Washington University in St.Louis

Electron-Probe Microanalysis: Instrumental Calibration, Standards, Quantitative Analysis, and Problem Systems

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The Big Picture for EPMA

- Instrumental issues for EPMA:
  - Column-spectrometer alignment
  - Detector linearity and stability (flow, sealed)
  - WDS deadtime calibration
  - Spectrometer resolution, reproducibility
  - New developments: SDD EDS mapping and quantitative analysis
- EPMA Standards:
  - Proper selection of standards (sample vs. standard)
  - Internal consistency of stds in your lab vs. international environment
- Problem Systems:
  - Peak overlaps, high-order WDS interferences
  - Analytical problems, high absorption correction
  - Correction algorithms and mass absorption coefficient data sets
- Solutions:
  - Interlaboratory collaboration, education
  - Multiple KV and multiple spectrometer analysis of core std set
  - Payoff – proof of internal std comps and empirical macs

Washington University, Saint Louis
Earth and Planetary Sciences JEOL JXA-8200

Calibration Issues for Electron-Probe Microanalysis

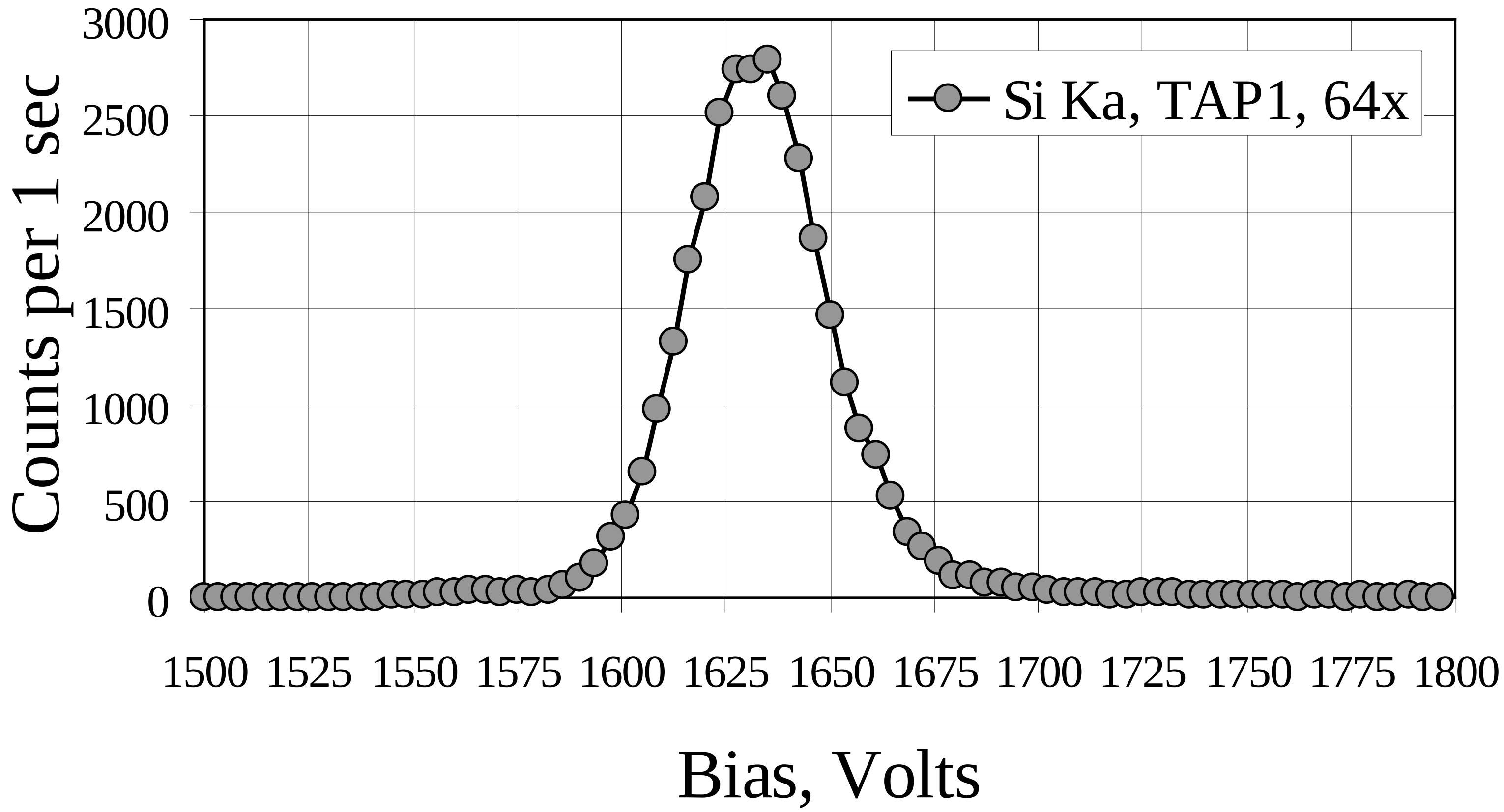
- Microprobe performance specifications are:
  - Driven by capabilities and address problem solving for customers
  - Capabilities are funded by purchases, user/vendor development
  - Realistic specifications for WDS vs. EDS systems
- Instrument calibration during installation and testing
  - Spectrometer alignment – to electron column and mutual agreement
  - Detector linearity with count rate and deadtime issues
  - Precision = reproducibility (mechanical, electronic)
  - Accuracy = correct K-ratio measured
- Instrument calibration – short vs. long term
  - Consistent performance with time
  - Accuracy in international interlaboratory environment
- Geological EPMA
  - CMAS silicate standards used for acceptance testing (CIT, WU)

Pulse-Height Analysis
Wavelength-dispersive spectrometer

WDS PHA Measurement

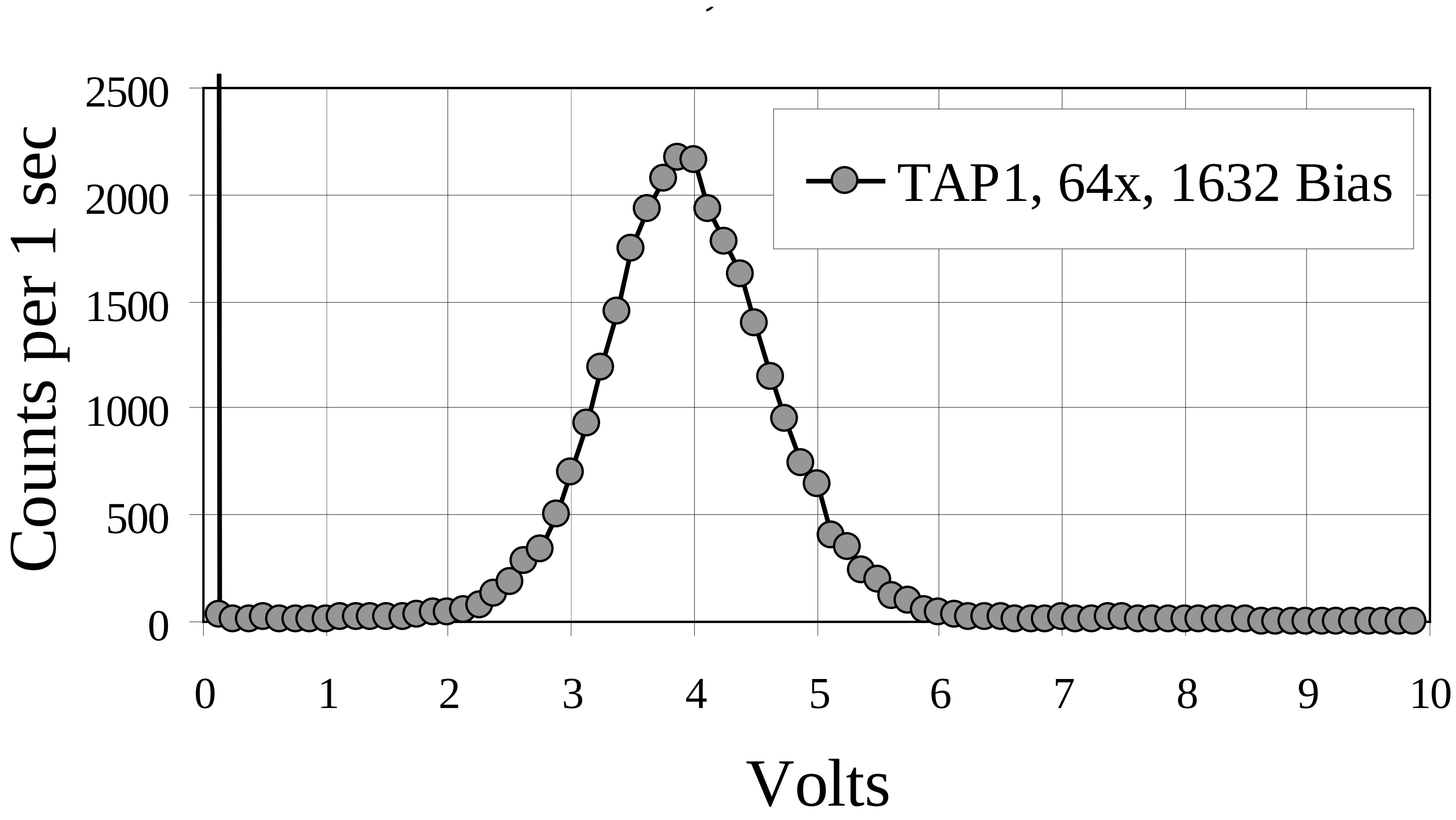
- Low energy pulses must be discriminated from baseline noise. Need proper setting of noise threshold, baseline, and window settings of WDS pulse height analyzer.
- The pulse processing circuitry of WDS does not need to deal with pulse shaping like that of EDS, and is inherently faster.
- Pulse energy shift with varying count rate results in instability. At high count rates pulses are poorly discriminated from baseline noise. Use similar count rates on standard and sample.
- Avoid tight PHA window, use integral mode unless a PHA interference is observed.
- The P-10 detector gas flow rate must be stable or else gas amplification factor varies, and so does count rate.
- Temperature variation will affect gas amplification factor as well as thermal expansion of analyzer crystal.
- Low energy peaks need to be integrated due to peak centroid and peak shape/area factors. Use area-peak factor or perform integration.

Detector Bias Scan Si Kα
Vary Bias at PHA Narrow Window



Detector bias scan using 3.9 volt baseline and 0.2 volt window on PHA.
Intended to minimize energy gain shift of PHA.
MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO_2 metal @ 10k cps.

Detector PHA Scan Si Kα

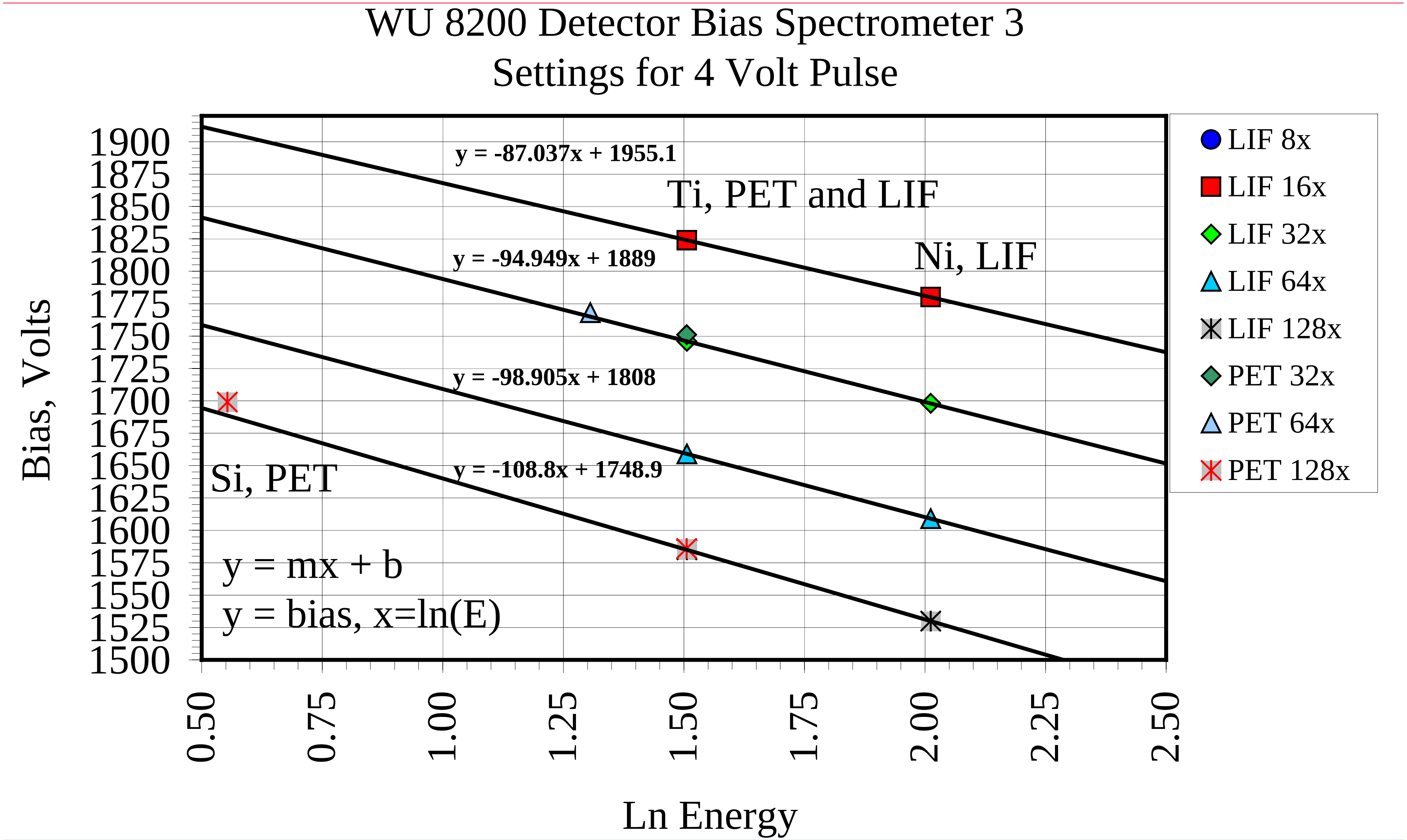


For Si Kα there is good separation between baseline and Si pulses.
Nominal baseline is 0.5 V with 9.5 V window (integral mode)
MSFC Spec 1, P-10 flow counter, TAP, 64x gain, Si Kα on SiO_2 @ 10k cps.

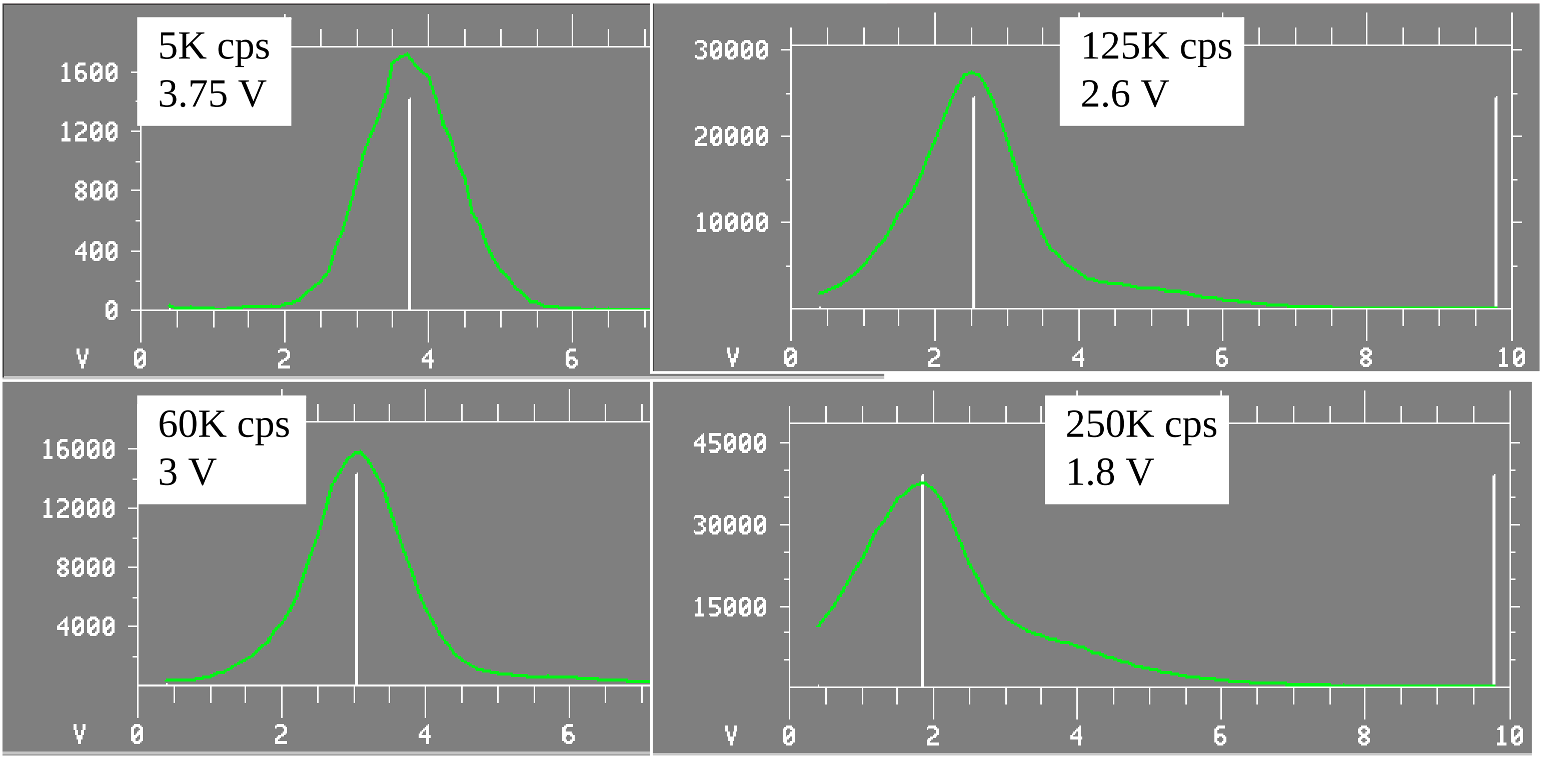
Calibration of PHA
Using Bias vs. ln(E) plots

- For JEOL microprobe want SCA pulse at 4 volts, Cameca at 2 volts
- Spectrometer at peak position
- Bias scan with 3.8v base, 0.2v window gives bias for 4 volt SCA
- Plot of bias vs ln of x-ray energy is linear
- Calibration performed for minimum element set which spans energy range of spectrometer for all analyzing crystals
- Detector should give same bias for Ti Kα on PET vs. LIF, others
- Calibration confirms systematic behavior of x-ray counter
- As P-10 tank empties and Ar/CH_4 changes, requires recalibration
- Use y = mx + b fit to bias data to provide quick calibration
- Similar plot for escape peak as function of x-ray energy

PHA Bias Plot for LIF/PET Data
Si, Ti, Ni Bias data at 8, 16, 32, 64, and 128x Gain



Gain Shift Due to Count Rate



Gain shift due to count rate, detector bias arbitrarily set to 1700 volts.

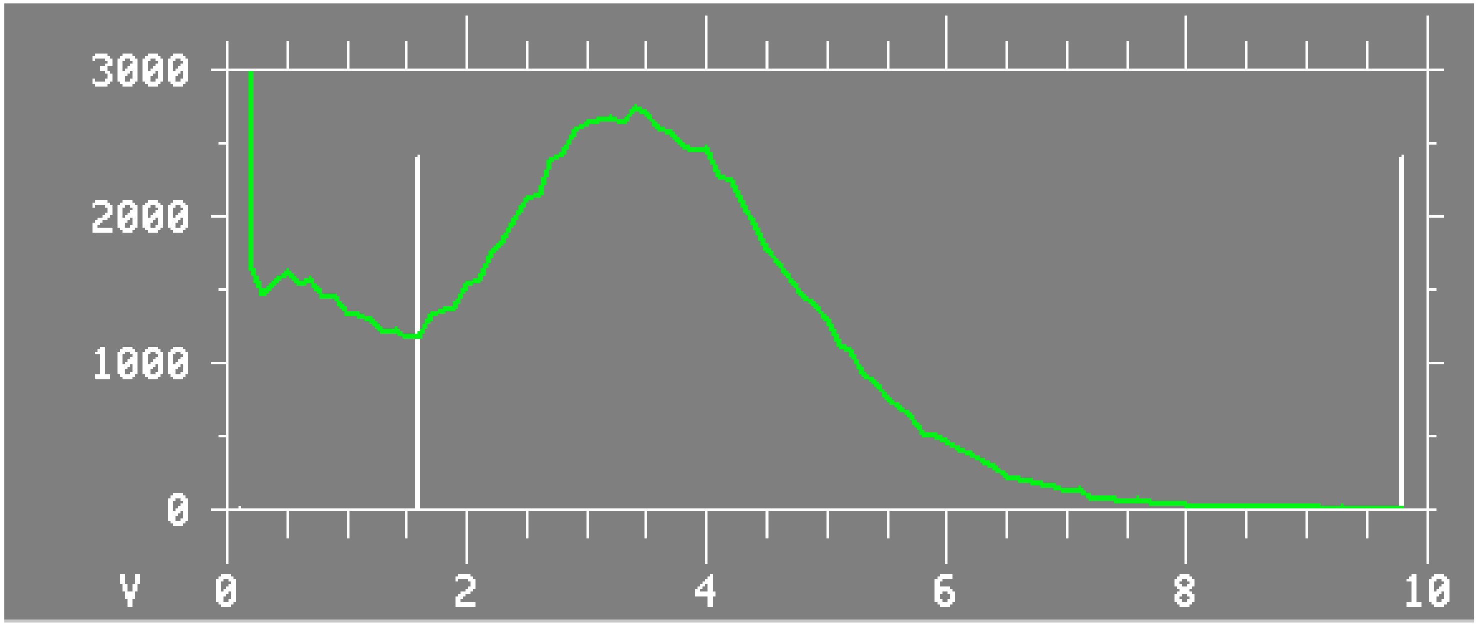
Observed shift is ~ 0.008 volts per 1 K cps (1.95 volt shift over 245 K cps range).

At ~125k cps baseline noise discrimination deteriorates.

Older PCS electronics exhibit complete shift into baseline noise.

MSFC Spec 1, P-10 flow counter, TAP, 32x gain, Si Kα on Si metal.

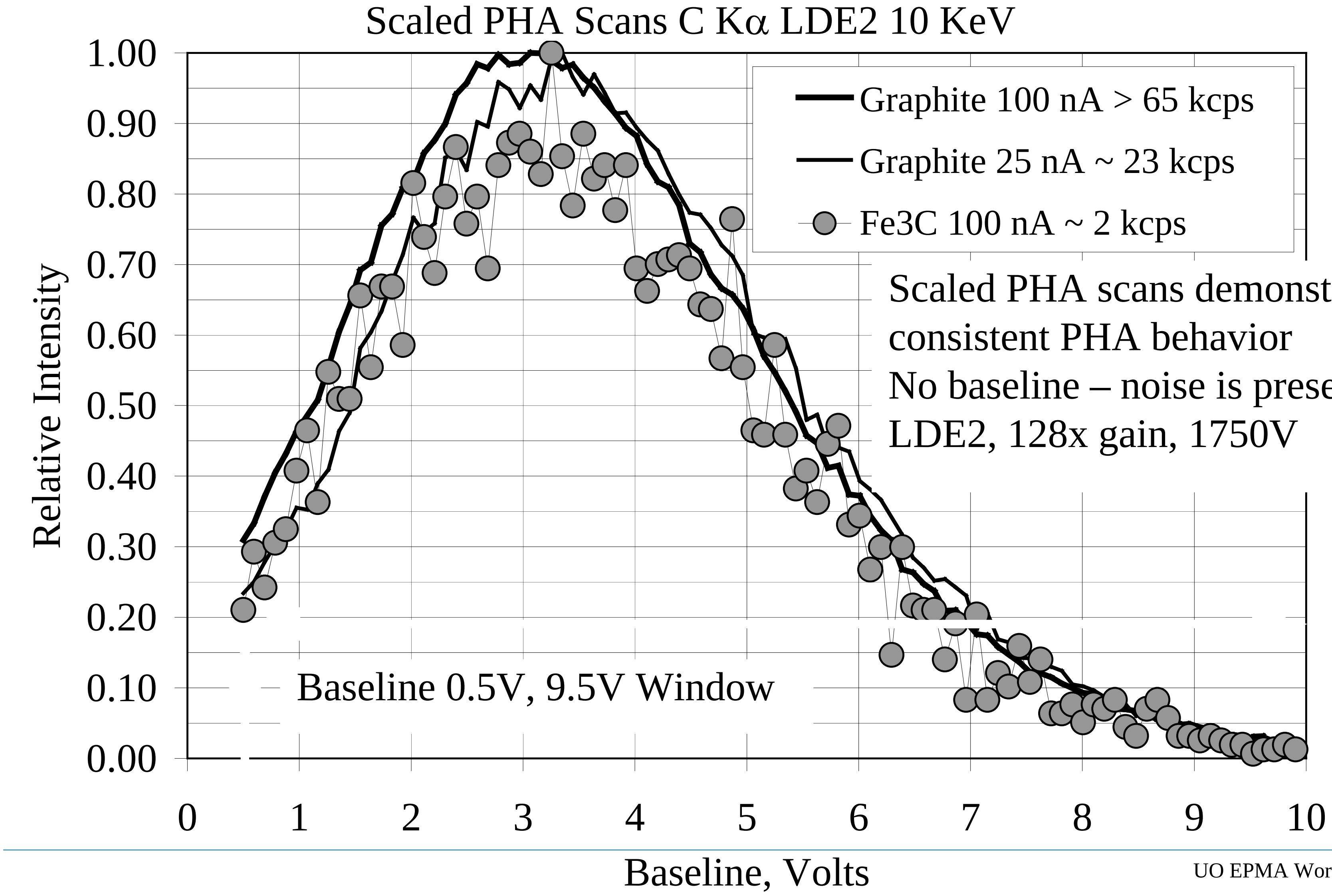
PHA Scan Ti Lα 20K CPS



Light element / low energy x-rays are poorly resolved from baseline noise. Gain shifts with count rate – PHA peak shifts toward baseline with increasing count rate. Use integral mode unless PHA energy discrimination required – counts extend to upper limit of PHA scan.

MSFC Spec 1 with P-10 flow counter, LDE2, 128x gain, Ti Lα on Ti metal @ 20k cps.

Carbon Kα PHA Scans Graphite, Fe3C



Scaled PHA scans demonstrate consistent PHA behavior

No baseline – noise is present

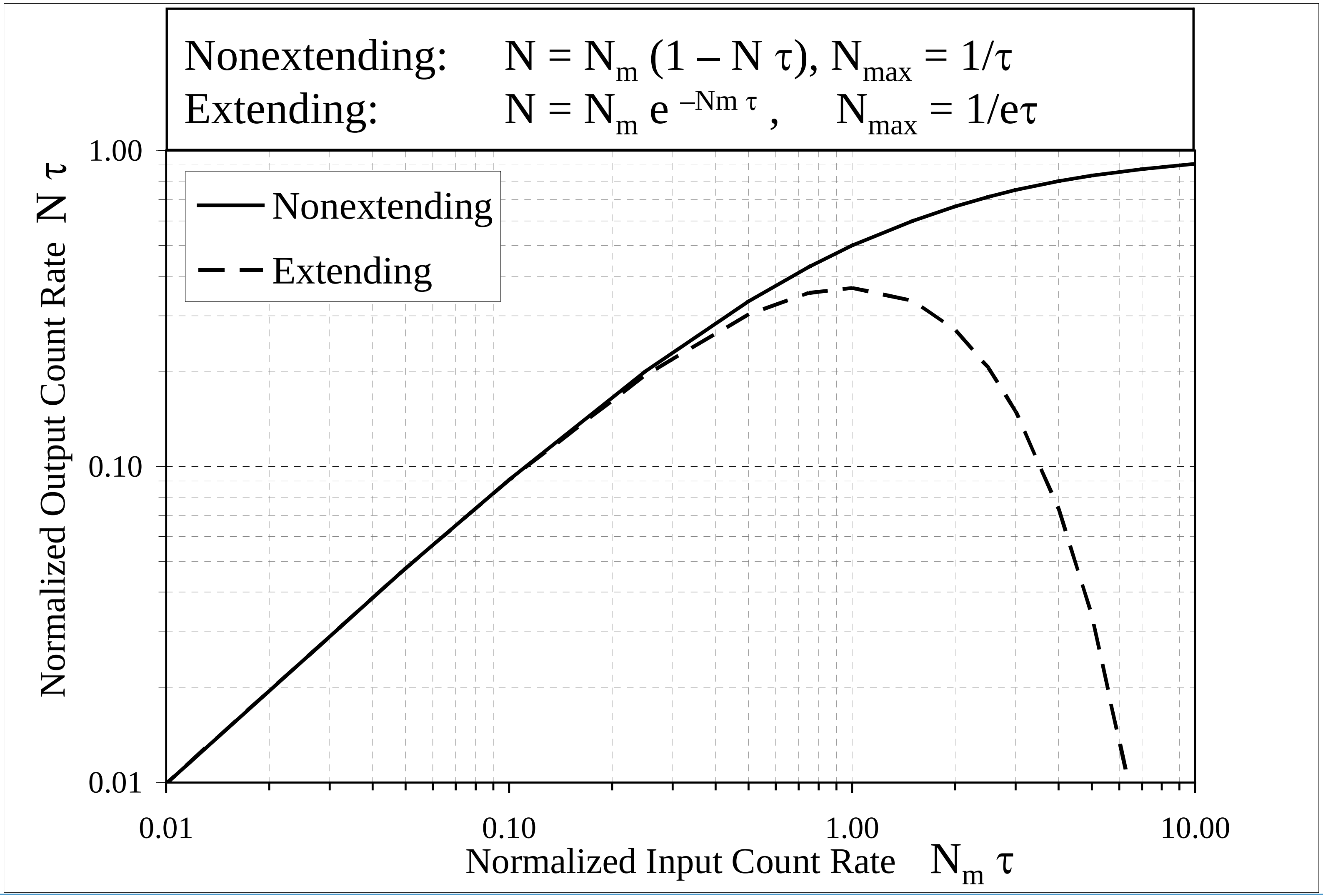
LDE2, 128x gain, 1750V

Deadtime Measurement on the Wavelength-Dispersive Spectrometer

WDS Deadtime Issues in EPMA

- Deadtime – time interval during which counting electronics are unable to process subsequent incoming pulses
- Deadtime error is non-negligible, systematic, affects all measurements
- General problem:
- Counting behavior of WDS systems is undocumented and poorly known
- End-users make measurements with assumed WDS deadtime behavior
- User knowledge of deadtime issues needs improvement
- Specific problem areas:
    - No software to conveniently evaluate deadtime on turnkey systems
    - No agreed method for setting bias, gain, and sca on systems
    - SCA pulse shift behavior with count rate undocumented
    - Deadtime dependence on X-ray energy undocumented and unknown
    - Low vs. high count rate behavior and deadtimes inconsistent

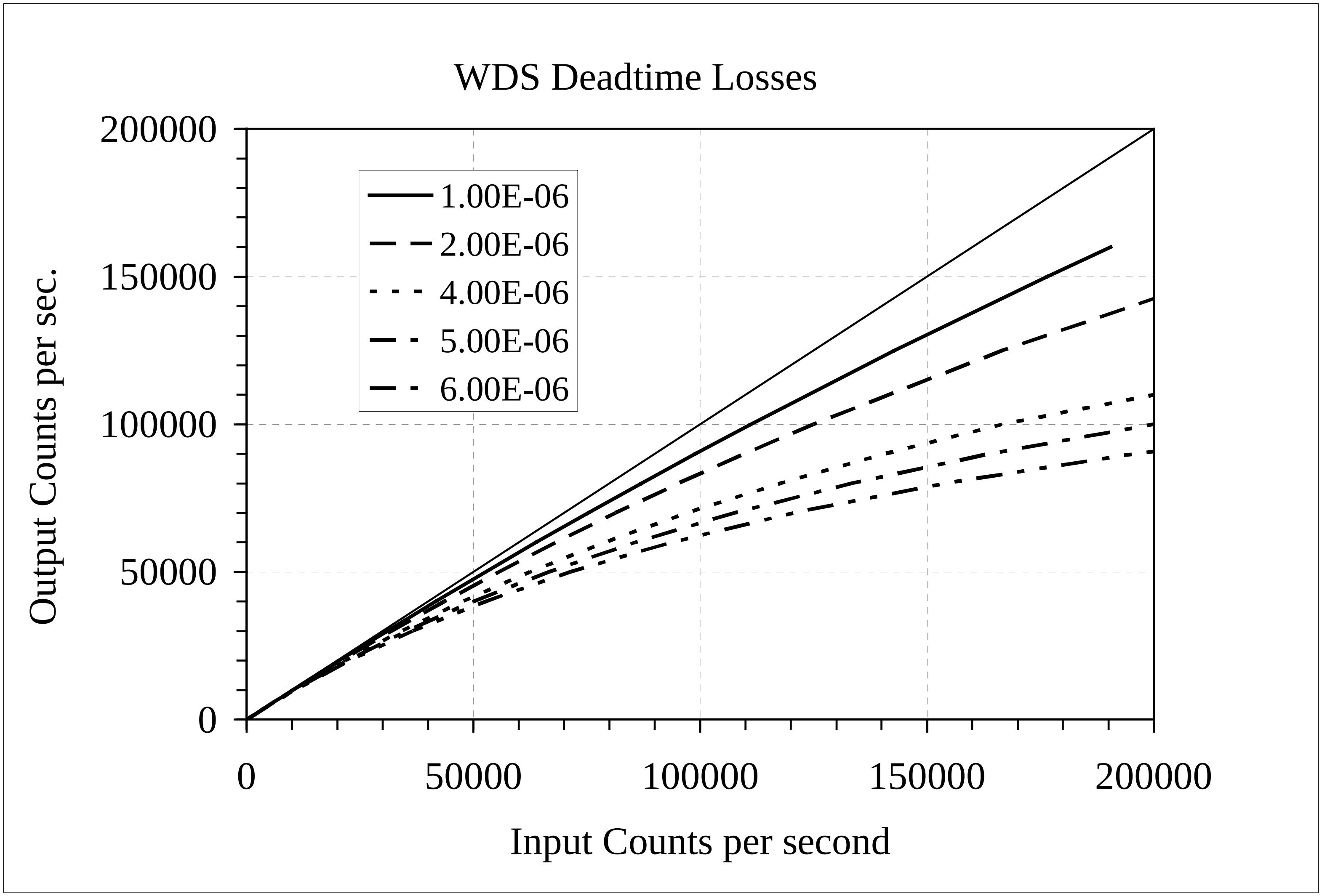
Deadtime Behavior:
Extending vs. Nonextending



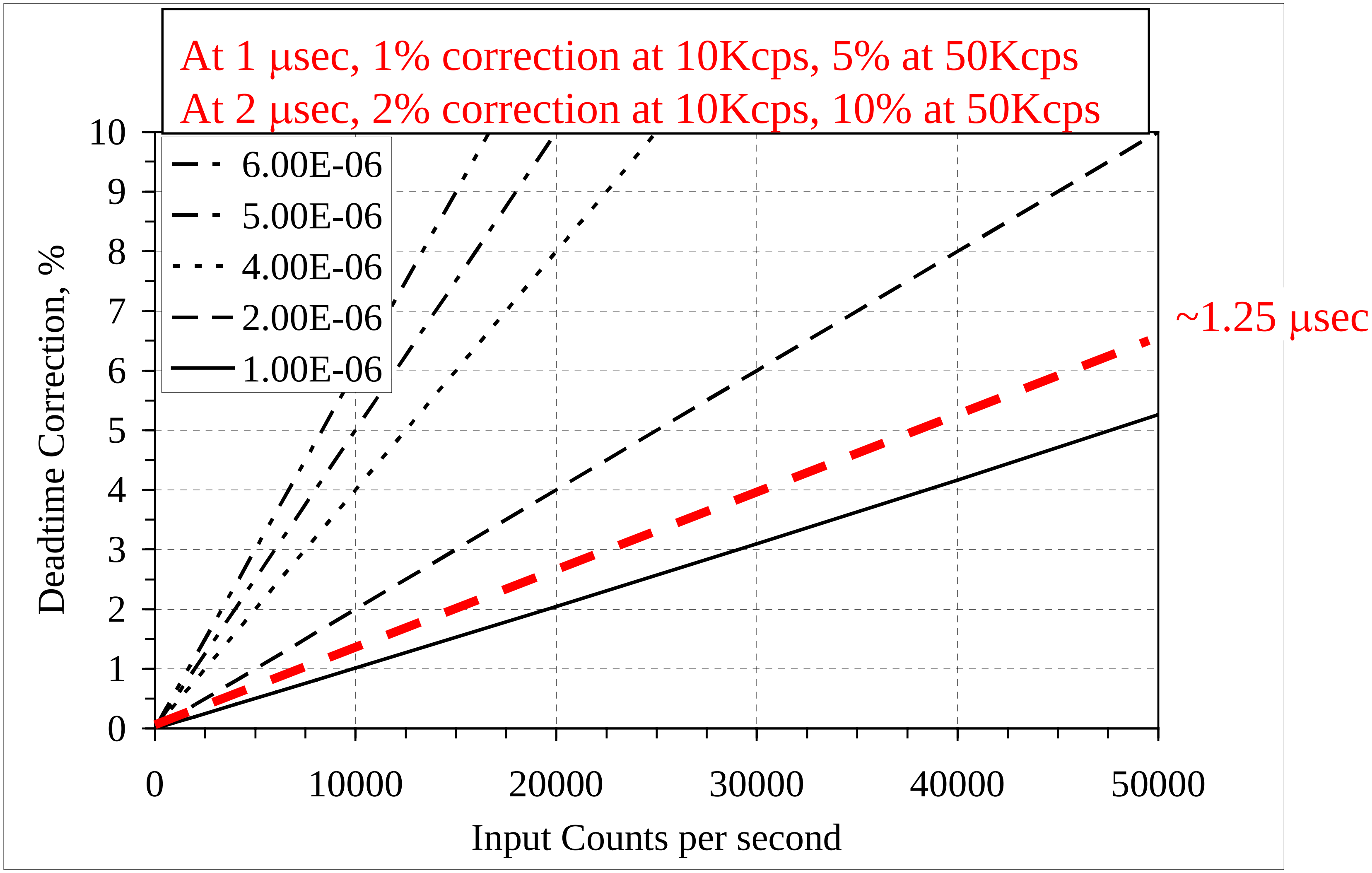
Nonextending: $N = N_m (1 - N \tau)$, $N_{max} = 1/\tau$

Extending: $N = N_m e^{-N_m \tau}$, $N_{max} = 1/e\tau$

Deadtime Losses
Input – Output Curves for μsec Deadtime Constants



Percentage Deadtime Losses
Percent Level Corrections Apply to All Measurements



At 1 µsec, 1% correction at 10Kcps, 5% at 50Kcps

At 2 µsec, 2% correction at 10Kcps, 10% at 50Kcps

~1.25 µsec

Deadtime Relations
Calculation of Deadtime Constant

$$N = \frac{N_m}{(1 - N_m \tau)}$$

- N = true count rate, N_m = measured count rate with deadtime losses ($N_m < N$), and τ is the deadtime constant, which ranges from 1 to several μsec for WDS counting systems. It is necessary to know N_m and N to calculate τ. We assume the proportionality of N to the probe current i is constant. This may not be true at low count rates.

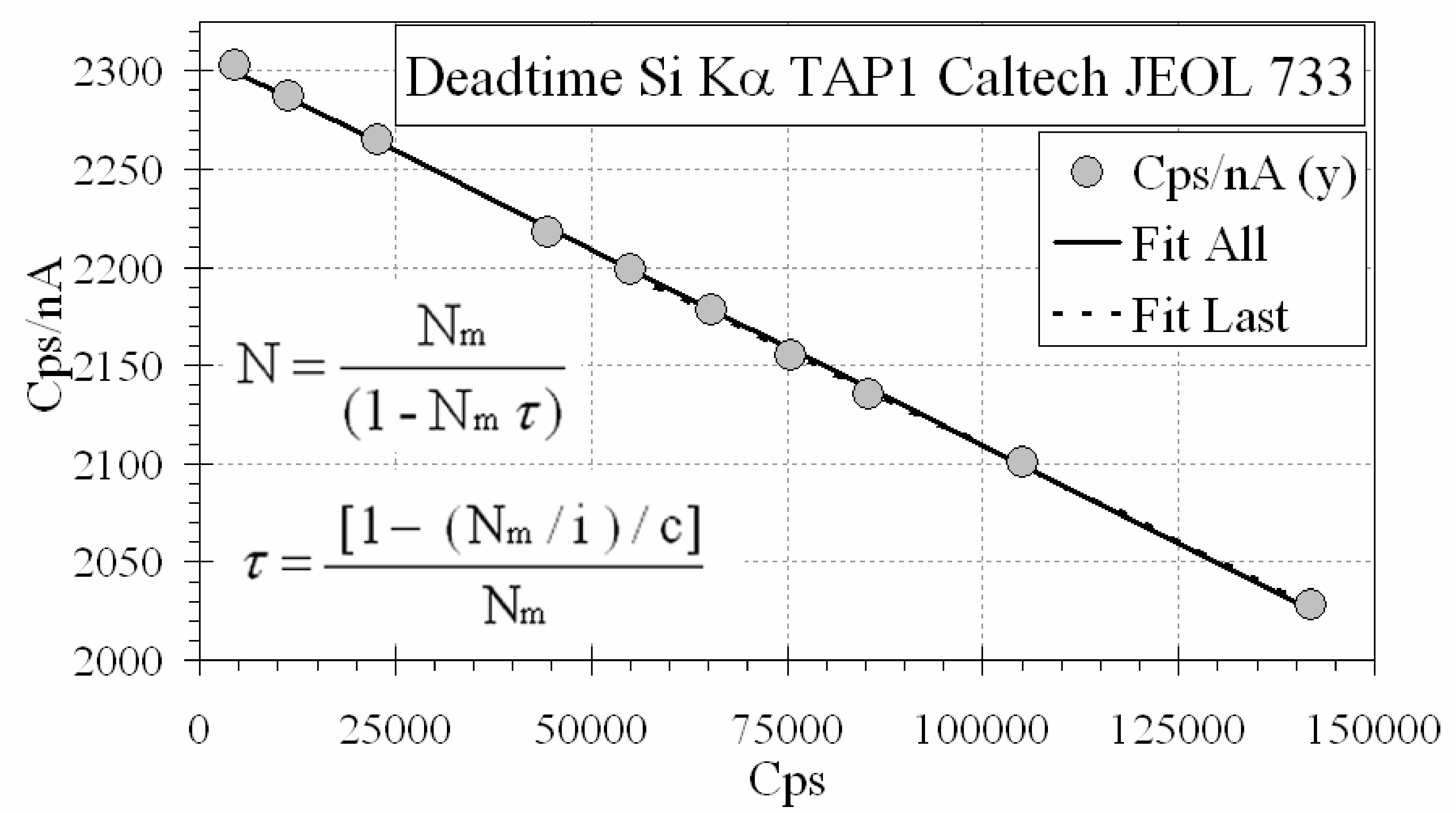
$$\frac{N_m}{i} = c(1 - N_m \tau)$$

- N_m / i = measured count rate in counts per second per nA, and c is the constant N / i
  Form: y = mx +b
  (N_m / i) is y, x is N_m, y-intercept b is constant c (= N / i).

$$\tau = \frac{[1 - (N_m / i) / c]}{N_m}$$

- Equivalent to τ = (1 – y / b) / x
  Measure x-ray intensity at increasing probe current
  Use count rate N_m and N_m / i to evaluate the deadtime constant τ over a range of intensity values

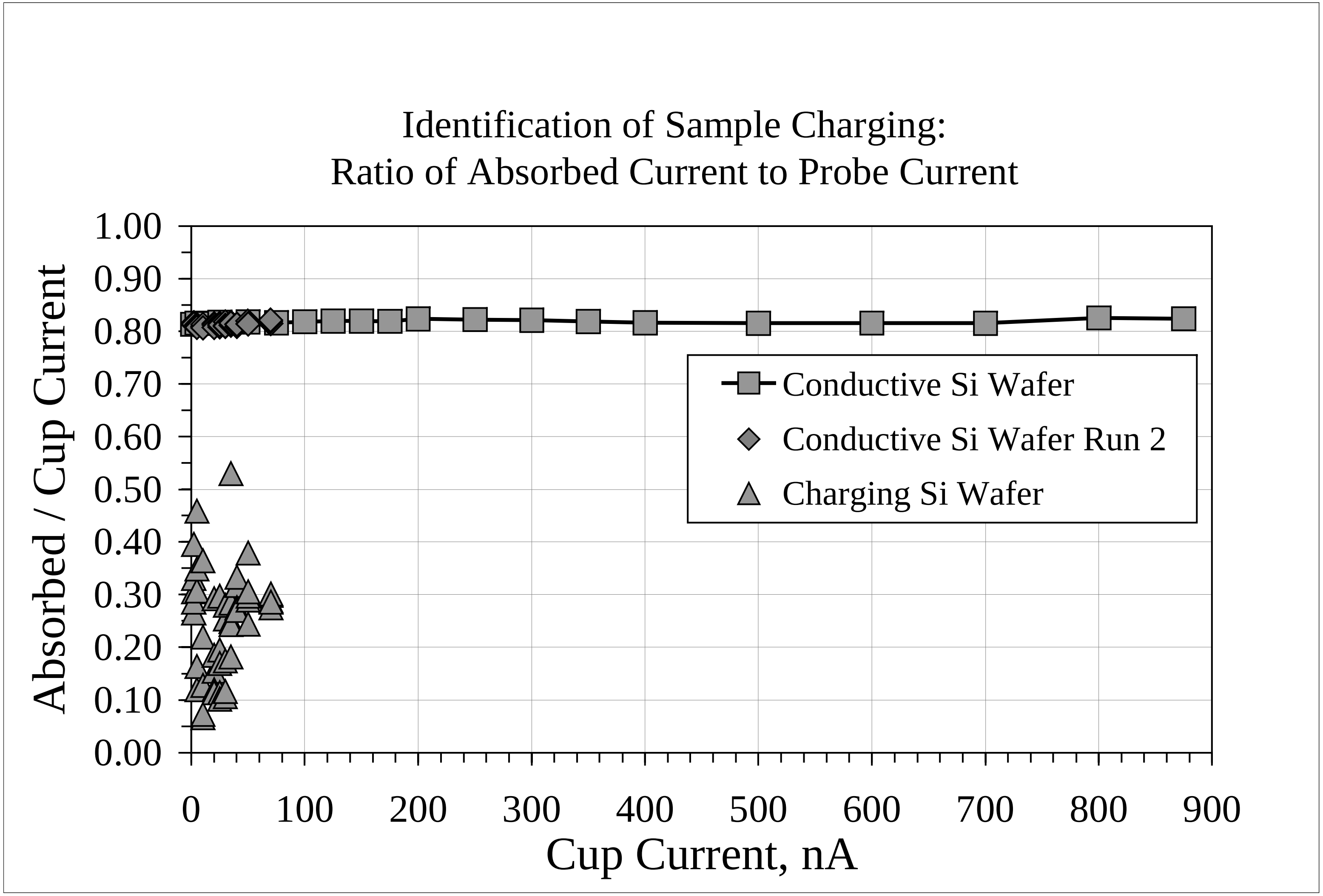
Deadtime Evaluation Plot
N_m vs. N_m / i to determine LS Fit to τ



$$N = \frac{N_m}{(1 - N_m \tau)}$$

$$\tau = \frac{[1 - (N_m / i) / c]}{N_m}$$

Verification of Probe Current vs. Absorbed Current Linearity and/or Detection of Sample Charging

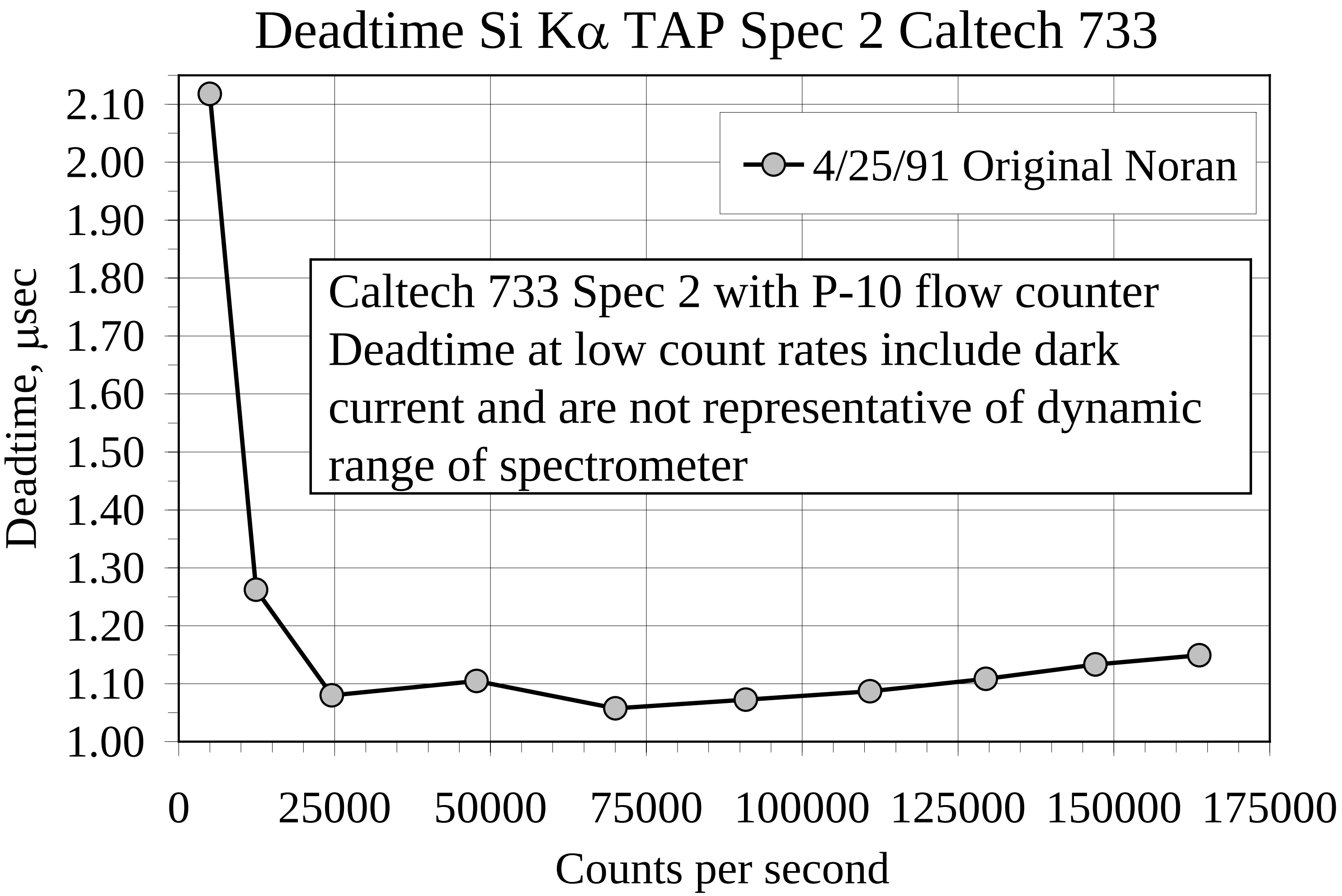


Deadtime Calculation from Excel Spreadsheet

nA	Abs Cur	Abs/Probe	Time	Cps (x)	Cps/nA (y	Fit All	Fit Last	DT us All	DT Last
2.00	1.63	0.82	100	4607.9	2302.57	2299.81		0.61	
5.00	4.05	0.81	80	11436.9	2287.20	2286.17		0.83	
10.01	8.10	0.81	80	22665.3	2264.44	2263.73		0.85	
20.05	16.25	0.81	60	44469.0	2217.95	2220.18		0.89	
25.00	20.29	0.81	60	54977.1	2199.08	2199.18	2197.08	0.87	0.83
29.98	24.34	0.81	30	65298.1	2177.91	2178.56	2177.00	0.87	0.84
35.02	28.54	0.81	30	75474.9	2155.07	2158.23	2157.20	0.88	0.86
40.05	32.53	0.81	30	85510.0	2134.97	2138.18	2137.67	0.88	0.86
49.99	40.74	0.81	30	105026.6	2101.04	2099.19	2099.70	0.86	0.84
69.98	57.25	0.82	30	141942.7	2028.45	2025.44	2027.88	0.86	0.84
Regression Output:						Mean deadtime		0.86	0.84
All	Y intercept		2309.01	Slope	-0.0020	Sigma		0.02	0.01
High CR	Y intercept		2304.04	Slope	-0.0019	Regression DT		0.87	0.84

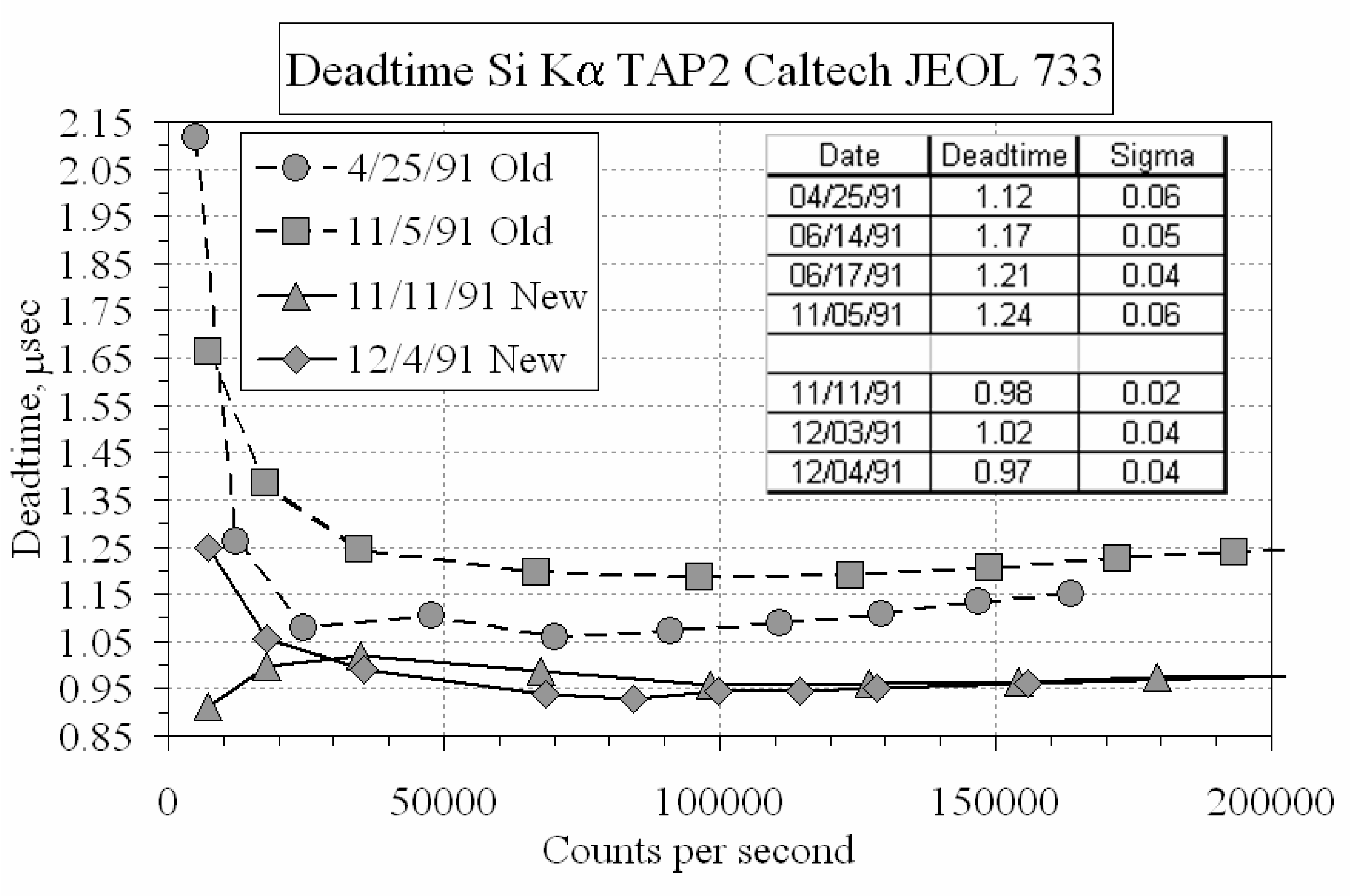
Excel Sheet: X is N_m and Y is N_m/i. Deadtime evaluated from each intensity (DT) and from least squares fit to data (Fit) using Excel *linest* function. All data and high intensity only data are compared with average values (Mean deadtime) and standard deviation. Ratio of absorbed/probe current checks conductivity. If linear all data agree.

Deadtime Variation with Count Rate



Caltech 733 Spec 2 with P-10 flow counter
Deadtime at low count rates include dark current and are not representative of dynamic range of spectrometer

Deadtime Variation With Time and P-10 Gas Chemistry
Comparison of Original and New Tracor PCS Electronics



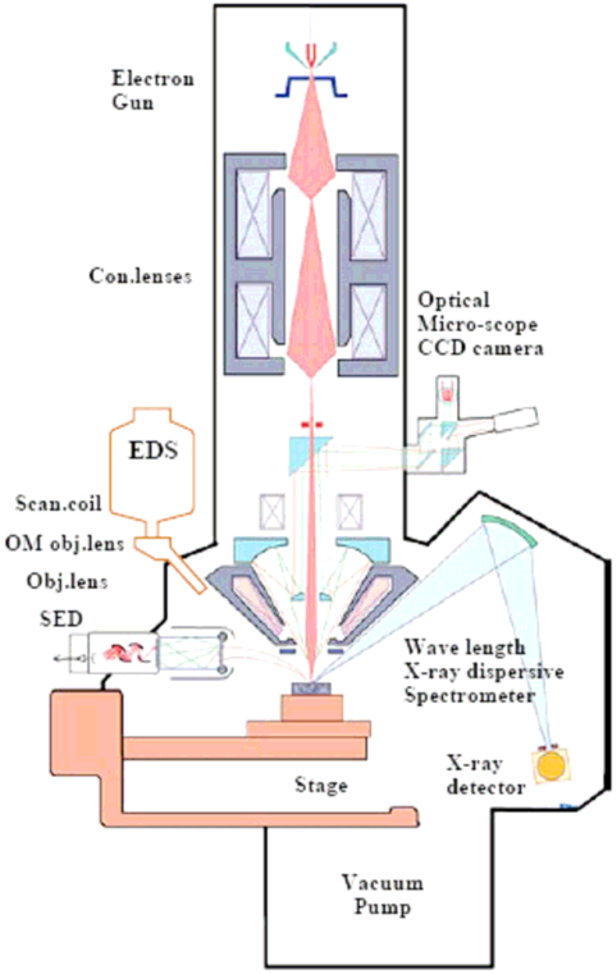
Date	Deadtime	Sigma
04/25/91	1.12	0.06
06/14/91	1.17	0.05
06/17/91	1.21	0.04
11/05/91	1.24	0.06
11/11/91	0.98	0.02
12/03/91	1.02	0.04
12/04/91	0.97	0.04

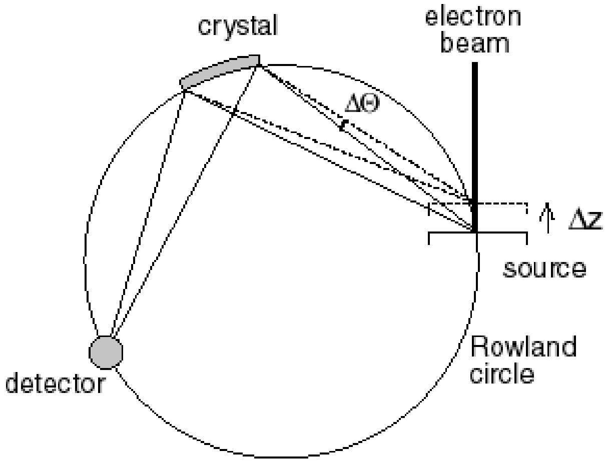
Alignment and Quantitative Analysis:
Wavelength-Dispersive and Energy-Dispersive Spectrometers

Establishing Calibration of an Electron Microprobe

- Wavelength spectrometer aligned vertically (baseplate) to coincide with optical microscope focal point in z-space
- Diffracting crystal aligned to be on Roland circle
- All WDS should focus on same z-axis and coincident xy area ~ 50 um in diameter
- Characteristics of correct alignment
  - All WDS & EDS have identical X-ray takeoff angle
  - Maximum X-ray intensity at z focus position, but also require:
  - Measure identical k-ratio within counting statistics
- Simultaneous k-ratio measurement is ultimate test of alignment
- Initial CMAS standard set used on Caltech MAC and JEOL JXA-733
- Expanded CMASTF standard set used for Wash U JXA-8200

Electron Microprobe Column
Spectrometer Alignment: Baseplate and Crystal





Baseplate: Place Rowland circle at Z focus

Crystal: Align all crystals on Rowland circle

Spectrometer design keeps detector on RC

Note: Different K-ratio = misalignment

Multiple spectrometer comparison required to demonstrate all WDS and EDS are mutually aligned

CMASTF Silicate Standards
Geological materials are multicomponent

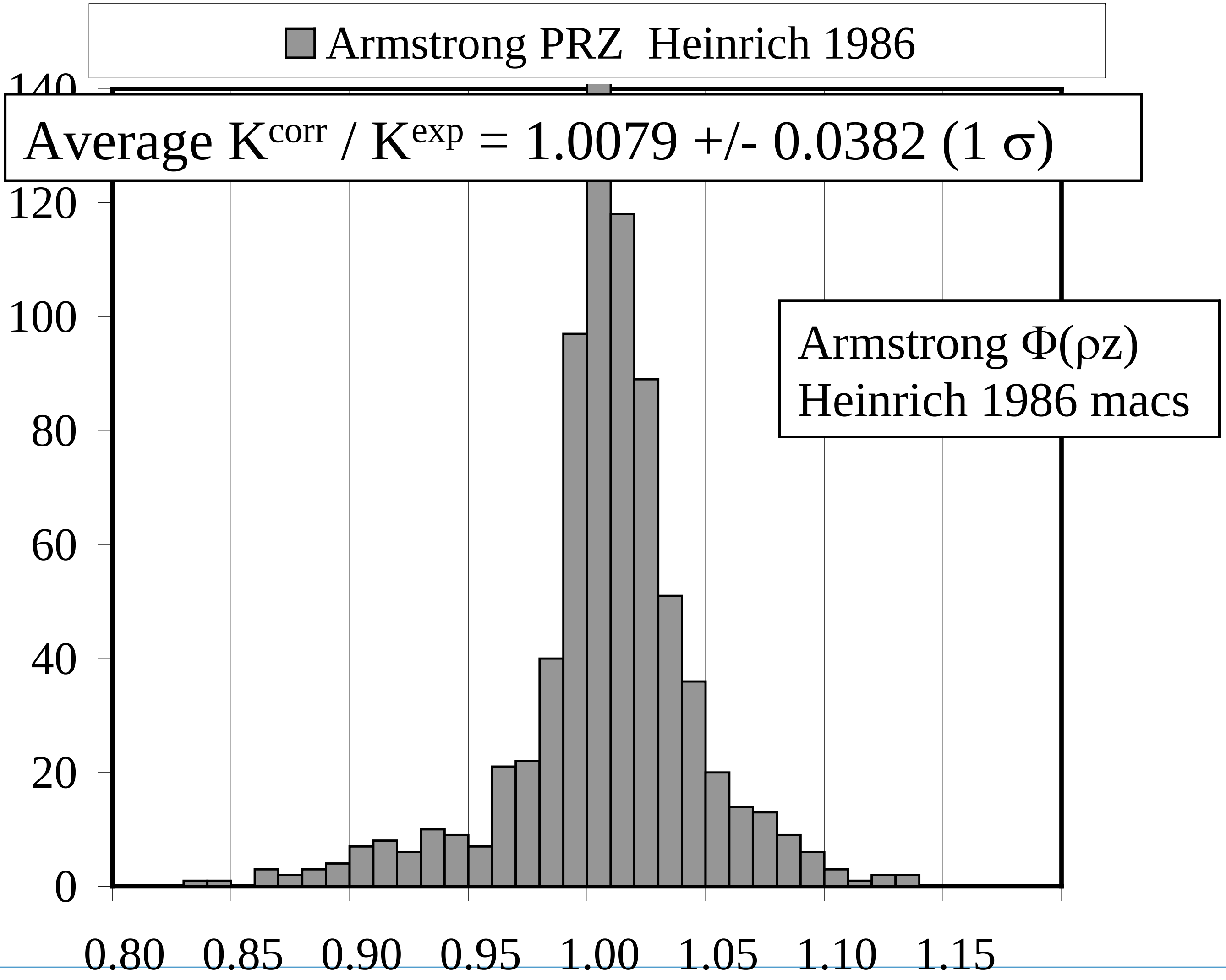
- End-member stoichiometric silicate and oxide mineral standards
- Primary standards:
  MgO, Al_2O_3, SiO_2, $CaSiO_3$ (CaO 48.27, SiO_2 51.73), TiO_2, and Fe_2O_3
- Analyzed suite of stoichiometric standards, natural and synthetic materials:
  Second set of primary standards on different mounts
  Spinel $MgAl_2O4$, Enstatite $MgSiO_3$, Forsterite Mg_2SiO_4
  Kyanite Al_2SiO_5
  Fayalite Fe_2SiO_4
- Well characterized natural mineral standards and glasses:
  Olivines $(Mg,Fe)_2SiO_4$
  Diopside $CaMgSi_2O_6$, Anorthite $CaAl_2Si_2O_8$, Sphene $CaTiSiO_5$
  Ilmenite $FeTiO_3$
  Synthetic glasses in CMAS and CMASF system:
    Weill CMAS glasses, NBS K411, K412

CMASTF Standard Inventory: Natural & Synthetic

Composition in Wt% Oxide

Standard	MgO	Al2O3	SiO2	CaO	TiO2	FeO* or Fe2O3
Alaska Anorthite		36.03	44.00	19.09		0.62
Boyd Olivine	51.63		40.85			7.17
Ilmen Mtns Ilmenite	0.31				45.70	46.54
K411 Glass	14.67	0.10	54.30	15.47		14.42
K412 Glass	19.33	9.27	45.35	15.25		9.96
Kyanite P236		62.91	37.09			
Natural Bridge Diopside	18.31	0.06	55.40	25.78	0.01	0.26
ORNL, RDS Fayalite			29.49			70.51
San Carlos Olivine	49.42		40.81			9.55
Shankland Forsterite	57.30		42.70			
Springwater Olivine	43.58		38.95			16.62
Taylor Kyanite	0.00	62.70	37.00			0.16
Taylor Olivine	50.78		41.15			7.62
Taylor Sphene		1.36	30.83	28.82	37.80	0.66
Taylor Spinel	28.34	71.66				
Weill A	11.05	16.07	49.72	23.15		
Weill B	13.99	16.05	48.99	20.97		
Weill D	17.97	20.96	45.07	16.00		
Weill E*	6.00	8.99	79.97	5.04		
Weill Enstatite Glass	40.15	0.00	59.85			
Weill F	10.07	30.93	52.06	6.94		
Weill G	32.69	3.31	61.12	2.89		
Weill H	5.22	41.90	30.91	21.97		
Weill I	19.03	2.01	52.95	26.01		
Weill J	1.01	19.02	42.98	36.99		

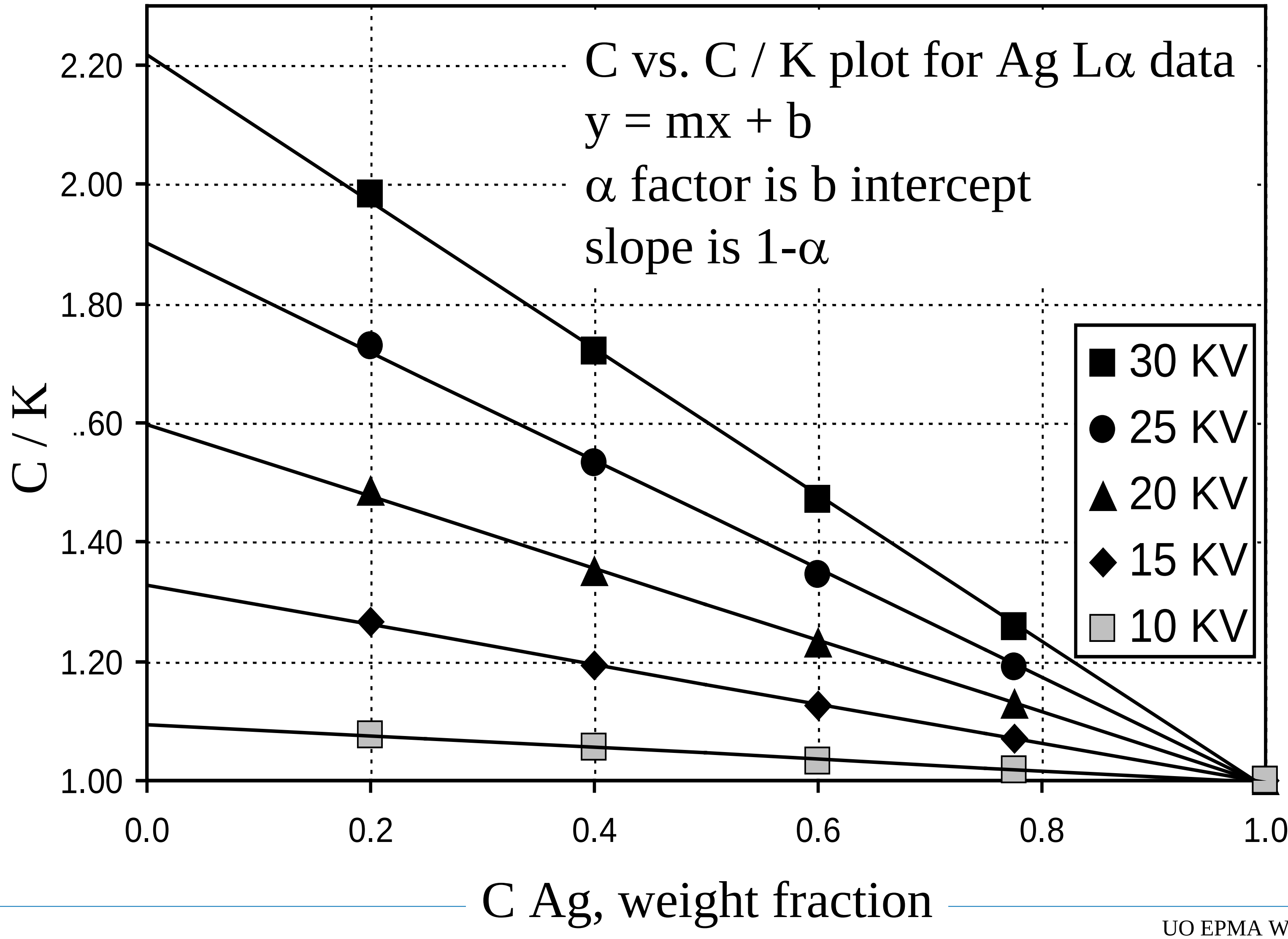
Pouchou Experimental Binary K-ratio Data Set (n=756)
$\Phi(\rho z)$ Algorithm – No silicates or multi-element materials



Average K^{corr} / K^{exp} = 1.0079 +/- 0.0382 (1 σ)

Armstrong $\Phi(\rho z)$
Heinrich 1986 macs

Ag Lα NIST SRM 481 AgAu Alloy (ψ=40)



C vs. C / K plot for Ag Lα data

y = mx + b

α factor is b intercept

slope is 1-α

Accuracy Study for EPMA
Comparison of Measured to Calculated K-ratio

- $K_{measured}$ dependent on:
  - Accelerating Potential
  - Probe current
  - Detector (gas, sealed)
  - Pulse processing
  - PHA calibration
  - Deadtime
  - Spectrometer alignment
  - Sample homogeneity
  - P-B determination, stripping, counting statistics
  - Other sampling/drift factors
- $K_{calculated}$ dependent on:
  - Correct composition of standard
  - Correction algorithms
  - Data sets, mass absorption coefficients
  - Other algorithmic factors

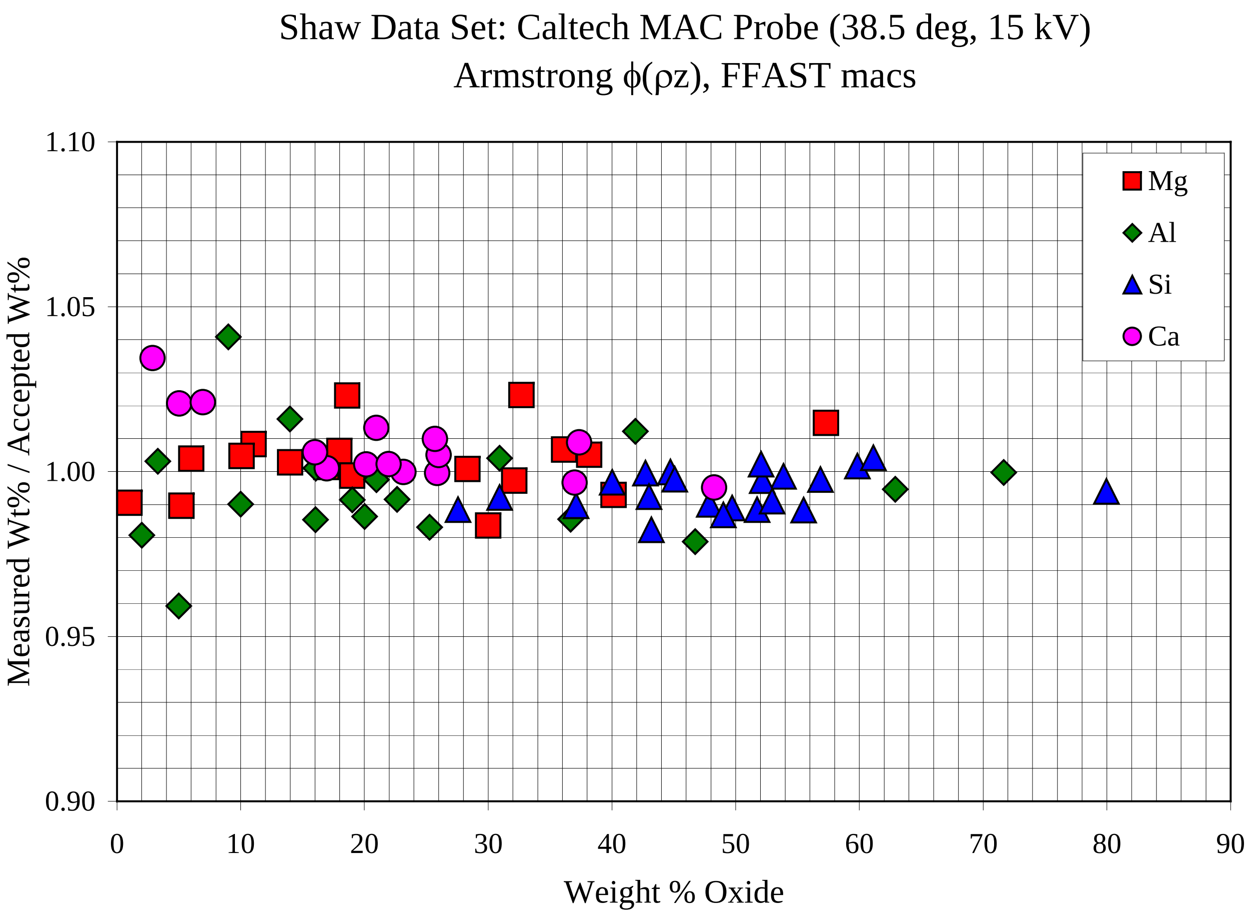
$$K_{measured} = \frac{(P - B)^{sample}}{(P - B)^{standard}}$$

$$C = K * ZAF$$

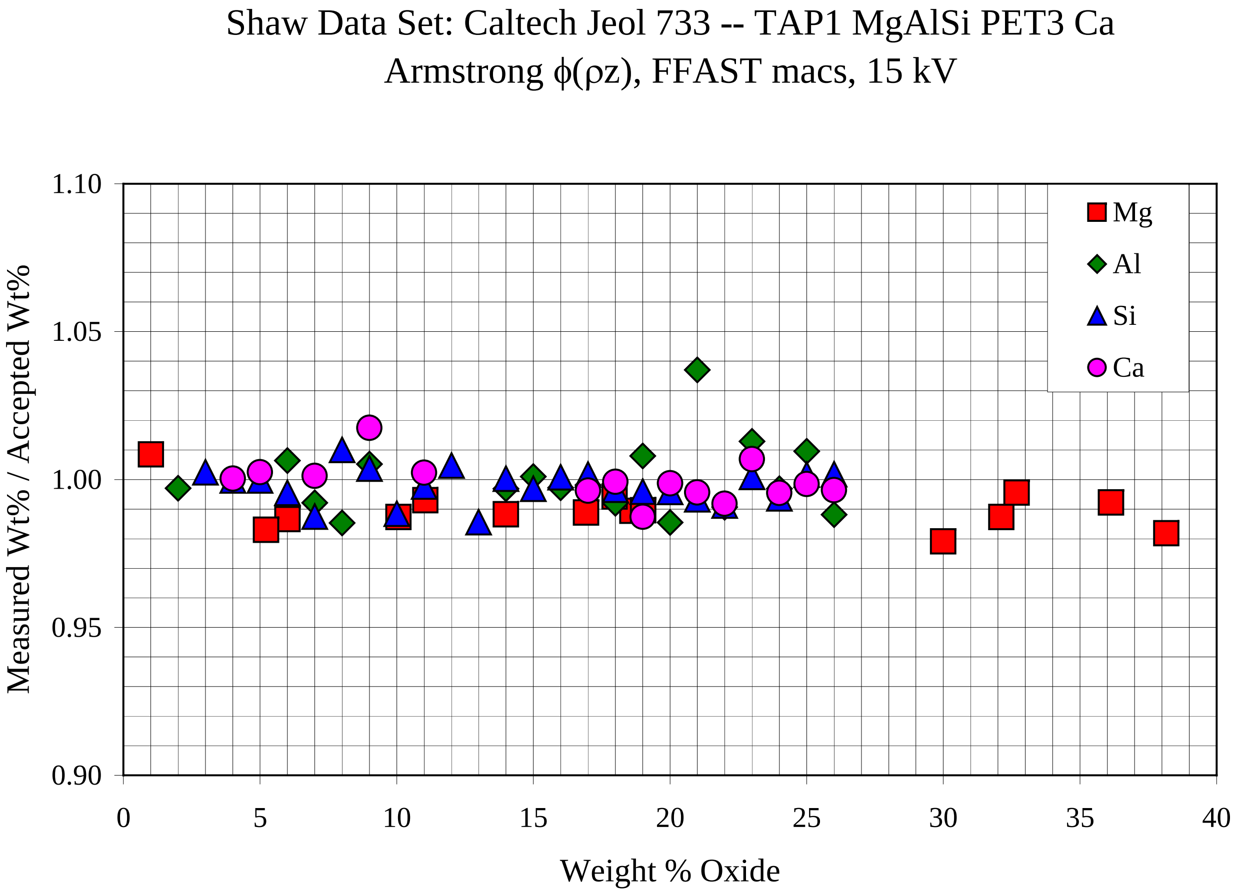
$$K_{calculated} = C / ZAF$$

$$\text{Evaluate}: \frac{K_{measured}}{K_{calculated}}$$

Historical CMAS Data
Caltech MAC Probe, Circa 1980's

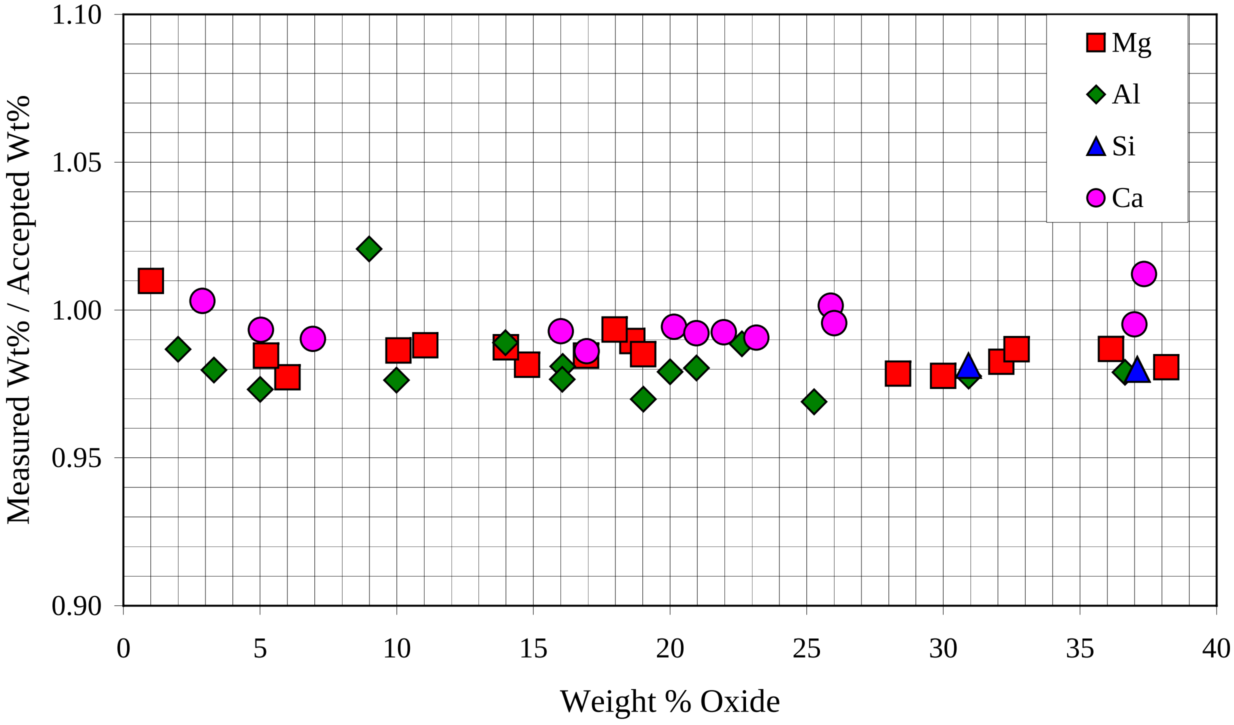


Caltech JEOL 733 1990’s
Spectrometer 1 TAP for Mg Al Si (Ca PET)



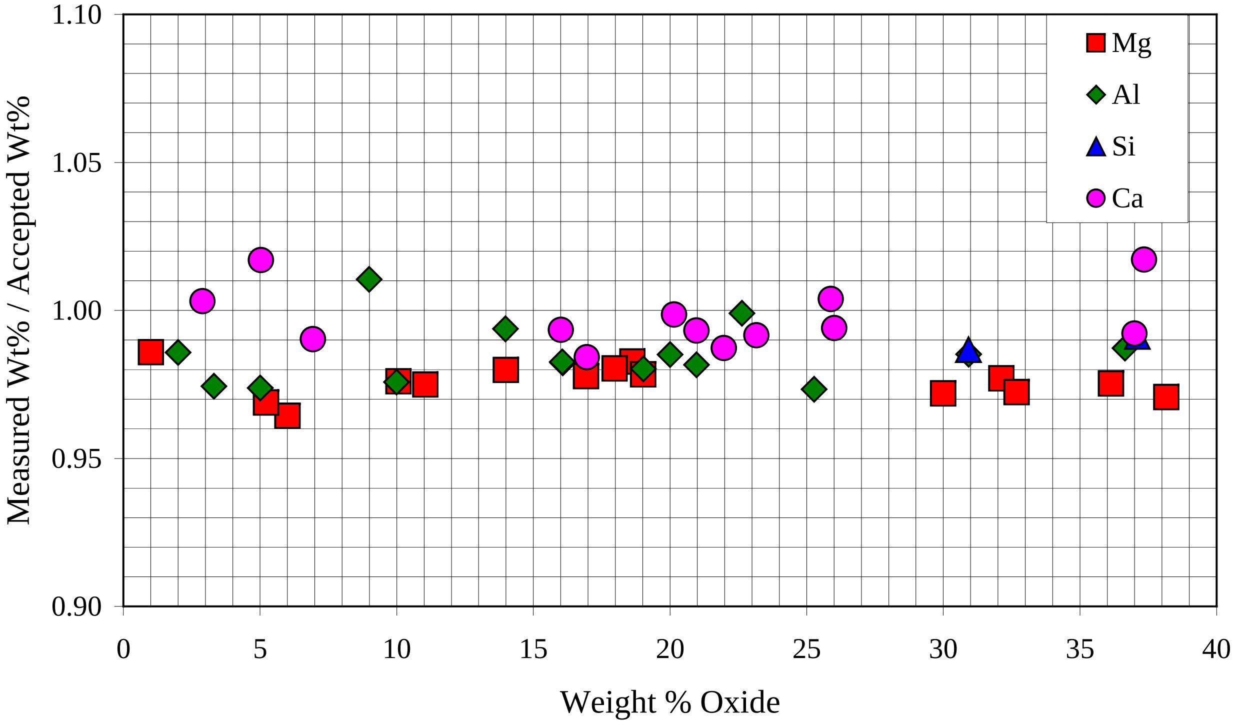
Caltech JEOL 733 1990’s
Spectrometer 2 TAP for Mg Al Si (Ca PET)

Shaw Data Set: Caltech Jeol 733 -- TAP2 MgAlSi PET5 Ca
Armstrong ϕ(ρz), FFAST macs, 15 kV

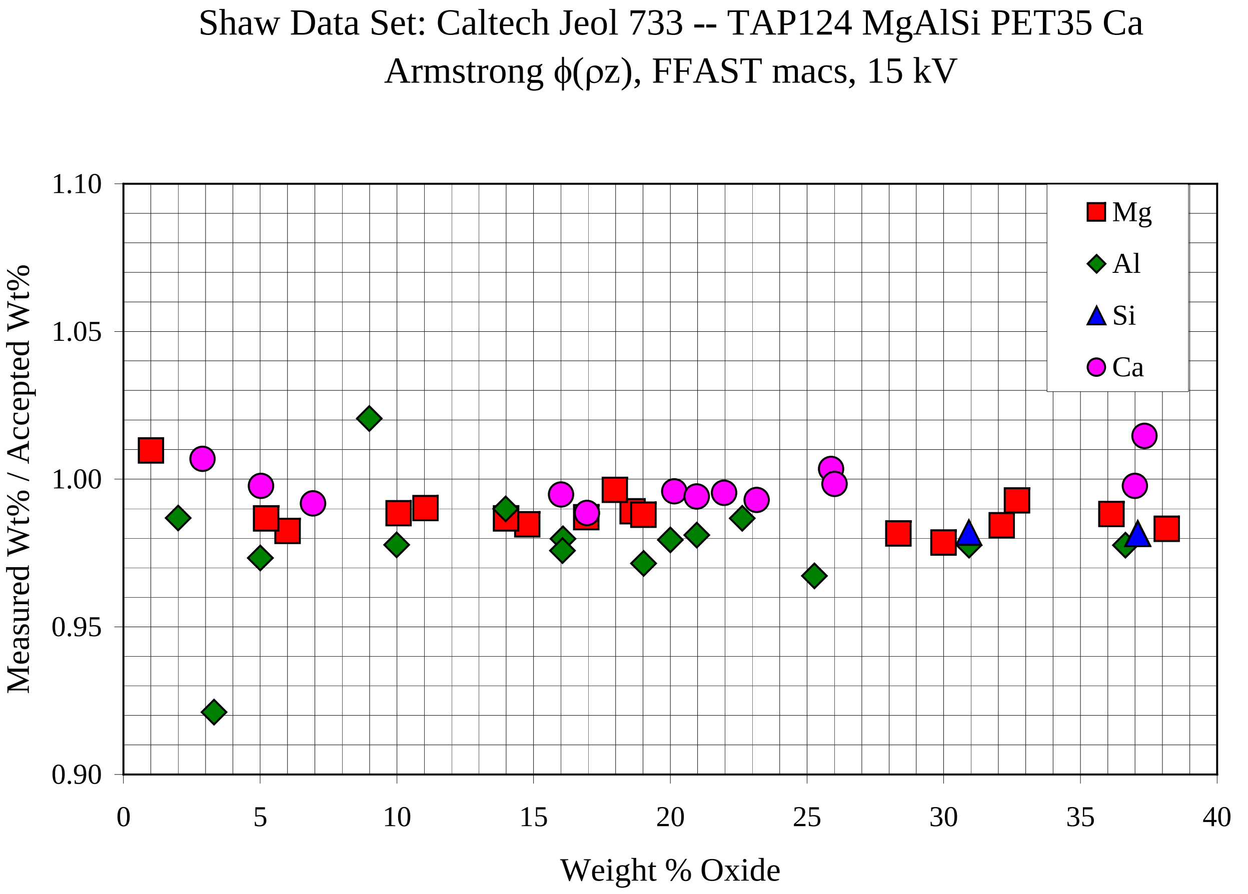


Caltech JEOL 733 1990's
Spectrometer 4 TAP for Mg Al Si (Ca PET)

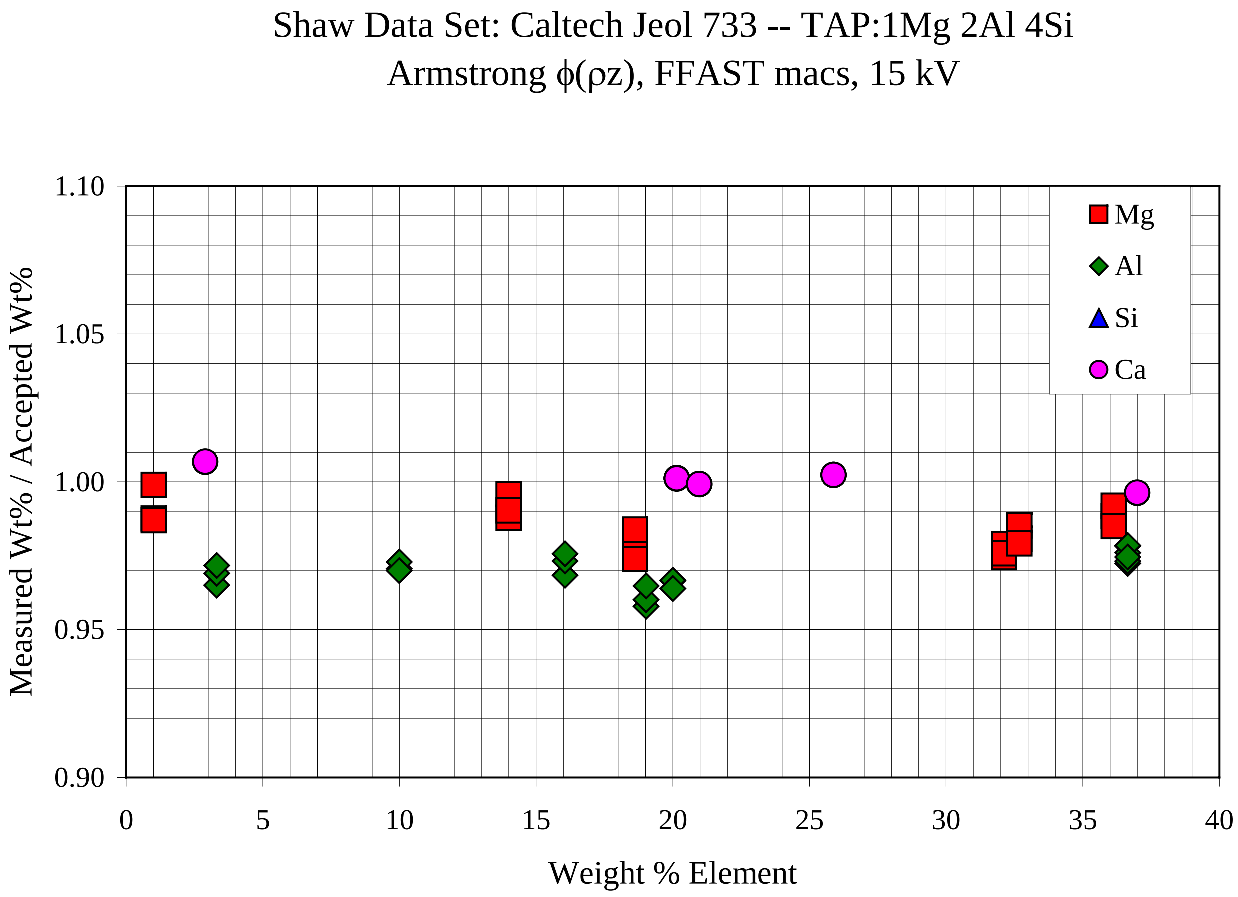
Shaw Data Set: Caltech Jeol 733 -- TAP4 MgAlSi PET5 Ca
Armstrong ϕ(ρz), FFAST macs, 15 kV



Caltech JEOL 733 1990's
Spectrometer 124 TAP for Mg Al Si (Ca PET)



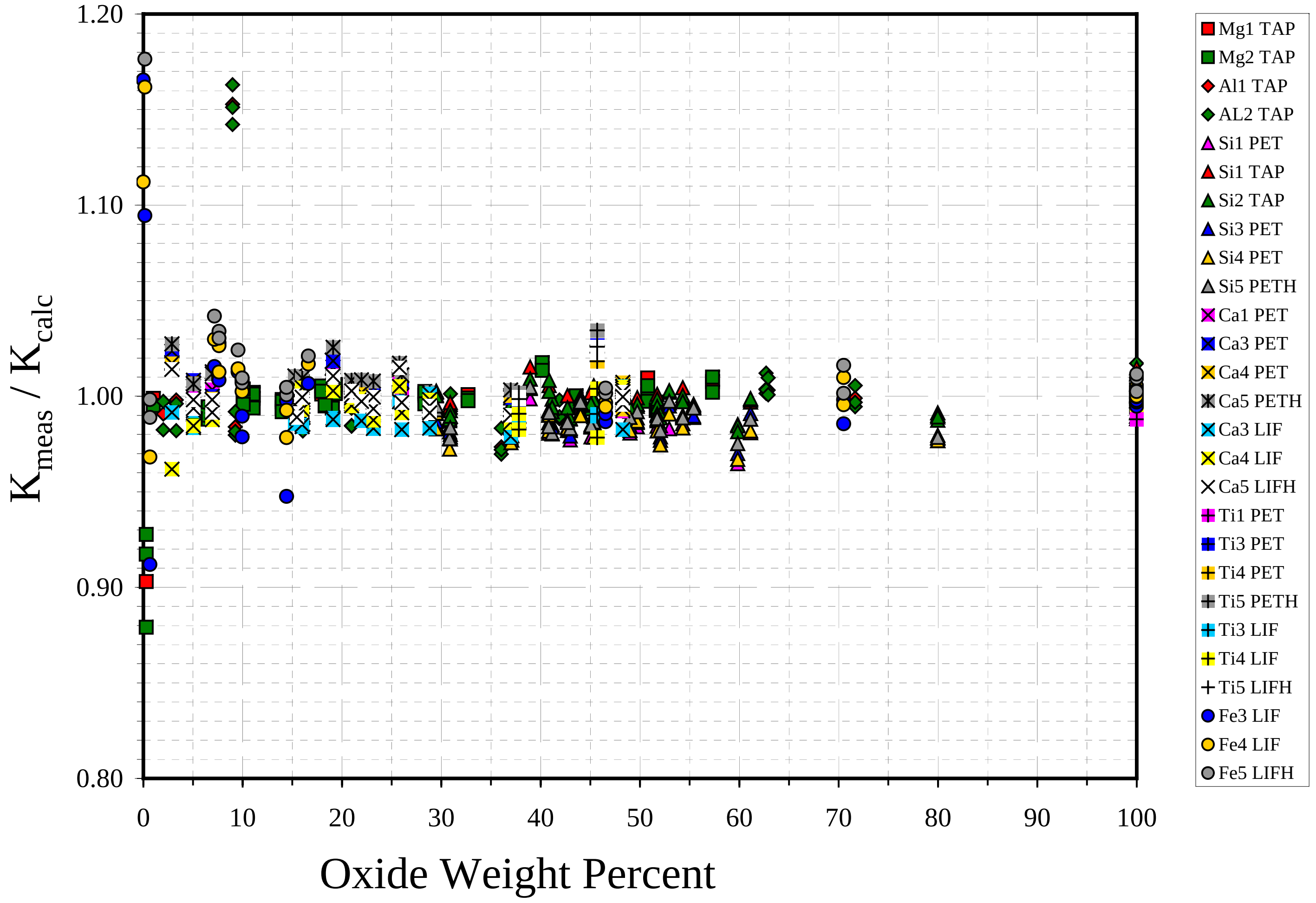
Caltech JEOL 733 1990’s
Spectrometer 124 TAP for Mg Al Si (Ca PET)



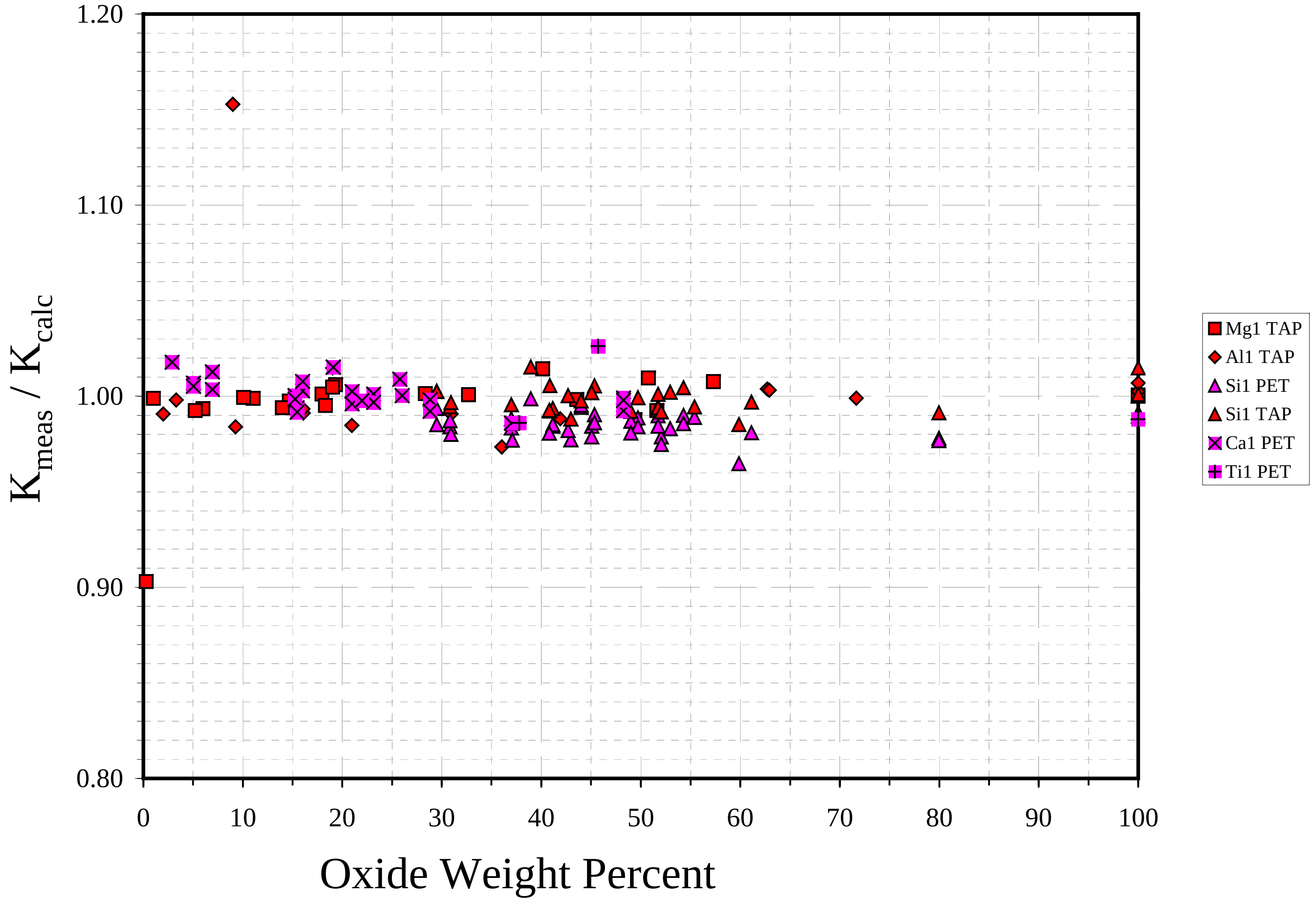
Intercomparison of Measured vs. Accepted Concentration for Standards on Microprobes

Instrument	C_{meas}/C_{calc} Mg	C_{meas}/C_{calc} Al	C_{meas}/C_{calc} Si	C_{meas}/C_{calc} Ca
MAC, avg	1.0030	0.9948	0.9940	1.0077
MAC, 1sd	0.0105	0.0171	0.0058	0.0107
Caltech 733 Spec 1 MgAlSi, avg	0.9909	1.0000	0.9977	0.9993
Caltech 733 Spec 1 MgAlSi, 1sd	0.0083	0.0123	0.0058	0.0068
Caltech 733 Spec 2 MgAlSi, avg	0.9877	0.9847	0.9901	0.9963
Caltech 733 Spec 2 MgAlSi, 1sd	0.0086	0.0122	0.0064	0.0064
Caltech 733 Spec 4 MgAlSi, avg	0.9783	0.9862	0.9938	0.9971
Caltech 733 Spec 4 MgAlSi, 1sd	0.0095	0.0101	0.0059	0.0096
Caltech 733 Mg1Al2Si4, avg	0.9894	0.9817	0.9905	0.9984
Caltech 733 Mg1Al2Si4, 1sd	0.0077	0.0188	0.0061	0.0063

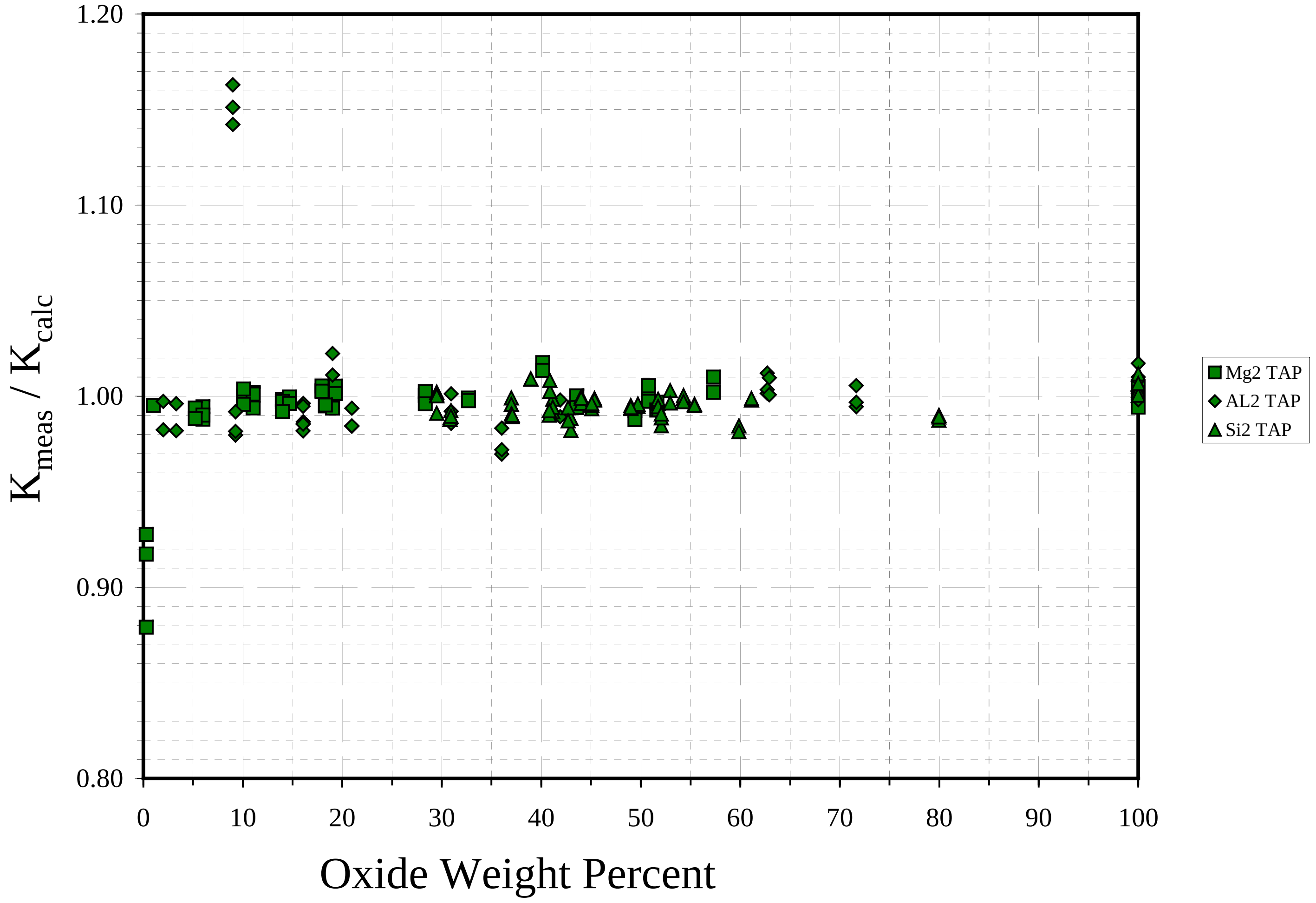
WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed



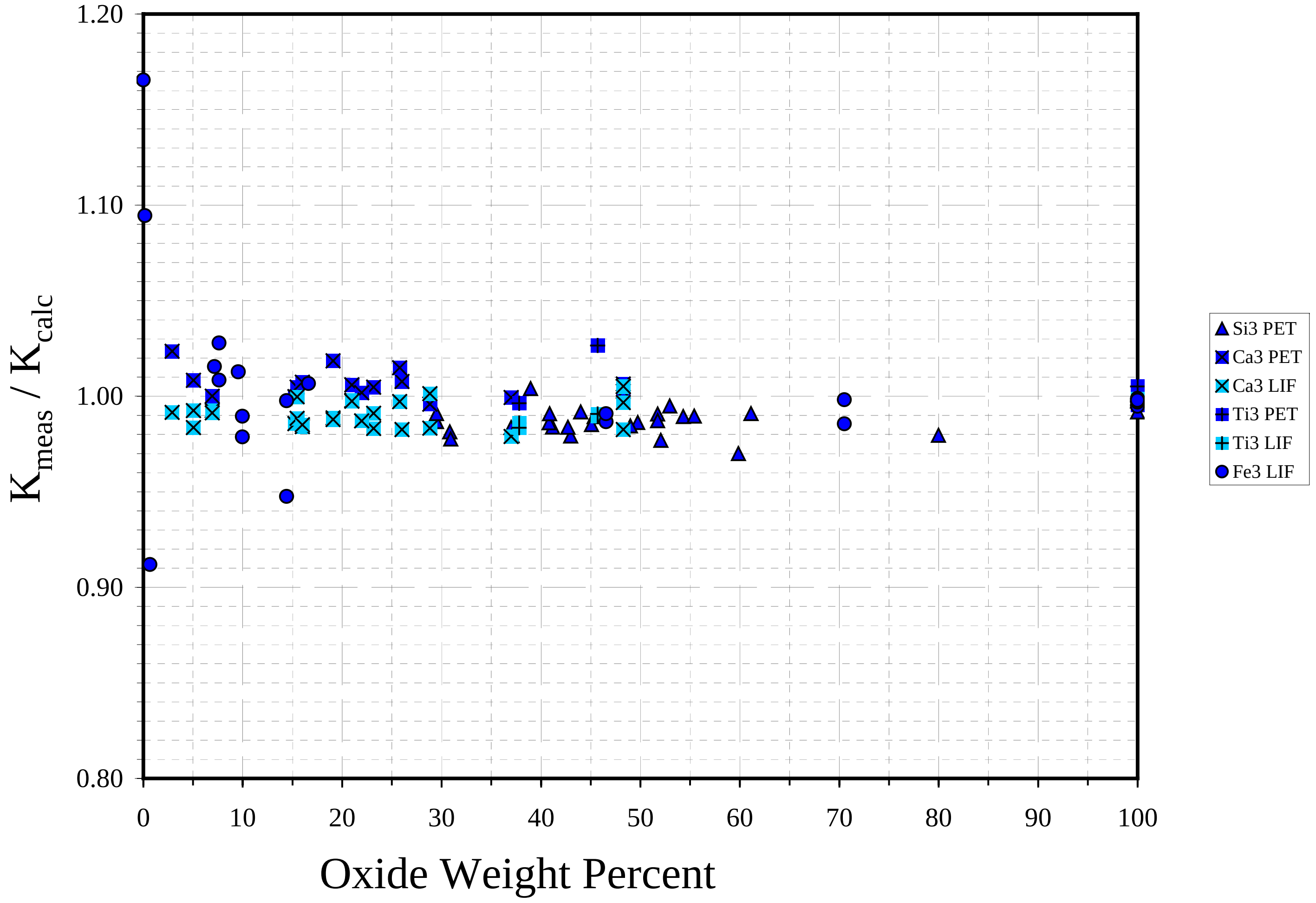
WU JXA-8200 CMASTF Data Set
Spectrometer 1 PET and TAP



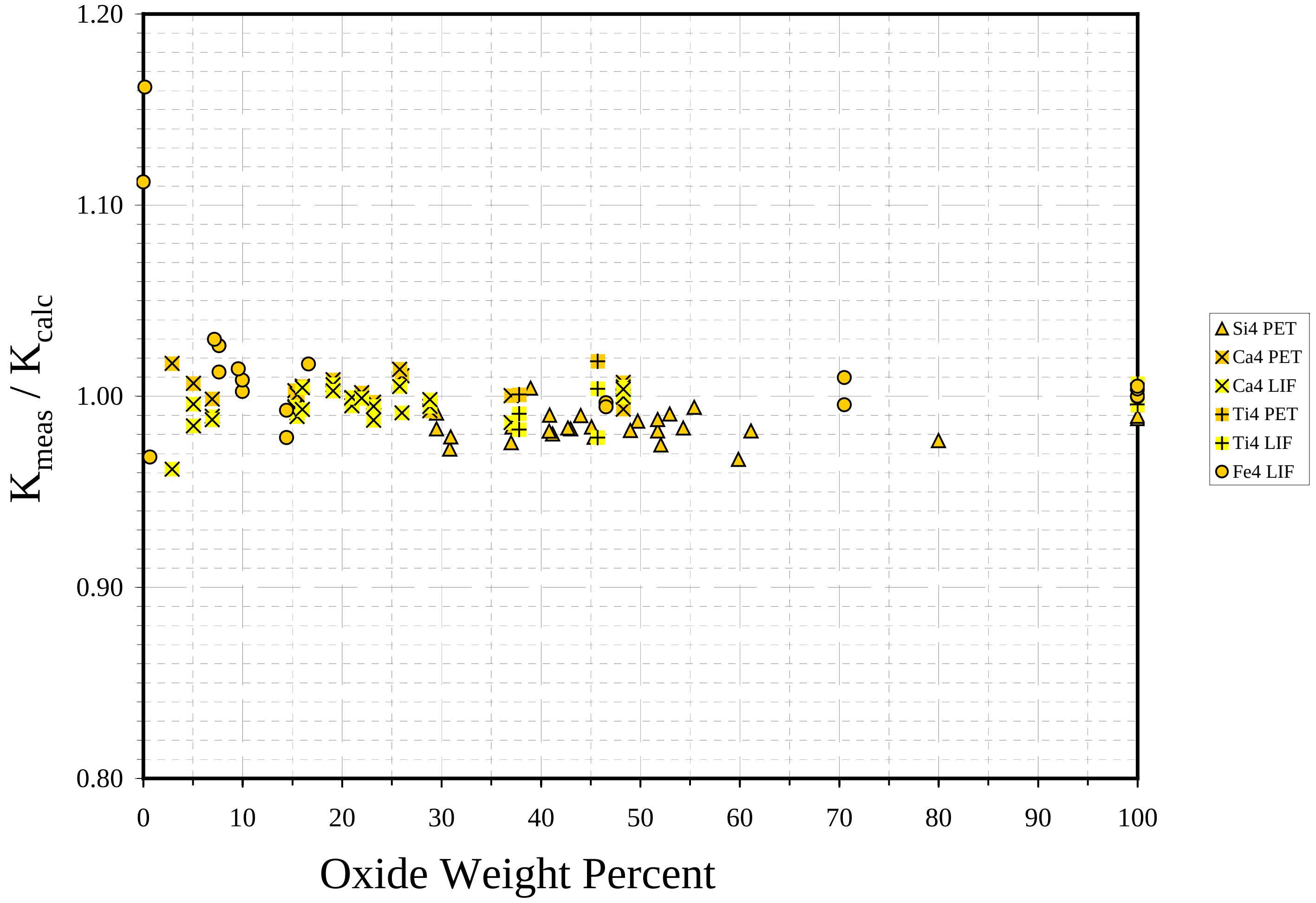
WU JXA-8200 CMASTF Data Set
Spectrometer 2 TAP



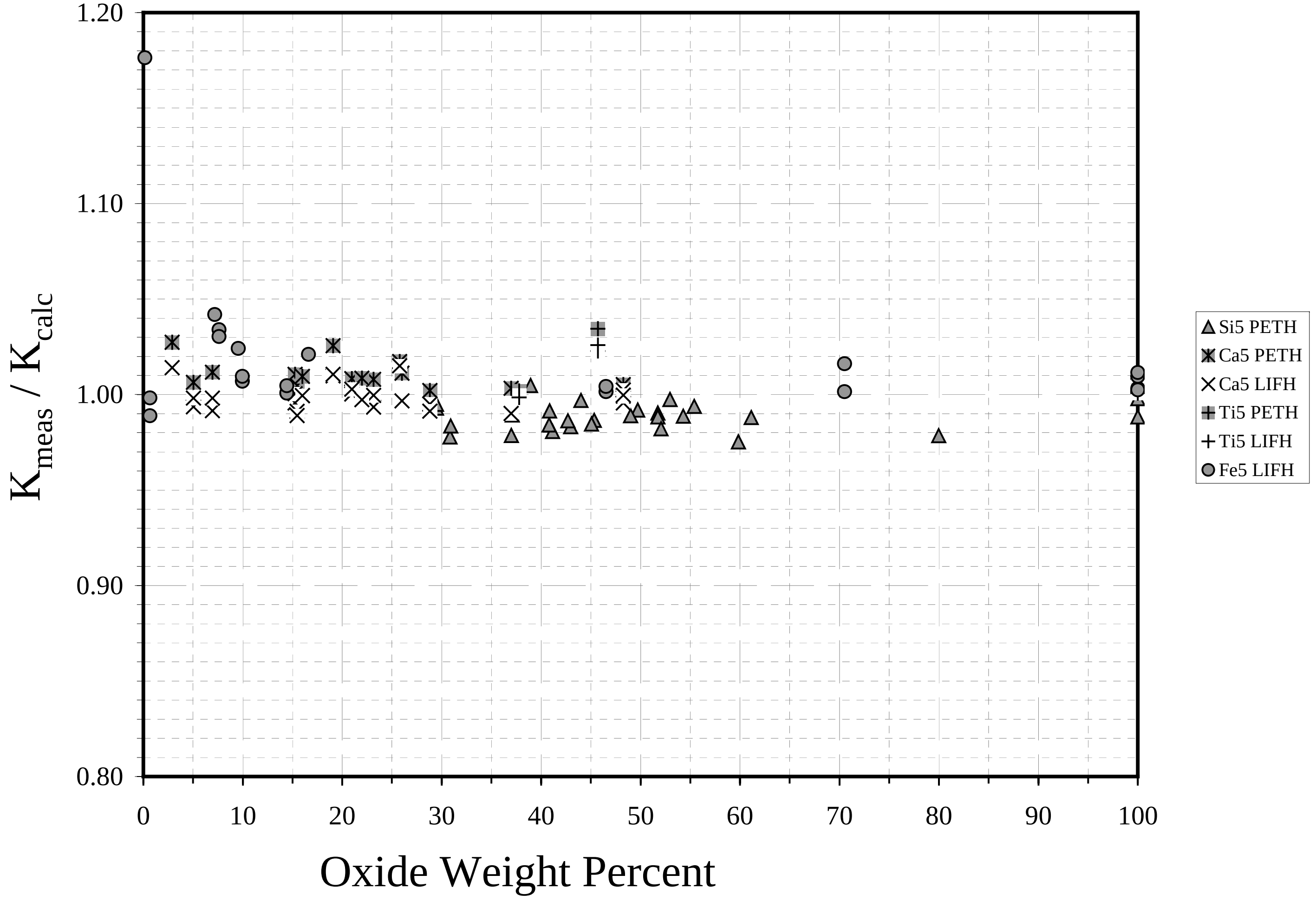
WU JXA-8200 CMASTF Data Set
Spectrometer 3 PET and LIF



WU JXA-8200 CMASTF Data Set
Spectrometer 4 PET and LIF



WU JXA-8200 CMASTF Data Set Spectrometer 5 PETH and LIFH



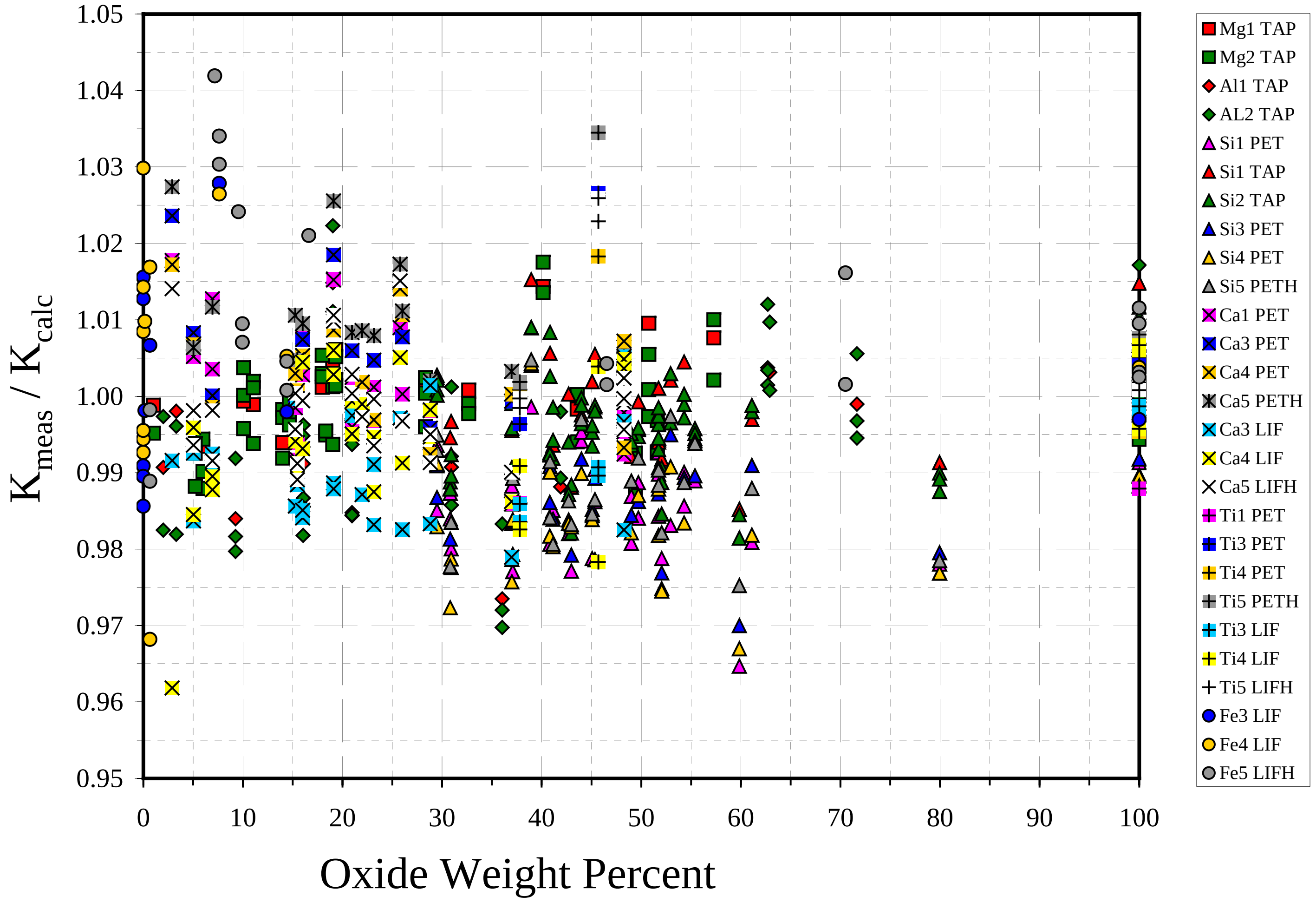
Average K_{meas} / K_{calc} for CMASTF Standards Washington University JEOL 8200

WDS	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5
Mg TAP	0.9997	0.9971			
Al TAP	0.9950	0.9946			
Si TAP	0.9981	0.9955			
Si PET	0.9855		0.9865	0.9837	0.9880
Ca PET	1.0013		1.0064	1.0035	1.0101
Ca LIF			0.9908	0.9948	0.9989
Ti PET	1.0000		1.0059	1.0044	1.0115
Ti LIF			0.9919	0.9949	1.0084
Fe LIF			0.9962	1.0051	1.0131

Accuracy, 1σ % Error in K_{meas} / K_{calc} CMASTF Standards Washington University JEOL 8200

WDS	Spec 1	Spec 2	Spec 3	Spec 4	Spec 5
Mg TAP	0.65	1.30			
Al TAP	1.06	1.22			
Si TAP	0.74	0.64			
Si PET	0.71		0.71	0.75	0.70
Ca PET	0.79		0.73	0.70	0.74
Ca LIF			0.74	0.92	0.69
Ti PET	2.27		1.44	0.98	1.54
Ti LIF			0.61	1.15	1.14
Fe LIF			1.75	1.27	1.26

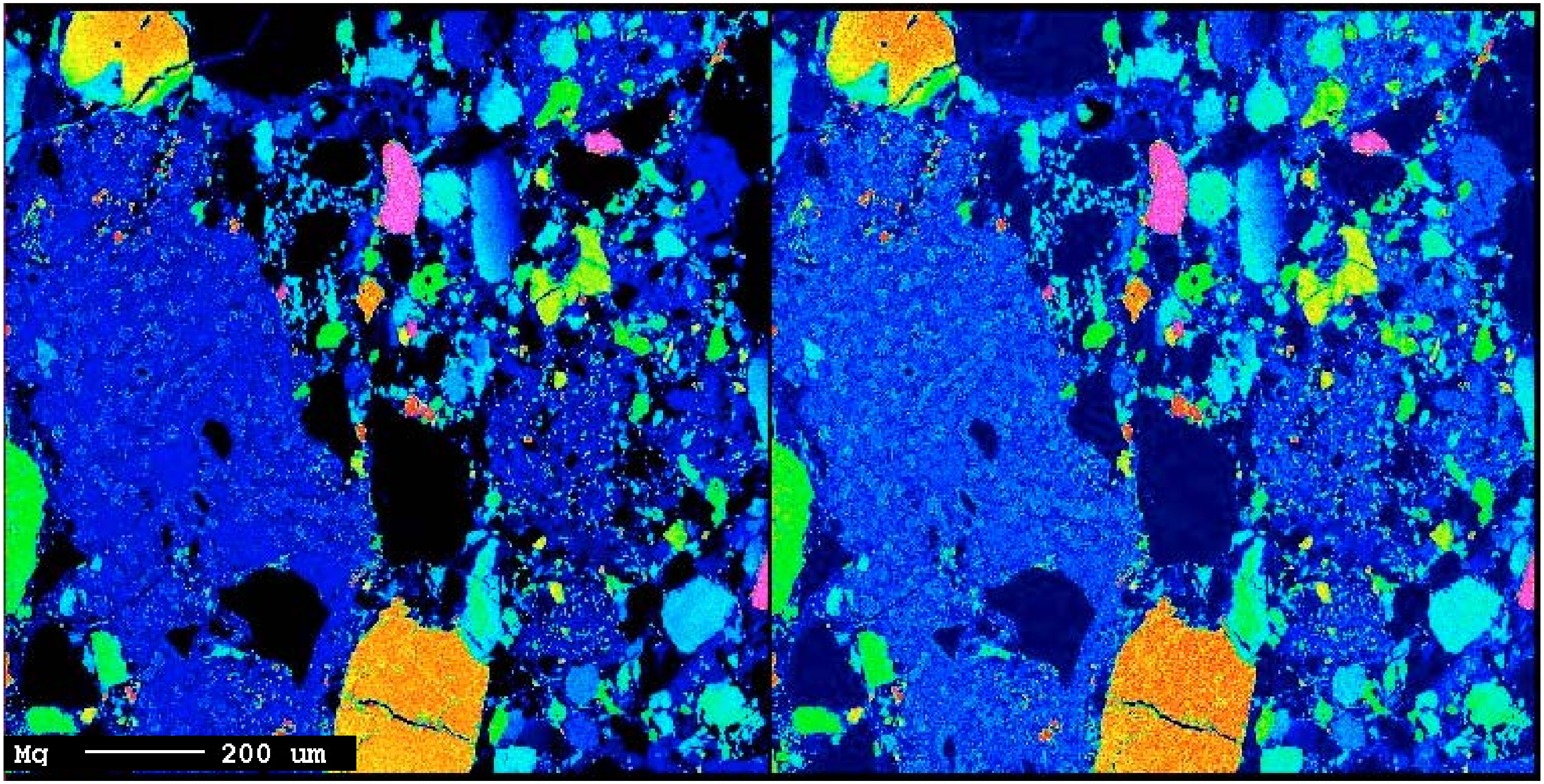
WU JXA-8200 CMASTF Data Set
All WDS Data Superimposed Expanded Scale



Washington University
Earth and Planetary Sciences JEOL JXA-8200 SDD

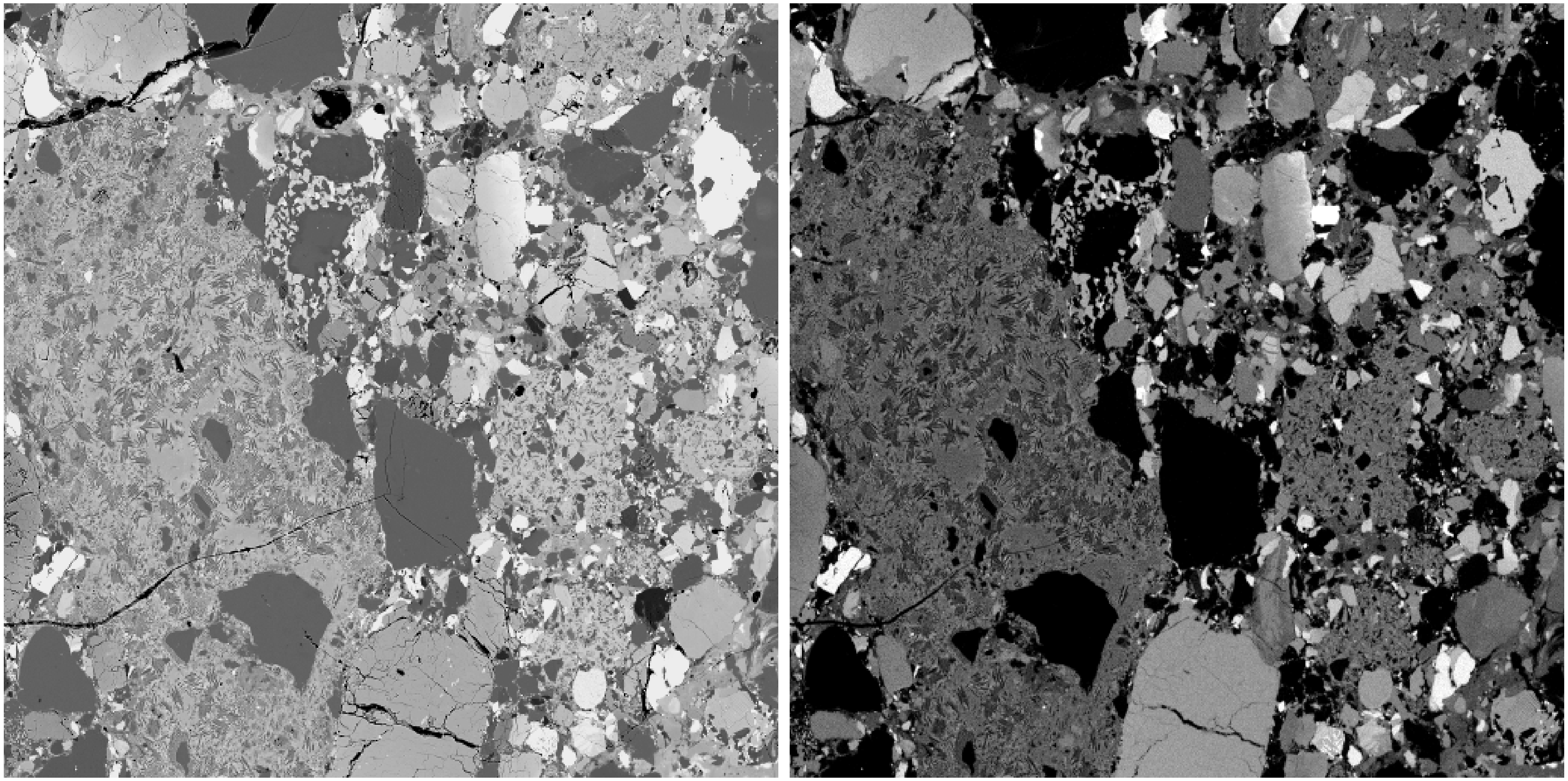
JEOL e2v Silicon Drift Detector
130 eV resolution
3 time constants T3 T2 T1
Stage and beam mapping
Quantitative EDS analysis LLSQ

JEOL 8200 Stage Maps: Lunar Meteorite SAU169 WDS vs. SDD Mg @ 15KV, 120nA, 25ms dwell



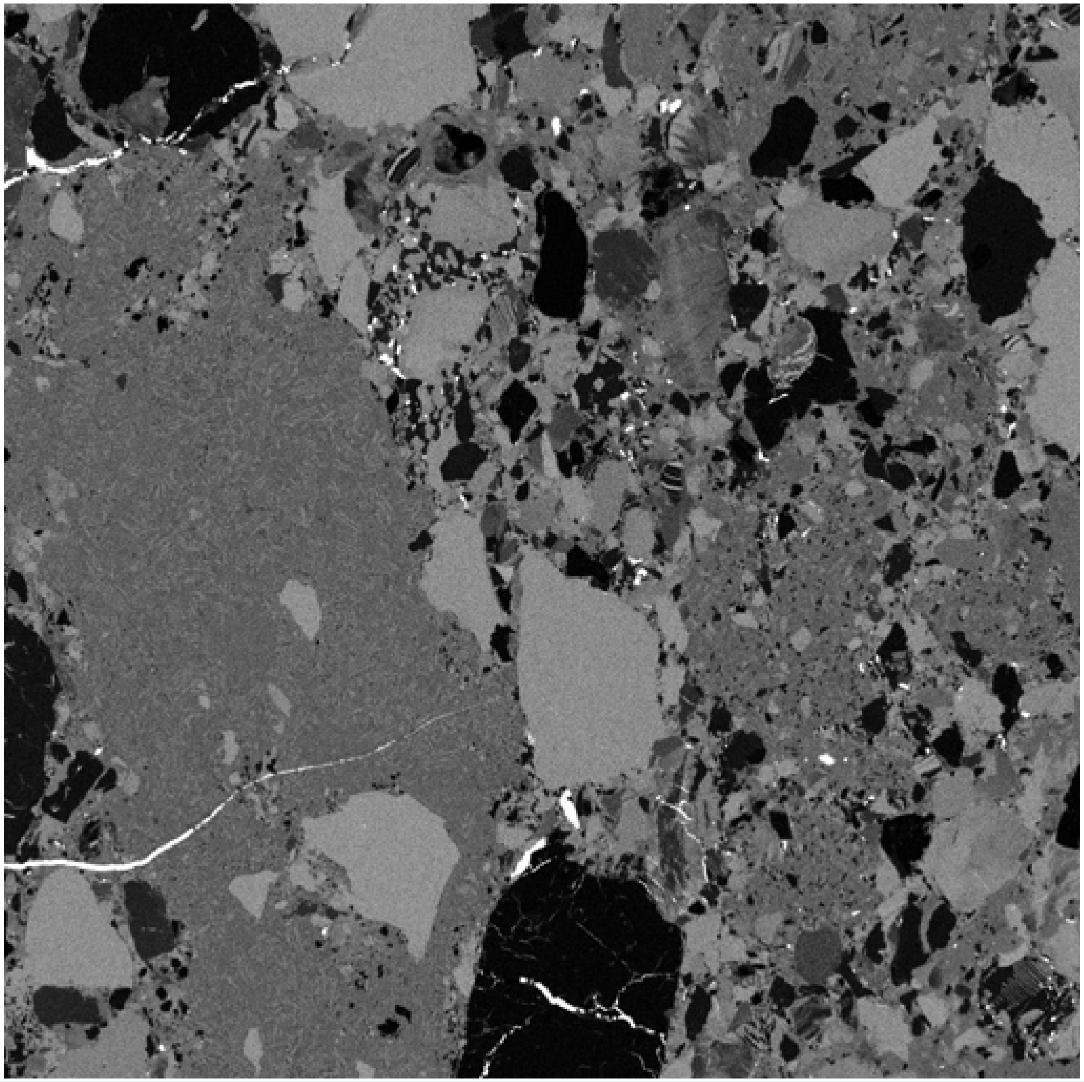
Mg WDS 1061 max counts, Mg SDD 527 max counts
1024x1024 stage map, 8 hours

Lunar Meteorite SAU169
Stage map 1024x1024, 25 ms, 8 hr run

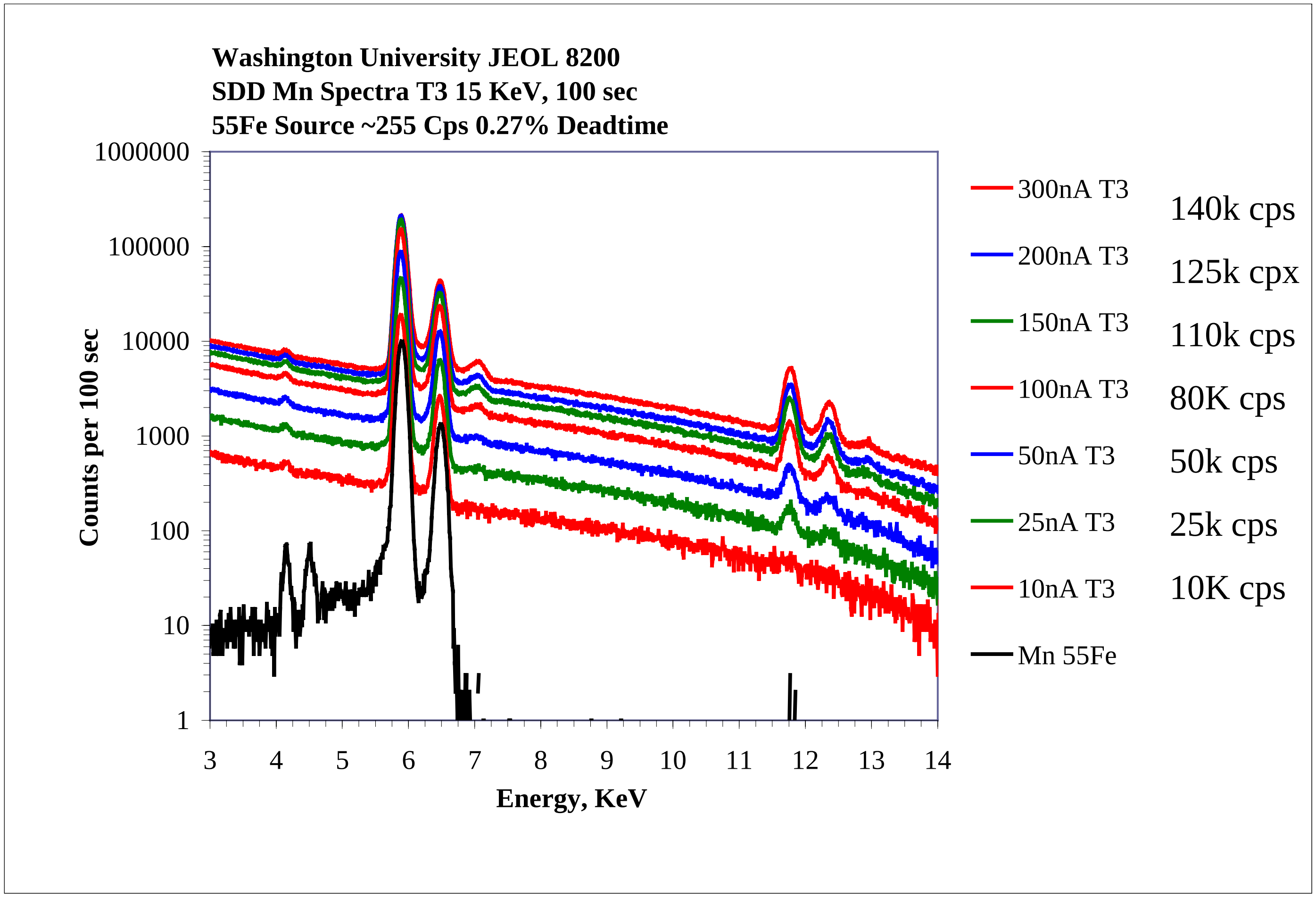


Backscattered electron vs. Fe SDD maps

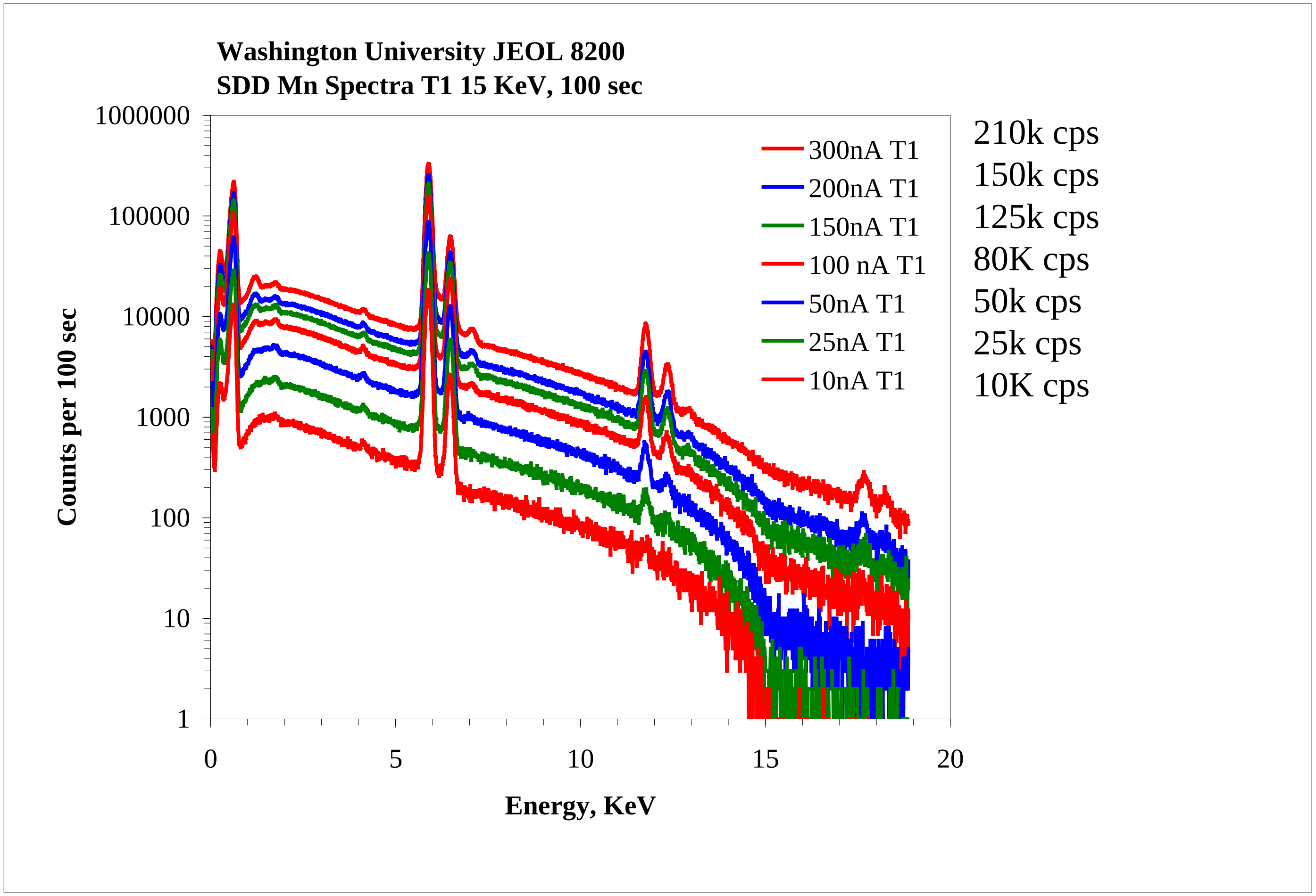
Lunar Meteorite SAU169
Stage map 1024x1024, 25 ms, 8 hr run: Ca SDD



WU8200 JEOL SDD
^{55}Fe Source Mn Kα Resolution 130 eV

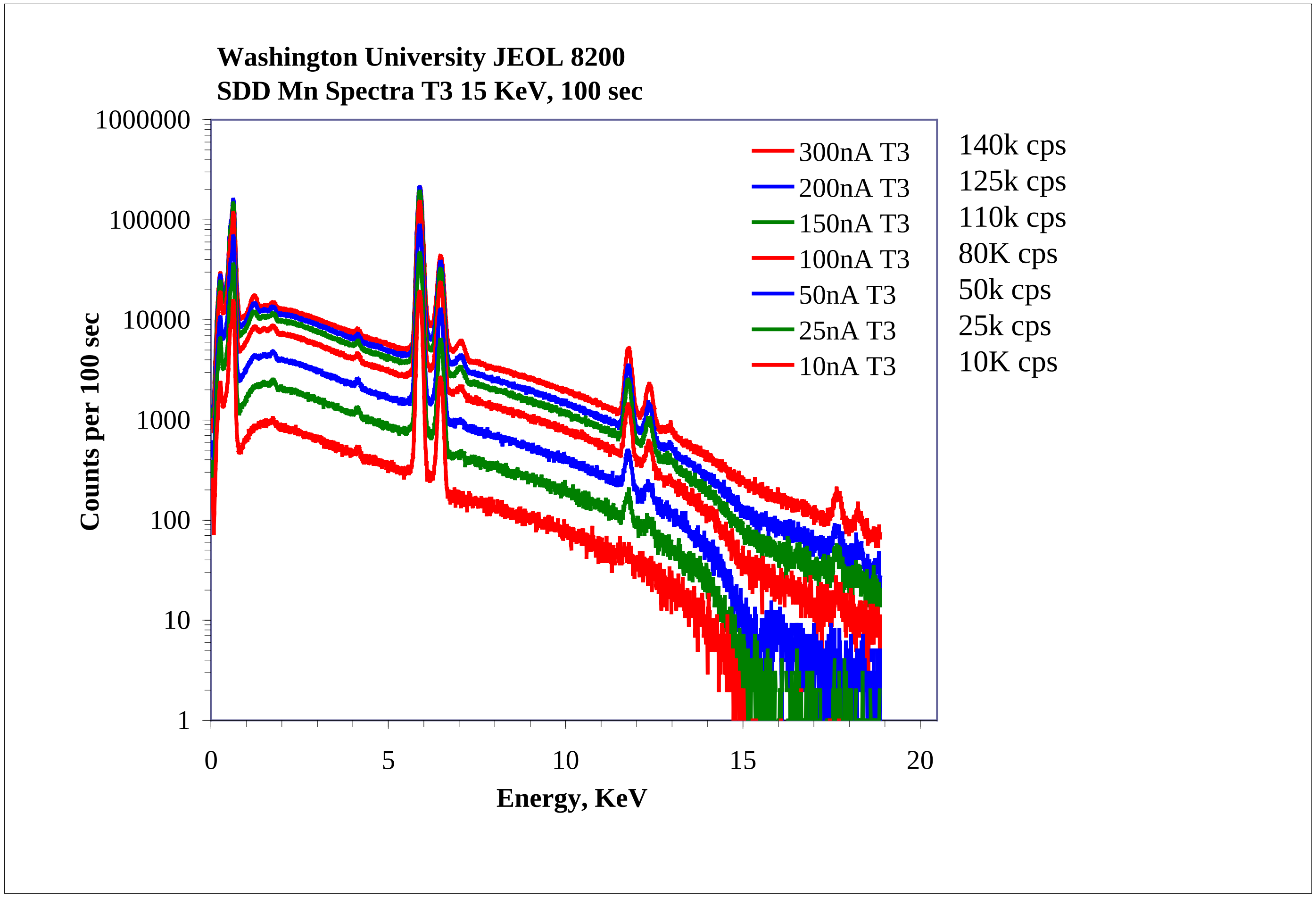


SDD Performance Data:
WU8200 SDD Mn Target, T1 15 KeV, 100 sec



210k cps
150k cps
125k cps
80K cps
50k cps
25k cps
10K cps

SDD Performance Data:
WU8200 SDD Mn Target, T3 15 KeV, 100 sec



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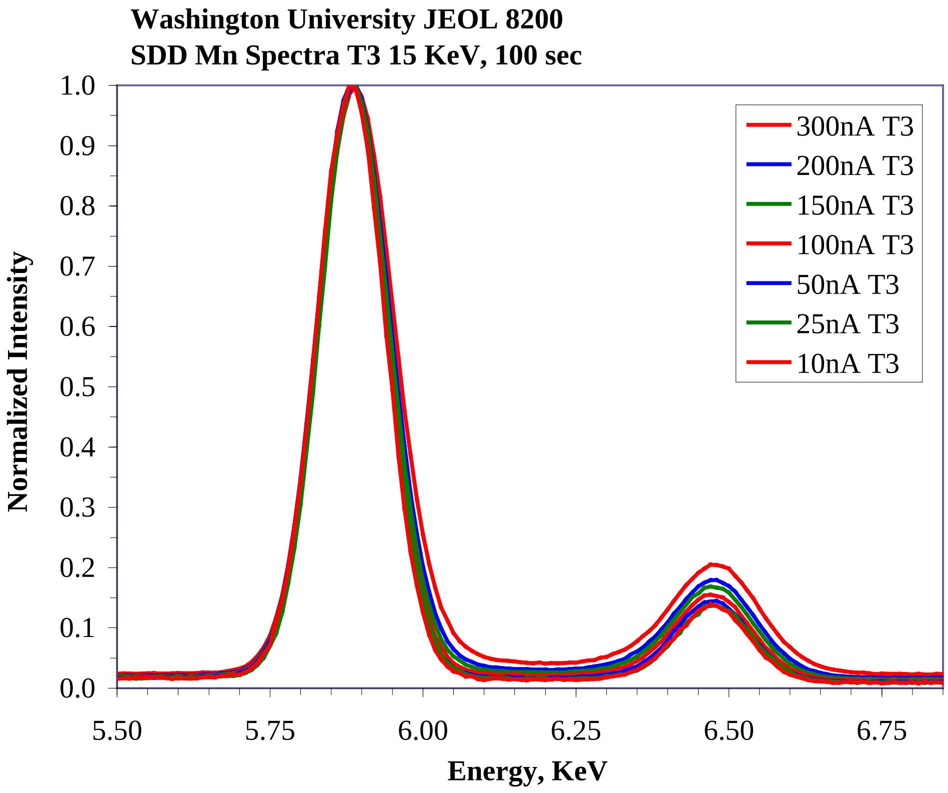
10K cps

WU8200 SDD Mn K Spectra
T3, 100 sec



Washington University JEOL 8200
SDD Mn Spectra T3 15 KeV, 100 sec

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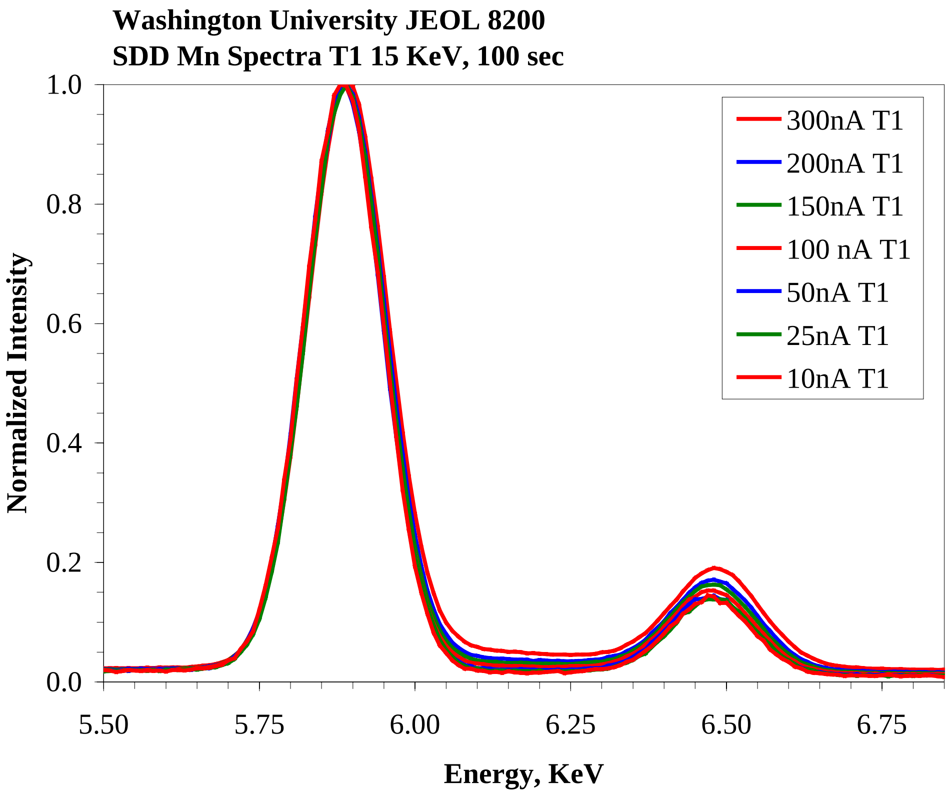
80K cps
50k cps
25k cps
10K cps

WU8200 SDD Mn K Spectra
T1, 100 sec



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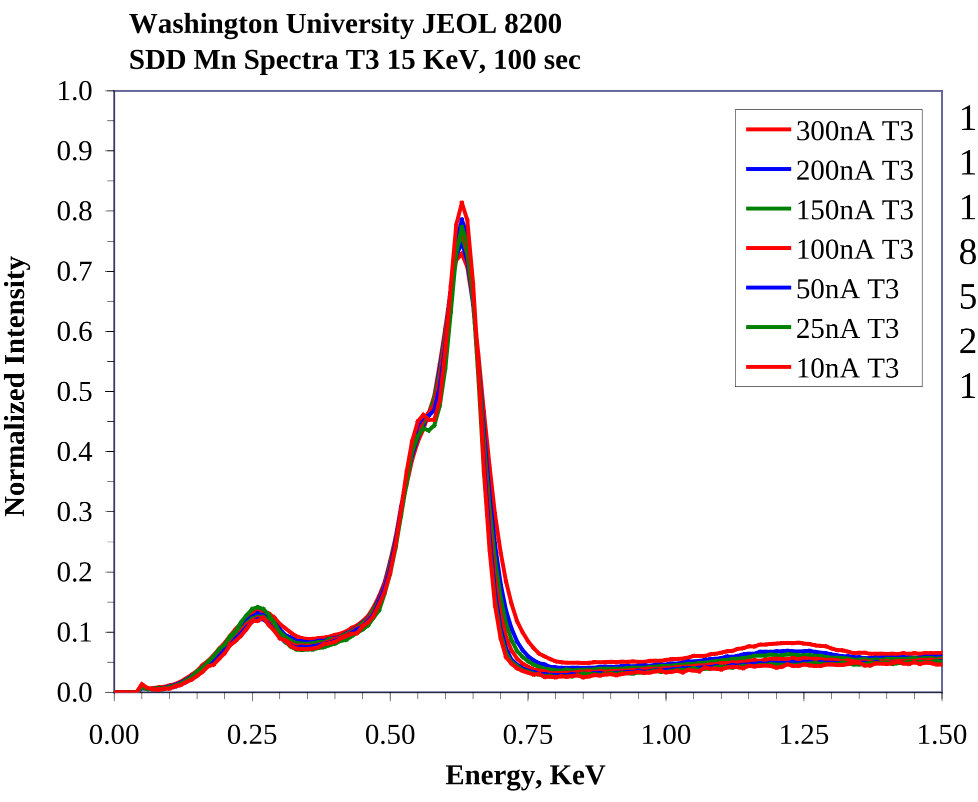
WU8200 SDD Mn L Spectra
T3, 100 sec



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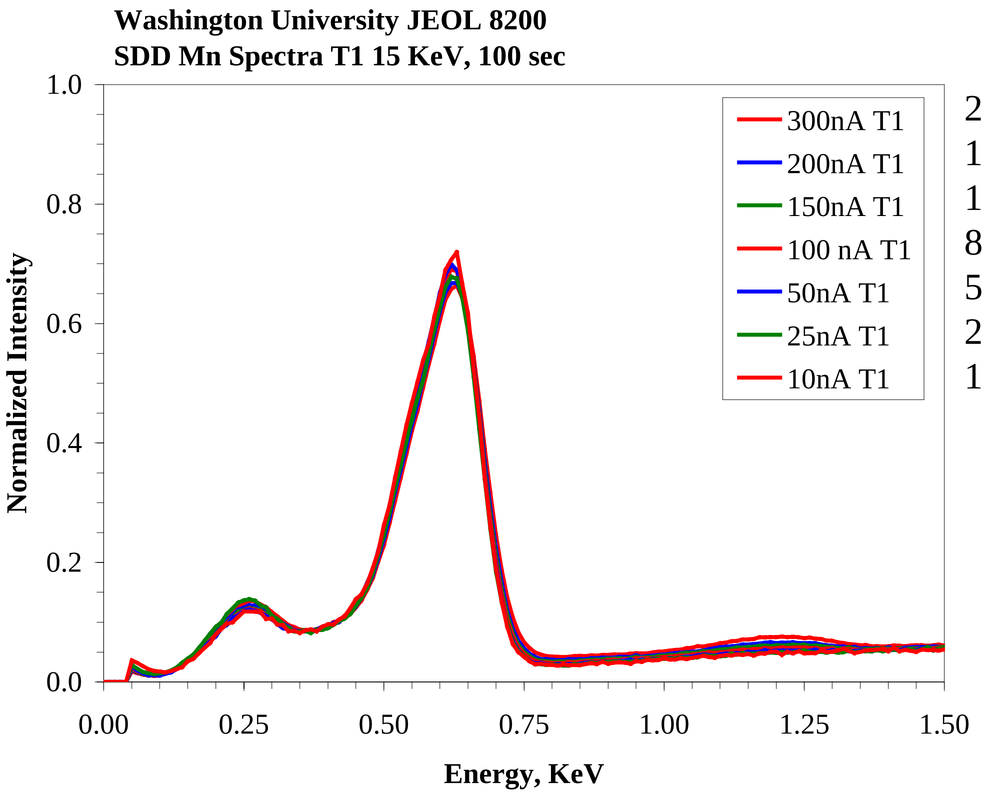
25k cps
10K cps

WU8200 SDD Mn L Spectra
T1, 100 sec



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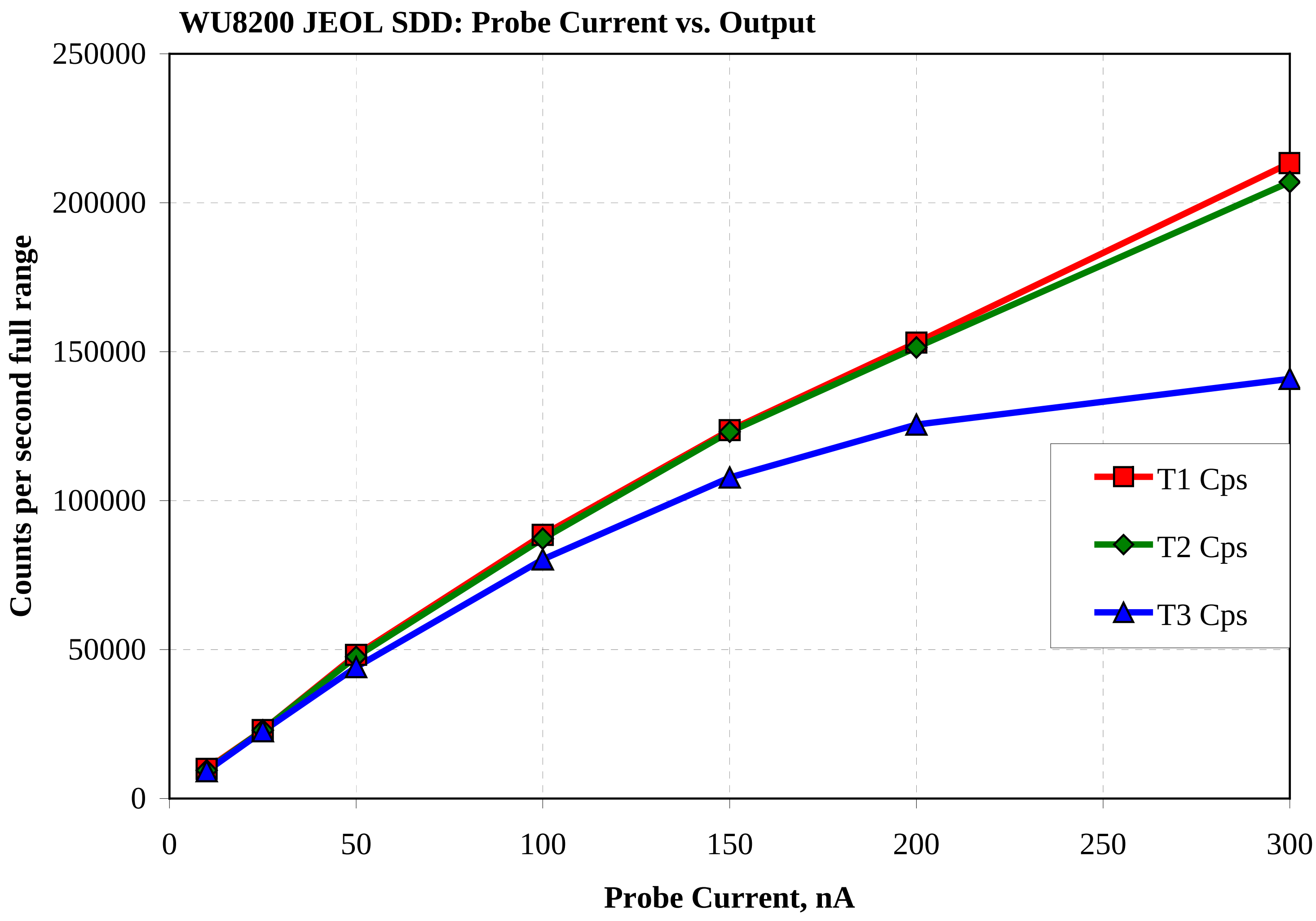
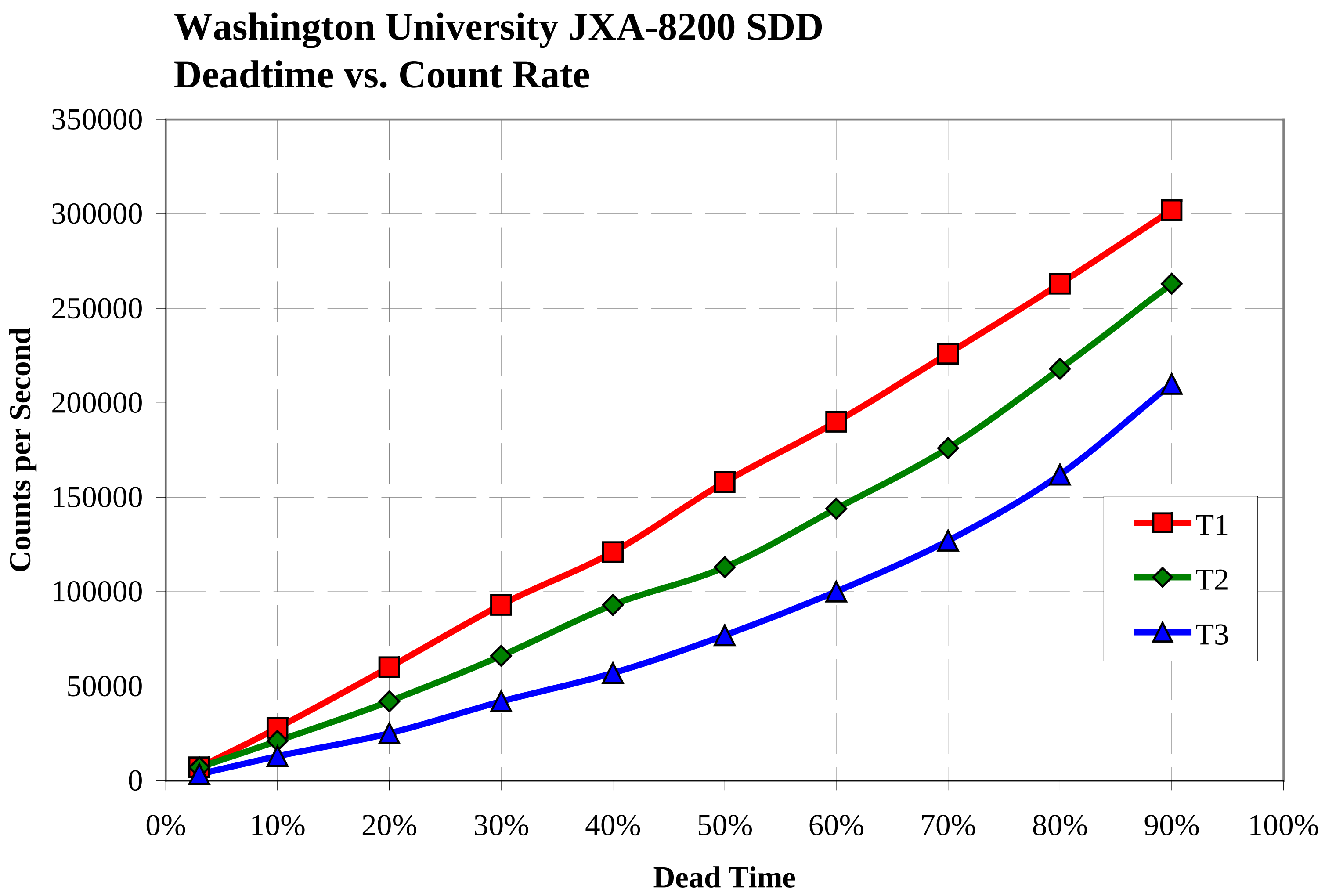
80K cps
50k cps
25k cps
10K cps

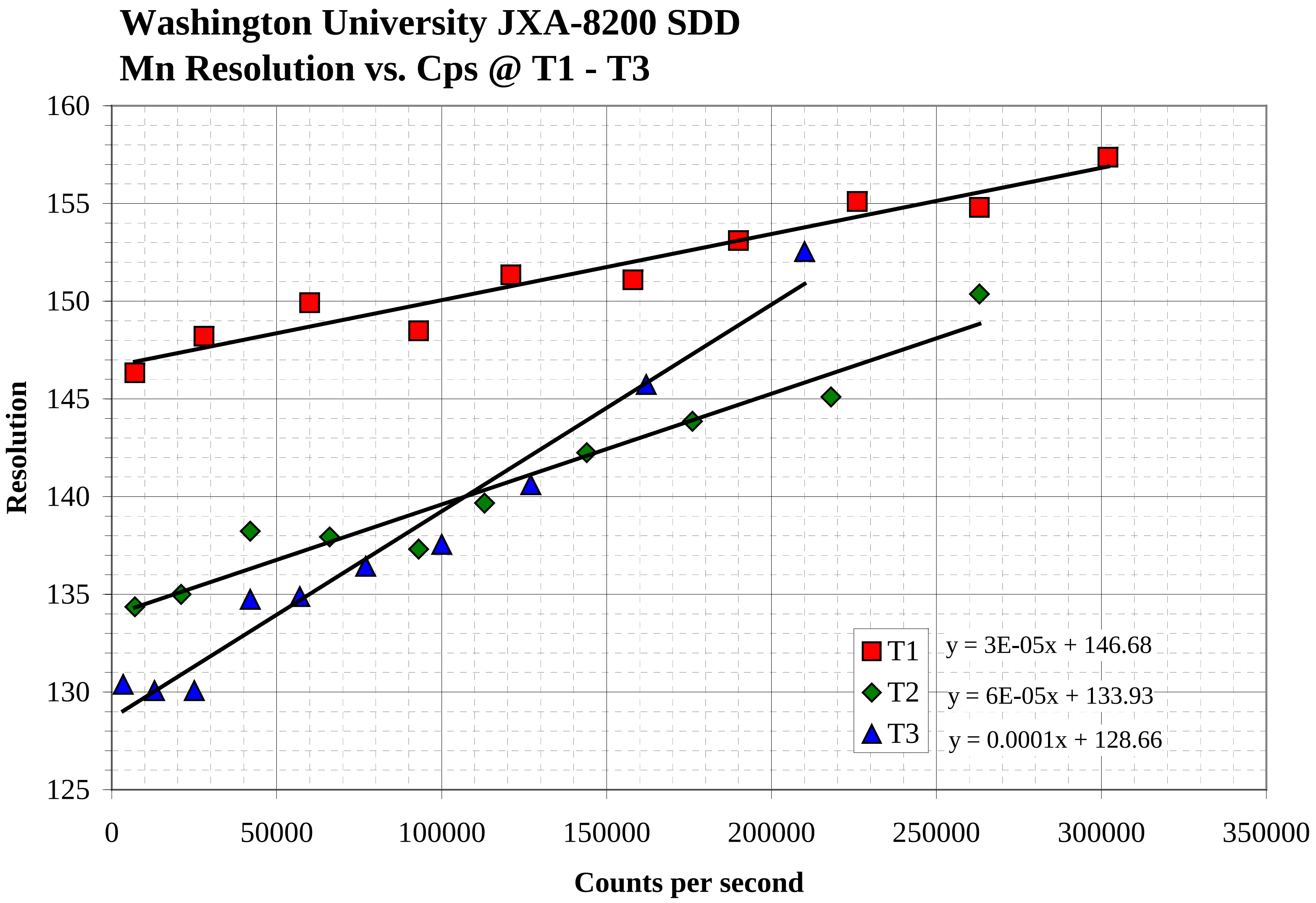
WU8200
Probe Current vs. Count Rate



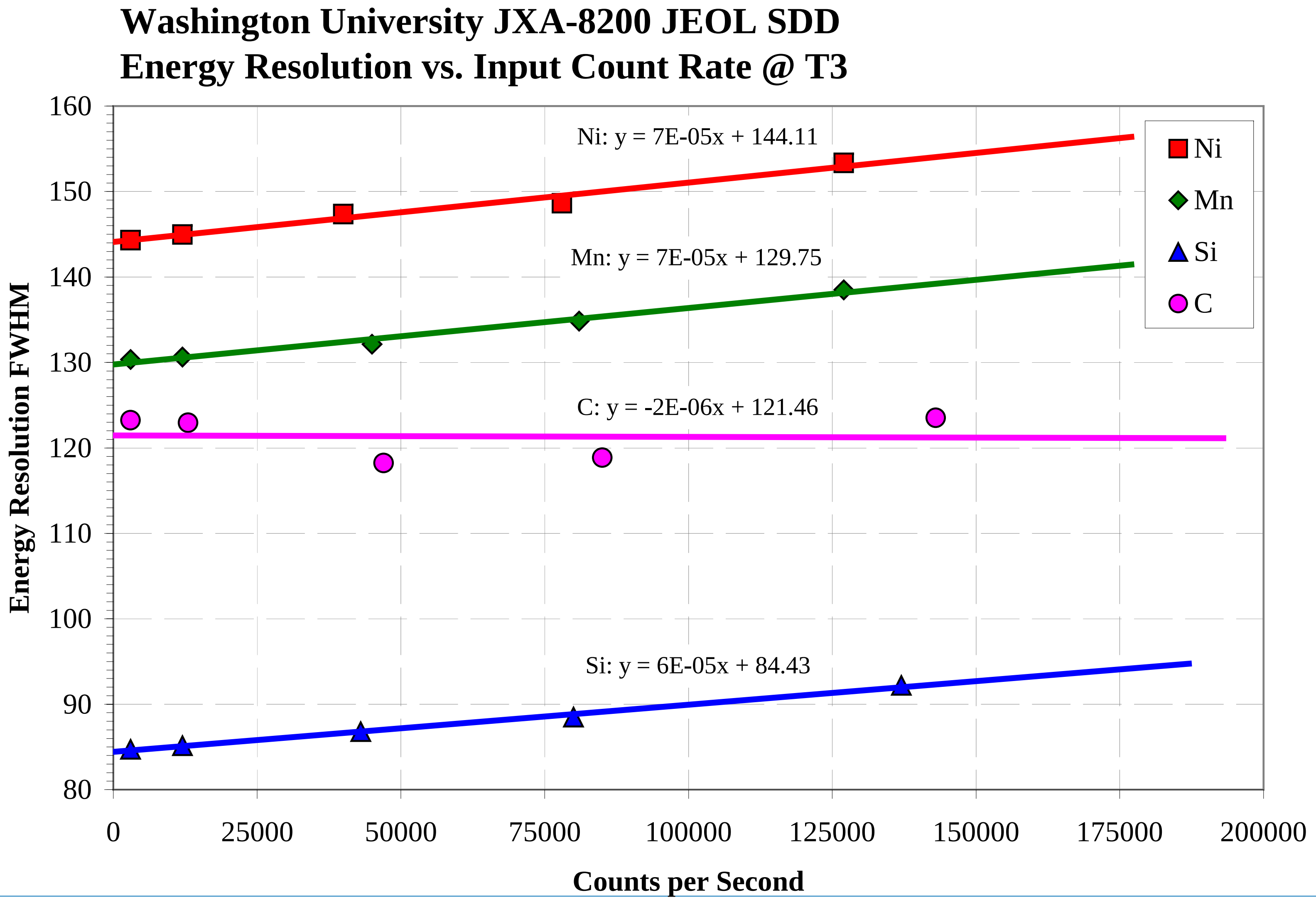
WU8200 SDD
Deadtime vs. Count Rate



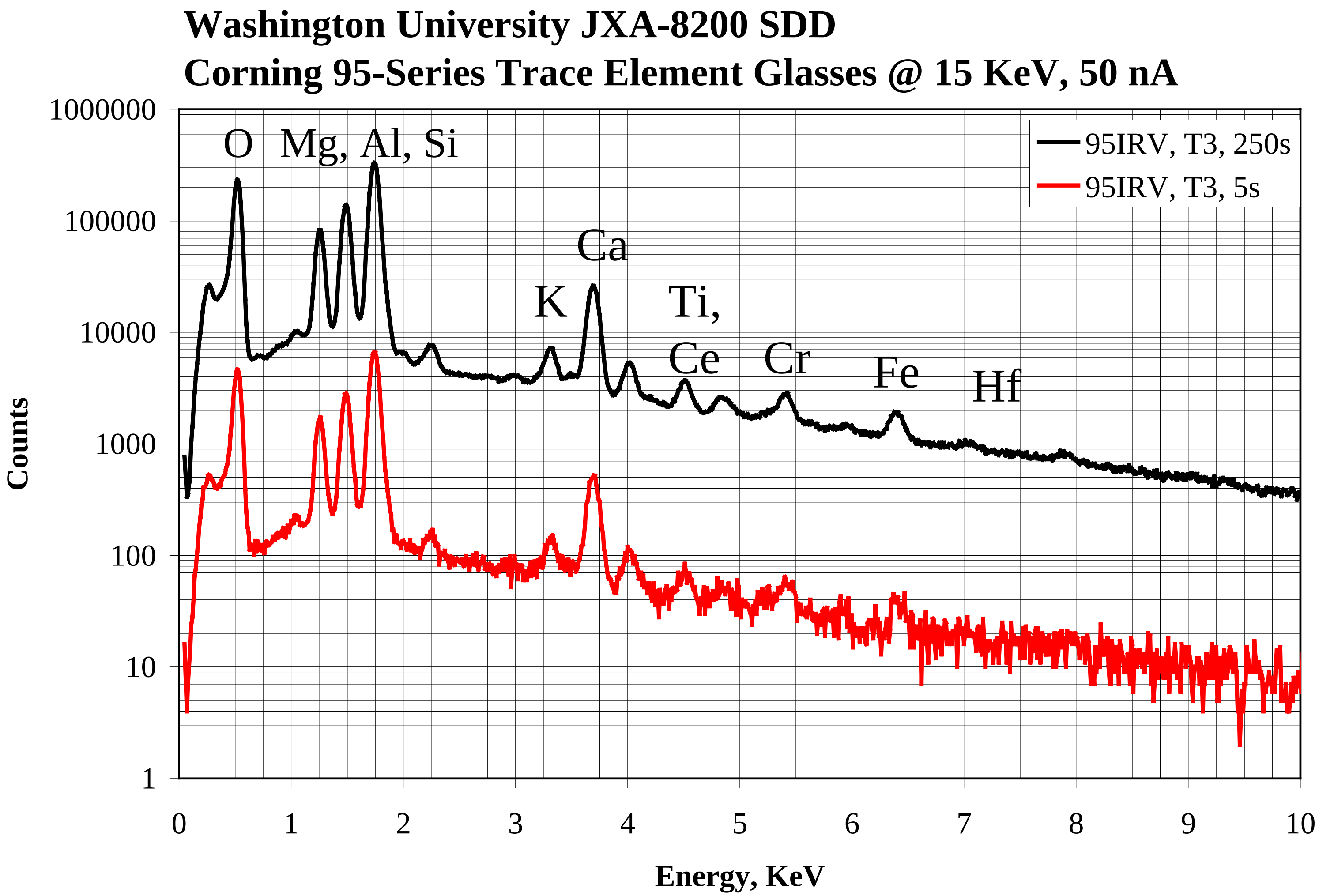
WU8200 SDD
Count Rate vs. Resolution



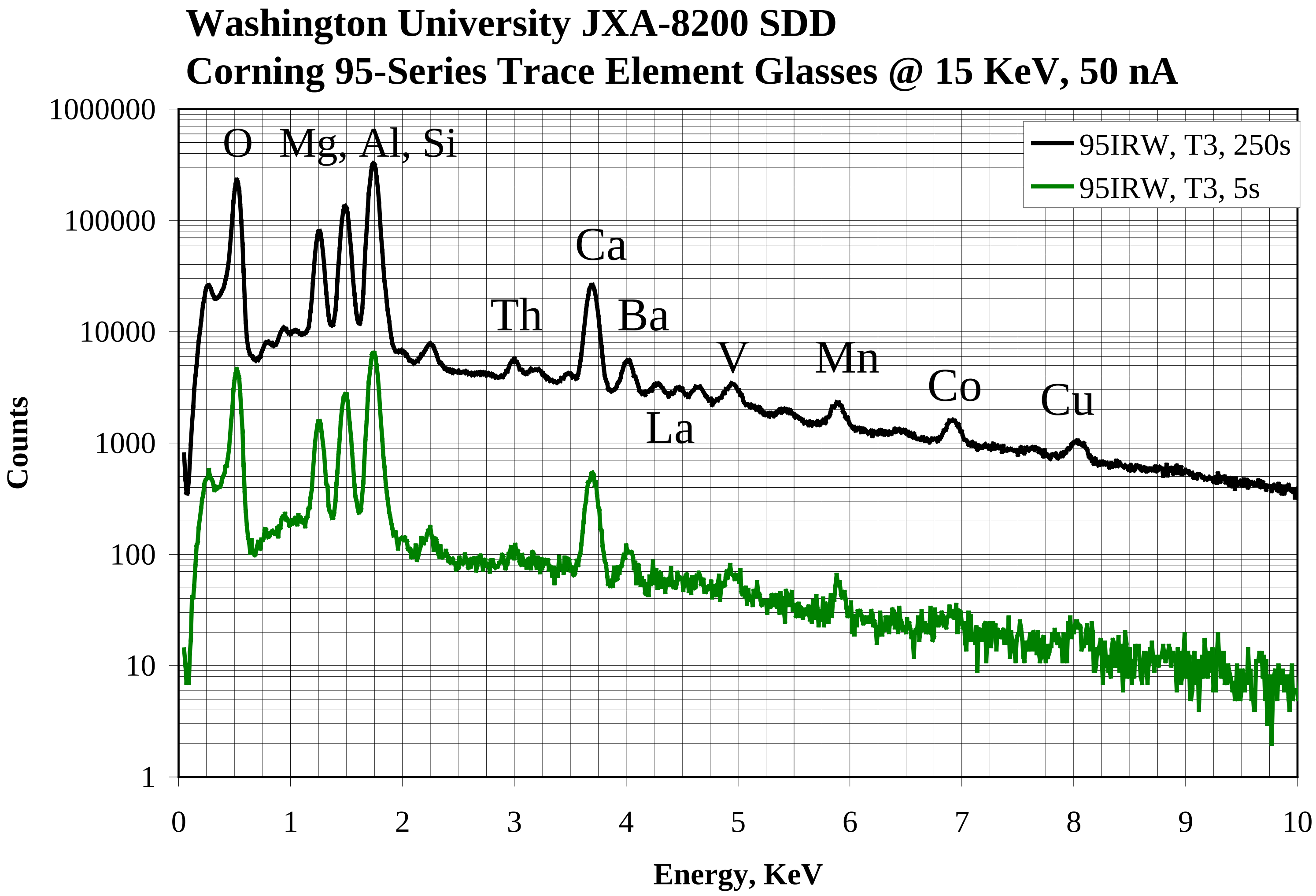
WU8200 SDD
Count Rate vs. Resolution for C, Si, Mn, Ni



Washington University JXA-8200 SDD
Corning 95IRV: K, Ti, Cr, Fe, Ce, Hf



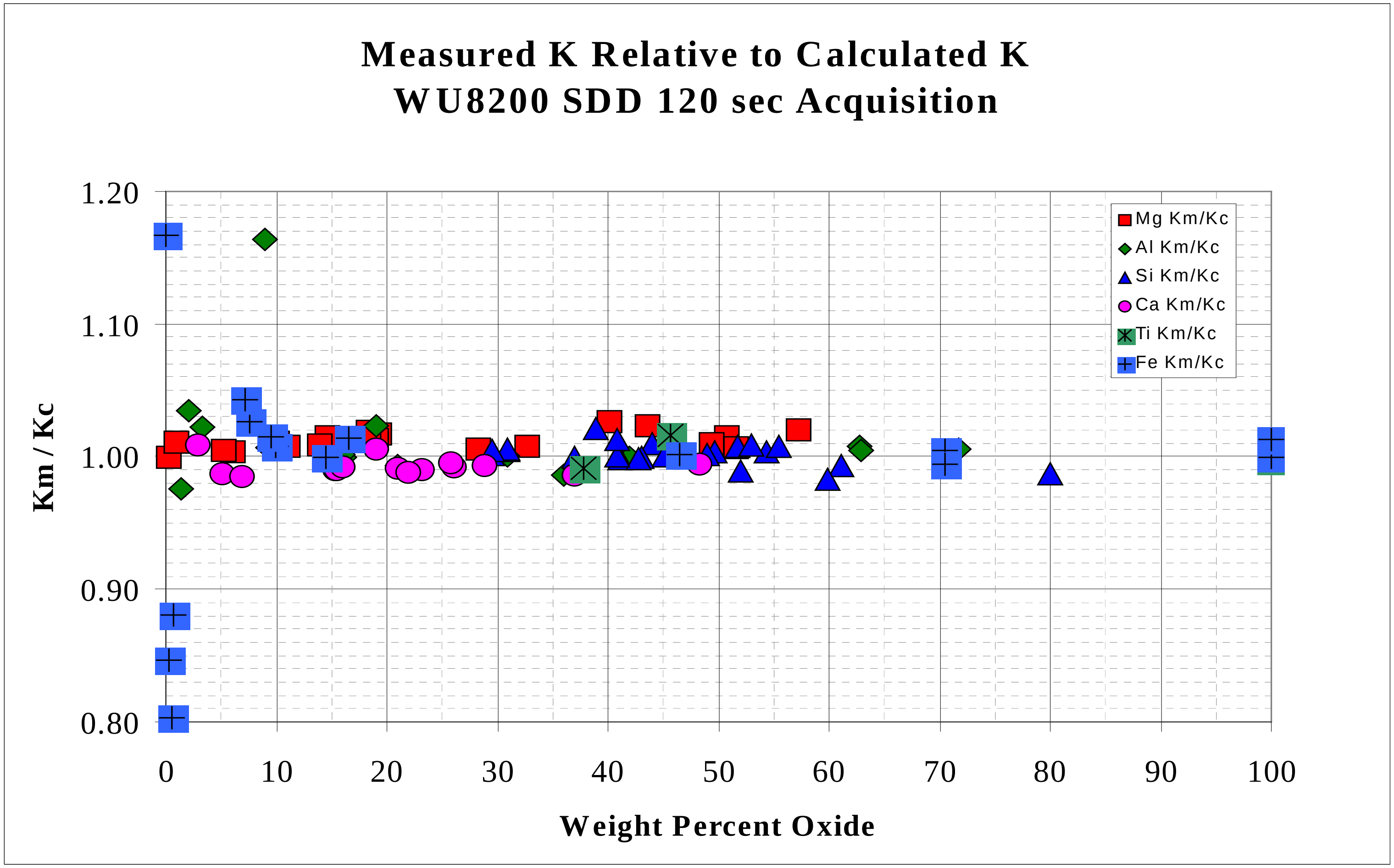
Washington University JXA-8200 SDD
Corning 95IRW: V, Mn, Co, Cu, Cs, Ba, La, Th



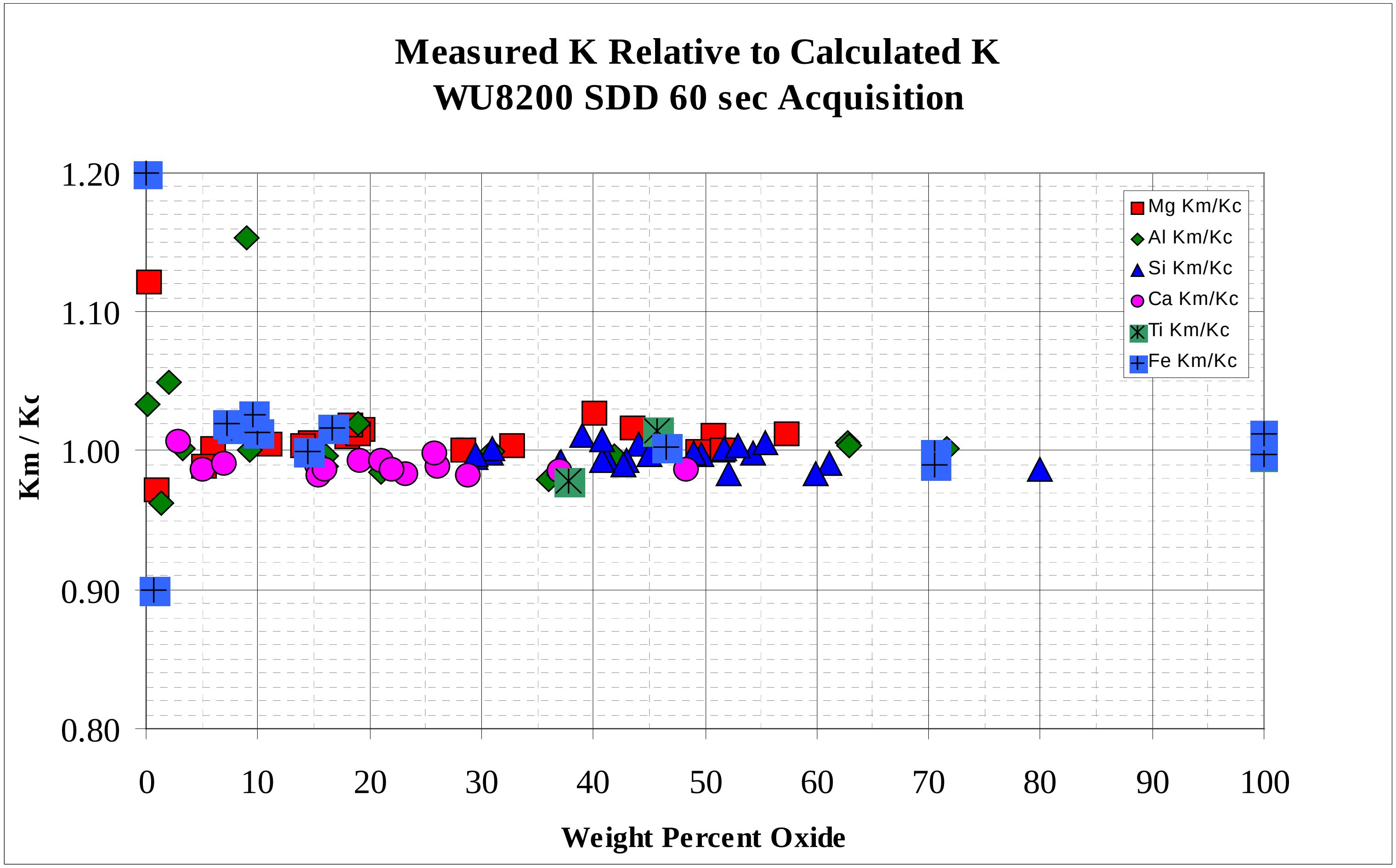
Washington University JEOL JXA-8200 SDD Quantitative Analysis Data

- SDD great for mapping, what about quantitative analysis?
- SDD EDS data acquired at 120s, 60s, and 3s acquisitions at T3
- Standards used: MgO, Al_2O_3, SiO_2, $CaSiO_3$ (CaO 48.27, SiO_2 51.73), TiO_2, and Fe_2O_3
- Linear least-squares peak deconvolution (JEOL software)
- Extracted raw K-ratios processed using Armstrong $\Phi(\rho z)$ and FFAST macs for comparison with WDS data

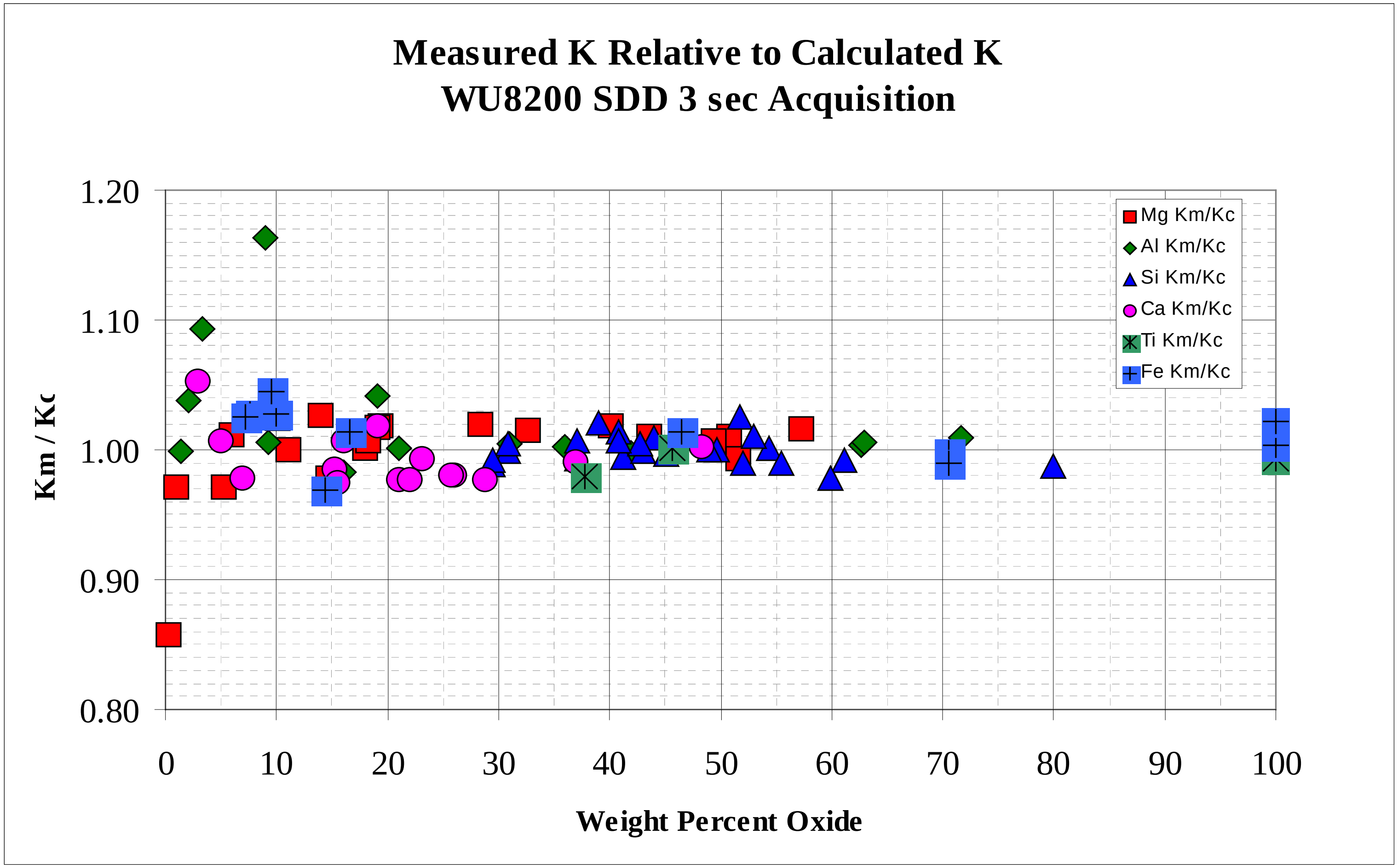
CMASTF Standard Analyses
WU8200 SDD LLSQ 120 sec. Acquisition T3



CMASTF Standard Analyses
WU8200 SDD LLSQ 60 sec. Acquisition T3



CMASTF Standard Analyses
WU8200 SDD LLSQ 3 sec. Acquisition T3



Average Kmeas / Kcalc for CMASTF Standards WU8200 SDD Data @ 120, 60, 3 sec acquisition T3

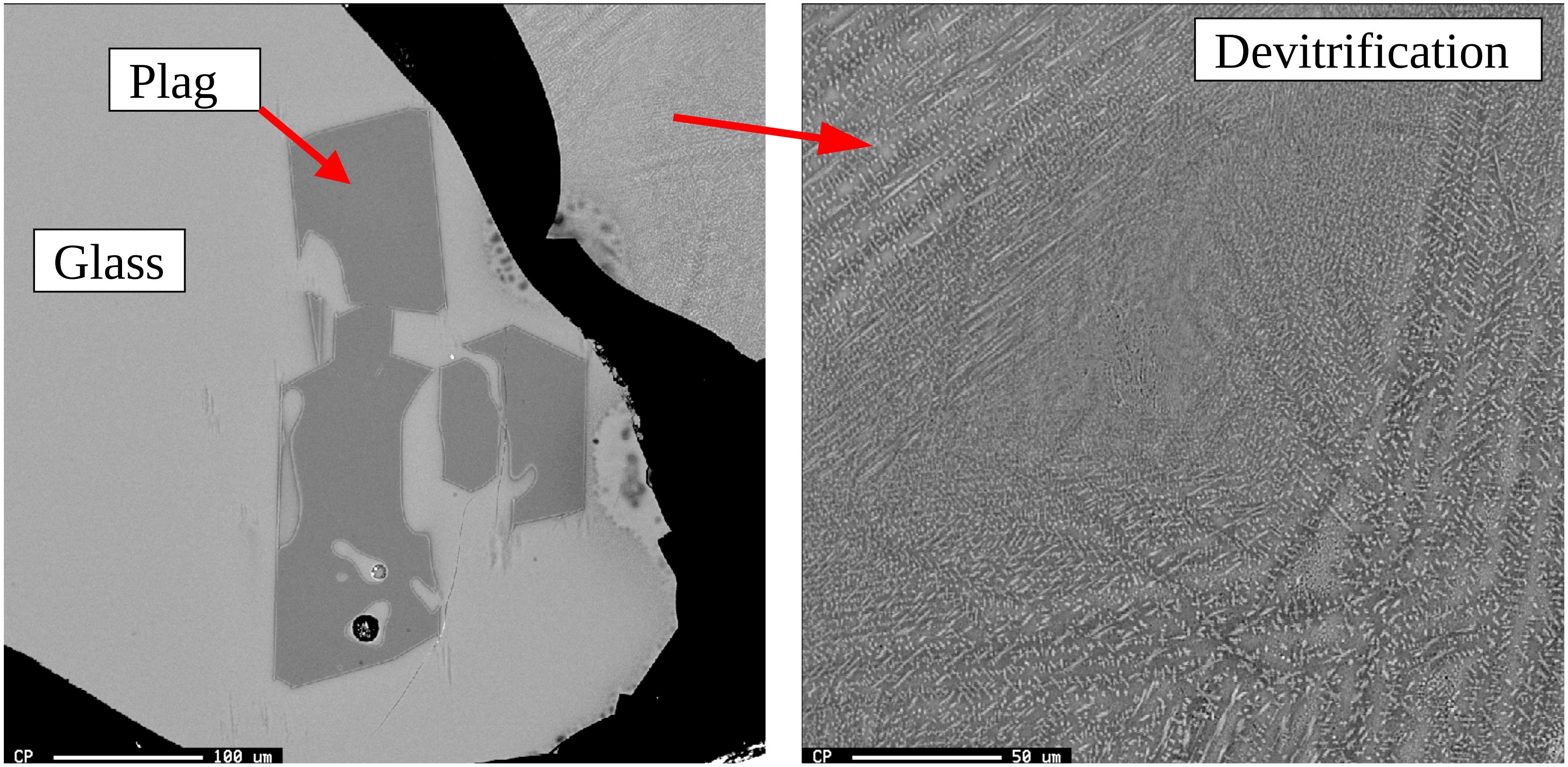
120s Data	**Mg**	**Al**	**Si**	**Ca**	**Ti**	**Fe**
Average	1.0122	1.0064	1.0017	0.9926	1.0021	1.0108
1 σ	0.0063	0.0122	0.0078	0.0066	0.0106	0.0140
Relative %	0.62	1.21	0.78	0.67	1.06	1.38
60s Data						
Average	1.0058	1.0022	0.9969	0.9895	0.9975	1.0083
1 σ	0.0118	0.0162	0.0069	0.0066	0.0150	0.0113
Relative %	1.17	1.61	0.69	0.67	1.51	1.12
3s Data						
Average	1.0061	1.0135	1.0001	0.9933	0.9947	1.0123
1 σ	0.0162	0.0263	0.0104	0.0213	0.0118	0.0211
Relative %	1.61	2.59	1.04	2.14	1.19	2.09

EPMA Standards

Advances in EPMA:
Geological Materials -- Standards

- EPMA standards requirements: Homogeneous on micron scale, grain to grain, well characterized on both scales, and available in large enough quantity to be used by microanalysis communities.
- Most materials fail one or more of these requirements.
- Natural and synthetic minerals, oxides, and glasses.
  Minerals impose stoichiometry but may be inhomogeneous
  Glasses lack stoichiometric control but can be homogeneous
- Glasses: targeted compositions that can be made in bulk and utilized by the microanalysis community.
  (Corning 95-series trace element glasses)
- Internal consistency of EPMA standards used by the community is poorly known. Few comparison reports, generally anecdotal.
- Solution: calculate expected x-ray intensity for element of interest in suite of standards, compare measured intensities relative to end-member standard (oxide), i.e., k = ZAF / C. This highlights errors in composition as well as systematic errors in algorithm.

Basalt Glass Indian Ocean USNM 113716: EPMA vs. Wet Chemistry Data



Of the 3-5 mounts of UNSM 113716, this is the first observation of mineral inclusions or crystallites in the glass. This is otherwise a homogeneous standard, consistent with EPMA of other glasses, but based on wet chemistry comparison. **How representative is this of the wet chemical analysis?**

Olivine Standards: Mg-rich $(Mg,Fe)_2SiO_4$

Standard	Nat./Syn.	Minor/Trace Els.
Shankland forsterite Fo_{100}	Synthetic	Fe?
Boyd olivine Fo_{93}	Natural	Mn, Co, Ni, Zn?
LLNL "Fo85" (Fo_{93})	Synthetic	<none>
San Carlos olivine Fo_{90}	Natural	Na?, Mg, Al, Ca, Ti?, Cr, Mn, Co, Ni
Fujisawa sintered Fo_{90}	Synthetic	Al, Ca, Mn, Zn
LLNL "Fo80" (Fo_{85})	Synthetic	Al, Ca, Cr, Mn, Co?, Ni?
Springwater olivine Fo_{82}	Natural	Ca, Cr, Mn
LLNL "Fo67" (Fo_{70})	Synthetic	<none>

Shankland from ORNL
LLNL olivines from George Rossman, Boyd and Fujisawa from Caltech
San Carlos and Springwater olivine from Smithsonian

Olivine Standards: Mn, Fe, Ni

Standard	Nat./Syn.	Minor/Trace Els.
Mn-olivine GRR-392	Synthetic	Fe
Mn-olivine RDS P-1087	Synthetic	Mg, Ca, Fe
Fayalite GRR-391	Synthetic	Mn
Fayalite RDS P-1086	Synthetic	Mg, Cr, Mn
Rockport Fayalite	Natural	Mg, Ca, Cr, Mn, Zn
Fayalite ORNL	Synthetic	Al?, Ca?, Cr
Ni-olivine P-877	Synthetic	Cr?, Fe, Co

GRR and RDS from George Rossman, P numbers Caltech probe standards
Rockport Fayalite from Smithsonian

Rockport Fayalite

- RF is widely used as primary Fe standard
  But Mg and Zn present, not in wet chemistry analysis
  [Low level oxides suspected to be variable not reported in wc analysis]
- Is ferric iron present? – apparently not:
  Wet Chemistry: Fe_2O_3 1.32, FeO 66.36 %, Tot: 99.18
  Dyar XANES: RF iron is completely reduced.
- Grunerite in separate: $Fe_7^{2+}Si_8O_{22}(OH)_2$
- Magnetite at locality, in separate ($Fe_2^{3+}Fe^{2+}O_4$) ??
- Analysts should use EPMA analysis when using RF as primary standard.

Fayalite Standards

Oxide	Rockport Wet Chemistry	Rockport EPMA	RDS P-1086 EPMA	GRR391 EPMA**
MgO	Not reported	0.046	0.385	0
SiO_2	29.22	29.99	30.04	(29.49)
CaO		0.045	0	0.004
Cr_2O_3		0.059	0	0.010
MnO	2.14	2.13	0.092	0.212
FeO*	67.55	67.62	69.61	(70.34)
NiO		0.007	0.012	0.011
ZnO	Not reported	0.575	0.006	0.007
Total	99.18	100.48	100.16	(100.04)
ΣM^{2+}	1.999	1.982	1.979	1.999
Si	1.001	1.009	1.010	1.000

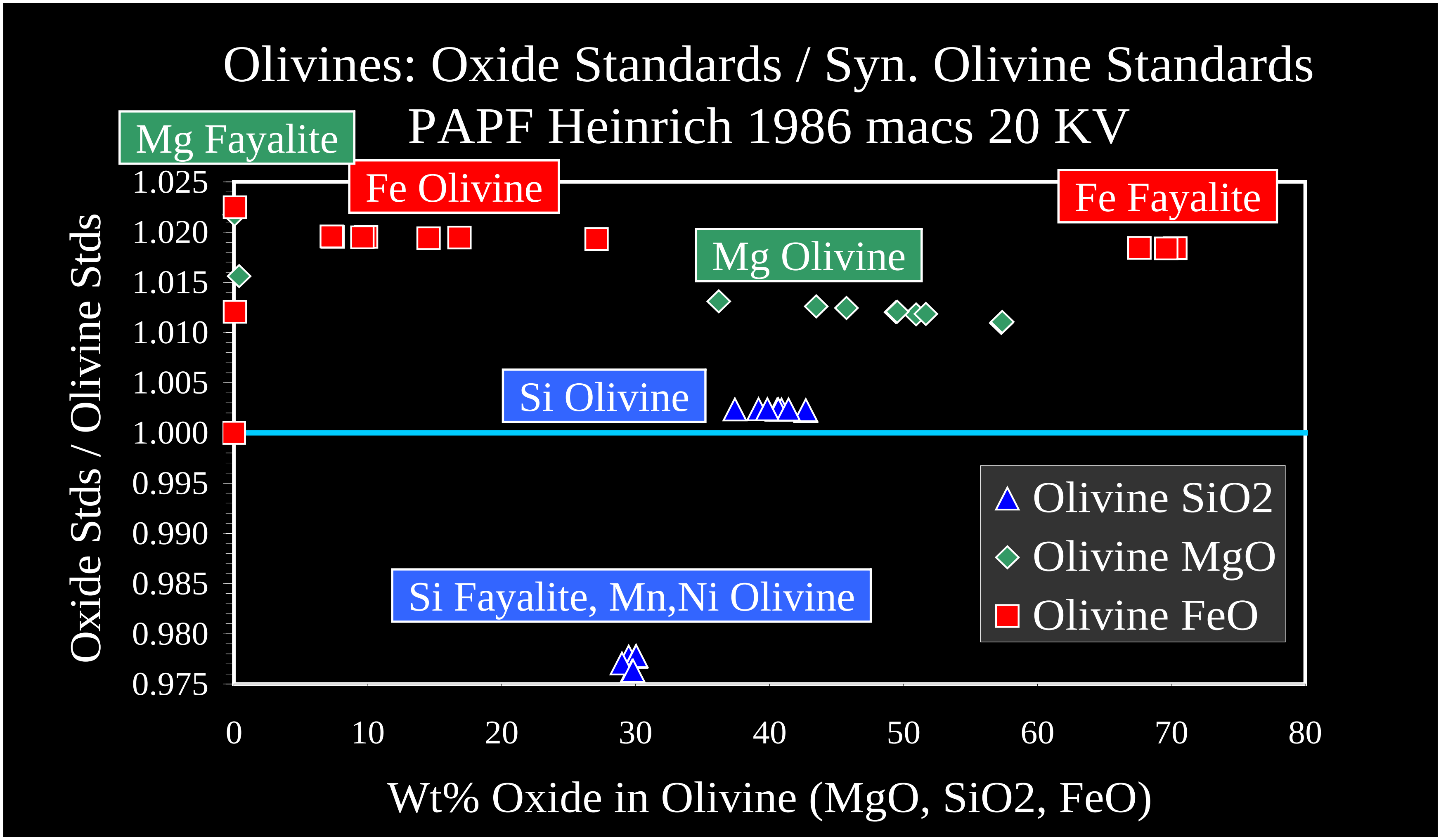
Rockport WC: FeO 66.36, Fe_2O_3 1.32, FeO* 67.55. TiO_2 0.04, H_2O 0.1
EPMA: PAPF, olivine stds, Heinrich 1986 macs, 20KV, n=4 **GRR391 std Si, Fe

Systematic Errors in Olivine $M^{2+}{}_2SiO_4$
PAPF, Heinrich 1986 macs @ 20 KV, 40 TOA

Olivine Group	Standard Type	Analysis Total	σ, wt%	Si cations 1 ideal	σ	Σ M^{2+} 2 ideal	σ
Olivines	Oxide	101.14	0.42	0.989	0.004	2.023	0.007
	Syn. Olivine	100.22	0.37	0.994	0.003	2.012	0.006
Fayalites	Oxide	100.93	0.20	0.990	0.001	2.022	0.001
	Syn. Olivine	100.34	0.23	1.010	0.001	1.981	0.003
Mn,Ni Olivines	Oxide	99.32	0.33	0.991	0.003	2.018	0.006
	Syn. Olivine	100.07	0.30	1.002	0.003	1.995	0.005

Averages of total and cation stoichiometry for all olivines from test data set.
For olivines, Mg/(Mg+Fe) = 0.860 ± 0.080 (ox) vs. 0.861 ± 0.079 (oliv).
Identical k-ratios corrected using PAP full Φ(ρz) and Heinrich 1986 macs, relative to oxide vs. synthetic olivine standards.
Olivine Formula: $M^{2+}{}_2SiO_4$

Systematic Error Using Oxide Standards



Status Report: EPMA of Olivine

- EPMA using synthetic olivine standards better than oxide standards:
  Superior analysis total, Si cation ~1.0, and ΣM^{2+} ~ 2.0
- Improvement in EPMA accuracy for olivine using
  Armstrong $\Phi(\rho z)$ coupled with FFAST mac data set.
- Using oxide standards we observe:
  Overcorrection of Mg and Fe in olivine across Fo-Fa binary
  Undercorrection of Si in low-Mg olivine (Fayalite, Mn-ol, and Ni-ol)
  Marginal underestimation of Mg/(Mg+Fe).
- These relationships extend to all MgFe silicates relative to composition.
- Alpha-factor analysis of systematic errors in Fo-Fa system:
  EPMA and wet chemistry of natural olivines are not internally consistent.
  Worst: Boyd Forsterite Mg and Fe not consistent (Caltech standard)
  Best: Springwater Mg,Fe, and Mg in San Carlos (Fe in SC less so)

Accuracy of EPMA:
Quantitative Analysis of Olivine

Olivine EPMA Accuracy Study:
Alpha factor method extended to olivine

- Alpha factor (α-factor) method used to evaluate:
  - Systematic errors for $\Phi(\rho z)$ correction algorithms
  - Internal consistency of EPMA-only data and EPMA vs. wet chemistry.
- Compositional end-members for α-factor systems:

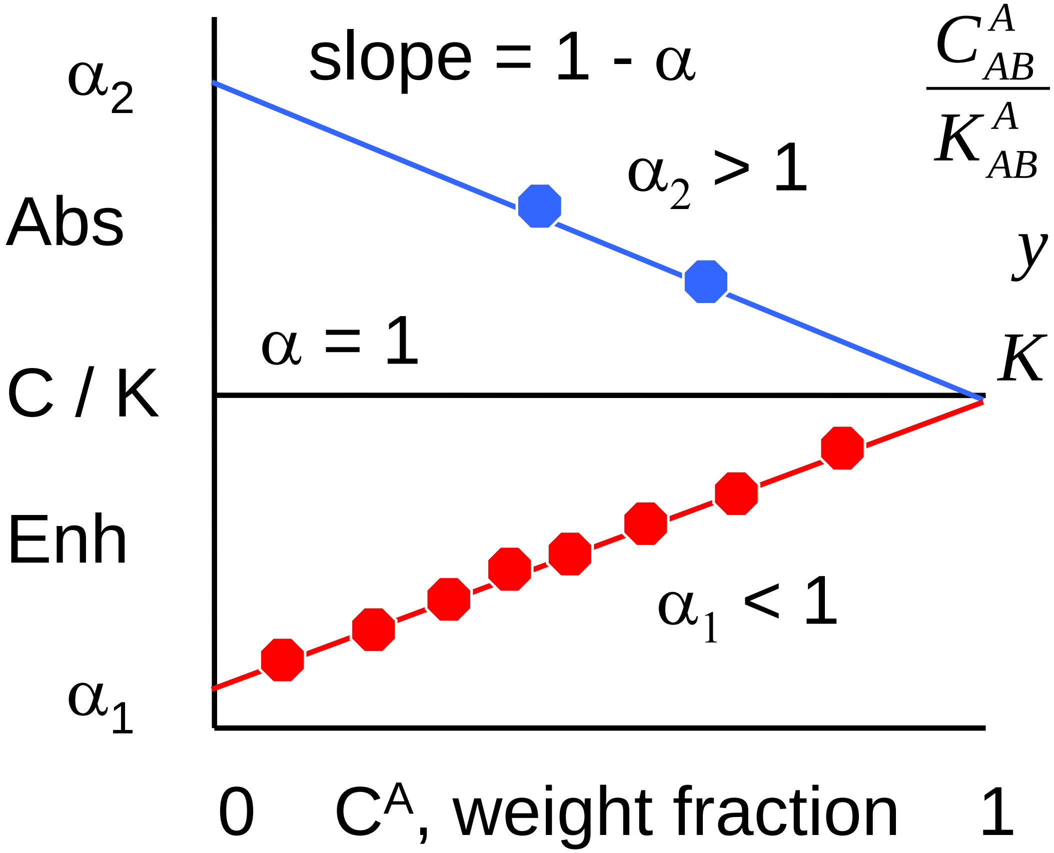
Pure elements	Mg – Fe, i.e., Ziebold-Ogilvie
Pure oxides	MgO – FeO, i.e., Bence-Albee
Olivine binary	Mg_2SiO_4 – Fe_2SiO_4

- Synthetic olivines, pure Fo and Fa, used as primary standards for α-factor analysis.
- Natural olivines require projection onto Fo-Fa binary for comparison.
- Anticipate decreased reliance on correction algorithm and fundamental parameters as one moves from pure element end members to olivine end members. Measurement errors ultimately control accuracy.

Olivine Alpha Factor Study:
Comparison of Calculated and Measured Concentration

- Calculated α-factors using $\Phi(\rho z)$ algorithms and mass absorption coefficients and a polynomial fit to the individually calculated values.
  - C known, K calculated.
- Experimental α-factors extracted from olivine analyses.
  - K measured, C calculated.
  - Compared with calculated α-factors.
  - If measurements, algorithms, and data sets are correct, all experimentally determined analyses would lie on theoretical lines.
- Wet chemistry data evaluated.
  - K measured, C obtained from wet chemistry.
  - If wet chemistry data, algorithms and data sets are correct, all wet chemistry analyses would also lie on the theoretical lines.

Extraction of α-factors from Experimental Measurements



$$\frac{C_{AB}^{A}}{K_{AB}^{A}} = \alpha_{AB}^{A} + \left(1 - \alpha_{AB}^{A}\right) C_{AB}^{A}$$

$$y = b + mx$$

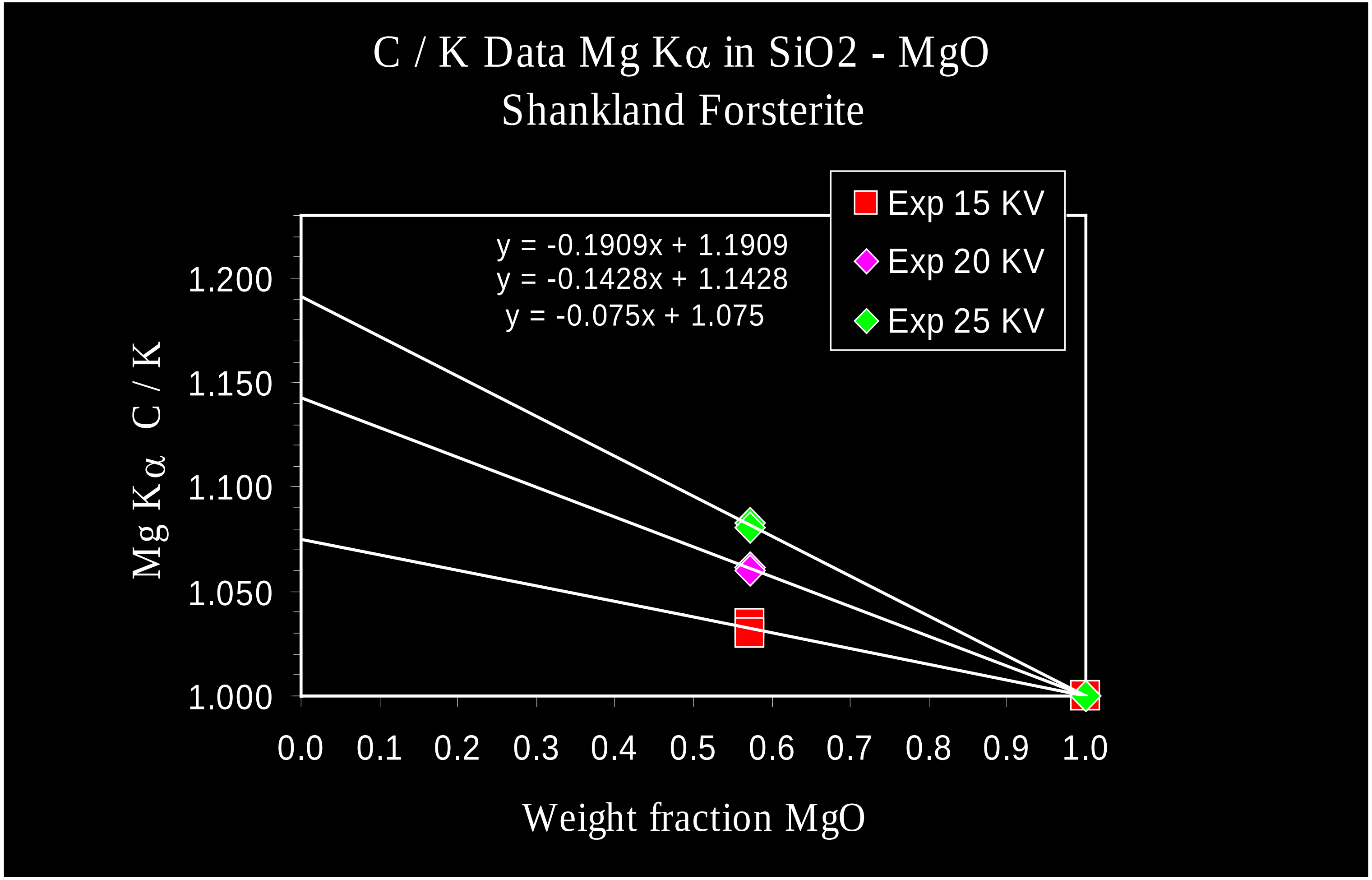
$$K = (P - B)^{smp} / (P - B)^{std}$$

$$\alpha_{AB}^{A} = \frac{\left[\frac{C_{AB}^{A}}{K_{AB}^{A}} - C_{AB}^{A}\right]}{1 - C_{AB}^{A}}$$

For olivine:
Forsterite: C = Wt Fraction MgO / [MgO in Mg_2SiO_4]
Fayalite C = Wt Fraction FeO / [FeO in Fe_2SiO_4]

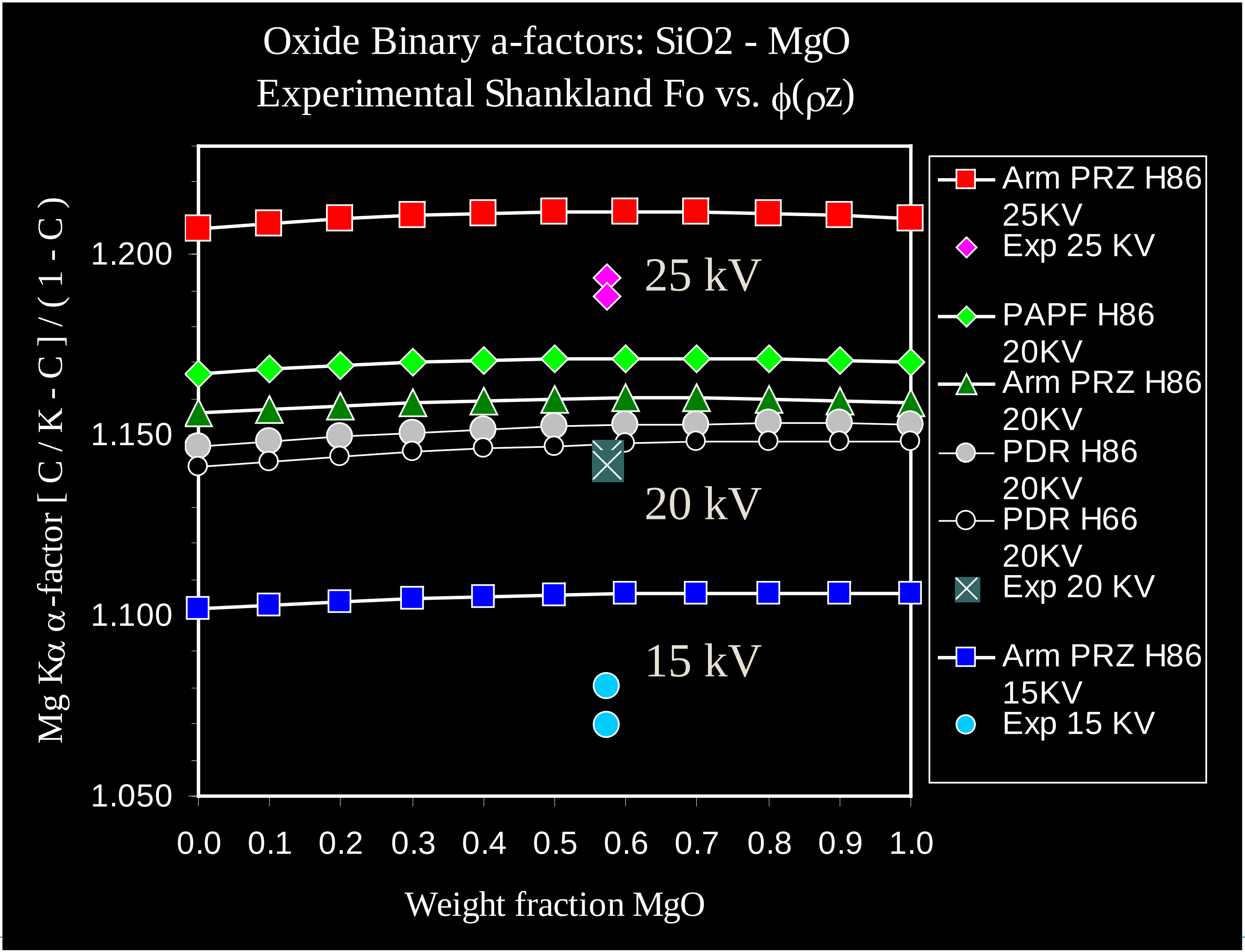
Analysis of Mg Kα in Shankland Forsterite using MgO Std: Experimental Determination of α-factors

Bence-Albee Analysis of Forsterite for Mg Kα using MgO

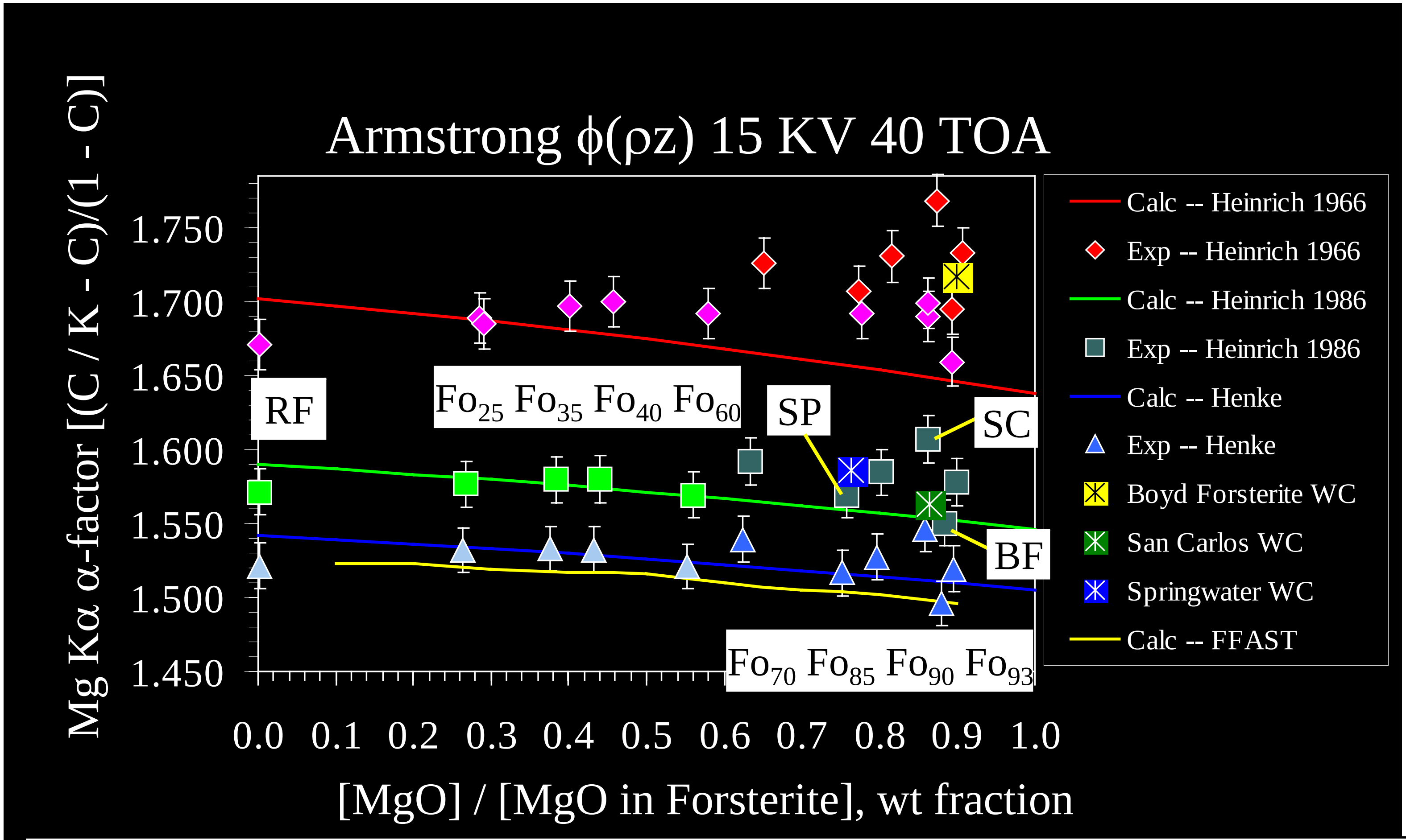


MgO Std – Shankland Fo Mg Kα
Variation of α-factors with Composition, kV

Multiple kV Analysis Highlights X-ray Absorption Errors

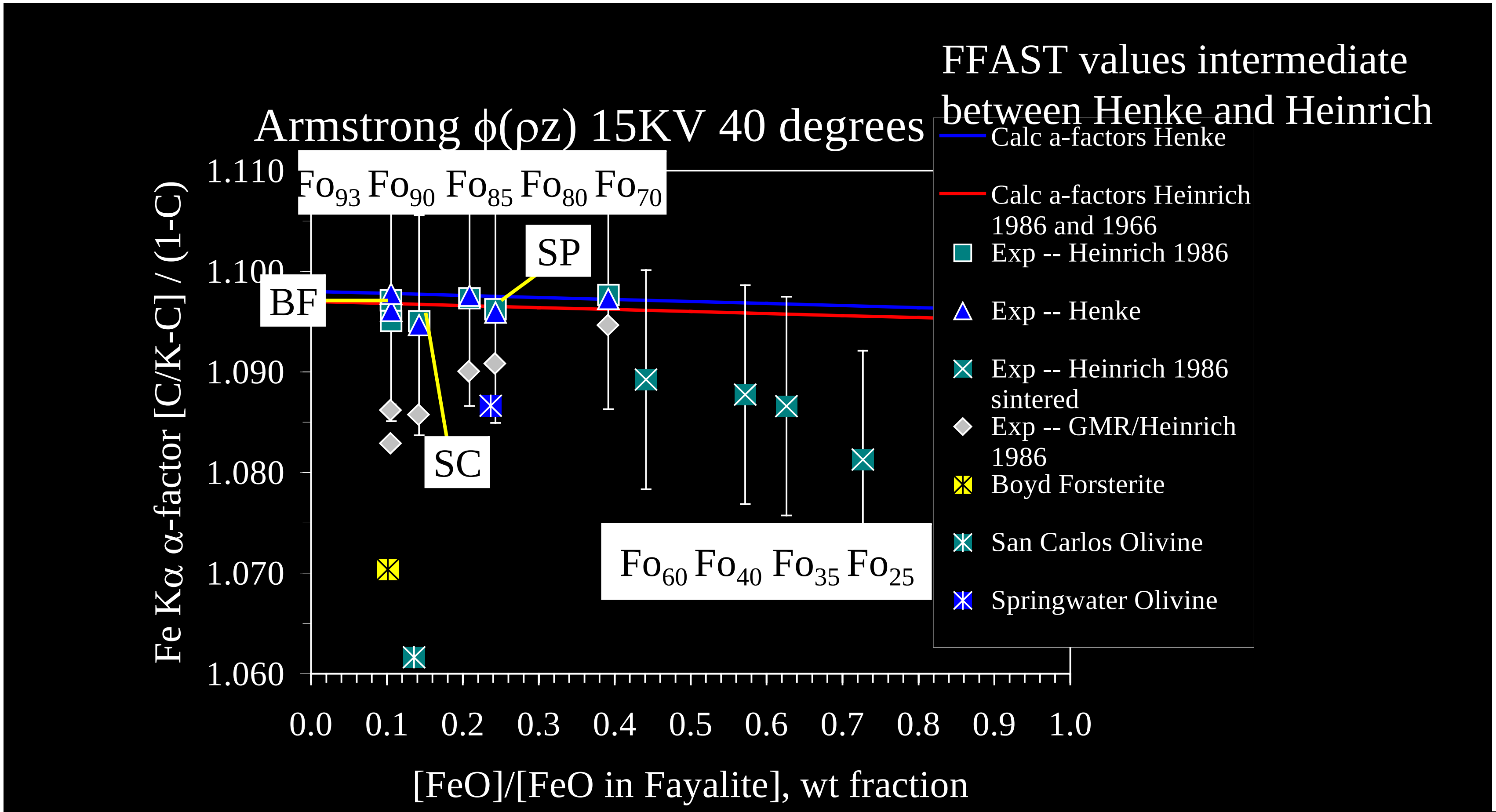

Oxide Binary a-factors: SiO2 - MgO
Experimental Shankland Fo vs. ϕ(ρz)

Mg Kα in Olivine Using Forsterite Standard Calculated and Experimental Data, Effect of MAC's



1. Historical overcorrection, esp. H66 at Fo-rich, FFAST macs reduce overcorrection.
2. Good agreement EPMA of syn. and natural olivines, esp. H86, Henke using Armstrong Φ(ρz).
3. Boyd Forsterite Mg value of wet chemistry inconsistent with wc of San Carlos and Springwater.

Fe Kα A-factors in Fo-Fa Binary
Better accuracy compared to Mg



FFAST values intermediate between Henke and Heinrich

1. Minimal dependence on mac data set. Could calculate Mg by 2-Fe for binary olivines only.
2. Good agreement EPMA of syn. and natural olivines with Armstrong Φ(ρz).
3. Continuum fluorescence important for Fo-rich olivines.
4. Boyd Forsterite and San Carlos Fe value of wet chemistry least consistent with others.

EPMA of San Carlos Olivine
Correction Method and macs @ 20 KV, 40 TOA

Oxide	Wet Chem	PDR	PAPF-1	Arm-1	PAPF-2	Arm-2	PAPF-3	Arm-3
		Ox / H66	Ox / H86	Ox / H86	Ol / H86	Ol / H86	Ol / FF	Ol / FF
MgO	49.42	50.10	50.04	49.82	49.44	49.44	48.98	49.00
SiO_2	40.81	40.74	40.66	40.07	40.56	40.58	40.34	40.69
FeO*	9.55	10.13	10.08	9.89	9.89	9.89	9.89	9.74
Total	100.29	101.66	101.47	100.47	100.60	100.60	99.90	100.12
ΣM^{2+}	2.005	2.025	2.025	2.034	2.016	2.016	2.014	2.003
Si	0.997	0.986	0.986	0.982	0.991	0.991	0.992	0.997
Mg/(Mg+Fe)	0.902	0.898	0.899	0.900	0.899	0.901	0.898	0.900

PDR: Philibert-Duncumb-Reed ZAF, oxide stds, Heinrich 1966 macs

PAPF-1 and Arm-1: $\Phi(\rho z)$ algorithms, oxide stds, Heinrich 1986 macs

PAPF-2 and Arm-2: synthetic olivine stds, Heinrich 1986 macs

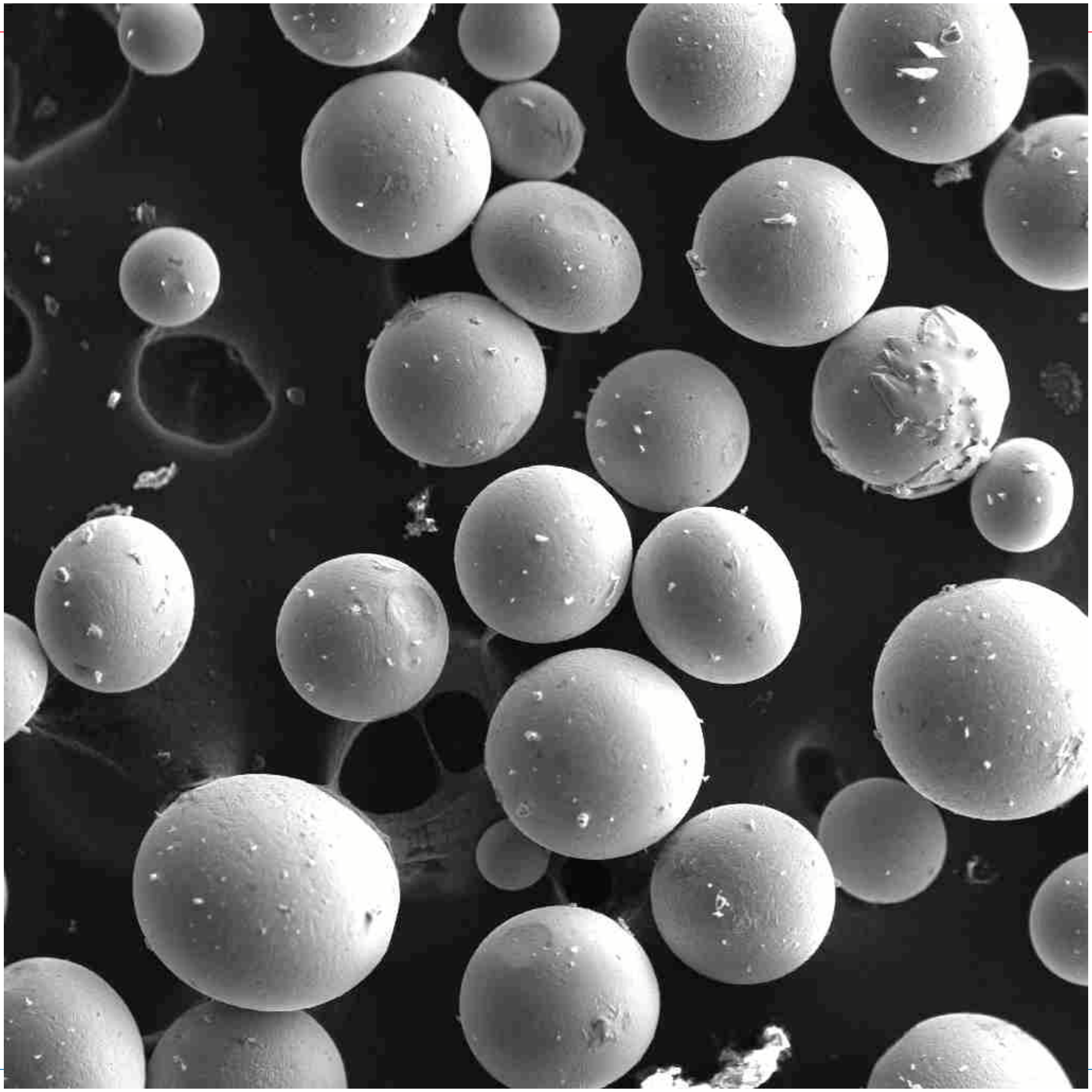
PAPF-3 and Arm-3: synthetic olivine stds, FFAST macs

Same k-ratios, n=4, CaO 0.09, Cr_2O_3 0.06, MnO 0.14, NiO 0.37 (wt %)

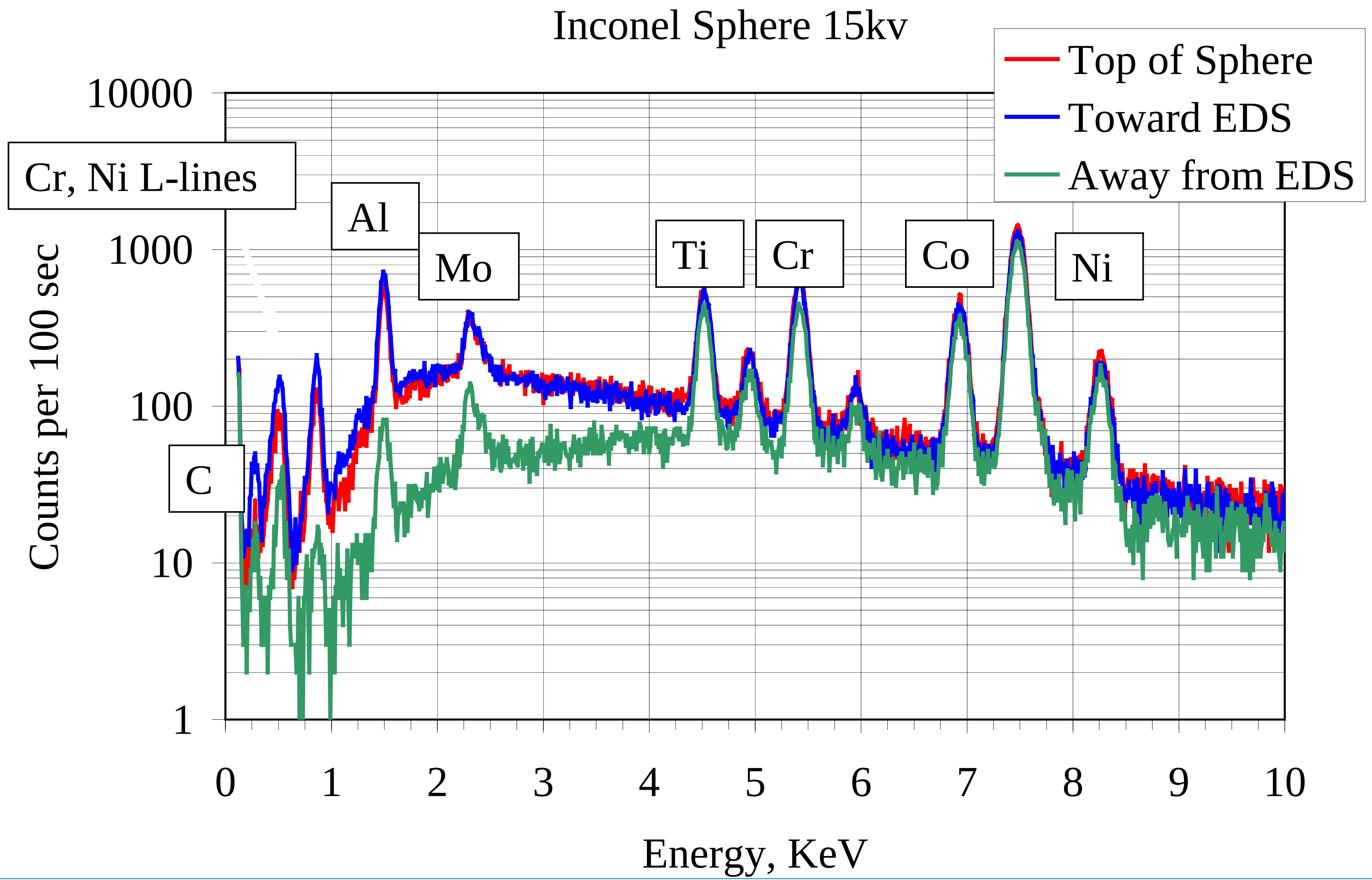
Olivine Formula: $M^{2+}{}_2SiO_4$ [PFW 7/2004, PDR and PAPF algorithm errors corrected]

Effect of Tilting and Particle Effects

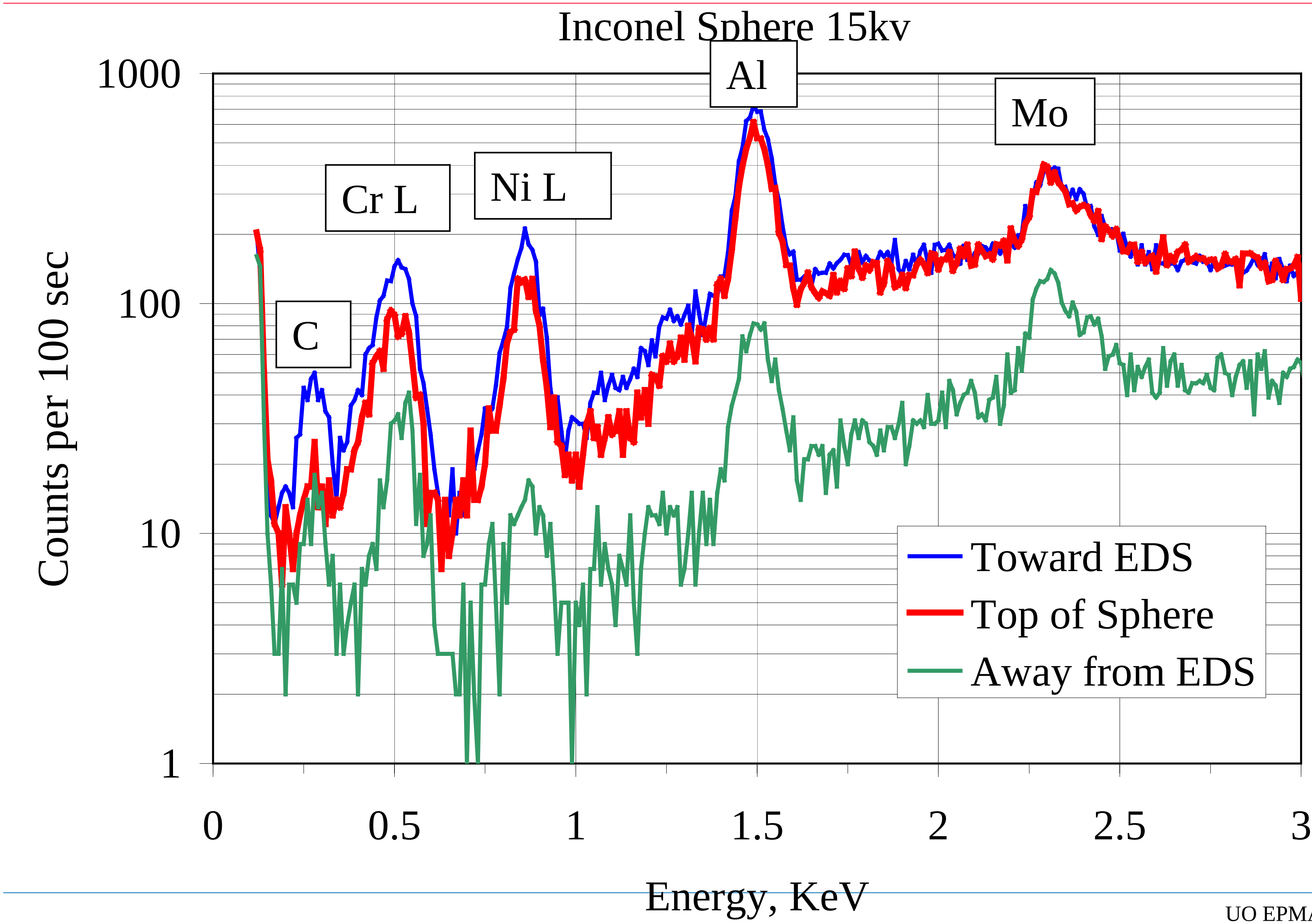
Inconel Spheres: Diameter ~ 30 um



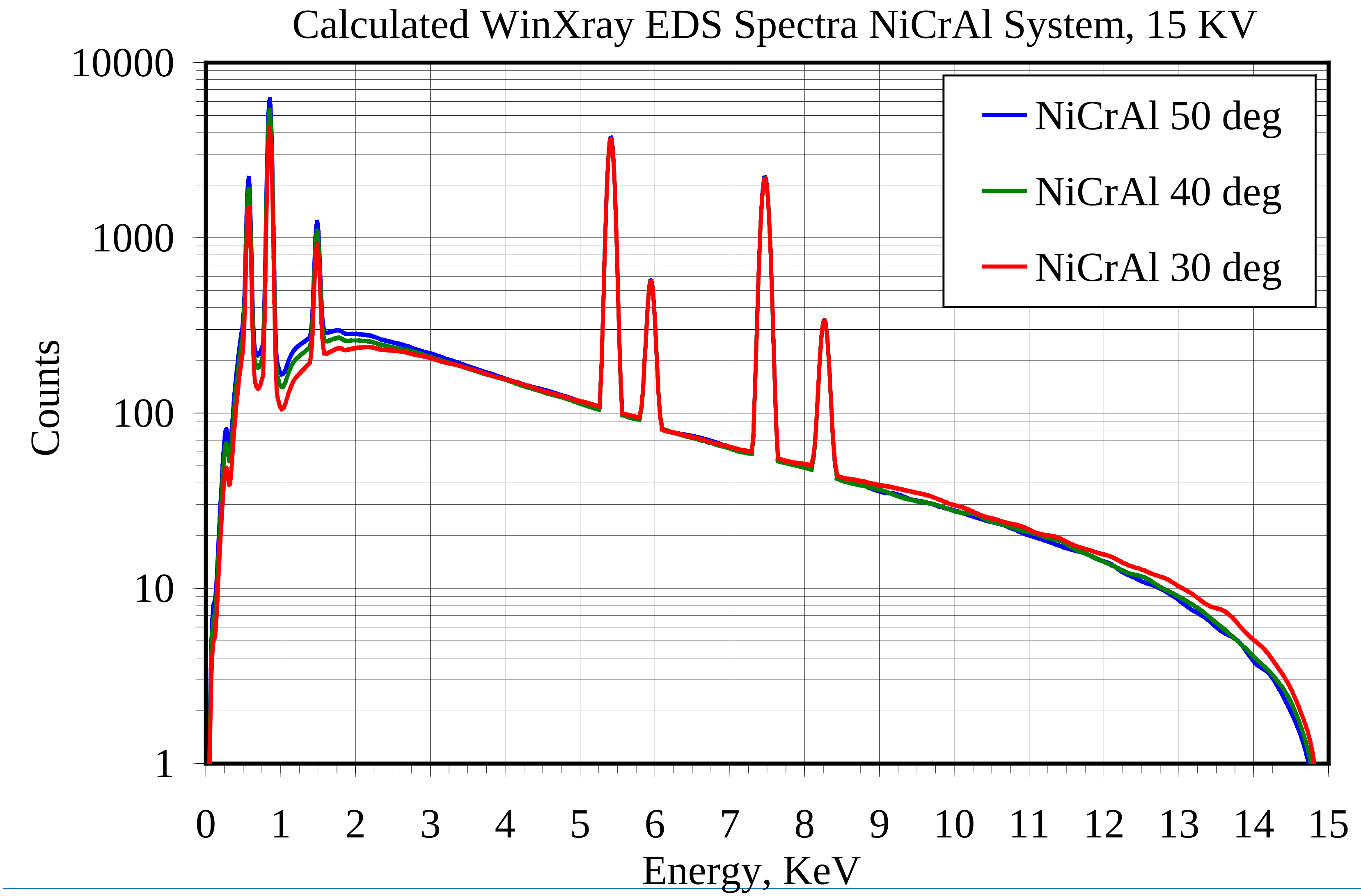
Inconel Sphere EDS Spectra: Effect of Takeoff Angle



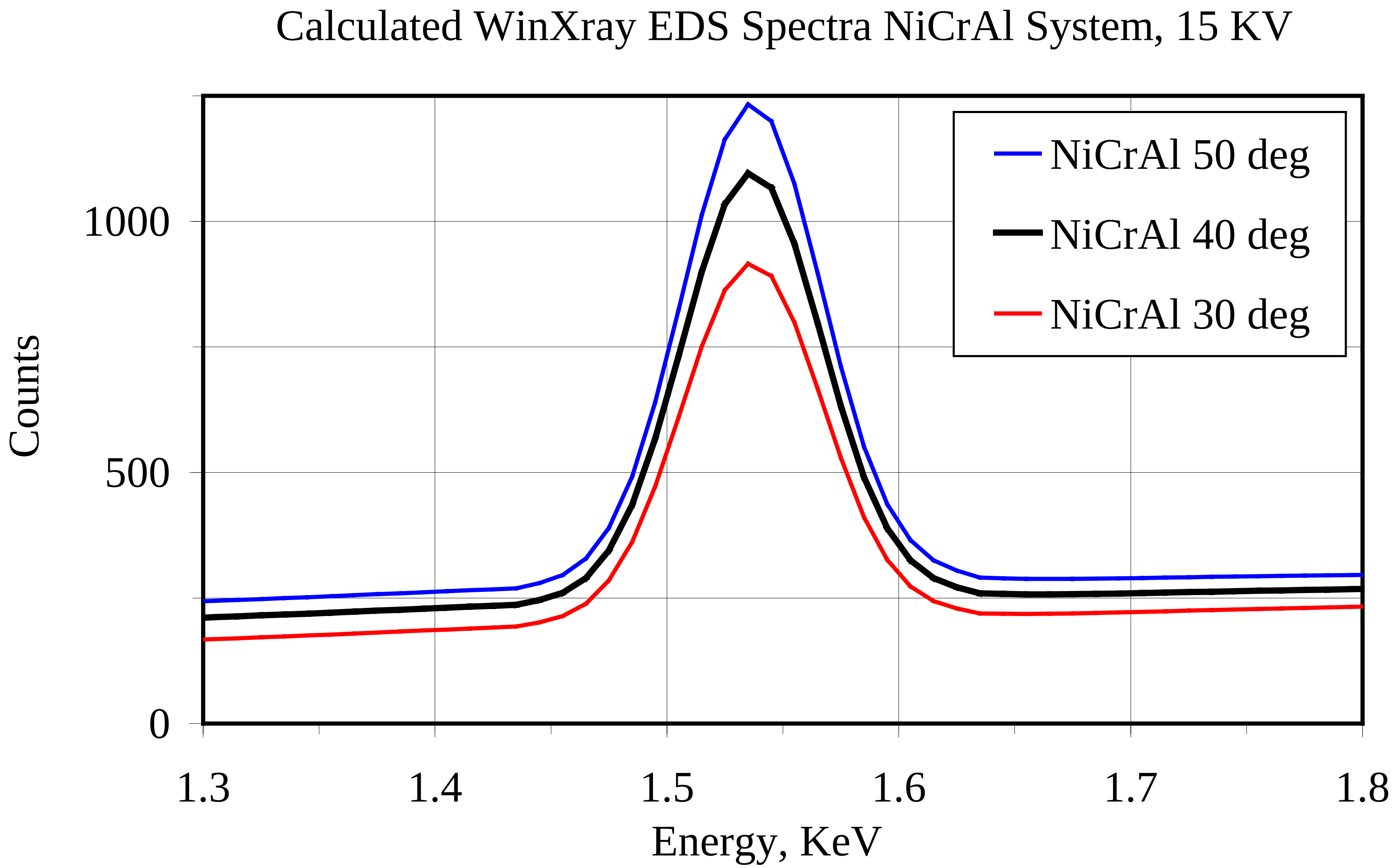
Inconel Sphere Low Energy EDS Region



WinXray: EDS Spectra at 30, 40, 50 degree TOA



Al Kα Peak Intensity at -10º to +10º Tilt Relative to 40º



Calculated Tilt Effect on Al-Cr-Ni Alloy Composition

	Takeoff Angle	Al Kα Intensity	Al Wt %	Cr Kα Intensity	Cr Wt %	Ni Kα Intensity	Ni Wt %
	30	59.85	2.45	437.57	37.28	263.80	58.43
	35	66.52	2.73	441.18	37.58	265.79	58.87
Nominal	**40**	**72.21**	**2.96**	**443.95**	**37.82**	**267.31**	**59.21**
	45	77.04	3.16	446.13	38.01	268.49	59.47
	50	81.12	3.33	447.86	38.15	269.42	59.68

GMR Thin Film program: calculate emitted intensity at each takeoff angle.
(We don’t want k-ratio relative to standard at each takeoff angle)
X-ray intensity relative to 40 degree value used to scale weight %
Al range 0.88 wt% / 20 degrees = 0.044 wt% per degree = 1.5% relative/deg.
Cr range 0.88 wt%, = 0.12% relative/degree
Ni range 1.25 wt%, = 0.063 wt% per degree = 0.11% relative/degree
Conclusion: 10 degree tilt error results in percent level analytical errors

Problem Systems

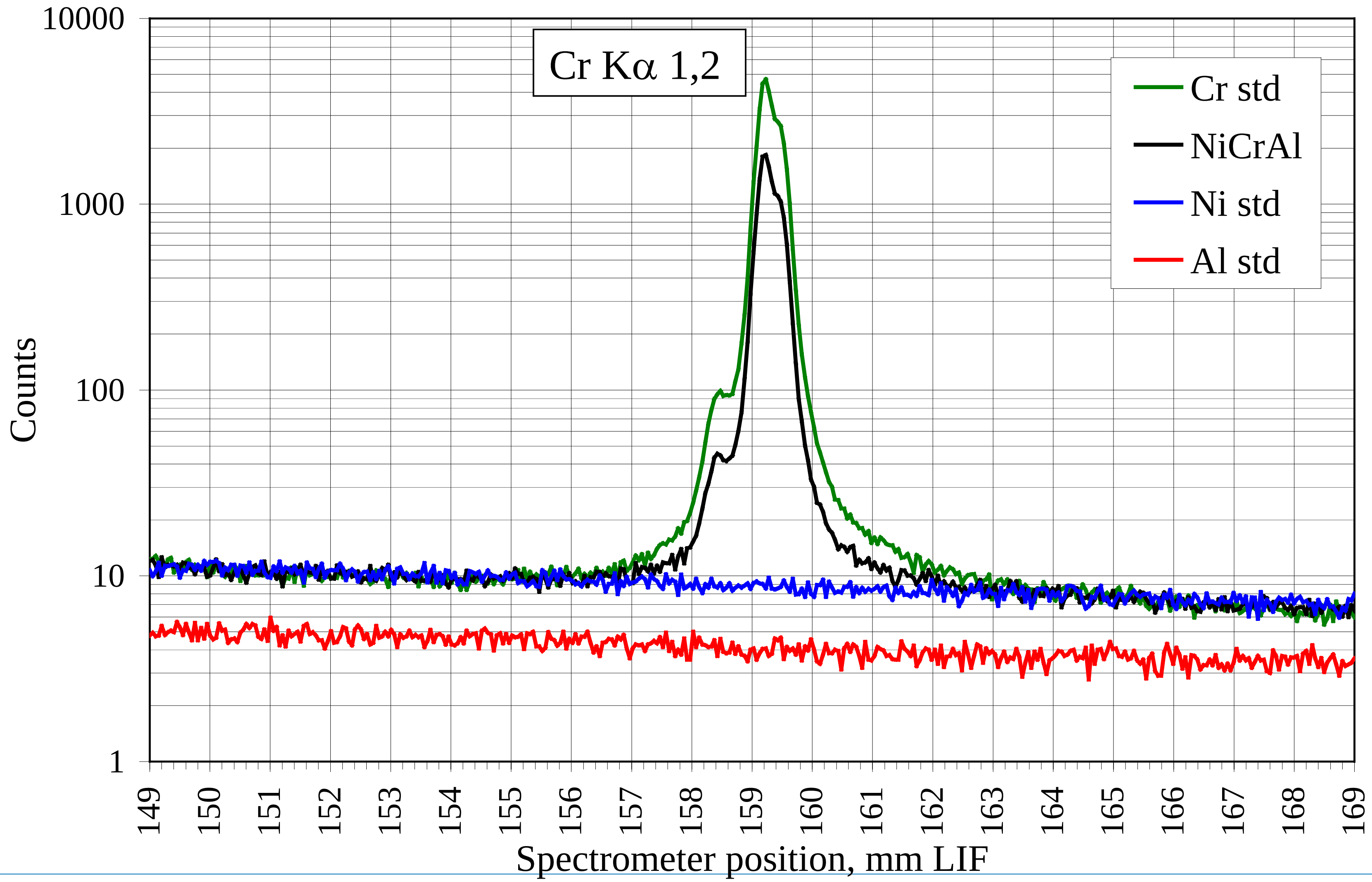
Problem Systems in EPMA: Analytical Elements in Problem Matrices

- Analytical Problems:
- X-ray peak overlaps
- High x-ray absorption
- Spatial issues, inhomogeneity
- Particle, thin film, etc.
- ----
- Perform proper measurement to obtain correct k-ratio
- Use standard as close to sample for high correction analysis
- Necessary to evaluate all correction algorithms and mass absorption coefficients – do not blindly accept one pairing as the best

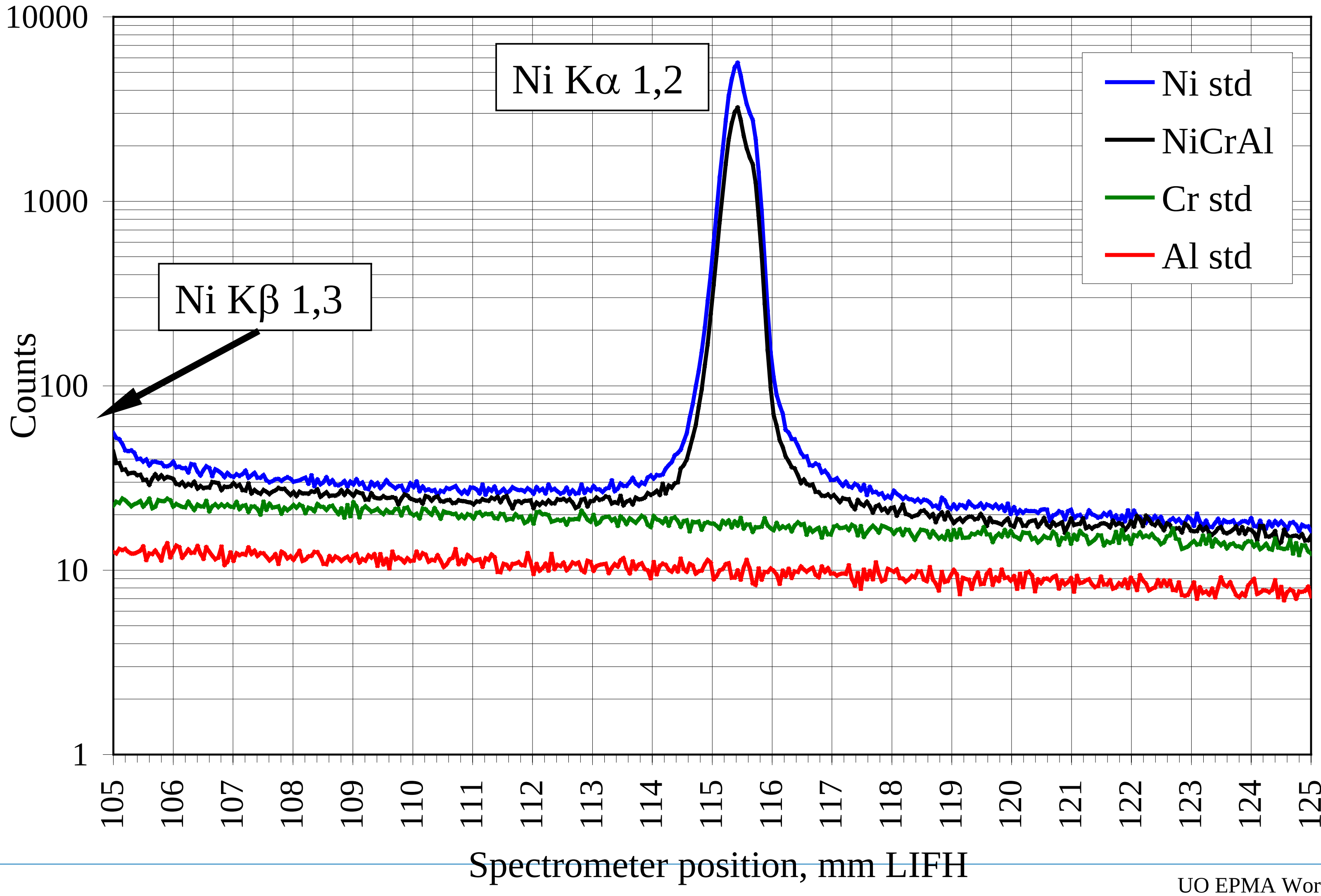
WDS Background Selection (Natural Peak Width) And High Order WDS Interferences

- Example AlCrNi alloy used in Lehigh Microscopy School lab
- WDS scan on pure Al necessary to establish full natural peak width
- People choose backgrounds too close to peak
  - If background is not true on pure element, also not true on any sample
- Cr Kb IV reflection observed at Al Ka peak position on TAP

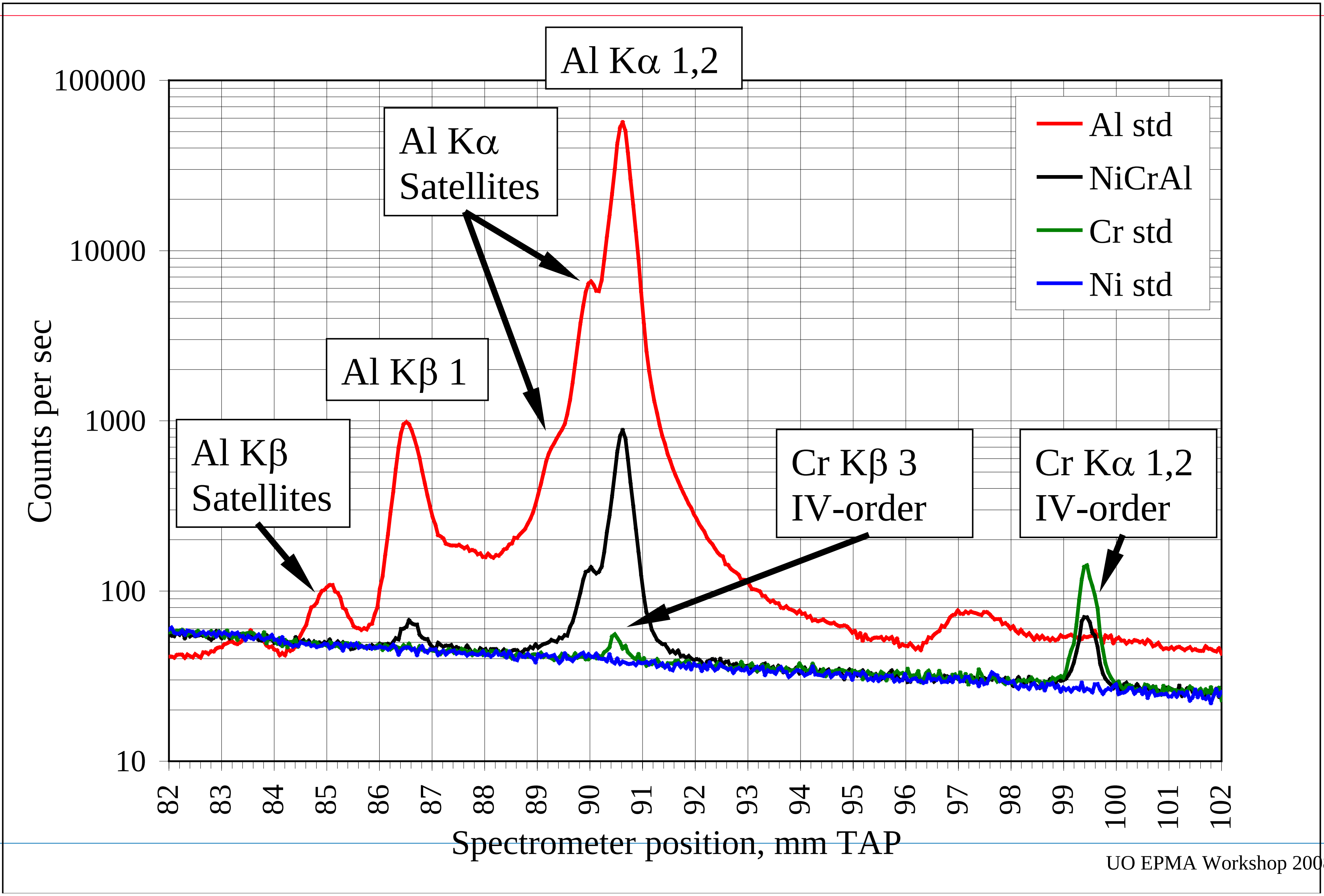
WDS Scan LIF: Al, Cr, Ni and NiCrAl Sample
Note background intensity as function of Z



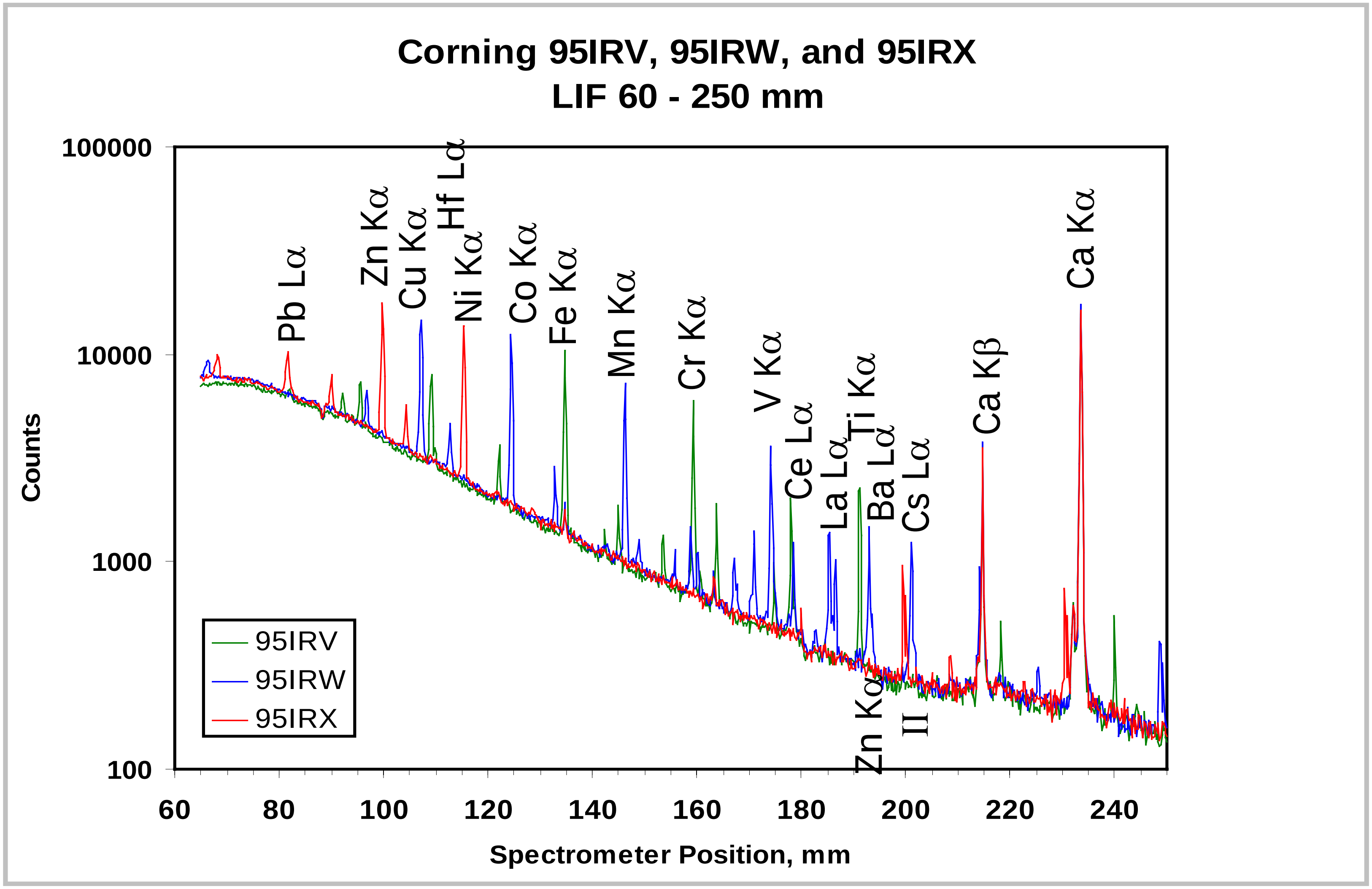
WDS Scan LIF: Al, Cr, Ni, and NiCrAl Sample
Note background intensity as function of Z



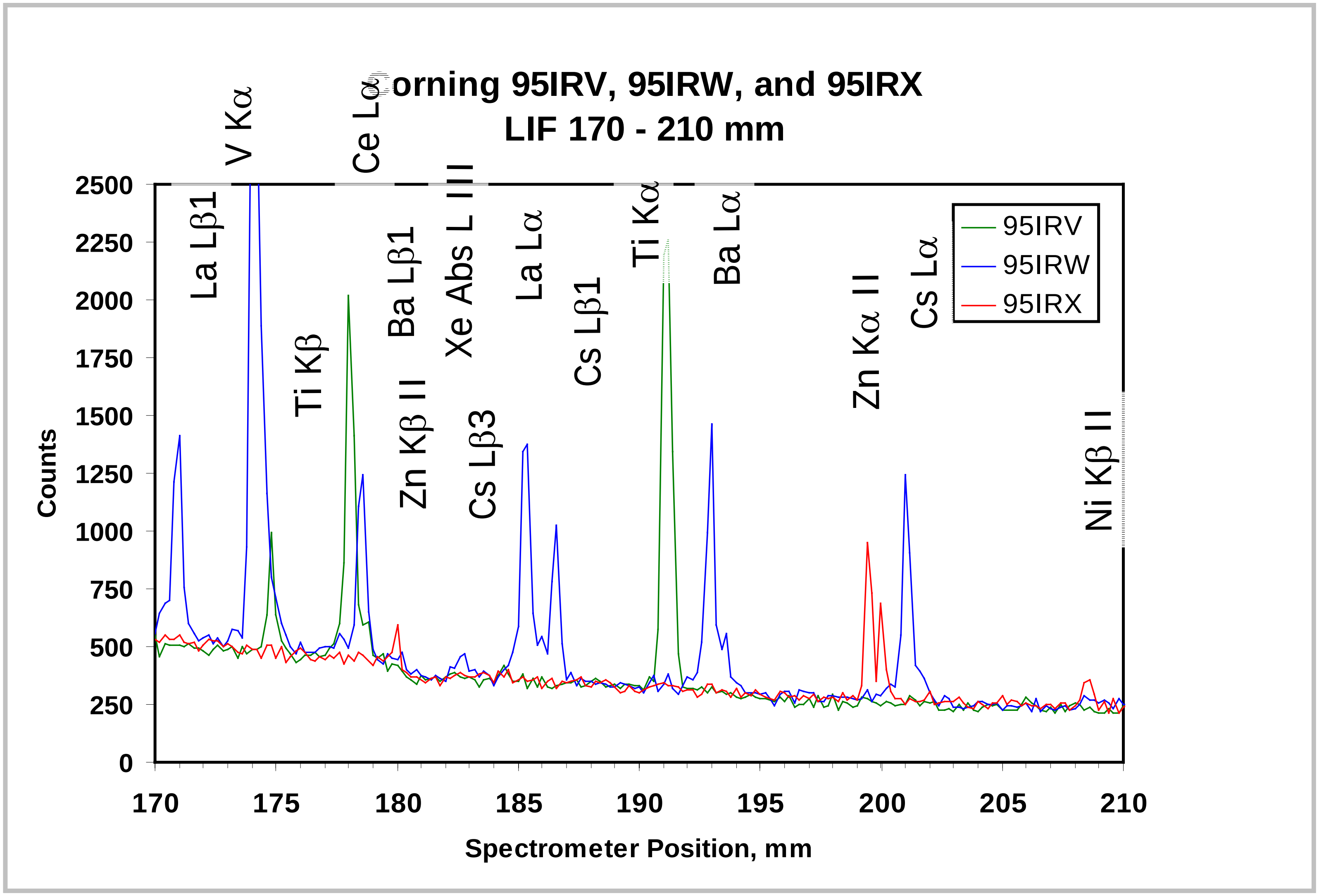
WDS Scan TAP: Al, Cr, Ni, and NiCrAl Sample
Note Cr Kβ IV-order interference on Al Kα, Full Al peak width



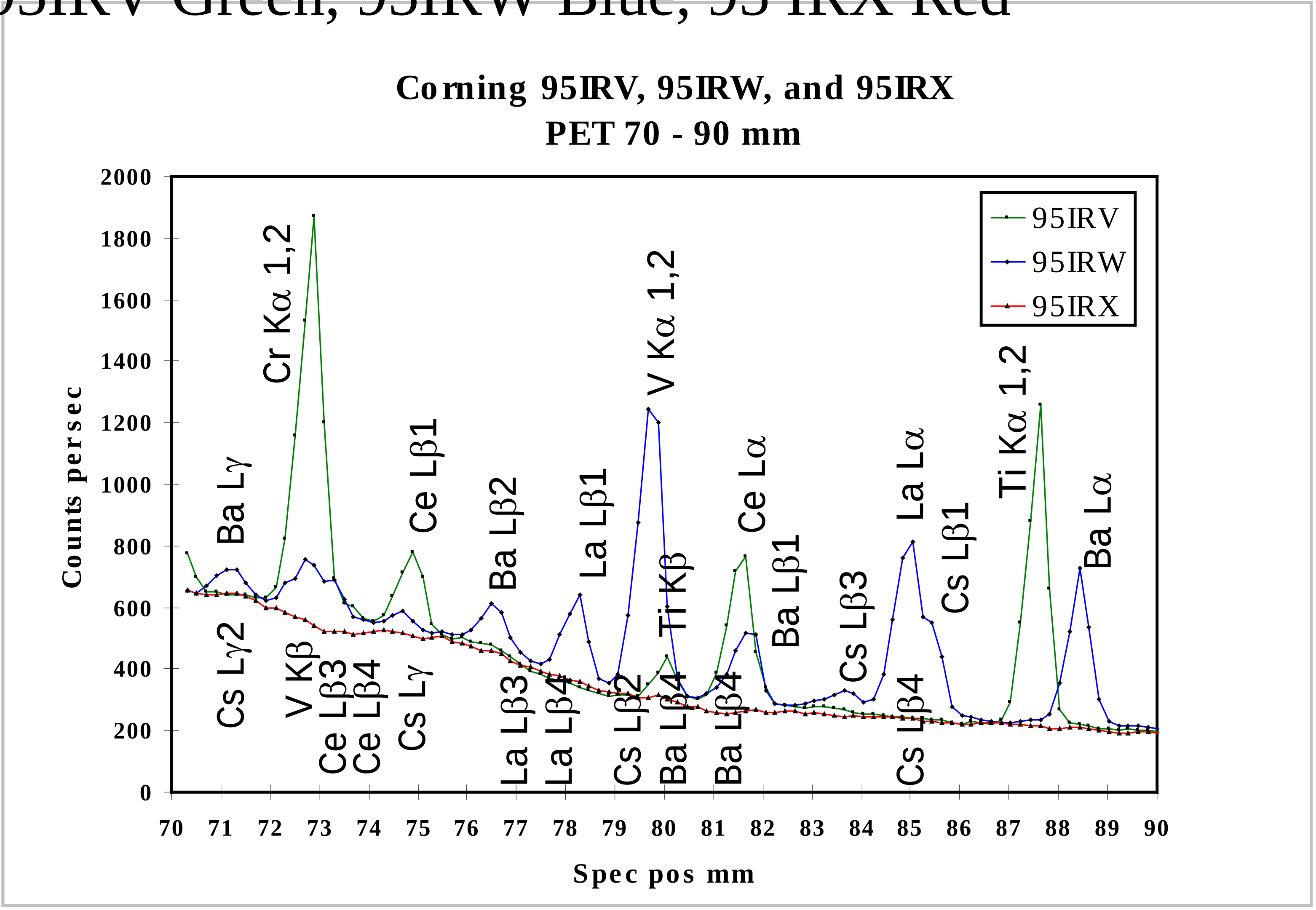
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red



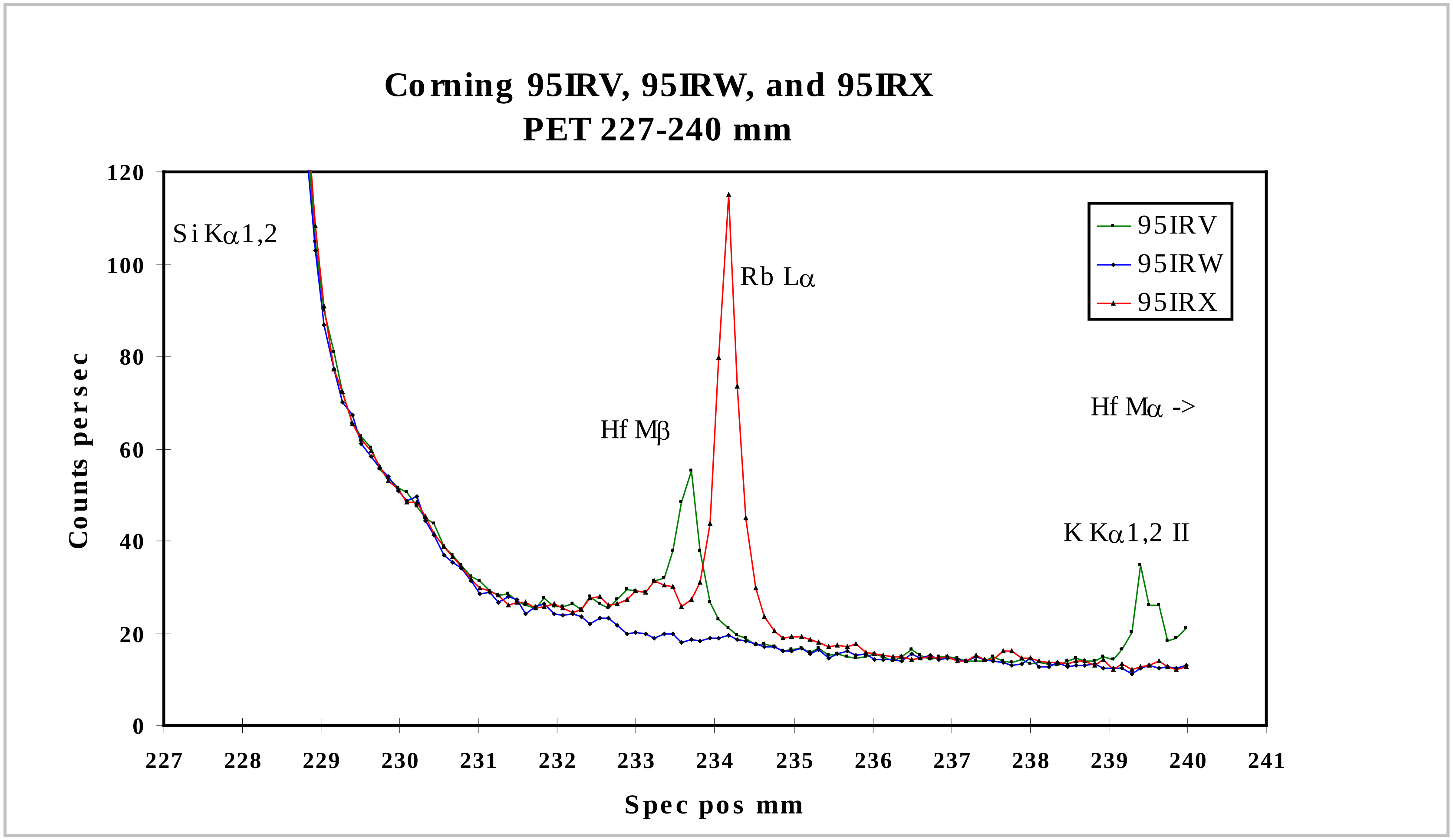
WDS Scan: LiF Crystal
95IRV Green, 95IRW Blue, 95IRX Red



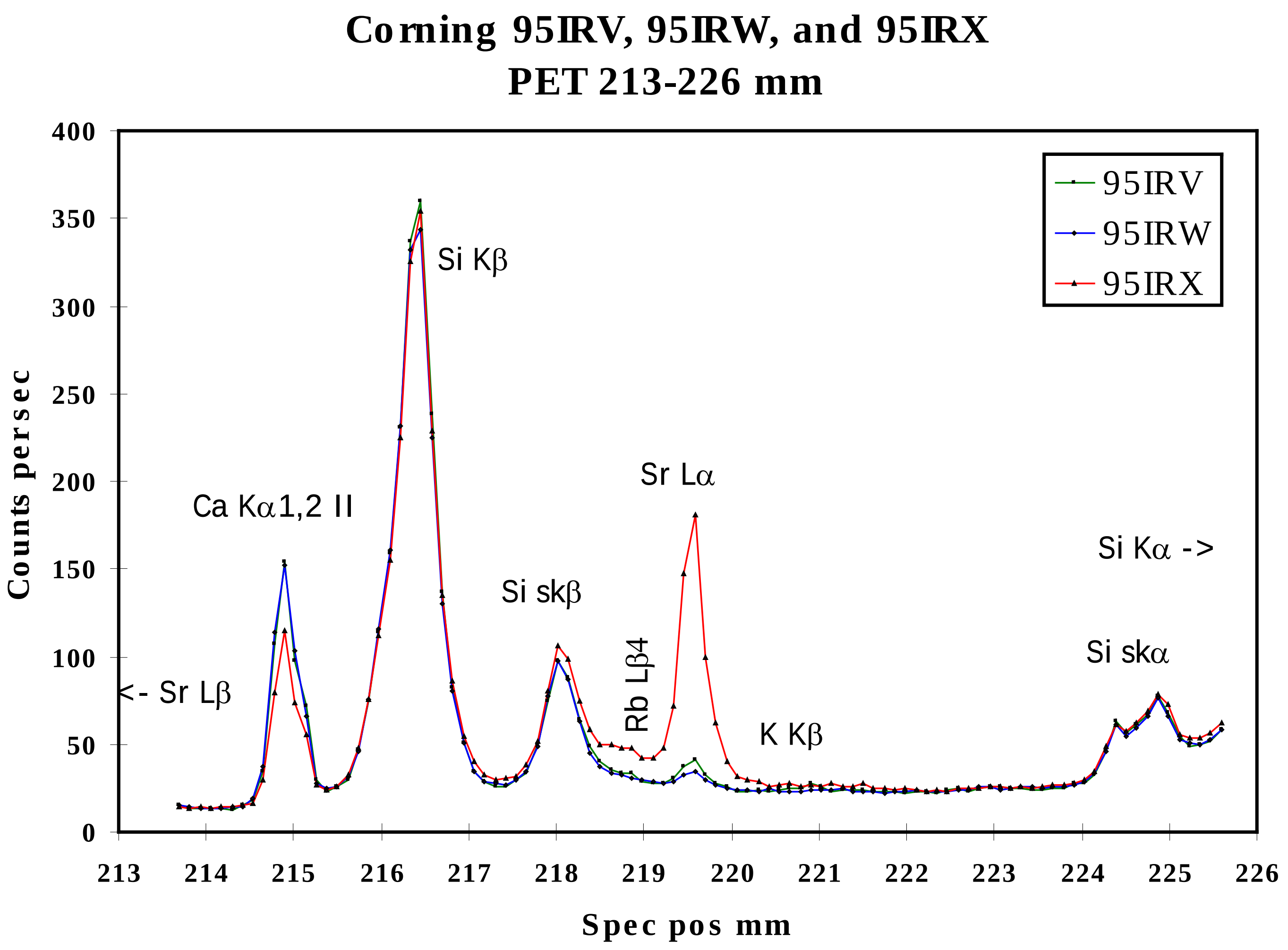
WDS Scan: PET Crystal
95IRV Green, 95IRW Blue, 95 IRX Red



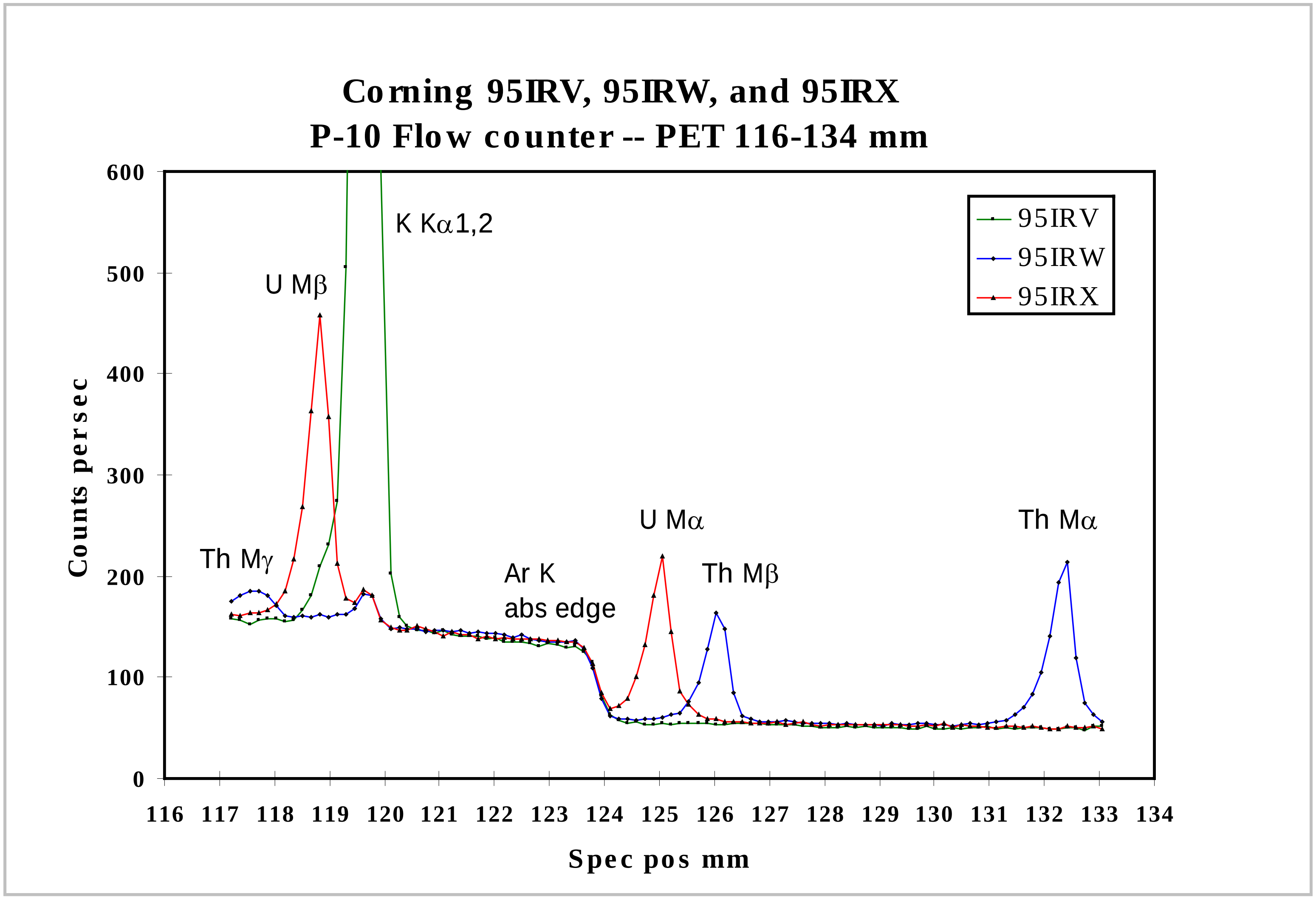
WDS Scan: PET Crystal
Si Kα limb and Hf Mβ Overlap on Rb Lα



WDS Scan: PET Crystal
Sr Lα Peaks, Rb Lβ family overlaps



WDS Scan: PET Crystal
Th Mβ on U Mα, K Kα Peaks & Ovlp U Mβ



Elevated and Uncertain MAC Values for K, L, M Lines: Proximity to Absorption Edge of Matrix Element

K-Lines and absorber for K, L, M edge

Li	Be											B Be,S,Y	C B,Ar,Tc	N C,Ca,Ag	O N,V,Sn	F O,Mn,I	Ne F,Co,La
Na Ne,Zn,Nd	Mg Na,Ge,Gd											Al Mg,Se,Er	Si Al,Kr,Hf	P Si,Sr,Re	S P,Zr,Au	Cl S,Mo,Pb	Ar Cl,Ru,Rn
K Ar,Pd,Ac	Ca K,Cd,U	Sc Ca,Sn	Ti Sc,Sb	V Sc,Xe	Cr Ti,Ba	Mn V,Ce	Fe Cr,Nd	Co Mn,Sm	Ni Fe,Gd	Cu Co,Dy	Zn Ni,Er	Ga Cu,Lu	Ge Zn,Ta	As Ga,Re	Se Ge,Ir	Br As,Au	Kr As,Hg
Rb Se,Pb	Sr Br,Po	Y Kr,Rn	Zr Rb,Ra	Nb Sr,Th	Mo Y,U	Tc Fr	Ru ~Ac										

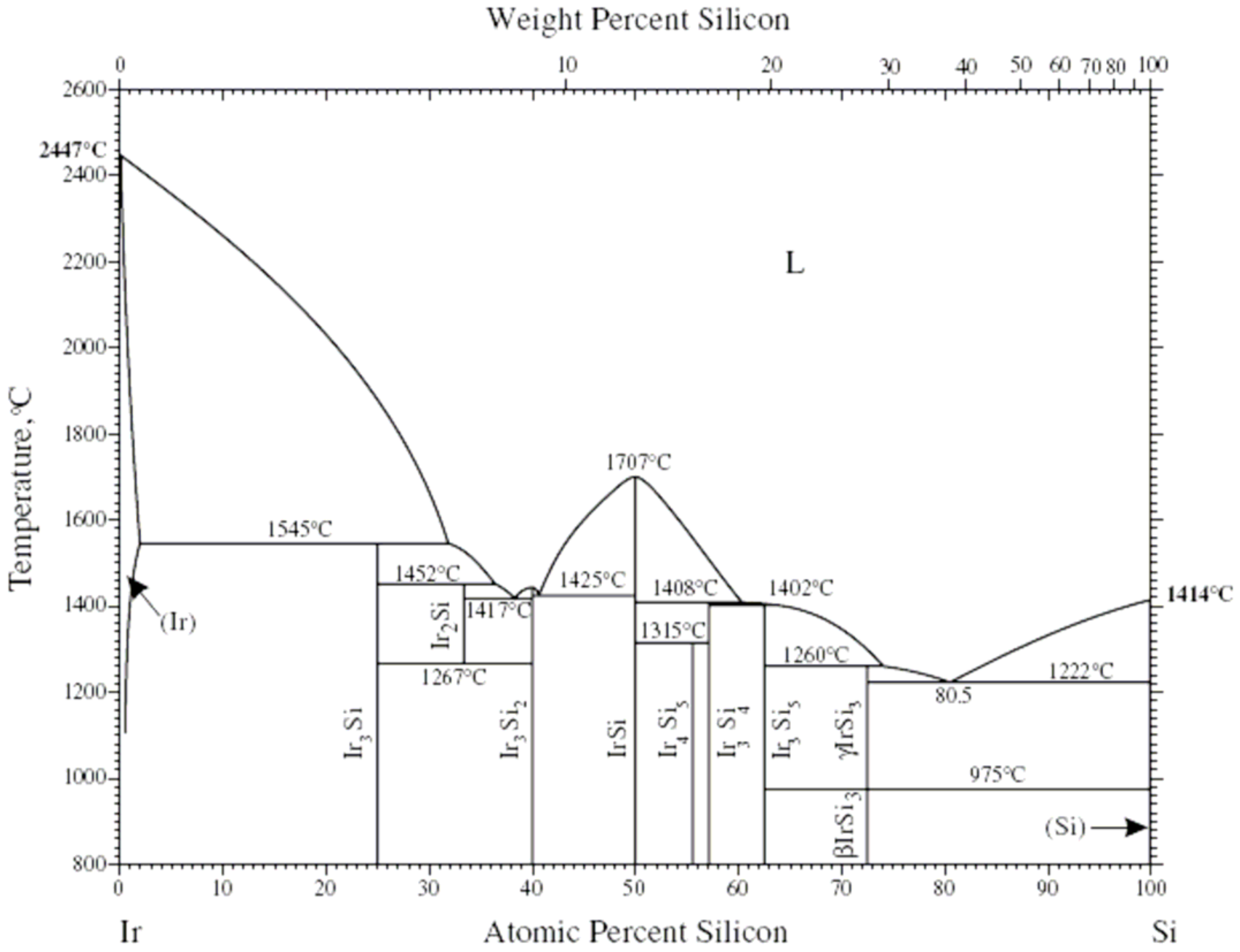
L-Lines and absorber for K, L, M edge

			Ti N,Sc,In	V N,Ti,Sn	Cr O,V,Sb	Mn O,Cr,I	Fe F,Mn,Xe	Co F,Fe,Ca	Ni F,Co,La	Cu Ne,Ni,Ce	Zn Ne,Cu,Nd	Ga Na,Zn,Pm	Ge Na,Ga,Eu	As Na,Ge,Tb	Se Mg,As,Dy	Br Mg,Se,Er	Kr Al,Br,Yb
Rb Al,Kr,Lu	Sr Si,Rb,Ta	Y P,Rb,W	Zr Si,Sr,Os	Nb P,Y,Ir	Mo P,Zr,Au	Tc P,Nb,Tl	Ru S,Mo,Pb	Rh S,Tc,Po	Pd Cl,Ru,At	Ag Cl,Ru,Rn	Cd Cl,Rh,Ra	In Ar,Pd,Ac	Sn Ar,Ag,Pa	Sb Ar,Cd,U	Te K,In,Np	I K,Sn,Np	Xe Ca,Sn
Cs Ca,Sb,	Ba Ca,Te	▨	Hf Co,Dy	Ta Co,Ho	W Ni,Er	Re Ni,Tm	Os Ni,Tm	Ir Cu,Yb	Pt Cu,Lu	Au Zn,Hf	Hg Zn,Ta	Tl Zn,W	Pb Ga,Re	Bi Ga,Re	Po Ge,Os	At Ge,Ir	Rn Ge,Pt
Fr As,Au	Ra As,Hg	▨															
		La Sc,I	Ce Sc,Xe	Pr Ti,Cs	Nd Ti,Cs	Pm Ti,Ba	Sm V,La	Eu V,Ce	Gd Cr,Pr	Tb Cr,Nd	Dy Cr,Pm	Ho Mn,Sm	Er Mn,Sm	Tm Fe,Eu	Yb Fe,Gd	Lu Fe,Tb	
		Ac As,Hg	Th Se,Tl	Pa Se,Pb	U Br,Bi	Np Br,Po	Pu Br,At										

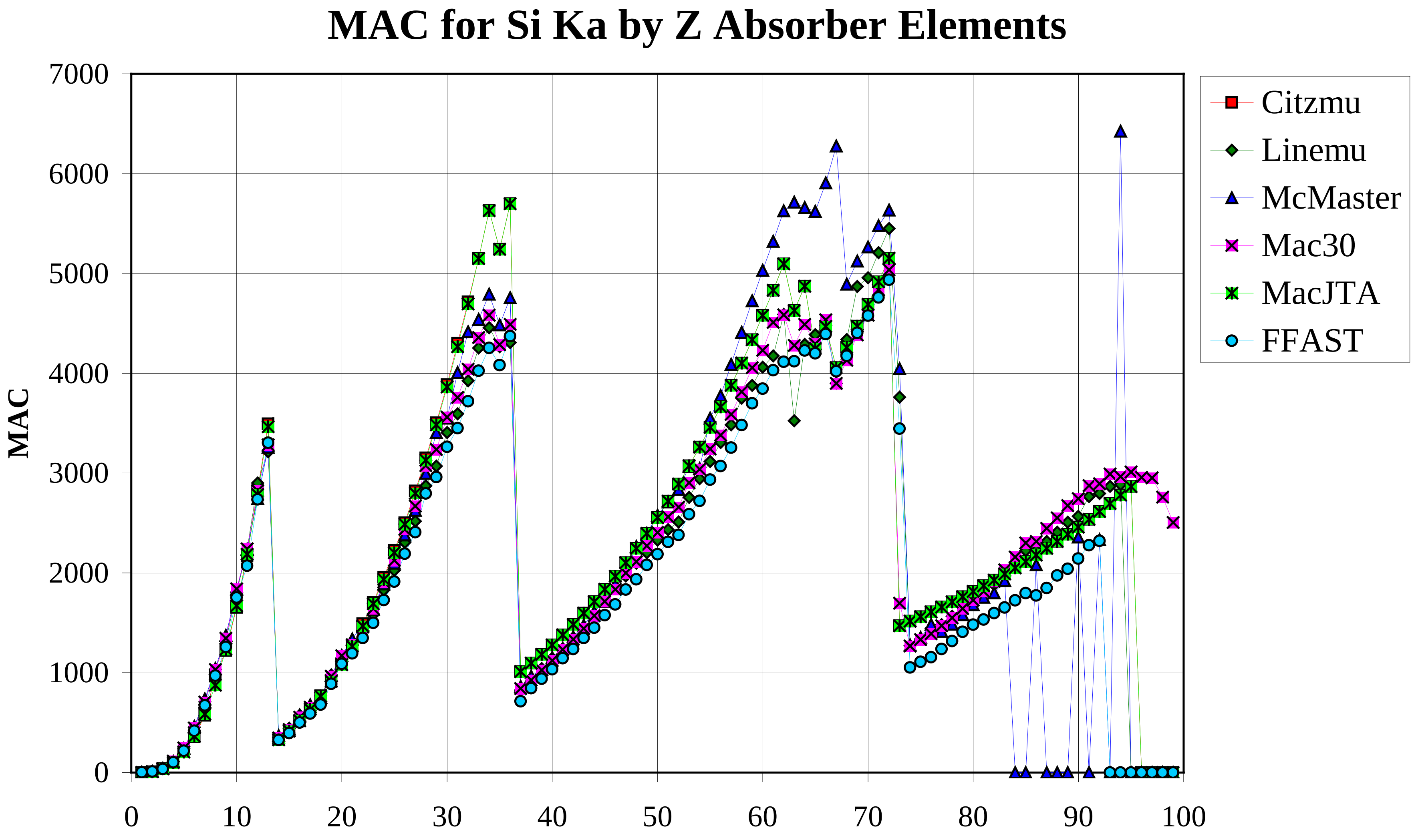
M-Lines and absorber for K, L, M edge

		▨	Hf Al,Br,Lu	Ta Al,Kr,Lu	W Al,Kr,Hf	Re Si,Rb,Ta	Os Si,Rb,W	Ir Si,Sr,Re	Pt Si,Sr,Os	Au Si,Y,Ir	Hg P,Y,Pt	Tl P,Zr,Pt	Pb P,Zr,Au	Bi P,Nb,Hg	Po S,Nb,Tl	At S,Mo,Pb	Rn S,Mo,Pb
Fr S,Tc,Po	Ra Cl,Tc,At	▨															
		La F,Co,Ba	Ce Ne,Ni,La	Pr Ne,Ni,Ce	Nd Ne,Cu,Pr	Pm Ne,Ni,Nd	Sm Na,Zn,Pm	Eu Na,Ga,Sm	Gd Na,Ga,Eu	Tb Na,Ge,Gd	Dy Na,Ge,Tb	Ho Mg,As,Dy	Er Mg,As,Ho	Tm Mg,Se,Er	Yb Mg,Se,Tm	Lu Al,Br,Yb	
		Ac Cl,Ru,Rn	Th Cl,Ru,Rn	Pa Cl,Rh,Fr	U Cl,Rh,Ra												

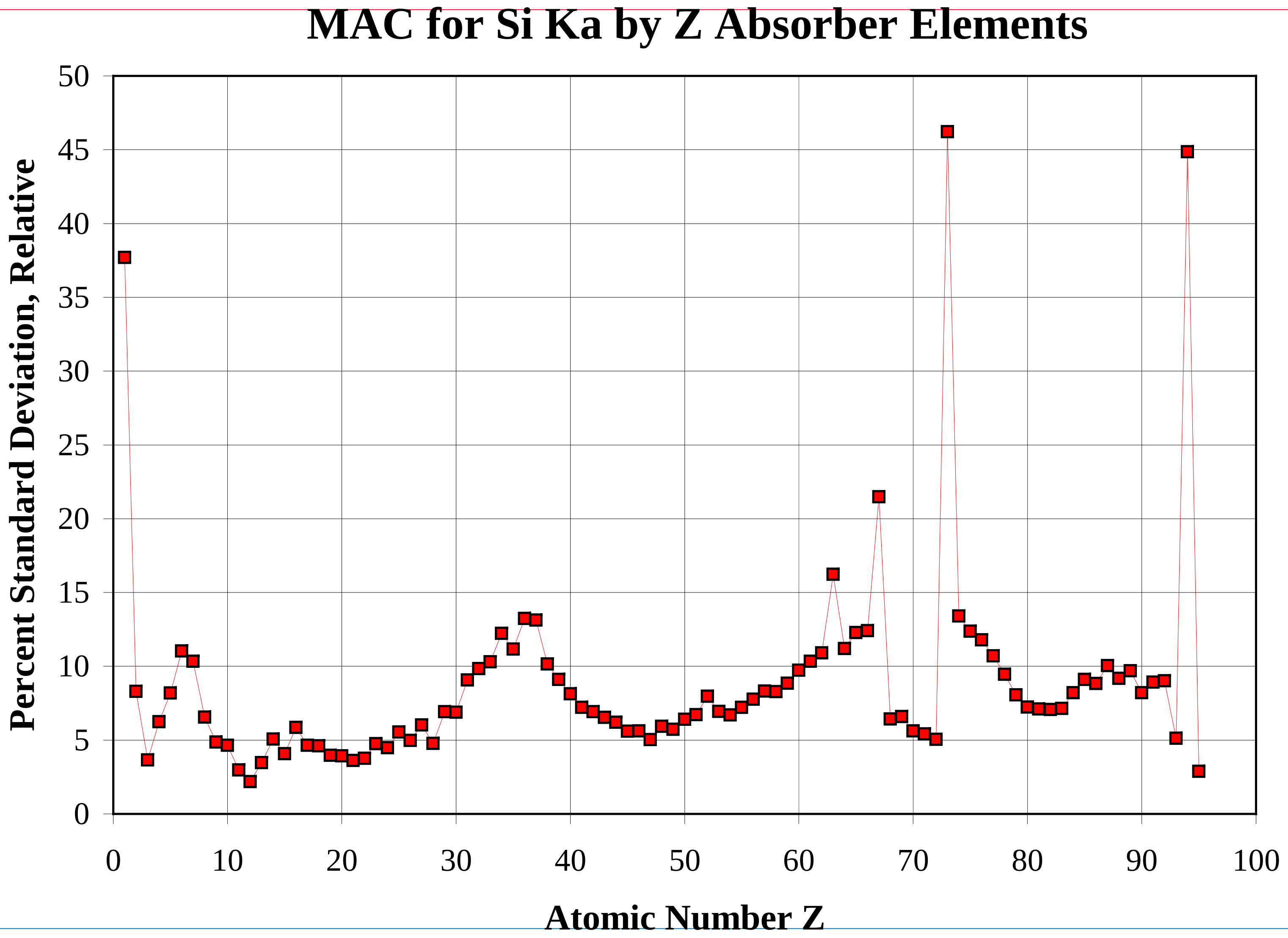
Example problem:
Identification of Ir_xSi_y unknown



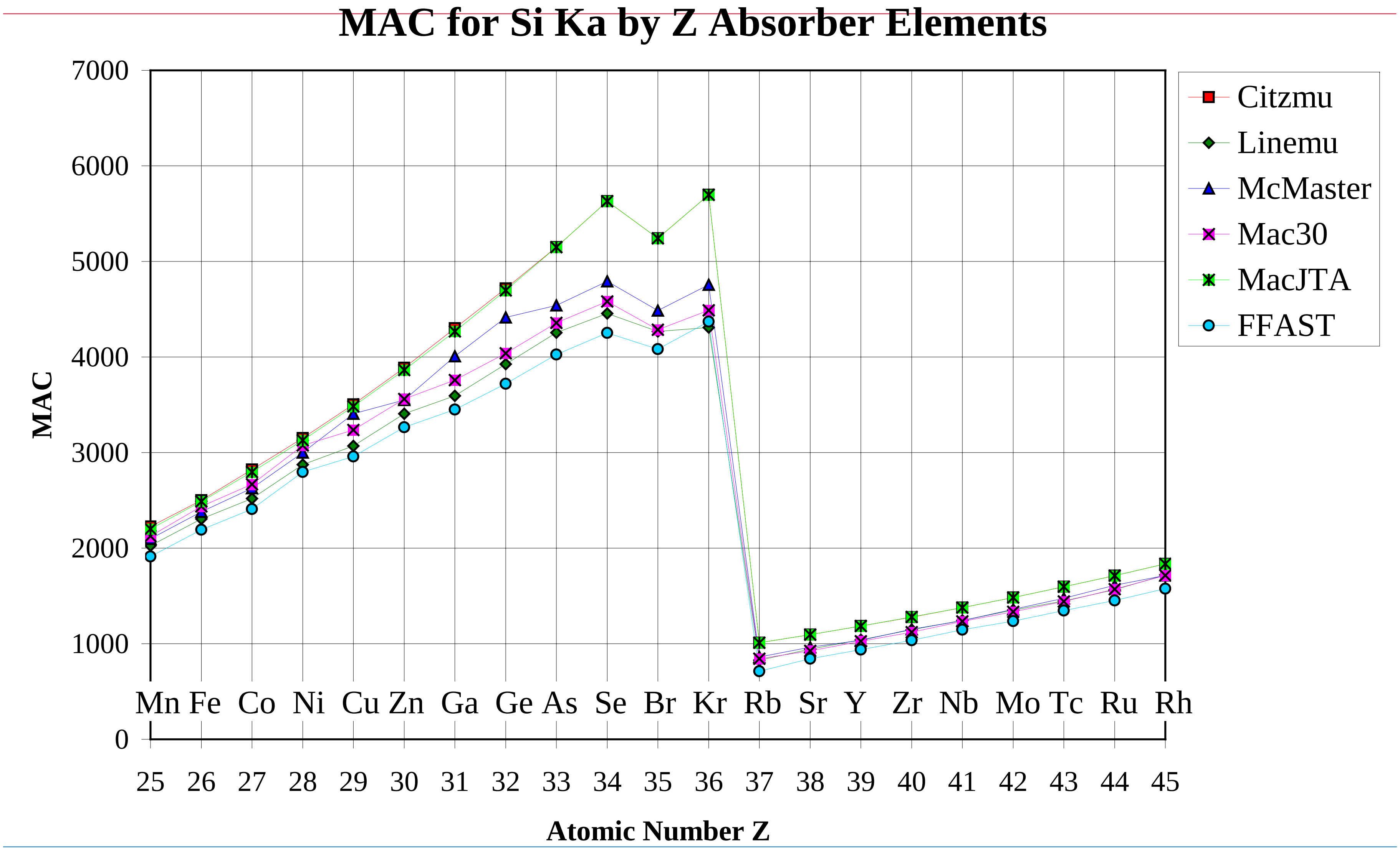
Mass Absorption Coefficients for Si Kα
By Absorber Z, All MAC Data Sets Compared



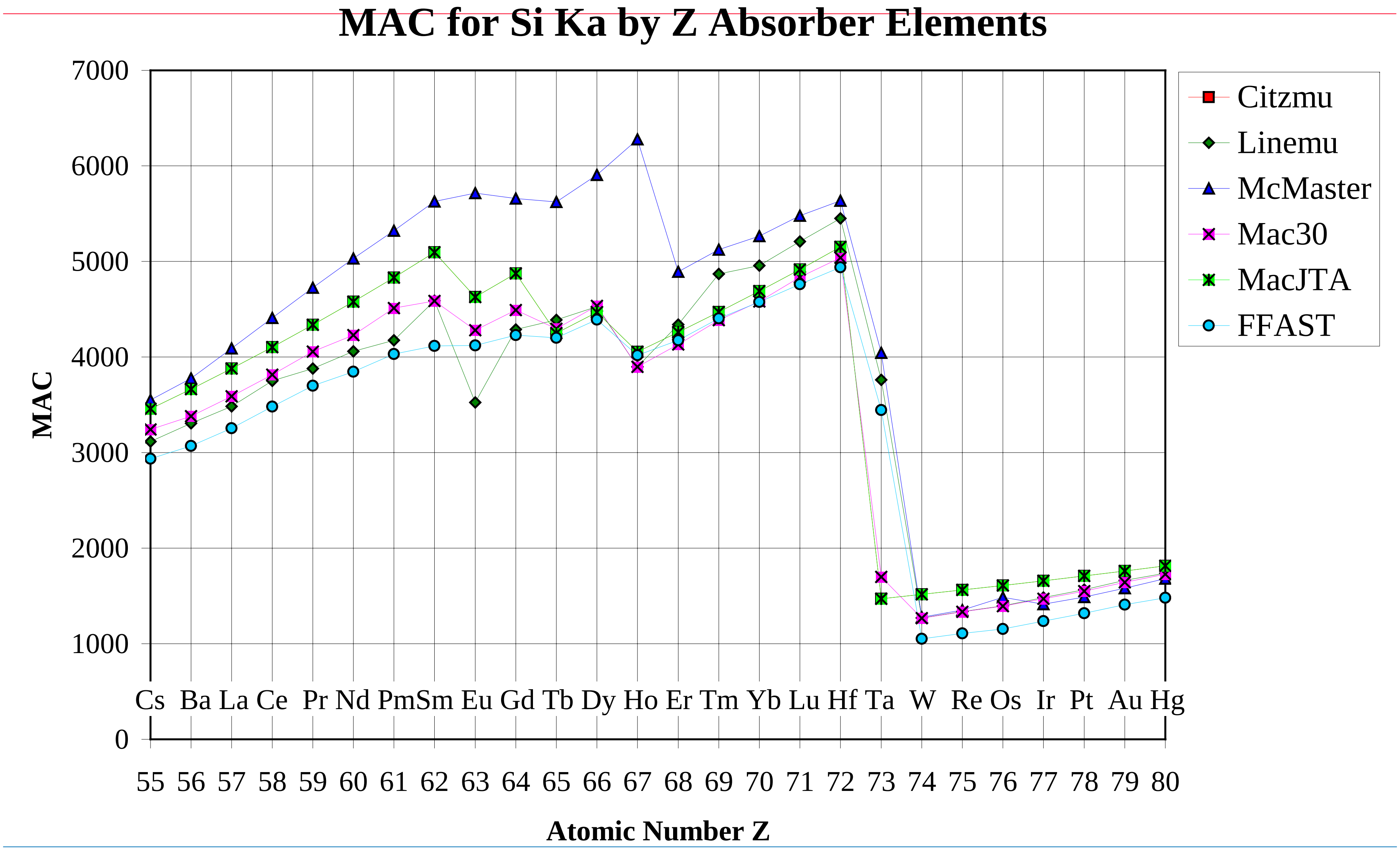
Comparison of Si Kα MACS
Relative percent σ



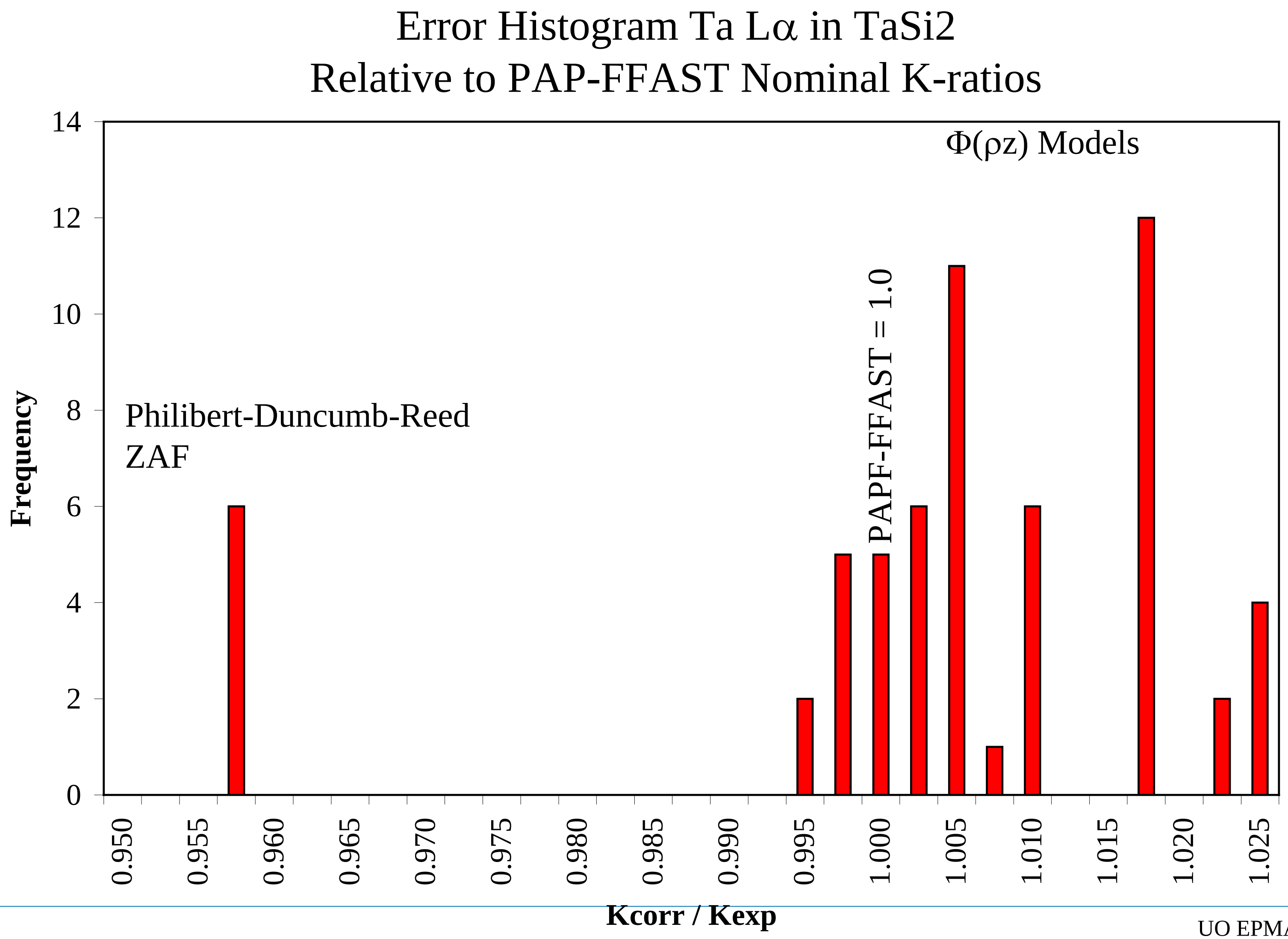
Silicon Kα MAC at L-edge of Absorber



Silicon Kα MAC at M-edge of Absorber



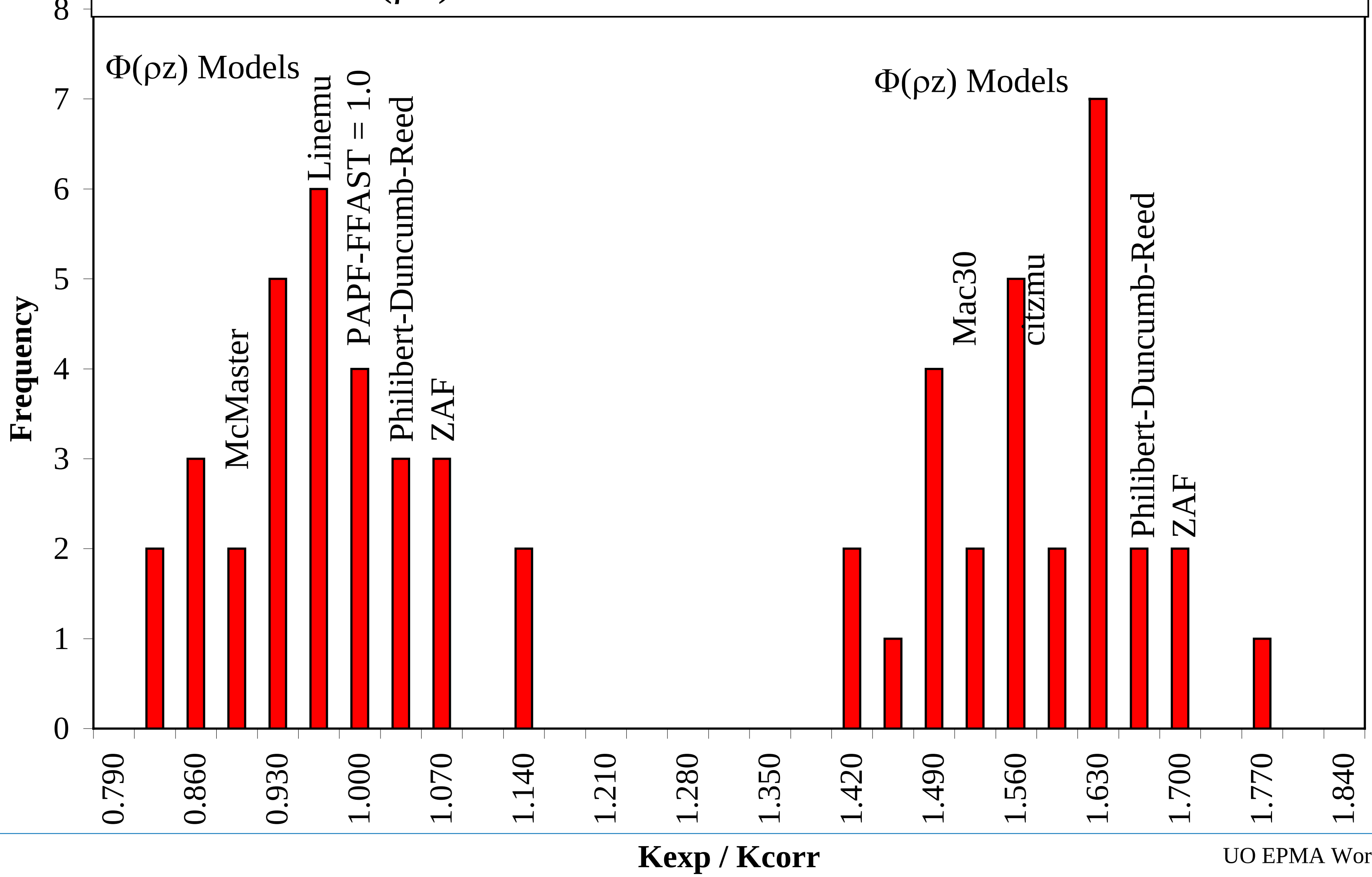
Error Analysis Ta Lα in $TaSi_2$
All algorithms and MAC sets (PAPF-FFAST = 1.0)



Error Analysis Si Kα in $TaSi_2$
All algorithms and MAC sets (PAPF-FFAST=1.0)

Dramatic demonstration of choice of MAC data set:

Variation of Φ(ρz) models and 4 mac data sets



Calculated Compositions of TaSi2 Relative to PAP—FFAST Nominal K-ratios

PAPF with MAC	Wt% Si	Wt% Ta	Total
CM	14.74	73.74	88.48
M30	15.64	74.02	89.66
(FFAST)	23.69	76.31	100
LM	24.87	76.52	101.39
MM	25.96	76.85	102.81

Conclusions

- Geological applications require multicomponent accuracy evaluation
- Use of K_{meas}/K_{calc} plot used for data analysis, WDS and EDS
- CMASTF standards provide instrument calibration data set
- Experimental K-ratio data set available for development and testing
- Identification of inconsistent compositions
- Accuracy of analysis in CMASTF system better than 2%, precision limited
- SDD quantitative analysis data highly competitive with WDS
- Excellent prospects for high speed SDD quantitative analysis in particle, mapping applications