A Critical Review of Popular XPS Data-Banks

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I. Preface

Information derived or interpreted from analyses of X-ray Photoelectron Spectroscopy (XPS) data is frequently used to make valuable decisions in business and research. It is important that this information be as reliable as possible. For this reason, it is important to understand the characteristics of the XPS data in the data-banks which are currently used to obtain this information.

This review mainly discusses the characteristic features and problems of the data listed in several popular XPS data-banks with special emphasis on the reliability of the electron binding energy (BE) data in the data-banks. There are basic three types of XPS data-banks: numerical data-banks, spectral data-banks, and spectral-numerical data-banks. The first and third types will be discussed in this review. The second type, spectral data-banks, will not be discussed because there are currently none that exist as independent data-banks.

The data in the numerical and spectral-numerical types of data-banks are considered to be reference data which were obtained from a wide variety of materials that were considered to be commonplace materials with a high degree of purity. Very few of the commonplace materials used to generate these XPS reference data are certified reference materials (CRM) or standard reference materials (SRM).

In this review, the author uses the common phrase "chemical state" when discussing the assignment of an XPS signal, but the author wishes to clarify the point that XPS is used to infer the relative presence or absence of an element in a variety of different atomic environments, not just the chemical oxidation state of an element. This is important to point out because XPS is useful to identify differences in many materials which do not have any formal oxidation states, e.g., polymers, alloys, intermetallics, or compound semi-conductors.

The data-banks described in this review are available in various types of publications, i.e., handbooks, scientific journals, computer-based data-bases, and computer based data-banks.

This review is designed to be read mainly by scientists, but the details are designed so that non-experts can also understand the basic contents of this review.

At the end of this review there are a few suggestions on the potential design and content of future data-banks and experimental methods used to collect XPS reference data.

II. Purpose

The main objective of this review is to outline the features and problems in the content and structure of several popular XPS numerical data-banks and XPS spectral-numerical data-banks with special emphasis on the reliability of electron binding energy (BE) data in the data-banks because these data are routinely used by scientists and engineers in their efforts to produce useful information from raw XPS spectra.

The basic intention of this review is to provide comments and criticisms which can be used in a constructive manner to improve the quality and reliability of all XPS data-banks.

III. Introduction and Background

Surface scientists in research and industry use reference data in commercially-made *XPS numerical data-banks* to help them to assign chemical states to XPS signals. As a result, these data-banks are used to generate useful, but not always exact, information from experimentally measured XPS spectra.

The reliability of the information obtained from new sets of XPS spectra are directly affected by the reliability of the XPS reference data stored in XPS data-banks. The reliability of the reference data is directly affected by the experimental methods used to collect the XPS reference data. This, in turn, means that the reliability of the information is directly limited and controlled by the reliability of the experimental methods used to collect the XPS reference data.

The most simple type of XPS reference data, i.e., high resolution electron binding energies, in commonplace XPS data-banks are known to have various uncertainties due to the uncertainties in the experimental methods used to collect those reference data.[1,2] Those uncertainties limit or directly control the reliability of chemical state assignments. Even so, many analysts still assume that those uncertainties are small enough to allow reliable assignments of chemical states.

Sometimes it is difficult for the scientist to make reasonable assignments based on the limited amounts and uncertainties of the reference data. Because of these difficulties and the fact that similar chemical states give similar binding energies (BEs), many scientists must do extra work to maximize the accuracy of their chemical state assignments. They must use their XPS instruments to collect complete sets of XPS spectral data from high purity reference materials. They then use these complete sets of spectra from the pure materials to help them to assign chemical states to the XPS signals which are the true target of their work. This in-house generation of a small scale XPS spectral data-bank greatly improves the accuracy and usefulness of their interpretations, but this method requires extra work, time, and cost.

At this time, commercially-made *XPS spectral data-banks* are not readily available, therefore most chemical state assignments must be made by using either numerical or spectral-numerical data-banks.

When sufficiently large and reliable XPS spectral data-banks become commercially available, then those spectral data-banks will greatly assist analysts to make more reliable chemical state assignments and to generate reliable fully detailed numerical data-bank

Several different *spectral-numerical data-banks* are commercially available and they are the main subject matter of this review.

As mentioned above, the main objective of this review is to outline the features and problems in the content and structure of XPS numerical data-banks and XPS spectral-numerical data-banks which are used by scientists and engineers in their efforts to produce useful information from raw XPS spectra.

Before beginning the discussion section, it is necessary to explain the differences between XPS numerical data-banks, XPS spectral data-banks, and XPS spectral-numerical data-banks. The author's definitions of these three different types of data-banks are given here:

XPS numerical data-banks are data-banks of numbers only. This type of XPS data-bank normally contains simple one dimensional tables of high resolution electron binding energy (BE) numbers, Auger parameter numbers, or kinetic energy (KE) numbers which are listed next to the relevant chemical states. These numbers were derived from processing raw XPS spectra. Advanced numerical data-banks also contain data other than just BEs which are useful for more detailed analyses of XPS data.

XPS spectral data-banks are data-banks of spectra only. This type of data-bank normally contains actual spectra obtained under various analyses conditions from various energy regions which can be analyzed to generate the numbers listed in numerical data-banks. Useful spectral data-banks should include collections of spectral data known as: depth profiles, line profiles, images, maps, angle-resolved analyses, and many details of the analysis conditions.

XPS *spectral-numerical data-banks* are a combination of XPS spectral and XPS numerical data-banks. This type of data-bank contains both actual spectra and numerical data-tables and is the most useful type of XPS data-bank. Three of the data-banks that will be discussed in this review are spectral-numerical data-banks. One of these three data-banks, the Common Data Processing System, currently has a limited collection of data processing routines and also a small collection of data-tables.

During the last 10 years there have been several papers that discuss various aspects of XPS data-banks.[1-8] The author of this review has read and summarized details from some of those papers, but has not made an attempt to expand on or follow the logic used in those reviews.

IV. Discussion

A. General Details about XPS Data-Banks

Information derived from XPS data is similar to information derived from many other types of spectroscopic data because most forms of spectroscopy need reliable reference data to make reliable chemical state assignments.

To make reliable elemental and chemical state assignments, many XPS analysts have bought, use, and rely on the numerical data-banks included in the *NIST XPS Database* developed by the US National Institute of Standards and Technology (NIST, formerly NBS), the *Handook of XPS* (1st and 2nd editions) written by the Physical Electronics (PHI) company, the book *Practical Surface Analysis* edited by Briggs and Seah, and the *Handbook of XPS* written by the Japan Electron-Optics Laboratories (JEOL) company.

Whenever possible, they also rely on a variety of XPS related science journals and other books. These books and journals include various types of small numerical data-banks, and some include small collections of actual spectral data from many different classes of materials. These small collections are not really organized as data-banks and will not be considered here.

Some scientists possess and rely on their private collections of spectral and numerical data-banks, but those data-banks are not available publicly and can not be critiqued in this review.

Very recently, some XPS analysts have also been able to use and take advantage of two spectral-numerical data-banks, i.e., a book titled *High Resolution XPS of Organic Polymers* published by Wiley & Sons and a journal called *Surface Science Spectra* (SSS) published by the American Vacuum Society (AVS). The SSS journal will soon be available as an electronic data-base.

However, even though XPS has been widely used by industry and research for more than 20 years, its users and all XPS data-banks still suffer from various problems. See Table 1 for details.

Despite these and other serious problems, errors, and uncertainties, the current popular XPS data-banks still appear to be useful to solve a wide variety of surface chemistry problems and to analyze the surface chemistry of the top 2-20 atomic layers of any solid material.

Table 1. Problems in Many XPS Data-Banks

- no international or national standards for the calibration of energy scales,
- no international or national standards for the intensity scales produced by XPS instruments,
- uncertainties and systematic errors in spectral data are undefined,
- problems in the exchange of spectral data between different instruments,
- no standards that define *data quality* or *data reliability*,
- very few spectral data from commonplace materials, and
- no valid method to reference BEs from insulators.

This must be true because a simple review of the reference citations used in recent journal publications clearly shows that many analysts do indeed appear to solve a variety of problems by relying upon and using BE numbers published in numerical data-banks that were commercially assembled.

This situation suggests that many analysts have assumed that the BE numbers in those commercially-assembled numerical data-banks are sufficiently accurate and have uncertainties and errors which are small enough to generate reliable assignments.

It is quite possible that those analysts do not realize or do not worry that the BE numbers listed in those handbooks and commercially-assembled numerical data-banks were generated by many hundreds of different analysts, who used many different non-standardized calibration methods and analysis conditions to generate those BE numbers.[9,10] Those numbers, as a natural result, must suffer from a variety of errors that include random and systematic errors.[1] The instruments used by those same analysts are also known to suffer from significant differences in instrument response functions, and energy resolution settings.[1,11]

The fact that many scientists have published their research results does not mean that those research results and assignments are correct or that all research results are free of errors. It simply means that the results are accepted by fellow scientists who based their acceptance on currently available knowledge and limits.

In fact, a group of scientists have performed several 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.[9,10, 12-14] These errors and uncertainties are most probably the major driving force behind the current national and international efforts to develop international standards for XPS.

One of the major reasons for these efforts to standardize XPS is that many experienced XPS users have been having too much difficulty to make chemical state assignments by using XPS reference data that were generated by too many different people who used too many different instruments without sufficient control of the experimental conditions. As a result of much frustration, the experienced users have finally begun the pursuit of standards. Unfortunately, this situation suggests that many XPS reference data are questionable.

Simple interviews of many experienced analysts by this author clearly indicates that the more experienced analysts already know that many of the BE numbers in various data-banks are not reliable enough to use to assign chemical states correctly.

Because of this problem, the experienced analysts tend to build their own in-house spectral data-banks, which provide the many details needed to solve the more difficult problems caused by the overlap of BE signals and the similarity of many chemical states. Unfortunately, in-house spectral data-banks usually require many years to complete because the normal work of each scientist is not to collect reference grade spectral data even though it is actually needed.

These secretly generated in-house spectral data-banks, when used in conjunction with the numerical data-banks, allow the scientists and their companies or universities to minimize the chance of error.

These internally generated spectral data-banks are normally self-consistent sets because many experimental parameters remain constant. By being self-consistent, the reliability of a data-bank is greatly improved and is therefore more useful to generate reliable information from raw XPS spectra.

This situation indicates once more that XPS is the same as many other types of spectroscopy where the scientist requires both numerical data-banks and spectral data-banks to maximize the reliability of chemical state assignments and the resulting information.

As mentioned at the start, the main objective of this review is to outline the features and problems of the content and structure of XPS numerical data-banks and XPS spectral-numerical data-banks which are used by scientists and engineers in their efforts to produce useful information from raw XPS spectra. The XPS numerical data-banks and XPS spectral-numerical data-banks, which are included in this review, are listed in Table 2 below.

Sample pages from the data-banks discussed in this review are included below as Figures 1-18.

The following two sections discuss the basic features and problems of the numerical data-banks and spectral-numerical data-banks which are widely used to make chemical state assignments.

A later section describes the specific features and problems of each of the data-banks listed above.

B. Basic Features and Problems in XPS Numerical Data-Banks

Numerical data-banks are data-banks of numbers only. This type of XPS data-bank normally contains simple one dimensional tables of high resolution electron binding energy (BE) numbers, which are listed next to the relevant chemical states.

This type of data table is widely used by many surface scientists for the purpose of assigning chemical states to XPS signals because spectral-numerical data-banks, which provide more data (i.e., complete sets of spectra), are still very few and very small.

The numerical data-bank made by NIST, i.e., *NIST XPS Database*, is a good example of a numerical data-bank which has many high resolution electron BE data tables (see figures 3-4).

Most of the books discussed in this review are mainly designed to be numerical data-banks, but they also contain a 2-3 spectra from each of the pure elements which are meant to serve as a rough guide to the XPS analyst. These few spectra are not very useful for solving problems or assigning chemical states.

Table 2. Numerical and Spectral-Numerical Data-Banks[15-24] Discussed in this Review

1979: *Handbook of XPS* published by the Physical Electronics (PHI) Corp.
1989: *NIST X-ray Photoelectron Spectroscopy Database Version 1.0* developed by the
1990: *Practical Surface Analysis 2nd Edition, Appendix 5* published by Wiley and Sons, Co.
1990: *Common Data Processing System Version 3.1* developed by the National Research Institute for Metals (NRIM) and VAMAS-SCA Japan members
1991: *Handbook of XPS* published by the Japan Electron Optics Laboratory (JEOL) Co.
1991: *Practical Handbook of Spectroscopy - Section 2* published by CRC Press, Inc.
1992: *Handbook of XPS 2nd Edition* published by the Physical Electronics (PHI) Corp.
1992: *High Resolution XPS of Organic Polymers* published by Wiley and Sons, Co.
1992: *Surface Science Spectra* journal and electronic database developed by the AmericanVacuum Society (AVS)
1992: *NIST X-ray Photoelectron Spectroscopy Database Version 2.0* published by the National Institute of Science and Technology (NIST)

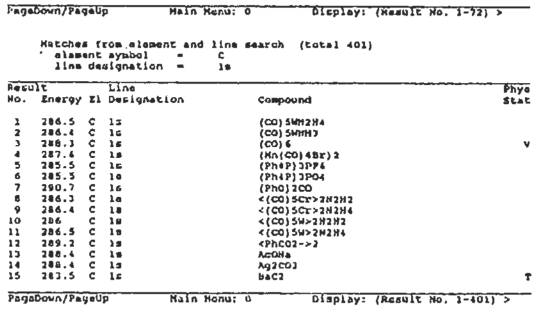
Before continuing further, it is important to note that one scientist, Dr. Charles D. Wagner, is mainly responsible for tabulating nearly all of the BEs listed in the high resolution electron BE data tables included in most of the popular handbooks and the NIST database. Dr. Wagner spent many years reviewing the literature, evaluating, and correcting the BE values which are now listed in those high resolution electron BE data tables. He corrected those BEs by using a practical set of reference energies so that the BE data tables can be used in a practical manner.

Even so, the many hundreds of BEs in the tables of today's XPS numerical data-banks were, in fact, measured by many different scientists who used many different XPS instruments under many different experimental conditions to collect XPS spectral data from many different high purity reference materials. These scientists, unfortunately, seldom reported any statistical analysis of their BE numbers which were usually the result of single run experiments. As a result, the repeatability, reproducibility, and uncertainty of the BEs in these data-banks are, in effect, poorly defined.

The high resolution electron BE data tables, provided in the various handbooks, usually only include BEs from a single XPS signal (e.g., an electron energy level called: 1s, 2p3/2, 3d5/2, or 4f7/2) that were obtained from many different chemical compounds. The XPS signal that is normally listed in each data table is usually that XPS signal which gives the smallest full-width-at-half-maximum (FWHM) values and the most intense XPS signal. This type of signal is the most useful to decide which chemical state is present or absent. In the case of the element carbon, the high resolution electron BE data table would report BEs for the C (1s) XPS signal. That data table includes, for example, high resolution electron BEs attributed to the presence of carbides, hydrocarbons, or carbonates, which are similar, but different enough to be resolved. For more detail, please refer to the example shown below in Table #3.

Much of the uncertainty and reliability problems in these simple one dimensional tables of high resolution electron BEs is due, in particular, to the differences in the reference energies used to calibrate XPS instruments.[9] These problems exist because there are currently no international standard reference energies for calibrating XPS instruments. This particular problem will, however, be solved in the next few years by the development of internationally accepted standards which are being developed by the International Standards Organization (ISO).

Table 3. A Typical High Resolution Electron BE Binding Energy Table for C (1s) Signals



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PageDown/PageUp          Main Menu: 0          Display: (Result No. 1-72) >

     Matches from element and line search  (total 401)
     ' element symbol     =     C
       line designation   =     1s

Result         Line                                                    Phys
No.   Energy El Designation          Compound                          Stat

 1    286.5  C  1s                   (CO)5WN2H4
 2    286.4  C  1s                   (CO)5WNH3
 3    288.3  C  1s                   (CO)6                              V
 4    287.6  C  1s                   (Mn(CO)4Br)2
 5    285.5  C  1s                   (Ph4P)3PF6
 6    285.5  C  1s                   (Ph4P)3PO4
 7    290.7  C  1s                   (PhO)2CO
 8    286.3  C  1s                   <(CO)5Cr>2N2H2
 9    286.4  C  1s                   <(CO)5Cr>2N2H4
10    286    C  1s                   <(CO)5W>2N2H2
11    286.5  C  1s                   <(CO)5W>2N2H4
12    289.2  C  1s                   <PhCO2->2
13    288.4  C  1s                   AcONa
14    288.4  C  1s                   Ag2CO3
15    283.5  C  1s                   BaC2                               T

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After studying various XPS data-banks and publications,[9-24] the reader will find that during the past 44 years the XPS reference energies reported for pure gold (Au°) ranged from 44.7 eV ±0.2 eV to 84.07 eV. Please note the 83.7 eV ±0.2 eV value implies a range of 83.5 eV to 83.9 eV. Older publications indicate that pure gold was also reported to have a BE of 83 eV.[20] During the same time, the reference energy for pure copper (Cu°) ranged from 932.2 eV to 932.8 eV.[9-24] As a result, it is possible that many published BEs for pure conductive materials (alloys, metallic elements, semiconductors, steels, etc.) may vary by as much as ±0.3 eV. With the <0.3 eV energy resolution capability of today's monochromatic XPS systems a ±0.3 eV range is large enough to cause wrong assignments for materials that are chemically similar (similar alloys with different ratios of elements, similar compound semi-conductors). These ranges of uncertainty were probably inevitable because of instrument design tolerances, low precision electron volt standards, the large FWHM of conventional X-ray sources, and other related limitations. Unfortunately, the same reference energies are still being used today because the "de facto" internationally accepted reference energy standards from the National Physical Laboratory in the UK are still not used by many researchers.

As a partial solution to this calibration problem, Dr. Wagner has corrected the BEs that he has referenced in many numerical data-banks so that all BEs are referenced to a single set of defined reference energies. This approach is useful, but only partially decreases one aspect of the energy referencing problem.

Another energy referencing problem is due to differences in the linearity of the energy scales used on different instruments. This linearity is easy to correct for if the researcher reported reference energies for both Cu (2p3) and Au (4f7), but it is difficult to correct for in already published data because most workers normally report only one reference energy in their publications.

A much more serious problem of uncertainty in BEs exists for insulators which unfortunately represent the most common type of material that need to be analyzed by XPS. Insulators develop a charge during XPS analysis. To correct for the charge effect on the BEs, various secondary energy referencing methods have been used to energy reference raw BEs from insulators, but none of the current methods provide uncertainties which are reliable enough to avoid mistaking one chemical state for a similar, but different, chemical state.

The most common and apparently the useful method for energy referencing XPS BEs from insulators involves the hydrocarbon moieties in non-conductive carbon-based contaminants which exist on the surface of nearly every material. In the past, these hydrocarbon moieties were assumed to have a C (1s) BE that occurs between 284.5 eV and 285.5 eV.[21] A few years later, many users assumed that the C (1s) BE of hydrocarbon moieties was between 284.6 eV and 285.2 eV. [10,14] Now, however, many scientists prefer either 284.8 eV or 285.0 eV.[16, 17, 19-22] Unfortunately, there are no studies which clearly define a valid reference energy for the hydrocarbon moieties in non-conductive carbon-based contaminants.[9] This author has some unpublished results which indicates that the BE of the hydrocarbon moiety depends on the surface dipole moment of the underlying material. It seems that large surface dipole moments in certain materials together with other surface effects may cause the BE to rise to more than 286 eV. Other workers have found that the BE of the C (1s) of these hydrocarbon moieties may increase by as much as 1 eV as the thickness of the hydrocarbon layer increases.[26-28]

This range of uncertainty in the C (1s) BE of hydrocarbon moieties found in non-conductive carbon-based contaminants infers that the range of uncertainty in the BEs of already published results for many insulators should be considered to have an uncertainty of at least ± 0.5 eV and perhaps as much as ± 1.0 eV. These two potentially ranges of uncertainty are large enough that it is possible to assign the wrong chemical state to a chemical group or species which is a part of an insulating material.

The numerical data-banks that exist now suffer from the above-mentioned limitations. The same numerical data-banks also do not provide several useful numerical variables which can be easily obtained if a complete set of XPS spectral data is available for a reference material.

A partial list of numerical variables, which can greatly enhance the accuracy and the process of the chemical state assignment of XPS signals, is given here in Table 4.

Because the numerical data (i.e., simple high resolution electron BE data tables) in many *XPS numerical data-banks* appear to have significant amounts of uncertainty and do not include information about their statistical validity, they seem to be data which are difficult to use in a fully reliable manner. Many scientists have been aware of these limitations for the past 20 years and as a result a lot of work and research has been done to eliminate these limitations[1-3, 7, 10-14, 29] but it is a difficult task.

Based on the aforementioned limitations of numerical data-banks, surface scientists have realized that they need *XPS spectral data-banks* of raw spectral data with a sufficient amount of calibration data. Complete sets of raw spectral data from a material together with the sufficient amount of calibration spectral data are very valuable because they can be processed by various softwares at any time and thus greatly improve the reliability of chemical state assignments. For these reasons and the reasons that micro-computers and data storage have become inexpensive, it is now possible to greatly improve the reliability of chemical state assignments by using XPS spectral-numerical data-banks.

Table 4. Numerical Variables Needed to Enhance the Process and Accuracy of Chemical State Assignments

- the full width at half maximum (FWHM) value of all major XPS signals,
- the degree of asymmetry of a peak,
- the relative ratio of Gaussian and Lorentzian (G/L) peak-shapes in each peak,
- the peak areas and peak area ratios of the major XPS signals,
- the BE and FWHM of the C (1s) signal due to hydrocarbon moieties ,
- the uncorrected raw binding energies of the major signals, and
- shape of the electron energy loss region.

Very recently a few groups are working to produce XPS spectral-numerical data-banks with different degrees of reliability. Some of the features of these spectral-numerical data-banks are discussed below and in the later sections which directly address specific data-banks.

C. Basic Features and Problems in XPS Spectral-Numerical Data-Banks

In this section we shall discuss some of the basic features and problems of XPS spectral-numerical data-banks, but first we need to discuss briefly some of the features of spectral data-banks, the meaning of "a set of coordinated spectra", and the usual makeup of a single spectrum. Afterwards, we shall turn to the features and problems of the two basic forms of spectra (printed form and computer readable form) stored in spectral-numerical data-banks.

Spectral data-banks are data-banks of spectra, which are the source of all the BE numbers in all the numerical data-banks. Spectral data-banks should contain thousands of complete sets of spectra obtained from many different commonplace materials. Each set of spectra should be a set of coordinated spectra. A set of coordinated spectra is a set of spectra obtained from a single material which were generated during a single experimental run by using identical or almost identical experimental conditions (e.g., same pass energy, same charge-up conditions, same electron take-off-angle, same vacuum conditions, same beam intensity, same beam size, etc.). At this time, there are no commercially produced spectral data-banks, so spectral data-banks are only briefly discussed in this review.

A single spectrum is actually a set of sequential voltage settings and electron impact induced current measurements (i.e., data points) which have been converted into a contiguous line of ink on a piece of paper or a series of numbers encoded onto paper or various types of recording media (e.g., magnetic hard disks used by computers). The sequential voltage settings are used to generate the BE scale of an XPS spectrum and the electron impact induced current are used to generate the electron counts scale.

In XPS, there are two basic types of spectra: i.e., high resolution narrow scan XPS energy spectra and low resolution wide scan XPS survey spectra which usually have different experimental conditions that match the needs of the scientist.

The number of data points in a single low resolution wide scan XPS survey spectrum, which is usually 1,000 eV in width, normally ranges from 1,000 to 2,000 data points. These low resolution wide scan XPS survey spectra are routinely used by scientists to determine which elements are present or absent and also the relative amount of the different elements contained in the surface of a material.

The number of data points in a single high resolution narrow scan XPS energy spectrum, which is usually 20 electron-volts (eV) in width, normally ranges from 200 to 500 data points. The high resolution XPS energy spectra are considered to be the most useful type of spectra because they can be routinely used by scientists to determine the number and relative amount of the different chemical states contained in the surface of a material.

The BE value in a numerical data-bank, which is associated with a particular element contained in a particular reference material, is normally attributed to the single (1) most intense data point which has the greatest number of electron counts in the high resolution narrow scan XPS spectrum containing 200-500 data points. The other 199-499 data points in that spectrum are deliberately ignored. This approach of relying on a single data point to make a chemical state assignment would be useful if all XPS signals had very small FWHM values, had very simple peak-shapes, and seldom suffered from signal overlap, but that is not the usual case. Therefore, the scientist should not ignore the hundreds of other data points provided in each spectrum if he or she wants to maximize the reliability of the data and the information that can be obtained from a single XPS spectrum or a coordinated set of XPS spectra. For this reason and others, spectral-numerical data-banks are being developed.

A major problem with nearly every spectral and spectral-numerical XPS data-bank is that each data file in a data-bank usually contains just a single set of spectral data (that is: one wide scan survey spectrum, one high resolution spectrum from each of the primary element signals, one valence band spectrum, and one Auger signal spectrum, if present) for each material because the analyst has analyzed the sample just one time. The reason for making a single set of spectra is that XPS analysis time is very expensive so it is difficult to justify repeating the same set of spectra five times to produce a set of BE numbers which are statistically meaningful.

Spectral-numerical data-banks are available in two distinct forms, i.e., printed paper form and computer readable form.

To learn as much as possible from the XPS spectra obtained from a material it is necessary to compare an already published spectrum to a spectrum that was just measured. For maximum benefit it is most useful if one spectrum can be directly overlaid on the other. This can be done manually with two sheets of paper or digitally with software and a computer system.

The printed form of a spectrum in a reference book or data-bank can be manually overlaid with the spectral data from the target material by placing both spectra on top of a light-box. If the two spectra were collected and plotted under nearly identical conditions, then the comparison of two printed spectra is useful. However, identical styles of data collection and plotting are <u>not</u> common because there are currently no standardized conditions for collecting or plotting spectral data. Therefore, the printed form, by itself, can be very difficult to use to determine the relative amount of or the absence of a minor or a major chemical state in a target material which is identical or chemically similar to a reference material. The printed form can therefore be very limiting. With only paper copies of the target spectral data and the reference spectral data, it is also difficult or impossible to perform the data analyses listed in Table 5:

Table 5. Data Analyses Which are Difficult to Perform on Printed Paper Form of Spectra

- add or subtract spectra from target and reference materials
- verify that energy scale shifts were performed correctly for insulating materials
- correct the BE scale of the spectra from the target and reference materials
- normalize the electron counts in the spectra from the target and reference materials
- reduce the noise level to reveal hidden features
- fit signals to the data envelop to resolve the presence or absence of signals

All of the above and other data processing methods are useful to help the scientist to maximize the reliability of the information, but none of them can be directly applied to spectra in printed form.

If, however, the scientist could convert the printed form into a computer readable form then it would be possible to analyse the converted printed form by using any of the above mentioned data processing methods. It is, in fact, possible to convert printed data into computer readable form. The conversion process requires an optical image scanner and software. One such software is available from the American Chemical Society. The software converts a contiguous line of data points on paper into a series of data points encoded on computer readable media in either ASCII or HPGL data formats.[30]

By comparison to the printed form, the computer readable form of spectral data is much more useful and reliable than the printed form because it can be readily analyzed, processed, and interconverted in many different ways as long as the necessary data processing software routines are available.

Until recently computer readable forms of spectral-numerical data-banks were not available. Fortunately spectral-numerical data-banks can now be produced and distributed in a variety of inexpensive computer readable forms, e.g., removable floppy magnetic disks, fixed magnetic hard disks, removable hard-disks, WORM disks, CD-ROM disks, re-writable magneto-optical disks, phase-change optical disks, and other computer readable disk formats.

The computer readable form normally consists of XPS data in its original raw state just as it was produced by the XPS instrument. These original raw data naturally suffer from various amounts of instrument induced systematic errors and human induced random errors. These types of errors occur in all types of spectroscopy, including XPS and their numerical and spectral-numerical data-banks. These types of errors can be partially compensated for or diminished in spectral data stored in computer readable form, but not those stored in printed paper form.

The printed paper form of a spectral-numerical data-bank is, of course, much more useful than a simple numerical data-bank, but the computer readable form is much more versatile and as a result is most useful and most reliable. Therefore, as long as there is sufficient calibration data and statistical data with each set of coordinated raw spectra, the computer readable form is the most useful and the most reliable for making chemical state assignments.

From firsthand experience and by interviewing the more experienced analysts, this author has learned that the best and most reliable information comes from analyzing a new set of coordinated raw spectra by comparing them to a complete set of coordinated raw spectra from reference materials in their computer readable form. These experienced analysts have found that coordinated sets of actual raw spectra from reference materials can be directly compared and correlated with the spectra generated by a target material. By taking full advantage of the spectral and the numerical data contained in this type of data-bank, the analyst can more readily solve various problems and make more reliable chemical state assignments. These are only some of the advantages of having and using XPS spectral-numerical data-banks.

Unfortunately, spectra in the spectral-numerical type of data-bank are <u>not</u> frequently used for assigning chemical states to XPS signals because the number of actual spectra in these data-banks is still small.

In the following discussion section the author has reviewed three of the common XPS data-banks which are useful spectral-numerical data-banks.

Of these three, the journal called *Surface Science Spectra* (SSS) is the best example of a useful spectral-numerical data-bank. This data-bank will soon be available in a computer data-base form. The SSS journal has most of the features of a high quality spectral-numerical data-bank. It has the advantage of containing useful numerical data (e.g., BEs, FWHMs, and atom percentages) which were derived from processing the spectra contained in the spectral data-bank. Unfortunately, it is not yet known if the data-base version will include data processing software.

Unfortunately, many of the problems, that were outlined in the earlier section that discusses numerical data-banks, are duplicated in the SSS journal and also in the other spectral-numerical data-banks that are discussed in this review.

In the following synopses, which are presented in chronological order, the author has summarized the merits and minor problems in the numerical and spectral-numerical data-banks which are today widely used by many XPS analysts.

D. Specific Comments and Criticisms of XPS Numerical and Spectral-numerical Data-banks

The objective of this section is to present specific comments and criticisms about the content and structure of the numerical and spectral-numerical data-banks which are currently used by many scientists.

XPS data-banks exist in various forms (e.g., handbooks, standard journals, and computer based databases). As mentioned above, XPS spectral-numerical data-banks frequently suffer from the same problems that exists in many numerical data-banks. The most notable problem is due to the problem of not being able to determine reasonably reliable BEs from insulators. This is a very serious problem because more than 50% of all useful materials are insulators. At this time all current methods of generating BEs from insulators rely on secondary energy referencing methods which have uncertainties which are frequently as large as ± 0.5 eV,[10, 17, 26, 27] but can be as large as ± 1.0 eV[28] for a few materials. This degree of relative uncertainty is large enough to cause scientists to assign a wrong structure to many different insulating materials. This problem is indeed a serious and ongoing problem that exists in all data-banks that report BEs for insulators.

In the following synopses there are two sub-sections. The first sub-section summarizes most of the contents and structure of the data-bank. The second sub-section summarizes the problems in each data-bank and some features that could have been included with each particular data-bank.

1. *Handbook of XPS* by Physical Electronics (PHI) Corporation (1979)[15]

(1a) Contents and Structure of the 1979 PHI *Handbook of XPS*

This data-bank includes spectra and numerical data tables which contain high resolution electron BE data from many kinds of materials. This data-bank is a spectral-numerical data-bank.

In 1979, Physical Electronics (PHI) Corp. released the first edition of their handbook of XPS. It has been cited in many hundreds of publications. Until 1989, it was the best single source of high resolution electron BE numbers for more than 1500 different materials. To construct the high resolution BE data tables (i.e., photoelectron BE charts) for the primary XPS signal of each element, the authors, C. D. Wagner, W. M. Riggs, L. E. Davis and J. F. Moulder, had to evaluate the BE data published in thousands of different publications by hundreds of different scientists. The original publications cited in this data-bank were published between the years 1967 and 1978. In this 1979 edition, the reference energy values for Au° (4f7/2), Cu° (3p3/2), Cu° (2p3/2) and adventitious hydrocarbon C (1s) signals were reported to occur at 83.8 eV, 74.9eV , 932.4 eV, and 284.6 eV, respectively, with the energies of the Mg° and Al° X-ray sources reported to be 1253.6 eV and 1486.6 eV, respectively. The

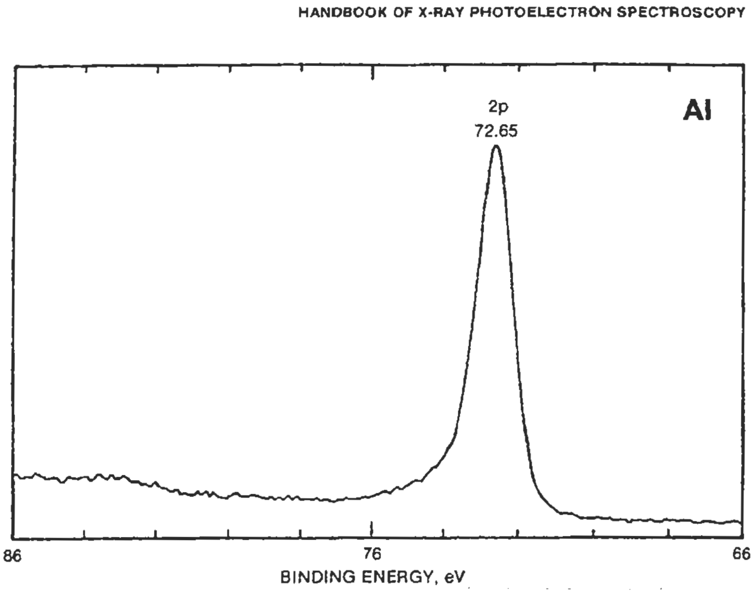
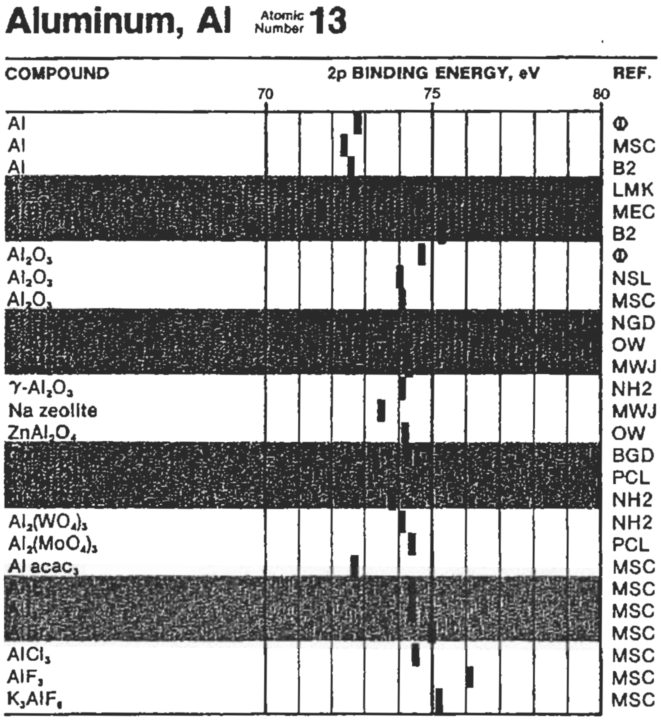


Figure 1. A Typical Spectrum from the 1979 PHI *Handbook of XPS.*



Aluminum, Al Atomic Number **13**

COMPOUND	2p BINDING ENERGY, eV	REF.
Al		Φ
Al		MSC
Al		B2
[illegible]		LMK
[illegible]		MEC
[illegible]		B2
Al_2O_3		Φ
Al_2O_3		NSL
Al_2O_3		MSC
[illegible]		NGD
[illegible]		OW
[illegible]		MWJ
γ-Al_2O_3		NH2
Na zeolite		MWJ
$ZnAl_2O_4$		OW
[illegible]		BGD
[illegible]		PCL
[illegible]		NH2
$Al_2(WO_4)_3$		NH2
$Al_2(MoO_4)_3$		PCL
Al $acac_3$		MSC
[illegible]		MSC
[illegible]		MSC
[illegible]		MSC
$AlCl_3$		MSC
AlF_3		MSC
K_3AlF_6		MSC

Figure 2. A Typical BE Data Table from the 1979 PHI *Handbook of XPS.*

authors suggested that the reference energy values might need to be increased by as much as 0.2 eV sometime in the future. The authors have used error bars which are 0.2 eV (±0.1 eV) in width for each BE entry in all high resolution electron BE data tables. Scattered throughout the first 30 pages of the book the reader can find most of the experimental parameters needed to understand the reliability and quality of the spectral data which were obtained from almost clean surfaces of the conductive elements, a few binary inorganic compounds, and organic polymers. As a result, the spectral data represent a self-consistent set of data which enhances the reliability the chemical state assignments made by using the spectra data that were made by the Physical Electronics authors.

In this handbook, there are approximately 210 different spectra which form a small spectral data-bank that includes wide scan, narrow scan, and, in some cases, Auger band spectra for 46 different elements, 21 different binary oxides, 4 different binary halides, 1 polymer and 6 chemical compounds. The data tables and example spectra for each element are presented in the order of the atomic number of the element. Most spectra were obtained by using a non-monochromatic Magnesium K_α X-ray source which has a FWHM of approximately 0.7 eV. This X-ray source produces several X-ray satellite signals which are readily observed in all spectra. A few spectra were measured by using a non-monochromatic Aluminium K_α X-ray source which minimized the overlap of the Auger signals with the XPS signals. The authors reported that the instrumental contribution to the natural line width (FWHM) of each high resolution signal was 0.5 eV. They reported that the instrumental contribution to the line width for the wide scan survey spectra should be 1.0 eV. Most of the wide scan survey spectra were shown with 1,000 eV wide energy ranges, and most of the high resolution electron energy spectra, which were shown with 20 eV wide energy ranges. All of the major XPS and major AES signals were clearly labeled on each of the wide scan spectra. The high resolution electron energy spectra for each element included a chemical group structure, which was usually the pure element, together with a binding energy value placed near the top of the most intense data point. The BE value listed on each high resolution spectrum normally included one decimal figure, but in a few cases included two decimal figures. When there were a pair of spin-orbit coupled signals within the 20 eV wide spectrum, the authors reported the difference in energy between the two spin-orbit coupled signals. When Auger signals are present, the authors also produced a high resolution analysis of the major Auger signals which are presented as gray colored boxes inserted onto the wide scan survey spectra. This handbook contains approximately 2,000 high resolution electron BE numbers, and about 250 Auger KE numbers from more than 1500 materials. Nearly every XPS BE and Auger KE numbers in this handbook was extracted from approximately 200 different scientific publications. The original source of the BE or Auger KE number can be found by referring to the authors' initials which are listed on the same line as the BE and then the index of publications. Many of the BE data tables contain 2 or 3 and sometimes more multiple entries for a particular chemical group or species. The range in BE for these multiple entries varied from 0.0 eV to 0.8 eV for conductive elements and from 0.0 eV to >1.0 eV for insulators. Some of the elements which gave Auger signals had Auger parameter data tables which are meant to help the analyst to make more reliable chemical state assignments. In the appendices there are BE data tables that report the line positions of the major XPS signals for each of the elements. There is also a data table of atomic sensitivity factors (ASF) which range from 0.012 to 30.0. The ASF values are normalized to the F (1s) peak area which has a ASF of 1.0.

To understand part of the structure and content of this database, please refer to figures 1-2.

(1b) Problems and Features Missing in the 1979 PHI *Handbook of XPS*

The major problem with this handbook is that errors and uncertainties associated with the BEs reported in the high resolution electron BE data tables are not reported. The authors only report an estimate of the error.

The errors and uncertainties associated with the BE are directly due to the work done by the original workers, not the authors of this handbook. Please recall the earlier discussions about the problems associated with simple one dimensional data tables of BEs. This problem is a serious one because this handbook was designed to be a major source of BEs to be used to make chemical state assignments.

Line position error bars for each BE signal in the high resolution data tables do not qualify as a sufficient report of uncertainty. The 1979 handbook seems to indicate that the uncertainty in the measured and referenced BEs are ±0.1

eV by showing line position error bars which are 0.2 eV wide.

Statistical information about the quality or reliability of those BEs is also missing. If included, it would have greatly improved the intended purpose of the data tables contained in this XPS data-bank.

The spectral data measured by the authors are a mixture of practical and research grade qualities, but the spectra appear to be reliable because the authors have made a serious effort to make reliable data through their careful attention to calibration.

Many of the wide scan survey spectra contain a relatively large amount of noise making it difficult to observe small signals, but the high resolution spectra have very little noise. The noise in the wide scan survey spectra is due mainly to the lack of sufficient total counting time. The electron counts scale of all spectra were deliberately removed.

There are several missing very valuable peak shape parameters. i.e.. FWHM, degree of asymmetry, ratio of Gaussian:Lorentzian curves needed to fit the individual XPS signals, and peak area ratios of spin-orbit coupled signals. The inclusion of FWHMs for the BEs listed in the high resolution electron BE data tables would have been an excellent tool to help scientists to analyse their raw spectral data.

There is no list of BEs for the energy loss signals that occur after all major XPS signals in each spectrum.

There are no valence band spectra, which are very valuable for theoretical studies and also allow cross-checks on the energy scale calibrations.

There is no table of BEs for the main C (1s) and O (1s) signals even though they are observed in nearly all of the wide scan survey spectra. This book only includes data from non-monochromatic sources which directly limits the quality of the spectral data and in some cases may have caused damage to some of the oxide or polymer samples while the spectra were being acquired. The low resolution of the X-ray source has most probably hidden most of the damage effects if indeed any occurred.

The actual FWHM of the narrow scan spectra from pure elements were estimated, by this author, to range from 1.1 eV to 1.5 eV for those signals which did not have a spin-orbit doublet nearby. The high resolution FWHM for the Ag (3d5) signal, which was taken with a 25 eV pass energy, was 1.1 eV. The FWHM for several insulators ranged from 1.7 eV to 3.0 eV with a typical FWHM of approximately 1.9-2.0 eV. This range of FWHM directly limits the user's ability to resolve the presence or absence of minor species and overlapping signals.

The uncertainties and errors for the reference energy numbers and the BE numbers listed in all the data tables were not clearly specified. The number of significant figures used to report the BEs seems to be somewhat randomly decided by the authors. The authors normally use 4 significant figures, but sometimes, there are 3 and 5 significant figures (e.g., 55.5 eV for the Li (1s) signal of LiF, and 511.95 eV for the V (2p3) signal of pure Vanadium (V) metal). Based on the fact that the reference energy for the Cu° (2p3) was reported to be 932.4 eV, it would have been better to use four significant figures. A similar problem with significant figures exists in the atomic sensitivity factor table in the appendix.

There are no uncertainties reported for line positions listed in appendices.

By comparing the BEs for pure conductive elements published in the new and old version, it was easy to find noticeable differences in the BEs in the high BE range. This is mainly due to the use of new reference energies in the new edition. This is a potential problem for new scientists because many new publications are using the new reference energies but many old scientists may still be using the old reference energies. The problem can be corrected by rescaling either set of data because they have provided sufficient calibration data.

A detailed statistical analysis of the pure element BEs listed in the old 1979 and new 1992 versions of this handbook was made by this author after correcting for differences in the BE scales and the reference energies used in the two different versions. The results are shown below in Table 6.

Table 6. Statistical Analysis of the Differences in BEs Listed in the 1979 and 1992 PHI Handbooks

Number of Data Points	38
Standard Deviation	0.1533
Median	0.1518
Mean	0.1452
Standard Error	0.02488
Variance	0.02352
RMS	0.2097
Skewness	-1.997
Kurtosis	8.109

Despite the various problems and missing features of this 1979 edition, the original 1979 handbook has proved to be very valuable and very useful to many scientist throughout the world. The authors are commended for their efforts to provide the surface analysis community with a useful data-bank.

2. *NIST X-ray Photoelectron Spectroscopy Database* Version 1.0 (1989)[16]

(2a) Contents and Structure of the *NIST XPS Database* Version 1.0

This data-bank is a dedicated numerical data-bank which contains high resolution electron BE data from all kinds of materials. There are no spectra in this data-bank.

In 1989, the US National Institute of Standards and Technology (NIST) released the first version of their *NIST X-ray Photoelectron Database*, which contains more than 13,000 numbers (i.e., BEs, KEs, Auger parameters, chemical shifts and splittings) and the chemical state assignments which are from the work and assignments made by thousands of workers between 1958 and 1985. The BEs are assumed to come from high resolution electron energy studies of the primary XPS signals.

This database is the result of a collaboration between NIST and Charles D. Wagner, Ph.D. (Surfex Co., Ltd.) an expert is surface analysis. By himself, Dr. Wagner selected the BEs from many thousands of publications after determining the reliability of the energy scale and the charge referencing techniques used by the original workers.

Published BE numbers were not included unless the original work included at least one of four preferred reference energy signals, i.e., Au° (4f7/2), Ag° (3d5/2), Cu° (2p3/2), and adventitious hydrocarbon C (1s) signals which were defined to appear at 84.0 eV, 368.2 eV, 932.6 eV, and 284.8 eV, respectively. If only one such reference energy was reported, then he corrected all observed BEs by using the one single reference energy. If additional reference energies were provided in the original publication, then he would "re-scale" the BEs if necessary to bring the published reference energies into agreement with the preferred reference energies listed above.

The database is currently available in formats which can be loaded onto personal computers that run with Microsoft or Apple disk operation software. It features more than 15 different ways to search the available data files.

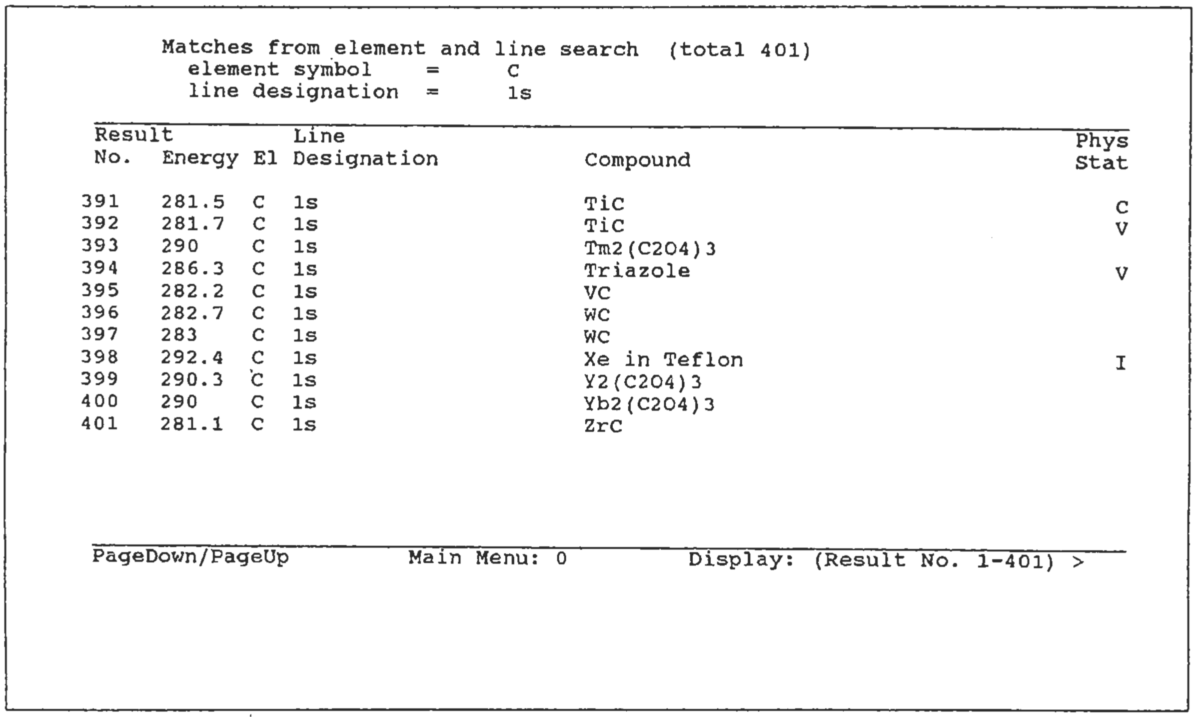
Each data file includes:

- the name and formula for a given compound or element, atomic number
- BE value, KE value, difference between BEs, or difference between KEs
- experimental details on calibration, physical state, treatments, charge referencing
- compound structure, compound type (e.g., carbide), empirical formula
- statement about energy corrections, rescaling, and data quality
- materials used for energy referencing (e.g., pure Pd°, Cu°, Au°, etc.)
- method of charge referencing insulating materials
- complete listing of original reference work
- the type of signal (e.g., spin-orbit, spin-orbit splitting, Auger parameter, or Auger transition)

Based on the above list of parameters, the software can perform searches for single or multiple parameters and single or multiple numbers of elements. Energy values can include various tolerances in the energy range. The six (6) main categories for searching are listed below:

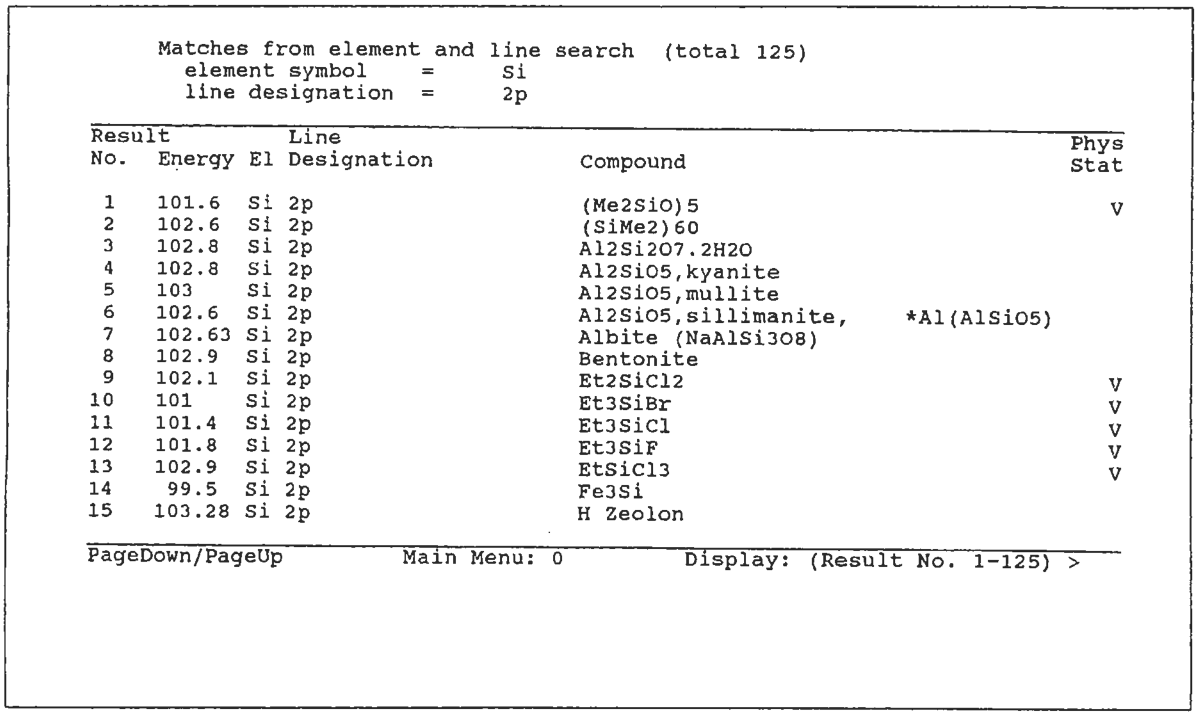
Identify:
  1. One unknown spectral feature
  2. A set of unknown spectral features
Search and Display for an Element:
  3. Binding energy data
  4. Auger kinetic energy data
  5. Chemical shifts
Browse:
  6. Individual data fields

A typical search of the database on a modern computer system requires only a few seconds. The number of line results that can be displayed is 999. Each line includes a Result No., the Energy, the Element abbreviation, the Line Designation, the Compound's empirical formula or its common name, and an abbreviation that reports the Physical State of the compound. A typical search for a specific common chemical compound (e.g., Al_2O_3 or CaO) will return a list of one (1) to ten (10) data sets. The full data file for any data set can be read by selecting the result number for that data set. Depending on the search routine the data sets are organized by numeric or alphabetic ordering. One of the interesting



```
      Matches from element and line search  (total 401)
        element symbol    =     C
        line designation  =     1s

   Result          Line                                                  Phys
   No.   Energy El Designation               Compound                    Stat

  391    281.5  C  1s                        TiC                          C
  392    281.7  C  1s                        TiC                          V
  393    290    C  1s                        Tm2(C2O4)3
  394    286.3  C  1s                        Triazole                     V
  395    282.2  C  1s                        VC
  396    282.7  C  1s                        WC
  397    283    C  1s                        WC
  398    292.4  C  1s                        Xe in Teflon                 I
  399    290.3  C  1s                        Y2(C2O4)3
  400    290    C  1s                        Yb2(C2O4)3
  401    281.1  C  1s                        ZrC



   PageDown/PageUp         Main Menu: 0         Display: (Result No. 1-401) >
```

Figure 3. A Typical BE Data Table from the *NIST XPS Database* Version 1.0.



```
      Matches from element and line search  (total 125)
        element symbol    =     Si
        line designation  =     2p

   Result          Line                                                  Phys
   No.   Energy El Designation               Compound                    Stat

    1    101.6  Si 2p                        (Me2SiO)5                    V
    2    102.6  Si 2p                        (SiMe2)60
    3    102.8  Si 2p                        Al2Si2O7.2H2O
    4    102.8  Si 2p                        Al2SiO5,kyanite
    5    103    Si 2p                        Al2SiO5,mullite
    6    102.6  Si 2p                        Al2SiO5,sillimanite,    *Al(AlSiO5)
    7    102.63 Si 2p                        Albite (NaAlSi3O8)
    8    102.9  Si 2p                        Bentonite
    9    102.1  Si 2p                        Et2SiCl2                     V
   10    101    Si 2p                        Et3SiBr                      V
   11    101.4  Si 2p                        Et3SiCl                      V
   12    101.8  Si 2p                        Et3SiF                       V
   13    102.9  Si 2p                        EtSiCl3                      V
   14     99.5  Si 2p                        Fe3Si
   15    103.28 Si 2p                        H Zeolon

   PageDown/PageUp         Main Menu: 0         Display: (Result No. 1-125) >
```

Figure 4. A Typical BE Data Table from the *NIST XPS Database* Version 1.0.

and useful features is the ability to search by compound type, e.g., Polymer, Carbide, Alloy, Sulfide, Sulfate, Oxide, Element, Carbonate, Nitrate, Nitrite, Silicate, etc.

The number of BEs from primary XPS signals for most of the metallic elements ranges from 10-70. More than 15 elements (i.e., C, N, O, F, Si, P, S, Cl, Cr, Fe, Ni, Cu, Mo, Rh, Pd, Sn, and Pt) have more than 120 BEs from their primary XPS signal. Out of those 15 elements, several (i.e., O, N, P, S, Cl, Ni, and Rh) have more than 200 BEs from their primary XPS signal. The elements with more than 400 BEs are C, O, P, and S. Oxygen has the most data with more than 999 BEs.

This data-bank is especially useful because it contains many reasonably reliable BEs which were selected and evaluated by the same person, C. D. Wagner. The number of BEs from primary XPS signals totals more than 8,000. Most of the remaining numbers are Auger KEs, Auger parameters, spin-orbit splittings, and chemical shifts. There are also useful numbers of BEs for the rare earths which are seldom studied.

To understand part of the structure and content of this database, please refer to figures 3-4 which are copies of the actual video displays used by the database.

(2b) Problems and Features Missing in *NIST XPS Database* Version 1.0

Most of the problems and limitations of a simple one dimensional numerical data-bank that are fully discussed earlier in this review are directly applicable to this numerical data-bank.

In addition to those problems we have described other problems which are specific to this numerical data-bank.

Because the original publication authors did not report sufficient detail about binding energy scale calibration, Dr. Wagner's method of evaluation was usually limited to a single reference energy which may or may not have been verified by the original authors during the time actually used to collect the reported BE numbers. This means that Dr. Wagner's efforts to make a common energy scale are limited by the quality, accuracy, and content of the original publications that he reviewed.

Relative degrees of uncertainties and errors in the BE numbers were not specified anywhere in the database or the handbook that accompanies it.

The number of significant figures included in the data base varied from two (2) to five (5) with no mention of the actual uncertainties or errors associated with each BE or KE number.

International Union of Pure and Applied Chemistry (IUPAC) based formulae were not included. The empirical formula system devised by Wagner is significantly different from the IUPAC system, but is still familiar to many chemists.

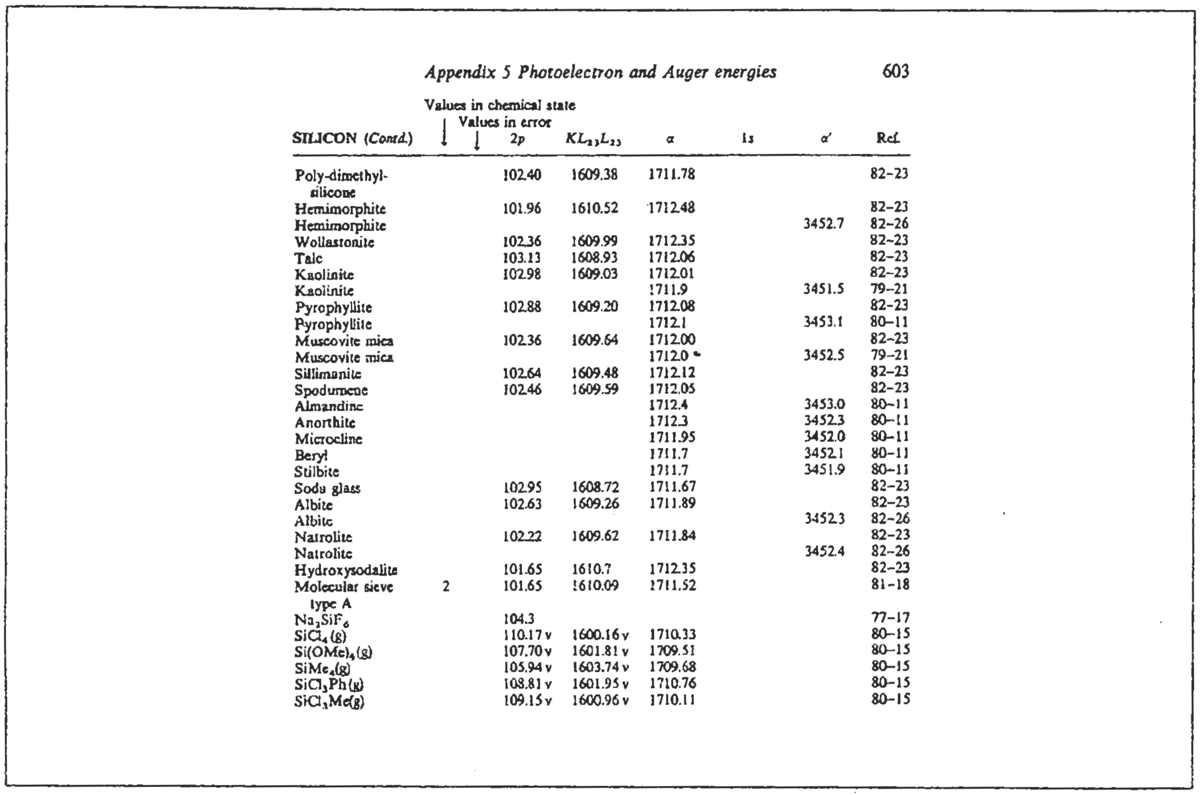
A good number of mineral names were used without their empirical formula which makes it difficult for users to take direct advantage of the BE information because he/she may not have access to a book that reveals the empirical formula or the structure of the groups contained in the mineral. Common chemical names (quartz), and trade names (e.g., Cab-O-Sil), which are helpful, but were used randomly.

There are no statistical analyses (reproducibility checks) for the BEs obtained a identical chemical compounds measured by different scientists. From a set of 10 BE numbers from identical compounds it is possible to generate several statistically meaningful numbers that would help the database user to decide the best number (BE or KE) to use for the chemical state assignment of the signals in his spectra.

This database was constructed in conjunction with the US government National Institute for Science and Technology, but it is not clearly reported that the data are not truly high quality data that is expected from a national body that is responsible for making various kinds of *standards* (e.g., standard reference materials).

The quality of the data became clearer after we measured the statistical mean BE value from all available BEs for 59 different elements listed in the database and compared those mean BE values to the list of preferred BEs published by NIST workers in a special ECASIA 91 issue of the Surface and Interface Analysis journal published in 1992 (p.241-246). From that comparison-we realized that most of the preferred BEs were taken from one particular source (i.e., N. Martensson, Uppsala University in Sweden), and that the other preferred BEs were taken from other reference sources (NIST internal document: C.D. Wagner, The NIST X-ray Photoelectron Spectroscopy Database, NIST Technical Note Number 1289. US Department of Commerce, Gaithersburg, MD (1991)). Our statistical analysis of the BE differences between the mean BEs in the database and the preferred BEs gave a standard deviation of 0.3872, a variance of 0.1499, and a standard error of 0.0504.

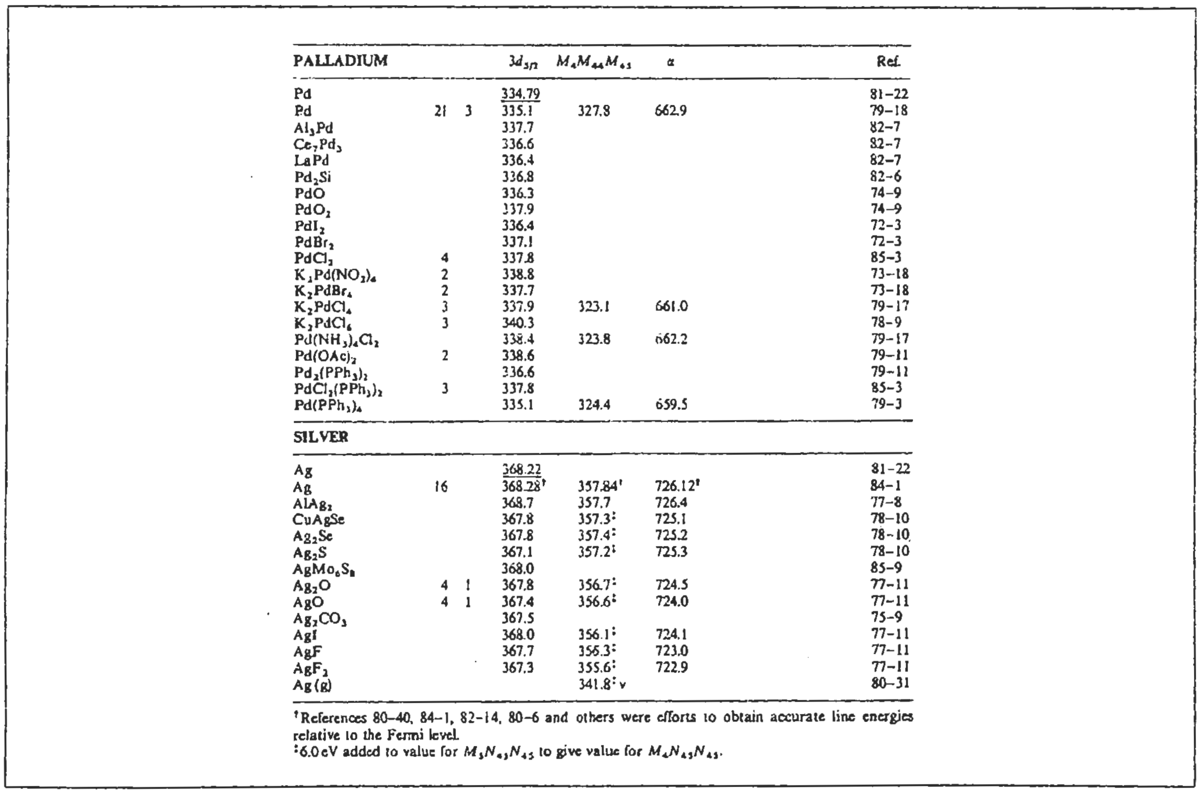
Despite the various problems and features missing from this data-bank, it is very useful and contains reasonably reliable BEs. If statistical analyses that indicate which BE is "most"



Appendix 5 Photoelectron and Auger energies 603

SILICON (*Contd.*)	Values in chemical state	Values in error	$2p$	$KL_{23}L_{23}$	α	$1s$	α'	Ref.
Poly-dimethyl-silicone			102.40	1609.38	1711.78			82–23
Hemimorphite			101.96	1610.52	1712.48			82–23
Hemimorphite							3452.7	82–26
Wollastonite			102.36	1609.99	1712.35			82–23
Talc			103.13	1608.93	1712.06			82–23
Kaolinite			102.98	1609.03	1712.01			82–23
Kaolinite					1711.9		3451.5	79–21
Pyrophyllite			102.88	1609.20	1712.08			82–23
Pyrophyllite					1712.1		3453.1	80–11
Muscovite mica			102.36	1609.64	1712.00			82–23
Muscovite mica					1712.0 •		3452.5	79–21
Sillimanite			102.64	1609.48	1712.12			82–23
Spodumene			102.46	1609.59	1712.05			82–23
Almandine					1712.4		3453.0	80–11
Anorthite					1712.3		3452.3	80–11
Microcline					1711.95		3452.0	80–11
Beryl					1711.7		3452.1	80–11
Stilbite					1711.7		3451.9	80–11
Soda glass			102.95	1608.72	1711.67			82–23
Albite			102.63	1609.26	1711.89			82–23
Albite							3452.3	82–26
Natrolite			102.22	1609.62	1711.84			82–23
Natrolite							3452.4	82–26
Hydroxysodalite			101.65	1610.7	1712.35			82–23
Molecular sieve type A	2		101.65	1610.09	1711.52			81–18
Na_2SiF_6			104.3					77–17
$SiCl_4$ (g)			110.17 v	1600.16 v	1710.33			80–15
$Si(OMe)_4$(g)			107.70 v	1601.81 v	1709.51			80–15
$SiMe_4$(g)			105.94 v	1603.74 v	1709.68			80–15
$SiCl_3Ph$(g)			108.81 v	1601.95 v	1710.76			80–15
$SiCl_3Me$(g)			109.15 v	1600.96 v	1710.11			80–15

Figure 5. A Typical BE Data Table from Appendix 5 in *Practical Surface Analysis* 2nd Edition.



PALLADIUM			$3d_{5/2}$	$M_4M_{45}M_{45}$	α	Ref.
Pd			334.79			81–22
Pd	21	3	335.1	327.8	662.9	79–18
Al_3Pd			337.7			82–7
Ce_7Pd_3			336.6			82–7
LaPd			336.4			82–7
Pd_2Si			336.8			82–6
PdO			336.3			74–9
PdO_2			337.9			74–9
PdI_2			336.4			72–3
$PdBr_2$			337.1			72–3
$PdCl_2$	4		337.8			85–3
$K_2Pd(NO_2)_4$	2		338.8			73–18
K_2PdBr_4	2		337.7			73–18
K_2PdCl_4	3		337.9	323.1	661.0	79–17
K_2PdCl_6	3		340.3			78–9
$Pd(NH_3)_4Cl_2$			338.4	323.8	662.2	79–17
$Pd(OAc)_2$	2		338.6			79–11
$Pd_2(PPh_3)_2$			336.6			79–11
$PdCl_2(PPh_3)_2$	3		337.8			85–3
$Pd(PPh_3)_4$			335.1	324.4	659.5	79–3
SILVER						
Ag			368.22			81–22
Ag	16		368.28†	357.84†	726.12†	84–1
$AlAg_2$			368.7	357.7	726.4	77–8
CuAgSe			367.8	357.3‡	725.1	78–10
Ag_2Se			367.8	357.4‡	725.2	78–10
Ag_2S			367.1	357.2‡	725.3	78–10
$AgMo_6S_8$			368.0			85–9
Ag_2O	4	1	367.8	356.7‡	724.5	77–11
AgO	4	1	367.4	356.6‡	724.0	77–11
Ag_2CO_3			367.5			75–9
AgI			368.0	356.1‡	724.1	77–11
AgF			367.7	356.3‡	723.0	77–11
AgF_2			367.3	355.6‡	722.9	77–11
Ag (g)				341.8‡ v		80–31

†References 80–40, 84–1, 82–14, 80–6 and others were efforts to obtain accurate line energies relative to the Fermi level.

‡6.0 eV added to value for $M_5N_{45}N_{45}$ to give value for $M_4N_{45}N_{45}$.

Figure 6. A Typical BE Data Table from Appendix 5 in *Practical Surface Analysis* 2nd Edition.

accurate were included then this data-bank would be even more useful.

3. *Practical Surface Analysis* Second Edition Appendix 5 (1990)[16]

(3a) Contents and Structure of Appendix 5 - *Practical Surface Analysis* 2nd Ed.

This data-bank is a dedicated numerical data-bank that contains high resolution electron BE data from inorganic materials mainly. There are no spectra in this data-bank.

In 1983, Charles. D. Wagner, Ph.D. (Surfex Co., Ltd.) published the original version of this chapter[30] in the first edition of *Practical Surface Analysis*. (Note: Dr. Wagner is also directly responsible for most of the work done to assemble the numerical data tables in the 1979 and 1992 PHI *Handbook of XPS* and the *NIST XPS Database.*).

The BE data in this series of data tables were extracted from 295 different publications published between 1967 and 1985.

Those BEs were evaluated and assembled into useful data tables by Wagner. In this numerical data-bank, the reference energies for Au° (4f7/2), Ag° (3d5/2), Cu° (2p3/2) and adventitious hydrocarbon C (1s) signals were assumed to occur at 84.00 eV, 368.20 eV, 932.60 eV, and 284.8 eV, respectively.

The "permissible error" for the BEs reported throughout this data-bank is ≥ 0.5 eV. This means that the permissible error range is $\geq \pm 0.5$ eV (e.g., SiO_2 is reported to have a BE of 103.4 eV ± 0.5 eV).

This version of the data-bank contains 1086 lines of data which includes BEs, KEs, and Auger parameters. The overall sequence of presentation is based on the atomic number of the element. There are usually 5-10 different chemical compounds listed under each element. There are BEs for nearly every non-radioactive elements. For a particular element, the row sequence starts with the pure element, followed by the other compounds without any particular order. About half of the lines of data include an entry called "values in chemical state". The number for this entry ranges from 1 to 26, but averages around 2-3. The "values in chemical state" number is the total number of different references that were used to determine the "median" BE assigned to that particular chemical compound. This number serves as a rough guide to the reliability of the reported BE. The "permissible error" for the these BEs seems to be ≥ 0.5 eV. The columns for each data line include: an empirical formula, which uses common chemical names and abbreviations, the Values in chemical state, the Values in error, an XPS BE, an Auger KE if available, an Auger parameter if available, a secondary XPS BE if available, a modified Auger parameter if available, and finally the an abbreviation for the original reference work.

Some of the BEs listed for the pure elements are underlined, which means that that BE is the result of careful calibration work by Nils Martensson or another researcher.

This data-bank is most useful to scientists who need reasonably reliable BEs for inorganic materials.

To understand part of the structure and content of this database, please refer to figures 5-6.

(3b) Problems and Features Missing in Appendix 5 - *Practical Surface Analysis* 2nd Edition

Most of the problems and limitations of a simple one dimensional numerical data-bank that are fully discussed earlier in this review are directly applicable to this numerical data-bank. This means that the user does not have access to any useful peak-shape (signal) parameters such as: FWHM, ratio of Gaussian:Lorentzian curve shapes, degree of asymmetry, or the shape of underlying background.[31]

In addition to those problems we have described other problems which are specific to this numerical data-bank.

BEs for most organic materials were deliberately excluded. This severely limits the usefulness of the data-bank to at least two major groups of potential users, i.e., scientists who study polymers and catalysts.

The logic for choosing a permissible error range of ± 0.5 eV is not fully explained and is therefore difficult to accept as being meaningful because there are no statistical values known as "permissible error".[17]

It is also not clear if the author has indeed listed median values for the BE associated with each chemical compound. As a result, the user is still left wondering about the uncertainties and accuracy of the data summarized in this data-bank.

The author has used a second decimal place for each of the defined reference energies which appears as a zero (0) value, but has not explained the reasoning for the use of a zero decimal place which does not have any true mathematical significance.

And despite the author's intention to make the "... line energy data in as self-consistent a manner as possible" it is, in fact, very difficult to generate a self-consistent set of data from data generated by many different users using many different instruments and many different energy referencing methods.

A good number of mineral names were used without their corresponding empirical formulae which makes it difficult for users to take direct advantage of the BE information because he/she may not have access to a book that reveals the empirical formula or the structure of the mineral.

Despite the various problems and missing features this appendix is perhaps more reliable than the NIST XPS Database because it appears to have been more severe in the admittance of BEs to their data tables. It would have been better to include BEs from organic materials as a second database instead of excluding them from this quite useful data-bank.

4. *Common Data Processing System - Version 3.1* by NRIM and VAMAS-SCA (1990)[17]

(4a) Contents and Structure of the *Common Data Processing System - Version 3.1*

The Common Data Processing System[3,17,43] which is software designed to process spectral data taken by using different instruments, was constructed by using Microsoft's Visual Basic programming language and is compatible with MS-Windows 3.1. This software was initially developed in 1989 under the direction of K. Yoshihara of the National Research Institute for Metals (NRIM) which is directly supported by the Science and Technology Agency (STA) of Japan. Dr. Yoshihara and several Japanese members of the Surface Chemical Analysis (SCA) division of the international Versailles Project for the Advancement of Materials and Science (VAMAS) worked together to develop the initial data processing software and attached data-banks. This software is already being used by more than 200 Japanese researchers.

This software is distributed free of charge to all users and has recently been installed on a computer based electronic bulletin board which is part of the Inter-Ministry Network (IMNet) system located at NRIM in Tsukuba City, Japan. Now the Common Data Processing System can be accessed by using the Internet at the World-Wide-Web site known as: "www.sekimori.nrim.go.jp".[32]

The Common Data Processing System has also been given free of charge to the American Standards and Testing Methods (ASTM) E-42 committee on Surface Analysis. The E-42 committee installed it on their computer based electronic bulletin board.

This software can convert different spectral data file formats into a common data file format known as the "VAMAS-SCA Standard Data Transfer Format".[34] The resulting data can then be treated in various ways, i.e., (a) characterize the relative electron transmission behavior of each instrument, (b) calibrate spectra by using that relative behavior, (c) analyze spectral data by various data processing softwares, or (d) obtain correction factors from the database.

The main focus of this software is to develop data processing tools which enable users to analyze spectra obtained by different instruments. This software includes a routine called "Analyzer" which determines in a relative manner the characteristics of an instrument by comparing sets of spectral data with spectral data defined to be standard spectra.

The capabilities and appearance of this software is nicely presented in the Journal of Surface Analysis, Vol. 1, p.459 (1995). This software is designed so that any user can add new source code to the original Visual Basic source code. Some of the features of this software are listed here:

- analyzer (to setup energy or intensity scale correction schemes used in "calibration")
- multi-spectra processing (to overlay several spectra)
- expand (to look at a less intense or less wide region of data)
- display (to display more than one spectrum at a time)
- add or subtract (to add or subtract two spectra)
- divide (to help develop the calibration scheme)
- curve fitting (to fit two reference spectra onto a spectrum of two mixed compounds)
- file convert (to convert original file format into VAMAS file format)
- print (to print paper copies of spectra)
- background (to apply a linear, Shirley, Tougarrd, or Sickafus background to a spectrum)
- intensity (to change the intensity scale)
- de-convolution (to remove signal broadening effects)
- smoothing (to smooth noisy data)
- calibration (to apply a recorded scheme to calibrate energy and intensity scales)
- quantify (to quantify the atom % based on signal areas or heights)
- check transmission (to compare electron transmission of two instruments)
- reference (to access the "reference" grade spectral data-bank of >500 spectra)

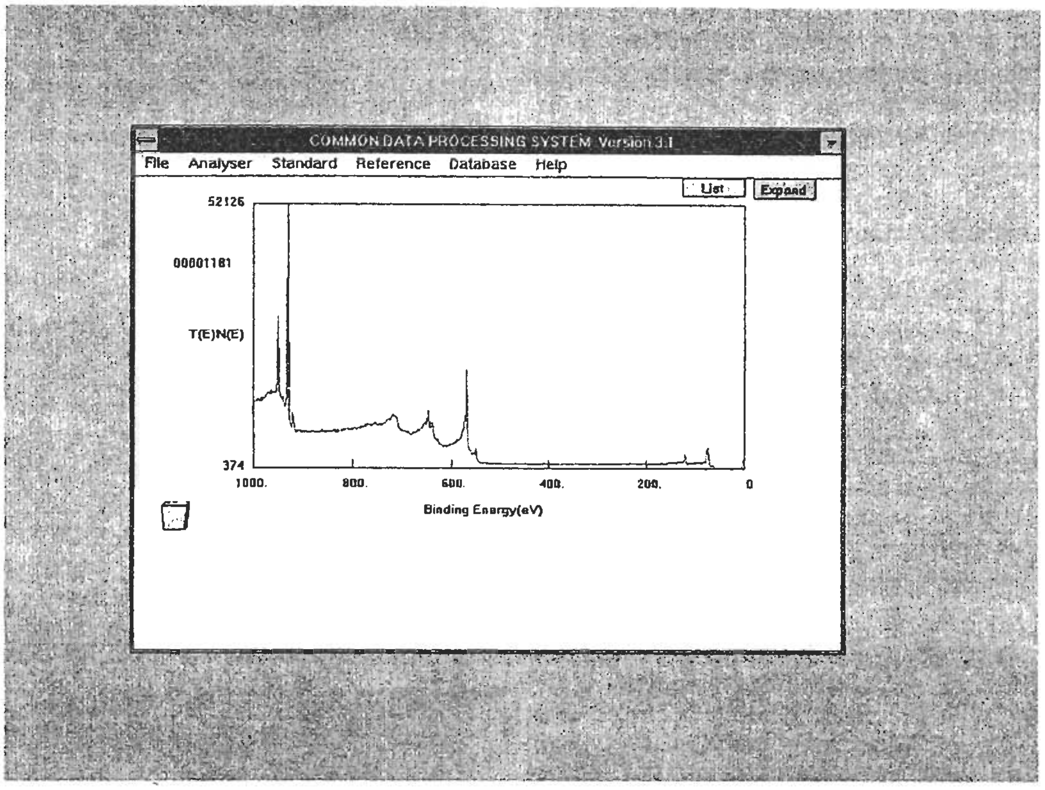
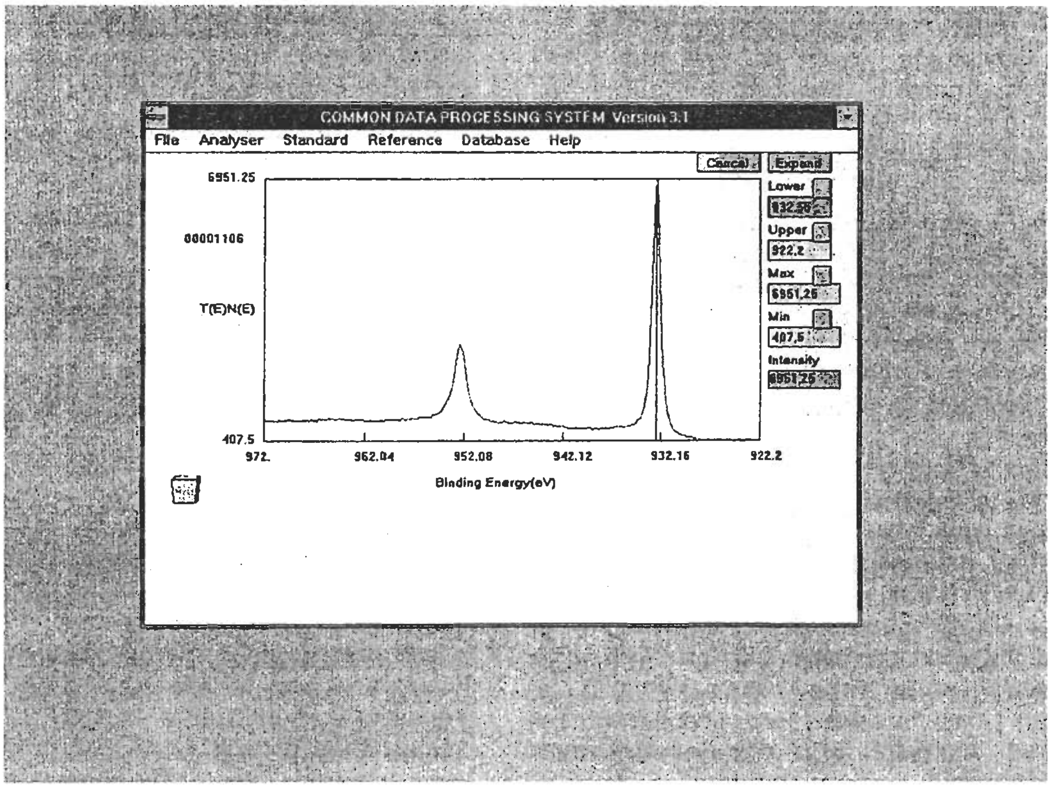


Figure 7. A Typical Spectrum from the Common Data Processing System - Version 3.1



Lower 932.56

Upper 922.2

Max 6951.25

Min 407.5

Intensity 6951.25

Figure 8. A Typical Spectrum from the Common Data Processing System - Version 3.1

- list (to access information about the sample, analysis conditions, and instrument)
- help (to access on-line guiding remarks about each routine)
- database (to access information about each element including IMFP, Backscatter
- factors, BEs, atomic number, atomic weight, valence electrons, band gap
- atomic density, and weight density)

The "List" routine is very useful because it brings up all the details about the sample, the instrument, the analysis conditions, and a comment line which can be used to bring up much more information about the sample and the spectral data after it is fully developed.

The system includes a spectral data-bank of "standard" AES spectra (>40) which were obtained from a custom-made mechanically well-defined CMA type of AES instrument[35, 36] and a spectral data-bank of "standard" of XPS spectra (>10) which were obtained from a commercially made double-pass CMA type of XPS instrument.[37]

The system also includes a small temporary spectral data-bank of >500 "reference" grade XPS and AES spectra which were supplied by various Japanese VAMAS members to assist with the testing and development of the total software system.

To assist the development of the Common Data Processing System software and to test its data processing capabilities, Dr.Crist has donated more than 300 practical grade spectra from a private data-bank of more than 15,000 spectra.[28] Another 150 spectra were generously donated by several private companies here in Japan.[18]

Most of the reference grade spectra are from pure elements but none of the current spectra are meant to be permanent entries in the databank.

There are currently a total of 99,999 file numbers available for a maximum of 99,999 different individual spectra.

One of the nice features of the data-bank is the method to select the major element of interest. The system uses the elemental periodic table which is very natural to use for scientists.

In mid-1994, the Science and Technology Agency agreed to provide extensive funding for a five year period to develop the data-bank attached to the Common Data Processing System into a useful, large scale spectral data-bank.

More than 100 Japanese researchers are currently collecting spectra and developing routine methods for collecting practical grade spectral data to submit to the spectral data-bank.

The Common Data Processing System is therefore considered to be a spectral-numerical data-bank, which can be separated into a true spectral data-bank and the Common Data Processing System. It is important to note that the Common Data Processing System also includes numerical data-banks of IMFP and Backscatter data which are very useful.

Once the spectral data-bank and the telecommunication software are fully developed, this system should become a very powerful tool for surface analysis.

To understand part of the structure and content of this database, please refer to figures 7-8 which are copies of the actual video displays used by the database.

(4b) Problems and Features Missing in *Common Data Processing System - Version 3.1*

The problems and features which are missing from the data processing software and the spectral data-bank will be discussed sequentially in the following two sub-sections.

Data Processing Software Problems: Some of the names used for the data processing routines need to be reworded so that the capability of the routine is more easily understood. The "Help" menu is indeed helpful to understand the capability of the different processing routines, but the help menu disappears when another menu is accessed.

When a spectrum is displayed there is no way to understand the chemical contents of the spectrum because all the information which describes the data are hidden in a separate display (which can be accessed by selecting the "List" button). It would be much better if a minimum amount of useful information was displayed together with the spectra at the bottom of the video screen.

A problem exists when we want to find the energy of a peak position. We must use a routine called "Expand" to get an on-screen cursor that can be used to find the energy of a peak position. The initial non-functional screen should be eliminated.

Another problem occurs when we try to select a spectrum that we are interested to study. The problem is that there are only 10 characters used to describe the chemical composition of the sample. This problem must be corrected before the software can be used with a true large scale data-bank which will include many complicated chemical compounds.

The periodic table system used to locate major elements of interest is convenient but it can not deal with the names used for organic polymers. A special sub-menu option to search for polymers and other organic materials will have to added to when the user selects the element carbon.

There are a few other minor problems with the data processing software which occurred because the original problem-free software was translated from Quick-Basic into Visual Basic for Windows.

The last comment is that it may be worthwhile to offer separate listings of the AES from the XPS spectral data-files because it should be quite seldom that many users will want to access AES and XPS spectra at the same time.

Spectral Data-Bank Problems: There are two types of spectral data in the spectral data-bank part of the Common Data Processing System. The "Reference" spectra data-bank is currently test data which is temporary data. It is almost meaningless to discuss the problems associated with these spectral data. It is worthwhile to point out a few minor details, such as the noise level. All spectra submitted to the data-bank should have a certain minimum level of noise which is acceptable.

The spectral data should also have an upper limit for the eV/channel step size which is small enough to allow the user to perform advanced data reduction methods such as: peakwidth analysis, smoothing, Fourier transformations, deconvolution, peak-fitting, subtraction of one spectrum from another, peak removal, peak shifting. For example: the maximum eV/channel step size should be <0.05 for 20 eV wide spectra.

To maximize the reliability of the BE data it is essential to include a valence band spectrum that ranges from -10 eV to +40 eV so that BE calibration can be checked for each set of coordinated spectra.

An adequate method for cross referencing sets of coordinated spectra must be included in the data-bank and the data processing software. A list of other recommended features is included at the end of this review.

Despite the minor problems and missing features, this data-bank has a great potential to become an excellent self-consistent source of reliable spectral data by avoiding the mistakes made by other efforts and by developing reliable methods to collect reliable spectral data.

5. *Handbook of XPS* by JEOL Co. (1991)[19]

(5a) Contents and Structure of the JEOL *Handbook of XPS*

This data-bank includes spectra and numerical data tables which contain high resolution electron BE data from all kinds of materials. This data-bank is a spectral-numerical data-bank.

In 1991, the Japan Electron Optics Laboratory (JEOL) Co., Ltd. produced an XPS handbook which includes spectra obtained by using a non-monochromatic Magnesium K_α X-ray source and a non-monochromatic Aluminium K_α X-ray source. As reference energy values, the authors, N. Ikeo, Y. Iijima, N. Niimura, M. Shigematsu, T. Tazawa, S. Matsumoto, K. Kojima, and Y. Nagasawa, assigned Au° (4f7/2), Ag° (3d5/2), Cu° (2p3/2) and adventitious hydrocarbon C (1s) signals to occur at 83.8 eV, 368.2 eV, 932.8 eV, and 285.0 eV, respectively.

In this handbook, there are approximately 330 different spectra which form a spectral data-bank that includes wide scan, narrow scan, valence band and/or Auger band spectra of 33 different pure elements, 11 different binary halides, 7 different binary oxides, 17 different polymers and 9 other types of chemical compounds. The spectra obtained from various polymers and a few forms of carbon were included as a special section, #5.

Many of these spectra include actual peak-fit results and peak assignments which are very helpful to beginners.

The analysis conditions used to collect the spectral data are only partially defined on page 21 of the handbook. The pass energy was set to 10 eV for high resolution electron energy scans which gave a 0.9 eV FWHM for the Ag (3d5) signal. The pass energy for the wide scan survey spectra was set to 50 eV. A step size of 0.1 eV/channel and a step size of 1.0 eV/channel were used for the narrow scan work and the wide scan work, respectively.

Valence band spectra, which can be very useful for checking the BE accuracy and for research purposes, were included by scanning from -4 eV to + 20 eV with a 30 eV pass energy and a 0.1 eV/channel step size.

The signal/noise ratio of the wide scan and narrow scan spectra are in general better than those provided in the 1979 PHI Handbook of XPS.

The spectra that were acquired by JEOL represent a self-consistent set of spectra which have been used together with three other self-consistent sets of BEs from pure elements to

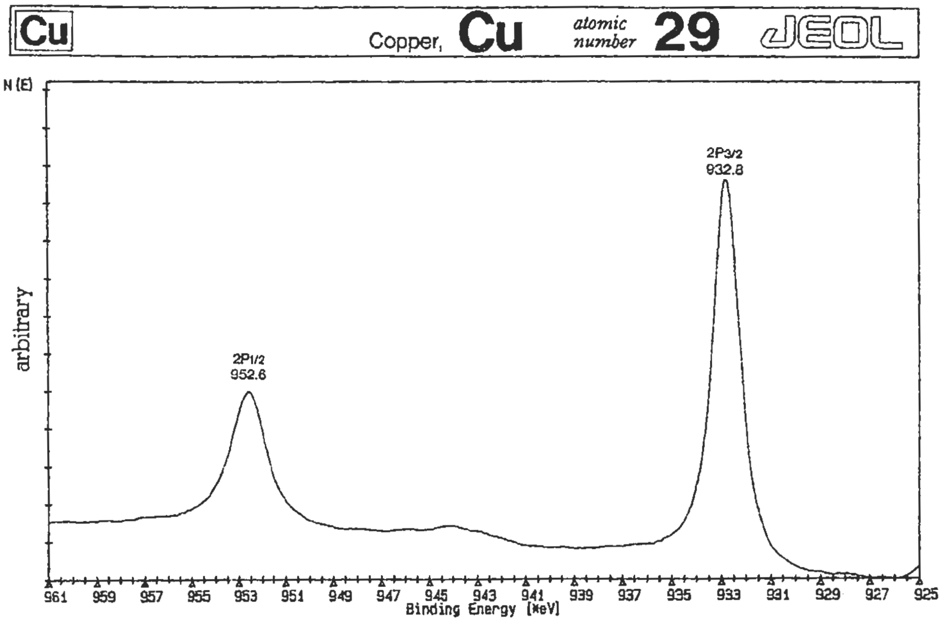


Figure 9. A Typical HIgh Resolution Spectrum from the JEOL *Handbook of XPS.*

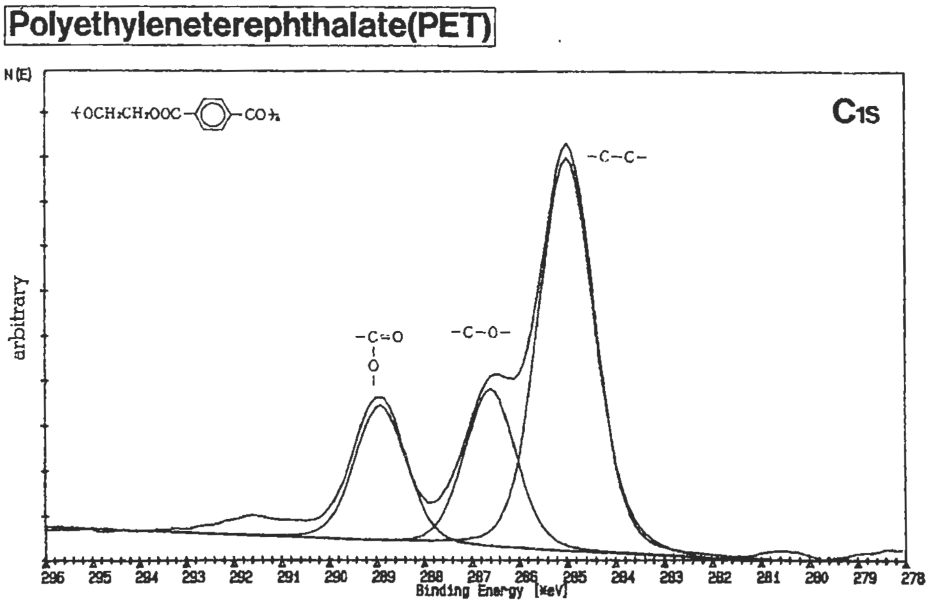


Figure 10. A Typical Polymer Spectrum from the JEOL *Handbook of XPS.*

determine reliable secondary reference energies for a series of pure elements.[38]

Relative sensitivity factors (RSFs) are in a chart in Appendix 5 of the handbook All RSFs, which were determined from peak areas, are normalized to the Ag (3d5) peak area which has a RSF of 1.0.

This handbook also contains a self-education section on practical methods for sample preparation, data collection and data interpretation in the front of the book.

In the appendices there are numerical data tables about pure element electron binding energies, calculated atomic photoionization cross-sections, calculated asymmetry parameters, calculated electron inelastic mean free path, calculated number of valence electrons, band-gap energies of nonconductors and semiconductors, relative sensitivity factors, ion beam etch and sputtering rates, a table of FWHM values measured from high resolution spectra of the main XPS signals produced by various elements, tables extensive tables of BEs and chemical shifts from >700 different chemical compounds.

The BE numbers reported in an appendix in this handbook came from 700 different chemical compounds and 70 elements.

Nearly all of the BE numbers were extracted, with permission, from the *NIST XPS Database* and the book *Practical Surface Analysis* edited by D. Briggs and M. P. Seah.

There is also an appendix (#8) on polymer materials which reports 60 different C (1s) BEs and FWHMs for the different functional groups contained in those polymers. There is also a brief table on O (1s) BEs and FWHMs for a few polymers.

This data-bank is similar to the 1979 handbook produced by PHI but includes many practical data tables, which can be useful to experienced users, and also includes a small collection of spectra from polymers and the valence band region of many elements.

To understand part of the structure and content of this database, please refer to figures 9-10.

(5b) Problems and Features Missing in the JEOL *Handbook of XPS*

The authors have decided to include the simple one dimensional high resolution electron BE data tables provided by the *NIST XPS Database* and the book *Practical Surface Analysis*. This means that the user suffer the same limits and problems that exist for those two sets of BE data.

The uncertainties for their reference energy numbers or any BE numbers were not clearly specified, but the authors wrote that the reference energy number for the adventitious hydrocarbon C (1s) signal was 285.0 eV ±0.2 eV.

The authors have used reference energies which are different than those accepted and used by most other researchers. The chosen reference energy for Au (4f7) is 83.8 eV which is 0.2 eV smaller than the more common 84.0 eV value. The chosen reference energy for the Cu (2p3) signal is 932.8 eV which is 0.1-0.2 eV larger than the more common 932.6-932.7 eV value. These differences cause an relative increase in the BE scale and requires rescaling their XPS data to allow comparison with BE data obtained from most other instruments.

The book only contains spectra from 60 different elements, which is less than the number of elements included in the relatively old 1979 handbook produced by PHI.

The FWHM of the primary XPS signals for each element are clearly provided in Appendix 7. This table shows FWHM for most of the conductive elements which are typically 1.0 eV to 1.2 eV. The FWHM from insulators ranged from 1.4-3.5 eV with a typical value between 1.4-2.0 eV. The poor resolving power and poor charge control ability of non-monochromatic X-ray sources is clearly revealed by comparing these FWHM values to those obtained by using a monochromatic X-ray source.[21,28]

The peak-fitted spectra provided in the section #5 reveals some of the problems that exist when peak-fitting is done on data obtained from a non-monochromatic source. The peak-fit results indicates charging problems and reveal an unusual problem which is seen as a shoulder and some asymmetry on the low BE side of the main hydrocarbon signal of the C (1s) spectra.

A number of wide scan spectra for various elements (r.f., Zn, Al, Si, and As) seem to indicate some instability in the system when collecting electrons with BEs greater than 700 eV. The unusual increase in the background in that region does not appear in the spectra reported in other handbooks.

Despite the various problems and missing features this data-bank of spectra and numerical data-tables is still useful, especially to people who frequently use both magnesium and aluminium X-ray sources. It is also very useful to advanced users who need some of the unusual data-tables provided in the appendices.

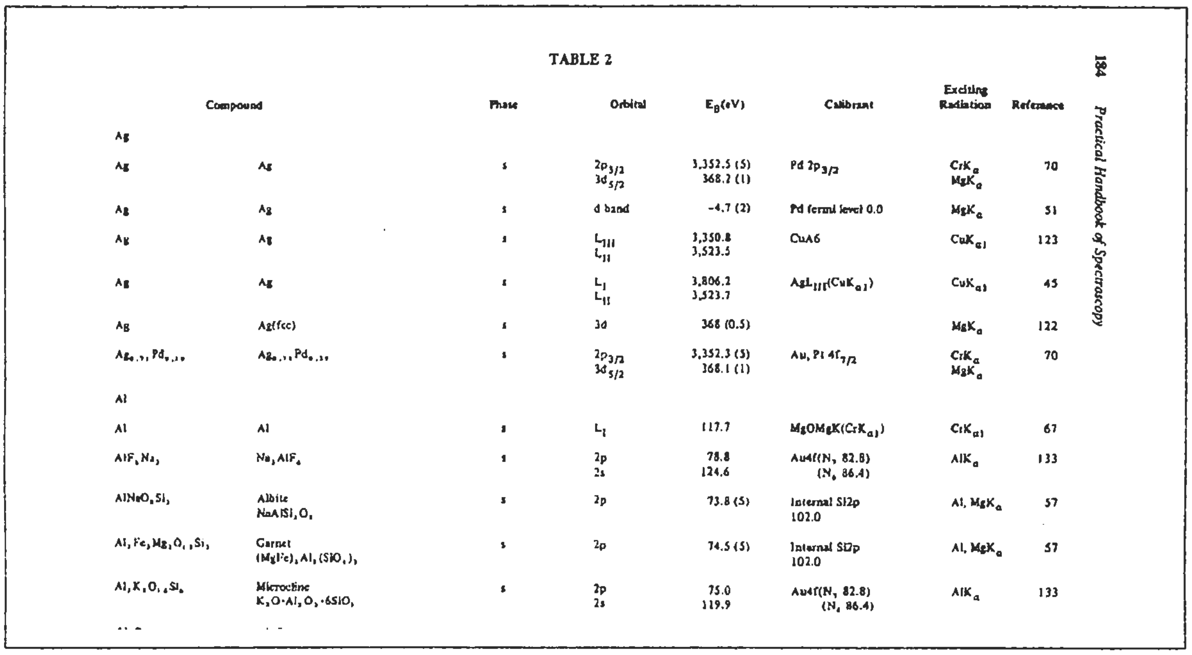


TABLE 2

Compound		Phase	Orbital	E_B(eV)	Calibrant	Exciting Radiation	Reference
Ag							
Ag	Ag	s	$2p_{3/2}$ $3d_{5/2}$	3,352.5 (5) 368.2 (1)	Pd $2p_{3/2}$	CrK_α MgK_α	70
Ag	Ag	s	d band	−4.7 (2)	Pd fermi level 0.0	MgK_α	51
Ag	Ag	s	L_{III} L_{II}	3,350.8 3,523.5	CuA6	$CuK_{\alpha 1}$	123
Ag	Ag	s	L_I L_{II}	3,806.2 3,523.7	$AgL_{III}(CuK_{\alpha 1})$	$CuK_{\alpha 1}$	45
Ag	Ag(fcc)	s	3d	368 (0.5)		MgK_α	122
$Ag_{0.71}Pd_{0.29}$	$Ag_{0.71}Pd_{0.29}$	s	$2p_{3/2}$ $3d_{5/2}$	3,352.3 (5) 368.1 (1)	Au, Pt $4f_{7/2}$	CrK_α MgK_α	70
Al							
Al	Al	s	L_I	117.7	$MgOMgK(CrK_{\alpha 1})$	$CrK_{\alpha 1}$	67
AlF_6Na_3	Na_3AlF_6	s	2p 2s	78.8 124.6	Au4f(N_7 82.8) (N_6 86.4)	AlK_α	133
$AlNaO_8Si_3$	Albite $NaAlSi_3O_8$	s	2p	73.8 (5)	Internal Si2p 102.0	Al, MgK_α	57
$Al_2Fe_3Mg_3O_{12}Si_3$	Garnet $(MgFe)_3Al_2(SiO_4)_3$	s	2p	74.5 (5)	Internal Si2p 102.0	Al, MgK_α	57
$Al_2K_2O_{16}Si_6$	Microcline $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$	s	2p 2s	75.0 119.9	Au4f(N_7 82.8) (N_6 86.4)	AlK_α	133

184 *Practical Handbook of Spectroscopy*

Figure 11. A Typical BE Data Table from the *Practical Handbook of Spectroscopy.*

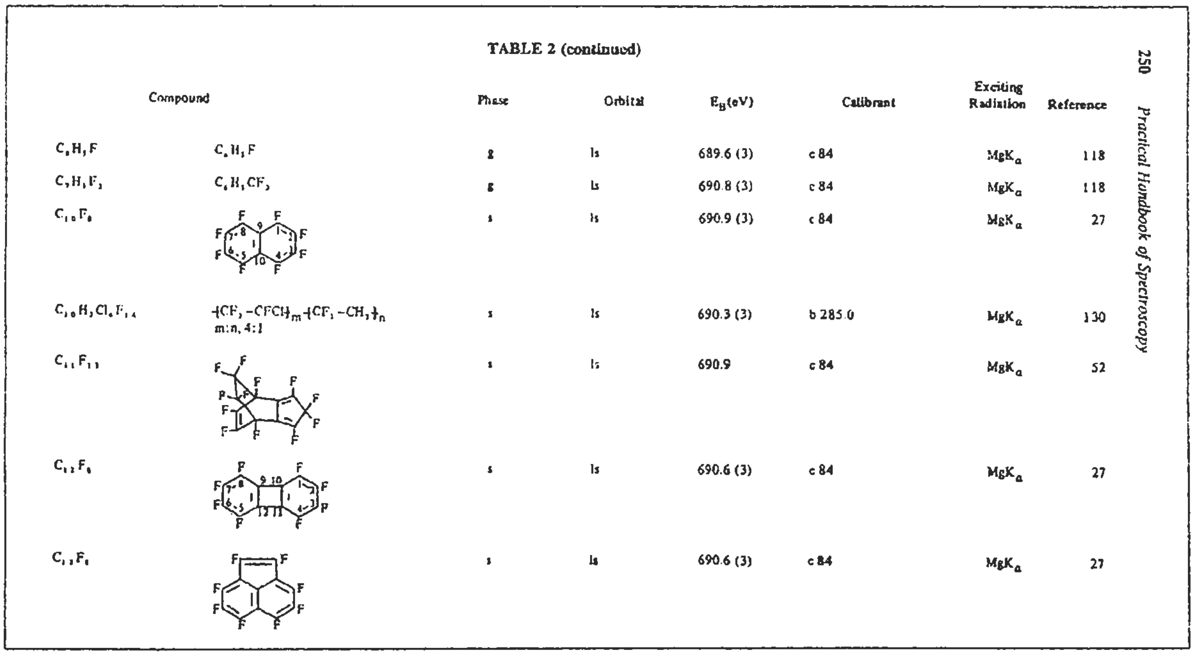


TABLE 2 (continued)

Compound		Phase	Orbital	E_B(eV)	Calibrant	Exciting Radiation	Reference
C_6H_5F	C_6H_5F	g	1s	689.6 (3)	c 84	MgK_α	118
$C_7H_5F_3$	$C_6H_5CF_3$	g	1s	690.8 (3)	c 84	MgK_α	118
$C_{10}F_8$		s	1s	690.9 (3)	c 84	MgK_α	27
$C_{10}H_2Cl_4F_{14}$	$-(CF_2-CFCl)_m-(CF_2-CH_2)_n$ m:n, 4:1	s	1s	690.3 (3)	b 285.0	MgK_α	130
$C_{11}F_{11}$		s	1s	690.9	c 84	MgK_α	52
$C_{12}F_8$		s	1s	690.6 (3)	c 84	MgK_α	27
$C_{12}F_8$		s	1s	690.6 (3)	c 84	MgK_α	27

250 *Practical Handbook of Spectroscopy*

Figure 12. A Typical BE Data Table from the *Practical Handbook of Spectroscopy.*

6. *Practical Handbook of Spectroscopy - Section 2* by CRC Press (1991)[20]

(6a) Contents and Structure of the *Practical Handbook of Spectroscopy*

This data-bank is a dedicated numerical data-bank which contains high resolution electron BE data from all kinds of materials. There are no spectra in this data-bank. In 1991, the Chemical Rubber Company (CRC) published the *Practical Handbook of Spectroscopy* which includes a 244 page section called "ESCA - Photoelectron Spectroscopy" (pp. 175-418). The authors of this section were Kai Siegbahn, David A. Allison, and Juanita H. Allison. There are two data tables which are eight columns wide with individual lines of data associated with each chemical.

The first data table is a small table of low energy data (5 pages) from the valence band region of an XPS spectrum.

The second data table is the main data table which is 235 pages in length which lists BEs for > 2,500 different chemical compounds which were obtained from 150 different publications dating from 1958 to 1973. More than 10 percent of all the references are from K. Siegbahn's laboratory. Most of Siegbahn's publications involved organic materials.

Many compounds have multiple BEs listings which are from different spin-orbit signals (e.g., 2s, 2p1, 2p3, 3d3, 3d5) which might be useful whenever there are overlapping signals.

Each line of data in each data table is headed by a chemical formula derived from the Chemical Abstracts Service (CAS) method of chemical nomenclature.

The data tables are organized alphabetically by using the chemical abbreviation of the element (Ag-Zr) and then the CAS empirical formula system. Adjacent to the CAS formula, the authors have included the more common molecular formula or a molecular structure drawing which are very convenient and do not require very much printing space.

The physical state of the sample (gas or solid) is then listed.

The next line items are the orbital assignments (e.g., 1s, 2s, 2p3, etc.) and the BEs. Adjacent to the BEs column, there is a column which reports very brief details of the energy referencing methods used to reference the reported BE values. Some of the BE numbers have an error value in parentheses which were reported to be either estimates or rigorously determined limits of the absolute value. The authors of this article suggest that the reader refer to the original literature for proper interpretation of the errors.

The last two items on each line were the type of exciting radiation and a reference to the original literature.

There are 11 different energy referencing calibrants which include "3M Scotch Tape" (Scotch is the brand name used by the 3M company in the USA), pump oil, gold (Au°), internal carbon, copper Auger line (KLL), graphite (C°), the Pb (4f7) signal in PbO, the P (2p) signal in $Na_4P_2O_7$, the N (1s) signal in KNO_3, deposited carbon, and the Magnesium K-α X-ray signal.

The inclusion of the original energy reference method helps the reader to learn the whether or not the sample behaved as an insulator. The inclusion of the original energy referencing method also helps the reader to compare the original referencing method to modern practices of energy referencing without having to go to the library to find the original reference. When the compound was analyzed in a gaseous state, one of several gases (Ar, Ne, CHF3, C6H6, CO2, etc.) was used as the energy reference.

All of the BEs were extracted from publications that were originally published between 1958 and 1972. Approximately 50% of all the BE data are from organic or organometallic compounds. BEs from several higher energy types of X-ray sources (e.g., Cr, Cu, and Mo), which penetrate deeper into the core level region and also deeper into the surface, are included for several pure elements and a few chemical compounds.

This data-bank is a useful to analysts who need BE values for hundreds of organic materials. This data-bank includes actual chemical structure drawn next to each of the organic materials. It is also useful because it clearly reports the original energy referencing method used for each compound. This data-bank also includes BE values from higher energy X-ray sources.

To understand part of the structure and content of this database, please refer to figures 11-12.

(6b) Problems and Features Missing in the *Practical Handbook of Spectroscopy*

Most of the problems and limitations of a simple one dimensional numerical data-bank that are fully discussed earlier in this review are directly applicable to this numerical data-bank.

In addition to those problems we have described other problems which are specific to this numerical data-bank.

This data-bank was not designed to use a self-consistent set of reference energies. The reference energies listed with the different energy referencing calibrants vary by as much as 1.5 eV for the C (1s) signal in the 3M Scotch tape which was used as the reference energy value (i.e., 284.0 eV versus 285.5 eV). These differences are large enough to allow scientists to make significant errors in chemical state assignments of insulators. The reference energies listed for the C (1s) of pump oil was predominantly at 285.0 eV, but there were are a few cases where it was listed as 284.6 eV.

The reference energies listed for pure gold (Au°), which is a true conductor, varied by as much as 1.0 eV (i.e., from 83.0 eV to 84.0 eV).

There are very few BEs for the pure elemental forms of the conductive metals which limits internal statistical checks to find the most valid BE for the pure element.

The few error values that are given in parentheses are undefined. The reader can not decide if the error value of "3" shown for in the BE value, 297.5 (3) eV, means ±0.3 eV or ±0.15 eV.

It is a somewhat difficult to locate a chemical compound by using the alphabetical system mixed with the CAS system of nomenclature.

Each compound and each BE are normally listed just once, which means that the reader does not have multiple data points to help decide which BE is the most accurate one to use.

A random comparison the BE reported for a particular chemical compound in this data-bank and the BEs reported for the same compound in Appendix 5 of the book *Practical Surface Analysis* reveals that there are significant differences between the two BEs. The differences can be as large as 2-3 eV after normalizing the energy referencing methods to be the same. The difference can also be relatively small, 0.1 - 0.5 eV. There is no obvious reason for these differences.

Despite the various problems and missing features because it contains hundreds of BEs from organic materials which are listed next to their chemical structure drawings. But caution is needed when studying organic materials with X-rays because they are easily damaged by the X-rays, the heat from the nearby anode, and the Bremmstrahlung that accompanies non-monochromatic X-ray sources. Low power density monochromatic X-ray sources used with a cold stage are recommended to scientists who need to study organic materials.

7. *Handbook of XPS - Second Edition* by Physical Electronics (PHI) Corporation (1992)[20]

(7a) Contents and Structure of the PHI *Handbook of XPS - Second Edition*

This data-bank includes spectra and numerical data tables which contains high resolution electron BE data from all kinds of materials. This data-bank is a spectral-numerical data-bank.

Many of the positive comments previously made about the original 1979 edition are also true for this 1992 edition.

In addition to the original features, the second edition includes more than 400 wide scan, narrow scan and Auger band spectra of 81 elements, and 12 valence band spectra of polymers and chemical compounds.

Spectra from very reactive metals (Na, K, Rb, Cs, Ca, Sr, and Ba) were included in the new edition along with spectra from nearly all the rare earth metals.

Signals from carbon and oxygen contamination in the wide scan spectra are very low, and the noise in the wide scan spectra are quite low.

The spectral data for the elements were obtained by using monochromatic and non-monochromatic. The photon energy of the non-monochromatic Magnesium X-ray source and the monochromatic Aluminium X-ray source were reported to occur at 1253.6 eV and 1486.6 eV, respectively.

The chemical state assignment tables, shown with each element's spectra, were redesigned in this new edition. The new style tables include range bars for each of the chemical compounds listed. The range bars indicate variation in BEs for a particular compound. The range bars are usually 0.6 eV in width (i.e., ±0.3 eV). These variations are presumably due to the errors associated with the original reference data. A few of the range bars are as large as 2 eV (i.e., ±1 eV). This new style of reporting BE ranges appears to reflect the uncertainty in BEs for a particular chemical compound or a group of similar compounds which are listed in detail in the BE data tables in Appendix B.

The new edition includes more Auger parameter charts and data tables in Appendix A. These charts are very useful to improve the reliability of a chemical state assignment.

This new edition also includes a new large data table in Appendix B which contains more than 3,000 BE numbers, of which 1,500 were newly added. The new data table is organized alphabetically by using the standard abbrevia-

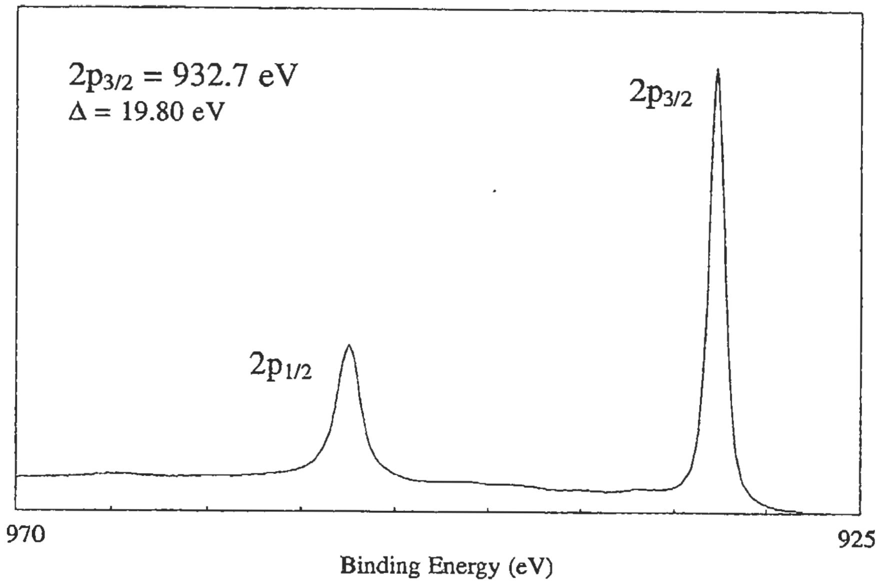


Figure 13. A High Resolution Spectrum from the PHI *Handbook of XPS - 2nd Edition.*

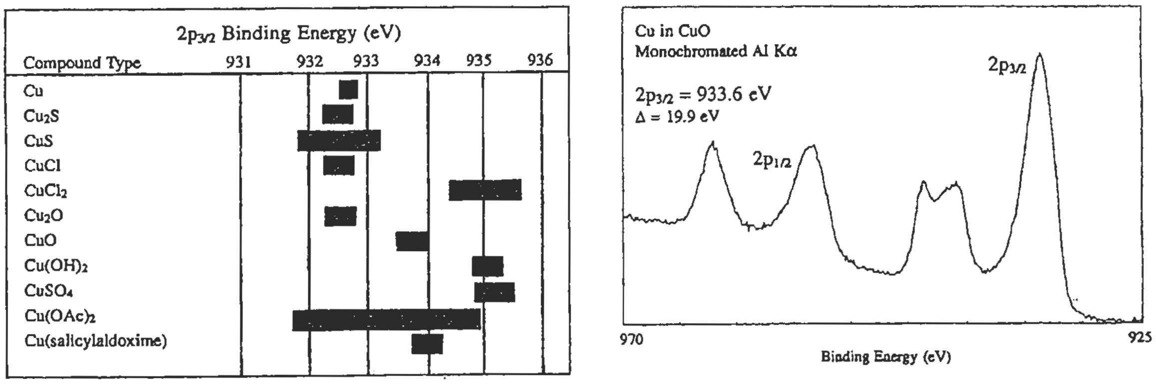


Figure 14. A Typical BE Data Table from the PHI *Handbook of XPS - 2nd Edition.*

tions for the chemical names (e.g., Ag, Al, As...Zr).

The appendices also hold two new tables of atomic sensitivity factors. The range of energies provided for each different chemical state was derived from the data tables included as Appendix B.

This edition uses new reference energies where Au° (4f7/2), Ag° (3d5/2) and Cu° (2p3/2) are reported to occur at 84.0 eV, 368.3 eV, and 932.7 eV, respectively. This change in reference energies produces noticeable changes in the BEs of pure conductive elements that have BEs in the high energy range. The difference can be as large as 0.4 eV.

The C (1s) energy of adventitious hydrocarbons was again defined to occur at 284.8 eV.

As mentioned above, the spectra that were acquired by PHI represent a self-consistent set of spectra.

The BEs obtained from the pure elements in this set have been statistically analyzed together with three other self-consistent sets of BEs from pure elements to determine reliable secondary reference energies for a series of pure elements.[38] The other large sets of pure element BEs were provided by JEOL,[19] B.V.Crist,[28] and N. Martensson.[39-42]

To understand part of the structure and content of this database, please refer to figures 13-14.

(7b) Problems and Features Missing in the PHI *Handbook of XPS - Second Edition*

Most of the problems and limitations of a simple one dimensional numerical data-bank that are fully discussed earlier in this review are directly applicable to the numerical data-banks included in this otherwise excellent handbook.

The new style of reporting BE ranges does not reflect any true statistical analysis of the BEs listed in Appendix B. Even though the number of BEs listed for a particular chemical compound may be small, it is still worthwhile to include statistical results for a small set of data points (i.e., BEs) that indicate the reliability (e.g., confidence intervals, Student T-test results, standard deviation, the weighted median, a BE vs. occurrence histogram etc.) of a particular BE for a chemical compound.

A major problem with this handbook is that errors and uncertainties associated with the BEs reported in the high resolution electron BE data tables are not reported. These errors and uncertainties are directly due to the work done by the original workers, not the authors of PHI's handbook. This problem is a serious one because this handbook was designed to be a major source of BEs to be used to make chemical state assignments. Statistical information about the quality or reliability of those BEs is also missing. If included, it would have greatly improved the intended purpose of the data tables contained in this XPS data-bank.

Many features, which could have added, but were not included, are missing from both the 1979 edition and the 1992 edition. For completeness, the relevant comments are repeated here. The electron counts scale of all spectra were deliberately removed. There are several missing very valuable peak parameters. i.e.. FWHM, degree of asymmetry, ratio of Gaussian:Lorentzian curves needed to fit the individual XPS signals, and peak area ratios of spin-orbit coupled signals. The inclusion of FWHMs for the BEs listed in the high resolution electron BE data tables would have been an excellent tool to help scientists to analyse their raw spectral data. There is no list of BEs for the energy loss signals that occur after all major XPS signals in each spectrum. There are no valence band spectra, except for 12 spectra included in Appendix D.

Despite the various problems and missing features this handbook is still useful for cursory assignments of chemical states to XPS signals. The addition of spectra for the reactive alkali and alkaline metals is an excellent addition to the spectral data-bank. The near absence of signals from oxygen and carbon from nearly all of the wide scan spectra clearly shows that it is possible to obtain and to record spectra which are effectively free of contamination. It would be very useful if the authors included a detailed section about the techniques required to produce these excellent pure element spectra.

8. *High Resolution XPS of Organic Polymers* by Wiley and Sons, Co. (1992)[22]

(8a) Contents and Structure of *High Resolution XPS of Organic Polymers*

This data-bank includes spectra and numerical data tables which contains high resolution electron BE data from all kinds of materials. This data-bank is a spectral-numerical data-bank.

In 1992, G. Beamson and D. Briggs published this XPS handbook of organic polymers, which is composed of a self-consistent numerical data-bank and a self-consistent spectral data-bank. The data-bank contains about 530 spectra from a set of 110 standard homopolymers. This spectral-numerical data-bank pro-

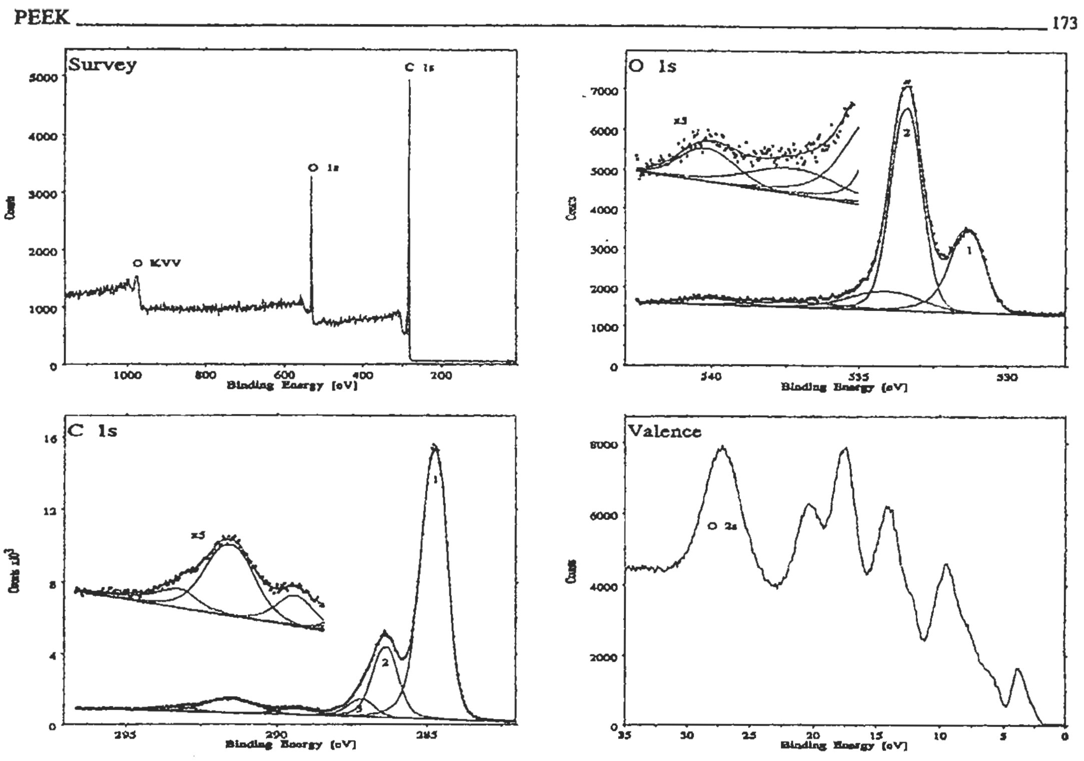
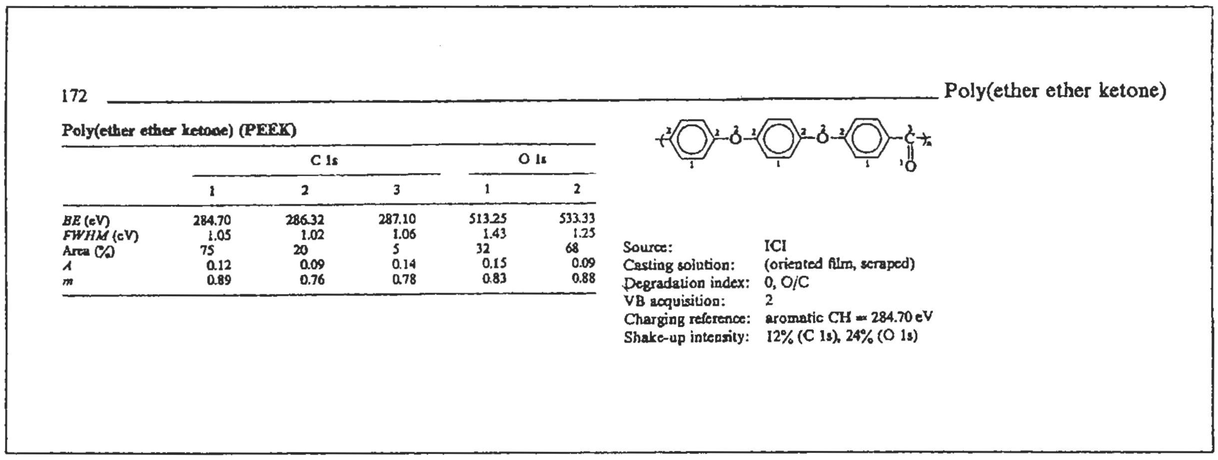


Figure 15. A Typical Spectra Page from the *High Resolution XPS of Organic Polymers.*


172 Poly(ether ether ketone)

Poly(ether ether ketone) (PEEK)

	C 1s			O 1s	
	1	2	3	1	2
BE (eV)	284.70	286.32	287.10	513.25	533.33
FWHM (eV)	1.05	1.02	1.06	1.43	1.25
Area (%)	75	20	5	32	68
A	0.12	0.09	0.14	0.15	0.09
m	0.89	0.76	0.78	0.83	0.88

Source:	ICI
Casting solution:	(oriented film, scraped)
Degradation index:	0, O/C
VB acquisition:	2
Charging reference:	aromatic CH = 284.70 eV
Shake-up intensity:	12% (C 1s), 24% (O 1s)

Figure 16. A Data Summary Page from the *High Resolution XPS of Organic Polymers.*

vides complete sets of coordinated spectra for a given compound and also provides sufficient detail and information about the sample and the peak-fitted results to be defined as a spectral-numerical data-bank with data quality that is good.

This handbook contains many operational details about the Scienta ESCA300 instrument, various performance tests, experimental protocol, data processing information, and an X-ray degradation section. The degradation section suggests that the X-ray power level should be kept below 1.5 kW to avoid excessive damage during the 4-5 hours used to collect each data set. The first 48 pages of the handbook include nearly all the details necessary to repeat the same analyses and to make full use of the spectra provided in the handbook.

These authors, whenever possible, chose to cast non-conductive thick films (a few micrometers in thickness) of most of the polymers. The reference energy of saturated and aromatic hydrocarbon C (1s) signals were defined to occur at 285.00 eV and 284.70 eV, respectively. Reference energy values for the Ag° (3d5/2) and the Ag° (M4VV) signals were reported to be 386.27 eV and 1128.84 eV, respectively. The photon energy for the monochromatic Al° X-ray energy of 1486.7 eV. The energy at the Fermi edge of Ag° was reported to occur at 0.02 eV.

Except for the valence band spectra, all high resolution spectra include the actual peak-shapes that were used to determine the peak parameters reported in each data summary chart. This is an excellent way to help the reader to learn about the relation between XPS signals and the functional group components that are present in the sample. This helps to teach the reader how to perform valid curve-fits.

The handbook also contains a useful index because includes the common abbreviation and the common name of each polymer.

A structural drawing of each polymer is placed next to the data summary charts for each polymer. Each structural drawing has identifying numbers adjacent to each atom which correspond to the different chemical state assignments made in the data summary chart.

The data summary charts report BE, FWHM, relative peak area, asymmetry, and the degree of mixing Gaussian and Lorentzian peak shapes for each peak.

On each page just under the structural drawings there is detailed information about the source of the polymer, how the sample was prepared for analysis, the tendency to degrade under the X-ray beam, the time spent to acquire the valence band spectrum, the C (1s) signal that was used for energy referencing, and the actual BE defined as the reference energy.

The appendices have several chemical shift tables to assist curve-fitting. Each table includes a structural drawing of several different functional groups adjacent to the minimum, maximum, and mean chemical shift values associated with each functional group. For each functional group there is also a listing for the number of different polymers that contained that particular functional group. The mean chemical shift values were determined by using the BEs associated with each functional group and the number of different polymers that contained that particular functional group.

This data-bank is very useful, and would be a very powerful tool if was provided in software form so that any scientist can perform detailed analyses on the original spectral data. The contents of this handbook can be used to guide the development of other XPS data-banks.

To understand part of the structure and content of this database, please refer to figures 15-16.

(8b) Problems and Features Missing in *High Resolution XPS of Organic Polymers*

Uncertainties for the reference energy numbers and the observed BE numbers for all of the polymers were not clearly specified, but were indirectly inferred to be less than ±0.05 eV by using a step size per channel of 0.05 eV/channel. Previous publications by Briggs et al in the journal of Surface and Interface Analysis indicated that the charge control of polymers on the ESCA300 can vary by as much as 0.2 eV during a consecutive series of analyses on the exact same polymer sample.

It is difficult to find many serious problems or features that are missing from this excellent handbook, but there are a few. The handbook does not report atomic percentages for either the individual elements or the individual functional groups. If the atomic percentages were included along with the theoretical ratios of the individual functional groups, then the reader would indeed have a powerful tool.

There is a problem with the electron transmission behavior or the X-ray power stability of the system because we can see slight fluctuations in the background above 500 eV of several wide scan spectra. This problem is easily noticed by comparing the wide scan spectra from their polyethylene or polypropylene spectra with their spectra from other pure hydrocarbon polymers such as polyisobutylene or poly-1-butene.

Another problem is that many valence band spectra have too much noise which makes them difficult to use for overlaying with experimental spectra. Another problem with the valence band data is that there are no BEs reported for the many valence band peaks that are easy to see.

The authors, G. Beamson and D. Briggs, have introduced different ratios of Gaussian and Lorentzian peak shapes for curve-fitting the various signals contained in the peak envelop of the primary XPS signals (e.g., C (1s), O (1s)). There is no information that the Gaussian:Lorentzian ratio was based on existing reference data or on a theoretical behavior. By allowing random ratios in the amount of Gaussian and Lorentzian peak shapes the author has probably hidden a variety of impurities that exist in low abundance at the surface of the polymer films.

The reliability of the BE numbers reported in this handbook are somewhat questionable because there was no obvious statement on the frequency of calibration during the many months required to produce this spectral-numerical data-bank.

The reliability of the BE numbers is questionable because the author has used only the Ag (3d5) signal for determining the energies of the XPS signals. If the author had calibrated his instrument with the Au (4f7) and Cu (2p3) reference energies, 83.98 eV and 932.67 eV, which are the "de facto" standard reference energies, then the BEs reported in this handbook would be a little more reliable.

The author's use of a Auger signal for calibration was a logical choice at that time, but has been shown to have some chance for error. Recent research by a round robin group led by NIST has shown that the Auger generated KEs for a monochromatic X-ray source are frequently different from, the Auger KEs obtained by using a non-monochromatic X-ray source by as much as 0.3 eV. This means that the use of the Ag (M4VV) signal may introduce more uncertainty in some of the BEs.

9. *Surface Science Spectra* Journal by AVS (1992)[23]

(9a) Contents and Structure of the AVS *Surface Science Spectra* Journal

This data-bank includes spectra and numerical data tables which contains high resolution electron BE data from all kinds of materials. This data-bank is a fully functional spectral-numerical data-bank which is used to generate a journal called *Surface Science Spectra* (SSS) published by the American Vacuum Society.

This data-bank is currently the only data-bank that used the true peer review process to evaluate the quality of the spectral data and the information by unseen experts who can reject or accept sets of spectra for inclusion into the data-bank.

The *Surface Science Spectra* journal and data-bank system is designed as a long term project which will, in the future, meet the needs and expectations of many users who use a variety of instruments under a variety of conditions.

The SSS data-bank publishers use a two fold approach to provide data to subscribers. They produce a hard copy (journal) and a soft copy (electronic data-bank) of all numerical and spectral data contributed by each author. The soft copy is a living and growing set of data which can be sold to subscribers, but the hard copy is fixed and forever linked to whatever features, information, errors or problems it may have.

Over the long run, the soft copy version is much more useful because it can be modified at any time by various algorithms and/or "standardized" whenever the AVS editors and its board of advisor's want to offer a "standardized" set of the original data. (Note: international standards do not yet exist.)

This spectral-numerical data-bank normally provides complete sets of coordinated spectra for a given chemical compound or element, and also provides sufficient detail and information about the specimen sample, the data, the instrument, analysis conditions, calibration energies, data processing conditions and spectral features (BE, FWHM, peak areas, and atomic percentages) that resulted from data processing.

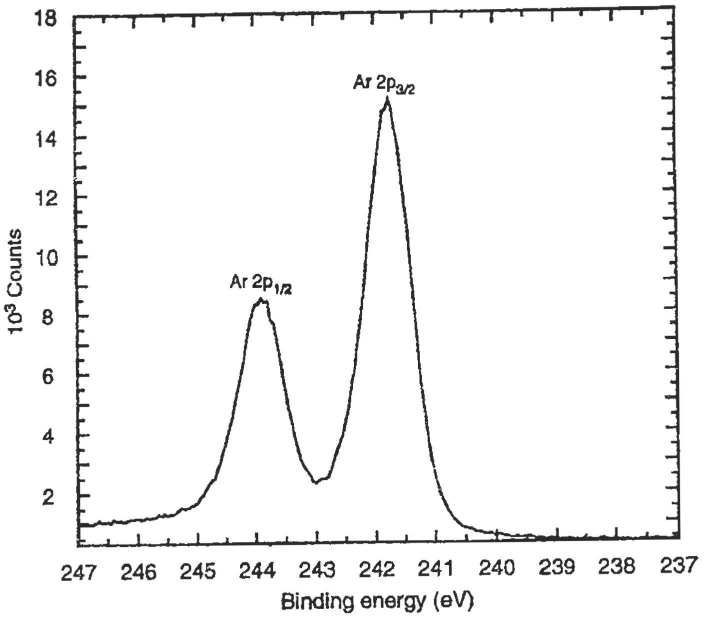
All submissions, which undergo expert peer review, are classified as "technical, comparison or reference" grade spectra.

In 1992, this database system archived and published more than 400 individual XPS spectra from 65 chemical compounds or elements. In general, most submissions included complete sets of coordinated spectra for a given chemical compound, but there are a few cases where only a limited number of spectra were submitted.

In 1993, a similar number of individual XPS spectra were archived and published.

In 1994 and 1995, the database started to publish SIMS and AES spectra.

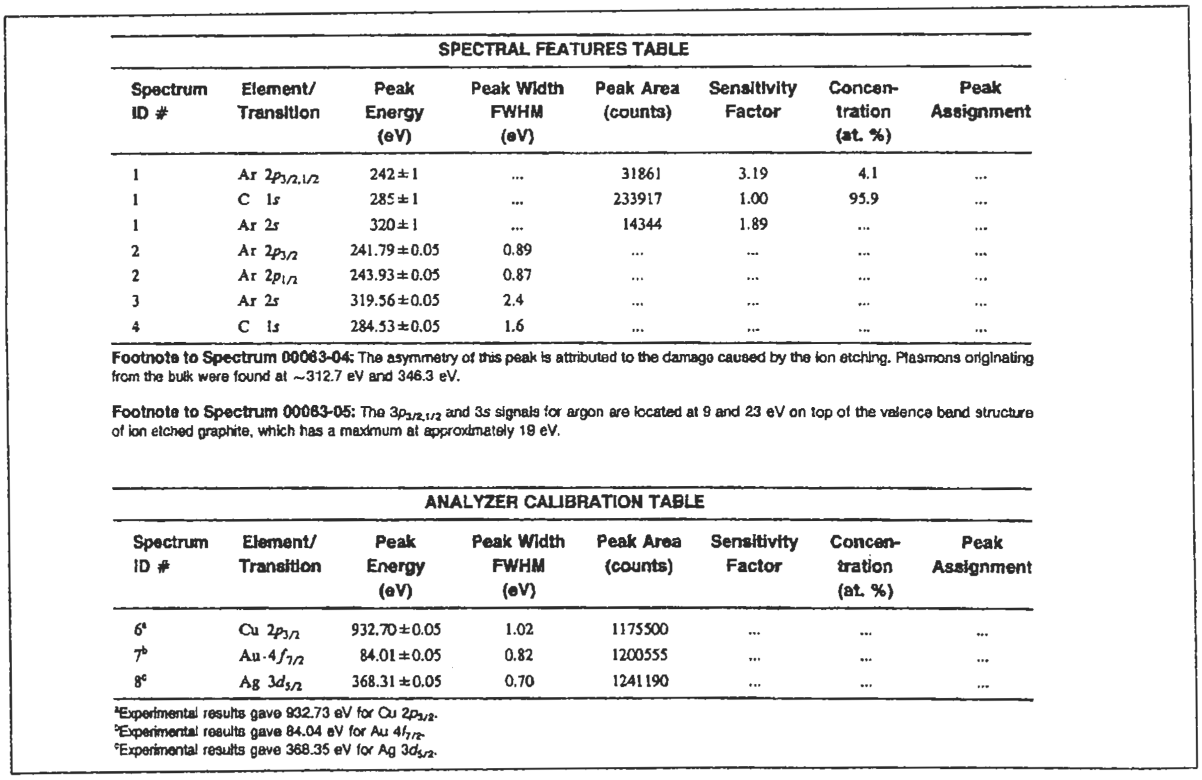
As of January 1996, the total number of individual XPS spectra is estimated to be more



- **Accession #:** 00063-02
- **Host Material:** natural graphite crystal
- **Technique:** XPS
- **Spectral Region:** Ar $2p_{3/2}$; Ar $2p_{1/2}$

Instrument: Fisons Instruments S-Probe E-2703
Excitation Source: Al K_α monochromatic
Source Energy: 1486.7 eV
Source Strength: 200 W
Source Size: 250 μm × 700 μm
Incident Angle: 20°
Analyzer Type: spherical sector
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.50 eV
Emission Angle: 0°
Data Acquisition Time: 800 s
Dead Time Correction: none
Number of Scans: 20

Figure 17. A High Resolution Spectrum from the *Surface Science Spectra* Journal.



SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
1	Ar $2p_{3/2,1/2}$	242±1	...	31861	3.19	4.1	...
1	C $1s$	285±1	...	233917	1.00	95.9	...
1	Ar $2s$	320±1	...	14344	1.89	...	...
2	Ar $2p_{3/2}$	241.79±0.05	0.89	...	...	...	...
2	Ar $2p_{1/2}$	243.93±0.05	0.87	...	...	...	...
3	Ar $2s$	319.56±0.05	2.4	...	...	...	...
4	C $1s$	284.53±0.05	1.6	...	...	...	...

Footnote to Spectrum 00063-04: The asymmetry of this peak is attributed to the damage caused by the ion etching. Plasmons originating from the bulk were found at ~312.7 eV and 346.3 eV.

Footnote to Spectrum 00063-05: The $3p_{3/2,1/2}$ and $3s$ signals for argon are located at 9 and 23 eV on top of the valence band structure of ion etched graphite, which has a maximum at approximately 19 eV.

ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
6[a]	Cu $2p_{3/2}$	932.70±0.05	1.02	1175500	...	...	...
7[b]	Au $4f_{7/2}$	84.01±0.05	0.82	1200555	...	...	...
8[c]	Ag $3d_{5/2}$	368.31±0.05	0.70	1241190	...	...	...

[a] Experimental results gave 932.73 eV for Cu $2p_{3/2}$.
[b] Experimental results gave 84.04 eV for Au $4f_{7/2}$.
[c] Experimental results gave 368.35 eV for Ag $3d_{5/2}$.

Figure 18. A BE Data Table from the *Surface Science Spectra* Journal.

than 1,000. As expected and desired by the database owners, there are several cases where spectra were obtained from the same chemical compound, but by different workers who used a different instrument and different analysis conditions.

As a journal, this data-bank is very useful, and will become a very powerful tool once it is routinely available in software form so that any scientist can perform detailed analyses on the original spectral data.

The contents of this journal can be used to guide the development of other XPS databanks. The electronic database which stores the raw spectra is already very well designed. There are only a few features which are missing which would greatly improve the utility and reliability of the data included in this database.

The journal includes an excellent set of cross-referenced indices which are divided a Subject Index (e.g., optics, dielectric properties and materials, materials science etc.), an Author Index, and an Electronic Transition Index (e.g., Al (2p), C (1s), N (KLL)).

Each issue of the journal also includes a Contributors Form for anyone to use to make a submission to the journal and database.

To understand part of the structure and content of this database, please refer to figures 17-18.

(9b) Problems and Features Missing in the AVS *Surface Science Spectra* Journal

The hard copy printout from the AVS approach currently suffers from many of the problems that have caused trouble in other older sources of numerical data.

Because there are many different contributors using many different energy referencing methods, different uncertainties, and different analysis conditions on instruments with various transmission functions, it is very difficult for the spectral data that they provide to be considered as a self-consistent set of spectral data. A large set of spectral data that is not self-consistent is limited in its ability to produce reliable data with a high degree of precision.

At this time, estimated uncertainties are frequently not specified, and the eV/step size is not provided for each spectrum. Therefore, it is difficult to estimate the uncertainty in the observed BE numbers.

The analyzer calibration table is normally used by the authors to report reference energy numbers that should be used, not experimentally observed energies from reference energy signals, i.e., Au° (4f7/2), Ag° (3d5/2) or Cu° (2p3/2).

Depending on the contributing author preference, the reference energy for the adventitious hydrocarbons C (1s) signal was reported to occur at 284.6 eV, 284.8 eV, or 285.0 eV.

This arbitrary variation in the reference energy for the adventitious hydrocarbons C (1s) signal makes it very difficult to maximize the reliability of chemical state assignments for all kinds of non-conductive materials which are very frequently analyzed by XPS.

In some cases the energy scale of the spectral data was shifted to align with the preferred BE number for the adventitious hydrocarbons C (1s) signal. This means that the original raw spectral data were obscured.

Valence band spectra, which are invaluable, are frequently included, but are not required for submission.

The peak fit results are presented only in table form. It would be useful to include the actual peak-fitted results in the printed journal to help scientists to learn how to do peak-fitting and to see if the reported peak-fit results actually match the spectral data.

Non-monochromatic and monochromatic X-ray sources cause various amounts of damage during the time it usually takes to generate reference or comparison grade XPS spectra, but at this time, there is no category which addresses the actual or potential errors on BE numbers and/or atomic percentages which might be caused by the analysis conditions.

The various contributing authors have used various calibration methods and have rounded off the number of significant figures in BE numbers by undefined methods which makes it difficult to compare reported BE numbers to BE numbers derived from the same chemical compound but obtained by using different reference energies and/or different energy scales. This approach is not truly self-consistent and partially defeats the desired objectives of the hard copy journal form of the database. With the proper algorithms, the electronic version can be made to generate BEs based on some interim standard set of reference energies until the ISO committees define true international standard reference BE numbers for XPS.

There is significant figure problem with the FWHM values. Peak energy values are reported with one decimal place, but FWHM values are frequently reported with two decimal places.

A major problem with reliability in the BE values because contributors are not required to collect spectra from reference energy materials (Cu°, Au°, and Ag°) just prior to and after collecting the spectra from the target material. As a minimum, the contributor should collect the Cu° (2p3) and Cu° (3p) BEs from freshly ion etched Copper metal just prior to collecting the spectra from the target material. The actual BEs from the freshly analyzed copper sample should be submitted together with the reference energy that are used to setup the BE scale of the instrument.

The is currently no requirement to include estimates of BE uncertainties. When uncertainties or error ranges are given, there is no explanation as how the uncertainty or error range was determined. This is currently no requirement to include reference energies that span a large range of the BE spectrum.

A problem with nearly every XPS data-bank and also this one is that each data file in this data-bank probably contains just one set of spectral data for each contribution because each author has most likely only analyzed the sample just one time. The reason for this submitting just a single experimental run is that XPS analysis time is very expensive so it is difficult to justify repeating the same set of spectra five times to produce a set of BE numbers which are statistically meaningful.

From the users point of view, a problem with this journal and database is that it is growing too slowly. It will be many years before the data-bank is big enough to assist scientists working in many different fields.

Despite the various problems and missing features the Surface Science Spectra journal and database are very valuable tools for any scientist analyzing materials by XPS. These tools will become even more valuable once the number of data files grows to include many different data sets from hundreds of different commonplace materials such as: binary inorganic compounds, semi-conductor related materials, polymers, ceramics, glasses, catalyst systems, minerals, alloys, steels, standard reference materials, certified reference materials, etc.)

10. *NIST XPS Database - Version 2.0* by NIST (1992)[24]

(10a) Contents and Structure of the *NIST XPS Database - Version 2.0*

This data-bank is a dedicated numerical data-bank which contains high resolution electron BE data from all kinds of materials. There are no spectra in this data-bank.

In 1992, NIST announced version 2.0 of their NIST XPS with some new user interface features and updates to data.[5] The new user interface features was reported to include a self-intuitive "trainingless" user interface, pull-down menus, lists of all options, Wagner plots, enhanced chemical searching, the ability to calculate chemical shifts from on-board reference data, new display options, and a list of reference energies for the principal photoelectron lines and Auger lines for the elements.

The updates to the data tables were reported to include data published after 1985 by NIST and will later include data from a joint effort by the NIST and the Institute for Chemical Metallurgy in China which was scheduled to start in 1992. This database will be made available to instrument makers who can incorporate it into their data processing softwares.

It is difficult to evaluate this data-bank further because it has not yet been released. The reader is referred to the publication in Surface and Interface Analysis which presents many of the new features of this new version of the *NIST XPS Database.*[5]

(10b) Problems and Features Missing in *NIST XPS Database - Version 2.0*

Most of the problems and limitations of a simple one dimensional numerical data-bank that are fully discussed earlier in this review should be directly applicable to this numerical data-bank.

Within a NIST publication[23] there is a table titled: "Reference energies for the principal photoelectron lines and Auger lines for the elements". This table lists the BEs for Au° (4f7/2), Ag° (3d5/2), and Cu° (2p3/2) XPS signals to occur at 83.97 eV, 368.23 eV, and 932.57 eV, respectively. It is very interesting that the 943.57 eV Cu° (2p3) reference energy is 0.1 eV below the internationally recognized "de facto" standard (NPL) value of 932.67 eV. It is also slightly different from the 932.60 eV value reported in Appendix 5 of Practical Surface Analysis.

The reference energies for nearly all of the pure elements listed in this table are previously published values which C. D. Wagner evaluated as the best reference measurements for the principal photoelectron lines of those elements. Unfortunately, the uncertainties and errors in the reference energies were not clearly specified.

It is difficult to evaluate this data-bank further because it has not yet been released, but it appears that makers have made several improvements in the user interface which should make this database quite easy to use.

E. Recommended Features for Future XPS Spectral Data-banks

Useful data-banks should include both practical and research grade spectra. Self-consistent sets of specific classes of materials collected by individuals from a single instrument are an excellent way to maximize the reliability of spectral data and the information obtained from raw XPS spectra.

A partial list of the main components desired in a high quality and reliable XPS spectral-numerical data-bank is presented below in Table 7A-C.

Table 7A. Desirable Features and Components of Useful XPS Spectral-numerical Data-Banks

- Spectra obtained from monochromatic X-ray sources
- Spectra with practical levels of signal/noise ratios
- Spectra with practical levels of energy resolution
- Detailed descriptions of the sample, its history, and any sample treatments
- Detailed descriptions of the instrument and its fixed capabilities and geometry's
- Detailed descriptions of the experimental analysis conditions for each spectrum
- Detailed descriptions of the instrument calibration methods
- Descriptions of the statistical validity of the spectral data
- Descriptions of any problems experienced during the analysis
- Tables of numerical data obtained by routine processing of the spectra
- Detailed descriptions of the data processing methods used
- Spectra from reference materials used for energy and intensity scale calibrations
- Dates for all calibration data and all spectra
- Color photographs of the actual sample at low and high optical magnification
- Drawings of the chemical structure with detailed labeling
- Valence band spectra
- Peer reviewing of each set of spectra
- Minimum quality levels for the admission of data to the database
- Data quality should be centered around practical grade data
- Detailed indices with extensive cross-referencing
- Include data sets from "clean" and "as-received" materials
- All high resolution narrow scan spectra should include peak-fit results

Table 7B. The spectra for each data set should include the following conditions as a minimum set:

- The 0-1200 eV range (a survey scan) for systems with Magnesium X-ray sources
- The 0-1400 eV range (a survey scan) for systems with Aluminum X-ray sources
- The -10 to +40 eV range (a valence band scan)
- A 20 eV range for any primary XPS signal used to make chemical state assignments (These types of spectra are known as high resolution scans.)
- A 100 eV energy range for any Auger signal
- A maximum step size of 0.05 eV/data point for each high resolution spectrum

Table 7C. Useful spectral-numerical data-banks should also include collections of data or practical studies known including:

- Depth profiles,
- Line profiles,
- Maps,
- Images,
- Angle-resolved analyses,
- Extensive charge control studies,
- Damage studies,
- Contamination studies,
- Instrument performance studies,
- Examples of bad data,
- Effects of varying experimental analysis conditions,
- Tables of work functions and band gaps,
- Tables of calculated and experimentally found IMFP and AL values.

A critical review published by C. J. Powell (NIST) and M. P. Seah (NPL) that discusses precision, accuracy, and uncertainty in quantitative surface analysis by AES and XPS is an excellent source of guidelines for the development of any XPS spectral data-bank.[1] In addition to the aforementioned critical review, any XPS data-bank development project should also carefully review the contents of the *Surface Science Spectra* journal, the *NIST XPS Data-*

base, and the *High Resolution XPS of Organic Polymers.*

Because spectral data-banks offer greater reliability and utility, it is very important that all spectra be collected by using reliable experimental conditions which are confirmed by repeatedly analyzing a small set of spectra obtained on the same day from a single pure reference material, which is confirmed by a different scientist in a different laboratory using a similar but different XPS instrument.

The minimum acceptable data quality should be tied to several experimental parameters which provide the same quality of data as that used on a daily basis in most laboratories. That level of quality should be equal or slightly better than a practical level which needs to be defined.

Any set of data submitted to a spectral data-bank must include practical level data, and whenever possible, a second data set, which is near research grade level.

It is not essential that the data be collected under high performance conditions. In fact, it may be detrimental because the cost to collect the data may be too great to bear by the laboratory that produces the research grade data and the laboratory that tries to collect similar data.

Useful spectral data-banks include collections of data such as: depth profiles, line profiles, maps, images, angle-resolved analyses, charge control studies, damage studies, contamination studies, instrument performance studies, examples of bad data, and studies of the effects of varying the experimental analysis conditions.

One of the most important variables to control is surface charging in insulating materials. This is a serious issue because most of the materials that need to be analyzed by XPS are insulators, and we still do not have a reliable method for correcting the BEs from insulators. It is therefore very important to use a well-defined protocol for collecting XPS spectral data from insulators which will allow for the correction of charging effects at a later time if necessary.

V. Summary

We have outlined and critically reviewed the specific content and structure of several popular XPS data-banks with the goal of helping others to learn from this critical review of data-banks so they can improve existing data-banks and develop better, more reliable XPS data-banks that include spectra as well as data tables of numbers.

Some general details about XPS data-banks and some of the basic features and problems in numerical and spectral-numerical data-banks have been reviewed.

Self-consistent sets of specific classes of materials collected by individuals from a single instrument were suggested as an excellent way to maximize the reliability of spectral data and the information obtained from raw XPS spectra

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Footnotes

(I) Definition and Usage of Phrase: *Chemical State*

In this review, the author uses the common phrase "chemical state" when discussing the assignment of an XPS signal, but the author wishes to clarify the point that XPS is used to infer the relative presence or absence of an element in a variety of different atomic environments, not just the chemical oxidation state of an element. This is important to point out because XPS is useful to identify differences in many materials which do not have any formal oxidation states, e.g., polymers, alloys, intermetallics, or compound semi-conductors.

XPS is a technique that yields indirect measurements of the electrodynamic forces and interactions that hold groups of atoms together in the form of a chemical compound.

XPS is not capable of directly identifying oxidation states of an element in a straightforward manner even though it has been frequently used to identify the different oxidation states of many elements. To understand this point of view, please consider the fact that XPS is not capable of revealing the oxidation state difference between the pure element form and the oxidized form of some commonplace metals, such as: Ca vs. CaO, Cd vs. CdO, and Cu vs. Cu2O.

Based on this point of view it is better to say that XPS is capable of revealing differences in the distribution of the electron density that exists between adjacent atoms. The capability of XPS to reveal differences in electron density between adjacent atoms becomes even more obvious when XPS is used to observe the difference between different forms of carbon which have covalent bonds with their adjacent atoms.

To understand this capability, consider the XPS spectra obtained from polymeric carbon bonded to fluorine (e.g., Teflon) and polymeric carbon bonded to hydrogen (e.g., polyethylene), where the differences in the C (1s) electron binding energy (BE) is approximately 7 electron volts (eV).

(ii) XPS Data-Banks and Databases Not Discussed in this Review

- *Auger Electron Spectrometry Data Bank* is a spectral-numerical data-bank currently still under development by M.P. Seah at the National Physical Laboratory (NPL) in the UK.
- *VG Scientific Handbooks of XPS* is a spectral-numerical data-bank published by VG. Scientific.
- *XPS Spectral Data-Bank System*, which is a spectral data-bank of more than 15,000 spectra is now under development by XPS International.
- *Handbooks of XPS Spectra* Volumes 1-4 are spectral-numerical data-banks published in draft form by XPS International.
- *Photo-electron Spectra Induced by X-rays of Above 600 Non-metallic Compounds Containing 77 Elements* published by The Royal Danish Academy of Sciences and Letters in 1972.

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