XPS – BE Calibration and Atom % Accuracy Checks
All We Need is Copper (Cu)

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This poster explains that BE Calibration and Atom % Accuracy can be quickly and reliably checked by using just one piece of freshly cleaned, ion-etched, pure (~99.9%) Copper (Cu) for both tasks.

Existing methods are valid, but are tedious and time consuming, and therefore seldom used. The end result of this conundrum is that published BEs and atom % values are unnecessarily inaccurate.

As evidence that the problem continues, please review the Statistical Analyses of the BEs shown in Periodic Table format. The results were derived from the on-line version of NIST Database of XPS BEs.

The NIST database and other collections of BEs all suffer from the use of maker recommended calibration energies (i.e. Cu 2p3 ranges from 932.2 eV to 932.8 eV), and the assumption that the hydrocarbon C 1s BE should equal (=) 284.8 ±0.2 eV. The evidence of this still ongoing problem is revealed in the Histograms.

To escape the BE error problems, and to publish, have and use reliable XPS BEs to assign chemical states reliably, we must start to check and calibrate our Energy Scales, so a fast and reliable method is needed.

The Atom % (TF) Check:

After collecting, either one routine, wide-scan survey spectrum (0-1000 eV), or two smaller, wide-scan spectra (i.e. 50-150 eV and 900-1,000 eV), we can check Atom % Accuracy by generating atom% values from two or more of the 4 major XPS signals produced from freshly cleaned and strongly ion-etched pure (>99.9%) Copper (Cu).

If the Transmission Function (TF) or Instrument Response Function (IRF) is setup correctly, and we are using Scofield's theoretically calculated, relative sensitivity factors (RSFs), then each Copper peak must have the same value within 10% of that value. If any of the Atom% values differ by ≥12%, then there is, most likely, a problem with either the Transmission Function or the RSFs at one or more pass energies or collection angles.

Copper — Atom % Test: Based on RSFs for Pure Copper (Cu) — Copper

Relative Sensitivity Factors (RSFs) by James Scofield (LLNL) were theoretically derived. These RSFs are the most widely used and trusted. Kratos, VG, JEOL, Scienta, SSI and others use Scofield RSFs.

Even though PHI instruments use Wagner's "empirically" measured RSFs, renormalization to give RSF = 1.0 for the C 1s signal, in place of the usual RSF = 1.0 for F 1s, produces RSFs that are almost identical.

But the Real Questions are: (1) Does my instrument give reliable Atom % results? and
(2) How can I check the Atom% results for my instrument ?

Pure Copper (Cu)

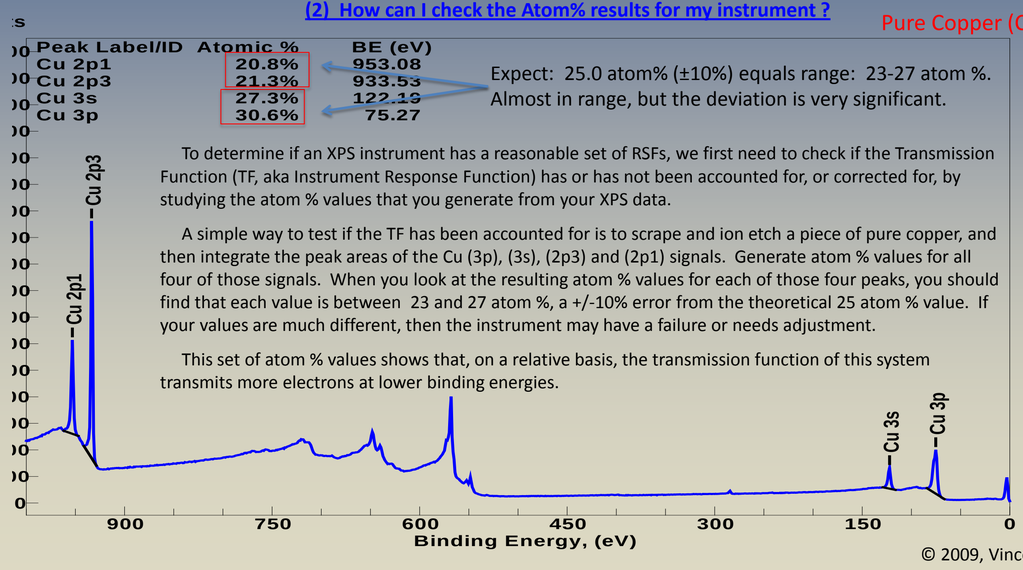
Peak Label/ID	Atomic %	BE (eV)
Cu 2p1	20.8%	953.08
Cu 2p3	21.3%	933.53
Cu 3s	27.3%	122.13
Cu 3p	30.6%	75.27

Expect: 25.0 atom% (±10%) equals range: 23-27 atom %.
Almost in range, but the deviation is very significant.

To determine if an XPS instrument has a reasonable set of RSFs, we first need to check if the Transmission Function (TF, aka Instrument Response Function) has or has not been accounted for, or corrected for, by studying the atom % values that you generate from your XPS data.

A simple way to test if the TF has been accounted for is to scrape and ion etch a piece of pure copper, and then integrate the peak areas of the Cu (3p), (3s), (2p3) and (2p1) signals. Generate atom % values for all four of those signals. When you look at the resulting atom % values for each of those four peaks, you should find that each value is between 23 and 27 atom %, a +/-10% error from the theoretical 25 atom % value. If your values are much different, then the instrument may have a failure or needs adjustment.

This set of atom % values shows that, on a relative basis, the transmission function of this system transmits more electrons at lower binding energies.



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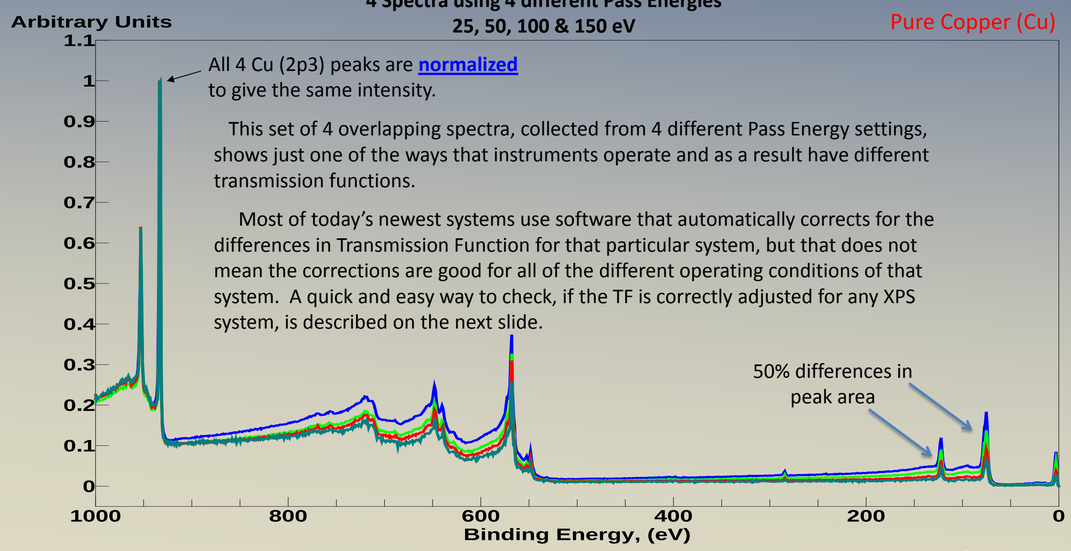
Copper — Atom % Test: Instrument Response Function & RSFs — Copper

The Instrument Response Function (aka transmission function, TF) of each XPS instrument in the world is normally slightly different or greatly different from all other XPS instruments. This has to do with the subtleties of actually building electron collection lenses, electron energy analyzers (hemispheres) and detectors. Transmission functions (or IRFs) directly affect the atom % values produced by every XPS system. In a perfect XPS system, all 4 spectra (shown below), which were taken at different PEs, should overlap exactly.

4 Spectra using 4 different Pass Energies
25, 50, 100 & 150 eV

Pure Copper (Cu)



This set of 4 overlapping spectra, collected from 4 different Pass Energy settings, shows just one of the ways that instruments operate and as a result have different transmission functions.

Most of today's newest systems use software that automatically corrects for the differences in Transmission Function for that particular system, but that does not mean the corrections are good for all of the different operating conditions of that system. A quick and easy way to check, if the TF is correctly adjusted for any XPS system, is described on the next slide.

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The BE Calibration Check:

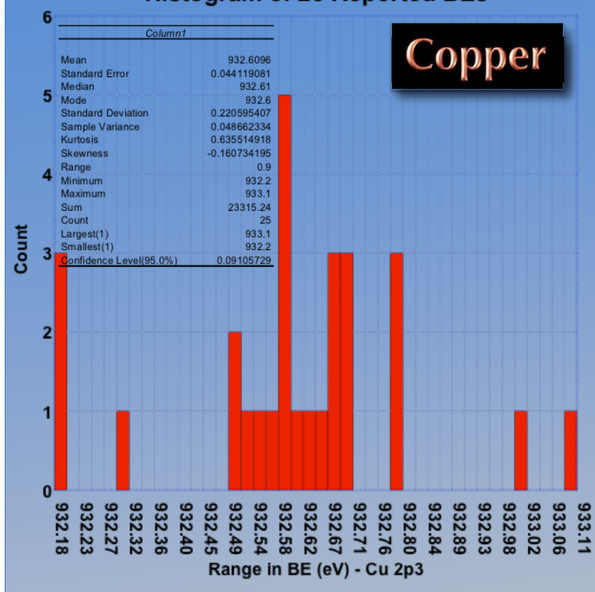
Check BE Calibration by using the routine conditions used to separate and identify different chemical states. If more than one pass energy and step size (eV/step) is routinely used, then consider checking those settings at least one time.

Check the Energy Scale by measuring the Cu 2p3 peak (932.67 eV) and either the Cu 3s peak (122.45 eV) or Cu 3p3 peak (75.14 eV) from pure (>99.9%) Copper metal that was freshly cleaned (e.g. scraped) and strongly ion-etched.

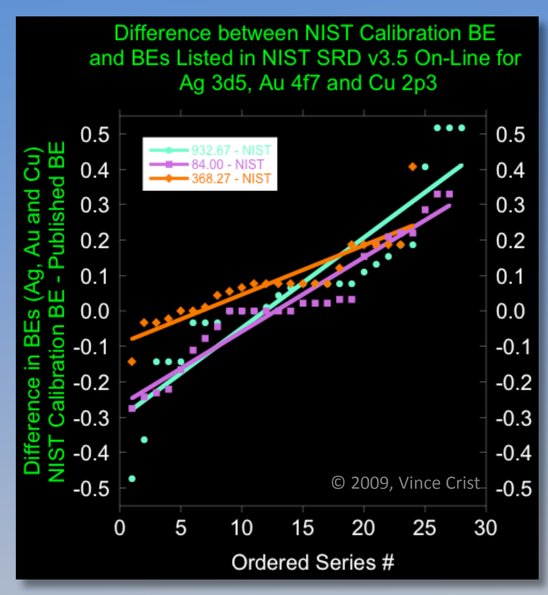
If any BE is wrong by more than >0.15 eV (practical conditions), we can use the measured BEs to adjust the work function (energy offset), energy scale factor (DAC) or pass energies of that XPS instrument.

Each time one instrument voltage is adjusted, the Cu 2p3 BE and Cu 3p3 (or Cu 3s) must be re-measured.

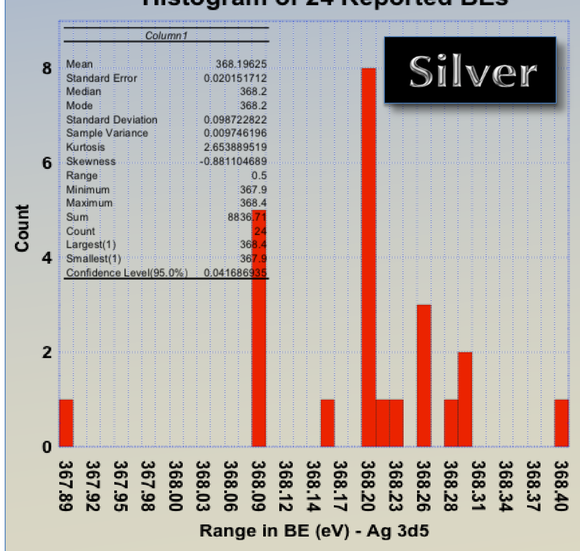
Cu (2p3/2) BE as Listed in NIST SRD v3.5 On-Line
Histogram of 25 Reported BEs



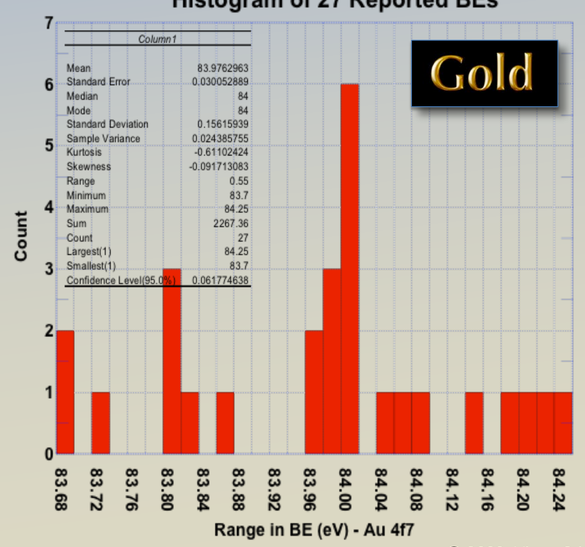
Summary of BE Uncertainties
for Ag 3d5, Au 4f7 and Cu 2p3 as Listed
in NIST SRD XPS Database of BEs v3.5 On-Line (free)



Ag (3d5/2) BE as Listed in NIST SRD v3.5 On-Line
Histogram of 24 Reported BEs



Au (4f7) BE as Listed in NIST SRD v3.5 On-Line
Histogram of 27 Reported BEs



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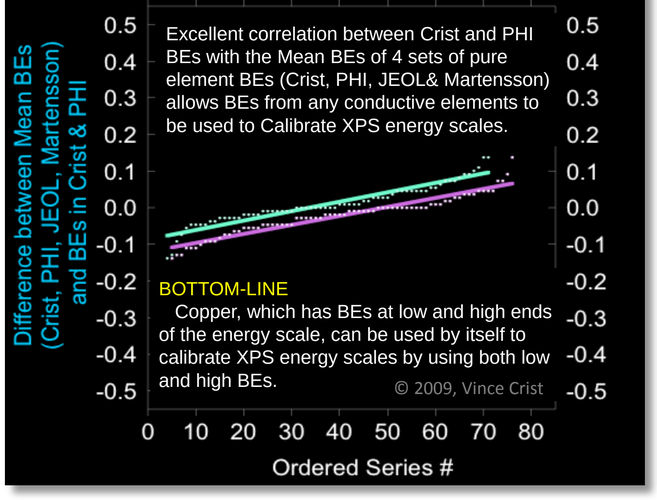
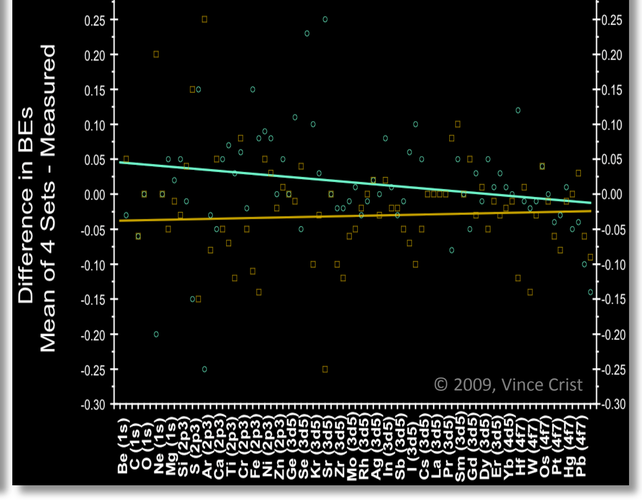
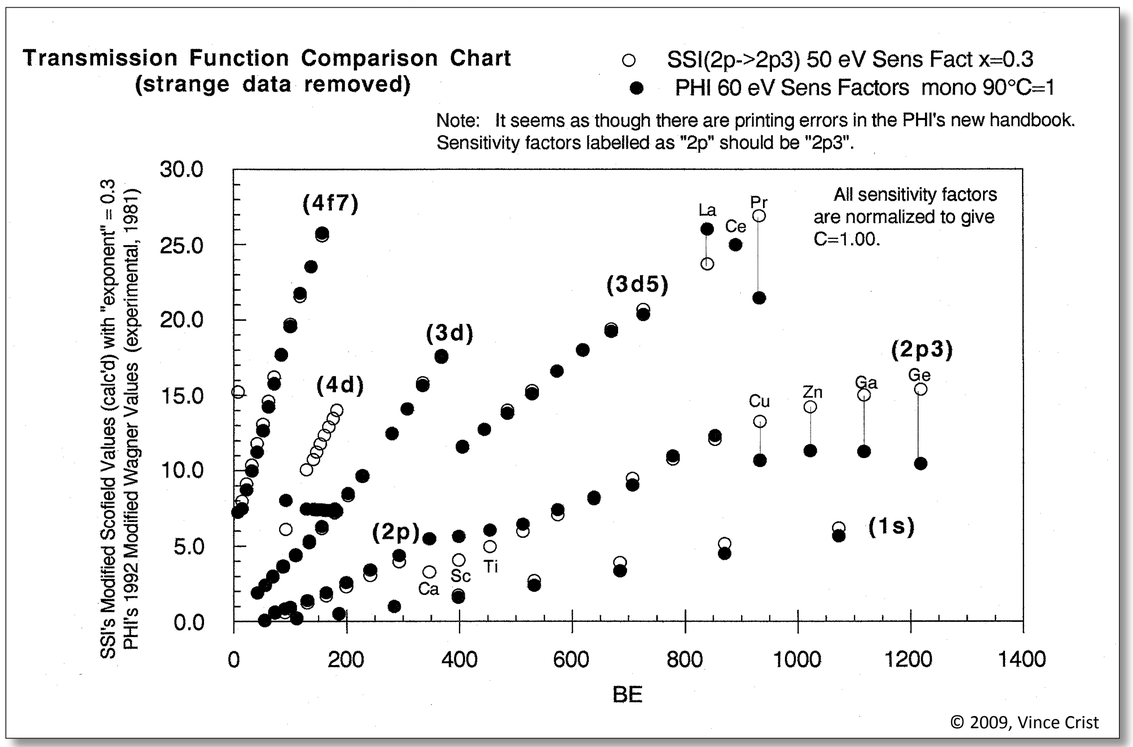
Difference between Mean BEs (4 data sets) and BEs listed in Crist XPS Database & PHI XPS Handbook (conductive elements only)



Uncertainties in Element BEs
Crist and PHI Handbooks of XPS



Comparison of Scofield's Theoretical RSFs and PHI's RSFs after Normalizing PHI RSFs to give C 1s RSF = 1.00



Statistical Analyses of Binding Energies (BEs) Listed in NIST XPS Database of BEs (SRD-20) v3.5 On-Line (free)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	LiCl	Be°											B°	C°	Si_3N_4	SiO_2	MF	Ne(+)
Mean BE	56.03	111.57											187.28	284.63	397.82	532.88	684.12	962.40
Std. Dev.	0.21	0.25											0.85	0.42	0.48	0.42	1.04	0.75
Range	*0.40*	*0.50*											*2.00*	*1.52*	*1.72*	*2.30*	*3.50*	*1.80*
# of Values	3	3											5	15	35	51	20	4
95% Confid	0.52	0.63											1.06	0.23	0.17	0.12	0.49	1.19
	NaCl	Mg°											Al°	Si°	P°	S°	KCl	Ar(+)
Mean BE	1071.90	49.64											72.90	99.40	130.18	163.91	196.70	241.32
Std. Dev.	0.56	0.21											0.19	0.26	0.32	0.60	2.82	0.63
Range	*1.60*	*0.65*											*0.80*	*1.30*	*1.00*	*1.90*	*6.50*	*1.90*
# of Values	8	11											16	51	10	9	9	11
95% Confid	0.47	0.14											0.10	0.07	0.23	0.46	2.17	0.43
	KCl	$CaCO_3$	Sc°	Ti°	V°	Cr°	Mn°	Fe°	Co°	Ni°	Cu°	Zn°	Ga°	Ge°	As°	Se°	KBr	Kr(+)
Mean BE	292.67	346.87	398.55	453.86	512.44	574.19	639.67	707.28	778.18	852.73	932.61	1021.70	18.64	29.17	41.71		68.80	207.45
Std. Dev.	0.19	0.15	0.34	0.32	0.25	0.27	1.02	0.93	0.25	0.40	0.21	0.35	0.20	0.28	0.20		0.12	0.21
Range	*0.40*	*0.30*	*0.50*	*1.10*	*0.76*	*0.90*	*2.22*	*4.20*	*0.70*	*1.80*	*0.90*	*1.30*	*0.56*	*1.05*	*0.50*		*0.20*	*0.30*
# of Values	4	4	2	8	9	15	10	27	9	25	28	15	8	11	16		4	2
95% Confid	0.30	0.24	3.18	0.27	0.19	0.15	0.73	0.37	0.19	0.17	0.08	0.19	0.17	0.19	0.12		0.18	1.91
	RbCl	SrF_2	Y°	Zr°	Nb°	Mo°	Tc°	Ru°	Rh°	Pd°	Ag°	Cd°	In°	Sn°	Sb°	Te°	LiI	Xe(+)
Mean BE	110.00	133.90	155.87	178.91	202.18	227.82		280.91	307.02	335.21	368.20	404.94	443.78	484.95	527.96	573.00	619.30	669.78
Std. Dev.	0.14	0.21	0.11	0.31	0.35	0.46		0.57	0.43	0.37	0.10	0.22	0.34	0.51	0.63	0.34	0.57	0.56
Range	*0.20*	*0.30*	*0.30*	*1.01*	*1.10*	*2.50*		*1.80*	*1.30*	*1.70*	*0.50*	0.7	*1.45*	*2.42*	*2.00*	*1.44*	*0.80*	*1.80*
# of Values	2	2	7	16	13	22		7	10	28	24	11	18	23	9	20	2	7
95% Confid	1.27	1.91	0.10	0.17	0.21	0.21		0.53	0.31	0.14	0.04	0.47	0.17	0.22	0.48	0.16	5.08	0.52

	Cs°	Ba°	La°	Hf°	Ta°	W°	Re°	Os°	Ir°	Pt°	Au°	Hg°	Tl°	Pb°	Bi°
Mean BE		780.10	835.90	14.32	21.73	31.35	40.55		60.78	71.10	83.98	99.83	117.61	136.84	156.93
Std. Dev.		0.67	0.00	0.06	0.13	0.20	0.29		0.19	0.13	0.16	0.10	0.27	0.30	0.16
Range		*1.42*	*0.00*	*0.17*	*0.30*	*0.70*	*0.90*		*0.70*	*0.47*	*0.55*	*0.20*	*0.50*	*1.50*	*0.52*
# of Values		4	2	5	9	13	8		10	31	27	4	3	19	9
95% Confid		1.07		0.08	0.10	0.12	0.25		0.13	0.05	0.06	0.15	0.67	0.15	0.12

Periodic table of the elements showing statistical analyses of BEs listed in NIST "*SRD-20 XPS Database*" v3.5. The column at the far left side lists the mean BE for the element or compound together with its standard deviation, the range in the mean BE, the number of database values that were available (minus any gross outliers) and the resulting 95% confidence values.

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