



Designation: E2735 – 14 (Reapproved 2020)

Standard Guide for Selection of Calibrations Needed for X-ray Photoelectron Spectroscopy (XPS) Experiments¹

This standard is issued under the fixed designation E2735; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide describes an approach to enable users and analysts to determine the calibrations and standards useful to obtain meaningful surface chemistry data with X-ray photoelectron spectroscopy (XPS) and to optimize the instrument for specific analysis objectives and data collection time.

1.2 This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This guide cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide will be applicable in all circumstances.

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 is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This guide is under the jurisdiction of ASTM Committee E42 on Surface Analysis and is the direct responsibility of Subcommittee E42.03 on Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy.

Current edition approved Dec. 1, 2020. Published December 2020. Originally approved in 2013. Last previous edition approved in 2014 as E2735–14. DOI: 10.1520/E2735-14R20.

2. Referenced Documents

2.1 ASTM Standards:²

E995 Guide for Background Subtraction Techniques in Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

E996 Practice for Reporting Data in Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

E1078 Guide for Specimen Preparation and Mounting in Surface Analysis

E1127 Guide for Depth Profiling in Auger Electron Spectroscopy

E1217 Practice for Determination of the Specimen Area Contributing to the Detected Signal in Auger Electron Spectrometers and Some X-Ray Photoelectron Spectrometers

E1523 Guide to Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy

E1577 Guide for Reporting of Ion Beam Parameters Used in Surface Analysis (Withdrawn 2020)³

E1634 Guide for Performing Sputter Crater Depth Measurements

E1636 Practice for Analytically Describing Depth-Profile and Linescan-Profile Data by an Extended Logistic Function (Withdrawn 2019)³

E1829 Guide for Handling Specimens Prior to Surface Analysis

E2108 Practice for Calibration of the Electron Binding-Energy Scale of an X-Ray Photoelectron Spectrometer

2.2 ISO Standards:⁴

ISO 10810 Surface Chemical Analysis—Depth Profiling—Measurement of Sputtered Depth

ISO 14606 Surface Chemical Analysis—Sputter Depth Profiling—Optimisation Using Layered Systems as Reference Materials

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.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

- ISO 14701 Surface Chemical Analysis—X-ray Photoelectron Spectroscopy—Measurement of Silicon Oxide Thickness
- ISO 14976 Surface Chemical Analysis—Data Transfer Format
- ISO 15470 Surface Chemical Analysis—X-ray Photoelectron Spectroscopy—Description of Selected Instrumental Performance Parameters
- ISO 15472 Surface Chemical Analysis—X-ray Photoelectron Spectrometers—Calibration of Energy Scales
- ISO/TR 15969 Surface Chemical Analysis—Depth Profiling—Measurement of Sputtered Depth
- ISO 18115-1 Surface Chemical Analysis—Vocabulary—Part 1: General Terms and Terms Used in Spectroscopy
- ISO 18115-2 Surface Chemical Analysis—Vocabulary—Part 2: Terms Used in Scanning-Probe Microscopy
- ISO 18116 Surface Chemical Analysis—Guidelines for Preparation and Mounting of Specimens for Analysis
- ISO 18117 Surface Chemical Analysis—Handling of Specimens Prior to Analysis
- ISO 18118 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Guide to the Use of Experimentally Determined Relative Sensitivity Factors for the Quantitative Analysis of Homogeneous Materials
- ISO/TR 18392 Surface Chemical Analysis—X-ray Photoelectron Spectroscopy—Procedures for Determining Backgrounds
- ISO 18516 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Determination of Lateral Resolution
- ISO 19318 Surface Chemical Analysis—X-ray Photoelectron Spectroscopy—Reporting of Methods Used for Charge Control and Charge Correction
- ISO/TR 19319 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Determination of Lateral Resolution, Analysis Area and Sample Area Viewed by the Analyser
- ISO 20903 Surface Chemical Analysis—Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy—Methods Used to Determine Peak Intensities and Information Required when Reporting Results
- ISO 21270 Surface Chemical Analysis—X-ray Photoelectron and Auger Electron Spectrometers—Linearity of Intensity Scale
- ISO 22335 Surface Chemical Analysis—Depth Profiling—Measurement of Sputtering Rate: Mesh-Replica Method Using a Mechanical Stylus Profilometer
- ISO 24237 Surface Chemical Analysis—X-ray Photoelectron Spectroscopy—Repeatability and Constancy of Intensity Scale

3. Terminology

3.1 *Definitions*—For definitions of surface analysis terms used in this guide, see ISO 18115-1 and ISO 18115-2.

4. Significance and Use

4.1 The purpose of this guide is assist users and analysts in selecting the standardization procedures relevant to a defined

XPS experiment. These experiments may be based, for example, upon material failure analysis, the determination of surface chemistry of a solid, or the composition profile of a thin film or coating. A series of options will be summarized giving the standards that are related to specific information requirements. ISO 15470 and ISO 10810 also aid XPS users in experiment design for typical samples. ASTM Committee E42 and ISO TC201 are in a continuous process of updating and adding standards and guides. It is recommended to refer to the ASTM and ISO websites for a current list of standards.

5. Procedure

5.1 *General Sample Characterization:*

5.1.1 *Sample History*—The analyst should obtain a summary of the background information of the sample, including descriptors, history, sample cleaning and handling, existing application data, bulk composition, and any prior analysis that has been conducted. The sample history, especially handling, packing and storage, can impact the approach needed to obtain the desired information. Because inadequate sample collection can sometimes destroy or minimize the ability to collect the desired information, it is often necessary to identify the needed information and establish the procedures to be used (5.2) before the surface analysis is performed.

5.1.2 *Vacuum Compatibility*—The compatibility of sample with instrument vacuum should be considered. Although some samples have inappropriately high vapor pressures for ambient temperature operation, some instruments may include a sample cooling stage, which allows these types of materials to be analyzed. Additionally, newer XPS systems often have improved vacuum pumps coupled with monochromatic X-ray sources (that do not heat the sample) and a small X-ray spot size (requiring less sample for analysis). As a result, strongly outgassing or subliming samples can often be examined.

5.2 *Design of Experiment:*

5.2.1 The goal of the experiment should be defined. Experimental goals may include data relating to the surface chemical composition and chemical state, surface segregation, quantification, layer thickness, nanostructures, and so forth. The identification of the specific analysis objectives influences sample handling, instrument setup, the approach to data collection, and finally the methods of data analysis.

5.2.1.1 **Table 1** is a summary of possible experiments along with different calibrations required to obtain meaningful data or to optimize the instrument for the best data in the time available.⁵ Also included are the ASTM and ISO standards for checking the parameter. In the table, an X indicates applications where a calibration is required. Additionally, the calibrations are ranked with X = generally important and XX = generally very important calibrations for a given task.

5.2.2 *General System Check*—The analyst should perform a general system health check (including mechanical components, sample holders, vacuum level, and performance check) as recommended by the instrument manufacturer. Many

⁵ Castle, J. E., Powell, C. J., Report on the 34th IUVSTA Workshop, XPS: From Spectra to Results—Towards an Expert System, *Surface and Interface Analysis*, Vol 26, 2004, pp. 225–237.

TABLE 1 Recommended XPS Calibrations for Defined Experiments

NOTE 1—The X indicates applications where a calibration is required. X = generally important, XX = generally very important. Local methods^A are procedures developed by an individual laboratory or the instrument manufacturer. NPL software for the calibration of the intensity scales of XPS instruments is available from the UK National Physical Laboratory.^B BCR 261^C is a certified reference tantalum oxide/tantalum foil calibration sample and NIST SRM 2135c^D is a certified nickel/chromium thin-film depth profile standard.

Instrument Calibrations and Checks	ASTM Standard	ISO Standard	Additional Sources	Elemental Composition	Chemical State	Low Level Detection	Quantification	Layer Thickness	Nano-structures
General System Check			Local Method	XX	XX	XX	XX	XX	XX
Sample Preparation	E1829 E1078	18116 18117		X	X	X	X	XX	X
Binding Energy	E2108 E1523	15472 19318		XX	XX		X		X
Intensity Repeatability and Constancy		24237		X	X	XX	XX	X	X
Intensity/Energy Response Function			NPL Software				XX	X	XX
Linearity of Intensity Scale		21270 18118		X	X		XX	X	XX
Peak Intensities	E995	18392 20903	Local Method	X	X	XX	X	X	X
Ion Gun and Sputter Rate	E1577 E1127 E1634	15969 22335 14606 14701	BCR 261					XX	XX
Depth Resolution	E1577 E1127 E1634 E1636	14606	BCR 261 NIST SRM 2135c					XX	XX
Analysis Area	E1217	19319		X			X	X	XX
Lateral Resolution		18516		X			X	X	X
Data Reporting	E996	14979		X	X	X	X	X	X

^A Manual from the system manufacturer.

^B National Physical Laboratory (NPL), <http://www.npl.co.uk/science-technology/surface-and-nanoanalysis/services/calibration-software-and-reference-materials-for-electron-spectrometers>.

^C European Institute for Reference Materials and Measurements, BCR261, certified reference material.

^D National Institute of Standards and Technology, NIST-SRM 2135c Ni/Cr Thin Film Depth Profile Standard, <http://www.nist.gov>.

analysts have also developed their own methods to verify the general operational health of an instrument. This might be done, for example, by testing a specimen commonly analyzed by the instrument to quickly verify the binding energies of few photoelectron peaks and overall count rates. Based upon the experiment to be performed, the relative importance of the parameters in Table 1 should be assessed, including calibration of the binding-energy scale, intensity repeatability and constancy, intensity/energy response function (IERF), linearity test of the intensity scale, energy resolution for the desired intensity, lateral resolution, charge compensation, depth resolution, and depth profile rate calibration.

5.2.3 Sample Transport and Preparation—As a surface analysis technique, X-ray photoelectron spectroscopy (XPS) is sensitive to the outermost few atomic layers of the sample being characterized. Specimens should be transported to the analyst in a container that does not come into direct contact with the surface of interest. In most cases, the analysis will be performed on the as-received specimen; therefore, the goal

must be to preserve the state of the surface so that the analysis remains representative of the original surface. Care must then be taken to ensure that no outside agents come in contact with the surface to be investigated. These agents include: fingers, solvents or cleaning solutions, gases (including compressed air) or vapors, metals, tissue or other wrapping materials, tape, cloth, tools, packing materials or the walls of containers. Handling of the surface to be analyzed should be eliminated or minimized whenever possible.

5.2.3.1 Proper preparation and mounting of specimens is particularly critical for surface analysis. Improper preparation of specimens can result in alteration of the surface composition and unreliable data. In addition, specimen mounting techniques have the potential to affect the intended analysis. Guides E1078 and E1829 and/or ISO 18116 and ISO 18117 describe methods the surface analyst may need to minimize the effects of specimen preparation when using any surface-sensitive analytical technique. Also described are methods to mount specimens so as to ensure that the desired information is not

compromised. Because of the wide range of types of specimens and desired information, only broad guidelines and general examples are included in the standards. The optimum handling procedures will be dependent on the particular specimen and the needed information. It is recommended that the specimen supplier consult the surface analyst as soon as possible with regard to specimen history, the specific problem to be solved or information needed, and the particular specimen preparation or handling procedures required.

5.2.4 Binding Energy, Energy Scale Linearity, and Charge Compensation—Calibrations of the binding energy (BE) scales of XPS instruments are required for four principal reasons. First, meaningful comparison of BE measurements from two or more XPS instruments requires that the BE scales be calibrated, often with an uncertainty of about 0.1 to 0.2 eV. Second, identification of chemical state is based on measurement of chemical shifts of photoelectron and Auger-electron features, again with an uncertainty of typically about 0.1 to 0.2 eV; individual measurements, therefore, should be made and literature sources need to be available with comparable or better accuracies. Third, the availability of databases of measured BEs for reliable identification of elements and determination of chemical states by computer software requires that published data and local measurements be made with uncertainties of about 0.1 to 0.2 eV. Finally, the growing adoption of quality management systems, such as ISO 9001, in many analytical laboratories has led to requirements that the measuring and test equipment be calibrated and that the relevant measurement uncertainties be known. As described in the ASTM and ISO procedures below, the accuracy of the BE calibration can be determined by the analyst and depends on the specific analysis objectives. If, for example, changes to a BE of 0.1 eV are important, the degree of instrument calibration needs to be more carefully adjusted than if changes of 0.2 eV or greater are adequate. Annex A of ISO 19318 also describes methods of charge control and charge correction.

5.2.4.1 A procedure is given in Practice E2108 and ISO 15472 for calibrating the BE scale of an X-ray photoelectron spectrometer equipped with one or more of the following sources of characteristic $K\alpha$ X-rays: magnesium (Mg) source, unmonochromated aluminum (Al) source, or monochromated Al source. In a first calibration for particular operating conditions of the instrument, or after the instrument has been modified, measurements are made of the binding energies of specified core levels of copper and gold, and these values are then compared with corresponding reference energies. The linearity of the BE scale is checked at a single point on the scale using a measurement of the position of either a specified core level of silver (monochromated Al source) or a specified Auger-electron transition of copper (Mg source or unmonochromated Al source). Additional checks can be made, if desired, with secondary standards. Procedures are given for determining the uncertainties of BE measurements (at the 95 % confidence level) at various times following a calibration. The analyst can therefore establish tolerance limits at the same level of confidence, based on the instrument stability and the analyst's needs. Then, BE measurements statistically are likely to be made within these limits during specified time intervals

following a calibration. The instrument is then adjusted or subsequent BE measurements are corrected. For a routine check of the instrumental calibration, either one or two measurements are made each of the same core levels of copper and gold. In Practice E2108 and ISO 15472, a flow chart is given that summarizes the steps of the calibration procedure; references are given to relevant sections of this standard. An optional procedure is provided for determining the average energy of the X-rays from a monochromated Al X-ray source, using a measured position of a copper Auger peak in order to determine modified Auger parameters.

5.2.4.2 As discussed in Guide E1523 and ISO 19318 and ISO 21270, the emission of photoelectrons following X-ray excitation may result in a buildup of a positive surface charge on insulating specimen surfaces. 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 are generally larger for spectrometers equipped with monochromatic X-ray sources because of the often lower flux of low-energy electrons impinging on the specimen surface. 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 availability of neutralizing electrons. Methods of charge control include using an electron flood gun, an ultraviolet flood lamp, specimen heating, improving the electrical connection (grounding and enhanced conduction path, isolation from ground, and biasing), a low-energy ion source or a source utilizing combined low energy electrons and low energy inert ions such as argon. Methods of charge correction include adventitious hydrocarbon referencing, gold deposition, implantation with inert gases, internal referencing, and substrate referencing.

5.2.5 Intensity Energy Response Function (IERF, Transmission Function)—Because spectrometers of different designs have responses that vary differently with electron energy and settings, it is essential to know the instrument-energy response function (or transmission function) for quantitative analyses. Some instruments have methods included in the software that allows the response function to be tested and appropriate parameters linked to a specific set of data. The National Physical Laboratory (NPL, United Kingdom) has developed software⁶ for intensity calibration of cylindrical mirror analyzer (CMA) or hemispherical sector analyzer (HSA) spectrometers. With spectra acquired from copper, silver, and gold reference materials, the software can be used to calculate the intensity response function (or transmission function) of the spectrometer. The calibration gives the transmission function

⁶ National Physical Laboratory (NPL), <http://www.npl.co.uk/science-technology/surface-and-nanoanalysis/services/calibration-software-and-reference-materials-for-electron-spectrometers>.