

Calculating the uncertainty due to matrix corrections in electron probe microanalysis

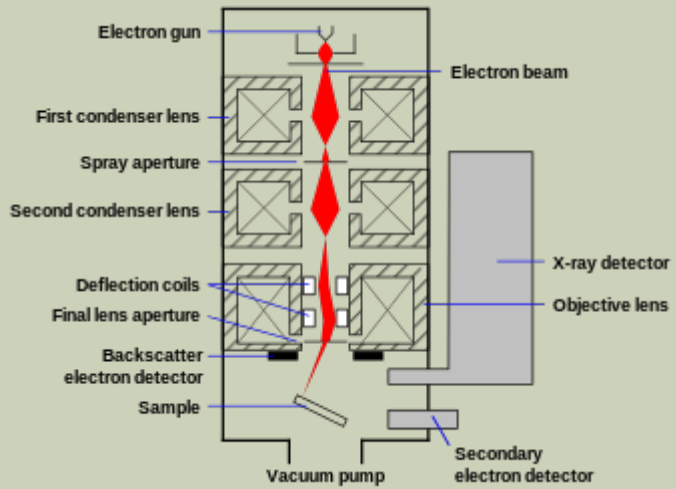
Nicholas W. M. Ritchie & Dale E. Newbury
National Institute of Standards and Technology
Gaithersburg, MD 20899
nicholas.ritchie@nist.gov

We can calculate uncertainties,

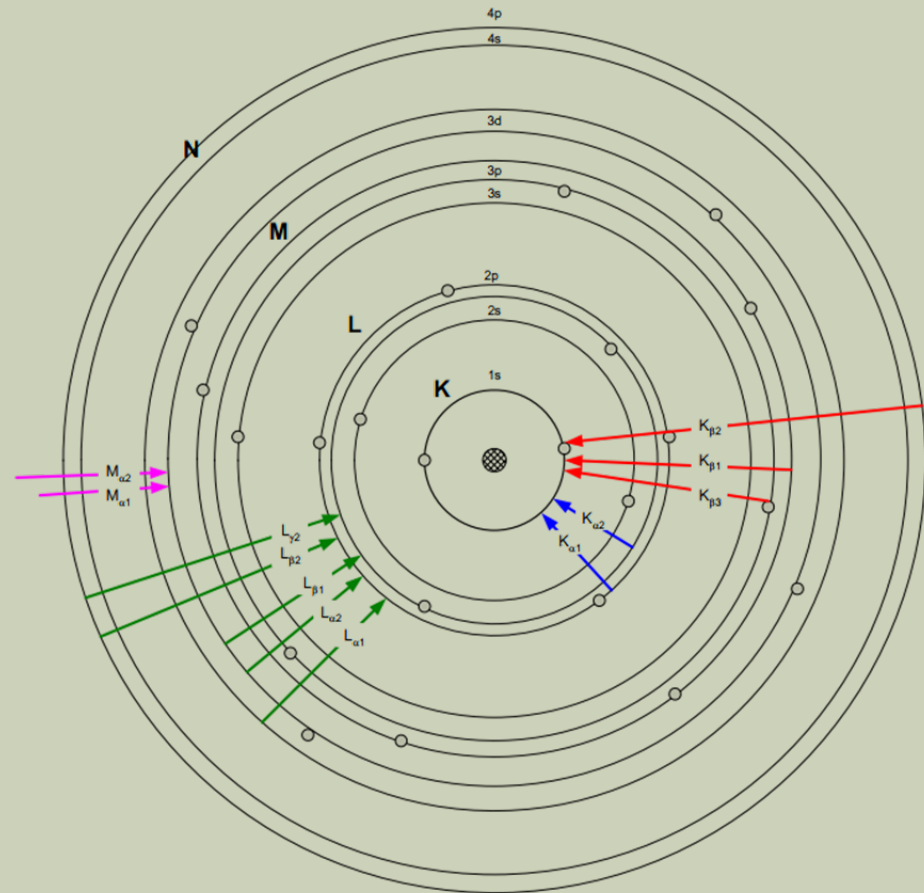
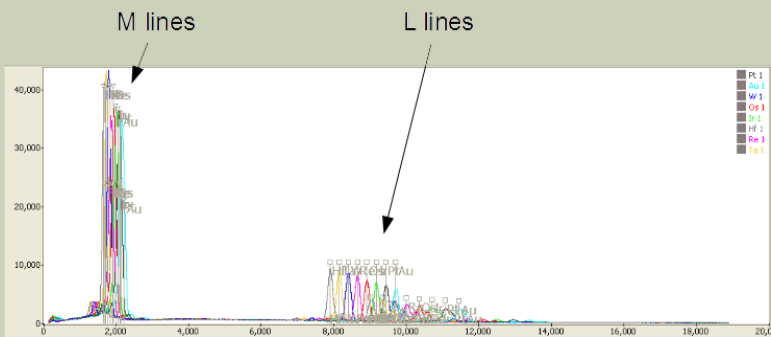
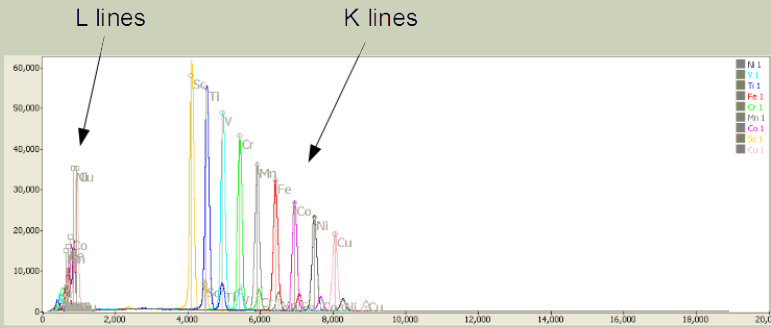
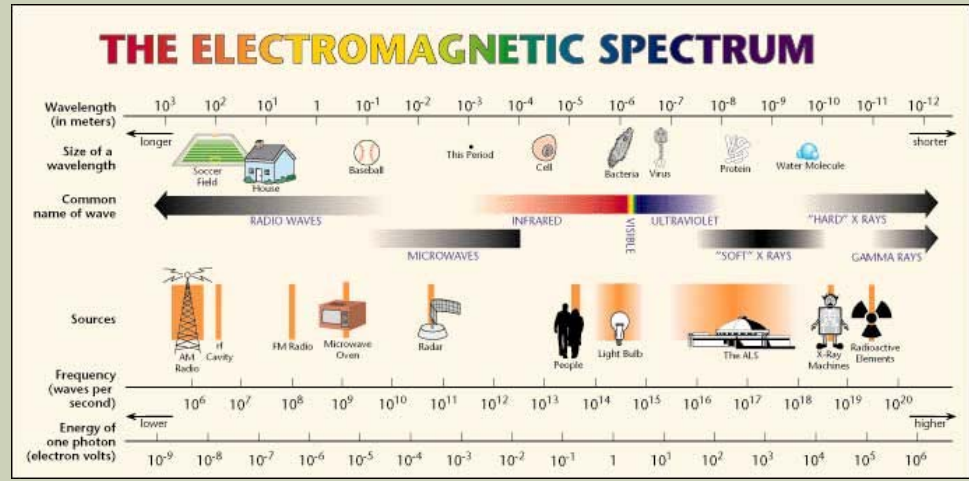
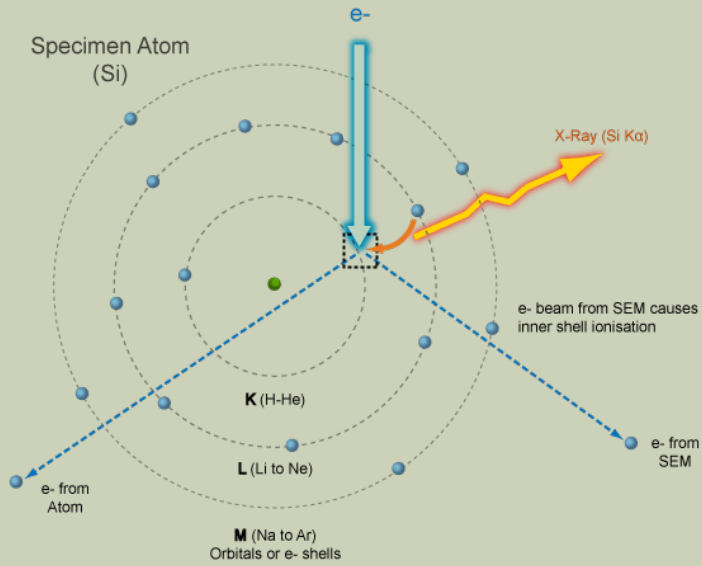
so what?

That and \$6 will get you an beer at Dogfish Head...

SEM



Characteristic X-Ray Production



k-ratios



0.1076



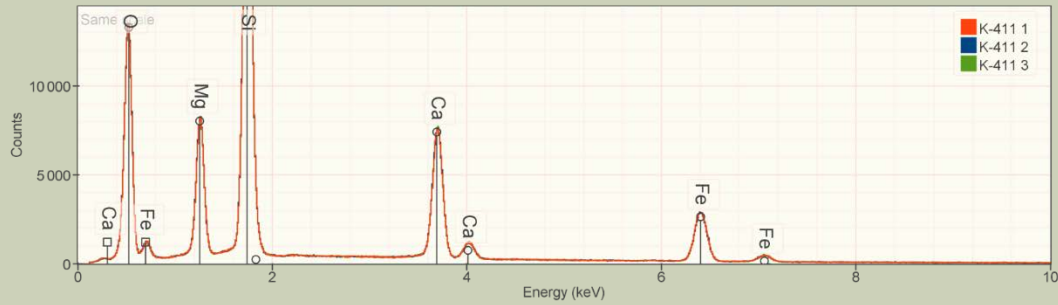
0.1792



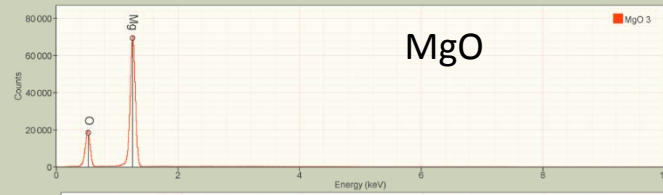
0.2947



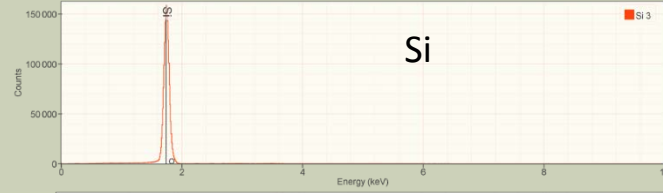
0.0921



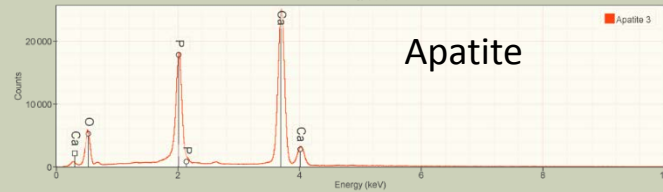
=



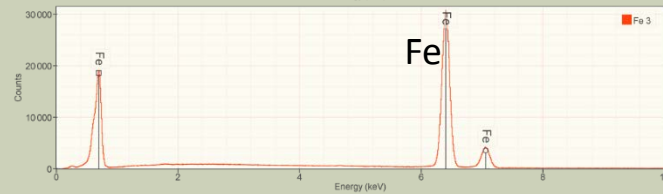
+



+

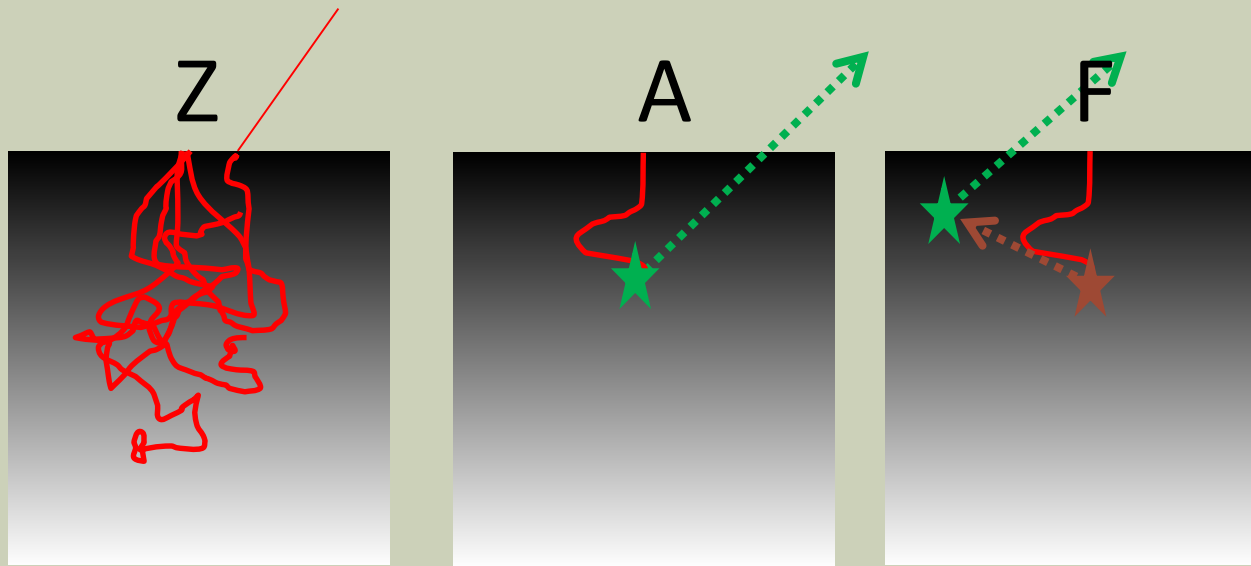


+



+

Matrix correction



Stopping / backscatter

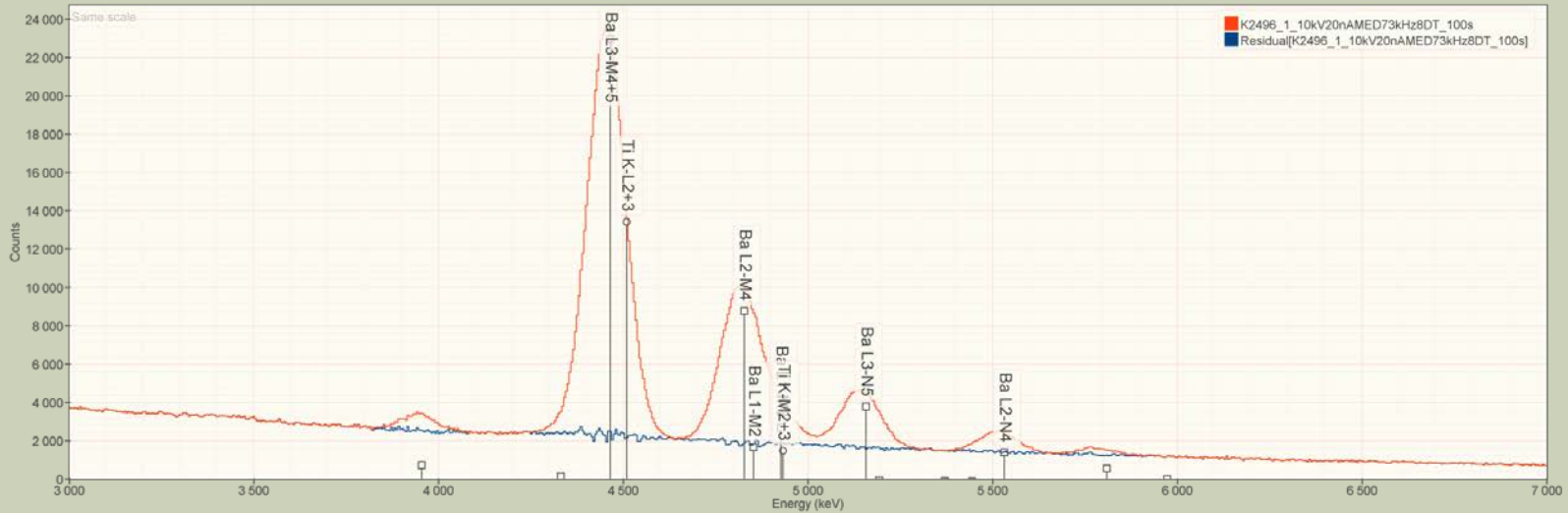
X-ray absorption

Secondary fluorescence

$$k_A = \frac{\{Z \cdot A \cdot F\}_{Unk,A}}{\{Z \cdot A \cdot F\}_{Std,A}} C_A$$

IUPAC	Seigbahn	Standard	Energy	ZAF	Z	A	F	k-ratio
O K-L3	O Kα1	MgO	0.5249	0.5777	1.0240	0.5650	0.9985	0.616525
Mg K-L3	Mg Kα1	MgO	1.2536	0.7593	1.0240	0.7365	1.0069	0.111390
Si K-L3	Si Kα1	Pure Si	1.7397	0.7039	0.9817	0.7157	1.0018	0.178651
Si K-M3	Si Kβ1	Pure Si	1.8290	0.7302	0.9817	0.7424	1.0019	0.185337
Ca K-L3	Ca Kα1	CaF2	3.6917	0.9169	0.9637	0.9460	1.0057	0.197481
Ca K-M3	Ca Kβ1	CaF2	4.0127	0.9275	0.9637	0.9565	1.0063	0.199775
Fe K-L3	Fe Kα1	Pure Fe	6.4039	0.8348	0.8422	0.9912	1.0000	0.093572
Fe K-M3	Fe Kβ1	Pure Fe	7.0580	0.8367	0.8422	0.9934	1.0000	0.093780
Fe L3-M5	Fe Lα1	Pure Fe	0.7045	0.2557	0.8574	0.2980	1.0009	0.028659

Minor element quantification with major element overlap



K2496 glass

- $E_0 = 10$ keV
- 1000 nA-s
- 0.1-10keV integral = 12,175,000 counts
- Standards:
 - SiO_2
 - BaSi_2O_5 (Sanbornite) for Ba
 - Ti

Raw total (mass fraction)	O, mass conc (stoichiometry)	Si, mass conc	Ti, mass conc	Ba, mass conc
0.9836±0.0011	0.3195±0.0004	0.2251±0.0004	0.0180±0.0003	0.4374±0.0012
0.9824±0.0011	0.3202±0.0004	0.2260±0.0004	0.0178±0.0003	0.4360±0.0012
0.9828±0.0011	0.3197±0.0004	0.2259±0.0004	0.0170±0.0003	0.4374±0.0012
0.9828±0.0011	0.3196±0.0004	0.2255±0.0004	0.0176±0.0003	0.4374±0.0012
0.9814±0.0011	0.3197±0.0004	0.2256±0.0004	0.0175±0.0003	0.4372±0.0012
0.9811±0.0011	0.3199±0.0004	0.2257±0.0004	0.0178±0.0003	0.4366±0.0012
0.9819±0.0011	0.3194±0.0004	0.2254±0.0004	0.0173±0.0003	0.4379±0.0012
average	0.3197	0.2256	0.0176	0.4371
s		0.00028	0.00031	0.00058
s (relative)		0.13%	1.8%	0.13%
synthesized		0.2291	0.0180	0.4299
Relative error		-1.5%	-2.4%	1.7%
Error in k (counts)		0.0001 (0.044% relative)	0.0003 (1.7% relative)	0.0007 (0.16% relative)
Error in Z (estimate)		1.1E-5 (0.0049% rel)	2.5E-7 (0.0014% relative)	2.1E-7 (4.8E-5% relative)
Error in A (estimate)		0.0015 (0.66% relative)	3.9E-6 (0.022% relative)	1.9E-5 (0.0044% relative)

Same scale

K2115_1_10KV20nAMED_119kHz10DT_100s
Residual(K2115_1_10KV20nAMED_119kHz10DT_100s)

K2115

$E_0 = 10 \text{ keV}$

2,000 nA-s (20 nA, 100 s)

0.1 – 10 keV integral = 15,297,000 counts

Fitting with SiO_2 , PbSe and Bi

$\text{PbM}\alpha = 2.346 \text{ keV}$

$\text{BiM}\alpha = 2.422$

$\Delta = 76 \text{ eV}$

$\text{PbM}\beta = 2.443$

$\Delta = 21 \text{ eV}$

$\text{BiM}\beta = 2.526$

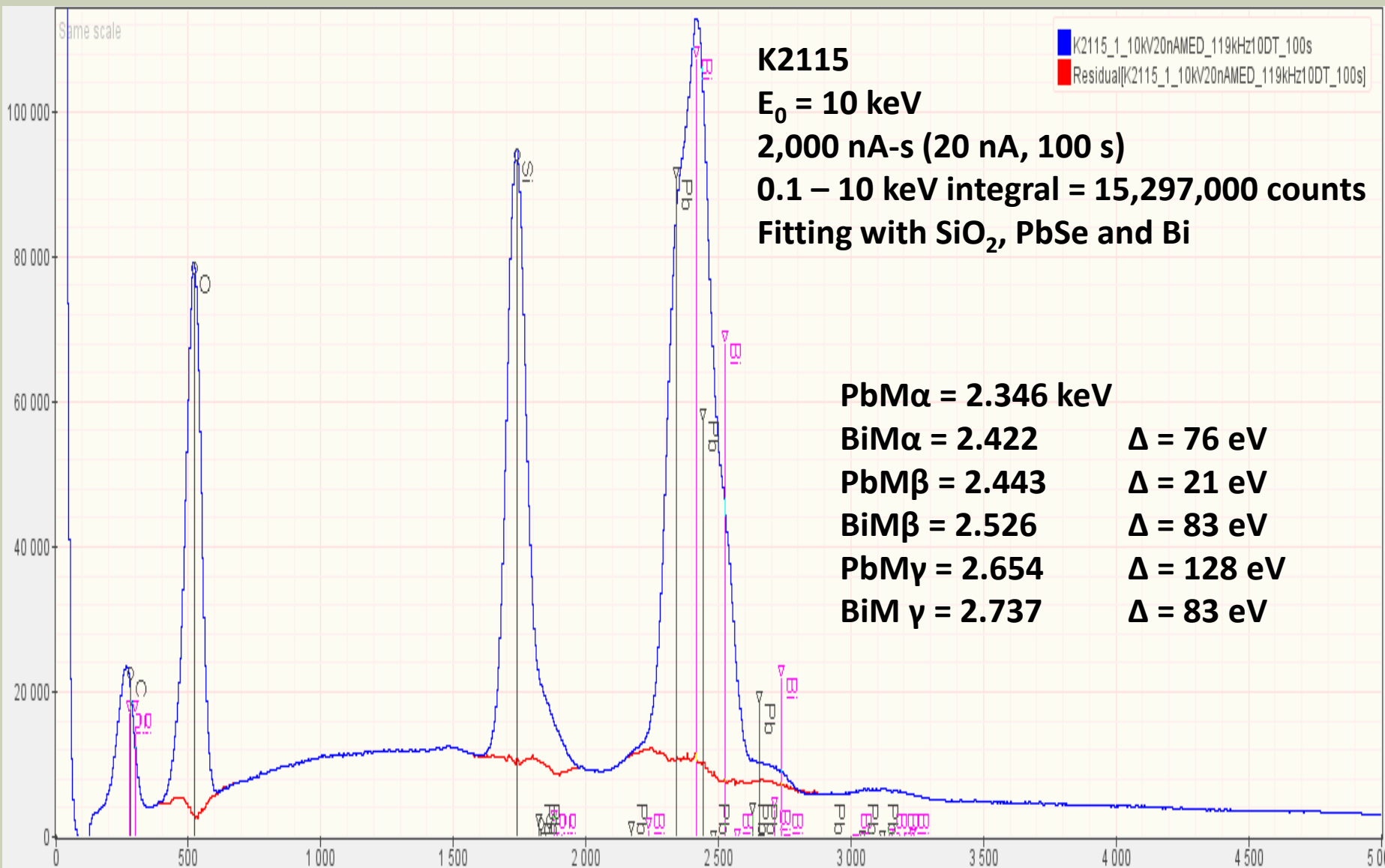
$\Delta = 83 \text{ eV}$

$\text{PbM}\gamma = 2.654$

$\Delta = 128 \text{ eV}$

$\text{BiM}\gamma = 2.737$

$\Delta = 83 \text{ eV}$



Unknown: NIST Glass K2115

Raw total	O, atom conc	Si, atom conc	Pb, atom conc	Bi, atom conc
0.9979±0.0013	0.6159±0.0009	0.1828±0.0004	0.1035±0.0003	0.0979±0.0003
0.9977±0.0013	0.6159±0.0009	0.1828±0.0004	0.1032±0.0003	0.0981±0.0003
0.9960±0.0013	0.6159±0.0009	0.1829±0.0004	0.1033±0.0003	0.0979±0.0003
0.9965±0.0013	0.6160±0.0009	0.1830±0.0004	0.1029±0.0003	0.0981±0.0003
0.9963±0.0013	0.6159±0.0009	0.1829±0.0004	0.1032±0.0003	0.0979±0.0003
0.9969±0.0013	0.6158±0.0009	0.1826±0.0004	0.1036±0.0003	0.0981±0.0003
0.9975±0.0013	0.6158±0.0009	0.1825±0.0004	0.1036±0.0003	0.0981±0.0003

Measurement

- $E_0 = 10 \text{ keV}$
- Standards:
 - SiO_2
 - PbSe
 - Bi

Silicon

- Average = 0.1828
- $\sigma = 0.00016$
- $\sigma_{\text{rel}} = 0.090\%$
- Synthesis = 0.1863
- Rel error = -1.9%

Bismuth

- Average = 0.0980
- $\sigma = 0.00009$
- $\sigma_{\text{rel}} = 0.10\%$
- Synthesis = 0.0961
- Rel error = 2.0%

Lead

- Average = 0.1033
- $\sigma = 0.00024$
- $\sigma_{\text{rel}} = 0.23\%$
- Synthesis = 0.1003
- Rel error = 3.0%

The Big Question

Given that EDS with an SDD can produce such amazingly good results *when applied correctly**, how do we encourage people to do the right thing?

* Standards-based analysis with carefully prepared standards and unknowns under well-controlled and well-selected conditions.

My Answer:

Make doing the right thing as easy as possible.

What did we gloss over?

- ✓ Selection of beam energy
- ✓ Selection of standards
- ✓ Necessity for references
- ✓ Selection of transition (K vs. L, L vs. M)
- ✓ Selection of probe dose (for the unknown, the standards and the references)

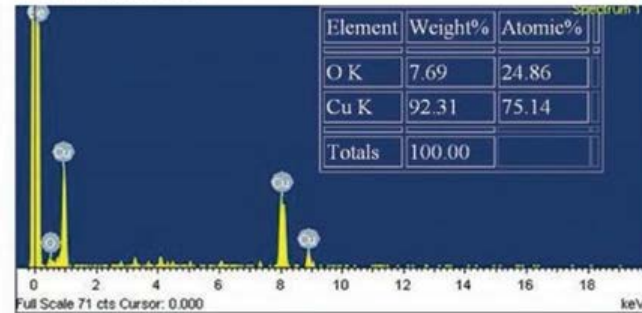
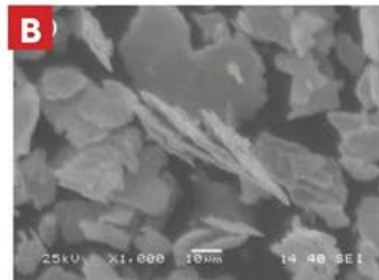
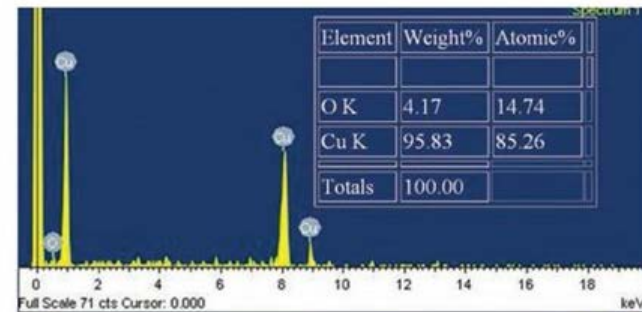
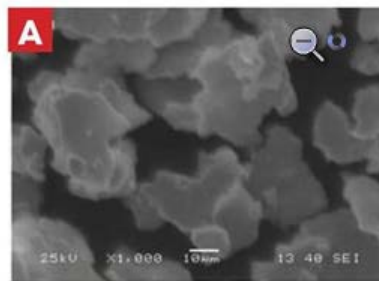
No wonder people are intimidated by the prospect of performing a standards-based EDS measurement.

What is wrong with this picture?

Development of copper-based metal matrix composites: An analysis by SEM, EDS and XRD

Syed Nasimul Alam and Harshpreet Singh

Department of Metallurgical and Materials Engineering, National Institute of Technology Raichur, Raichur, Chik. State



What is wrong with this picture?

Really? Exactly 100%

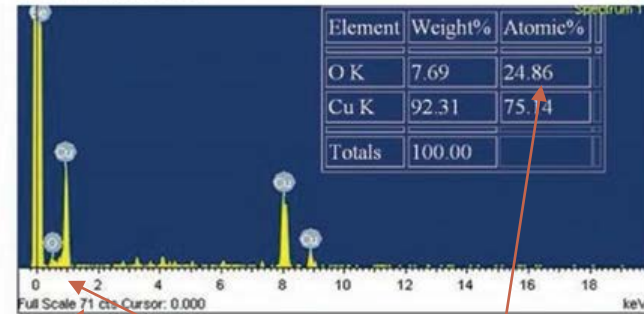
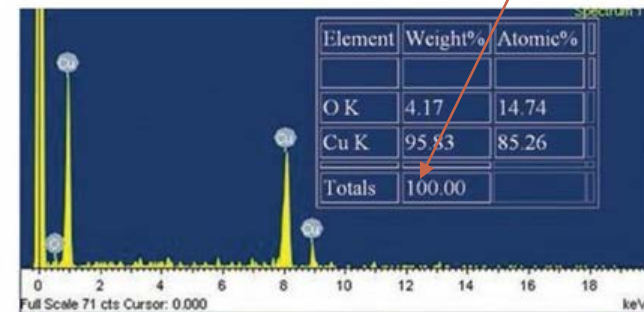
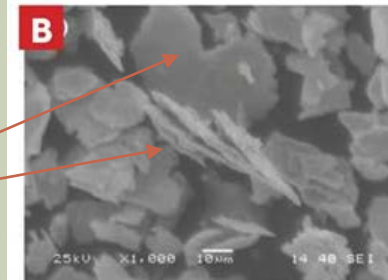
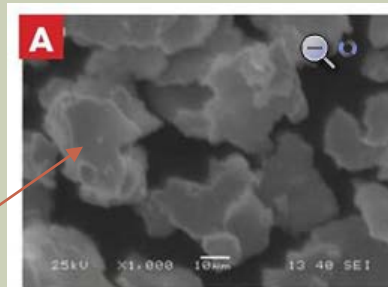
What about this peak

Development of copper-based metal matrix composites: An analysis by SEM, EDS and XRD

Syed Nasimul Alam and Harshpreet Singh
Department of Production and Materials Engineering, National Institute of Technology Raichur, Raichur, Chik. State

Doesn't look flat, polished, bulk to me...

Doesn't look homogeneous



71 counts full scale!

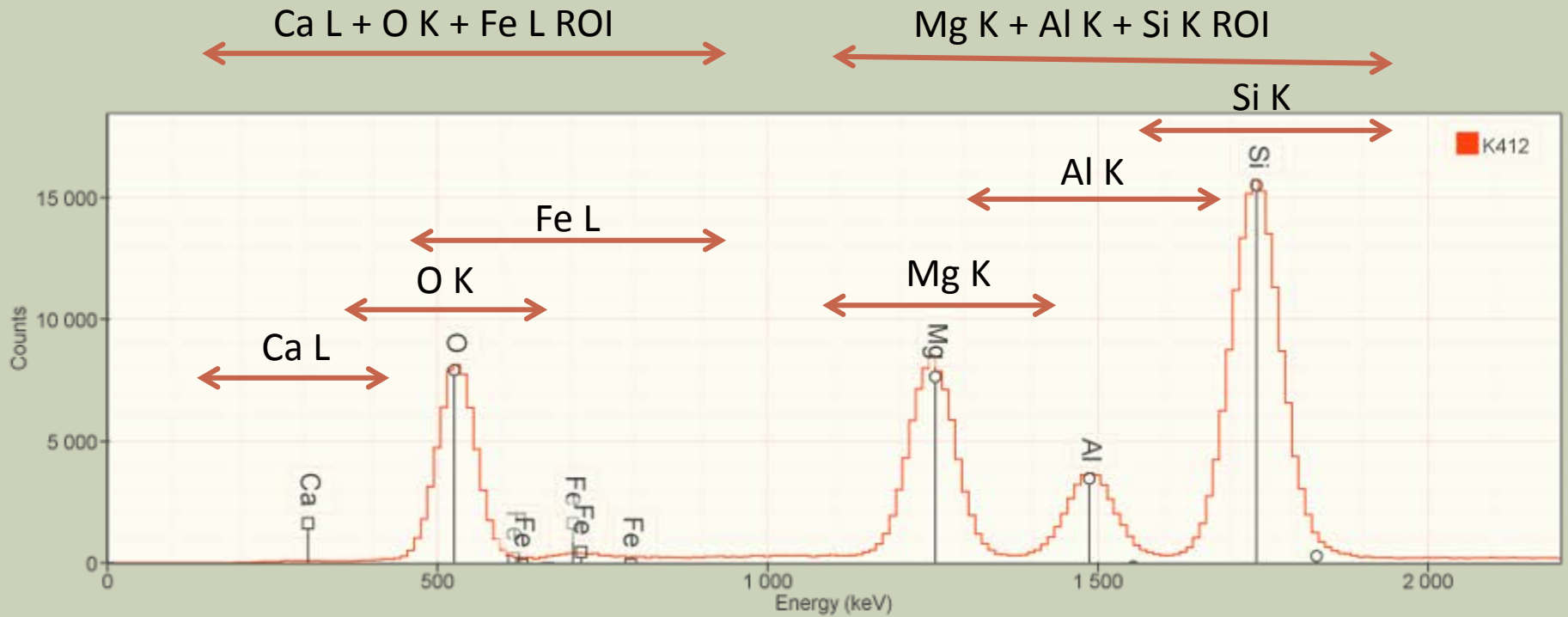
10 counts for how many digits of precision?

Crisis in microanalysis

- EPMA is only one of many techniques for which the typical technician is responsible
- Many labs fail to provide adequate training
- Instrument vendors are not motivated to ensure that their instruments produce reliable results in the field
- EPMA is conceptually simple but the devil is in the details

The literature is awash with poor quality EPMA measurements

K412



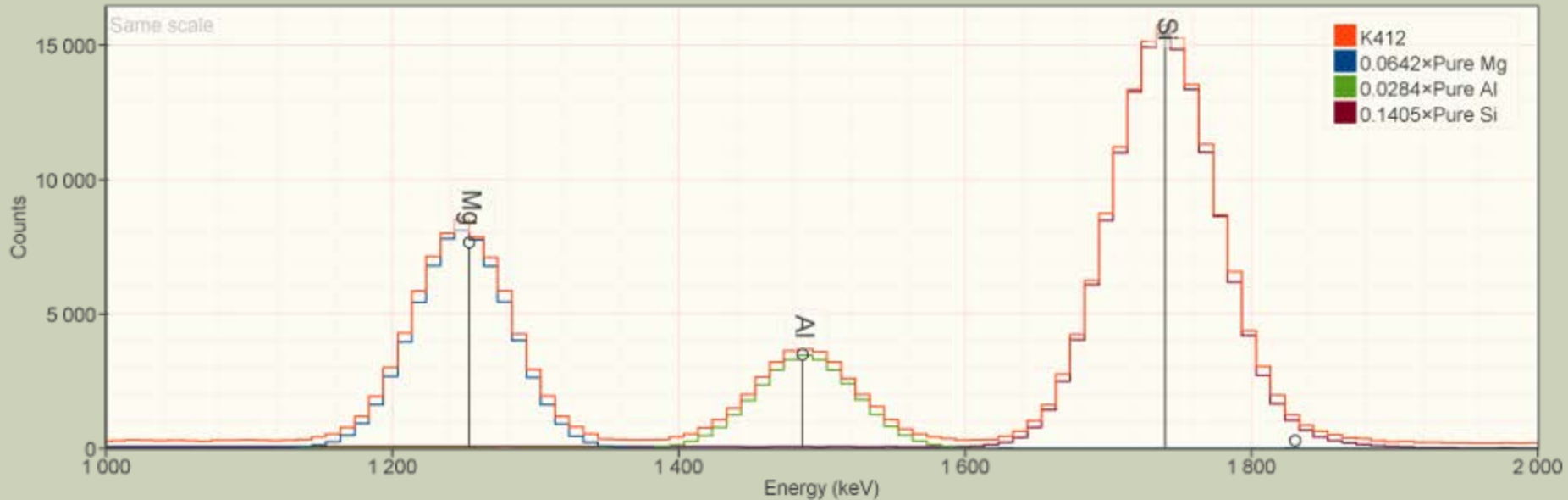
An accurate fit requires both peak and background

To extract the O K intensity we need references for Ca L, O K and Fe L \rightarrow CaF_2 , Al_2O_3 and Fe
Mg K intensity we need references for Mg K, Al K and Si K \rightarrow Mg, Al_2O_3 and Si

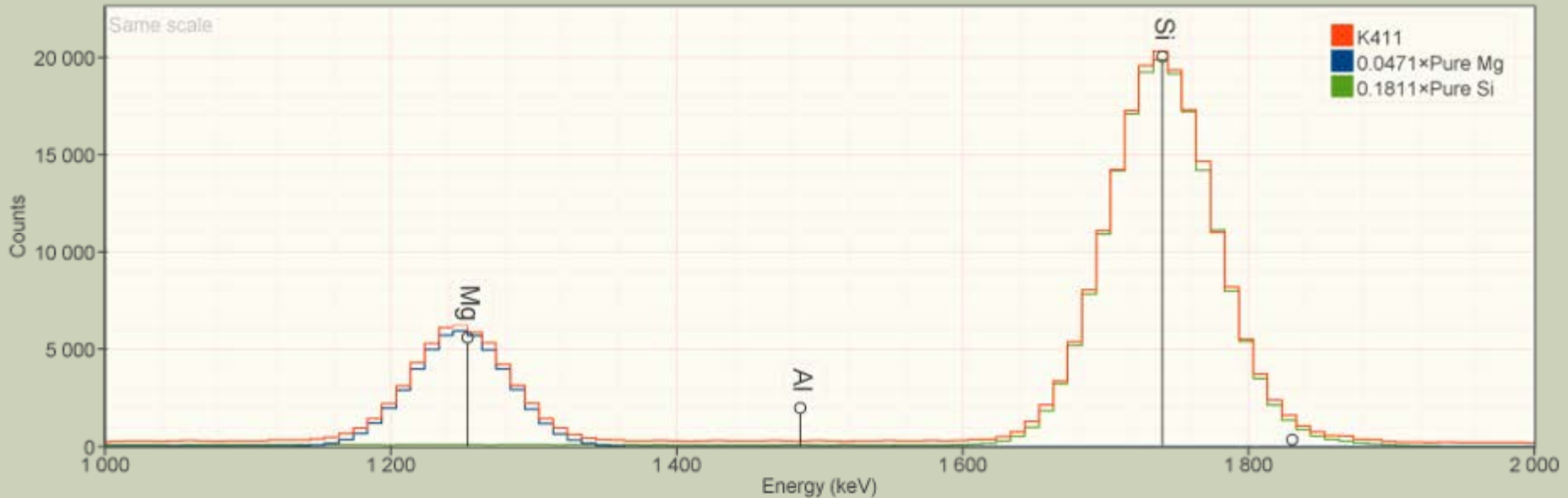
Standards and References

- Standards provide **intensity** information
- References provided **peak shape** information
- Sometimes the standard can provide both intensity and shape information (in which case the standard can act as reference too.)
- You may need references for elements that **aren't even in the unknown** (but are in the standard.)
- Using standards **similar in composition** to the unknown typically produces more accurate measurements.

Fit the references to the standard



Fit the references to the unknown



$$k (\text{Mg in K411 vs K412}) = 0.0471 / 0.0642 = 0.7344$$

$$k (\text{Si in K411 vs K412}) = 0.1405 / 0.1811 = 1.2889$$

Why like standards?

<i>IUPAC</i>	<i>Seigbahn Standard</i>		<i>ZAF</i>	<i>Standard</i>	<i>ZAF</i>
O K-L3	O K α 1	K412	0.9973	Al ₂ O ₃	0.652
Mg K-L3	Mg K α 1	K412	0.9543	Mg	0.5259
Si K-L3	Si K α 1	K412	1.0676	Si	0.7039
Si K-M3	Si K β 1	K412	1.0614	Si	0.7302
Ca K-L3	Ca K α 1	K412	1.0058	CaF ₂	0.9169
Ca K-M3	Ca K β 1	K412	1.0061	CaF ₂	0.9275
Fe K-L3	Fe K α 1	K412	1.0045	Fe	0.8348
Fe K-M3	Fe K β 1	K412	1.0046	Fe	0.8367
Fe L3-M5	Fe L α 1	K412	1.011	Fe	0.2557

Small corrections (ZAF \sim 1) typically lead to accurate measurements.

What can we do?

- Education
 - Works but up to a point...
- More helpful tools
 - Help the user to a select a suitable beam energy
 - Help to select good standards
 - Inform the user about reference requirements
 - Help to determine suitable probe doses
 - Warn about potential pitfalls
- Better tools
 - Eliminate the need for references

Measurement Uncertainties

- Precision
 - Count statistics in the standard, the reference and the unknown
 - Instrument stability
 - Sample stability
- Accuracy
 - Suitability of the matrix correction
 - Accuracy of the physical parameters ($[\mu/\rho]$ & η)
 - Sample preparation (Coatings, surface roughness...)



Precision



Uncertainties in electron probe microanalysis

R B Marinenko^{1,3} and S Leigh²

¹ National Institute of Standards and Technology (NIST), Surface and Microanalysis Science Division, US-20899 Gaithersburg, MD, U.S.A.

² National Institute of Standards and Technology (NIST), Statistical Engineering Division, 100 Bureau Drive, US-20899 Gaithersburg, MD, U.S.A.

E-mail: ryna.marinenko@nist.gov

Abstract. We determined uncertainties for WDS-EPMA (wavelength-dispersive X-ray spectroscopy - electron probe microanalysis) data using the globally accepted ISO/GUM (International Standards Organization/Guide to the Expression of Uncertainty in Measurement). For each calculation, such as the current drift correction and deadtime correction that precede the calculation of a k -value (net corrected X-ray counts of unknown/net corrected X-ray counts of standard), uncertainties were calculated from contributing factors and combined until a final combined standard uncertainty for the k -value was calculated. Our example used data from the analysis of the Ge $L\alpha$ X-ray line in a SiGe alloy. Additional contributions to uncertainties in EPMA results, such as the matrix correction procedure and mass absorption coefficients (MACs) are considered. All statistical calculations used in the process of arriving at the combined uncertainty are included, and the basic steps of the ISO/GUM are described.

Accuracy



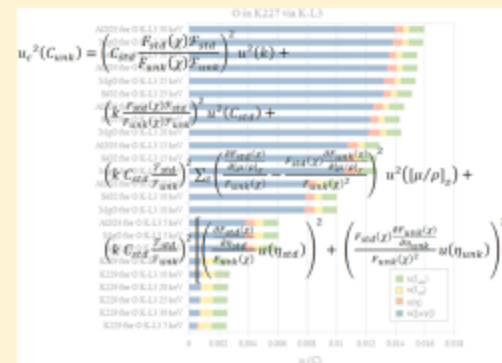
Uncertainty Estimates for Electron Probe X-ray Microanalysis Measurements

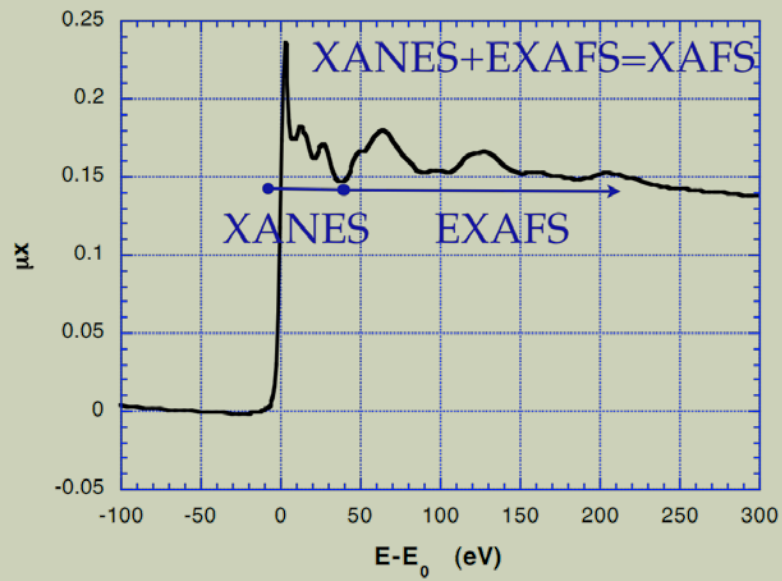
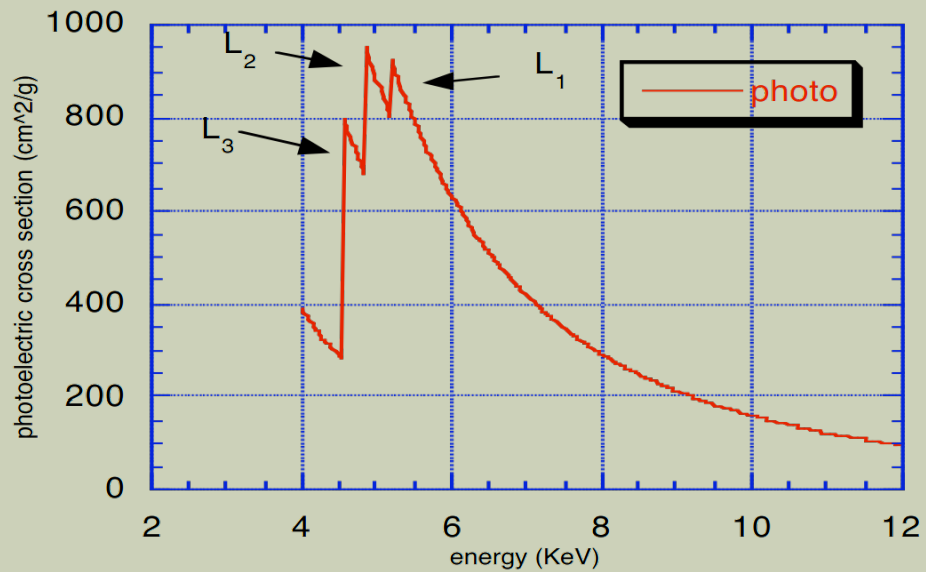
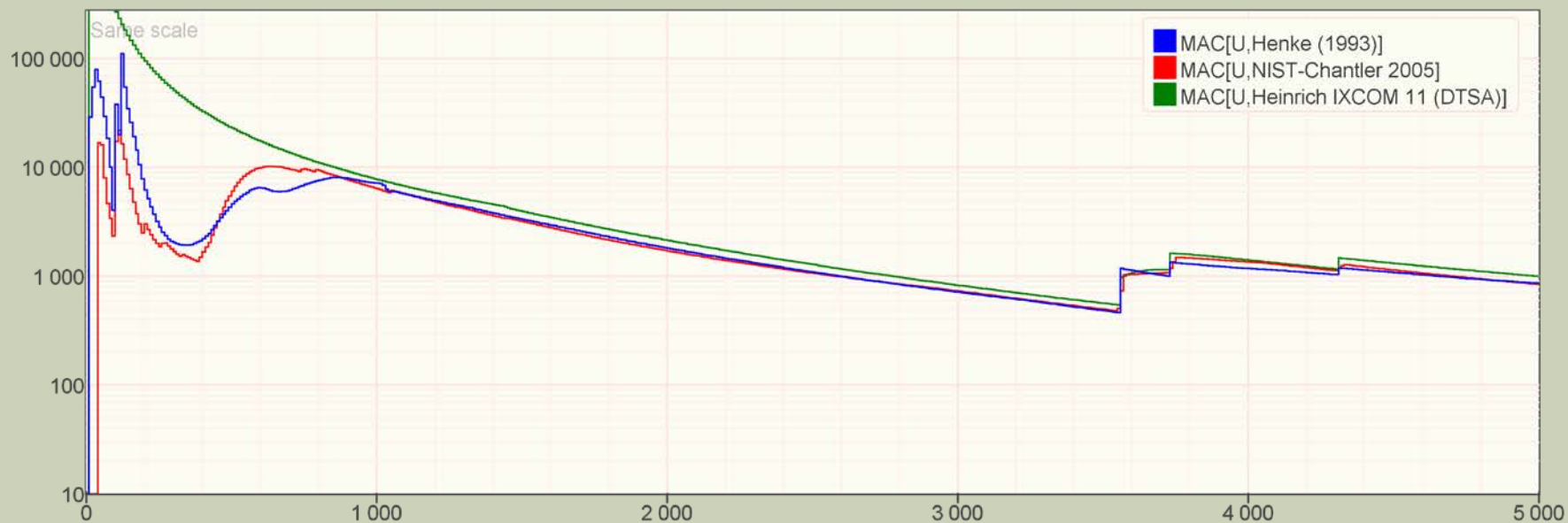
Nicholas W. M. Ritchie* and Dale E. Newbury

Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Drive, MS 8372, Gaithersburg, Maryland 20899-8372, United States

S Supporting Information

ABSTRACT: It has been over 60 years since Castaing (Castaing, R. Application of Electron Probes to Local Chemical and Crystallographic Analysis. Ph.D. Thesis, University of Paris, Paris, France, 1951; translated by P. Duwez and D. Wittry, California Institute of Technology, 1955) introduced the technique of electron probe X-ray microanalysis (EPMA), yet the community remains unable to quantify some of the largest terms in the technique's uncertainty budget. Historically, the EPMA community has assigned uncertainties to its measurements which reflect the measurement precision portion of the uncertainty budget and omitted terms related to the measurement accuracy. Yet, in many cases, the precision represents only a small fraction of the total budget. This paper addresses this shortcoming by considering two significant sources of uncertainty in the quantitative matrix correction models—the mass absorption coefficient, $[\mu/\rho]$, and the backscatter coefficient, η . Understanding the influence of these sources provides insight into the utility of EPMA measurements, and equally important, it allows practitioners to develop strategies to optimize measurement accuracy by minimizing the influence of poorly known model parameters.





Gauss' Formula

$$u(y(x_i, j, \dots))^2 = \sum_{i=1, n} c_i^2 u(x_i)^2 + \sum_{\substack{i, k=1, n \\ i \neq k}} c_i c_k u(x_i, x_k)$$

$$c_i = \frac{\partial y}{\partial x_i} \quad \text{Sensitivity coefficient with respect to } x_i$$

$$u(x_i) \quad \text{Uncertainty in } y \text{ arising from uncertainty in } x_i$$

$$u(x_i, x_k) = u(x_i) u(x_k) r_{i,k} \quad \text{The covariance between } x_i \text{ and } x_k$$

$$-1 \leq r_{i,k} \leq 1 \quad \text{The correlation between } x_i \text{ and } x_k$$

$$u(a + b) = \sqrt{u(a)^2 + u(b)^2}$$

If the source of uncertainty in a and b are uncorrelated

$$u(a + b) = u(a) + u(b)$$

If the source of uncertainty in a and b are 100% correlated.

Applying Gauss' Formula

Applying Gauss' Formula to XPP

This is the sensitivity of XPP to uncertainty in $[\mu/\rho]_z$.

Measurement Optimization

$$M = \{ C_i \pm \Delta C_i \}$$

C_i

Mass fraction of element i

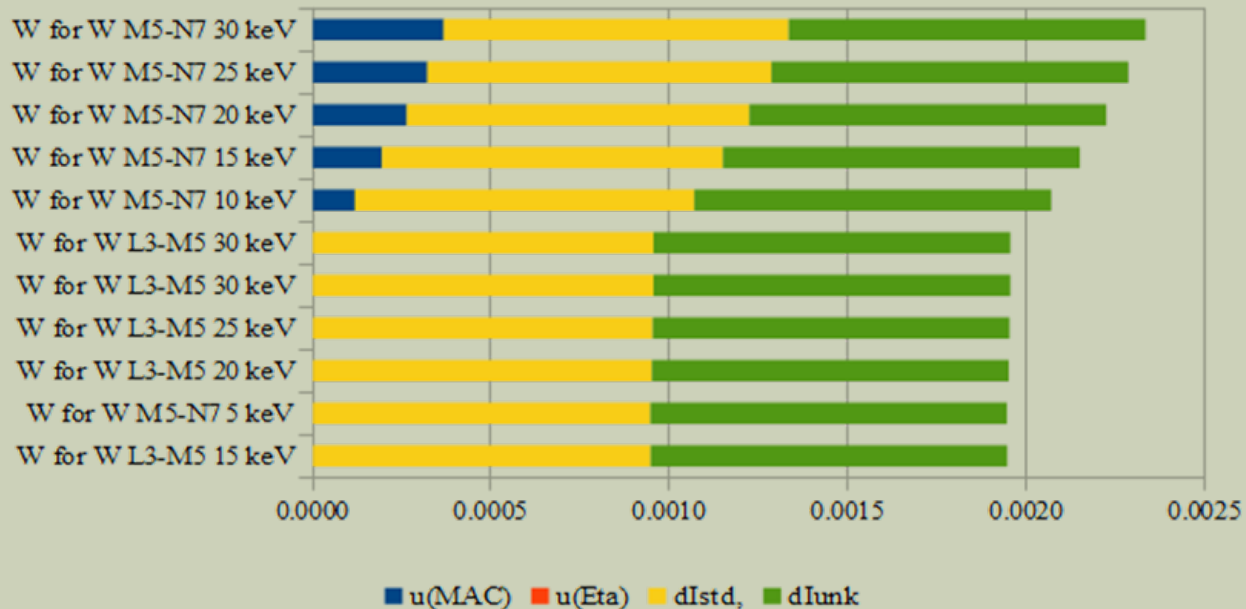
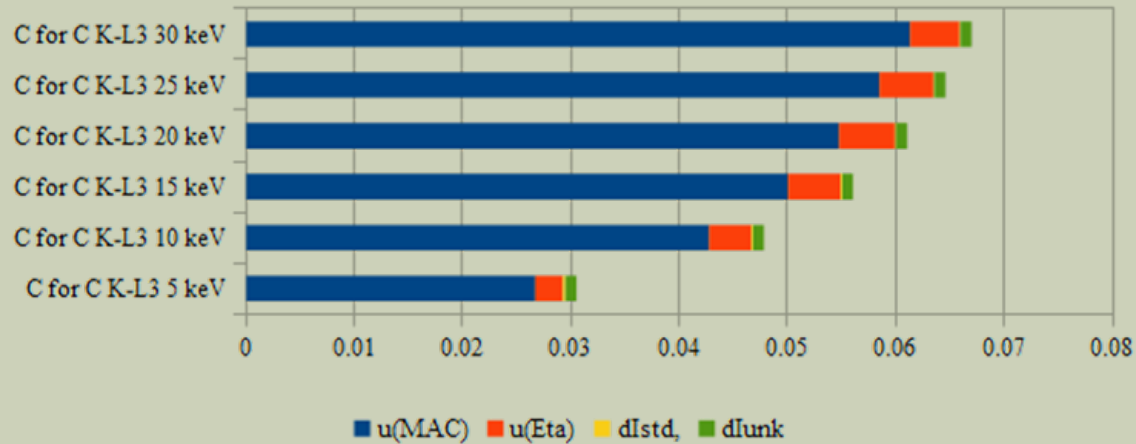
ΔC_i

Measurement uncertainty in
the mass fraction of element i

$$\min(f(\{\Delta C_i\}; P))$$

Select the measurement parameters
 P such that a function f of the
measurement uncertainties is minimized.

Example: Tungsten Carbide



Optimizing Precision

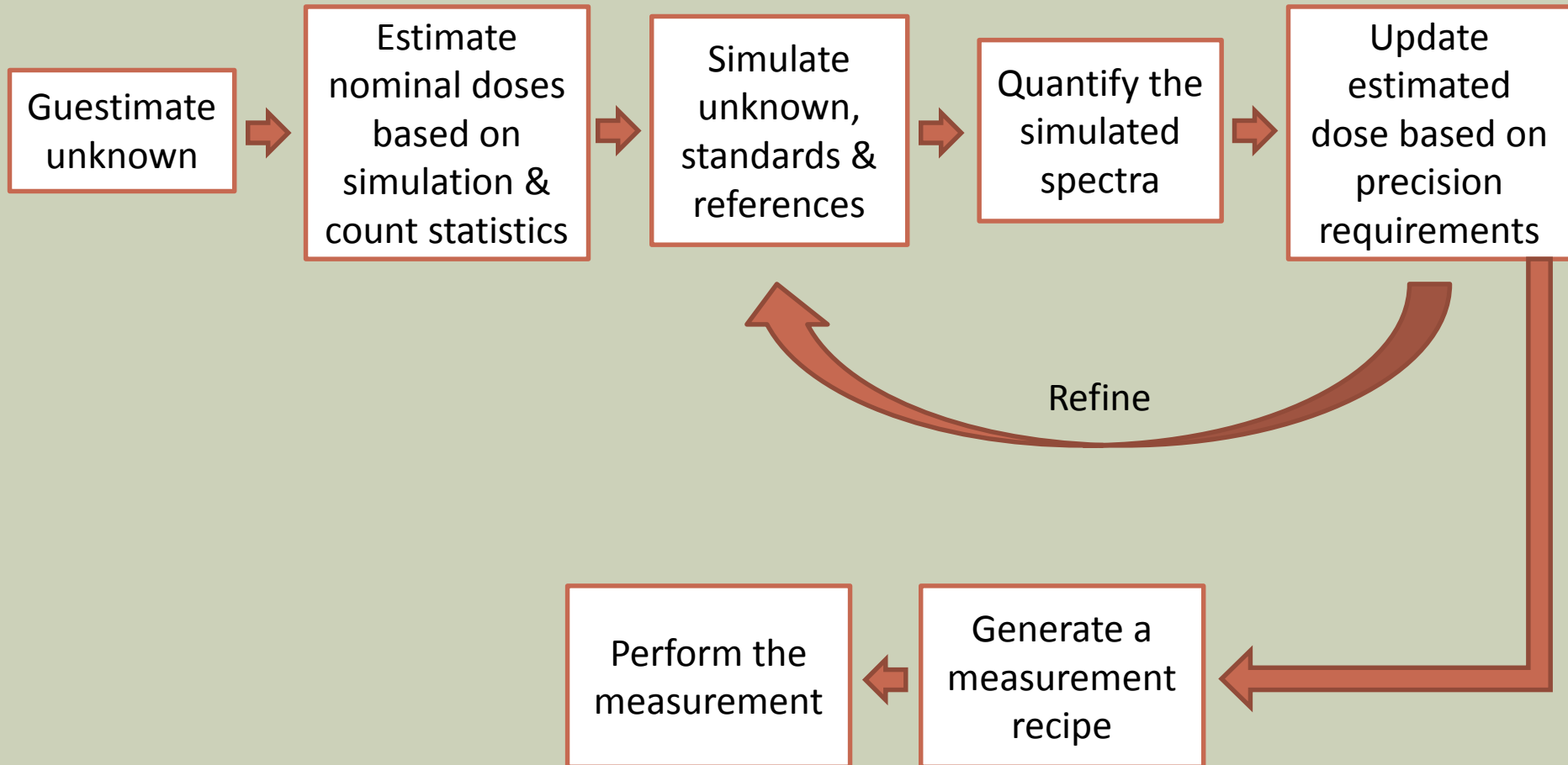
How do I pick the probe doses
(live time \times probe current)
to produce the desired measurement precision?

- Not all elements need to be measured with the same precision
- We probably want to optimize the choices to minimize the total measurement time
- Dose correct spectrum simulation can help

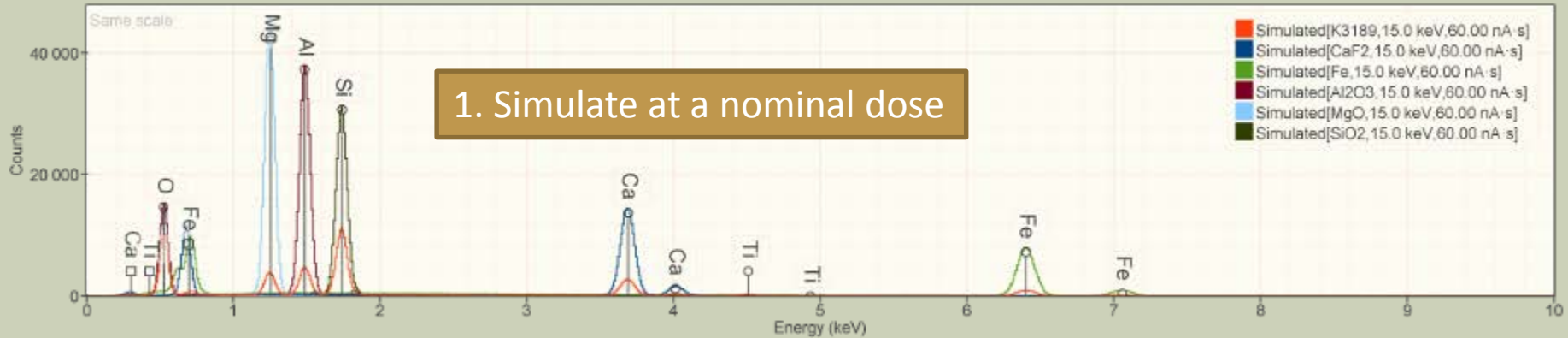
Rules of Thumb:

- ✓ Precision scales with the square root of counts / probe dose.
- ✓ Precision depends on the standard, the unknown and any references.
- ✓ The references (if any) contribute to the error budget twice.

Estimating Dose Requirements



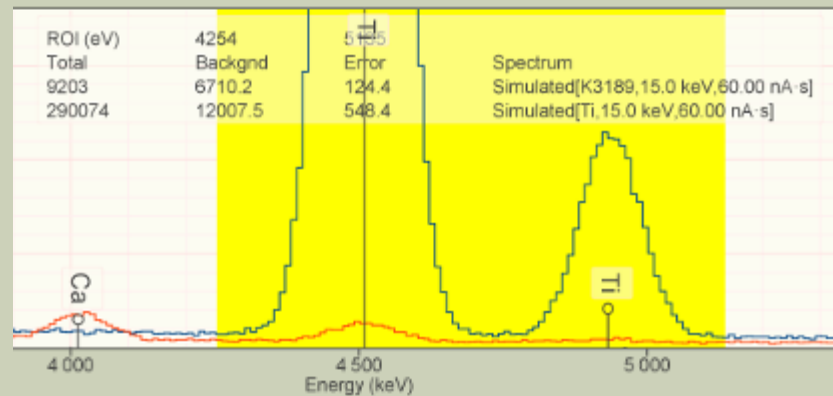
Estimating dose requirements



2. Perform the simulated quant.

3. Combine with data from the simulated spectra

Name	k	dk	dk/k (%)	Dose (tot)
O All	0.65978	0.0018	0.3%	4.87
Mg All	0.08065	0.0004	0.5%	14.75
Al All	0.11902	0.0005	0.5%	12.81
Si All	0.35037	0.0008	0.2%	3.699
Ca K-family	0.18338	0.0009	0.5%	14.77
Ca L-family	0.22206	0.0120	5.4%	
Ti K α	0.00976	0.0002	2.8%	459.1
Ti K β	0.01142	0.0018	15.8%	
Ti L-family	0.04432	0.0056	12.7%	
Fe K α	0.11745	0.0011	1.0%	54.5
Fe K β	0.10297	0.0043	4.2%	
Fe L-family	0.05958	0.0017	2.9%	



3. Estimate the standard & unknown doses

$$D_{\text{Ti,unk}} = 441 \text{ s} \quad D_{\text{Ti,std}} = 19 \text{ s} \rightarrow k/dk = 99.2$$

Acquisition Optimization

- Minimize total acquisition time

$$T_{Total} = T_{unk} + \sum_z T_{std,z} + \sum_j T_{ref,j}$$

- Constrained by precision requirements

$\frac{U(k_z)}{k_z} < p_z$ where p_z is the desired fraction precision for element z .

- The precision scales with \sqrt{T} and the individual contributions can be determined from simulated spectra by fitting a noise-free simulated reference to the unknown, standard and references.

Output

- Sample preparation requirements
- Instrument settings
- Standard spectrum requirements
- Reference spectrum requirements
- Recommendations on the number of unknown spectra to collect
- Suggestion on which lines to use for the quantification

What does the analyst need to know?

- What elements are in the unknown
 - Collect a quick qual spectrum
- The approximate composition of the unknown
 - Quick standardless analysis
- Which standard materials are available
 - Labs can distribute this to users as a DTSA-II standard database

Why not standardless?

Compound	Metal	Analysis	Relative Error(%)	Sulfur	Analysis	Relative Error (%)
FeS	0.635	0.629	-1	0.365	0.371	1.8
FeS ₂	0.466	0.642	38	0.534	0.358	-33
CuS	0.665	0.764	15	0.335	0.236	-30
ZnS	0.671	0.762	14	0.329	0.239	-28
SrS	0.732	0.758	3.6	0.268	0.242	-10
CdS	0.718	0.808	3.8	0.222	0.192	-13
Sb ₂ S ₃	0.717	0.739	3.1	0.283	0.261	-7.8
PbS	0.866	0.914	5.5	0.134	0.086	-36

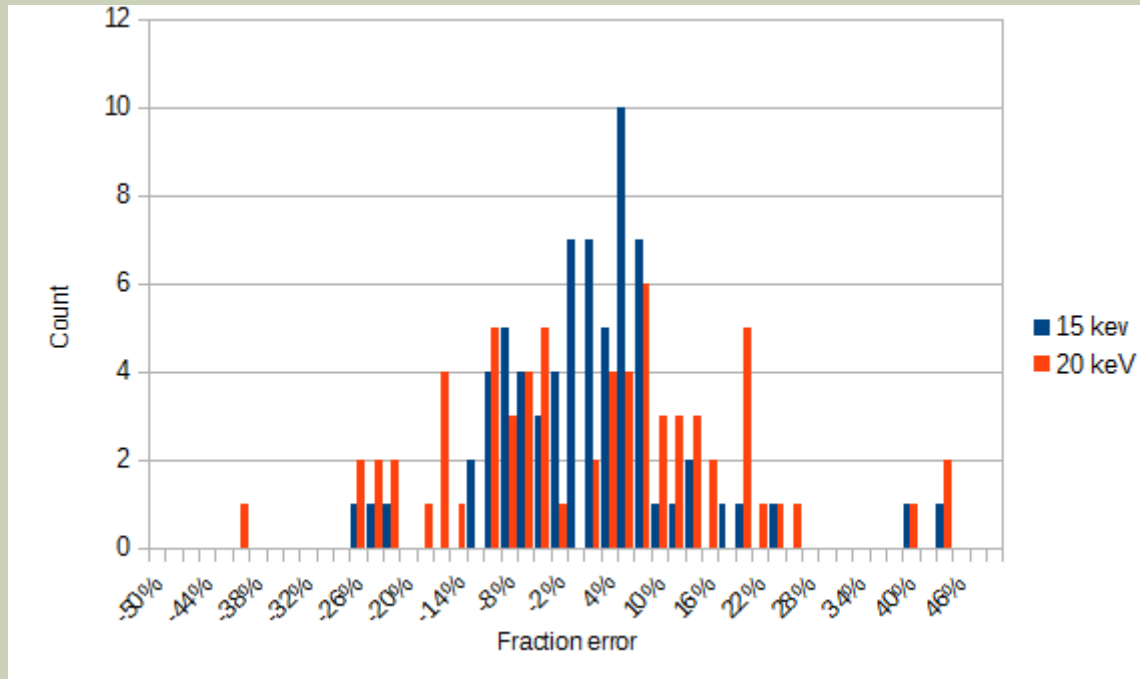
Vendor "A" standardless analysis

Thanks Dale.

Vendor A

Measure O directly

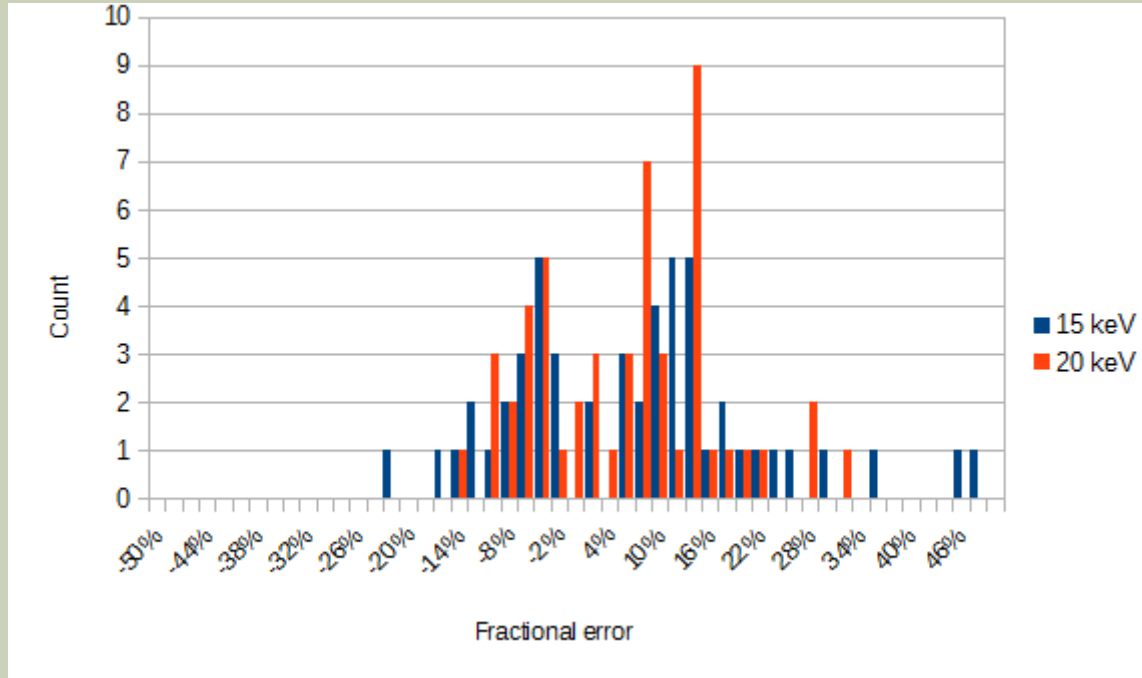
142 measurements



Vendor B

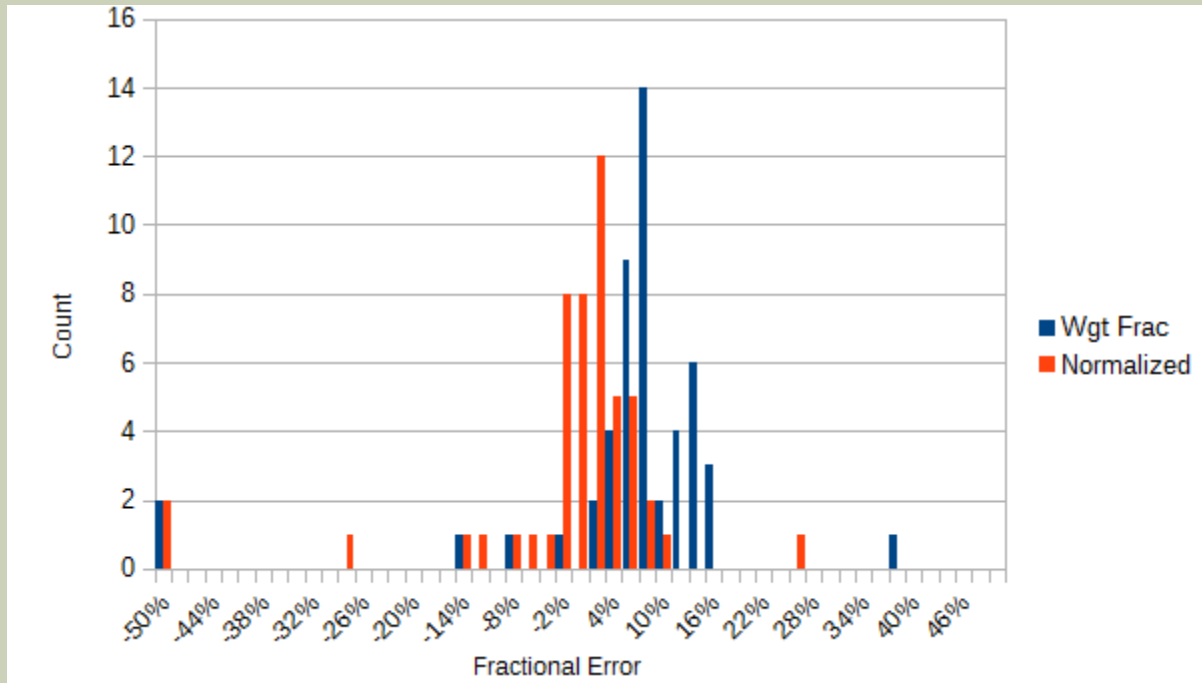
Measure O directly

104 measurements



Vendor C

15 keV – Unnormalized vs normalized



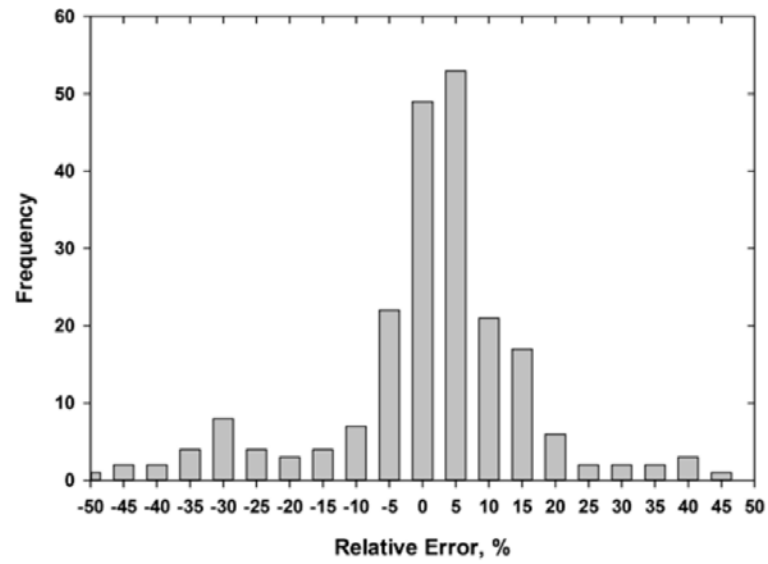
Why standards-based?

Compound	Metal	Analysis	Relative Error(%)	Sulfur	Analysis	Relative Error (%)
FeS	0.635	0.635	0	0.365	0.365	0
FeS ₂	0.466	0.463	-0.6	0.534	0.537	0.6
CuS	0.665	0.667	0.3	0.335	0.333	-0.6
ZnS	0.671	0.674	0.4	0.329	0.326	-0.9
SrS	0.732	0.737	0.7	0.268	0.263	-1.9
CdS	0.778	0.786	1	0.222	0.214	-3.6
Sb ₂ S ₃	0.717	0.727	1.4	0.283	0.273	-3.5
PbS	0.866	0.87	0.5	0.134	0.13	-3

NIST DTSA-II standards-based analysis

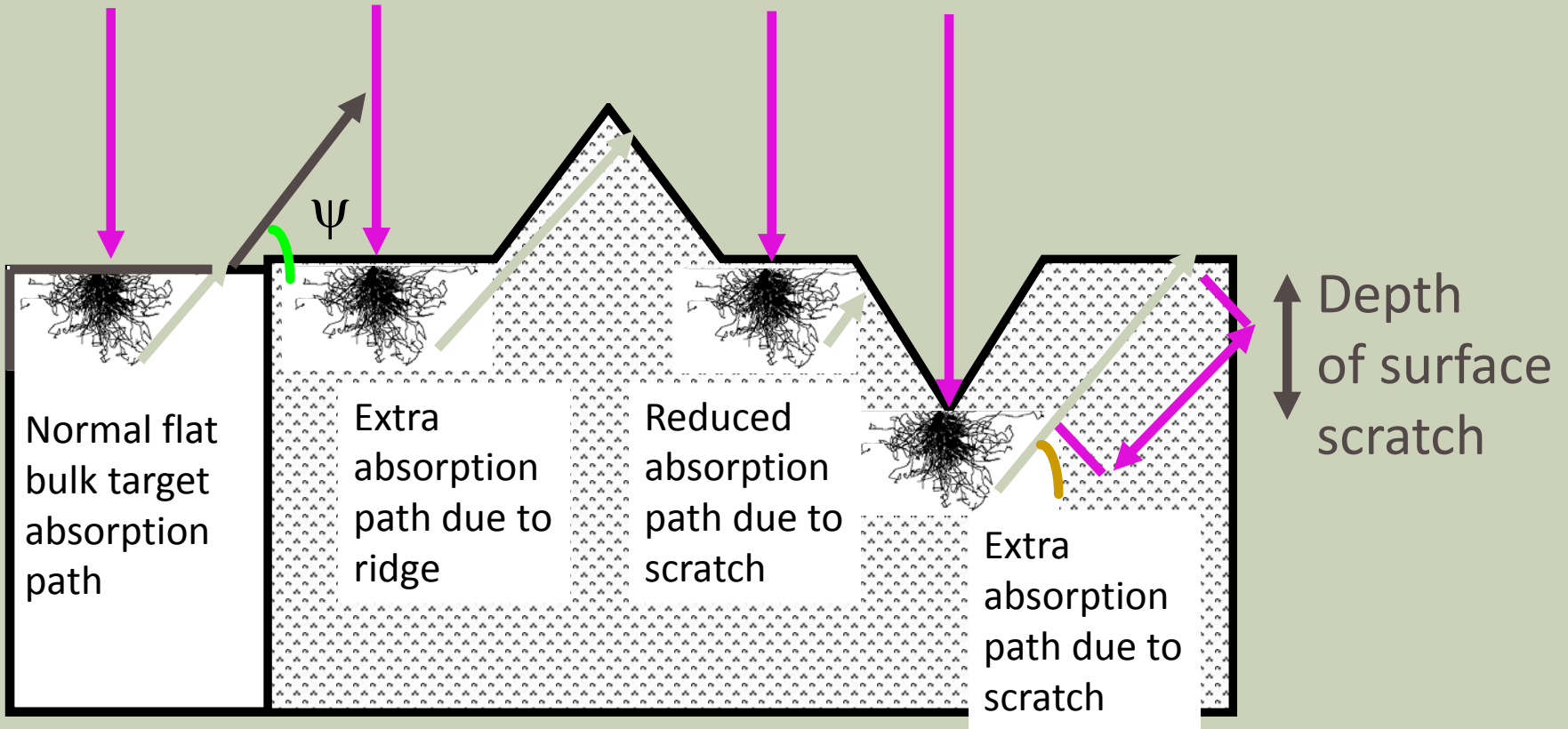
Thanks Dale.

Standardless Analysis



Geometric Effects

Common, practical examples: surface roughness, scratches





Element

Ideal mass concentration

S

0.5345

Fe

0.4655

Errors in Normalized Analysis (k-ratio protocol with CuS and Fe, DTSA-II)

Location 10

Norm conc relative error

S

0.2727

-49%

Fe

0.7273

56%

Raw Total

0.0391

Location 11

Norm conc relative error

S

0.5015

-6%

Fe

0.4985

7%

Raw Total

0.8773

Location 7

Norm conc relative error

S

0.0381

-93%

Fe

0.9619

107%

Raw Total

0.1121

Location 9

Norm conc relative error

S

0.3654

-32%

Fe

0.6346

36%

Raw Total

0.5244

Location 3

Norm conc relative error

S

0.5352

0.13%

Fe

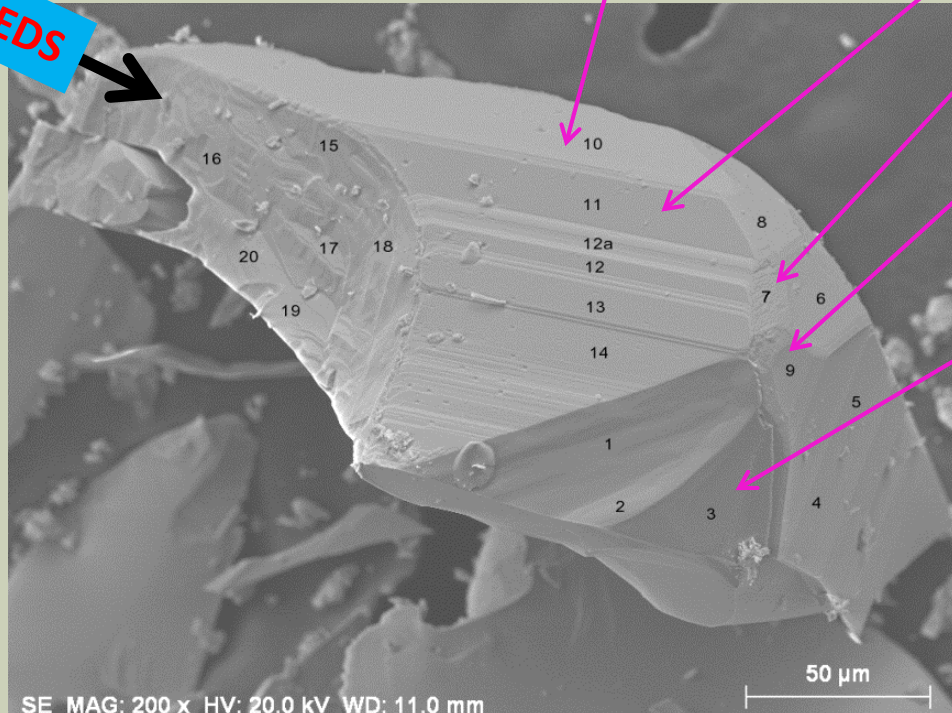
0.4648

-0.15%

Raw Total

0.9892

EDS

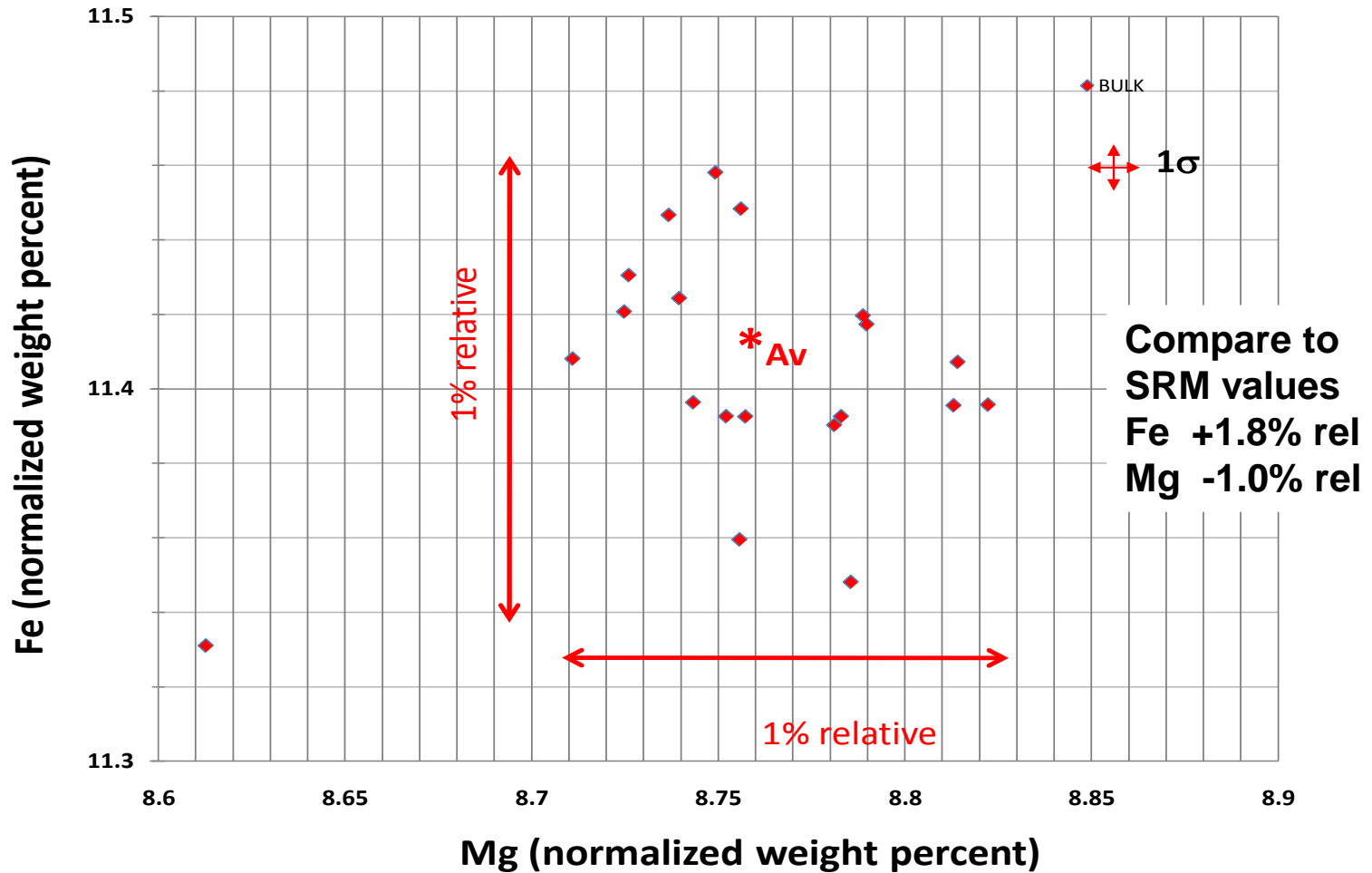


SE MAG: 200 x HV: 20.0 kV WD: 11.0 mm

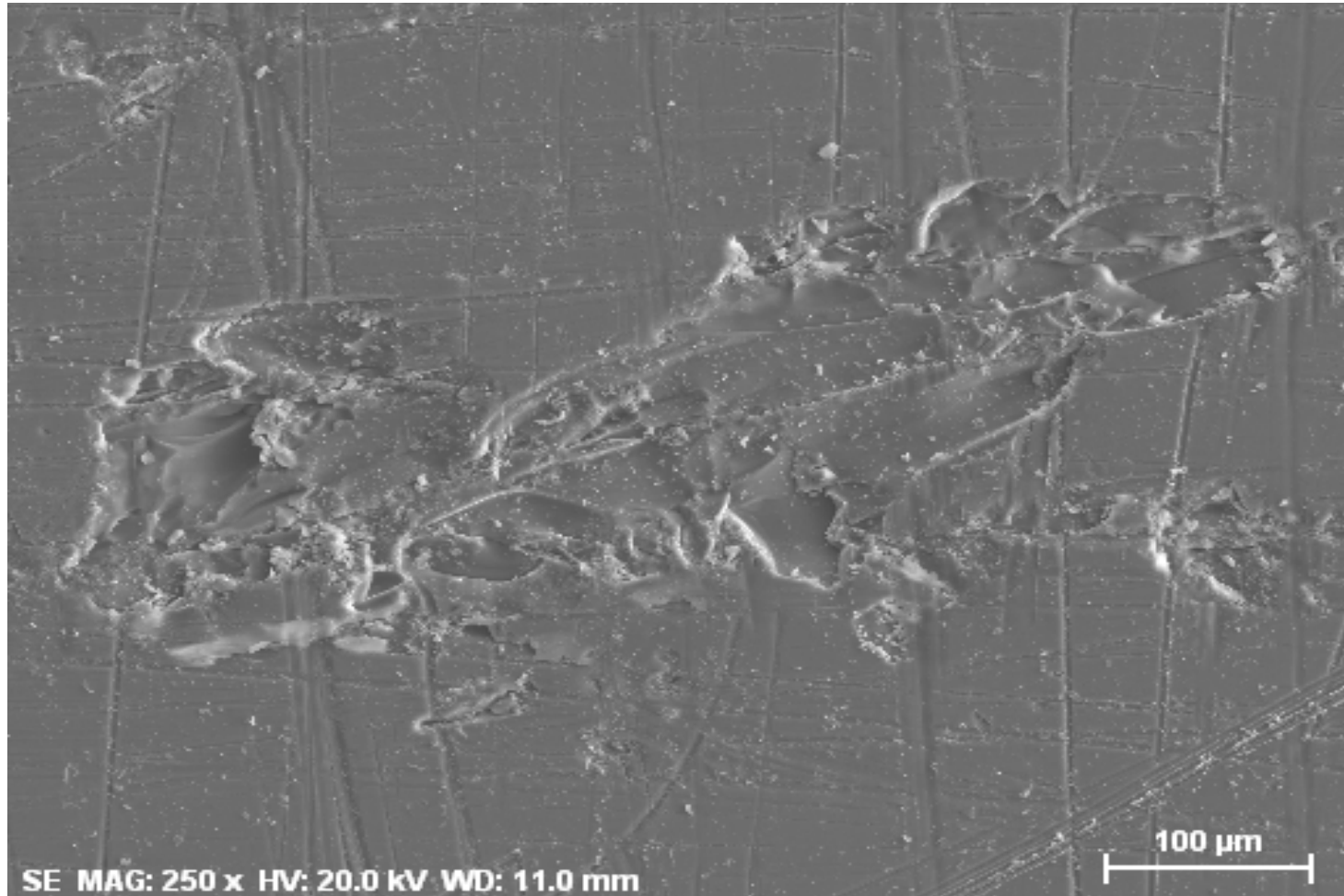
50 µm

Analysis with the ideal flat polished sample shape

Analysis of K411: Bulk polished

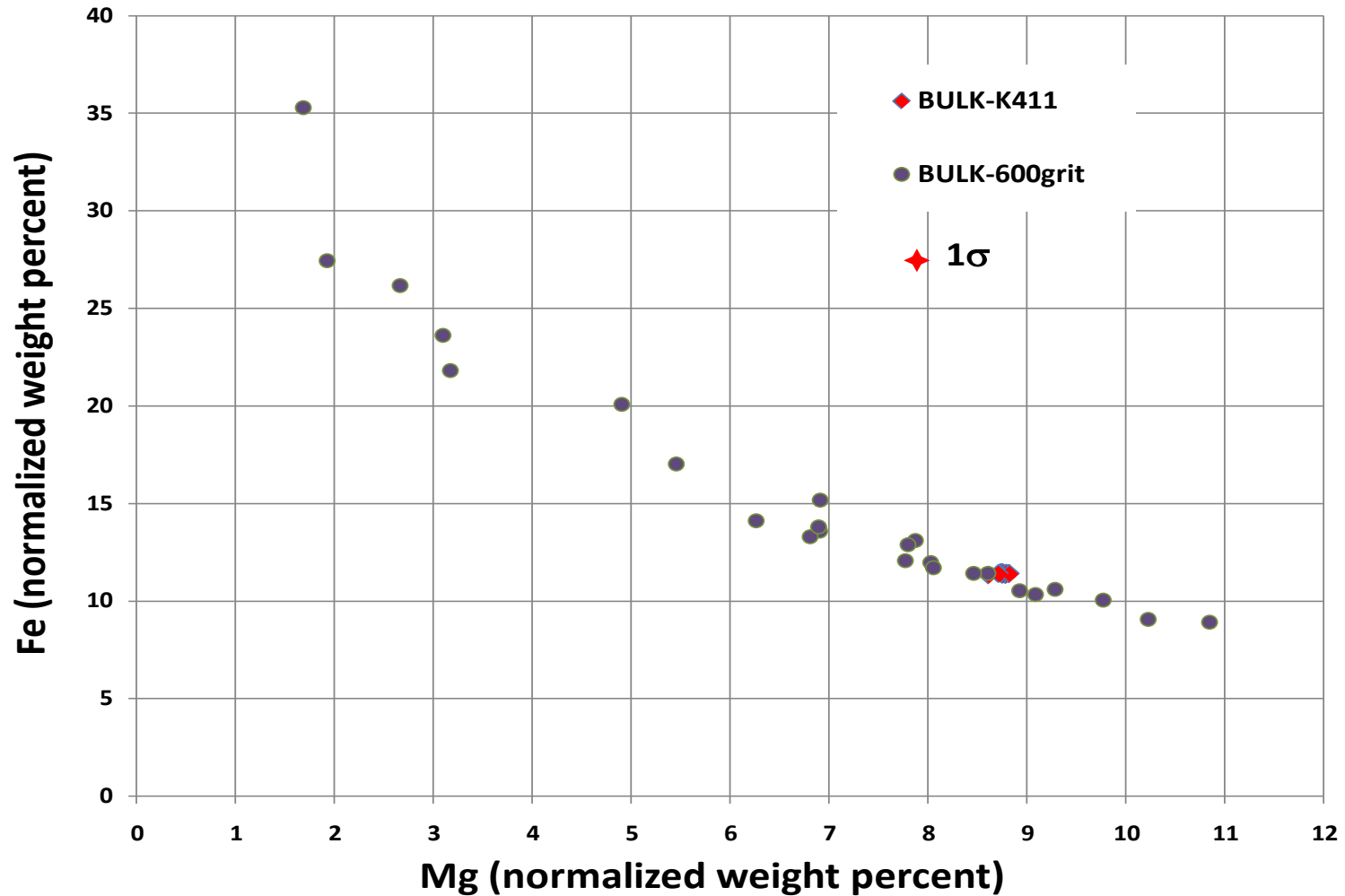


Analysis with a compromised sample shape: surface abrasion



Analysis with a compromised sample shape: surface abrasion

Analysis of K411: Bulk polished and 600 grit abraded



Only the beginning

- Better estimates of uncertainty for sub-optimal samples
- Better estimates of uncertainty for standardless analysis
- Make better use of redundant data
- Make better use of simulation to identify

Is there a better way?

Assume the ideal

- Assume that the user will make the optimal choices
- Don't provide information about consequences
- Don't present alternatives or consequences
- Let the user sink or swim

A Better Way

Assume the ideal

- Assume that the user will make the optimal choices
- Don't provide information about consequences
- Don't present alternatives or consequences
- Let the user sink or swim

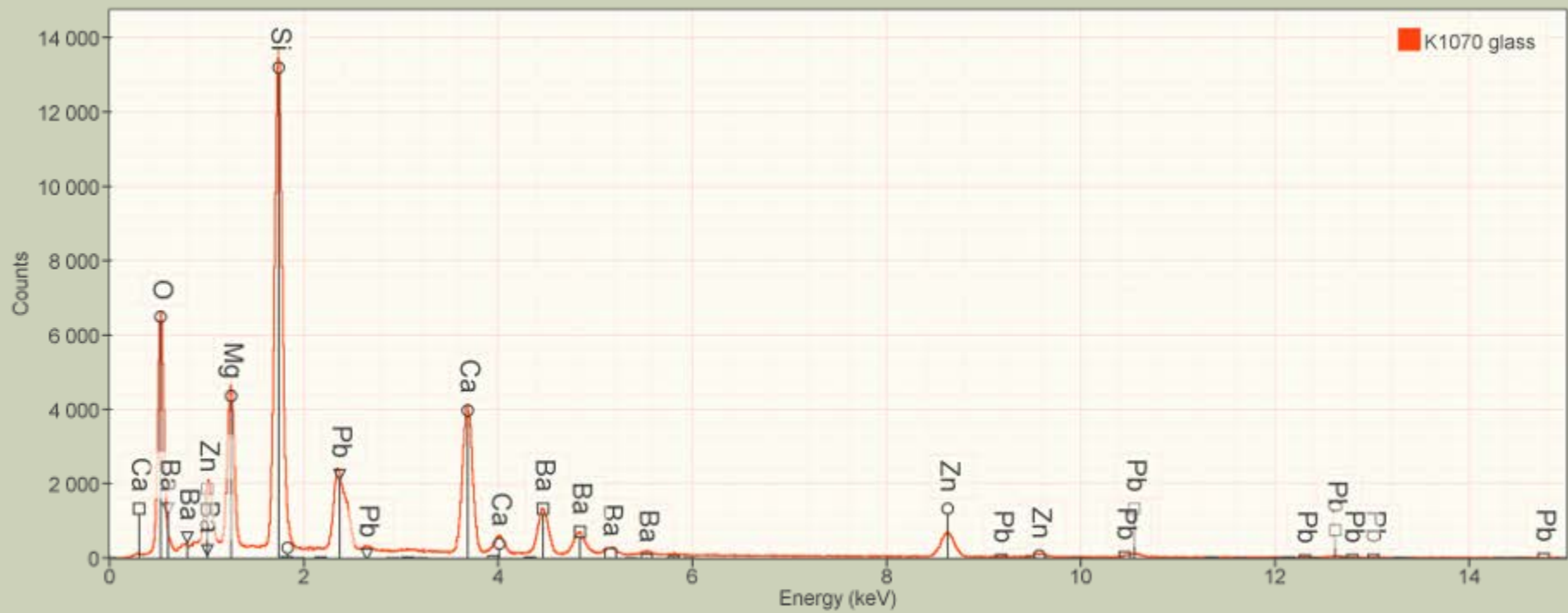
Work towards ideal

- Assume that the user will make sub-optimal choices
- Present the consequences of those choices
- Present alternative choices and the consequences
- Allow the user to make the choices suited to their application – expeditious to optimal

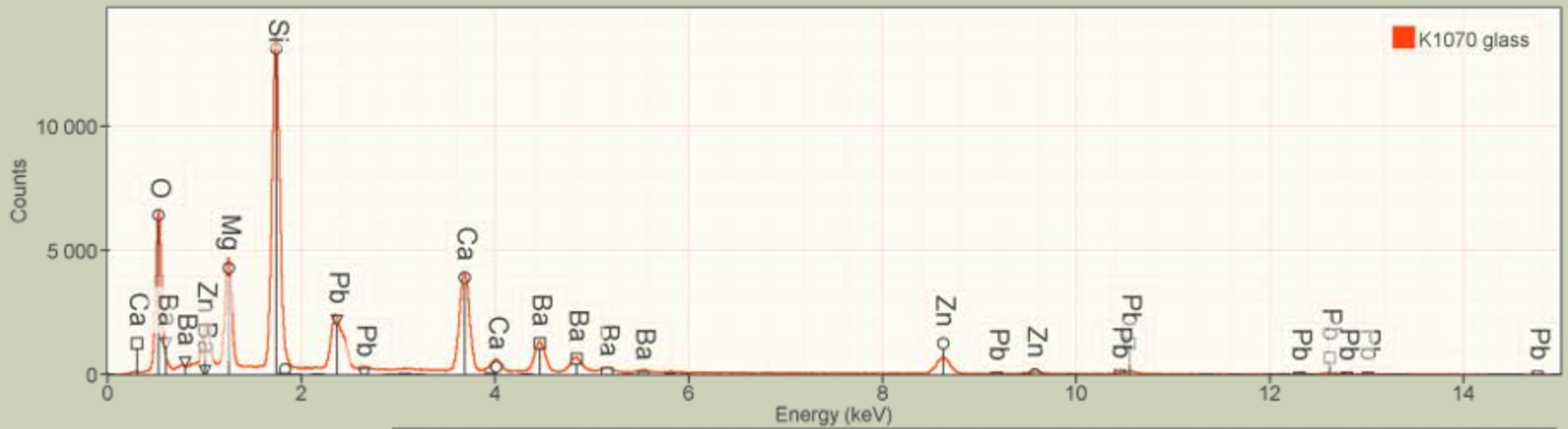
Conclusion

- Being able to calculate uncertainties is all very well and good
 - How we use the uncertainties is critical
- Being able to calculate realistic uncertainties will help users to:
 - Identify bad measurement practices
 - Avoid bad measurement practices
 - Be more realistic about measurement tradeoffs
 - Be more realistic about the utility of the measurement
 - Plan better measurements
- Better designed tools can help
 - Simply being able to produce good results isn't enough

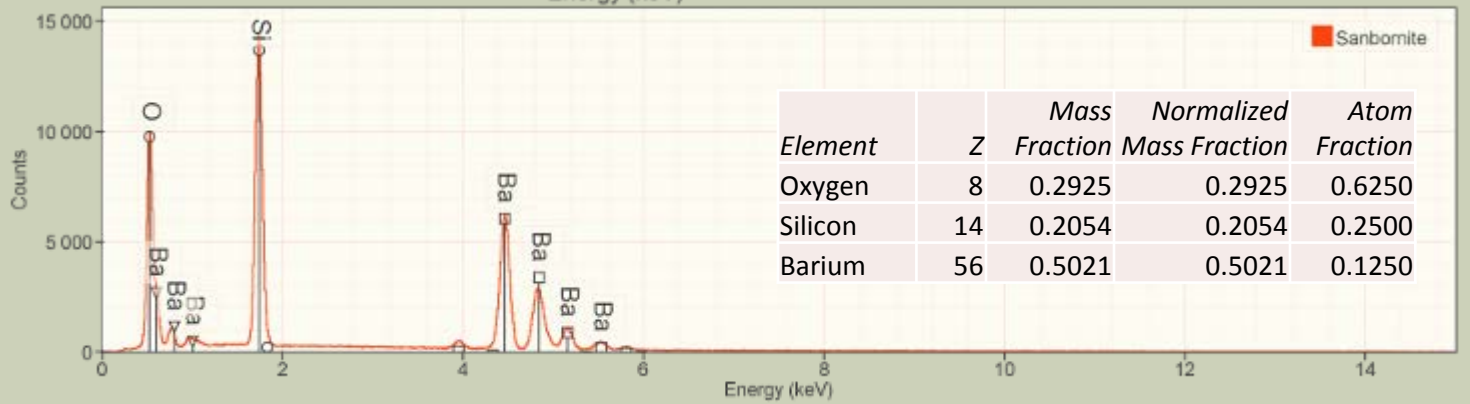
Extra slides



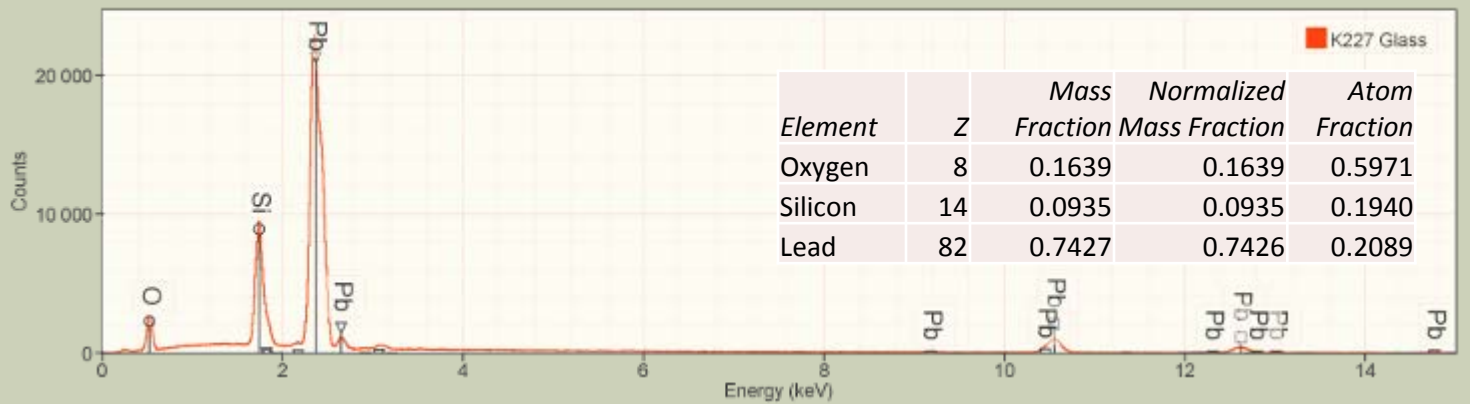
<i>Element</i>	<i>Z</i>	<i>Mass Fraction</i>	<i>Normalized Mass Fraction</i>	<i>Atom Fraction</i>
Oxygen	8	0.3431	0.3431	0.5919
Magnesium	12	0.0754	0.0754	0.0856
Silicon	14	0.1870	0.1870	0.1838
Calcium	20	0.0893	0.0893	0.0615
Zinc	30	0.1004	0.1004	0.0424
Barium	56	0.1120	0.1120	0.0225
Lead	82	0.0928	0.0928	0.0124



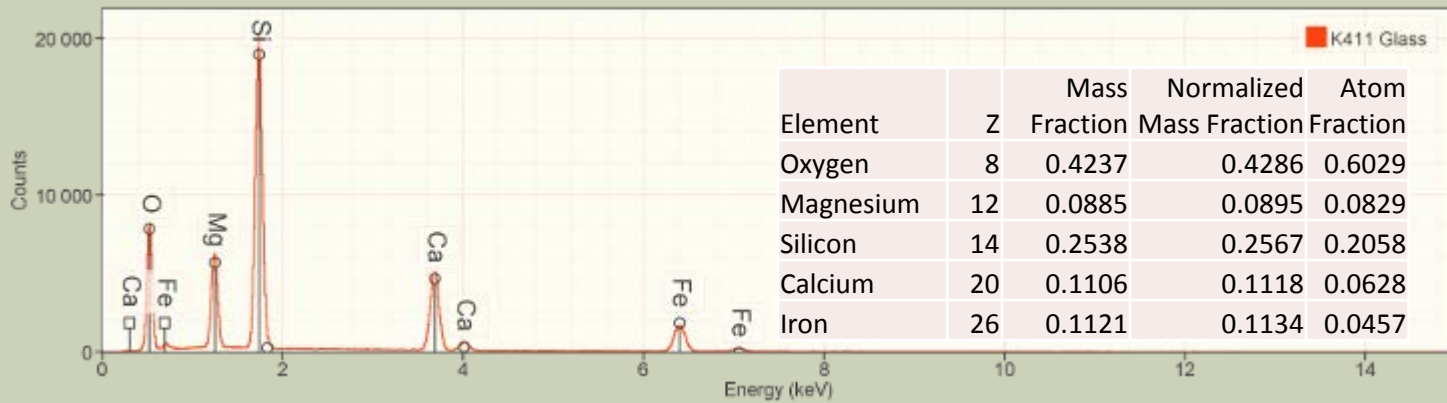
Ba, Si, O



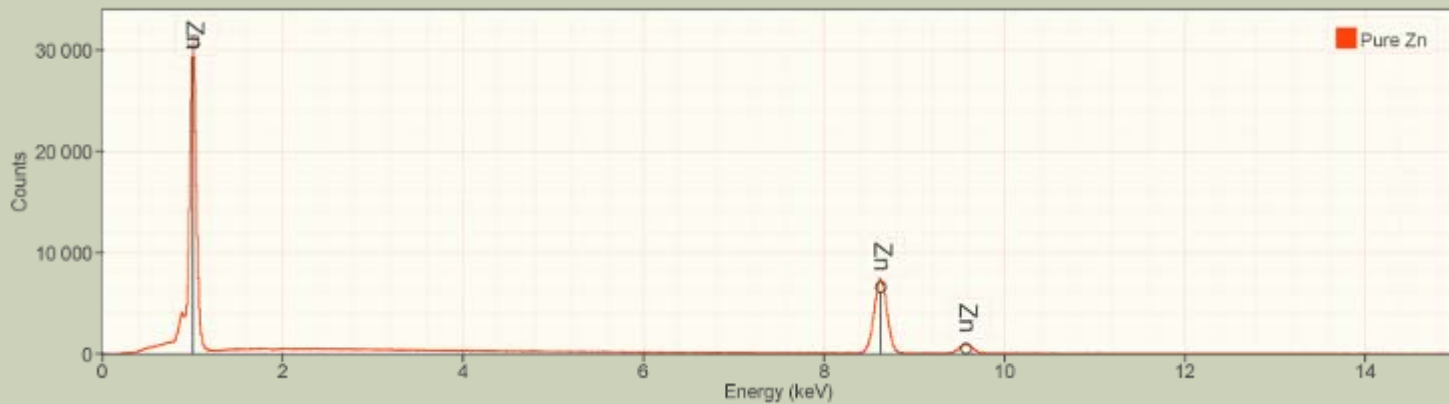
Pb

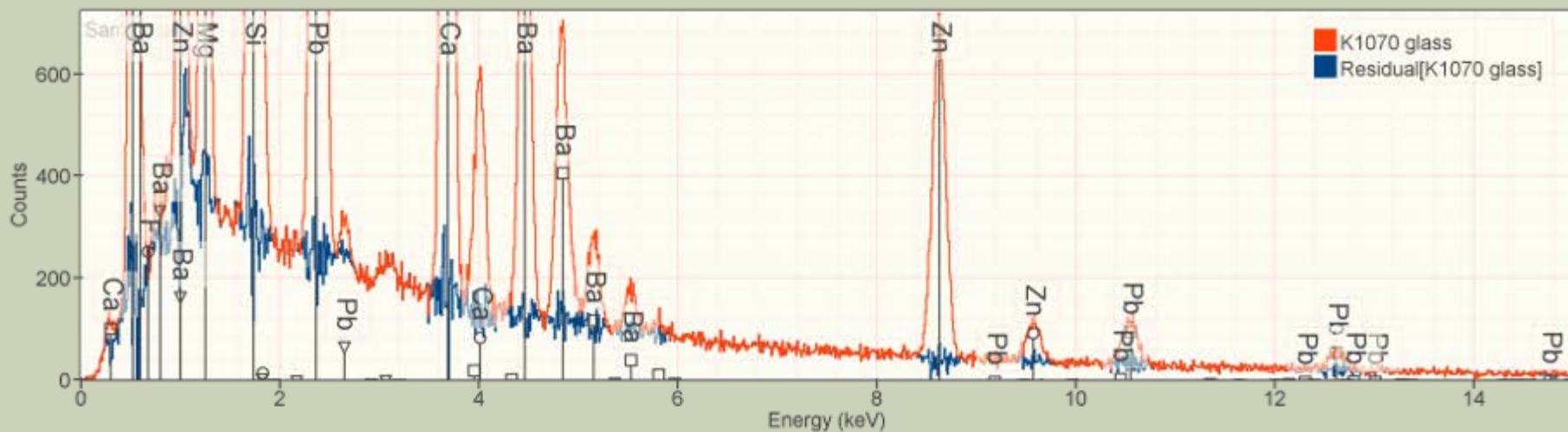


Mg, Ca



Zn





Name	K1070 glass Relative to
Mg All	0.7108 Mg in K411
Si All	0.9502 Si in Sanbornite
Ca K-family	0.8156 Ca in K411
Ca L-family	1.0031 Ca in K411
Zn K α	0.0889 Zn in Pure Zn
Zn K β	0.0891 Zn in Pure Zn
Zn L3-M5 + 6 others	0.0581 Zn in Pure Zn
Ba L3-M5 + 5 others	0.2012 Ba in Sanbornite
Ba L2-N4 + 2 others	0.2389 Ba in Sanbornite
Ba L3-M1	0.2118 Ba in Sanbornite
Ba M-family	0.1533 Ba in Sanbornite
Pb L2-M4 + 13 others	0.0963 Pb in K227
Pb L2-N4 + 1 others	0.0849 Pb in K227
Pb L3-M1	0.0245 Pb in K227
Pb L α	0.0878 Pb in K227
Pb M5-N7 + 6 others	0.0964 Pb in K227
Pb M4-N2 + 1 others	0.1056 Pb in K227

The peak in the unknown has k times the number of counts (per nA·s) as the peak in the standard.

<i>IUPAC</i>	<i>Seigbahn</i>	<i>Standard</i>	<i>Energy</i>	<i>ZAF</i>	<i>Z</i>	<i>A</i>	<i>F</i>	<i>k-ratio</i>
O K-L3	O K α 1	Sanbornite	0.5249	0.5823	0.9339	0.6234	1.0004	0.6831
Mg K-L3	Mg K α 1	K411	1.2536	0.865	1.0665	0.8134	0.9972	0.7373
Si K-L3	Si K α 1	Sanbornite	1.7397	1.0532	0.9327	1.1298	0.9994	0.959
Si K-M3	Si K β 1	Sanbornite	1.829	1.0459	0.9327	1.122	0.9994	0.9523
Ca K-L3	Ca K α 1	K411	3.6917	1.0168	1.0727	0.9444	1.0036	0.8213
Ca K-M3	Ca K β 1	K411	4.0127	1.0242	1.0727	0.9513	1.0036	0.8272
Zn K-L3	Zn K α 1	Pure Zn	8.6389	0.8746	0.8753	0.9882	1.011	0.0878
Zn K-M3	Zn K β 1	Pure Zn	9.572	0.8779	0.8753	0.9909	1.0121	0.0881
Zn L3-M5	Zn L α 1	Pure Zn	1.0116	0.4637	0.8886	0.5205	1.0026	0.0466
Ba L3-M5	Ba L α 1	Sanbornite	4.4663	0.8983	0.927	0.968	1.001	0.2004
Pb L3-M5	Pb L α 1	K227	10.5512	0.7611	0.7547	1.0099	0.9986	0.0951
Pb M5-N7	Pb M α 1	K227	2.3459	0.7699	0.8213	0.9375	0.9999	0.0962

<i>Element</i>	<i>Standard</i>	<i>Measured</i>	<i>Difference</i>	<i>% Difference</i>
Si	18.7	18.39	-0.31	-1.7
Pb	9.28	8.57	-0.71	-7.6
O	34.31	33.67	-0.64	-1.9
Ba	11.2	11.18	-0.02	-0.1
Zn	10.04	10.18	0.14	1.4
Ca	8.93	8.82	-0.11	-1.3
Mg	7.54	7.21	-0.33	-4.4