General EM

- So far we are up to about 1970, albeit we have not gone to higher levels of diffraction that were known then
  - Basic Diffraction (+CBED)
  - Basic Bright Field
  - Basic Dark Field
- Kinematical is OK, but better (Bethe theory) was known even in 1928, the year ED was confirmed
- These are *always* a good place to start, but there is far more

Overview: Experimental

Chemical/Electronic

- X-ray microanalysis (EDS)
- Electron Energy Loss Spectroscopy (EELS)
- ND Spectroscopies (EDS/EELS + position)
- Other (mainly SEM)
  - Cathodoluminescence
  - Phonon
  - Acoustic

Structural

- Conventional High Resolution (HREM or HRTEM)
- Annular Dark Field (ADF)
- High Angle ADF (HAADF)
- Annular Bright Field
- Aberration Correction
- Lorentz & Other
- 4D STEM
- Vortex Beam

Overview: Theoretical

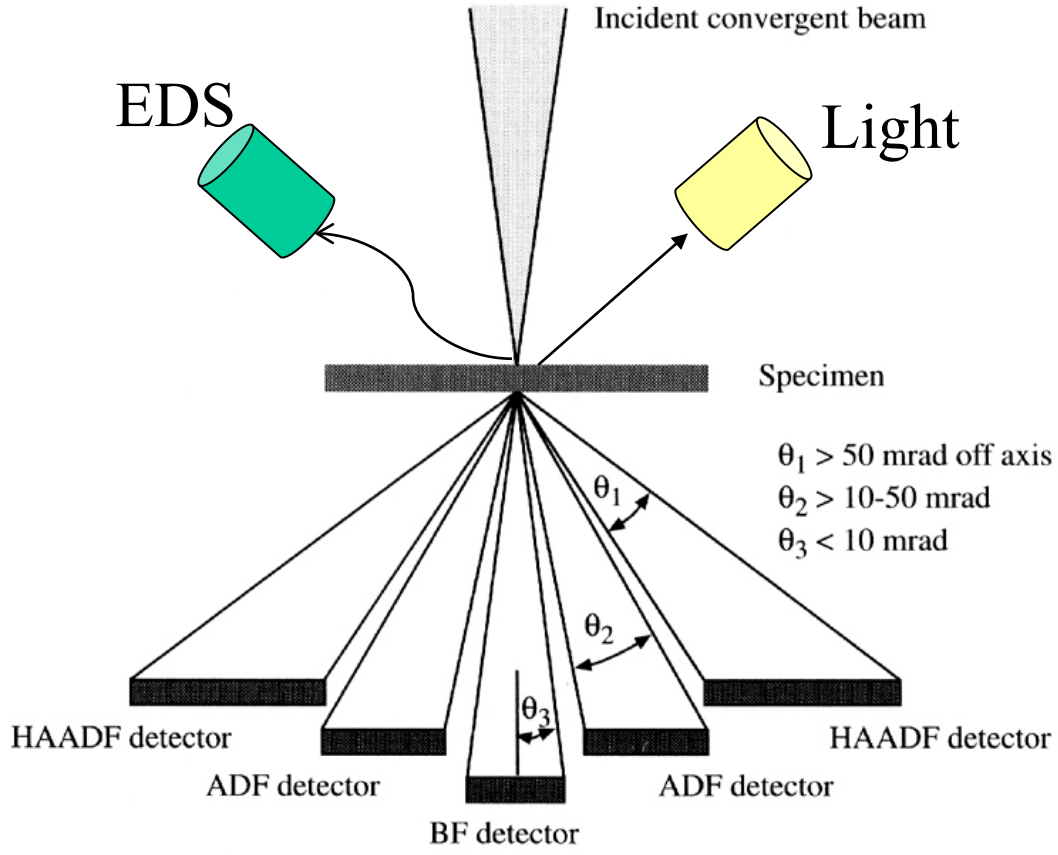
Chemical/Electronic

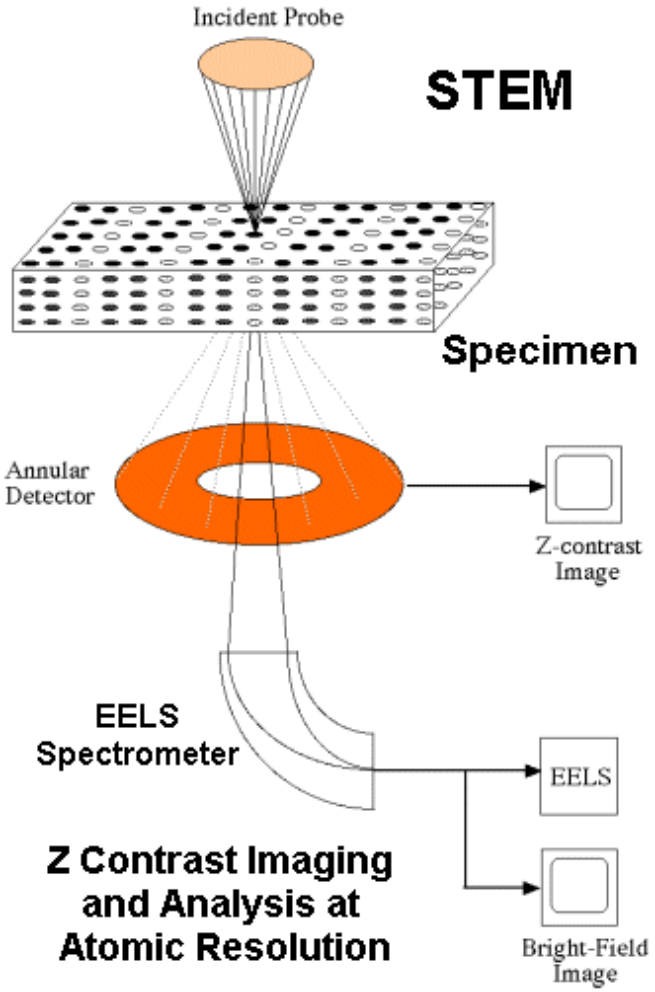
- Classical Cross Sections
- Transition Matrix Methods (Fermi Golden Rule)
- Selection Rules
- Coupling with Diffraction
- Coupling with DFT
- Relativistic contributions

Diffraction

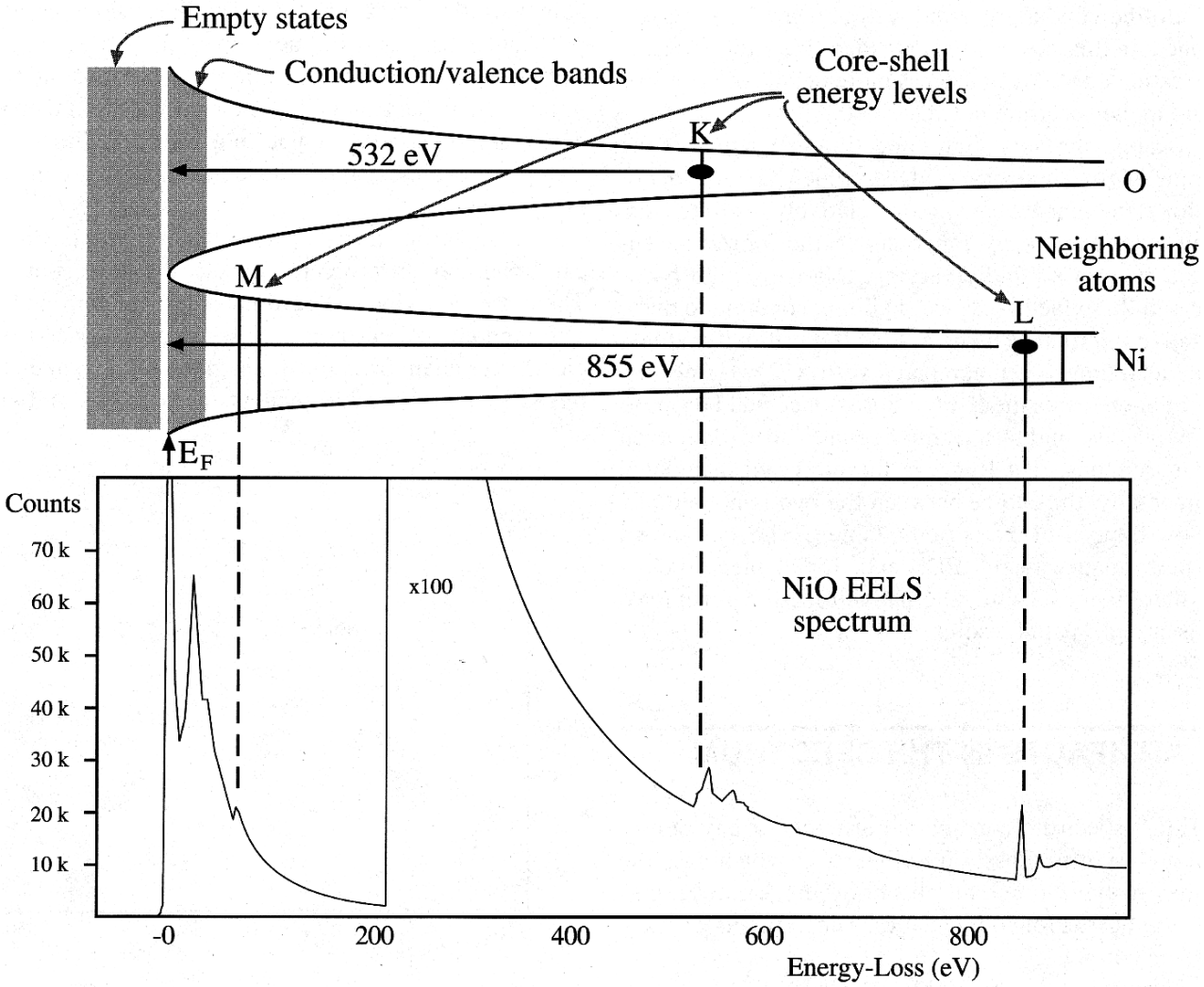
- 2-Beam theory
- General dynamical diffraction (Bloch wave)
- Multislice Method
- Tight Binding & Channeling Method
- 1s Channeling

Generic Structure of STEM





Energy Levels and Energy-Loss Spectrum



from Williams and Carter, *Transmission Electron Microscopy*, Springer, 1996

What Matters?

Initial State

- Core Electron
- Valence Electron
- Selection Rules
- Bonding
- Local Environment
- Sample

Final State/Detector

- X-ray
- Light
- Heat/Sound
- Electrons which have lost energy
- Background
- Efficiency for different elements/modes
- $$ On detector

What Matters?

Initial State

- Core Electron
- ~~Valence Electron~~
- ~~Selection Rules~~
- ~~Bonding~~
- ~~Local Environment~~
- Sample

Final State/Detector

- X-ray
- ~~Light~~
- ~~Heat/Sound~~
- ~~Electrons which have lost energy~~
- Background
- Efficiency for different elements/modes
- $$ On detector

X-ray Microanalysis

Adapted from slides from

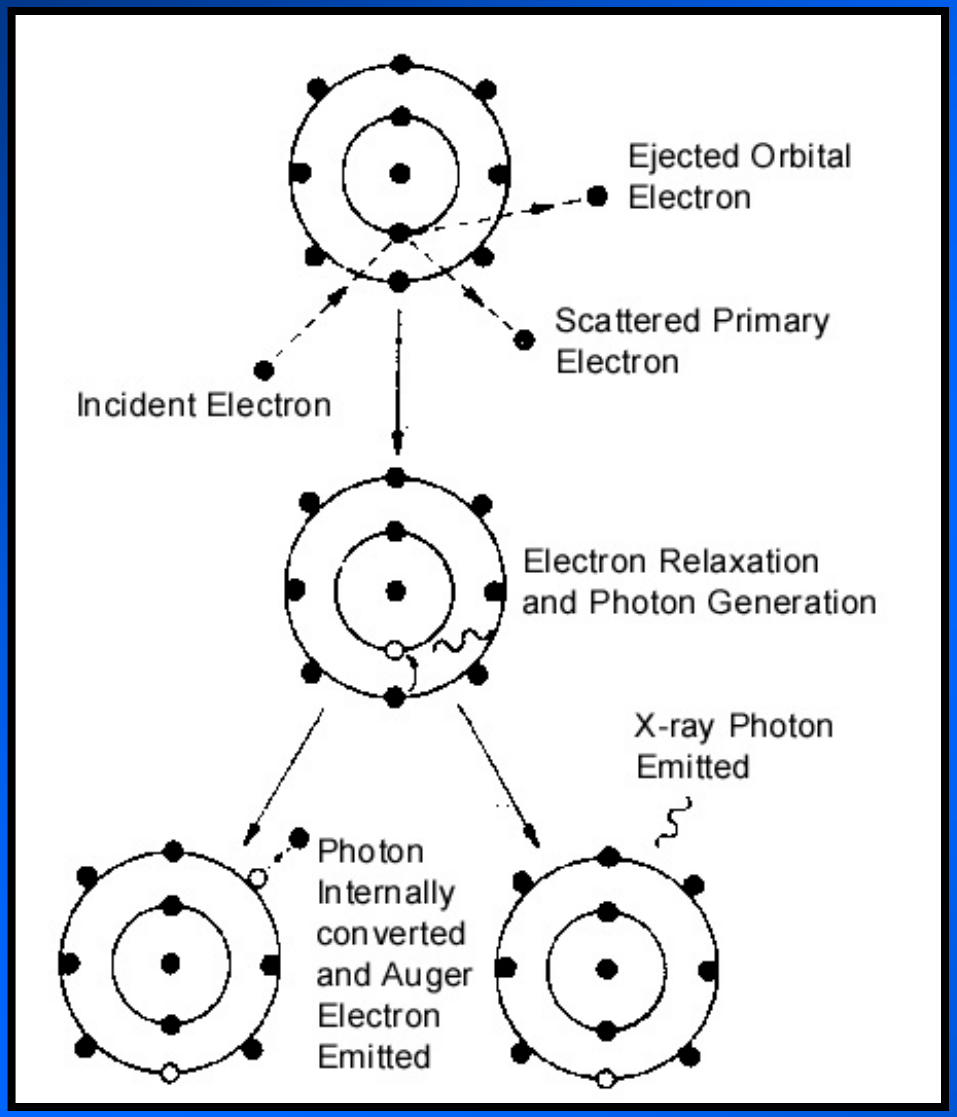
Mark Farmer, University of Georgia

Charles Lyman and Alwyn Eades,
Lehigh University

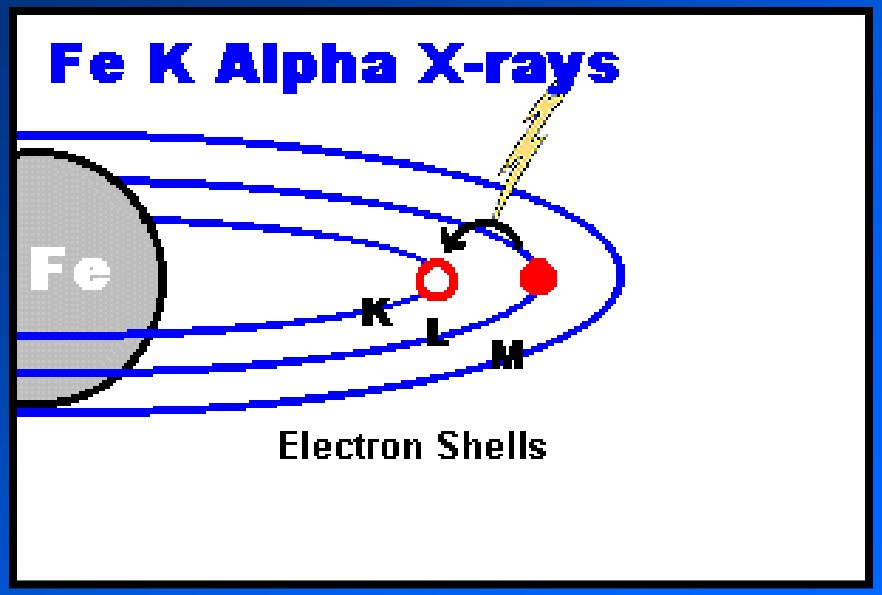
Natasha Erdman, JEOL

(and others…)

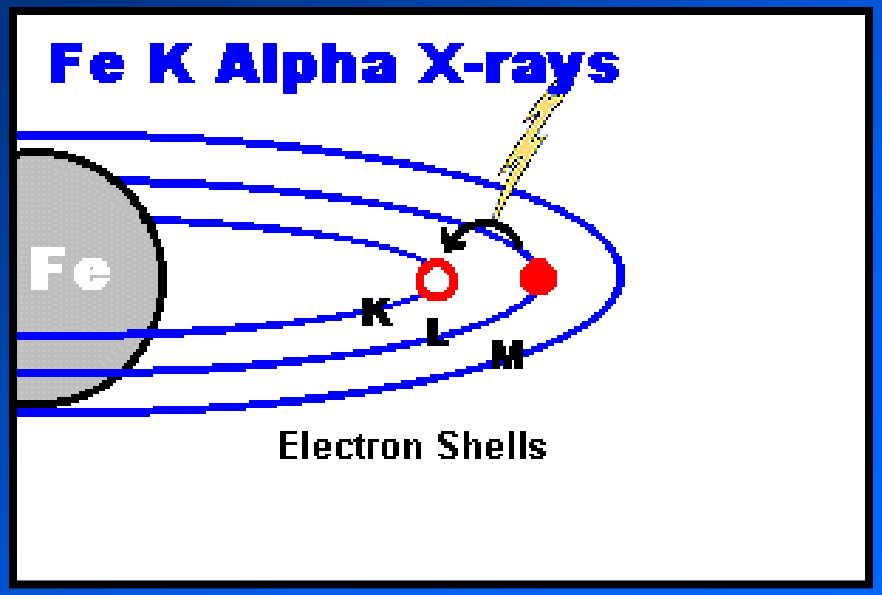
X-ray Microanalysis

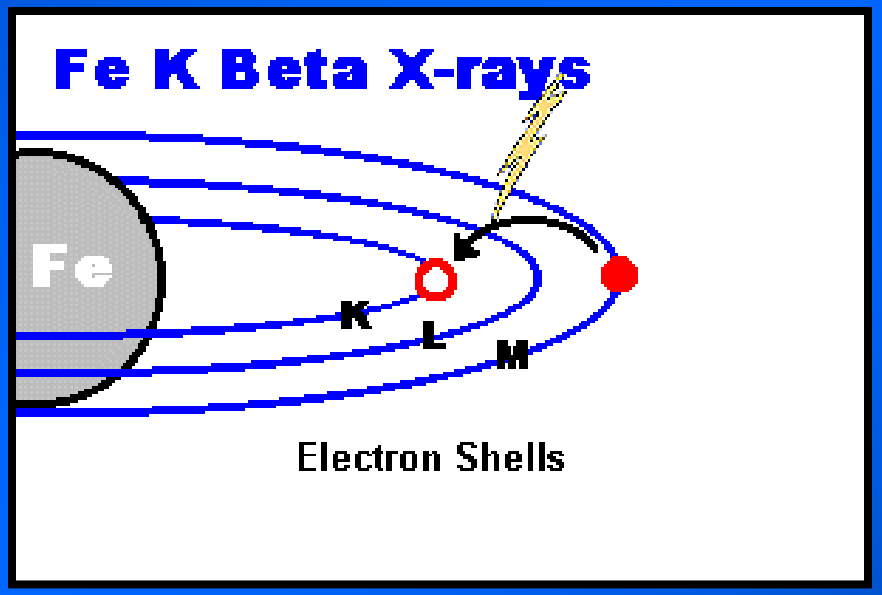


An inelastic collision between a primary beam electron and an inner orbital electron results in the emission of that electron from the atom, the energy released from an electron replacement event produces a photon with an energy exactly equal to the drop in energy.



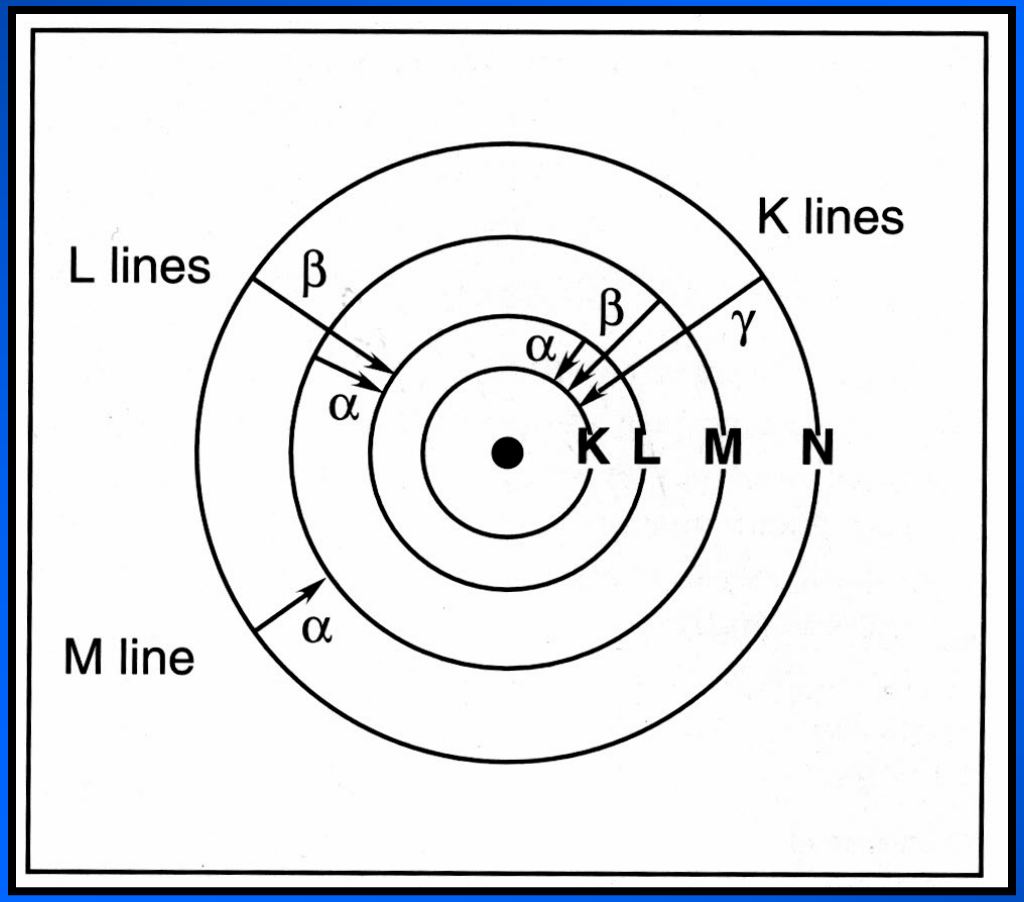
When an electron from a K-shell is replaced by one from the next closest shell (L), it is designated as a Kα event





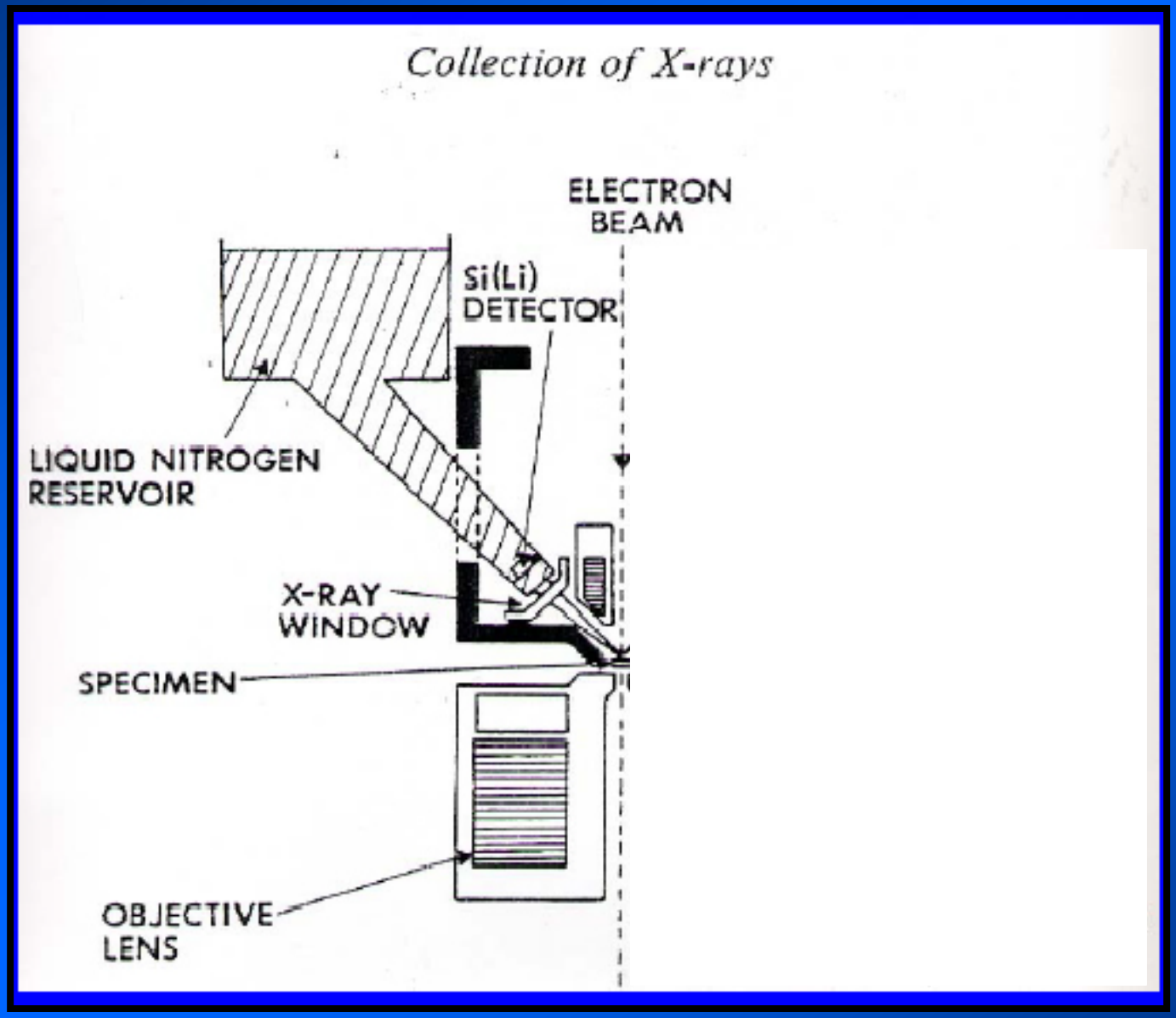
When an electron from a K-shell is replaced by one from the second closest shell (M), it is designated as a Kβ event

X-ray Microanalysis

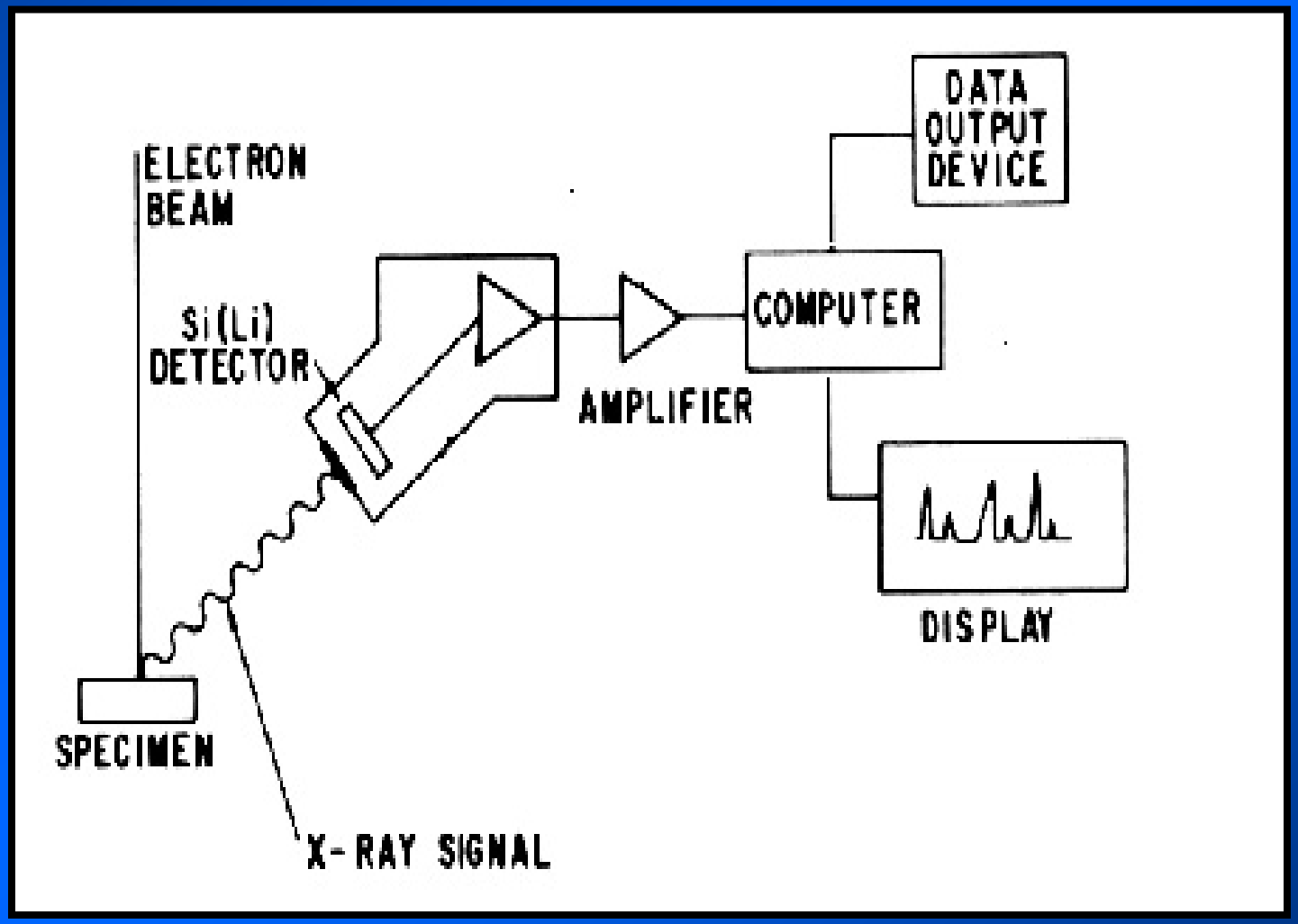


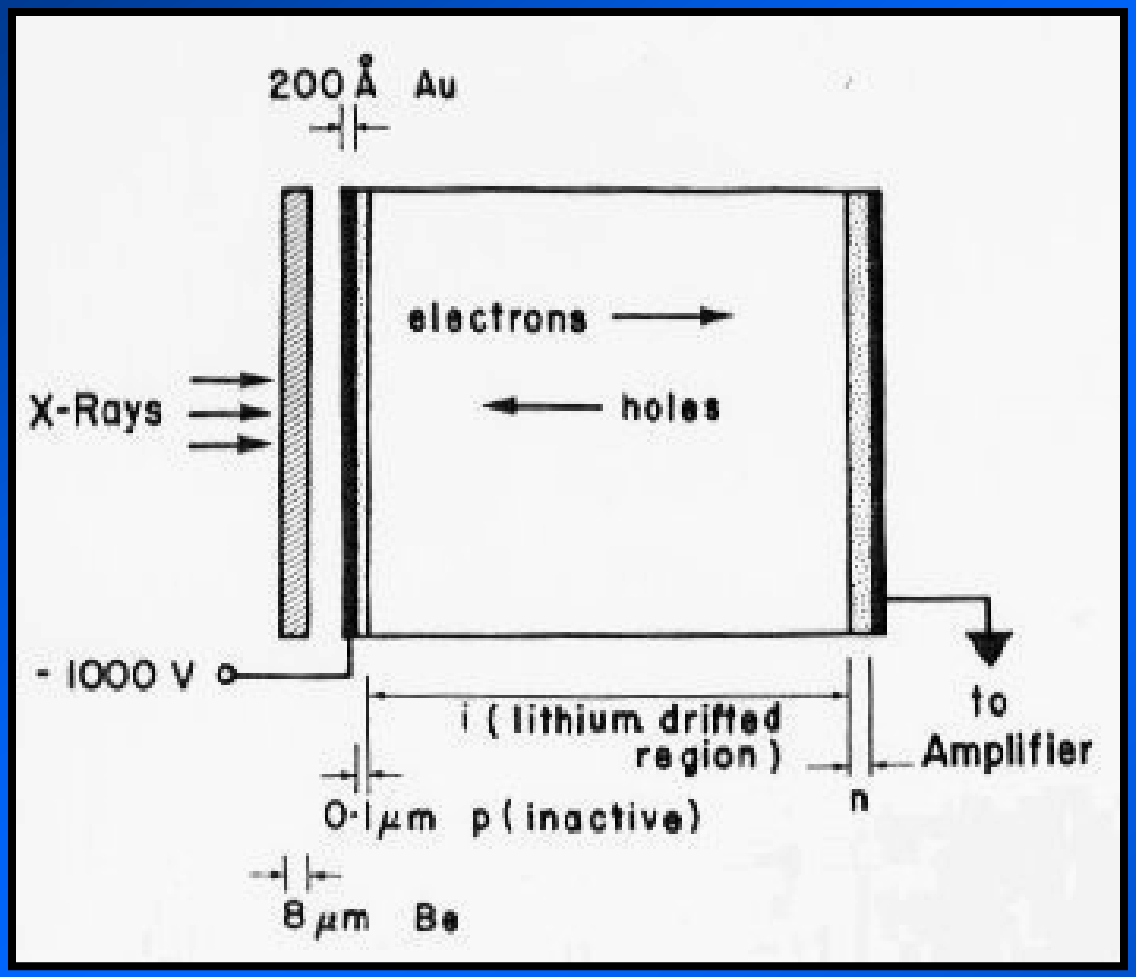
Certain events such as Mα, Lβ, and Kγ are only possible in atoms of sufficient atomic weight

EDS


Collection of X-rays
ELECTRON BEAM
Si(Li) DETECTOR
LIQUID NITROGEN RESERVOIR
X-RAY WINDOW
SPECIMEN
OBJECTIVE LENS

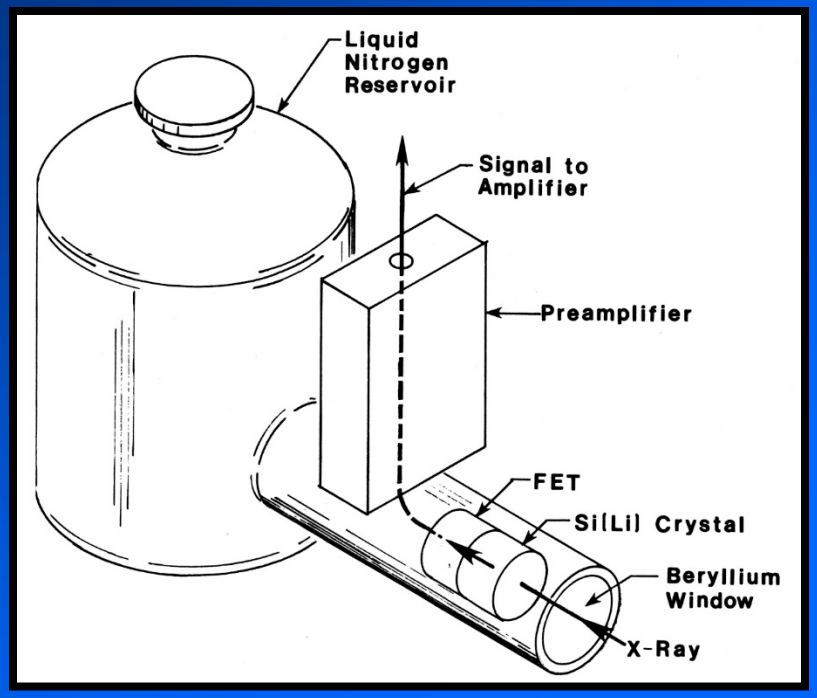
X-ray Microanalysis
Energy Dispersive Spectroscopy (EDS)





Each ionized atom of silicon absorbs 3.8 eV of energy, so an X-ray of 3.8 KeV will ionize approximately 1000 silicon atoms.

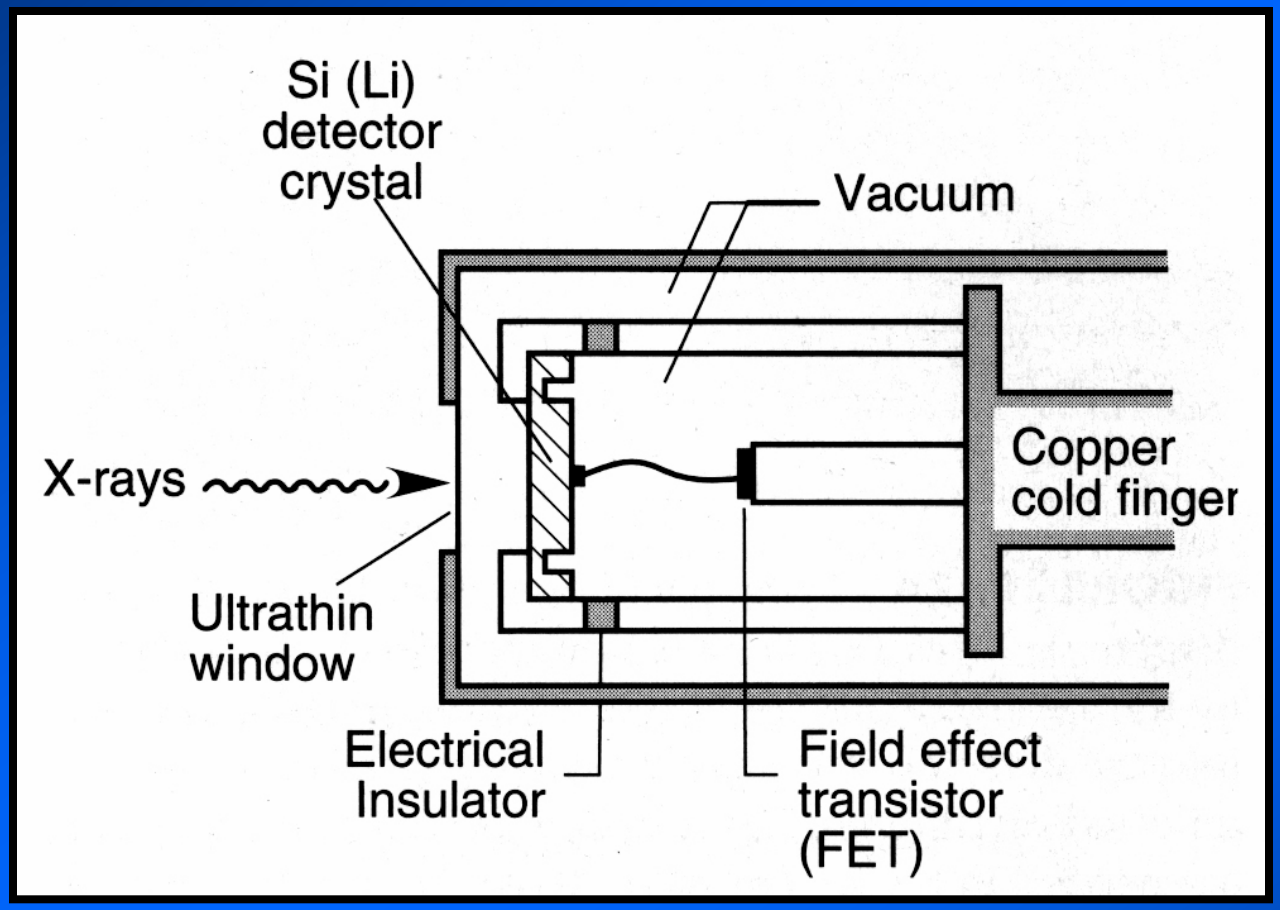
Energy Dispersive Spectroscopy



Collimator to limit BSE and stray X-rays

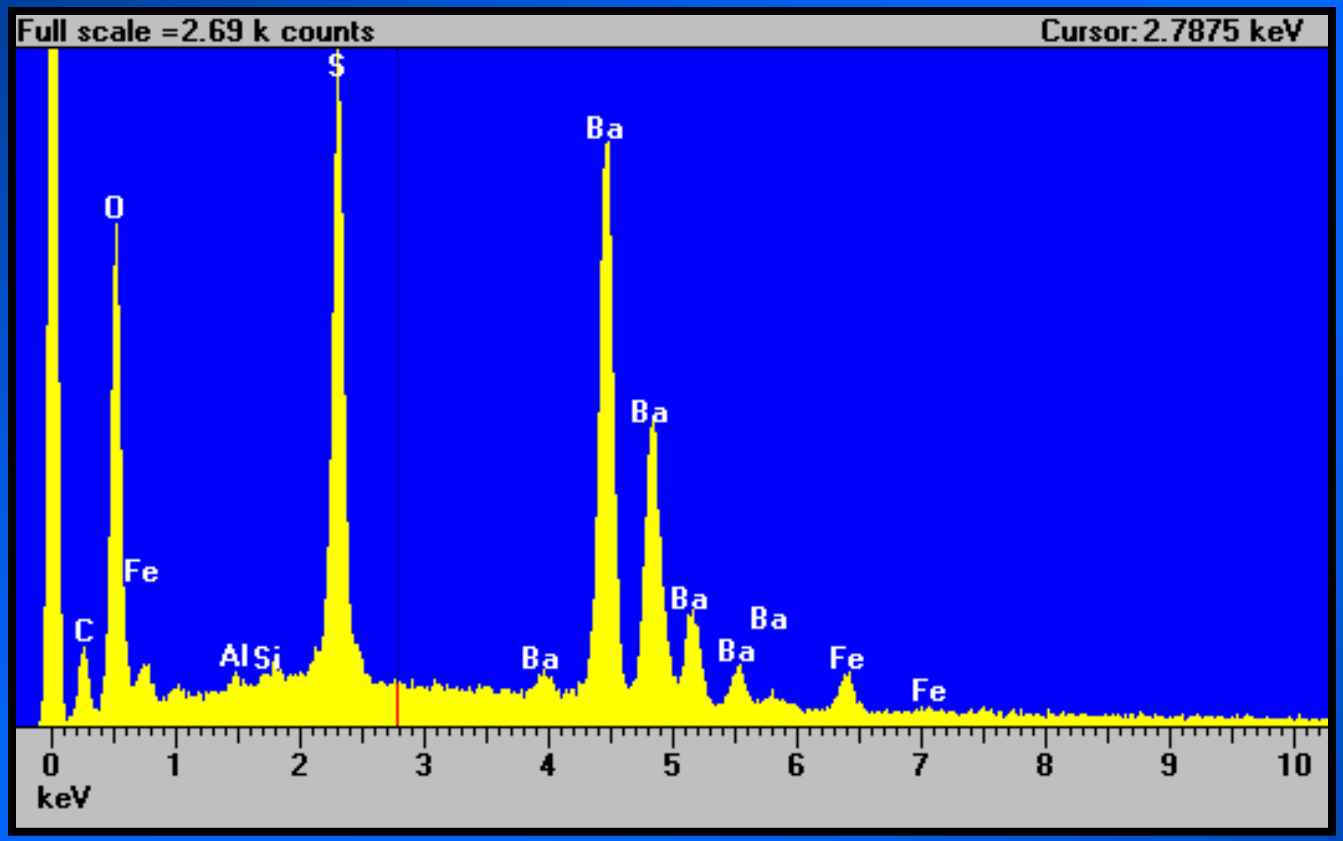
Window usually made of beryllium (limited to sodium, atomic number 11) or thin plastic to detect down to boron (Atomic number 5) protects cooled crystal from air.

Detector crystal silicon wafer with lithium added in. For each 3.8 eV from an X-ray, produce an electron and hole. This produces a pulse of current, the voltage of which is proportional to the X-ray energy. Must keep the crystal at LN temperature to keep noise to a minimum.



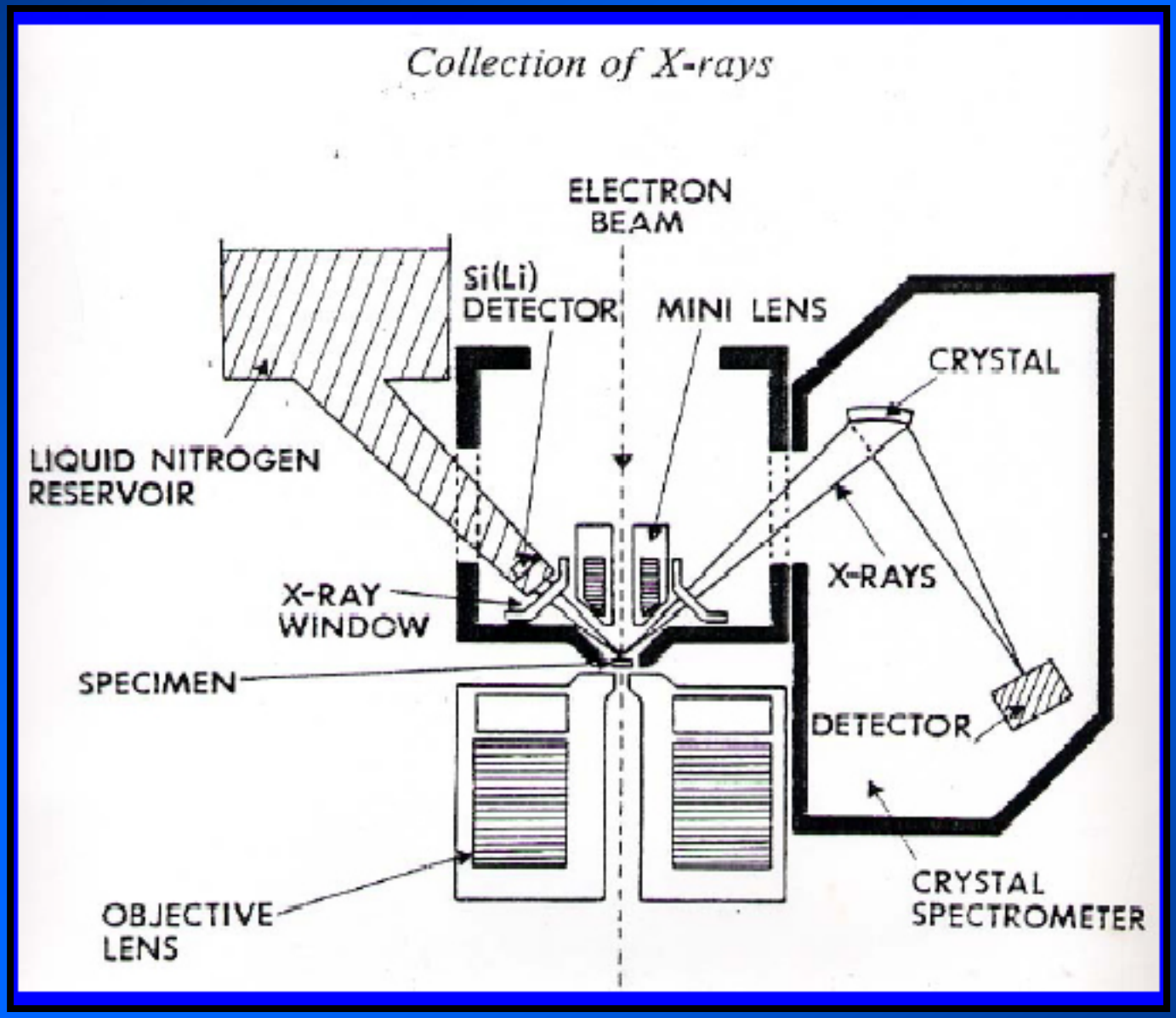
Expanded view of an EDS detector

Multichannel Analyzer (MCA)

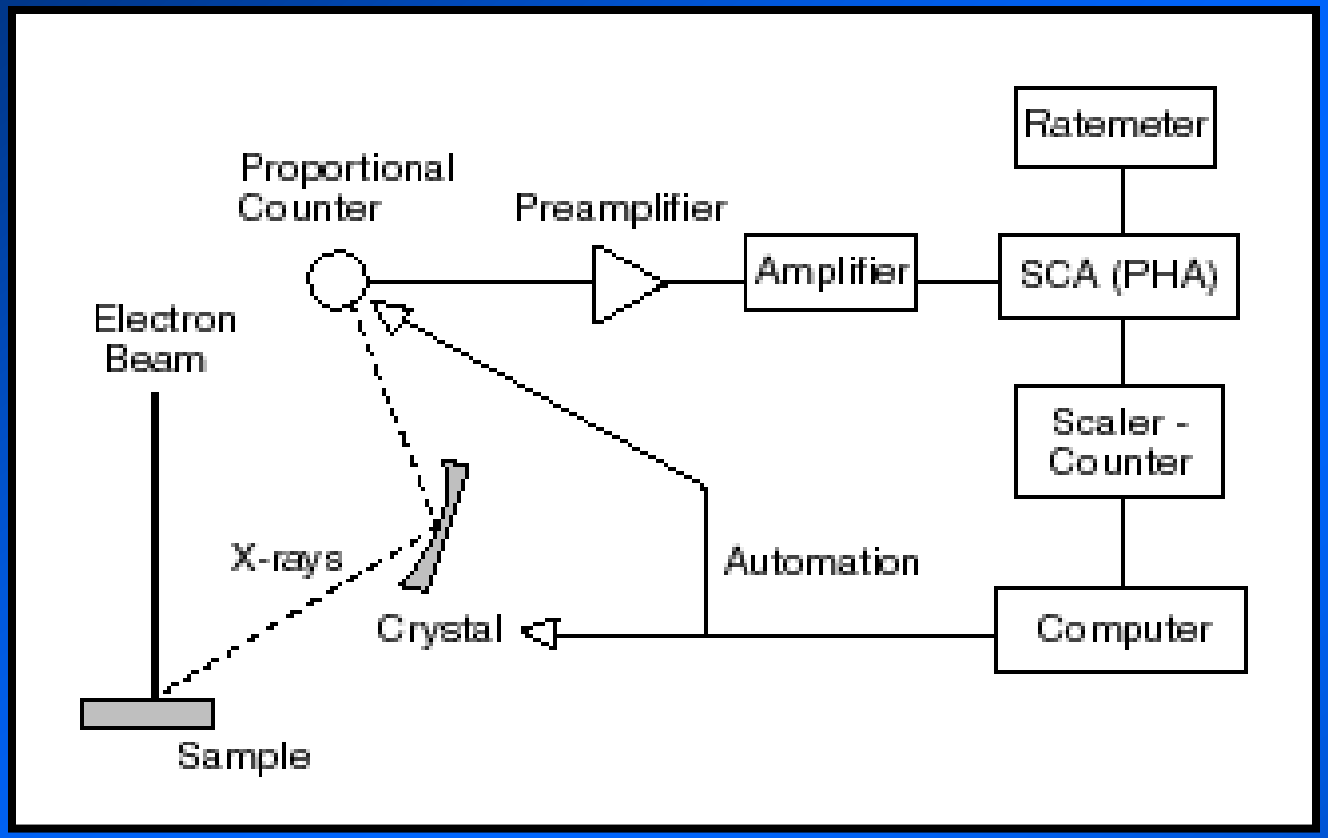


The changes in conductivity of the SiLi crystal can be counted for a given time and displayed as a histogram using a multichannel analyzer.

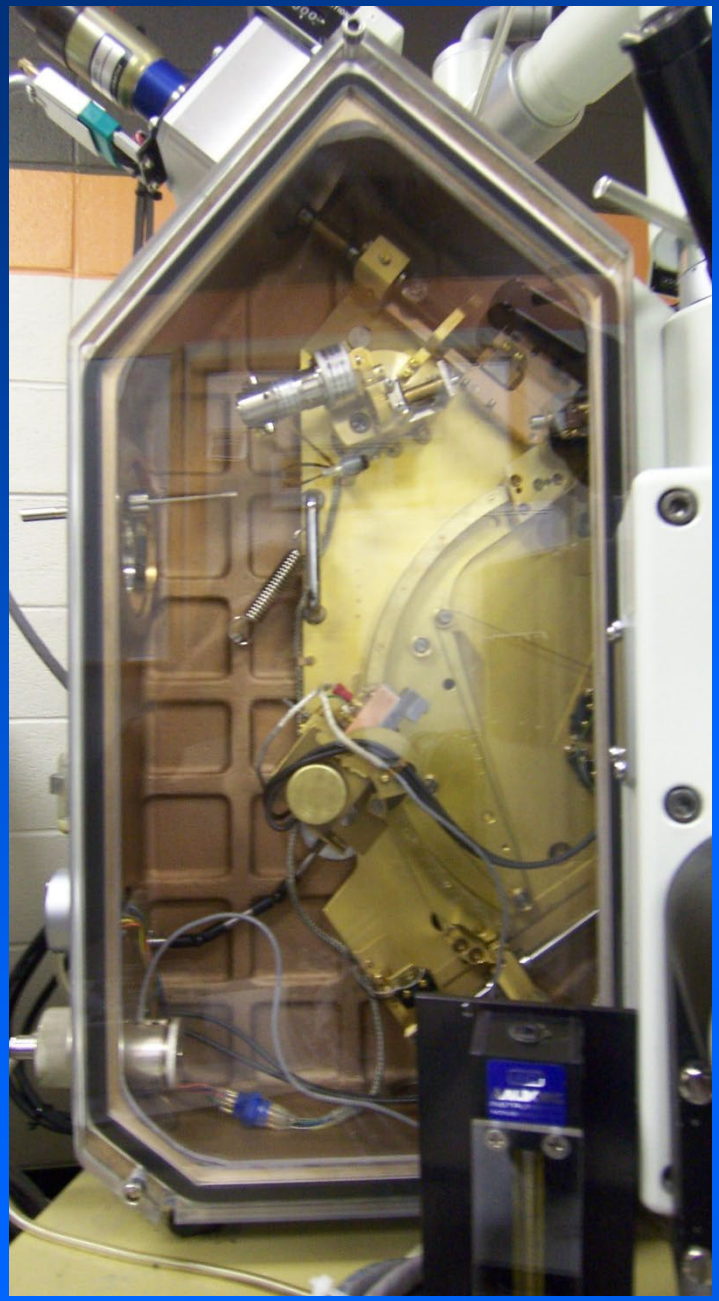
EDS

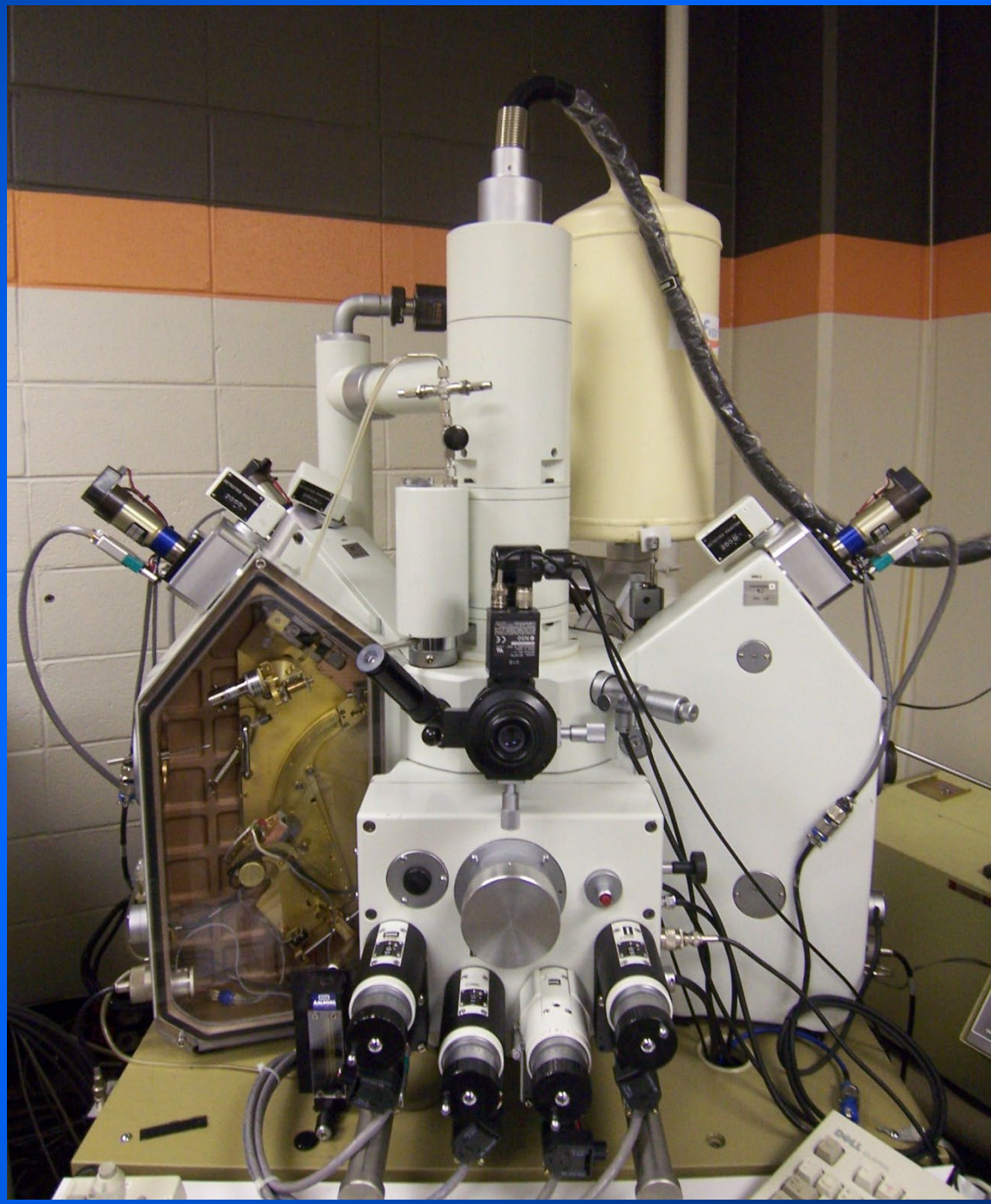

Collection of X-rays
ELECTRON BEAM
Si(Li) DETECTOR
MINI LENS
CRYSTAL
LIQUID NITROGEN RESERVOIR
X-RAY WINDOW
X-RAYS
SPECIMEN
DETECTOR
OBJECTIVE LENS
CRYSTAL SPECTROMETER

WDS



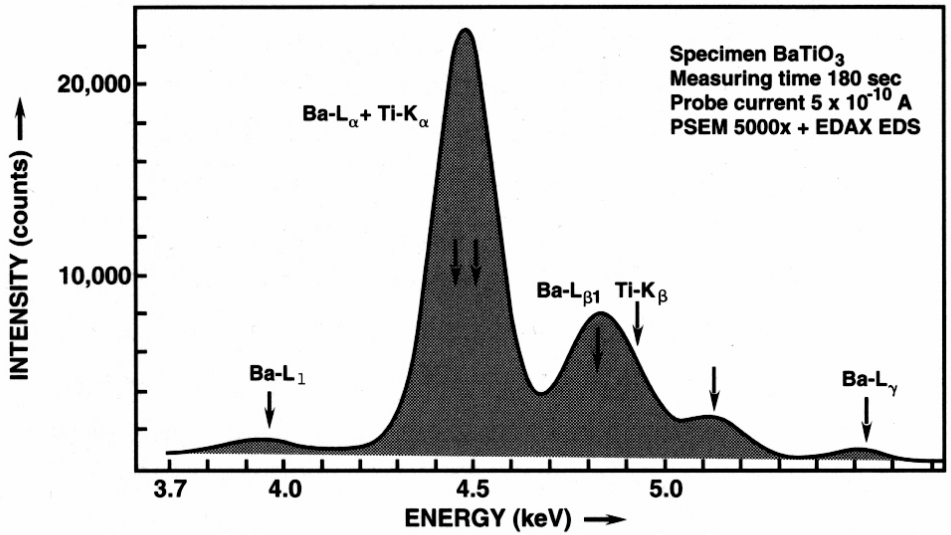
A WDS detector takes advantage of the fact that an X-ray of a given wavelength can be focused by a crystal if it encounters the crystal at the proper Bragg's angle.

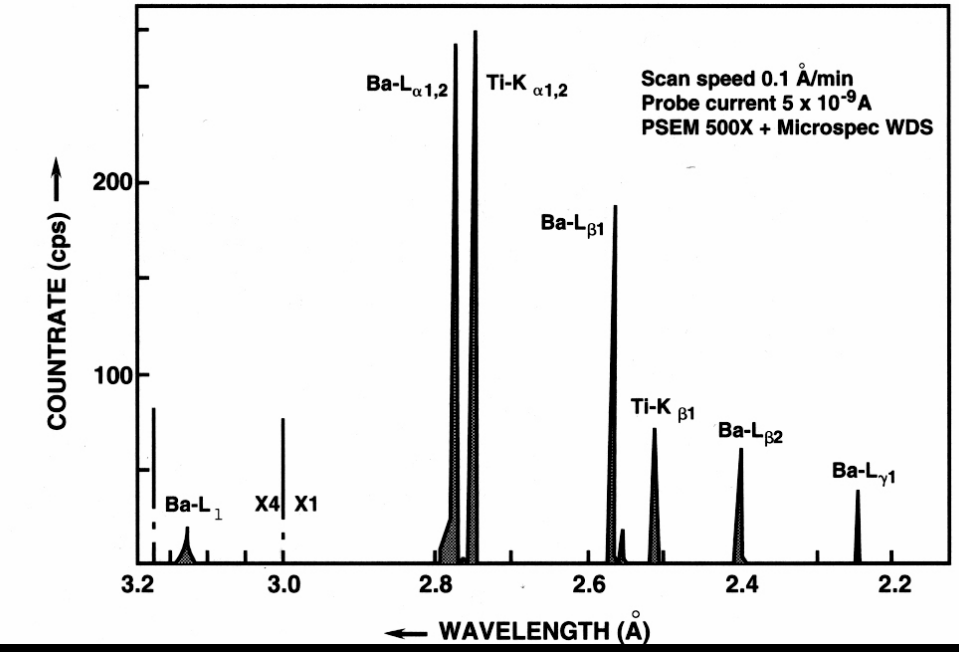




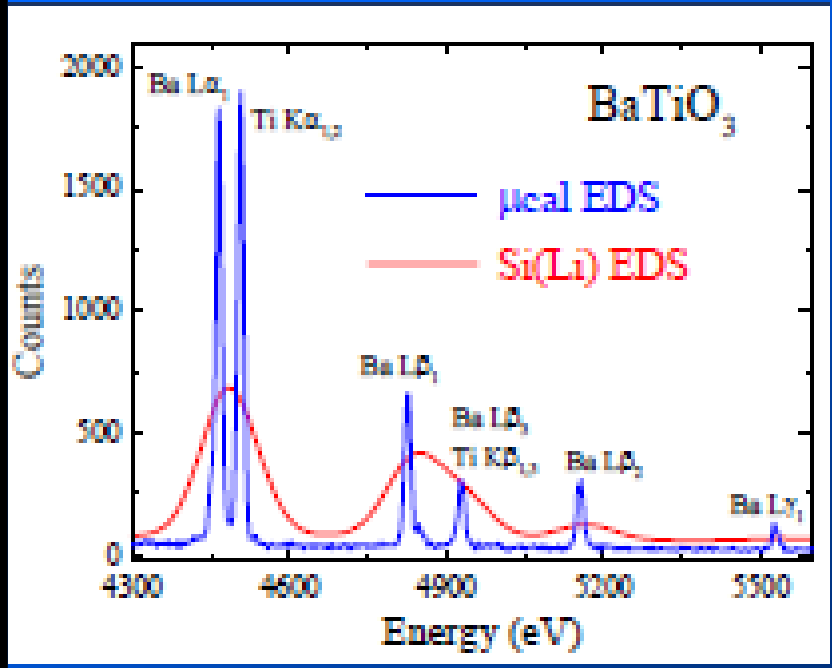
WDS vs. EDS

WDS	EDS
1. High spectral resolution (2-6 eV)	1. Low spectral resolution (130-155 eV)
2. Low collection efficiency (slower)	2. High collection efficiency (faster)
3. Higher P/B	3. Lower P/B
4. Highly sensitive to geometric effects	4. Low sensitivity to sample geometry
5. Few spectral artifacts	5. Several spectral artifacts
6. No LN required	6. LN required*
7. Moving mechanical parts	7. No moving mechanical parts**
8. Relatively high beam current typical	8. Lower beam current feasible
9. Great for majors and traces	9. Great for majors, poor for traces
10. Very expensive to purchase	11. Less expensive to purchase
	* Some recent claims of LN-free new models
	** Except for retractable models





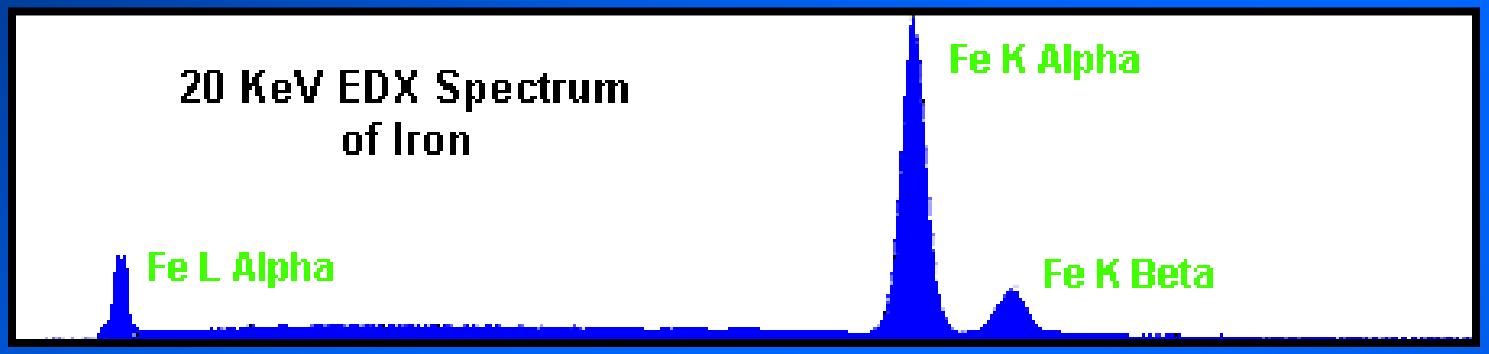
A comparison of three spectra collected with EDS, WDS & an experimental bolometer shows how peak overlap and energy spread can serve to obscure the information in an EDS spectrum



Z		name	Ka1	Ka2	Kß1	Kß2	KL	KM	Ec(K)	La1	Lß1	Lß2	Lg1	Ll	Lg3	LK	LM	Ec(L3)
3	Li	Lithium	0.054						0.055									
4	Be	Beryllium	0.108					38	0.112									
5	B	Boron	0.183					42	0.188									
6	C	Carbon	0.277				19	46	0.284									
7	N	Nitrogen	0.392				22	50	0.401									0.01
8	O	Oxygen	0.525				23	54	0.532									0.007
9	F	Fluorine	0.677				26	57	0.685									0.009
10	Ne	Neon	0.849				28	58	0.87									0.022
11	Na	Sodium	1.041		1.067		30	61	1.072									0.031
12	Mg	Magnesium	1.254		1.302		33	66	1.305									0.051
13	Al	Aluminium	1.487		1.557		35	70	1.56									0.073
14	Si	Silicon	1.74	1.739	1.835		37	74	1.839					0.09				0.099
15	P	Phosphorus	2.014	2.013	2.139		40	78	2.145					0.117				0.135
16	S	Sulfur	2.308	2.307	2.464		42	82	2.472					0.1487		5	40	0.164
17	Cl	Chlorine	2.622	2.621	2.816		44	86	2.822					0.1826		5	42	0.2
18	Ar	Argon	2.958	2.956	3.191		47	90	3.203					0.221		5	43	0.249
19	K	Potassium	3.314	3.311	3.59		49		3.607					0.2603		6	45	0.294
20	Ca	Calcium	3.692	3.688	4.013		52		4.038	0.341	0.345			0.3027		6	47	0.347
21	Sc	Scandium	4.091	4.086	4.46		54		4.493	0.395	0.3996			0.348		7	48	0.402
22	Ti	Titanium	4.511	4.505	4.932		56		4.966	0.452	0.458			0.395		7	51	0.455
23	V	Vanadium	4.952	4.945	5.427		59		5.465	0.511	0.519			0.447		8	54	0.513
24	Cr	Chromium	5.415	5.405	5.947		61		5.989	0.573	0.583			0.5		8	55	0.574
25	Mn	Manganese	5.899	5.888	6.49		63		6.539	0.637	0.649			0.556		9	57	0.64
26	Fe	Iron	6.404	6.391	7.057		66		7.113	0.705	0.719			0.615		9	57	0.708
27	Co	Cobalt	6.93	6.913	7.649		68		7.709	0.776	0.791			0.678		10	57	0.779
28	Ni	Nickel	7.478	7.461	8.265		70		8.333	0.851	0.869			0.743		10	58	0.855
29	Cu	Copper	8.048	8.028	8.905	8.977	73		8.979	0.93	0.95			0.811		10	59	0.931
30	Zn	Zinc	8.639	8.616	9.572	9.658	75		9.659	1.012	1.035			0.884		11	61	1.02

Each element has a family of characteristic X-rays associated with it, some overlap

Counts

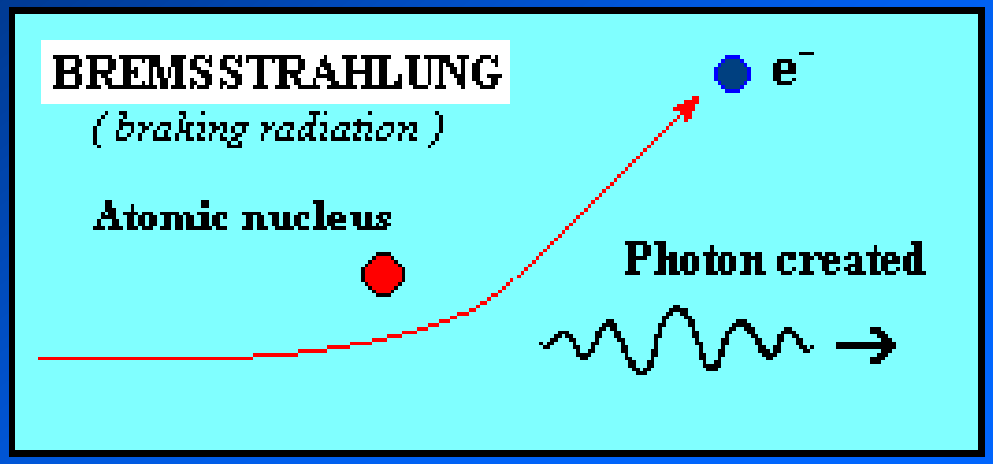


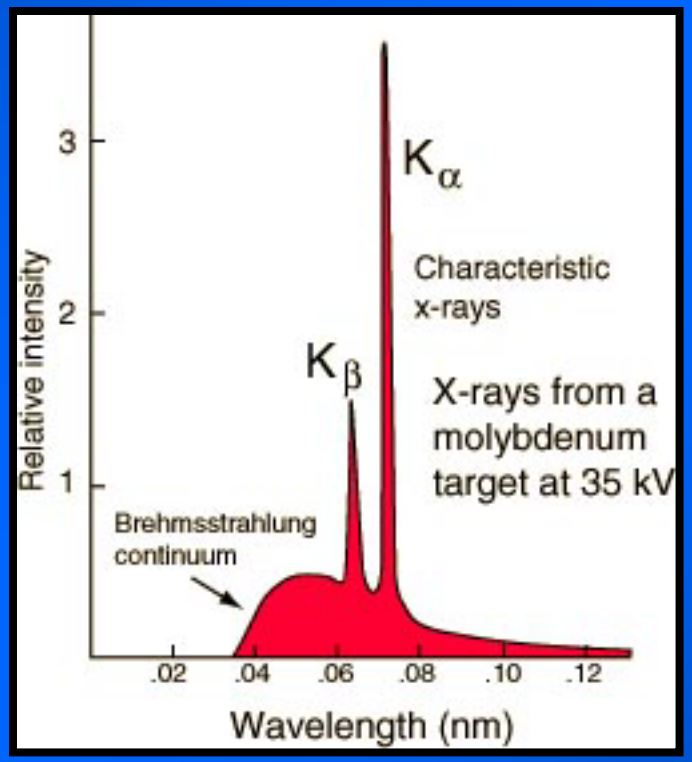
X-ray Energy in KeV

Need to consider probability of X-ray production for quantitation.

And artifacts….

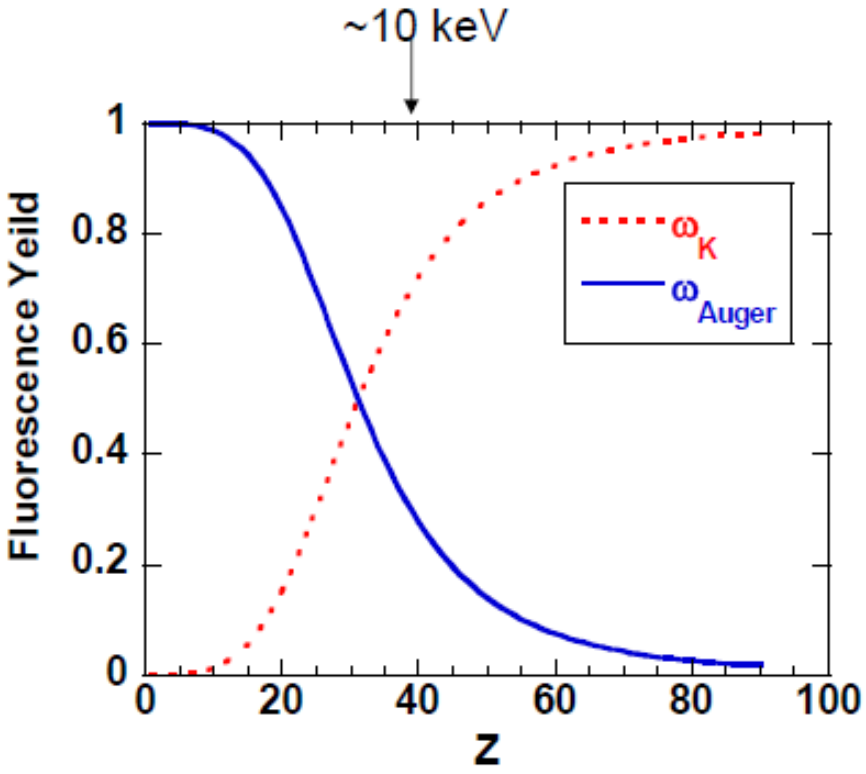
Background





"Bremsstrahlung" means "braking radiation" and comes from the original German to describe the radiation which is emitted when electrons are decelerated or "braked" when they interact with the specimen. Although they contribute to the total X-ray signal they contain no useful information because their energies are nonspecific and therefore are considered as part of the background .

Auger vs X-ray Yield

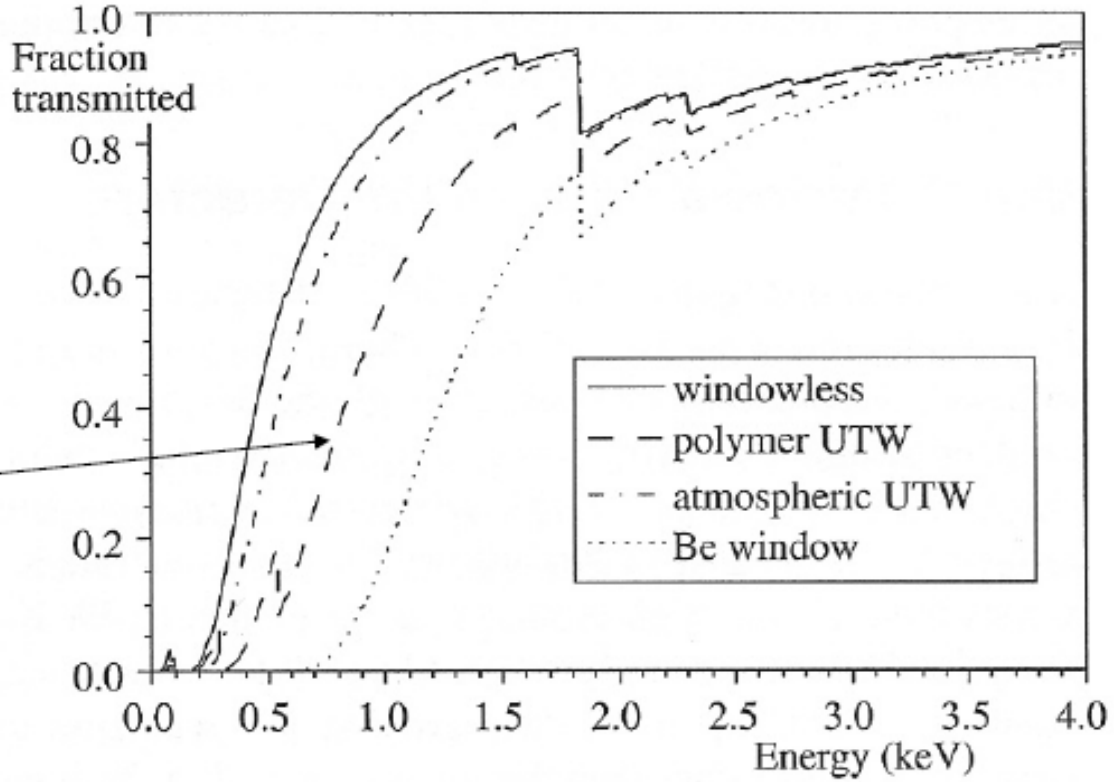


Below ~10 keV, Auger emission dominates and very few x-rays are emitted.

X-ray fluorescence is most efficient for detecting high-Z elements

Eqn 3.13 of *Rev. Mod. Phys.* **44**, 716 - 813 (1972)

Losses in the X-Ray Detector



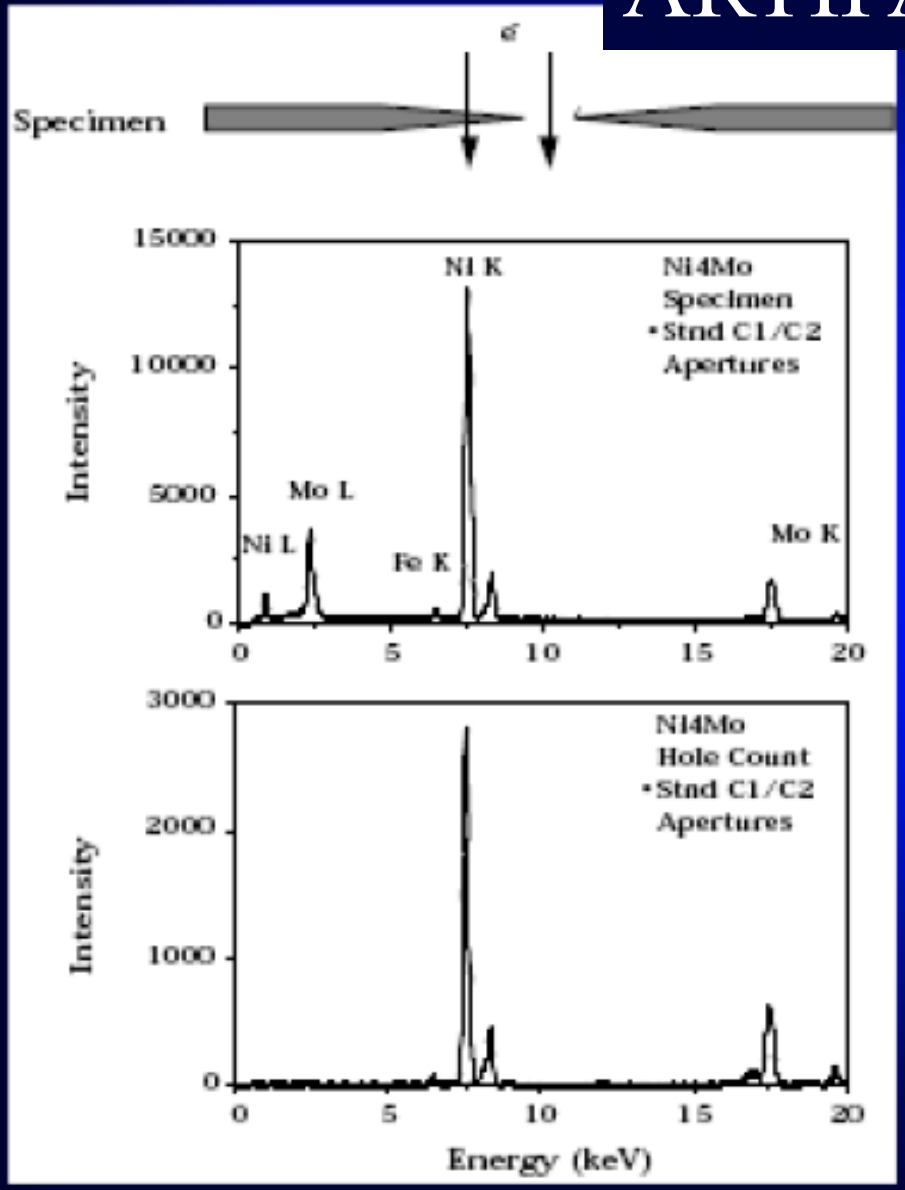
Strong Attenuation for low Z

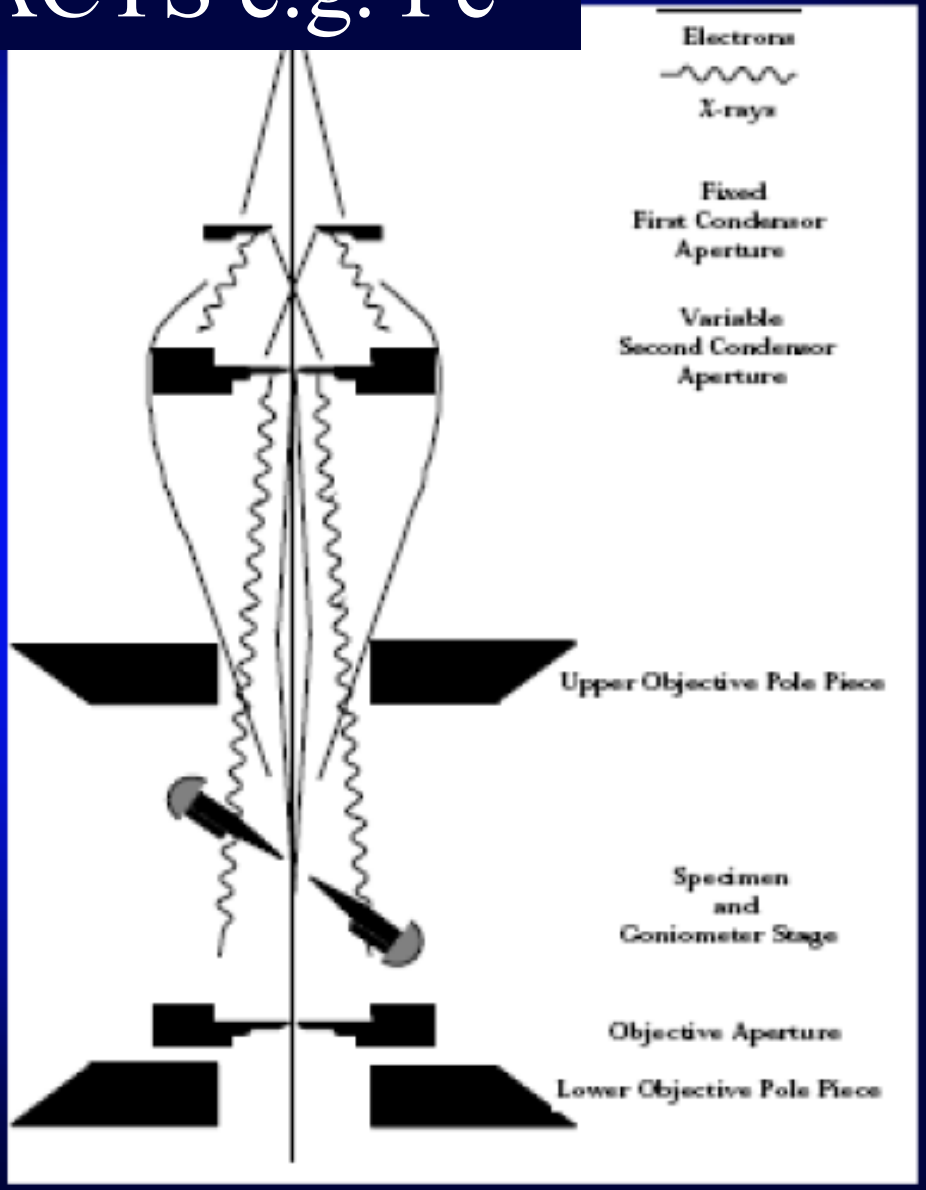
Figure 32.6. Low-energy efficiency calculated for a windowless detector, UTW detector (1 μm Mylar coated with 20 nm of Al), an ATW detector and a 13-μm Be window detector. Note that the efficiency is measured in terms of the fraction of X-rays transmitted by the window.

Williams and Carter, Vol 4

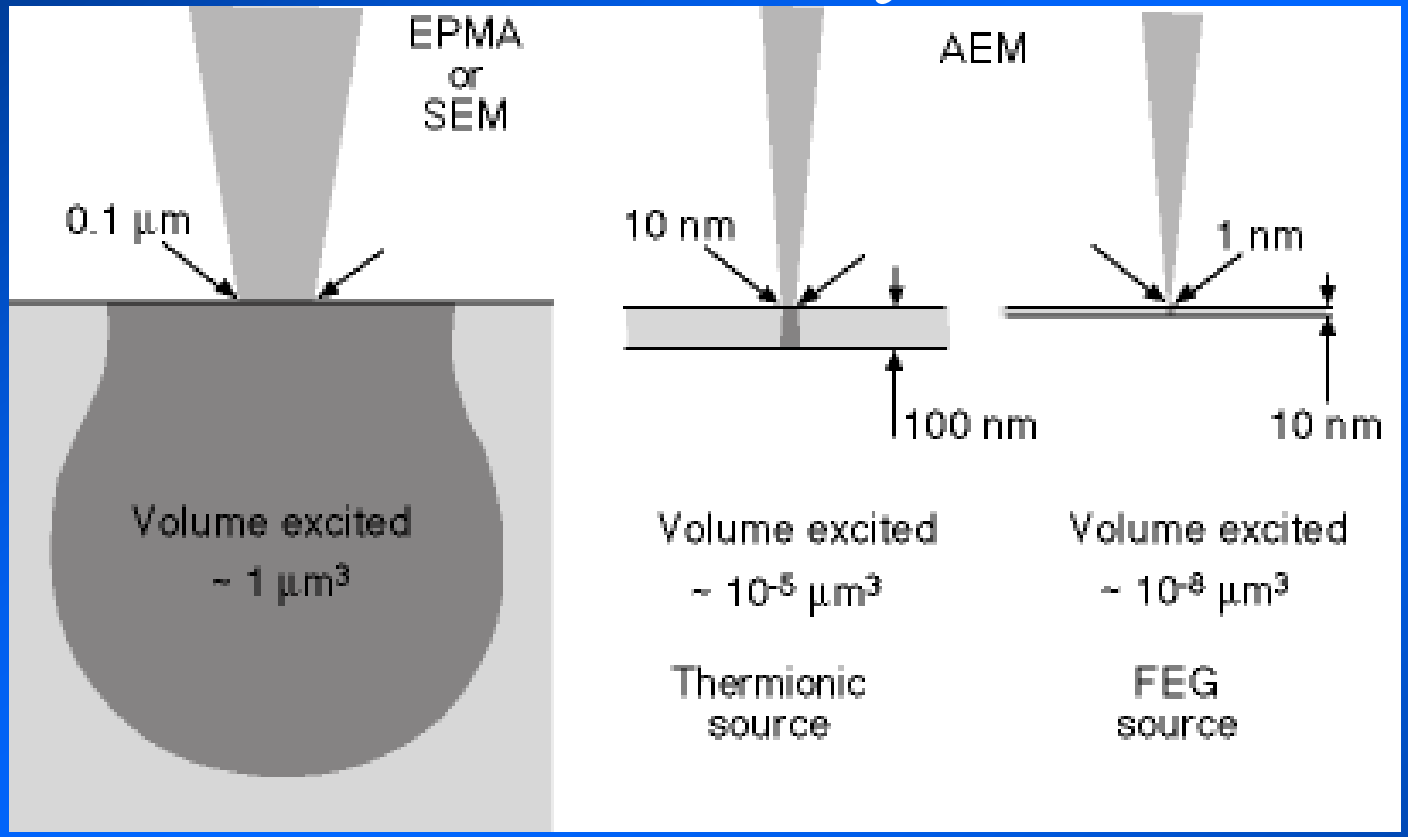
Spectral Artifacts in the AEM
Uncollimated Radiation: The Hole Count

ARTIFACTS e.g. Fe





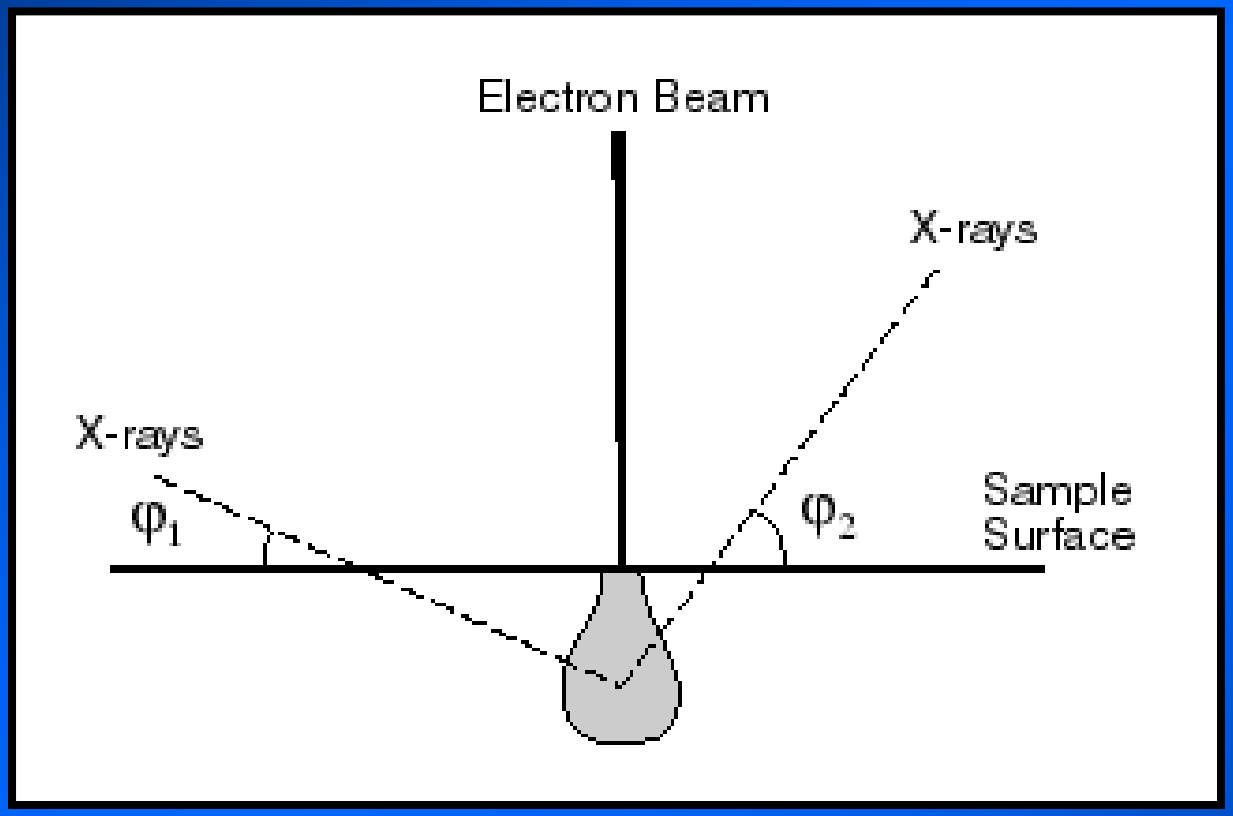
Spatial Resolution vs. Analytical Sensitivity



Conditions that favor high spatial resolution (thinnest specimen) result in poorer analytical sensitivity and vice versa. For example to obtain equivalent analytical sensitivity in an AEM to an EPMA, the X-ray generation and detection efficiency would have to be improved by a factor of 10^8

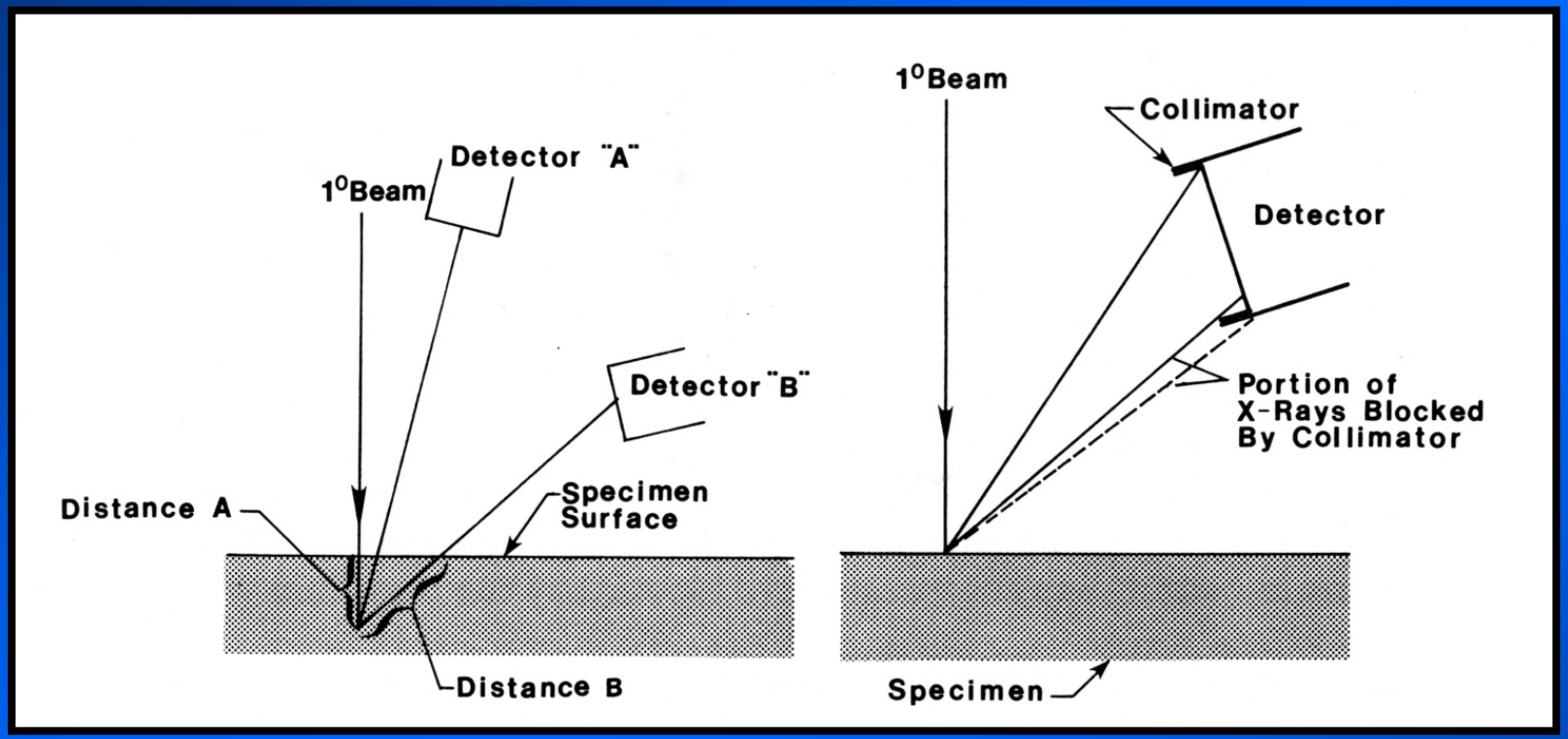
from Williams and Carter, *Transmission Electron Microscopy*, Springer, 1996

Take-off Angle



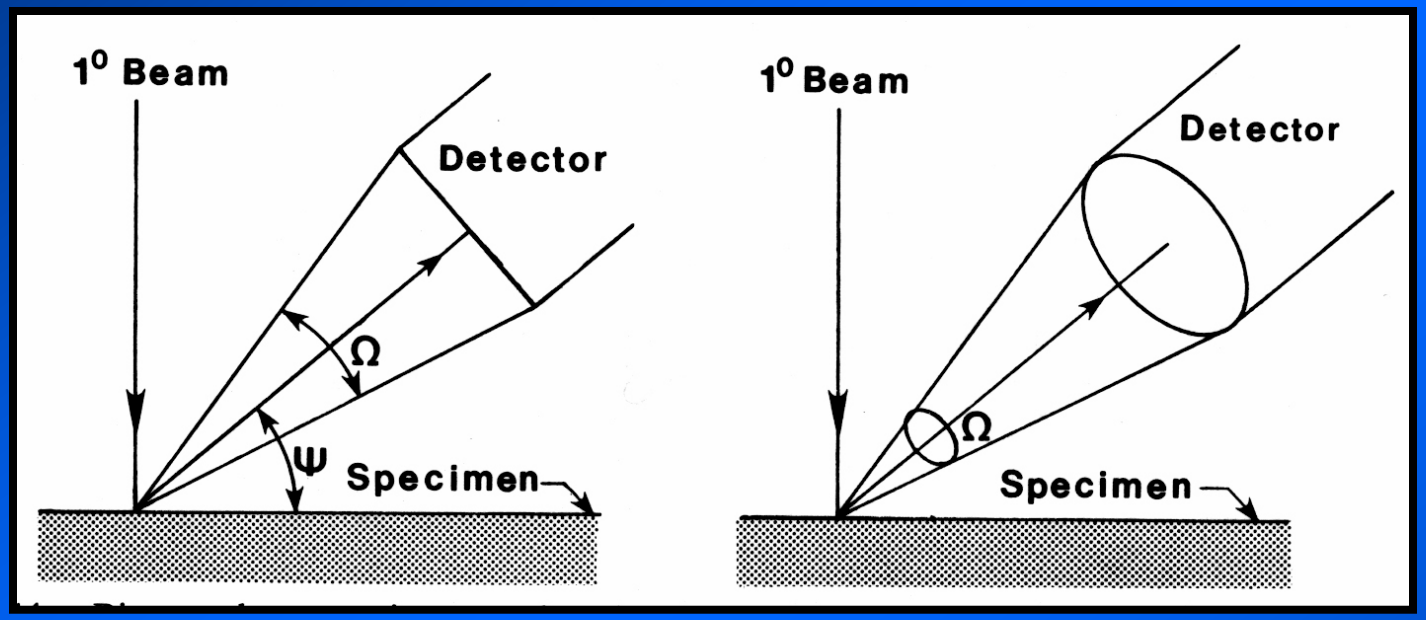
For a given angle of electron incidence, the length of the absorption path is directly proportional to the cosecant of the take-off angle, φ

Factors affecting signal collection

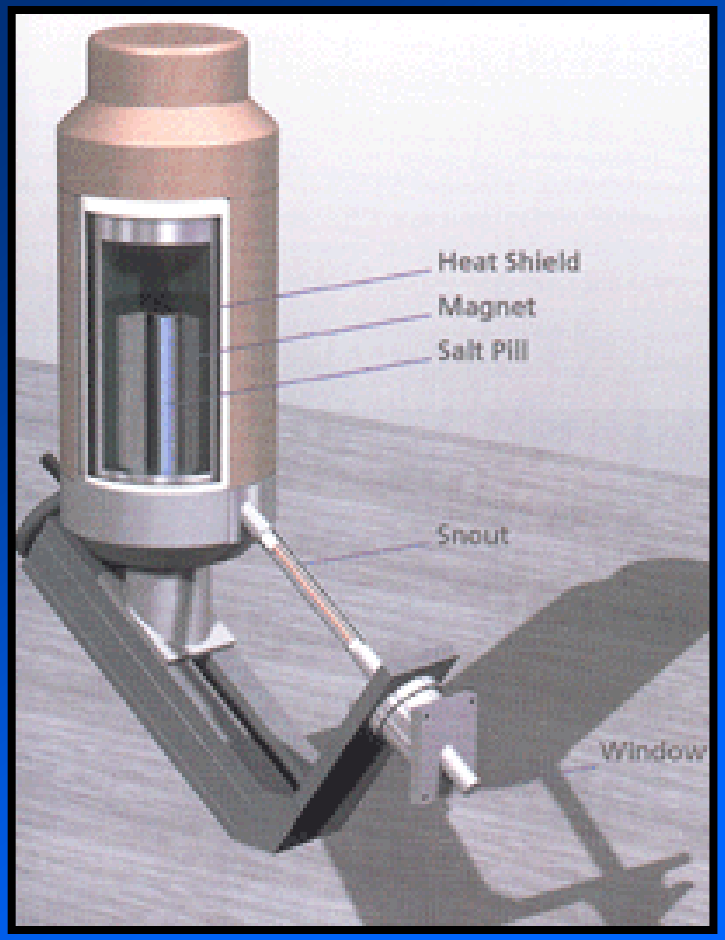


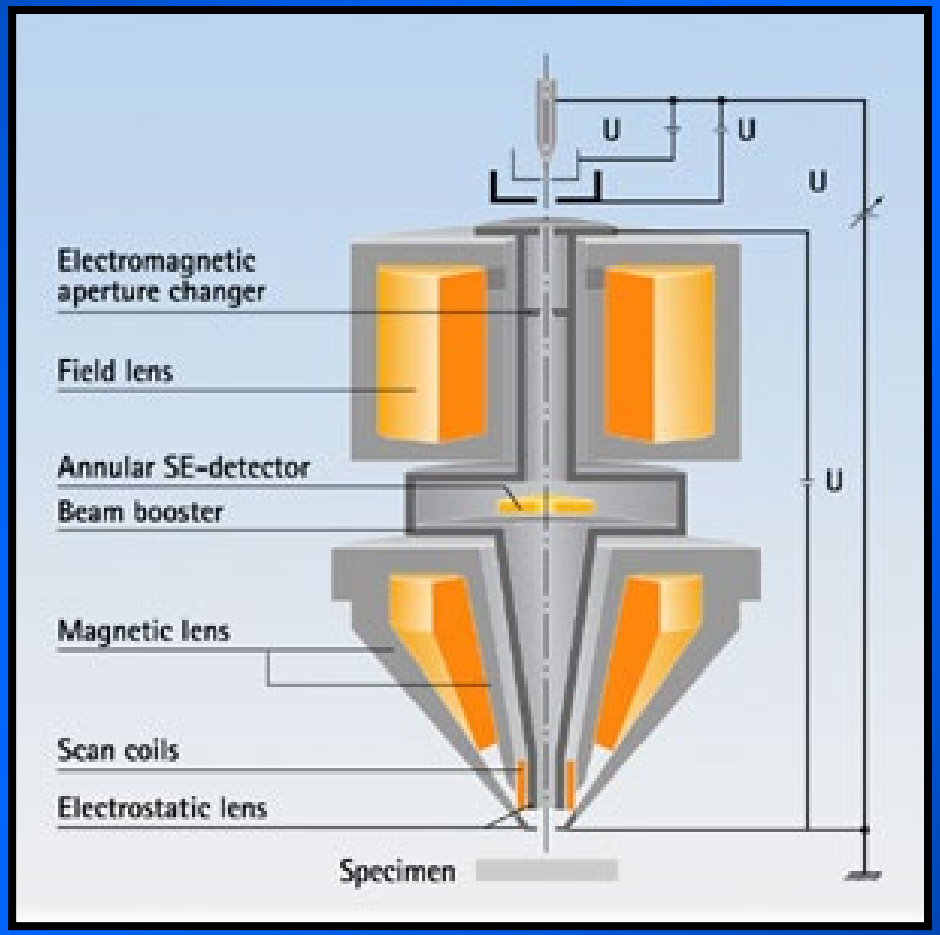
Distance between detector and X-ray source, angle at which detector is struck, and volume of signal collected.

Solid Angle

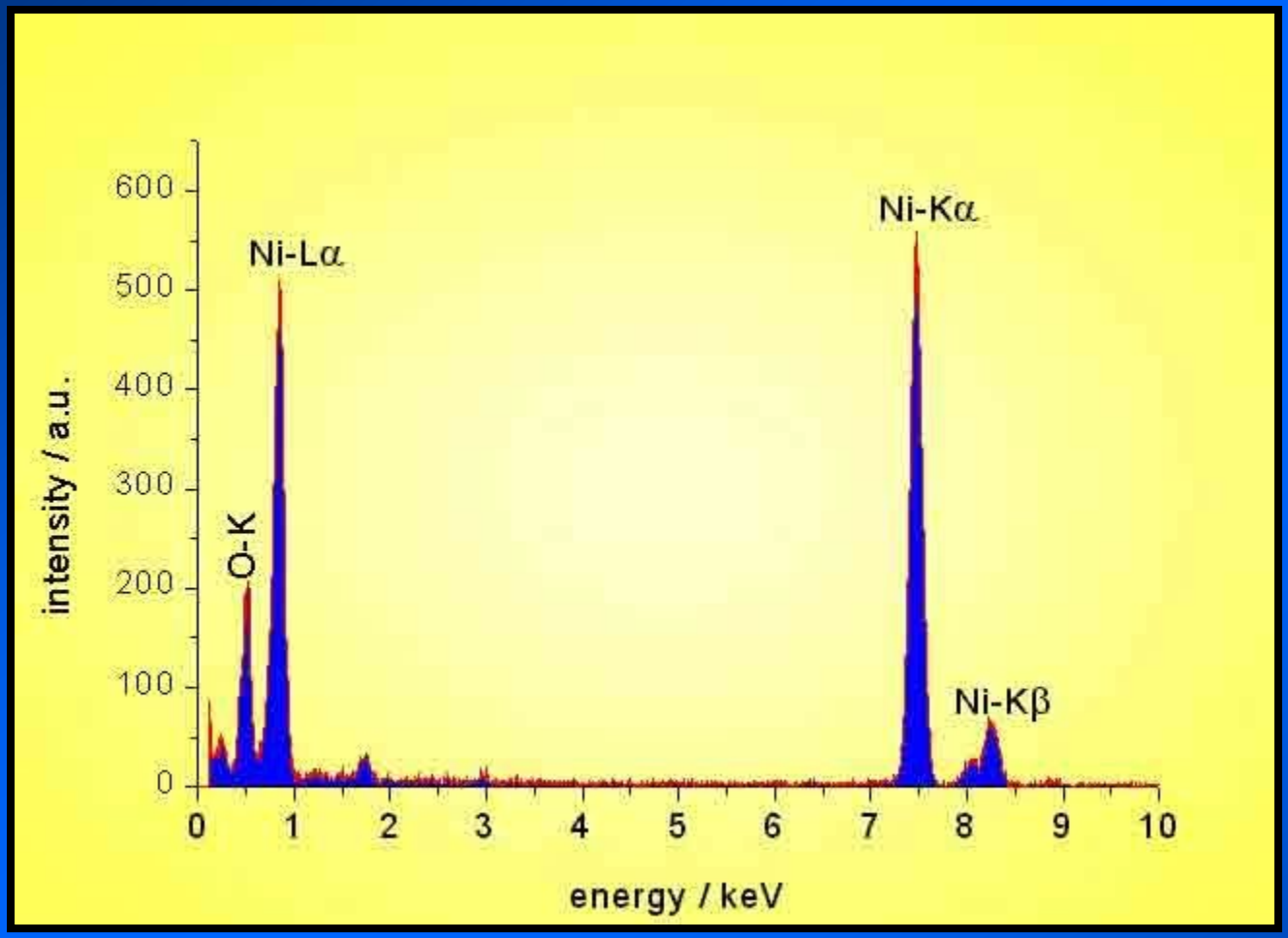


The solid angle Ω of a detector is defined as angle of the cone of signal entering the detector. The greater the size of the detector surface area the greater will be the solid angle.





One reason that the final lens of an SEM is conical in shape is so that the EDS detector can be positioned at a high take-off angle and inserted close to the specimen for a high solid angle.



Positive identification of an element is best done by collection of the entire family of peaks for a given element.

Quantitative X-ray Analysis

How much of each element is present?

- Aim of quantitative analysis: **to transform the** intensities **in the X-ray spectrum into** compositional **values, with known precision and accuracy**

- Cliff-Lorimer method:

$$C_A/C_B = k_{AB}\, I_A/I_B$$

C_A = concentration of element A
I_A = x-ray intensity from element A
k_{AB} = Cliff-Lorimer sensitivity factor

- Precision: **collect at least 10,000 counts in the smallest peak to obtain a counting error of less than 3%**
- Accuracy: **measure k_{AB} on a known standard and find a way to handle x-ray absorption effects**

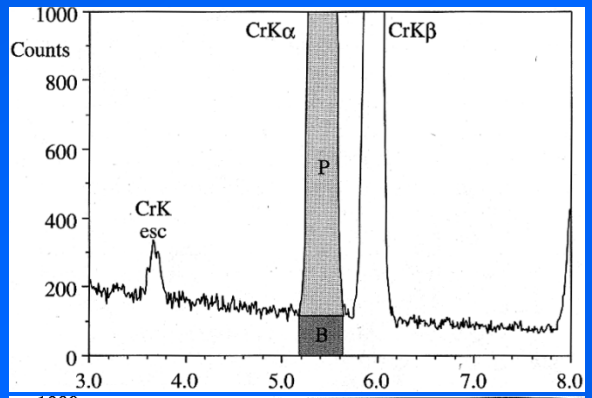
Assumptions

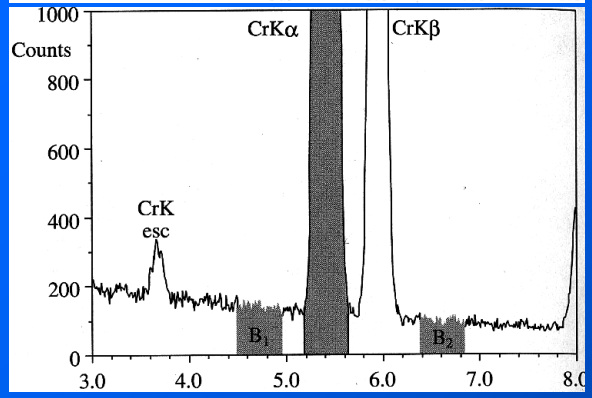
- Basic assumptions
  - X-ray intensities for each element are measured simultaneously
  - Ratio of intensities accounts for thickness variations
  - Specimen is thin enough that absorption and fluorescence can be ignored

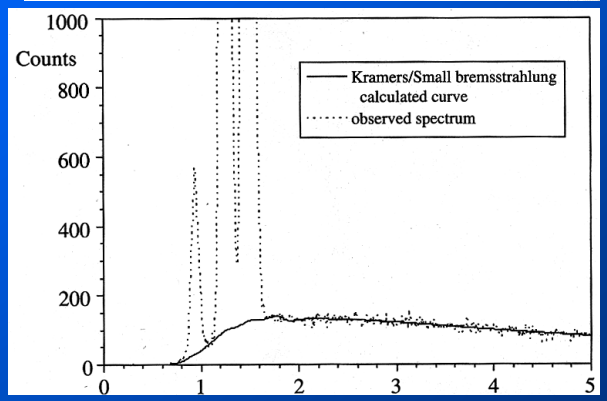
- Cliff-Lorimer equation:
  - C_A and C_B are weight fractions or atomic fractions (choose one, be consistent)
  - k_{AB} depends on the particular TEM/EDS system and kV (use highest kV)
    - k-factor is most closely related to the atomic number correction
  - Can expand to measure ternaries, etc. by measuring more k-factors

Calculate Background, Subtract

- Gross-Net Method
  - Draw line at ends of window covering full width of peak
  - Impossible with peak overlap
  - Should work better above 2 keV where background changes slowly
- Three-Window Method
  - Set window with FWHM (or even better 1.2 FWHM)
  - Average backgrounds B_1 and B_2
  - Subtract B_{ave} from peak
  - Requires well-separated peaks
- Background Modeling
  - Mathematical model of background as function of Z and E
  - Useful when peaks are close together

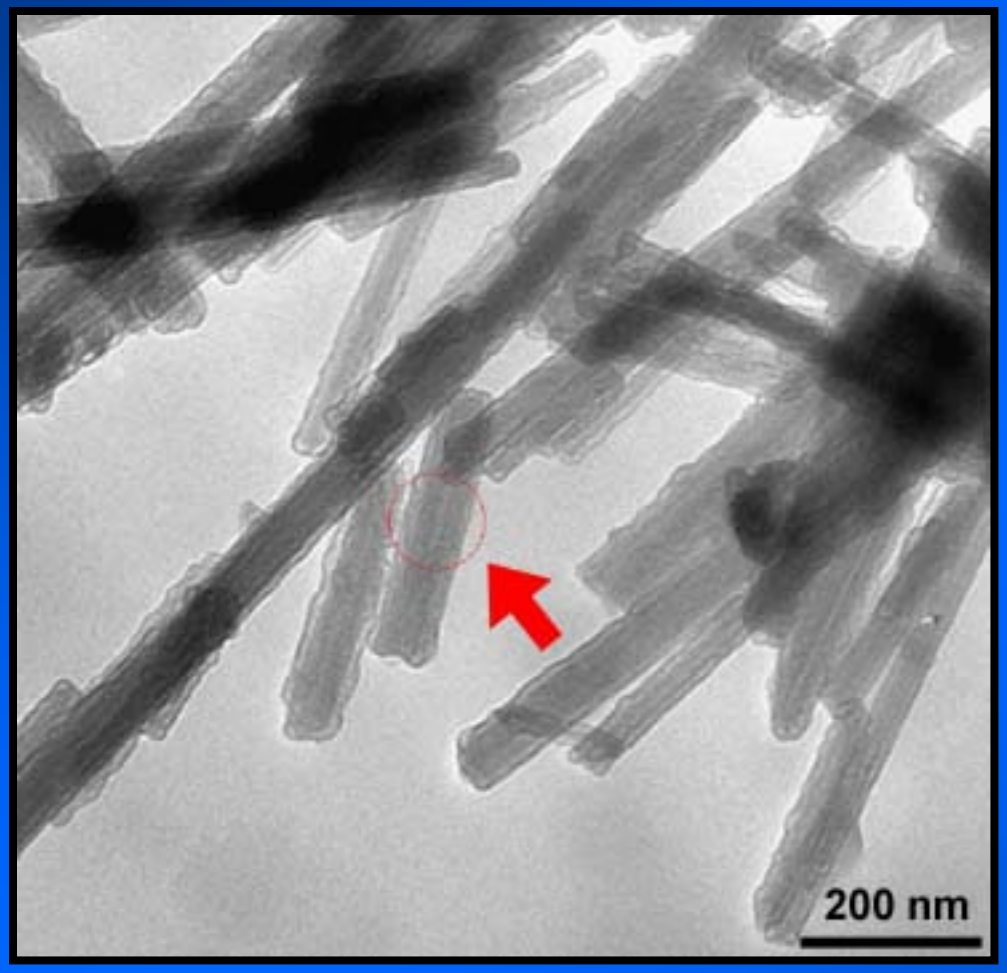




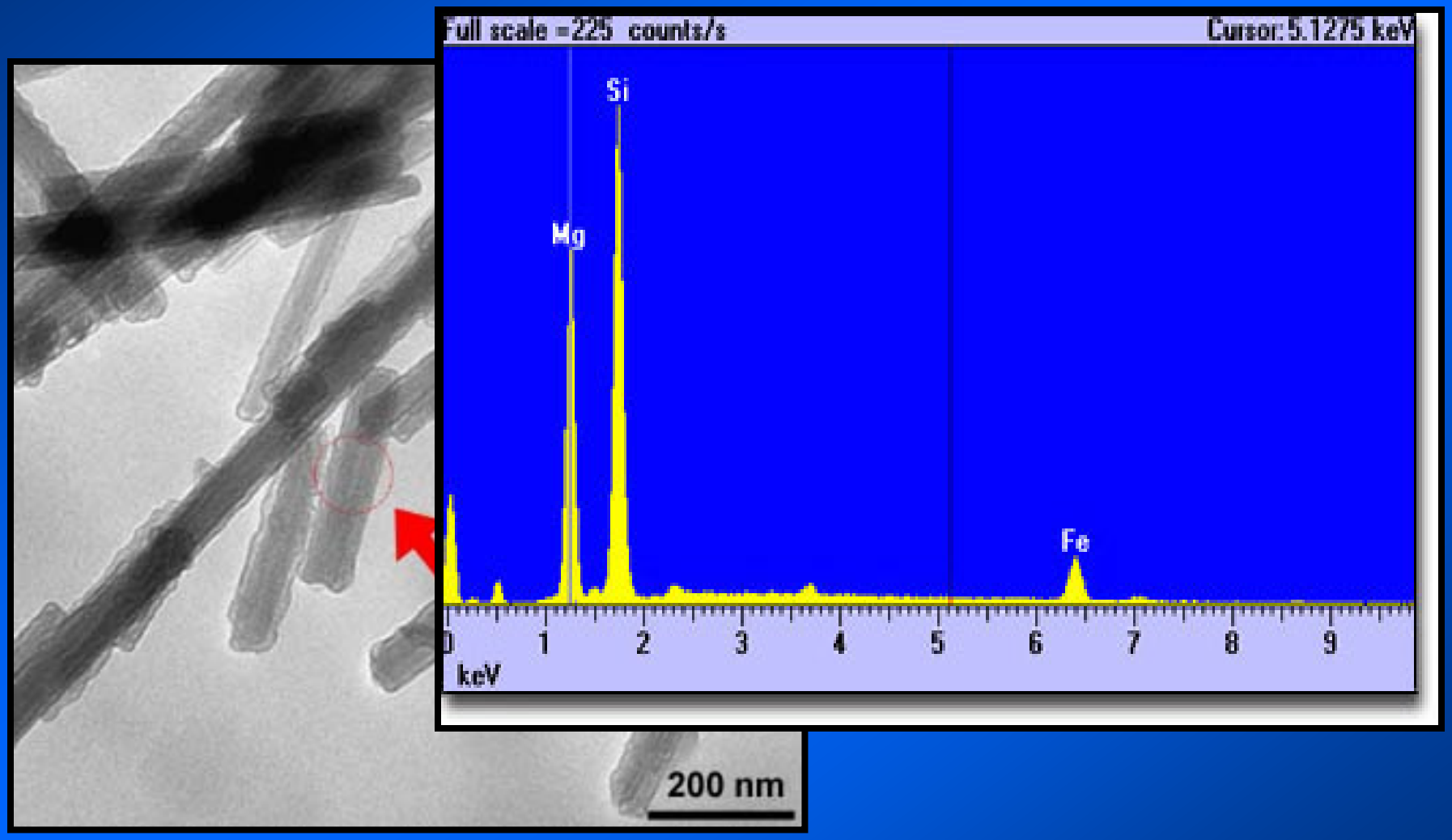


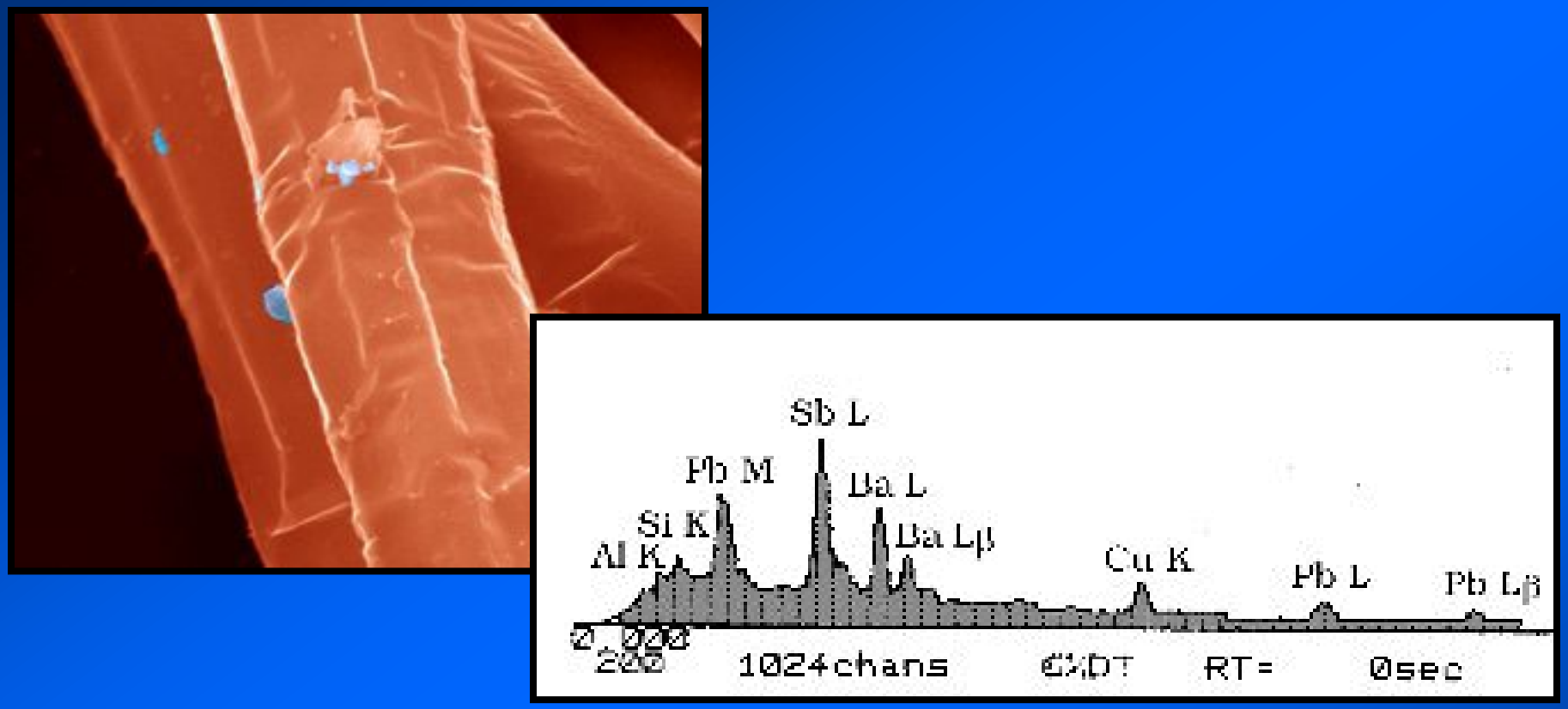
from Williams and Carter, *Transmission Electron Microscopy*, Springer, 1996

Chrysotile Asbestos Fibers



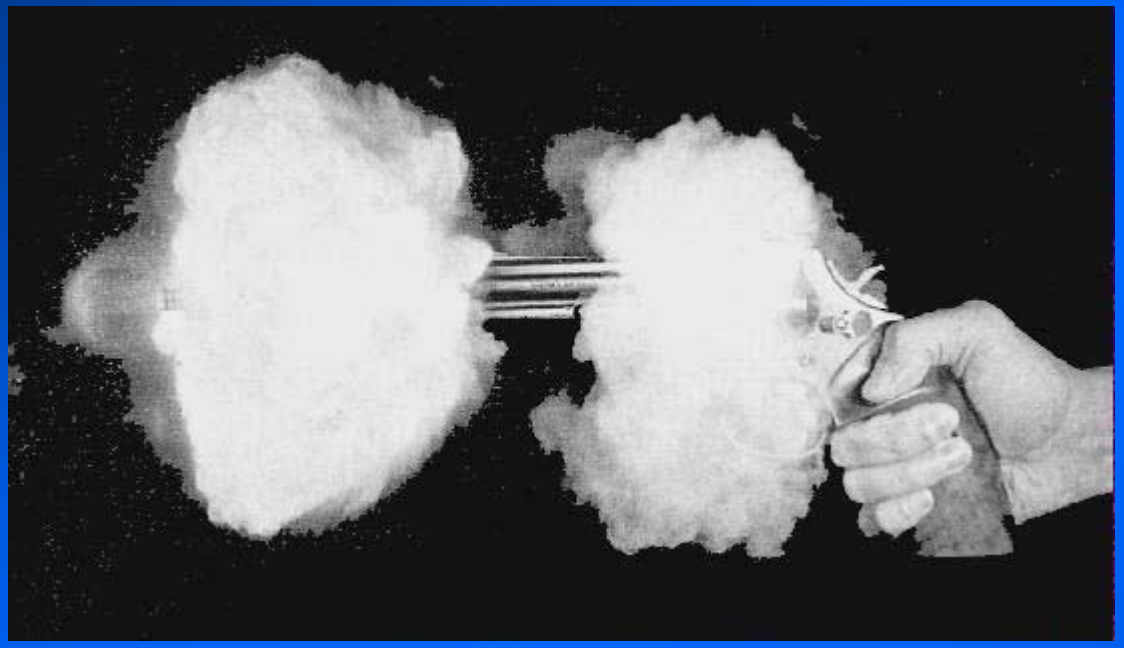
Chrysotile Asbestos Fibers



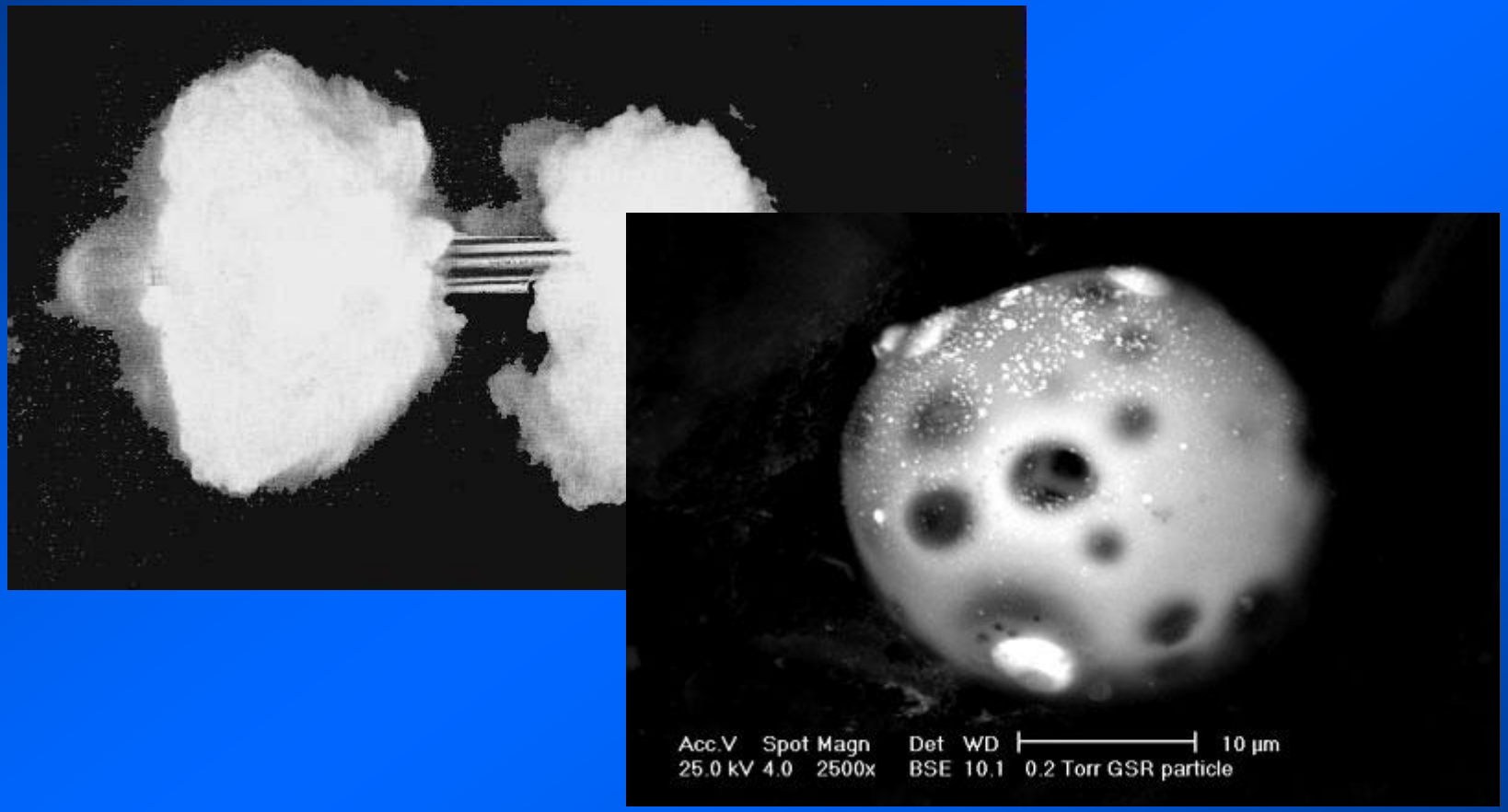


Bullet fragments (blue) can be identified on cloth fibers and distinguished from other metal pieces by their elemental composition

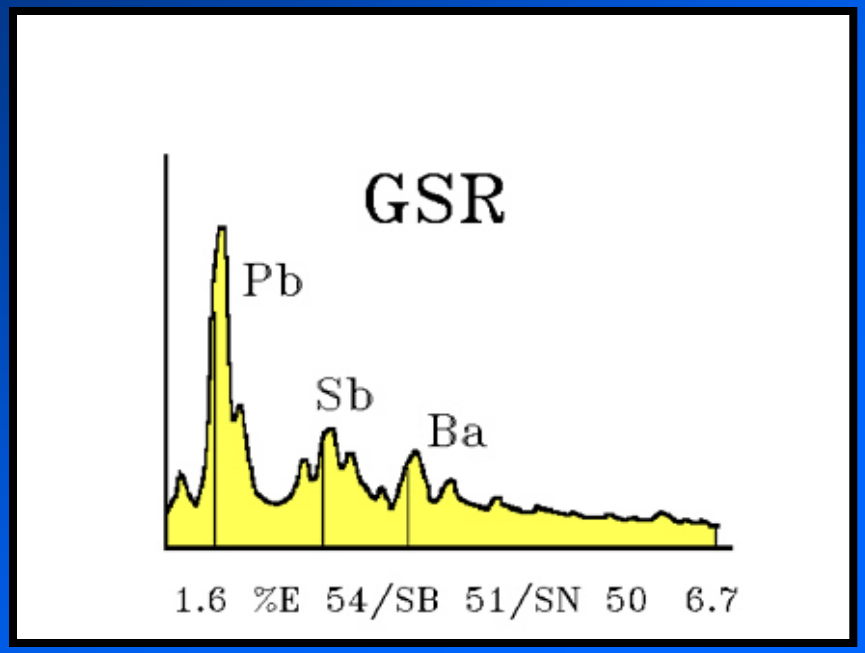
Gunshot Residue (GSR) Analysis



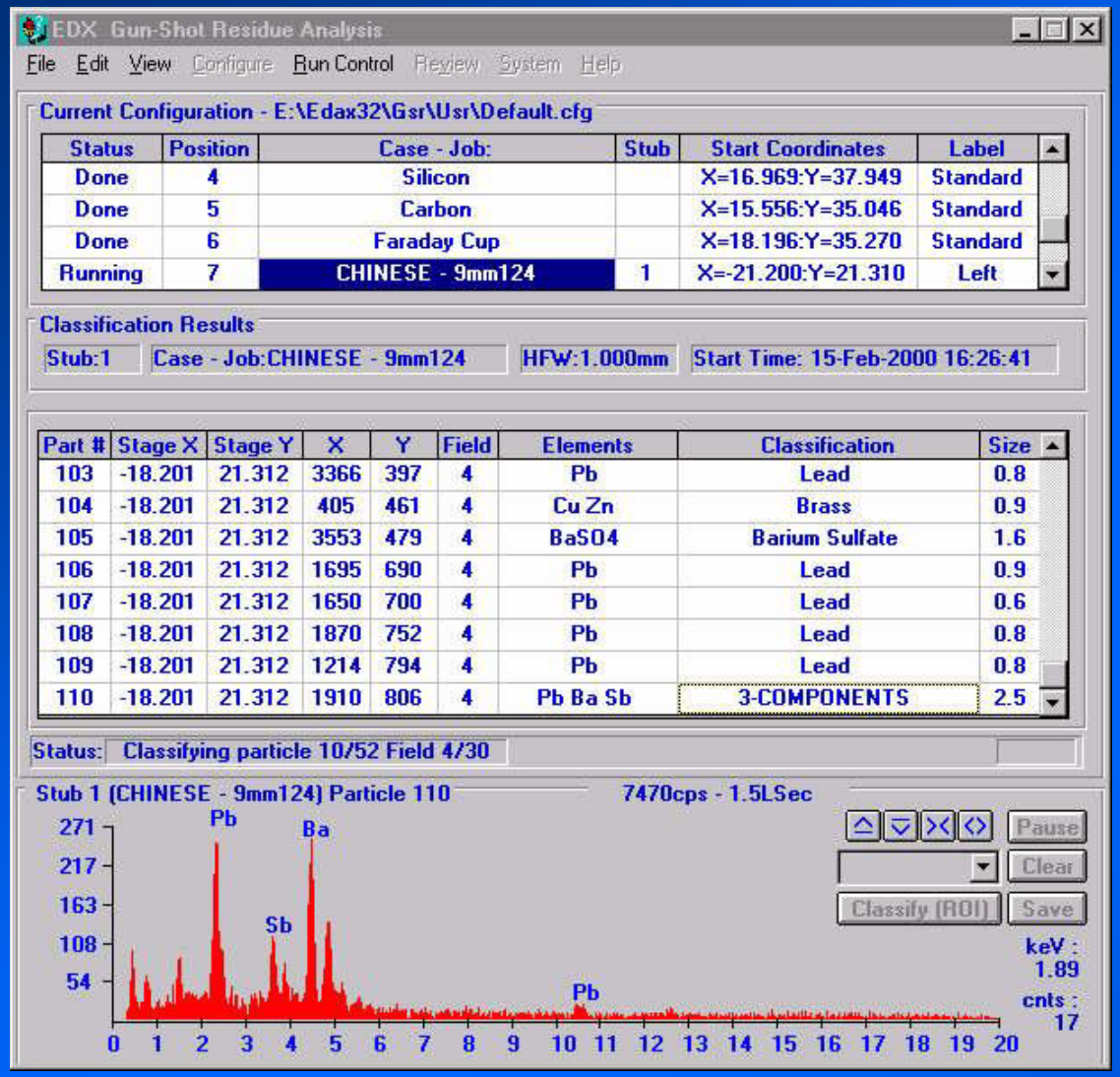
Gunshot Residue (GSR) Analysis



Gunshot Residue (GSR) Analysis



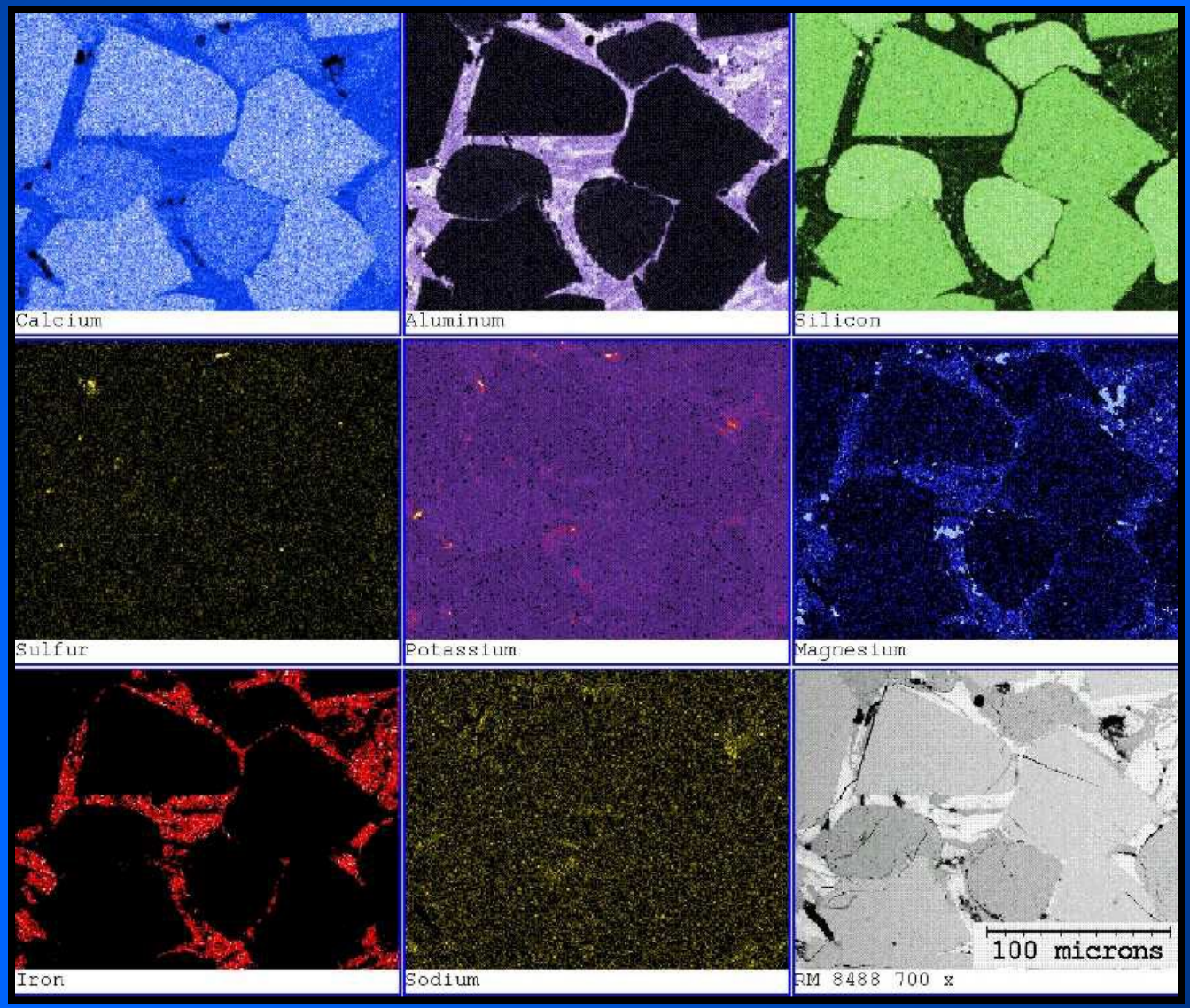
- Particles are very characteristic, therefore presence of these particles forms evidence of firing a gun.
- Particles normally consist of Pb (lead), Sb (antimony) and Ba (barium).
- New ammunition: environmentally friendly (no Sb).



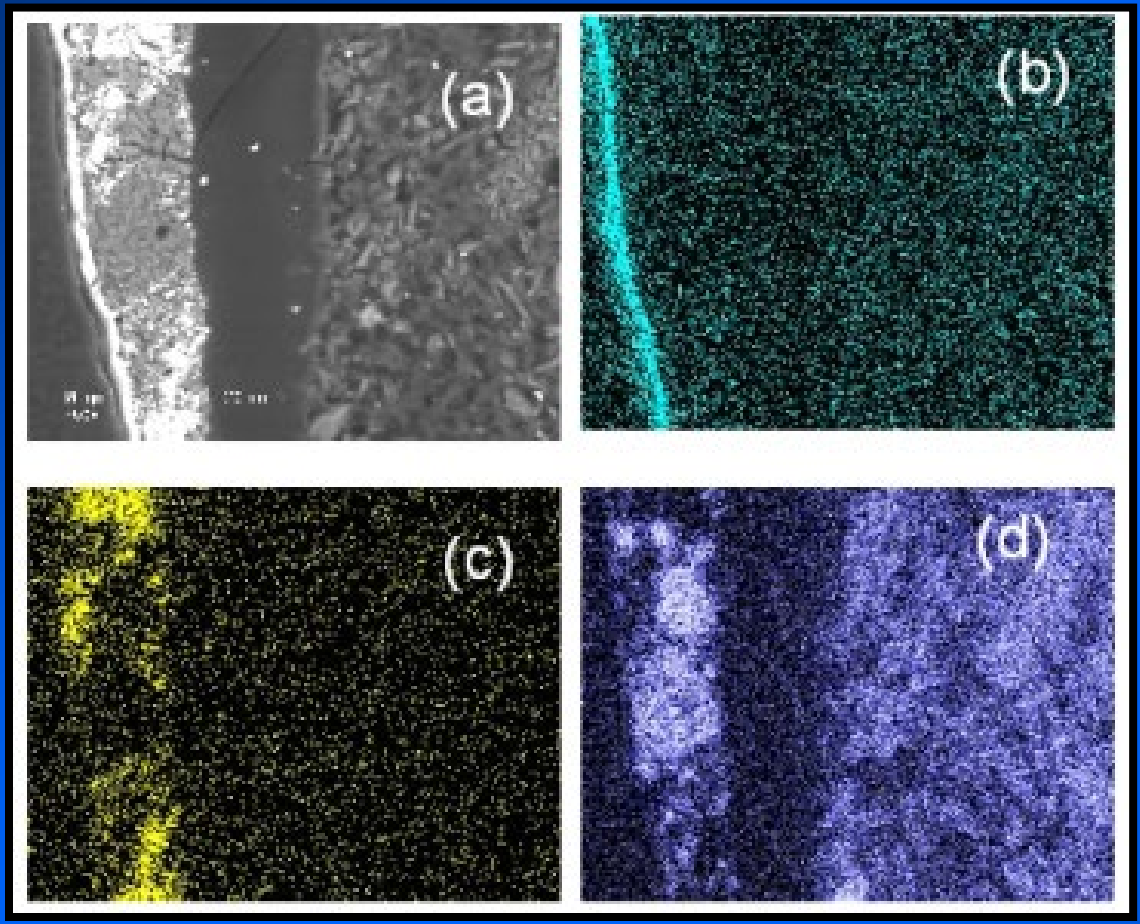
The proportion of elements present in GSR differ slightly and databases of GSR from different manufacturers can be used to identify what ammunition was used in a crime.

GSR is often found on criminals and also on victims if shot at close range.

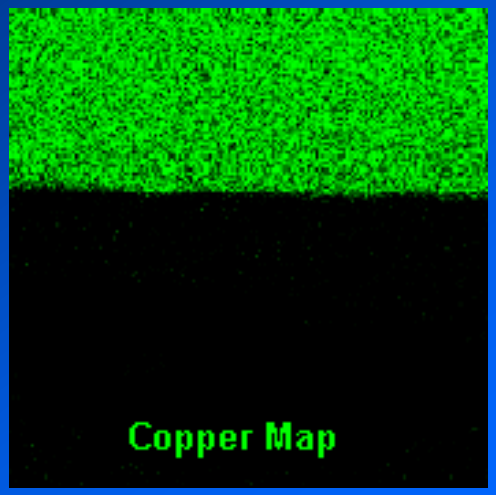
X-ray Mapping

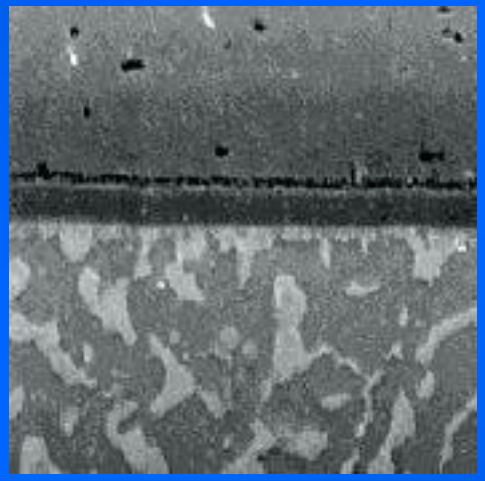


X-ray analysis of paint fragments

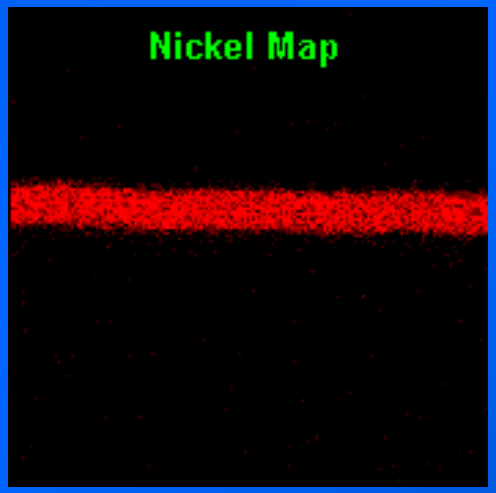


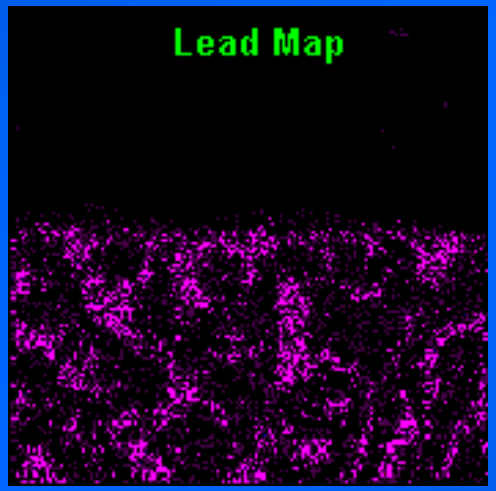
Combined with backscatter imaging and X-ray maps of (a) Au, (b) Ba and (c) Ca different layers of paint can be identified

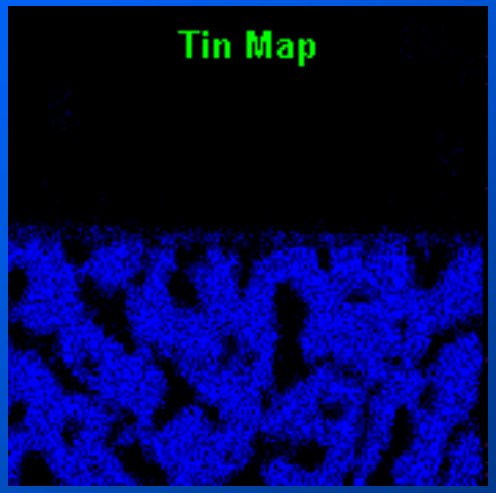




Secondary Electron

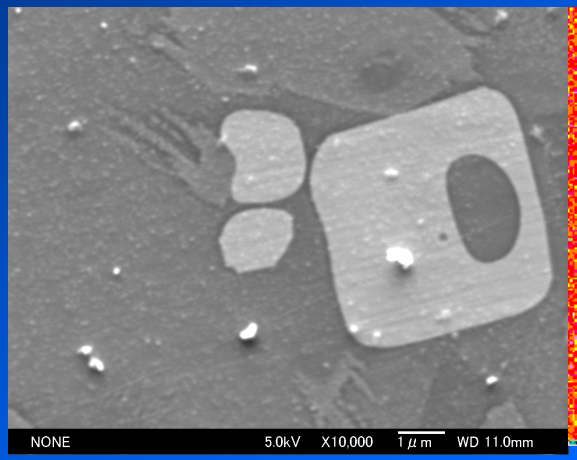




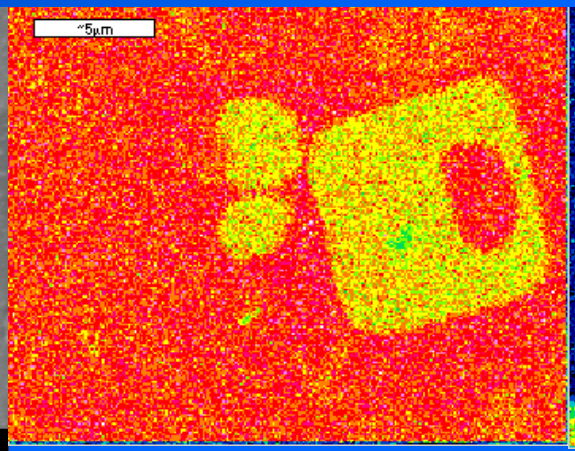


Low kV WDS Mapping

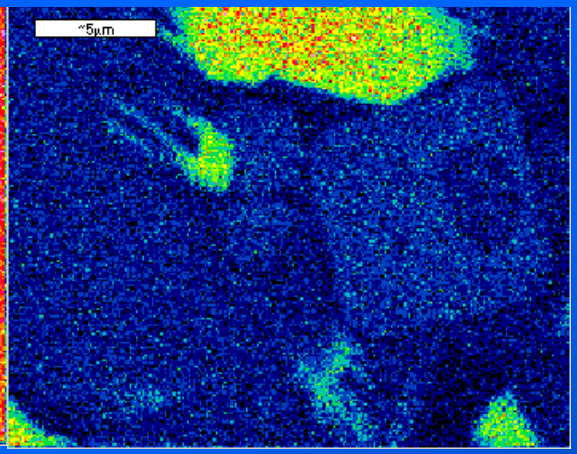
- **Accelerating Voltage : 5kV, Magnification 10,000X**



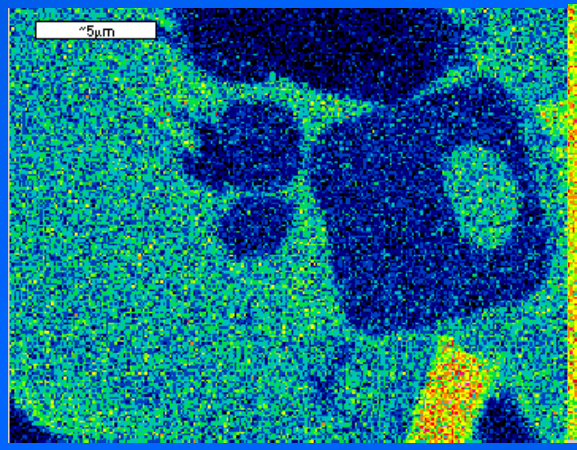
BSE



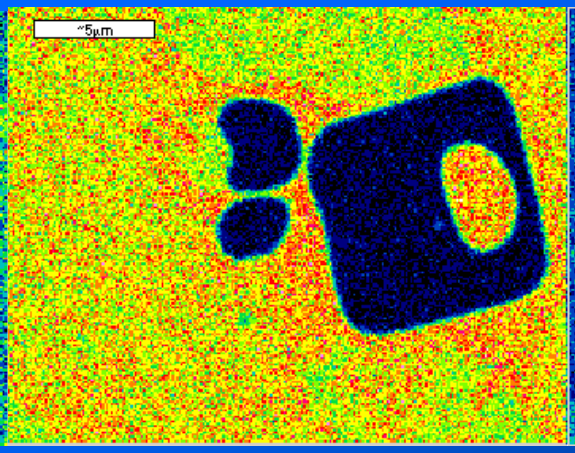
O



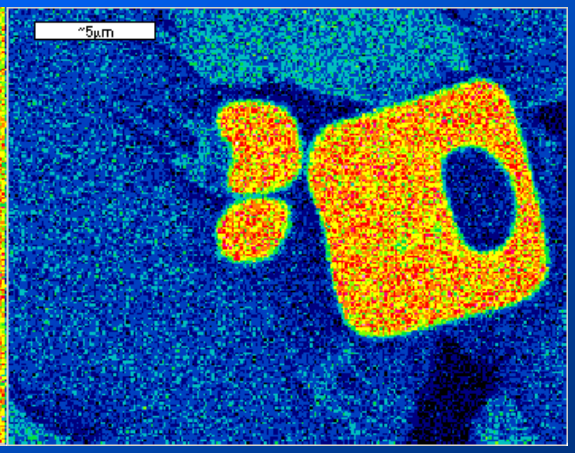
Mg



Al



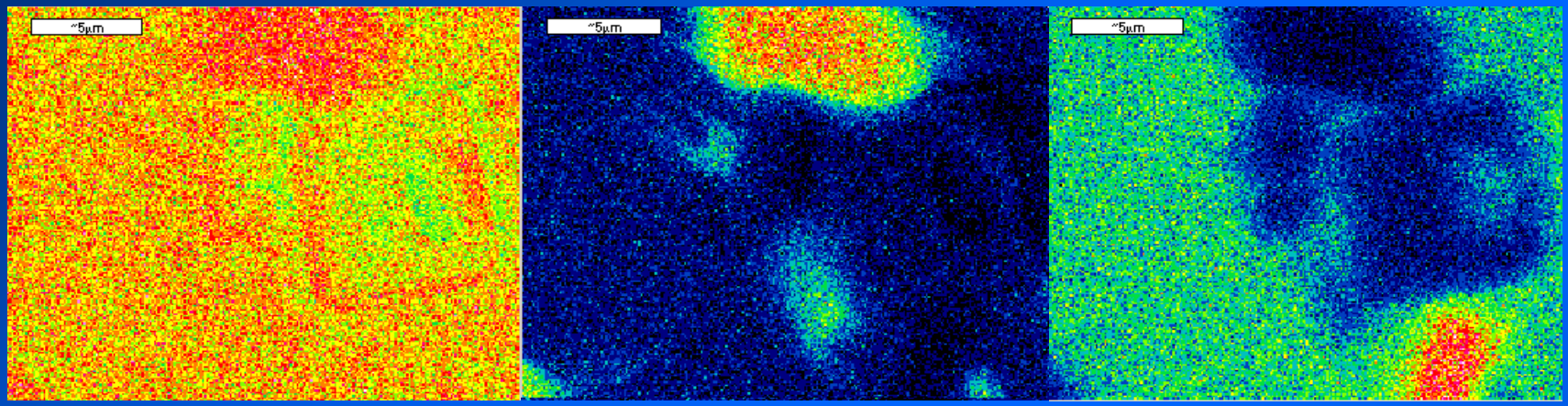
Si



Fe L

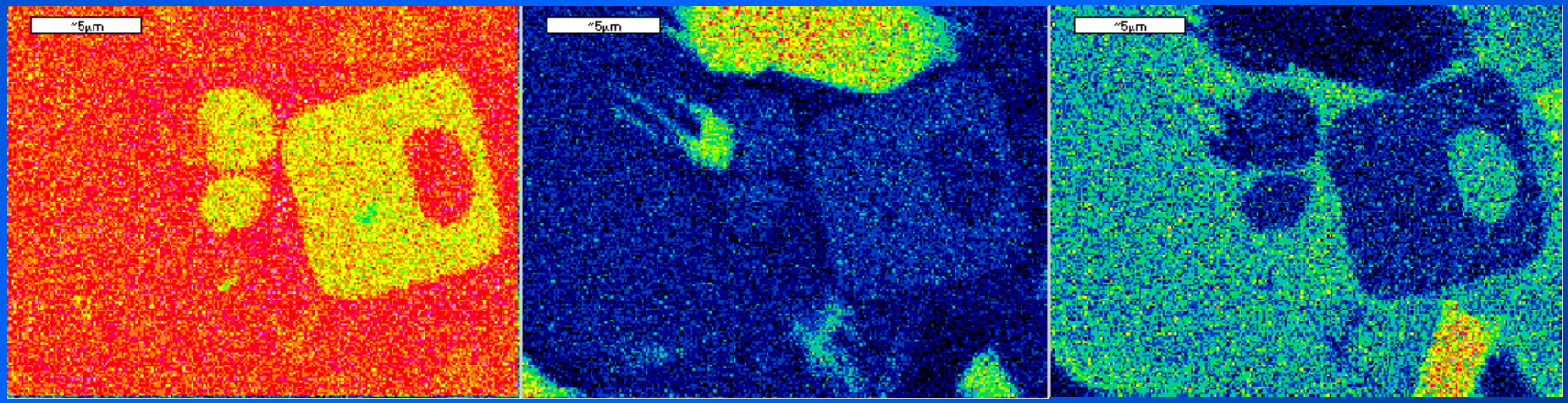
kV Comparison

15kV



O Mg Al

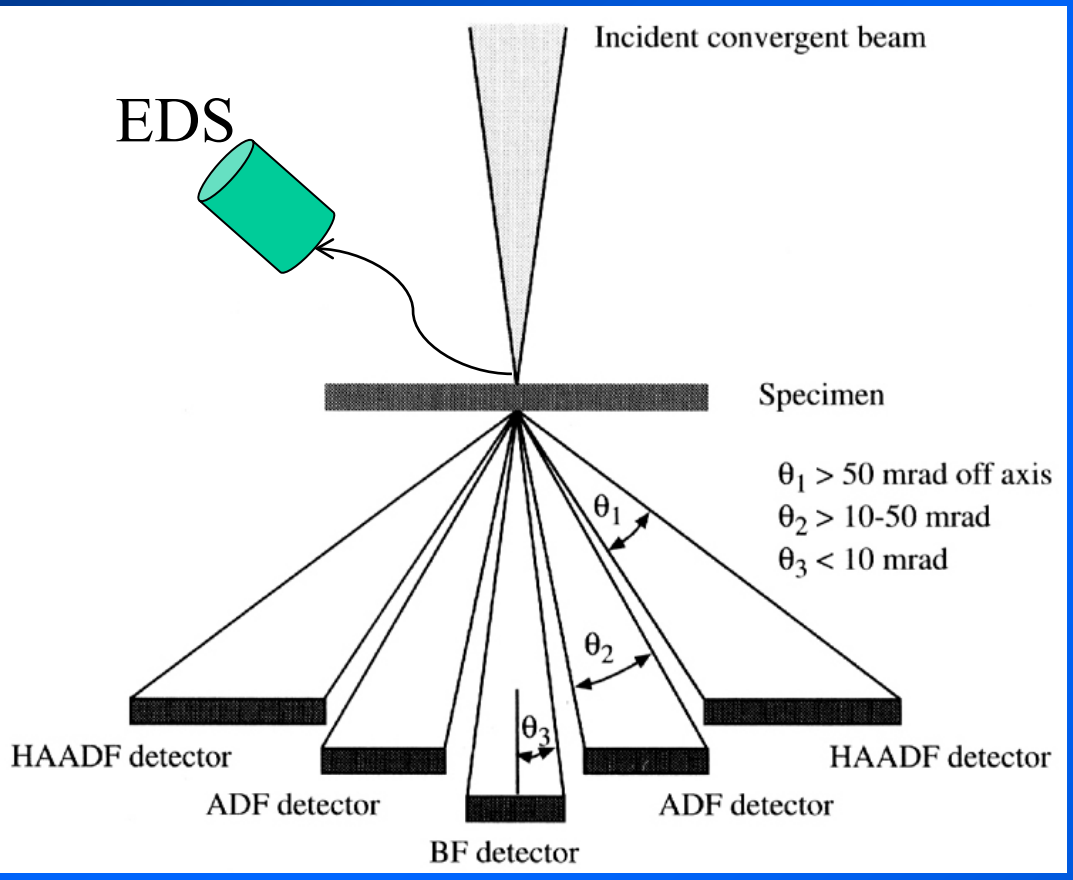
5kV

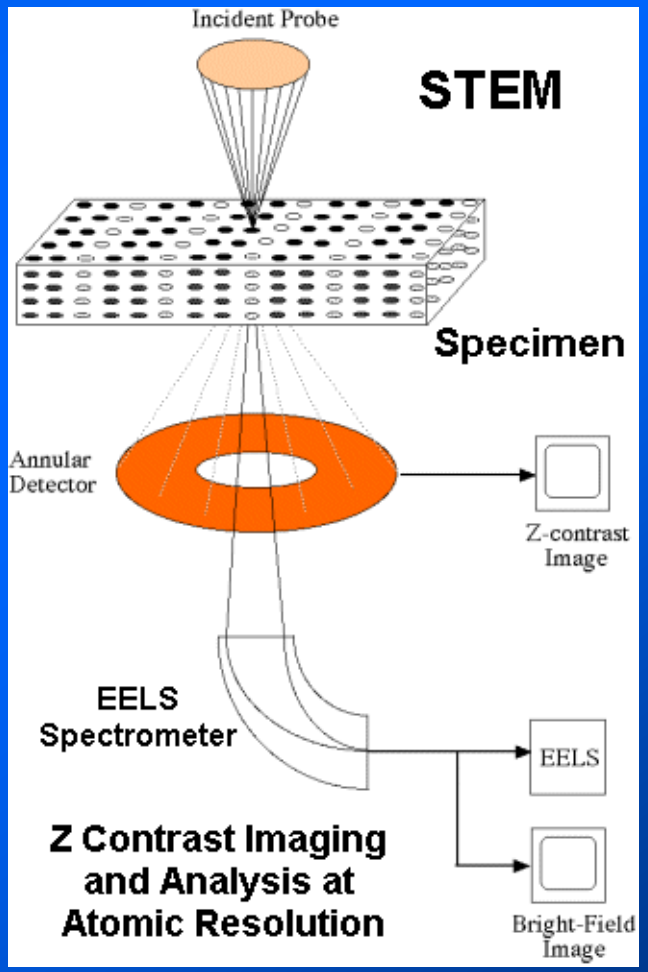


O Mg Al

Note the dramatic improvement in spatial resolution at low kV. Thermal FEG allows high count rates (high Ip) while maintaining a small spot size at low kV.

STEM


Incident convergent beam
EDS
Specimen
$\theta_1 > 50$ mrad off axis
$\theta_2 > 10$-50 mrad
$\theta_3 < 10$ mrad
θ_1
θ_2
θ_3
HAADF detector
HAADF detector
ADF detector
ADF detector
BF detector

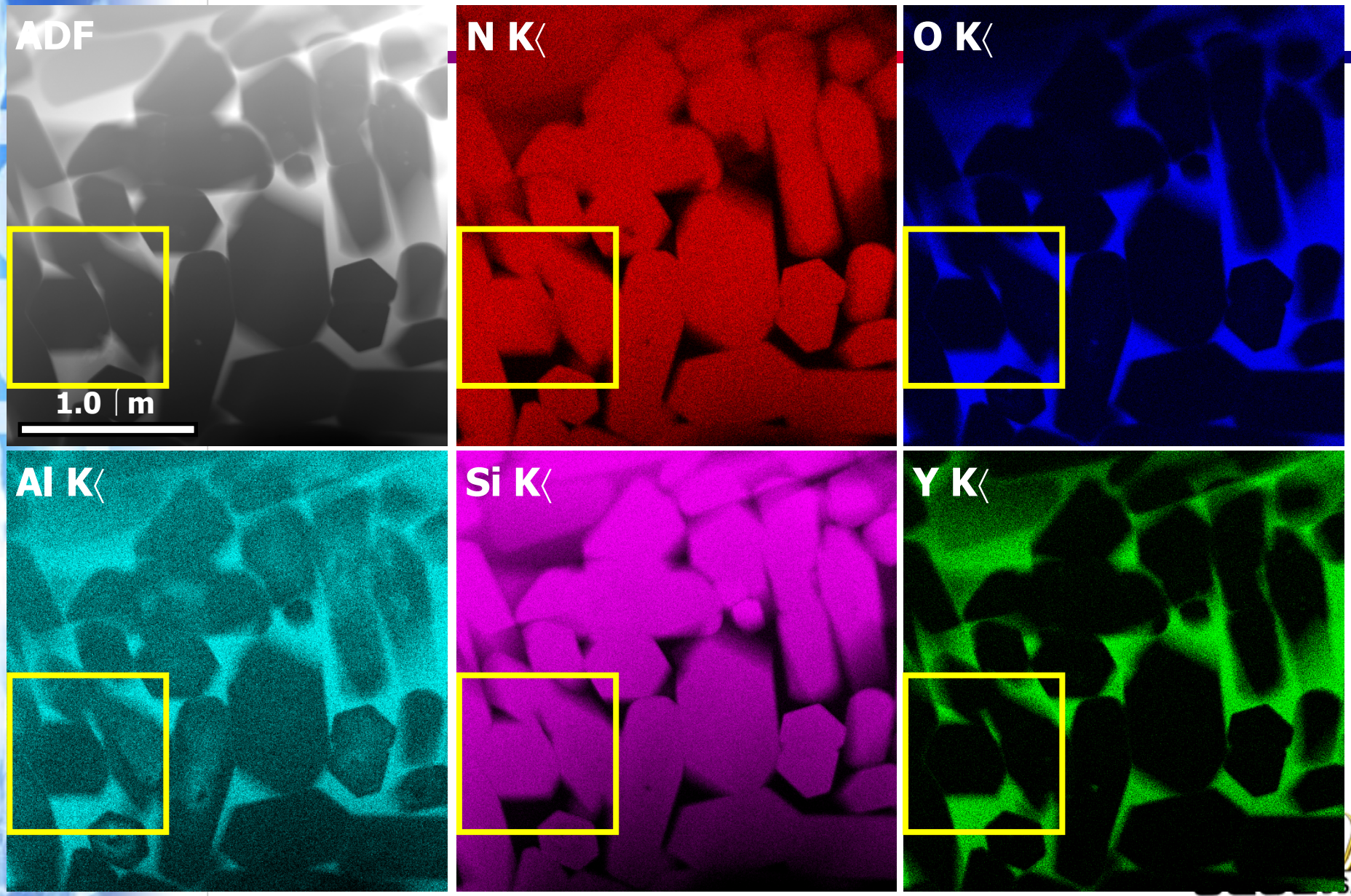

Incident Probe
STEM
Specimen
Annular Detector
Z-contrast Image
EELS Spectrometer
EELS
Bright-Field Image
Z Contrast Imaging and Analysis at Atomic Resolution

JEM-ARM200F & 100mm² SDD

1024x1024 pixel（15 frames）

About 28 min

Large pixel EDS mapping

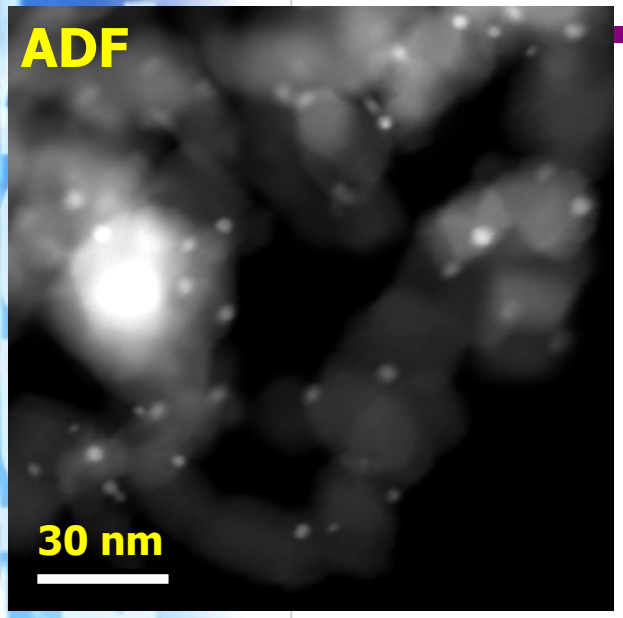


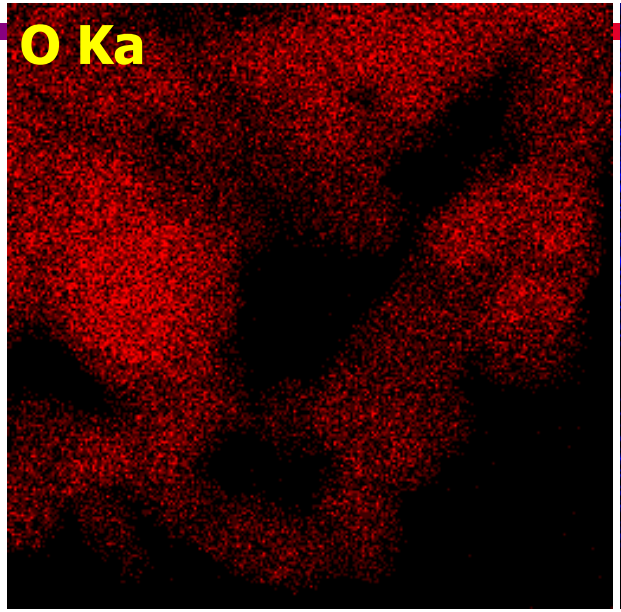
Specimen: SIALON

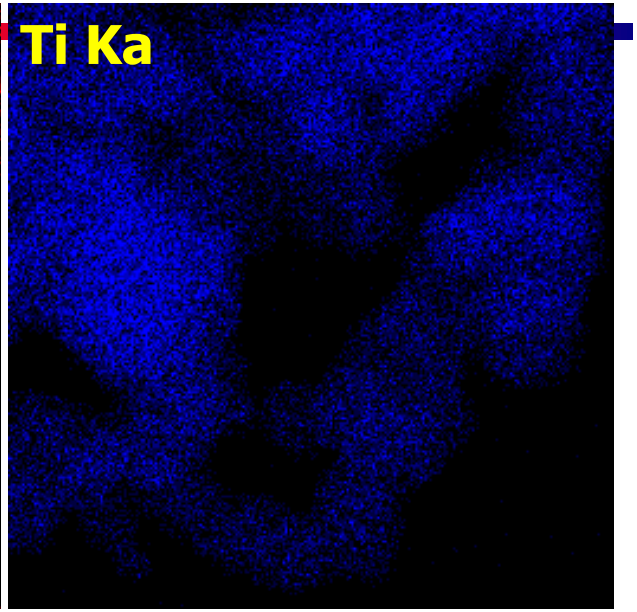
Mag: X1.5M
Probe current: ~1nA
(SS: 4C, CLA: 50(m))

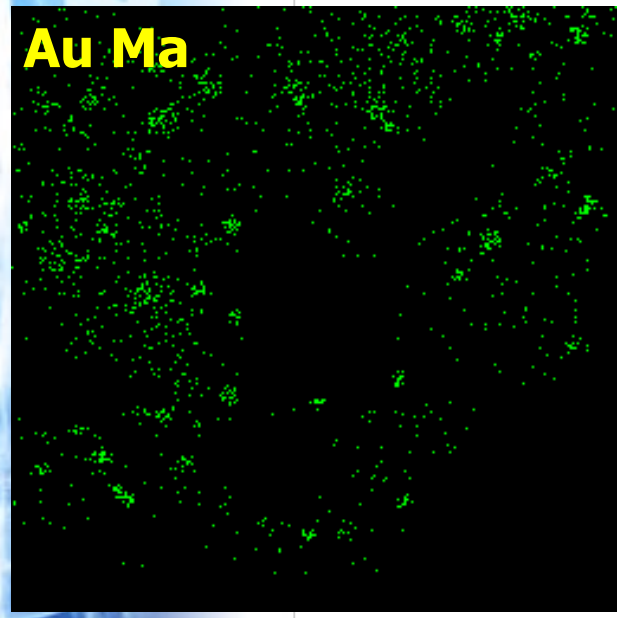
Au on TiO_2 Catalyst

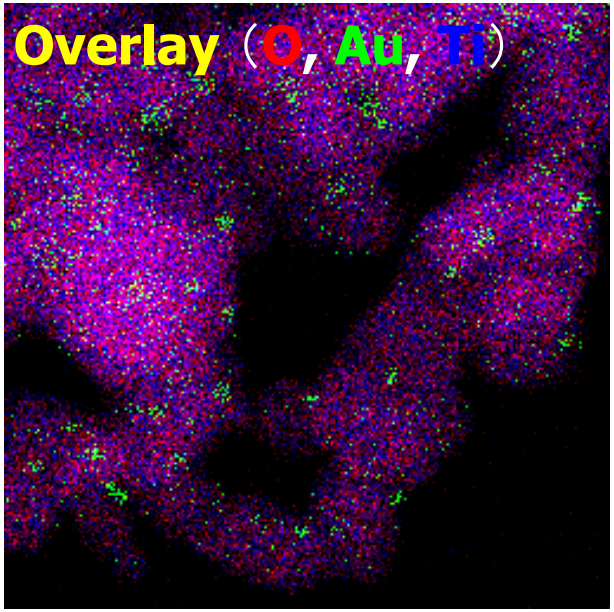
256x256, 5f, T4, 0.2ms
RT: 1m5s, DT: 12.02%
Count rate: 4368.17cps











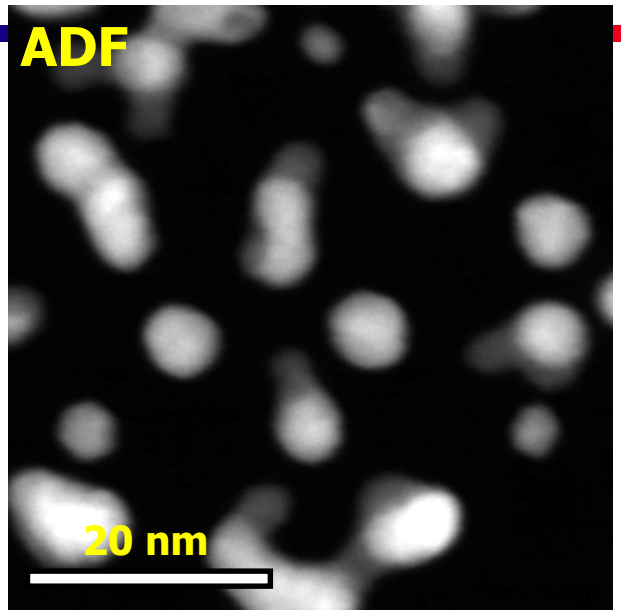
Particle size :
2~5nm
1 min mapping time

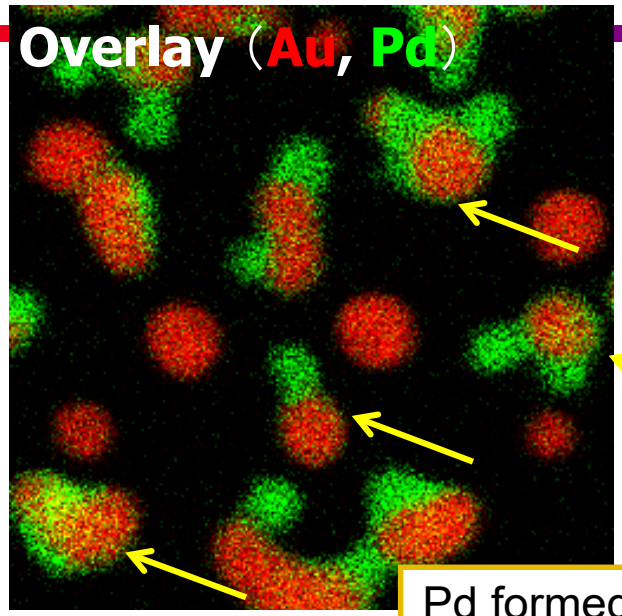
50 JEOL USA

Mag: X4.0M
Probe current: ~1nA
(SS: 4C, CLA: 50(m))

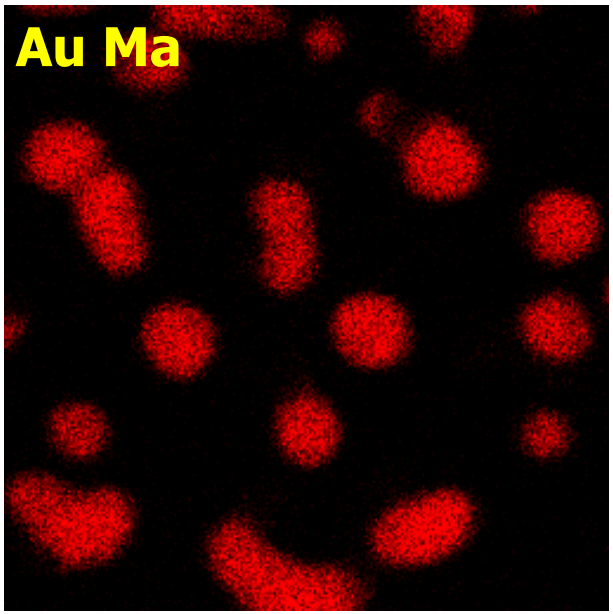
Au/Pd Catalyst

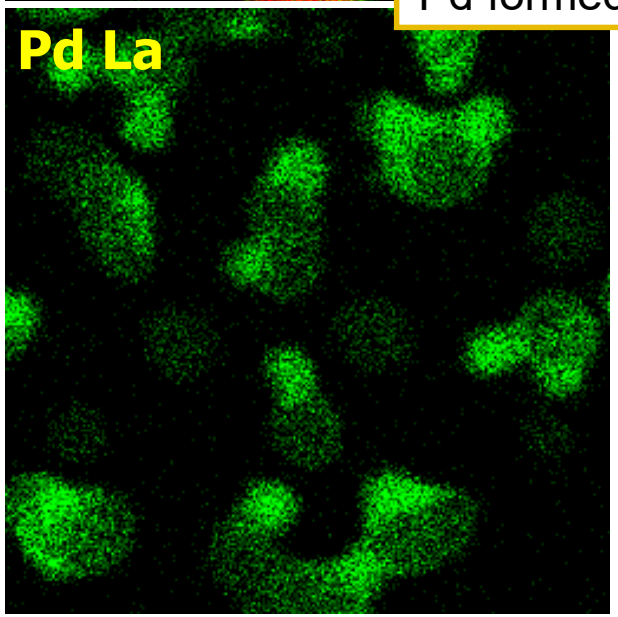
256x256, 89f, T4, 0.1ms
RT: 9m42s, DT: 5.70%
Count rate: 1689.80cps



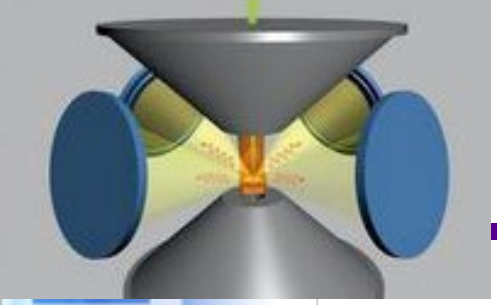


Pd formed shell(very thin)



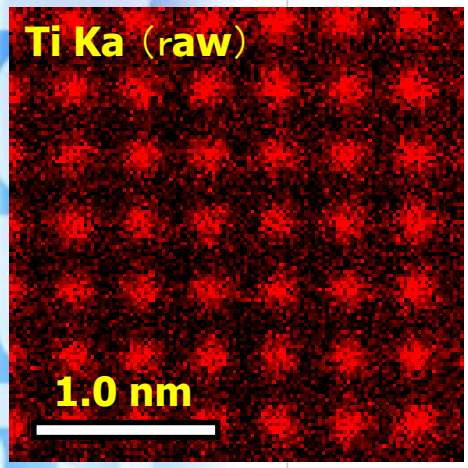


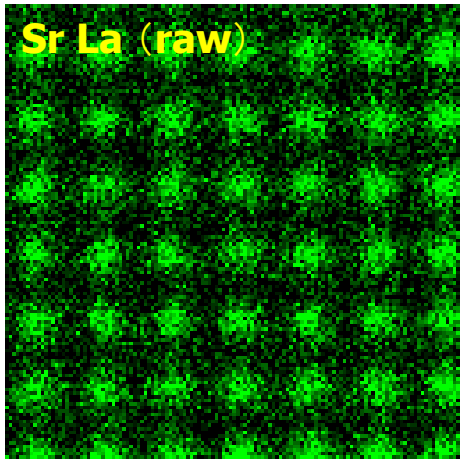
50 JEOL USA

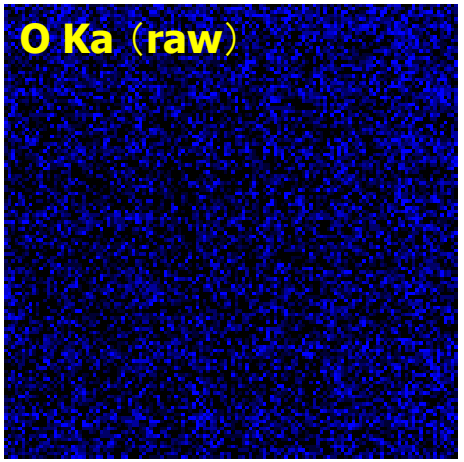


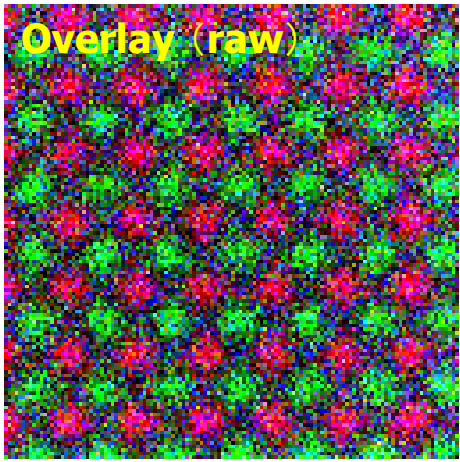
128x128, 175f, T4, 0.2ms
RT: 9m33s, DT: 3.71%
Count rate: 1119.57cps

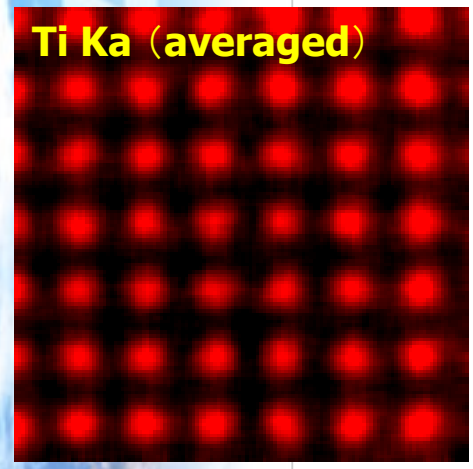
Atomic Resolution EDS

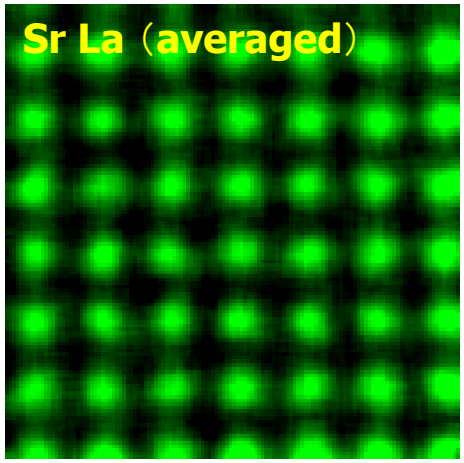


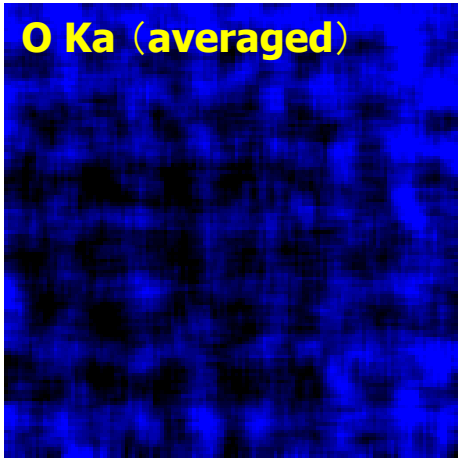


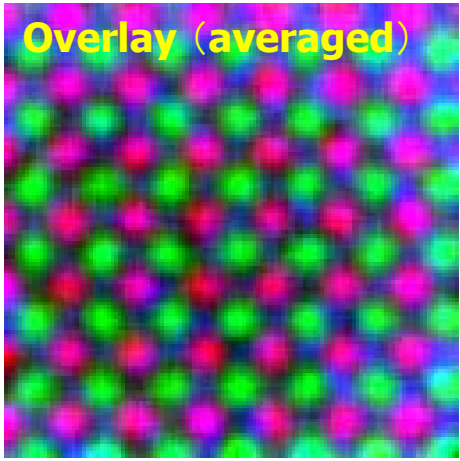






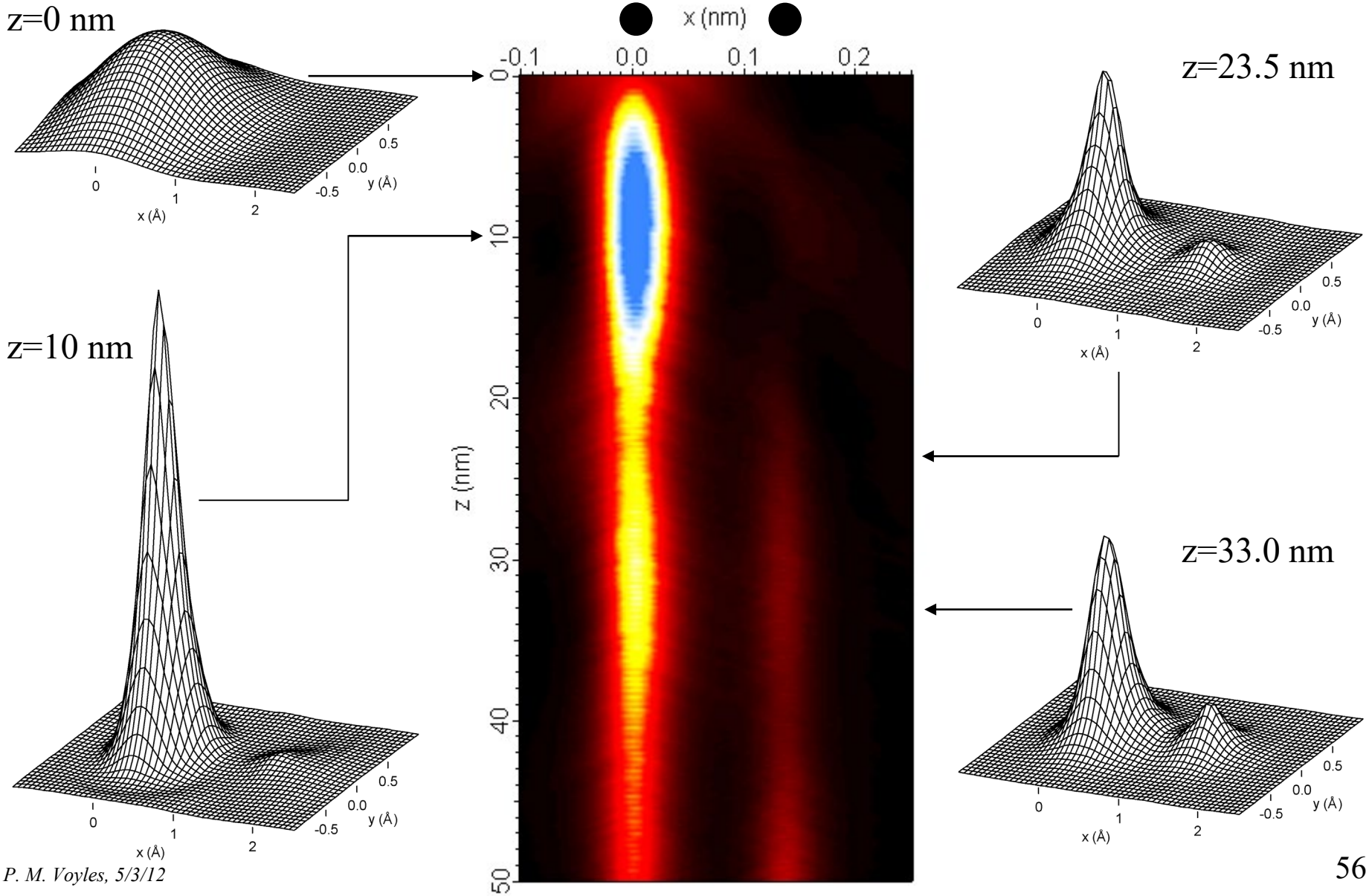






50 JEOL USA

Probe Channeling



Summary

- Qualitatively good, except for light elements
- Resolution can approach atomic
- Better ($$) detectors, better results
- Need calibrants even with “best” microscope & detectors
- Beware the black-box output
- Nothing can save a bad sample