Handbooks of Monochromatic XPS Spectra

Volume 1 - *The Elements and Native Oxides*

by

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INTRODUCTION

This handbook contains wide scan spectra and narrows scan spectra from the elements and native oxides of the elements. The elements have been analyzed under conditions that have maximized the accuracy of the binding energies. The binding energies for the pure elements are referenced to the reference energies recommended by the National Physical Laboratory in the UK. Please refer to section "F" (Energy Scale Reference Energies and Calibration Details) for more details about calibration.

"The Elements" Section:

Includes wide scan survey spectra , high energy resolution spectra, and valence band spectra for the elements Ag, Al, Ar(+), As, Au, B, Ba(+), Be, Bi, Br(-), C, Ca(2+), Cd, Ce(4+), Cl(-), Co, Cr, Cs (+), Cu, Dy, Er, Eu, F(-), Fe, Ga, Gd, Ge, Hf, Hg, Ho, I(-), In, Ir, K(+), La(3+), Li(+), Lu, Mg, Mn, Mo, N(3-), Na(+), Nb, Nd, Ni, O(2-), P, Pb, Pd, Pr, Pt, Rb(+), Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr(2+), Ta, Tb, Te, Ti, Tl, Tm. V, W, Y, Yb, Zn, and Zr. If the element is part of insulating chemical compound, then a C (1s) spectrum is also provided to allow the user to correct for sample charging. All narrow scan spectra are peak-fitted to reveal FWHM, peak asymmetry, and peak separation for spin-orbit pairs. The strong signals observed in the wide scan survey spectra are labeled and tabulated together with rough BE values of those strong signals. The details of the experimental protocol used to produce each these spectra are provided in the "Instrument and Analysis Details" section. All pure elements, except for Silicon and Selenium, were ion etched prior to analysis.

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The "Native Oxides" Section:

Includes wide scan survey spectra, high energy resolution spectra for principal signals of each element, carbon (1s) high energy resolution spectra, and oxygen (1s) high energy resolution spectra found in/on naturally formed native oxides of the elements Ag, Al, As, B, Be, Bi, Cd, Co, Cu, Fe, Ga, Ge, Hf, In, Ir, Mg, Mn, Mo, Nb, Ni, Pb, Pd, Pt, Re, Rh, Ru, Sb, Sc, Se, Sn, Ta, Te, Ti, Tl, V, W, Y, Zn, and Zr. Atomic percentage based tables of surface composition, which reveal the natural oxidative tendencies of the elements and the tendencies of these elements to capture various gases from the air and/or various contaminants introduced to the surface from handling by the original chemical producers. To enhance traceability and to try to determine chemical shifts it was deemed essential to observe the pure metal signal for a set of spectra to be included in this Native Oxide section. The samples used for these measurements were, in general, naturally formed native oxides that were analyzed as received without any treatment of any kind. All of these samples had been stored in a set of drawers which were not air-tight and so the samples were exposed to the normal atmosphere of a laboratory for many months or years.

Note: Most of the native oxides are naturally formed native oxides, but a few of the native oxides are actually "freshly formed" native oxides that were produced by scraping the surface of the oxidized metal with a clean knife and exposing the freshly cleaned surface to the normal atmosphere of the laboratory for a time period between 5 minutes and several days. This scraping was done because the naturally formed native oxide or carbonate film was thick enough to hide the pure metal signal when the samples were analyzed by XPS. This method produces freshly formed native oxides which have probably not reached a thermodynamically stable state.

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ORGANIZATION AND DETAILS OF SPECTRAL SETS

Organization of Spectra

A set of spectra for a particular chemical is located by looking for the chemical formula abbreviation written in the upper right hand corner of each page. For the element called “aluminium (Al)" the user will find its chemical abbreviation “Al" in the upper right corner of the pages that belong to that set of data and spectra. The spectra are organized by using the chemical abbreviation. This means that spectra for "antimony (Sb)" can be found by looking for the chemical formula: “Sb".

Contents of Each Set of Spectra

The spectra are presented exactly as printed by the Spectral Data Processor software which is provided in each XI SpecMaster Data-Base system. The first page of a set includes the “Detailed Surface Composition Table” which reports the peak assignments, binding energies, relative sensitivity factors, and Atom % abundance of each major signal contained in the wide scan survey spectrum for that chemical. In the title line of this first page the user will find the full chemical name along with other basic information about the chemical, such as Formula Weight, Chemical Abstract Services number, common name, and the Latin language name of the element if available.

The second page of each set is the wide scan survey spectrum with peak labels for each of the strong signals.

Detailed information about the operating capabilities of the SSI systems and the instrument and analysis conditions used to collect these data are presented in the "Instrument and Analysis Details" section of this book.

The remaining pages of each set are the high energy resolution narrow scan spectra which were obtained by measuring the strongest signals found in the wide scan survey spectrum. These spectra include detailed peak-fit results in a table and display the actual peak-fit results for each spectrum. The binding energies of insulating materials are reported in both raw and corrected form. Based on our research we have used a 285.0 eV value for the C (1s) signal of hydrocarbons for charge referencing spectra. The FWHM values for each peak of a high energy resolution spectrum is adjacent to the binding energy for that peak. The percentage numbers given for each peak is a relative percentage that is based on the intensity of that signal only (It is not an atom % value).

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Philosophy of Data Collection Methods

Our philosophy is to collect spectra under analysis conditions that are practical, readily reproduced, and typically used in laboratories that use monochromatic X-ray sources and work under real world practical analysis conditions. We have assumed that the most XPS laboratories need practical reference spectra and will not spend the time or money to produce and to analyze pure, clean surfaces under ultimate energy resolution conditions. However, we did spend extra time to collect data with above average signal to noise (S/N) ratios which reveal the presence of minor components that might otherwise be missed. In the production of these spectra we did not attempt to clean the surfaces of the native oxides or the insultors which would make charge referencing a difficult task. For practical reasons we used the C (1s) spectra from the naturally formed layer of adventitious hydrocarbons because that signal is the "de facto" standard for charge referencing insulating materials.

The spectral data contained within these handbooks are designed to assist engineers, scientists, analysts, theoreticians, and teachers who use XPS on an everyday basis under practical working conditions. We believe that these spectra will help XPS users to analyze industrial problems, gather reference data, perform basic research, test theories, and teach others. These spectra are designed to be practical tools for everyday use and were obtained under practical working conditions. No attempt was made to produce research grade spectra, but many of the spectra are actually research grade spectra because of the self-consistent methods used.

In the production of some spectra no attempt to produce a pure, clean surface, but some effort was made to produce surfaces with a minimum amount of natural surface contamination if needed. When ion etching was used to clean a material that contained more than one element, then ion etching was done with conditions that should minimize preferential sputtering. For the spectra of pure elements, the surface was strongly ion etched.

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Peak-Fitting (Curve-Fitting) of High Energy Resolution Spectra

Peak-fitting was performed by using the software provided with the Surface Science Instruments XPS system. That software allows the user to control the full width at half maxima (FWHM) value of any peak, the binding energy (BE) of any peak, peak areas, the ratio of two peak areas, the energy difference between two peak maxima, the shape of a peak as a sum-function of Gaussian and Lorentzian peak shapes in any peak, and the percentage of asymmetry in any peak.

By empirically peak-fitting the spectra from large sets of closely related materials in a trial and error method and analyzing the trends, it was possible to recognize several fundamental peak-shape and peak-fitting parameters for pure elements, binary oxides, polymers, and semiconductors. We used those empirical results to guide our efforts to peak-fit many of the spectra which had complicated peak shapes. In some cases we used the theoretical ratio of spin-orbit coupled signals to assist the peak-fitting of some spectra and also the energy interval between spin-orbit coupled signals that were derived from pure element spectra. No attempt was made to fit the spectra in accordance with theoretical expectations or calculations.

A reduced "chi-squared" value, which indicates the goodness of a peak-fit, was used to determine if a peak-fit was reasonable or not. Based on practical experience a "chi-squared" value between 1 and 2 implies a relatively good peak-fit. A "chi-squared" value between 2 and 4 implies that the fit has not yet been optimized. A "chi-squared" value larger than 4 implies that one or more signals may be missing from the peak-fit effort.

A Shirley-type baseline was used for all peak-fits. Peak shapes for the main XPS signals obtained from chemical compounds (e.g. oxides, halides, etc.) were typically optimized by using a Gaussian:Lorentzian ratio between 80:20 and 90:10. For pure metals, the Gaussian:Lorentzian ratio for the main XPS signals was normally between

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50:50 and 70:30. The main XPS signals for semi-conductor materials usually required a Gaussian:Lorentzian peakshpae between 70:30 and 80:20.

From the peak-fitting of the binary oxides, we have observed that FWHM for the C (1s), O (1s) and the main metal signal from the binary oxide are usually in range 1.0-1.4 eV. This trend helped us to decide if we had good charge compensation.

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Charge Compensation of Insulating Materials

Charge compensation of insulating materials was normally handled by using the patented SSI mesh-screen together with a low voltage flood gun of electrons which used an acceleration voltage that was adjusted to 3-4 eV for optimum results. The mesh-screen device uses a 90% transmission electro-formed mesh made of nickel metal that is supported above the surface of the sample by mounting the mesh on a conductive metal frame that is grounded to the sample mount. To achieve good charge compensation the mesh-screen is positioned so that the distance between the mesh and the surface of the sample is between 0.5 - 1.0 mm. When the distance between the mesh-screen and the surface of the sample is greater than 1.2 mm, the usefulness of the mesh screen flood gun system was normally null.

The mesh-screen is understood to function as an electron cut-off lense with some tendency to allow incoming flood gun electrons to focus onto the area being irradiated with monochromatic X-ray beam. This occurs because the X-ray beam does not have a uniform flux density over the area of the beam. In effect, the mesh-screen produces a nearly uniform electric potential at the surface of the sample and allows incoming flood-gun electrons to pass through whenever they are needed (on demand).

The mesh-screen was used on every insulating material except for a few materials that were analyzed before the flood gun mesh-screen method was developed.

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Abbreviations Used

Due to the limited space provided to describe each sample in each electronic data-file, it was necessary to use various abbreviations. The abbreviations are:

scr = screen used for charge compensation
scrn = screen used for charge compensation
TOA = take-off-angle for the electrons
Aldr = Aldrich Chemical Co.
RMC = Rare Metallics Co.
SPP = Scientific Polymer Products Co.
MS Co. = Metal Samples Company
FG = flood gun,
mesh = mesh-screen used for charge control,
1mm=1 mm height used for the mesh-screen,
semi-con = semi-conductive behavior
conduc, = conductive behavior
Tech = technical grade purity,
pellet = sample pressed into pellet form by pellet press used to make Infrared KBr pellets,
plt = pellet
pel = pellet

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INSTRUMENT AND ANALYSIS DETAILS USED TO MAKE XPS SPECTRA

A. Instrument Details (ref 1)

Manufacturer:	Surface Science Instruments (SSI)
Model:	X-Probe
	S-Probe (upgraded from M-Probe model 2703)
Software Version;	1.36.05 (Compiled in MS-DOS "C" version 6.0)
Analyzer Type:	Fixed Analyzer Transmission (FAT)
	Fixed Pass Energy = Constant Analyser Energy (CAE)
	180° Hemi-spherical (truncated)
Input Lens Field of View:	30° for sample normal to lens axis (1" diameter port)
	(always larger than X-ray beam; retarding potential scanned)
X-ray Type:	Al° monochromatic (one 2 " diameter thin natural SiO2
	crystal wafer glued onto Zerodur substrate heated to 65° C)
X-ray kV and mA Emission:	10 KV, 1.5-22.0 mA (depending on spot size used)
X-ray Energy Defined as:	1486.7 eV (8.3393 Å), Bragg Angle=78.5°
Excitation Source Window:	0.6 μ aluminum in S-Probe (10μ mylar i n X-Probe)
Angle of X-ray Incidence:	α = 71° (relative to sample normal)
Electron Emission Angle:	β = 0° (relative to sample normal)
Angle Between X-ray Axis and Electron Analyzer Axis:	ϕ =71° (fixed, non-variable)

Pass Energy of Analyzer:	150 V for Resolution 4 setting
	100 V for Resolution 3 setting
	50 V for Resolution 2 setting
	25 V for Resolution 1 setting
Type & Size of Input Slit:	Fixed (2 mm X 35 mm); magnetic compression
Type & Size of Output Slit:	None (dispersion limited by hemisphere voltages)
Electron Collection Lens	
Field of View:	~ 1 mm^2 for a take off angle = 0° at 1000 eV KE
Electron Collection Lens Efficiency:	7% over 2π steradians
Sample Surface to Tip of Electron	
Collection Lens Distance:	~33 mm
Crystal to Sample Surface Distance:	~190 mm
Crystal to X-ray Anode Distance:	~190 mm
True Background Count of Noise:	<10 electrons/second at -50 eV (shot noise limited)
Detector Type:	SSI Position Sensitive Detector (PSD), resistive anode,
	40 mm X 40 mm, electronically defined as 128 active channels
	with a maximum electron count rate of 1,000,000
Dead Time:	zero (unless ion etching pure element while collecting data)
Base Pressure:	4.0×10^{-10} torr
Normal Operating Pressure:	1.6×10^{-9} torr
FWHM Diffracted by Natural SiO2:	~0.25 eV

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Power Settings:	200 Watts in a 250 x1100 μ X-ray beam
	100 Watts in a 150 x 800 μ X-ray beam
	45 Watts in a 80 x 350 μ X-ray beam
	15 Watts in a 40 x 250 μ X-ray Beam
X-ray Induced Current:	1.1×10^{-9} amps for a 600 μ spot in X-Probe
Approximate True X-ray Power :	$\sim 6 \times 10^{-6}$ W in a 600 μ spot
Approximate True X-ray Irradiance:	$\sim 8\ W/m^2$
Approximate True X-ray Photon Flux:	$\sim 7 \times 10^9$ photons/sec

B. Experimental Details

Electron Take-Off-Angle:	90° relative to sample surface (unless otherwise reported)	
Pass Energies Used:	Wide scans were done at PE = 150 eV	
	Narrow scans were normally done at PE = 50 eV	
	Valence band scans were done at PE=150 eV	
X-ray Beam Size Used:	Wide scans:	250 x 1500 μ ellipse (at 90° TOA)
(for S-Probe)		250 x 1100 μ ellipse (at 35° TOA)
	Narrow Scans:	250 x 1500 μ ellipse (at 90° TOA)
		150 x 1000 μ ellipse (at 90° TOA)
SSI Mesh-Screen:	A 85% transmission (20 μ diameter wire with 200 μ spacing) nickel metal mesh screen was adhered to a small 25 mm x 25 mm x 1.5 mm (W x L x H) aluminum plate over a 20 mm x 20 mm aperture.	

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The mesh-screen was placed over all oxide samples so that the distance between the sample surface and the mesh-screen was <1.0 mm but >0.3 mm.

Dwell Time (counting time):	200 milliseconds/channel (usual setting)
Data Transfer Time:	4 milliseconds
Max. Number of Channels:	5000 (channels = data points)
Scan Time for One Wide Scan:	~ 3.5 minutes (using 1024 data points)
Scan Time for One Narrow Scan:	~100 seconds (using 256 data points)
Energy Range:	-100 to +1400 eV (BE range)
Typical Step Size:	0.1 eV/step (i.e. 0.1 eV/data point)

C. Data Processing Details

Baseline Subtraction:	None, unless S/BG gave a small display. When the baseline was removed, the intensity of the lowest point was subtracted from all points.
Data Smoothing:	None
Energy Shifting:	None

D. Sample Details (for Volumes 1-5)

The "Description" given on each XPS spectrum reports the empirical elemental formula for the oxide, purity, source, production lot number, a note, if appropriate, about being conductive or semi-conductive, the abbreviation "scrn" which means that the SSI mesh-screen was used, and a number, and “90”: which means that a 90° electron take-off-angle used to collect the data for that sample. Abbreviations used in the description and their full meaning include: Aldr = Aldrich Chemical Co., RMC = Rare Metallics Co., semi-con = semi-conductive behavior, scrn = SSI mesh-screen used, TOA = electron Take-Off-Angle, Tech = technical grade purity, pellet = sample pressed into pellet form, plt = pellet, pel = pellet, MS Co. = Metal Samples Company in Munford, Alabama USA (Tel 205-358-4202), SPP = Scientific Polymer Products Inc. in Ontario, New York state, USA (Tel 716-265-0413)

Sources of Elements and Chemical Compounds (for Volume 1)

The pure element samples were obtained from various sources without any specific information about sample purity so pure element samples must be assumed to be pure at the 99%+ level. The "halide" salts used to produce spectra from gaseous or highly reactive elements were also obtained from various sources. These halide samples were obtained as crystalline "windows" which are normally used in Infrared spectroscopy and have purities at the 99% level. The Boron Nitride (BN) sample was a white ceramic electrical standoff which was fractured in air. The copper foil material, which was always used to determine reference energies, were obtained as 99% pure foil which was designed as a multiple purpose foil for use around the home. The gold ingot material, which was also used to determine reference energies was obtained as a 99.999% pure sample from Aldrich Chem. Co..

Source of Polymer Materials (for Volume 4)

A special kit (#205) of the 100 polymer materials was obtained from Scientific Polymer Products, Inc. which is located at 6265 Dean Parkway, Ontario, New York, USA 13519 (Tel 716-265-0413).

Source of Alloys (for Volume 6)

A special kit of 54 metallic alloys was obtained from the Metal Samples Co., which is located at Route #1, Box 152, Munford, Alabama, USA, 36268 (Tel 205-358-4202). This kit includes a materials analysis report on each alloy in weight percents. The National Research Institute for Metals (NRIM) in Tsukuba, Japan has provided a series of various binary alloys made of AuCu and CoNi alloys.

Sources of Semi-Conductor Materials (for Volume 3)

Over the course of many years, many people in the Japanese semi-conductor business have given samples of various semi-conductor materials in crystalline wafer form. Various samples were donated by the Oki Electric Company, Mitsubishi Materials, Canon, and various universities. The source of each material is included with the individual sample descriptions whenever that information was provided.

Sources of Commercially Pure Binary Oxide Samples (for Volume 2)

Most of the commercially pure binary oxides were purchased from the Aldrich Chem. Co.. The packages from the Aldrich Chemical Co. included an "Analytical Information" sheet which described an ICP or AA analysis summary, a production lot number, the Aldrich product number, sample purity number (e.g. 99+%), sample appearance (color and physical form), date of chemical analysis, formula weight and a label on the bottle that reports the melting point, toxicity, Chemical Abstracts registry number and density. The samples from Aldrich were generally quite pure at the surface. Other oxide samples were obtained from either Cerac Inc. (USA) or Rare Metallics Co., Ltd. (Japan). The packages from Cerac Inc. included a "Certificate of Analysis" with an ICP or AA analysis summary, a production lot number, a product number, purity (e.g. 99+%),and mesh size. The packages from Rare Metallics Co. did not include analytical data reports, but instead had stock numbers and a purity statement. Two samples (i.e. SiO2 natural crystal and Al2O3 fused plate) were obtained from in-house sources and do not have any purity reports.

Powdered Samples Pressed into 3mm Diameter Pellet

Until analyzed, all finely powdered samples were kept stored in their original glass or plastic containers, which were packaged inside of plastic-lined aluminum bags. Just prior to XPS analysis, each bottle was opened in the normal air of the room where the XPS system was kept, and a small 50-100 mg portion of the sample was removed via a clean nichrome spatula and placed in the compression chamber of a hand-operated, stainless steel pellet press. All finely powdered samples were compressed without any chemical treatments, which, if done, may have introduced unusual contamination or produced some change in the samples. The resulting pellets varied in thickness from 0.3 - 0.8 mm.

To avoid iron and /or chromium contamination from the anvil, a thin sheet of paper was placed over the sample in the compression chamber. Any powders, which were clumped together, were very gently pressed into a powder just prior to compression. To avoid unnecessary heat-induced oxidation, those samples which were hard and granular were very gently ground into a fine powder in a agate marble mortar and pestle. As soon as each sample was removed from the compression chamber, it was mounted onto silver (Ag°) paint inside of a 5mm wide round brass boat which was 1.3 mm in height. Silver paint was used so that conductive oxides could behave as true conductors thereby providing true electron binding energies for those oxides that were indeed conductive. In general, each oxide was exposed to room air for <15 min..

Benefits of Pressing Powders into Pellets (increased counts and simple charge control)

A comparison of the electron counts obtained from powdered samples pressed onto double-sided adhesive tape and positioned at a 35° electron take-off-angle with the electron counts obtained from hand-pressed glossy or semi-glossy pellets positioned at a 90° electron take-off-angle (TOA) revealed that a pellet at a 90° electron TOA produces 3-5 times higher electron counts than a powdered sample pressed onto double-sided tape at a 35° electron TOA.

By pressing the finely powdered oxides into pellets, it was also found the surface charging behavior of these glossy or semi-glossy samples was very easy to control by using the mesh-screen electron flood-gun combination with the flood gun set to 4-6 eV acceleration energy and approximately 0.5 mA filament current.

Problems Caused by Pressing Samples into Pellets

By pressing the finely powdered oxides into pellets, the surface of the resulting samples were usually smooth enough to appear glossy or semi-glossy, but some samples had iron or chromium contamination which indicated that the oxide had undergone a pressure induced reaction with the stainless steel anvil. Very strong hand pressure caused some oxides to react with the stainless steel anvil, but medium hand pressure usually did not produce undesired iron and chromium contamination. All analyses that showed any unexpected contamination were repeated. Other forms of accidental contamination (chlorine or previously analyzed oxides) were caused by insufficient cleaning of the stainless steel anvil, which was normally cleaned with a metal polishing solution (Pikal) and rinsed with distilled water and isopropanol. All analyses that showed any unexpected contamination were repeated.

Solution to Pressure Induced Contamination of Pellets

Experiments on ways to avoid the pressure-induced iron or chromium contamination, produced pellets with semi-smooth non-glossy surfaces which required more effort to produce good charge control. These non-glossy surfaces also gave electron count rates that were about 10-50% lower than the glossy or semi-glossy surfaces. As a result, it appears that very smooth surfaces, which appear glossy or semi-glossy, greatly simplify efforts to control surface charging under the charge-control mesh-screen and also enhance the electron count rate by 10-50% more than a pellet that has a semi-rough non-glossy appearance.

Extensive experiments on different methods to avoid contamination of the pellets revealed that contamination is minimized or avoided by using freshly cleaned aluminum foil as a "buffer" between the oxide powders and the metals in the steel anvil components. The aluminum foil, which is sold as a kitchen wrap material, is cleaned with 100% isopropanol (isopropyl alcohol) just prior to use. The foil is cut to a size that is readily useful with the pellet press device after it is cleaned. Alternately, we have also used a type of "glycine" paper which is commonly used to as a paper to hold powders when weighing a powdered sample. This "weighing" paper is common in many chemical laboratories and can be substituted for the aluminum foil whenever the pressing results with the aluminum foil produce undesired binding results. The glycine paper method sometimes introduces very small amounts of contaminants which produce a N (1s) and C (1s) signals. The amount of these contaminants is much smaller than the amount of contaminants that occur by simply pressing the powder without any sort of paper or aluminum foil buffers.

Source of Pellet Press Equipment

"Qwik Handi-Press" from Barnes Analytical Division, Spectra-Tech, Inc.652 Glenbrook Road, Stamford, Connecticut, 06906 (FAX 203-357-0609) Kit: Part # 0016-111 to 0016-121 contains 1,3, and 7 mm die sets. Originally purchased through Aldrich Chem. Co. in 1989.

E. Energy Resolution Details

Table 1: Experimentally Observed Relation Between Energy Resolution

Element (XPS signal)	Resulting FWHM	Resolution Setting	Pass Energy	X-ray Spot Size
Si ($2p_{3/2}$) crystal - fractured edge	0.38 eV	5	10 eV	40 x 250µ
Si ($2p_{3/2}$) crystal - fractured edge	0.43 eV	1	25 eV	80 x 350µ
Au ($4f_{7/2}$) foil - ion etched clean	0.64 eV	5	10 eV	250 x 1000µ
Au ($4f_{7/2}$) foil - ion etched clean	0.79 eV	1	25 eV	250 x 1000µ
Au ($4f_{7/2}$) foil - ion etched clean	0.86 eV	2	50 eV	250 x 1000µ
Au ($4f_{7/2}$) foil - ion etched clean	1.40 eV	4	150 eV	250 x 1000µ
Ag ($3d_{5/2}$) foil - ion etched clean	0.42 eV	5	10 eV	40 x 250µ
Ag ($3d_{5/2}$) foil - ion etched clean	0.64 eV	1	25 eV	40 x 250µ
Ag ($3d_{5/2}$) foil - ion etched clean	0.75 eV	2	50 eV	40 x 250µ
Ag ($3d_{5/2}$) foil - ion etched clean	1.00 eV	3	100 eV	40 x 250µ
Ag ($3d_{5/2}$) foil - ion etched clean	1.30 eV	4	150 eV	40 x 250µ
Cu ($2p_{3/2}$) foil - ion etched clean	0.85 eV	5	10 eV	250 x 1000µ
Cu ($2p_{3/2}$) foil - ion etched clean	0.94 eV	1	25 eV	250 x 1000µ
Cu ($2p_{3/2}$) foil - ion etched clean	1.06 eV	2	50 eV	250 x 1000µ

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Cu ($2p_{3/2}$) foil - ion etched clean	1.60 eV	4	150 eV	250 x 1000μ
Cu ($2p_{3/2}$) foil - ion etched clean	0.85 eV	5	10 eV	150 x 800μ
Cu ($2p_{3/2}$) foil - ion etched clean	0.96 eV	1	25 eV	150 x 800μ
Cu ($2p_{3/2}$) foil - ion etched clean	1.05 eV	2	50 eV	150 x 800μ
Cu (3s) foil - ion etched clean	2.35 eV	2	50 eV	250 x 1000μ

Table 2: Theoretical Analyzer Resolution versus Pass Energy Settings

Theoretical Analyser Resolution	Pass Energy	Effective Detector Width
0.25 eV	25.0 eV	3.5 eV
0.50	50	7.0
1.00	100	14.0
1.50	150	21.0

F. Energy Scale Reference Energies and Calibration Details (ref. 8)

From May 1986 to January 1993

Energy Scale Reference Energies: 932.47 eV for Cu ($2p_{3/2}$) signal
122.39 eV for Cu (3s) signal
83.96 eV for Au ($4f_{7/2}$) signal
Binding Energy Uncertainty: less than ±0.08 eV
Digital-to-Analog (DAC) Conversion Setting: 163.88

After January 1993 (Based on NPL reference energies published in 1990)

Energy Scale Reference Energies: 932.67 <±0.05 eV for Cu ($2p_{3/2}$) signal
122.45 <±0.05 eV for Cu (3s) signal
83.98 <±0.05 eV for Au ($4f_{7/2}$) signal
Observed Reference Energy: 75.01 <±0.05 eV for Cu (3p3) signal
Binding Energy Uncertainty: less than ±0.08 eV
Digital-to-Analog (DAC) Conversion Setting: 163.87

Note: NPL has recently revised reference energies to be 932.62 eV for Cu (2p3) and 83.96 eV for Au (4f7) for monochromatic systems using an electron take-off-angles of 45°

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Reference Energies of Adventitious Hydrocarbon Contaminants

From May 1986 to January 1993 the electron binding energy of adventitious hydrocarbons was assumed to occur at 284.6 eV based on SSI and C. D. Wagner's research and recommendations.

Publications by P. Swift (Surface and Interface Analysis **4**, 47 (1982), S. Kohiki and K. Oki (J. Electron Spectrosc. Related Phenom. 33, 375-380 (1984), and G. Barth, R. Linder and C. E. Bryson, III (Surface and Interface Analysis **11**, 307-311 (1988) have shown that the electron binding energy for various hydrocarbon contaminants and polymers is not necessarily a constant number. Research by this author indicates that the electron binding energy for adventitious hydrocarbons lies somewhere between 284.4 and 287.0 eV depending on the underlying (oxide) materials. By taking a simple average of all available binding energies, the author has found that 285.0 eV is preferred for hydrocarbons on ion etched metals where the hydrocarbon is many hours old. For naturally-formed native oxides the preferred binding energy is 285.2 eV. Oxide based materials at the far left of the periodic element table (columns 1-4) tend to have higher values (285.2-287.0 eV, while most of the transition metal oxides center around 285.0 eV. Near the far right of the periodic table, the binding energy seems to rise to a 285.2-286.5 eV range (columns 12-14) when the native oxides of those elements are analyzed.

In routine practice, this author prefers to use the 285.0 eV number. Some potential factors that may cause this rather large range of electron binding energies for adventitious hydrocarbon contamination includes the dipole moment at the surface of the oxide material, which is expected to be much stronger than the dipole moment of a pure metal, and also, in the case of naturally formed native oxide films, the thickness of the native oxide, any physical or chemical treatments, the thickness of the adventitious

hydrocarbon layer, and the type of instrument used to analyze the sample. The type of instrument being used may cause different shifts in the observed binding energy of the adventitious hydrocarbon contamination because the source may or may not generate different amounts of low energy secondary electrons from the window that protects the X-ray source. The heat from the source and contamination that degases from a just turned on source may also influence the observed binding energy. Electron flood guns and implanted ions may or may not influence the binding energy of semiconductive materials.

Instrument Stability and Long Term Calibration

Initially each of the two SSI systems, that we have used, was calibrated 2-3 times per week because its ability to maintain accurate voltage settings was unknown. Once it was determined that the systems could maintain reliable voltage settings for 1-3 months, it was decided that good calibration could be maintained by checking and, if necessary, correcting the pass energies of the system on a 2-4 week basis. Each of the two SSI XPS instruments, that we have used, have been calibrated on a routine basis every 2-4 weeks by using SSI's reference energies. By using this method over several years time, it was found that the maximum uncertainty (error in pass energies) was normally $<\pm 0.10$ eV, but a few times rose to ± 0.15 eV or less. In a very rare case, the uncertainty rose to 0.20 eV. Long term use of the SSI systems has shown that the DAC circuit does not change enough to be observed unless the room temperature changes by more than 10 degrees Centigrade. If the room temperature changes within a few hours time by more than 10 degrees or the temperature of the DAC chip is changed by more than 10 degrees, then a >0.1 eV shift, which is much smaller than the reliability of almost all literature BEs, can be observed. Variables, which seem to cause pass energy settings to change slightly, include building line-voltages, ion etching conditions, and the addition or removal of some electrical device.

G. Electron Counting and Instrument Response Function Details

Instrument Response Functions (for the X-Probe System only) (ref 3, 4, 5)

Instrument Response Function: $Q(E)=E^{+0.27}$ for 150 eV PE (ref.3)
Instrument Response Function: $Q(E)=E^{+1.0}$ for 50 eV PE (ref.3)

Signal/Background (S/BG) Ratios for Ion Etched Silver using a 250x1000 µ Spot*

Pass Energy	25 eV	50 eV	100 eV	150 eV
S/BG ratio**	>140	>110	>70	>50

* Using a 90° electron take-off-angle and a smooth Ag°/mylar film.
** The S/BG ratio is a simple numerical ratio of electrons counts at the peak maximum relative to the average electron counts observed at approximately 10 eV lower BE.

Lens Voltage Settings Available via Software under Instrument Calibration

Pass Energy*	29.6-29.8	54.7-54.9	105.1-105.3	155.9-156.2
Detector Widths	3.743	7.486	14.954	22.297
Sensitivity Exponent	-0.1	0.3	0.7	1.1
V1 Offset	30	55	105	155
V1 Slope	0.600	0.611	0.676	0.709

* These pass energies include corrections for instrument work function. True pass energies were set to 25, 50, 100, and 150 eV ±0.1 eV.

H. Effects of Poorly Focussing the Distance between the Sample and the Electron Lens

If the focus distance between the sample surface and the electron collection lens is poorly adjusted, then the number of electron counts drops very quickly. A 0.5 mm error in focus produces a >300% decrease in counts, but does not produce any observable error in binding energies, which is a common problem with many XPS instruments. A 0.1 mm error in focus produces a 15% decrease in peak area counts and is easily observed as a horizontal displacement in the static (un-scanned mode) XPS signal as observed on the standard CRT display of the detector response. Such a decrease in signal intensity generally urges the operator to correct the focus error so as to maximize the electron count rate. In this

manner, the operator has avoided any chance of obtaining false BE readings and has accurately reproduced a nearly absolute focus point which greatly increases the quantitative accuracy of any unknown sample. Experiments with the Bragg angle alignment of the crystal indicated that the maximum error due to an unusual bad alignment of the crystal would be <0.1 eV. To observe an error greater than 0.1 eV, the electron counts were found to decrease by >50%.

I. Quantitation Details and Choice of "Sensitivity Exponents" (ref 2, 4, 5)

By default, the SSI software uses a 0.7 number as the sensitivity exponent factor for each pass energy setting which are used in an equation that modifies theoretically calculated atomic photo-ionization cross-sections (John H. Scofield, Ph.D.) to generate relative sensitivity factors that are valid for this XPS systems and which can be used to generate valid atomic percentages. The 0.7 value produces a ±10% accuracy in quantitative results for XPS signals obtained by using a 150 eV pass energy and occur within the 0-700 eV BE range. For signals that occur at higher BEs, it is generally necessary to change the sensitivity exponent factor to a 1.1 or higher value (1.4). To measure signals obtained by using other pass energies for quantitation, it is necessary to use other sensitivity exponent factors, if the user desires to maximize quantitative accuracy.

To determine useful sensitivity exponents, it is useful to use freshly ion etched poly-crystalline copper foil to test the validity of the sensitivity exponent for larger BE ranges and different pass energies. By integrating the peak areas of the Cu (2p1), Cu (2p3), Cu (3s), Cu (3p) and Cu (3d) signals with a modest amount of attention to baseline end points, it is possible to perform trial and error choices of the sensitivity exponents until a useful number is determined. Once a useful number has

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been entered into the computer software routine, then the software can generate "fictional" atomic percentages for each of the integrated copper signals which will generate 20 atom % values with a uncertainty of ±1-2 atom %. If the exponent factor is severely wrong then the atomic percentages will generate numbers such as 10%, 11%, 26%, 24%, and 29% or perhaps 31%, 28%, 14%, 13%, and 14%.

This trial-and-error approach may require 1-2 hours time and can be done on either wide scan data or more preferably narrow scan data for each of the 4-5 pass energies. This method, in effect, assumes that all five of the relative sensitivity factors for copper are reasonably correct. If wide scan data are used, then this method requires a little extra effort to avoid the satellites of the Cu (2p) signals.

This method, in effect, pretends that the pure copper sample is a standard material that is composed of 5 components which are present in 20 atomic % concentration. The objective is to change the sensitivity exponent until the software generates a 20 atom % result for each of the five copper signals. After useful sensitivity exponents are found, they are tested by analyzing freshly exposed bulk regions of crystalline materials such as SiO2, Al2O3, and NaCl. The high and low BE signals of the NaCl crystal are especially useful to test the validity of the sensitivity exponents.

As further checks, the freshly exposed bulk of common polymers (e.g. mylar or PMMA) or a thin film of high purity silicone oil can also be analyzed. Teflon has repeatedly given a slightly larger than desirable error by comparison to the other materials listed above. For that reason Teflon seems to be a less desirable material to determine useful sensitivity exponent values.

J. Crude Tests of the Reliability of Relative Sensitivity Factors

Crude testing of Scofield's numbers are included in atomic percentage composition tables that give atomic percentages for only one element. This testing used the software's automatic peak area integration software that is reasonably accurate. The results indicate that some of the relative sensitivity factors for some of the weaker signals are less reliable. If, however, all factors are taken into account, then Scofield's numbers are reliable to a 95% accuracy level for truly homogeneous materials. These results are available when using the Spectral Data Processor software.

K. Traceability Details

The definition of traceability reported by Martin P. Seah and Cedric J. Powell in the J. Vac. Soc. Technol. Vol 8, p.736 (1990) publication is: "The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons." Based on this definition, the following correlations were envisioned.

Traceability of Reference Binding Energies (Calibration)

At this time, there are no international standards for binding energies or reference energies. Numbers which are considered to be standard binding energies (BE), which would lead to traceability in BEs, include (a) those provided by Martin P. Seah at the National Physical Laboratory (NPL) in the United Kingdom (England), and (b) those provided by the ASTM in the USA "Standard Practice for Checking

the Operating Characteristics of XPS Spectrometers" designated as "E 902-88". Other nations also have similar national standards, which tend to imitate those set by the USA and the UK. Recently, many people in the world have been using NPL's reference energies, which have become "de facto" standards but have not yet been accepted by the International Standards Organization (ISO).

There are still many workers and researchers using various numbers provided by the instrument makers. The author of this book was using Surface Science Instruments (SSI) Co. reference energies until December 1992 and then switched to NPL BEs in January 1993. SSI reference energies came from Hewlett-Packard (HP). SSI and HP both used high precision voltage meters from HP to calibrate their ESCA machines (i.e. X, M, and S-Probe and HP-5950 A-type and B-type, resp.). Hewlett Packard was the first company to offer a commercial ESCA system, which used reference energies developed in cooperation with Kai Siegbahn at Uppsala, who effectively developed ESCA into a useful science and received the Nobel Prize.

In a recent effort to improve the accuracy of BEs obtained from pure elements, the S-Probe pass energies were checked and corrected, if needed, almost every work-day for two months to obtain high precision and high accuracy BEs for the pure elements that are metals. This study used the NPL reference energies with Cu (2p3) at 932.67 eV with +/- 0.02 uncertainty and Au (4f7) 83.98 eV with +/-0.02 uncertainty by using 0.02 eV/pt. steps for the calibrations. To determine the "true" BE of each of the pure elements, which were scraped clean in air and then ion etched in vacuum, a 0.05 eV/pt. step was used. A repetitive ion etching (depth profile) style was used to collect wide scan, valence (Fermi edge) band, and narrow scans of the main signals for each metal at 50, 25 and 10 eV pass energies. Each repetitive experiment run lasted about 4 hours. Therefore, if NPL's BE numbers are

accepted as "de facto" international standards, then the ultimate traceability of BEs in this data collection can be related to NPL BE numbers for Cu (2p3) and Au (4f7). In a different, but similar manner, the BEs used to calibrate the S-Probe are traceable to Siegbahn's work and the high precision, high voltage meters produced by the Hewlett Packard Company.

Traceability Transfer from Pure Metals to Non-conductive Binary Oxides

A question that should be posed is traceability to the oxide BEs. Traceability begins with NPL's BEs for pure copper and gold as state above. Traceability then transfers to pure element BEs which are based on NPL reference BEs. Traceability then transfers to pure element BEs based on SSI's reference BEs, and then the naturally formed native oxide data published in Volume 2 of our XPS Spectral Handbook series where BEs were measured from pure element signals and also the naturally formed native oxide signals.

Naturally formed native oxides typically have thin oxide films (10-80Å) which, in general, behave as good or true electrical conductors, which allows a direct measure of the true binding energy of many, but not all, binary oxides. To determine if traceability can indeed be transferred to true binary oxides, it was necessary to study the behavior of the naturally formed native oxides by applying various flood gun settings with the samples grounded and insulated. The results from that study can be used to transfer traceability to the experimentally observed BEs of pure binary oxides. The most difficult transfer of traceability occurs for the naturally formed native oxide systems. If the flood gun study was not done, then it is difficult to transfer traceability in a reliable manner from a conductive metal to one of its corresponding non-conductive binary oxides.

Traceability of Instrument Response Function

Copper, gold and silver data obtained from the X-Probe system were submitted to Martin P. Seah at the NPL for a round robin test on transmission function; the results of which were published in Surface and Interface Analysis, p.243 (1993). In that publication, X-Probe data, which we contributed, were attributed to group #35. That paper reported that instrument has a Q(E) =$E^{0.27}$ for Rex 4 pass energy (PE=150 V)and a Q(E) =$E^{1.0}$ for the Res 2 pass energy (PE=50 V). If the NPL method is accepted as a "de-facto" standard, even though it is not an internationally recognized standard, then the transmission function and quantitation results of the S-Probe system are traceable to the "metrology spectrometer" at NPL.

Traceability of Relative Sensitivity Factors (RSFs) used for Quantitation

Scofield's theoretically calculated photo-ionization cross-sections are internationally used as the "de-facto" standard theoretical numbers, except in Russia and a few other places, where Band's numbers are preferred but are almost identical to Scofields. The SSI system uses a very simple equation that modifies Scofield's numbers to generate relative sensitivity factors that are used by the SSI software to calculate atom %s. That equation corrects for pass energy differences, transmission function differences, and inelastic mean free path versus kinetic energy dependency. The SSI system relies on Scofield numbers and that simple equation. Other instrument makers prefer to blend Scofield's numbers and experimentally determined numbers.

Traceability of Sample Purity

The purity of the commercially pure (99+%) binary oxides can be traced to Aldrich's ICP or AA analyses performed by Aldrich. Copies of their results are included in the handbook at the beginning of each group of spectra. Similar data sheets were also obtained for samples bought from Cerac. A set of gold, copper, and silver samples, i.e. "Reference Metal Samples SCAA90" set, kit #367, was obtained from the NPL and used to test the instrument response function of the M-Probe system. Binding energies obtained from those gold, copper, and silver samples were identical to binding energies obtained from our commonplace gold, copper, and silver samples within the expected uncertainty of ±0.08 eV used for routine instrument calibration.

L. Reference Papers Describing Capabilities of X-Probe, M-Probe, and S-Probe XPS Systems

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