Quantitative metrics for identifying characteristic GSR particles

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Summary

- Quantification of particles is difficult
  - Estimating the mass fraction of an element in a particle
- Fortunately, quantification isn't necessary to determine the presence of an element
  - K-ratios are sufficient
- Linear regression using standard spectra is our friend
  - Linear regression provides uncertainty metrics
- Uncertainty metrics can be used to make defensible, quantitative statements about the presence or absence of an element
  - Even in the presence of interfering elements!

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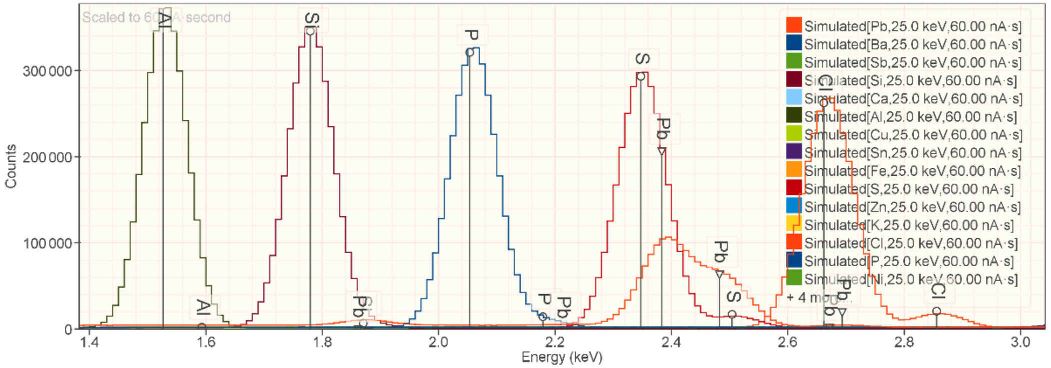
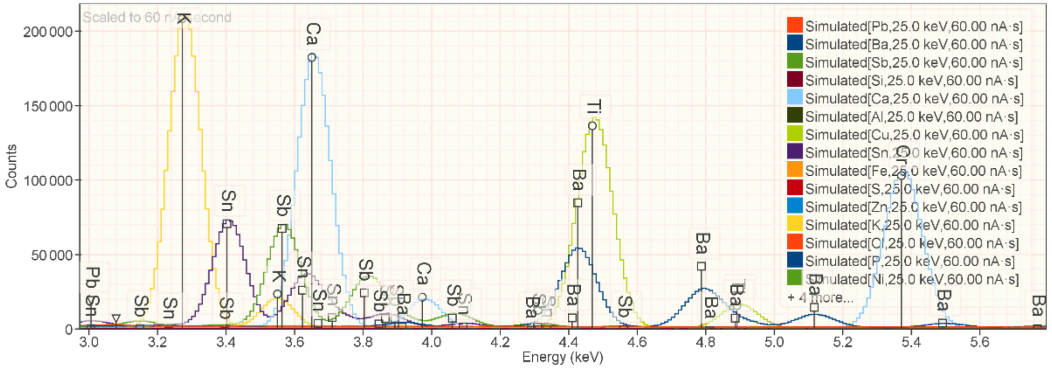
Characteristic Particle Types

Name	Required	Optional	Trace	Specials
Sinoxid	Pb, Ba, Sb	Si, Ca, Al, Cu, Sn	Fe, S, Zn, K, Cl, P, Ni	Co, Cr
SBP	Pb, Ba, Ca, Si, Sn	Cu, Fe, S, Zn, K, Cl		
Sintox – RUAG	Ca, Ti, Zn		Ca, S	
Sintox – MEN	Ca, Cu, Sn		K, S	



(S, Pb)



(Sn, K, Sb), (Sb, Ca), (Ba, Ti)

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Source: SWGGSR – Guide for Primer Gunshot Residue Analysis by Scanning Electron Microscope / Energy Dispersive X-ray Spectrometer.

Consistent Particle Types

- Barium, calcium, silicon (with no more than a trace of sulfur)
- Antimony, barium (usually with no more than a trace of iron or sulfur)
- Lead with levels of antimony greater than trace amounts
- Barium, aluminum
- Lead, barium
- Lead, barium, calcium, silicon (produced by antimony-free, lead styphnate, barium nitrate, and calcium silicide based primers like Hirtenberger)

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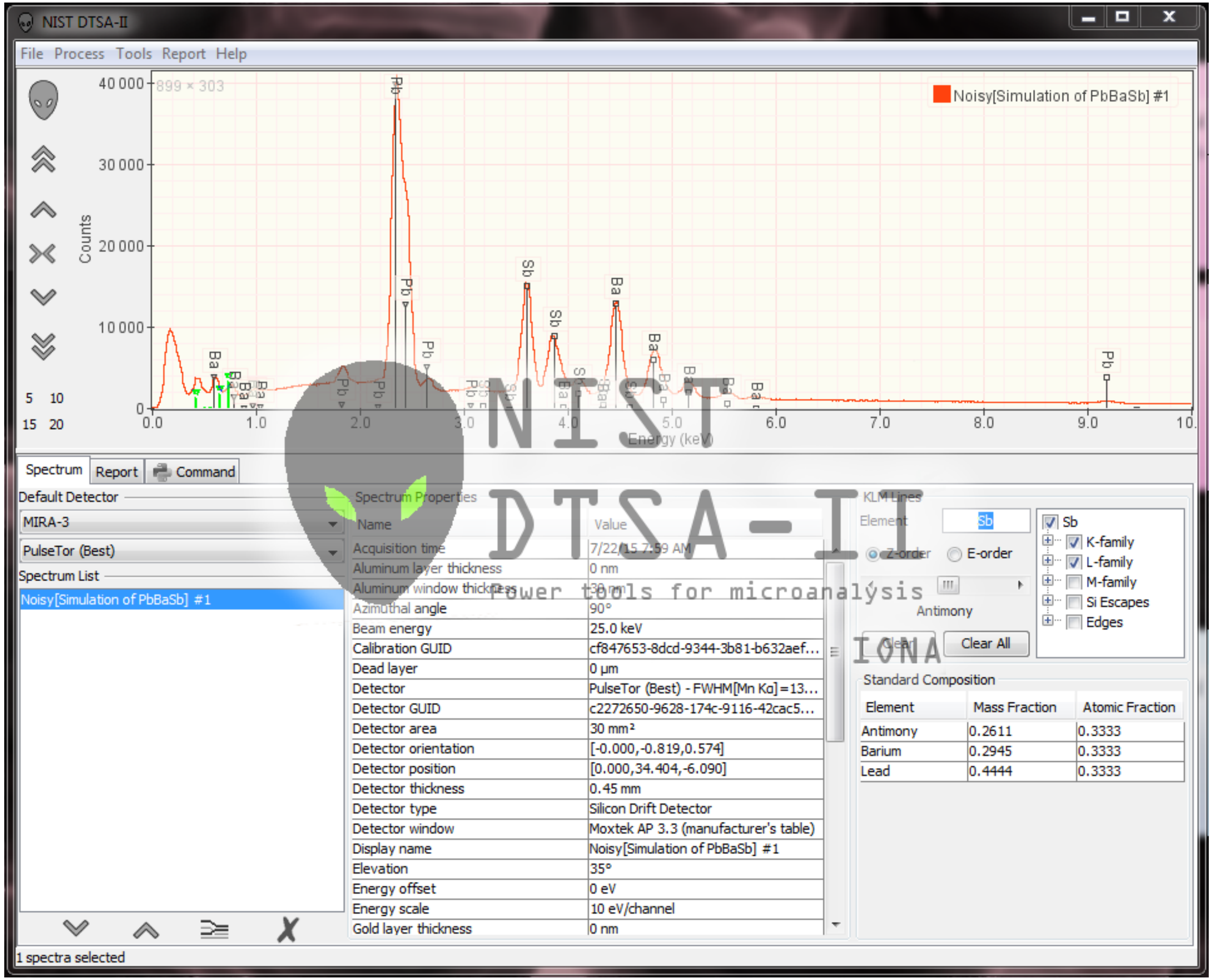
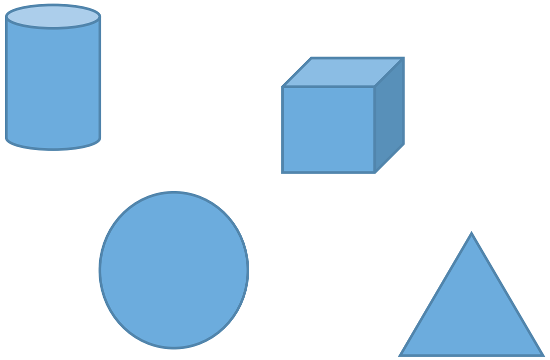
Source: SWGGSR – Guide for Primer Gunshot Residue Analysis by Scanning Electron Microscope / Energy Dispersive X-ray Spectrometer.



NIST DTSA-II

- Quantitative EDS spectrum analysis
- EDS spectrum simulation
  - Analytical models
  - Monte Carlo models
- Experiment optimization



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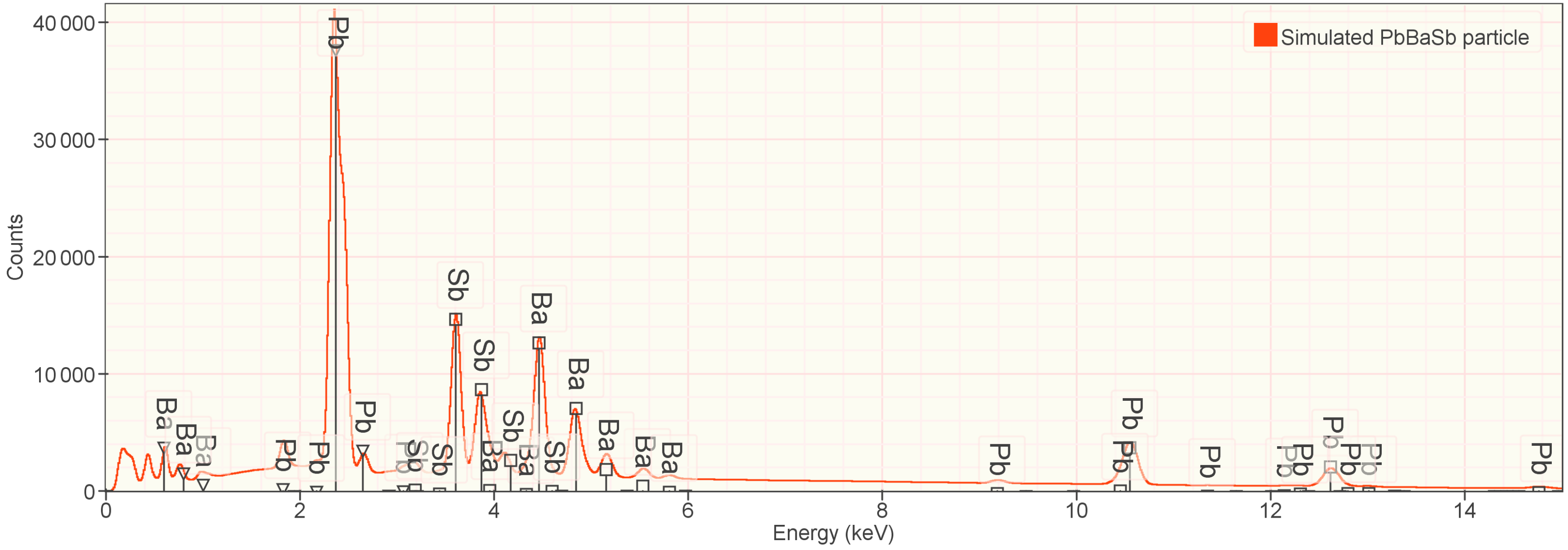
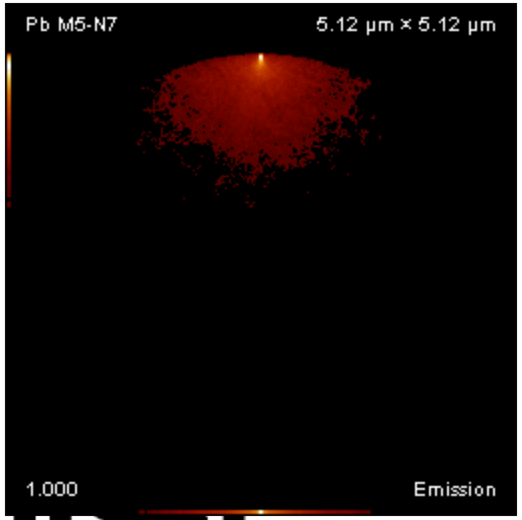
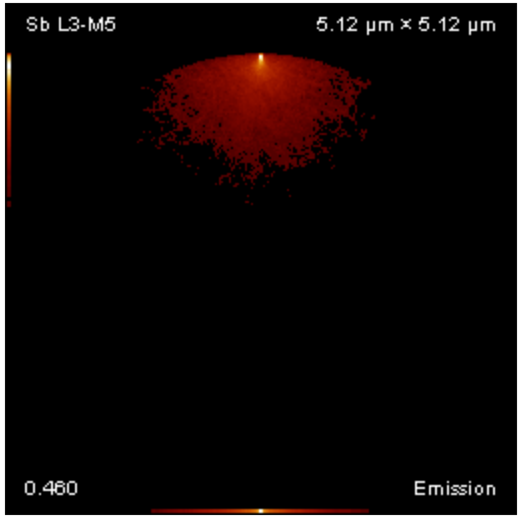
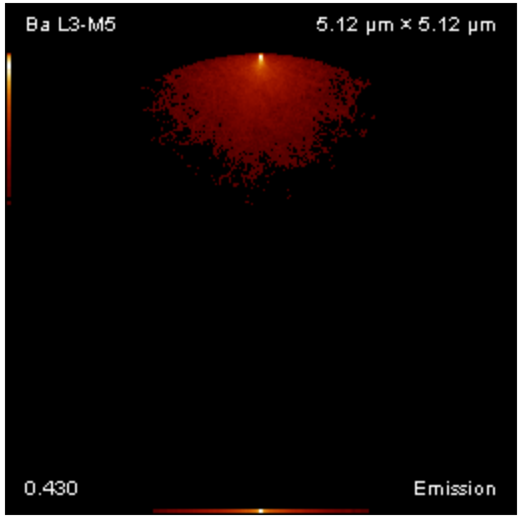
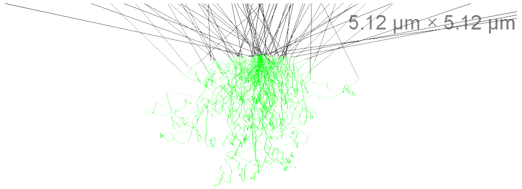
Google: "NIST DTSA-II" or http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html


Simulated PbBaSb particle
Counts
Energy (keV)
Pb
Sb
Ba


Pb M5-N7
5.12 µm × 5.12 µm
1.000
Emission


Sb L3-M5
5.12 µm × 5.12 µm
0.460
Emission

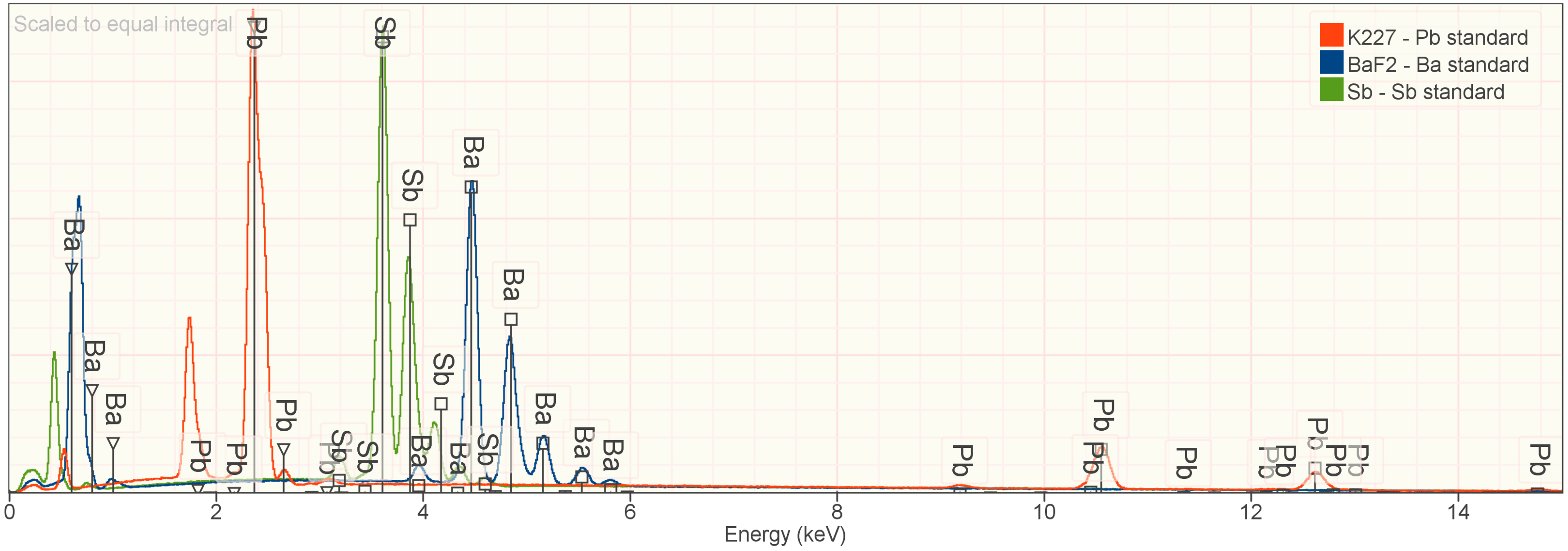

Ba L3-M5
5.12 µm × 5.12 µm
0.430
Emission


5.12 µm × 5.12 µm

Demonstration

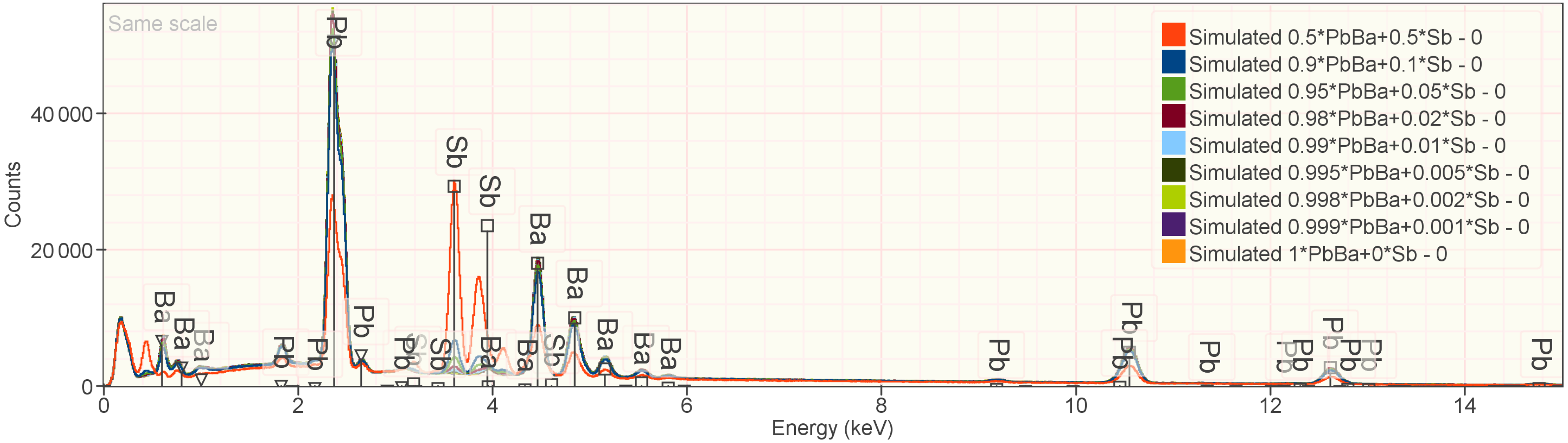
- Consider Sb in a Pb-Ba-Sb particle
  - Simulate spectrum from (1-k) PbBa + k Sb
    - for k = (0.5, 0.1, 0.05, 0.02, 0.01, 0.005, 0.002, 0.001)
  - Fit spectra with BaF_2, K227 (lead glass), Sb standard spectra

Standards

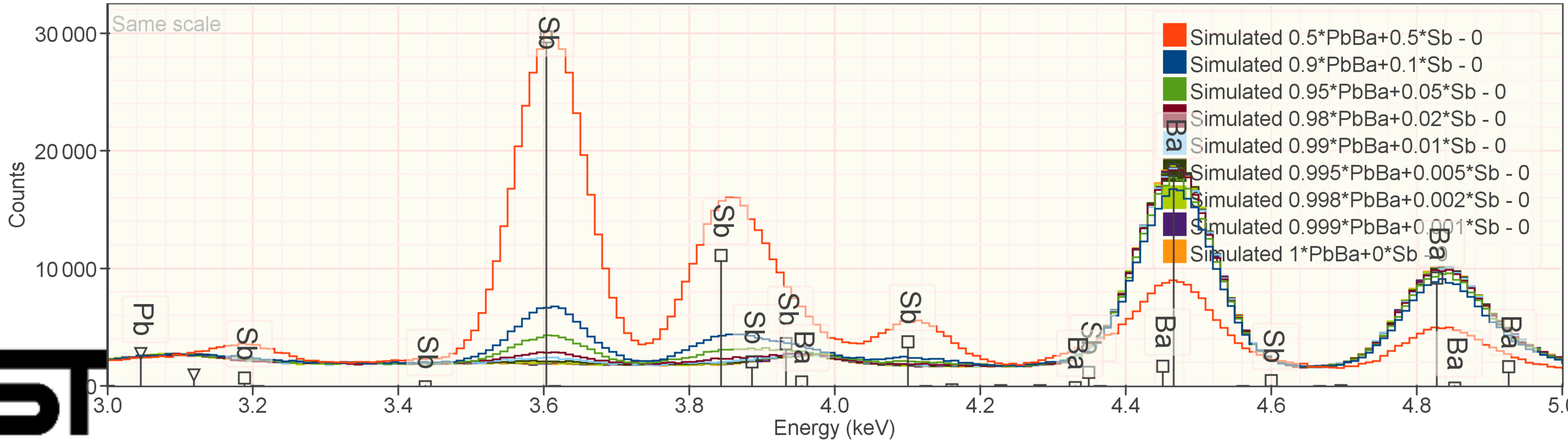


Scaled to equal integral
K227 - Pb standard
BaF2 - Ba standard
Sb - Sb standard
Pb
Sb
Ba
Energy (keV)
0
2
4
6
8
10
12
14

Unknowns



Same scale
Counts
Energy (keV)
Simulated 0.5*PbBa+0.5*Sb - 0
Simulated 0.9*PbBa+0.1*Sb - 0
Simulated 0.95*PbBa+0.05*Sb - 0
Simulated 0.98*PbBa+0.02*Sb - 0
Simulated 0.99*PbBa+0.01*Sb - 0
Simulated 0.995*PbBa+0.005*Sb - 0
Simulated 0.998*PbBa+0.002*Sb - 0
Simulated 0.999*PbBa+0.001*Sb - 0
Simulated 1*PbBa+0*Sb - 0



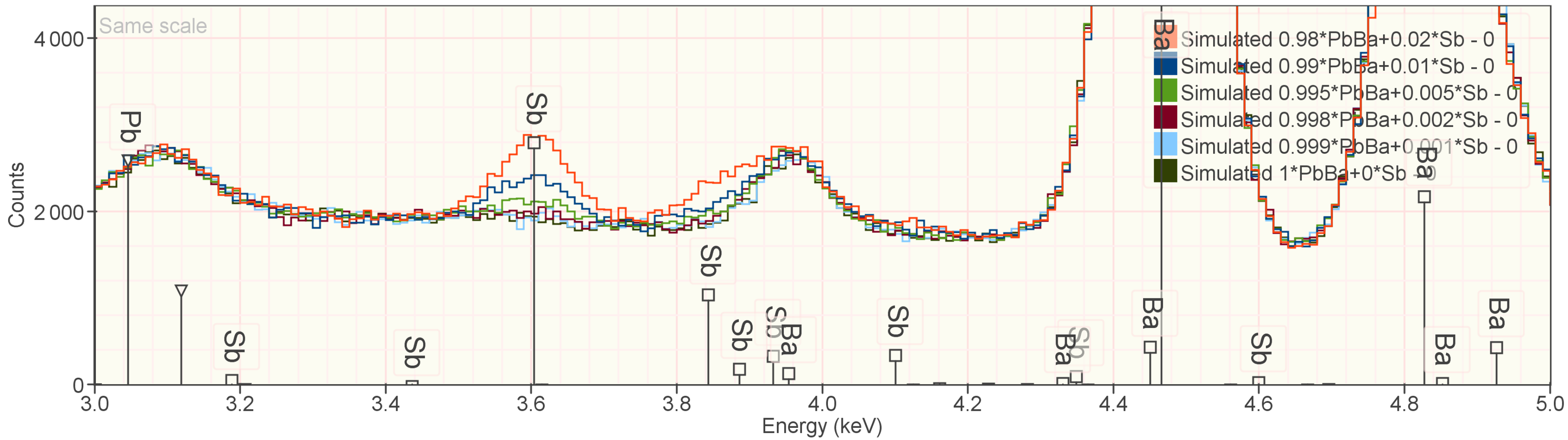
Same scale
Counts
Energy (keV)
Simulated 0.5*PbBa+0.5*Sb - 0
Simulated 0.9*PbBa+0.1*Sb - 0
Simulated 0.95*PbBa+0.05*Sb - 0
Simulated 0.98*PbBa+0.02*Sb - 0
Simulated 0.99*PbBa+0.01*Sb - 0
Simulated 0.995*PbBa+0.005*Sb - 0
Simulated 0.998*PbBa+0.002*Sb - 0
Simulated 0.999*PbBa+0.001*Sb - 0
Simulated 1*PbBa+0*Sb - 0

Standards

Element	Material	Req. References	Preferred ROI	Beam Energy	Spectrum
	CaF2				
C					
Sl					
B					
Pl					

Results

Spectrum	Quantity	Ca			Sb			Ba			Pb			Sum
Simulated 0.5 PbBa+0.5 Sb Bulk	Line	Ca K-family			Sb L3-M5 + 11 others			Ba L3-M5 + 5 others			Pb Lα			
	Z · A · F	-	-	-	1.041	0.774	1.004	1.087	0.650	0.999	1.043	0.993	0.998	
	k-ratios	0.0000	±	0.0007	0.4145	±	0.0008	0.1879	±	0.0008	0.4268	±	0.0047	
D-H = ? keV	mass fraction	0.0000	±	0.0007(I[unk,Ca]) [0.0007]	0.5110	±	0.0004(I[std,Sb]) 0.0009(I[unk,Sb]) 0.0036([μ/ρ]) $1.9 \cdot 10^{-5}$(η) [0.0037]	0.2079	±	0.0001(I[std,Ba]) 0.0009(I[unk,Ba]) 0.0077([μ/ρ]) $4.7 \cdot 10^{-6}$(η) [0.0078]	0.3066	±	0.0005(I[std,Pb]) 0.0034(I[unk,Pb]) 0.0002([μ/ρ]) $9.9 \cdot 10^{-7}$(η) [0.0034]	1.0255
I = 1.000 nA	norm(mass fraction)	0.0000	±	0.0007	0.4983	±	0.0036	0.2028	±	0.0076	0.2989	±	0.0033	-
LT = 60.0 s	atomic fraction	0.0000	±	0.0026	0.5837	±	0.0042	0.2106	±	0.0079	0.2058	±	0.0023	
Residual	C:\Users\nritchie.NIST\AppData\Local\NIST\NIST DTSA-II Reports\2015\July\7-Jul-2015\residual6292583148720905155.msa													
Simulated 0.9 PbBa+0.1 Sb Bulk	Line	Ca K-family			Sb L3-M5 + 11 others			Ba L3-M5 + 5 others			Pb Lα			
	Z · A · F	-	-	-	1.075	0.641	1.007	1.122	0.688	0.999	1.074	0.990	0.999	
	k-ratios	0.0000	±	0.0004	0.0726	±	0.0004	0.3845	±	0.0010	0.7978	±	0.0061	
D-H = ? keV	mass fraction	0.0000	±	0.0004(I[unk,Ca]) [0.0004]	0.1039	±	$7.6 \cdot 10^{-5}$(I[std,Sb]) 0.0006(I[unk,Sb]) 0.0013([μ/ρ]) $4.1 \cdot 10^{-6}$(η) [0.0014]	0.3885	±	0.0003(I[std,Ba]) 0.0010(I[unk,Ba]) 0.0038([μ/ρ]) $9.9 \cdot 10^{-6}$(η) [0.0040]	0.5575	±	0.0009(I[std,Pb]) 0.0041(I[unk,Pb]) 0.0002([μ/ρ]) $2.0 \cdot 10^{-6}$(η) [0.0042]	1.0500
I = 1.000 nA	norm(mass fraction)	0.0000	±	0.0004	0.0990	±	0.0014	0.3700	±	0.0038	0.5310	±	0.0040	-
LT = 60.0 s	atomic fraction	0.0000	±	0.0016	0.1339	±	0.0018	0.4439	±	0.0045	0.4221	±	0.0032	
Residual	C:\Users\nritchie.NIST\AppData\Local\NIST\NIST DTSA-II Reports\2015\July\7-Jul-2015\residual4290737460627 0039.msa													

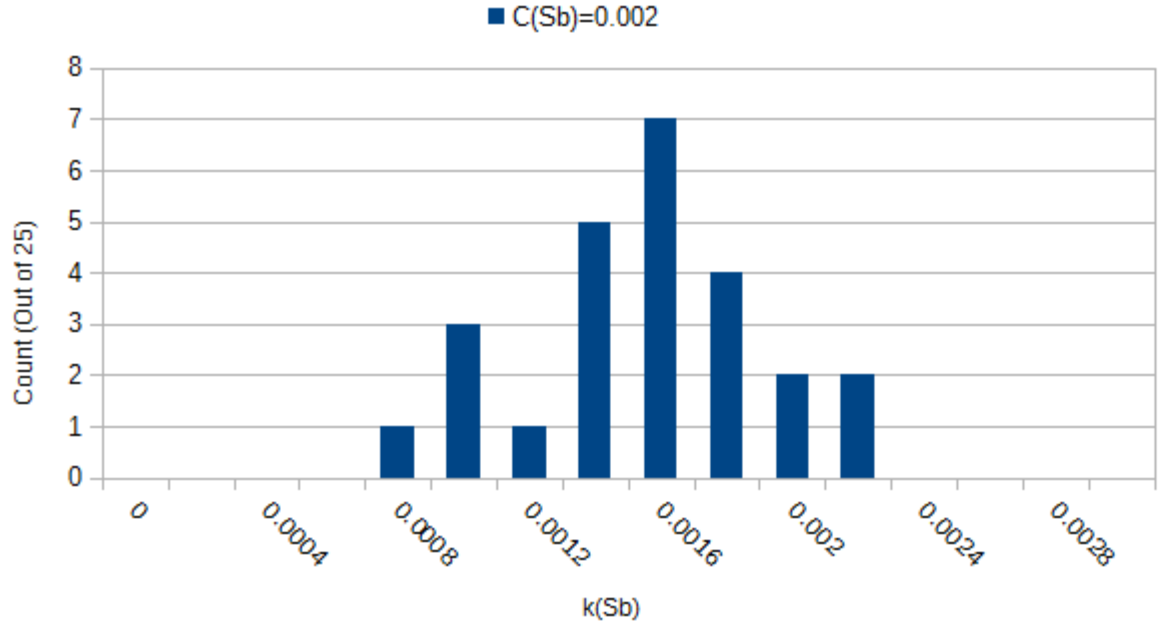


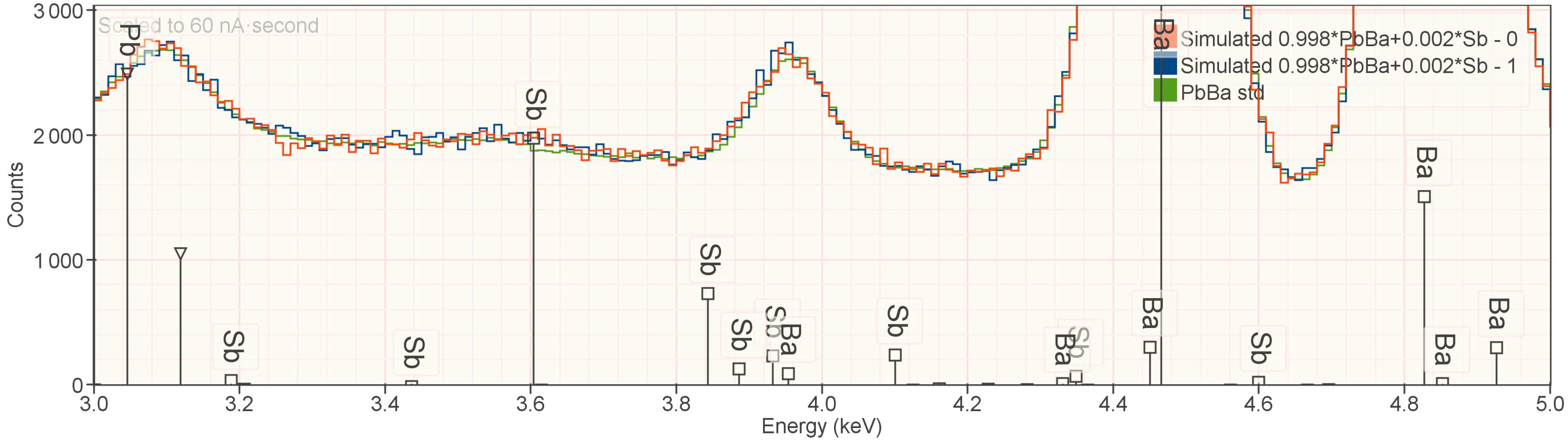
K-ratio

Std Dev of k (25 reps)

Uncertainty estimate (from MLLSQ fit)

C(Sb)	k(Sb)	dk(Sb)	[k/σ](Sb)	σ(Sb)	[k/σ](Sb)
50.0%	0.41416	0.00096	429.6	0.00080	517.7
10.0%	0.07267	0.00054	133.9	0.00040	181.7
5.0%	0.03575	0.00047	75.3	0.00040	89.4
2.0%	0.01416	0.00048	29.3	0.00030	47.2
1.0%	0.00702	0.00036	19.7	0.00030	23.4
0.5%	0.00351	0.00029	12.2	0.00030	11.7
0.2%	0.00150	0.00037	4.1	0.00030	5.0
0.1%	0.00049	0.00044	1.1	0.00030	1.6
0.0%	0.00012	0.00025	0.5	0.00030	0.4


C(Sb)=0.002
Count (Out of 25)
0
1
2
3
4
5
6
7
8
0
0.0004
0.0008
0.0012
0.0016
0.002
0.0024
0.0028
k(Sb)


Scaled to 60 nA·second
Simulated 0.998*PbBa+0.002*Sb - 0
Simulated 0.998*PbBa+0.002*Sb - 1
PbBa std
Counts
Energy (keV)
0
1 000
2 000
3 000
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
Pb
Sb
Ba

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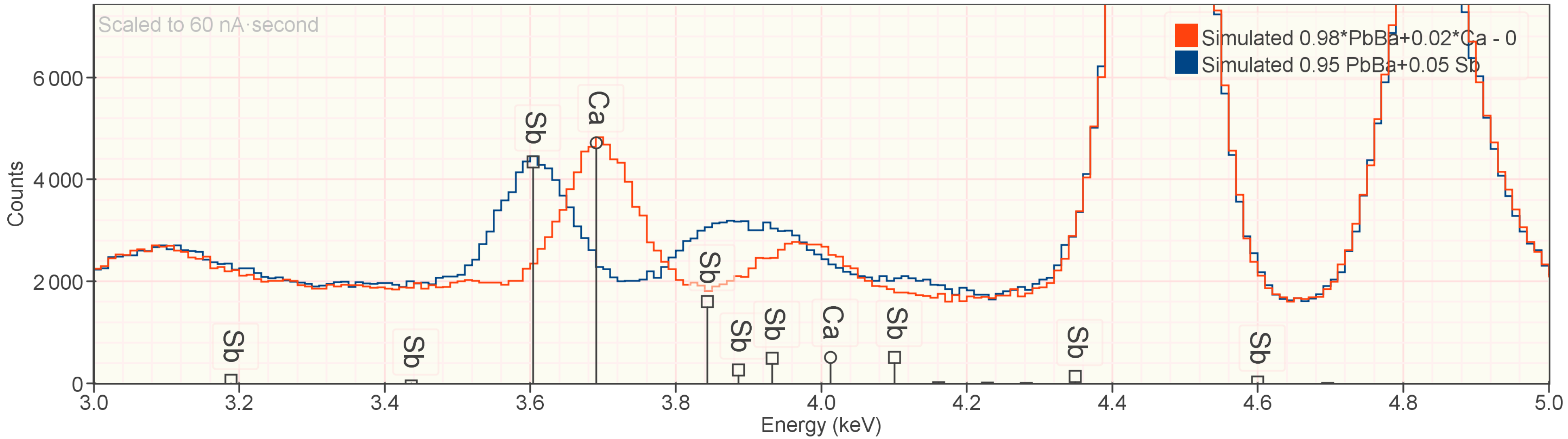
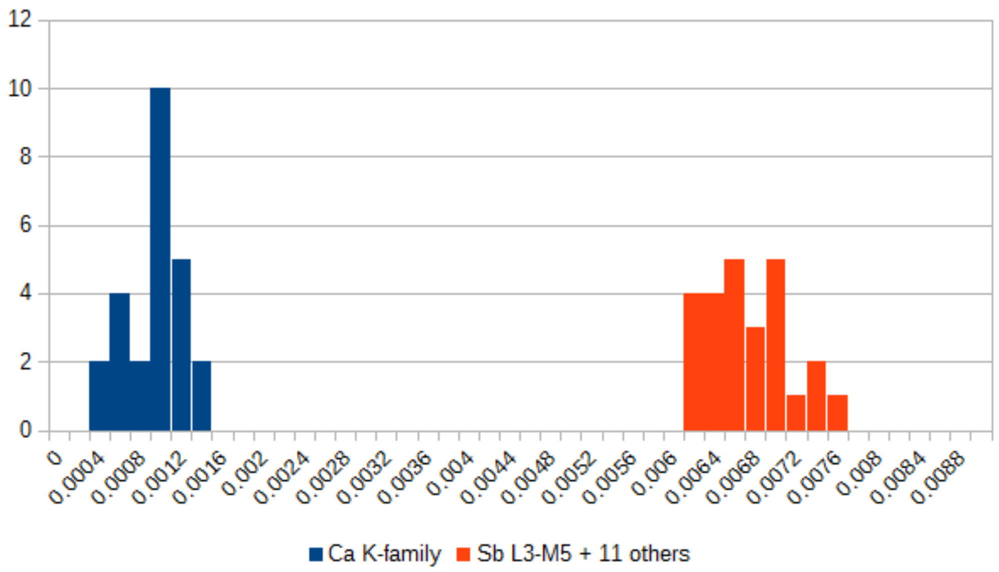
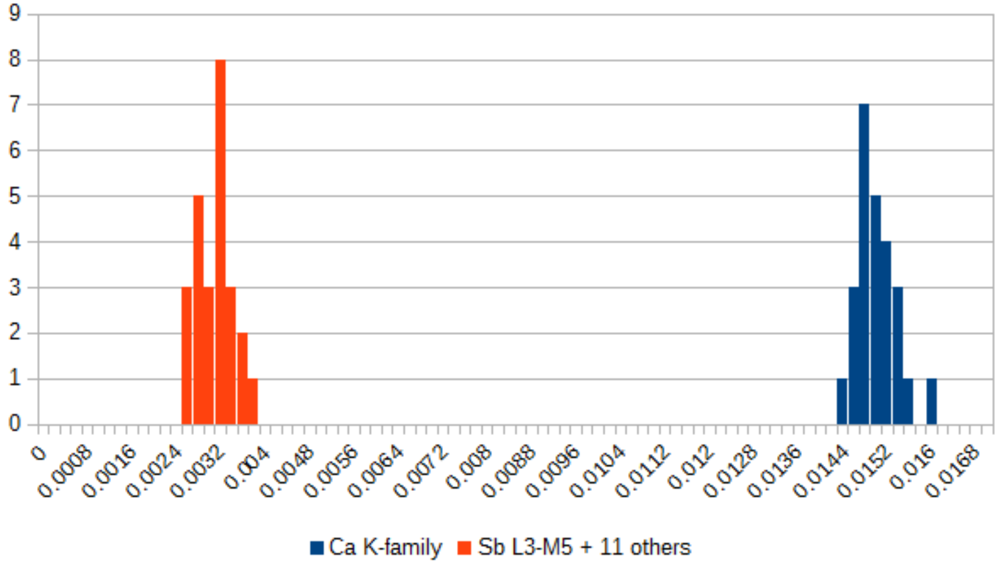
Ca / Sb interference



Mixtures of Sb and Ca in Pb-Ba



0.001 Ca and 0.01 Sb



0.01 Ca and 0.005 Sb

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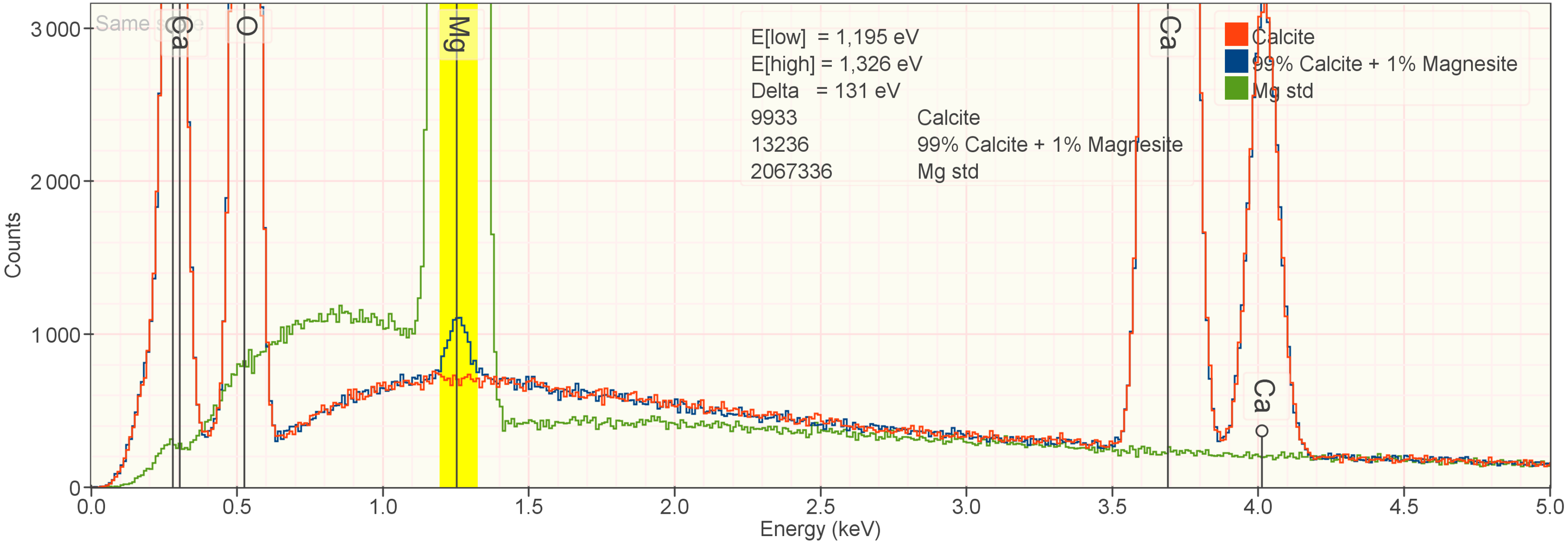
A quick lesson in what "detectable" means…



$$C_{DL} = \frac{3\sqrt{N(B)}}{\sqrt{n}\,(N_s - N(B))}\,C_S = \frac{3\sqrt{10^3}}{\sqrt{1}\,(2.1\times10^5 - 10^3)}\,1 = 4.5\times10^{-4} = 0.05\%$$

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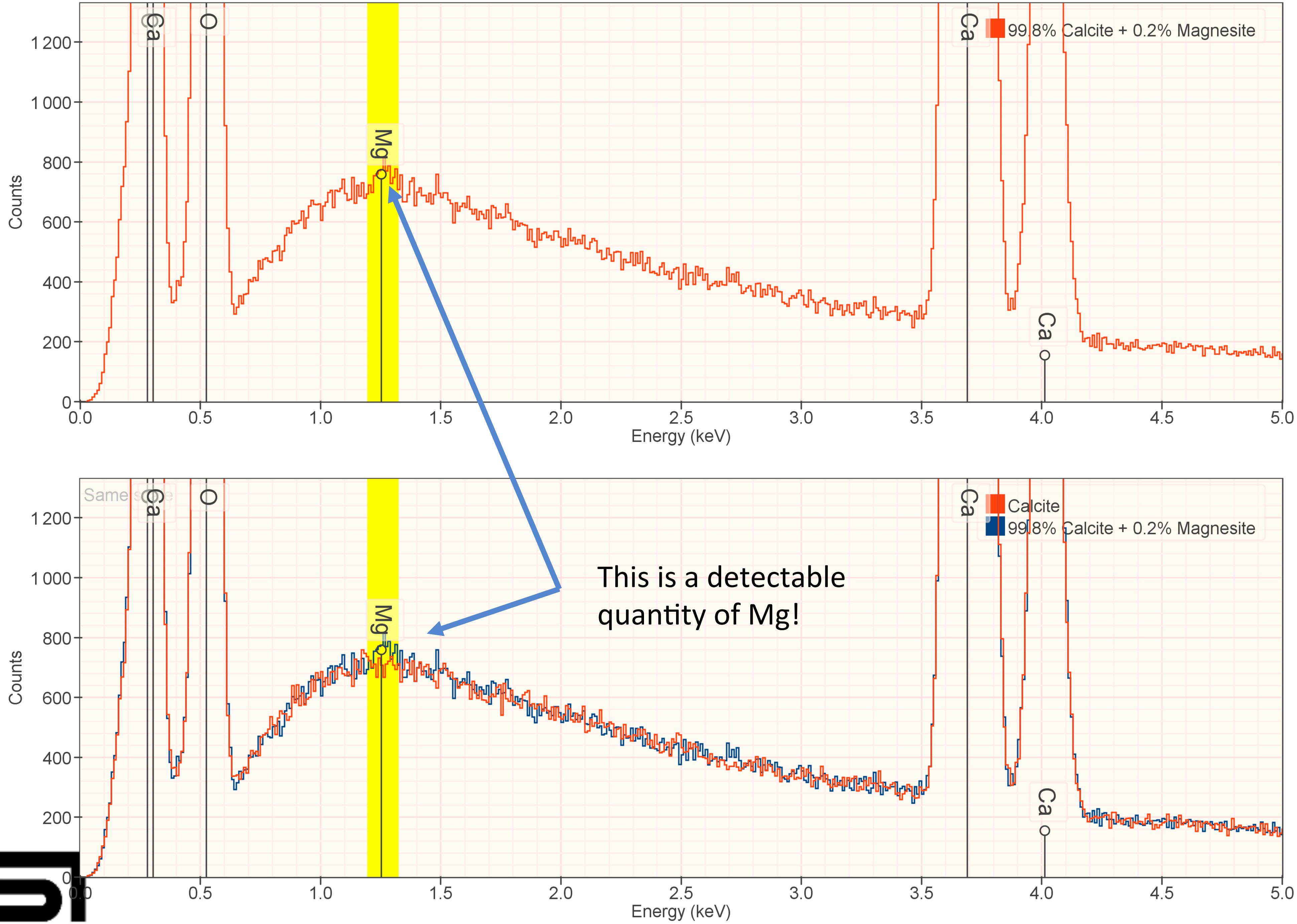
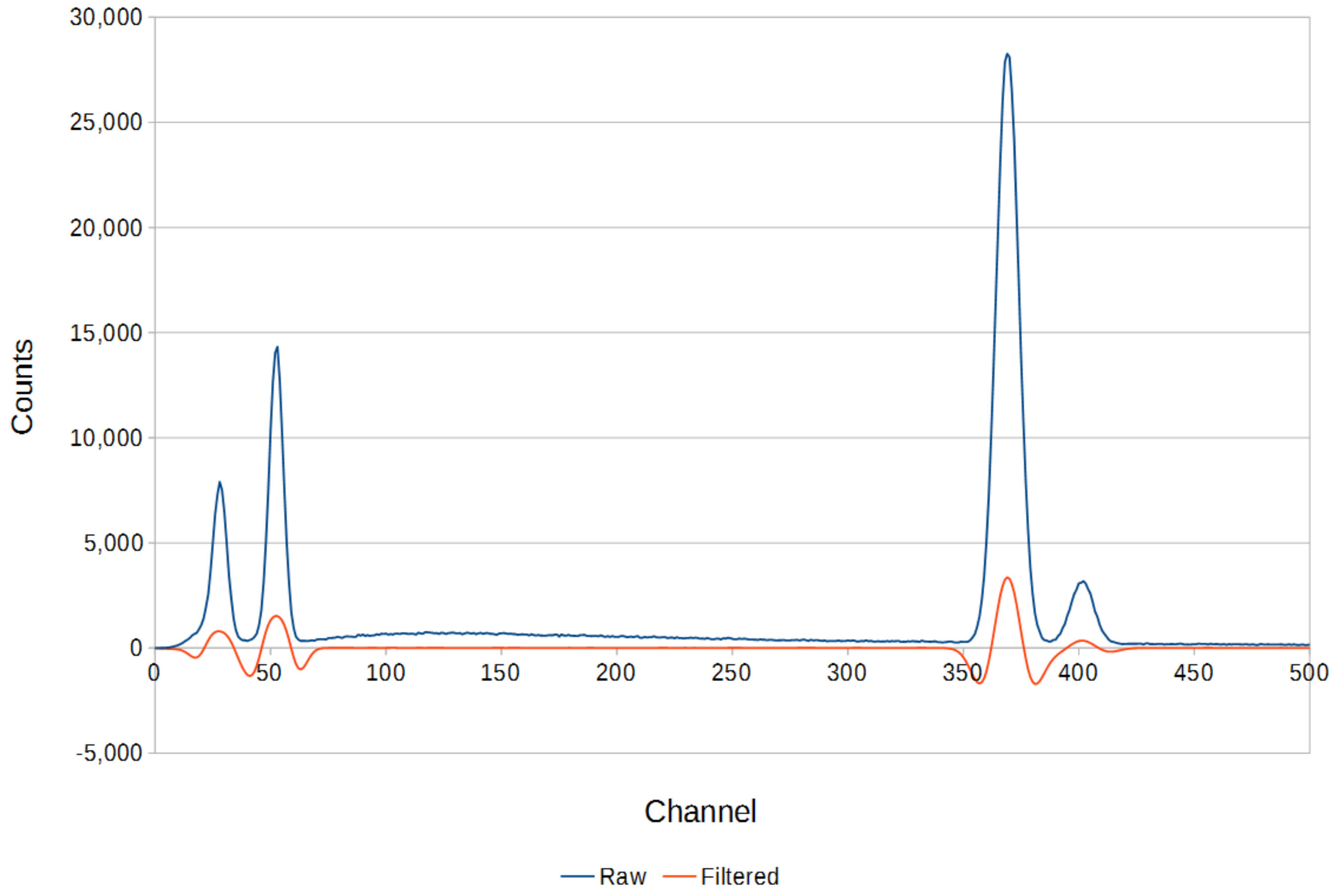
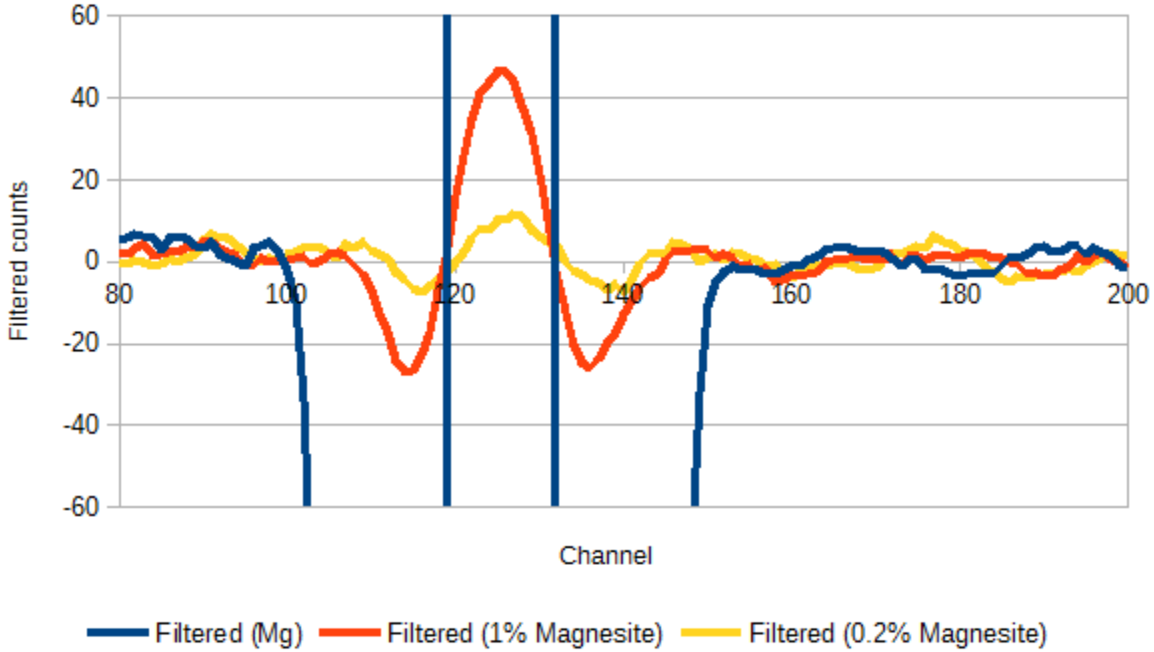
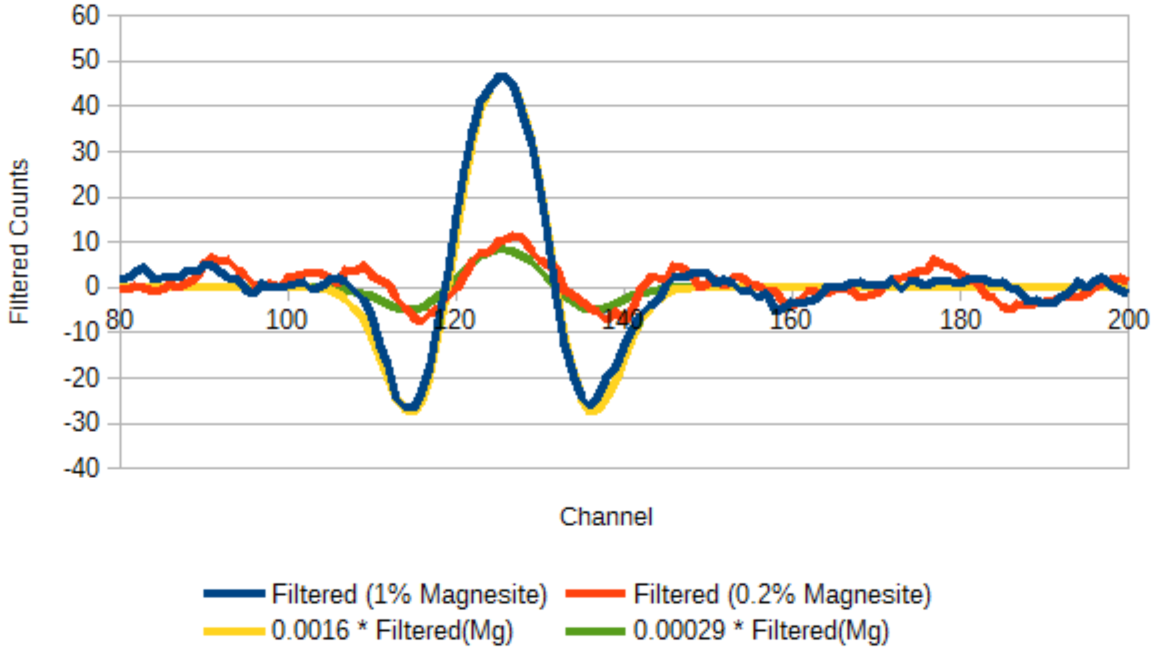

99.8% Calcite + 0.2% Magnesite
Calcite
Same scale
Ca
O
Mg
Counts
Energy (keV)
This is a detectable quantity of Mg!

MLLSQ Filter Fitting





Filtered spectra near Mg K



Filtered spectra near Mg K
with fitted Mg standard

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Results

Spectrum	Quantity	C			O			Mg			Ca			
99% Calcite + 1% Magnesite Bulk	Line	C All			O All			Mg All			Ca K-family			
	Z · A · F	1.247	0.429	1.001	0.989	0.340	0.999	0.951	0.604	1.001	0.931	1.030	1.000	
	k-ratios	0.0805	±	0.0003	0.3501	±	0.0011	0.0016	±	0.0001	0.7322	±	0.0017	
D-H = 14.831 keV	mass fraction	0.1503	±	0.0002(I[std,C]) 0.0006(I[unk,C]) 0.0165([μ/ρ]) 0.0002(η) [0.0165]	0.4918	±	0.0009(I[std,O]) 0.0012(I[unk,O]) 0.0121([μ/ρ]) 0.0002(η) [0.0122]	0.0028	±	$1.9\cdot10^{-6}$(I[std,Mg]) 0.0001(I[unk,Mg]) $1.1\cdot10^{-5}$([μ/ρ]) $3.3\cdot10^{-7}$(η) [0.0001]	0.3921	±	0.0006(I[std,Ca]) 0.0007(I[unk,Ca]) 0.0001([μ/ρ]) $6.8\cdot10^{-6}$(η) [0.0009]	1.0369
I = 1.000 nA	norm(mass fraction)	0.1449	±	0.0160	0.4742	±	0.0118	0.0027	±	0.0001	0.3782	±	0.0009	
LT = 60.0 s	atomic fraction	0.2354	±	0.0259	0.5783	±	0.0144	0.0021	±	0.0001	0.1841	±	0.0004	
Residual	C:\Users\nritchie.NIST\AppData\Local\NIST\NIST DTSA-II Reports\2015\July\8-Jul-2015\residual5794580825505575085.msa													
99.8% Calcite + 0.2% Magnesite Bulk	Line	C All			O All			Mg All			Ca K-family			
	Z · A · F	1.249	0.431	1.001	0.990	0.335	0.999	0.952	0.603	1.001	0.931	1.030	1.000	
	k-ratios	0.0818	±	0.0003	0.3441	±	0.0011	0.0003	±	0.0001	0.7419	±	0.0017	
D-H = 14.970 keV	mass fraction	0.1520	±	0.0002(I[std,C]) 0.0006(I[unk,C]) 0.0168([μ/ρ]) 0.0002(η) [0.0168]	0.4890	±	0.0009(I[std,O]) 0.0012(I[unk,O]) 0.0121([μ/ρ]) 0.0002(η) [0.0122]	0.0006	±	$4.0\cdot10^{-7}$(I[std,Mg]) 0.0001(I[unk,Mg]) $2.4\cdot10^{-6}$([μ/ρ]) $6.8\cdot10^{-8}$(η) [0.0001]	0.3972	±	0.0006(I[std,Ca]) 0.0007(I[unk,Ca]) 0.0001([μ/ρ]) $6.9\cdot10^{-6}$(η) [0.0009]	1.0387
I = 1.000 nA	norm(mass fraction)	0.1463	±	0.0161	0.4707	±	0.0117	0.0006	±	0.0001	0.3824	±	0.0009	-
LT = 60.0 s	atomic fraction	0.2381	±	0.0263	0.5750	±	0.0143	0.0004	±	0.0001	0.1865	±	0.0004	
Residual	C:\Users\nritchie.NIST\AppData\Local\NIST\NIST DTSA-II Reports\2015\July\8-Jul-2015\residual5488806498784311 25.msa													
Notes	Uncertainties are 1 σ and labeled by source. (I[std|unk]: Count statistics[standard|unknown], [μ/ρ]: Absorption correction, η: Backscatter correction, []: combined)													

Mg
Mg All
0.951 0.604 1.001
0.0016 ± 0.0001
$1.9\cdot10^{-6}$(I[std,Mg])

0.0016 ± 0.0001 = 16 σ

Mg All
0.952 0.603 1.001
0.0003 ± 0.0001
$4.0\cdot10^{-7}$(I[std,Mg])

0.0003 ± 0.0001 = 3 σ

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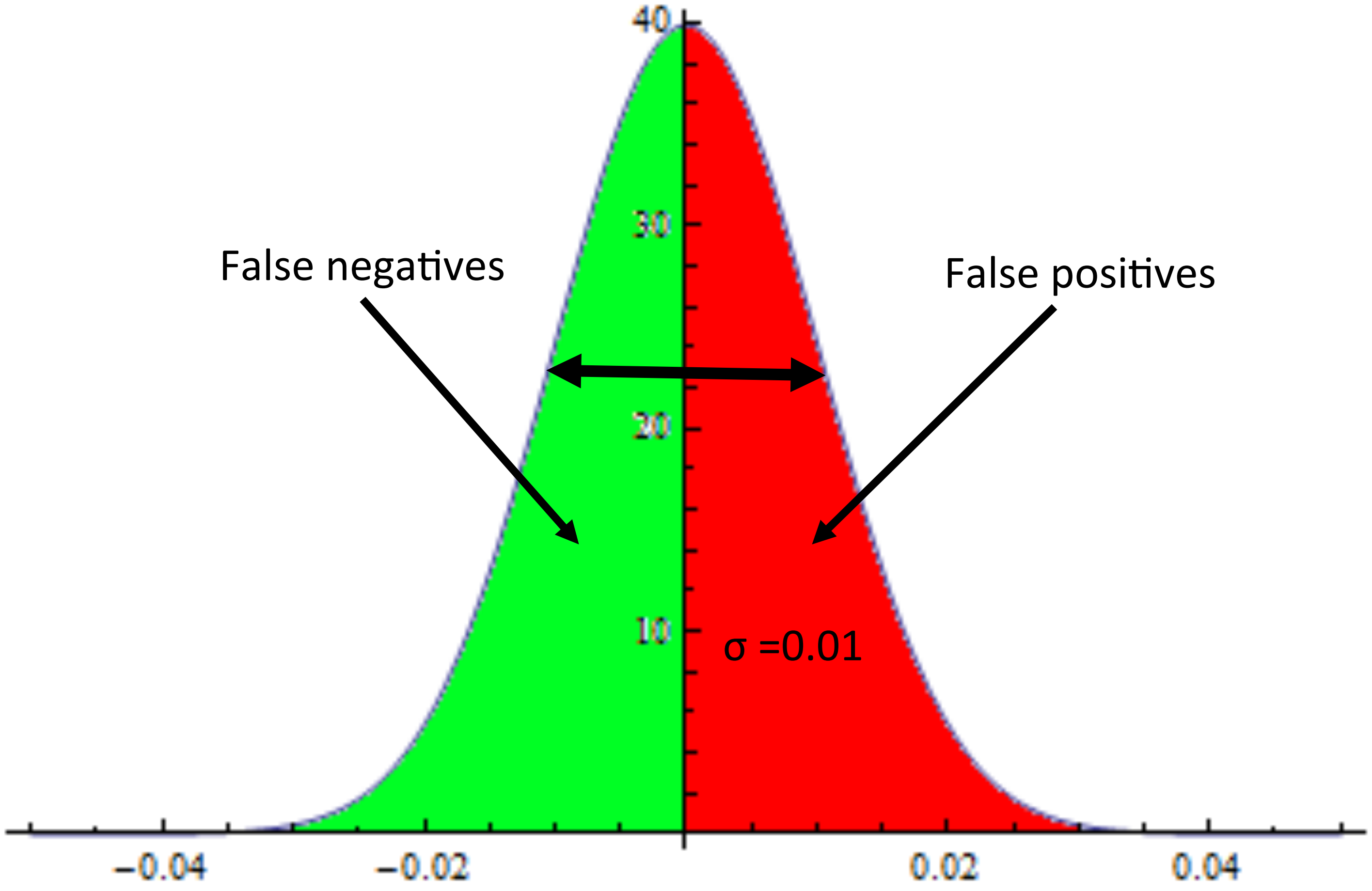
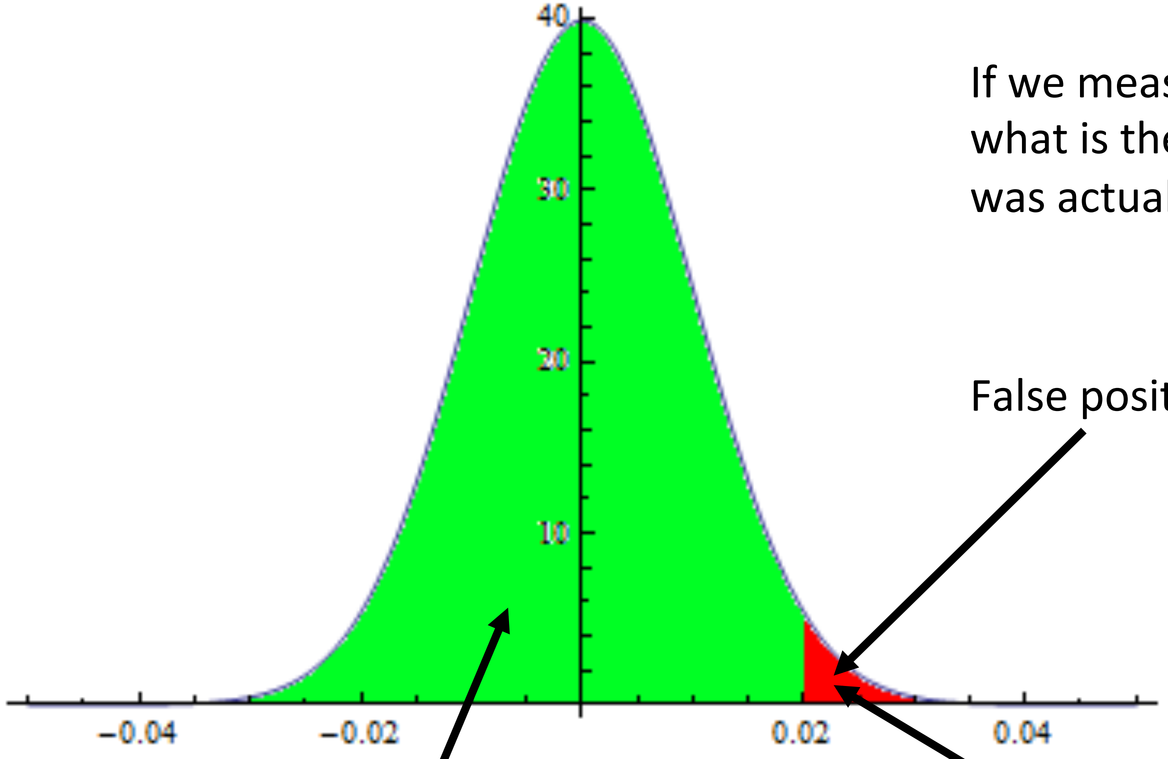
True value = 0


False negatives
False positives
40
30
20
10
σ =0.01
−0.04
−0.02
0.02
0.04



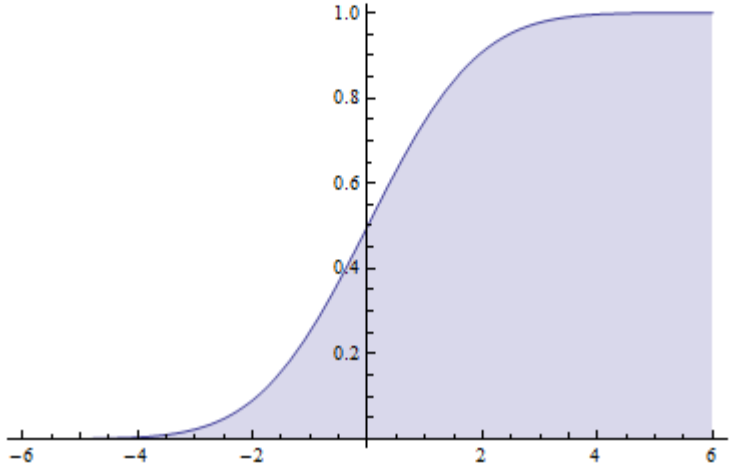
If we measure a value of 2 σ or larger, what is the chance that the true value was actually zero?

False positives

CDF[2σ] = 0.97725

1-CDF[2σ] = 1 - 0.97725 = 0.02275

~2% for 2 σ

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CDF[NormalDistribution[μ, σ], x]
```

$$\frac{1}{2}\,\mathrm{Erfc}\left[\frac{-x+\mu}{\sqrt{2}\,\sigma}\right]$$

	Limit	Error rate
Decision	$C_C = 1.64\,\sigma$	5 %
Detection	$C_D = 3.29\,\sigma$	0.05 %
Quantification	$C_Q = 10\,f\,\sigma$	

Currie, L. A., “Limits for Qualitative Detection and Quantitative Determination. Applications to Radichemistry” Anal Chem. 40: 586 (1968)

Conclusion

- Quantification of particles is difficult
  - Estimating the mass fraction of an element in a particle
- Fortunately, quantification isn't necessary to determine the presence of an element
  - K-ratios are sufficient
- Linear regression using standard spectra is our friend
  - Linear regression provides uncertainty metrics
- Uncertainty metrics can be used to make defensible, quantitative statements about the presence or absence of an element
  - Even in the presence of interfering elements!

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