

**Why Did We Spend 10 Years
to Make the Digital
“SpecMaster”
XPS Spectral Data-Base System?**

Outline of Seminar

- *XPS Data-Bases Currently Available*
- *Three Basic Types of XPS Data-Bases*
- *Summary of XPS Data-Base Contents*
- *Questions, Answers and Background Information*
- *Major Problems in Many XPS Data-Bases*
- *Main Causes of Problems in XPS Data-Bases*
- *Data-Base Needs of XPS Users*
- *Summary of Items Discussed*

List of XPS Data-Bases Available Now

- *PHI Handbook of XPS - 1st Edition (1979)* [mainly work of C.D. Wagner]
- *NIST SRD-20 XPS Database v1.0 (1989)* [C.D. Wagner]
- *Appendix #5 in Practical Surface Analysis (1990)* [C.D. Wagner]
- *Common Data Processing (ComPro) (1990)* [VAMAS-SASJ-NRIM]
- *JEOL Handbook of XPS (1991)* [C.D. Wagner]
- *CRC Practical Handbook of Spectroscopy (1991)* [Kai Siegbahn]
- *PHI Handbook of XPS - 2nd Edition (1992)* [C.D. Wagner]
- *High Resolution XPS of Organic Polymers (1992, out of print)* [Beamson & Briggs]
- *Journal of Surface Science Spectra (1992-present)* [AVS]
- *NIST SRD-20 XPS Database v3.4 (1989-present)* [C.D. Wagner]
- *XI "SpecMaster" XPS Spectral Libraries & Data-Base Systems (1997-present)* [XI LLC]

Three Basic Types of XPS Data-Base Systems

- **Numerical Type - Software**
 - Binding Energies Only (no FWHM, no spectra)
 - Example: NIST XPS Database
- **Spectral-Numerical Type - Books**
 - Mixture of spectra and numbers (no software)
 - Examples: Handbooks by PHI, JEOL, Beamson & Briggs, XI LLC
- **Spectral-Numerical Systems – Books & Software**
 - Examples: *XI SpecMaster XPS Spectral Data-Base system*, *Journal of Surface Science Spectra journal*, *SASJ-ComPro system*

Summary of XPS Data-Base Contents

	<i>Number of Spectra</i>	<i>Number of Materials</i>	<i>Number of BEs</i>	<i>FWHM Reported</i>	<i>Parameters Reported</i>	<i>Peak-Fitted Spectra</i>	<i>Number of Sources</i>	<i>Self Consistent</i>
PHI 1979	200+	1,500+	2,000+	None	Yes	No	200+	No
NIST 1989-present	0	1,500+	22,000+	None	No	No	1,000+	No
Wagner 1990	0	1,000+	1,500+	None	No	No	295	No
ComPro 1990	700+	250+	None	None	Yes	No	50+	No
JEOL 1991	300+	700+	1,000+	Yes	Yes	Yes	250+	No
CRC 1991	0	2,500+	3,000+	None	No	No	150+	No
PHI 1992	400+	2,000+	3,000+	None	Yes	No	500+	No
Briggs 1992	530	110	600+	Yes	Yes	Yes	1	Yes
SSS 1992- present	2,200+	300+	7,000+	Yes	Yes	No	300+	No
XPS International 1994-2007	40,000+	1,800+	>50,000	Yes	Yes	Yes	1	Yes

Questions:

1. Why did we spend 10 years to make the “SpecMaster” XPS Spectral Data-Base System?
2. Why do we talk about the reliability of chemical state assignments?
3. How can we solve the problem of inconsistent BEs?
4. What are the merits of the Self-Consistent method?
5. What do XPS users need from a XPS Data-Base System?

Question #1:

Why did we make the “SpecMaster” XPS Spectral Data-Base System?

Answer #1. The main reason is to help XPS users to make chemical state assignments that are more reliable. When assignments are more reliable, then the information derived from those chemical state assignments is much more valuable and useful. As a side benefit, XPS users save time and money.

Answer #2. The owner of XPS International has been responsible to try to make reliable chemical state assignments for more than 12 years. For the past 12 years he has had a variety of problems when he uses the BEs listed in many XPS handbooks and numerical databases.

The problems have not become smaller during the past 12 years, and we believe that many XPS users have the same problems today.

To help with this problem, the owner started 12 years ago to develop a “self-consistent” data-base of complete sets of correlated spectra which will help XPS users to make chemical state assignments that are more reliable.

Question #2:

Why do we talk about the Reliability of Chemical State Assignments?

Answer: Because XPS users often have problems to accept or believe the chemical state assignments that they make when they use the BEs listed in various XPS handbooks and numerical databases. Chemical state assignments based on the BEs from various XPS handbooks and numerical databases are frequently not logical and not reasonable. This is an extremely serious problem that must be corrected.

This problem exists because the BEs in XPS handbooks and numerical databases were made in a “inconsistent” manner by hundreds of different analysts using many different calibration energies, various charge referencing energies, many different charge compensation methods, hundreds of different instrument, and many different analysis conditions. This inconsistent style of producing spectra has naturally produced a range of BEs with large uncertainties (± 0.5 to ± 1.0 eV) and a range of systematic and random errors.

Major Problems in Many XPS Data-Bases - Part I

- ***BEs are reported to have uncertainties from ± 0.2 to ± 0.5 eV, but the more correct uncertainties are ± 0.5 to ± 1.5 eV for insulating materials. These large levels of uncertainty are large enough to cause wrong chemical state assignments. (Note: Insulators are 70-80% of all materials analyzed by XPS!)***
- ***BEs from main signals were collected from thousands of different journal publications from 1970-1983 by C. D. Wagner***
- ***BEs in those thousands of different publications were obtained***
 - by using many different calibration energies,
 - by using many different charge referencing energies,,
 - by using hundreds of different instruments,
 - by using hundreds of different analysts, and
 - by using many different analysis conditions.

Major Problems in Many XPS Data-Bases - Part II

- *Most workers do not report experimentally measured reference energies*
- *C 1s reference energies for hydrocarbons range from **284.2 to 285.3 eV***
- *Au 4f7 reference energies for pure Au range from 82.8 to 84.1 eV*
- *Cu 2p3 reference energies for Cu range from **932.2. to 932.8 eV***
- *The BE for Cu 2p3 at 932.67 eV is almost never checked. The Cu 2p3 BE is useful to check for errors in energy scale linearity which affect chemical state assignments in the high energy range.*
- ***Sources assumed to be reliable are sometimes not so reliable***
 - BEs for pure metallic elements in three publications by NIST have differences as large as 0.7 eV and standard deviations as large as 0.387
 - BEs for pure metallic elements in the two XPS handbooks by PHI are quite different

Main Causes of Major Problems in Many XPS Data-Bases

- ***No ISO Standards for Energy Scale Calibration until 2001***
- ***No ISO Standards for Correcting BE Charge-Shift***
- ***No ISO Standards for Reporting Uncertainties in XPS***
- ***No ISO Standards for Determining Reliability***

The International Standards Organization (ISO) is just now working to develop these standards. Japan controls the ISO Technical Committee 201 on Surface Chemical Analysis and receives help from STA, JISC, JSCA, and SASJ members.

“No Standards for Energy Scale Calibration” Calibration BEs Recommended by Makers

	<u><i>Cu 2p3</i></u>	<u><i>Au 4f7</i></u>	<u><i>Energy Difference</i></u>
<i>Shimadzu (1988)</i>	932.2	83.8	848.4
<i>SSI-HP (1972)</i>	932.47	83.96	848.51
<i>PHI (1979)</i>	932.4	83.8	848.6
<i>PHI (1992)</i>	932.7	84.0	848.7
<i>Scienta (1994)</i>	932.68	83.99	848.69
<i>VG (1984)</i>	932.5	83.7	848.8
<i>JEOL (1991)</i>	932.8	83.8	849.0
<i>Min-Max Difference</i>	<i>0.6</i>	<i>0.3</i>	<i>0.6</i>
<i>NPL (1985)</i>	932.67	83.98	848.69

Effect of Using Different Charge Referencing Methods

Range of BEs Found in XPS Handbooks and NIST Data-Base

	<u>Low BE (eV)</u>	<u>High BE (eV)</u>	<u>Range (eV)</u>
MgO	49.4*	51.5	2.1
Al₂O₃	73.5	74.3	0.7
Sc₂O₃	401.5	402.4	0.9
TiO₂	458.6	459.3	0.7
V oxide	515.7	517.6	1.9
Cr oxide	576.3	579.8	3.5
MnO₂	641.1	642.4	1.3
Fe₂O₃	710.7	710.9	0.2
Co₃O₄	779.5	780.2	0.7
NiO	853.5	854.4	0.9

*BE of metallic Mg is: 49.7 eV.

Question #3:

How can we Solve the Problem of Inconsistent BEs in XPS Databases?

Solution “A” Develop international BE standards (TC/201) and get all XPS users to use the new BE standards. Unfortunately, with this method it will be 10-20 years before XPS users can use a numerical database that contains a large number of reliable BEs based on ISO standards.

Solution “B” Make a “self-consistent” data-base of XPS spectra. This solution provides complete sets of correlated spectra that allow XPS users to check all of the features of all spectra collected from a chemical compound.

With this solution the user is NOT limited to a single BE. With this solution the XPS user can use complete sets of BEs, FWHMs, peak shapes, back-ground, valence band data, atom % data, and more.

XPS International LLC has used a “self-consistent” method to produce the SpecMaster Data-Base Systems. By using this method XI LLC has produced a source of BEs, which are more reliable.

Question #4:

What are the Merits of the Self-Consistent Method?

- Produces complete, correlated sets of spectra that allows XPS users to compare all spectral features including:
 - FWHMs, peak-shapes, backgrounds, energy loss features, valence band spectra, auger spectra, atom % values, inter-element energy differences, contamination studies, damage studies and BEs
- Avoids random and systematic errors in numerical databases of BEs
- Allows the user to check charge referencing
- Allows the user to choose a different method of charge referencing
- Minimizes uncertainties in all BE values
- Maximizes reliability of all numerical and spectral data

Question #5:

What do Users Need from an XPS Data-Base System?

- Complete sets of correlated spectra made with a high degree of reliability
- Advanced data processing abilities (e.g. peak-fit, peak labeling, BE shift, atom %, etc.)
- An organized, modular system of filenames and directory names that are easy to understand
- Ability to search and recall all spectra or data within a defined field of interest
- Ability to derive all key peak-fit parameters - including FWHMs, PEAKSHAPES, and BEs
- Detailed information about sample history, sample treatment, analysis conditions and detailed energy referencing information
- Ability to Export spectral data in various file formats (e.g. ASCII, TIFF, HPGL, PCT, WMF) to Word Processing software
- Ability to Import and Export a generic ASCII file format
- Ability to Import and Export ASCII file formats now being used by Ulvac-PHI, Thermo-VG, Shimadzu-Kratos, JEOL, Scienta, SSI, ISO, VAMAS, VSW, Specs, Omicron and others
- Advanced data printing capabilities with multiple spectra or full details printed on the same page

Summary

- ***What was discussed in this seminar***
 - Why we made SpecMaster XPS Spectral Database Systems
 - Three basic types of XPS databases
 - Features of XPS handbooks and XPS databases
 - Problems in BEs listed in XPS handbooks and numerical databases
 - Merits of Self-Consistent method
 - Database needs of XPS users