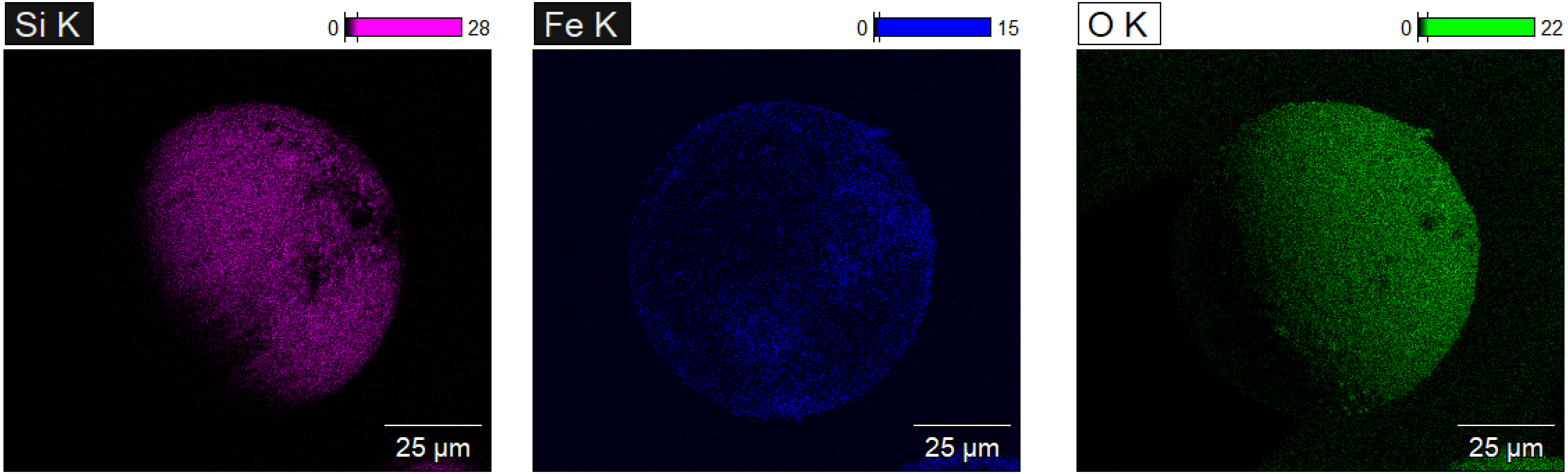
X ray analysis in the TEM and SEM.

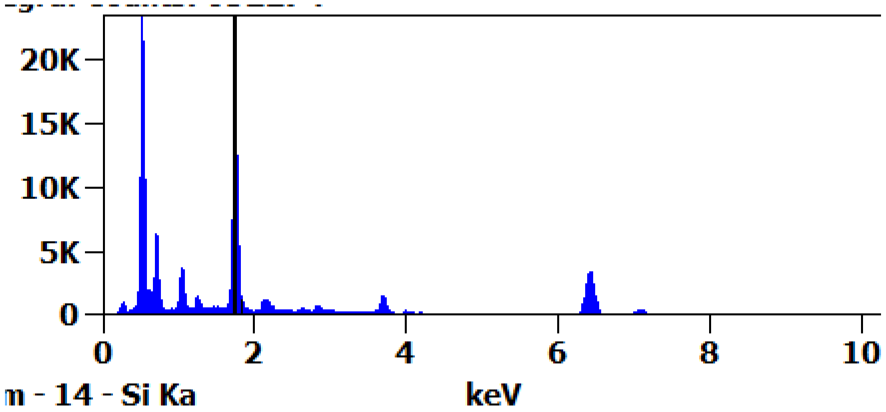


Iron oxide coated glass beads in Quanta 3D SEM using drift controlled Noran EDS

Jeff Nason environmental engineering group, OSU

Terminology

- X ray analysis in SEM is the same as :
- EDS energy dispersive spectroscopy
- EDX* energy dispersive x ray
- WDS wavelength dispersive spectroscopy, higher resolution cousin of EDS.



Energy Dispersive spectra of Figure 1 with characteristic 124 -130 eV resolution.

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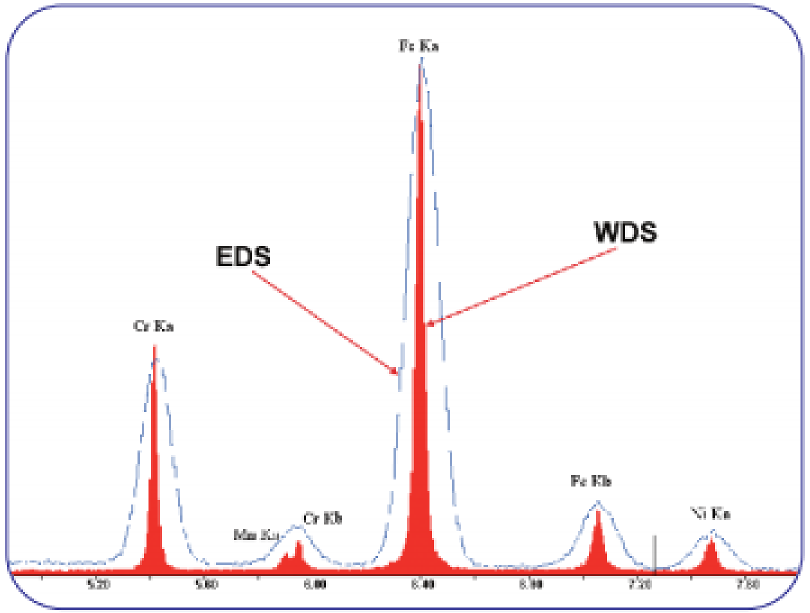
* Also EDAX which is a company name EDAX inc.

So, why would we bother with a lower resolution technique like EDS? When WDS is much higher resolution?

- WDS uses a crystal for the different energy, wavelength regions. You have to select the crystal before starting the analysis and there are 4 crystals. So, to get a complete scan you have to move the four crystals in and out of the x-ray path. This is slow compared with EDS.
- EDS detection systems are more efficient and require less beam and present less sample damage.
- EDS systems work well on standard SEM. WDS requires a special type of SEM called a microprobe. This type of SEM is tailored for high currents and fits the four crystals nicely in the system. An EDS-WDS system is available from Oxford, EDAX for conventional SEM, they are not commonly used but can be help in situations where overlap of peaks occurs, say Si(K) with Ta(L), or Mo(M) and S(K) lines.

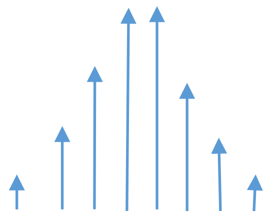


Example of spectra illustrating the resolution improvements of WDS versus EDS using a stainless steel example.

From EDAX inc literature on Neptune system integrated EDS and WDS.

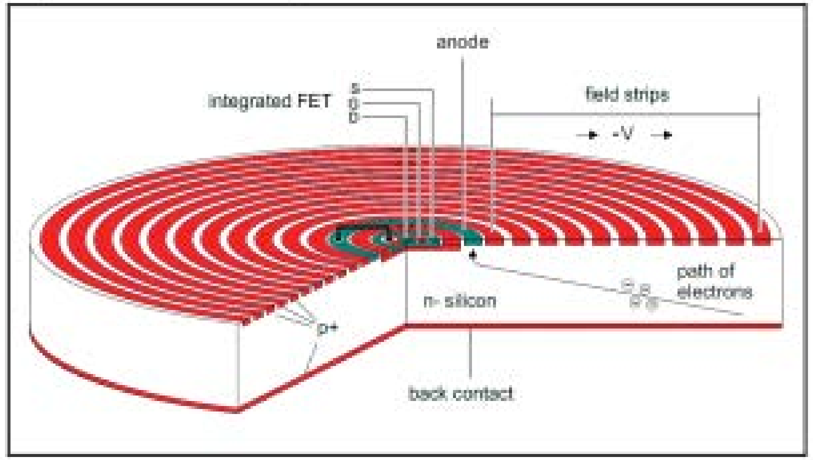
Basics of detecting x-ray energy.

- When the X ray hits a detector it creates a shower of electrons or electron hole pairs. The total number of these individual events that comprises the show is proportional to the X ray energy.
- Remember that most X rays have thousands of electron volts kinetic energy. While it only takes about 1 eV to create a free electron in a silicon detector. So, we get hundreds to free electrons per x-ray!
- Higher energy x ray creates a bigger shower of electrons and these electrons. Lower energy x-rays create less of a shower.
- So, if we add up all the pulses in a shower we get an intensity proportional to x-ray energy. This allows us to identify the element that created the shower in the detector.

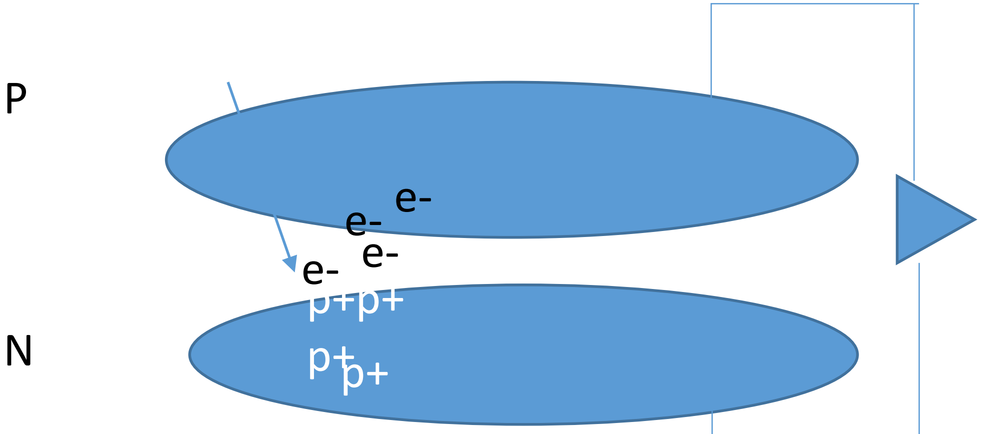


What pulses from an x ray look like in real time on a fast oscilloscope incident upon a silicon diode.

Silicon drift detector SDD vs Lithium drifted Si(Li) detectors



Credit to Thermo Fisher for drawing, same detector as on OSU Quanta 3D



We have this detector on the Quanta 600

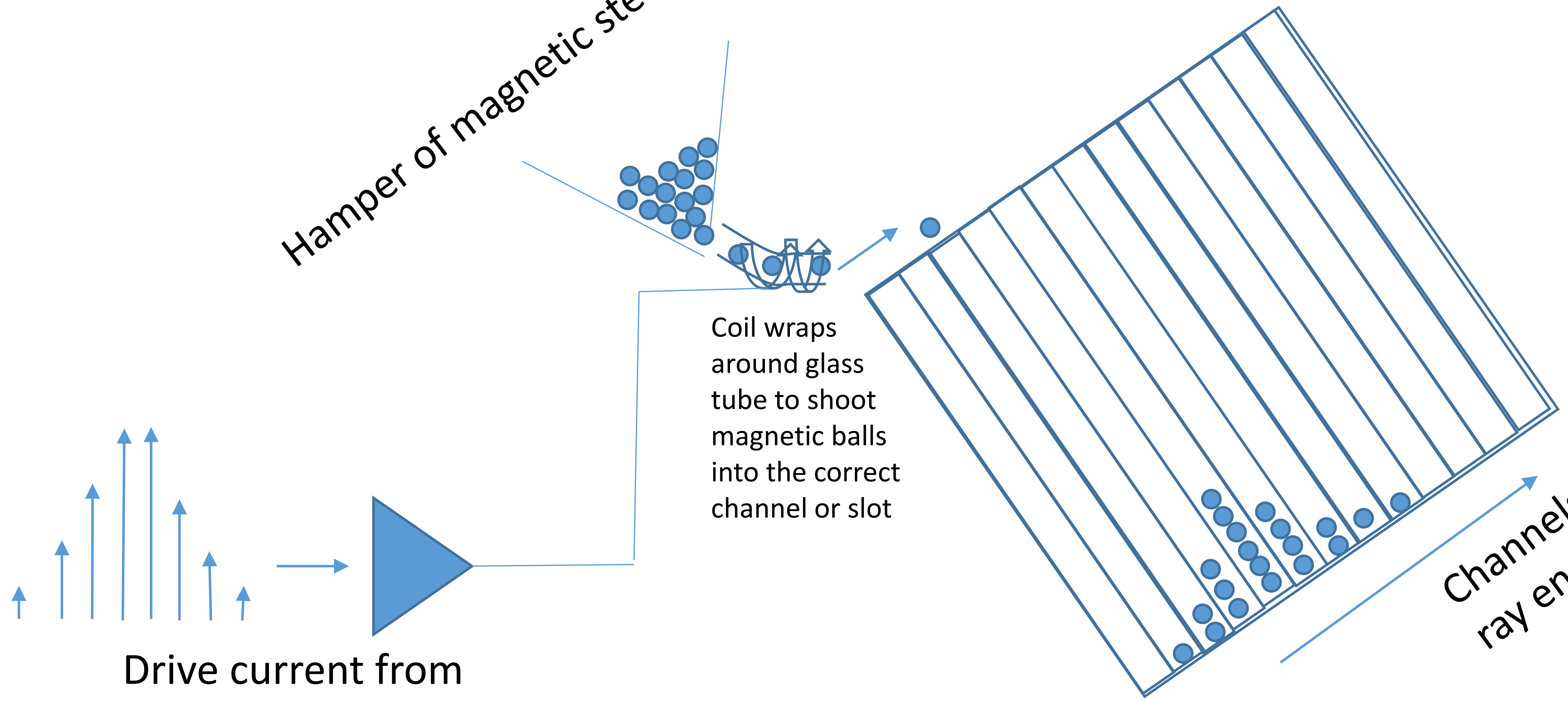
SDD detectors have always been very fast but suffered from non linear issues, distortion of low and high energy peaks. However, recent advances in design in last 10 years by PN Devices of Germany have made SDD the standard. PN devices probably makes 90% of SDD in world, all manufactures use them!

Lithium drifting Si(Li) makes the region between intrinsic semiconductor and so X ray hits it and charge separates to two plates, N and P side of junction. Capacitance is very high making it a slow detector but is highly linear.

Peter Eschbach

Oregon State University

Multi Channel Analyzer, MCA , action and how it works



Hamper of magnetic steel balls

Coil wraps around glass tube to shoot magnetic balls into the correct channel or slot

Drive current from pulse height of detected X ray

Channels are X ray energy

The kicksorter, an early version of the Multi Channel analyzer,
From Canberra, early MCA manufacturer. They credit Frazier Bronson with the original sketch

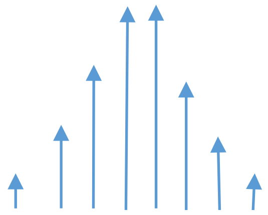
Peter Eschbach

Oregon State University

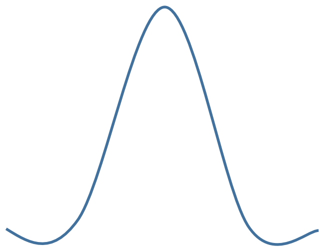
Oregon State University
OSU Electron Microscopy Facility

The Modern Multi Channel Analyzer. We use the same concept as the mechanical kicksorter. But, now we electronically sort the X rays and place them in bins of increasing energy. Then every few milli seconds read them out and update a graphical interface, your SEM EDS spectra.

X ray pulses are integrated into a peak with a charge sensitive pre amp. That peak height is measured with an analog to digital converter or multi channel analyzer.



What pulses from an x ray look like in real time on a fast oscilloscope.



Pulses are electronically integrated with charge sensitive pre amp

The analog pulse at left is converted to a digital signal with the voltage of step proportional to pulse height. More energetic x rays give higher height

Pulse shaping time and resolution

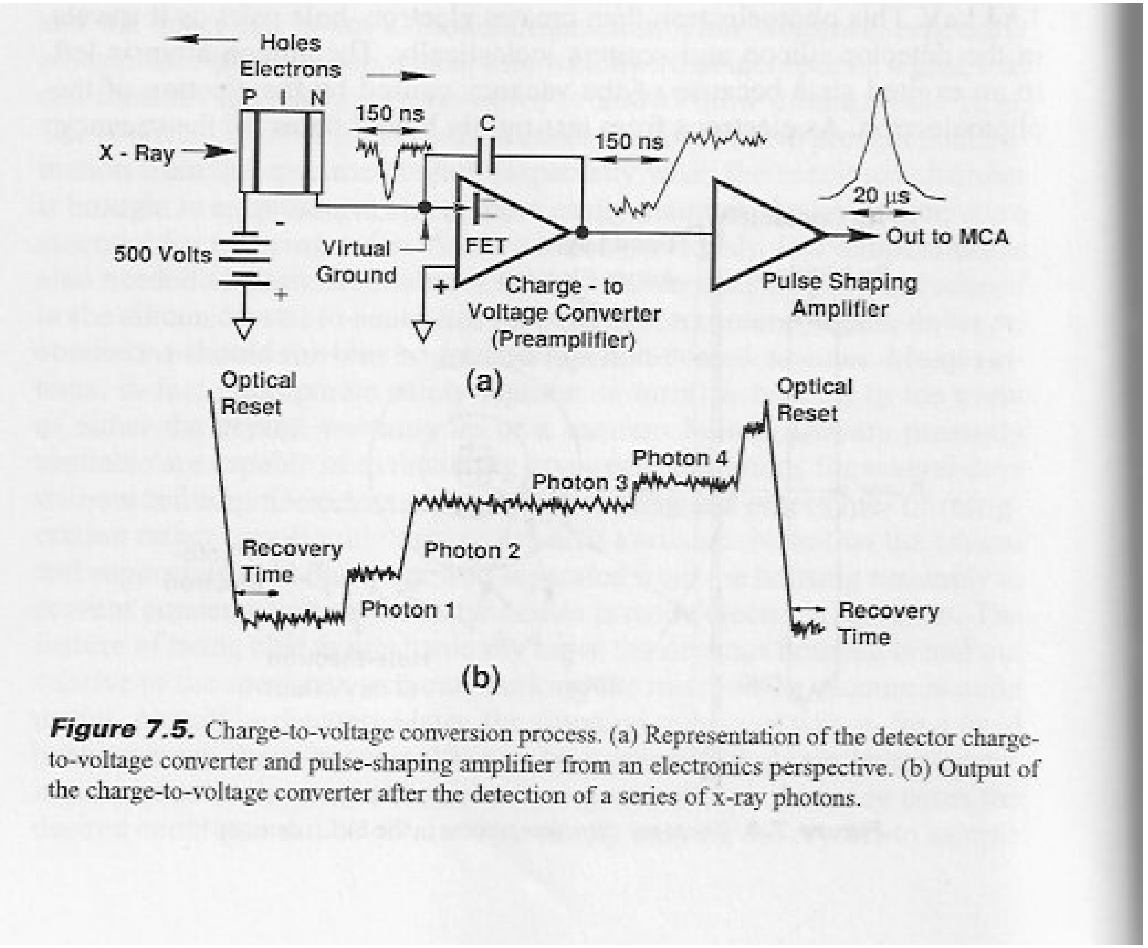


Figure 7.5. Charge-to-voltage conversion process. (a) Representation of the detector charge-to-voltage converter and pulse-shaping amplifier from an electronics perspective. (b) Output of the charge-to-voltage converter after the detection of a series of x-ray photons.

From Goldstein, Newbury, Joy, Lyman, SEM and X-ray micro analysis.

We get more resolution in heights with longer shaping time but then are subject to artifacts such as pulse pile up or Sum peaks. So, we set shaping time to as low as possible to still resolve peaks. Or if we have an SDD (Silicon Drift Detector) we don't worry so much until currents are very large!

Effect of shaping time, longer shaping time produces a higher resolution curve and pulls out weaker peaks like Carbon.

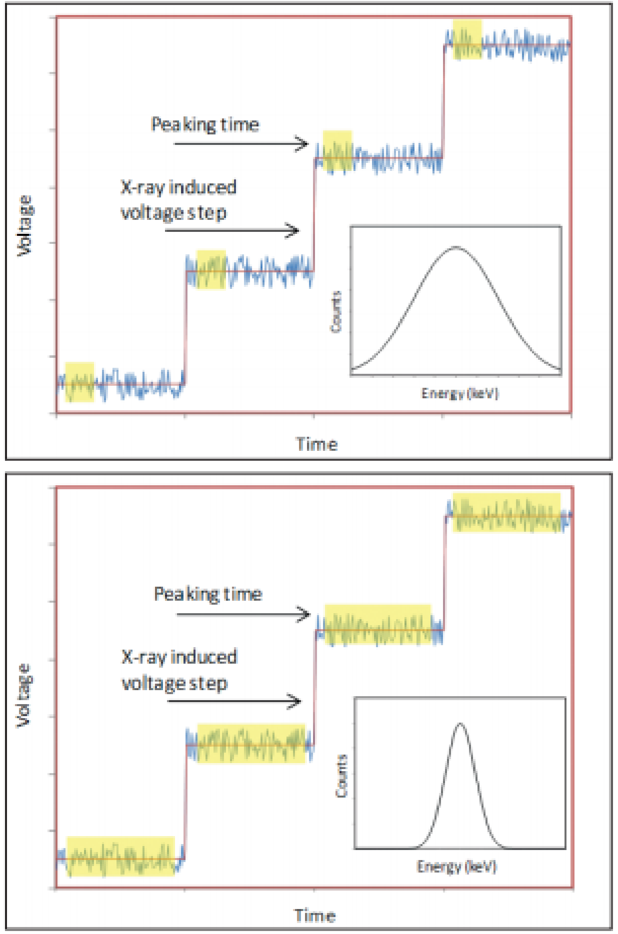
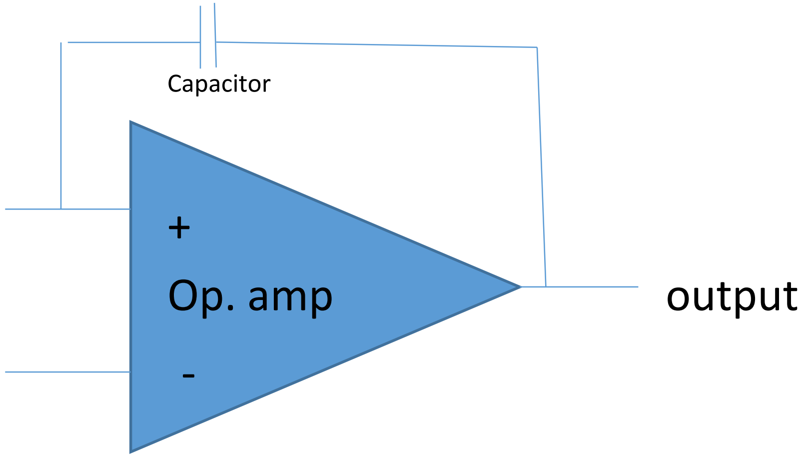


Figure 3: Illustration of voltage steps as a function of an absorbed X-ray. The noise fluctuations demonstrate the impact of noise and shaping time (top vs. bottom) on resolution.

Keith Thompson Thermo Scientific

Longer shaping time gives more accurate pulse height and tightens up distribution of energy!

- Shaping time is an important variable.
- Please play with shaping time.
- On the OSU Quanta 600 shaping times as low as 12 usec are necessary to resolve carbon peaks.



The larger the capacitor in our Operational amplifier feedback circuit, the longer the shaping time! For the Op. Amp and LF 355 JFET with low offset works nicely

Peter Eschbach

Oregon State University

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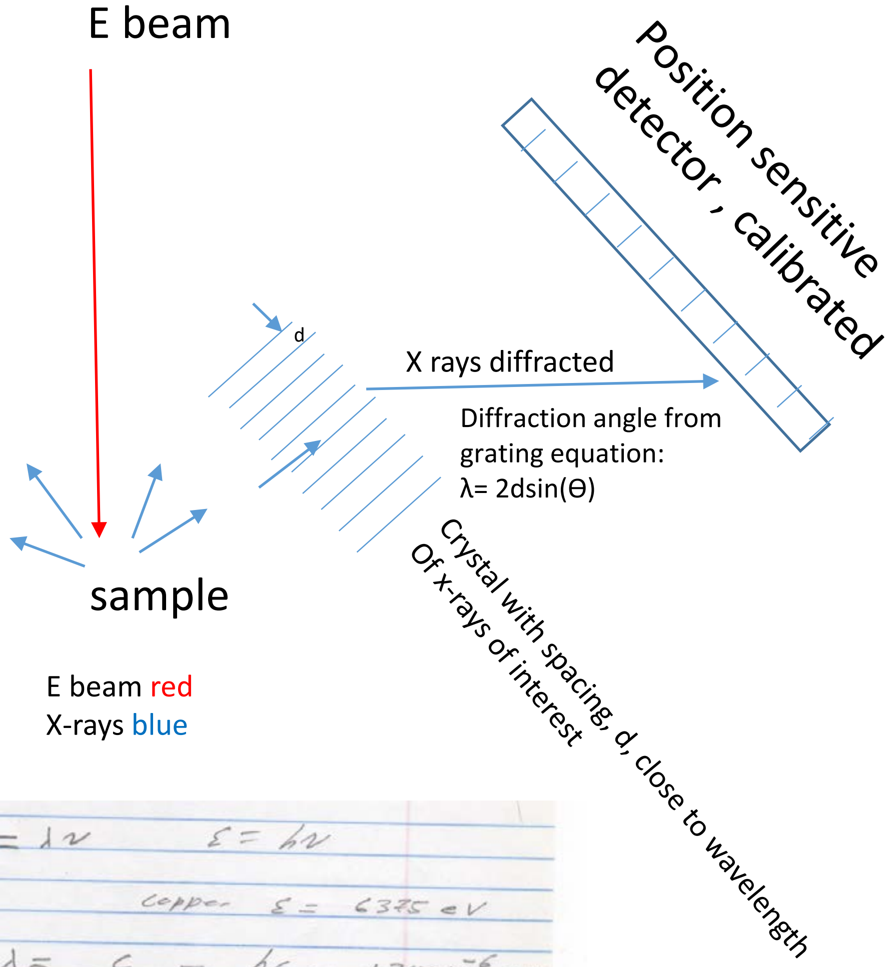
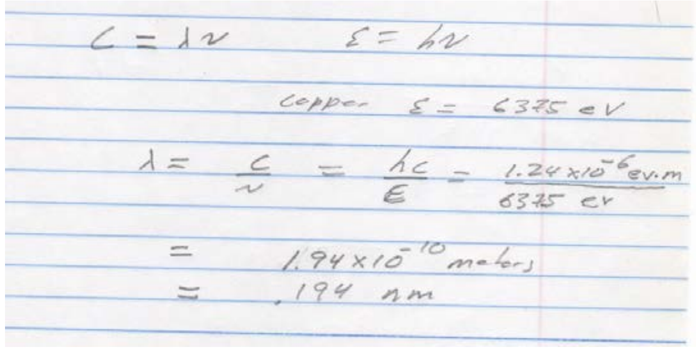
WDS process

- We do not use charge sensitive pre-amps and pulse height analysis to sort the energies.
- We use crystals that have carefully chosen lattice spacing's to diffract the x-rays into a simpler detector.
- Wavelength of Fe K alpha is solved at right, .194 nm.
- So, if we find a lattice with close to .2nm spacing we can get strong diffraction and detect elements near Iron with dramatic precision.



E beam red
X-rays blue



$c = \lambda \nu \qquad \varepsilon = h\nu$

copper $\varepsilon = 6375$ eV

$\lambda = \frac{c}{\nu} = \frac{hc}{\varepsilon} = \frac{1.24 \times 10^{-6} \text{ ev.m}}{6375 \text{ ev}}$

$= 1.94 \times 10^{-10}$ meters

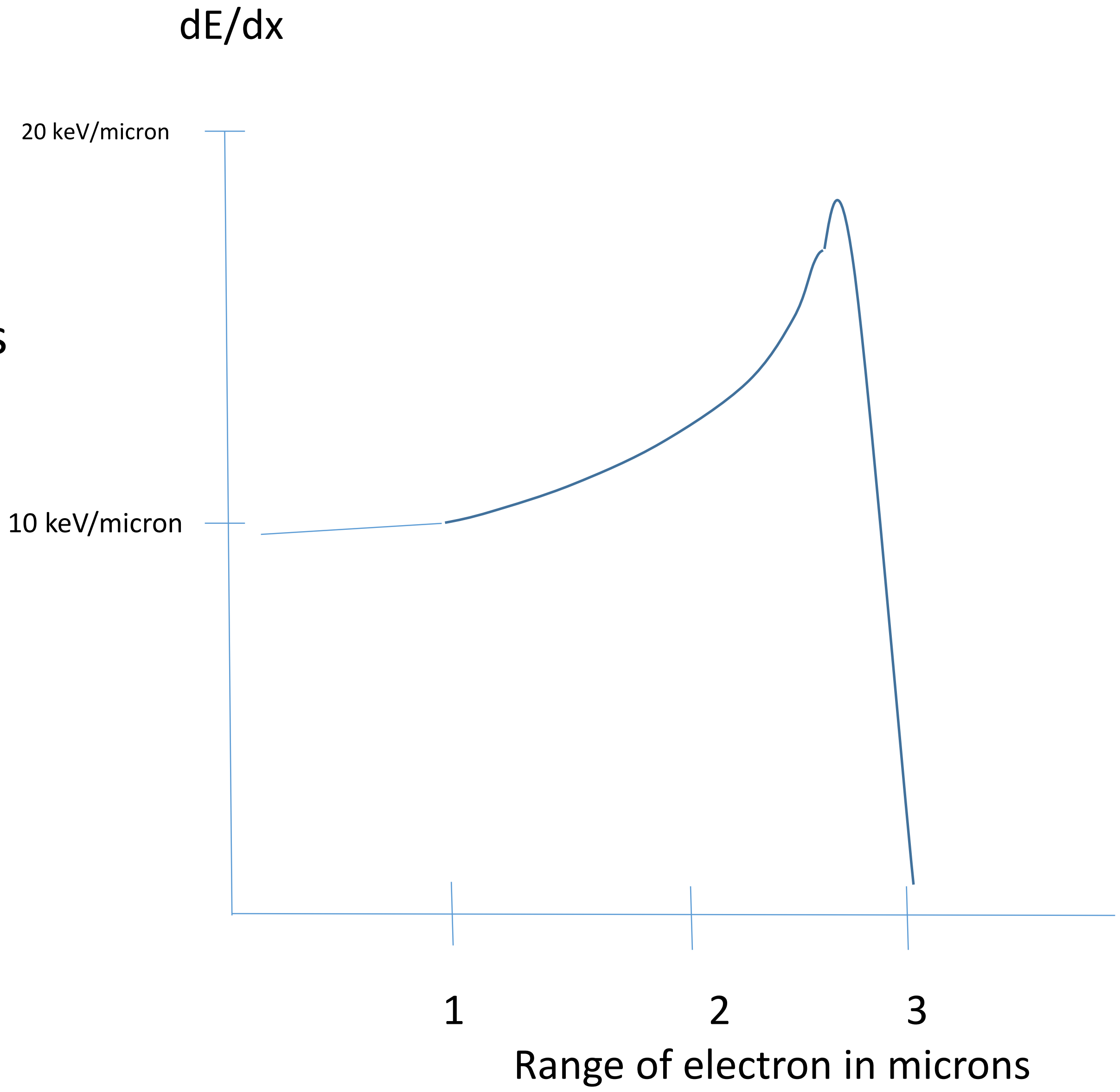
$=$ .194 nm

Peter Eschbach
Oregon State University

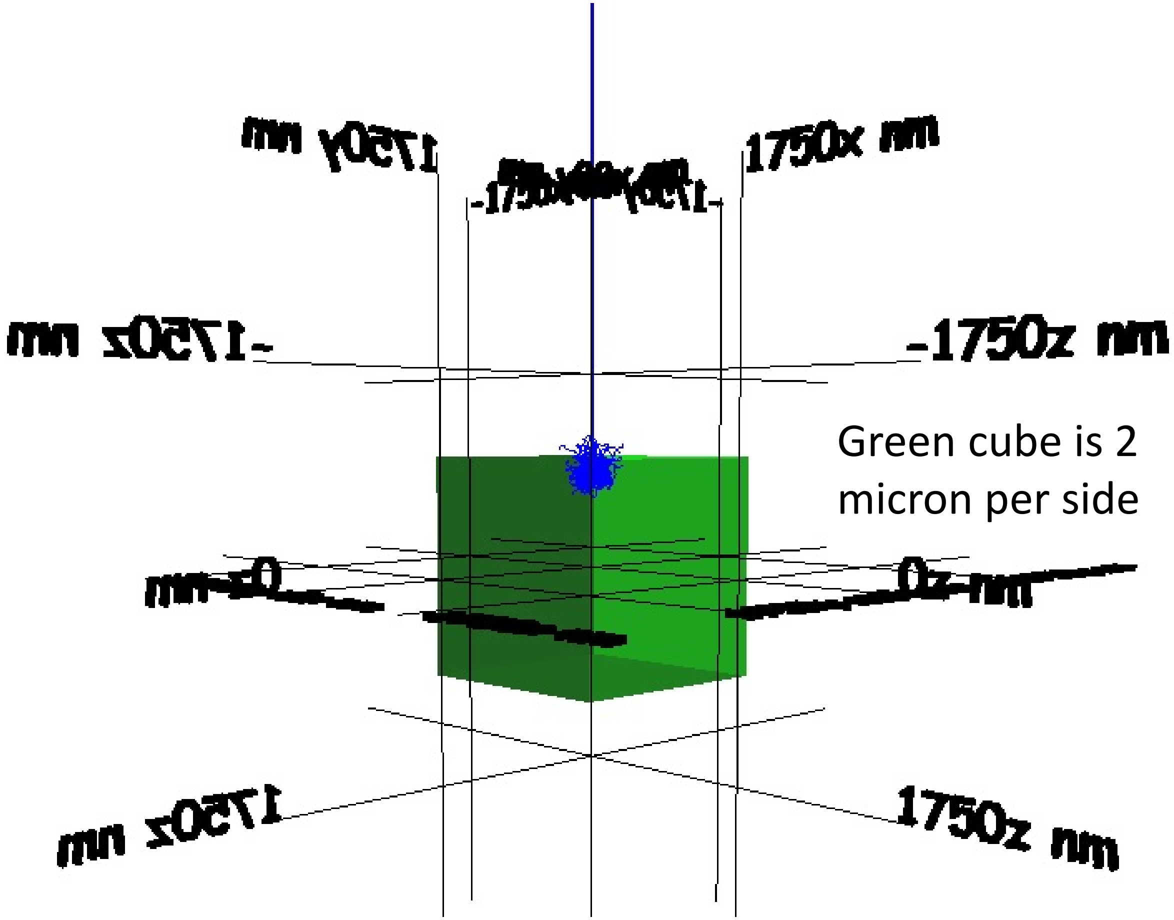
Now that we have a basic idea of X ray detectors and the difference between EDS and WDS, let us talk about X ray processes. We will review some basic atomic physics at the undergraduate physics or chemistry level.

Stopping Power

- Stopping power is roughly how many KeV per micron a beam looses in traversing a sample, -dE/dx.
- In radiation dosimetry, study of how ionizing radiation damages material there is a rule of thumb for gamma rays and electrons: 10 keV per micron in tissue equivalent material (bone, water), so called lineal energy transfer. So, a one electron beam deposits 10 KeV in a one micron sample.
- A more detailed description is provided by the Bragg Curve shown at right based upon lineal energy transfer of 10 keV/micron and representing an approximate 30 keV electron beam upon atomic number close to Silicon.



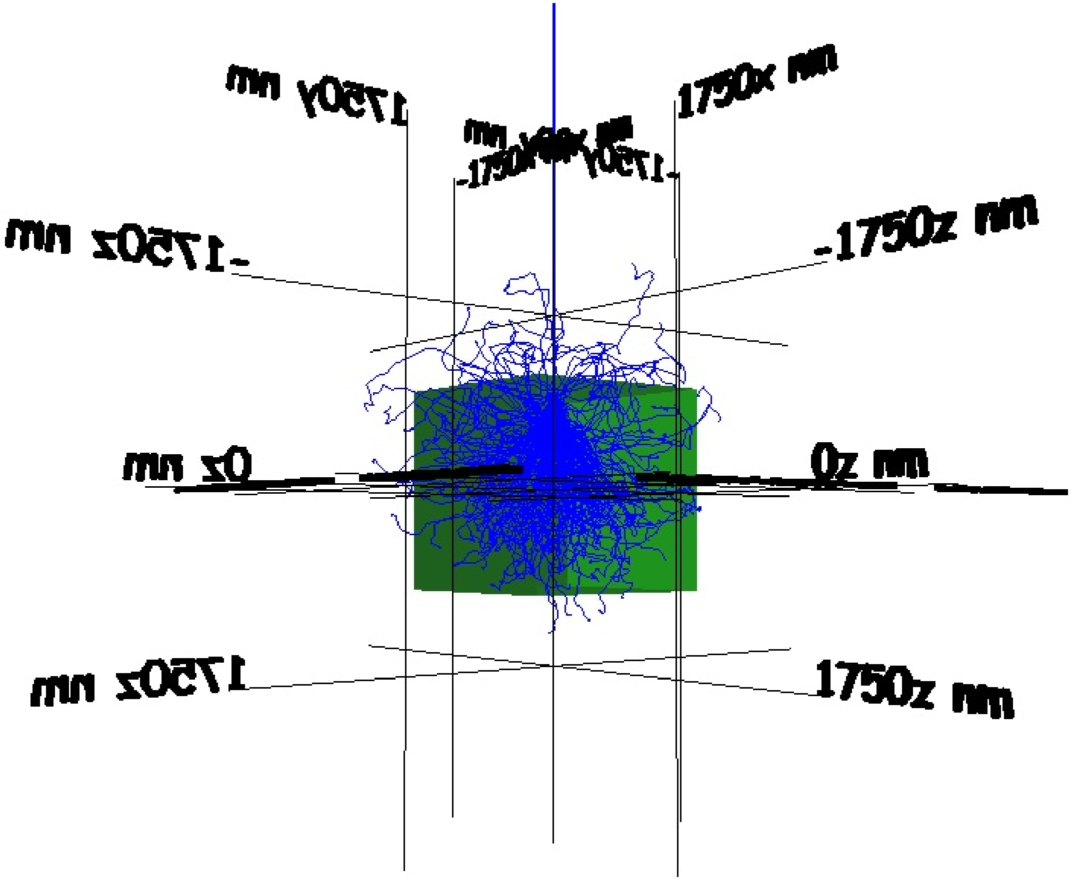
5 keV electron beam striking Silicon



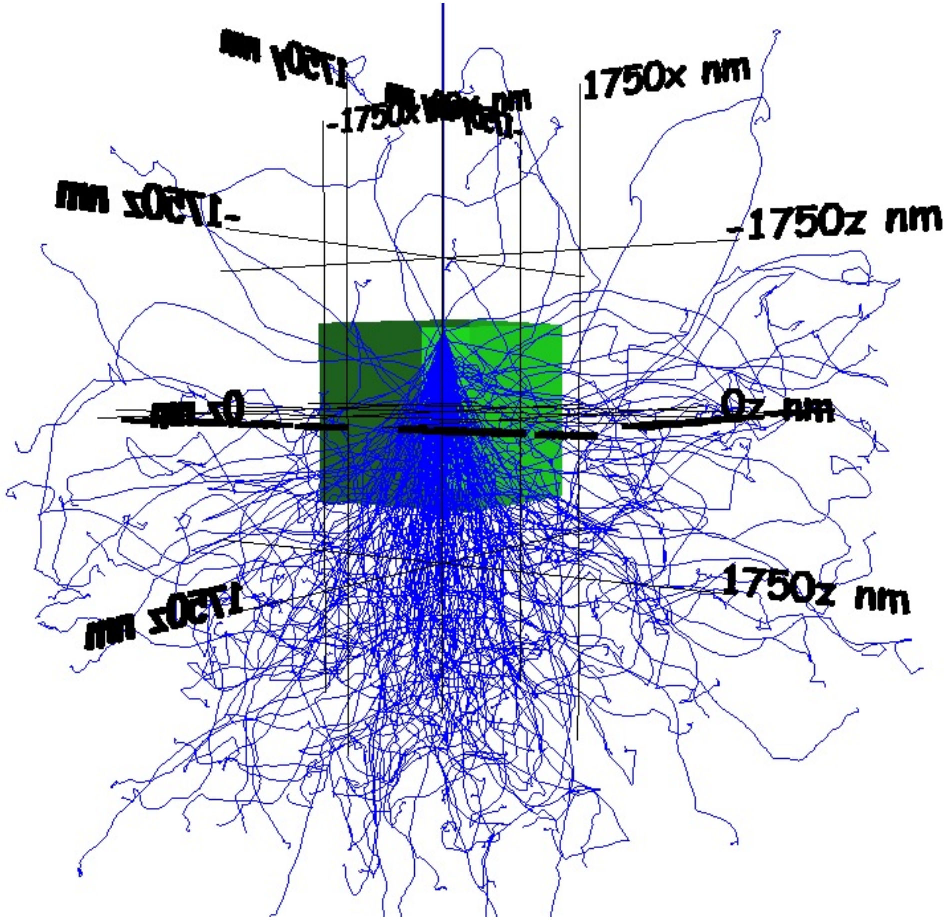
Green cube is 2 micron per side

Simulations from Win Casino, freeware for Monte Carlo simulations in electron microscopy.

15 keV beam in Si, now he penetration is past 1 micrometer.



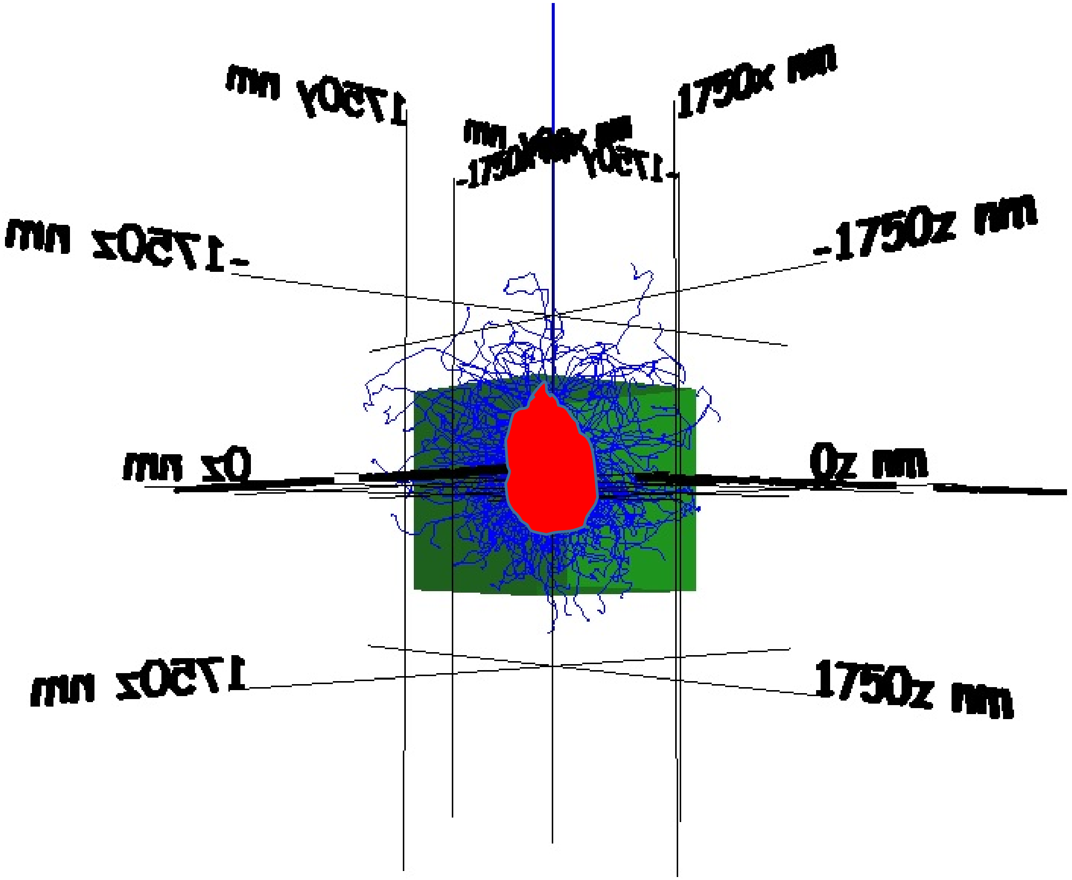
30 keV beam incident on Si. We can see the dramatic increase in secondary electron volume. How many of these secondary’s create X rays?



X ray volumes

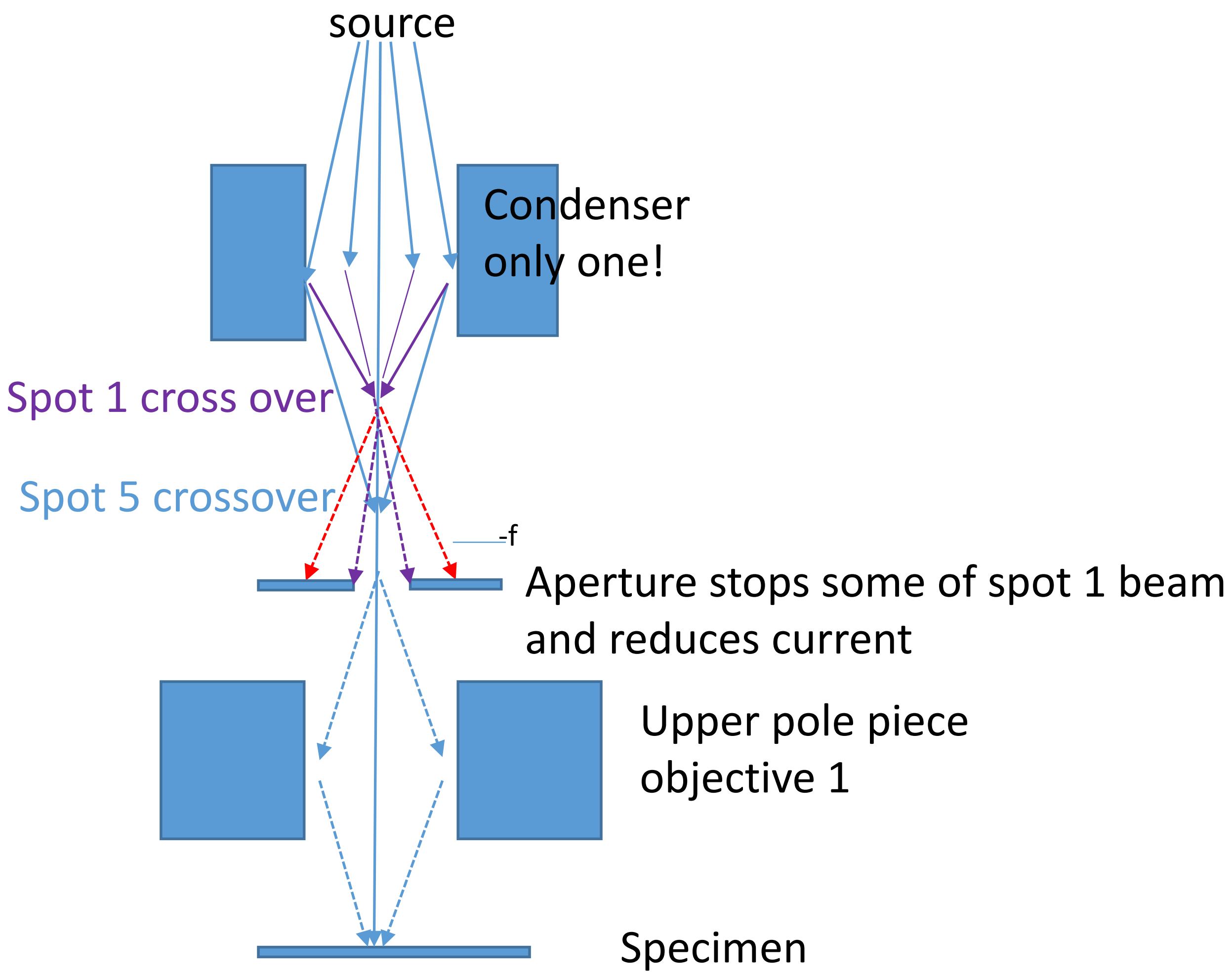
- For production of X rays, we have to surpass the ionization potential for the x ray of choice.
- For Si, this would be at least 1.74 keV plus an overvoltage factor of 1.3. We need roughly 2.5 keV. Using an LET of 10 keV per micron, only the first 1.2 micron will create x rays.
- This is born out by irradiating polymers like Acrylic with 15 keV beams then etching the polymers to reveal the x ray volume.

Win Casino secondary electrons in blue, and approximate Si K_α x ray volume in red. 15 keV beam on Silicon.



Green cube is 2 micron per side.

SEM spot size spot 5 vs spot 1. Be warned effect on current is opposite than TEM. In SEM spot 5 is a large current and spot 1 is a smaller current that focuses better.



source

Condenser
only one!

Spot 1 cross over

Spot 5 crossover

-f

Aperture stops some of spot 1 beam
and reduces current

Upper pole piece
objective 1

Specimen

So, we should always be spot 5 for SEM EDS?

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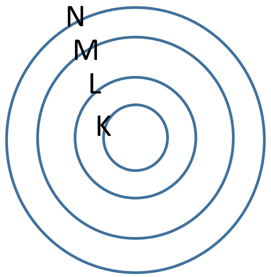
X ray process, Excite atom, electron falls from outer shell to inner shell to de-excite and x-ray is given off to conserve energy

Review of Atomic Physics

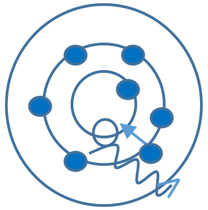


K, n = 1 ground state for hydrogen atom
L, n = 2 first excited state for hydrogen atom
M, n = 3 second excited state for hydrogen
N, n = 4 third excited state for hydrogen
l Occupancy * = 2*(2l+1)
Remember 2s , 3s, and 4s electrons so n = 2 shell
Has 8 electron capacity: $2s^2p^6$

* Occupancy, from Pauli Exclusion principle no electron can have same QN, Klebsch-Gordon Coefficients and the fact that electrons are spin ½ the occupancy of each shell is 2*(2l+1) , l = 0 K shell, l = 1 L shell, l = 2 for M shell …..

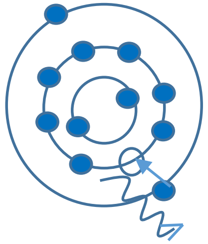
Examples of K, L, M transitions in common materials

K series Any decay to N= 1



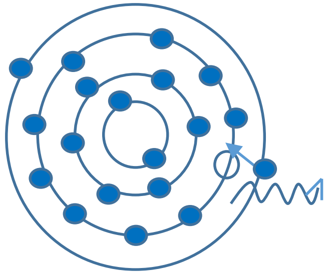
Oxygen atomic number 8

L series Any decay to N= 2



Titanium atomic number 22 not all Half of n = 2 electrons are shown

M series Any decay to N = 3



Cerium atomic number 58, not all of n= 2 and n =3 electrons are shown

Key

- ○ Hole, absence of electron in formally occupied state
- ● Electron*
- 〰 X ray or quantum of energy, pure energy no mass, high energy photon

* The electron has never been seen. However, based on its mass and density the nucleus would be a BB sitting on second base in a baseball stadium. The electrons would be grain of sand sized objects orbiting around the nucleus out in the bleachers. So, the atom is mostly comprised of empty space.

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OSU Electron Microscopy Facility
Peter Eschbach

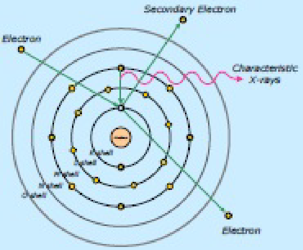
ISO 9001 Certificated
ISO 14001 Certificated

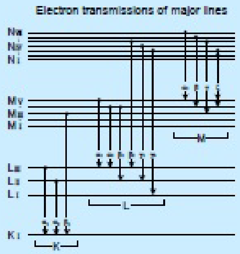
High technology for quality assurance and the environment

Energy table for EDS analysis

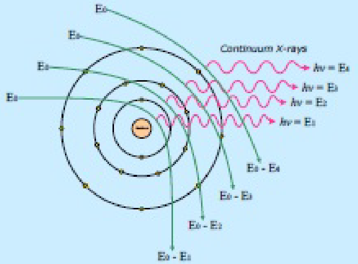
http://www.jeol.com/

Characteristic X-rays





Continuum X-rays



The electrons generated by the electron gun are accelerated and irradiate the sample. The electron has a kinetic energy proportional to the accelerating voltage. The kinetic energy dissipated within the sample generates characteristic signals from the specimen. The characteristic X-rays are the information used for EDS analysis.

If the incident electrons have sufficient acceleration and then have enough energy to strike an electron from the inner shell of the atom, it'll make an electron hole. An electron from the outer shell will fill up the hole and then, some characteristic X-rays will be emitted. The characteristic X-rays have different energy for each element, and the intensity will be proportional to the element concentration.

The continuum X-rays are emitted when the primary electrons are decelerated by the strong electric field existing close to atomic nucleus. The continuum X-rays have the energy of the kinetic energy lost during the deceleration. It will be observed as EDS spectrum background.

Number	Symbol	Name	Atomic mass	Density (kg/m³)	Characteristic X-ray (keV)	Minimum accelerating voltage
1	H	Hydrogen	1.01	0.08		⬜
2	He	Helium	4.00	0.19		⬜
3	Li	Lithium	6.94	0.53		⬜
4	Be	Beryllium	9.01	1.85	Kα 0.110	🟥
5	B	Boron	10.81	2.34	Kα 0.183	🟥
6	C	Carbon	12.01	2.25 *	Kα 0.277	🟥
7	N	Nitrogen	14.01	1.14	Kα 0.392	🟥
8	O	Oxygen	16.00	1.57	Kα 0.525	🟥
9	F	Fluorine	19.00	1.5	Kα 0.677	🟥
10	Ne	Neon	20.18	1.20	Kα 0.848	🟥
11	Na	Sodium	22.99	0.97	Kα 1.041	🟥
12	Mg	Magnesium	24.31	1.74	Kα 1.253	🟥
13	Al	Aluminium	26.98	2.70	Kα 1.486	🟥
14	Si	Silicon	28.09	2.42	Kα 1.739	🟥
15	P	Phosphorus	30.97	1.83 *	Kα 2.013	🟥
16	S	Sulphur	32.06	2.07 *	Kα 2.307	🟥
17	Cl	Chlorine	35.45	2.2	Kα 2.621	🟥
18	Ar	Argon	39.95	1.65	Kα 2.957	🟥
19	K	Potassium	39.10	0.87	Kα 3.312	🟥
20	Ca	Calcium	40.08	1.55	Kα 3.690	🟥
21	Sc	Scandium	44.96	2.99	Kα 4.088 Lα 0.395	🟥
22	Ti	Titanium	47.90	4.5	Kα 4.508 Lα 0.452	🟥
23	V	Vanadium	50.94	5.87	Kα 4.949 Lα 0.511	🟥
24	Cr	Chromium	52.00	7.14	Kα 5.411 Lα 0.573	🟥
25	Mn	Manganese	54.94	7.3	Kα 5.894 Lα 0.637	🟥
26	Fe	Iron	55.85	7.86	Kα 6.398 Lα 0.705	🟥
27	Co	Cobalt	58.93	8.71	Kα 6.924 Lα 0.776	🟥
28	Ni	Nickel	58.70	8.8	Kα 7.471 Lα 0.851	🟥
29	Cu	Copper	63.55	8.93	Kα 8.040 Lα 0.930	🟥
30	Zn	Zinc	65.38	6.92	Kα 8.630 Lα 1.012	🟥
31	Ga	Gallium	69.72	5.93	Kα 9.241 Lα 1.098	🟥
32	Ge	Germanium	72.59	5.46	Kα 9.874 Lα 1.188	🟥
33	As	Arsenic	74.92	5.73	Kα 10.530 Lα 1.282	🟥
34	Se	Selenium	78.96	4.82	Kα 11.207 Lα 1.379	🟥
35	Br	Bromine	79.90	4.2	Kα 11.907 Lα 1.480	🟥
36	Kr	Krypton	83.80	3.4	Kα 12.631 Lα 1.586	🟥
37	Rb	Rubidium	85.47	1.53	Kα 13.373 Lα 1.694	🟥
38	Sr	Strontium	87.62	2.60	Kα 14.140 Lα 1.806	🟥
39	Y	Yttrium	88.91	4.48	Kα 14.931 Lα 1.922	🟥
40	Zr	Zirconium	91.22	6.44	Kα 15.744 Lα 2.042	🟥
41	Nb	Niobium	92.91	8.4	Kα 16.581 Lα 2.166	🟥
42	Mo	Molybdenum	95.94	9.01	Kα 17.441 Lα 2.293	🟥
43	Tc	Technetium	(97)		Kα 18.325 Lα 2.424	🟥
44	Ru	Ruthenium	101.07	12.1	Kα 19.233 Lα 2.558	🟥
45	Rh	Rhodium	102.91	12.44	Lα 2.696	🟥
46	Pd	Palladium	106.4	12.16	Lα 2.838	🟥
47	Ag	Silver	107.87	10.49	Lα 2.984	🟥
48	Cd	Cadmium	112.40	8.65	Lα 3.133	🟥
49	In	Indium	114.82	7.28	Lα 3.286 M 0.368	🟩
50	Sn	Tin	118.69	7.30 *	Lα 3.443 M 0.691	🟩
51	Sb	Antimony	121.75	6.62	Lα 3.604 M 0.733	🟩
52	Te	Tellurium	127.60	6.25	Lα 3.769 M 0.778	🟩
53	I	Iodine	126.90	4.94	Lα 3.937	🟩
54	Xe	Xenon	131.30		Lα 4.109	🟩
55	Cs	Cesium	132.91	1.87	Lα 4.286	🟩
56	Ba	Barium	137.34	3.5	Lα 4.465 M 0.972	🟥
57–71		Lanthanoid				
72	Hf	Hafnium	178.49	13.3	Lα 7.898 M 1.644	🟥
73	Ta	Tantalum	180.95	16.6	Lα 8.145 M 1.709	🟥
74	W	Tungsten	183.85	19.3	Lα 8.396 M 1.774	🟥
75	Re	Rhenium	186.21	20.53	Lα 8.651 M 1.842	🟥
76	Os	Osmium	190.2	22.5	Lα 8.910 M 1.914	🟥
77	Ir	Iridium	192.22	22.42	Lα 9.174 M 1.977	🟥
78	Pt	Platinum	195.09	21.37	Lα 9.441 M 2.048	🟥
79	Au	Gold	196.97	18.88	Lα 9.712 M 2.120	🟥
80	Hg	Mercury	200.59	14.19	Lα 9.987 M 2.195	🟥
81	Tl	Thallium	204.37	11.86	Lα 10.267 M 2.267	🟥
82	Pb	Lead	207.2	11.34	Lα 10.550 M 2.342	🟥
83	Bi	Bismuth	208.98	9.78	Lα 10.837 M 2.419	🟥
84	Po	Polonium	(209)		Lα 11.129	🟦
85	At	Astatine	(210)		Lα 11.425	🟦
86	Rn	Radon	(222)		Lα 11.725	🟦
87	Fr	Francium	(223)		Lα 12.029	🟦
88	Ra	Radium	226.03	5	Lα 12.340	🟦
89–103		Actinoid				
57	La	Lanthanum	138.91	6.17	Lα 4.650 M 0.833	🟥
58	Ce	Cerium	140.12	6.66	Lα 4.839 M 0.883	🟥
59	Pr	Praseodymium	140.91	6.77	Lα 5.033 M 0.929	🟥
60	Nd	Neodymium	144.24	7.02	Lα 5.229 M 0.978	🟥
61	Pm	Prometium	(145)		Lα 5.432	🟩
62	Sm	Samarium	150.4	7.54	Lα 5.635 M 1.081	🟥
63	Eu	Europium	151.96	5.25	Lα 5.845 M 1.131	🟥
64	Gd	Gadolinium	157.25	7.90	Lα 6.056 M 1.185	🟥
65	Tb	Terbium	158.93	8.25	Lα 6.272 M 1.240	🟥
66	Dy	Dysprosium	162.50	8.56	Lα 6.494 M 1.293	🟥
67	Ho	Holmium	164.93	8.80	Lα 6.719 M 1.347	🟥
68	Er	Erbium	167.26	9.06	Lα 6.947 M 1.405	🟥
69	Tm	Thulium	168.93	9.32	Lα 7.179 M 1.462	🟥
70	Yb	Ytterbium	173.04	6.96	Lα 7.414 M 1.521	🟥
71	Lu	Lutetium	174.97	9.84	Lα 7.654 M 1.581	🟥
89	Ac	Actinium	(227)	10.07	Lα 12.650	🟦
90	Th	Thorium	232.04	11.00	Lα 12.967 M 2.991	🟥
91	Pa	Protactinium	231.04		Lα 13.288 M 3.077	🟥
92	U	Uranium	238.03	18.7	Lα 13.612 M 3.164	🟥
93	Np	Neptunium	237.05		Lα 13.942 M 3.260	⬜
94	Pu	Plutonium	(244)		Lα 14.276 M 3.348	⬜
95	Am	Americium	(243)		Lα 14.615 M 3.437	⬜
96	Cm	Curium	(247)		Lα 14.953 M 3.539	⬜
97	Bk	Berkelium	(247)		Lα 15.304 M 3.634	⬜
98	Cf	Californium	(251)		Lα 15.652 M 3.731	⬜
99	Es	Einsteinium	(254)			⬜
100	Fm	Fermium	(257)			⬜
101	Md	Mendelevium	(258)			⬜
102	No	Nobelium	(255)			⬜
103	Lr	Lawrencium	(262)			⬜

Gold
79 Au
196.97
18.88
Lα 9.712
M 2.120

Number
Atomic mass
Density (kg/m³)
Name
Symbol
Characteristic X-ray (keV)

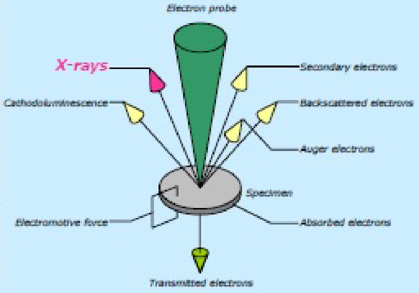
Note: Density
* 'C' as (graphite), 'P' as (white),
'S' as (alpha), 'Sn' as (white)

Minimum accelerating voltage

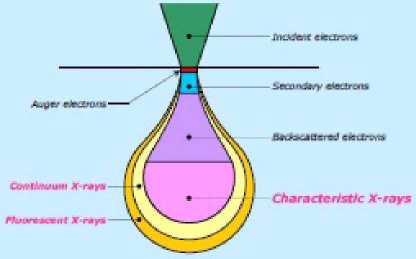
- ⬜ Unable to detect
- 🟥 5kV or higher
- 🟩 10kV or higher
- 🟦 15kV or higher

The colors mean to detect the characteristic X-ray of the lowest energy for each element.

Information from specimen



Generation depth and space resolution



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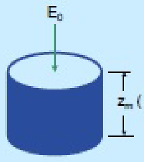
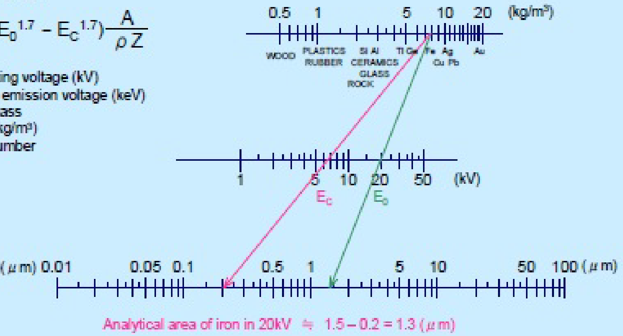
Analytical area

Castaing's formula

$$z_m = 0.033\,(E_0^{1.7} - E_C^{1.7})\frac{A}{\rho Z}$$

E_0 : Accelerating voltage (kV)
E_C : Minimum emission voltage (keV)
A : Atomic mass
ρ : Density (kg/m³)
Z : Atomic number

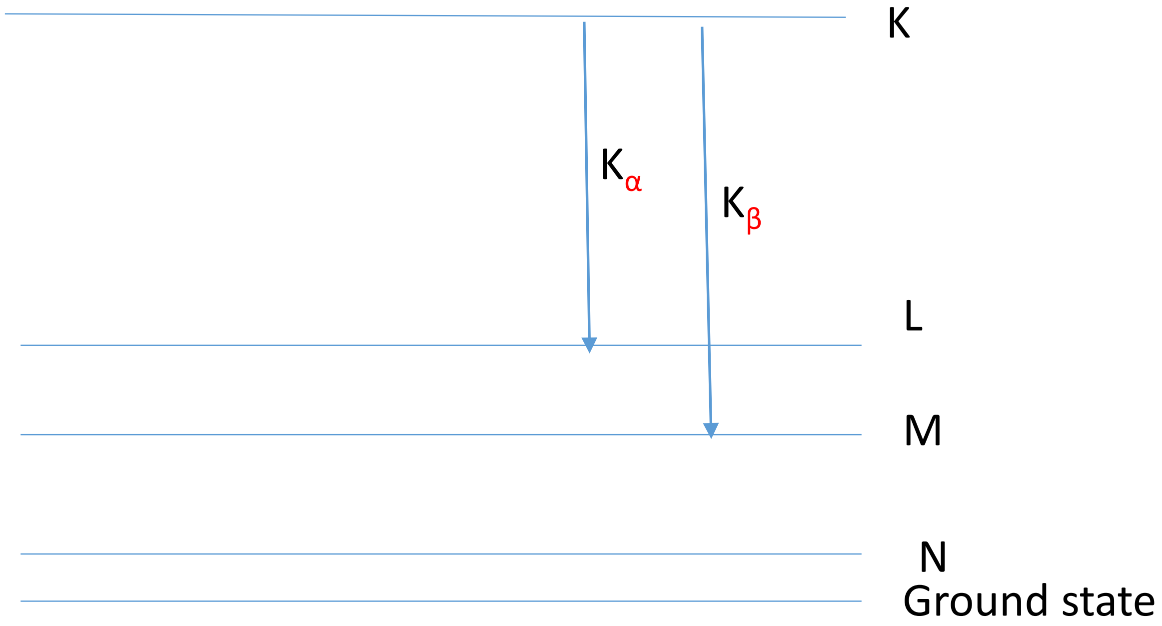


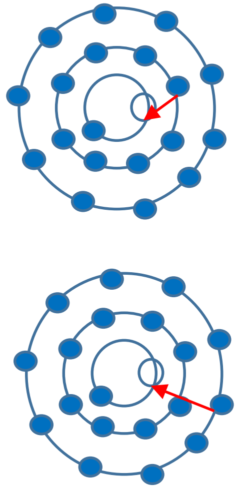


Analytical area of iron in 20kV ≒ 1.5 – 0.2 = 1.3 (μm)

Series, there are two K transitions, α, β, γ*

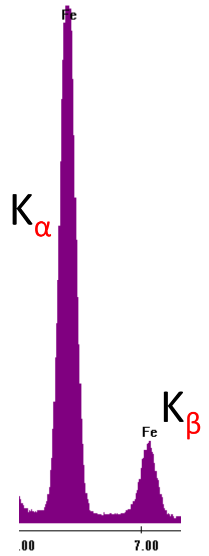
Atomic number 21,
Titanium, 4s^2 not shown





K_α n = 2 to n = 1

K_β n = 3 to n=1



Fe K_α K_β

* Gamma transitions are very improbable and generally not observed.

For reference, Goldstein, Newbury, Joy, Lyman, SEM and X-ray micro analysis.

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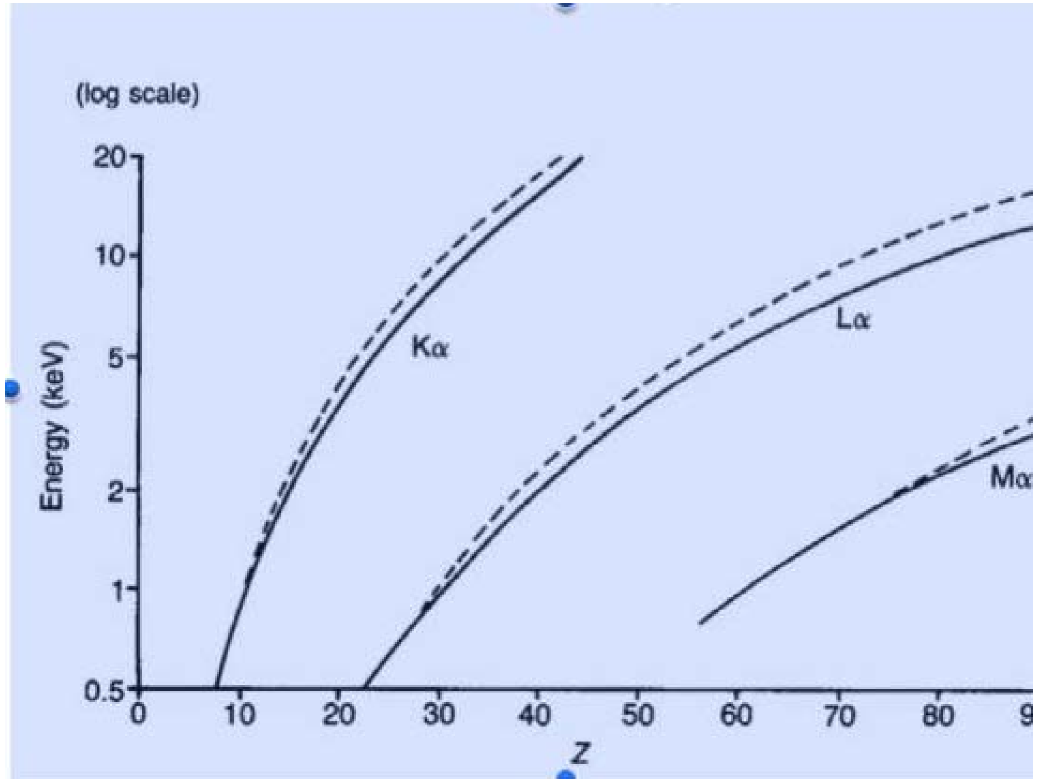
Complete series vs atomic number. Important to realize that elements below A.N. 21 do not have L lines, and those below A.N. < 56* do not have M lines.

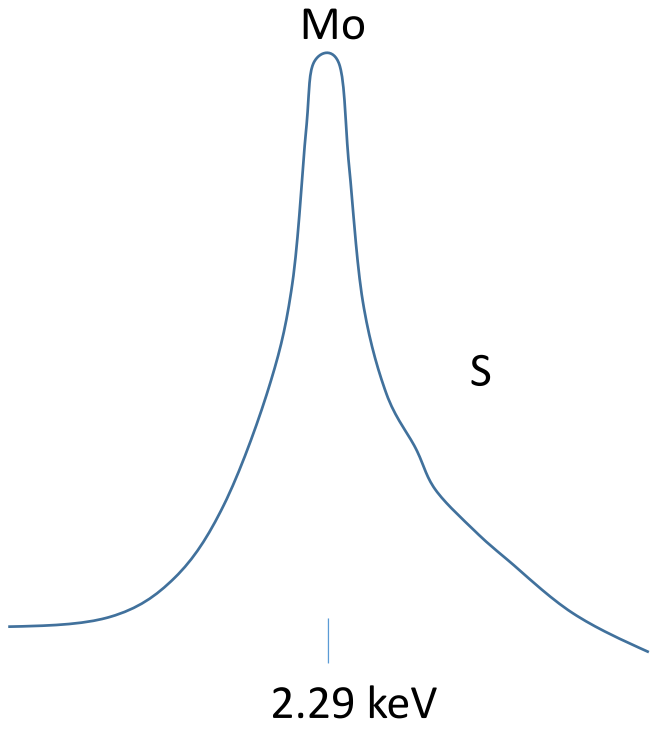


From Charlie Lyman’s notes on STEM EDS, Lehigh short course 2010.

* Except In, Sn, Sb, and Te as those have promotion to f electron shells

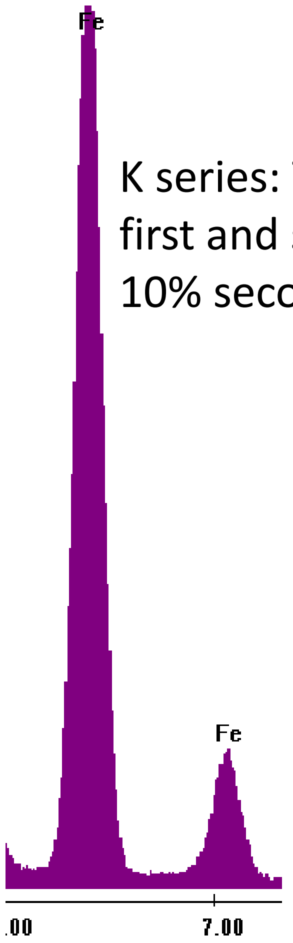
Line Overlap in EDS

- This can affect quantitation
- Be aware of this and add S into the Quantitation if you have a Mo peak. Compute your wt% of Mo.
- Now delete the S and see if it makes a difference.
- Or you can use HPD in EDAX software, Deconvolution view in Bruker software or artificial spectra in Noran-Thermo Fisher software. This will find insufficient identifications and hidden peaks.
- There was a freeware program to find overlaps, beerware. It was free software that if you found useful you could buy the gentleman a beer at the annual Microscopy and Micro Analysis meeting.



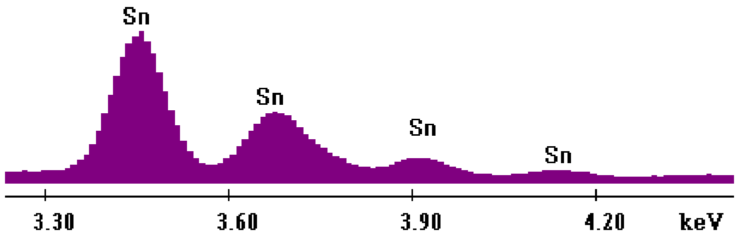
In Moly Sulfide , the shoulder on Mo peak looks funny. It is actually an overlap of Mo and Sulfur.

Atomic transitions and characteristic line shapes



K series: Tall first and shorter, 10% second

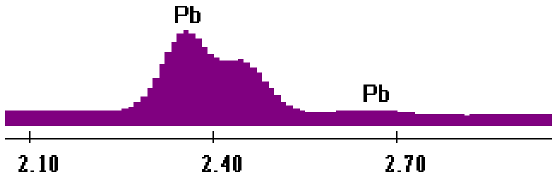
K



L series: Four lines Tall medium and then two shorts. Generally there will be corroborating K series at higher energy!

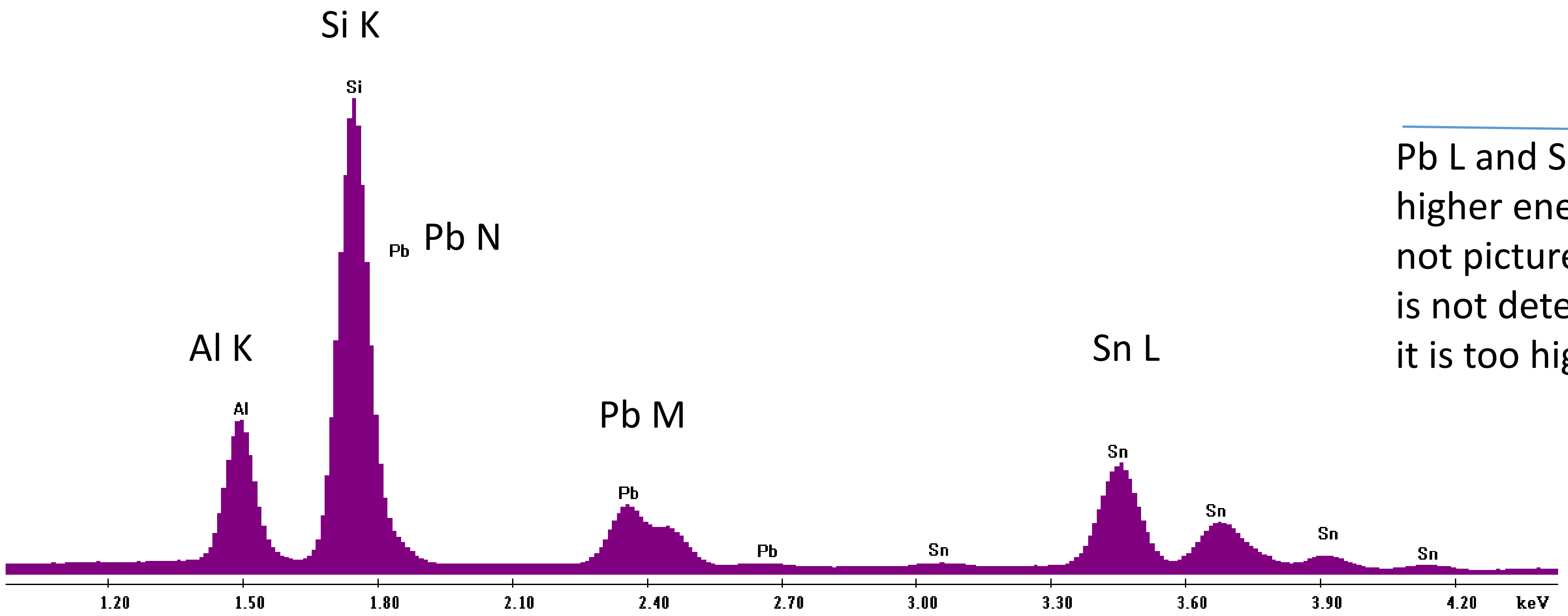
L

M series, heavy elements only, Tall and short. Don't confuse with K series of Sulfur or Phosphorous. Corroborate with higher energy L series that should be present!



M

Example with K,L,M,N lines



Pb L and Sn K are at higher energy and not pictured. Pb K is not detectable as it is too high energy.

Aside: What are the line strengths and why don’t we see the Kγ transition for example?

We see K_α and K_β from electron falling from n = 2 to n = 1 (L to K) and n = 3 to n = 1 (M to K) but why do we not see N to K transition or $K\gamma$?

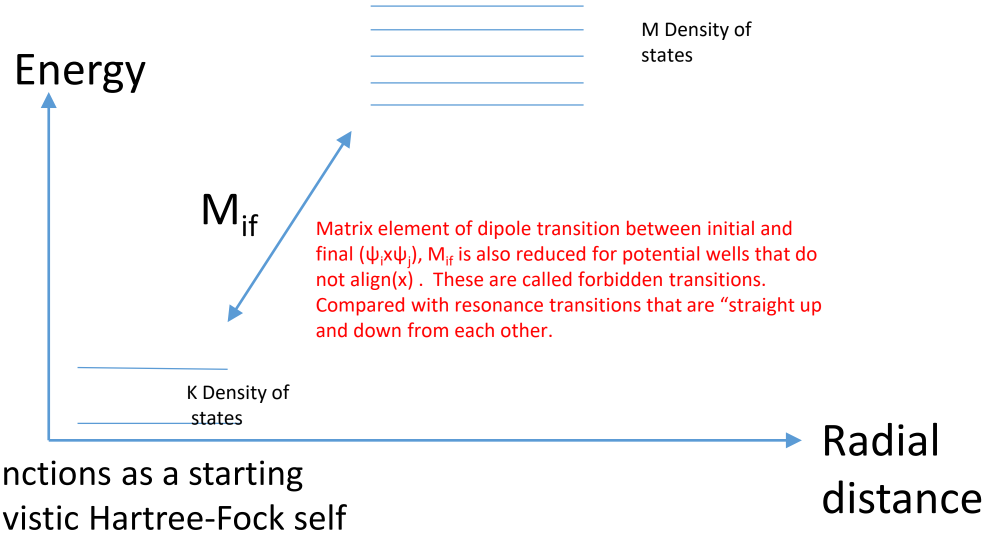
The cross section for decay from higher energy shells is smaller, K_α to K_β is 10 to 1. The higher energy $K\gamma$ is allowed but is not visible because it so very weak.

Plausibility argument: Fermi’s golden rule states the rate is proportional to Density of final state in K shell times density of states in N shell. With less DOS in K compared with N we get that the N to K shell transition is far less likely than the M to K transition β. For d electrons in the n = 4 state, l = 2. While the ground state is an S orbital with l = 0. This is not allowed by dipole selection rules l = +1,-1 and so the transition is forbidden and very slow depending upon quadrupole and higher terms that are small in comparison.

$$\lambda_{if} \quad = 2\pi \;\; 2\pi/h|M_{if}|^2\rho_{if}$$ *Fermi’s Golden Rule*

Probability

Overlap density of states



Matrix element of dipole transition between initial and final ($\psi_i x \psi_j$), M_{if} is also reduced for potential wells that do not align(x) . These are called forbidden transitions. Compared with resonance transitions that are “straight up and down from each other.

The full transition probability calculation is done by using Hydrogen atom wavefunctions as a starting point with radial functions(r) times Spherical harmonic Ylm(Θ,Φ). Then use relativistic Hartree-Fock self consistent fields to compute the N body Dirac equation for atomic numbers up to 95. $^{1-4}$

1 J. H. Scofield, “Radiative Decay Rates of Vacancies in the K and L Shells”, Phys. Rev., vol. 179, no. 1, pp. 9-16, 1969.
2 J. H. Scofield, “Relativistic Hartree-Slater Values for K and L X-ray Emission Rates”, Atom. Data Nucl. Data Tables, vol. 14, pp. 121-137, 1974.
3. J. H. Scofield, “Exchange corrections of K X-ray emission rates”, Phys. Rev. A, vol. 9, no. 2, pp. 1041-1049, 1974.
4. J. H. Scofield, “Hartree-Fock values of L X-ray emission rates”, Phys. Rev. A, vol. 10, no. 5, pp. 1507-1510, 1974

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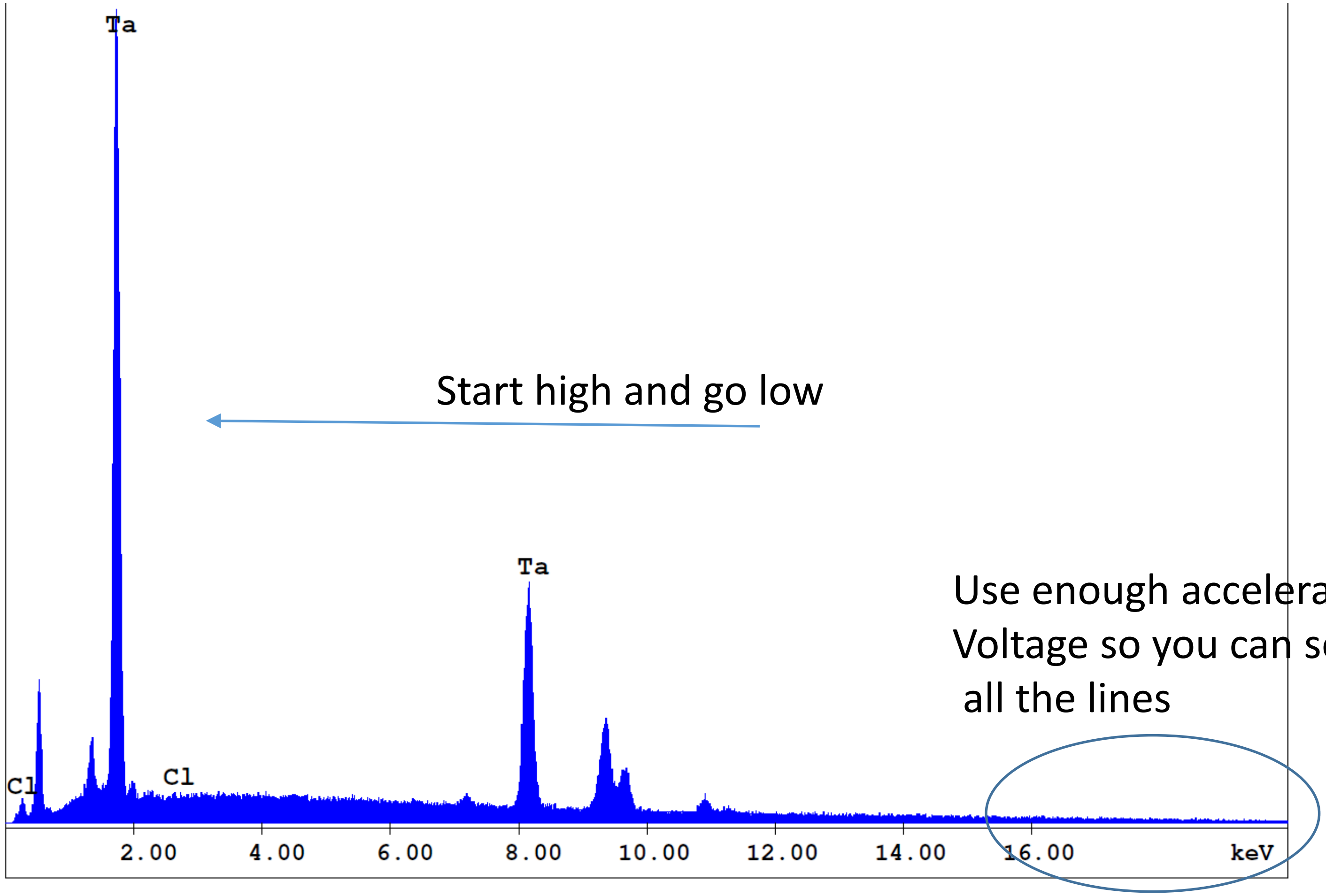
Identification strategies

- Use at least 20 keV, probably 30 keV for your first spectra.
- So often, students go straight from low keV imaging to EDS without increasing the energy. They then identify peaks based upon low energy only. Don’t fall into this trap. Increase the keV so you can verify peaks.
- Start at the right side and identify the highest energy peaks. In this case Ta L series.
- Then go down and look for the M series in Ta. Or if you have identified the K series in Nickel, then go the left and identify the L series in Nickel.
- Higher atomic numbers should have K and L lines, and even more massive atoms have M and possibly N lines. Identify as many as you can.



Start high and go low

Use enough accelerating
Voltage so you can see
all the lines

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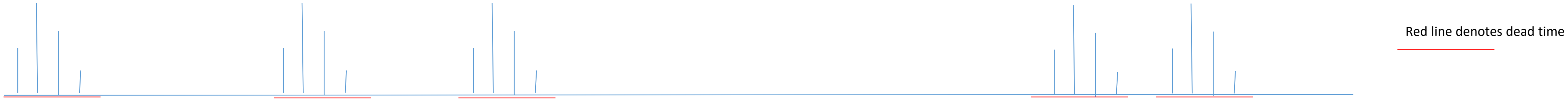
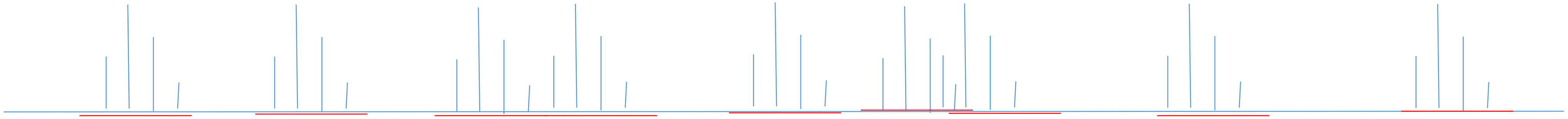
Dead time and Pulse Pile Up

20% dead time, pulse pile up or sum peaks are unlikely



50% dead time, pulse pile up or sum peaks occasionally occur!



70% dead time, pulse pile up or sum peaks are frequently occurring

Most EDS systems in the last 10 years have digital pulse processing and can handle up to 60% dead time. But, just to make sure we keep dead time below 40%.

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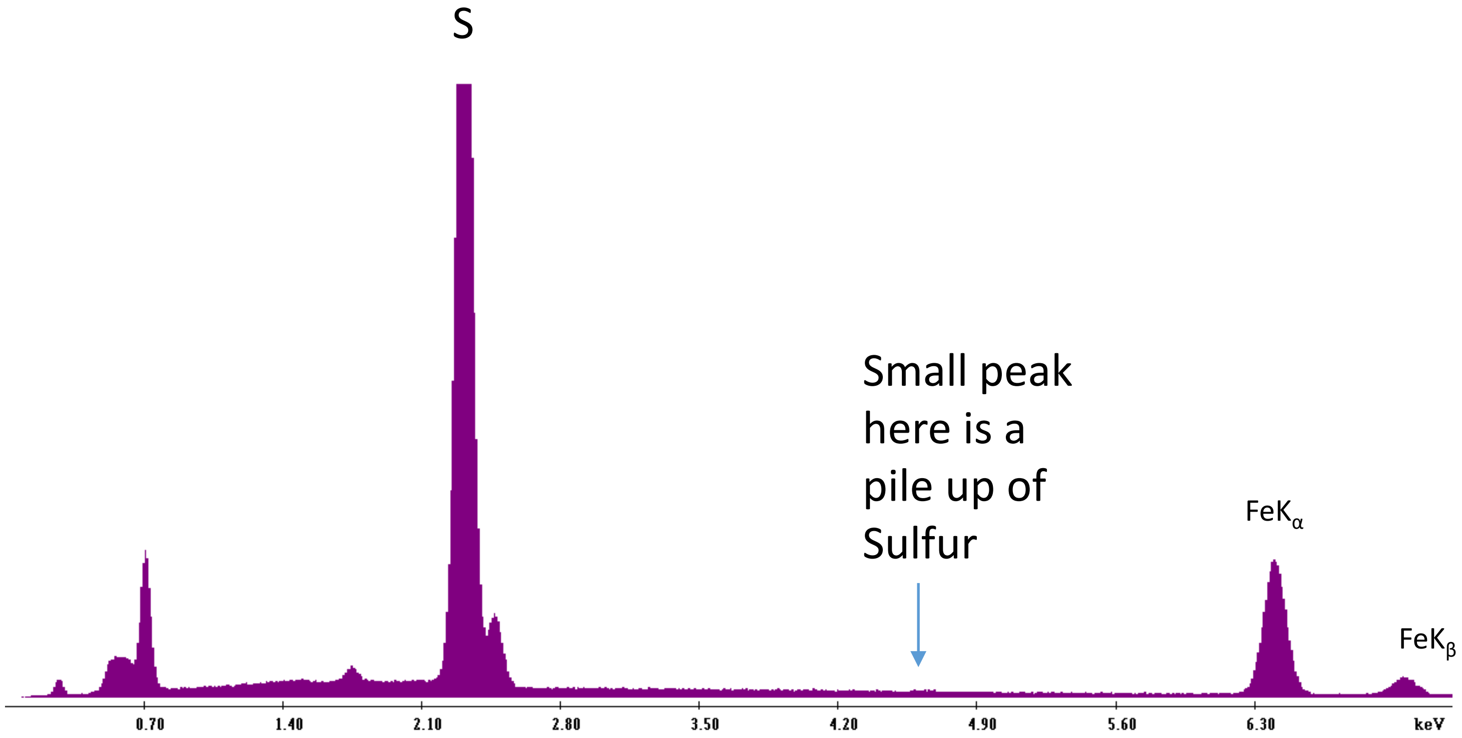
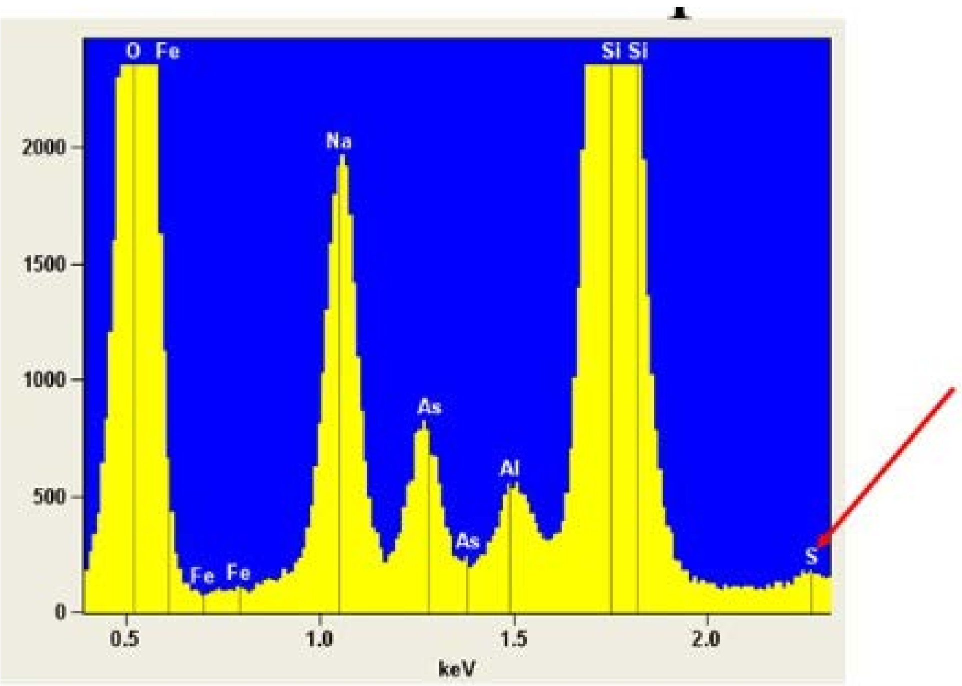
Consequences of too much Dead time, Pulse Pile Up or Sum Peaks.



Small peak here is a pile up of Sulfur

You can turn on sum peaks in EDS and Noran software, turn them on and be wary of them.

In some cases the Sum peaks can lead to mis-identifications: Argon, in an Aluminum sample? Probably not as Argon is a gas. Antimony, Sb in a Si sample? Both examples of Sum peaks, 2x energy. But there are more subtle peaks

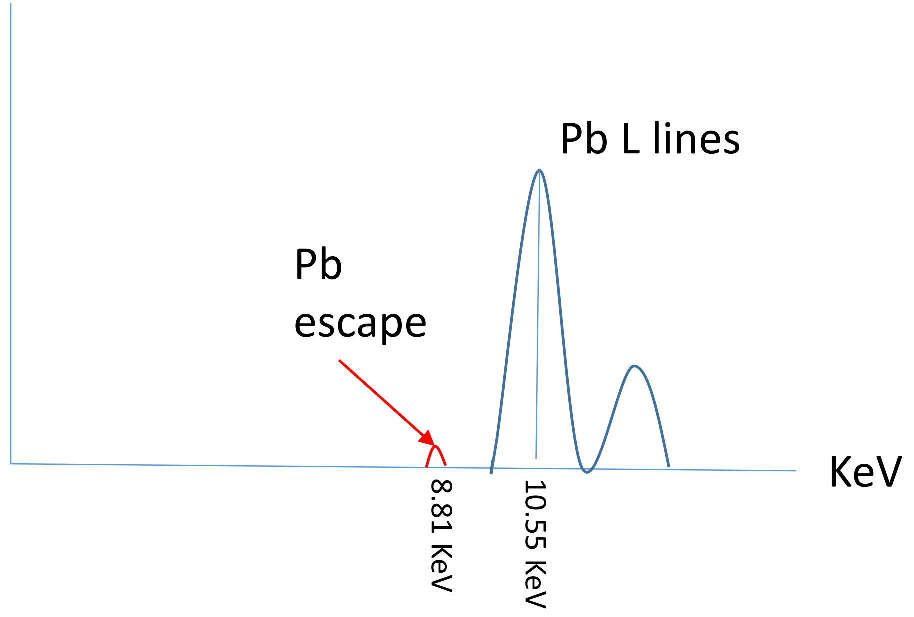


This example from UW Madison showing a “Sulfur” peak. It is actually the sum peak of O .63 KeV and Si at 1.74 KeV!

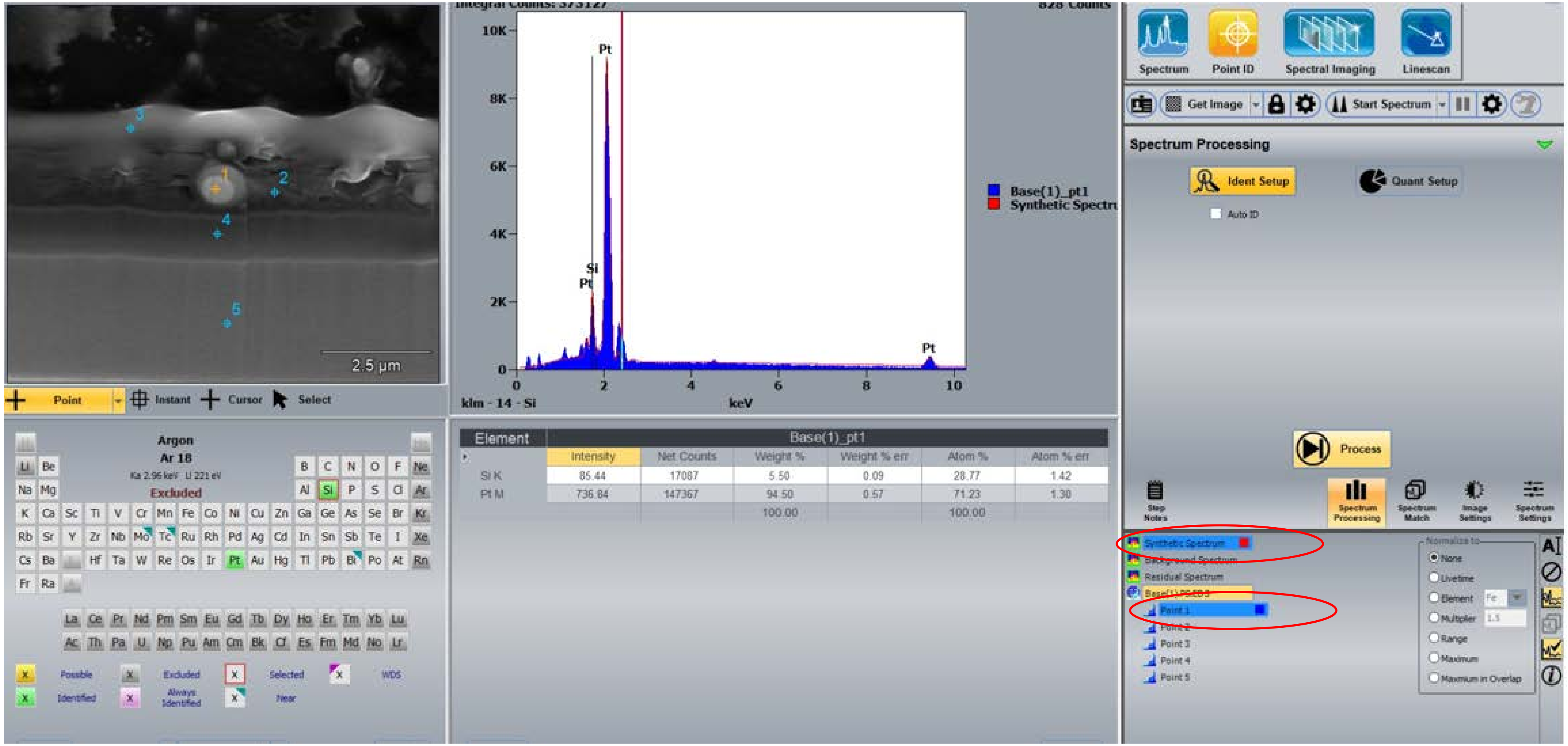
Just keep your dead time below 40% and you probably will never see these. If you do see a “mysterium peak.” Look at all possible sums..

Escape peak, Not readily observed on our systems with fairly thin detection areas, but here is what you should know about them.

- Higher energy x rays like Fe K or Pb L can induce fluorescence in the Si detector.
- Conservation of energy converts the Pb L to Pb L minus the Si K or 10.55 KeV – 1.74 KeV or 8.81 keV
- All you have to remember about escape peaks is minus 1.74 KeV. If you see a “mysterium peak” that is 1.74 keV below a strong, high energy peak it is an escape peak.



When in doubt over peak identifications, consult the known spectra that reside in the EDS software. These are found with the "HPD" button in EDAX, or "synthetic spectra" in the Noran-Thermo Fisher software.



Element	Intensity	Net Counts	Weight %	Weight % err	Atom %	Atom % err
Si K	85.44	17087	5.50	0.09	28.77	1.42
Pt M	736.84	147367	94.50	0.57	71.23	1.30
			100.00		100.00	

"Point and shoot mode" in Noran – Thermo Fisher software. By clicking on the synthetic spectra in red, you can see that all of the peaks have been properly identified. In this case the ball of material, point one, of the failed part cross section is comprised mostly of Platinum.

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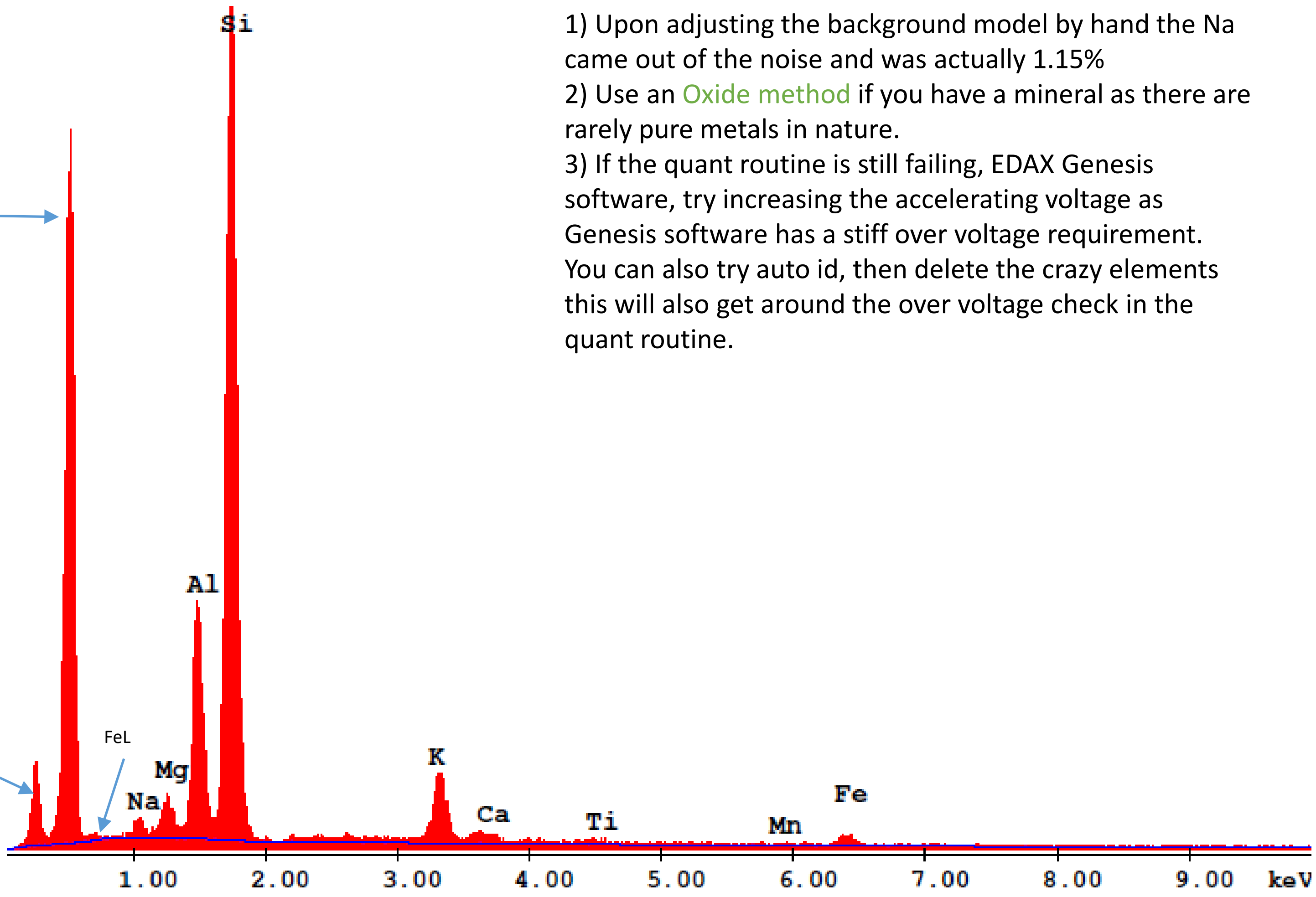
Finally, a tricky situation. Running Quant routines you will get zero results on peaks that exist. In this 8000 year old Indian artifact spectra the Na was coming out zero but was clearly present. Upon further examination the background model, blue line, was clipping the spectra.



Oxygen is not explicitly quantified in an Oxide method, it is implicit in the results

Carbon, ignored

1) Upon adjusting the background model by hand the Na came out of the noise and was actually 1.15%

2) Use an Oxide method if you have a mineral as there are rarely pure metals in nature.

3) If the quant routine is still failing, EDAX Genesis software, try increasing the accelerating voltage as Genesis software has a stiff over voltage requirement. You can also try auto id, then delete the crazy elements this will also get around the over voltage check in the quant routine.

Oxide	Wt%
Na_2O	1.15
MgO	2.46
Al_2O_3	14.95
SiO_2	67.55
K_2O	6.45
CaO	1.13
TiO_2	1
MnO	0.48
Fe_2O_3	4.83
Total	100

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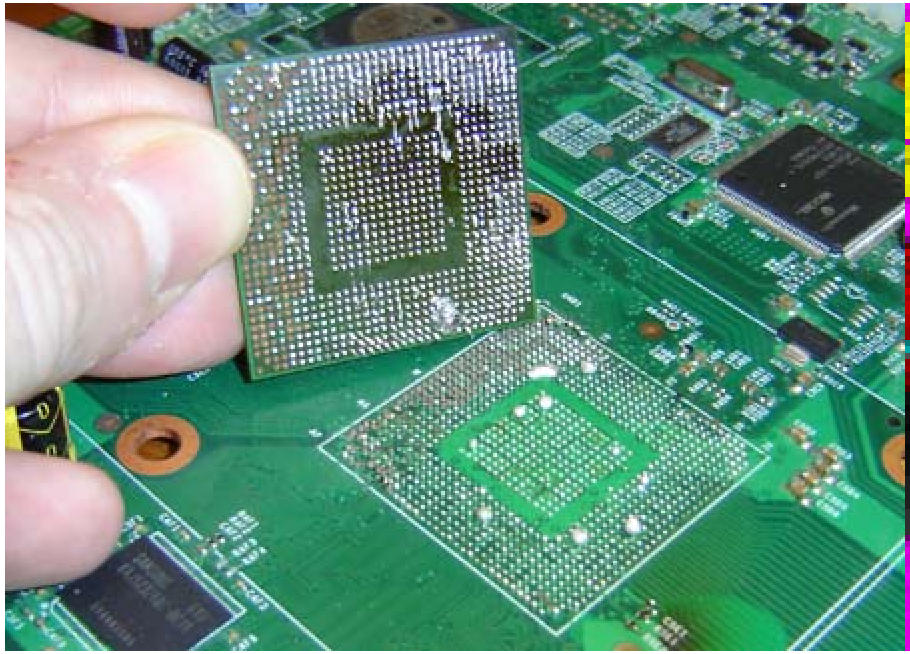
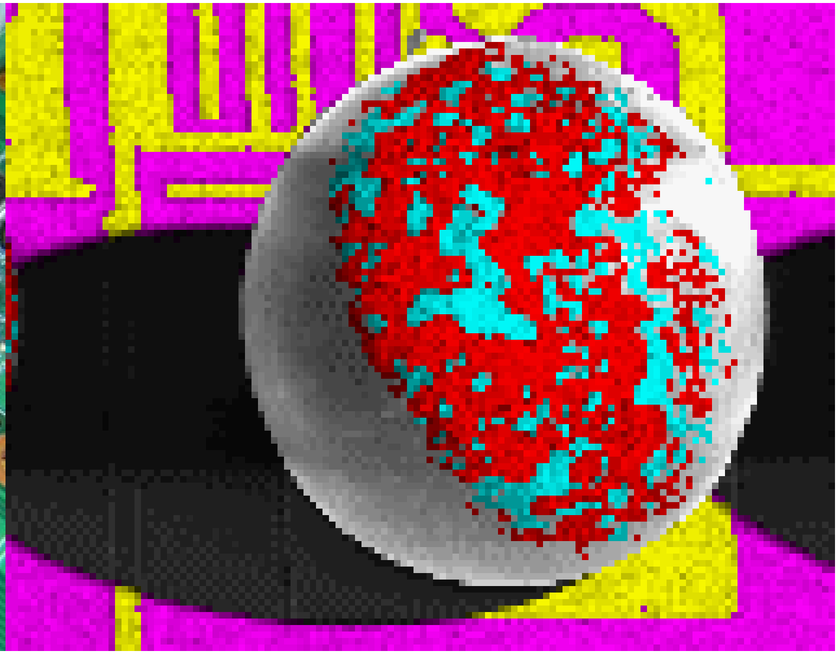
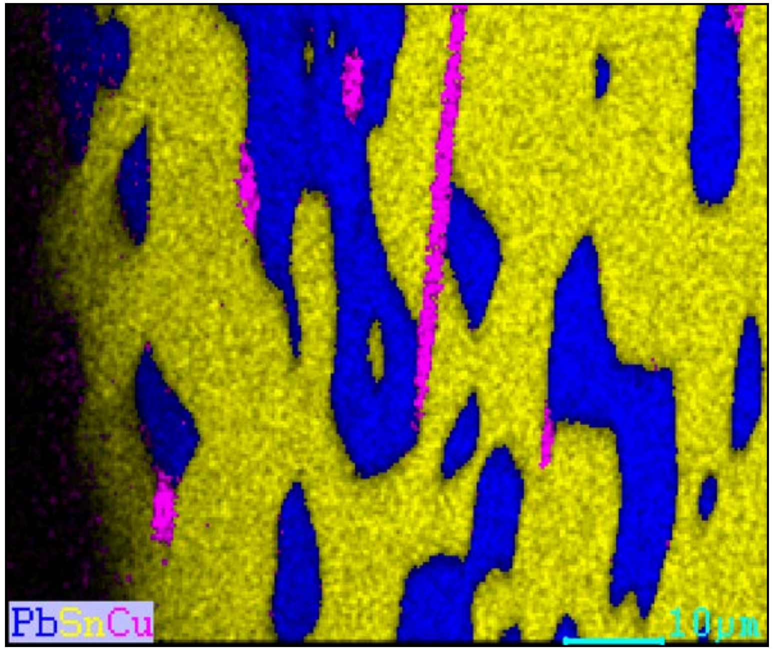
Mapping, use max current, drift control (only on Quanta 3D) and do post process to background subtract.



This is a flip chip Ball Grid Array (BGA). Or how to make Hundreds of reliable interconnects in a small space. Example of vertical integration. All modern processors are BGA. That is, until the next innovation.



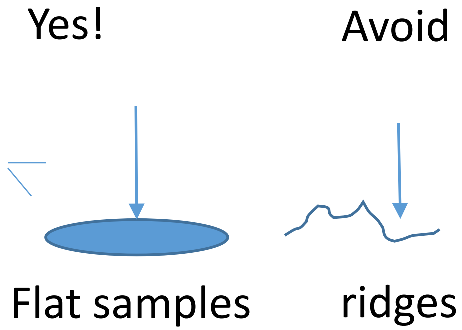
Quanta 3D example. Pb-Sn solder ball on Aluminum traces on Silicon, Medtronik pacemaker, medical devices can still use Pb-Sn solder!



Same ball grid array, higher magnification now of just the surface of the Pb-Sn ball. Now notice the Cu streaks.

Quantification or how we determine how much we have of every element. What we need for accurate quantification

1. We must do accurate qualitative analysis first. Study line shapes on page 21 and use them! How else is the algorithm going to compute Absorbance and Fluorescence corrections if peaks in the sample are not identified or ignored. The famous one I get is: my sample doesn’t have Na and Cl in it. Well, actually it does! And by ignoring those two elements you are degrading the accuracy of the quantitation.
2. Generally speaking we want to be above atomic number 11 for accurate quantification. This does not mean we can not get accurate quant on Oxygen. But we have to be careful and some of the tricks necessary for Carbon and Oxygen quantitation include, flat samples and standard checks to make sure the method is working.
3. Did I mention flat? If the sample is not flat, try tilting it towards the detector so that you are not sending X rays through topography.
4. Always run multiple spots and multiple KeV. At HP we had a rule for accurate quant: 3 locations and 2 keV. That is 6 measurements per sample. I know that many advisors give students 15 samples to analyze in limited time. But, on at least one of these, run 3 areas and 3 accelerating voltages: 15 keV and 30 keV to verify.
5. Standards. We have several standards from Tousimis and they are in the wood cabinets on the South side of the lab. Ask EM facility staff for one of these standards. There are up to 40 standards on one post so chances are we can find your compound and or something very close.



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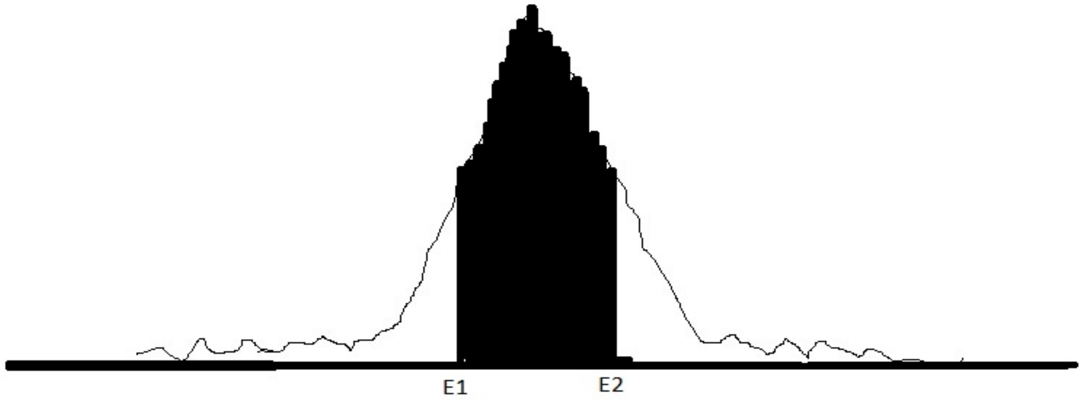
Quantification I, what is intensity?



Intensity is the total number of counts from Energy 1 to Energy 2. Or the Total Counts in a Region of Interest, ROI.

Quantification I continued, how we use Intensity

- First order approximation: $C_i/C_{(i)} = I_i/I_{(i)} = k_{(i)}$ equation 9.3 Goldstein where C_i is concentration in the unknown, $C_{(i)}$ is the concentration in the standard. Method of Castaing, 1951
- For example, ROI from 1.70 to 1.78 keV defines Si. Measure intensity of a pure Silicon standard, then put unknown in. If you get 10% of the intensity from the background subtracted Si ROI, then sample is 10% Silicon correct?
- This technique will lead to errors in SEM because of absorption and fluorescence.
- That is heavier elements in the matrix will absorb x-rays from lighter and lighter elements will fluoresce from heavier element x-rays.
- See next page

Downfall of Castaing’s K factor approach

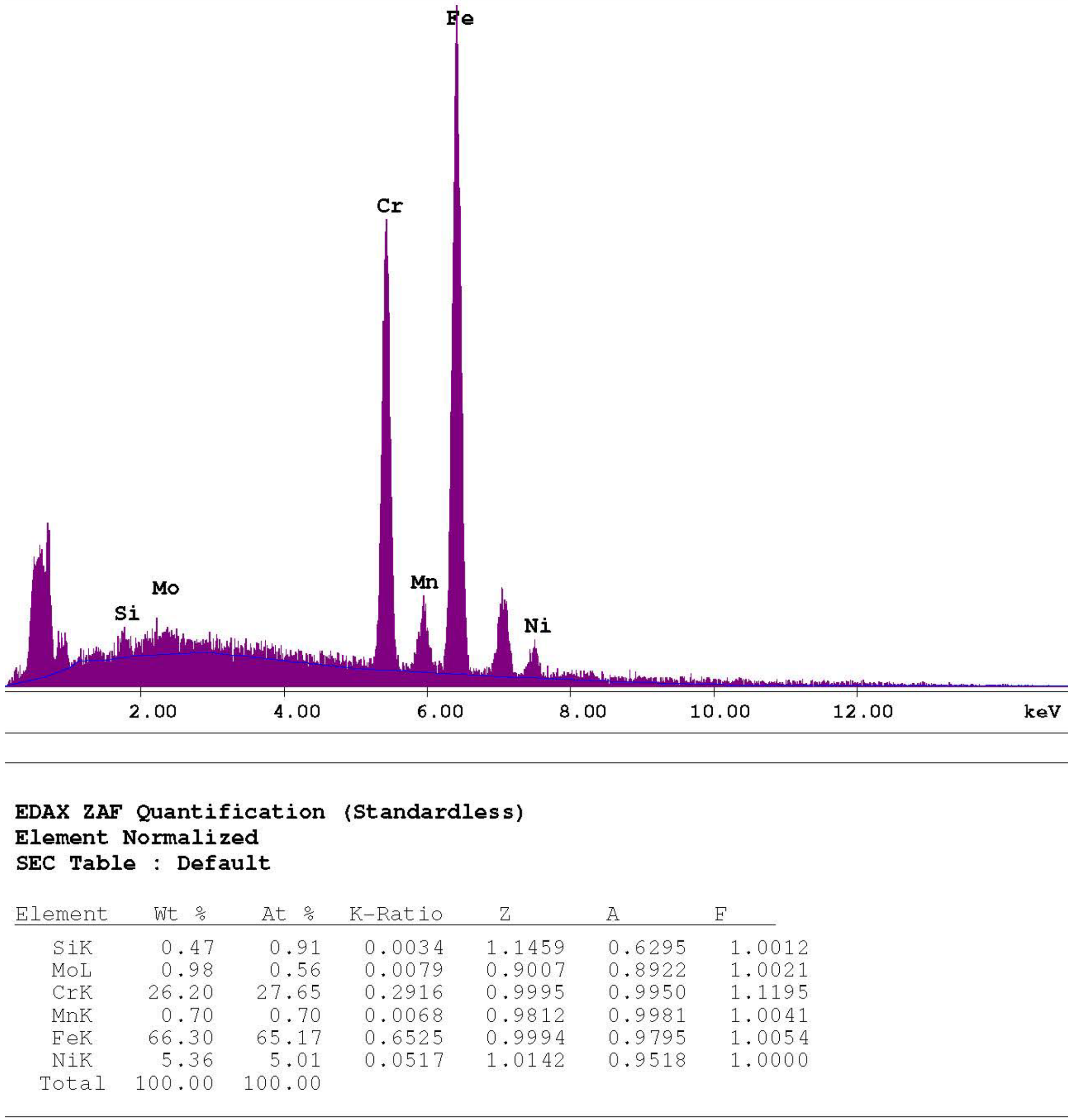
- Nickel K_{α} is higher energy than Fe and fluoresces Fe K_{α}
- And Fe will absorb Nickel K and so Nickel is diminished.
- When do K factors work?, TEM where sample is thin. Called Cliff-Lorimer method. K factor approach woefully in adequate for SEM.
- In SEM We use a series of three corrections of the K factor: Z for intensity difference due to different x ray yield, A for Absorbance say Iron absorbing Sulfur x-rays in a pyrite sample, and the final correction is due to fluorescence, F.

ZAF modification a second order more accurate determination than simple K factor of Castaing.

- $C_1/C_2 = \{ZAF\}I_1/I_2 = \{ZAF\}_1k_2$
- ZAF: Atomic number dependent stopping power and x-ray generation: Z, A for Absorption, F for Fluorescence
- Used in both EDS and WDS (electron microprobe analysis).
- Note a Z*A*F of less than one, typical for Si, Al, when heavier elements are in the material (matrix) … drives the response down.
- Wt% Concentration = K factor/Z*A*F will see an example of this on next page

Standardless quant, ZAF, alloy OSU Q600 on EDAX software

- Si Wt% = k/Z*A*F = .0034/1.1459*.6295*1.0012 = .0047 or .47% exactly what is given below. QED*
- Similarly for Mo, [Mo] = .0079/.9007*.8922*1.0021 = .0098 or 9.8%
- And so it goes, lighter elements get enhanced by A <1 as they are attenuated by heavier elements and A is in the denominator.
- Heavier elements generally have A and Z close to one but have some action with Flourescence, Chromium has F of 1.12 and that drives the Chromium concentration down as there is strong Fluorescence of Cr by higher energy Fe and Mo x rays.



```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %     At %   K-Ratio      Z          A         F

   SiK      0.47     0.91   0.0034   1.1459   0.6295   1.0012
   MoL      0.98     0.56   0.0079   0.9007   0.8922   1.0021
   CrK     26.20    27.65   0.2916   0.9995   0.9950   1.1195
   MnK      0.70     0.70   0.0068   0.9812   0.9981   1.0041
   FeK     66.30    65.17   0.6525   0.9994   0.9795   1.0054
   NiK      5.36     5.01   0.0517   1.0142   0.9518   1.0000
  Total   100.00   100.00
```

*QED , Quod Erat Demonstradum which was to be proven.

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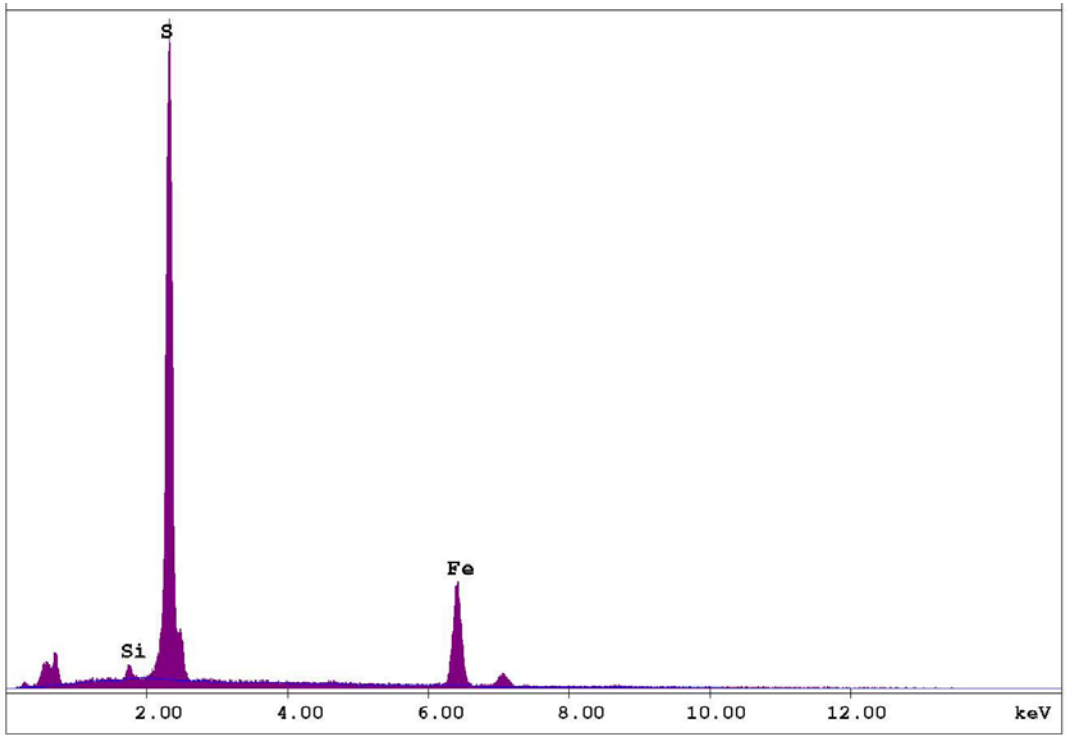
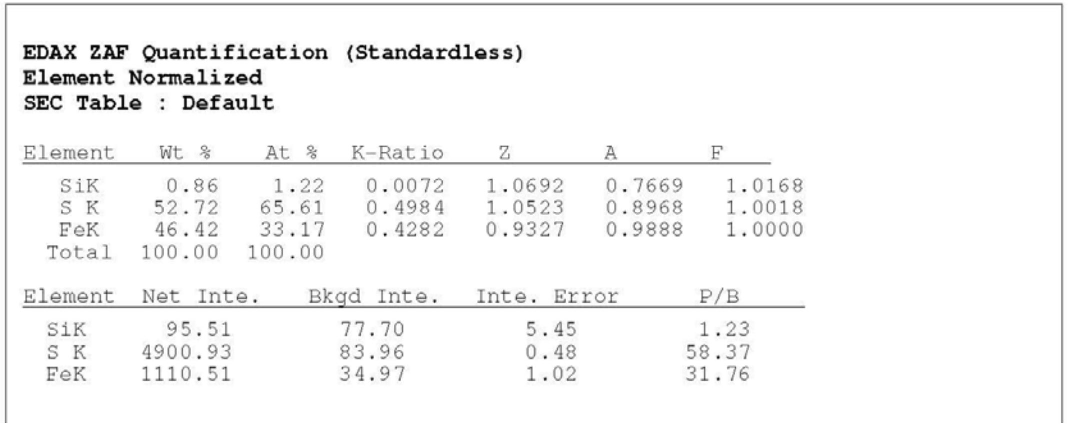
Quant Example II, Lab Standard Pyrite Notice A factor in Silicon, and Error in Si





```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element   Wt %    At %   K-Ratio    Z        A        F
  SiK     0.86    1.22   0.0072   1.0692   0.7669   1.0168
  S K    52.72   65.61   0.4984   1.0523   0.8968   1.0018
  FeK    46.42   33.17   0.4282   0.9327   0.9888   1.0000
 Total  100.00  100.00

Element  Net Inte.    Bkgd Inte.   Inte. Error      P/B
 SiK       95.51        77.70         5.45          1.23
 S K     4900.93        83.96         0.48         58.37
 FeK     1110.51        34.97         1.02         31.76
```

This is the second case for an A of much less than unity in a light element. What does this do to the K factor?

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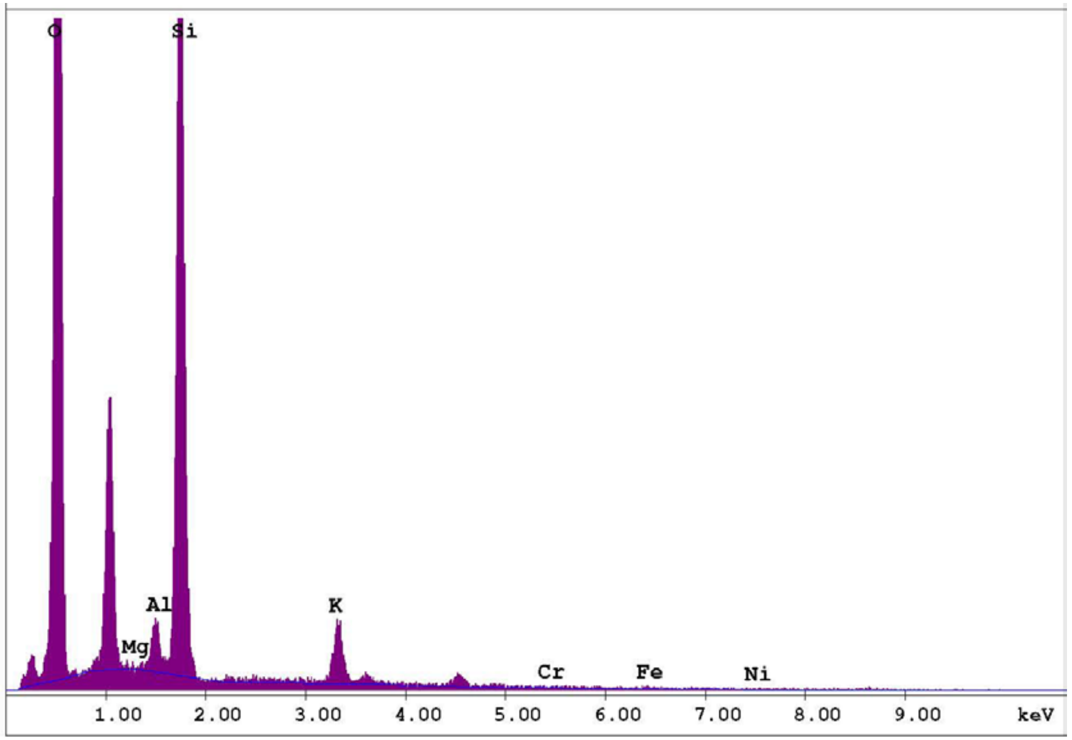
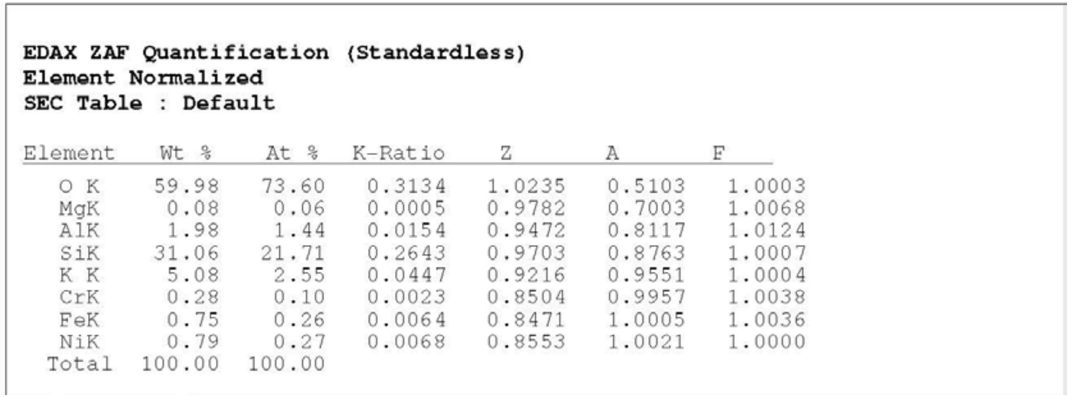
Example III a glass sample





```
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element    Wt %      At %    K-Ratio     Z          A          F
   O K     59.98     73.60   0.3134    1.0235    0.5103    1.0003
   MgK      0.08      0.06   0.0005    0.9782    0.7003    1.0068
   AlK      1.98      1.44   0.0154    0.9472    0.8117    1.0124
   SiK     31.06     21.71   0.2643    0.9703    0.8763    1.0007
   K K      5.08      2.55   0.0447    0.9216    0.9551    1.0004
   CrK      0.28      0.10   0.0023    0.8504    0.9957    1.0038
   FeK      0.75      0.26   0.0064    0.8471    1.0005    1.0036
   NiK      0.79      0.27   0.0068    0.8553    1.0021    1.0000
  Total   100.00    100.00
```

Note, Concentration should be equal to the K ratio divided by ZAF:

Si example: K ratio .2643
Z = .9703, A = .8763, F = 1.0007
Wt% = .2643*100/(.9703*.8763*1.0007) = 31.06%

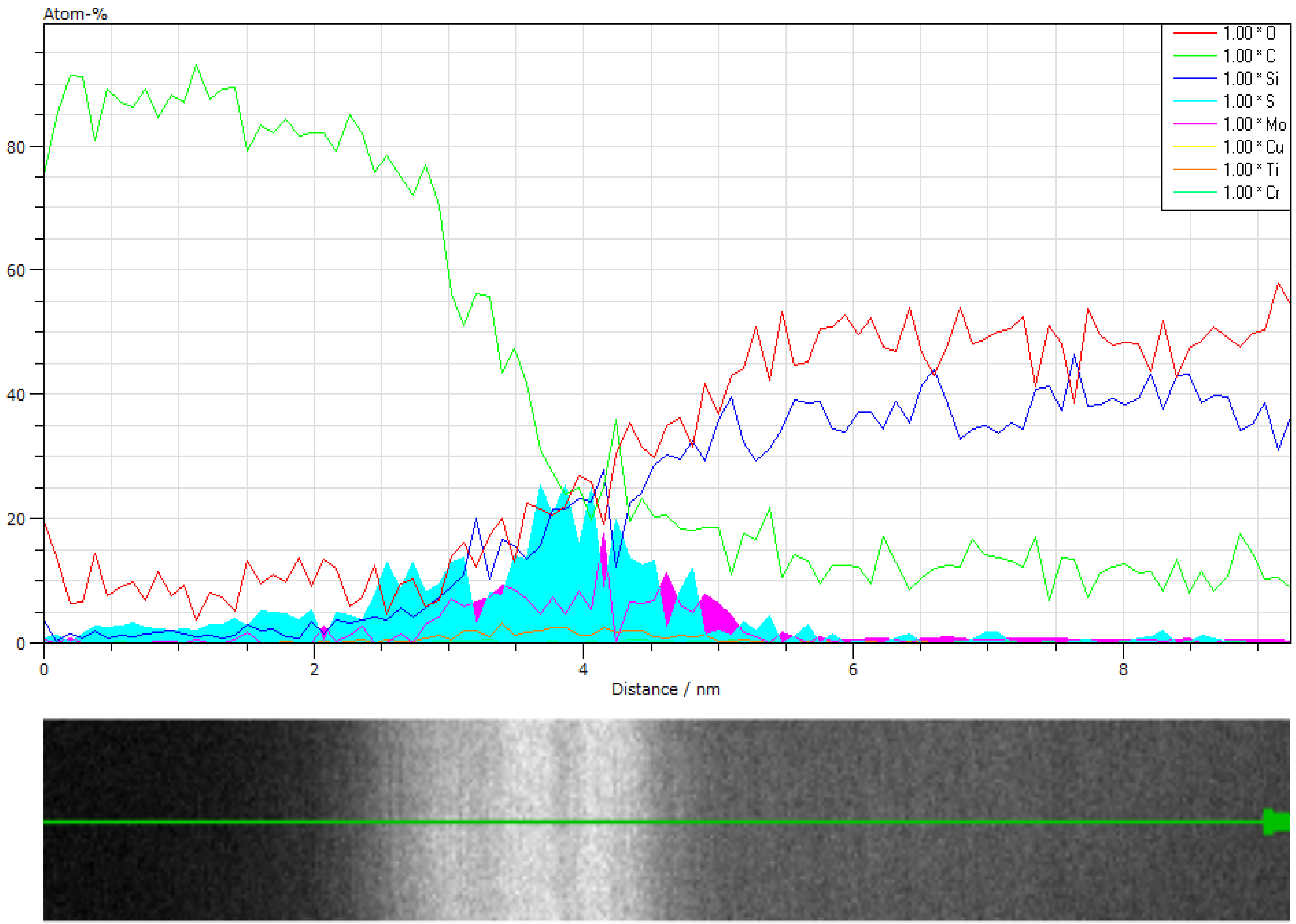
Fe example: K ratio .0064
Z = .8471, A = 1.0005, Z = 1.0036
Wt% Fe = .0064*100/(.8471*1.0005*1.0036) = 7.52%

Again, Z*A*F will drive up the concentration of a species as we know the response – x-rays- to this species will be lower.

Confidence in ZAF , standard less quantification method

- In many situations standardless quant in the SEM is superb for atomic numbers greater than 11. With an Iron Sulfite, pyrite, standard the EDAX, Si(Li) standard-less quant is typically within .2 At% of the correct answer, say 49.8% S and 50.2% Fe. With the Noran(SDD) and software the error is just a bit higher at say 49.4% and 50.6%.
- When in doubt, don’t do standardless quant. Instead, use a sample that you have hard data on say from XPS. Then we can show you how to turn this into a standardized method!
- For a complete dissertation on the performance of standard-less quant see Goldstein Chapter 9. They quote 5% error for atomic numbers 12 and above.

STEM EDS, the ultimate spatial resolution



1 nm thin bilayer of MoS_2 film on SiO_2 with a Chrome protect layer. Conley group OSU

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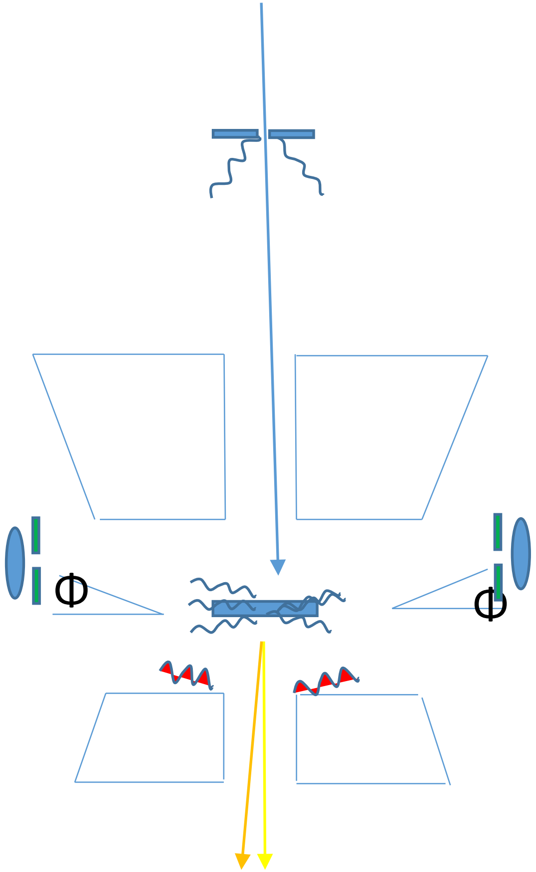
TEM x-ray analysis

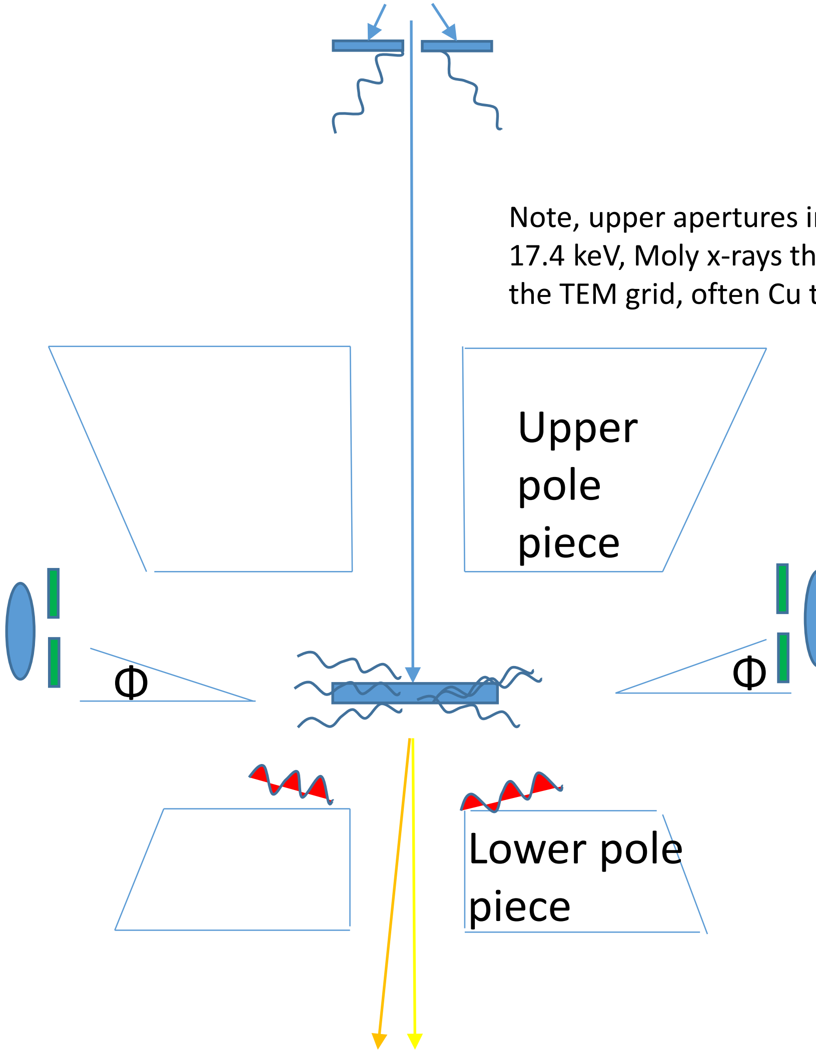
- Modern TEM's are generally a sandbox for analysis. You will have EDX and EELS on most. Some have cathode luminescence! You can also do diffraction. So, on hard problems we want to use all the tools. We don't want to just rely on TEM (STEM) EDS as it is not usually accurate enough for minor phase differences. That is we can't reliably tell In_2O_3 and InO phases. But, in diffraction we can distinguish those.
- In the TEM we put it in STEM mode do to the analysis. TEM mode floods the whole sample with the beam. We get an EDS signal but is from the whole sample. OK if your sample is homogenous but if you want small phases or thin film EDS, this is only done in STEM.



TEM quantification

- In TEM we can generally assume very little absorbance, very little fluorescence and stopping power and generation (Z) are approximately constant.
- Cliff-Lorimer realized that instead of ratio to a standard the response could be modelled by simply forming a ratio to subsequent peaks in the spectra.
- As such : $C_a/C_b = k_{ab}*(I_a/I_b)$ its really the k factor approach of Castaing
- Manufacturer provides a table of Cliff-Lorimer factors, K_{ab} from calculation and some experimental data.
- But, for maximum accuracy in your quantification do create a binary standard of your compounds of interest and measure the response in your system.
- Note, for slightly thick samples, greater than 50 nm, absorption effects will drive down response of low atomic numbers. Some manufactures, Bruker allows you to input a “fudge factor” thickness and density that will correct for this. Or try a ZAF method.
- Because of the poor take off angle in a modern STEM, with a small gap in pole pieces absorption effects are actually substantial. In god we trust, for all others we strongly suggest standards.

OSU ChemiSTEM* configuration, 4** x-ray detectors at Φ, take off angle of 22 degrees.



Note, upper apertures in condenser create “hard”, 17.4 keV, Moly x-rays that get to the sample and cause the TEM grid, often Cu to fluoresce

Upper pole piece

Collimator for unwanted pole piece x rays

SDD x- ray detector

Lower pole piece

Because this is a high resolution instrument, it has a narrow pole piece gap and so 22 degrees is it. A higher take off angle would be better for light element quantification!

Scattered beam for Diffraction or EELS

Transmitted beam

- ChemiSTEM is a trademark of FEI Thermo Fisher it is not a scientific name

** only 2 of the 4 detectors are pictured here

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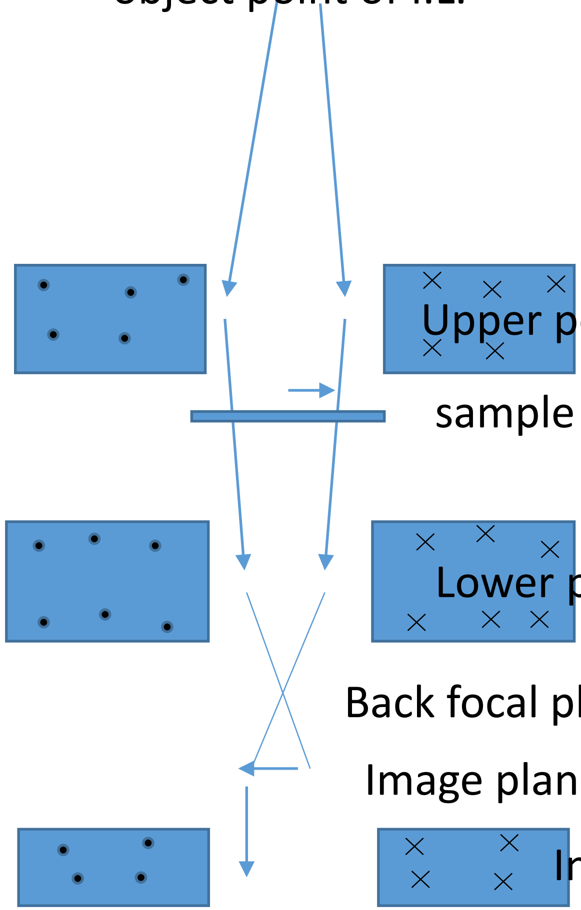
EDS on a TEM is done in STEM mode so we know where the x rays are coming from. Here is a comparison of TEM vs STEM modes. TEM parallel illumination, STEM converged. Only scattered beams go from sample into HAADF detector. The atomic number scattering into the HAADF is controlled by Camera length, crossover of Pole pieces.

TEM mode, parallel illumination Image plane of pole piece is object point of I.L.



Upper pole piece

sample

Lower pole piece

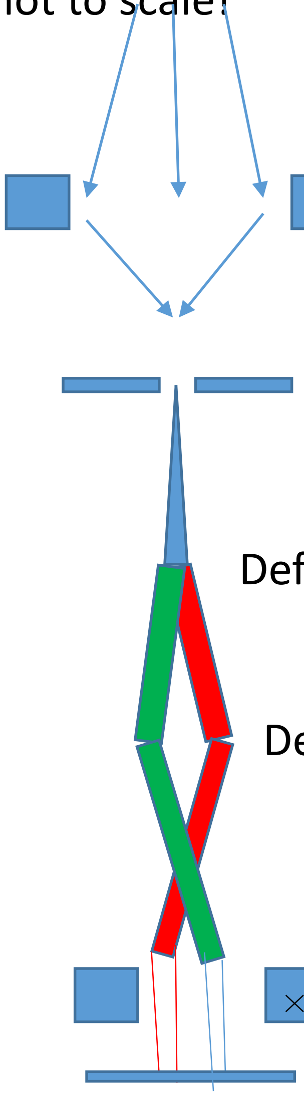
Back focal plane, diffraction pattern, ch 4, 5

Image plane

Intermediate lens

To projector lens and camera

STEM mode not to scale!



C.L. 2 or 3

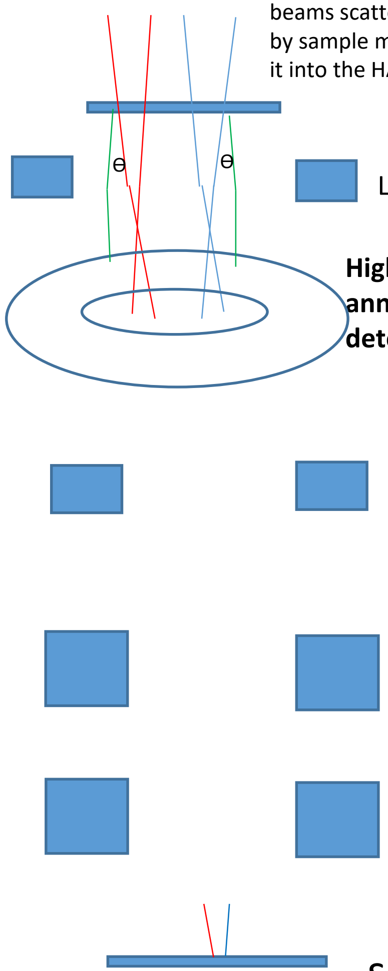
C.A.

Deflector 1

Deflector 2

Upper Pole piece

Continued to right



Only green beams scattered by sample make it into the HAADF

θ

θ

Lower pole

High angle annular dark field detector, STEM

I.L

PL 1

PL 2

screen

If you pause the scan, you see one disk for amorphous materials

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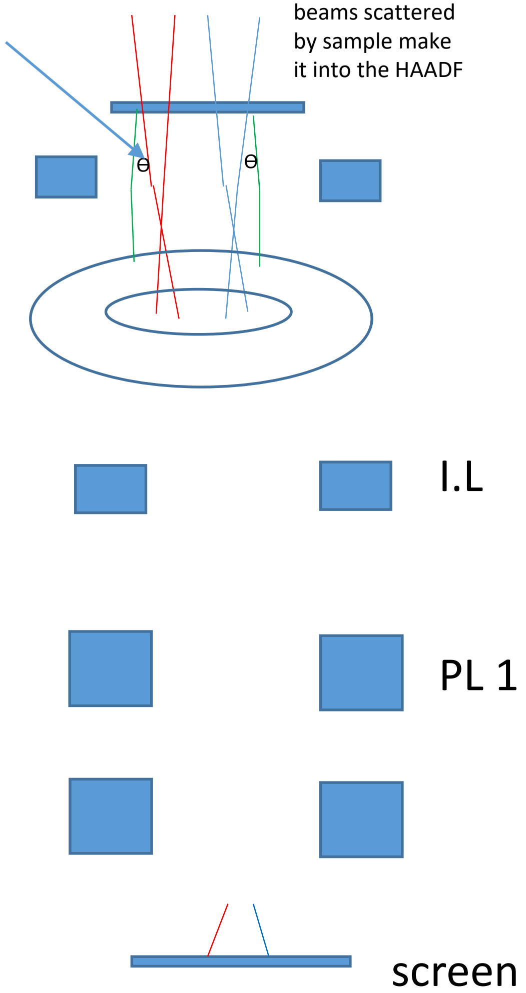
STEM EDS in TEM page 2

1. When you look at the screen the 000 spot you see is a disk and its size is relative to the convergence angle on the sample. CA 100 (20 milli radian convergence) means big spot, CA 50 (10 milli radian convergence) smaller spot, CA 10 (2 milliard convergence) smallest spot.
2. When you pause the beam on a crystalline and look on the screen with the eye pieces you will notice many disks, Bragg diffraction. How can this be? It has to be that $\Theta_{HAADF} >> \Theta_{bragg}$. The Z contrast, HAADF, signal is actually from Rutherford backscattering and that is a much higher angle than Bragg scattering, roughly 10 milli rad for .3 nm d spacing (Si 111) and 200 keV electrons, $\lambda = .0025$ nm. The Howie (1979) detector or HAADF has $\Theta > 50$ milli rad to avoid Bragg Scattering and only pick up Atomic, Z contrast via high angle Rutherford scattering.

3. Extra Credit! : By leaving the STEM scan on the OSU Titan and turning diffraction off you will actually see a shadow of the HAADF detector. The ray tracing for that is extra credit. Come see me if you get it and I will buy a cup of coffee for you at the OSU Ava's café.



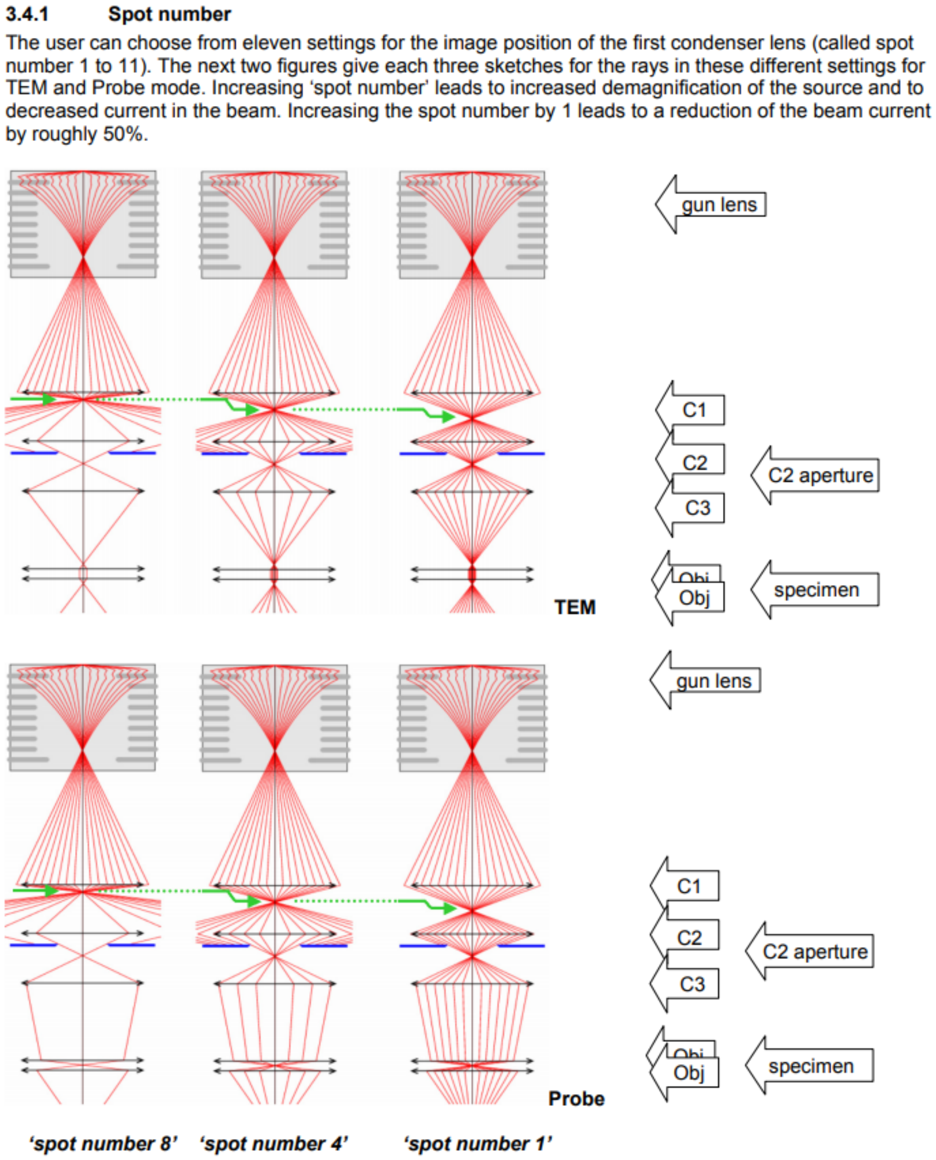
How large is Θ?

Only green beams scattered by sample make it into the HAADF

EDS in TEM-STEM differences vs EDS in SEM

- Spatial resolution! STEM EDS in the TEM has 100 times the spatial resolution of SEM.
- The TEM sample is generally 100 nm thin and so beam scatter that reduces horizontal resolution is reduced. STEM EDS resolution is typically 1-2 nm at 200 keV.
- Take off angle can be poor relative to SEM and so quantification of light elements suffers. Thus, a need for standards when quant of light and heavy elements is needed.
- More fluorescence effects in TEM than SEM. Hard X-rays from the Molybdenum foil apertures at the top of the column.

TEM Spot number diagrams from the Titan manual, in a TEM we strengthen C1 at higher spot number and this is more de-magnification and less current!



3.4.1 Spot number

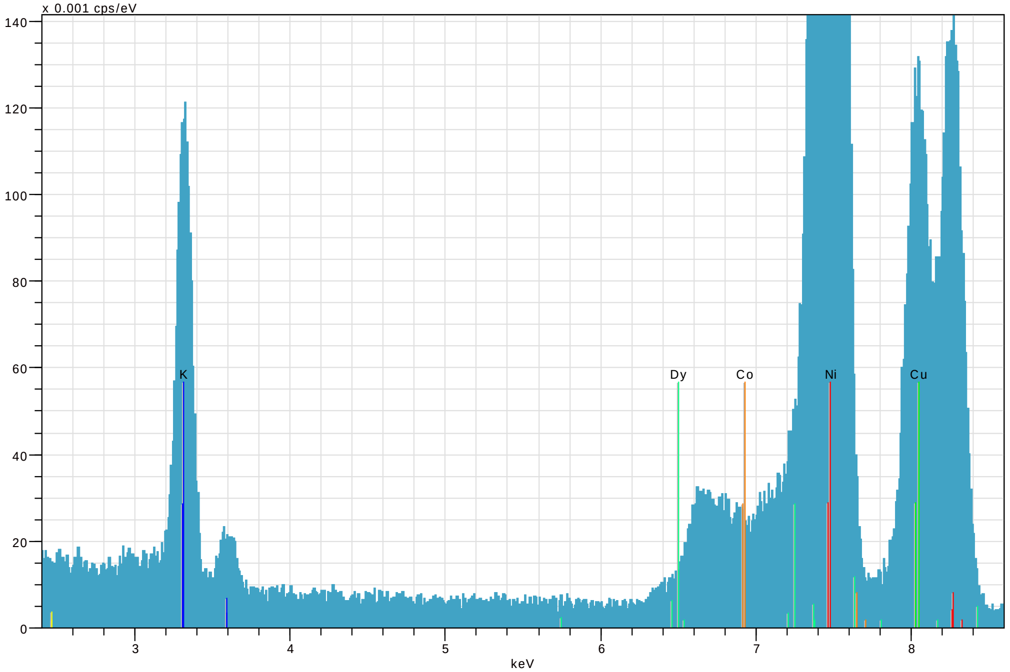
The user can choose from eleven settings for the image position of the first condenser lens (called spot number 1 to 11). The next two figures give each three sketches for the rays in these different settings for TEM and Probe mode. Increasing ‘spot number’ leads to increased demagnification of the source and to decreased current in the beam. Increasing the spot number by 1 leads to a reduction of the beam current by roughly 50%.

‘spot number 8’ *‘spot number 4’* *‘spot number 1’*

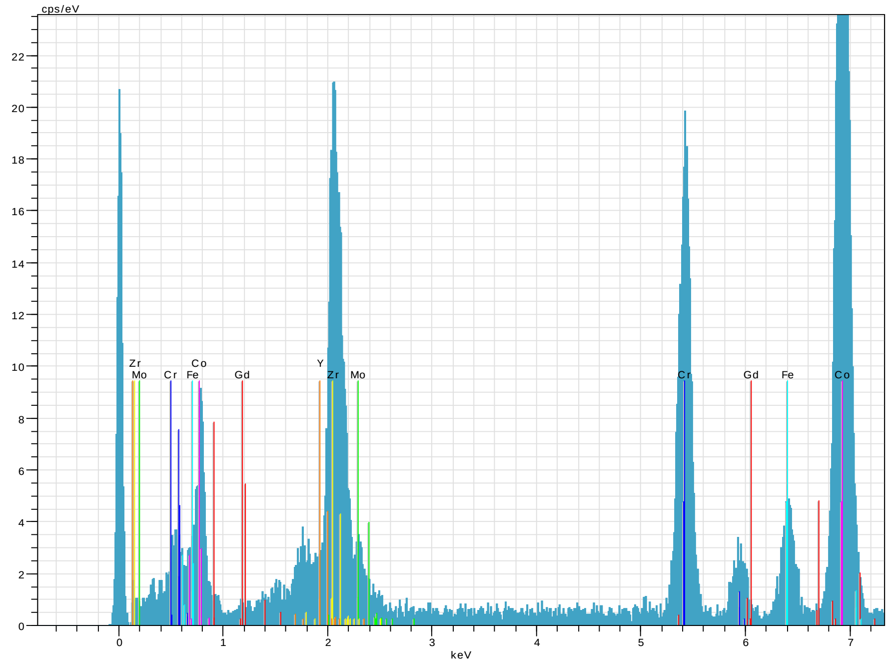
- Far left, spot 8 Condenser one is strongest and pulls crossover away from aperture underfilling and reducing current.
- Far right spot 1, Condenser one is weakest, this puts crossover nearer the aperture for near optimal filling and max current.
- Spot is a matter of preference. But, one thing to consider is beam coherence. Larger spot number on the TEM produces a more coherent beam and this can strengthen lattice fringes for example.
- For EDS maps, current is king, so spots less than 6 are typical.

OSU ChemiSTEM spectra.   Proper alignment of all four detectors is key to good spectra on a multi detector instrument.

Before an alignment. A Satellite peak of Ni between where Co and Dy would be.



Post alignment Cr, Ni, Fe artificial spectra fits now with no satellite peaks.



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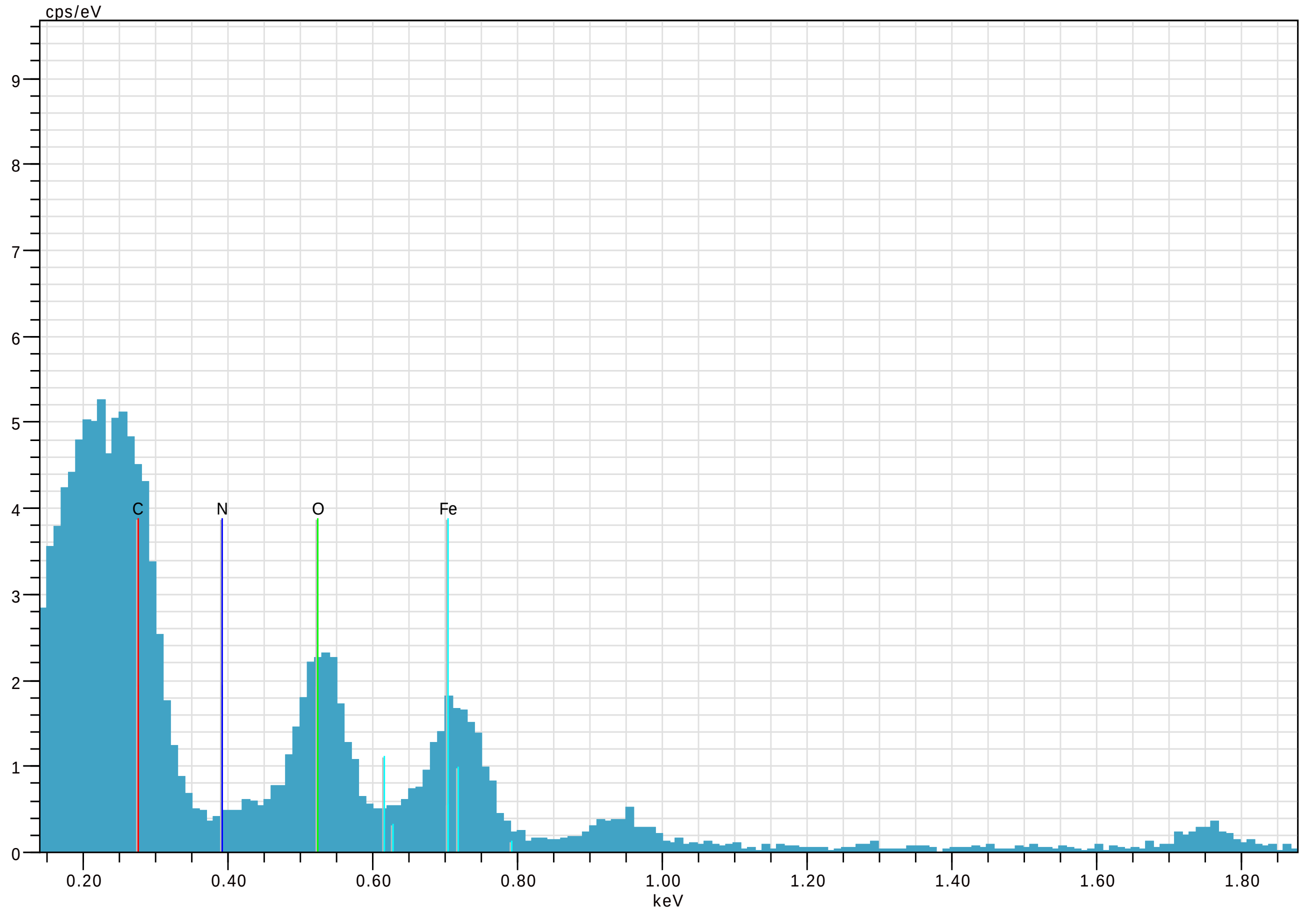
Low energy peaks also improved by alignment of all 4 detectors.

- In the no spectra is ever quite perfect to us career EDS folks, there is an issue with the Carbon peak.
- Can you spot it? My colleague at U Hawaii, John Bradley did, and suggests it is in the Bruker Pulse processing method.
- Note, for better Carbon results in the Bruker software, use the max 60,000 cps option. This effectively increases the shaping time we spoke of in the introductory SEM EDS portion of this chapter, page 9. That should improve the low energy line shape.



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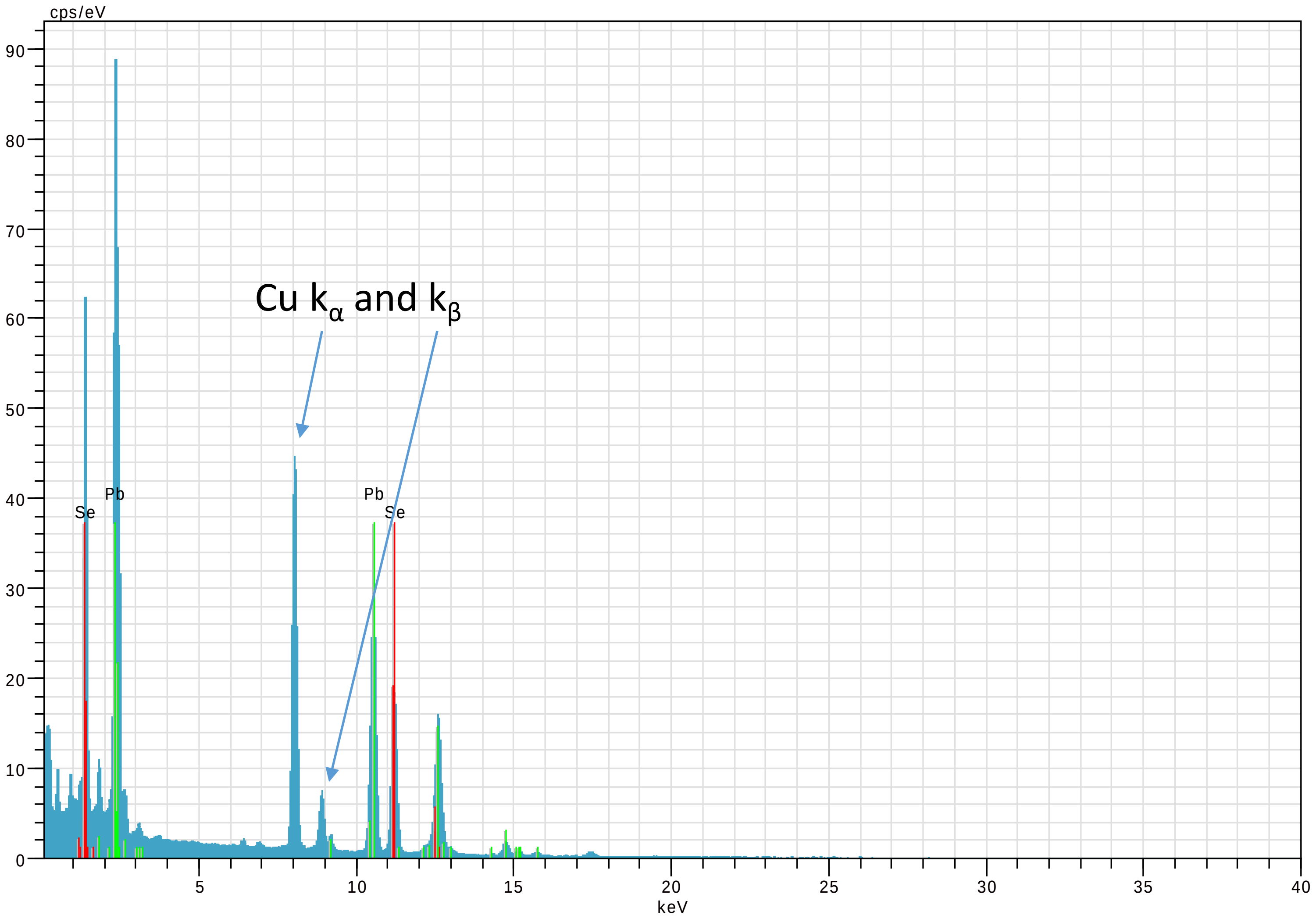
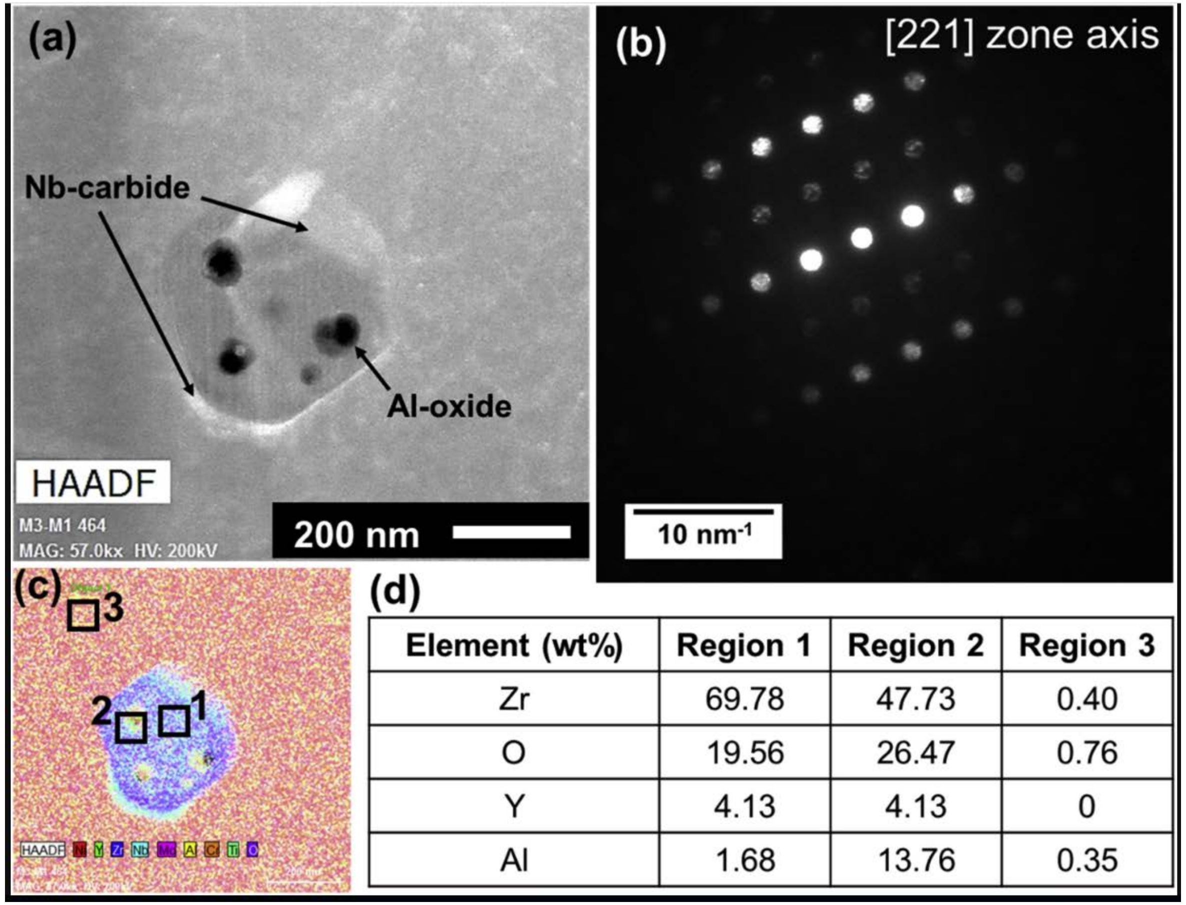
The Cu Fluorescence from the Cu grid is ever present in a TEM sample. You can "deconvolve" the Cu from the spectra using Bruker software. This uses the known ratio of the k_{α} and k_{β}. Using a method with Cu identified but later "deconvolved" is the best practice.



Cu k_{α} and k_{β}

In this case standardization was used to develop a method to quantify PbSe within .5% of the known stoichiometry. That result has been repeating for over one year on 30 plus samples.

Published result $_2$ for DOE NETL on additive manufacturing. In this case the OSU Titan TEM was used to show NbOx layer and Alumina segregation in ceramic added to a high temperature steel.



Element (wt%)	Region 1	Region 2	Region 3
Zr	69.78	47.73	0.40
O	19.56	26.47	0.76
Y	4.13	4.13	0
Al	1.68	13.76	0.35

Also, many peer reviewer's will ask for diffraction data to back up EDS data and a nice HAADF or TEM image as well!

2. H Rao R. P.Oleksak[ab]K. Favara[ac]A/ Harooni[d]B. Dutta[d]D. Maurice[a]Behavior of yttria-stabilized zirconia (YSZ) during laser direct energy deposition of an Inconel 625-YSZ cermet. Additive Manufacturing Vol 21, January 2020

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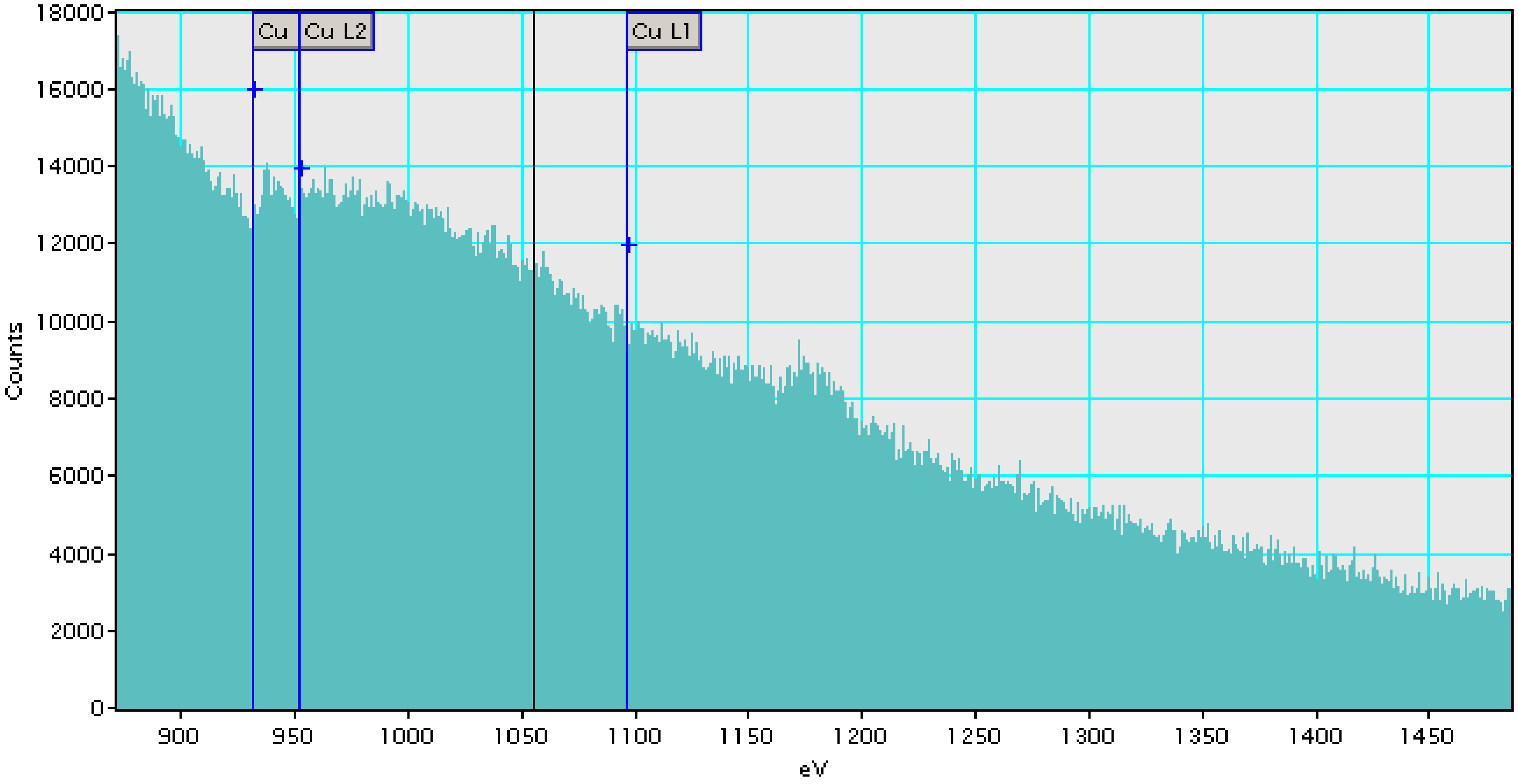
Other methods when EDS does not work.

Number 1 : EELS in STEM.
Number 2 : XPS
Number 3: WDS
Number 4: ICP MS or ICP AES
Number 5 and beyond: Accelerator techniques: PIXE, RBS (hydrogen), XANES (coordination number)

EELS In this case it was used to confirm a Copper contamination, a tough one in EDS because of Bronze parts in TEM or Cu in the grid.



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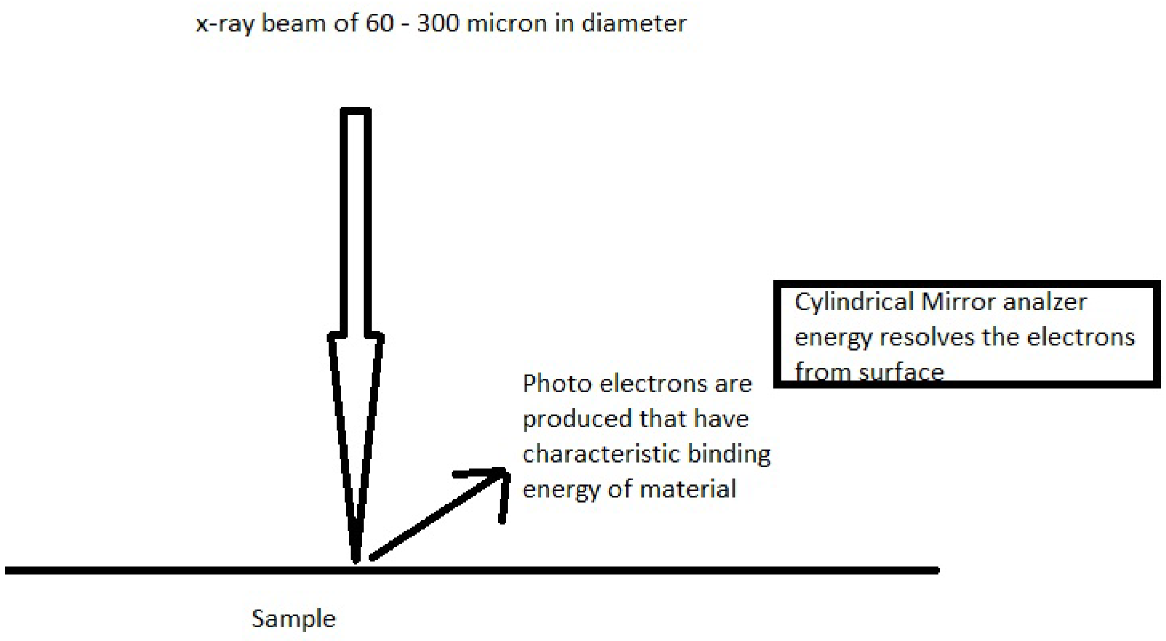
X-ray Photo electron spectroscopy, XPS

- Escape depth of photo electron is first 30 Angstrom, 3 nm.
- So, you must have a freshly cleaved surface or do some in situ sputtering.
- TEM or STEM EDS is more bulk sensitive, first 30 nm
- In spite of these difficulties the agreement between XPS and STEM EDS linescans can be startlingly good. Many examples of this in my failure analysis background.
- XPS excels at Carbon to Oxygen ratio. STEM EDS fails at this because STEM environment is not nearly as clean as Ultra High Vacuum of an XPS.
- Compliment to EELS. UPS (XPS with ultra-violet source). EELS will sense empty states. XPS only observes occupied states.
- Auger and SIMS are similar but not quantitative. Although Auger has superior spatial resolution. SIMS has extreme sensitivity



x-ray beam of 60 - 300 micron in diameter

Cylindrical Mirror analzer energy resolves the electrons from surface

Photo electrons are produced that have characteristic binding energy of material

Sample

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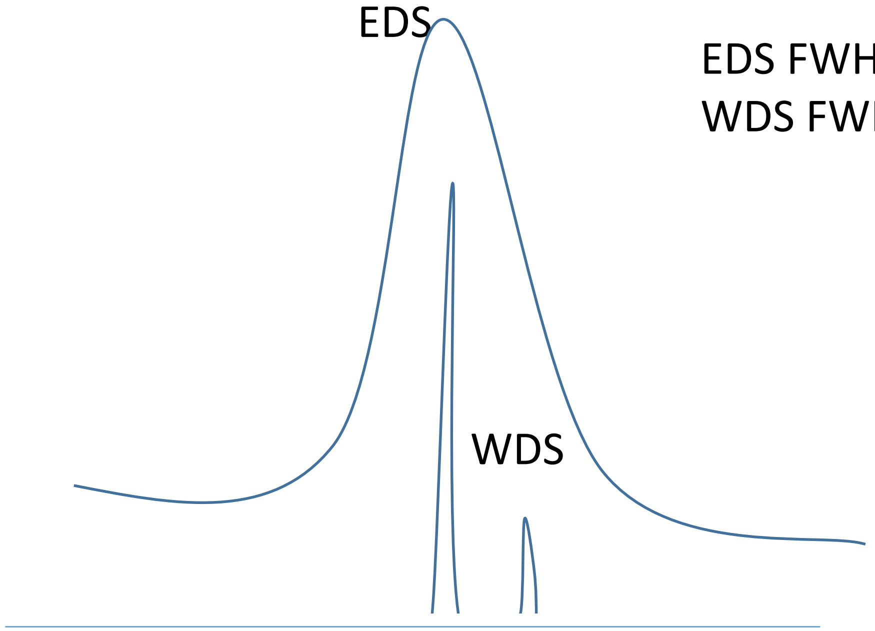
WDS EDS resolution You can actually see the Sulfur K_{α} and $K_{\beta.}$ This dramatically improves quantitation.



EDS FWHM typically 127 eV
WDS FWHM typically 10-15 eV

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Mass Spectroscopy techniques

- ICP-MS, accurate quantitation down to single ppm.
- ICP-AES is compliment for atoms that can’t be detected in MS.
- It is destructive and has very little spatial resolution.
- GC MS and LC MS, if you can rinse your sample and extract stuff these two techniques will produce fantastic results as mass spectra will give you a fingerprint of the exact compound.
- MALDI TOF, Matrix Assisted Laser ….

Accelerator Techniques

PIXE: Particle Induced X –ray emission: few part per million sensitivities. Lateral width is 1-10 microns in well collimated accelerators. Atomic numbers greater than sodium.

Rutherford backscattering, RBS, use the proton beam to sense backscatter events and quantify light elements and it excels at Hydrogen.

Conclusion:

EDS and WDS are useful tools for characterization of materials. WDS was only briefly discussed as our facility does not have a WDS onsite. Quantification errors are surprisingly low with SEM EDS, errors only in the .2 Wt% for the Pyrite sample discussed. STEM EDS in a TEM has 100 times the spatial resolution of SEM EDS. STEM EDS is more tricky because of lower take off angles. Standardization of TEM EDS does result in very low errors, one half percent or less if the samples analyzed do resemble the standard. Finally, consider other methods. And that is a perfect lead into the next chapter, chapter 7, EELS.

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