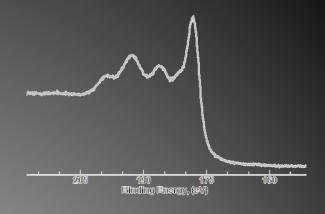
# Monochromatic XPS Spectra





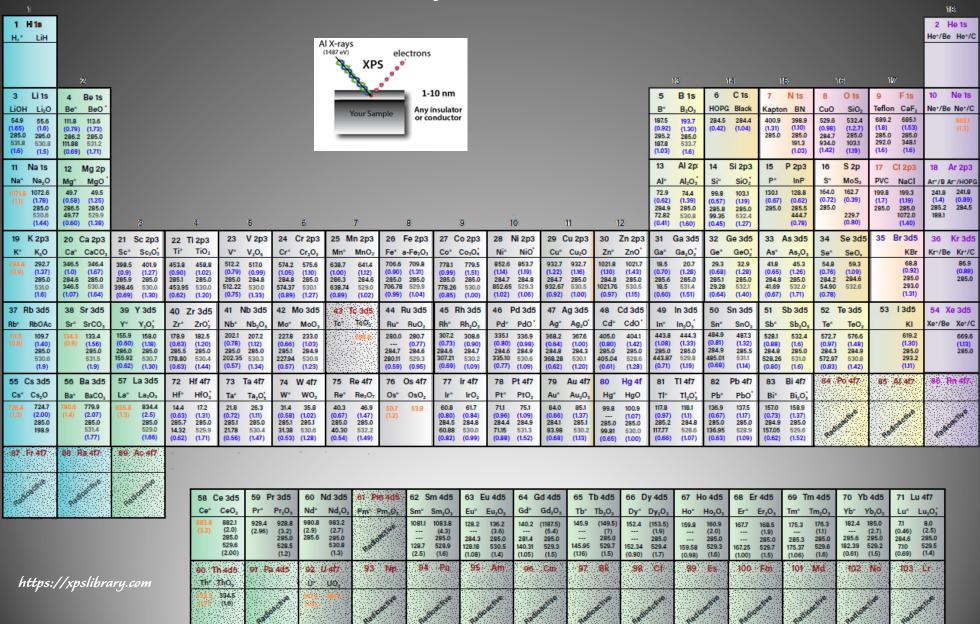
Miscellaneous: REOs, Carbonates, Hydroxides, Sulfides...

B. Vincent Crist

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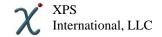
### Monochromatic XPS Spectra REOs, Carbonates, Hydroxides Sulfides, Nitrides...



## Handbooks of Monochromatic XPS Spectra

Volume 5 - Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides, Carbides, Borides, Acetates, & Miscellaneous Materials

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APPENDIX "A"



#### ALPHABETICAL LIST OF XPS SPECTRA IN VOLUME FIVE

### RARE EARTH OXIDES, HYDROXIDES, CARBONATES, NITRIDES, SULFIDES, ACETATES, CARBIDES, BORIDES, AND MISC MATERIALS

RARE EARTH (	<b>DXIDES</b>
--------------	---------------

$CeO_2$	(Cerium oxide, 99%, Rare Metallics, pressed pellet, insulator)	1
$Dy_2O_3$	(Dysprosium oxide, 99.99%, Aldrich, pressed pellet, insulator)	7
$Er_2O_3$	(Erbium oxide, 99.99%, Aldrich, pressed pellet, insulator)	14
$Eu_2O_3$	(Europium oxide, 99.95%, Aldrich, pressed pellet, insulator)	20
$Gd_2O_3$	(Gadolinium oxide, 99%, Aldrich, pressed pellet, insulator)	27
$Ho_2O_3$	(Holmium oxide, 99.999%, Aldrich, pressed pellet, insulator)	33
$Lu_2O_3$	(Lutetium oxide, 99.99%, Aldrich, pressed pellet, insulator)	38
$Pr_6O_{11}$	(Praseodymium oxide, 99.999%, Aldrich, pressed pellet, insulator)	43
$Sm_2O_3$	(Samarium oxide, 99%, Rare Metallics, pressed pellet, insulator)	49
Tb <sub>4</sub> O <sub>7</sub>	(Terbium (III,IV) oxide, gift, lump, semi-conductive)	56
$Tm_2O_3$	(Thulium oxide, 99%, Rare Metallics, pressed pellet, insulator)	63
$Yb_2O_3$	(Ytterbium oxide, 99.99%, Aldrich, pressed pellet, insulator)	69
HYDROXI	DES_	
Al(OH) <sub>3</sub>	(Aluminium hydroxide, technical grade, Perfect Parts Chemical, powder on adhesive tape, insulator)	75
$Cd(OH)_x$	(Freshly scraped cadmium metal soaked in concentrated H <sub>2</sub> O <sub>2</sub> for 4 hours, conductive)	80
$Co(OH)_2$	(Cobalt hydroxide, 95%, Aldrich, pressed pellet, insulator)	85
$Cu(OH)_2$	(Copper hydroxide, Technical grade, Aldrich, pressed pellet, insulator)	92
FeO(OH)	(α-Iron hydroxide, 99.999%, Rare Metallics, pressed pellet, insulator)	99
LiOH	(Lithium hydroxide, 95%, Rare Metallics, pressed onto indium foil, insulator)	106
$Mg(OH)_2$	(Magnesium hydroxide, 95%, Aldrich, pressed pellet, insulator)	111
$Ni(OH)_2$	(Nickel hydroxide, 99%, Aldrich, pressed pellet, insulator)	121



#### **MISCELLANEOUS** (continued)

<b>CARBONATES</b>		
BaCO <sub>3</sub>	(Barium carbonate, pressed onto indium foil, insulator)	128
(BiO) <sub>2</sub> CO <sub>3</sub>	(Bismuth sub-carbonate, 99%, Aldrich, pressed pellet, insulator)	135
CaCO <sub>3</sub>	(Calcium carbonate due to CO <sub>2</sub> attack on CaO from Aldrich, insulator)	140
CaCO <sub>3</sub>	(Calcium carbonate in the natural mineral Calcite, freshly exposed bulk, insulator)	146
CdCO <sub>3</sub>	(Cadmium carbonate, 99.999%, Aldrich, pressed pellet, insulator)	152
CuCO <sub>3</sub>	(Copper carbonate, Technical Grade, powder on adhesive tape, insulator)	160
$CuCO_3$ - $Cu(OH)_2$	(Copper carbonate – copper hydroxide in the natural mineral Azurite, freshly exposed bulk)	167
Li <sub>2</sub> CO <sub>3</sub>	(Lithium carbonate due to CO <sub>2</sub> attack on LiOH on Indium foil)	174
$MgCO_3$	(Magnesium carbonate-hydroxide in the natural mineral Magnesite, freshly exposed bulk, insulator)	179
$MgCO_3$	(Magnesium carbonate due to CO <sub>2</sub> attack on MgO powder from Aldrich, insulator)	186
MnCO <sub>3</sub>	(Manganese carbonate in the natural mineral Rhodochrosite, freshly exposed bulk, insulator)	194
PbCO <sub>3</sub>	(Lead carbonate in the natural mineral Cerrusite, freshly exposed bulk, insulator)	201
SrCO <sub>3</sub>	(Strontium carbonate due to CO <sub>2</sub> attack on SrO from Rare Metallics, insulator)	209
SrCO <sub>3</sub>	(Strontium carbonate, 99%, Rare Metallics, pressed on indium foil, insulator)	216
$Y_2CO_3$	(Ytrium carbonate trihydrate, 99%, Aldrich, pressed pellet, insulator)	220
Y <sub>2</sub> CO <sub>3</sub> -LaB <sub>6</sub>	(Yttrium carbonate on lanthanum hexaboride, ion etched away 50 angstroms, conductive)	227
<b>NITRIDES</b>		
AlN	(Aluminium nitride, 98+%, Aldrich, pressed pellet, insulator)	229
BN	(Boron nitride, 99%, white color, freshly exposed bulk, insulator)	236
CrN	(Chromium nitride film, old, ion etched 2 minutes, conductive)	242
$Si_3N_4$	(Silicon nitride coating, old, as received, insulator)	248
$Si_3N_4$	(Silicon nitride coating, old, ion etched 4 minites, insulator)	254
$Si_3N_4$	(Silicon nitride coating, metallic blue color, soaked 5 minutes in a solution of H <sub>2</sub> O <sub>2</sub> : HCl: H <sub>2</sub> O)	261
$Si_3N_4$	(Silicon nitride coating, metallic blue color, soaked 10 minutes in a solution of conc. HF: MeOH)	268
$Si_3N_4$	(Silicon nitride coating, old, gray color, as received, conductive)	275
$Si_3N_4$	(Silicon nitride coating, old, gray color, ion etched 10 minutes, conductive)	282



 $Si_3N_4$ 

TiN

284

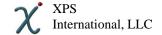
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(Silicon nitride coating, old, blue color, soaked 10 minutes in a solution of conc HF: MeOH)

(Titanium nitride coating, gold color, old, ion etched 2 minutes, conductive)

#### **MISCELLANEOUS** (continued)

#### **SULFIDES** (Silver sulfide in natural mineral Argentite from Guananuato, Mexico, freshly exposed bulk, conductive) $Ag_2S$ 298 $As_2S_2$ (Arsenic (II) sulfide in natural mineral Realgar from Nevada, USA, freshly exposed bulk, insulator) 307 (Arsenic (III) sulfide in natural mineral Orpiment from Nevada, USA, freshly exposed bulk, insulator) 317 As<sub>2</sub>S<sub>3</sub>(Copper (II) sulfide in natural mineral Covellite, dark blue region after ethanol wipe, conductive) CuS 326 (Copper (II) sulfide in natural mineral Covellite, dark blue region, ion etched 20 seconds, conductive) CuS 329 $FeS_2$ (Iron (IV) sulfide in natural mineral Pyrite, freshly exposed bulk, conductive) 340 (Mercury sulfide in natural mineral Cinnabar from Ukraine, Russia, freshly exposed bulk, insulator) HgS 348 (Molybdenum (IV) sulfide, freshly exposed bulk, conductive) MoS<sub>2</sub> 356 PbS (Lead (II) sulfide in natural mineral Galena from Missouri, USA, freshly exposed bulk, conductive) 360 TaS<sub>2</sub> (Tantalum (IV) sulfide "crystal", as received, conductive) 367 (Tantalum (IV) sulfide "crystal", after peeling away two surface layers, conductive) 374 $TaS_2$ (Zinc sulfide film, as received, insulator) ZnS 381 **CARBIDES** NbC (Niobium carbide, 97% Aldrich, ion etched to minimize oxygen content, conductive) 383 TaC (Tantalum carbide, 99%, Aldrich, ion etched 2 minutes to minimize oxygen content, conductive) 390 (Vanadium carbide, 98%, Aldrich, ion etched 2 minutes to minimize oxygen content, conductive) VC 397 **BORIDES** 404 Ni<sub>3</sub>B (Nickel boride powder, purity?, Kyoritsu Ceramic Materials, ion etched 2 minutes, conductive) (Tungsten boride powder, purity?, Japan New Metal, ion etched 2 minutes, conductive) WB 411 **ACETATES** BaOAc (Barium acetate powder, Kanto Chemical, pressed onto indium foil, insulator) 418 RbOAc (Rubidium acetate powder, freshly ground, insulator 426



#### MISCELLANEOUS MATERIALS

Cleaning agent	(MicroLab cleaning solution smeared onto gold plate as a very thin film, conductive)	430
Copper foil – heated in air	(Copper foil heated in air at >600C to produce dark brown wrinkled film, conductive)	438
Copper Phthalocyanine	(Copper phthalocyanine, as received, 4 monolayers on silicon wafer, conductive)	445
Double sided adhesive tape	e (Double sided adhesive tape from 3M Co., Scotch brand, as received, insulator)	452
Jewelry	(Metal ball on a ring became black after cleaning with jewelry cleanser)	458
Jewelry	(Metal ball on a ring became gray after cleaning with jewelry cleanser)	460
Loctite <sup>TM</sup> #414	(Loctite cyanoacrylate #414 instant glue on glass, as received, insulator)	462
Loctite <sup>TM</sup> #493	(Loctite cyanoacrylate #493 instant glue on glass, as received, insulator)	467
Mold release agent	("EASE" release 300 mold release agent smeared onto gold plate as very thin film, insulator)	473
Silicone remover agent	(Silicone oil remover from SLIDE Co. smeared onto gold plate as very thin film, conductive)	480
Tin plated wire	("Bad" sample with wrong color of tin plating coating, conductive)	486
Tin plated wire	("Good" sample with correct color of tin plating coating, conductive)	491
Black Widow spider web	(Black Widow spider web, non-sticky bundle, as received, insulator)	496
Contamination study	(Aluminium kitchen foil control sample, as received not touched with glove, conductive)	501
Contamination study	(Aluminium kitchen foil contaminated by touching surface with soft vinyl glove, conductive)	504
Borosilicate glass	("Soft" borosilicate glass from Asahi Glass, as received, insulator)	507
Pyrex <sup>TM</sup> glass	(Pyrex <sup>TM</sup> glass produced by Iwaki Glass, freshly exposed bulk, insulator)	510
Soda-lime glass	(Soda-lime glass used as microscope slide, as received, insulator)	518

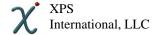


#### INTRODUCTION

This handbook contains wide scan spectra and narrows scan spectra from the Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides, Acetates, Carbides, Borides & Misc.. The elements have been analyzed under conditions that have maximized the accuracy of the binding energies. Please refer to section "F" (Energy Scale Reference Energies and Calibration Details) for more details about calibration.

#### Volume 5 – Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides, Carbides, Borides, Acetates, & Misc.

Includes wide scan spectra, principal metal signal high energy resolution spectra, some secondary metal signal high energy resolution spectra, carbon (1s) high energy resolution spectra, oxygen (1s) high energy resolution spectra, valence band spectra, and Auger signal spectra obtained from CeO<sub>2</sub>, Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub>, Tb<sub>3</sub>O<sub>7</sub>, Tm<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, Cd(OH)<sub>x</sub>, Co(OH)<sub>2</sub>, Cu(OH)<sub>2</sub>, FeO(OH), LiOH, Mg(OH)<sub>2</sub>, Ni(OH)<sub>2</sub>, (BiO)<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, CaCO<sub>3</sub>, CaCO<sub>3</sub>, CdCO<sub>3</sub>, CuCO<sub>3</sub>, CuCO<sub>3</sub>, CuCO<sub>3</sub>-Cu(OH)<sub>2</sub> (Azurite), Li<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub>, MgCO<sub>3</sub>, MgCO<sub>3</sub>, MgCO<sub>3</sub>, MgCO<sub>3</sub>, MgCO<sub>3</sub>, Y<sub>2</sub>CO<sub>3</sub>, Y<sub>2</sub>CO<sub>3</sub>-LaB<sub>6</sub>, AlN, BN, CrN, Si<sub>3</sub>N<sub>4</sub>, TiN, Ag<sub>2</sub>S (Argentite), As<sub>2</sub>S<sub>2</sub> (Realgar), As<sub>2</sub>S<sub>3</sub> (Orpiment), CuS (Covellite), FeS<sub>2</sub> (Pyrite), HgS (Cinnabar), MoS<sub>2</sub> (natural), PbS (Galena), TaS<sub>2</sub>, ZnS, NbC, TaC, VC, Ni<sub>3</sub>B, WB, BaOAc. RbOAc, Cleaning solution, Heat treated copper foil, Copper Phenyl Cyanine, Double sided adhesive tape (3M<sup>TM</sup>), Jewelry, Loctite<sup>TM</sup> #414, Loctite<sup>TM</sup> #493, Mold release agent, Silicone remover agent, Tin plated wire, Black Widow spider web. Borosilicate glass, Pyrex<sup>TM</sup> glass, and Soda-lime glass. Atomic percentage abundance tables are provided as guidelines for the user.



#### 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 binary oxide called "aluminium oxide" the user will find the chemical abbreviation " $Al_2O_3$ " 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 "Antimony Oxide" spectra will be found by looking for the chemical formula: " $Sb_2O_3$ ".

#### **Contents of Each Set of Spectra**

The spectra are presented exactly as printed by the Spectral Data Processor software 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 a few key words about the analysis conditions.

The second page of each set is the wide scan survey spectrum with information about the experimental conditions used to collect the spectrum, the history of the sample, the source of the sample if known, and peak labels. 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 next 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 normally contained 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 without any charge correction because there is currently no standard method or standard reference energy for charge referencing spectra from insulating materials. 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).

In this edition the spectra do not have labels which identify the XPS signal so the reader needs to refer to the energy range to determine which signal has been reported. In many cases valence band region spectra, Auger signal spectra, and spectra from weaker XPS signals are also included, but only for materials which were expected to be commercially pure.

#### **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 produce clean surfaces which would make charge referencing of insulators 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. Our spectra are designed to be practical tools for everyday use and were obtained under practical working conditions. We have not actually attempted to produce research grade spectra, but we have, in fact, produced research grade spectra because of our self-consistent methods.

In the production of these spectra no attempt to produce a pure, clean surface, but an effort was made to produce surfaces with a minimum amount of natural surface contamination. 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.

#### 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. This software allows the user to control 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 many spectra and also the energy interval between spin-orbit couple signals which were derived from pure element spectra. No attempt was made to fit the spectra in accordance with theoretical expectations or calculations.

The 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 most peak-fits. Peak shapes for the main XPS signals from chemical compounds (e.g. oxides or polymers,)were typically optimized by using a Gaussian:Lorentzian ratio between 80:20 and 90:10. For pure metals Gaussian:Lorentzian ratio for the main XPS signals was normally between 50:50 and 70:30. For the main XPS signals from semi-conductor materials, the Gaussian:Lorentzian ratio was usually 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.

#### **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 2-4 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 null.

The mesh-screen is understood to function as a electron cut-off lense with some tendency to allow incoming flood gun electrons to focus on the area being irradiated with monochromatic X-ray beam because the X-ray beam does not have a uniform flux density of 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.

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

#### **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. 1mm = 1 mm height used for the mesh-screen, semi-con = semi-conductive behavior conduc. = conductive behavior Tech = technical grade purity,



#### INSTRUMENT AND ANALYSIS DETAILS USED TO MAKE XPS SPECTRA

#### A. Instrument Details

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 (Constant) 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) Al $^\circ$  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 in X-Probe)

Angle of X-ray Incidence:  $\alpha = 71^{\circ}$  (relative to sample normal) Electron Emission Angle:  $\beta = 0^{\circ}$  (relative to sample normal)

Angle Between X-ray Axis and Electron Analyzer Axis:  $\phi = 71^{\circ}$  (fixed, non-variable)

X-ray Type:

Pass Energy of Analyzer: 150 V for Resolution 4 setting 100 V for Resolution 3 setting

50 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:  $\sim 1 \text{ mm}^2 \text{ for b} = 0^\circ \text{ at } 1000 \text{ eV KE}$ 

Electron Collection Lens Efficiency: 7% over  $2\pi$  steradians

Sample Surface to Tip of Electron Collection Lens Distance: ~33 mm



X-ray Crystal to Sample Surface Distance: ~190 mm X-ray 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, resistive anode, 40 mm X 40 mm

electronically defined as 128 active channels with max ct rate 1,000,000

Dead Time: normally zero (unless ion etching pure element while collecting XPS data)

Base Pressure: 4.  $\times 10^{-10}$  torr Normal Operating Pressure: 1.6  $\times 10^{-9}$  torr

FWHM of X-rays Diffracted by natural SiO2: ~0.25 eV

Power Settings: 200 Watts in a 250 x1100 µ X-ray beam

X-ray Induced Current:  $1.1 \times 10^{-9}$  amps for a 600  $\mu$  spot in X-Probe Converted from amps to watts

Approximate True X-ray Power :  $\sim 6 \times 10^{-6} \text{ W in a } 600 \text{ } \mu \text{ spot}$ 

Approximate True X-ray Irradiance: ~8 W/m<sup>2</sup>

Approximate True X-ray Photon Flux: ~7 x 10<sup>9</sup> 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 eVValence band scans were done at PE=150 eV

X-ray Beam Size Used: Wide scans:  $250 \times 1500 \,\mu$  ellipse (at  $90^{\circ}$  TOA)

(for S-Probe) 250 x 1100  $\mu$  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 90% transmission (20  $\mu$  diameter wire with 200  $\mu$ 

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. This 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)

XPS International LLC

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
Intensity Scaling: None

#### D. Sample Details

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, e.g. 90 which reports the 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 Used for Element Series

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 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**

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**

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 in Tsukuba Japan has provided a series of various binary alloys made of AuCu and CoNi alloys.

#### **Sources of Semi-Conductor Materials**

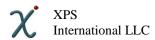
Over the course of many years, many people in the Japanese semi-conductor business have given samples of various semi-conductor materials in crystalline wafer form. Various samples were donated by the Oki Electric Company, Mitsubishi Materials, Canon, and various universities. The source of each material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

#### **Sources of Binary Oxide Samples**

Most of the commercially pure binary oxides were purchased from the Aldrich Chem. Co.. Many 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  $(Ag^{\circ})$  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 (FWHM) and Resolution Variables

Element (XPS signal)	Resulting FWHM	Resolution Setting	Pass Energy	X-ray Spot Size
Si (2p <sub>3/2</sub> ) crystal - fractured edge	0.38 eV	5	10 eV	40 x 250μ
Si (2p <sub>3/2</sub> ) crystal - fractured edge	0.43 eV	1	25 eV	80 x 350μ
Au (4f <sub>7/2</sub> ) foil - ion etched clean	0.64 eV	5	10 eV	250 x 1000μ
Au (4f <sub>7/2</sub> ) foil - ion etched clean	0.79 eV	1	25 eV	250 x 1000μ
Au (4f <sub>7/2</sub> ) foil - ion etched clean	0.86 eV	2	50 eV	250 x 1000μ
Au (4f <sub>7/2</sub> ) foil - ion etched clean	1.40 eV	4	150 eV	250 x 1000μ
Ag (3d <sub>5/2</sub> ) foil - ion etched clean	0.42 eV	5	10 eV	40 x 250μ
Ag (3d <sub>5/2</sub> ) foil - ion etched clean	0.64 eV	1	25 eV	40 x 250μ
Ag (3d <sub>5/2</sub> ) foil - ion etched clean	0.75 eV	2	50 eV	40 x 250μ
Ag (3d <sub>5/2</sub> ) foil - ion etched clean	1.00 eV	3	100 eV	40 x 250μ
Ag (3d <sub>5/2</sub> ) foil - ion etched clean	1.30 eV	4	150 eV	40 x 250μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	0.85 eV	5	10 eV	250 x 1000μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	0.94 eV	1	25 eV	250 x 1000μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	1.06 eV	2	50 eV	250 x 1000μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	1.60 eV	4	150 eV	250 x 1000μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	0.85 eV	5	10 eV	150 x 800μ
Cu (2p <sub>3/2</sub> ) foil - ion etched clean	0.96 eV	1	25 eV	150 x 800μ
Cu (2p <sub>3/2</sub> ) 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

#### From May 1986 to January 1993

Energy Scale Reference Energies: 932.47 eV for Cu (2p<sub>3/2</sub>) signal

122.39 eV for Cu (3s) signal

83.96 eV for Au (4f<sub>7/2</sub>) signal

Binding Energy Uncertainty: less than  $\pm 0.08$  eV Digital-to-Analog (DAC) Conversion Setting: 163.88

#### **After January 1993**

 $Energy \ Scale \ Reference \ Energies: \qquad 932.67 < \pm 0.05 \ eV \ for \ Cu \ (2p_{3/2}) \ signal$ 

 $122.45 < \pm 0.05$  eV for Cu (3s) signal

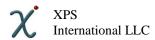
 $83.98 < \pm 0.05$  eV for Au (4f<sub>7/2</sub>) signal

Observed Reference Energy: 75.01 <±0.05 eV for Cu (3p3) signal

Binding Energy Uncertainty: less than  $\pm 0.08$  eV Digital-to-Analog (DAC) Conversion Setting: 163.87

#### 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 again rises to a 285.2-286.5 eV range (columns 12-14). 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 may or may not influence the binding energy as well.

#### **Instrument Stability and Long Term Calibration**

Initially each of the three 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 three 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  $<\pm0.10\,\mathrm{eV}$ , but a few times rose to  $\pm0.15\,\mathrm{eV}$  or less. In a very rare case, the uncertainty rose to  $0.20\,\mathrm{eV}$ . 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 deg Centigrade. If the room temperature changes within a few hours time by more than 10 deg or the temperature of the DAC chip is changed by more than 10 deg, then a  $>0.1\,\mathrm{eV}$  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 (for the X-Probe System only)

#### **Instrument Response Functions**

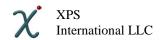
Instrument Response Function:  $Q(E)=E^{+0.27}$  for 150 eV PE (ref.3) Instrument Response Function:  $Q(E)=E^{+1.0}$  for 50 eV PE (ref.3)

#### Signal/Background 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

<sup>\*</sup> Using a 90° electron take-off-angle and a smooth Ag°/mylar film.

<sup>\*\*</sup> 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	0.7	1.1	1.3	1.5
V1 Offset	30	55	105	155
V1 Slope	0.600	0.611	0.676	0.709

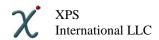
<sup>\*</sup> These pass energies include corrections for instrument work function. True pass energies were set to 25, 50, 100, and 150 eV ±0.1 eV.

#### 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 0.5mm 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 other instruments. A 0.1mm 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 causes 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"

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) 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  $\pm 10\%$  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. 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 possible 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 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  $\pm 1$ -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, this method requires a little extra effort to avoid the satellites associated with 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 slightly larger than desirable error by comparison to the other materials listed above. For that reason Teflon is a less desirable material to test the sensitivity exponents.

#### 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.

#### 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."

#### **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 t



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 HP's high precision, high voltage meters.

#### 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 (Throughput) Function

Copper, gold and silver data obtained from the M-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, M-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 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  $\pm 0.08$  eV used for routine instrument calibration.

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

1. Robert L. Chaney, Surface and Interface Analysis, 10, 36-47 (1987)

2. Noel H. Turner, Surface and Interface Analysis, 18, 47-51 (1992)

3. M. P. Seah, Surface and Interface Analysis, 20, 243-266 (1993)

4. L.T. Weng et al, Surface and Interface Analysis, 20, 179-192 (1993)

5. L.T. Weng et al, Surface and Interface Analysis, 20, 193-205 (1993)

6. B. Vincent Crist, Surface Science Spectra, 1, 292-296 (1993)

7. B. Vincent Crist, Surface Science Spectra, 1, 376-380 (1993)

[re: X-Probe]

[re: Quantitation]

[re: Response Function]

[re: Response Function]

[re: Response Function]

[re: KBr spectra]

[re: Ar/C spectra]



# Spectra of Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides, Carbides, Borides, Acetates, & Miscellaneous Materials



#### Detailed Surface Composition Table

File name: CEO2.MRS

Region:

Description: CeO2 RMC 3mm plt 90 TOA #70202-13

(mesh at 1mm)

Operator:

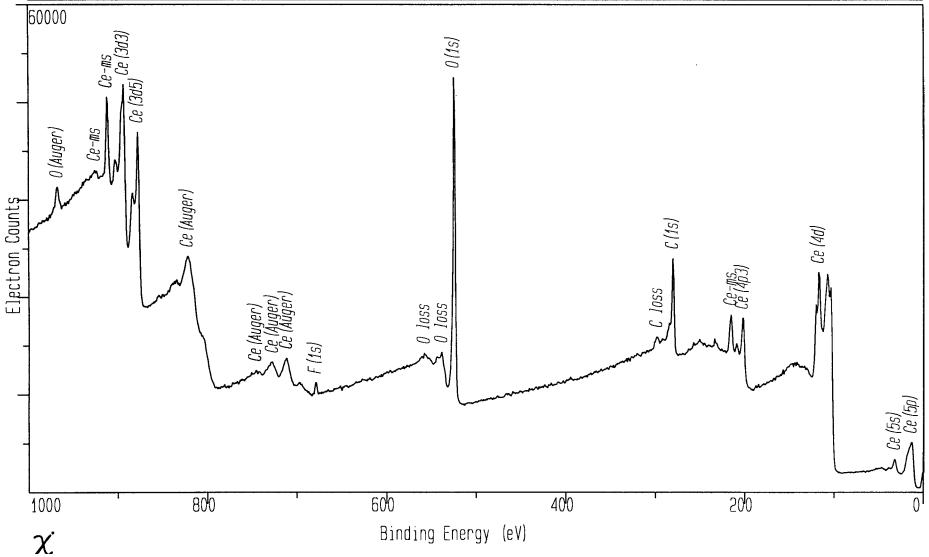
V. Crist

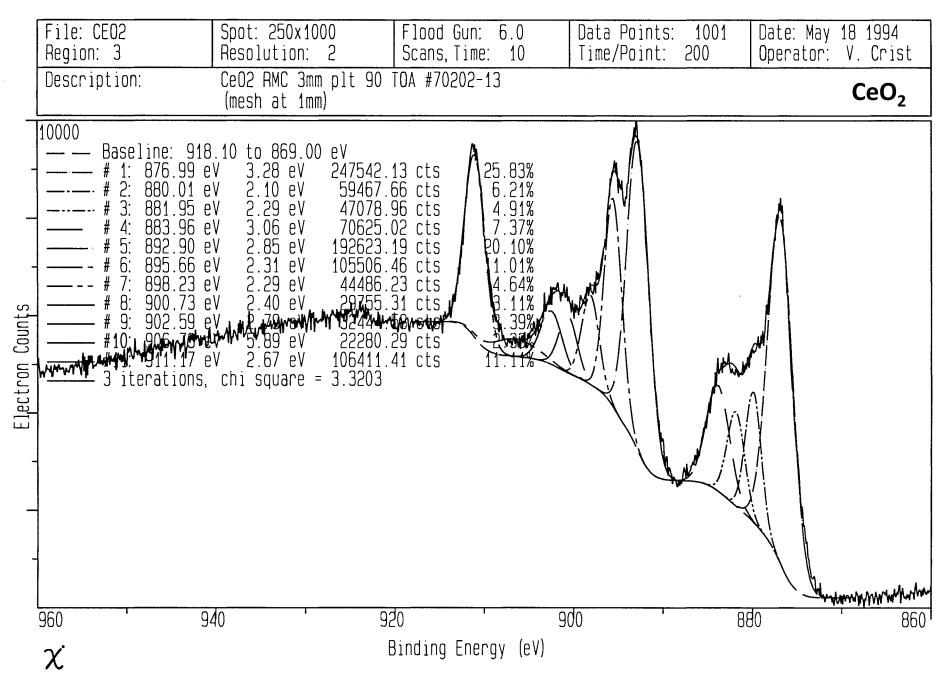
Date:

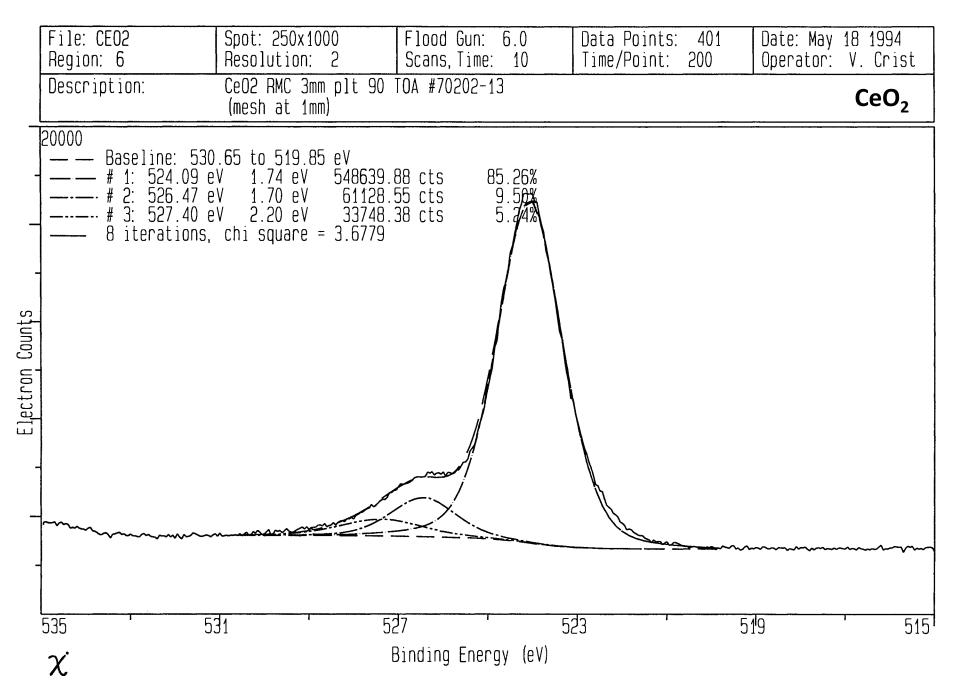
Wed May 18 22:26 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom &
O Auger	973.1	967.7	0.00	7546	0	
Ce-ms	931.1	925.7	0.00	2796	0	
Ce-ms	917.0	911.6	0.00	12908	0	
Ce3d3	898.9	893.6	9.71	36913	3802	
Ce3d5	883.0	877.6	14.44	58106	4024	
CeAuger	827.0	821.6	0.00	52841	0	
CeAuger	750.5	745.2	0.00	2102	0	
CeAuger	732.8	727.4	0.00	7295	0	
CeAuger	716.9	711.5	0.00	10557	0	
* F 1s	684.1	678.7	2.86	2060	720	1.12
O loss	562.9	557.5	0.00	4537	0	
O loss	543.6	538.2	0.00	11426	0	
* 0 1s	529.5	524.1	2.29	62352	27173	42.12
C loss	302.8	297.4	0.00	2693	0	
* C 1s	285.0	279.6	1.00	21617	21519	33.36
Ce-ms	219.9	214.5	0.00	8432	0	
Ce4p3	206.5	201.1	3.27	11066	3389	
* Ce4d	122.7	117.3	9.92	149823	15098	23.40
Ce5s	36.5	31.1	0.28	4114	14492	
Ce5p	17.7	12.3	0.83	19476	23573	

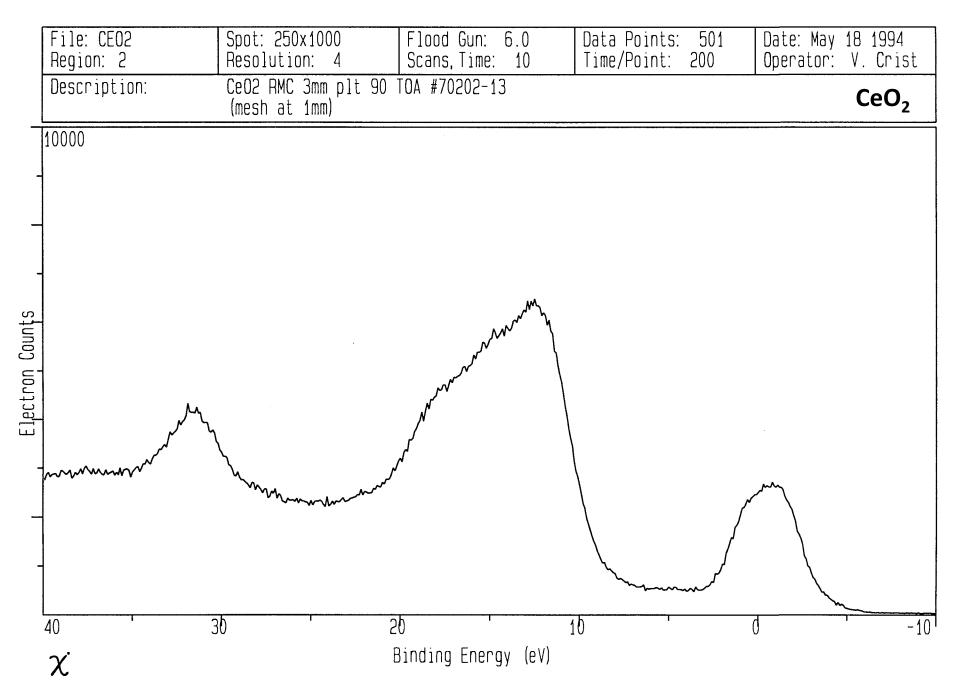
File: CEO2	Spot: 250x1000	Flood Gun: 6.0	Data Points: 1024	Date: May 18 1994
Region: 1	Resolution: 4	Scans, Time: 10	Time/Point: 200	Operator: V. Crist
Sample Description:	CeO2 RMC 3mm plt 90 T( (mesh at 1mm)	)A #70202-13		CeO <sub>2</sub>







	File: CEO2 Region: 5	Spot: 250x1000 Resolution: 2	Flood G Scans, T	ime: 5	Data Points: Time/Point:	201 200	Date: May 18 19 Operator: V. C	94 Crist
	Sample Description:	CeO2 RMC 3mm plt 90 TO (mesh at 1mm)	A #70202	2-13			Ce	<b>O</b> <sub>2</sub>
		1.50 eV 1754.30 1.31 eV 1218.69	cts cts	79.22% 4.10% 2.85% 13.82%				
Lipetron Counts	~~~~					V	M	~~~
	290 ' 28 <b>X</b> .	36 28 E		tnergy (eV)	<b>'8</b>	27	'4	270 <sup>1</sup>



#### Detailed Surface Composition Table

 $Dy_2O_3$ 

File name: D

DY203.MRS

Region:

Description: Dy203 99.99% Aldr lot# 02803KV 3 mm plt, 90 TOA

mesh at 1mm

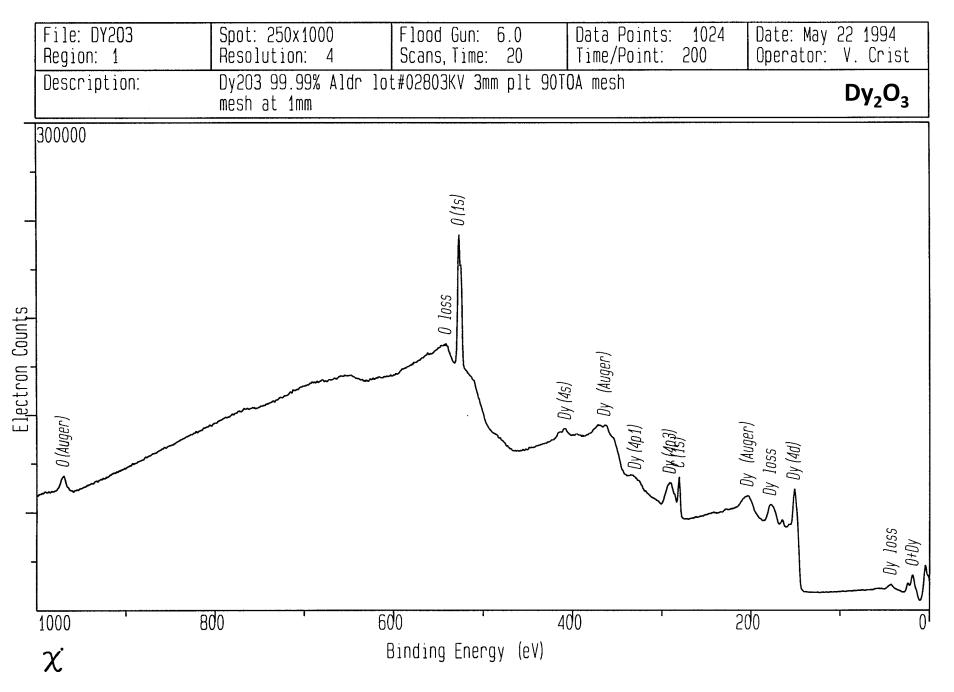
Operator:

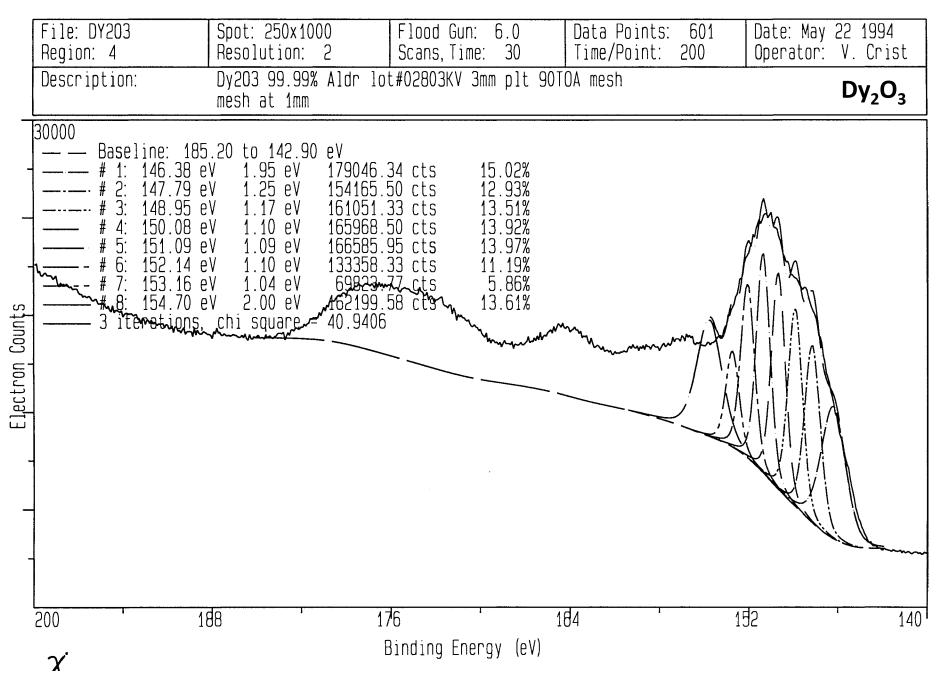
V. Crist

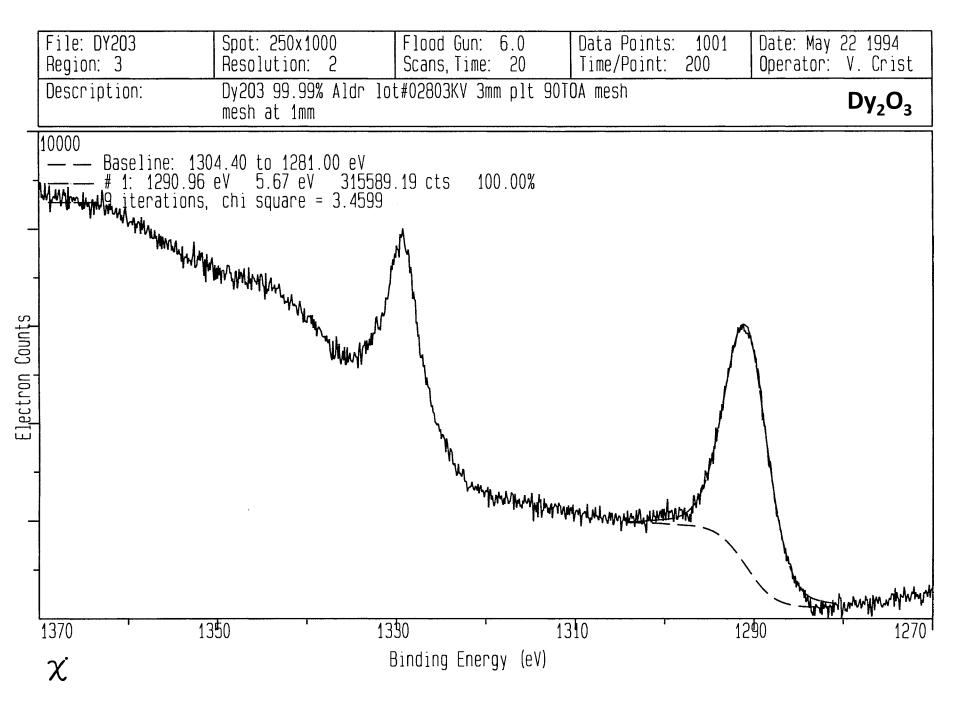
Date:

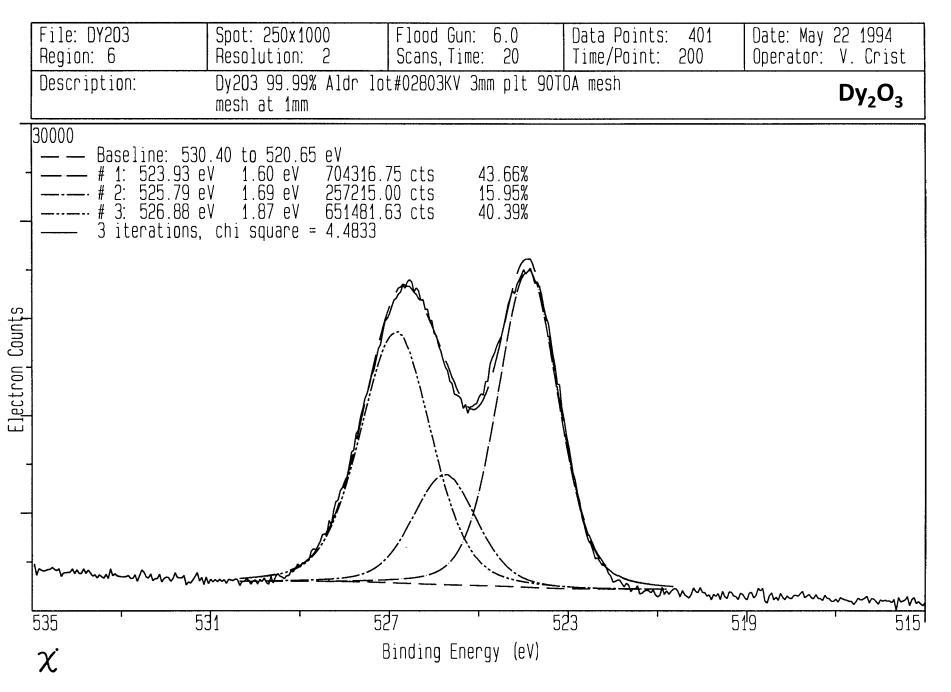
Sun May 22 06:58 1994

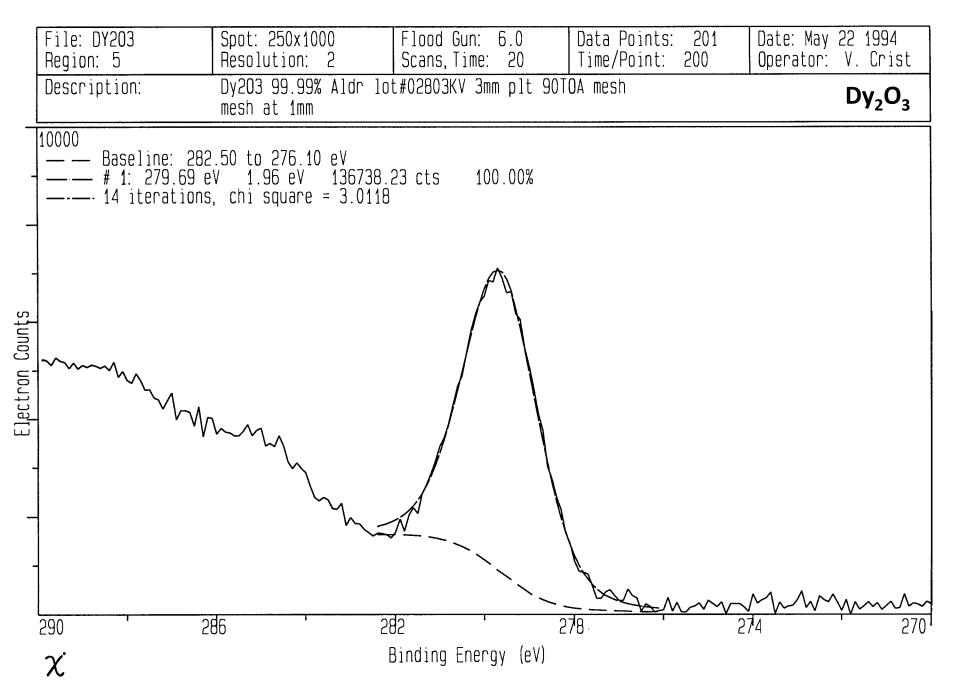
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom &
O Auger	97 <del>5.</del> 7	969.7	0.00	18882	0	
Dy Auger	660.9	654.9	0.00	15046	0	
* 0 1s	532.9	526.9	2.24	100434	44893	72.97
Dy Auger	413.6	407.6	0.00	15357	0	
Dy Auger	377.5	371.5	0.00	134373	0	
Dy auger	349.1	343.1	0.00	9142	0	
Dy4p3	296.3	290.3	4.09	21320	5207	
* C 1s	286.5	280.5	1.01	10219	10157	16.51
Dy auger	209.3	203.3	0.00	39552	0	
* Dy4d	157.5	<b>151.</b> 5	12.97	83932	6471	10.52
Dy5p	24.6	18.6	1.04	24734	23700	

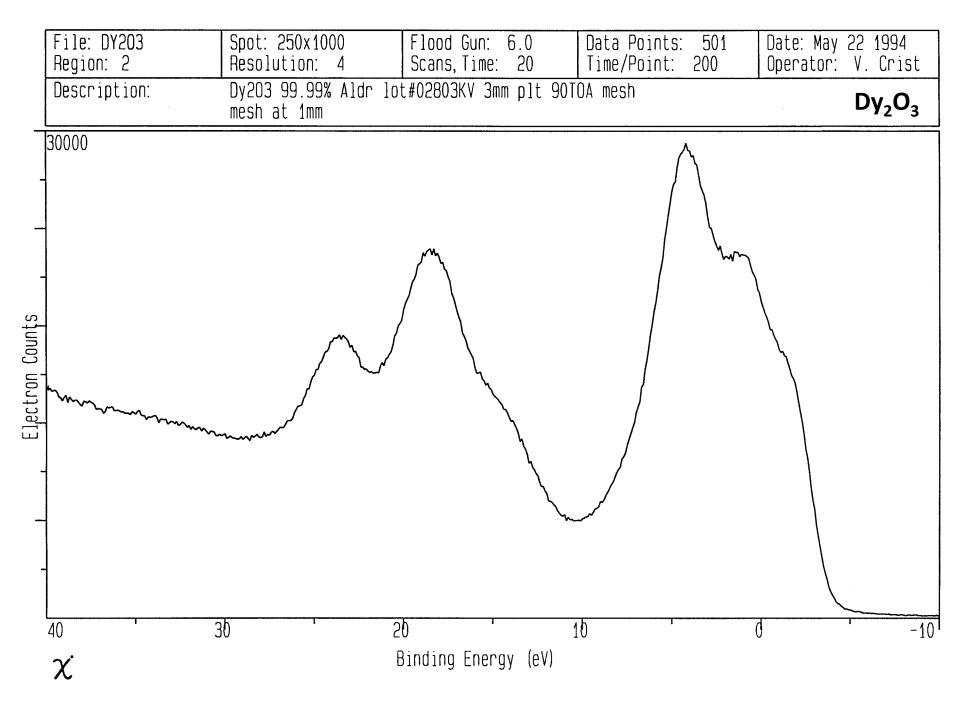












Er<sub>2</sub>O<sub>3</sub>

File name:

ER203\_2.MRS

Region:

1

Description: Er203 99.99% Aldr lot#02413KV 3 mm pellet 90 Deg TOA

mesh at 1mm

Operator:

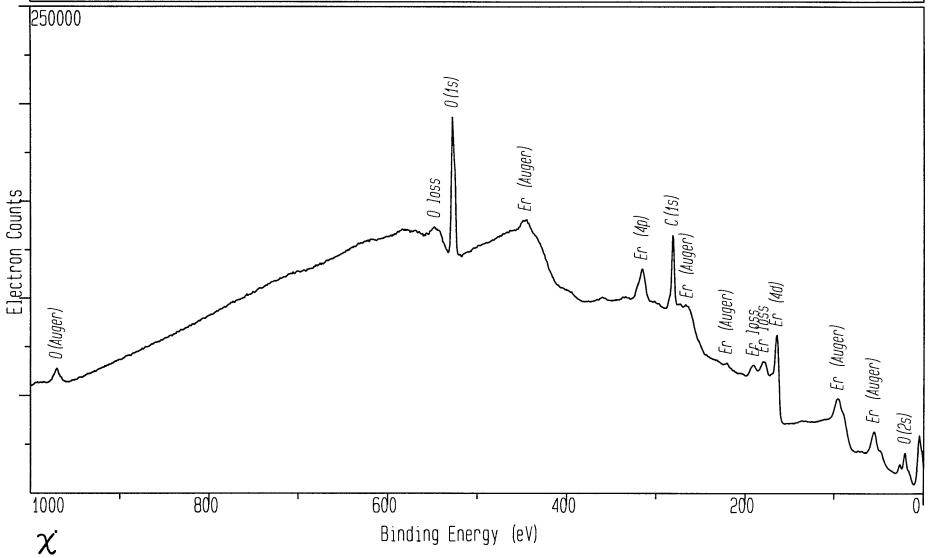
V. Crist

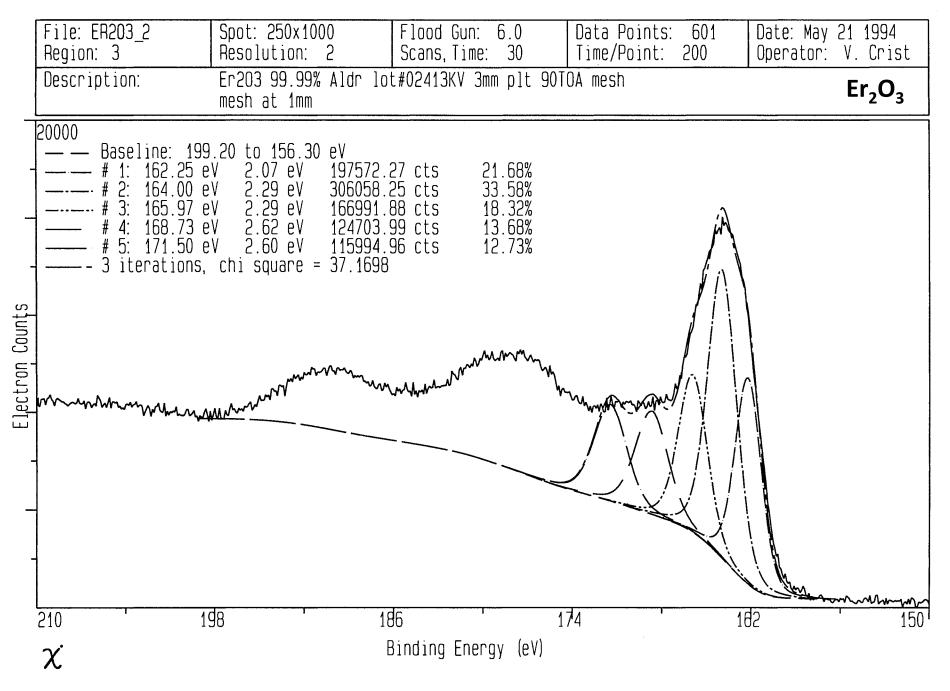
Date:

Sat May 21 06:25 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom %
0 Auger	975.2	970.6	0.00	13777	0	
O loss	551.9	547.4	0.00	28879	0	
* 0 1s	531.8	527.2	2.29	76135	33298	40.73
Er Auger	449.3	444.8	0.00	98378	0	
Er (4p)	319.5	315.0	6.33	36669	5795	
* C 1s	285.0	280.5	1.00	38216	38072	46.57
Er Auger	268.6	264.1	0.00	13794	0	
Er Auger	224.7	220.1	0.00	2101	0	
Er loss	194.4	189.9	0.00	5868	0	
Er loss	183.5	179.0	0.00	9501	0	
* Er (4d)	168.3	163.7	14.76	153183	10381	12.70
Er Auger	99.8	95.2	0.00	67118	0	
Er Auger	59.0	54.5	0.00	40333	0	
O+Er	24.5	19.9	0.00	25043	0	

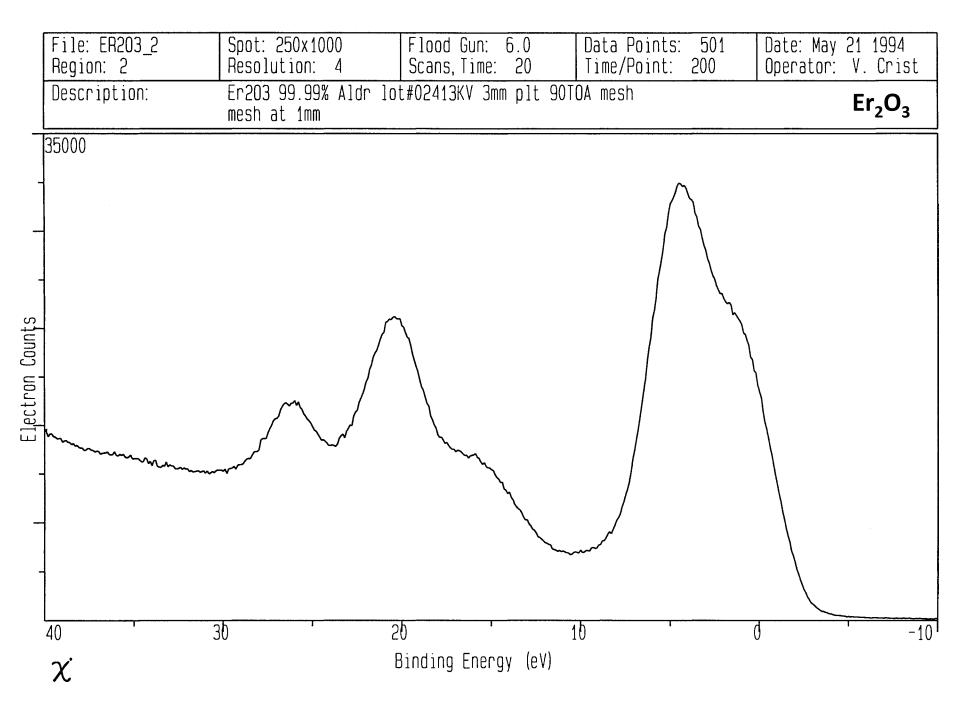
File: ER203_2 Region: 1	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 20	Data Points: 1024 Time/Point: 200	Date: May 21 1994 Operator: V. Crist
Description:				
250000				





File: ER2O3_2 Region: 5	Spot: 250x1000 Resolution: 2	Flood Gun: 6.0 Scans, Time: 20	Data Points: 401 Time/Point: 200	Date: May 21 1994 Operator: V. Crist
Description:		lot#02413KV 3mm plt		Er <sub>2</sub> O <sub>3</sub>
20000	110011 40 111111			
— — Baseline: 53 — — # 1: 524.51 — — # 2: 526.23 — # 3: 527.47	31.35 to 521.15 eV eV	3.34 cts 38.59% 1.81 cts 19.72% 4.75 cts 41.69%		
	Mary Marketing			Mmhmmmmmmm
535	531	527	523	519 ' 515
$\dot{\chi}$		Binding Energy (eV	)	

File: ER203_2 Region: 4	Spot: 250x1000 Resolution: 2	Flood Gun: 6.0 Scans, Time: 20	Data Points: 401 Time/Point: 200	Date: May 21 1994 Operator: V. Crist
Description:	Er203 99.99% Aldr l mesh at 1mm	ot#02413KV 3mm plt 90	TOA mesh	Er <sub>2</sub> O <sub>3</sub>
# 1: 280.01 e	V 1.81 eV 162963 V 1.80 eV 24909 V 2.28 eV 40492 chi square = 3.2628	282	278	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
χ̈́		Binding Energy (eV)		



 $Eu_2O_3$ 

File name:

EU203\_1.MRS

Region:

1

Description: Eu2O3 99.95% Aldr lot# 02914LV 3 mm plt 90 TOA

mesh at <1mm

Operator:

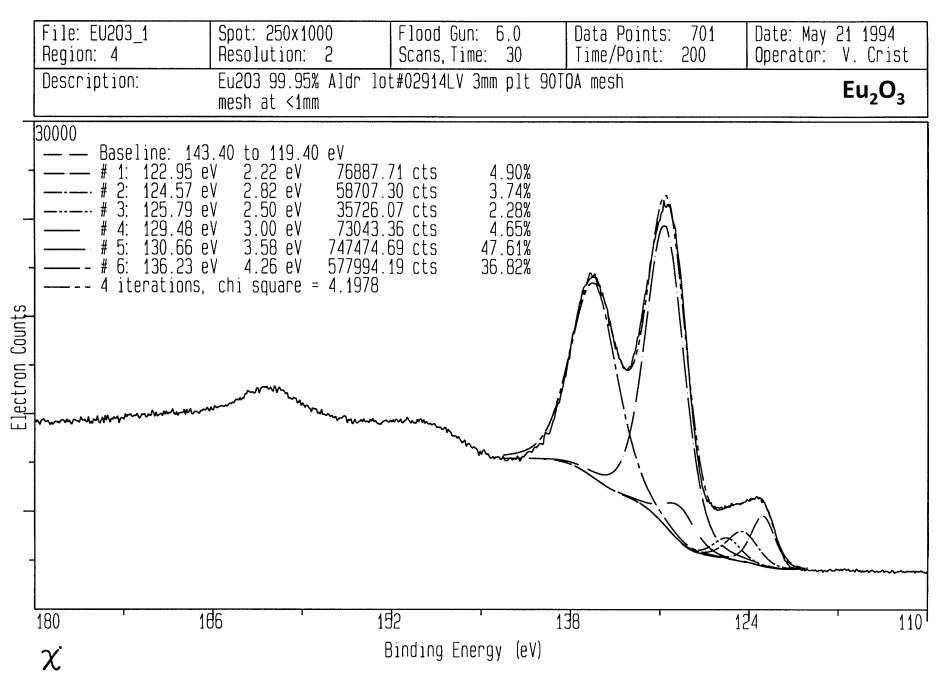
V. Crist

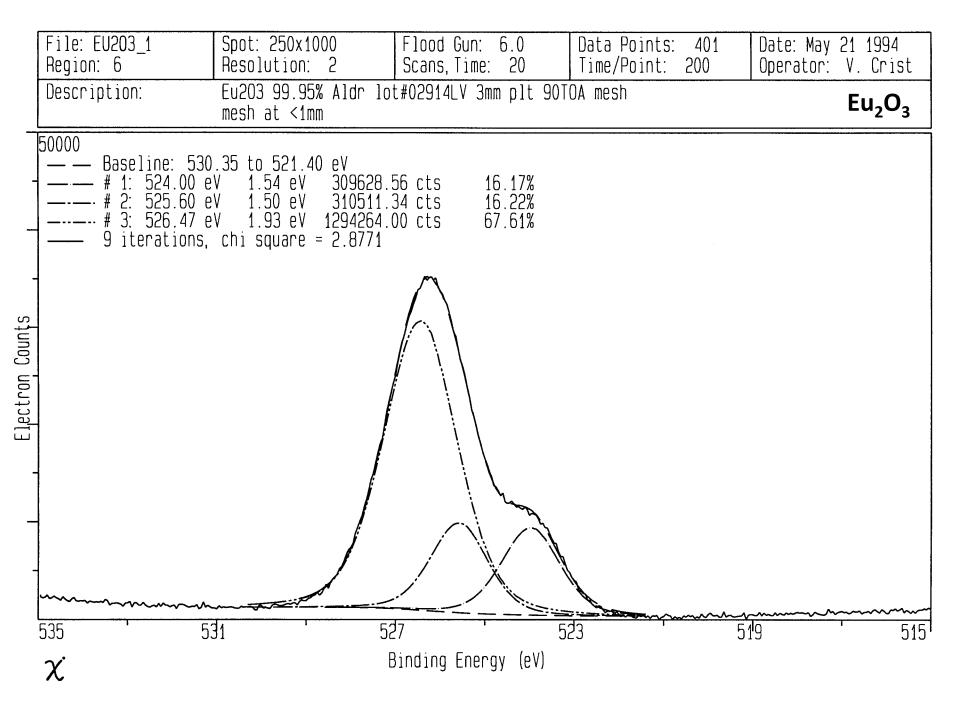
Date:

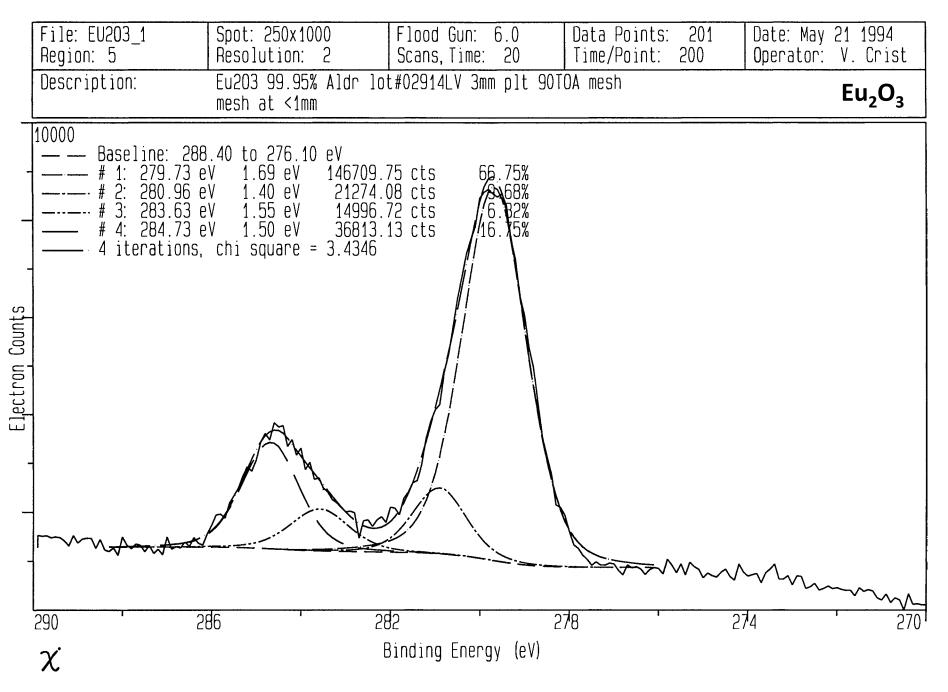
Sat May 21 23:55 1994

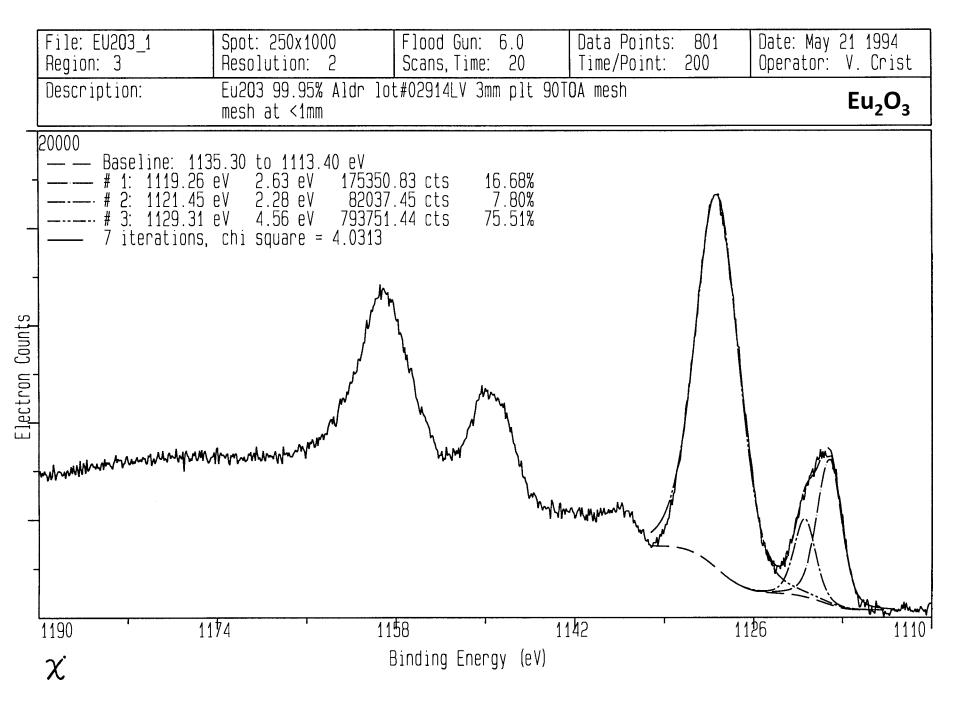
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom %
0 Auger	976.3	$9\overline{71}.2$	0.00	21515	0	
Eu Auger	762.7	757.5	0.00	6281	0	
Eu Auger	657.9	652.7	0.00	2774	0	
Eu Auger	637.0	631.9	0.00	40588	0	
O loss	549.1	544.0	0.00	22862	0	
* 0 1s	531.6	526.4	2.29	111319	48642	52.18
Eu Auger	516.8	511.7	0.00	9217	0	
Eu Auger	502.6	497.5	0.00	13127	0	
Eu Auger	479.8	474.7	0.00	6373	0	
Eu4s	364.6	359.5	1.36	27207	20001	
C loss	300.7	295.6	0.00	4211	0	
* C 1s	285.0	279.9	1.00	33334	33190	35.60
Eu4p3	260.6	255.5	3.82	35699	9347	
Eu loss	166.6	161.5	0.00	14082	0	
* Eu4d	135.6	130.5	10.24	116680	11391	12.22
O+Eu	21.6	16.4	0.00	22352	0	

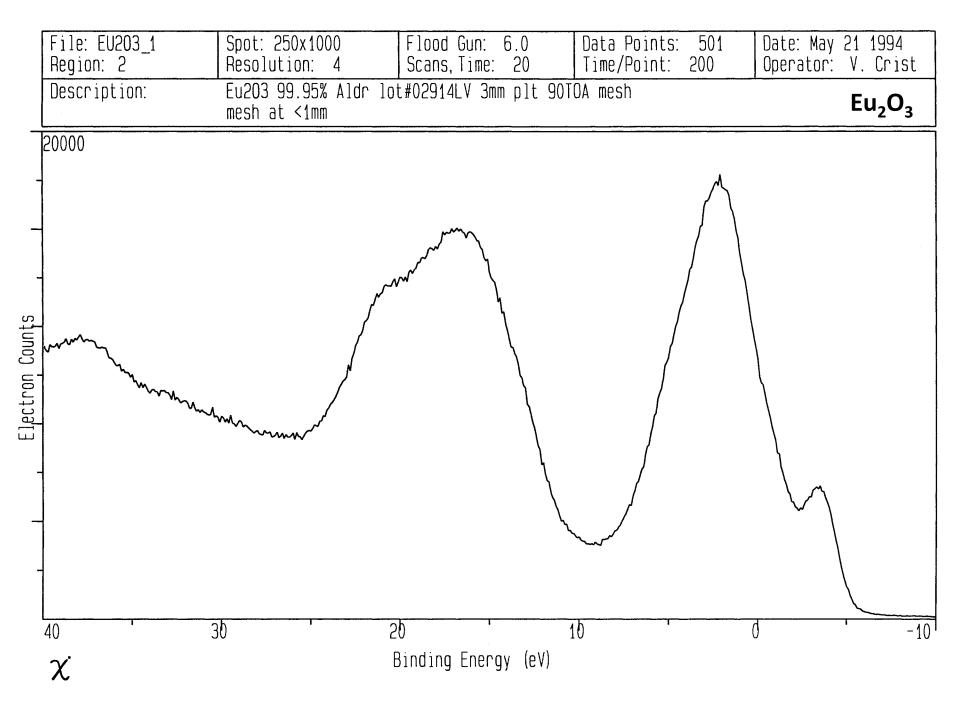
File: EU203_1 Region: 1	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 20	Data Points: 1024 Time/Point: 200	Date: May 21 1994 Operator: V. Crist
Description:	Eu203 99.95% Aldr lo mesh at <1mm	t#02914LV 3mm plt 90T	OA mesh	Eu <sub>2</sub> O <sub>3</sub>
Bectron Counts  (Auger)	$Fu \ (Auger)$ $Fu \ (Auger)$	Eu (Auger)	$ \begin{cases} Eu(4s) \\ C \log s \\ C(1s) \end{cases} $ $ Eu(4p3) $	$ \begin{array}{c} EU \ loss \\ 0 \ loss \\ 0 \ loss \end{array} $
1000 8		do ' 4 Binding Energy (eV)	do ' 2	200 01











File name: GD203\_1.MRS

Region:

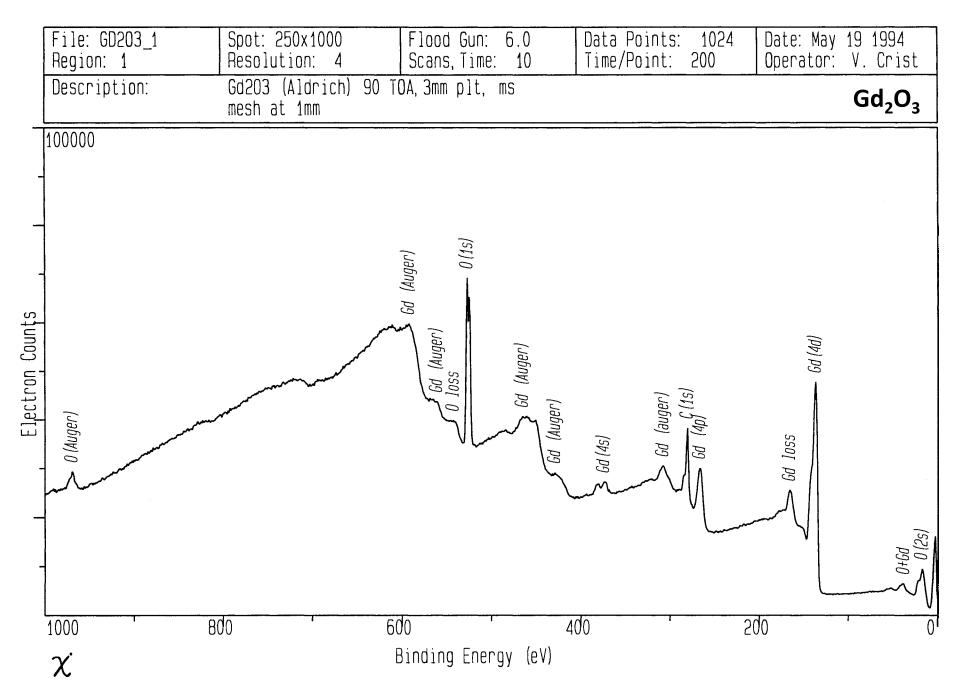
Description: Gd203 (Aldrich) 90 TOA, 3 mm plt,

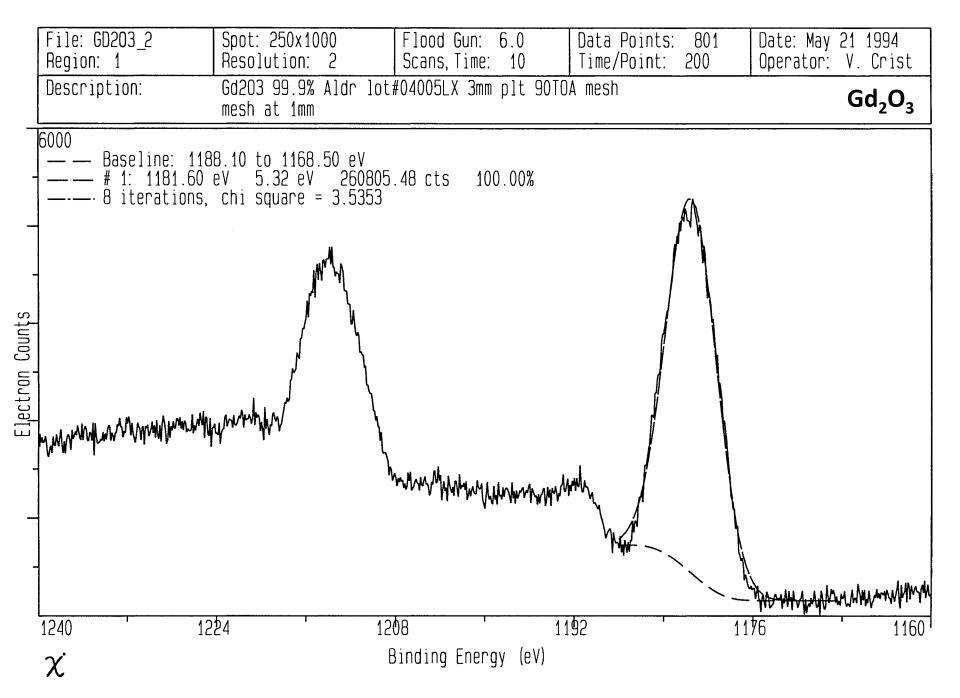
mesh at 1mm

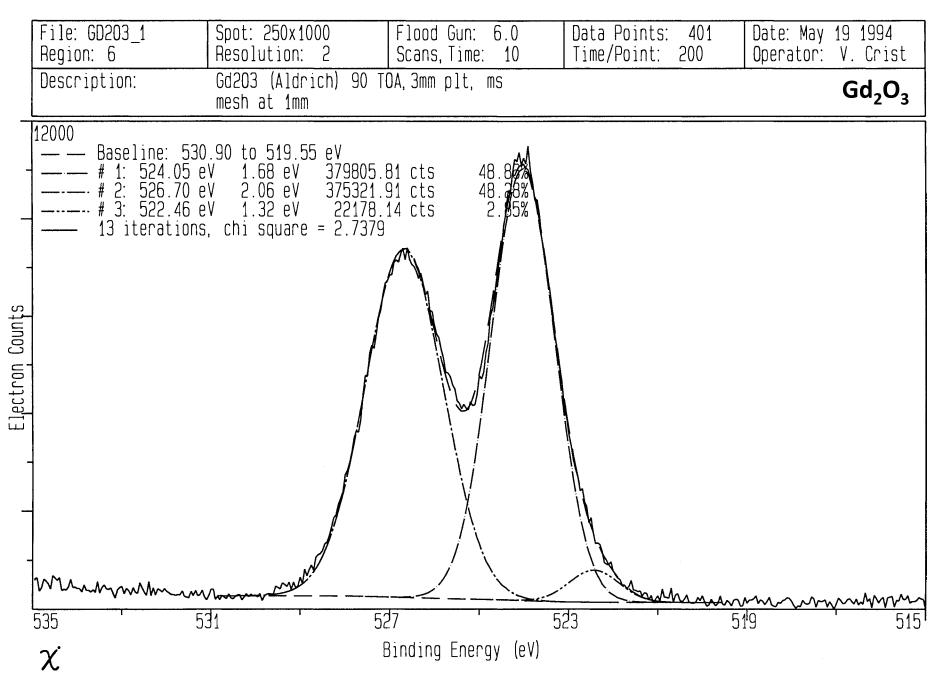
Operator: V. Crist

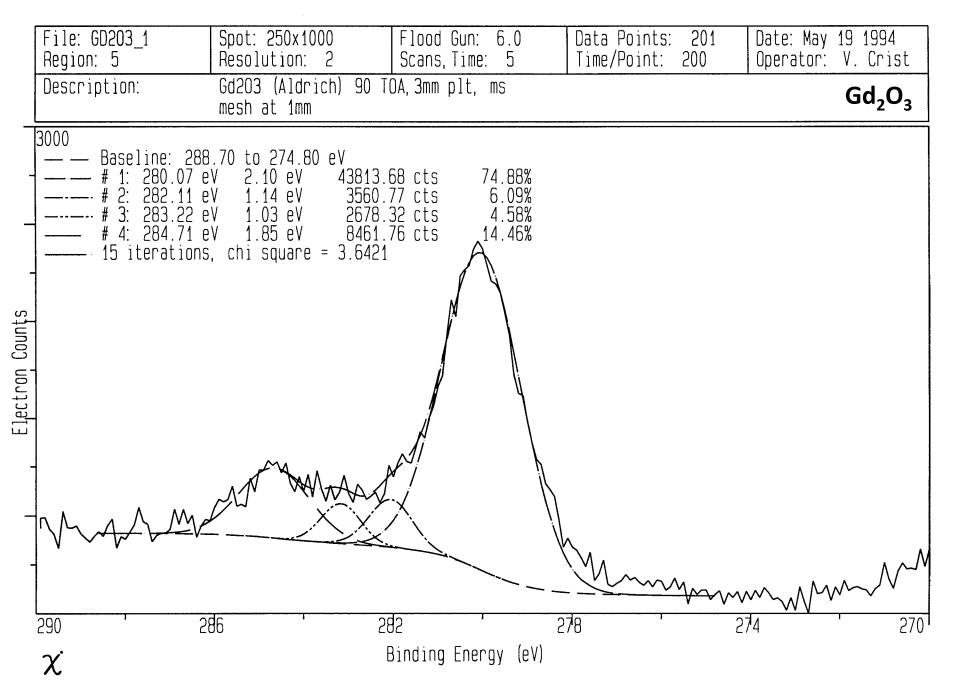
Date: Thu May 19 12:06 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom %
O Auger	974.3	969.3	0.00	13388	o	
Gd Auger	597.0	592.1	0.00	40237	0	
Gd Auger	565.8	560.8	0.00	6032	0	
O loss	547.2	542.2	0.00	9131	0	
* 0 1s	531.4	526.5	2.29	81942	35808	44.16
Gd Auger	469.5	464.6	0.00	17474	0	
Gd Auger	433.5	428.6	0.00	10345	0	
Gd4s	378.4	373.5	1.39	16228	11695	
Gd Auger	312.2	307.3	0.00	21933	0	
* C 1s	285.0	280.1	1.00	34177	34036	41.98
Gd (4p)	270.7	265.8	6.03	34737	5764	
Gd loss	170.1	165.2	0.00	17193	0	
* Gd4d	141.2	136.2	11.82	132870	11241	13.86
0+Gd	21.4	16.5	0.00	25704	0	









File: GD203_1 Region: 2	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 10	Data Points: 501 Time/Point: 200	Date: May 19 1994 Operator: V. Crist
Description:	Gd2O3 (Aldrich) 90 mesh at 1mm	TOA,3mm plt, ms		Gd <sub>2</sub> O <sub>3</sub>
20000				
Electron counts				
40 <b>X</b>	30	20 Binding Energy (eV)	10	d -10 <sup>1</sup>

File name: HO2O3.MRS

Region: 1

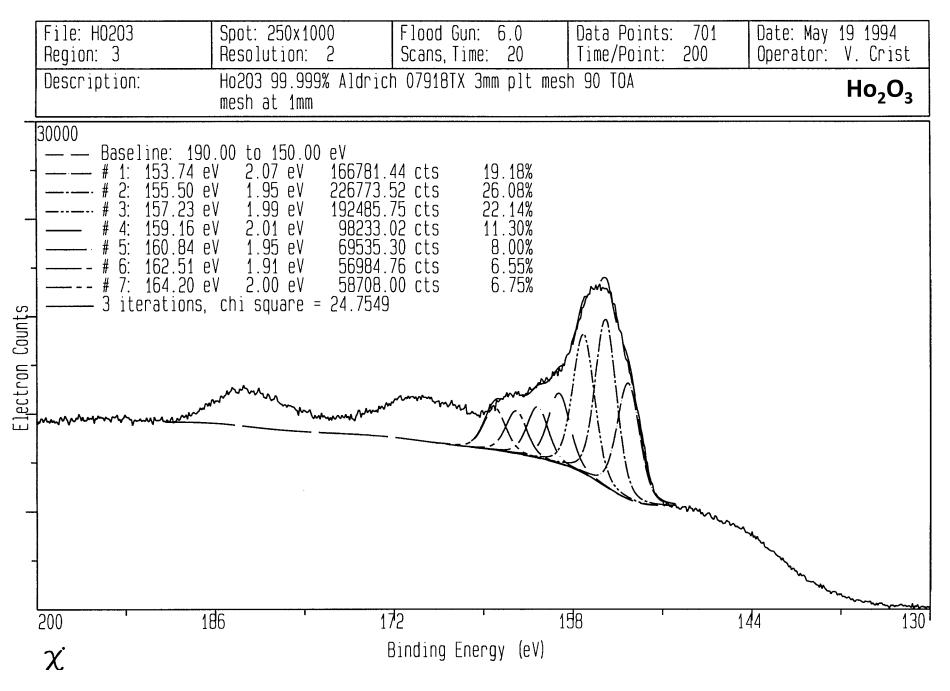
Description: Ho2O3 99.999% Aldrich 07918TX 3 mm pellet

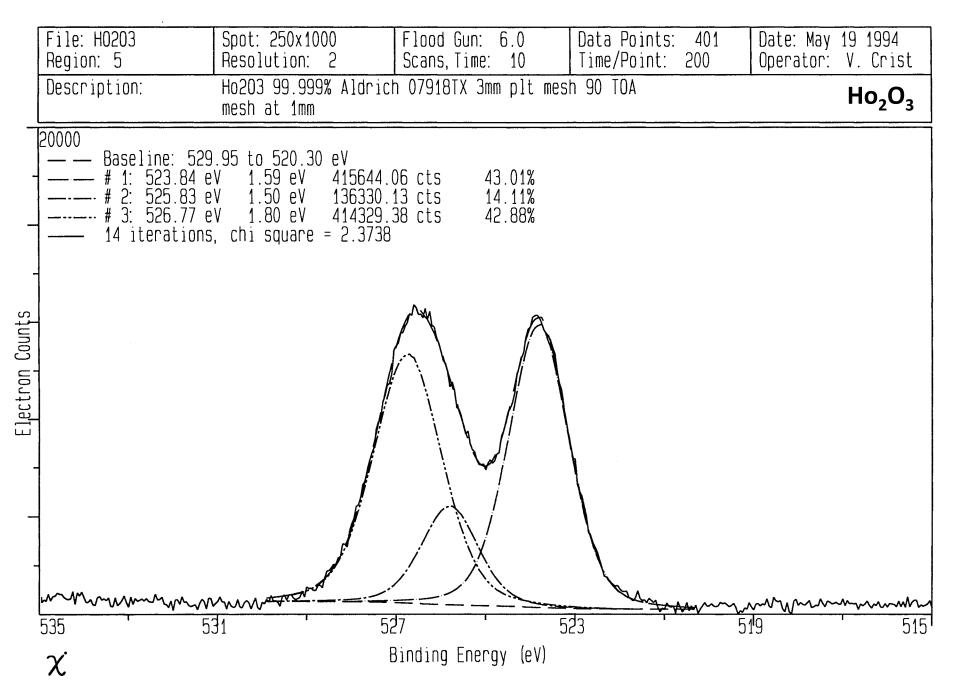
90 TOA mesh at 1mm

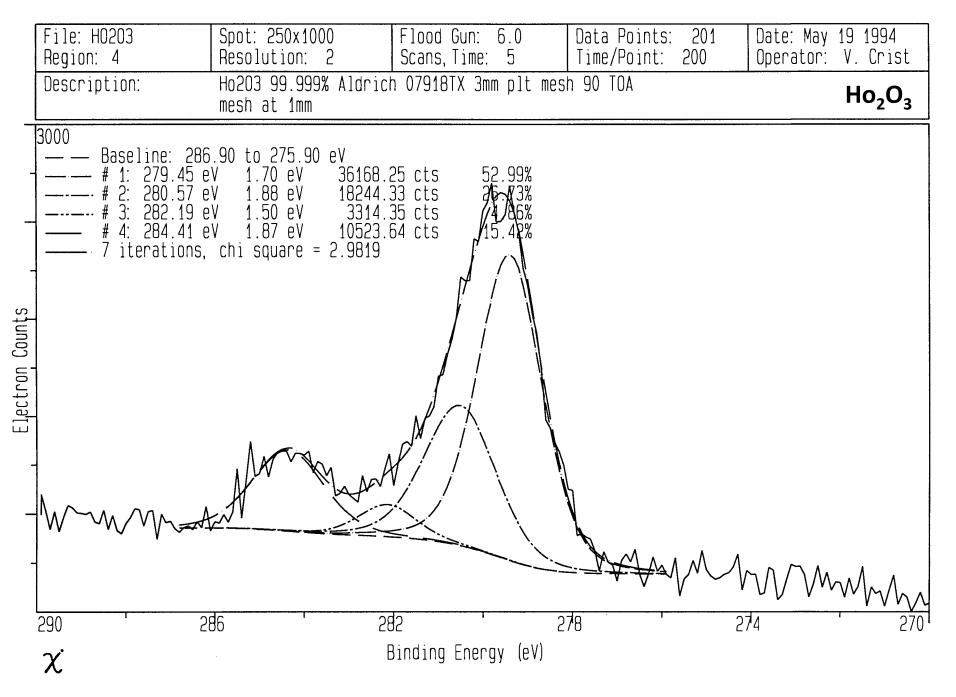
Operator: V. Crist

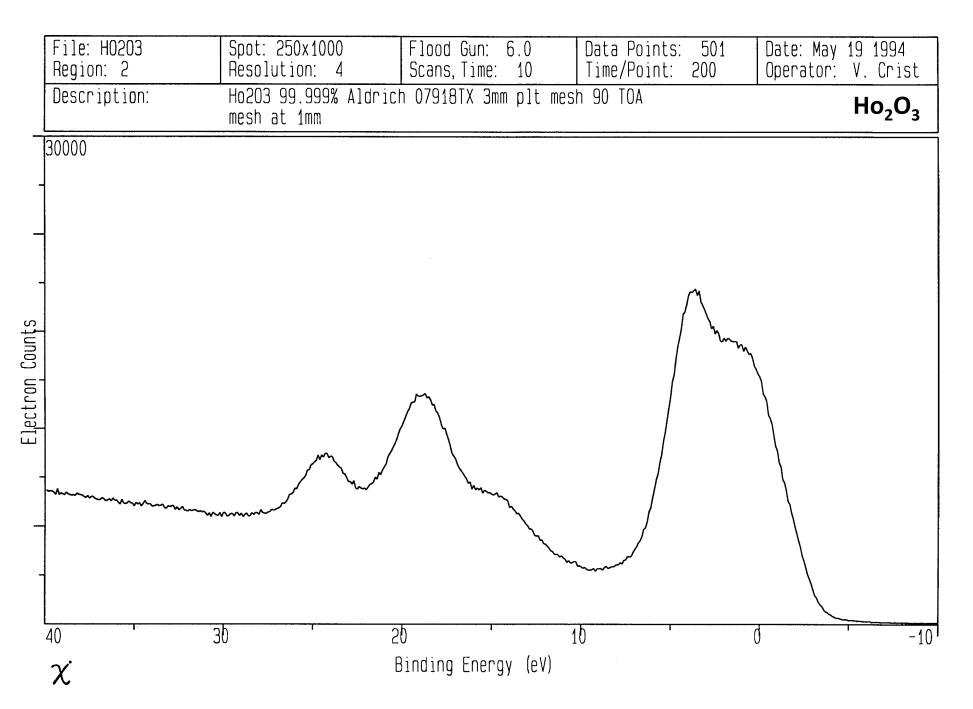
Date: Thu May 19 14:42 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom %
0 Auger	$97\overline{4.5}$	969.5	0.00	19278	0	
0 loss	547.9	542.9	0.00	15920	0	
* 0 1s	531.5	526.5	2.29	107365	46920	55.60
Ho Auger	482.6	477.7	0.00	61509	0	
Ho Auger	434.2	429.2	0.00	9610	0	
Ho Auger	349.4	344.4	0.00	8405	0	
Ho Auger	328.2	323.2	0.00	7261	0	
Ho Auger	307.7	302.7	0.00	80330	0	
* C 1s	285.0	280.0	1.00	30615	30487	36.12
Ho loss	188.8	183.8	0.00	12723	0	
Ho loss	174.4	169.4	0.00	6321	0	
* Ho4d	160.7	155.7	13.43	93803	6987	8.28
Ho Auger	119.5	114.5	0.00	39255	0	
O+Ho	23.5	18.5	0.00	32547	0	









File name: LU203.MRS

Region:

Description: Lu203 99.99% Aldr lot# 003208AV 3 mm plt 90 TOA

mesh at <1mm

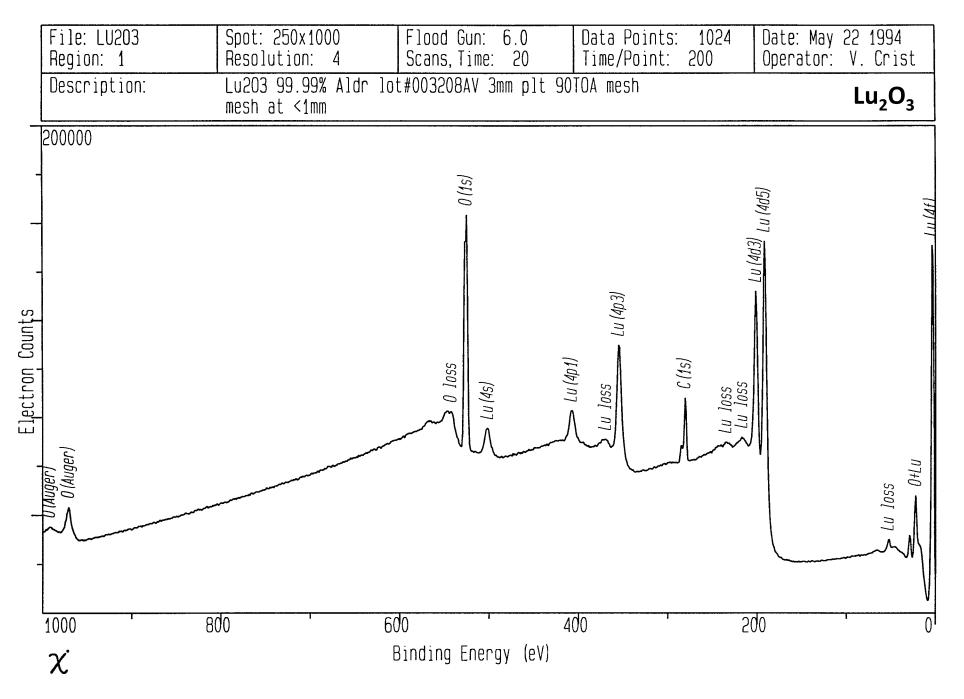
Operator:

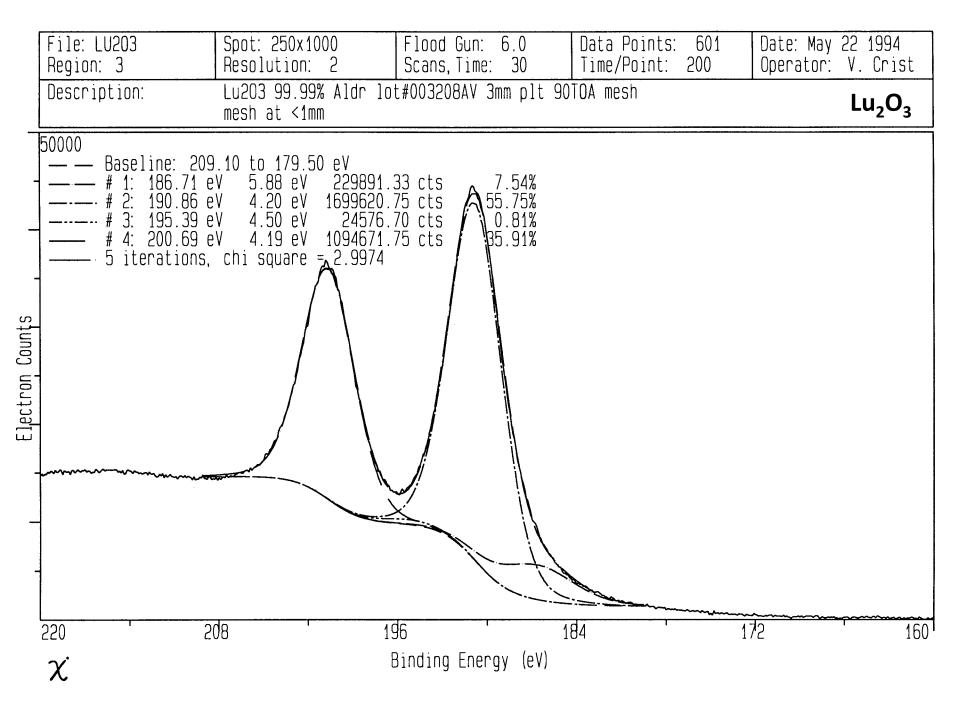
V. Crist

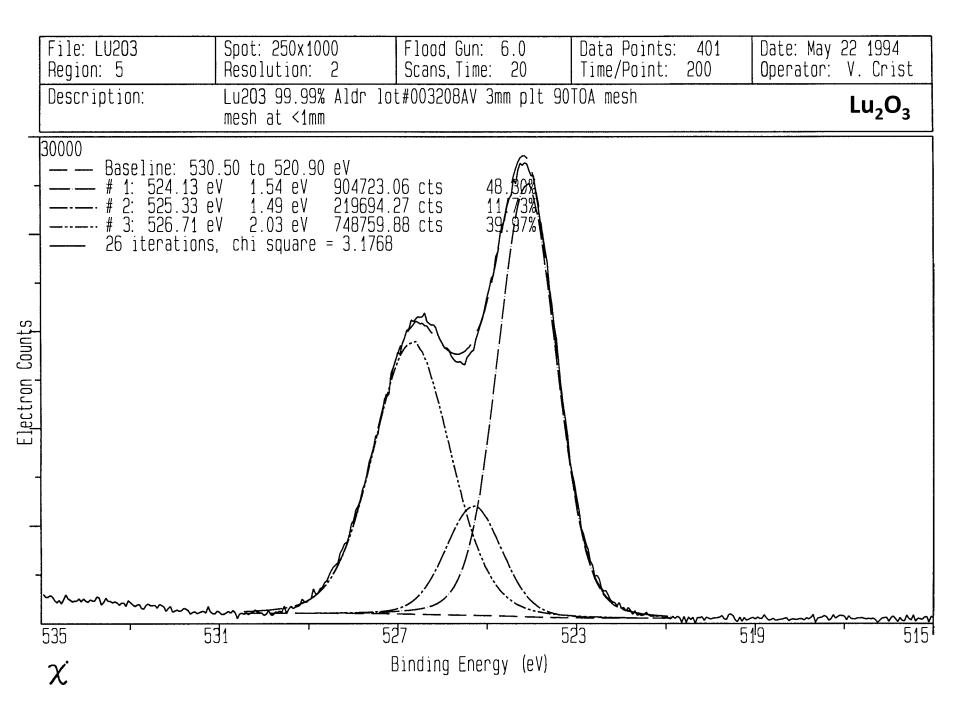
Date:

Sun May 22 12:04 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom 8
O Auger	997.2	991.9	0.00	4285	0	
O Auger	975.9	970.6	0.00	20348	0	
O loss	547.4	542.1	0.00	34682	0	
* 0 1s	530.0	524.7	2.29	106480	46438	56.24
Lu4s	506.7	501.4	1.39	21653	15576	
Lu4p1	412.1	406.8	1.80	27230	15093	
Lu loss	374.6	369.3	0.00	4500	0	
Lu4p3	359.1	353.8	4.44	72039	16223	
* C 1s	285.0	279.7	1.00	23975	23868	28.91
Lu loss	239.5	234.2	0.00	2490	0	
Lu loss	221.6	216.3	0.00	7138	0	
Lu4d3	205.9	200.6	6.32	69779	11036	
* Lu4d5	196.0	190.7	9.18	112573	12264	14.85
Lu loss	56.7	51.4	0.00	14518	0	
O+Lu	26.9	21.6	0.00	64941	0	
Lu4f	9.2	3.9	8.19	123622	15091	







	File: LU203 Region: 2	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 20	Data Points: 501 Time/Point: 200	Date: May 22 1994 Operator: V. Crist
	Description:	Lu203 99.99% Aldr lo mesh at <1mm	t#003208AV 3mm plt 90	TOA mesh	Lu <sub>2</sub> O <sub>3</sub>
Lipettron Counts	——— # 1: -1.05 e	7.80 to -4.40 eV eV 4.00 eV 136039. eV 2.97 eV 5477029. s, chi square = 13.585	30 cts 2.42% 50 cts 97.58% 3		
	40 3	30 2		10	-10
	χ̈́		Binding Energy (eV)		

File name: PR205.MRS

Region: 1

Description: Pr(III,IV) oxide 99.999% Aldrich lot# 09826LX

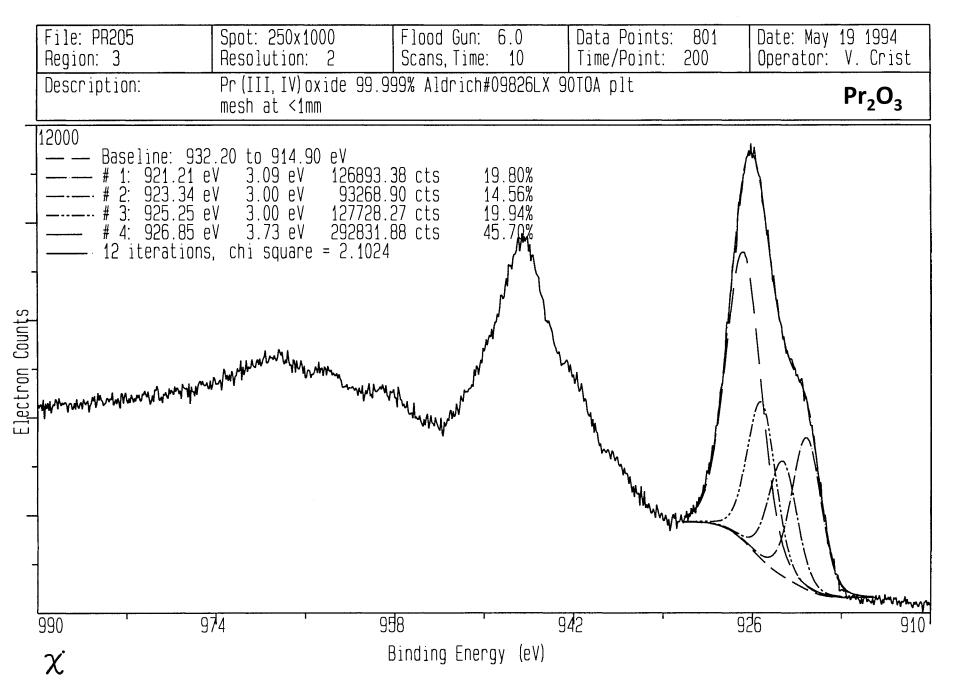
90 TOA, plt, mesh at <1mm

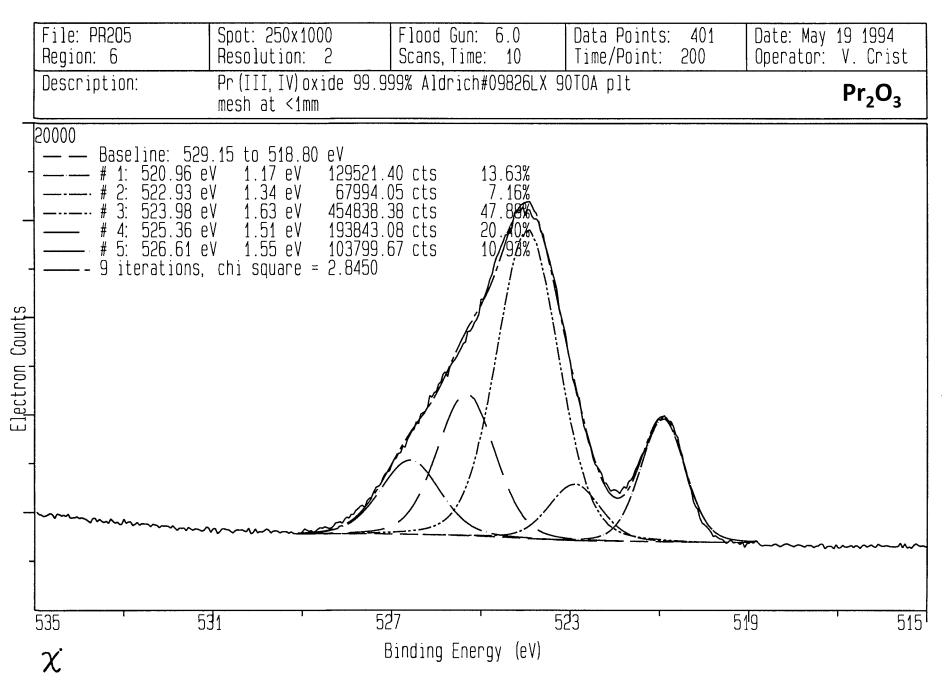
Operator: V. Crist

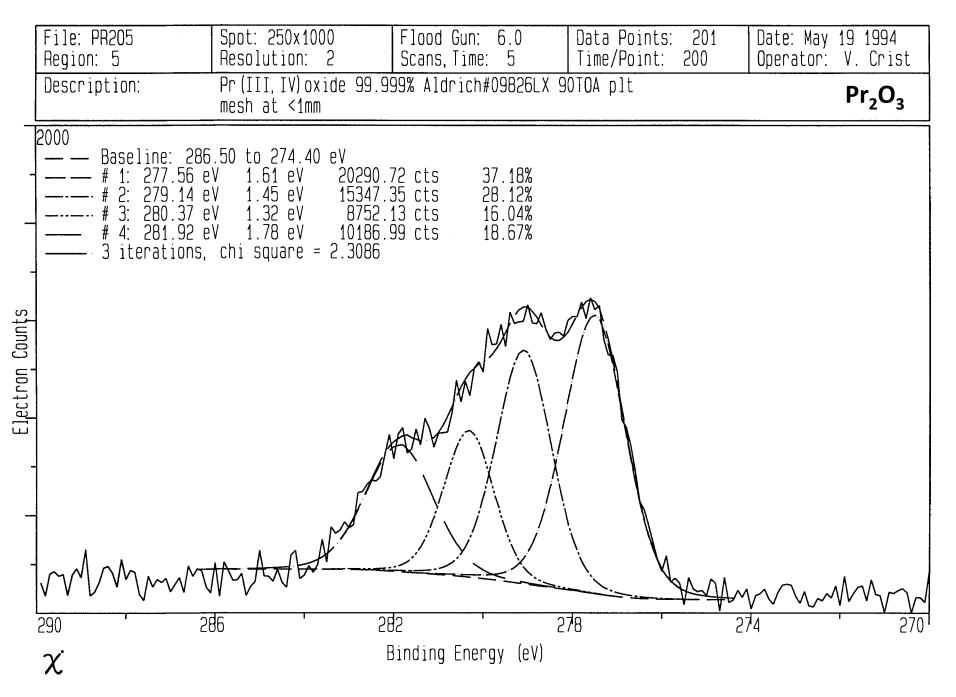
Date: Thu May 19 01:40 1994

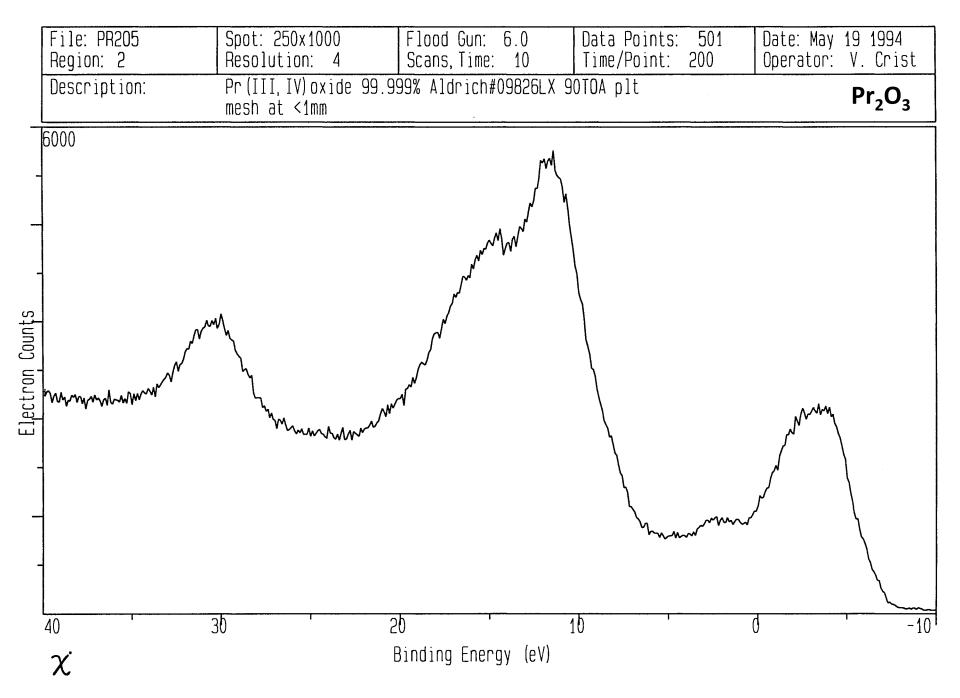
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom 8
0 Auger	975.2	968.8	0.00	25695	o	
Pr3d3	953.2	946.9	9.42	54292	5762	
Pr3d5	932.7	926.4	14.19	84952	5989	
Pr Auger	791.5	785.2	0.00	57129	0	
Pr Auger	689.5	683.2	0.00	4150	0	
Pr Auger	675.1	668.8	0.00	9077	0	
O loss	552.3	546.0	0.00	42570	0	
* 0 1s	530.3	524.0	2.29	102733	44765	58.26
Pr+C	303.5	297.2	0.00	14514	0	
* C 1s	285.0	278.7	1.01	27215	27069	35.23
Pr loss	231.6	225.3	0.00	7049	0	
* Pr (4p)	216.7	210.4	5.03	25147	5002	6.51
Pr loss	167.3	161.0	0.00	1843	0	
Pr loss	147.2	140.9	0.00	3624	0	
Pr loss	128.4	122.1	0.00	1613	0	
Pr4d	114.9	108.6	8.69	89453	10290	
Pr5s	36.1	29.8	0.29	2433	8276	
Pr+O	17.3	11.0	0.00	15511	0	

	File: PR205 Region: 1	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 10	Data Points: 1024 Time/Point: 200	Date: May 19 1994 Operator: V. Crist
	Description:	Pr(III, IV)oxide 99 mesh at <1mm	3.999% Aldrich#09826LX S	30TOA plt 	Pr <sub>2</sub> O <sub>3</sub>
Electron Counts		Pr Auger	0 1055	Pr+C (15)	Pr (55)
	1000 ' 8	90	600 Painding Energy (eV)	100 2	90 01









File name: SM203.MRS

Region:

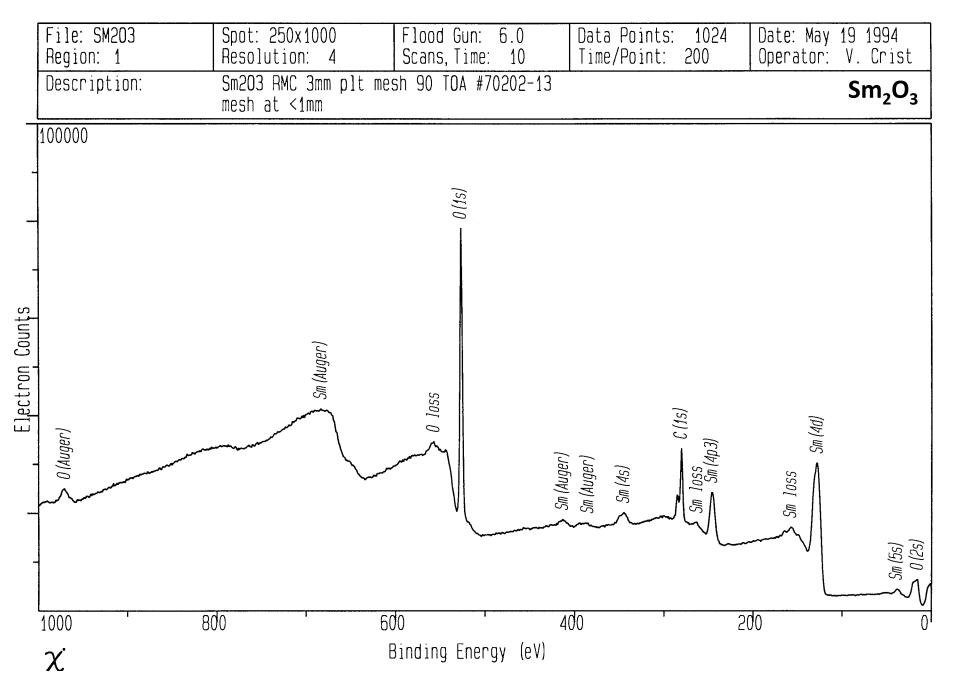
Description: Sm2O3 RMC, 3 mm plt mesh 90 TOA, lot #70202-13

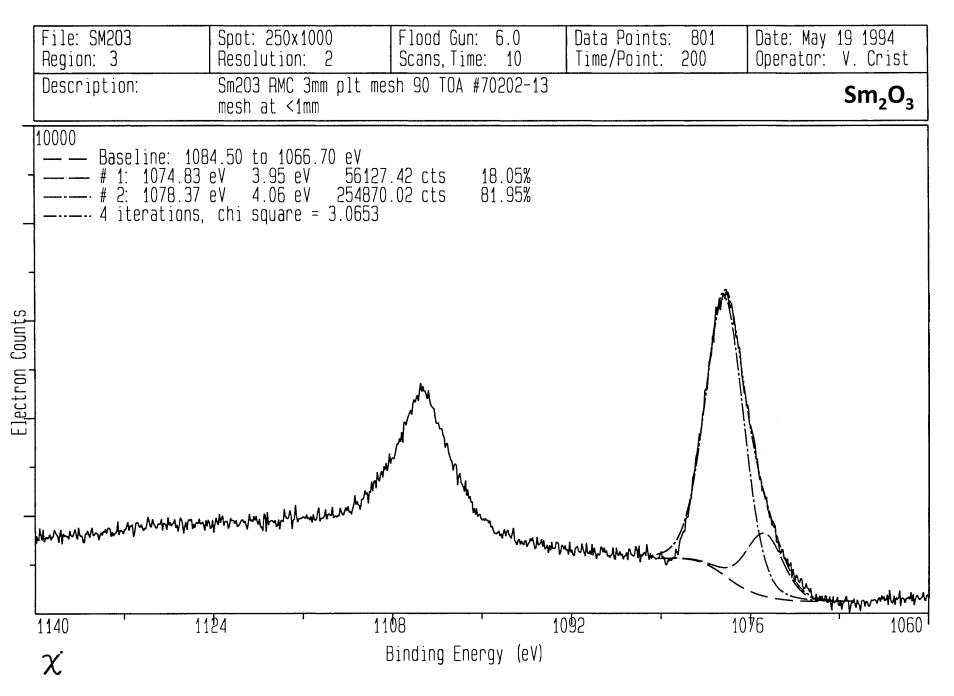
mesh at <1mm

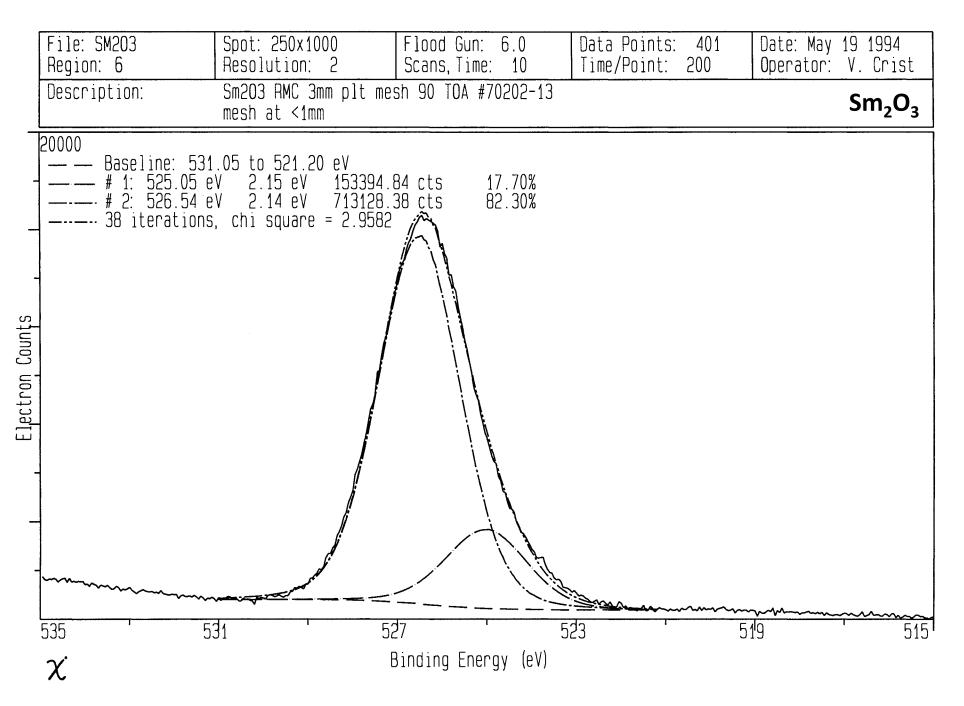
Operator: V. Crist

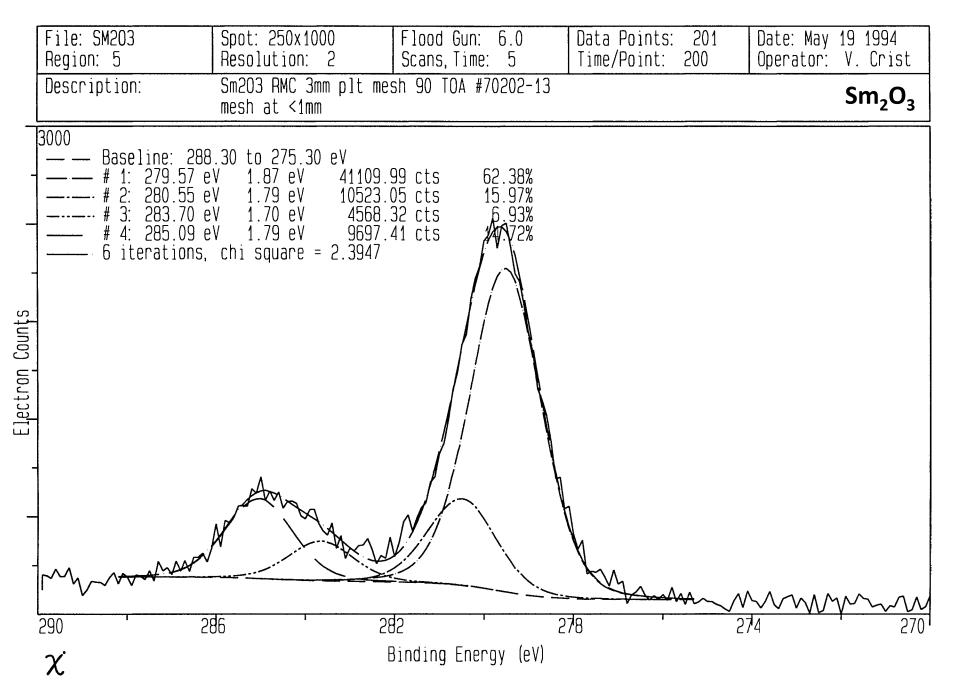
Date: Thu May 19 04:55 1994

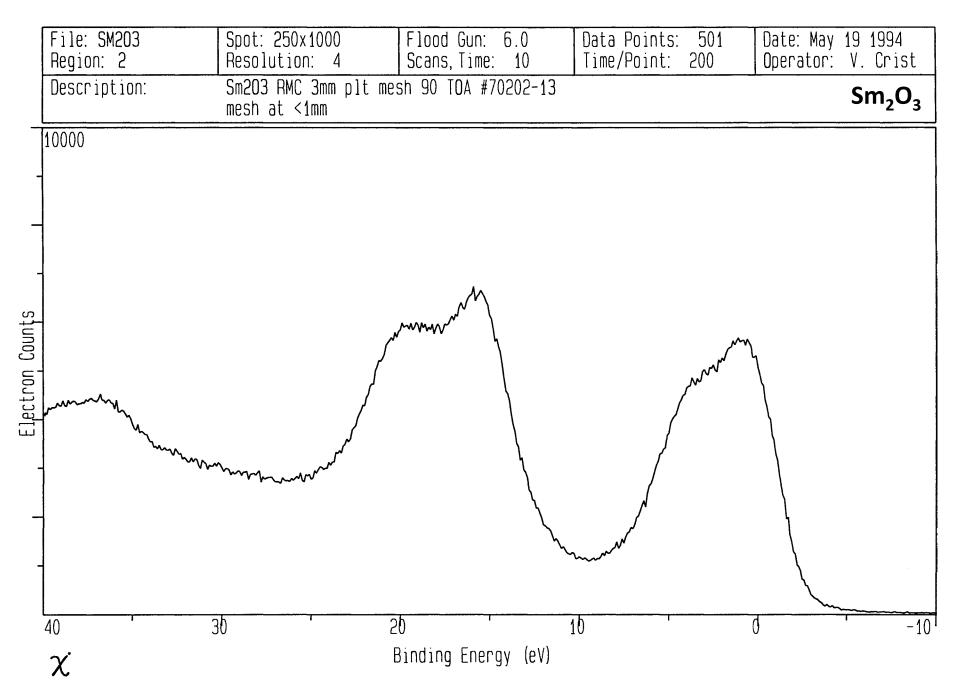
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	<u>Area</u>	Atom 8
O Auger	976.1	970.9	0.00	14008	0	
SmAuger	688.5	683.3	0.00	200113	0	
O loss	562.2	556.9	0.00	10705	0	
* 0 1s	531.7	526.4	2.29	93886	41024	48.81
SmAuger	418.7	413.5	0.00	7839	0	
SmAuger	390.4	385.1	0.00	3701	0	
Sm4s	349.6	344.4	1.34	8531	6355	
* C 1s	285.0	279.8	1.00	32760	32615	38.80
Sm loss	267.9	262.6	0.00	3963	0	
Sm4p3	250.5	245.3	3.72	31027	8347	
Sm loss	161.7	156.5	0.00	19679	0	
* Sm4d	132.8	127.5	10.48	109168	10412	12.39
Sm5s	43.1	37.8	0.32	4785	14929	
O+Sm	20.4	15.1	0.00	18719	0	

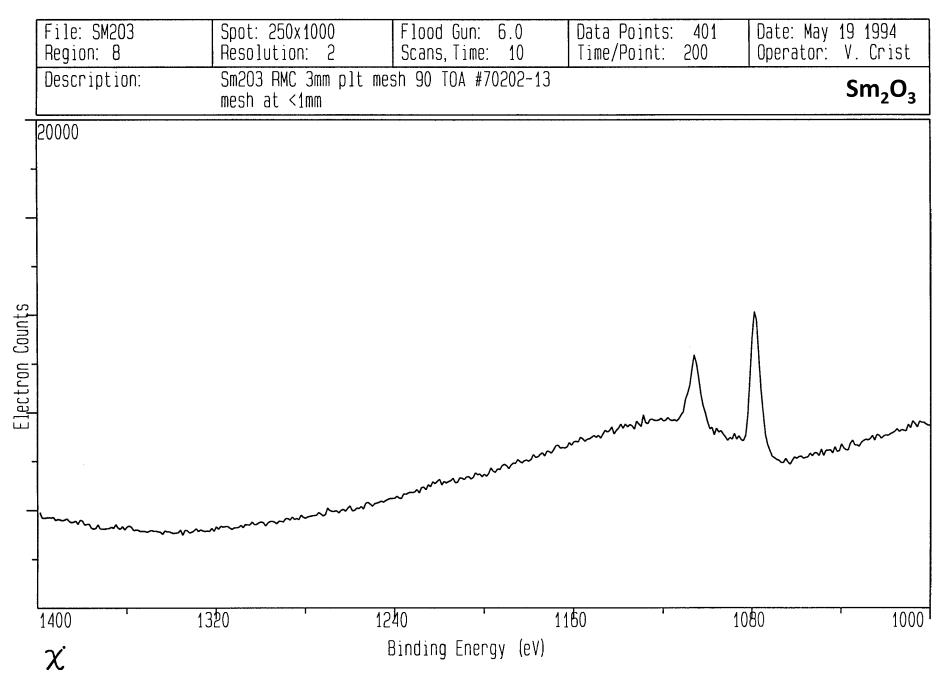












File name: TB307\_1.MRS

Region:

Description: Tb407 (brown lump) 3 mm plt, 90 TOA

mesh at <1mm

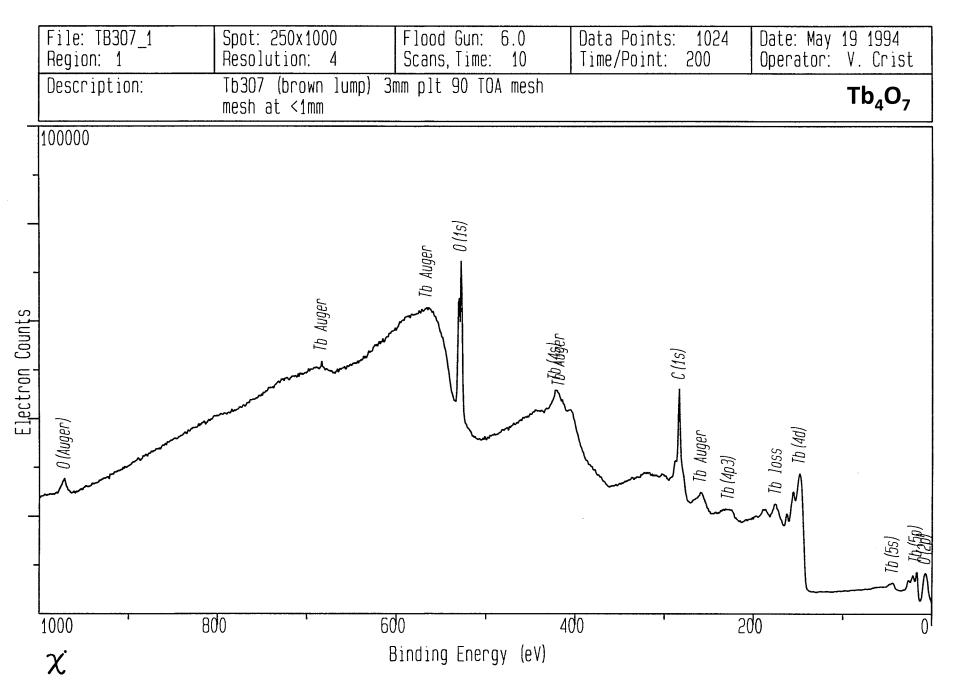
Operator:

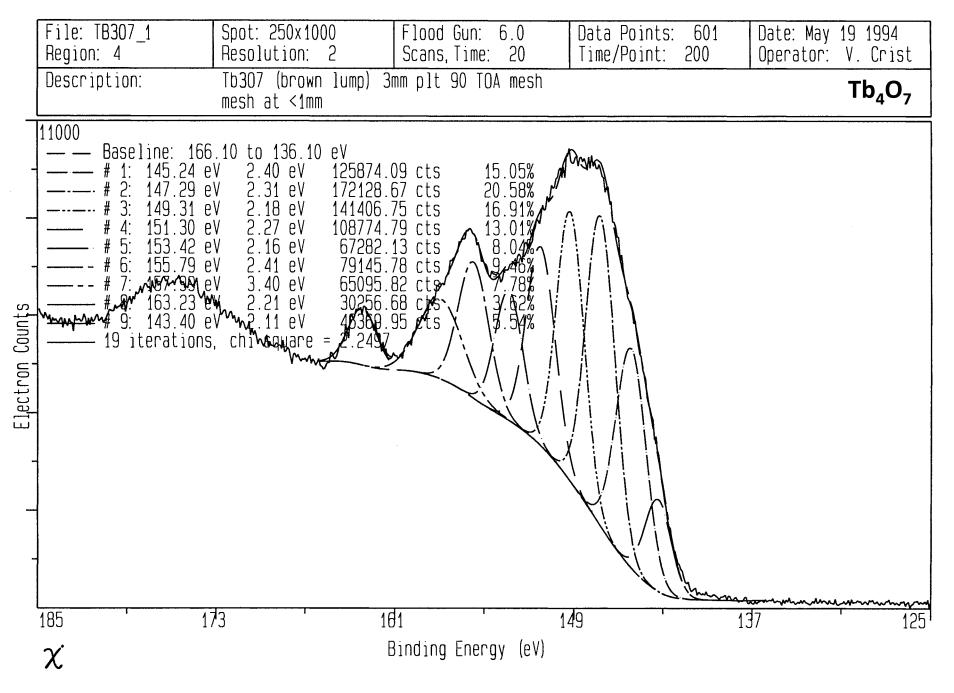
V. Crist

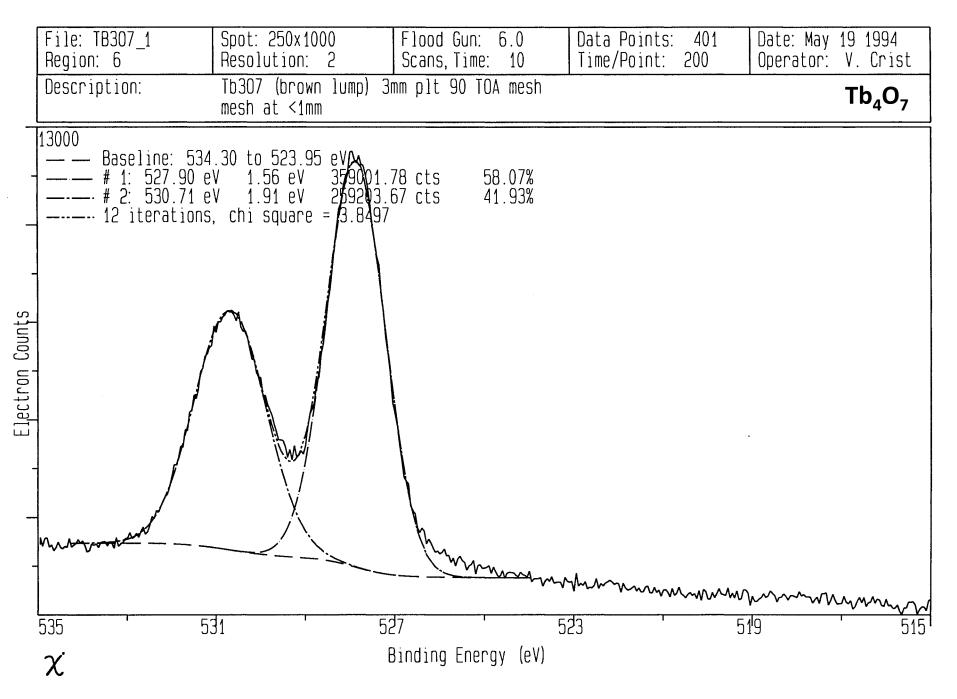
Date:

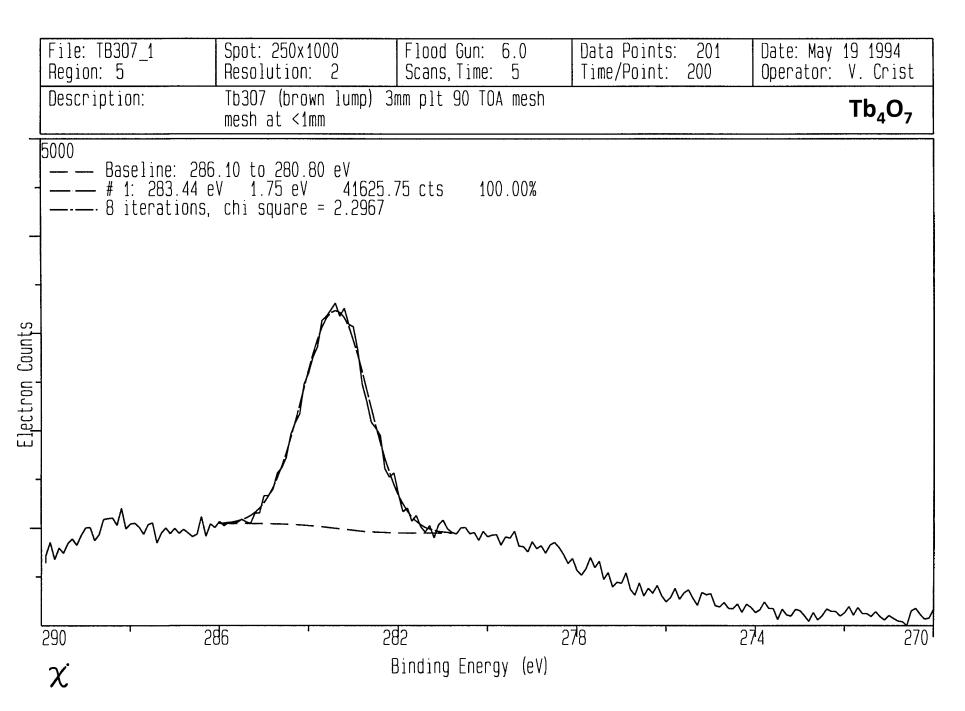
Thu May 19 08:32 1994

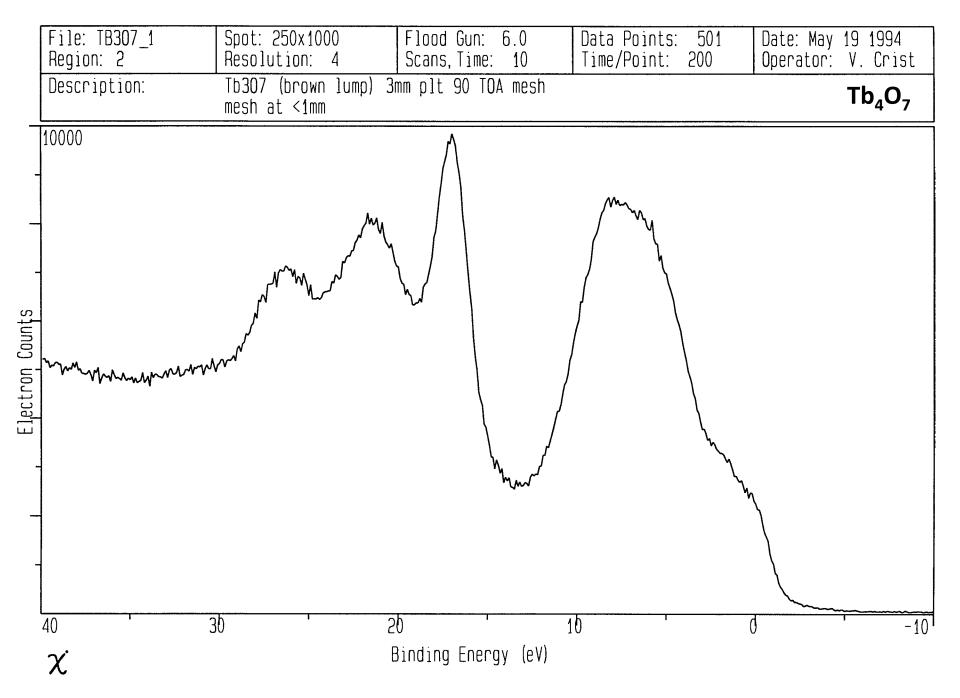
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	<u>Factor</u>	Area	Area	Atom &
O Auger	973.8	971.8	0.00	10467	0	
Tb Auger	685.3	683.3	0.00	50753	0	
Tb Auger	568.0	566.0	0.00	462486	0	
* 0 1s	529.3	527.3	2.14	69146	32360	33.48
Tb4s	423.4	421.4	1.30	11728	9019	
Tb Auger	419.4	417.4	0.00	11840	0	
* C 1s	285.0	283.0	1.00	54898	54793	56.70
Tb Auger	261.0	259.0	0.00	13322	0	
Tb4p3	228.9	226.9	4.26	5259	1234	
Tb loss	176.6	174.6	0.00	11508	0	
* Tb4d	149.9	147.9	12.64	119983	9489	9.82
Tb5s	45.3	43.3	0.36	3348	9222	
Tb5p	18.2	16.2	1.07	25366	23793	
O+Tb	8.5	6.5	0.00	17821	0	

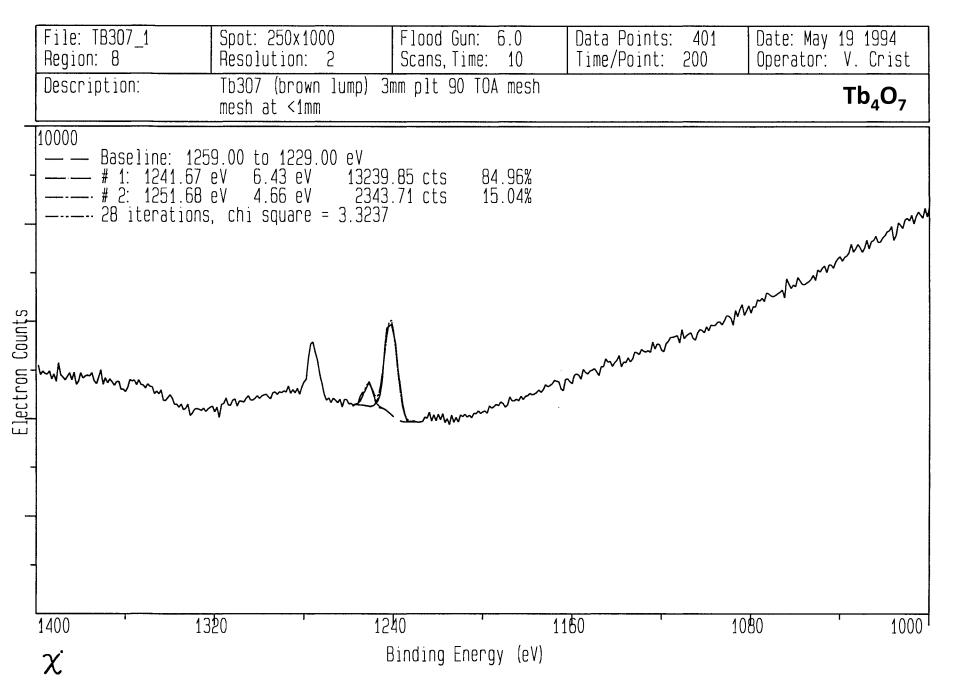












File name: TM203.MRS

Region: 1

Description: Tm2O3 99% RMC lot# 70202-13 3 mm plt, 90 TOA

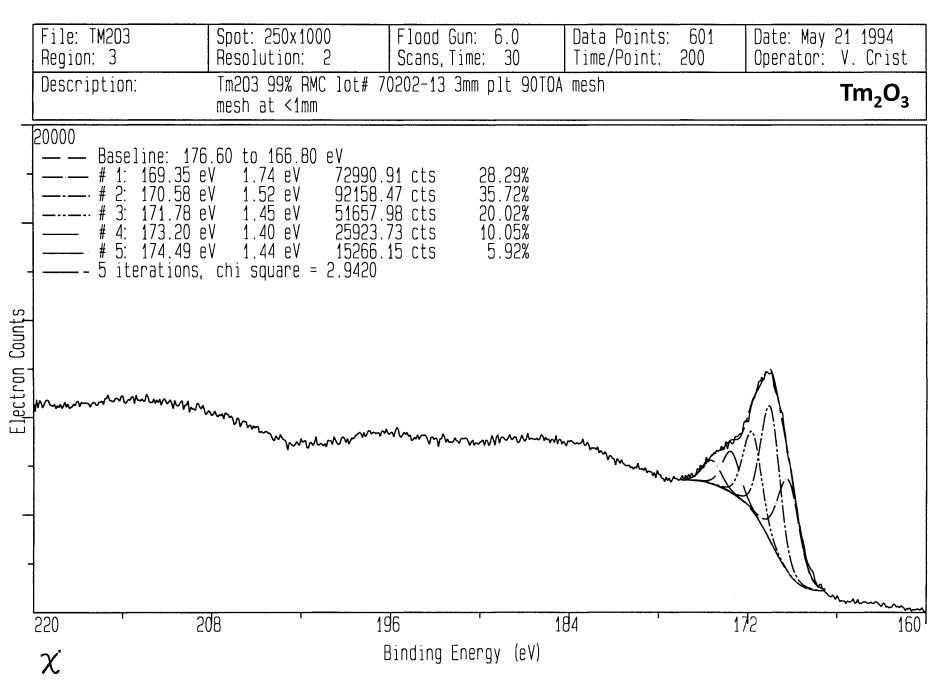
mesh at <1mm

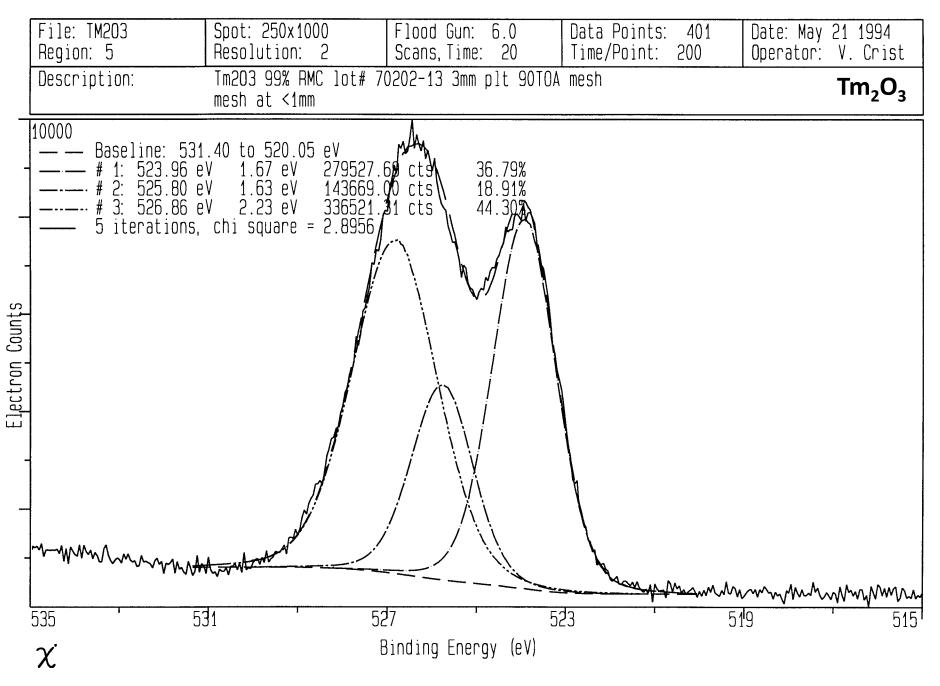
Operator: V. Crist

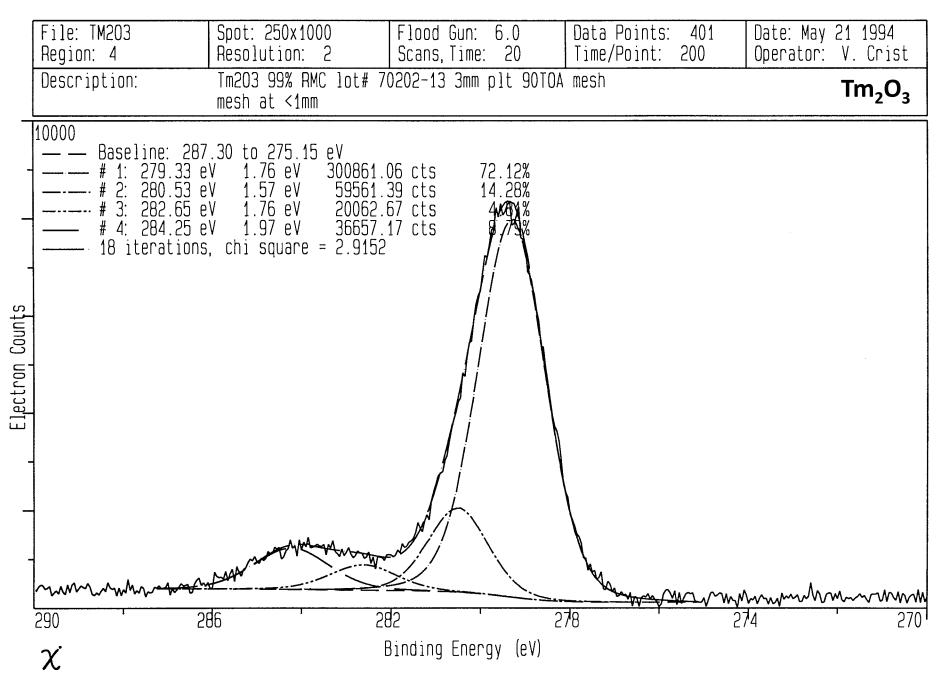
Date: Sat May 21 12:11 1994

	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	<u>Area</u>	Area	Atom 8
O Auger	$97\overline{5.4}$	969.8	0.00	7334	0	
0 loss	553.4	547.8	0.00	15236	0	
* 0 1s	532.1	526.5	2.29	39979	17470	37.10
Tm4s	468.4	462.8	1.40	6666	4768	
Tm Auger	393.2	387.6	0.00	5055	0	
* Tm4p3	332.6	326.9	4.30	20136	4680	9.94
* C 1s	285.0	279.4	1.00	25055	24936	52.96
Tm Auger	216.2	210.6	0.00	5122	0	
Tm loss	202.3	196.7	0.00	1328	0	
Tm4d	176.3	170.6	14.50	22395	1545	
Tm loss	53.0	47.4	0.00	1556	0	
Tm5s	43.4	37.8	0.37	5874	15786	
O+Tm	25.6	19.9	0.00	6077	0	

Electron Counts  O (Auger)  Im Auger  Im Auger  Im (403)  Im (404)	File: TM203 Region: 1 Description:	Spot: 250x1000 Resolution: 4 Tm203 99% RMC lot# mesh at <1mm	Flood Gun: 6.0 Scans, Time: 20 70202-13 3mm plt 90TOA	Data Points: 1024 Time/Point: 200 mesh	Date: May 21 1994 Operator: V. Crist $\mathbf{Tm_2O_3}$
1000 800 600 400 200	0 (Auger)	and of the same of	1m (4s)	Tm Auger  Tm (4p3)	74 m/055







[File: TWOO?	Cook 250,4000	Flood Cup. C A	Data Daiata: FOA	Deter May 04 4004
File: TM2O3 Region: 2	Spot: 250x1000 Resolution: 4	Flood Gun: 6.0 Scans, Time: 20	Data Points: 501 Time/Point: 200	Date: May 21 1994 Operator: V. Crist
Description:		0202-13 3mm plt 90TOA		Tm <sub>2</sub> O <sub>3</sub>
20000			<b>۸</b>	
TECHTON COUNTS		Many		
40 3 X	b ' 2	0	6	<b>0</b> ' −10

File name: YB203.MRS

Region: 1

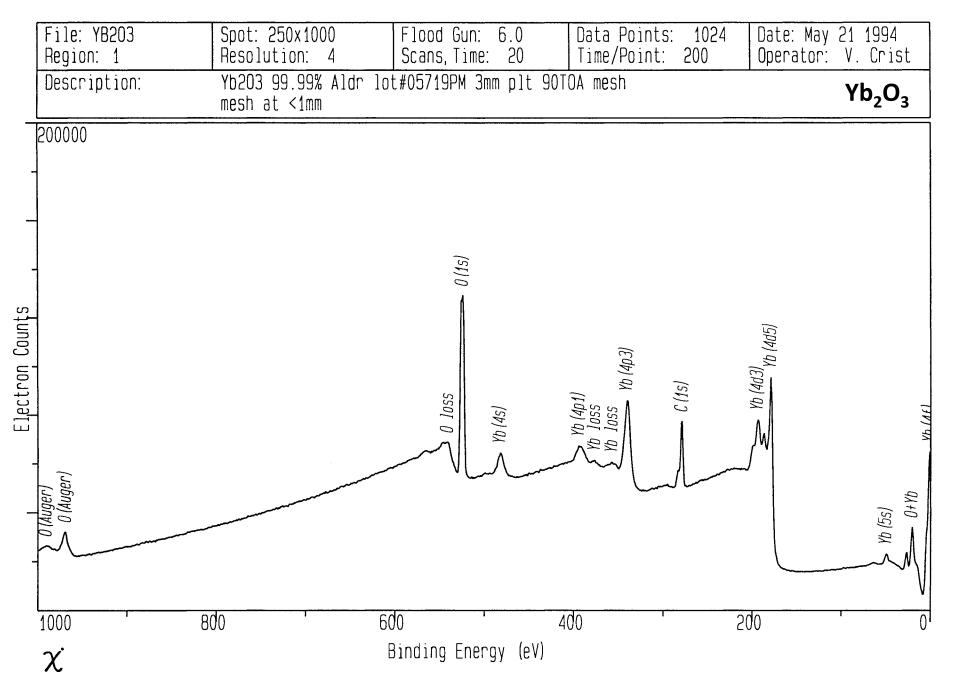
Description: Yb203 99.99% Aldr lot# 05719PM, 3 mm plt, 90 TOA

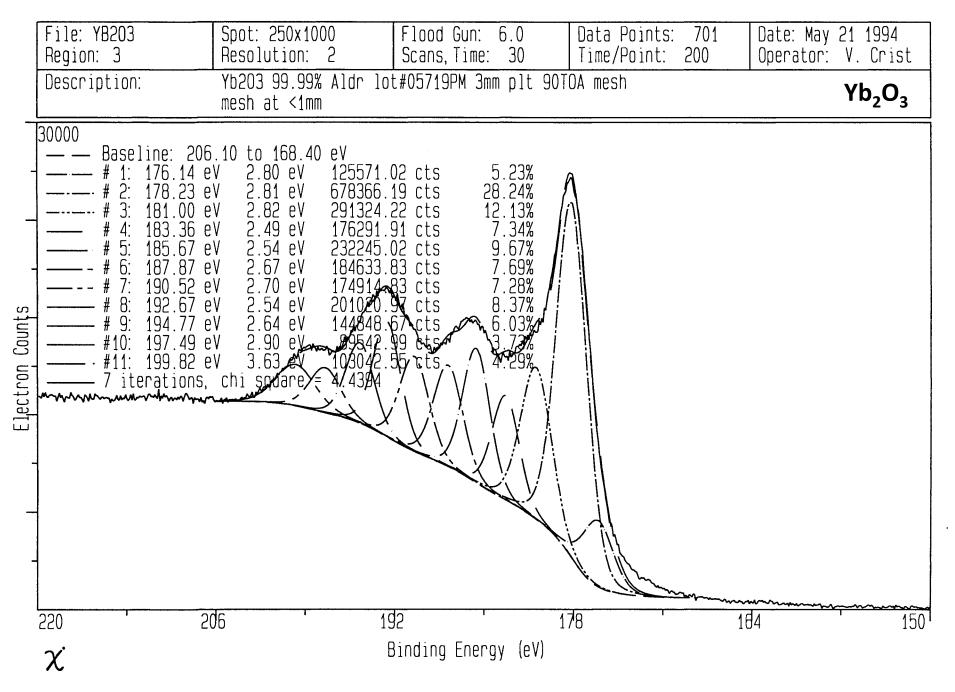
mesh at <1mm

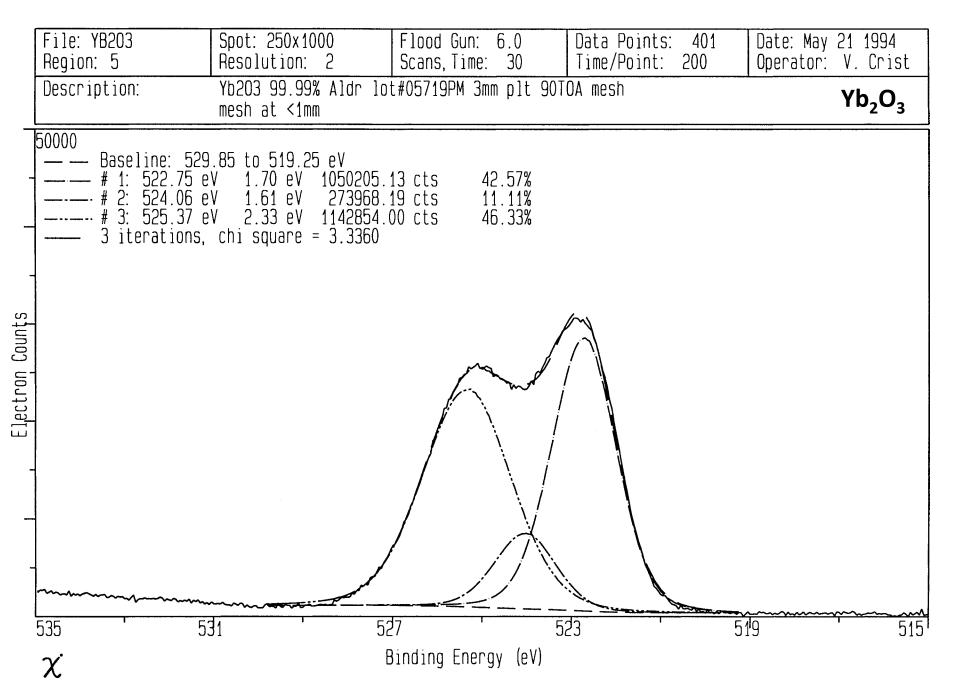
Operator: V. Crist

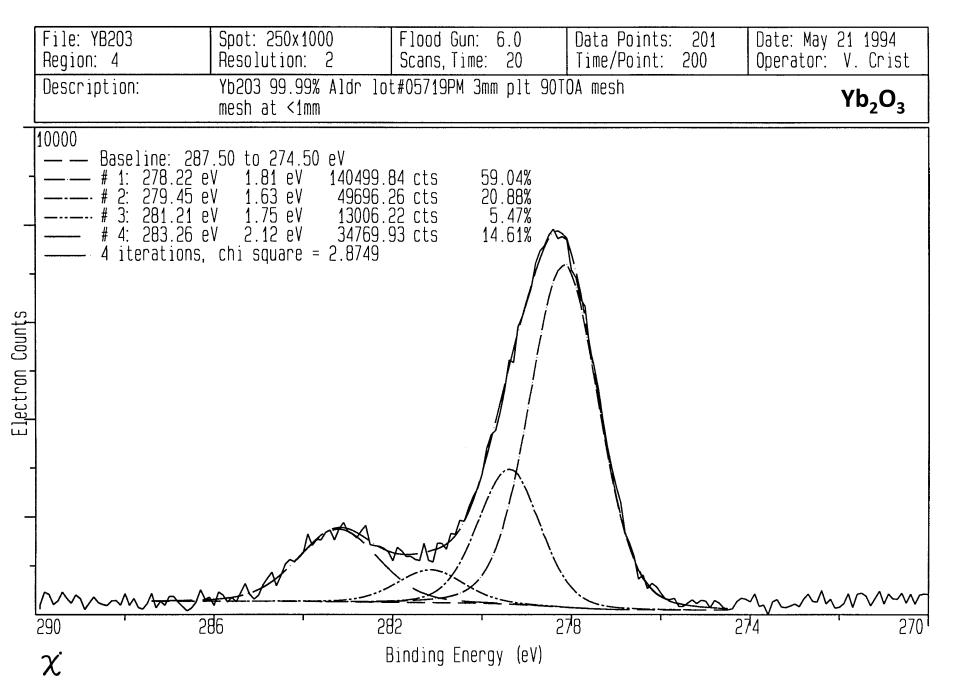
Date: Sat May 21 00:39 1994

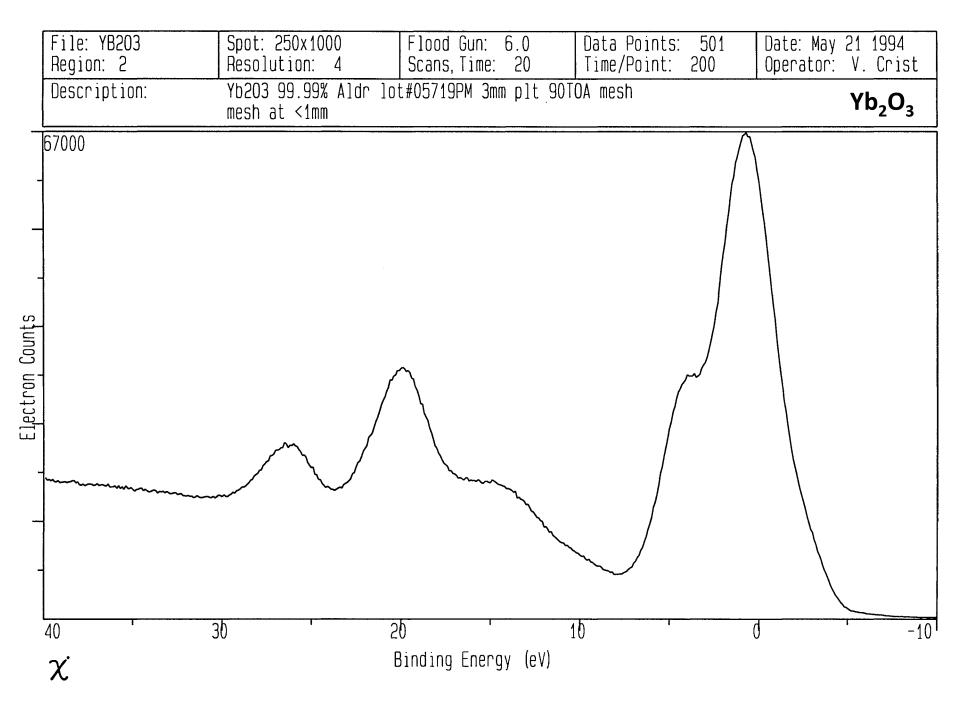
	Corrected	Exper.	Sens	Norm	Relative	
Signal	BE	BE	Factor	Area	Area	Atom %
0 Auger	996.9	990.2	0.00	5208	o	
O Auger	975.7	969.1	0.00	15655	0	
O loss	547.1	540.4	0.00	32245	0	
* 0 1s	530.5	523.8	2.30	91312	39781	49.29
Yb4s	487.9	481.2	1.40	18515	13256	
Yb4p1	399.9	393.3	1.80	18233	10118	
Yb loss	382.8	376.1	0.00	1118	0	
Yb loss	363.3	356.6	0.00	4229	0	
* Yb4p3	345.8	339.1	4.37	60263	13796	17.10
* C 1s	285.0	278.3	1.01	27281	27125	33.61
Yb4d3	199.2	192.6	6.08	22881	3761	
Yb4d5	184.8	178.2	8.86	52749	5954	
Yb5s	55.2	48.6	0.38	10006	26672	
O+Yb	26.2	19.5	0.00	43013	0	
Yb4f	7.7	1.0	7.04	10559	1499	











# **APPENDIX "A"**

# ALPHABETICAL INDEX OF XPS SPECTRA IN VOLUME FIVE

Rare Earth Oxides, Hydroxides, Carbonates, Nitrides, Sulfides, Carbides, Borides, Acetates, & Miscellaneous Materials

## ALPHABETICAL INDEX OF XPS SPECTRA IN VOLUME FIVE

# RARE EARTH OXIDES, HYDROXIDES, CARBONATES, NITRIDES, SULFIDES, ACETATES, CARBIDES, BORIDES, AND MISCELLANEOUS MATERIALS

#### RARE EARTH OXIDES CeO<sub>2</sub> $Dy_2O_3$ Er<sub>2</sub>O<sub>3</sub> $Eu_2O_3$ Gd<sub>2</sub>O<sub>3</sub> Ho<sub>2</sub>O<sub>3</sub> $Lu_2O_3$ $Pr_6O_{11}$ Sm<sub>2</sub>O<sub>3</sub> Tb<sub>4</sub>O<sub>7</sub> $Tm_2O_3$ Yb2O3 HYDROXIDES $Al(OH)_3$ $Cd(OH)_x$ $Co(OH)_2$ Cu(OH)<sub>2</sub> FeO(OH) LiOH $Mg(OH)_2$ Ni(OH)<sub>2</sub>

## MISCELLANEOUS (continued)

<b>CARBONATE</b>	<u>es</u>
BaCO <sub>3</sub>	(Barium carbonate, pressed onto indium foil, insulator)
$(BiO)_2CO_3$	(Bismuth sub-carbonate, 99%, Aldrich, pressed pellet, insulator)
$CaCO_3$	(Calcium carbonate due to CO <sub>2</sub> attack on CaO from Aldrich, insulator)
$CaCO_3$	(Calcium carbonate in the natural mineral Calcite, freshly exposed bulk, insulator)
$CdCO_3$	(Cadmium carbonate, 99.999%, Aldrich, pressed pellet, insulator)
$CuCO_3$	(Copper carbonate, Technical Grade, powder on adhesive tape, insulator)
CuCO <sub>3</sub> -Cu	(OH) <sub>2</sub> (Copper carbonate – copper hydroxide in the natural mineral Azurite, freshly exposed bulk)
$Li_2CO_3$	(Lithium carbonate due to CO <sub>2</sub> attack on LiOH on Indium foil)
$MgCO_3$	(Magnesium carbonate-hydroxide in the natural mineral Magnesite, freshly exposed bulk, insulator)
$MgCO_3$	(Magnesium carbonate due to CO <sub>2</sub> attack on MgO powder from Aldrich, insulator)
$MnCO_3$	(Manganese carbonate in the natural mineral Rhodochrosite, freshly exposed bulk, insulator)
$PbCO_3$	(Lead carbonate in the natural mineral Cerrusite, freshly exposed bulk, insulator)
$SrCO_3$	(Strontium carbonate due to CO <sub>2</sub> attack on SrO from Rare Metallics, insulator)
$SrCO_3$	(Strontium carbonate, 99%, Rare Metallics, pressed on indium foil, insulator)
$Y_2CO_3$	(Ytrrium carbonate trihydrate, 99%, Aldrich, pressed pellet, insulator)
Y <sub>2</sub> CO <sub>3</sub> -LaF	36 (Yttrium carbonate on lanthanum hexaboride, ion etched away 50 angstroms, conductive)
NUMBER	
NITRIDES AlN	(Aluminium nitride, 98+%, Aldrich, pressed pellet, insulator)
BN	(Boron nitride, 99%, white color, freshly exposed bulk, insulator)
CrN	(Chromium nitride film, old, ion etched 2 minutes, conductive)
Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, old, as received, insulator)
Si <sub>3</sub> N <sub>4</sub> Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, old, ion etched 4 minutes, insulator)
Si <sub>3</sub> N <sub>4</sub> Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, ord, for etened 4 finites, fisuator)
Si <sub>3</sub> N <sub>4</sub> Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, metallic blue color, soaked 10 minutes in a solution of conc. HF: MeOH)
Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, old, gray color, as received, conductive)
Si <sub>3</sub> N <sub>4</sub> Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, old, gray color, ion etched 10 minutes, conductive)
Si <sub>3</sub> N <sub>4</sub> Si <sub>3</sub> N <sub>4</sub>	(Silicon nitride coating, old, blue color, soaked 10 minutes in a solution of conc HF: MeOH)
TiN	(Titanium nitride coating, gold color, old, ion etched 2 minutes, conductive)
1111	(Trainant marac coating, gold color, old, foll ciched 2 minutes, conductive)

# MISCELLANEOUS (continued)

<u>SULFIDES</u>		
$Ag_2S$	(Silver sulfide in natural mineral Argentite from Guananuato, Mexico, freshly exposed bulk, conductive)	298
$As_2S_2$	(Arsenic (II) sulfide in natural mineral Realgar from Nevada, USA, freshly exposed bulk, insulator)	307
$As_2S_3$	(Arsenic (III) sulfide in natural mineral Orpiment from Nevada, USA, freshly exposed bulk, insulator)	317
CuS	(Copper (II) sulfide in natural mineral Covellite, dark blue region after ethanol wipe, conductive)	326
CuS	(Copper (II) sulfide in natural mineral Covellite, dark blue region, ion etched 20 seconds, conductive)	329
$FeS_2$	(Iron (IV) sulfide in natural mineral Pyrite, freshly exposed bulk, conductive)	340
HgS	(Mercury sulfide in natural mineral Cinnabar from Ukraine, Russia, freshly exposed bulk, insulator)	348
$MoS_2$	(Molybdenum (IV) sulfide, freshly exposed bulk, conductive)	356
PbS	(Lead (II) sulfide in natural mineral Galena from Missouri, USA, freshly exposed bulk, conductive)	360
$TaS_2$	(Tantalum (IV) sulfide "crystal", as received, conductive)	367
$TaS_2$	(Tantalum (IV) sulfide "crystal", after peeling away two surface layers, conductive)	374
ZnS	(Zinc sulfide film, as received, insulator)	
CARBIDES		
NbC	(Niobium carbide, 97% Aldrich, ion etched to minimize oxygen content, conductive)	383
TaC	(Tantalum carbide, 99%, Aldrich, ion etched 2 minutes to minimize oxygen content, conductive)	390
VC	(Vanadium carbide, 98%, Aldrich, ion etched 2 minutes to minimize oxygen content, conductive)	397
BORIDES		
Ni <sub>3</sub> B	(Nickel boride powder, purity?, Kyoritsu Ceramic Materials, ion etched 2 minutes, conductive)	404
WB	(Tungsten boride powder, purity?, Japan New Metal, ion etched 2 minutes, conductive)	411
ACETATES		
BaOAc	(Barium acetate powder, Kanto Chemical, pressed onto indium foil, insulator)	418
RbOAc	(Rubidium acetate powder, freshly ground, insulator	42 <del>6</del>

## MISCELLANEOUS MATERIALS

Cleaning agent	(MicroLab cleaning solution smeared onto gold plate as a very thin film, conductive)
Copper foil – heated in air	(Copper foil heated in air at >600C to produce dark brown wrinkled film, conductive)
Copper Phthalocyanine	(Copper phthalocyanine, as received, 4 monolayers on silicon wafer, conductive)
Double sided adhesive tape	e (Double sided adhesive tape from 3M Co., Scotch brand, as received, insulator)
Jewelry	(Metal ball on a ring became black after cleaning with jewelry cleanser)
Jewelry	(Metal ball on a ring became gray after cleaning with jewelry cleanser)
Loctite <sup>™</sup> #414	(Loctite cyanoacrylate #414 instant glue on glass, as received, insulator)
Loctite <sup>™</sup> #493	(Loctite cyanoacrylate #493 instant glue on glass, as received, insulator)
Mold release agent	("EASE" release 300 mold release agent smeared onto gold plate as very thin film, insulator)
Silicone remover agent	(Silicone oil remover from SLIDE Co. smeared onto gold plate as very thin film, conductive)
Tin plated wire	("Bad" sample with wrong color of tin plating coating, conductive)
Tin plated wire	("Good" sample with correct color of tin plating coating, conductive)
Black Widow spider web	(Black Widow spider web, non-sticky bundle, as received, insulator)
Contamination study	(Aluminium kitchen foil control sample, as received not touched with glove, conductive)
Contamination study	(Aluminium kitchen foil contaminated by touching surface with soft vinyl glove, conductive)
Borosilicate glass	("Soft" borosilicate glass from Asahi Glass, as received, insulator)
Pyrex <sup>TM</sup> glass	(Pyrex <sup>TM</sup> glass produced by Iwaki Glass, freshly exposed bulk, insulator)
Soda-lime glass	(Soda-lime glass used as microscope slide, as received, insulator)