



XPS in industry—Problems with binding energies in journals and binding energy databases

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This paper is dedicated to Dr. Charles D. Wagner for his pioneering efforts to build XPS data-banks.

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ABSTRACT

Experimentally measured BEs are commercially available in various forms, e.g. scientific journals, handbooks, internet based data-banks, computer-based data-banks of BEs or complete sets of actual spectra. This review addresses fundamental problems that exist in experimentally measured binding energies (BEs) stored in various numerical X-ray Photoelectron Spectroscopy (XPS) data-banks, including, for example: (1) PHI Handbook of XPS (1979), (2) NIST SRD-20 XPS Database, v1.0–4.1 (1989–2017), (3) Wiley Practical Surface Analysis 1st and 2nd ed. (1990), (4) SASJ ComPro v12 and Data-bank (1990–2017), (5) JEOL Handbook of XPS (1991), (6) CRC Practical Handbook of Spectroscopy (1991), (7) PHI Handbook of XPS, 2nd Ed. (1992), (8) AVS Surface Science Spectra (1993–2017), (9) LaSurface Web Site Database – XPS (2001–2017), and (10) Biesinger XPSfitting website (2012–2017). The 3 major problems in all existing data-banks are due to: (a) the widespread use of different calibration energies, (b) the widespread use of different energy scales, and (c) the widespread use of a “user-defined” BE for the C 1s peak attributed to hydrocarbon moieties. At the end of this review there is a list of recommendations for the design and content of future XPS data-banks.

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1. Introduction

X-ray Photoelectron Spectroscopy (XPS) is trusted as a method, as a tool, that provides reliable chemical state assignments.

Information derived or interpreted from analyses of XPS data is used to make valuable decisions in major industries for product development, process improvement and materials characterization. For this reason, it is important to understand the problems and characteristics that exist in: experimentally measured binding energies (BEs) published in peer reviewed scientific literature, calibration energies provided by instrument manufacturers, and calibration energies (CEs) recommended by various organizations (e.g. ISO, ASTM).

This review focuses on the fundamental problems that exist in binding energies that are published in the literature and subsequently used to make chemical state assignments.

The fundamental problems, that are discussed in this review, limit the usefulness of the information derived from XPS analyses when industry tries to use published BEs to develop new materials and to solve real world problems.

At the end of this review you will find a few suggestions on how to diminish those problems.

1.1. Industries that use XPS

Semiconductor, Polymers, Steel, Printing, Packaging, Fuel Cells, Catalysts, Medical, Bio-medical Devices, Coatings, Thin Films, Photovoltaic, Solar Cell, Paper, Paint, Dentistry, Cosmetics, Inkjets, Inks, Optical, Laser, Space, Automobile, Aerospace. . .

1.2. Common industrial applications of XPS

- Chemical State Identification
- Effects of Heat or Plasma Treatments
- Quality Control
- Contamination Analysis
- Chemical Structure of Multi-layered Films
- Stoichiometry of Bulk Material
- Thickness of Thin Films

In Table A1 in Appendix A, we list most of the problems that exist in the various numerical data-banks of BEs that are commercially available in handbooks, a government run database, scientific journals, and various websites.

2. Background

Data-banks of XPS data can be classified into two basic types: (1) numerical data-banks and (2) spectral data-banks. Each type can be stored in printed or digital form with or without data processing (e.g. smoothing, deconvolution, peak-fitting, atomic% summary, annotation. . .). In this review, we will discuss BEs in numerical data-banks, journals, and handbooks.

The BE numbers in numerical data-banks are often referred to as “measured BEs” because they were published in peer-reviewed scientific journals and because the authors reported at least one calibration (reference) energy, e.g. the BE of the Ag 3d5/2 peak, Au 4f7/2 peak, C 1s peak, or the Fermi edge at 0 eV.

Measured BEs, published in scientific journals, are often assumed to be accurate enough to allow reliable assignments of chemical states to be made even though the BE number was most likely measured only one time from a single sample, and were measured by a graduate student who has not checked the calibration energies for many months, if ever.

It is surprising that published measured BEs for various pure chemicals can have large ranges of uncertainty, but are still

assumed to be accurate to be reliable. Large ranges of uncertainty exist for pure chemicals because they were measured by a very large number of researchers and engineers around the world who used various energy scales, various calibration energies and various charge referencing energies.

Most of the measured BEs that are used to make chemical state assignments in industry and academia were published in a very wide variety of scientific journals between 1970 and 1985. The energy scales of the instruments in use during these years had a Cu 2p3/2 BE ranging from 932.2 to 932.8 eV, a Au 4f7/2 BE ranging from 83.8 to 84.2 eV and a hydrocarbon moiety C 1s BE ranging from 284.2 to 285.2 eV. Comparing these ranges to repeat measurements of CEs on any XPS instrument shows that 0.4–0.6 eV ranges will dramatically change chemical state assignments for a very wide variety of materials.

To minimize confusion in terminology, we use the following phrases and definitions:

- (a) measured binding energy (BE):
i.e. a BE experimentally measured from research materials, commonplace materials, standard reference materials, certified reference materials or secondary reference materials and published in the literature, a book or data-bank.
- (b) calibration energy (CE):
i.e. a BE used to calibrate or define the energy scale of an XPS instrument. These calibration energies (CEs) are measured from the principle XPS signals of pure, clean pieces of Au, Cu, or Ag. A CE value is **NOT** to be confused with a measured BE value.
- (c) hydrocarbon moiety C 1s charge referencing energy:
i.e. the C 1s BE of the hydrocarbon moiety (component) of adventitious, carbon-bearing materials used for the purpose of correcting measured BEs derived from non-conductive materials. This moiety is the fragment of an organic material that is composed of only C and H that are not directly bound to any other element.
- (d) chemical state ($\neq$ oxidation state):
i.e. the electronic, chemical, and physical nature of a chemical element as it exists in combination with a group of one or more other elements or in its natural “elemental” state. (Organic polymers have carbon–carbon covalent bonds with C 1s BEs close to 285.0 eV, whereas carbon–fluorine covalent bonds have a C 1s BE close to 292 eV. The difference is not related to a change in oxidation state.)
- (e) numerical data-bank:
i.e. a collection consisting of numbers only. It normally contains simple lists or tables of high energy resolution electron binding energy (BE) numbers, Auger parameter numbers or kinetic energy (KE) numbers that are attributed to or assigned to a group of one or more atoms, which, for example, are called a chemical state, a functional group or an oxidation state.
- (f) spectral data-bank:
i.e. a collection consisting of spectra only, stored in either raw or processed form with or without atom% composition tables, peak-fit tables, annotation or other information. This type of data-bank contains actual spectra obtained under various analysis conditions from various energy regions usually ranging from –10 to 1400 eV.

Dr. Charles Wagner [1], who dedicated much of his career to the field of XPS, reviewed countless journal publications for the sole purpose of extracting measured BEs derived from XPS measurements of many different materials. He cross-checked and organized those BEs into tables and charts of XPS BEs, which, in effect, formed the first XPS numerical data-bank. Most of the materials used to build this collection of measured BEs were commonplace materials that were expected or reported to have a high degree of bulk

or surface purity. Very few, if any, of those materials were certified reference materials, standard reference materials or secondary reference materials. Dr. Wagner's tables of experimentally measured BEs form the very core of all versions of the NIST SRD-20 XPS Database [2–4]. All of us who use XPS are greatly indebted to Dr. Wagner for his very significant efforts to assemble the 1st widely available data-bank of measured BEs derived from a wide host of commonplace materials.

His tables of measured BEs are partially or fully reproduced in both editions of PHI's Handbooks of XPS [5,6], both editions of Practical Surface Analysis [7,8], JEOL's Handbook of XPS [9], the website built by LaSurface [10], and the XPSfitting website built by M. Biesinger [11].

Scientists in research and industry routinely use Dr. Wagner's BE tables to assist them in their efforts to assign chemical state structures (e.g. CH₂ or CHF; SiO or SiO₂; Cu⁰ or Cu₂O) to XPS peaks obtained by peak-fitting high energy resolution (chemical state) spectra. As a result, data-banks of BEs published in scientific journals, handbooks and government supported data-banks, are still used to generate new information and new interpretations derived from experimentally measured XPS spectra.

The reliability of that new information is directly affected by and determined by the reliability of all measured BE numbers, which, in turn, are directly affected by the calibration (reference) energies used to calibrate the energy scales of the instruments that were used to measure those thousands of BEs. This means that the reliability of new information obtained from any measured XPS signal is limited by the random errors, systematic errors, and uncertainties of the calibration (reference) energies [12] used to collect those BEs.

Personal communications with experienced XPS scientists revealed that the systematic and random errors and uncertainties in measured BEs in numerical data-banks (e.g. NIST XPS SRD-20 data-bank), handbooks and journals are large enough to allow inexperienced XPS analysts to make chemical state assignments that are wrong or misleading. This problem is the main reason for writing this review.

If the reader reviews various BE data-banks and publications having tables of BEs [2–29], the reader will find that during the past 40 years the XPS calibration (reference) energies reported for pure gold (Au 4f7/2) have ranged from 83.7 ± 0.2 eV to 84.07 ± 0.05 eV, a range of BEs >0.3 eV. The reported ±0.2 uncertainty in the 83.7 eV value allows the BE to range 0.4 eV from 83.5 eV to 83.9 eV. An older publication, published by K. Siegbahn [36], indicates that pure gold was at one time reported to have a BE of roughly 83 eV.

During the same 40 year period the calibration energy for the Cu 2p3/2 signal of pure copper (Cu⁰) has ranged from 932.2 eV to 932.8 eV [2–29]. Therefore, it is reasonable to expect that the BEs for many conductive materials (alloys, metallic elements, semiconductors, steels etc.) should have an uncertainty as large as ±0.3 eV especially if its principal signal is in the higher end of the BE scale (700–1400 eV).

The objective of this review is to discuss a few of the problems in the numerical data-banks that are currently available to the public.

3. Data reliability and problems

Information derived from XPS spectra is similar to information derived from other types of spectroscopic data because the reliability of all forms of information depends directly on the reliability of the peer-reviewed literature values used to make chemical state assignments and the calibration (reference) energies used to calibrate the instruments (XPS, AES, IR, NMR, SIMS etc). When an institution (eg company, private lab, university, or government lab) purchases peer-reviewed scientific journals that report measured BEs and other surface science information, then those scientists in those institutions are expecting a high degree of reliability for BEs published in peer-reviewed scientific journals.

The surface science literature, that publishes XPS BEs, normally provides only small and un-organized tables of numerical BEs that are scattered over thousands of publications. As a result, many XPS analysts have, in the past, bought, use, and rely on the numerical data-banks provided in several versions of the NIST SRD-20 XPS Database (v1.0–v4.1), PHI Handbook of XPS (1st and 2nd Ed) and the literature to make valuable business decisions.

Because XPS is widely considered to be a mature science and a reliable tool to determine chemical state information, many XPS users suffer from the various problems described in Table A1 in Appendix A.

This section reviews key aspects of data reliability and reveals problems that exist in numerical data-banks and the literature.

As stated before, scientists and engineers, who are responsible for interpreting and converting raw XPS spectra into accurate or useful information, assume that the BE numbers in numerical data-banks are sufficiently reliable and have uncertainties and errors that are small enough to allow them to generate reliable chemical state assignments. This assumption indicates that many XPS users do not realize or know that the measured BEs listed in numerical data-banks suffer from a variety of significant, systematic and random errors, that exist because the BE numbers in those data-banks were generated by many hundreds of different instrument operators, who used different calibration energies, various C 1s charge referencing energies and various analysis conditions that affect measured BE numbers [12].

An example of the early problems that are due to variations in calibration energies is shown in Table 1 that lists the calibration energies provided by instrument makers soon after XPS became a viable analytical tool.

To understand the severity of the problem, the reader is asked to compare the 0.6 eV range in calibration BEs for the Cu 2p3/2 signal of pure elemental copper (Cu⁰) to the 0.2 eV difference in BEs between pure copper (Cu⁰) and Cu₂O found in [4], which lists 16 different BEs for Cu₂O that range from 932.2 to 932.7 eV. Such a difference means that beginning users, who use different energy scales

Table 1
Various calibration energies recommended by XPS instrument manufacturers before 1980 [29].

XPS Instrument	AEI	HP	Kratos	PHI	VG
Year	1972	1976	1977	1979	1980
Model	100	5950	200	550	Mk1
X-ray Type	Mg non-mono	Al mono	Mg non-mono	Mg non-mono	Mg non-mono
XPS Signal	BE (eV)	BE (eV)	BE (eV)	BE (eV)	BE (eV)
Cu 3p	75.2	75.1	–	74.9	75.1
Au 4f7/2	84.2	83.96	83.8	83.8	83.7
Ag 3d5/2	368.2	368.25	368.2	367.9	367.9
Cu 2p3/2	932.2	932.47	932.8	932.4	932.5
C 1s, adventitious	–	284.7	285.0	284.6	–

Table 2
Various calibration energies published by authors before 1980 [5,13–16].

XPS Signal	Wagner 1979 BE (eV)	Schon 1973 BE (eV)	Asami 1976 BE (eV)	Richter 1978 BE (eV)	Johansson 1973 BE (eV)
Au 4f7/2	83.8 eV	84.0 eV	84.07 eV	84.0	83.8
Ag 3d5/2	367.9	368.2	368.23	–	368.2
Cu 2p3/2	932.4	932.2	932.53	932.7	932.8
C 1s, adventitious	284.6	284.6	–	285.2	285.0
Reference	[5]	[13]	[14]	[15]	[16]

provided by different instruments, will make wrong chemical state assignments or will assume they have bad material.

Table 2 shows that authors used the calibration energies provided by the instrument manufacturers, which forms the basis of the systematic variations in measured BEs published in the literature, one of the problems listed in Table 1.

Table 2 also shows that authors have published measured BEs for non-conductive insulators by arbitrarily assigning the hydrocarbon moiety C 1s charge referencing peak to occur at C 1s BEs ranging from 284.6 to 285.2 eV. This 0.6 eV range in charge referencing non-conductive materials is large enough to confuse the assignment of 2 or more chemical states for a wide variety of materials. This totally arbitrary choice of C 1s BE is another of the problems listed in Table 1.

A less well-known problem, surface degradation [20–27] occurs while the surface of interest is inside high vacuum and exposed to an X-ray source. Degradation, when it occurs, often introduces new chemical states that may affect measured BEs due to the loss of various gases (eg H₂, HCl, HF, F₂, H₂O, CO₂).

The use of different calibration energies directly causes systematic errors in numerical data-banks especially when the contributor does not report the Cu 2p3/2 BE which reveals the energy scale of the instrument being used. These various systematic and random problems are being addressed by groups of experienced scientists who have performed national and international round-robin comparison tests and have reported that there are indeed a variety of significant errors and uncertainties in nearly all XPS data.

These errors and uncertainties are also the major driving force behind the current national and international efforts to develop international standards for XPS by various experienced scientists who donate their time and effort in the hope of improving future results and the pursuit of international standards. This level of activity clearly infers that many of the older measured BEs are questionable and need to be verified, corrected, or simply deleted.

In response to these now obvious problems, many companies and universities have begun building in-house data-banks of complete sets of self-consistent XPS spectra that provide more accurate BEs that are essential to solving the problems caused by the overlap of BE signals from similar chemical states having similar BEs. These sorts of private in-house spectral data-banks require many years to complete because the normal work of the industrial scientist is not to collect reliable, reference grade spectral data. However, by being self-consistent, the reliability of chemical state assignments is greatly improved, in turn improving the reliability of the information gained and the products being produced.

A few of the numerical BE data-banks, discussed in this review, are listed in Table A2 in Appendix A.

4. Numerical and spectral data-banks

As mentioned at the start, the objective of this review is to discuss the features and problems of the numerical data-banks that are readily available to the public. Spectral data-banks, which also provide BEs, are listed in Table A2 in Appendix A but are not part of the current review.

4.1. Numerical data-banks of measured binding energies

Numerical data-banks are data-banks of numbers only, no spectra. This type of data-bank normally contains simple tables of measured electron binding energy (BE) numbers, which, in certain data-banks, are listed adjacent to the attributed chemical states and a reference to the original publication. These chemical states are the ones being used to make chemical state assignments in industry, academia, and government labs.

The data-bank published by NIST (SRD-20 X-ray Photo-electron Spectroscopy Database, v1.0–v4.1) is a prime example of a numerical data-bank that contains thousands of measured BE numbers. This type of numerical data-bank is currently widely used by many scientists and engineers working to assign chemical state structures to BEs derived from peak-fitting with or without charge referencing to the hydrocarbon moiety C 1s peak.

Several books and handbooks [5–9] have appendices that contain the exact same numerical data-banks and references provided in the NIST database. Two of the handbooks include a few raw spectra from pure elements which serve as a rough guide for processing raw spectra, and a few chemical state spectra from well-known non-conductive polymers or non-conductive chemical compounds (eg TiO₂). Due to the complicated peakshapes of many chemical state spectra, actual spectra are valuable to determine if newly measured experimental results represent a pure chemical state or a mixture of chemical states. With this in mind, a library of actual XPS spectra is sorely needed to improve chemical state assignments derived from peak-fits of chemical state spectra of not only pure chemicals but also mixtures of chemicals.

Before delving into the specifics of the problems that plague numerical data-banks, we re-iterate the main causes of the problem that we all face when we try to use simple numerical data-banks of measured BEs. Today's numerical data-banks were, in fact, measured by many different analysts, who used many different XPS instruments having different calibration energies and energy scales, many different experimental conditions, and based BEs on the results from single run experiments. Because graduate students or analysts normally ran each analysis only once, the repeatability, reproducibility, and uncertainty of the BEs in these data-banks are, in effect, poorly defined or unknown.

4.2. Problems in XPS numerical data-banks

Of the problems (Table A1 in Appendix A) that might affect the BEs reported in various numerical BE data-banks, this section focuses on the 3 most critical and fundamental problems in those data-banks.

Now, just as in the past, many XPS instrument operators do not routinely check, document, track, publish or use more than 1–2 of the 6–8 calibration energies provided by instrument makers. There are many potential reasons for the lack of checking calibration energies. Reasons such as: (a) machine time is too expensive, (b) there's no time just now, (c) the machine is running just fine, (d) the energies have been the same the last 3 times we checked last year, etc.

Table 3

Various calibration energies published by authors between 1990 and 1998 [51–55].

Author	Strohmeier	Kelly	Beard	Sherwood	Sherwood
Year	1995	1993	1992	1998	1990
Instrument	Kratos	SSI	PHI	Kratos	VSW
Model	XSAM 800	S-Probe	5400	ES200 B	HA 150
X-ray Type	Mg non-mono	Al mono	Mg non-mono	Mg non-mono	Al mono
XPS Signal	BE (eV)	BE (eV)	BE (eV)	BE (eV)	BE (eV)
Cu 3p	74.9	–	74.95	75.14	75.1
Au 4f7/2	84.0	84.15	83.82	–	–
Ag 3d5/2	368.0	–	368.08	–	368.3
Cu 2p3/2	932.7	932.71	932.49	932.67	932.7
C 1s, adventitious	285.0	–	284.8	–	284.6
Reference	[51]	[52]	[53]	[54]	[55]

Table 4

Various calibration energies published by authors between 2000 and 2002 [56–60].

Author	Poirier	Kwok	Cox	Haasch	Silversmit
Year	2000	2000	2001	2000	2002
Instrument	PHI	Kratos	Leybold	PHI	PHI
Model	Quantum	AXIS-HS	LHS-11	5400	5500
X-ray Type	Al mono	Al mono	Al mono	Mg non-mono	Mg non-mono
XPS Signal	BE (eV)	BE (eV)	BE (eV)	BE (eV)	BE (eV)
Cu 3p	–	–	–	–	–
Au 4f7/2	84.0	84.00	–	83.7	84.2
Ag 3d5/2	–	–	368.1	–	368.47
Cu 2p3/2	–	–	–	932.4	932.8
C 1s, adventitious	–	–	–	–	284.6
Reference	[56]	[57]	[58]	[59]	[60]

A cursory check of the NIST numerical database indicates that a few laboratories around the world do indeed routinely check and routinely report two calibration energies to define and document the energy scale of their particular instruments. This is an improvement over the use of just one calibration energy, but may not address the energy scale variances (or voltage drifts) that occur in the high BE range (500–1400 eV) where several industrially important transition metals (e.g. Fe, Co, Ni, Cu, Zn) have strong signals that are often used to determine their chemical states.

5. Fundamental problem #1

5.1. Uncertainties in calibration (reference) energies

As early as 1969, commercial instrument makers provided calibration energies for the Ag 3d5/2, Ag 3d3/2, Au 4f7/2, Au 4f5/2, Cu 3p, Cu 3s, Cu 2p3/2 and Cu 2p1/2 signals and other useful signals, but the operators or owners, all too frequently, normally publish or check only one or two of the 6–8 calibration energies that were provided by the instrument makers for the sole purpose of routinely checking and correcting energy scale settings and linearity.

This operator-based practice of using just one or two calibration energies to check or define the energy scale calibration of an XPS instrument is a practice that is directly responsible for many of the errors in the BEs of conductive, semi-conductive and non-conductive materials listed in various numerical data-banks. This tendency is easily found by doing a random review of the calibration energies provided in the NIST SRD-20 database.

Calibration (reference) energies, developed by an international team of XPS experts, were published in 2001 by the International Standards Organization (ISO) Technical Committee (TC/201) for Surface Chemical Analysis as ISO document #15472 (titled: Surface chemical analysis – X-ray photoelectron spectrometers – Calibration of energy scales) [73]. The ISO calibration energies for a monochromatic Al K α 1 source for the Cu 2p3/2, Cu 3p3/2, Ag 3d5/2 and Au 4f7/2 signals are 932.62, 75.01, 368.21 and 83.96 eV, respectively. These ISO values are reported with ± 0.02 eV uncertainty, and they represent the first international effort to standardize the calibration energies used to calibrate the energy scales of XPS instruments worldwide. The lack of international calibration energy standards until 2001 means that most of the calibration energies used over the past 40 years, have uncertainties [12] that

Table 5

Various calibration energies published by authors between 2014 and 2017 [61–65].

Author	Marin	Muro	Watts	Salvi	Dillingham
Year	2016	2017	2015	2015	2014
Instrument	Ulvac-PHI	Scienta-Omicron	Thermo-Scientific	SPECS	PHI
Model	Quantera	R4000	Theta-Probe	PHOIBOS 100	5100
X-ray Type	Al mono	Synchrotron	Al mono	Al mono	Mg non-mono
XPS Signal	BE (eV)	BE (eV)	BE (eV)	BE (eV)	BE (eV)
Cu 3p	–	–	–	–	–
Au 4f7/2	–	Au fermi edge	83.85	84.05	–
Ag 3d5/2	–	–	368.16	–	368.27
Cu 2p3/2	–	–	932.61	932.67	–
C 1s, adventitious	284.8	–	285.0	285.0	–
Reference	[61]	[62]	[63]	[64]	[65]

Table 6
Subtle changes in BEs for AuCu Alloy Series. SpecMaster Database BEs versus NIST v4.1 BEs [38,4].

	SpecMaster Database Cu 2p _{3/2} BE (eV)	SpecMaster Database Au 4f _{7/2} BE (eV)	NIST v4.1 Range for Cu 2p _{3/2} BE (eV)	NIST v4.1 Range for Au 4f _{7/2} BE (eV)
25:75 AuCu	932.53	84.37	932.45–932.47	84.26–88.04
50:50 AuCu	932.41	84.21	932.40–932.52	84.25–87.96
75:25 AuCu	932.35	84.12	932.25–932.41	84.06–87.73
Reference	[38]	[38]	[4]	[4]

* — AuCu 25:75 (NIRM) scraped & etched 1 min 3KV 90TOA
 — AuCu 50:50 (NIRM) scraped & etch 1 min 3KV 90 TOA
 — AuCu 75:25 (NIRM) scraped & etched 1 min 3KV 90TOA

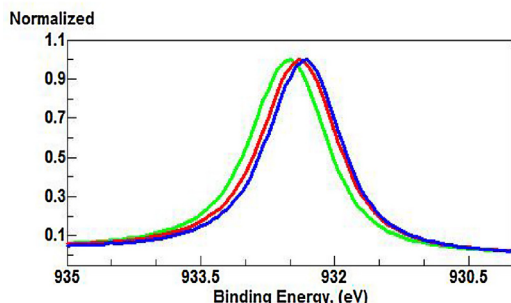


Fig. 1. Cu 2p_{3/2} spectra from AuCu alloys with Au:Cu ratios ranging from 25:75 to 50:50 to 75:25.

are large enough to affect the chemical state assignments of any material, including conductive ones.

Much of the uncertainty and reliability problems in numerical data-banks of high energy resolution electron BEs is due, in large part, to the fundamental differences in the calibration energies that have been and continue to be used to calibrate the BE scale of XPS instruments. This trend is documented in Tables 3–5.

After studying various BE data-banks and publications [2–29] the reader will find that during the past 40 years the XPS calibration (reference) energies reported for pure gold (Au 4f_{7/2}) have ranged from 83.7 ± 0.2 eV to 84.07 ± 0.05 eV, a range of BEs >0.3 eV. The reported ± 0.2 uncertainty in the 83.7 eV value allows the BE to range 0.4 eV from 83.5 eV to 83.9 eV. Still older publications indicate that pure gold was at one time reported to have a BE of roughly 83 eV [36].

During the same 40 years the calibration energy for the Cu 2p_{3/2} signal of pure copper (Cu⁰) has ranged in the literature between 932.2 eV and 932.8 eV [2–29]. Using a ± 0.2 eV uncertainty for each value means that the Cu 2p_{3/2} signal can have a 1.0 eV range between 932.0 eV and 933.0 eV.

Therefore, it is reasonable to expect that the BEs for many conductive materials (alloys, metallic elements, semiconductors, steels etc.) should have an uncertainty as large as ± 0.4 eV especially if its principal signal is located in the higher end of the scale (700–1400 eV).

With this ± 0.4 eV uncertainty range in published BEs and the <0.3 eV energy resolution capability of today's monochromatic or synchrotron based XPS systems it is very possible to make wrong chemical state assignments for conductive materials that are chemically similar.

This possibility is revealed as a reality by comparing the subtle changes in the BEs (Table 6) for Cu 2p₃ and Au 4f_{7/2} obtained from a series of CuAu alloys (see spectra in Figs. 1 and 2), which were compared to BEs included in the NIST XPS database v4.1 (rf Au 4f_{7/2} ranges from 84.26 to 88.04).

This type of problem occurs for alloys that contain the same elements, but contain different ratios of those elements, or compound semi-conductors mixed together in different ratios which are only slightly different in composition.

* — AuCu 25:75 (NIRM) scraped & etched 1 min 3KV 90TOA
 — AuCu 50:50 (NIRM) scraped & etch 1 min 3KV 90 TOA
 — AuCu 75:25 (NIRM) scraped & etched 1 min 3KV 90TOA

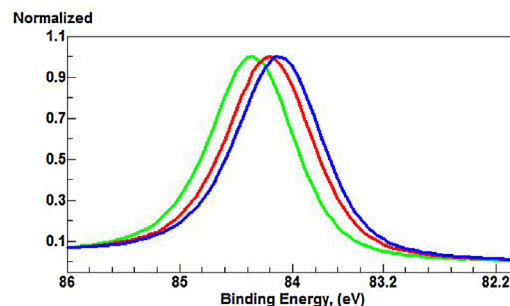


Fig. 2. Au 4f_{7/2} spectra from AuCu alloys with Au:Cu ratios ranging from 25:75 to 50:50 to 75:25.

In the past, the range of uncertainty in BEs was inevitable due to the large FWHM of non-monochromatic X-ray sources, previous instrument design tolerances, previous low precision electron volt standards and related limitations obscured such small chemical shifts. But today, the quality of electronics and monochromatic X-ray sources have improved significantly.

The resulting question is, “Are new scientific publications based on new, more accurate or old, more uncertain calibration energies?”

6. Fundamental problem #2

6.1. Separation between calibration (reference) energies

A second fundamental problem that affects the reliability and accuracy of the BEs in any numerical data-bank is the separation in calibration (reference) energies (SCE). An SCE value is the difference between a high calibration energy from the BE of Cu 2p_{3/2} and a low calibration energy from the BE of Cu 3p or Au 4f_{7/2}. The range in SCE values is normally the result of using different calibration (reference) energies, but may also be due to limitations in original, old electronics.

This systematic problem would be easy to compensate for if a publication included freshly measured calibration energies for both low BE and high BE calibration energies such as the BEs from the Cu 2p_{3/2}, Cu 3p or Au 4f_{7/2} signals, but it is difficult, if not impossible, to correct published data in the existing numerical data-banks because most authors normally reported only one calibration energy in their publications or they reported a low calibration energy from the Au 4f_{7/2} signal or a mid-range calibration energy, from signals such as the hydrocarbon moiety C 1s or Ag 3d_{5/2} signal.

Instruments used today, and in the past, have an SCE value between 848.0 and 849.0 for the Cu 2p_{3/2}–Au 4f_{7/2} signals. The 1 eV difference between these values has significant consequences toward the BEs reported. Poorly maintained instruments (e.g. oxidized sample mount, oxidized roller bearings) or dirty reference materials (e.g. Cu or Ag) can produce SCE values larger or smaller than those listed in Table 7. Such differences cannot be corrected for if the author reports only one calibration energy or reports calibration energies below 700 eV.

Table 7

Separation in calibration energies (SCE) used by instrument manufacturers [29].

	AEI	HP	Kratos	PHI	VG
Year	1972	1976	1977	1979	1980
Model	100	5950	200	550	Mk1
Calibration Peaks	SCE	SCE	SCE	SCE	SCE
Cu 2p _{3/2} – Cu 3p	857.0	857.4	na	857.5	857.4
Cu 2p _{3/2} – Au 4f _{7/2}	848.0	848.5	849.0	848.6	848.8

The SCE values derived from the ISO reference energies is 848.67 ± 0.01 for the Cu 2p_{3/2}–Au 4f_{7/2} energy separation. Maintaining this SCE value is critical to the production of new reliable BEs to be shared internationally.

7. Fundamental problem #3

7.1. C 1s charge referenced BEs from non-conductive materials

A third fundamental problem of uncertainty and error exists for non-conductive materials (insulators) which represents by far the most common type of material analyzed by XPS.

To use BEs measured from a non-conductive material, the XPS user must first use a method to compensate, offset or correct for the charge induced energy shift that occurs when the X-rays and/or a low voltage beam of electrons strike the surface of the area being analyzed. This method is commonly called “Charge Referencing”.

Charge referencing is performed by mathematically correcting all experimental peak values to a suitable reference energy, which in the case of non-conductive materials, is normally the C 1s BE of the covalently bonded, non-ionic, hydrocarbon (component) moieties (C–H, C–C, C=C, C_nH_m) that exist on the “as-received” surface of nearly all materials. This hydrocarbon moiety (component) is the dominant form of adventitious carbon on all materials if the sample has not been recently ion etched, fractured in vacuum, or specially treated to remove the adventitious carbon.

Table 8

C 1s binding energies for adventitious hydrocarbon moieties reported by Swift [30,34].

Reference	Year	C 1s BE (eV)	Substrate	Au 4f _{7/2} BE (eV)
Malmsten	1970	285.0 ± 0.4	Cu	na
Schön	1973	284.8	Ag, Au, Cu, Pd, Pt	84.0
Johansson	1973	285.0 ± 0.3	Au, Cu, Pd, Pt	83.8
Richter	1978	285.2 ± 0.2	Au, Cu, Pd	84.0
Wagner	1979	284.6	Au, Cu	83.8
Wagner	1980	284.8	(na)	84.0

This 3rd fundamental problem exists in all numerical data-banks, and is due to the 0.4–0.6 eV range in the reference energy of the hydrocarbon moiety C 1s peak BE that is used for charge referencing non-conductive materials. Table 8 shows the range of C 1s reference energies still in use today.

The hydrocarbon moiety C 1s reference energy that is used for charge referencing raw spectra obtained from non-conductive materials depends completely on the initial training of the operator, author, or scientist. Each beginner is trained to believe (accept) that the C 1s reference energy for the hydrocarbon moiety is one of the following values: 284.6, 284.7, 284.8 or 285.0 eV. At this time, there is no standard reference energy for the C 1s BE of the hydrocarbon moiety or any pure non-conductive hydrocarbon material, and there is no known method for ensuring a true Fermi level contact between the surface of a non-conductive material and a suitable reference material or a user deposited layer of some pure non-conductive hydrocarbon material.

The 0.6 eV range of hydrocarbon moiety C 1s reference energies (284.6–285.2 eV) shown in Table 8 is based on a summary published by Swift [30,34] and the work done between 1970 and 1980 by Malmsten, Schön, Johansson, Richter, and Wagner (referenced in Swift [30,34]), who reported hydrocarbon moiety C 1s BEs found by peak-fitting the C 1s signals attributed to the hydrocarbon moieties that exist on the “as-received” surfaces of several noble metals: Ag, Au, Cu, Pd, Pt (Table 8). The decision to use only noble metals was not defined in the original publication.

Legend																					
1		2														13	14	15	16	17	18
LiCl		Be°														B°	C°	Si ₃ N ₄	SiO ₂	MF	Ne(+)
Mean BE	56.03	111.57													187.28	284.63	397.82	532.88	684.12	962.40	
Std. Dev.	0.21	0.25													0.85	0.42	0.48	0.42	1.04	0.75	
Range	0.40	0.50													2.00	1.52	1.72	2.30	3.50	1.80	
# of Values	3	3													5	15	35	51	20	4	
95% Confid	0.52	0.63													1.06	0.23	0.17	0.12	0.49	1.19	
NaCl		Mg°														Al°	Si°	P°	S°	KCl	Ar(+)
Mean BE	1071.90	49.64													72.90	99.40	130.18	163.91	196.70	241.32	
Std. Dev.	0.56	0.21													0.19	0.26	0.32	0.60	2.82	0.63	
Range	1.60	0.65													0.80	1.30	1.00	1.90	6.50	1.90	
# of Values	8	11													16	51	10	9	9	11	
95% Confid	0.47	0.14													0.10	0.07	0.23	0.46	2.17	0.43	
KCl		CaCO ₃	Sc°	Ti°	V°	Cr°	Mn°	Fe°	Co°	Ni°	Cu°	Zn°	Ga°	Ge°	As°	Se°	KBr	Kr(+)			
Mean BE	292.67	346.87	398.55	453.86	512.44	574.19	639.67	707.28	778.18	852.73	932.61	1021.70	18.64	29.17	41.71		68.80	207.45			
Std. Dev.	0.19	0.15	0.34	0.32	0.25	0.27	1.02	0.93	0.25	0.40	0.21	0.35	0.20	0.28	0.20		0.12	0.21			
Range	0.40	0.30	0.50	1.10	0.76	0.90	2.22	4.20	0.70	1.80	0.90	1.30	0.56	1.05	0.50		0.20	0.30			
# of Values	4	4	2	8	9	15	10	27	9	25	28	15	8	11	16		4	2			
95% Confid	0.30	0.24	3.18	0.27	0.19	0.15	0.73	0.37	0.19	0.17	0.08	0.19	0.17	0.19	0.12		0.18	1.91			
RbCl		SrF ₂	Y°	Zr°	Nb°	Mo°	Tc°	Ru°	Rh°	Pd°	Ag°	Cd°	In°	Sn°	Sb°	Te°	Lil	Xe(+)			
Mean BE	110.00	133.90	155.87	178.91	202.18	227.82		280.91	307.02	335.21	368.20	404.94	443.78	484.95	527.96	573.00	619.30	669.78			
Std. Dev.	0.14	0.21	0.11	0.31	0.35	0.46		0.57	0.43	0.37	0.10	0.45	0.34	0.51	0.63	0.34	0.57	0.56			
Range	0.20	0.30	0.30	1.01	1.10	2.50		1.80	1.30	1.70	0.50	0.22	1.45	2.42	2.00	1.44	0.80	1.80			
# of Values	2	2	7	16	13	22		7	10	28	24	11	18	23	9	20	2	7			
95% Confid	1.27	1.91	0.10	0.17	0.21	0.21		0.53	0.31	0.14	0.04	0.11	0.17	0.22	0.48	0.16	5.08	0.52			
Cs°		Ba°	La°	Hf°	Ta°	W°	Re°	Os°	Ir°	Pt°	Au°	Hg°	Tl°	Pb°	Bi°						
Mean BE		780.10	835.90	14.32	21.73	31.35	40.55		60.78	71.10	83.98	99.83	117.61	136.84	156.93						
Std. Dev.		0.67	0.00	0.06	0.13	0.20	0.29		0.19	0.13	0.16	0.10	0.27	0.30	0.16						
Range		1.42	0.00	0.17	0.30	0.70	0.90		0.70	0.47	0.55	0.20	0.50	1.50	0.52						
# of Values		4	2	5	9	13	8		10	31	27	4	3	19	9						
95% Confid		1.07		0.08	0.10	0.12	0.25		0.13	0.05	0.06	0.15	0.67	0.15	0.12						

Fig. 3. Periodic table of the elements showing statistical analyses of BEs listed in NIST “SRD-20 XPS Database” v3.4.

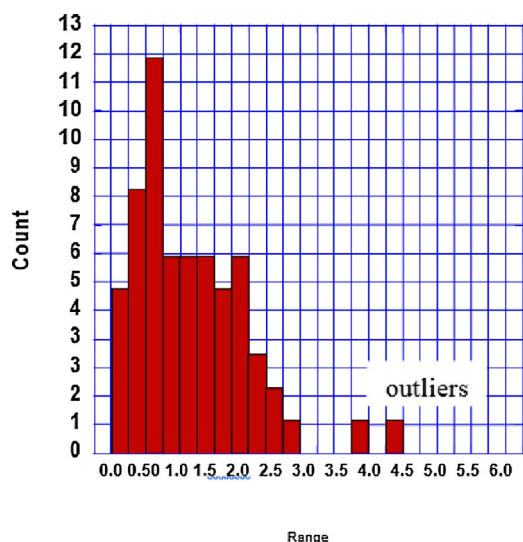


Fig. 4. Histogram of BE range values listed in the periodic table, Fig. 3. Two significant outliers (3.6 and 4.2) indicate a serious problem in the original data. A 3rd outlier (KCl crystal, at 6.5, not shown) suffers from an error in charge referencing.

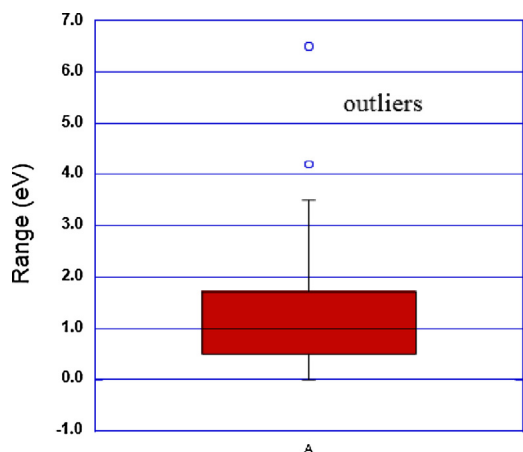


Fig. 5. Box plot of BE range values listed in the periodic table, Fig. 3. Boxed area represents 50% of the data points. Solid line in center of boxed area is the mean value. The top and bottom of the box mark the limits of $\pm 25\%$ of the variable population.

This 0.6 eV range in the “hydrocarbon moiety C 1s reference energy” is large enough to cause the mis-assignment of chemical state structures that exist within or on the surface of, not only non-conductive materials, but also carbon bearing materials (polymers) both of which constitute most of the materials analyzed by XPS. The effect of this 0.4–0.6 eV range is shown in the Periodic Table shown as Fig. 3. The reader is referred to the Range, Standard Deviation and Confidence Levels for the non-conductive materials which reveals the potential for mis-assigning chemical states.

The chemical composition of “adventitious carbon”, which is widely used for charge referencing, has never been definitively determined by any analytical method, even though ToF-SIMS and GC–MS could be used to reveal more about this type of carbon (Figs. 4–7).

It is interesting to note that the ratio of the different types of adventitious carbon chemical state moieties (hydrocarbon, alcohol, ether, ketone, ester, acid, carbonate) changes in accordance with the basic chemical nature of the substrate (e.g. metal, glass, ceramic, oxide, polymer). The as-received surface of a metal often has 40–60 at.% of adventitious carbon on it, whereas polished glasses and ceramics have 20–40 at.% of adventitious carbon and polymers have only 1–10 at.%. (Unpublished results by the author.)

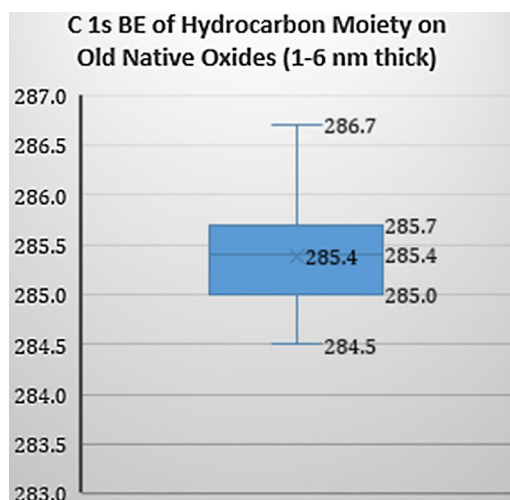


Fig. 6. Box plot of C 1s BEs from old, naturally formed native oxides showing quartiles and the median value, 285.4 eV.

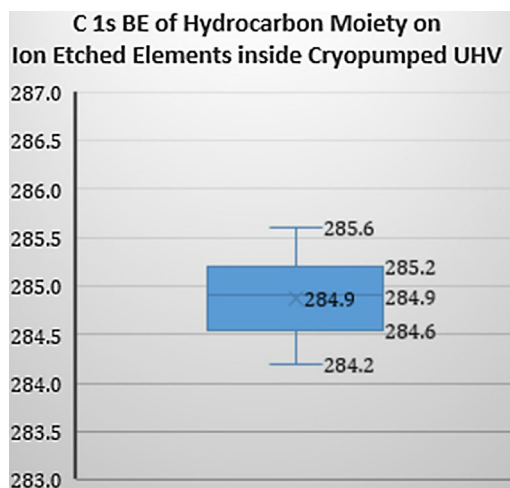


Fig. 7. Box plot of C 1s BEs from ion etched elements that captured gases from UHV showing quartiles and the median value, 284.9 eV.

To characterize the range of C 1s BEs that occur for native oxides, the author measured a series of old, naturally formed, native oxides that behaved conductively in an XPS system equipped with a monochromatic beam of X-rays and a low voltage beam of electrons (flood gun). A table of the hydrocarbon moiety C 1s BEs derived from those samples is provided as Table 9. The charge neutralizer (flood gun) was turned off during all measurements.

The same native oxide samples were removed, scraped clean in air, re-entered to the analysis chamber, strongly ion etched to remove residual surface contaminants, and left in the XPS analysis chamber under the X-ray beam overnight for >14 h allowing the surfaces to develop a new steady state native oxide and a new layer of carbon contamination that originated from the gases that are residual to the UHV analysis chamber and the contamination that existed elsewhere on the surface of the sample. (The instrument used for this study was an SSI X-Probe, equipped with a monochromatic Al $K_{\alpha 1}$ source of X-rays and a cryo-pump on the analysis chamber having a base pressure of 10^{-10} torr.)

The average of the C 1s BEs measured from those native oxide samples is 285.4 eV for the BE of the hydrocarbon moieties that exist on naturally formed, native oxides (Table 9).

The average of the C 1s BEs measured after ion etching the same samples is 284.9 eV for the hydrocarbon moieties that developed

Table 9

C 1s binding energies of the hydrocarbon moiety on naturally formed native oxides (note: pure metal signal is visible, used 90° electron take-off-angle, flood gun off).

Element	Old Native Oxide BE (eV)	In UHV >10 h after Ion Etch BE (eV)	BE Difference (eV)
Ag	285.5	284.7	0.8
Al	286.3	285.1	1.2
As	284.6	284.7	−0.1
B	284.6	285.2	−0.6
Be	285.6	284.4 ^a	1.2
Bi	285.4	284.8	0.6
Cd	286.0	285.0	1.0
Co	285.5	284.4 ^a	1.1
Cr	285.1	284.8	0.3
Cu	284.7	284.7	0.0
Fe	285.2	284.4 ^a	0.8
Ga	286.1	285.6	0.5
Ge	285.7	284.5	1.2
Hf	286.2	286.1	0.1
In	285.4	284.9	0.5
Ir	285.4	285.4	0.0
Mg [Fresh]	286.5	284.4 ^a	2.1
Mn	284.8	286.3	−1.5
Mo	284.8	285.5	−0.7
Nb	285.1	284.9	0.2
Ni	285.4	284.9	0.5
Pb [Fresh]	285.6	285.2	0.4
Pd	285.3	284.2	1.1
Re	284.5	285.0	−0.5
Sb [Fresh]	285.0	284.4	0.6
Si	285.7	284.9	0.8
Sn	285.2	284.8	0.4
Ta	284.8	284.6	0.2
Te	284.8	284.2	0.6
Ti	285.2	285.3	−0.1
Tl [Fresh]	285.4	285.2	0.2
V [Fresh]	285.1	285.2	−0.1
W	285.0	285.1	−0.1
Y [Fresh]	286.7	286.7	0.0
Zn	285.8	284.9	0.9
Zr	285.9	285.5	0.4
Mean BE	285.4	284.9	
Std Dev	0.55	0.56	
Std Error	0.092	0.093	
High–Low Range (eV)	2.2	2.3	

[Fresh] means the original native oxide was more than 100 Å thick so the sample was scraped clean in the air and then immediately entered for analysis by XPS.

^a Based on full data analysis this C 1s BE is potentially due to a carbide species.

on the surface of ion etched metals after many hours (>14 h) in cryo-pumped UHV (Table 9).

Based on these statistics, the 284.9 eV value, which is free from any native oxide effects, is probably a more reliable number to be assigned to the hydrocarbon moiety. The higher 285.4 eV number from native oxides is probably due to unexpected charging effects or surface dipole moments, neither of which have been studied.

7.2. Problems in NIST SRD-20 XPS data-bank v1.0–v4.1

This data-bank suffers from most, if not all, of the systematic and random errors that trouble many old sources of BE numbers. This occurs because the database incorporated data measured by using different calibration energies, different charge referencing values for the C 1s hydrocarbon moiety, various charge control methods and various analysis conditions on many different instruments. The degree of these problems is partially revealed by the data shown in the Periodic Table, Fig. 3.

Each data-file in the NIST numerical data-bank includes a category called “Energy Uncertainty”. A random review of 50 files revealed that only half of the files had an Energy Uncertainty value, and there is no indication as to whether the value is the total range or half of the range of uncertainty.

Under the category called “Energy Scale Evaluation”, the system uses the term “Reliable”. The definition, as it is written, i.e. “...within 300 eV of a reference point on the energy scale...” sug-

gests that any BE outside of that 300 eV span should be suspect and may have a large degree of uncertainty especially since most of the measured BEs are referenced to low calibration energies for Ag 3d5/2 (~368 eV) and Au 4f7/2 (~84 eV). Therefore, BEs above 700 eV are more uncertain.

Under the definition for “Energy Scale Evaluation”, the sentence begins with: “Literature data will not ordinarily be included unless correspondence with at least one point on this energy scale can be determined. . .” The indirect double negative wording reveals that some data will be included even if it does not have “. . .at least one point on this energy scale”.

The “General Information” category in this database is said to report the “overall energy resolution”. A random review of 30 data-files for pure elements gave a null result. And, regrettably, the definitions on the “Data Field Definitions” page do not include a definition of “overall energy resolution”.

Another random review of 30 data-files from conductors and insulators indicates that authors seldom report more than one calibration energy and they reported either the Au 4f7/2 or C 1s BE as the sole source of energy calibration. This tendency, if pervasive, greatly increases the uncertainty in BEs greater than 285 eV, the BE for C 1s.

Under the “Charge Reference” category, the database reports that gold (Au) deposition is accepted as a method for charge referencing insulators. Unfortunately, work reported by Kohiki [66,67] shows that the use of gold (Au) decoration for charge referenc-

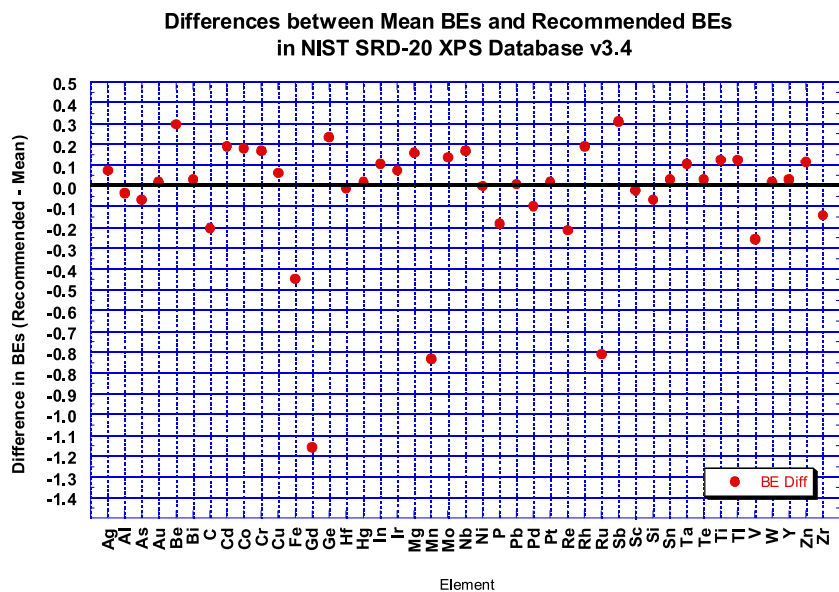


Fig. 8. Chart showing differences between “Recommended BEs” and “Mean BEs Derived from NIST SRD-20 Database” for pure metals. Derived from analyzing v3.4 of NIST SRD-20.

ing is not reliable since data derived from this method of charge referencing was found to produce a large degree of uncertainty.

A literature source that defines the justification for using C 1s BE = 284.8 eV for the adventitious hydrocarbon moiety is not provided even though it is used to charge reference thousands of BEs from non-conductive materials. Any government institute for standards (e.g. NIST) should provide a series of references to significant literature work that justifies the use of this value, along with an appropriate uncertainty value. Unfortunately, this sort of supporting documentation is missing.

The NIST use of the term “adventitious hydrocarbon” implies the presence of a chemical compound that is a pure hydrocarbon. Based on this author’s experience, “adventitious carbon” materials are always accompanied by an oxygen-bearing component. A more correct phrase is “adventitious hydrocarbon moieties or components” which better reflects the true nature of “adventitious carbon”.

Version 4.1 of the NIST database provides a list of “Elemental Referenced Data” including a category called “Recommended binding energies for principal photoelectron lines (85 elements)”. These BEs are the result of correcting (scaling) the BEs obtained from an instrument run by Prof. Martensson’s students at the University of Uppsala, Sweden [68–71]. These recommended BEs were compared to the mean BEs derived from the BEs of all available pure element BEs listed in v3.4–v4.1 of the SRD-20 NIST XPS Database. A chart showing the differences between these two sets of numbers is shown as Figs. 8 and 9. Approximately 40% of the difference values shown in the chart are ≥ 0.15 eV, which is significantly larger (7X) than the ≤ 0.02 eV uncertainty attributed to the calibrant BEs [4] listed in the Method of Energy-Scale Calibration.

Based on this fact, it is difficult to understand how to use the BEs of pure conductive elements provided in the NIST SRD-20 XPS database.

A publication by Dr. Powell [72] (NIST) reports a detailed comparison of the BEs of pure elements originally published by JEOL, PHI, Crist and Martensson that provides extensive inter-comparisons of those BEs and a mean BE derived from those BEs. The comparison produced mean differences of 0.02 and a standard deviation of 0.06. Based on the number of professional contributors, this result would make a useful addition to the Recommended BEs section.

Despite the problems and missing features, this dedicated numerical data-bank is useful as a guide for making chemical state assignments.

If statistical analyses or histogram plots that indicate which BE is “most” accurate or most likely, were included then the usefulness of the BEs in this data-bank would be clear. Otherwise, the user of this data-bank needs to be cautious.

8. Discussion

XPS instruments are still expensive tools to run and maintain, and are relatively slow to collect spectra, so many instrument owners and operators find it necessary to spend a minimum amount of time collecting reference grade spectra or maintaining energy scale calibration. Despite these high cost and time factors, we all need BEs and spectra that are not only reliable, but also reproducible so we can produce accurate and reliable information for the companies

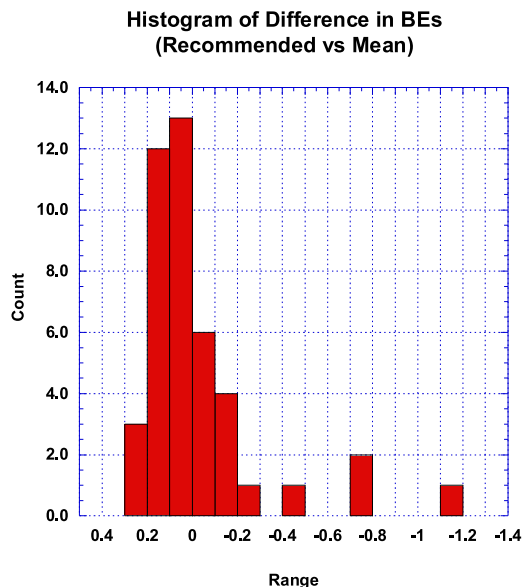


Fig. 9. Histogram showing differences between “Recommended BEs” and “Mean BEs Derived from NIST SRD-20 Database” for pure metals. Derived from analyzing v3.4 of NIST SRD-20.

and universities that we work for, in turn, justifying the ongoing cost of operating the XPS instruments.

Most of our current resources of BEs and spectral data in various data-banks and journals have one or more problems with energy scale calibration. A natural question is: What can be done to fix this problem? The answer is: It is difficult, if not impossible, to correct the existing tables of BEs. We should look forward and develop a system that, in effect, forces the authors to submit spectra with a truly sufficient number of calibration spectra measured on the same day as the material of interest.

An international group of XPS experts and specialists have been working together, under the ISO umbrella, for the past 15 years to develop international documentary standards designed to guide academic and industrial scientists to produce reliable BE numbers and spectral data, but they are not policemen who can force authors to measure energy scale calibration spectra.

The ISO effort represents Phase 1 of an international plan to produce XPS spectra and BEs that are reliable enough to help future scientists and engineers to produce more advanced materials and solve more difficult problems by having and using reliable and reproducible XPS spectra and BEs.

Phase 2 of this plan has been to promote the use of ISO standards by publishing short reports about the existence of standards that will help us move forward to our goals. Promoting the use of any documentary standard, such as energy scale calibration, by publishing summaries is relatively easy to do but does not guarantee that progress will be made, i.e. the existence of a standard without a means to encourage it to be used often produces a negative result or zero action.

To make measurable progress toward our goals we need instrument owners, who publish XPS spectra or BEs, to spend a relatively short amount of time to maintain (i.e. record, document, track and correct) the BE scale of their instruments once or twice per month. This can be done in a very simple manner by using a piece of copper (Cu) foil and measuring the Cu 2p_{3/2} and Cu 3p_{3/2} BEs under high energy resolution conditions after removing the surface contamination by either argon ion etching or severe physical scraping in the air immediately prior to loading. Because energy scales can vary with pass energy settings, spectra need to be collected from at least two high energy resolution pass energy settings. The high energy resolution spectra from these 4 measurements need to be stored digitally and on paper with the peak-fitted results.

Several new XPS instruments have pieces of Au, Ag and Cu installed on or near the analysis stage. The operator can activate a software routine that checks and automatically corrects calibration energies. If the software is automated to run a calibration routine overnight when the machine is not busy collecting routine spectra then the author-user would have excellent tracking and accountability of calibration energies that can be published.

Phase 3 is to establish a system of verification that would require an extensive, but valuable, bit of brain-storming and time to set up, but would serve as a model for other instruments that need verification of calibration. Because peer-reviewed scientific journals are the major source of numerical BEs, we need a system that strongly encourages the authors of a publication to include a bi-weekly, verifiable summary of the energy scale calibration that supports the BEs or spectra to be published. This system could be connected to or the responsibility of the editors of the journal, the peer reviewing members or an independent body that is paid to certify that the energy scales have indeed been routinely maintained and recorded.

9. Future data-banks and suggestions

To advance material science, we must produce reliable BEs and peak-widths (FWHMs) from now. This means that XPS users and

operators must check and correct energy scale calibration on the same day that research spectra are collected.

Peak-widths are next in line of value because FWHMs from monochromatic X-ray sources can be used to reveal the presence or absence of various chemical states resolved by peak-fitting high energy resolution chemical state spectra. FWHM is a key parameter for discerning relative abundances. At this time, the only journal that publishes FWHM is the Journal of Surface Science Spectra (AVS). However, the BEs in this journal suffer all the errors and uncertainties caused by the existence of multiple calibration energies and related problems.

To establish the accuracy of the full range of the energy scale of an instrument, the author of a work or a publication must collect or request a minimum set of spectra that reveal the calibration energies of the Cu 2p_{3/2} and Cu 3p_{3/2} peaks at the same settings used to collect the research spectra, and most importantly on the same day. For the benefit of all users, academic, industrial and government, the author must also reveal the energy resolution conditions of the instrument by supplying a FWHM of a suitable calibration peak (e.g. Ag 3d_{5/2}) that can be reproduced on the other XPS instrument by using the pass energy settings on different instruments that produce the same FWHM as the author's instrument.

In the building of future data-banks, it is not practical to collect spectra under ultimate energy resolution conditions. In fact, it is detrimental because the cost and time needed to collect such ultimate grade spectra are too great to the laboratory that tries to produce those spectra, and the laboratory that tries to reproduce them.

To minimize random and systematic errors in our future data-bank, all operators need a standard set of analysis conditions that must be used for any BEs or spectra to be accepted into any data-bank. These conditions must not be overly constraining, but must be able to minimize the entry of BEs or spectra into the data-bank that are of little value to those who need to use the spectra. This is a task for a company that is tasked to build an international data-bank of complete sets of spectra having complete calibration details.

In any future data-bank of reliable spectra, survey spectra should have step sizes ranging from 1 to 1.3 eV per step. High energy resolution (chemical state) spectra should have step sizes between 0.05 eV/step and 0.10 eV/step. High energy resolution analysis conditions for chemical state spectra should produce a FWHM between 0.60–0.75 eV for the Ag 3d_{5/2} peak. Chemical state spectra must be collected from the C 1s, O 1s, key Auger signals, the valence region and the main signals from the chemical being measured. The angle between the primary axis of the electron collection lens and the plane of the sample should be between 70–90° for bulk analyses.

The first spectrum to be run should be a single scan survey spectrum, followed by normal survey spectrum, then chemical state spectra and finally the same single scan survey spectrum must be measured again to reveal any sample degradation that may have occurred during the full analysis. Calibration energy spectra must be recorded on the same day that the research material is analyzed. Calibration energy spectra must be submitted with the target spectra.

The C 1s BE to be used for charge referencing BEs from non-conductive materials has been studied only to a limited extent in the past, and it is still not yet reliably defined. Without a reliable C 1s BE for the hydrocarbon moiety, all data from non-conductive materials will suffer excessive uncertainty and error. Our future data-bank and all future spectra from non-conductive materials must be based on a reliable C 1s BE of the hydrocarbon (moiety) component as it exists on various chemically different materials (e.g. native oxides, ceramics, pure metals, polymers). Definitive research on adventitious carbon is essential and must precede the future data-bank.

10. Summary

Experimentally measured binding energies (BEs) are commercially available in various forms, e.g. handbooks, scientific journals, internet-based data-banks, software-based data-banks of BEs, or complete sets of actual spectra. This review addresses fundamental problems that exist in peer-reviewed published binding energies stored in various numerical X-ray Photoelectron Spectroscopy (XPS) data-banks, including, for example: (1) PHI, Handbook of XPS (1979), (2) NIST SRD-20 XPS Database, v1.0–4.1 (1989–2017), (3) Wiley, Practical Surface Analysis 1st and 2nd ed. (1990), (4) SASJ, ComPro v8 and Data-bank (1990–2017), (5) JEOL, Handbook of XPS (1991), (6) CRC, Practical Handbook of Spectroscopy (1991), (7) PHI, Handbook of XPS, 2nd Ed. (1992), (8) AVS, Journal of Surface Science Spectra (1993–2017), (9) LaSurface Web Site Database – XPS (2001–2017), and (10) M. Biesinger's XPSfitting website (2012–2017).

The 4 major problems in all peer-reviewed data-banks of BEs and journals are due to: (a) the widespread use of different calibration energies, (b) the widespread use of different energy scales, (c) the widespread use of a “user-defined” BE for the C 1s peak attributed to hydrocarbon moieties, and (d) the inability of the professors who publish, the reviewers and journal editors to perform their expected functions and responsibilities. Hopefully, professors, journal editors and reviewers will find a way to get all new authors to use the ISO Calibration Energies [73] so that all of us can improve the accuracy and reliability of our chemical state assignments. If you review recently published papers you will find only one calibration BE. When was that single calibration BE measured? The same day as the key data, or was it last year, or was it never measured. Did the tool owner ever check BE scale or calibration energies? What calibration energies did they use? At the end of this review there is a list of recommendations for the design and content of future spectra based XPS data-banks.

Appendix A.

Table A1

Problems that exist and persist in XPS Knowledge, Technology, and Publications.

- Energy scales of old, still operational XPS instruments are still calibrated using original calibration energies (CEs) where its' energy scale is 0.6 eV larger than others
- Old literature reports list various CEs that define energy scales where Au 4f7/2 CE ranges between 83.7 and 84.2 eV, a 0.5 eV difference, and where Cu 2p3/2 CE ranges between 932.2 and 932.8 eV, a 0.6 eV difference
- The BE assigned to the Carbon 1s BE of the adventitious hydrocarbon moiety is crucial to defining BEs of insulators, but is always arbitrarily defined (no standard) even though most materials analyzed by XPS are insulators. This BE has been defined to occur between 284.6 and 285.2 eV
- The C 1s BE of the hydrocarbon moiety on native oxides is sometimes used to correct measured BEs of conductive materials even though the C 1s BE of the hydrocarbon moiety on naturally formed native oxides varies from 284.4 to 286.5 eV
- Authors often report calibration energies provided by the instrument maker or CEs checked many weeks earlier. Experimentally measured CEs are seldom measured the same day as the material being studied
- Publication reviewers often accept publications that report expected calibration energies, not recently measured calibration energies
- Publications often do not provide calibration energies that define the energy scale in the 400–1486 eV BE range
- NIST SRD 20 v4.1 data-bank of XPS measured BEs has significant uncertainties that are not documented or characterized by any statistics (e.g. histogram)
- BEs of metal signals measured from conductive native metal oxides differ from pure non-conductive metal oxides
- Surface degradation during actual analysis can affect BE results but is seldom measured or reported

Table A2

XPS data-banks commercially available. (Year published, Title, Publisher, Reference).

1979	Handbook of XPS, by Physical Electronics (PHI) Corp. [5].
1983	Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Appendix D, by John Wiley and Sons [7].
1989	SRD-20 X-ray Photoelectron Spectroscopy Database, by National Bureau of Science (NBS, now NIST) and Surflex Co. Ltd. [2].
1990	Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy 2nd Edition, Appendix E, by John Wiley and Sons [8].
1990	ComPro v8 and Databank by Surface Analysis Society of Japan (SASJ) [35].
1991	Handbook of XPS by Japan Electron Optics Laboratory (JEOL) Co. [9].
1991	Practical Handbook of Spectroscopy – XPS, Section 2 by CRC Press, Inc. [36].
1992	Handbook of XPS 2nd Edition by Physical Electronics (PHI) Corp. [6].
1992	High Resolution XPS of Organic Polymers – The Scienta ESCA 300 Database by Wiley and Sons [37].
1993	SpecMaster Pro XPS Database System by XPS International (XI) LLC [38].
1993	Surface Science Spectra journal by American Vacuum Society (AVS) [39].
1997	XPS International Web Site by XPS International (XI) LLC [40].
1999	Handbooks of Monochromatic Spectra – The Elements and Native Oxides – Vol 1 in PDF by XPS International (XI) LLC [41].
2000	Handbook of Monochromatic XPS Spectra: The Elements and Native Oxides by John Wiley and Sons, Co. [42].
2000	Handbook of Monochromatic XPS Spectra: Polymers and Polymers Damaged by X-rays by John Wiley and Sons, Co. [43].
2000	Handbook of Monochromatic XPS Spectra: Semiconductors by John Wiley and Sons, Co. [44].
2000	NIST SRD-20 X-ray Photoelectron Spectroscopy Database v3 by National Institute of Science and Technology (NIST) [4].
2001	LaSurface Web Site – Database – XPS by Centre National de la Recherche Scientifique (CNRS) [10].
2004	Handbooks of Monochromatic XPS Spectra: The Elements and Native Oxides – Volume 1 by XPS International (XI) LLC [45].
2004	Handbooks of Monochromatic XPS Spectra: Commercially Pure Binary Oxides – Volume 2 by XPS International (XI) LLC [46].
2004	Handbooks of Monochromatic XPS Spectra: Semiconductors – Volume 3 by XPS International (XI) LLC [47].
2004	Handbooks of Monochromatic XPS Spectra: Polymers and Polymers Damaged by X-rays – Volume 4 by XPS International (XI) LLC [48].
2004	Handbooks of Monochromatic XPS Spectra: Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides and Miscellaneous – Volume 5 by XPS International (XI) LLC [49].
2005	Handbooks of Monochromatic Spectra – Commercially Pure Binary Oxides – Vol 2 in PDF by XPS International (XI) LLC [50].
2012	XPSfitting website by M.C. Biesinger [11].

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