284.8 eV is often used for the carbon 1s level of this contamination and the difference between the measured position in the energy spectrum and the reference value, above, is the amount of surface potential shift caused by charging. This reference energy is based on the assumption that the carbon is in the form of a hydrocarbon or graphite and that other carbon species are either not present or can be distinguished from this peak.

7.3.1.2 A significant disadvantage of this method lies in the uncertainty of the true nature of the carbon and the appropriate reference values which have a wide range as reported in the literature (**13, 24, 25**) that ranges from 284.6 to 285.2 eV for the carbon 1s electrons. Therefore, it is recommended that if adventitious carbon is to be used for referencing, the reference binding energy should be determined on the user's own spectrometer. Ideally, this measurement should be carried out on a substrate similar in its chemical and physical properties to the material to be analyzed and covered by only a thin, uniform contamination layer (that is, of the order of a monolayer).

7.3.1.3 Care must be taken where adventitious hydrocarbon can be chemically transformed, as, for example, by a strongly oxidizing specimen (**25**). With less than one monolayer coverage of adventitious carbon, the carbon 1s binding energy sometimes decreases (**26**). The carbon binding energy may also shift as a consequence of ion sputtering; evidence has been found for carbon of lower binding energy, possibly graphite or, more likely, carbon in domains approaching atomic dimensions (**20**). One method for distinguishing the presence of more than one type of carbon is to monitor the FWHM of the carbon 1s photoelectron peak. Abnormally broad peaks suggest the presence of more than one type of carbon or differential charge. Broadened carbon 1s peaks may result from the presence of more than one type of carbon or differential charging. Despite the limitations and uncertainties associated with the use of adventitious carbon for static-charge referencing, it is the most convenient and commonly applied technique.

7.3.2 *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 (**23**). 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 shift factor, 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. In many circumstances, the oxygen 1s photoelectron peak is useful as a reference (**28**).

7.3.3 *Substrate Referencing*—For work involving thin films, the observed binding energies of the substrate provide a suitable reference for thin overlayers. Where available, this referencing should be employed since it accounts for band bending and overall charging. Interface dipoles may shift the energies of the material in the overlayer relative to the substrates (**29, 30**). Those dipoles are, however, part of the sample (**3**). The strength of the dipole could be 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.

7.3.4 *Gold Deposition (**13, 14, 23, 31-34**)*—Gold deposition refers to the application of a uniform thin layer (0.5 to 0.7 nm) of elemental gold to the entire surface of an insulator in order to provide a metal calibrant on the sample surface. This layer is also connected to the spectrometer by mechanical contact with the sample 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 is sufficient to establish a path that removes the specimen surface charge and positions the specimen binding energy position at a value that can be referenced to the gold binding energy. In practice, it has been found that for gold coverages, often less than one monolayer, there may be a reaction with the substrate. In addition to producing changes in the specimen, binding energies, such reactions may cause a chemical shift of the gold 4f peak (**32, 33**), and result in a different binding energy than expected for the gold metal reference. The influence of such reactions with the gold calibrant should decrease as the gold overlayer thickness increases. However, shifts in the gold 4f peak can occur with thickness of the deposited material and with changes in its morphology. In addition, it must be remembered that thick gold coverages may not form continuous layers and differential charging between the gold "islands" and the specimen may occur. Because of the many sources of uncertainty, this method is no longer widely used for XPS measurements.

7.3.5 *Implantation with Inert Gases (**35**)*—Assumed binding energies of inert gases in solids have been used to measure the amount of charging in insulating specimens if the specimens are implanted with such a gas (**35**). However, such implantation may change the chemistry of the specimen and induce binding energy shifts in the sample. It has also been demonstrated that measured binding energies for an implant species can vary in different matrices because of varying relaxation effects (**36**).

7.4 *Bias Referencing (**21**)*—This method involves both charge control and charge correction and it is therefore listed separately, even though the basic elements have been described in 7.2. Use is made of a calibrant material introduced onto a specimen surface (as described in 7.3) and charge-control methods (7.2) are utilized and optimized for a particular specimen and particular measurement conditions. This technique was developed in an effort 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 (7.3.4) was not independent of the voltage applied to an electron flood gun. In several cases, (**21**) 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 diameter between 1 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 may 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_{meas} for the gold $4f_{7/2}$ 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, gold $4f_{7/2}$ 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 may not be independent of the surface work function (**21**).

7.5 *Auger Parameter (**37-39**):*

7.5.1 The Auger parameter is defined as the kinetic energy of the sharpest Auger peak in the spectrum minus the kinetic energy of the most intense photoelectron peak from the same element (**37**). (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 static charging of the specimen surface, hence, the calculation of the Auger parameter results in a value that is independent of charging for most spectrometers. Because the Auger parameter may change with chemical bonding, this charge-independent value can sometimes be used to assist in the identification of the chemical state of an element (**37, 38**).

7.5.2 The modified Auger parameter is defined as the sum of the Auger parameter and the incident photon energy. (Or, alternately, as the sum of the kinetic energy of the sharpest Auger peak in the spectrum plus 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.

7.5.3 Although charging does not modify the Auger parameter, 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 could 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.

8. Keywords

8.1 charge control; charge referencing; charging; X-ray photoelectron spectroscopy

ANNEXES

(Mandatory Information)

A1. REPORTING INFORMATION RELATED TO CHARGE CONTROL

A1.1 Many of the methods commonly used to control the surface potential and to minimize surface charging are summarized in 7.1. The following critical specimen and experimental parameters are to be reported as appropriate:

A1.1.1 *Sample Information:*

A1.1.1.1 *Sample Type*—(for example, powder, thin-film, macroscopic specimen).

A1.1.1.2 *Sample Dimensions:*

(1) Sample Mounting Method(s)—(for example, powder pressed into foil, deposit on silicon, conductive adhesive tape type xyz, electrical connection to spectrometer).

(2) Sample Treatment Prior To or During Analysis—(for example, any physical or chemical treatment of the specimen prior to or during XPS measurements made to affect charging of the specimen during XPS measurements). Such treatment to the sample may modify the surface composition as well as the electrical conductivity of the surface region.

A1.1.2 *Instrument and Operating Conditions*—(for example, the particular XPS instrument and its operating conditions, including the X-ray energy (or choice of anode), use or otherwise of an X-ray monochromator, approximate size of the X-ray beam on the specimen surface, analyzer pass energy, a measure of energy resolution such as the FWHM of the silver $3d_{5/2}$ photoelectron line for the selected operating conditions and use of magnetic lens).

A1.1.3 *General Methods for Charge Control*—(for example, use of electron flood gun, ion gun, sample heating, or irradiation with ultraviolet light). The particular instrumental component(s) used for charge control shall be identified. If these components are not standard components of the XPS instrument, information should be provided on the manufacturer or on the relevant design characteristics.

A1.1.4 *Reasons for Choosing the Particular Method for Charge Control*—(for example, bulk insulating material, insulating powder, parts of specimen thought to be insulating, sample was mounted and isolated from ground, experience with similar samples, initial spectra without compensation showed surface charging, etc.).

A1.1.5 *Experimental Parameters of the Method Used for Charge Control*—(for example, cathode voltage and emission current for an electron flood gun and proximity to sample, conditions for minimization of the FWHM of a particular photoelectron line, etc.). Parameters as well as tests (or the experience base) used to establish these parameters should be indicated.

A1.1.6 *Information on the Effectiveness of Method of Charge Control*—(for example, 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). To document the effectiveness of the charge-control procedure(s), a measurement shall be reported of the FWHM of at least one photoelectron peak (preferably for a peak in the sample of interest) in another sample that is known to be conductive or for which the method of charge control is believed to be effective; this measurement should be made with the same operating conditions of the XPS instrument as for the original sample. Evidence of the presence or absence of sample damage should be noted.

A2. REPORTING OF METHOD(S) USED FOR CHARGE CORRECTION

A2.1 Many of the methods commonly used for charge correction are summarized in 7.2 – 7.4. The following critical specimen and experimental parameters are to be reported:

A2.1.1 *Approach*—The general method for correcting measured binding energies (peak positions) for charging effects must be specified. If a method is used that is not listed in 7.2 – 7.4, it should be described in some detail.

A2.1.2 *Value of Correction*—Information must be given on the magnitude of the correction energy (Δ_{corr}) for each spectrum and how this correction energy was determined. In addition, 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 ($BE_{meas,\ ref}$) and the accepted or reference value for this binding energy (BE_{ref}) using the following relation:

$$\Delta_{corr} = BE_{ref} - BE_{meas,\ ref}$$

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 energy for that peak (BE_{meas}) and the correction energy:

$$BE_{corr} = BE_{meas} + \Delta_{corr}$$

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