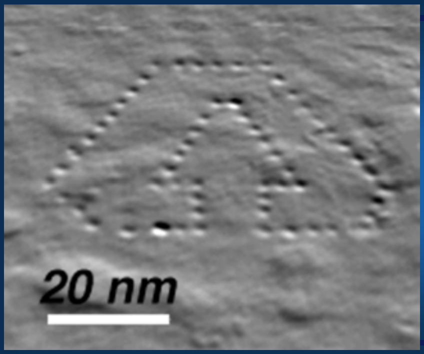
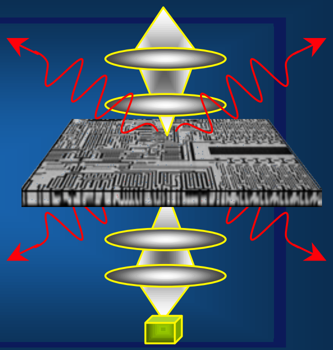
X-Ray Energy Dispersive Spectroscopy In the Electron Microscope



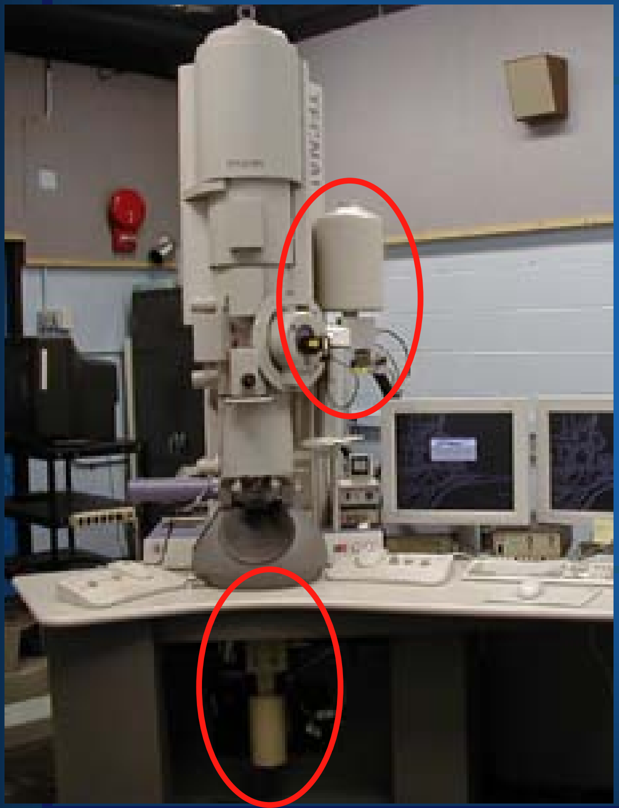


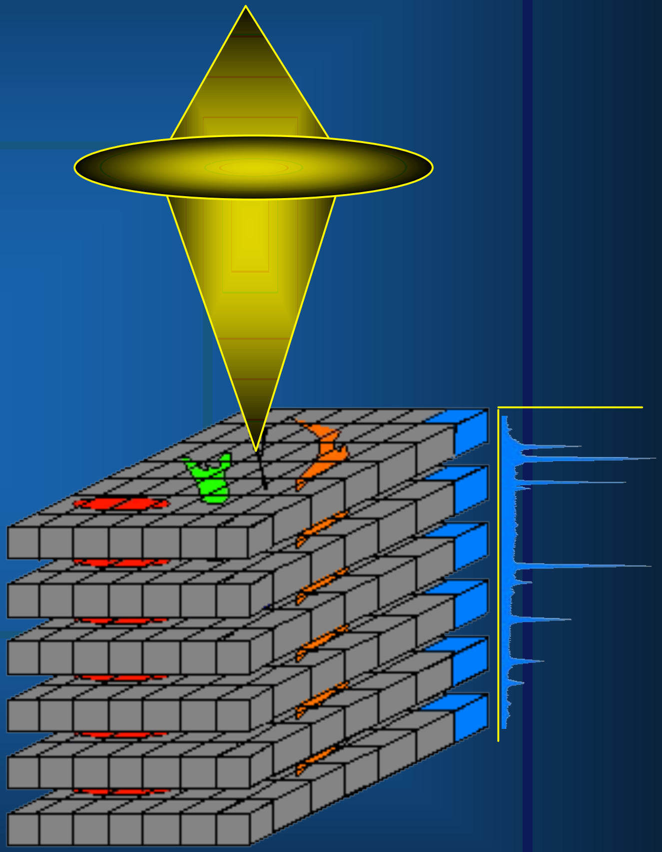
Nestor J. Zaluzec

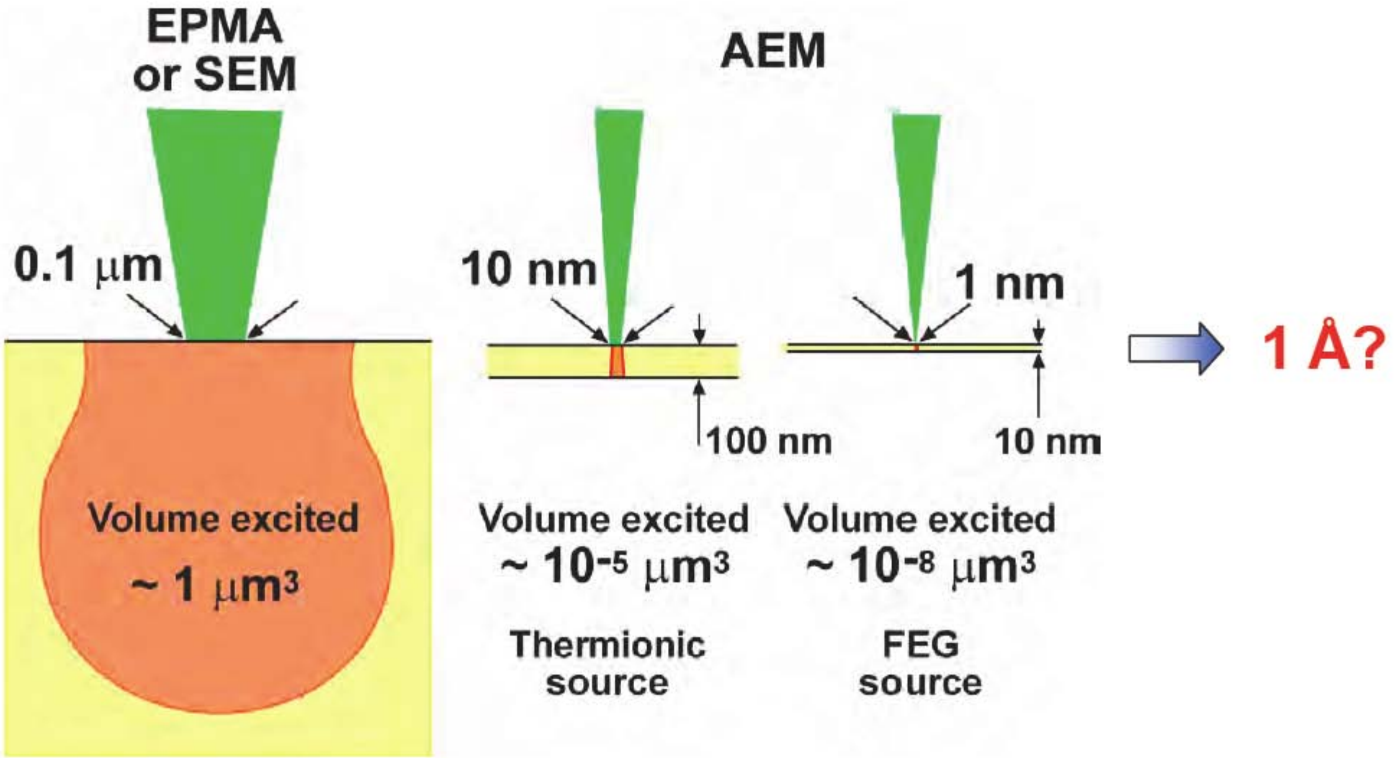
zaluzec@microscopy.com

zaluzec@aaem.amc.anl.gov

Micro-Analytical Capabilities







EPMA or SEM

0.1 μm

Volume excited

~ 1 μm³

AEM

10 nm

100 nm

Volume excited

~ 10⁻⁵ μm³

Thermionic source

1 nm

10 nm

Volume excited

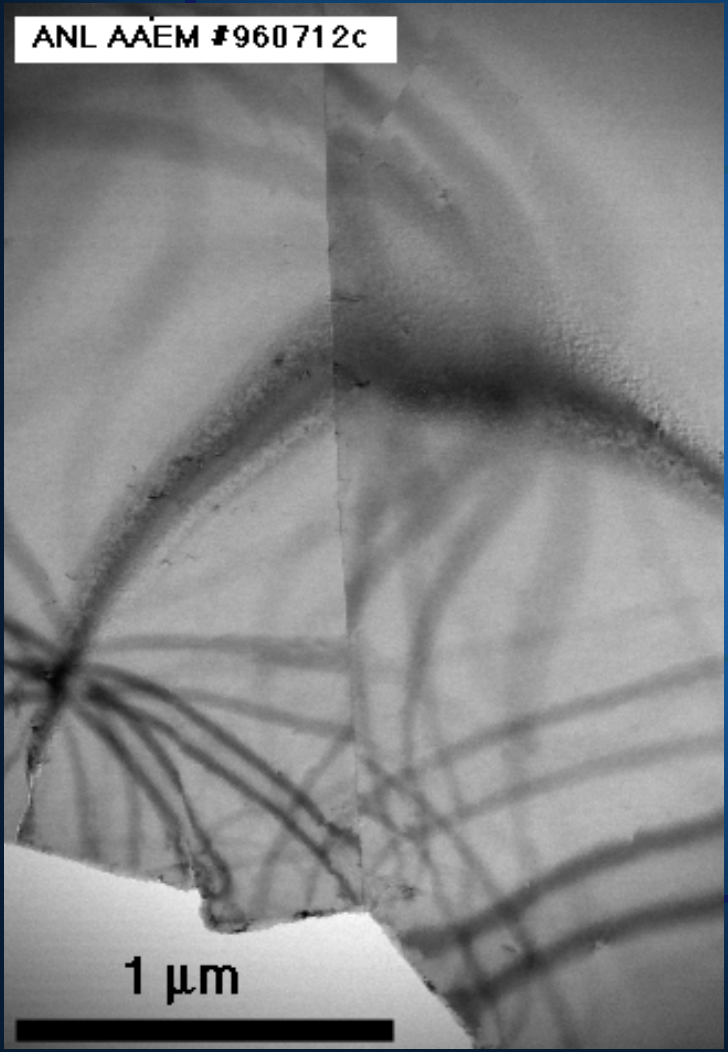
~ 10⁻⁸ μm³

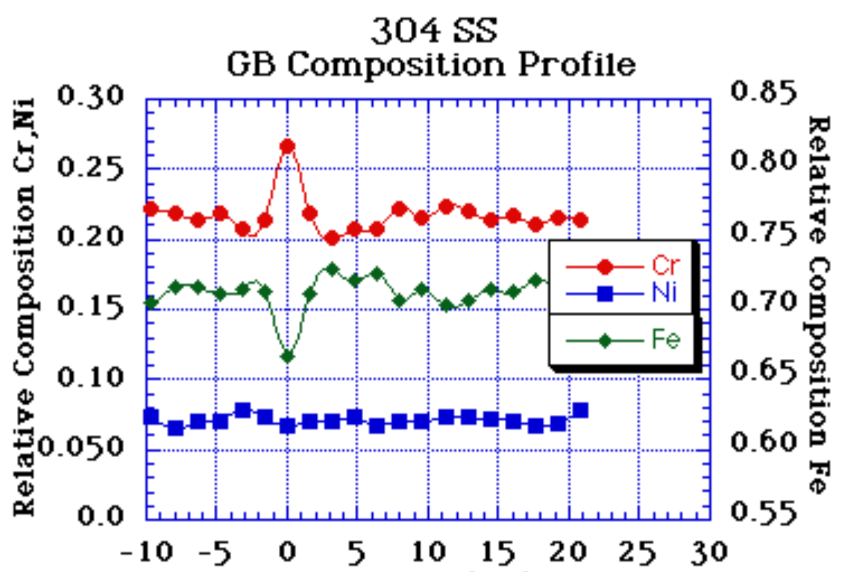
FEG source

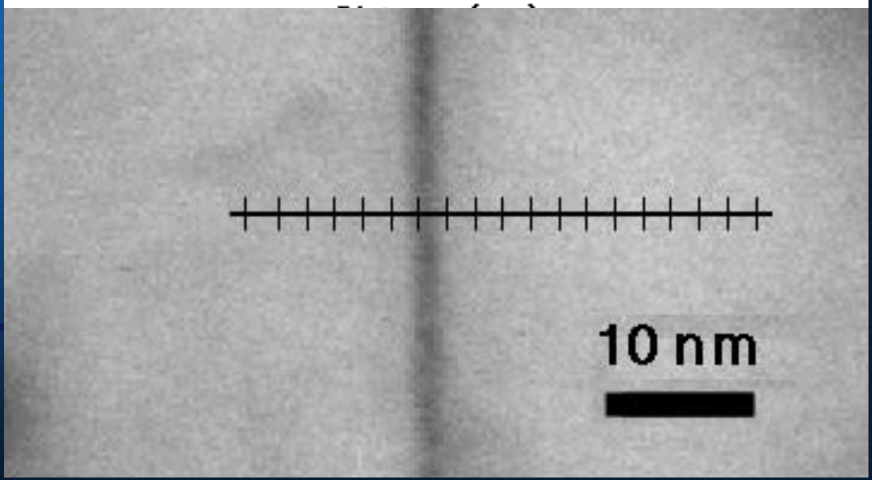
→ 1 Å?

Spatial resolution ↑ → Analytical sensitivity ↓

High Spatial Resolution Quantitative Microanalysis







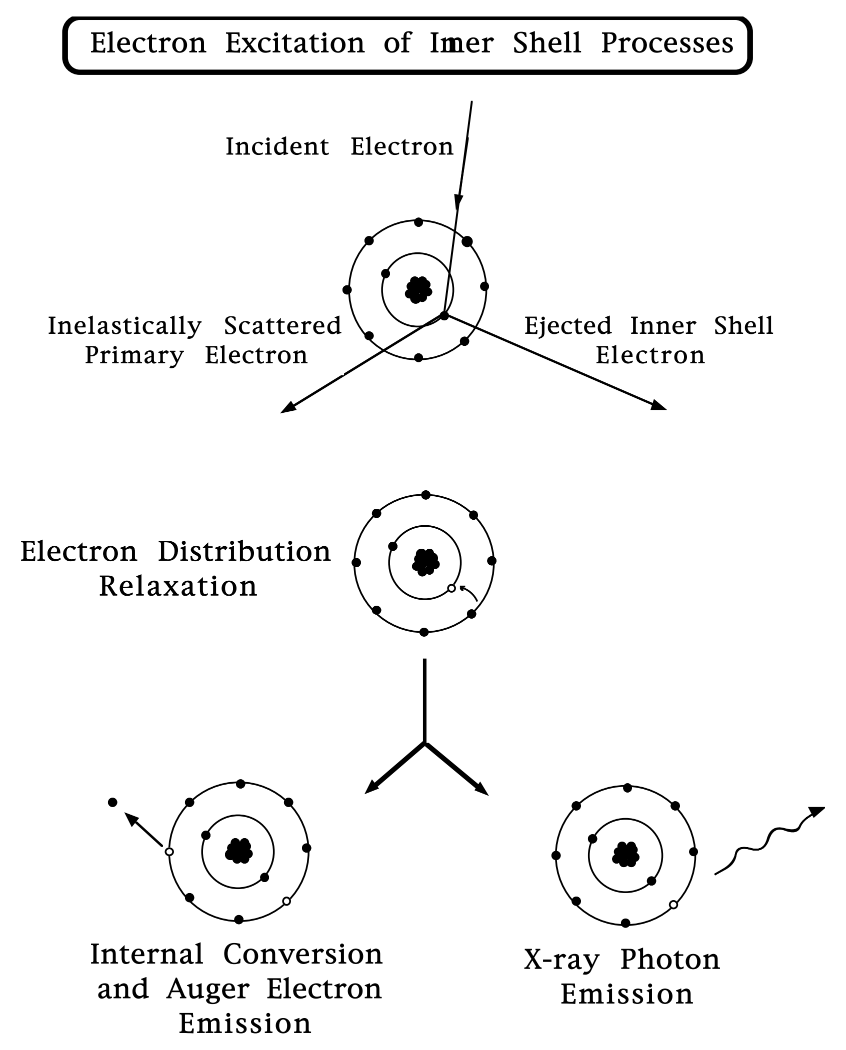
Brief Review of X-ray Generation

Instrumentation: Detector Systems

Instrumentation: EM Systems

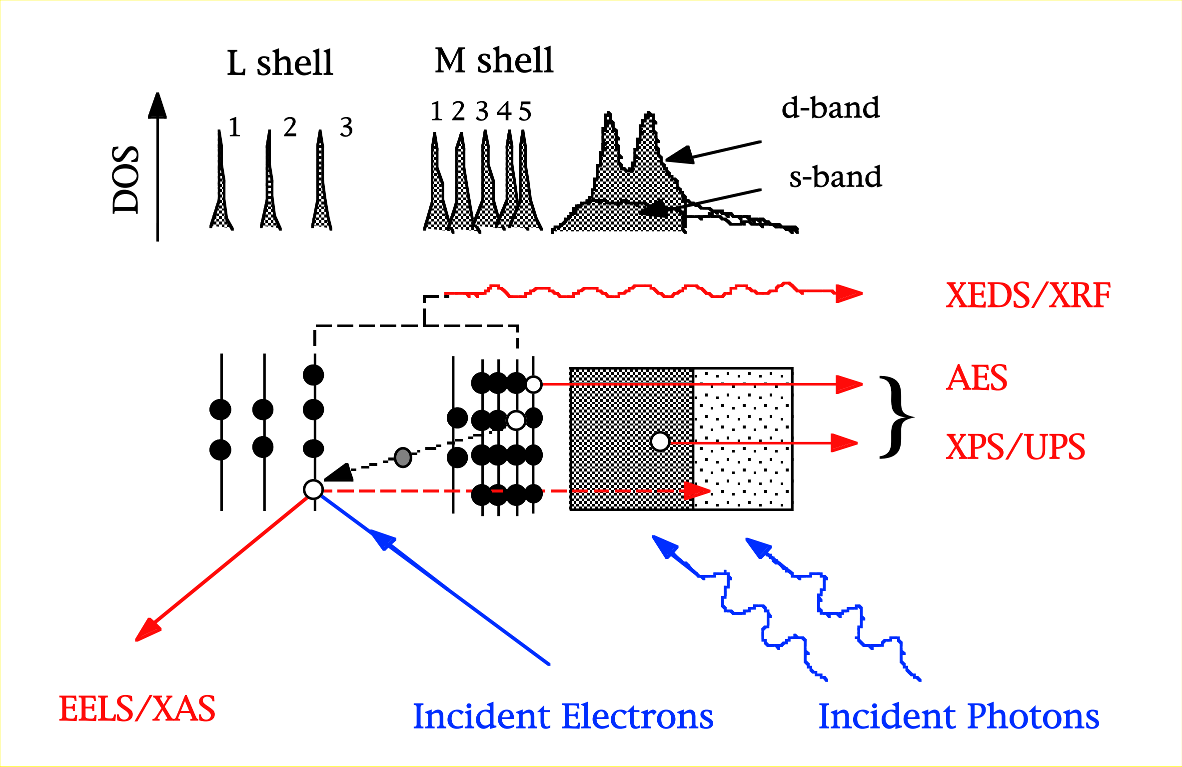
Data Analysis and Quantification:

Additional Topics



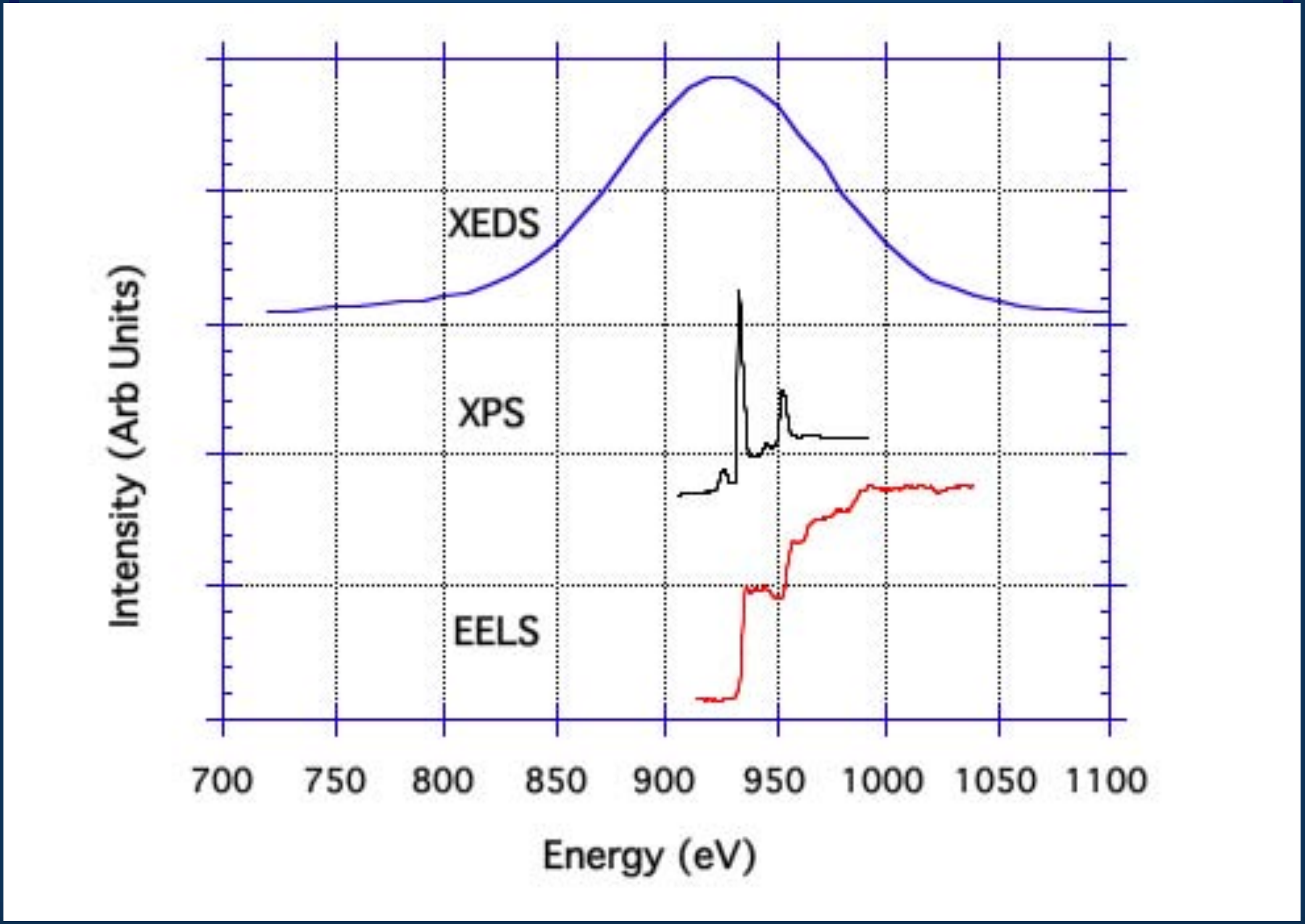
The Emission Process:

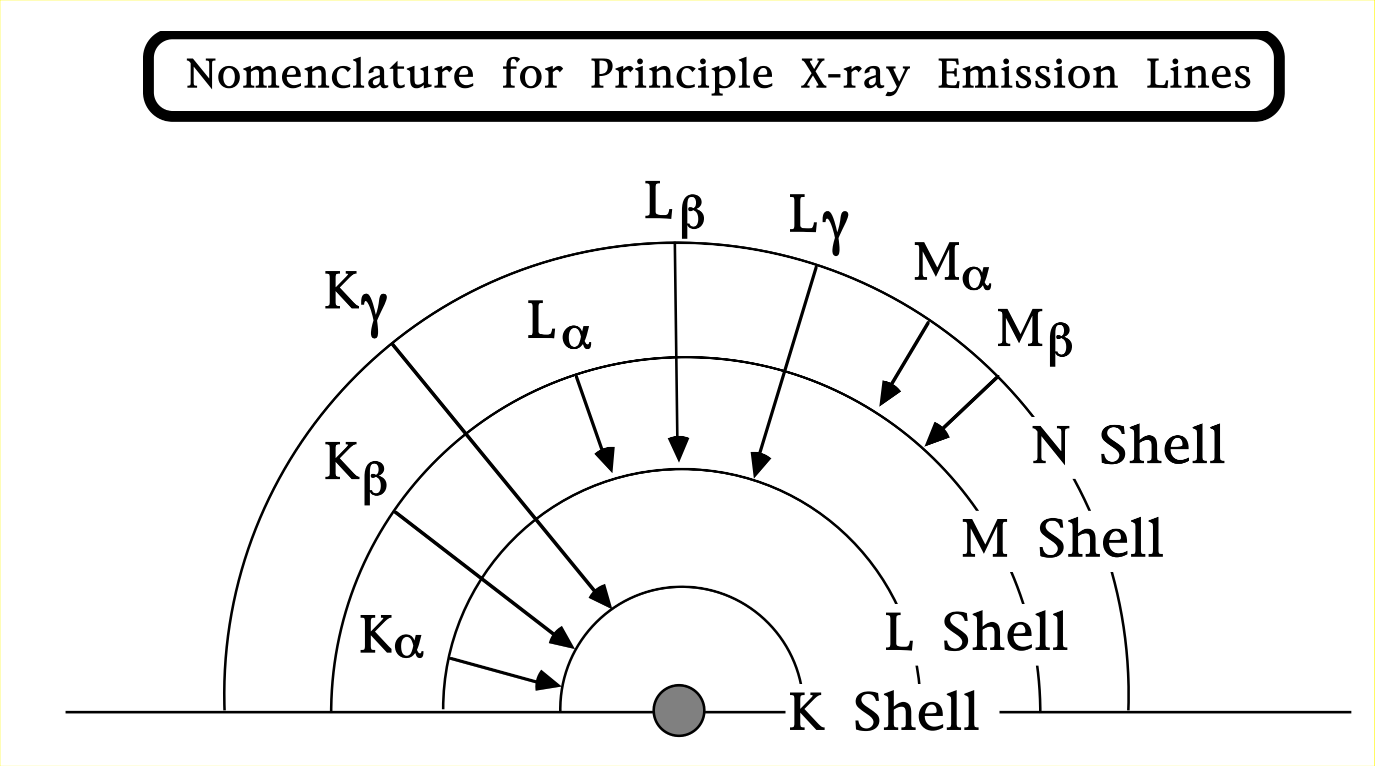
1. *Excitation*
2. *Relaxation*
3. *Emission*



Schematic Diagram Illustrating Sources of Signals Resulting from Inelastic Scattering

Experimental XEDS, XPS, and EELS data from the Copper L shell. Note the differences in energy resolution, and spectral features.





Characteristic X-ray Line Energy = $E_{final} - E_{initial}$

Recall that for each atom every shell has a unique energy level determined by the atomic configuration for that element.

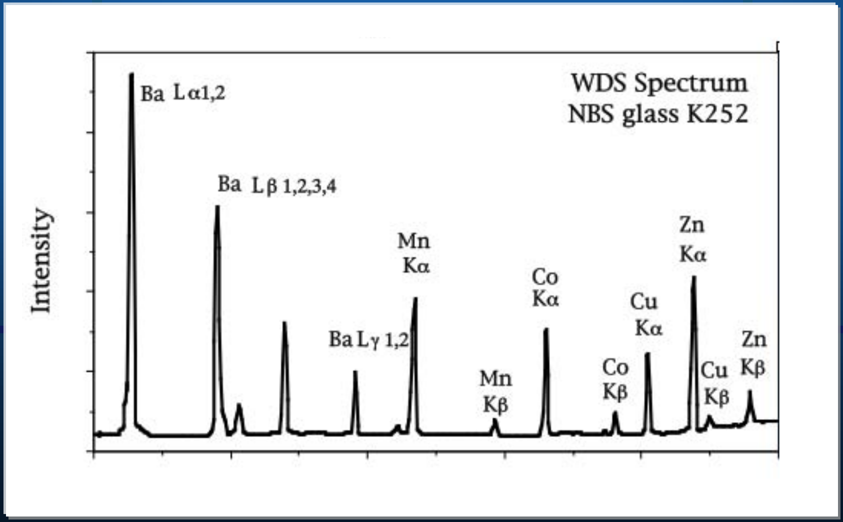
∴ **X-ray line energies are unique.**

Relative Intensities of Major X-ray Lines

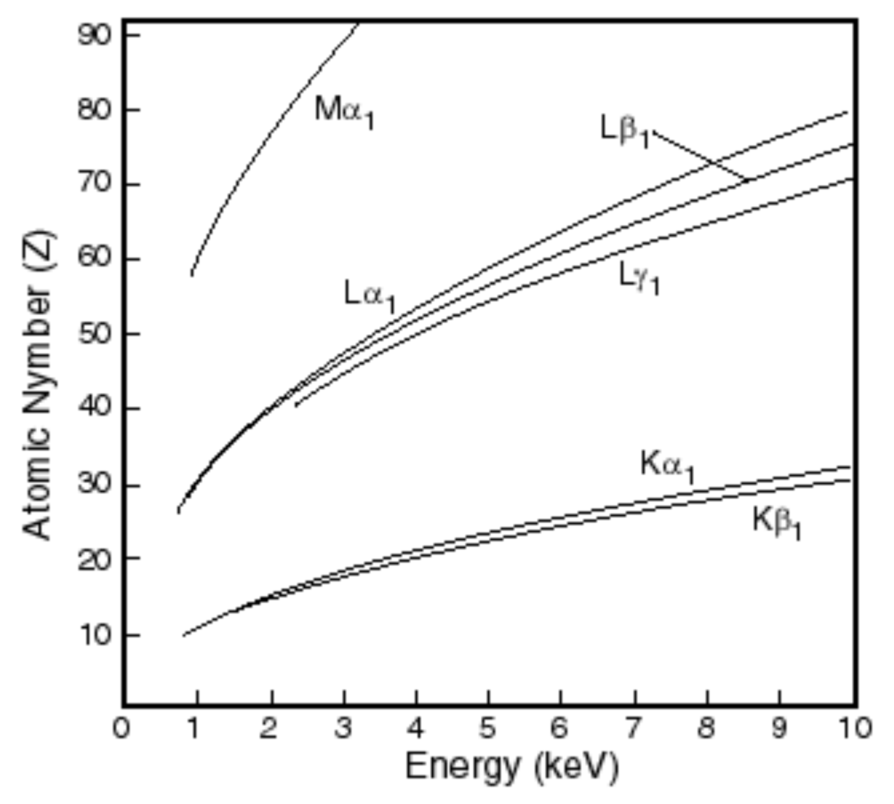
$K_{\alpha 1}$ = 100
$K_{\alpha 2}$ = 50
$K_{\beta 1}$ = 15-30
$K_{\beta 2}$ = 1-10
$K_{\beta 3}$ = 6-15

$L_{\alpha 1}$ = 100
$L_{\alpha 2}$ = 50
$L_{\beta 1}$ = 50
$L_{\beta 2}$ = 20
$L_{\beta 3}$ = 1-6
$L_{\beta 4}$ = 3-5
$L_{\gamma 1}$ = 1-10
$L_{\gamma 3}$ = 0.5-2
L_{η} = 1
L_{ι} = 1-3

$M_{\alpha 1,2}$ = 100
M_{β} = 60



Mosley's Law



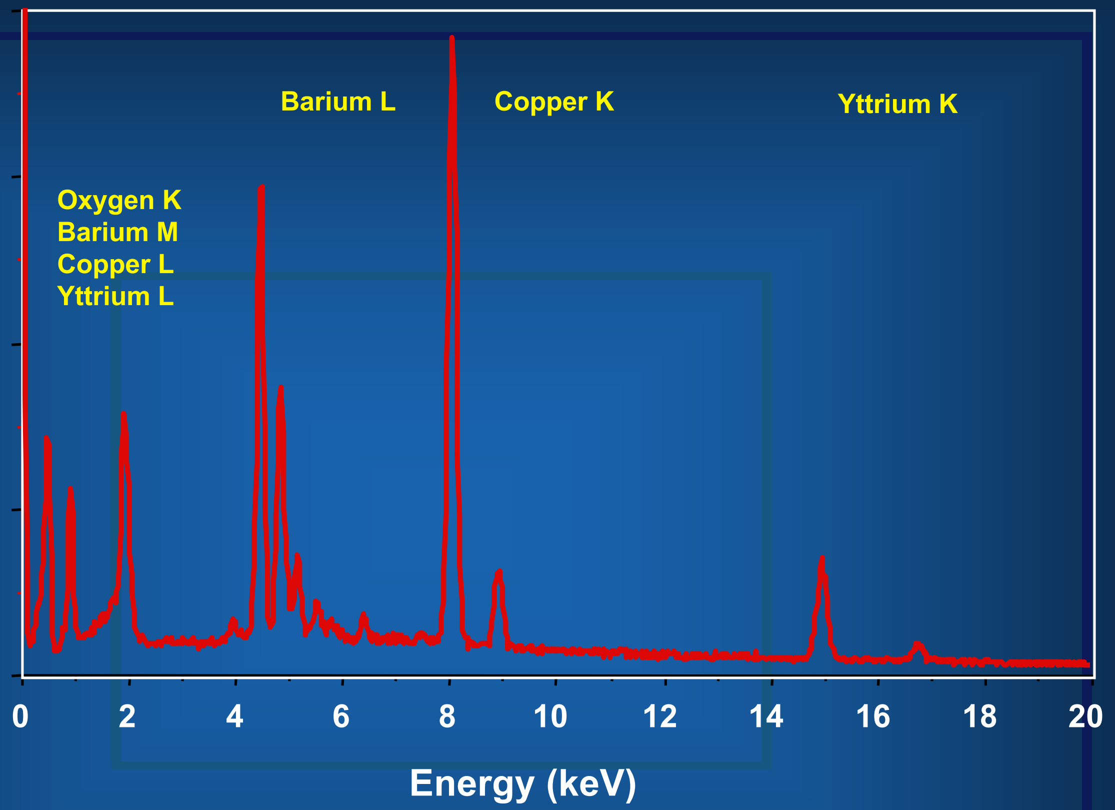
$$\lambda = \frac{K}{(Z - \sigma)^2} \; ,$$

where K and σ are constants for a given spectral line.

$$E\ (\text{kev}) = K\,(Z - 1)^2$$

where Z = atomic number and
$K = 1.042 \times 10^{-2}$ for the K-shell
$K = 1.494 \times 10^{-3}$ for the L-shell
and $K = 3.446 \times 10^{-4}$ for the M-shell.

Characteristic X-Ray Spectrum
Illustrating KLM lines

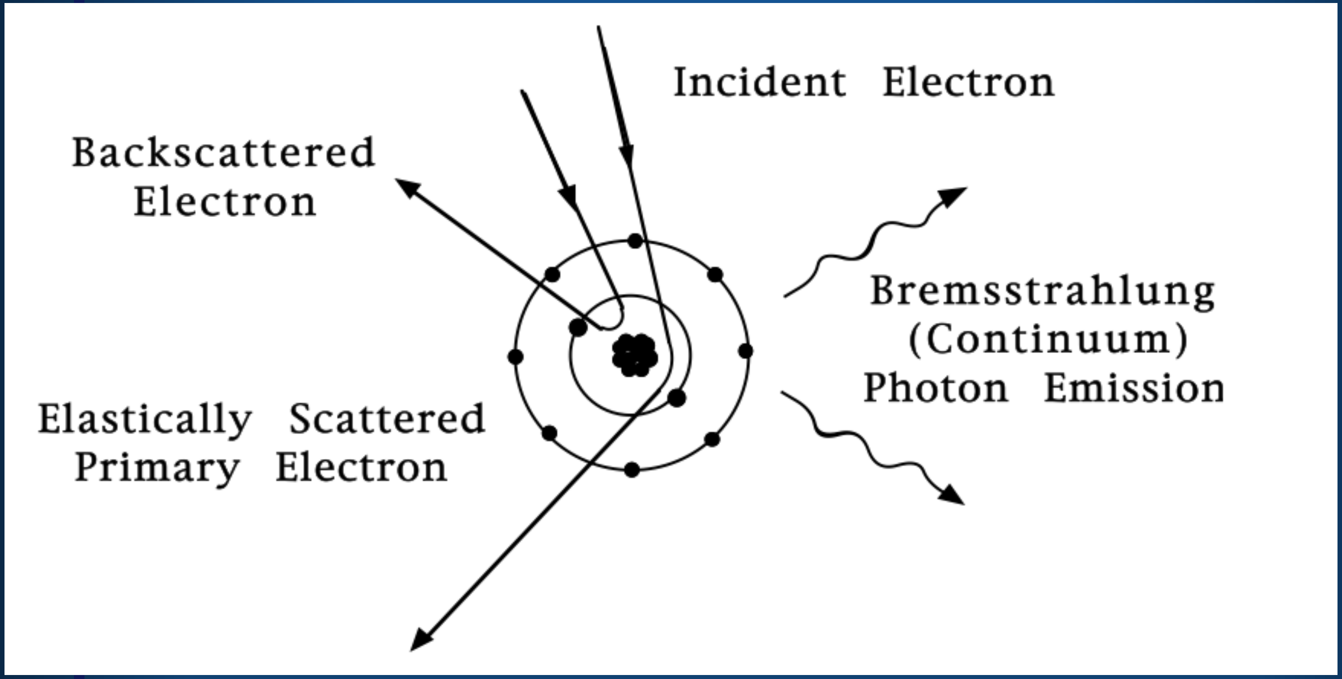


TEM Specimen: $Y_1Ba_2Cu_3O_{6.9}$ Superconductor - 120 kV - UTW Detector

Note:

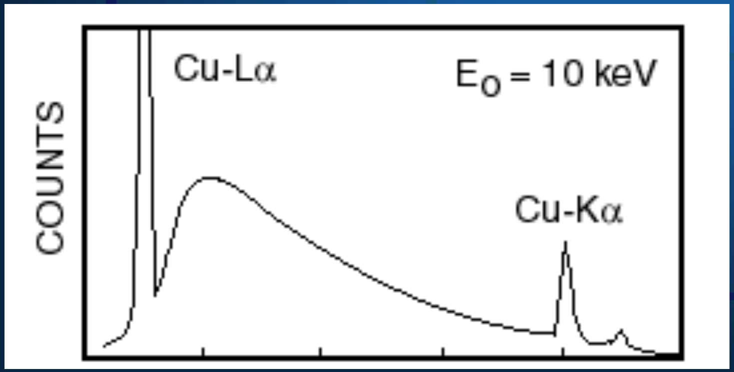
As Z increases the Kth shell line energy increases.
If K-shell is excited then all shells are excited (Y, Cu, Ba)
but may not be detected.
Severe spectral overlap may occur for low energy lines.

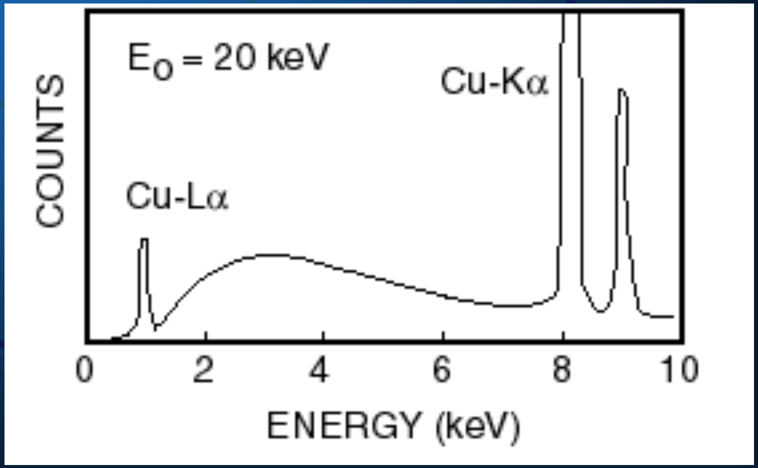
Electron Excitation also generates Continuum (background) signal

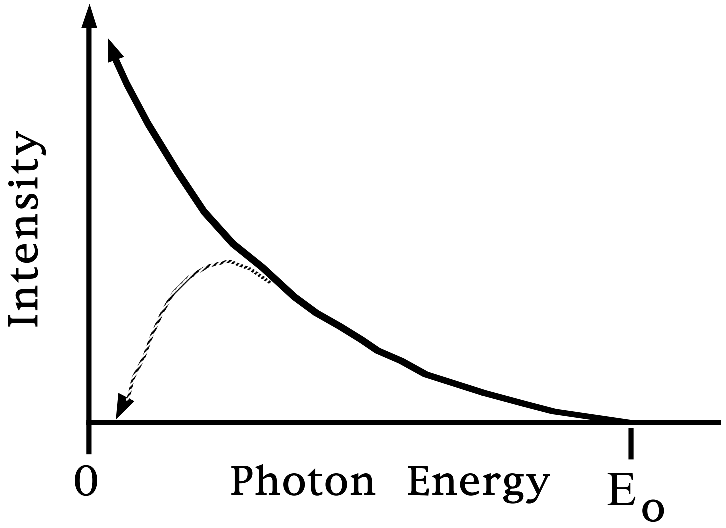


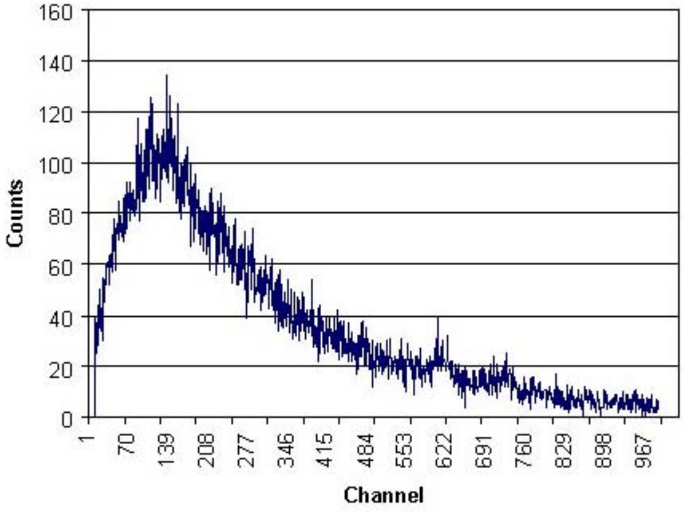
$$I = C\, i_b\, (E_o - E_c)^p,$$

where I = intensity of the line of interest,
C = a constant, i_b = beam current,
E_c = critical excitation potential of the line of interest,
E_o = accelerating voltage (keV),
and $p = 1.7$ for $E_o < 1.7\, E_c$ (and smaller for higher values of E_o).









Energy Range - Continuous Distribution

Maximum = Incident Electron Energy (Least Frequent)
Minimum = E_{plasmon} ~ 15-30 eV (Most Frequent)

Spectral Distribution will reflect this range, modified by detector response function

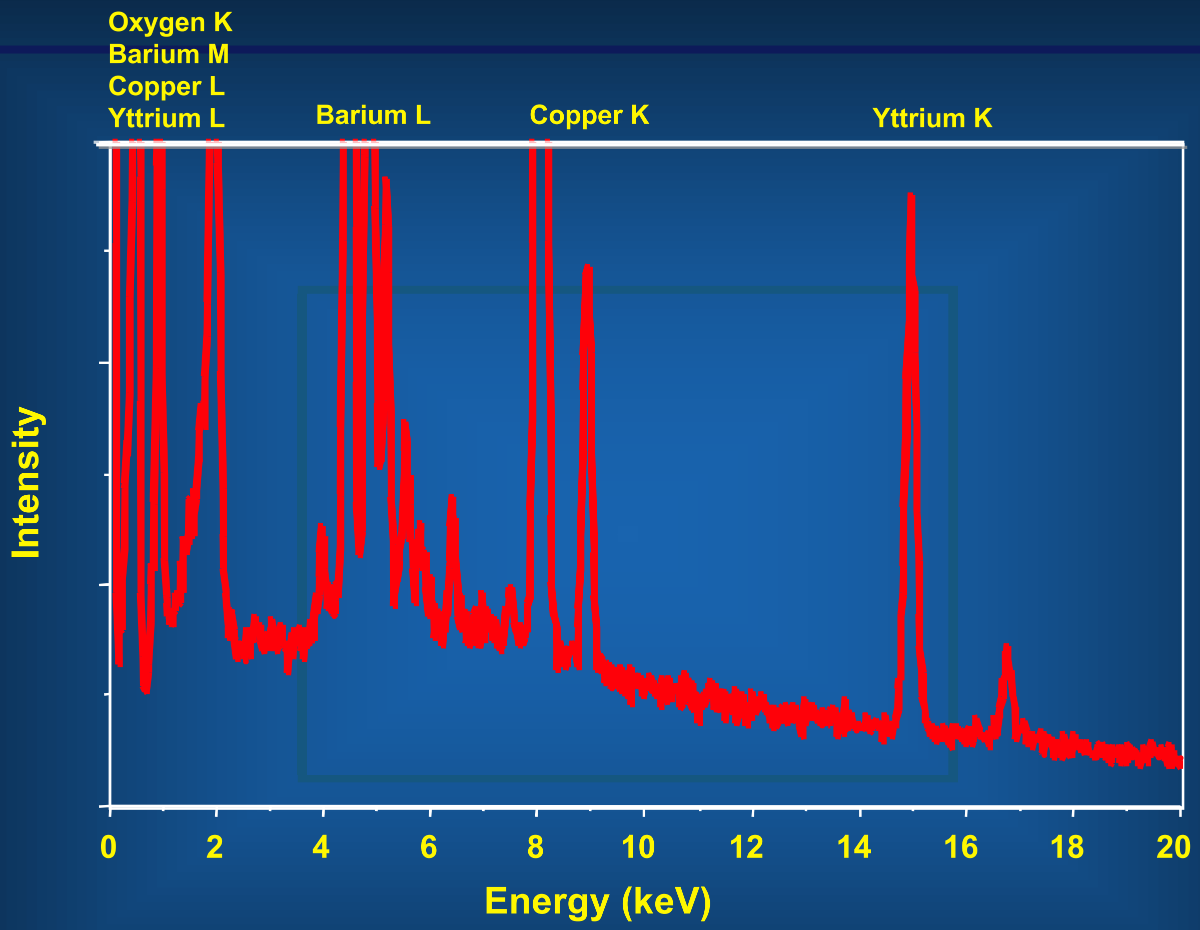
$$\lambda_{swl} = \frac{hc}{E_o},$$

where E_o = acclerating voltage.

$$I_c = i_b\, Z\, \frac{(E_o - E)}{E}$$

where i_b = beam current,
E = energy of interest,
and E_o = accelerating voltage (keV).

Electron Excitation of Continuum (Background) Intensity



Spectral background will be influenced by:

1.) Specimen composition
2.) Detector efficiency
3.) TEM generated artifacts

Instrumentation: Detector Systems

Wavelength Dispersive Spectrometers (WDS)
Energy Dispersive Spectrometers (EDS)
    Si(Li) Detectors
    HPGe Detectors
    Spectral Artifacts of the EDS System
    Detector Efficiency Functions
    Light Element Detectors
Superconducting Calorimeters/Bolometers
Silicon Drift Detectors

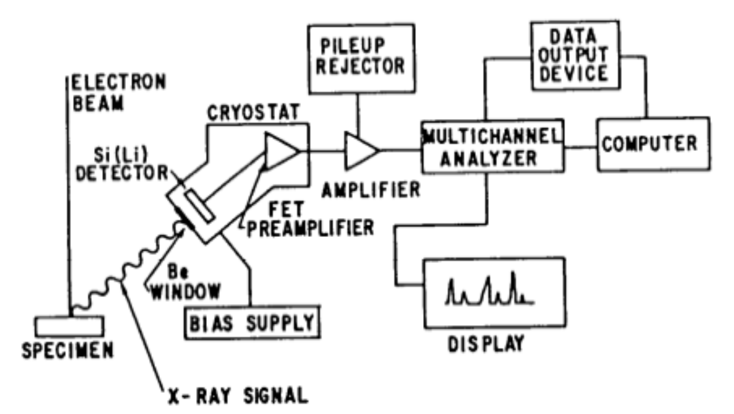
Multichannel Analyzers

Energy Dispersive Spectrometers: (Solid State Detector)

Operates on Energy Deposition Principle

Simple, Nearly Operator Independent
Large Solid Angles (0.05-0.5 sr)
Virtually Specimen Position Independent
No Moving Parts
Parallel Detection
Quantification by Standardless or Standards Methods

Poor Energy Resolution (~ 130 eV)
** SuperConducting Systems (~ 20 eV)
Poor Peak/Background Ratios (100:1)
Detection Efficiency Depends upon X-ray Energy

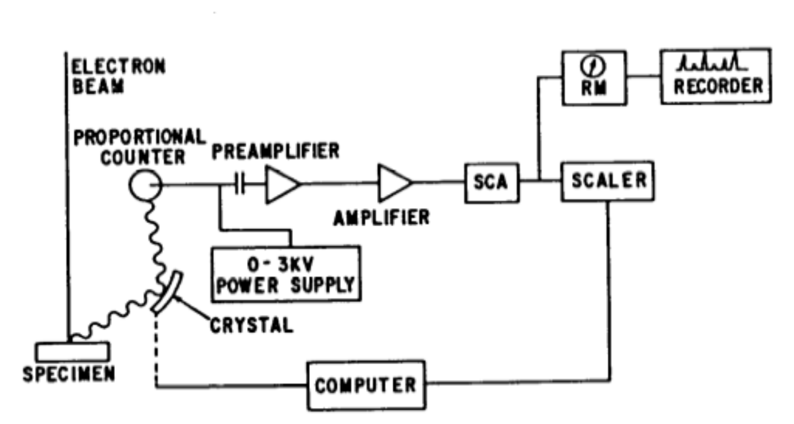


Wavelength Dispersive Spectrometers : (Diffractometer)

Operates using Diffraction Principles (Bragg's Law)

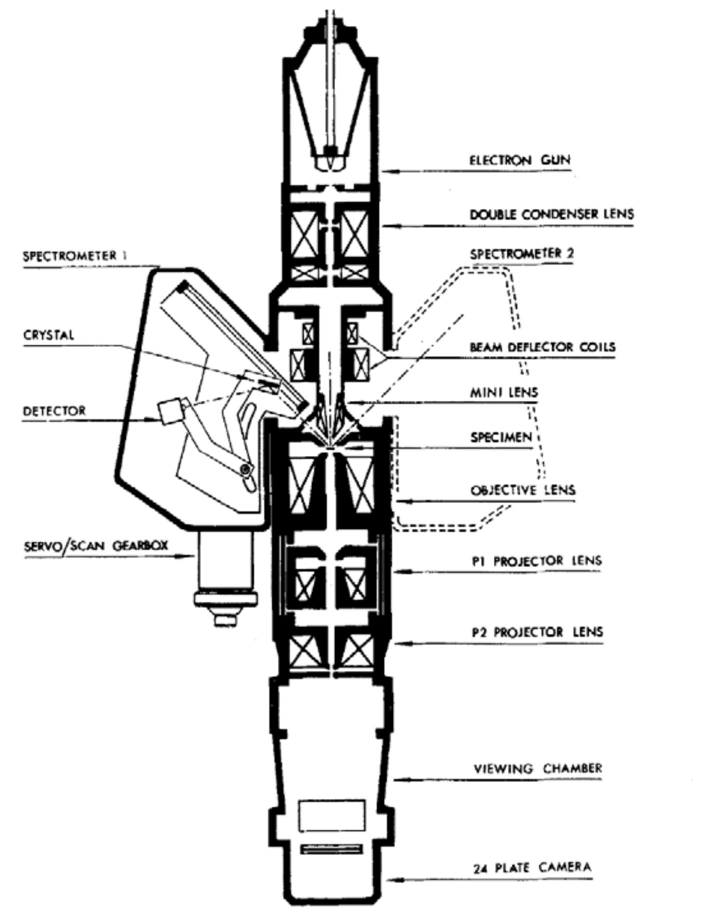
Excellent Energy Resolution (~ 5 eV)
High Peak/Background Ratios (10000:1)
Good Detection Efficiency for All X-rays
High Counting Rates
Good Light Element Capabilities

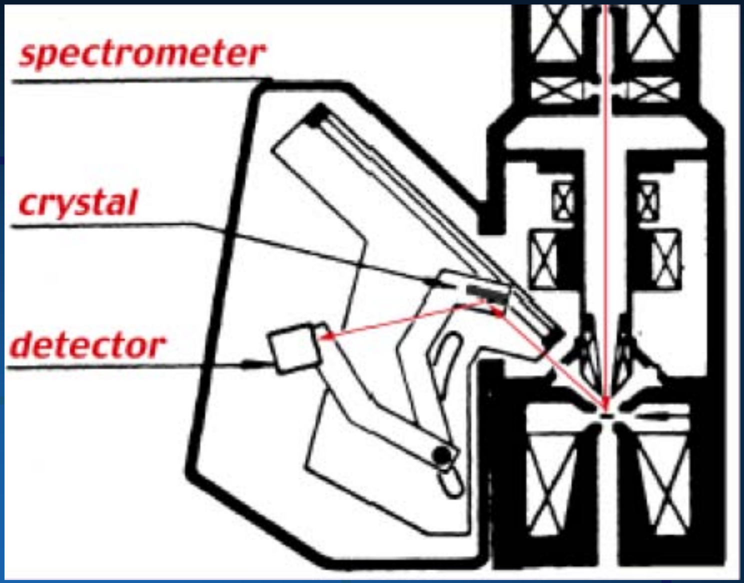
Complex Mechanical Devices, Operator Intensive
Specimen Height dependant focus
Moving Components in the AEM
Limited Solid Angles (<0.01 sr)
Serial Detection
Quantification Requires Standards

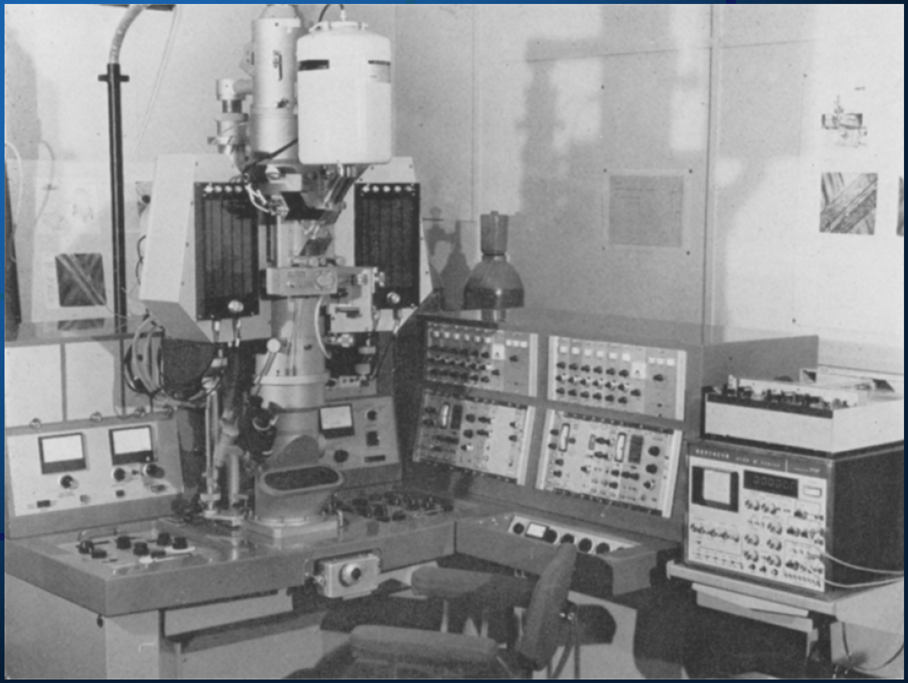



Link
Oxford Instruments
TECNAI

WDS system in a TEM
EMMA-4 System

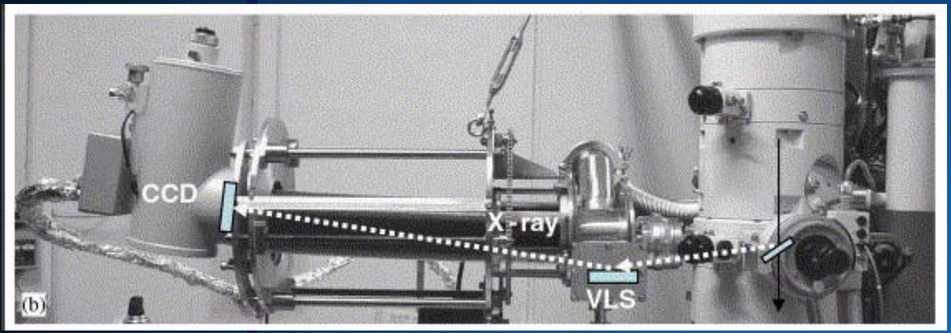


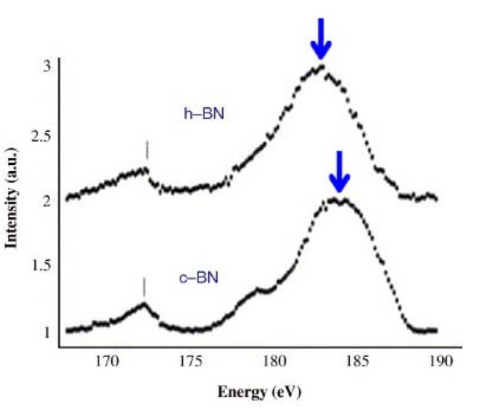


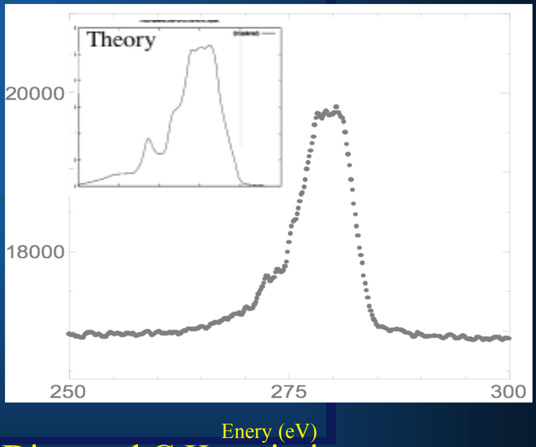


Circa 1972

Modern Applications WDS Valence Band/Electronic Structure Measurements







Diamond C K-emission spectrum

M. Terauchi , M. Kawana – Tohoku University

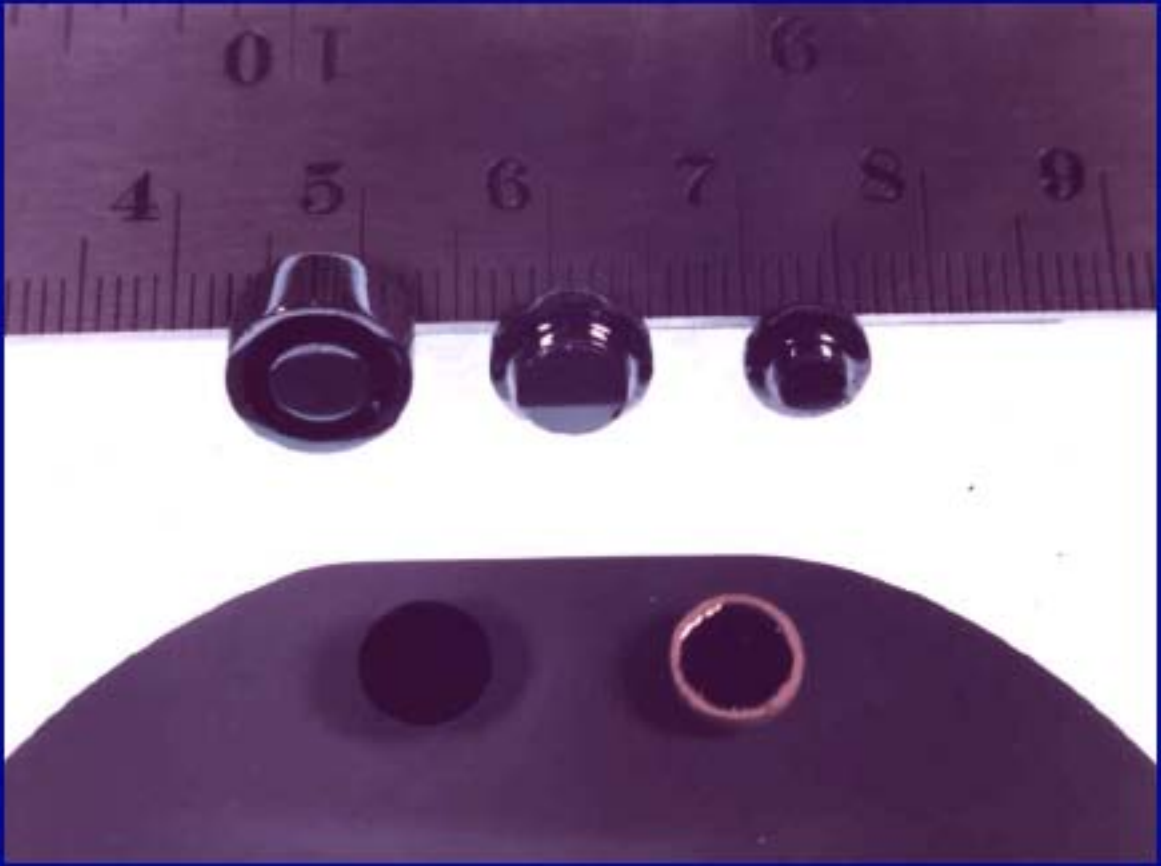
Y. Ito NIU Physics

Comparison of EDS and WDS Spectrometers

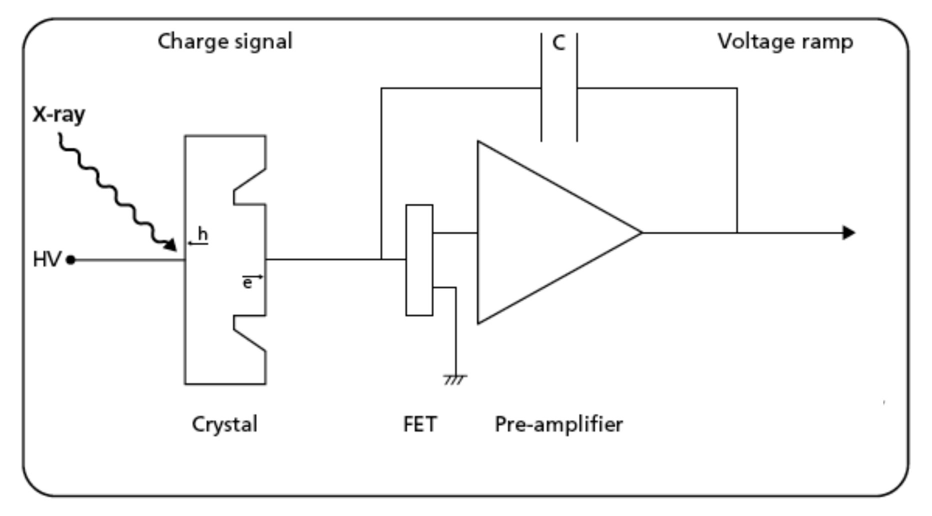
Parameter	Wavelength Dispersive	Energy Dispersive
Construction	Mechanical Device moving components	Solid State no moving parts
Energy Resolution	5 eV	130 eV
Efficiency	$\leq$ 30 %	100 % (3-15keV)
Input Count Rate	30-50 K cps	10 K cps
Peak/Background*	10000	100
Atomic Number Range	$Z \geq 4$ (Be)	$Z \geq 11$ (Na) $Z \geq 5$ (B)
Number of Elements	1 per Detector	All in Energy Range
Solid Angle	0.001-0.01 sr	0.02-0.3 sr
Collection Time	Tens of Minutes	Minutes
Beam Current	High Stability Required	Low Stability Required
Detector Stability	Good Short Term	Excellent
Spectral Artifacts	Neglegible	Important
Operation	Skilled (?)	Novice

* Values depend on definition, specimen, and operating conditions

Fabrication of Si(Li) Crystals



How is the X-ray Signal Measured?



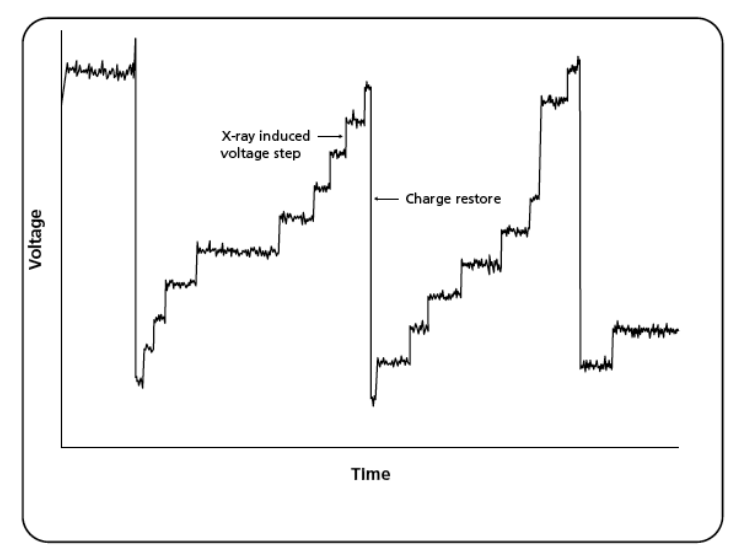
Properties of Intrinsic Silicon

.

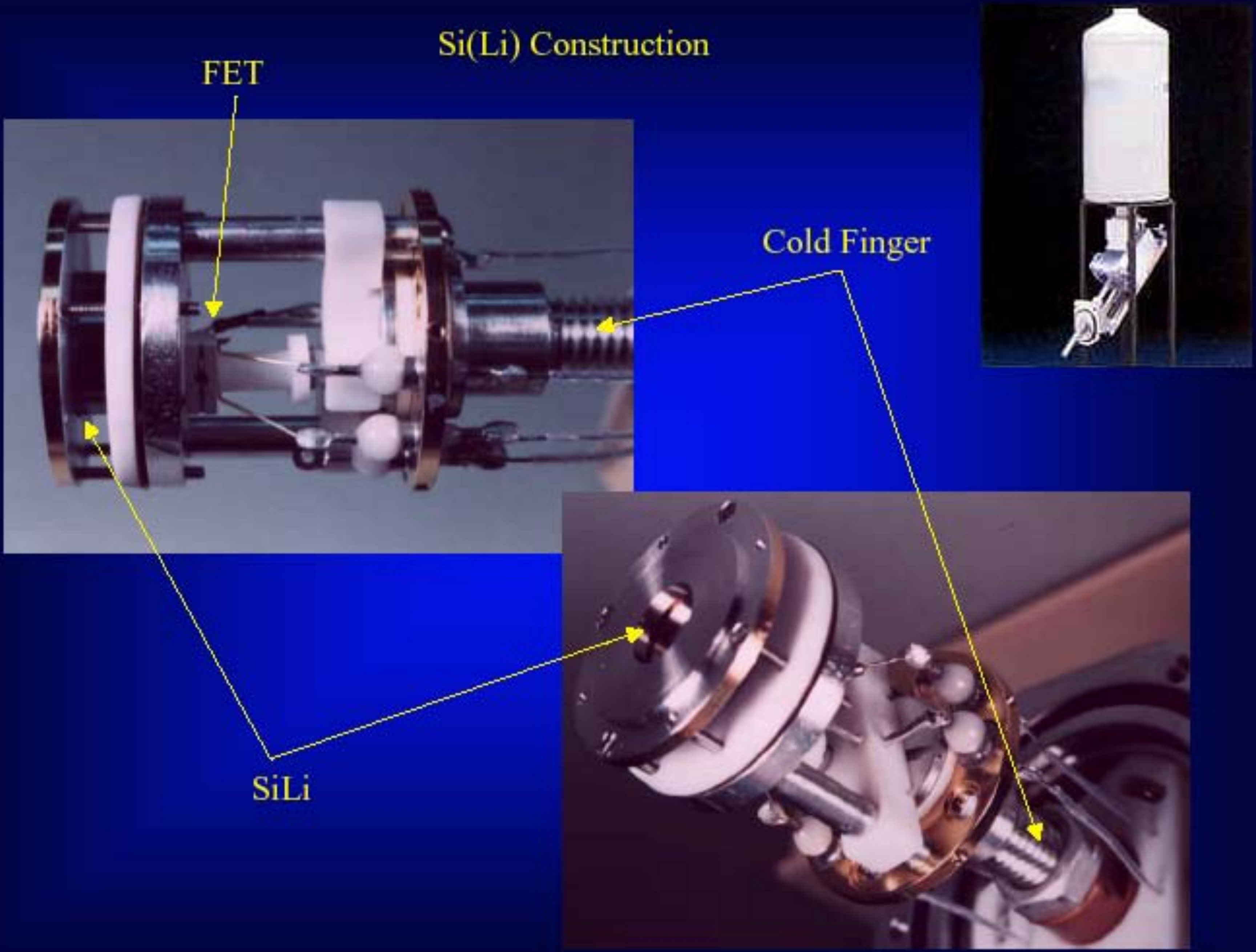
Attaching HV electrodes to the two surfaces the Si(Li) crystal will act similiar to a capacitor with free charges developing on the electrical contacts.

Charge developed in the crystal is N = E/ε. (E= x-ray Energy, ε = 3.8 eV/e-h pair)

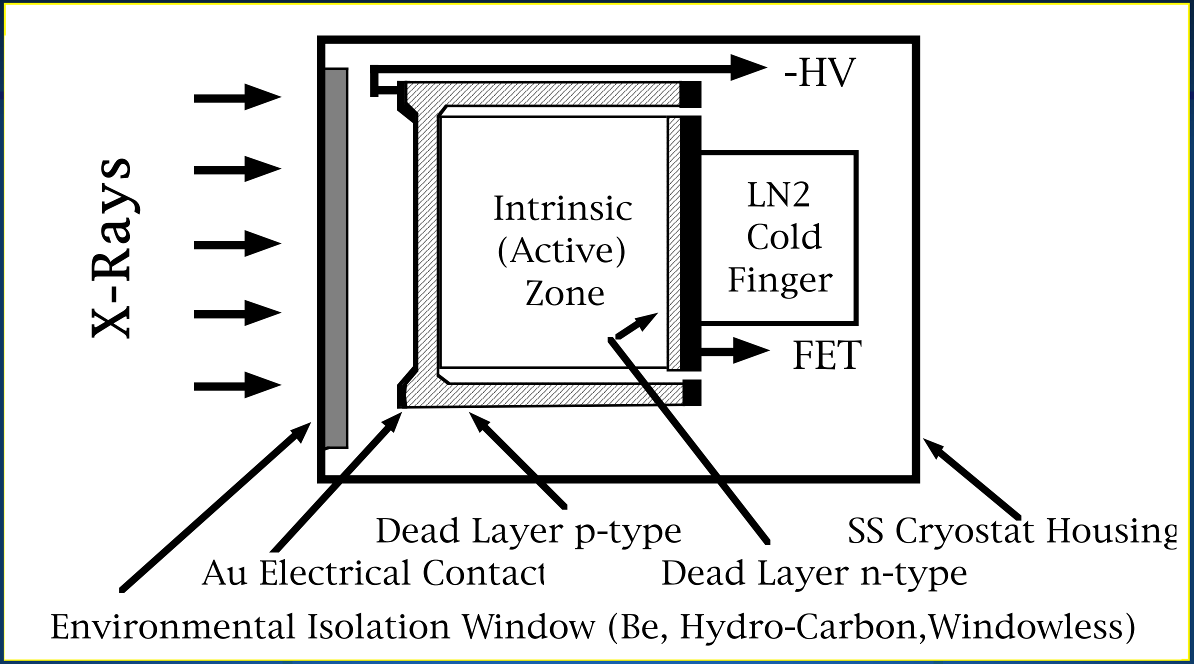
==> 10 kV X-ray produces ~2630 electrons = 4.2 x 10 -16 Coulombs.



Si(Li) Construction



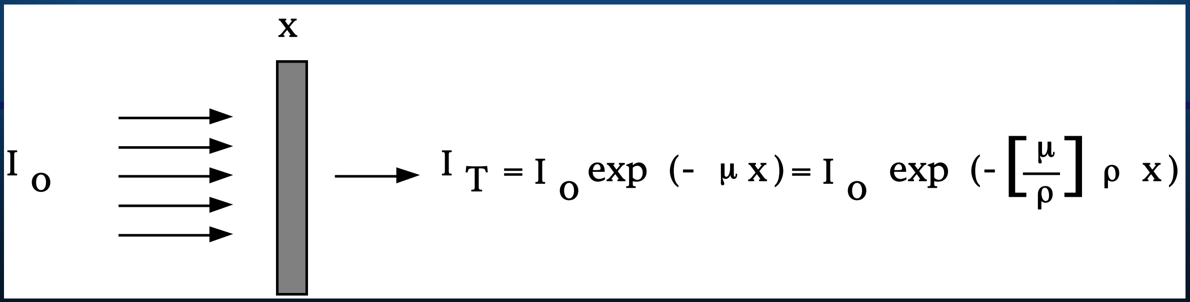
Solid State Detector Construction



Relative Detection Efficiency

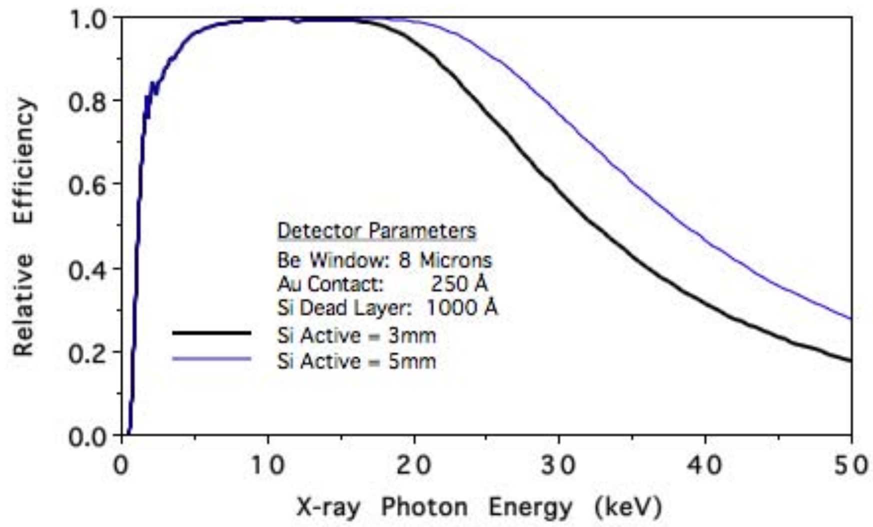
Solid State Detectors: Si(Li) or Instrinsic (High Purity) Ge

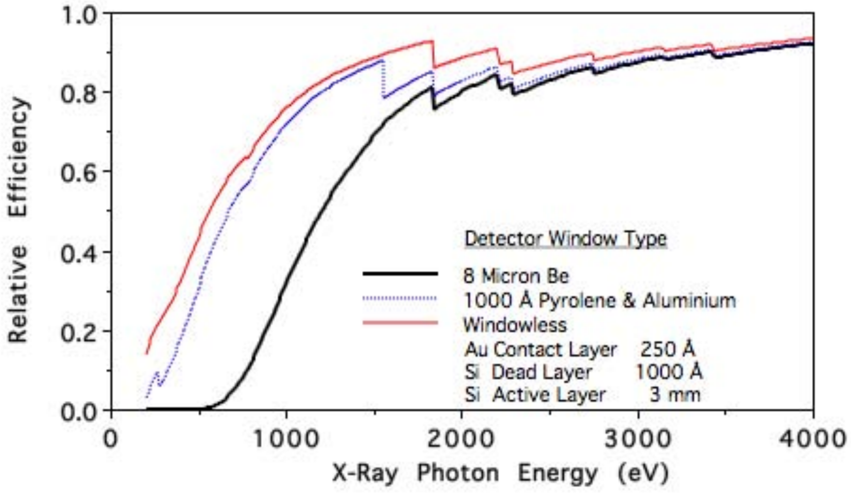
Using a simple absorption model define the relative detector efficiency ε(E) by the following procedure:



$$I_T = I_o \exp(-\mu x) = I_o \exp\left(-\left[\frac{\mu}{\rho}\right]\rho x\right)$$

Calculated Si(Li) Detector Efficiency by Active Layer Thickness & Window Type



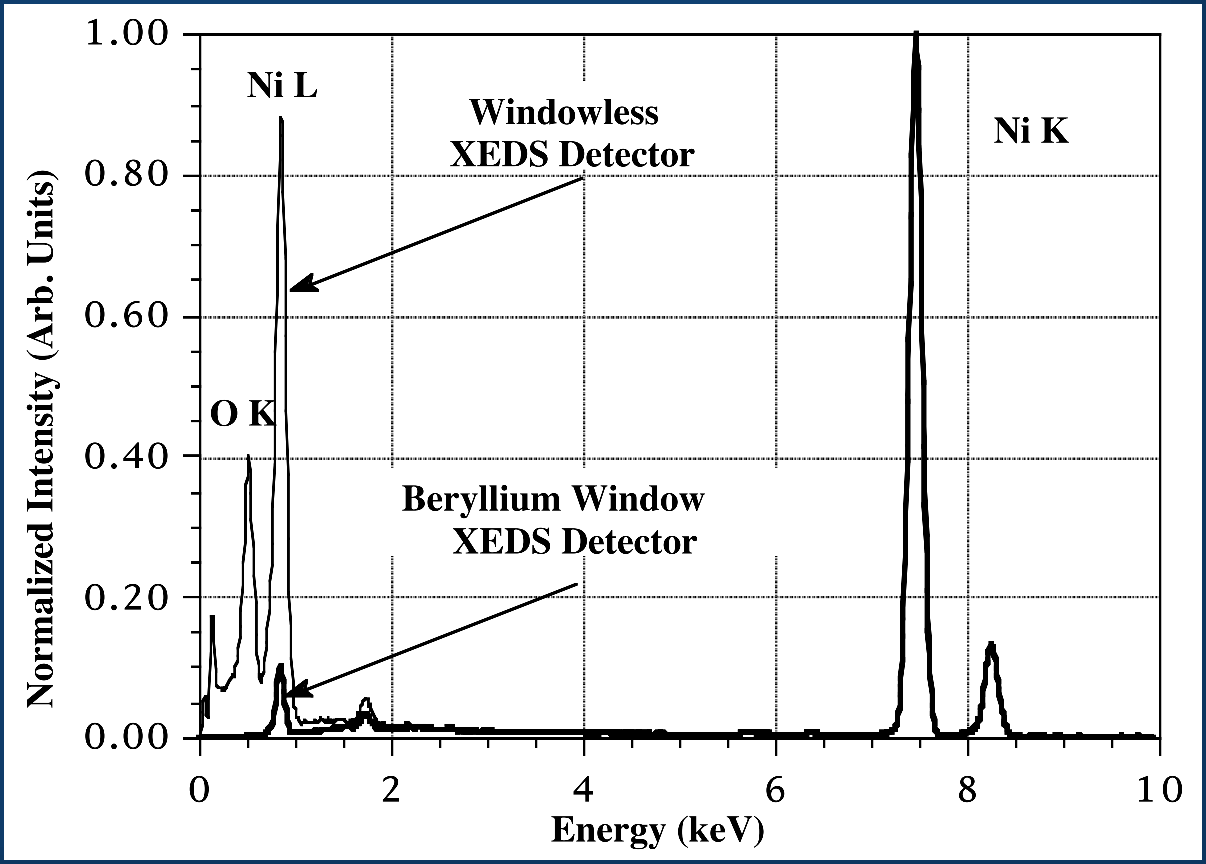


$$\varepsilon(E) = \frac{I_A * I_T}{I_o} = \exp\left(\sum_{i}^{HC/Be/Au/DL} -\left(\frac{\mu(E)}{\rho}\right)_i * \rho_i * t_i\right) * \left\{1-\exp\left(-\left(\frac{\mu(E)}{\rho}\right)_j * \rho_j * t_j\right)\right\}$$

<--Absorption--> <-- Transmission-->

$\frac{\mu(E)}{\rho}$ = mass absorption coefficient for Energy E; ρ = density; t = layer thickness

Windowless vs. Conventional Detectors
Comparision of XEDS measurement on NiO using a Windowless versus Beryllium Window detector



Note the enhanced detection efficiency below 1 keV for the WL detector. Both spectra are normalized to unity at the Ni Kα Line (7.48 keV)

Windowless vs. Conventional Detectors

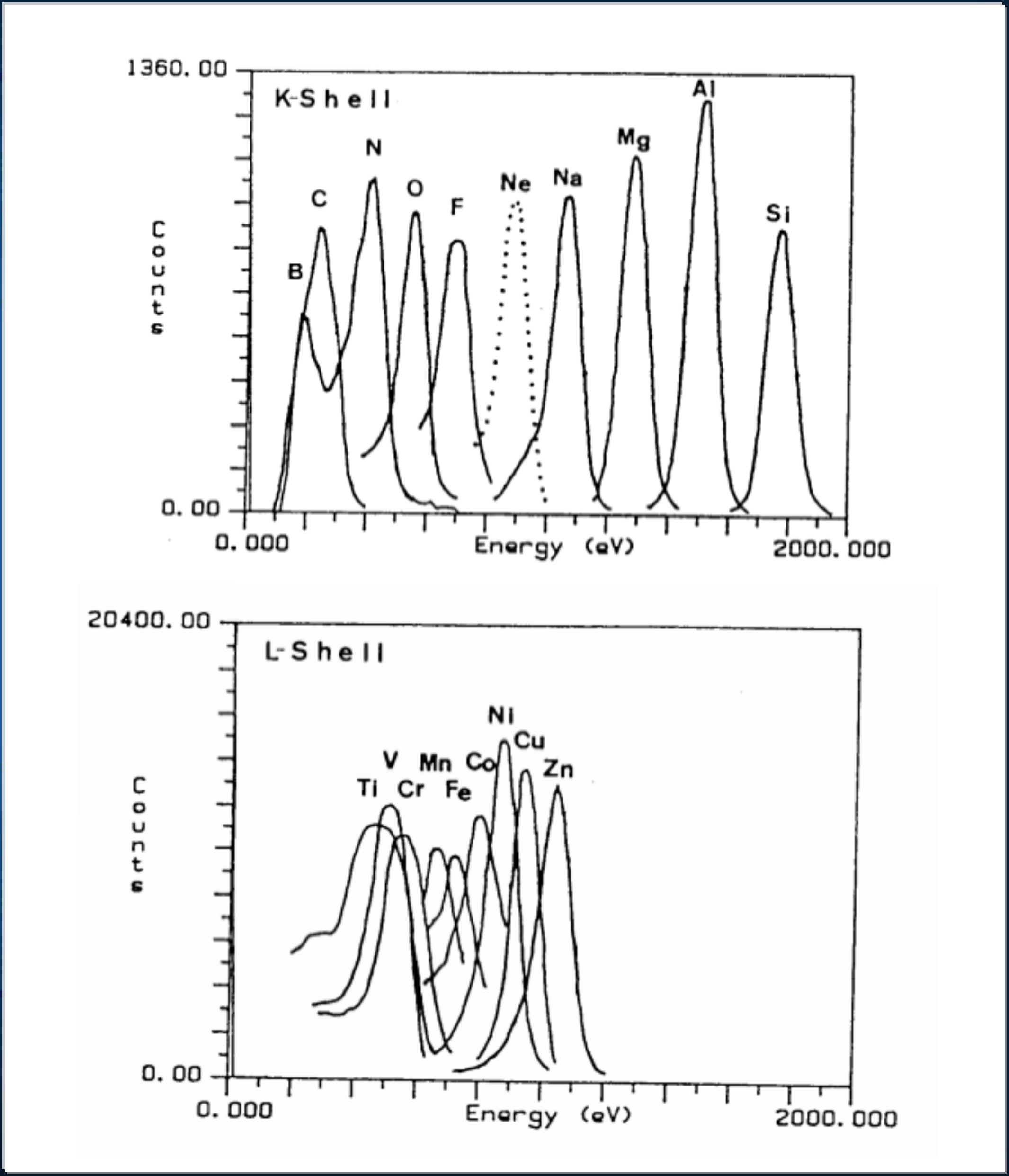
K Shell Spectra using Windowless Detector

Boron -> Silicon

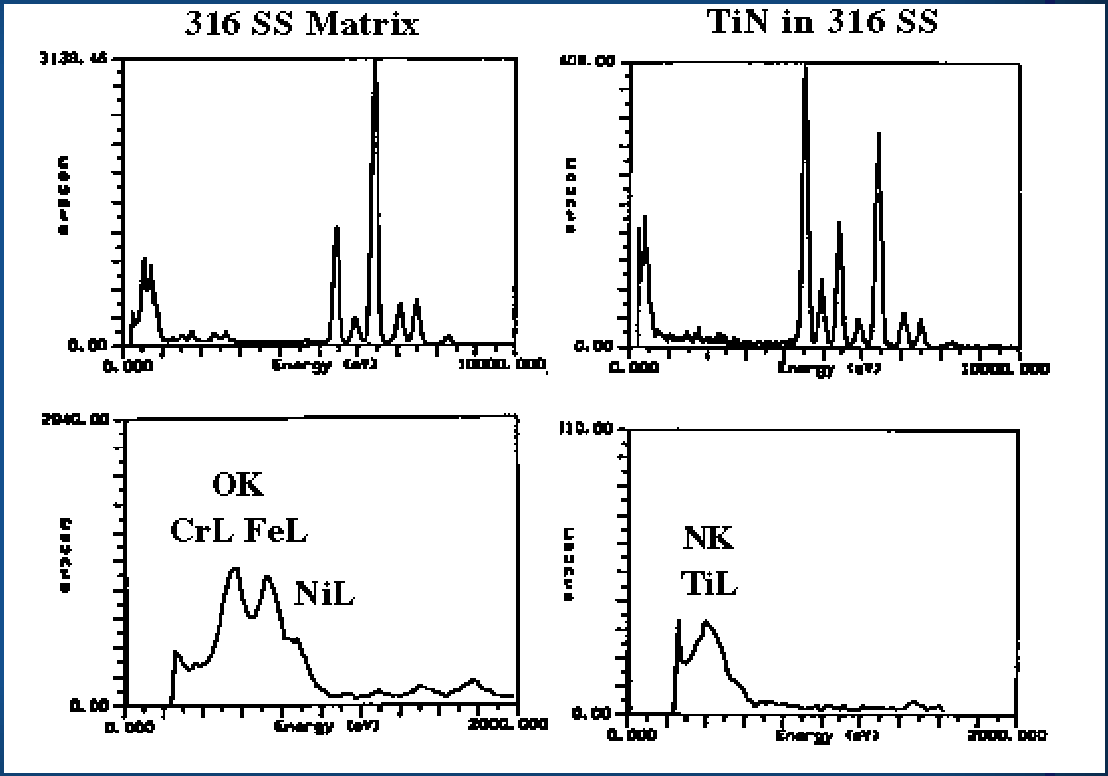
L Shell Spectra Using Windowless Detector

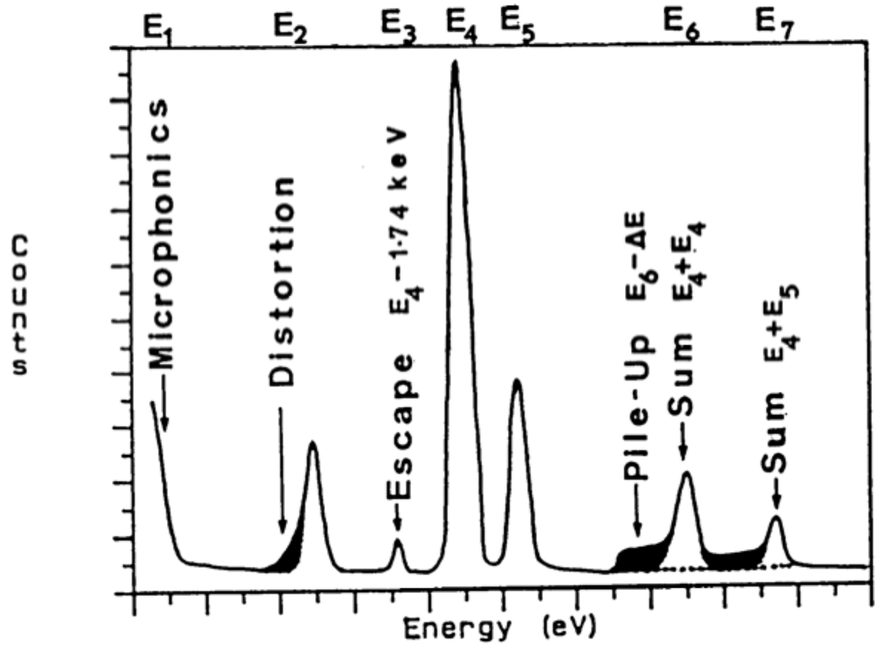
Titanium ->Zinc

Note Potential Overlaps with K shell Lines



Comparision
Light Element
Spectroscopy
Resolution
XEDS





$$\text{Resolution} = \text{FWHM} = \sqrt{\text{Noise}^2 + 2.35^2 \varepsilon F E}$$

ε= 3.8 eV (in Si) / 2.9 eV (in Ge)

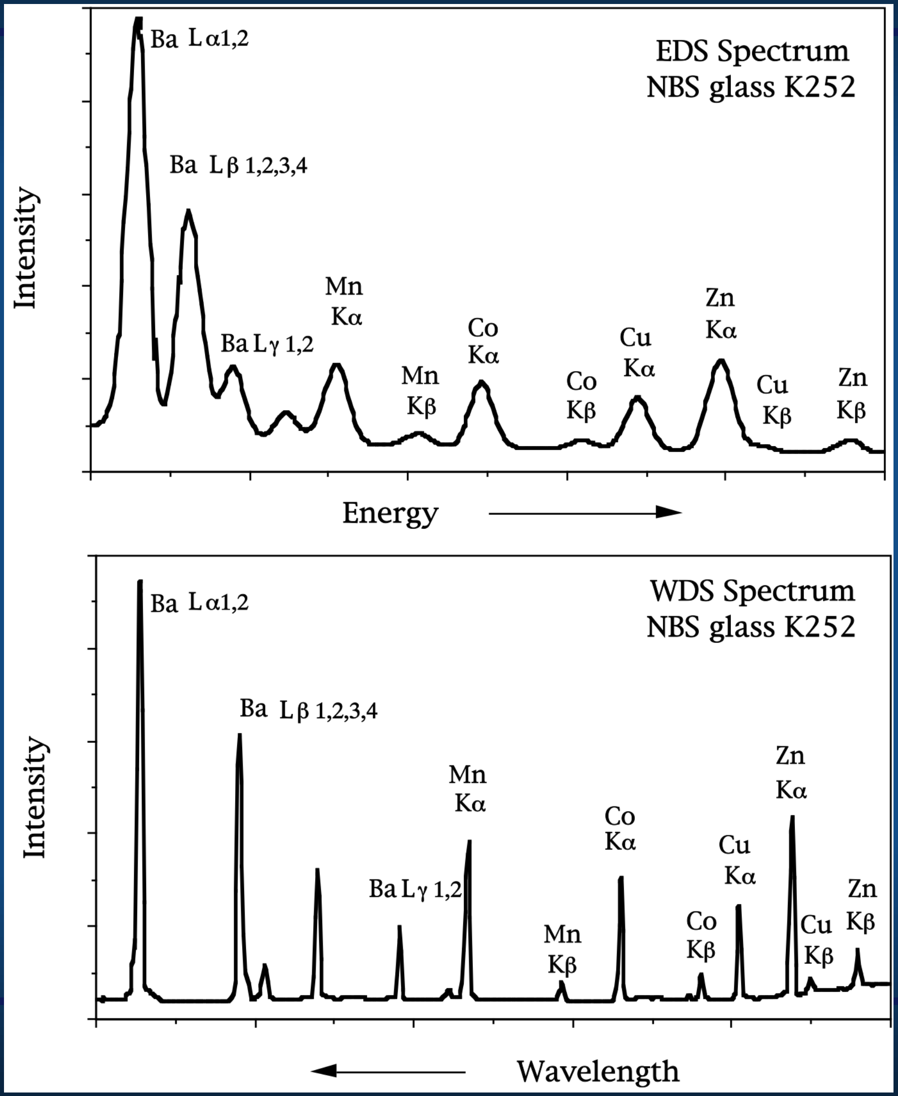
-> But the electrons produced are in a Poissson Distribution this gives rise to a spread in the number of electron

F = Fano Factor ~ 0.1
E= X-ray Energy
Noise = Electronic Noise (mainly in the FET)

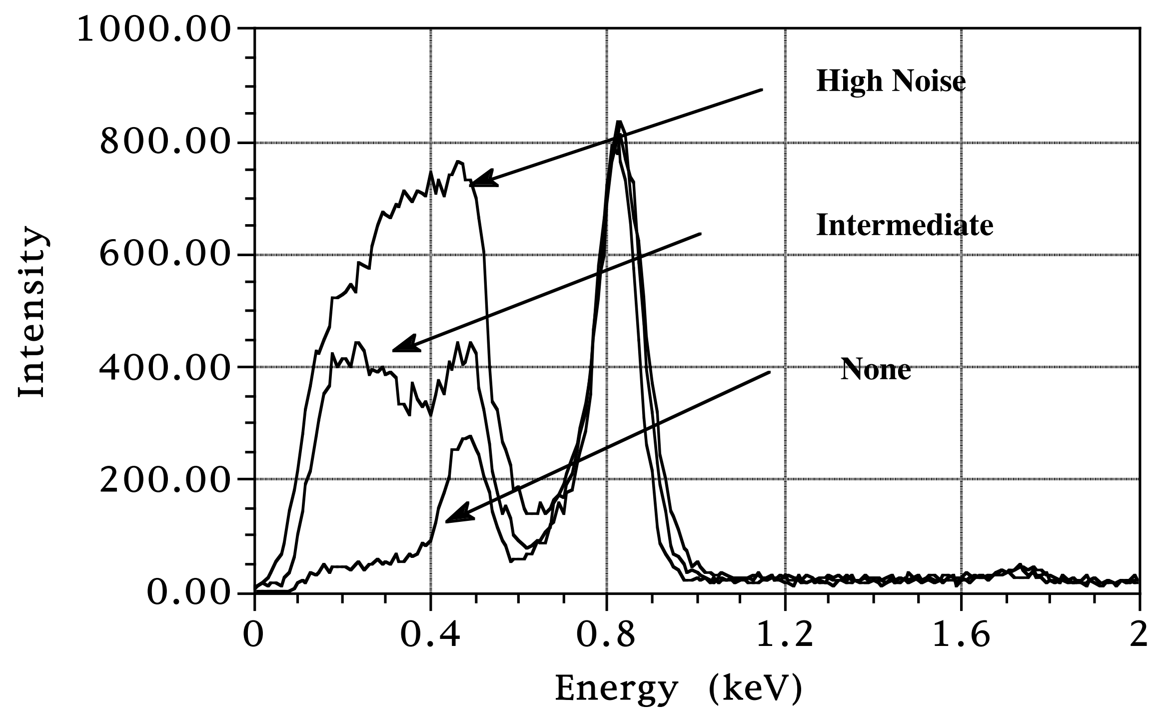
Nominal FWHM Values in Modern Si(Li) Detectors:

O Kα (0.52 keV) = 80 to 100 eV
Mn Kα (5.9 keV) = 140 to 160 eV
Mo Kα (17.5 keV) = 210 to 230 eV

Comparison of EDS and WDS Spectra

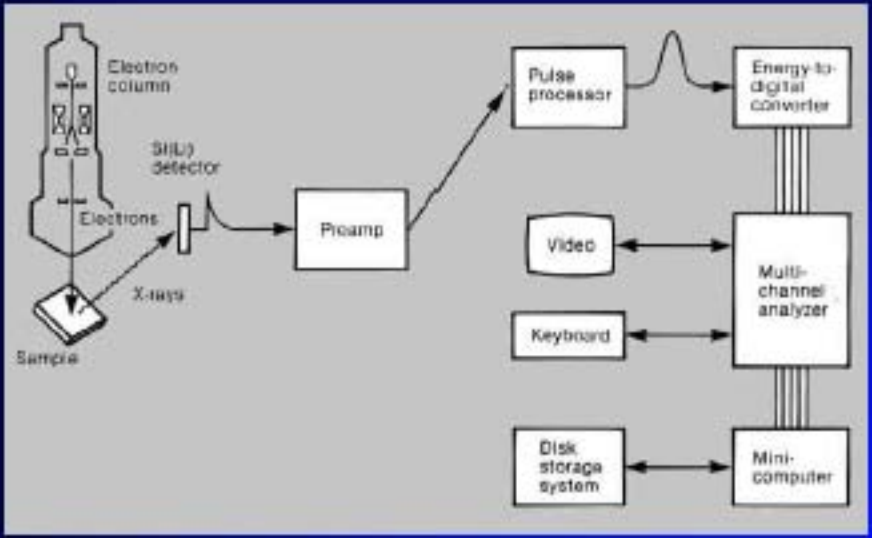


Resolution will also vary with Microphonic & Electronic Noise, and Counting Rate!

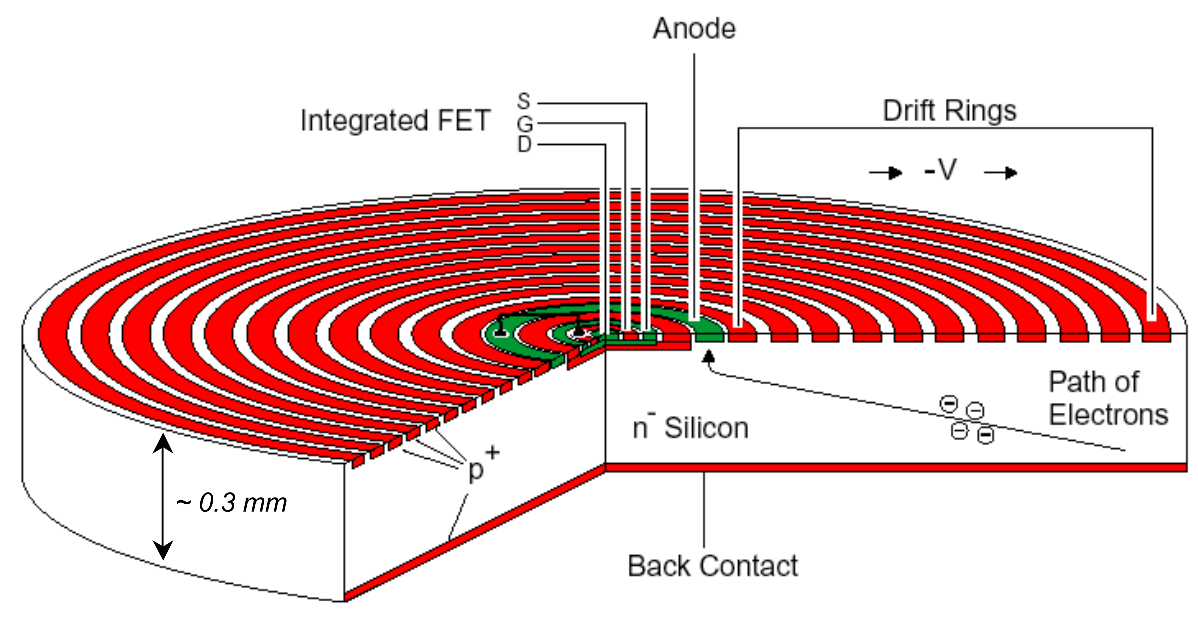


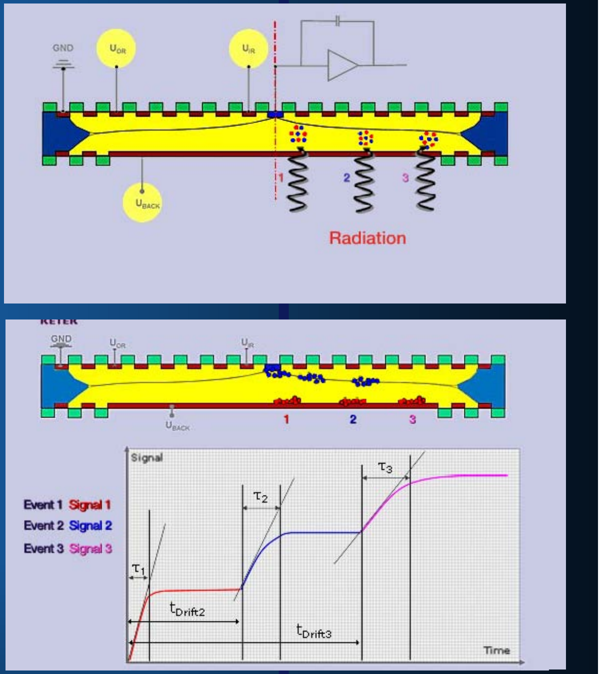
WL & UTW detectors are particuliarly sensitive to low energy noise and microphonics. Observe the changes in the spectra (width of the peaks)

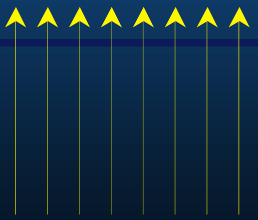
The Multi-Channel Analyzer



Silicon Drift Detector

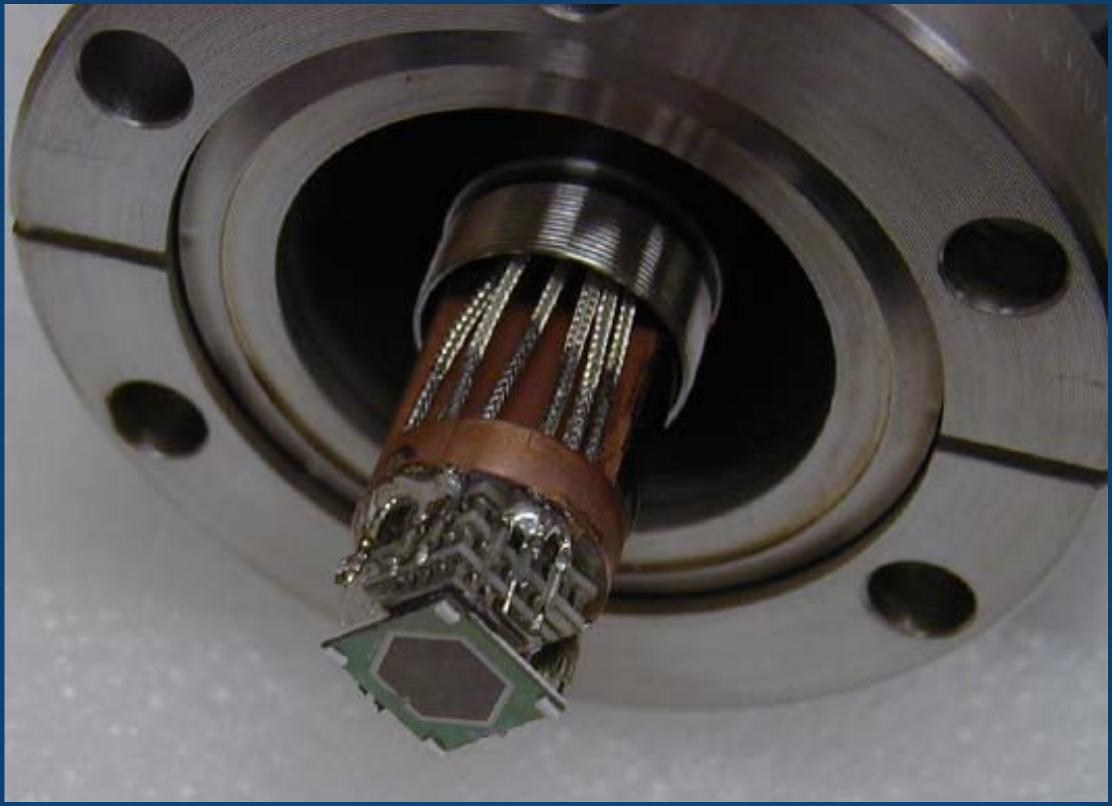






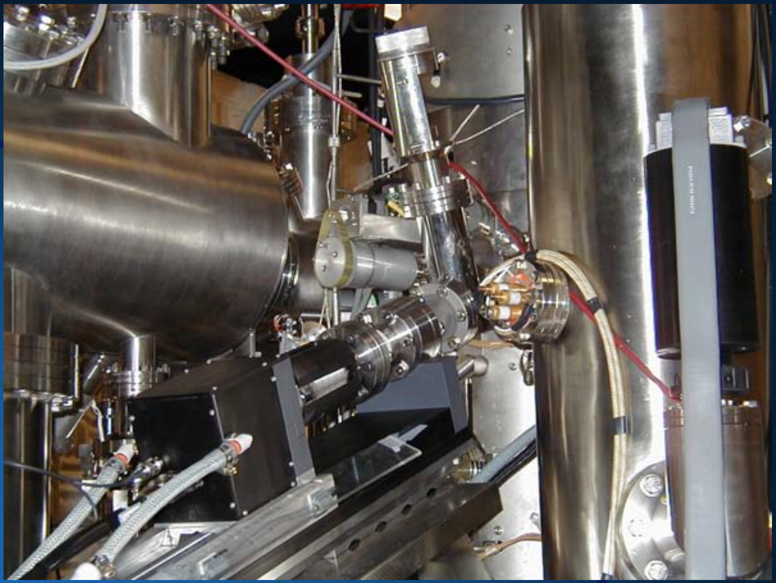
Both sides are reversed biased
Electrons travel along the central potential well
Radial drift gradiant sweeps electrons to the Anode

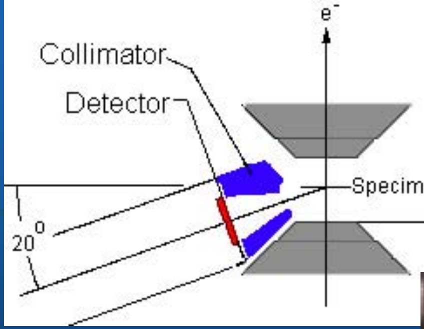
Silicon Drift Detector Construction



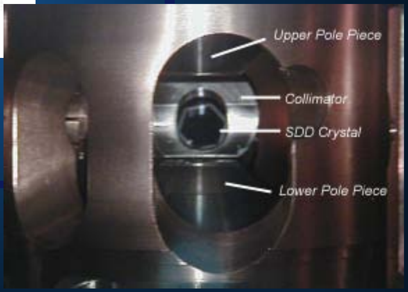
Detector Area = 50 mm^2
Peltier Cooled -> No LN$_2$
Low Capacitance (250 fF)

Silicon Drift Detector Construction

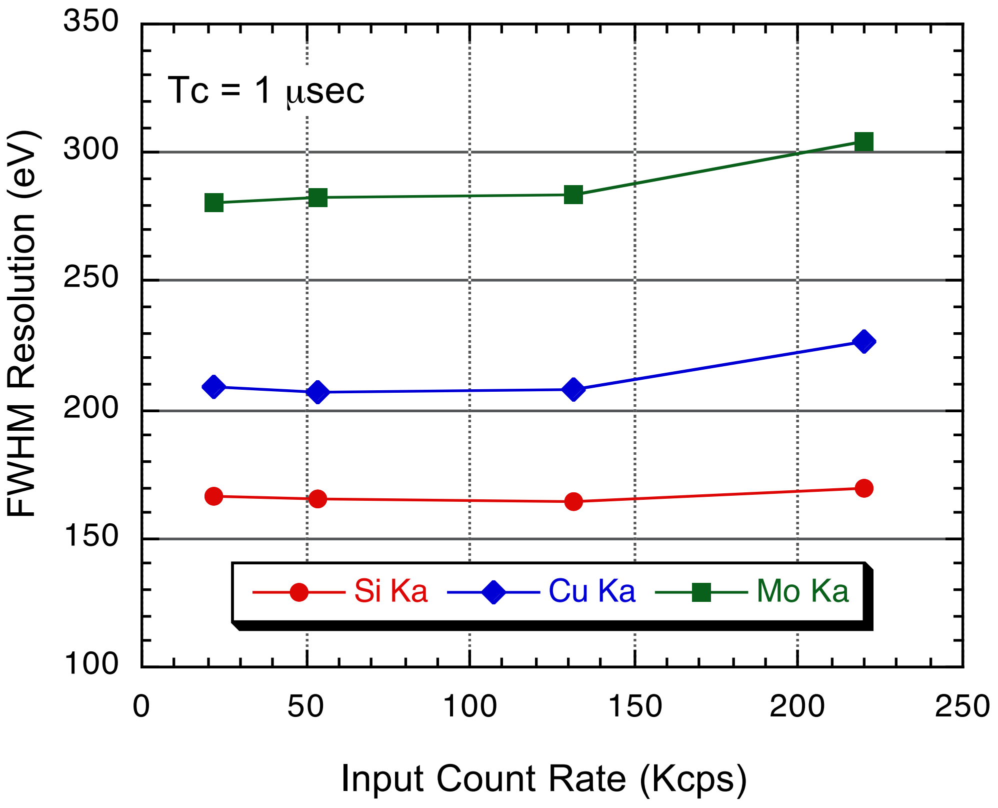




$\Omega_{\mathrm{ANL}} \sim 0.41$ sr



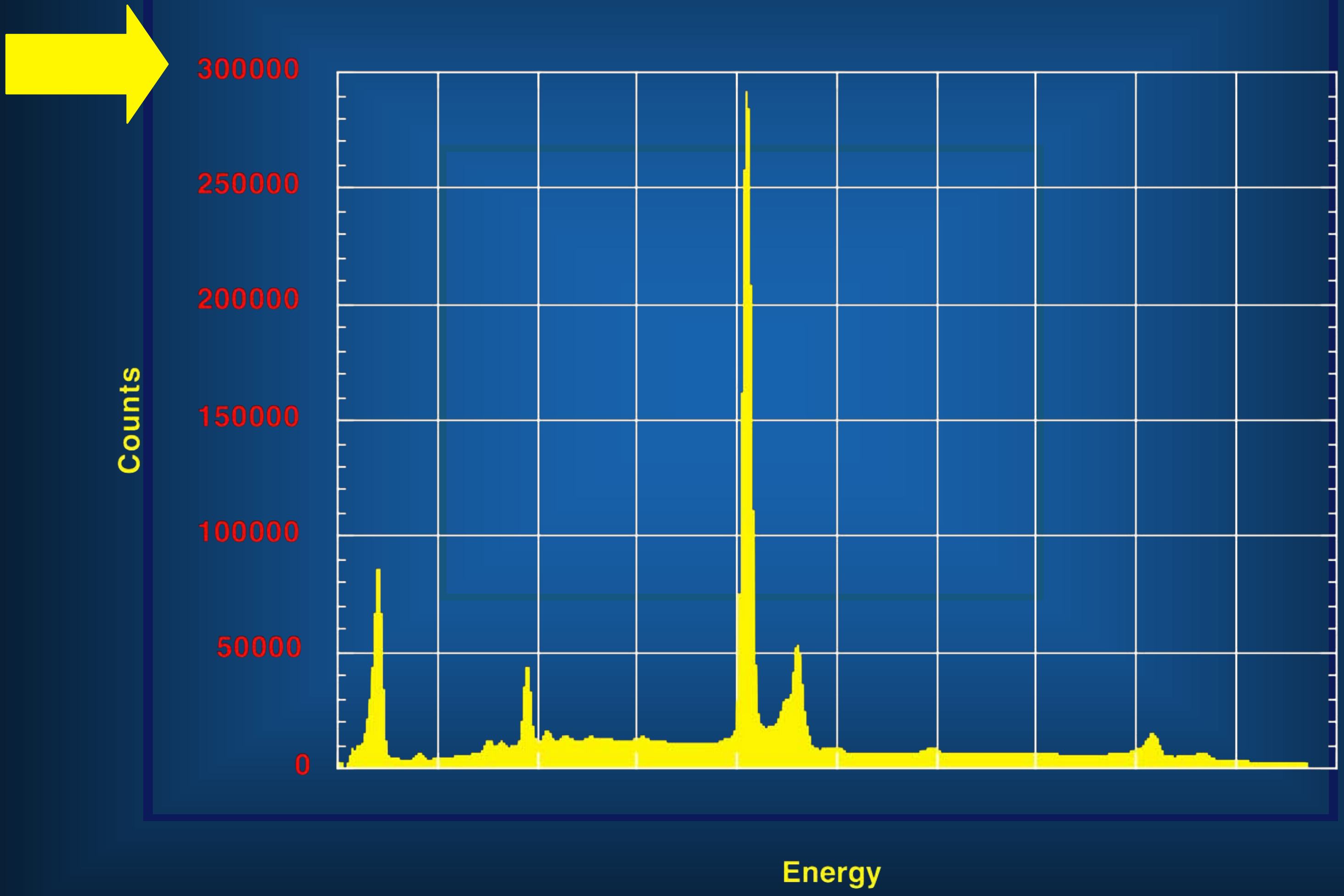
Resolution vs Count Rate



Count Rate = ~ 200 Kcps

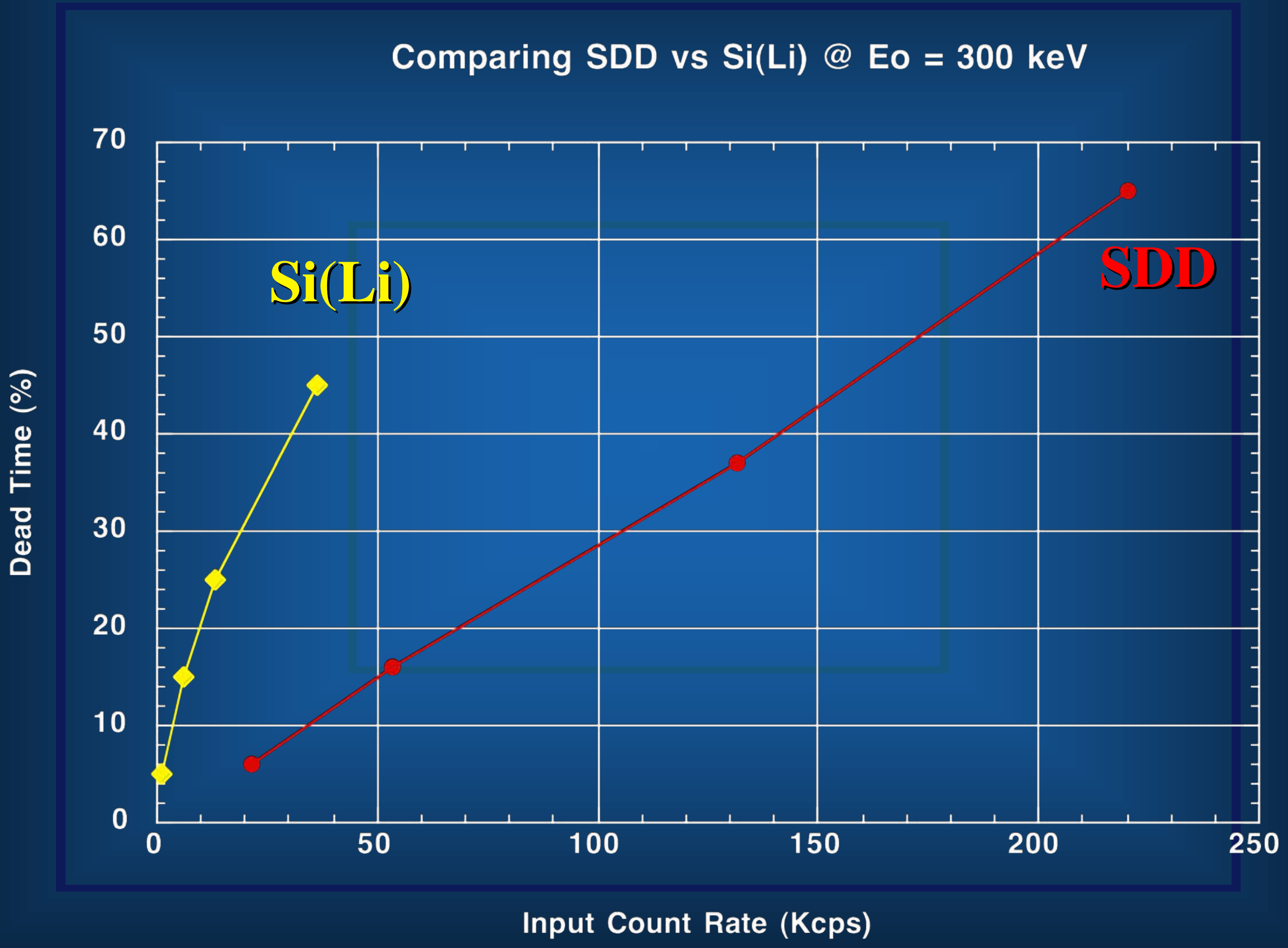
Time = 100 sec

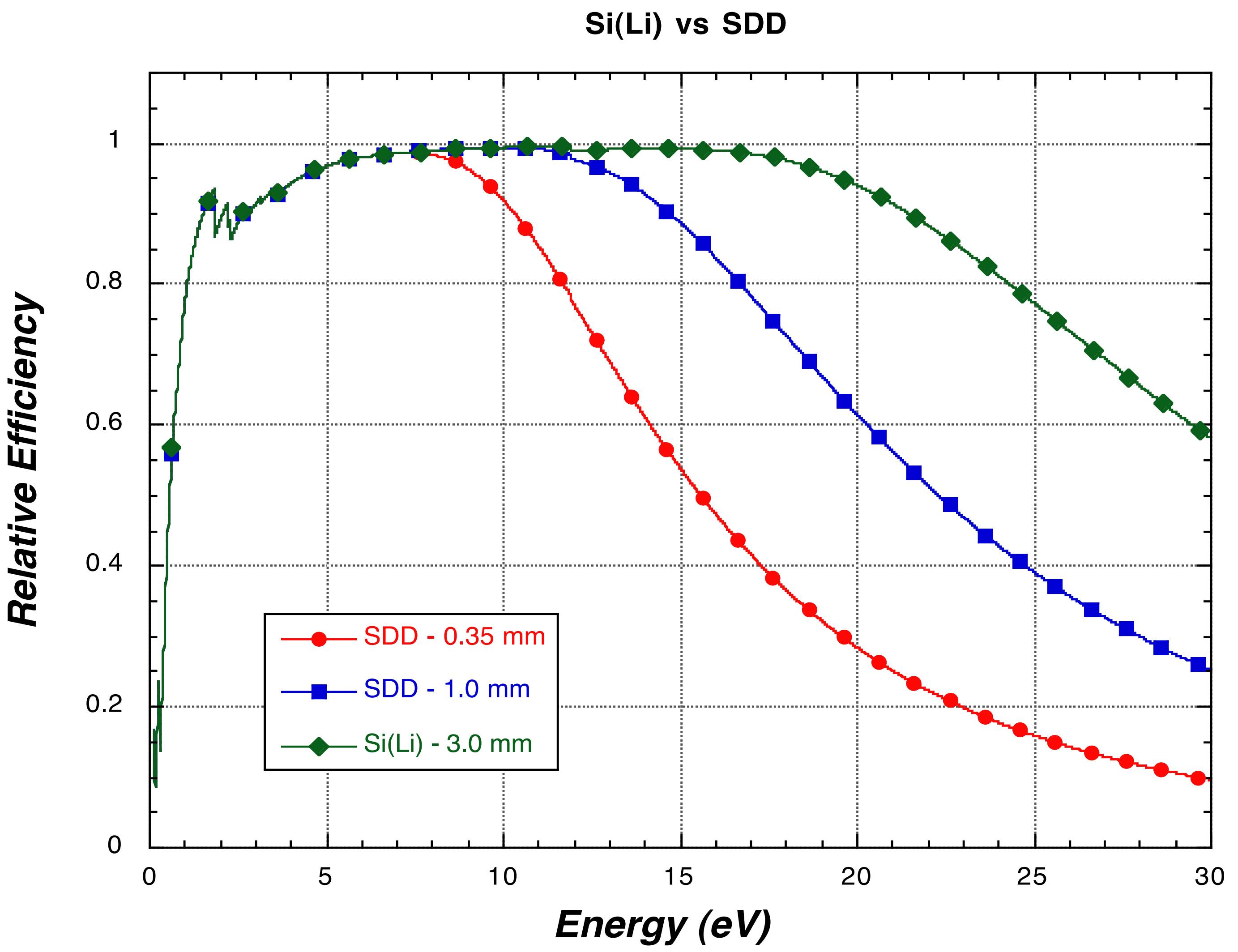
Integral = 20, 000, 000 counts !



Mo-Si/Cu Slot Grid

Dead Time vs Count Rate



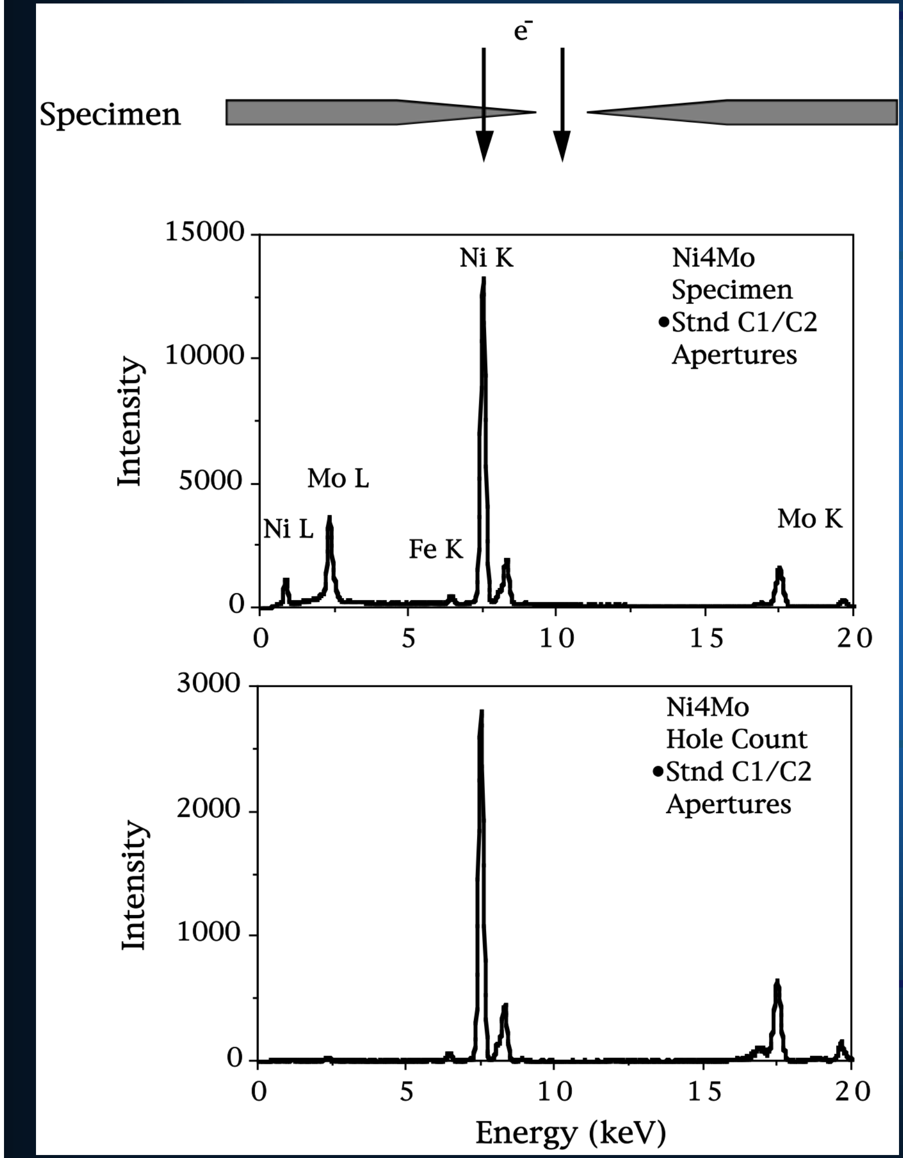


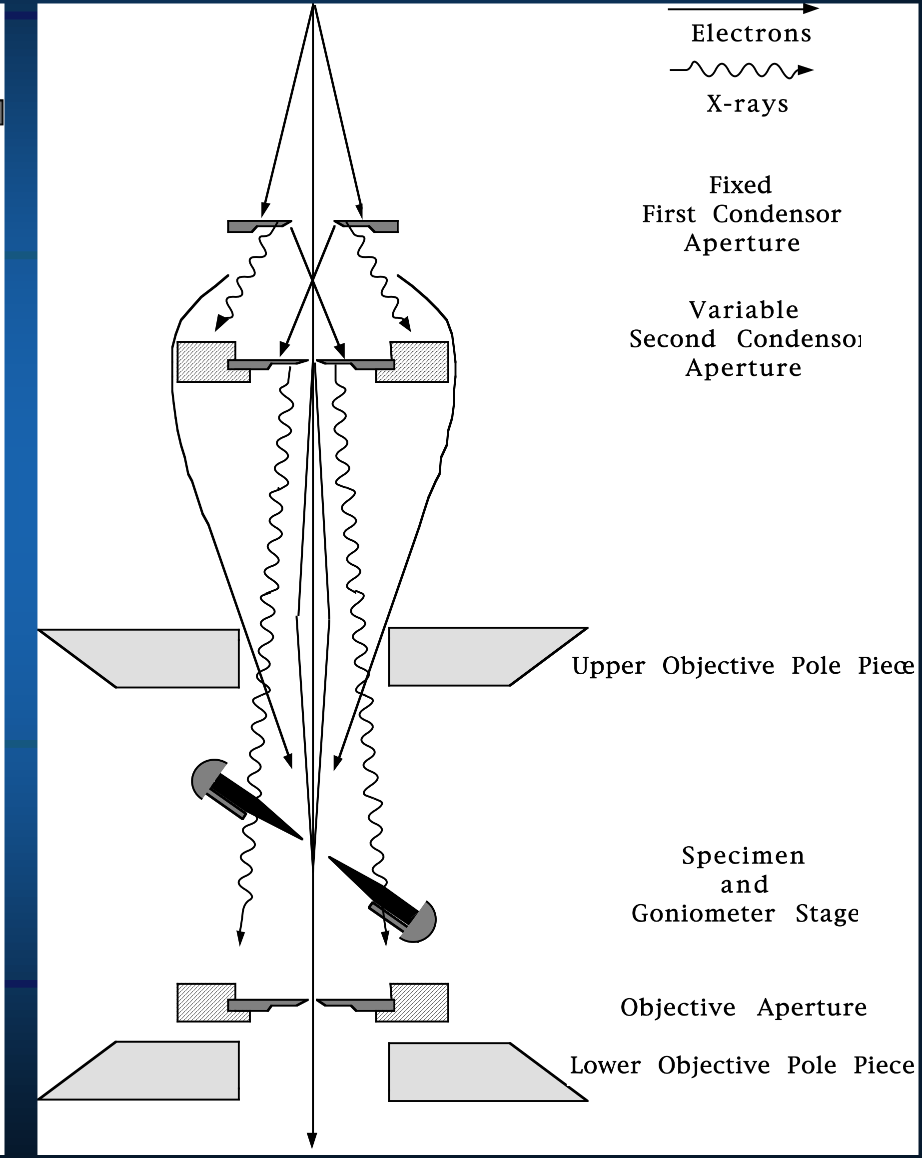
UTW Comparison Si(Li) vs SDD

Instrumentation: AEM Systems

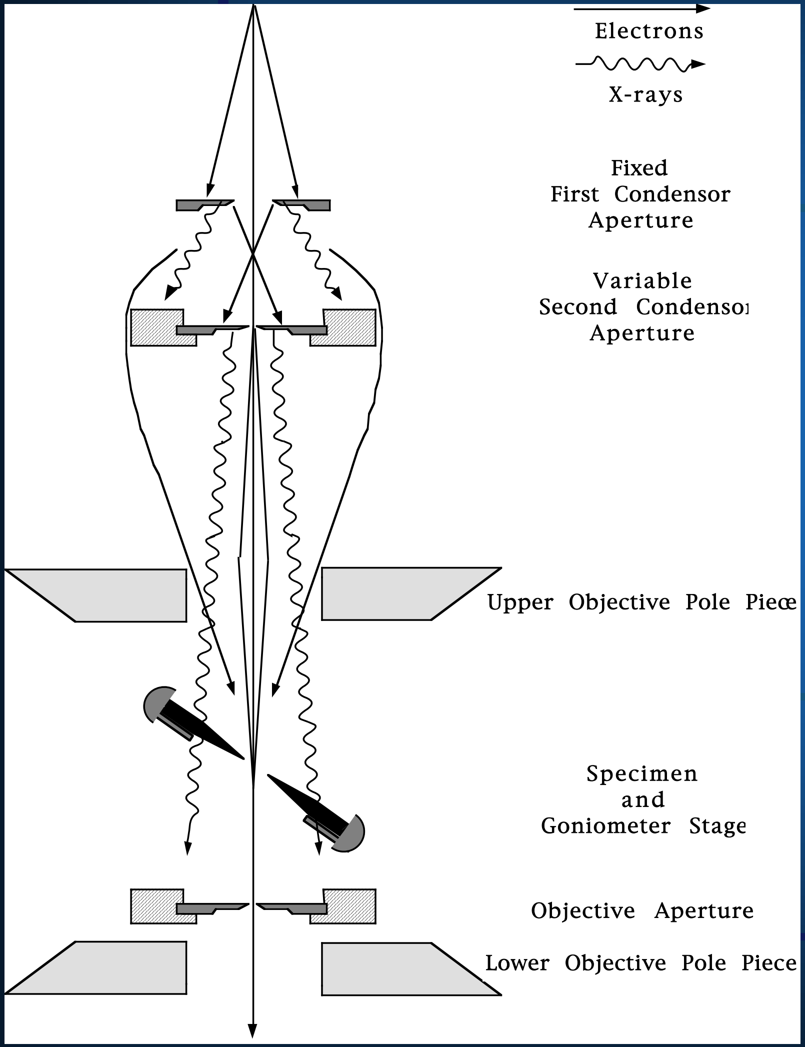
- The AEM as a system
- Spectral Artifacts in the AEM
  - Uncollimated Radiation
  - Systems Peaks
  - Artifacts at High Electron Energy
- Specimen Contamination & Preparation
- Optimizing Experimental Conditions

Spectral Artifacts in the AEM
Uncollimated Radiation: The Hole Count





Spectral Artifacts in the AEM
Uncollimated Radiation Solutions



Electrons

X-rays

Fixed
First Condensor
Aperture

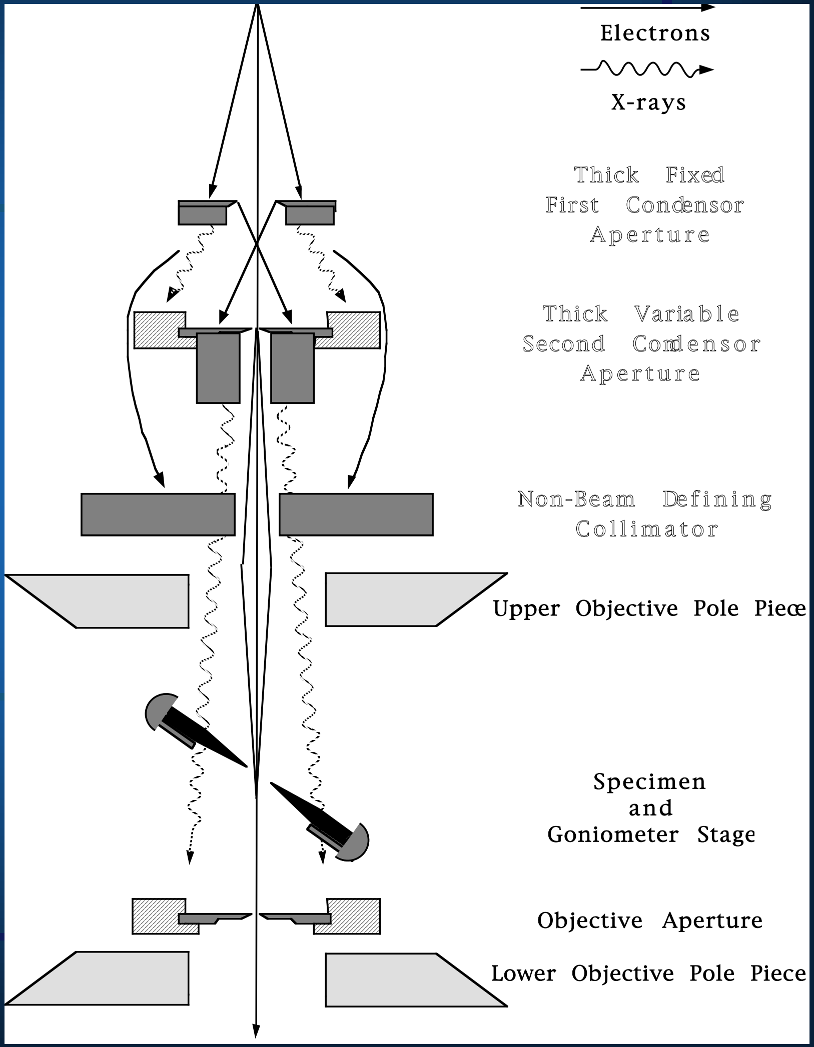
Variable
Second Condensor
Aperture

Upper Objective Pole Piece

Specimen
and
Goniometer Stage

Objective Aperture

Lower Objective Pole Piece



Electrons

X-rays

Thick Fixed
First Condensor
Aperture

Thick Variable
Second Condensor
Aperture

Non-Beam Defining
Collimator

Upper Objective Pole Piece

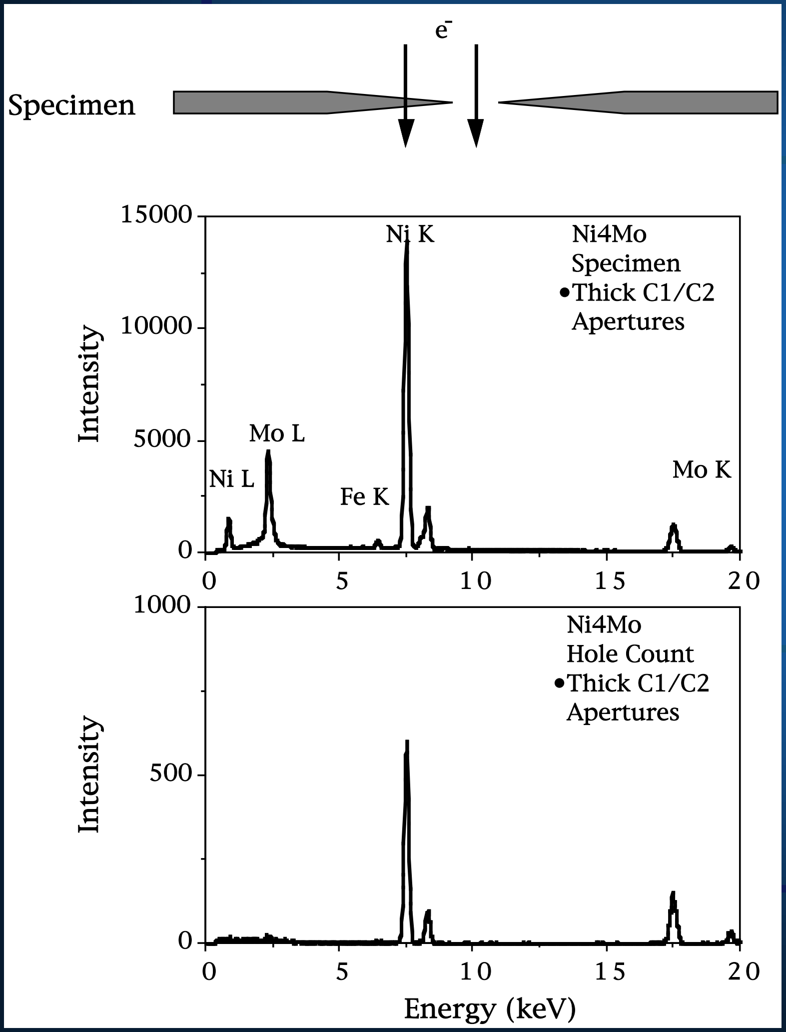
Specimen
and
Goniometer Stage

Objective Aperture

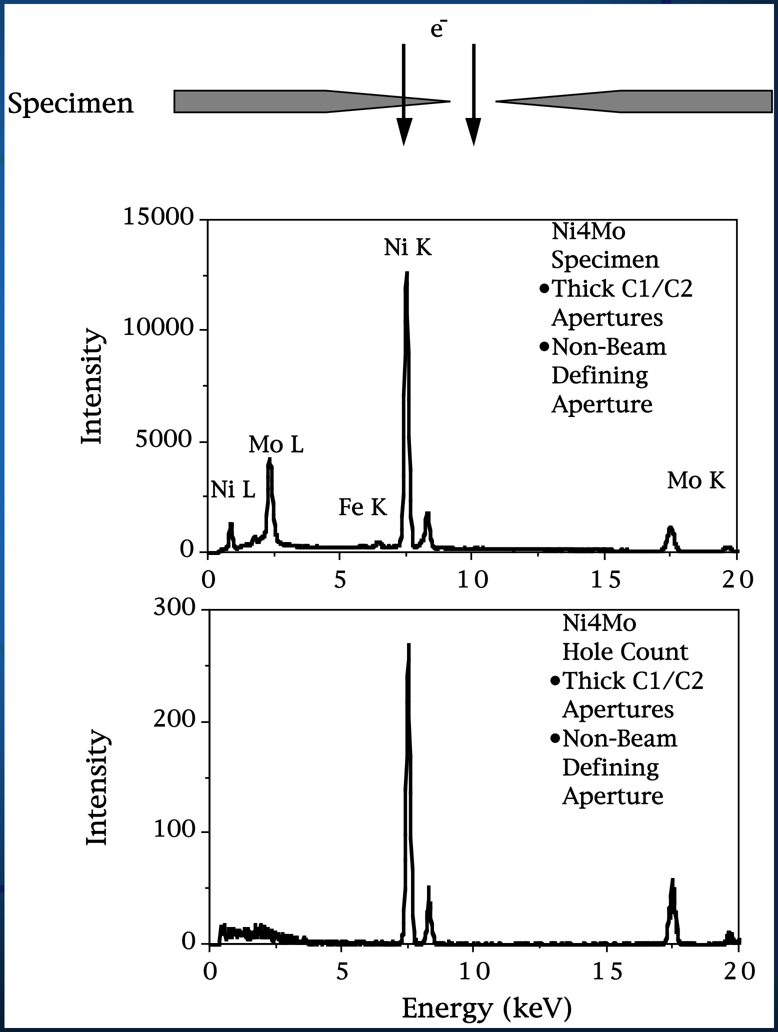
Lower Objective Pole Piece

Spectral Artifacts in the AEM

Hole Count Effects: Modified C_1 and C_2 Apertures



Hole Count Effects: Modified C_1 and C_2 & Non-Beam Defining Apertures



Optimizing Experimental Conditions

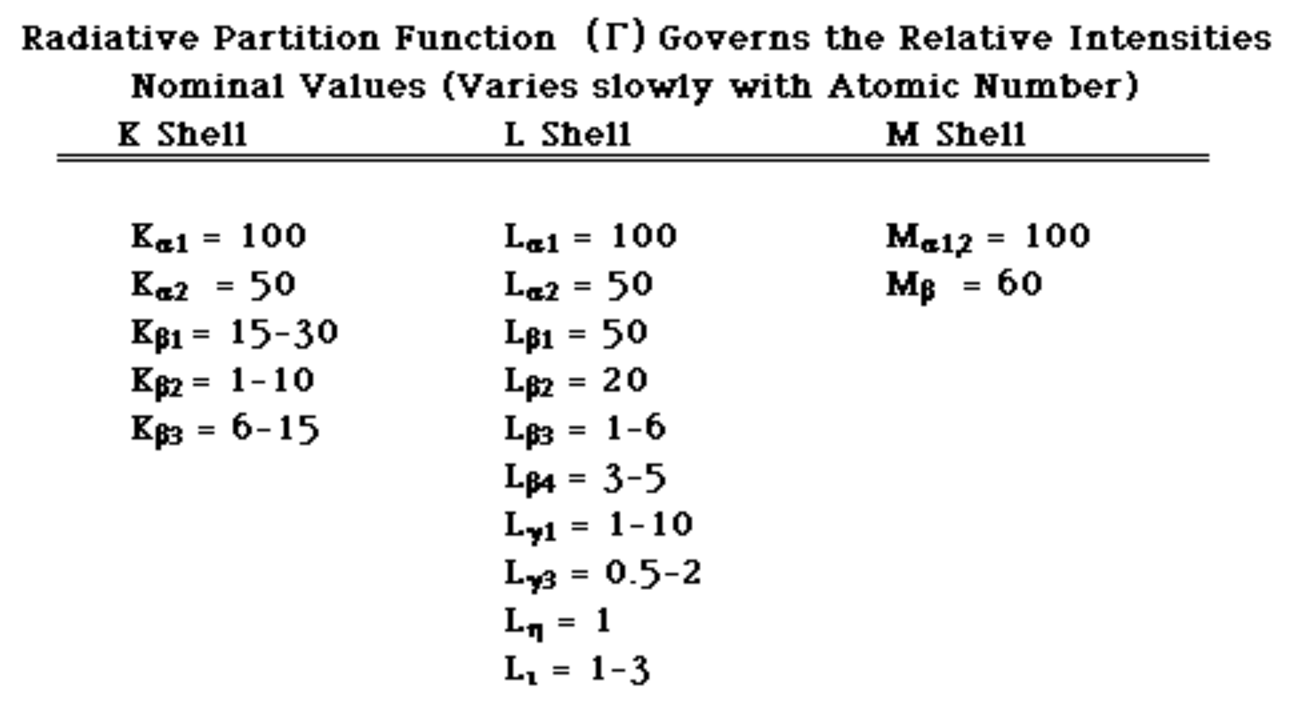
Choice of X-ray Line
- K- series
- L- series
- M- series

Detector/Specimen Geometry
- Elevation Angle
- Solid Angle

Detector Collimation

Choice of Accelerating Voltage
- Relative Intensity
- Peak/ Background
- Systems Peaks/Uncollimated Radiation

Choice of Electron Source
- Spatial Resolution
- Tungsten Hairpin
- LaB_6
- Field Emission

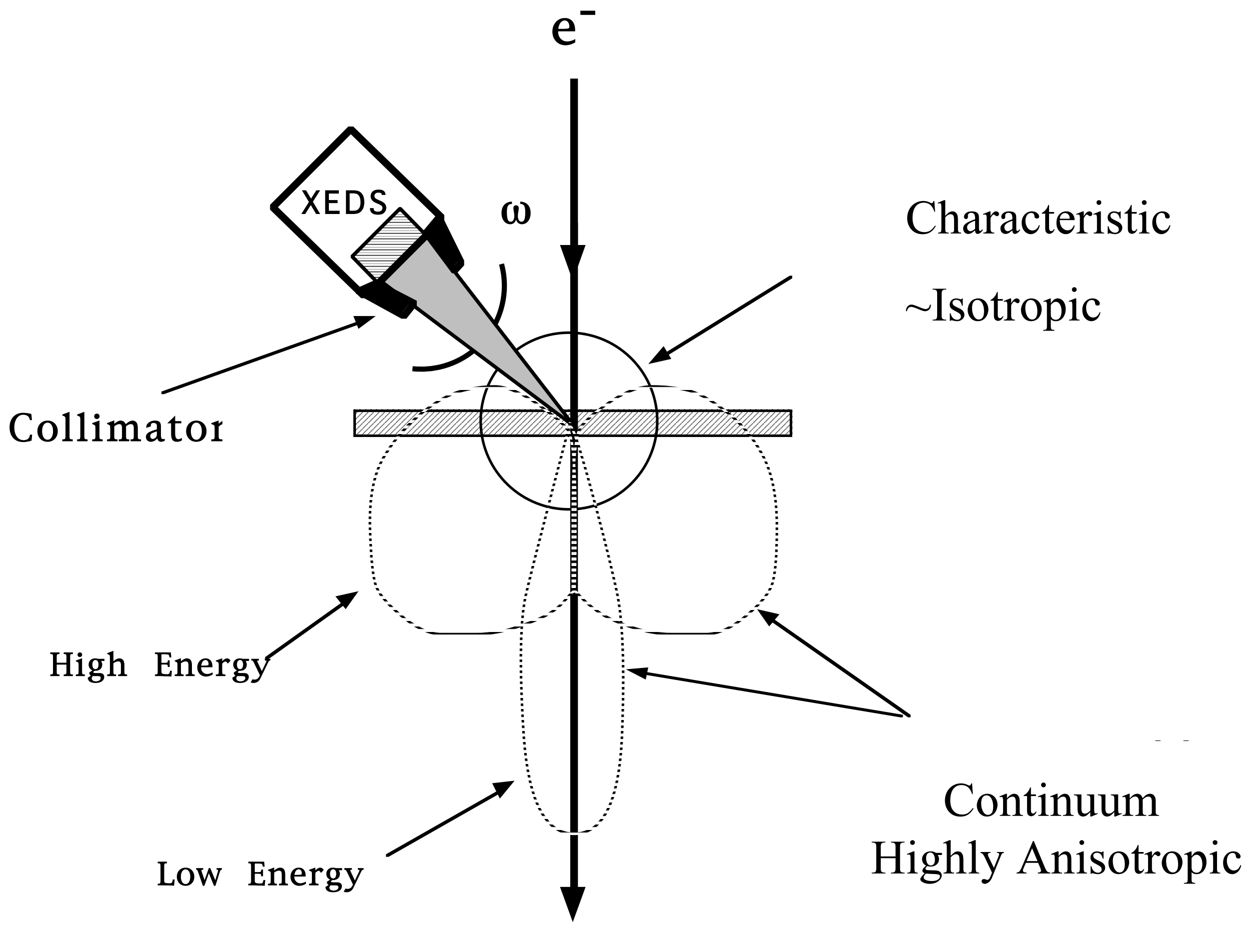


Radiative Partition Function (Γ) Governs the Relative Intensities

Nominal Values (Varies slowly with Atomic Number)

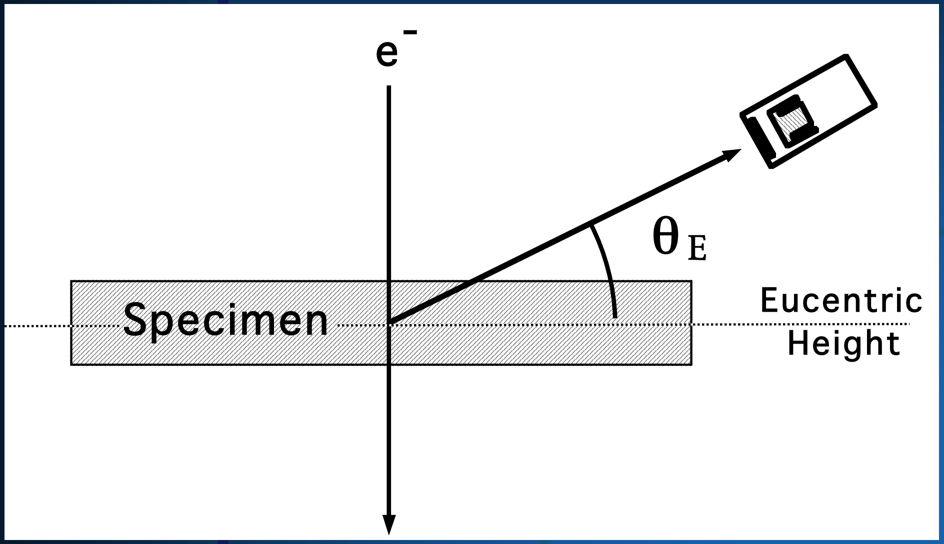
K Shell	L Shell	M Shell
$K_{\alpha1}$ = 100	$L_{\alpha1}$ = 100	$M_{\alpha1,2}$ = 100
$K_{\alpha2}$ = 50	$L_{\alpha2}$ = 50	M_{β} = 60
$K_{\beta1}$ = 15-30	$L_{\beta1}$ = 50	
$K_{\beta2}$ = 1-10	$L_{\beta2}$ = 20	
$K_{\beta3}$ = 6-15	$L_{\beta3}$ = 1-6	
	$L_{\beta4}$ = 3-5	
	$L_{\gamma1}$ = 1-10	
	$L_{\gamma3}$ = 0.5-2	
	L_{η} = 1	
	L_{ι} = 1-3	

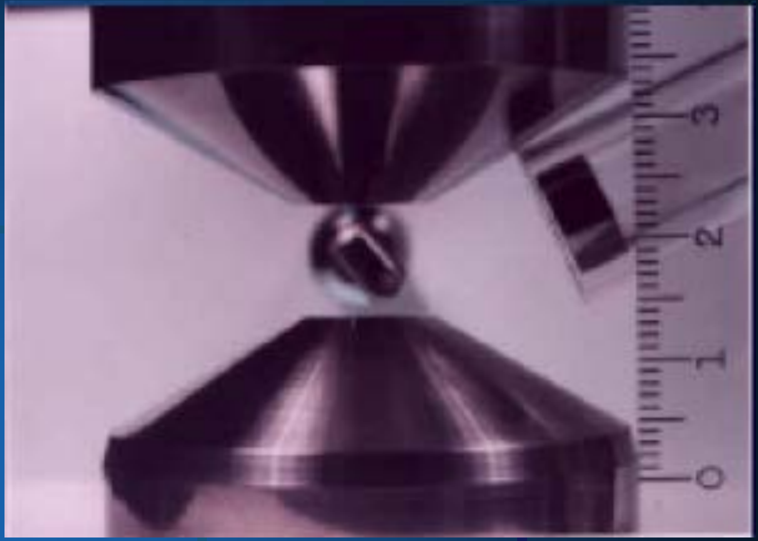
Detector/Specimen Geometry



Detector/Specimen Geometry

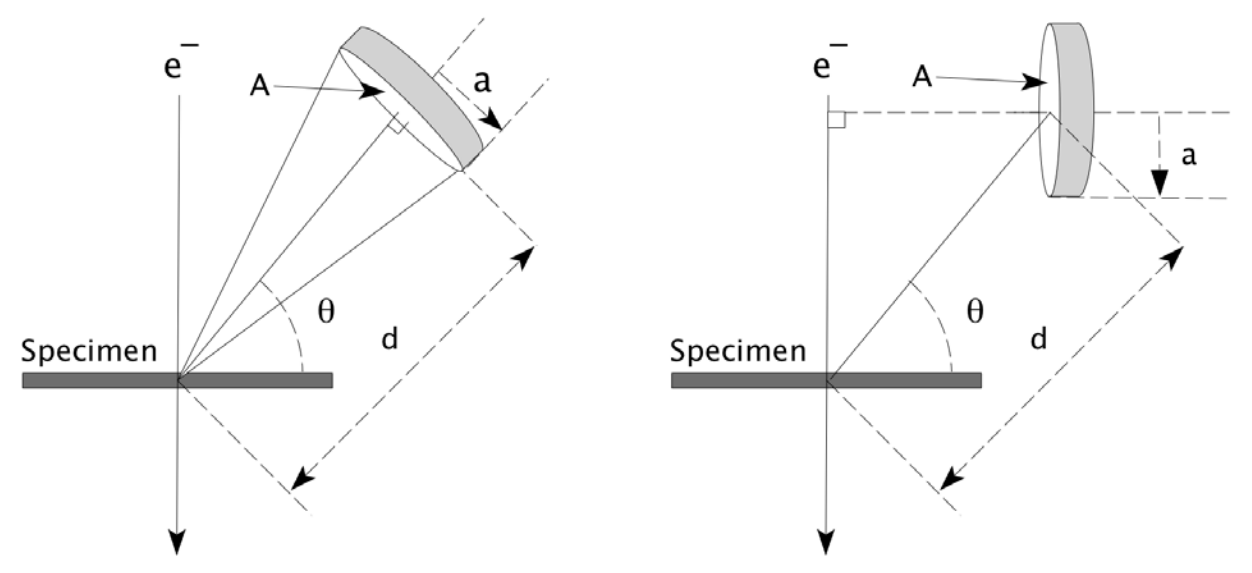
TEM





Designation	Elevation Angle θ_E	Azimuthal Angle θ_A	Manufacturer
Low	0° 0°	45° 90°	JEOL JEOL, FEI, VG
Intermediate	15-30°	90°	FEI, JEOL, Hitachi,VG
High	68-72°	0°	Hitachi, JEOL

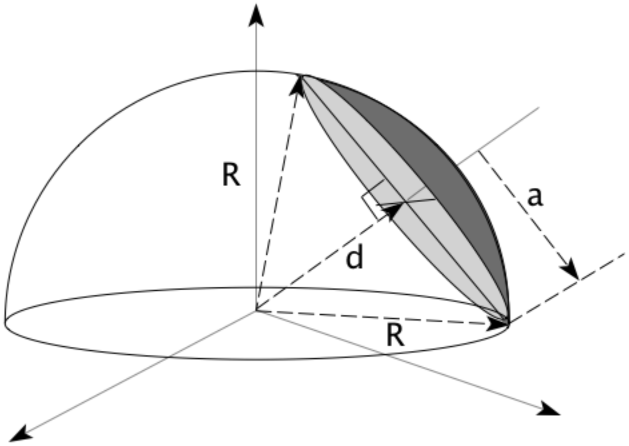
Geometrical / Collection Solid Angle



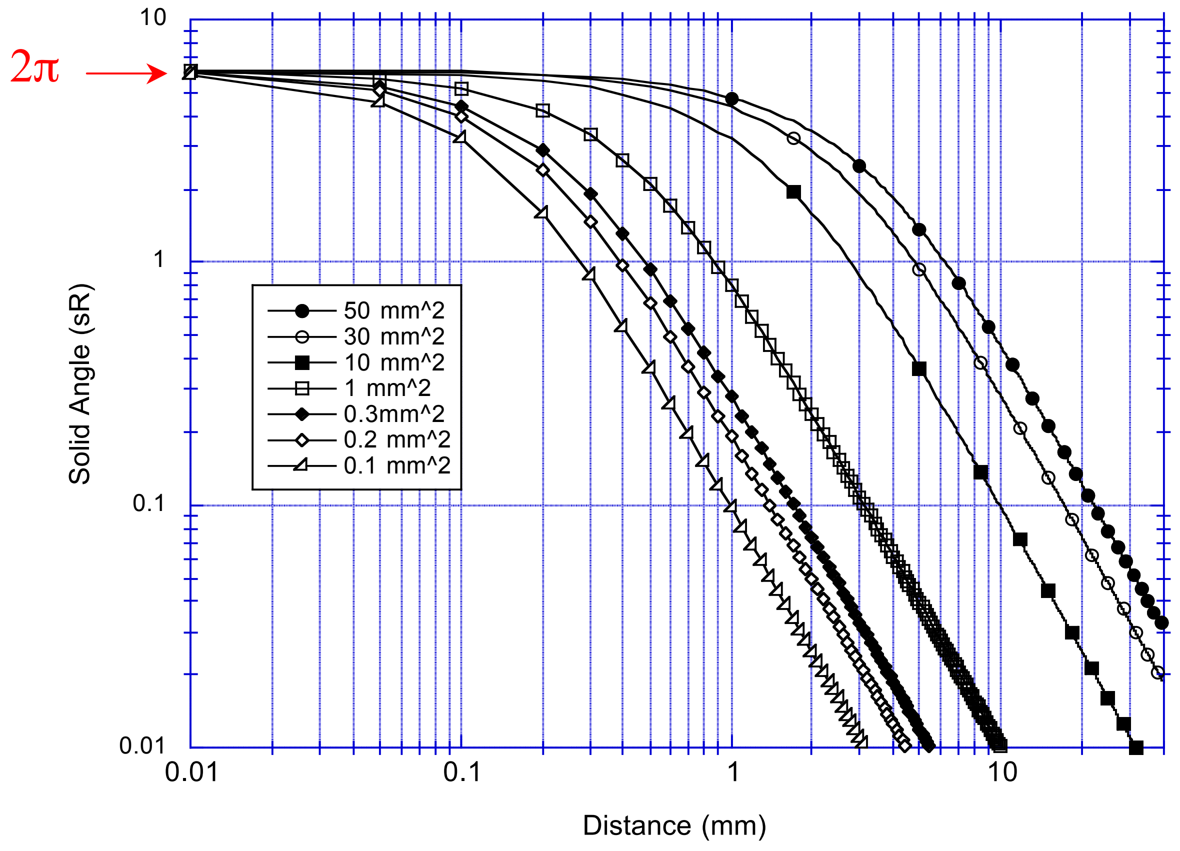
$$\Omega = \frac{S}{R^2} = \frac{2\pi\left(a^2+d^2-d\sqrt{a^2+d^2}\right)}{a^2+d^2}$$

$a^* = a\cos(\theta)$

$d^* = d - a\sin(\theta)$

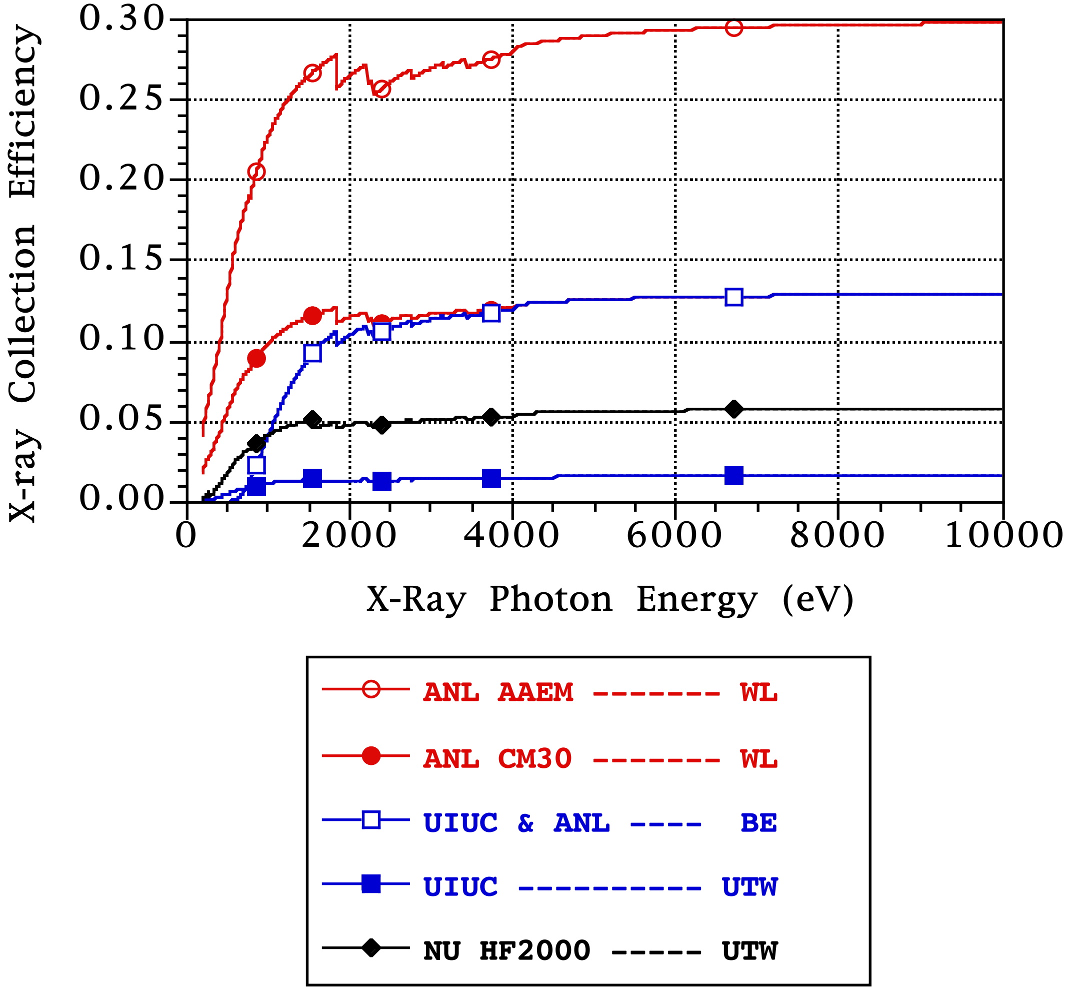


Geometrical / Collection Solid Angle

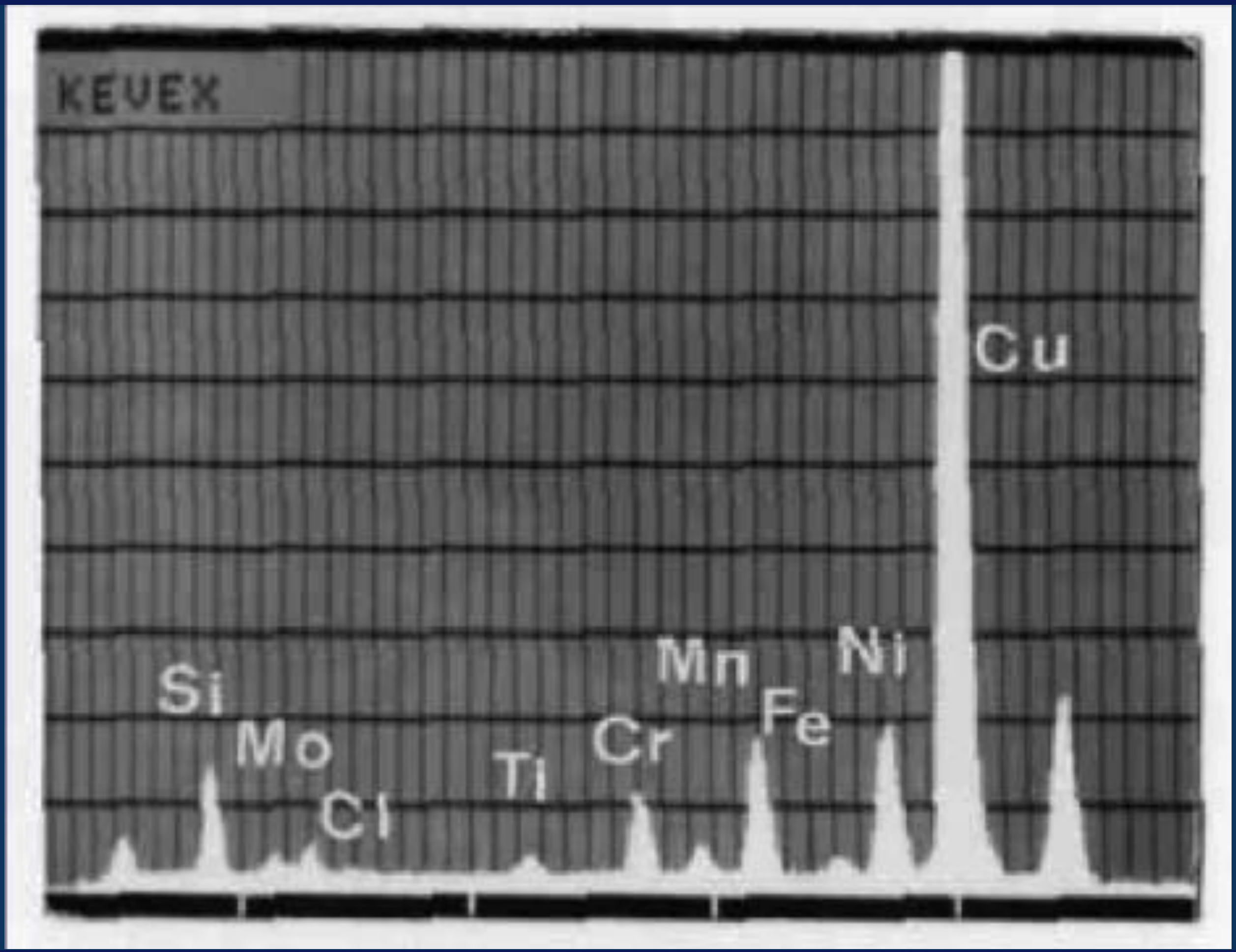


$$\Omega = \frac{S}{R^2} = \frac{2\pi\left(a^2+d^2-d\sqrt{a^2+d^2}\right)}{a^2+d^2}$$

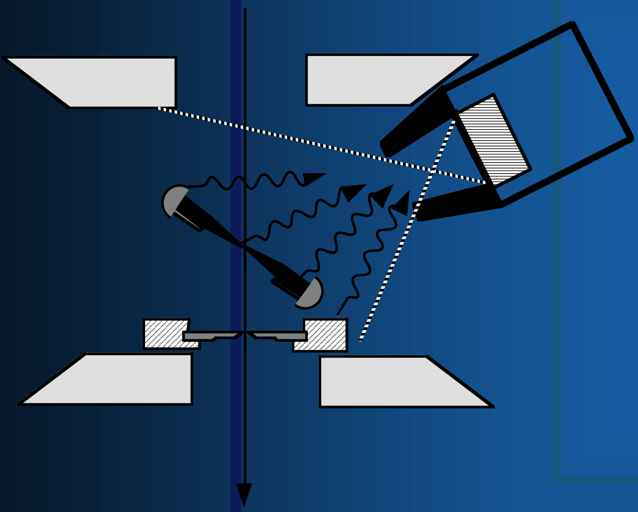
Comparison of AEM Systems with XEDS Detectors
ANL/UIUC/NU



Cu? In Steel ?
What is the source

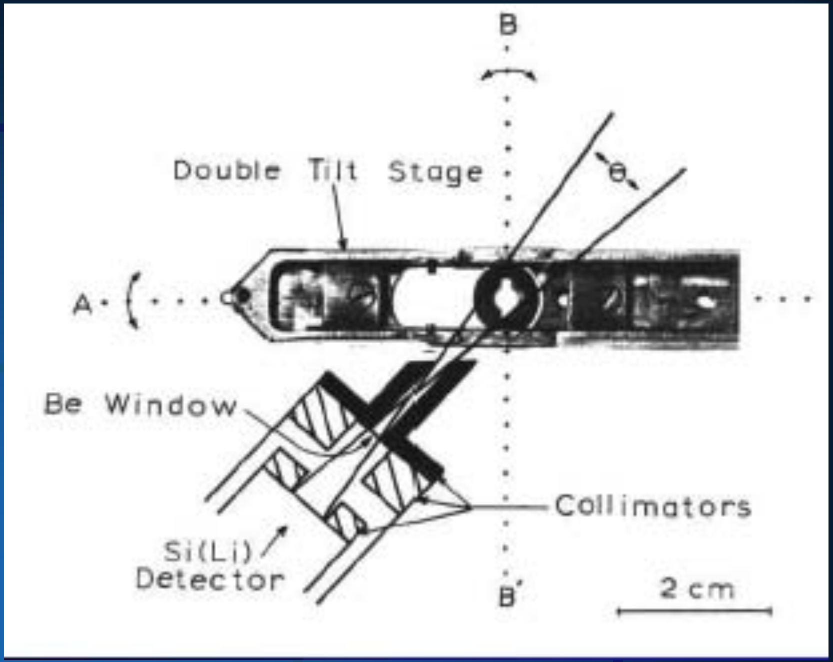


Subtending Solid Angle

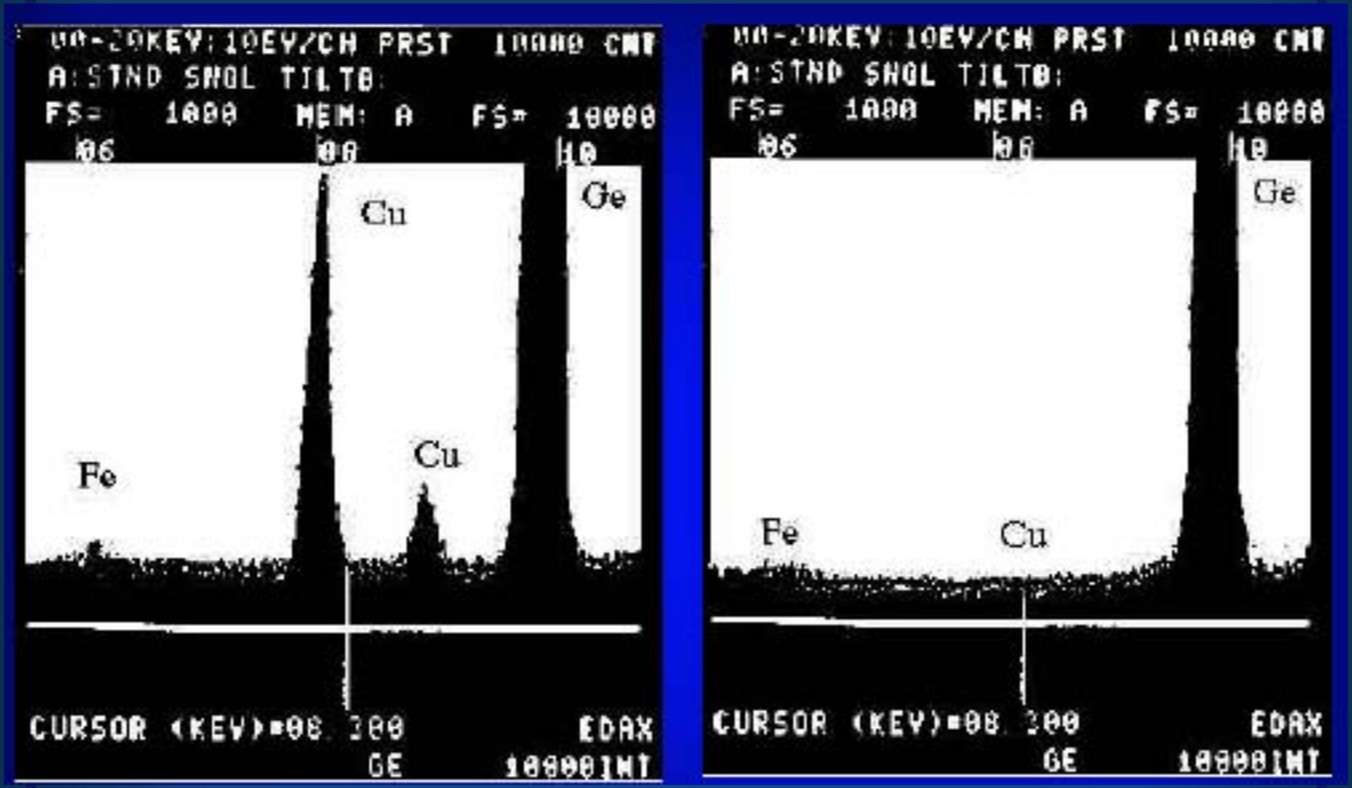


Where do Systems Peaks Come from?

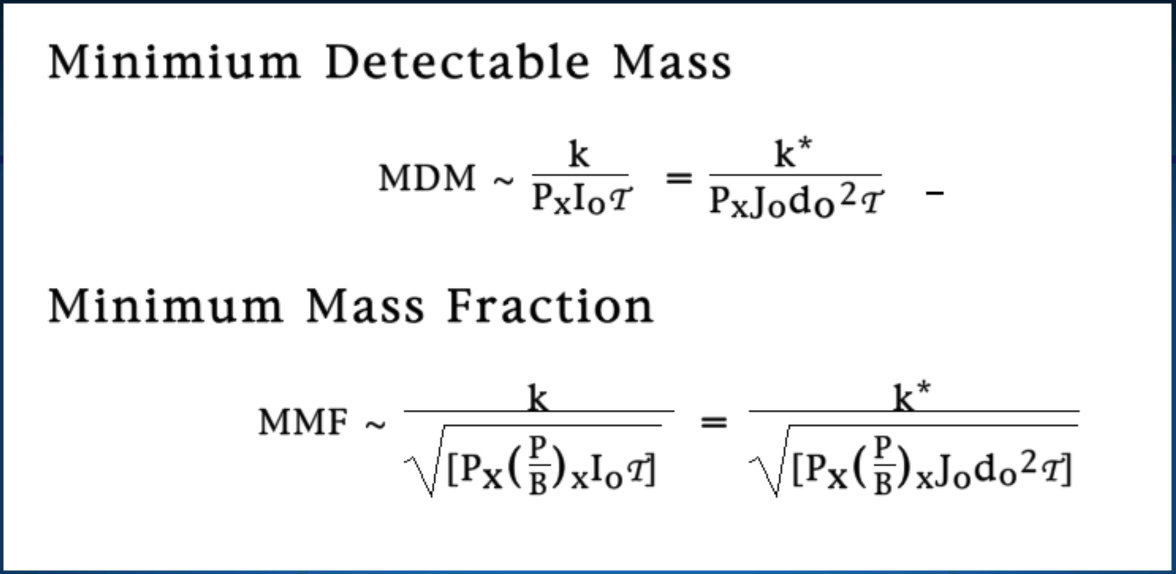
Detection of System Peaks
Effects of the Collimator & Stage



Detection & Removal of System Peaks



Removal of Stage System Peaks by use of Beryllium Gimbals
Ge specimen 10,000 in Ge Kα peak in both spectra
Left Standard Single Tilt Cu Stage, Right Be Gimbal DT Stage



Minimium Detectable Mass

$$\mathrm{MDM} \sim \frac{k}{P_x I_o \tau} = \frac{k^*}{P_x J_o d_o^2 \tau} \; -$$

Minimum Mass Fraction

$$\mathrm{MMF} \sim \frac{k}{\sqrt{[P_x \left(\frac{P}{B}\right)_x I_o \tau]}} = \frac{k^*}{\sqrt{[P_x \left(\frac{P}{B}\right)_x J_o d_o^2 \tau]}}$$

k,k^* = Constants

P_x = Characteristic Signal from element X

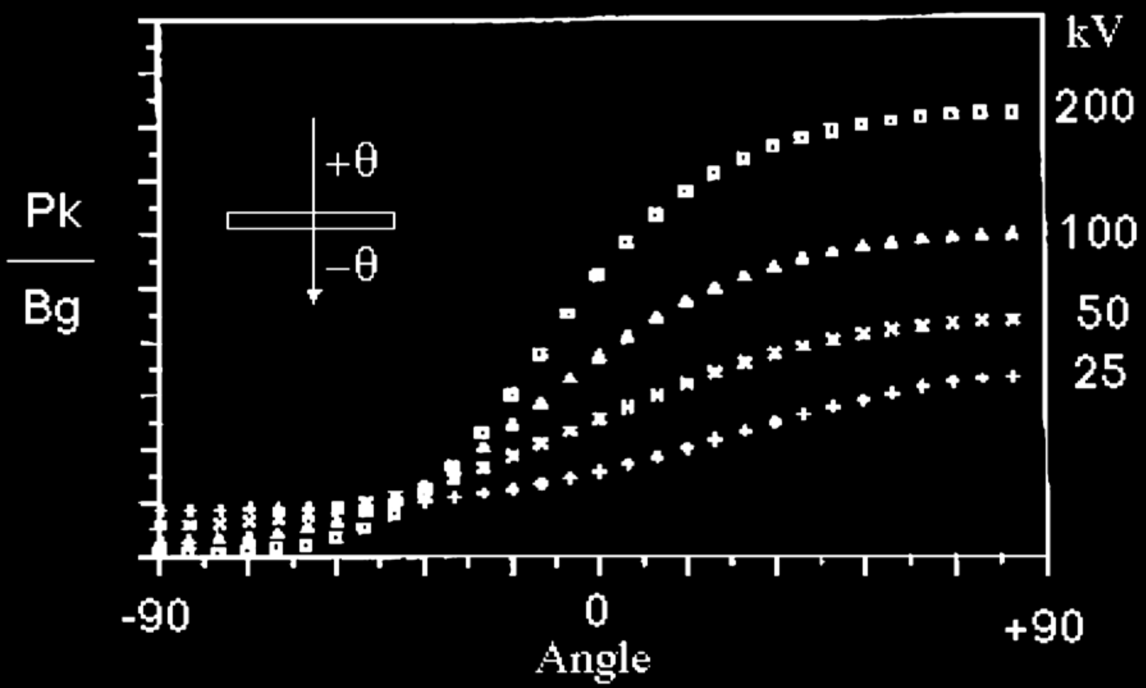
$(P/B)_x$ = Peak to Background ratio for element X

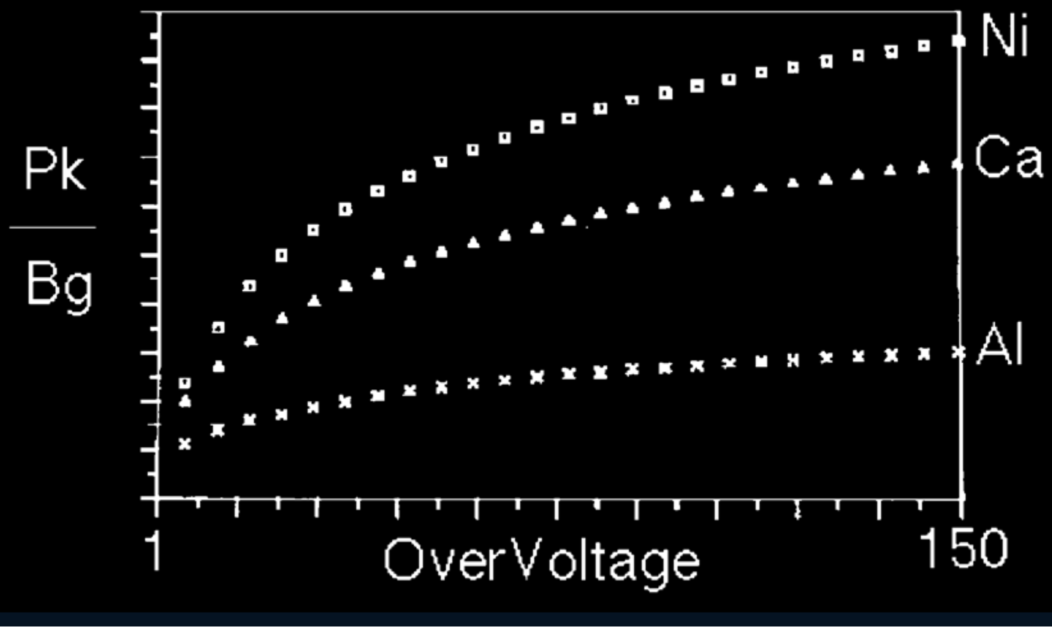
I_o = Incident electron flux

J_o = Incident electron current density

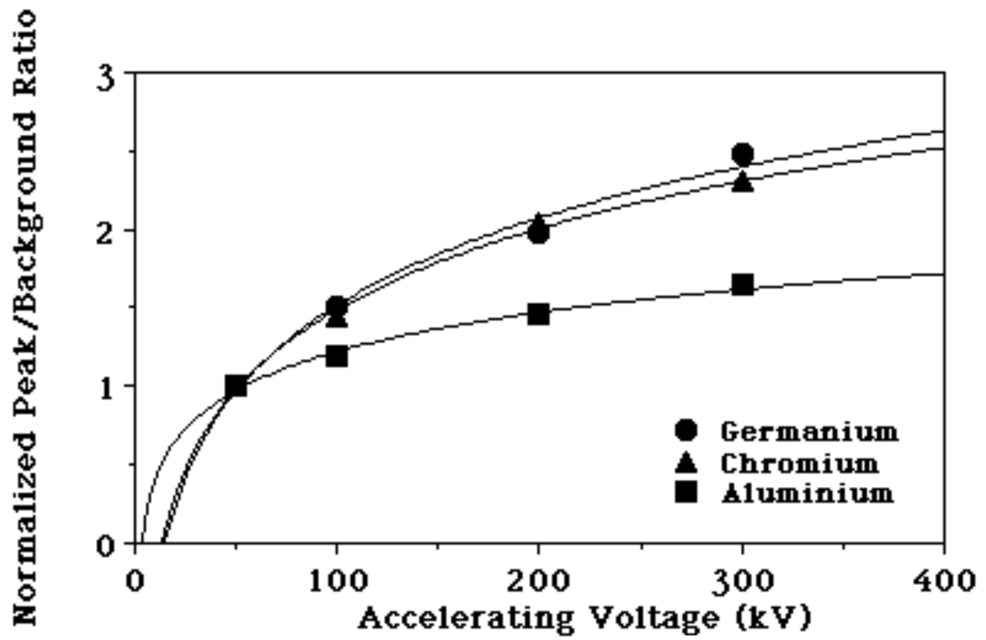
d_o = Probe diameter

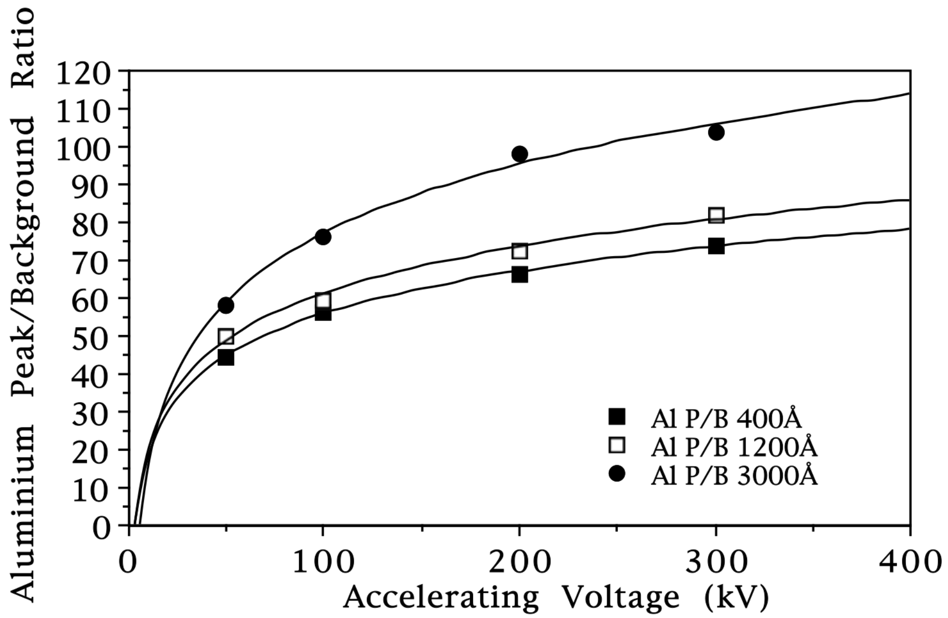
τ = Analysis time

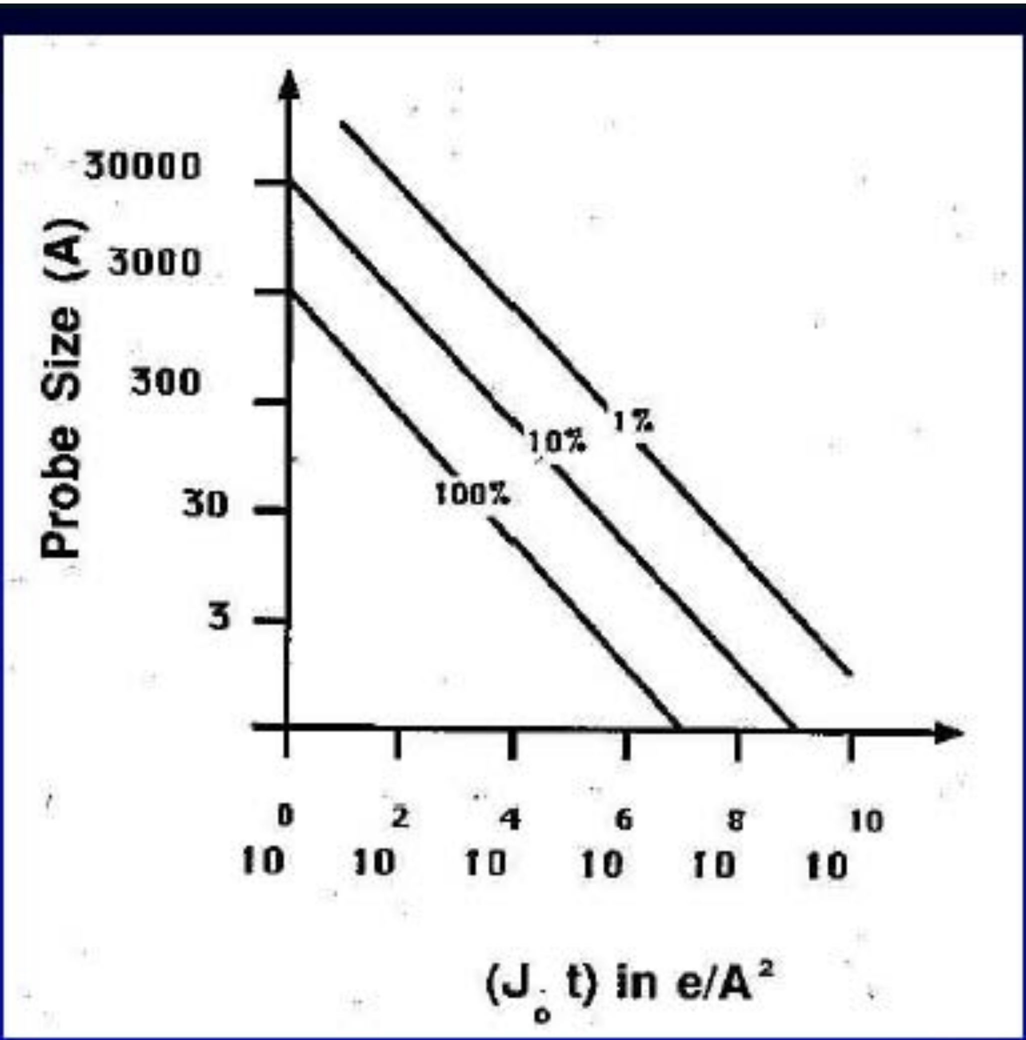

Pk
Bg
+θ
−θ
kV
200
100
50
25
-90
0
+90
Angle


Pk
Bg
Ni
Ca
Al
1
OverVoltage
150

Experimental Peak/Background Variation with Voltage

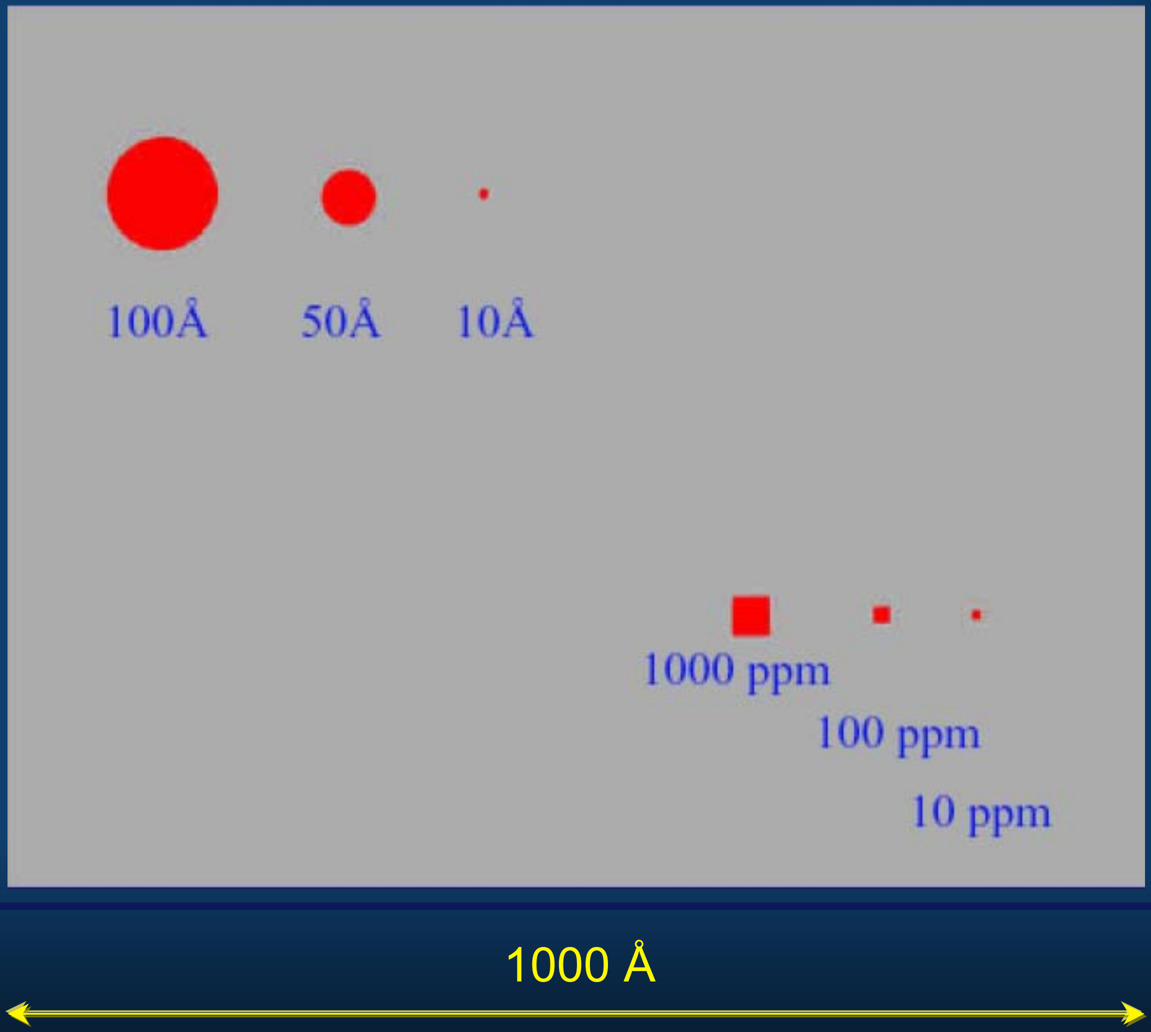


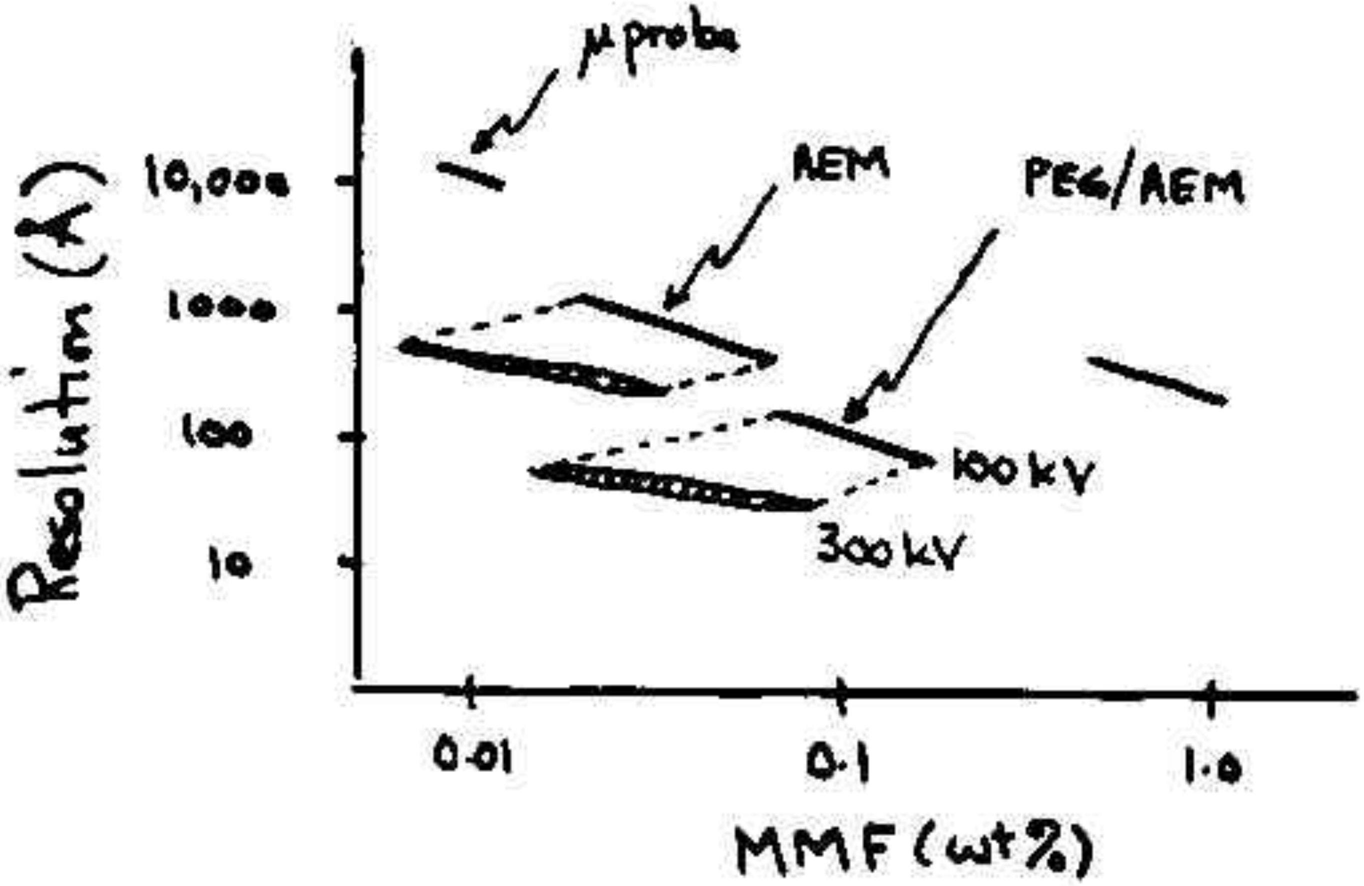




$$d_o \sim \frac{k^*}{MMF^*\sqrt{[P_X\left(\frac{P}{B}\right)_x J_o \tau]}}$$

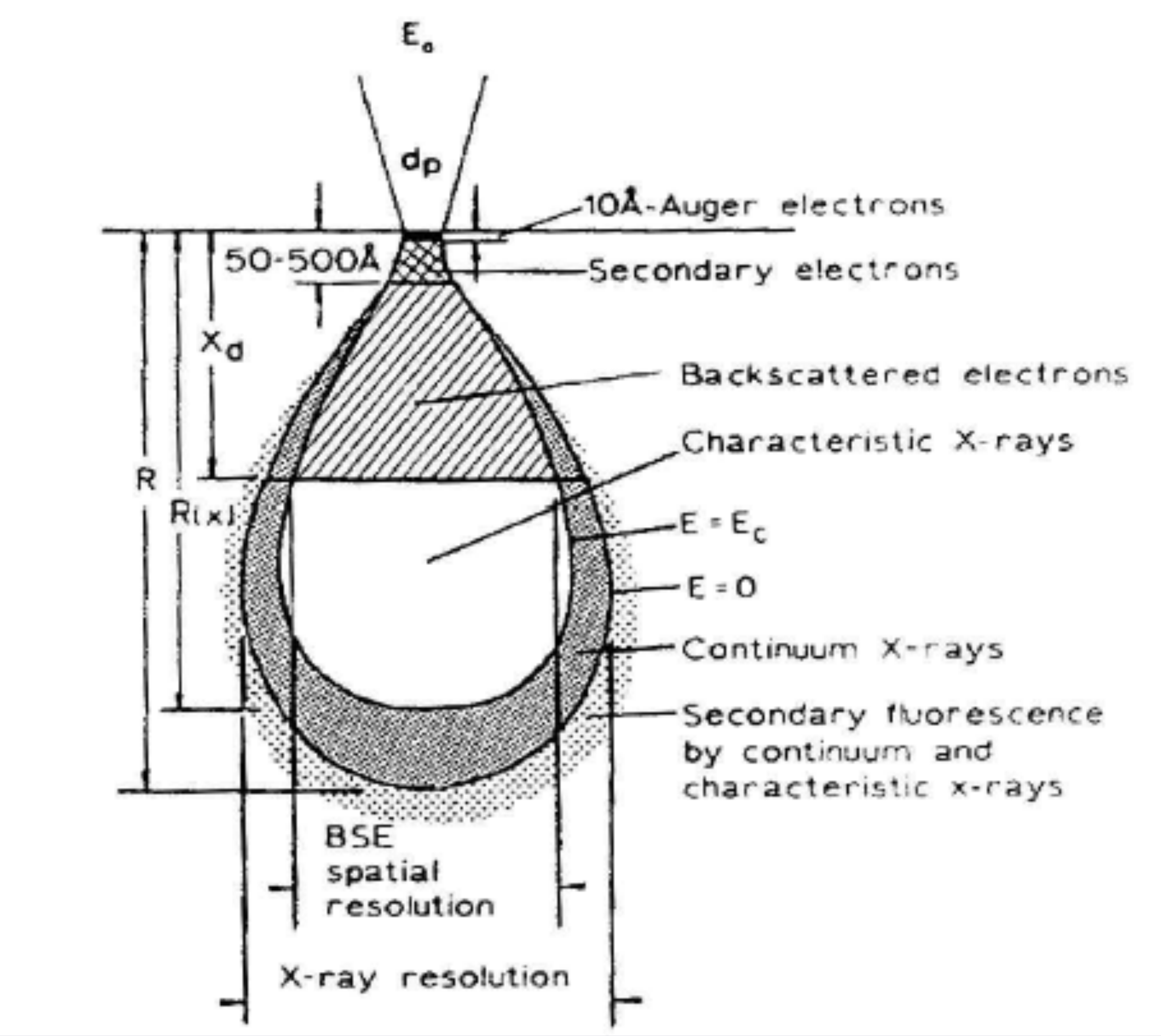
Visualizing Minimum Detectable Mass



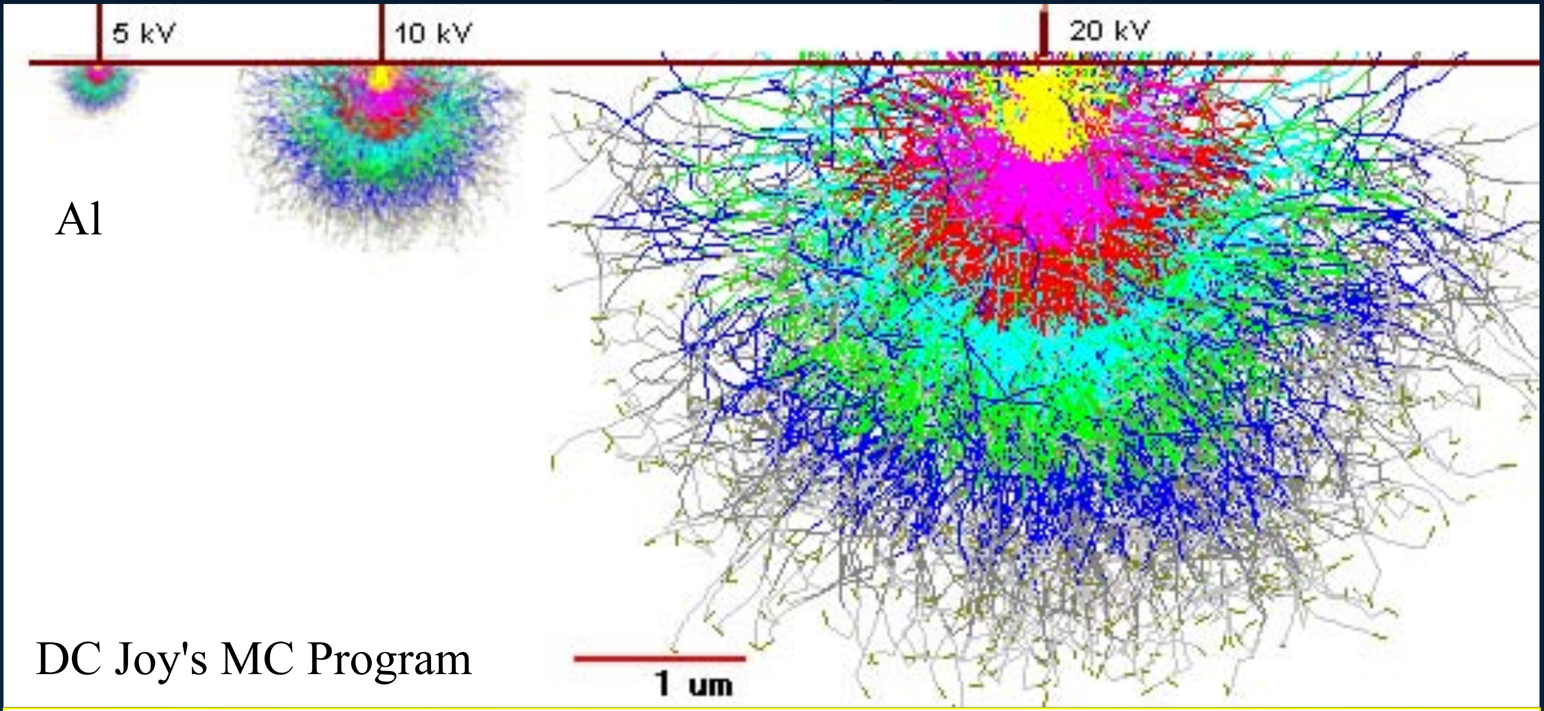

μ probe
AEM
PEG/AEM
Resolution (Å)
10,000
1000
100
10
100 kV
300 kV
0.01
0.1
1.0
MMF (wt%)

Lyman 1986

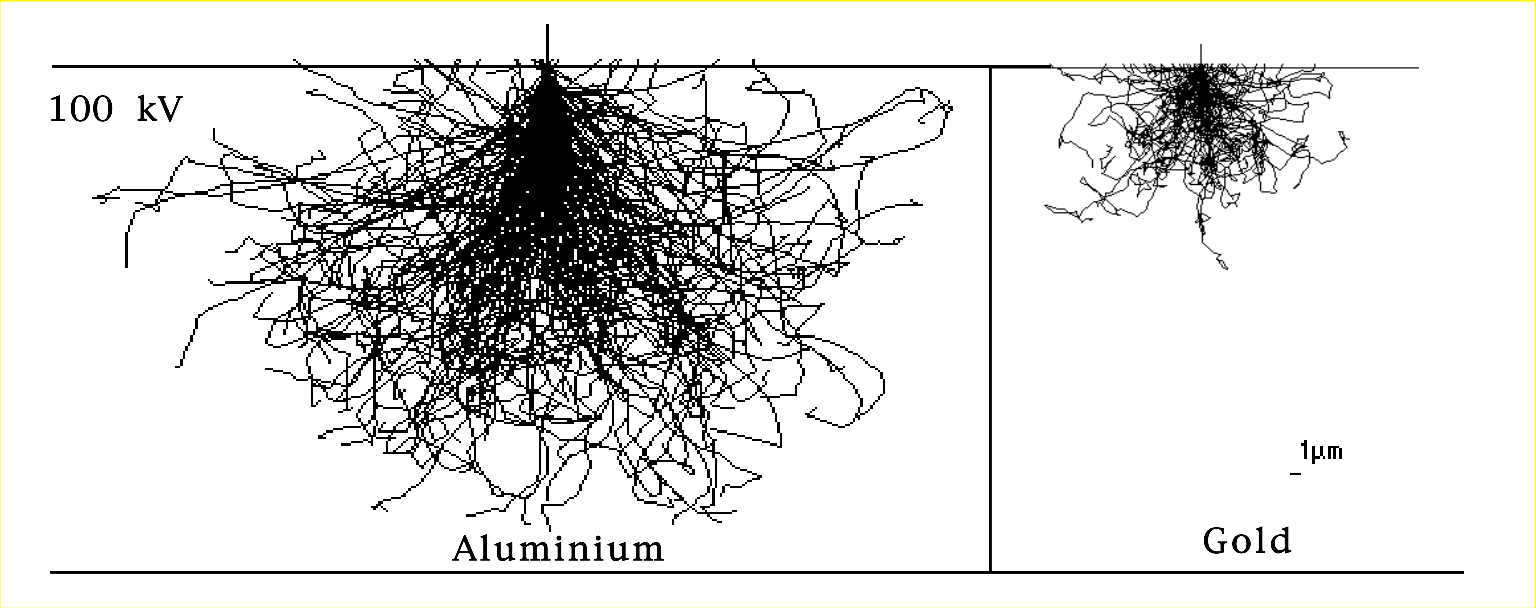
What is your spatial resolution?

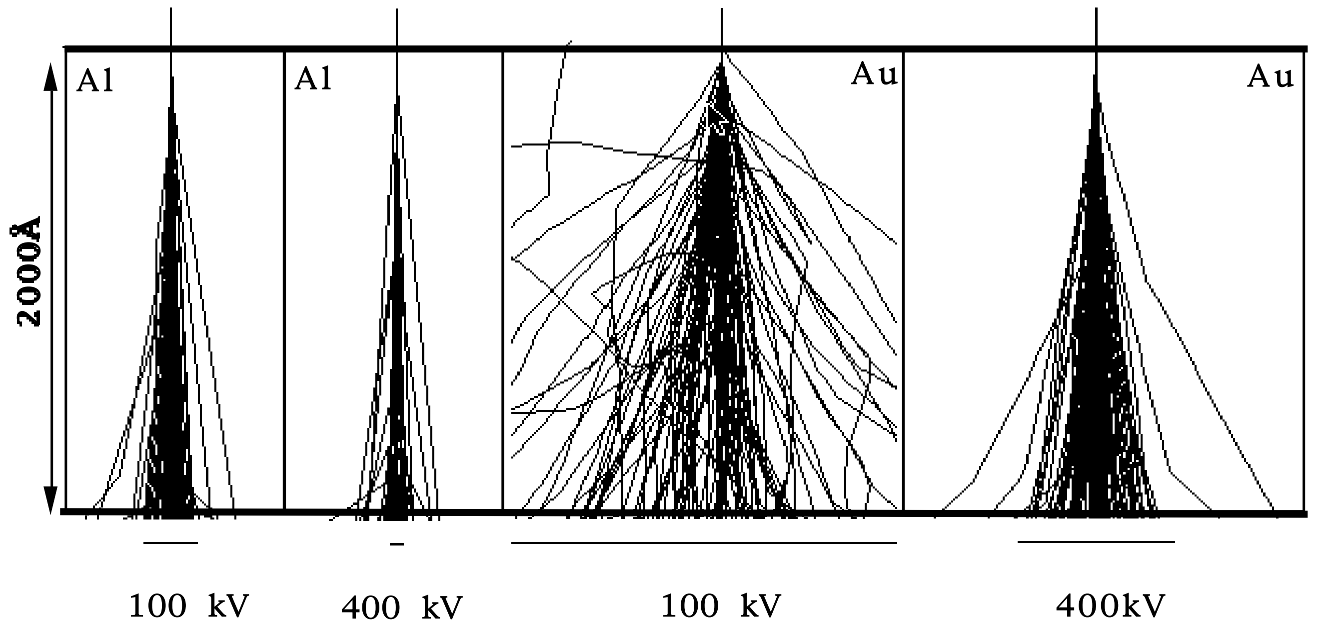


Spatial Resolution /Beam Spreading Monte Carlo Calculations



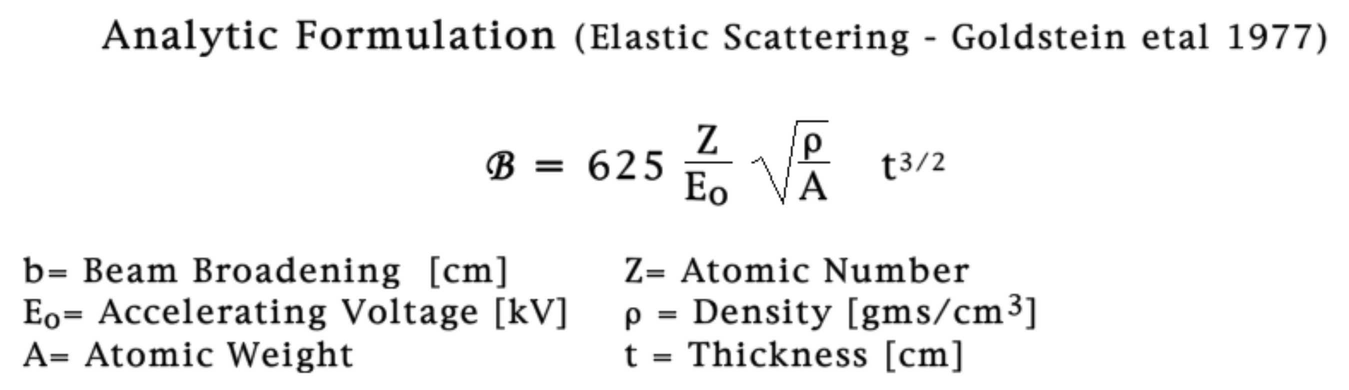
DC Joy's MC Program





Monte Carlo Calculations of $\mathcal{B}$ (Newbury & Myklebust -1979)

			Thickness		
Element	Z	10nm	50nm	100nm	500nm
Carbon	6	0.22	1.9	4.1	33.0
Aluminium	13	0.41	3.0	7.6	66.4
Copper	29	0.78	5.8	17.5	244.0
Gold	79	1.71	15.0	52.2	1725.0

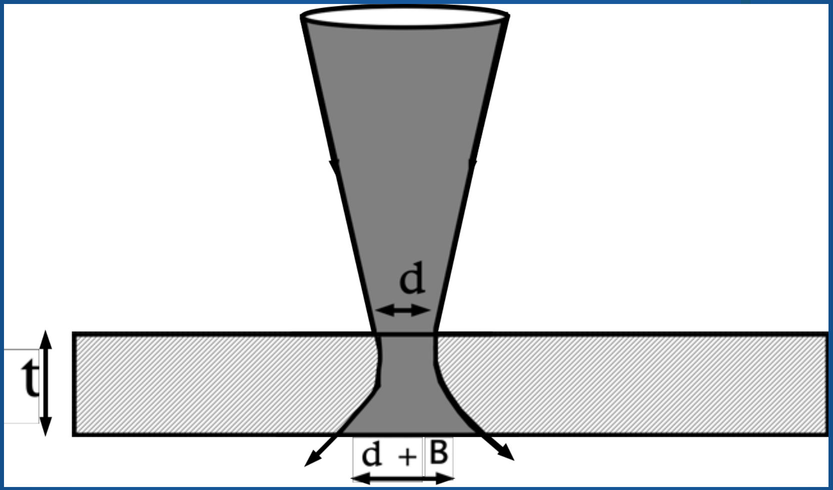


Analytic Formulation (Elastic Scattering - Goldstein etal 1977)

$$\mathcal{B} = 625 \frac{Z}{E_o} \sqrt{\frac{\rho}{A}} \quad t^{3/2}$$

b= Beam Broadening [cm]
E_o= Accelerating Voltage [kV]
A= Atomic Weight

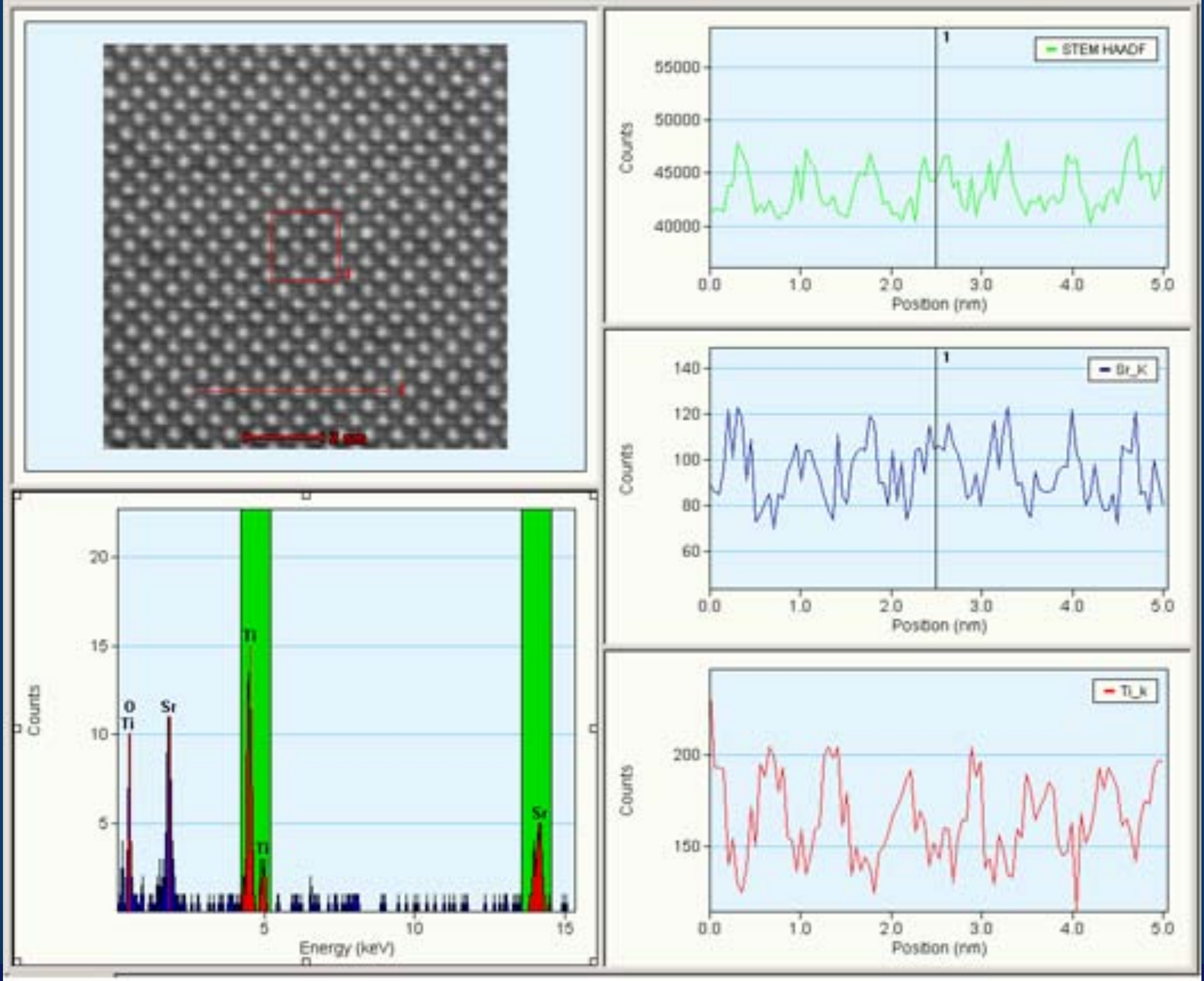
Z= Atomic Number
ρ = Density [gms/cm^3]
t = Thickness [cm]



Element	Z	10nm	50nm	100nm	500nm
Carbon	6	0.16	1.8	5.13	57.4
Aluminium	13	0.26	1.9	8.12	90.9
Copper	29	0.68	7.6	21.4	*
Gold	79	15.5	17.3	*	*

*model invalid at higher kV and/or high scattering angles

What are the Limits - Today?



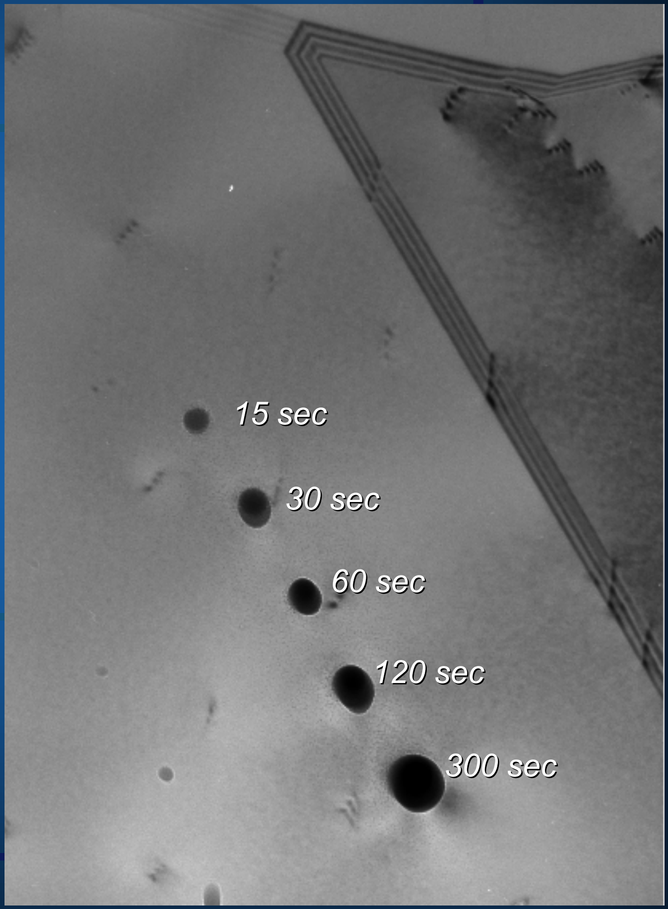
Dmitri Klenov B.Freitag,FEI

Specimen Contamination

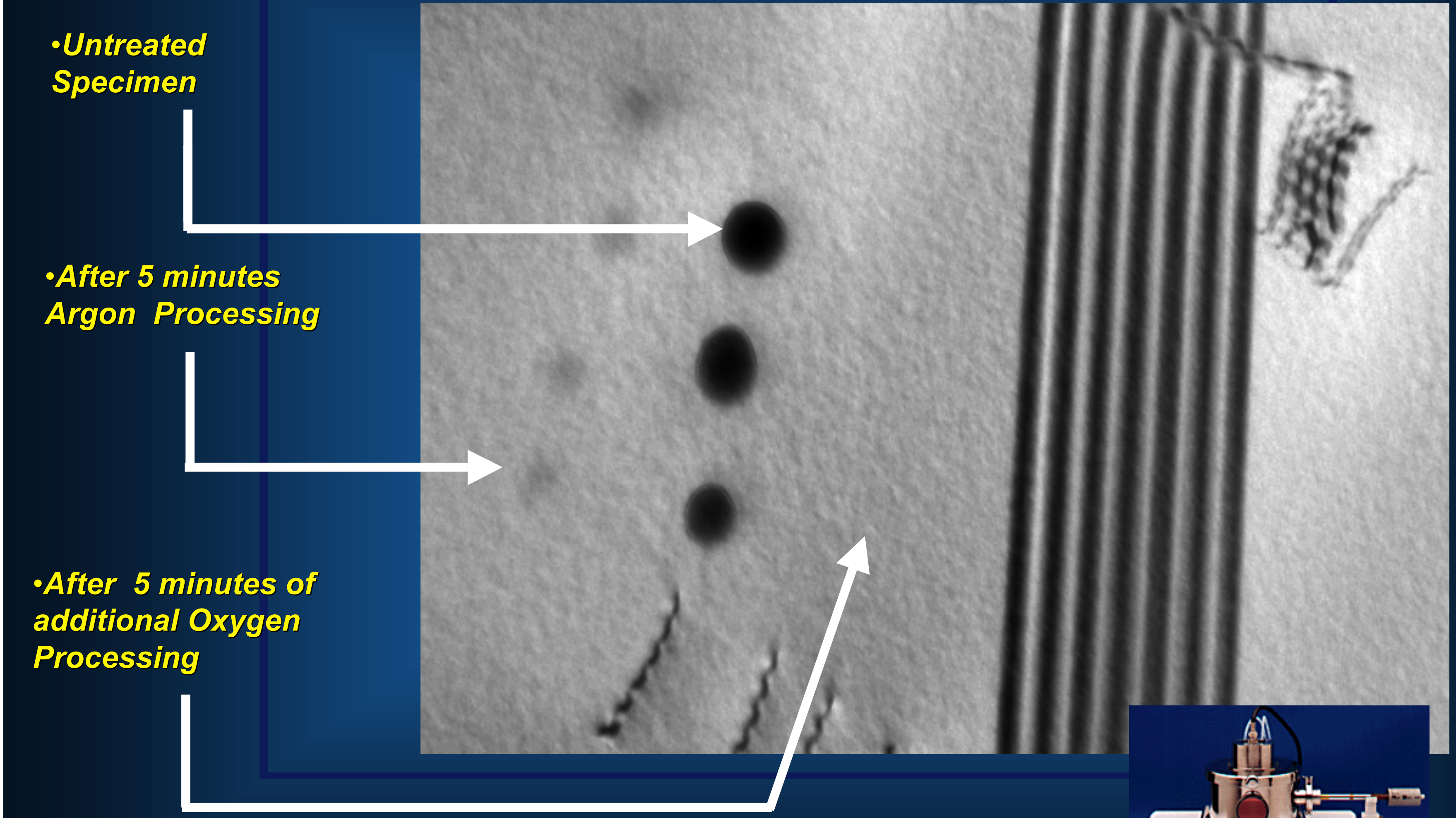
Example:

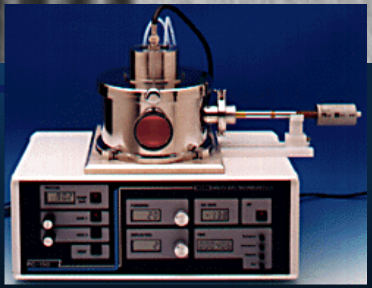
- *The figure at the right shows the results of contamination formed when a 300 kV probe is focussed on the surface of a freshly electropolished 304 SS TEM specimen.*

- *The dark deposits mainly consist of hydrocarbons which diffuse across the surface of the specimen to the immediate vicinity of the electron probe. The amount of the contamination is a function of the time spent at each location. Here the time was varied from 15 - 300 seconds.*

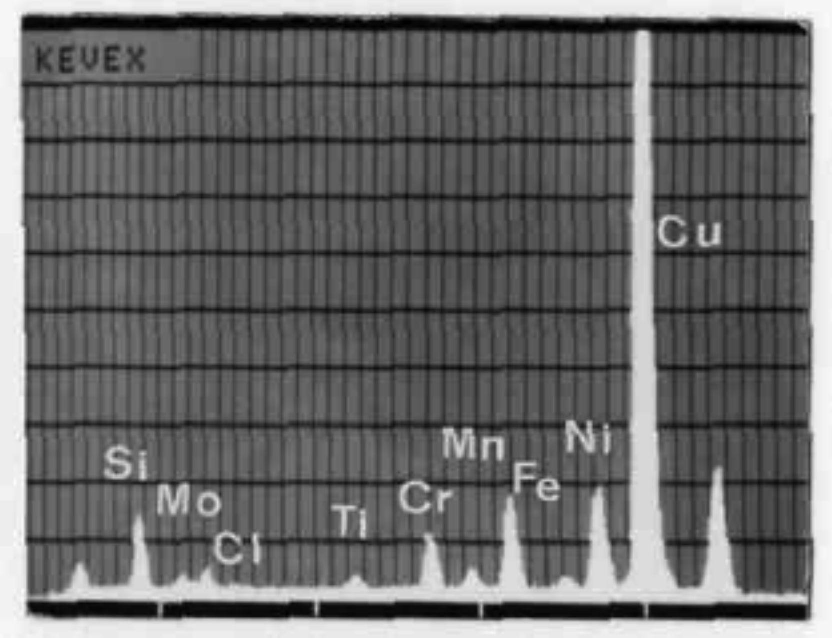


Plasma Cleaning of Electropolished 304 SS

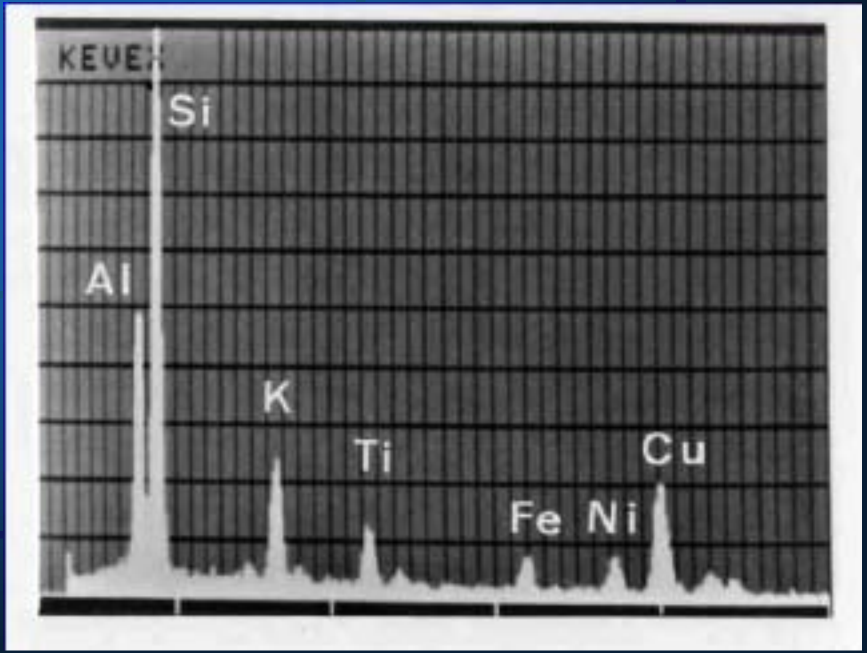




Specimen Preparation Artifacts



Electropolishing: HCl residue



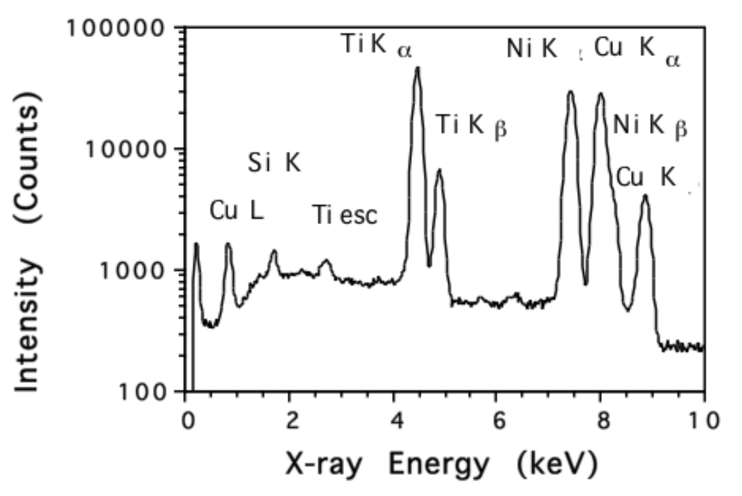
Ion Milling:Redeposition of Fe,Ni, Cu from SS holder

Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects:
    Absorption
    Fluorescence

Spectral Processing : XEDS

Spectrum = Characteristic Peaks + Background



Data Reduction

Simple: Linear Background Fit & Integration

Curve Fitting: Non-Linear Background & Profile Matching

Frequency (Digital) Filtering: Background Suppression
& Reference Spectra Fitting

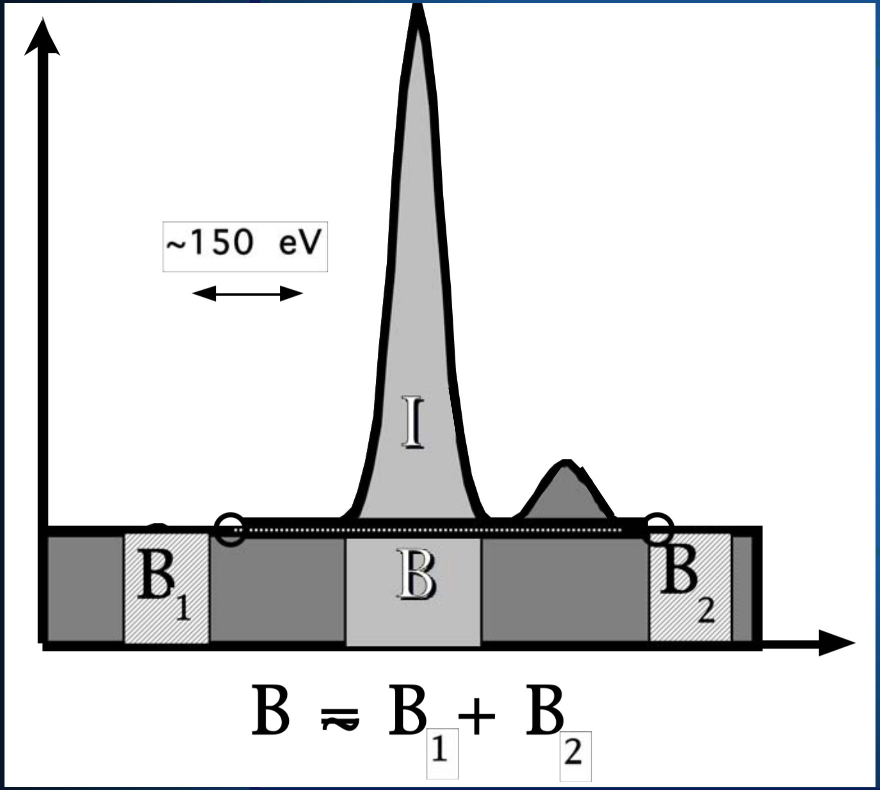
Deconvolution: Fourier Method for Resolution Enhancement

Background Modeling

Simple - Linear and/or Polynominal Interpolation

Modeling - Parametric Fits of Analytic Expressions
Phenomenological Expressions
Modified Bethe Heitler Model
Digital Filtering - Mathematical Supression

Spectral Processing : XEDS
Simple Data Reduction



Note: Must use peak integrals (I) and not peak amplitudes (A)

Recall that for a Gaussian Peak

$$I = \int_{-\infty}^{+\infty} A \exp\left(\frac{-x^2}{2\sigma^2}\right) dx = \sqrt{2\pi}\,\sigma A$$

Hence for the ratio of Intensities

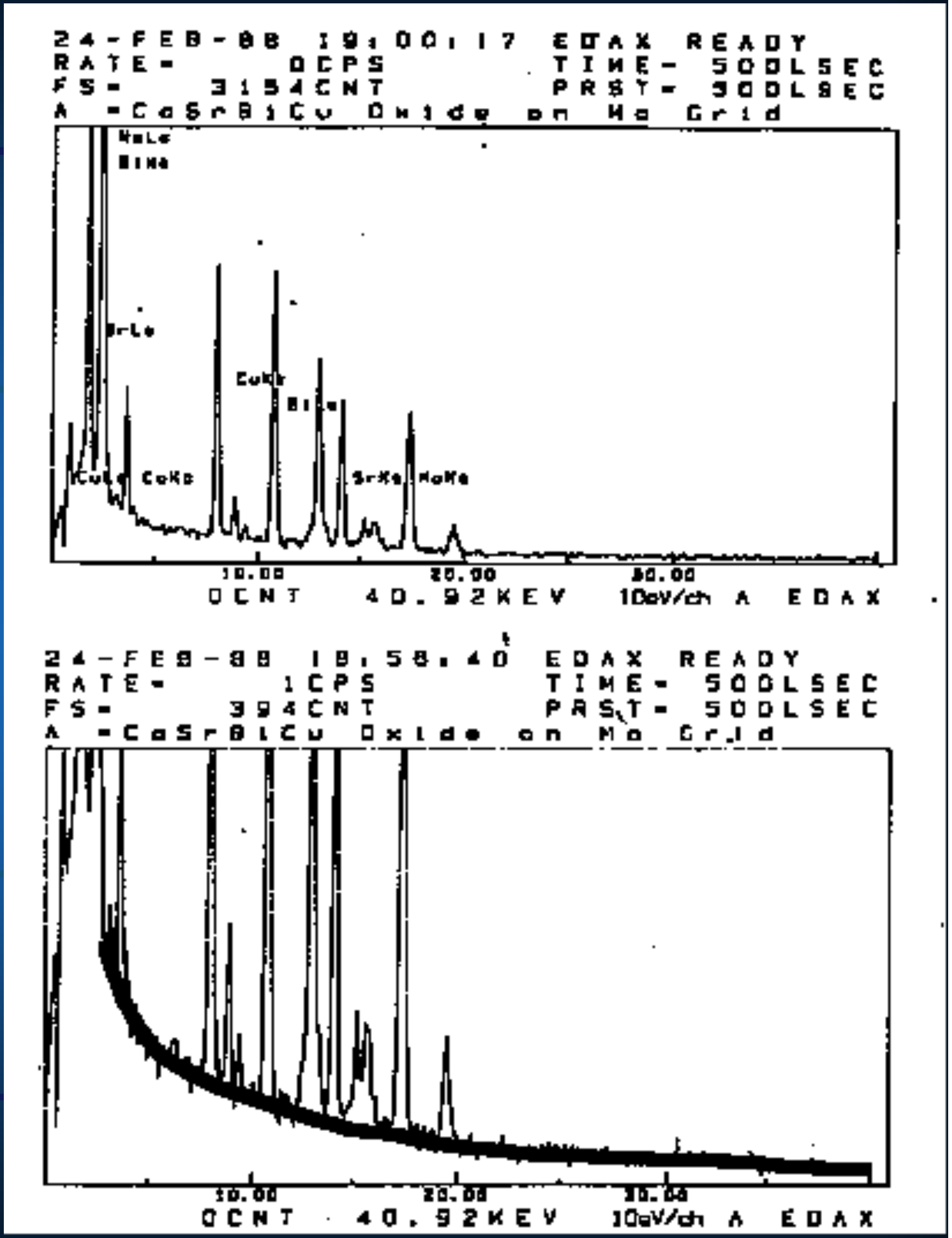
$$\frac{I_1}{I_2} = \frac{\sigma_1 * A_1}{\sigma_2 * A_2} \neq \frac{A_1}{A_2}$$

Spectral Processing : XEDS

Background Modeling :
Power Law/Parametric Fits

$$\text{Bgnd} = \varepsilon * \left\{ A\left(\frac{E-E_o}{E}\right)^2 + B\left(\frac{E-E_o}{E}\right) + C \right\}$$

Polynominal expansion
of Kramers Law



```
24-FEB-88  19:00:17  EDAX  READY
RATE=        0CPS          TIME-  500LSEC
FS=       3154CNT          PRST=  500LSEC
A  =CaSrBiCu Oxide on Mo Grid
```

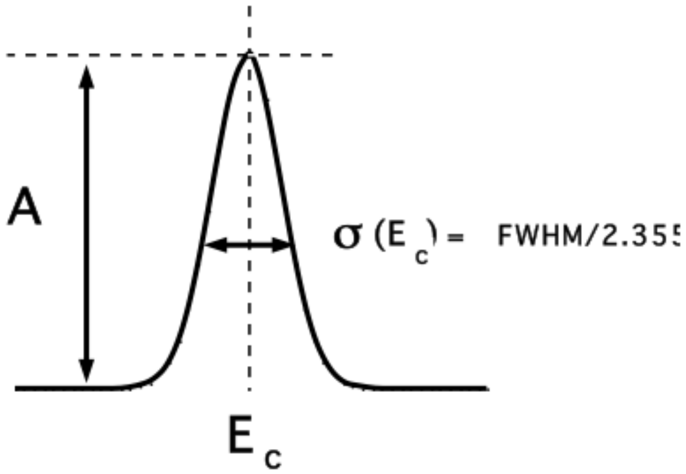
```
0CNT    40.92KEV    10eV/ch  A  EDAX
```

```
24-FEB-88  18:58:40  EDAX  READY
RATE=        1CPS          TIME=  500LSEC
FS=        394CNT          PRST=  500LSEC
A  =CaSrBiCu Oxide on Mo Grid
```

```
0CNT    40.92KEV    10eV/ch  A  EDAX
```

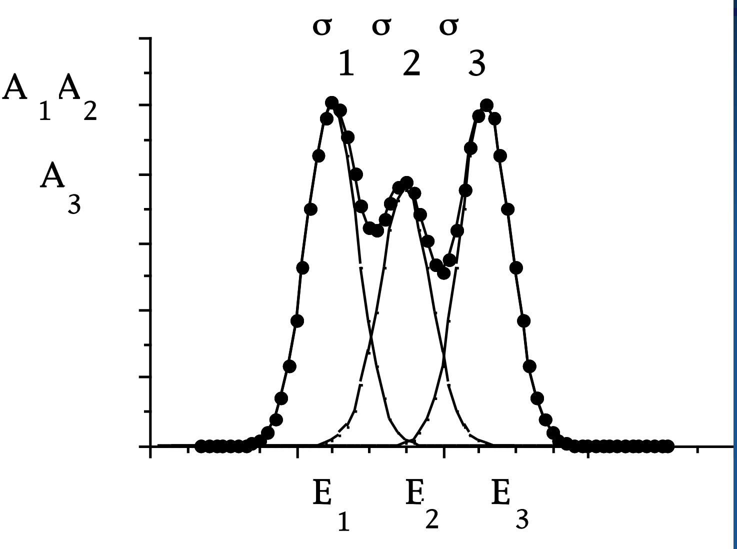
- Remove Background
- Describe Peaks as Gaussians

$$I(E) = A \exp\left(\frac{-(E-E_C)^2}{2\sigma_{E_C}{}^2}\right)$$



- Implement a Least-Squares Minimization to Theoretical or Reference Spectra
  - Linear Modeling:
    Solve for best A with E_C, σ_{E_C}, as known values
  - Non-Linear Modeling:
    Solve for best values of A, E_C, σ_{E_C}

Spectral Processing : XEDS
Curve Fitting : Linear Modeling



Let

$$G_{ij} = \exp\left(\frac{-(E_j - E_i)^2}{2\sigma_{Ei}^2}\right)$$

then

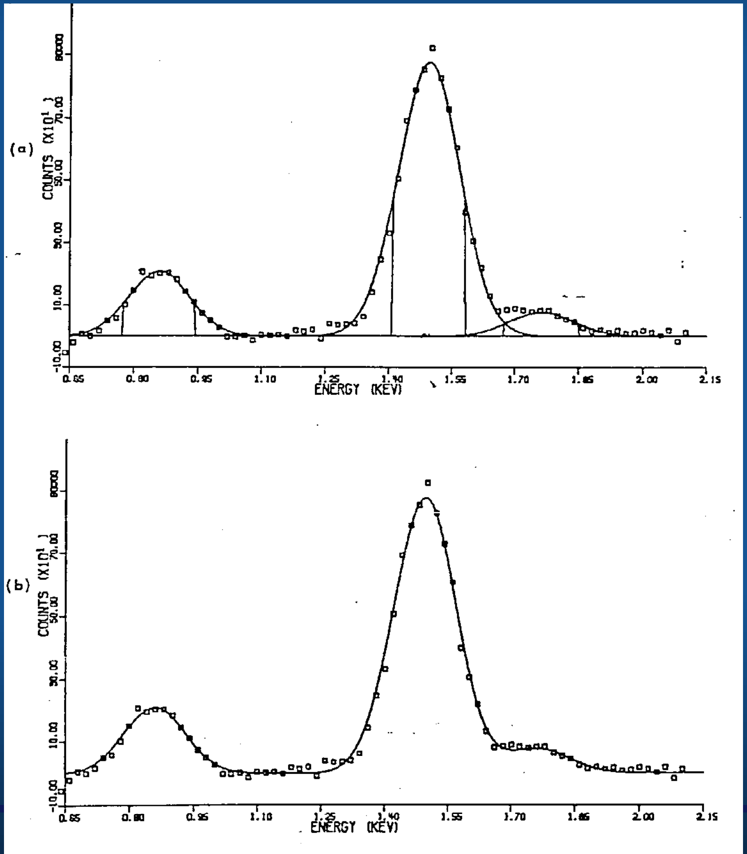
$$\begin{aligned} Y_1 &= A_1 * G_{11} + A_2 * G_{21} + A_3 * G_{31} \\ Y_2 &= A_1 * G_{12} + A_2 * G_{22} + A_3 * G_{32} \\ Y_3 &= A_1 * G_{13} + A_2 * G_{23} + A_3 * G_{33} \end{aligned}$$

Using simple matrix algebra solve for A

- **Fast and simple procedure**
- **Presumes operator knows all elements present**

*** System must be calibrated**
(i.e. E_c and σ_E must be accurately known)

Spectral Processing : XEDS
Curve Fitting : Linear Modeling

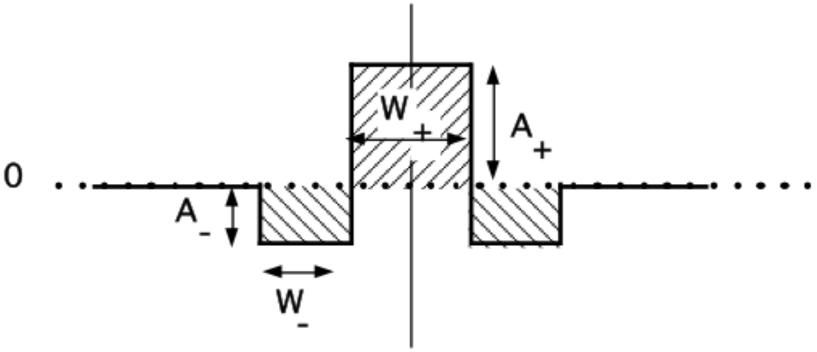


Spectral Processing : XEDS
Digital Filtering

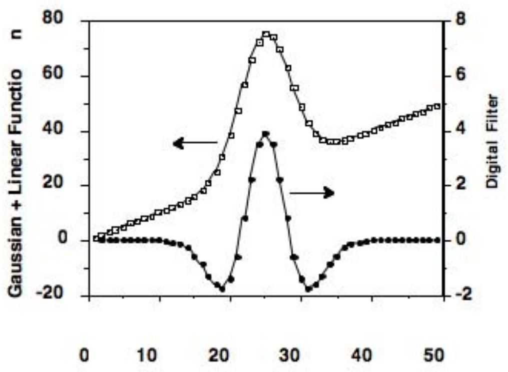
Background Suppression by Mathematical modeling
- Replace Data by new spectra formed by the following linear operation.

$$G(x_i) = [F(x_{+1}) - 2*(\frac{W_-}{W_+})* F(x_0) + F(x_{-1})] \quad \text{where } F(x_j) = \Sigma f(x_j)$$

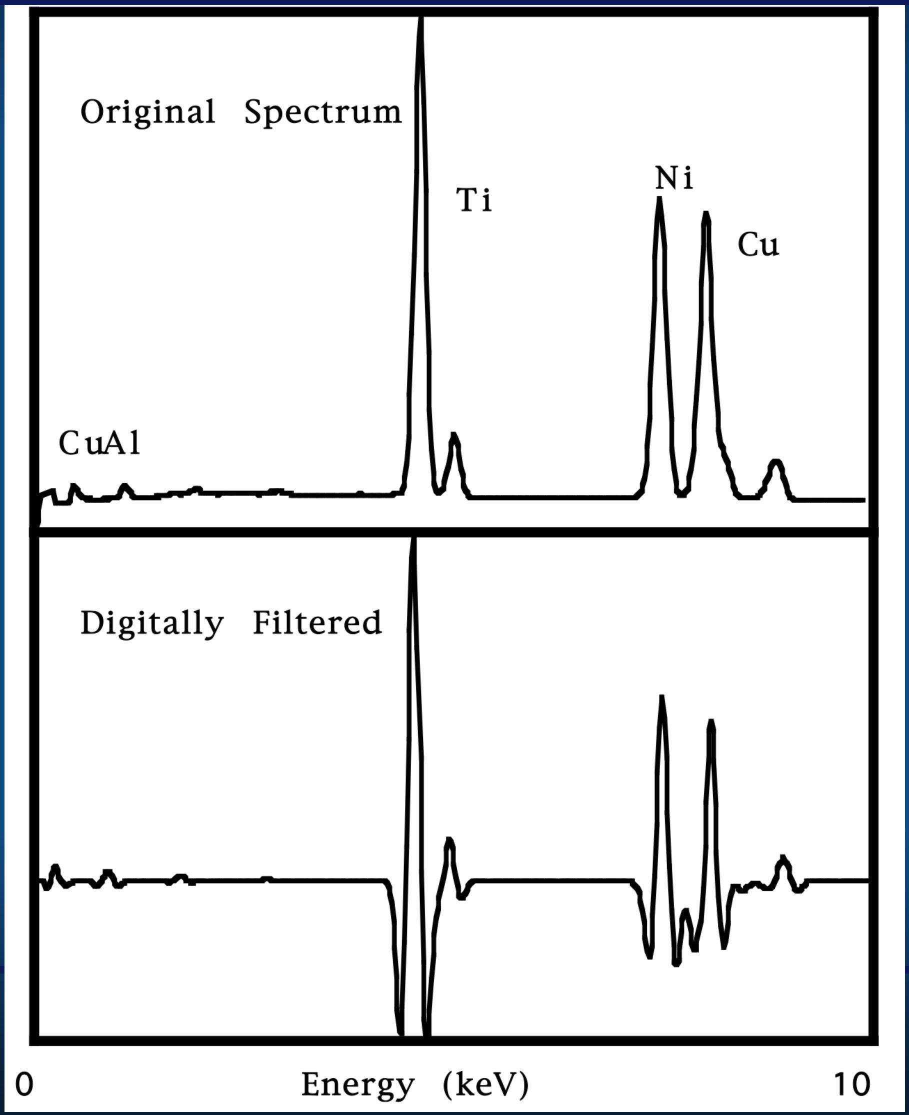
First Order (Top Hat) Digital Filter



Operator independent
Introduces severe spectral distortion



Spectral Processing : XEDS
Digital Filtering



Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects:

Okay we can detect elements
How do we Quantify things?

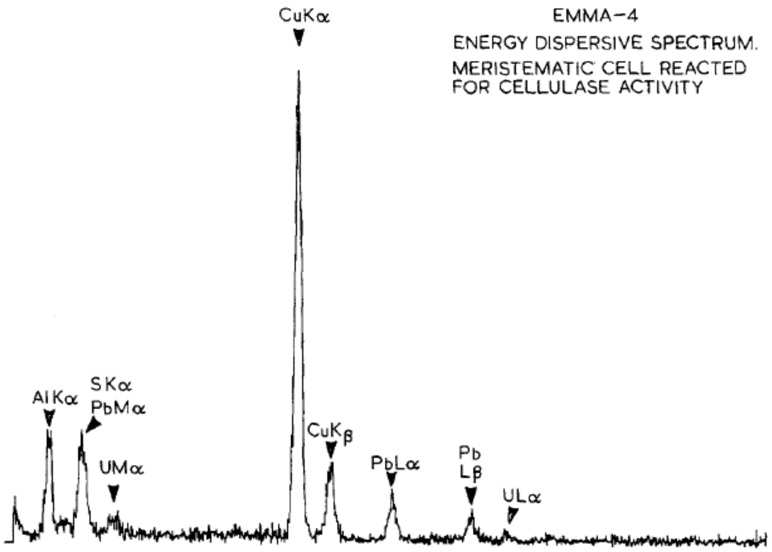
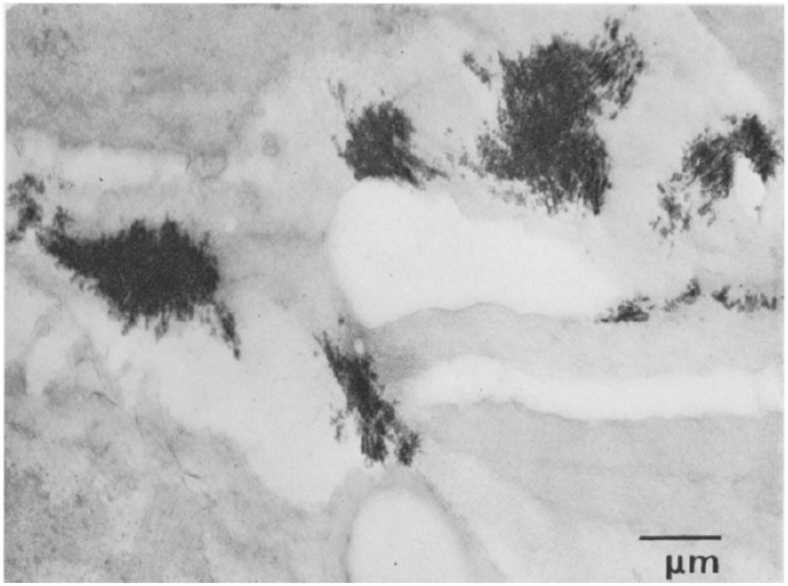
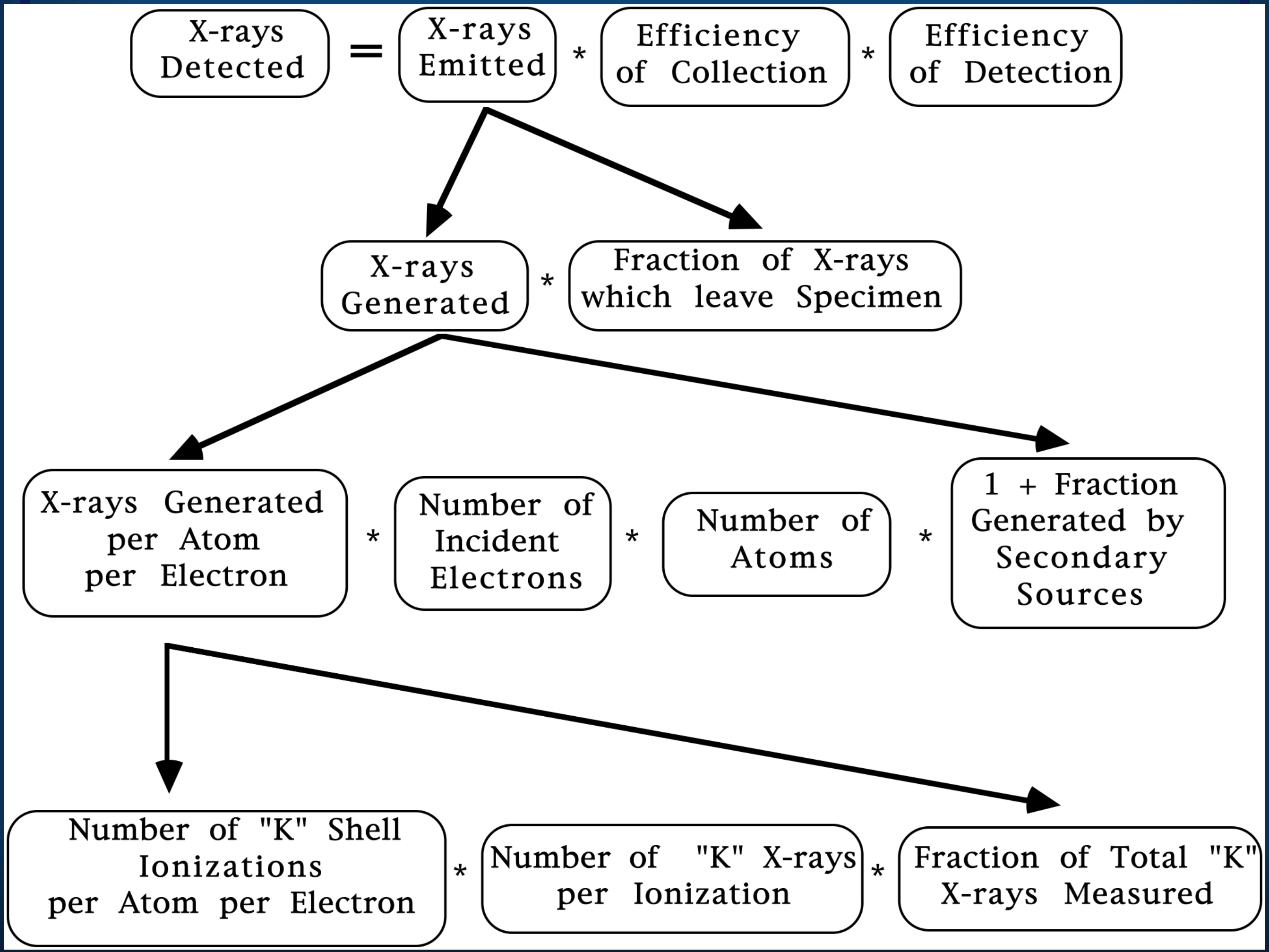


Figure 9. Energy dispersive spectrum of the final reaction product of cellulase activity (Bal, 1972; Weavers & Bal, 1972).



X-Ray Production



X-rays Detected = X-rays Emitted * Efficiency of Collection * Efficiency of Detection

X-rays Generated * Fraction of X-rays which leave Specimen

X-rays Generated per Atom per Electron * Number of Incident Electrons * Number of Atoms * 1 + Fraction Generated by Secondary Sources

Number of "K" Shell Ionizations per Atom per Electron * Number of "K" X-rays per Ionization * Fraction of Total "K" X-rays Measured

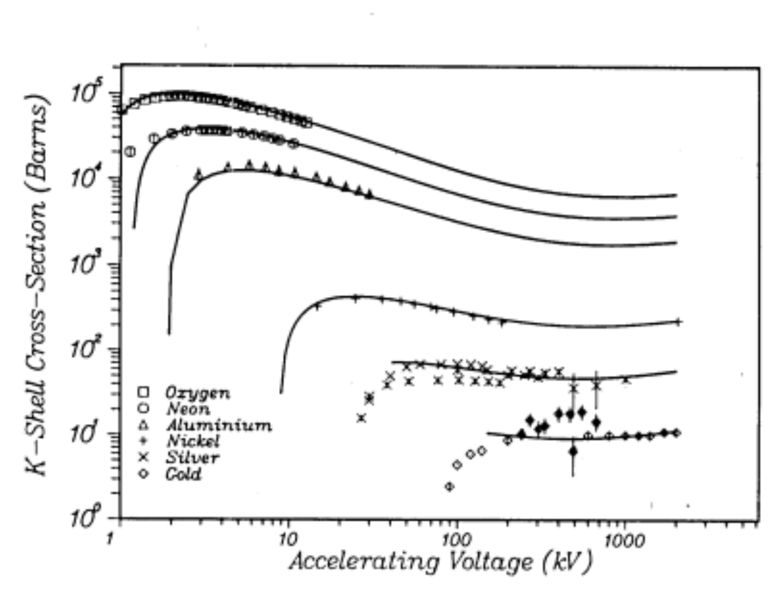
Quantitative Analysis Equations

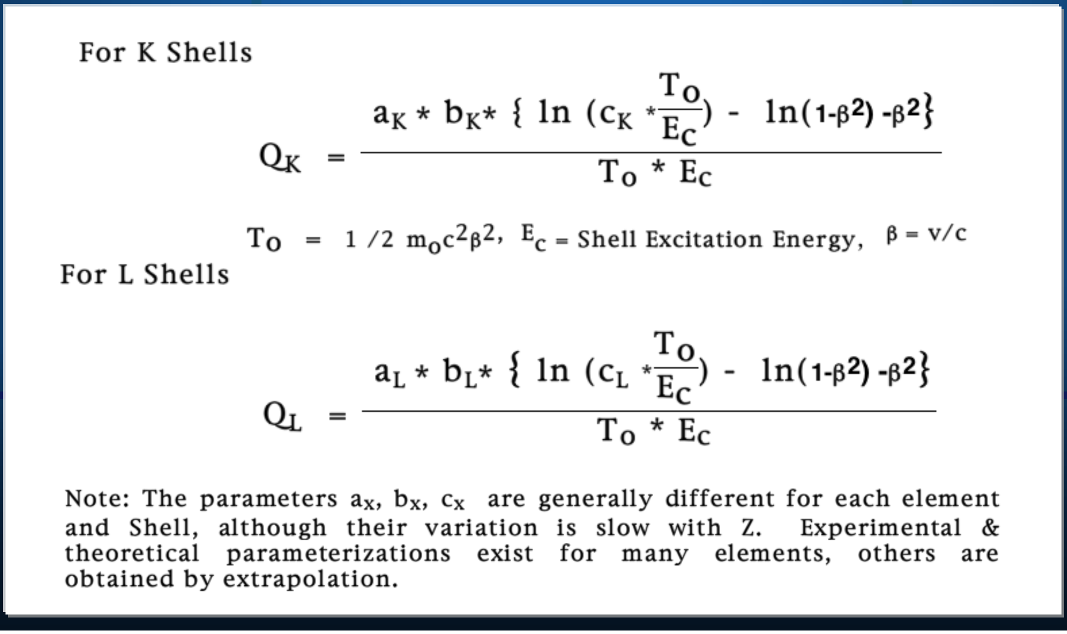
For a thin specimen

$$I_A^{K\alpha} = \{\sigma_A(E,Z)\Gamma_A\omega_A\}C_A\left\{\frac{N_o\rho}{W_A}\right\}\{\eta_o\ t\}\{\ \varepsilon_A\ \Omega\}$$

I_A = Measured x-ray intensity per unit area
σ = Kth-shell ionization cross-section
ω = Kth-shell fluorescence yield
Γ = Kth-shell radiative partition function
W = Atomic Weight
N_o = Avagodro's number
ρ = Density
C = Composition (At %)
η_o = Incident electron flux
t = Specimen thickness
ε = Detector efficiency
Ω = Detector solid angle

Ionization Cross-Section





For K Shells

$$Q_K = \frac{a_K * b_K * \{ \ln (c_K * \frac{T_o}{E_c}) - \ln(1-\beta^2) - \beta^2 \}}{T_o * E_c}$$

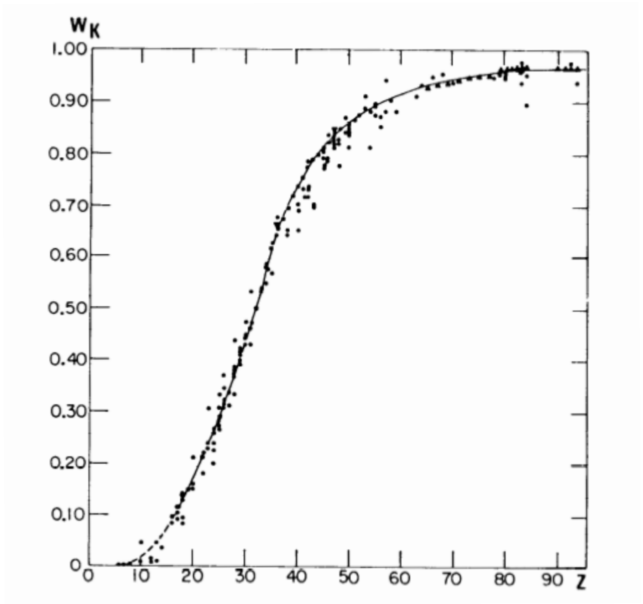
$T_o = 1/2\, m_o c^2 \beta^2$, E_c = Shell Excitation Energy, $\beta = v/c$

For L Shells

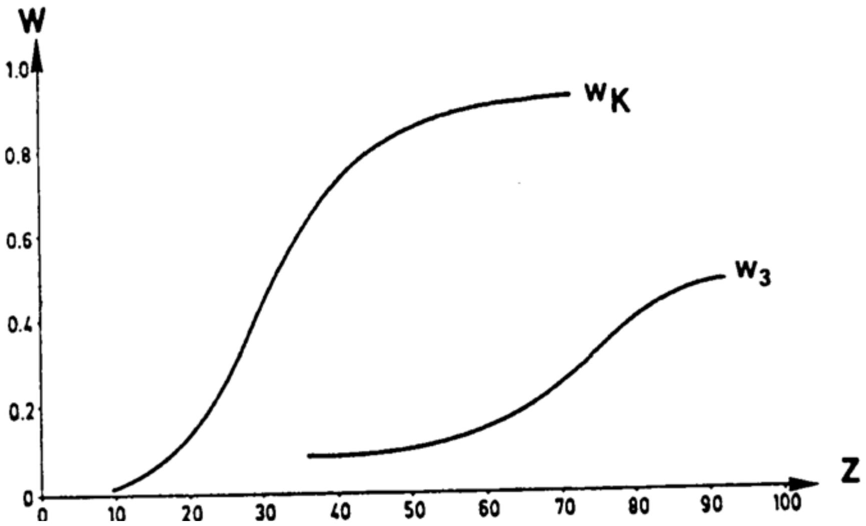
$$Q_L = \frac{a_L * b_L * \{ \ln (c_L * \frac{T_o}{E_c}) - \ln(1-\beta^2) - \beta^2 \}}{T_o * E_c}$$

Note: The parameters a_x, b_x, c_x are generally different for each element and Shell, although their variation is slow with Z. Experimental & theoretical parameterizations exist for many elements, others are obtained by extrapolation.

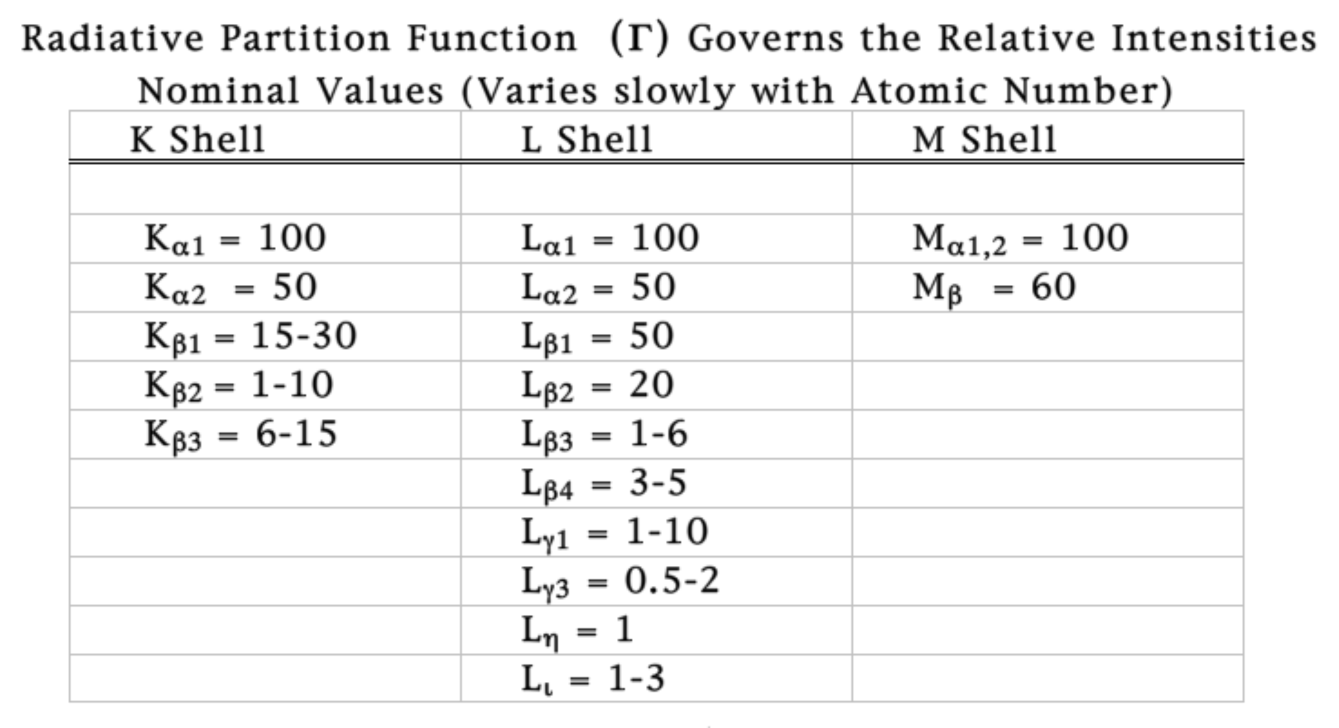
X-ray Fluorescence Yield has Systematic Variation With Atomic Number



ω_K shell



ω_K vs ω_L shell



Radiative Partition Function (Γ) Governs the Relative Intensities

Nominal Values (Varies slowly with Atomic Number)

K Shell	L Shell	M Shell
$K_{\alpha1}$ = 100	$L_{\alpha1}$ = 100	$M_{\alpha1,2}$ = 100
$K_{\alpha2}$ = 50	$L_{\alpha2}$ = 50	M_{β} = 60
$K_{\beta1}$ = 15-30	$L_{\beta1}$ = 50	
$K_{\beta2}$ = 1-10	$L_{\beta2}$ = 20	
$K_{\beta3}$ = 6-15	$L_{\beta3}$ = 1-6	
	$L_{\beta4}$ = 3-5	
	$L_{\gamma1}$ = 1-10	
	$L_{\gamma3}$ = 0.5-2	
	L_{η} = 1	
	L_{ι} = 1-3	

Quantitative Analysis using XEDS
Standardless Method

Invoke the Intensity Ratio Method, that is consider the ratio of x-ray lines from two elements

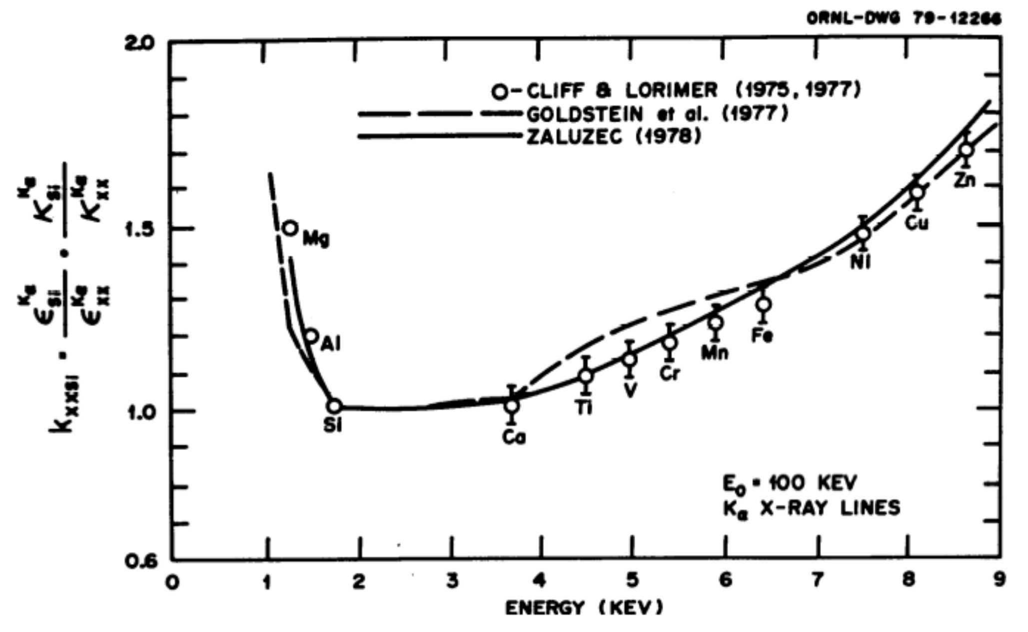
$$\frac{I_A}{I_B} = \frac{\kappa_A\, \varepsilon_A\, C_A}{\kappa_B\, \varepsilon_B\, C_B} = k_{AB}{}^{-1}\,\frac{C_A}{C_B}$$

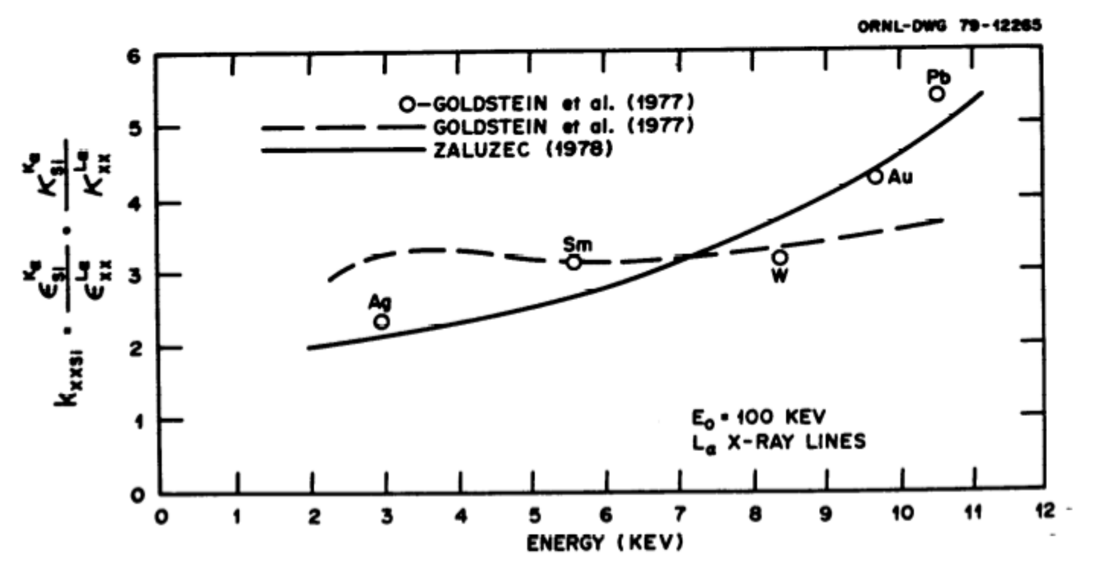
$$\kappa_A = \frac{\sigma_A \omega_A \Gamma_A}{W_A}$$

$$\frac{\kappa_A\, \varepsilon_A}{\kappa_B\, \varepsilon_B} = k_{AB}{}^{-1} \quad \text{(k-factor)}$$

This simple equation states that the relative intensity ratio of any two characteristic x-ray lines is directly proportional to the relative composition ratio of their elemental components multiplied by some "constants" and is independent of thickness.

NOTE: **The k_{AB} factor is not a universal constant!!**
Only the ratio of κ_A/κ_B is a true physical constant and is independant of the AEM system. The ratio of $\varepsilon_A/\varepsilon_B$ is not a constant since no two detectors are identical over their entire operational range. This can cause problems in some cases as we shall see.


ORNL-DWG 79-12266
O- CLIFF & LORIMER (1975, 1977)
GOLDSTEIN et al. (1977)
ZALUZEC (1978)
$k_{xxSi} = \frac{\epsilon_{Si}^{K_\alpha}}{\epsilon_{xx}^{K_\alpha}} \cdot \frac{K_{Si}^{K_\alpha}}{K_{xx}^{K_\alpha}}$
2.0
1.5
1.0
0.6
Mg
Al
Si
Ca
Ti
V
Cr
Mn
Fe
Ni
Cu
Zn
E_0 = 100 KEV
K_α X-RAY LINES
0
1
2
3
4
5
6
7
8
9
ENERGY (KEV)


ORNL-DWG 79-12265
O- GOLDSTEIN et al. (1977)
GOLDSTEIN et al. (1977)
ZALUZEC (1978)
$k_{xxSi} = \frac{\epsilon_{Si}^{K_\alpha}}{\epsilon_{xx}^{L_\alpha}} \cdot \frac{K_{Si}^{K_\alpha}}{K_{xx}^{L_\alpha}}$
6
5
4
3
2
1
0
Ag
Sm
W
Au
Pb
E_0 = 100 KEV
L_α X-RAY LINES
0
1
2
3
4
5
6
7
8
9
10
11
12
ENERGY (KEV)

The analysis to this point has only yielded the **relative compositions** of the specimen. We need one additional assumption to convert the relative intensity ratio's (I_i/I_j) into compositions namely:

$$\sum_{i=1}^{N} C_i = 1.0$$

One now has a set of N equations and N unknowns which be solved algebraically solved for the individual composition values.

Thus for a simple two element system we have:

$$\frac{I_A}{I_B} = k_{AB}^{-1} \frac{C_A}{C_B}$$

and

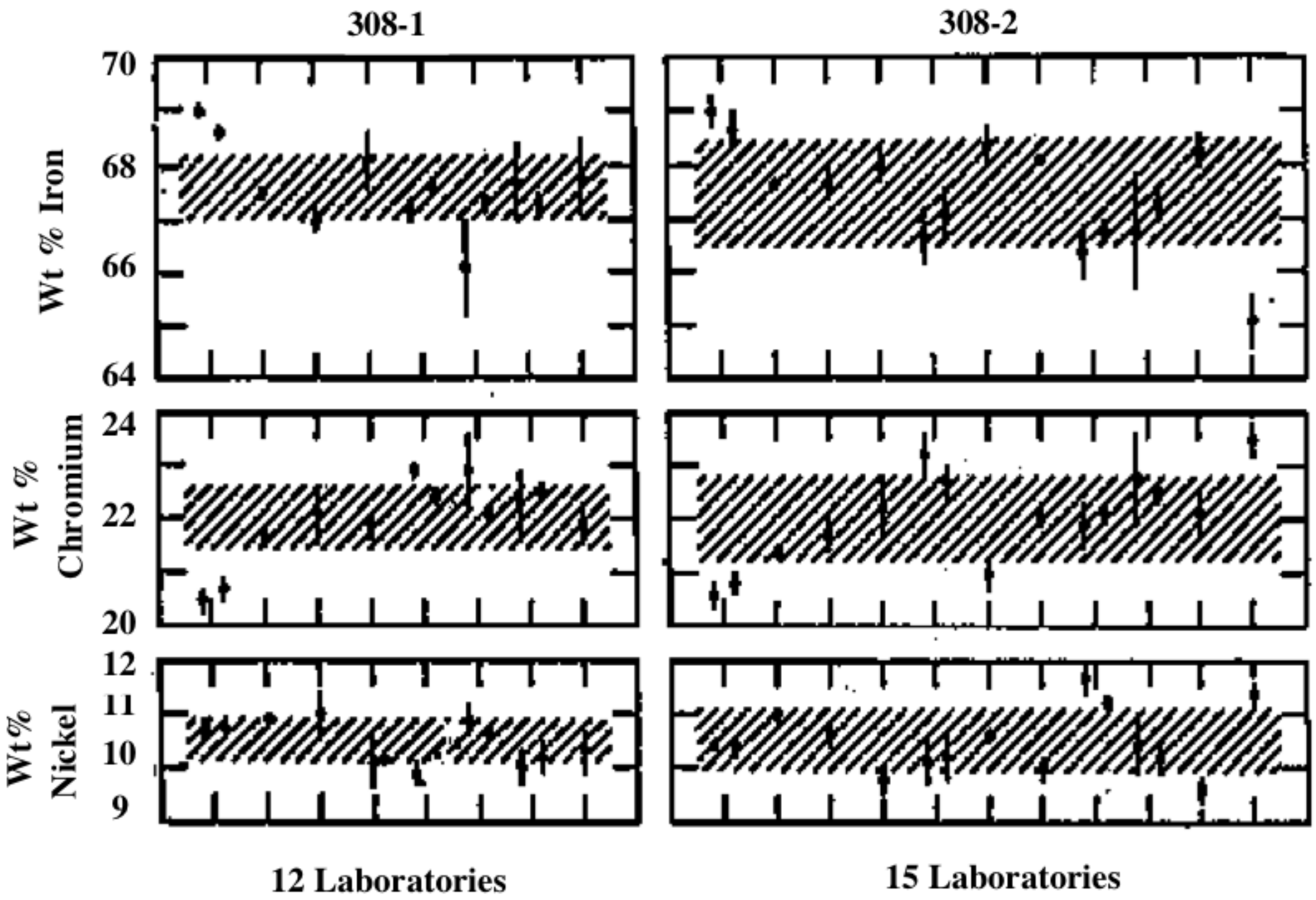
$$C_A + C_B = 1.$$

or

$$C_B \left(\frac{C_A}{C_B} + 1\right) = 1$$

Solving for C_B and C_A

$$C_B = \left(\frac{1}{(1+\frac{C_A}{C_B})}\right) = \left(\frac{1}{(1+\frac{I_A}{I_B} * k_{AB})}\right) \quad \text{and} \quad C_A = C_B - 1$$



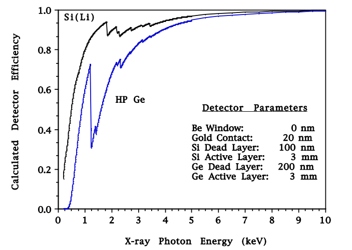
Vitek et al, AEM, 1984

Variation in Measured Composition on 308 SS for Different Labs

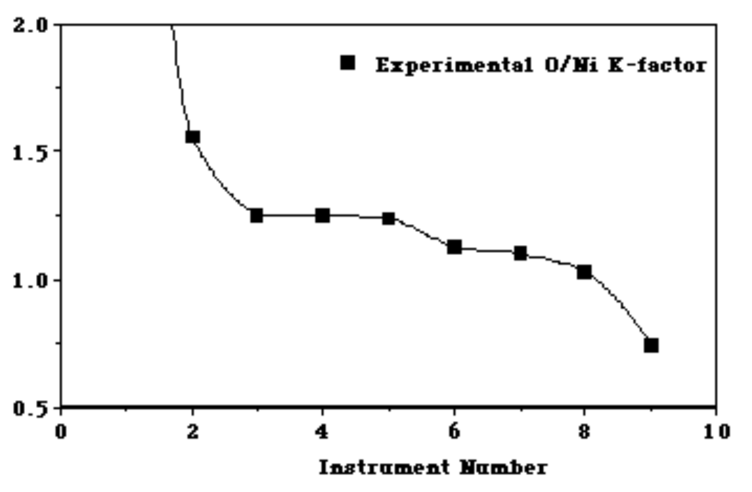
Example in which K-factor is stable

Cr, Fe, Ni

Note: Detector efficiency ~ 100% in this energy range



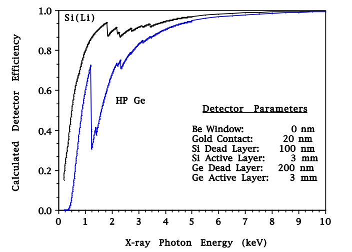
Variation in K-factor with AEM/Detector System
Specimen: Uniform NiO film on Be Grid



Instrument	Experimental K -Factor	Apparent Variation in Composition
1	5.17	80.9/19.1
2	1.56	56.1/43.9
3	1.25	50.6/49.4
4	1.25	50.6/49.4
5	1.24	50.4/49.5
6	1.13	48.1/51.9
7	1.10	47.4/52.6
8	1.03	45.8/54.2
9	0.74	37.8/62.2

From: Comparison of UTW/WL X-ray Detectors on TEM/STEMs and STEMs

Thomas, Charlot, Franti, Garratt-Reed, Goodhew, Joy, Lee, Ng, Plicta, Zaluzec.
Analytical Electron Microscopy-1984



Determining the k_{AB}^{-1} **Factor**

Experimental Measurements

Prepare thin-film standards of known composition then measure relative intensities and solve explicitly for the k_{AB} factor needed. Prepare a working data base.

This is the "best" method, but
- specimen composition must be verified independently
- must have a standard for every element to be studied

Theoretical Calculations

Attempt first principles calculation knowing
some fundamental parameters of the AEM system

Start with a limited number of kAB factor measurements,
then fit the AEM parameters to best match the data.
Extrapolate to systems where measurements and/or
standards do not exist.

- **Method 1**. (Goldstein etal) Assume values for Γ,ω,ε and determine the best s to fit $k_{AB.}$ This procedure essentially iterates the fit of s to the data.

Method 2. (Zaluzec) Assume values for Γ,ω,σ determine the best e to fit $k_{AB.}$ This procedure essentially iterates the fit of e (detector window parameters) to the data.

Sources of values for k_{AB} Calculations

W - International Tables of Atomic Weights

Γ(K) - Schreiber and Wims , X-ray Spectroscopy (1982)
Vol 11, p. 42

Γ(L) - Scofield, Atomic and Nuclear Data Tables (1974)
Vol 14, #2, p. 121

ω (K) - Bambynek etal, Rev. Mod. Physics, Vol 44, p. 716
Freund, X-ray Spectrometry, (1975) Vol 4, p.90

ω(L) - Krause, J. Phys. Chem. Ref. Data (1974) Vol 8,
p.307

σ(Eo) - Inokuti, Rev. Mod. Physics, 43, No. 3, 297 (1971)
- Goldstein etal, SEM 1, 315, (1977)
- Chapman etal, X-ray Spectrometry, 12,153,(1983)
- Rez, X-ray Spectrometry, 13, 55, (1984)
- Egerton, Ultramicroscopy, 4, 169, (1969)
- Zaluzec, AEM-1984, San Fran. Press. 279, (1984)

ε (E) - Use mass absorption coefficients from:
-Thinh and Leroux; X-ray Spect. (1979), 8, p. 963
-Henke and Ebsiu, Adv. in X-ray Analysis,17, (1974)
-Holton and Zaluzec, AEM-1984, San Fran Press,353,(1984)

Quantitative Analysis using XEDS

Thin Film Standards Method

Invoke the Intensity Ratio Method, but now consider the ratio of the same x-ray line from two different specimens, where one is from a **standard** of known composition while the other is **unknown**:

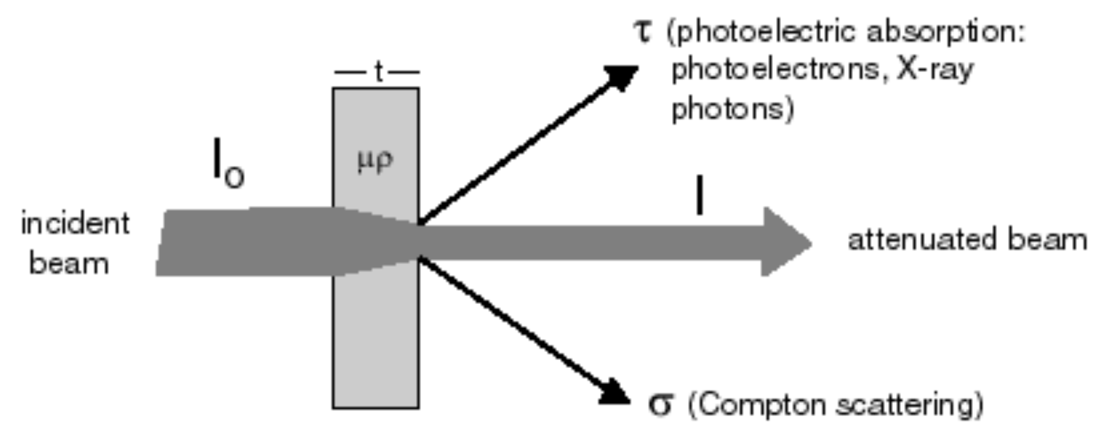
$$\frac{I_u}{I_s} = \frac{\eta_u \rho_u t_u}{\eta_s \rho_s t_s} * \frac{C_u}{C_s}$$

$$C_u = \frac{\eta_s \rho_s t_s}{\eta_u \rho_u t_u} * \frac{I_u}{I_s} * Cs$$

This simple equation states that the relative intensity ratio of same characteristic x-ray line is directly proportional to the relative composition ratio of the two specimens multiplied by a some new parameters.

η = incident beam current
ρ = local specimen density
t = local specimen thickness

X-ray Absorption

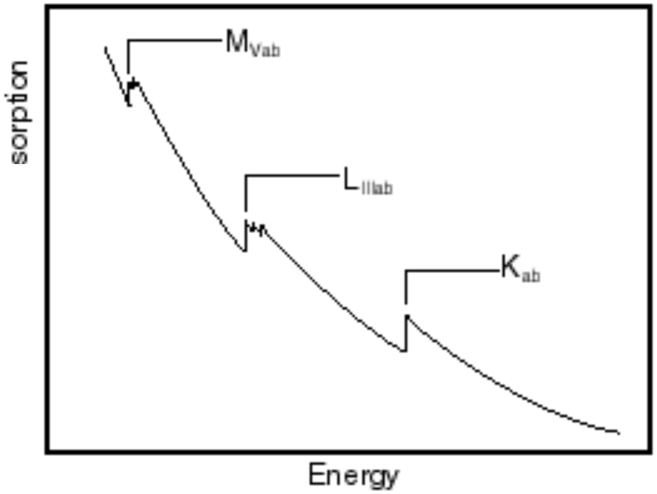


$$\mu = \tau + \sigma$$

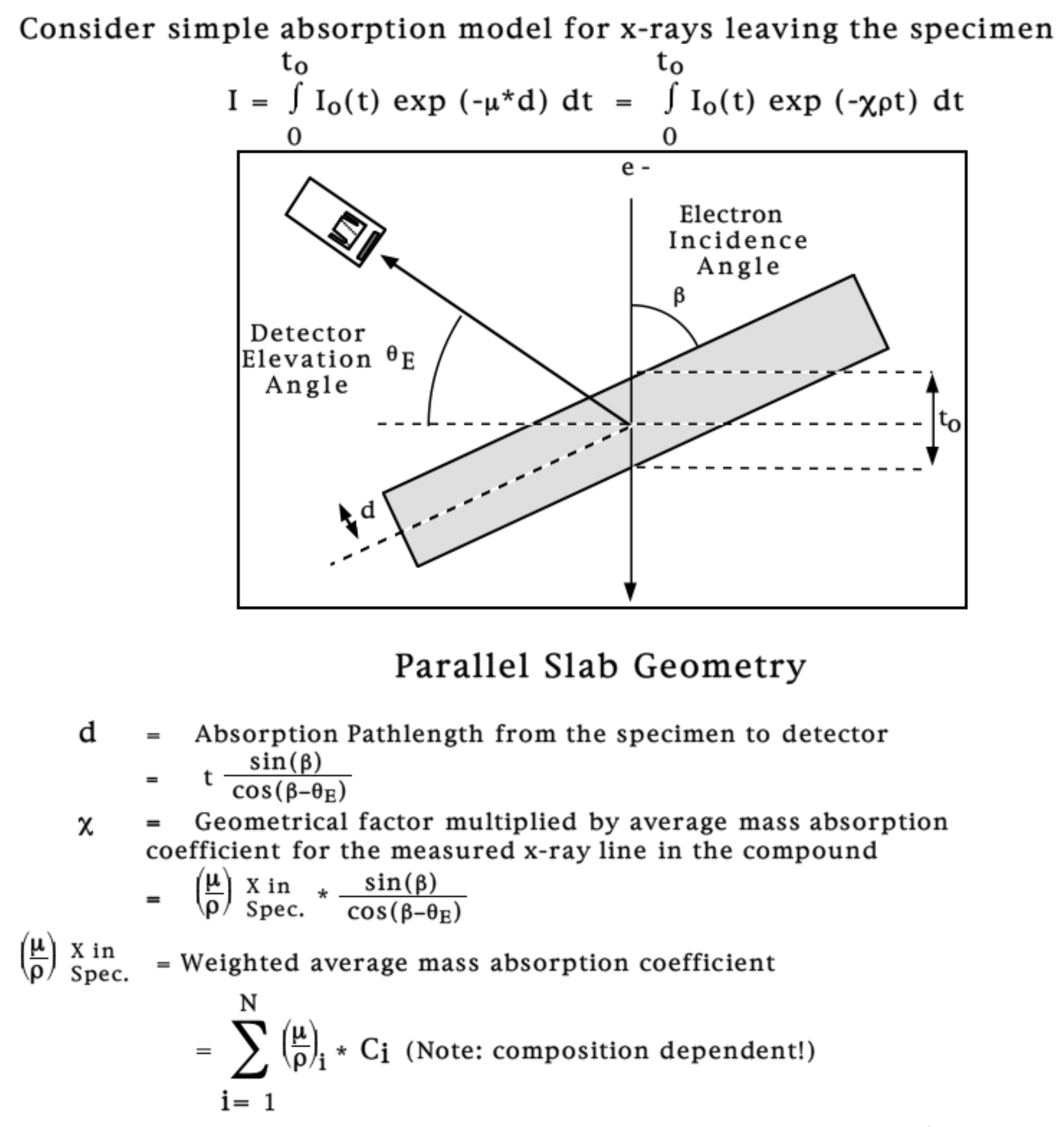
where μ = bulk mass absorption coefficient,
τ = photoelectric absorption coefficient,
σ = Compton scattering coefficient.

$$I = I_O e^{-\mu\rho t}$$

where I_O = initial intensity (cps),
I = final intensity (cps),
μ = bulk mass absorption coefficient of the material (cm^2/g),
ρ = density of the material (g/cm^3),
and t = thickness onf the material (cm).



Quantitative Analysis using XEDS : Absorption Correction



Consider simple absorption model for x-rays leaving the specimen

$$I = \int_{0}^{t_o} I_o(t)\,\exp(-\mu^* d)\,dt = \int_{0}^{t_o} I_o(t)\,\exp(-\chi\rho t)\,dt$$

Parallel Slab Geometry

d = Absorption Pathlength from the specimen to detector

$$= t\,\frac{\sin(\beta)}{\cos(\beta-\theta_E)}$$

χ = Geometrical factor multiplied by average mass absorption coefficient for the measured x-ray line in the compound

$$= \left(\frac{\mu}{\rho}\right)_{\text{X in Spec.}} * \frac{\sin(\beta)}{\cos(\beta-\theta_E)}$$

$\left(\frac{\mu}{\rho}\right)_{\text{X in Spec.}}$ = Weighted average mass absorption coefficient

$$= \sum_{i=1}^{N} \left(\frac{\mu}{\rho}\right)_i * C_i \quad \text{(Note: composition dependent!)}$$

Now rederive the standardless equations to include absorption.

$$\frac{I_A}{I_B} = \frac{\varepsilon_A}{\varepsilon_B} * \frac{\kappa_A}{\kappa_B} * \frac{\delta_A}{\delta_B} * \frac{C_A}{C_B}$$

with

$$\frac{\delta_A}{\delta_B} = \frac{\left(\frac{\mu}{\rho}\right)^{\text{B in}}_{\text{AB}}}{\left(\frac{\mu}{\rho}\right)^{\text{A in}}_{\text{AB}}} \frac{\left(1 - \exp(-\chi\rho t^*)^{\text{A in}}_{\text{AB}}\right)}{\left(1 - \exp(-\chi\rho t^*)^{\text{B in}}_{\text{AB}}\right)}$$

$$t^* = t_o \frac{\sin(\beta)}{\cos(\beta - \theta_E)}$$

$$\chi = \left(\frac{\mu}{\rho}\right)^{\text{X-ray in}}_{\text{Compound}} = \sum_{i=1}^{N} \left(\frac{\mu}{\rho}\right)_i * C_i$$

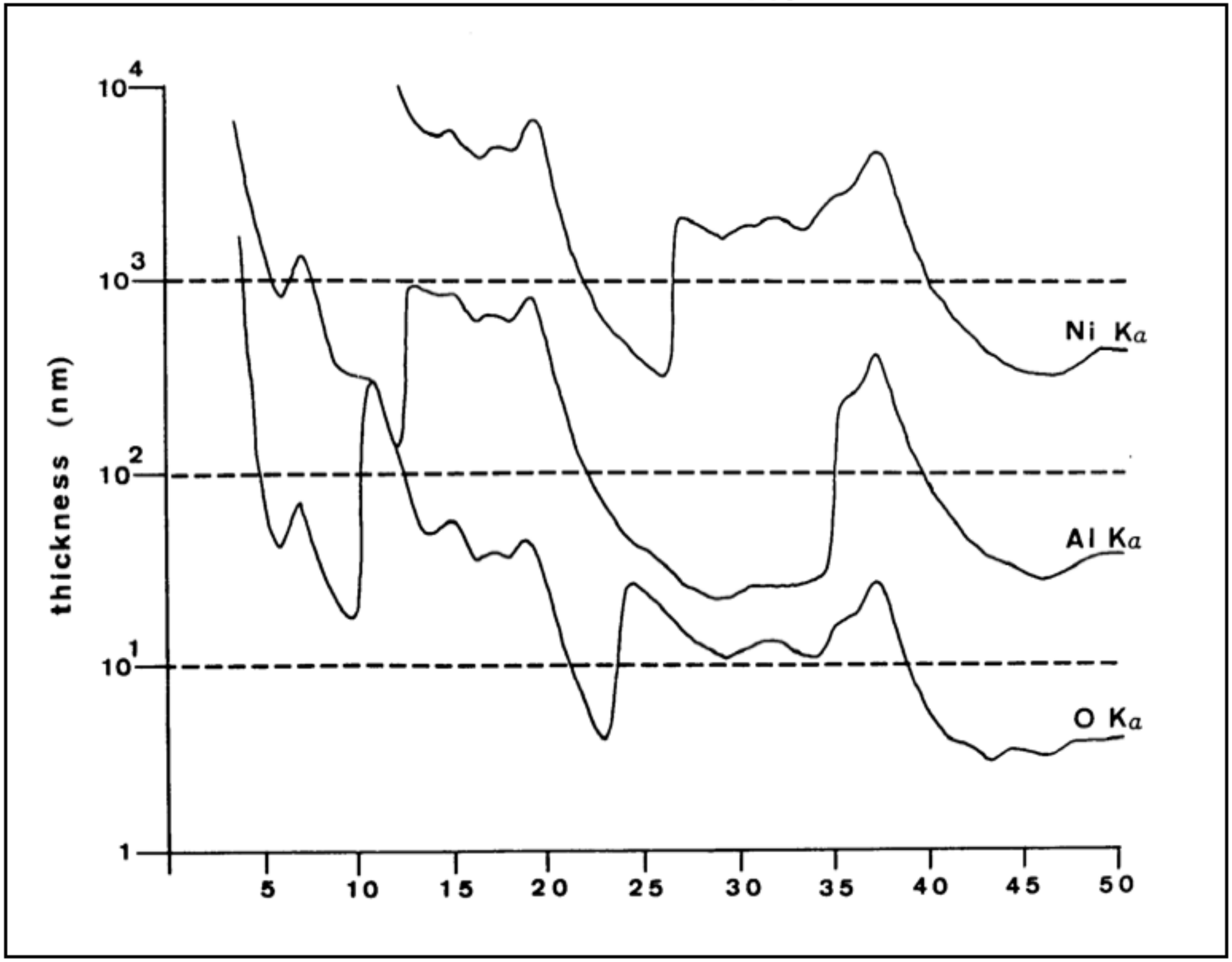
β = Electron Incidence Angle

= Function of Stage Tilts: ϕ_x, ϕ_y, & Detector Azimuth θ_A)

θ_E = Detector Elevation Angle

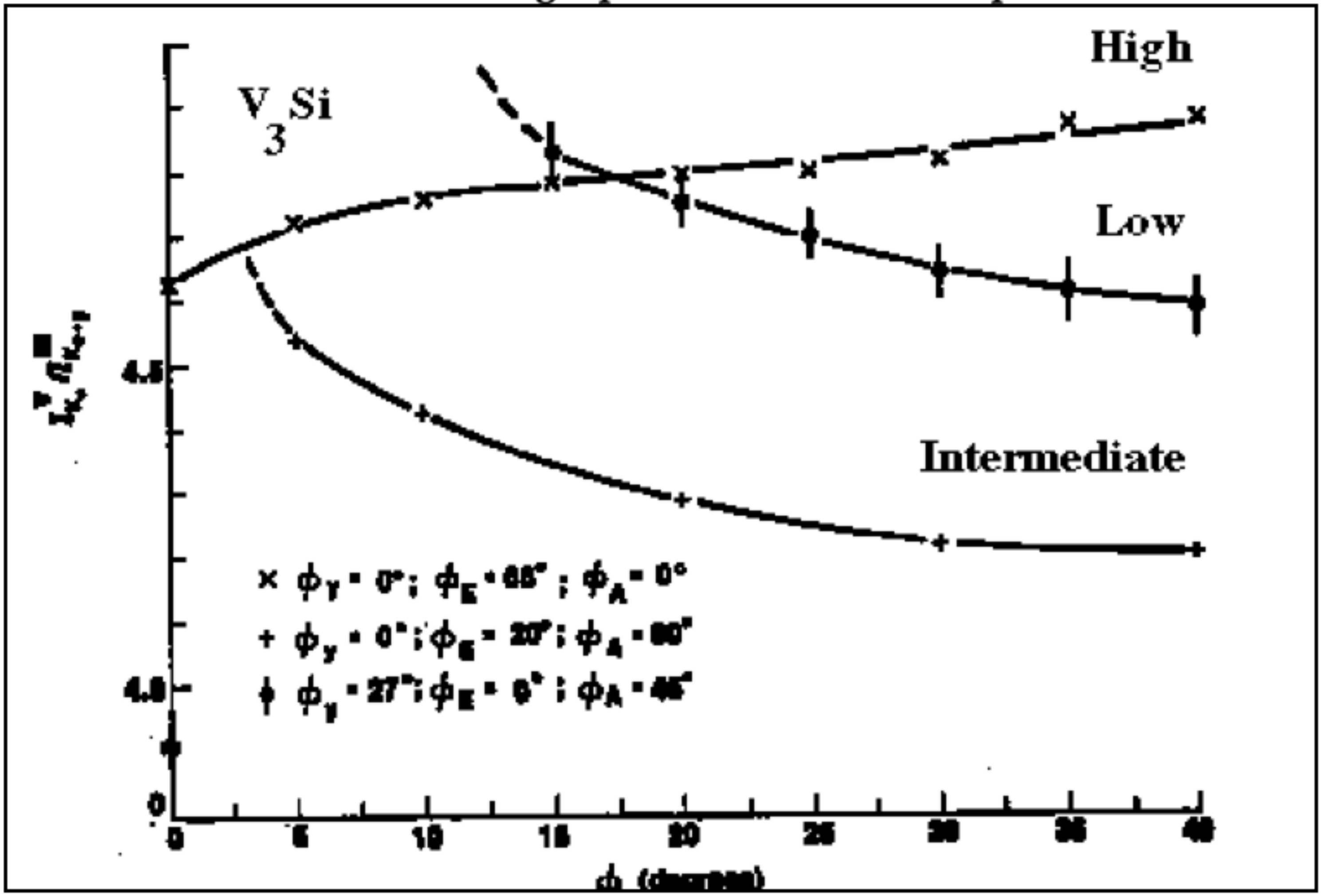
Define the Thin Film approximation: $\chi\rho t^* < 0.1$

Thin Film approximation: $\chi\rho t^* < 0.1$

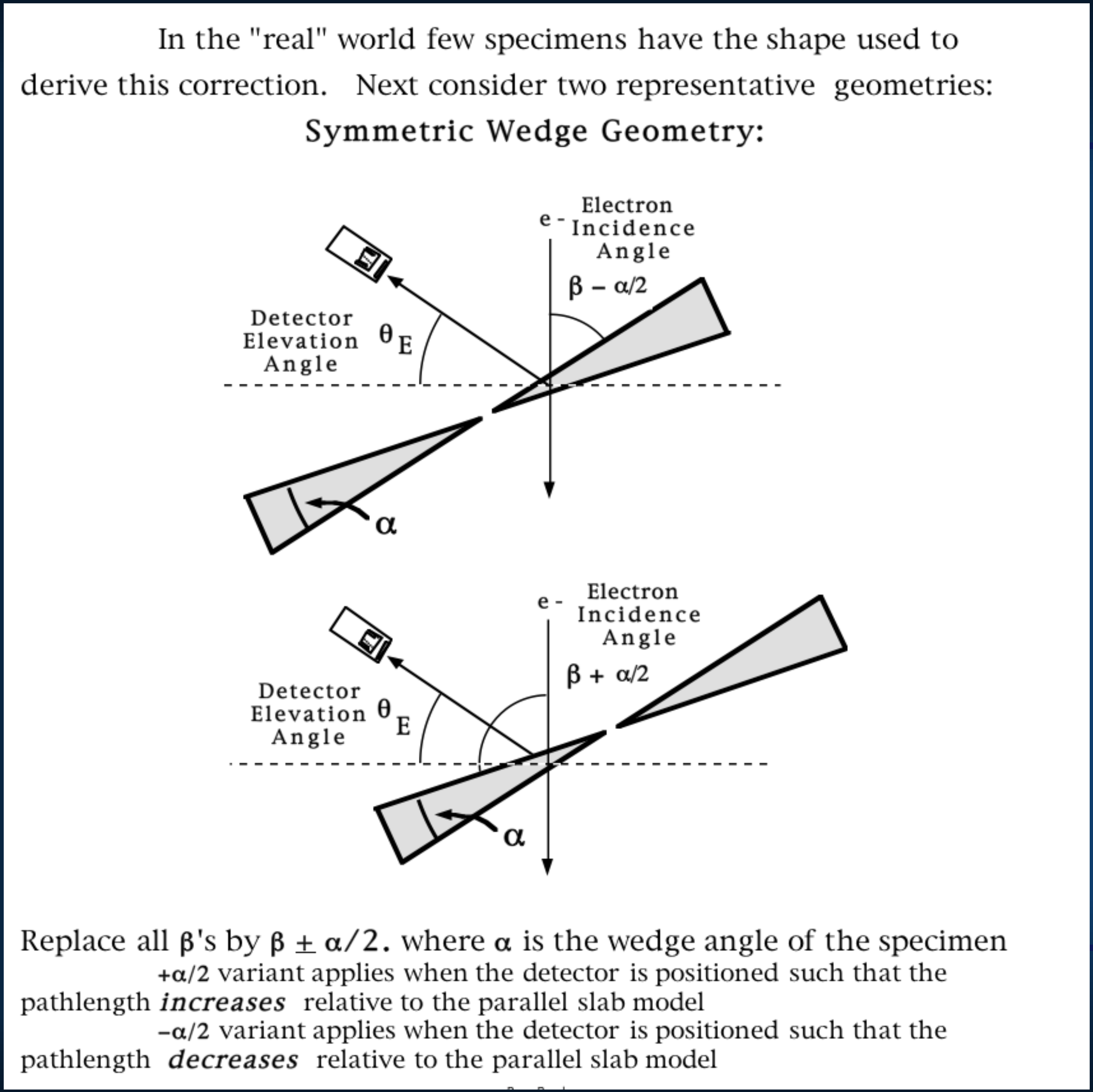


$$t^* \leq \frac{0.1}{\chi\rho}$$

Effect of Tilting Specimen on Absorption



For a plane parallel slab specimen, tilting has the effect of increasing the Specimen Thickness.
Different Detector/Specimen Geometries will enhance/reduce the Absorption Effects



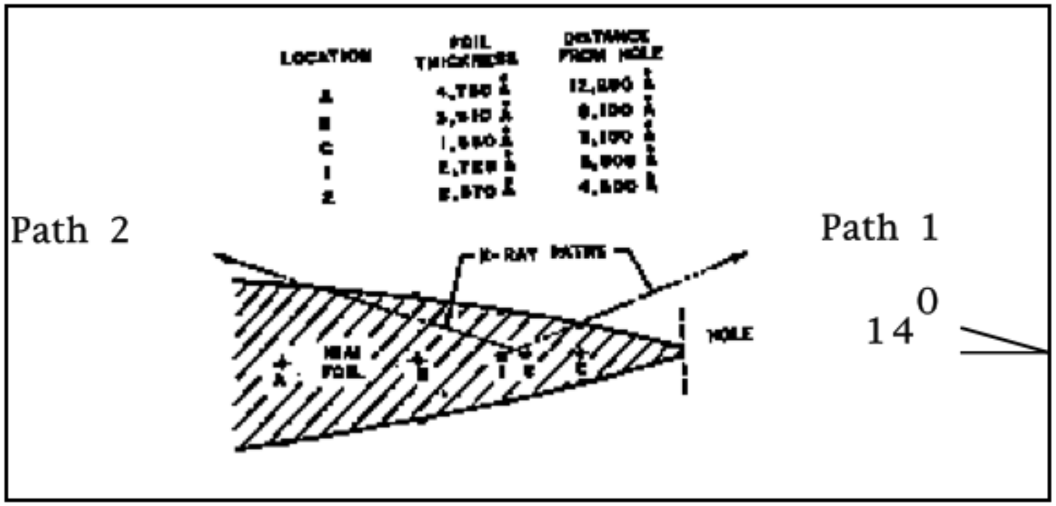
In the "real" world few specimens have the shape used to derive this correction. Next consider two representative geometries:

Symmetric Wedge Geometry:

Replace all β's by $\beta \pm \alpha/2$. where α is the wedge angle of the specimen

$+\alpha/2$ variant applies when the detector is positioned such that the pathlength ***increases*** relative to the parallel slab model

$-\alpha/2$ variant applies when the detector is positioned such that the pathlength ***decreases*** relative to the parallel slab model



Glitz etal (MAS-1981)

Attempt a Wedge Model Correction using previous formulae.

Path #1	Path #2
$\frac{I_{Ni}}{I_{Al}} = 2.64$	$\frac{I_{Ni}}{I_{Al}} = 5.18$
Thin Film Model $\frac{Ni=60.9}{Al=39.1}$	Thin Film Model Error!
Parallel Slab $\frac{Ni=45.3}{Al=54.7}$	Parallel Slab $\frac{Ni=60.5}{Al=39.5}$
Wedge Model $\frac{Ni=50.6}{Al=49.4}$	Wedge Model $\frac{Ni=42.6}{Al=57.4}$
$\chi \rho t_{Ni} = 0.016$	$\chi \rho t_{Ni} = 0.081$
$\chi \rho t_{Ni} = 0.925$	$\chi \rho t_{Ni} = 4.24$

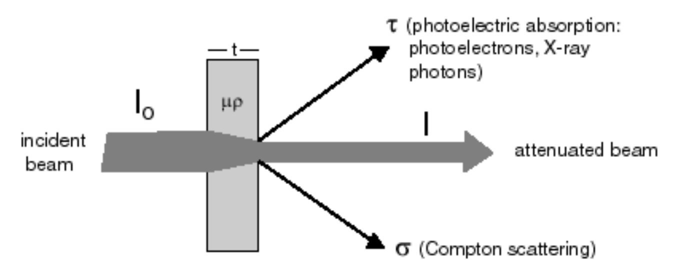
Absorption Correction has limited applications keep $\chi \rho t < 1$

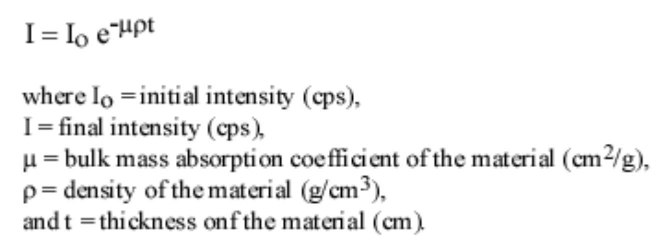
Quantitative Analysis using XEDS
Specimen Thickness Effects

For finite thickness specimens, what is a thin film?

Previous Assumptions:

Energy loss,
X-ray absorption,
No X-ray fluorescence

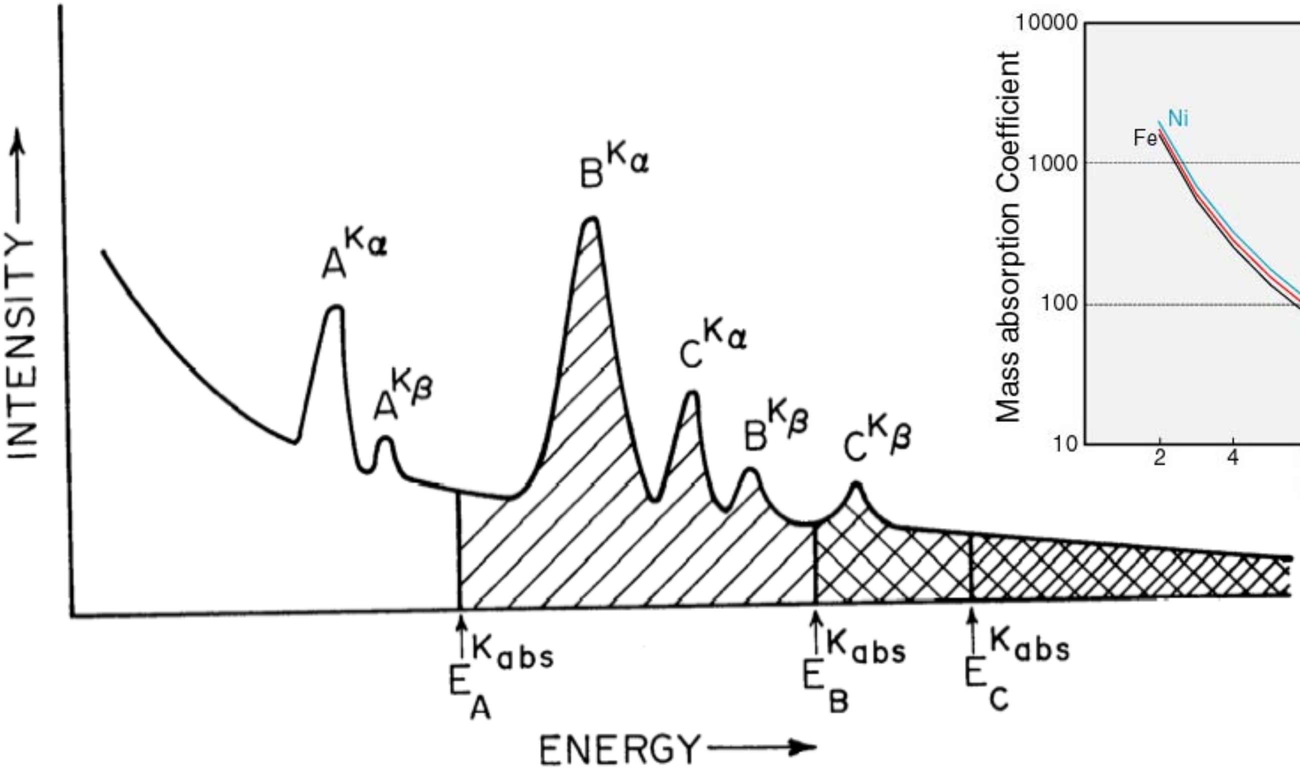


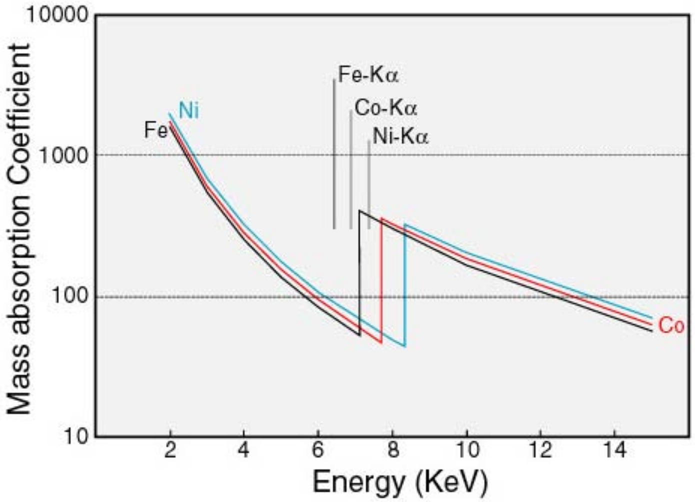


$$I = I_o\, e^{-\mu\rho t}$$

where I_o = initial intensity (cps),
I = final intensity (cps),
μ = bulk mass absorption coefficient of the material (cm^2/g),
ρ = density of the material (g/cm^3),
and t = thickness onf the material (cm).

X-Ray Fluorescence Correction





$$I_A^{\text{Measured}} = I_A^{\text{Electron}} + I_A^{\text{XRF by B}}$$

$$I_A^{\text{Measured}} = I_A^{\text{Electron}} \left(1 + \frac{I_A^{\text{XRF by B}}}{I_A^{\text{Electron}}} \right)$$

Next rederive the standardless equations to include x-ray fluorescence and you can show.

$$\frac{I_A}{I_B} = \frac{\varepsilon_A}{\varepsilon_B} * \frac{\kappa_A}{\kappa_B} * \frac{\delta_A}{\delta_B} * \frac{\gamma_A}{\gamma_B} * \frac{C_A}{C_B}$$

as in the case of x-ray absorption this requires iterative solution because the ratio of γ's are composition dependent..

When is the XRF Correction important?

- When fluorescing line is near the absorption edge of the lower energy line. Typically within a few atomic numbers (i.e. Z+2 to Z+6)
- When specimen is thick or path length is long

Define a thin film approximation for XRF as:

$$\frac{I_A^{\text{XRF by i}}}{I_A^{\text{Electron}}} < 0.05$$

$$C_i \ \omega_i \ \Gamma i \ \frac{A_A}{A_i} \frac{Q_i}{Q_A} \left(\frac{\Delta\mu}{\mu}\right)_A \left(\frac{\mu^i}{\rho}\right)_A \frac{\rho T}{2}\left[1.12 + \left(\frac{\mu^i}{\rho}\right)_{Ai} \bullet \frac{\rho T}{4} - \ln\left(\left(\frac{\mu^i}{\rho}\right)_{Ai} \bullet \rho T\right)\right] < 0.05$$

Specimen Homogenity

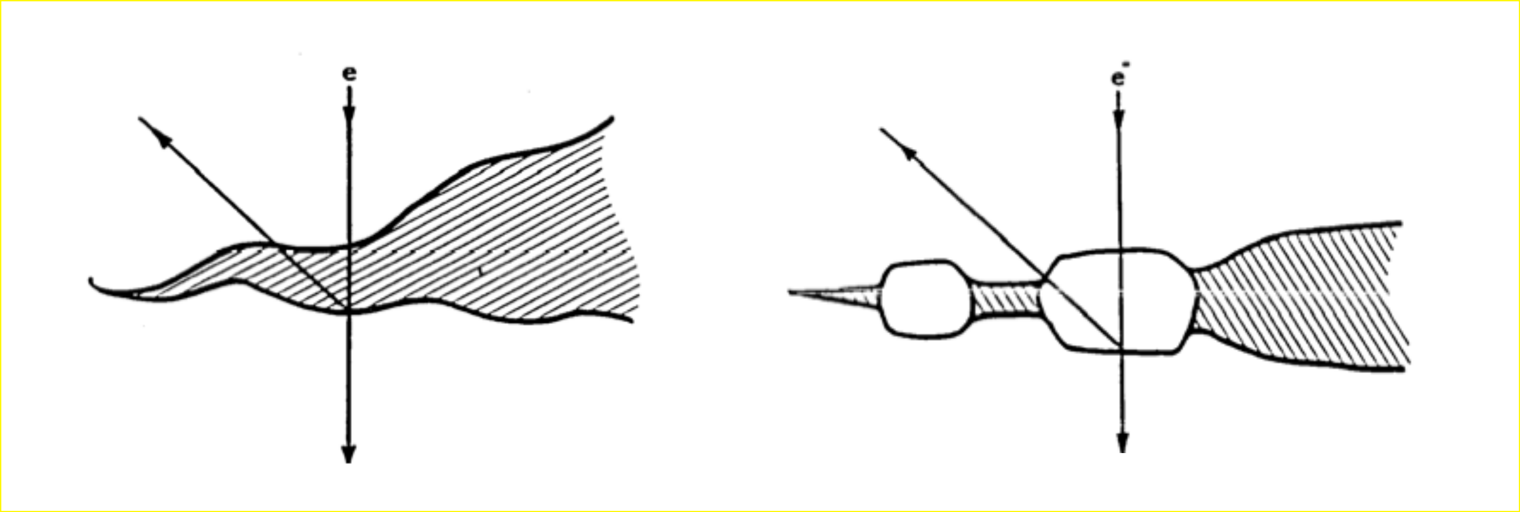
In this and all other derivations we have assumed that over the excited volume, as well as along th exiting pathlength, the specimen is homogeneous in composition. If this assumption is invalid, one must reformulate the absorption correction and take into account changes in : μ/ρ, ρ, and t along the exiting pathlength.

Effects of Beam Broadening

Parallel Slab Model: No Change in absorption pathlength
Wedge Model: There is a correction the magnitude of which varies with the wedge angle.

Effects of Irregular Surface

This cannot be analytically modeled but must be understood!

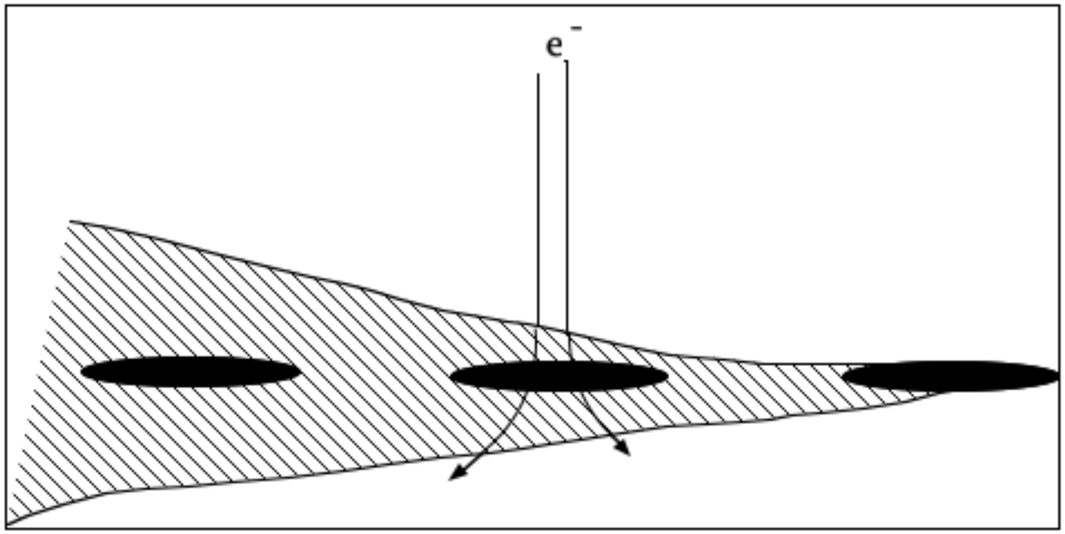


Additional Topics

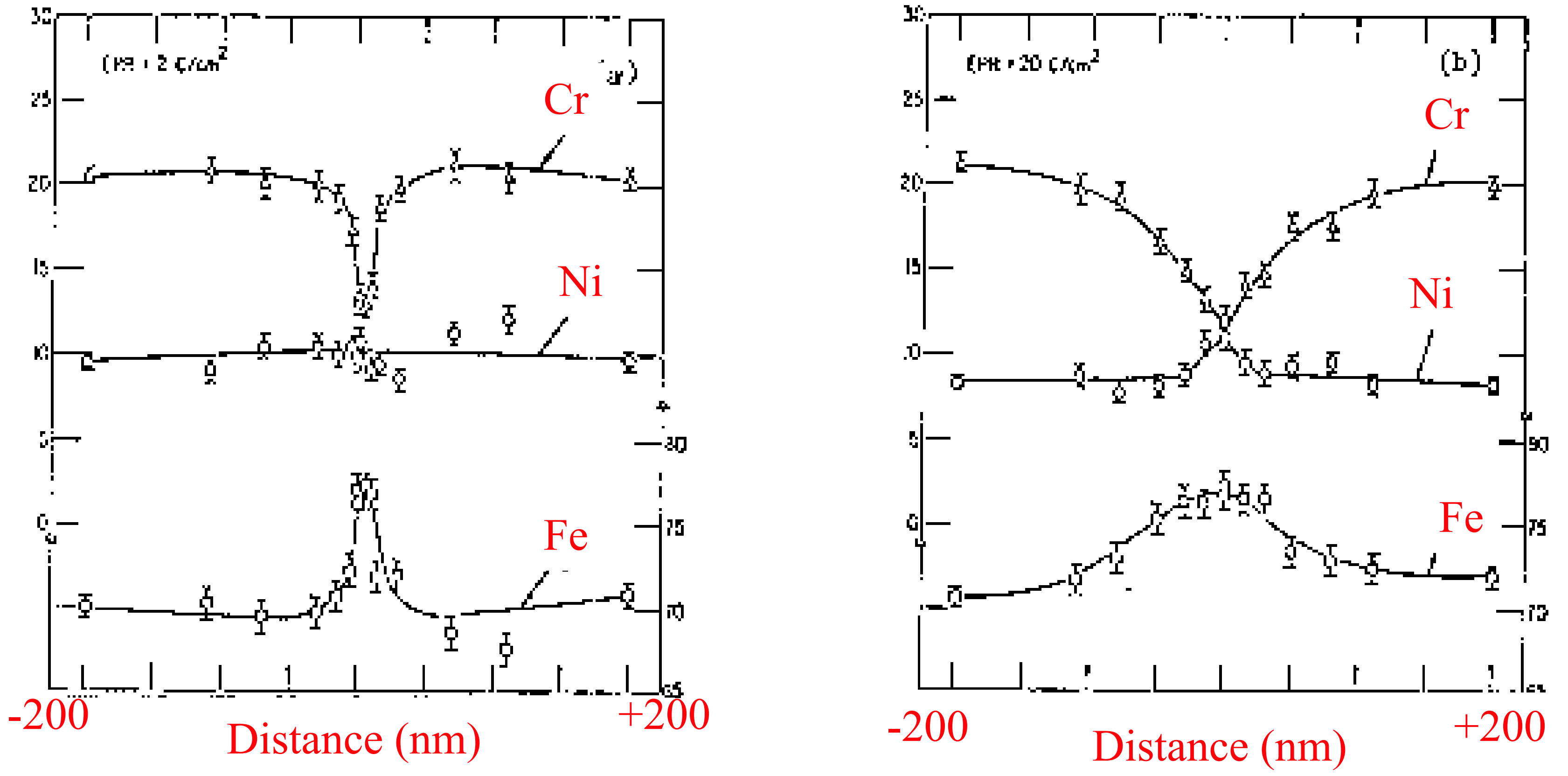
Heterogeneous Specimens
Composition Profiles
Electron Channeling
Radiation Damage
Spectral Imaging

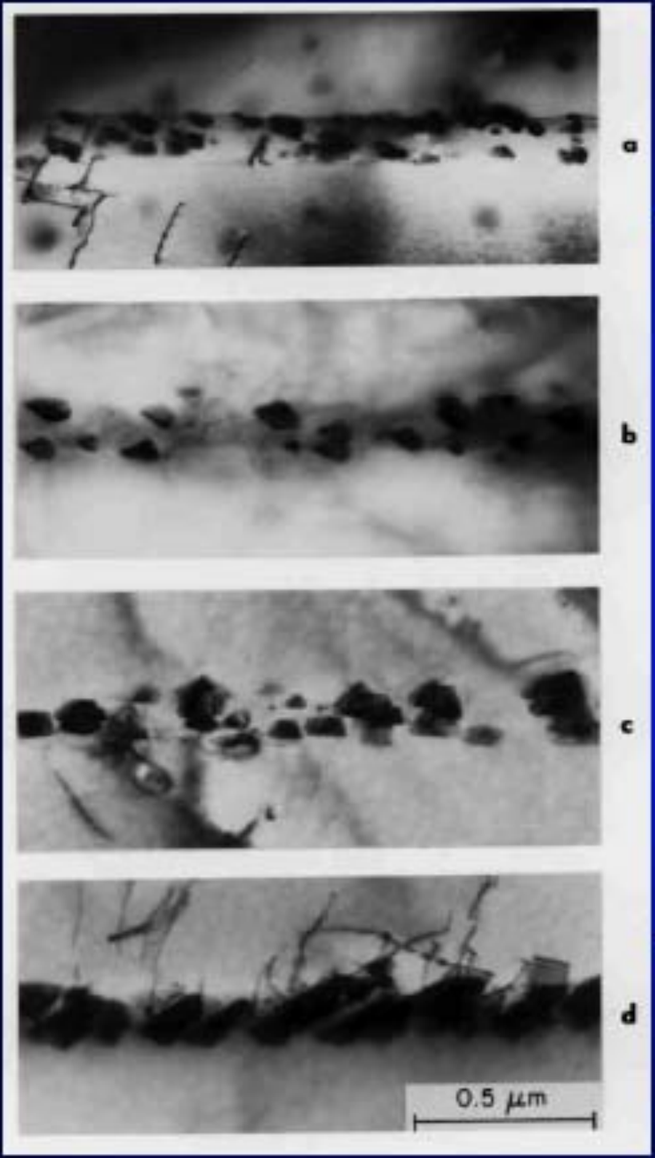
All quantitative analysis equations were derived assuming that the specimen is homogeneous over the exited volume

Application of the these equations to heterogenous specimens effectively averages the composition over the excited volume.



Grain Boundary Segregation





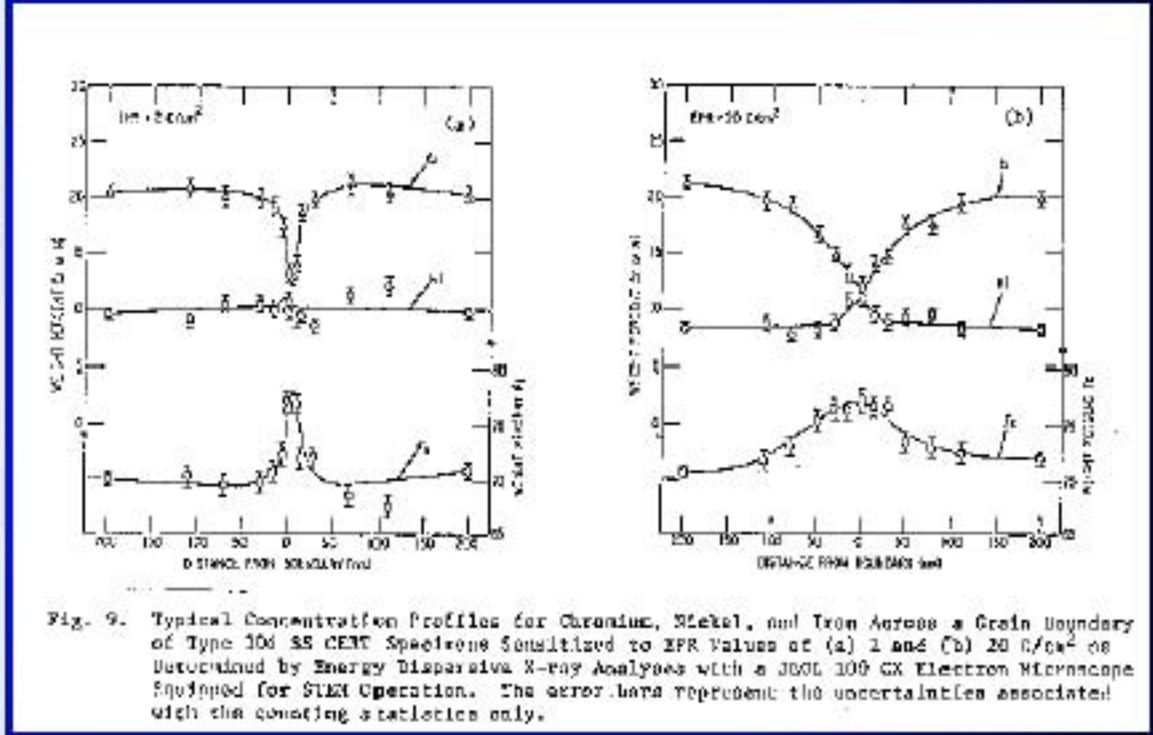


Fig. 9. Typical Concentration Profiles for Chromium, Nickel, and Iron Across a Grain Boundary of Type 304 SS CERT Specimens Sensitized to EPR Values of (a) 1 and (b) 20 C/cm² as Determined by Energy Dispersive X-ray Analyses with a JEOL 100 CX Electron Microscope Equipped for STEM Operation. The error bars represent the uncertainties associated with the counting statistics only.

$$C^*(x,y) = C(x,y,z) * d(x,y,z)$$

$C^*(x,y)$ = Apparent profile measured
$C(x,y,z)$ = Actual composition profile
$d(x,y,z)$ = Incident beam profile

$*$ = Convolution operator

F, F^{-1} = Fourier and Inverse Fourier Transforms

In the 2 dimensional limit one can deconvolute the measured profile using:

$$C(x,y) = F^{-1}\left\{\frac{F\{C^*(x,y)\}}{F\{d(x,y)\}}\right\}$$

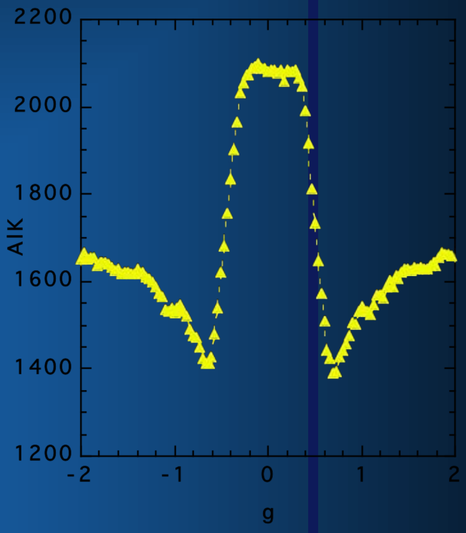
Realistically, it is better to decrease the probe diameter and specimen thickness

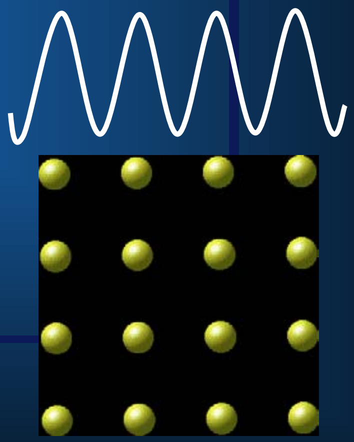
Electron Channeling Induced X-ray Emission

- Characteristic X-ray Emission is not truly isotropic in crystalline materials!

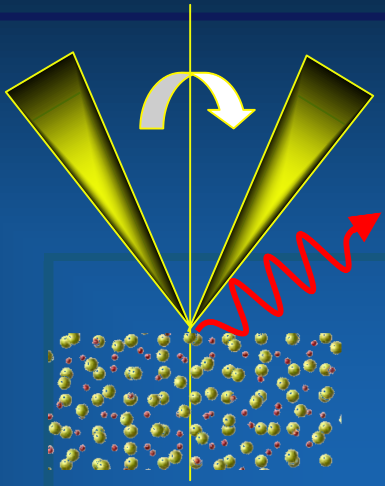
- Original Observations of Effect
  - Duncumb ‘62, Hall ‘66, Cherns etal ‘73
- Predicted Applications
  - Cowley ‘64, ‘70
- ACHEMI Technique -
  - Tafto ‘79, Spence & Tafto ‘83
- Multi-Variate Statistical Analysis -
  - Rossouw etal , Anderson and others

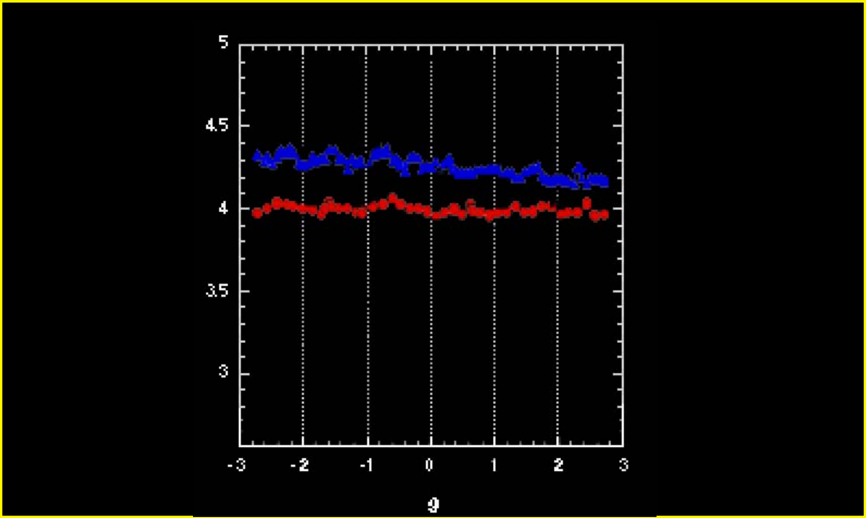
    late80’-90’s

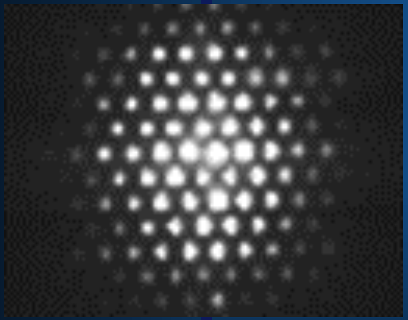


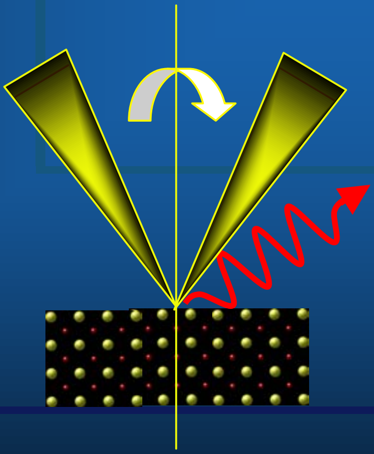


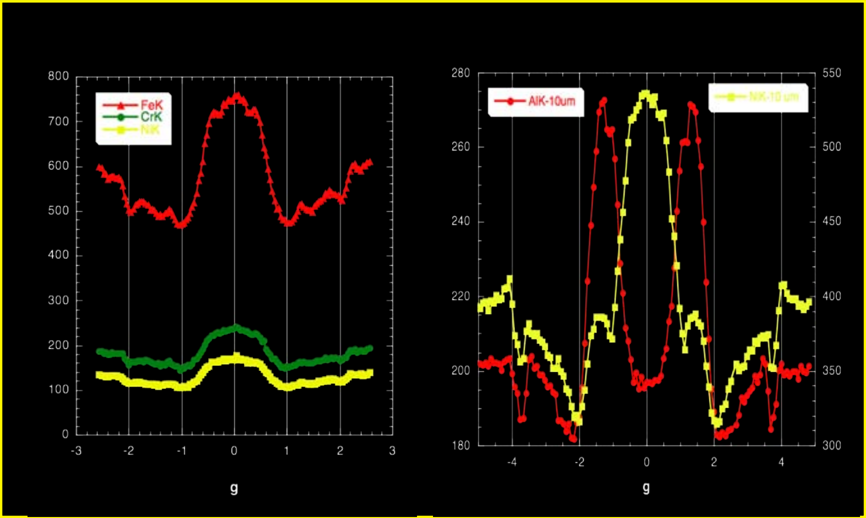
High Angular Resolution Electron Channeling X-ray Spectroscopy



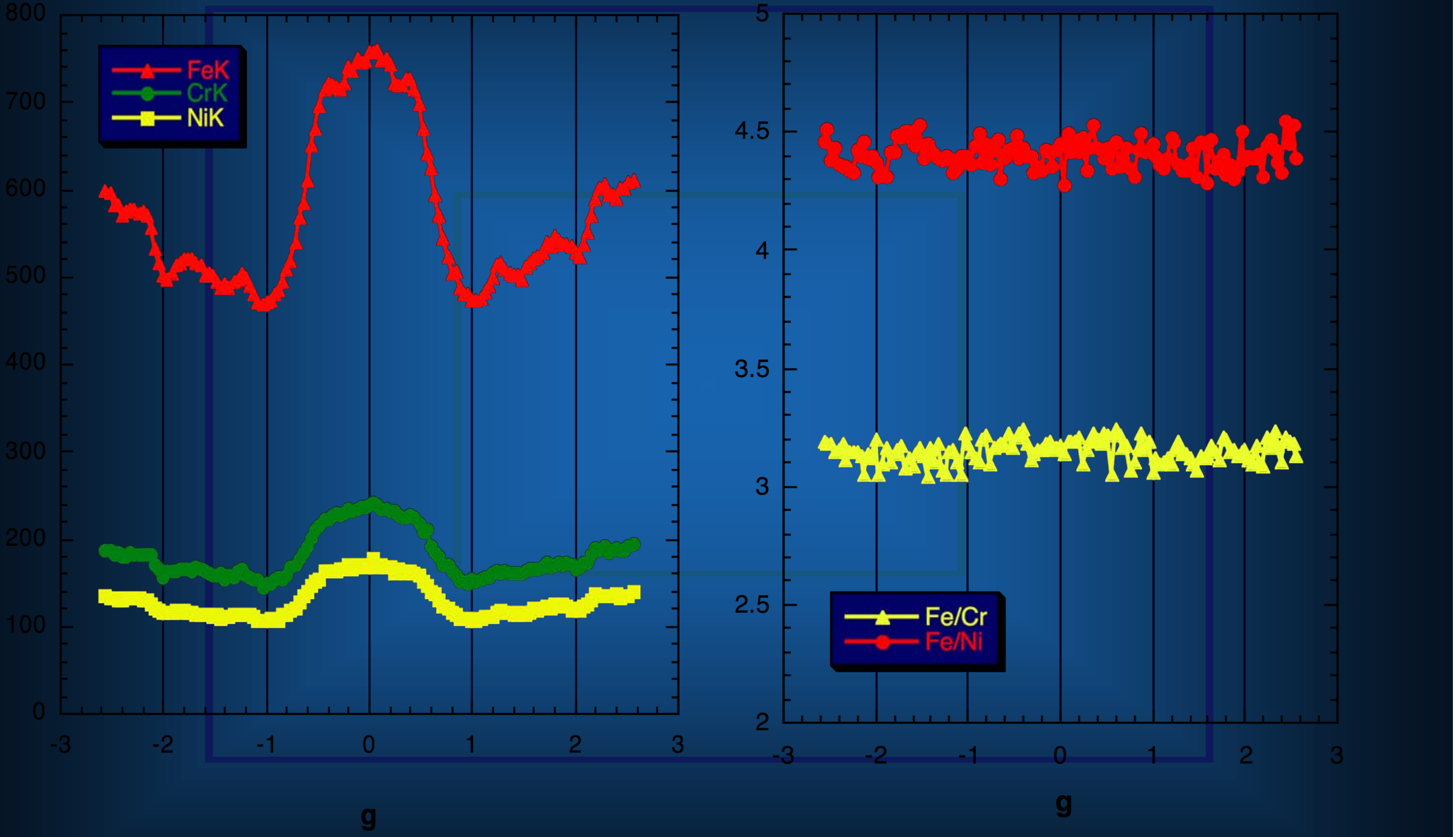




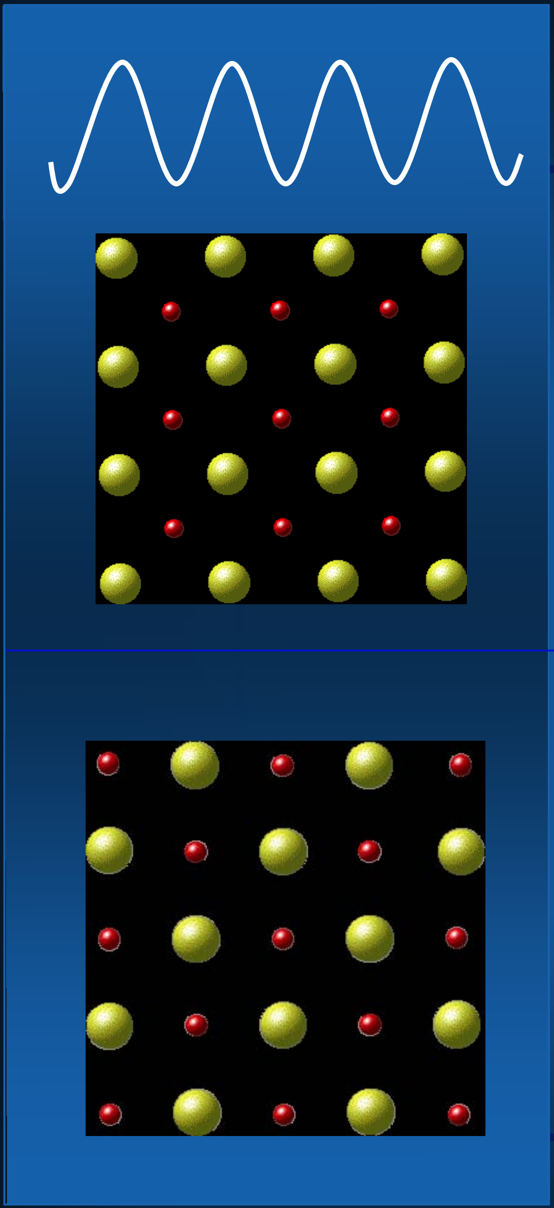


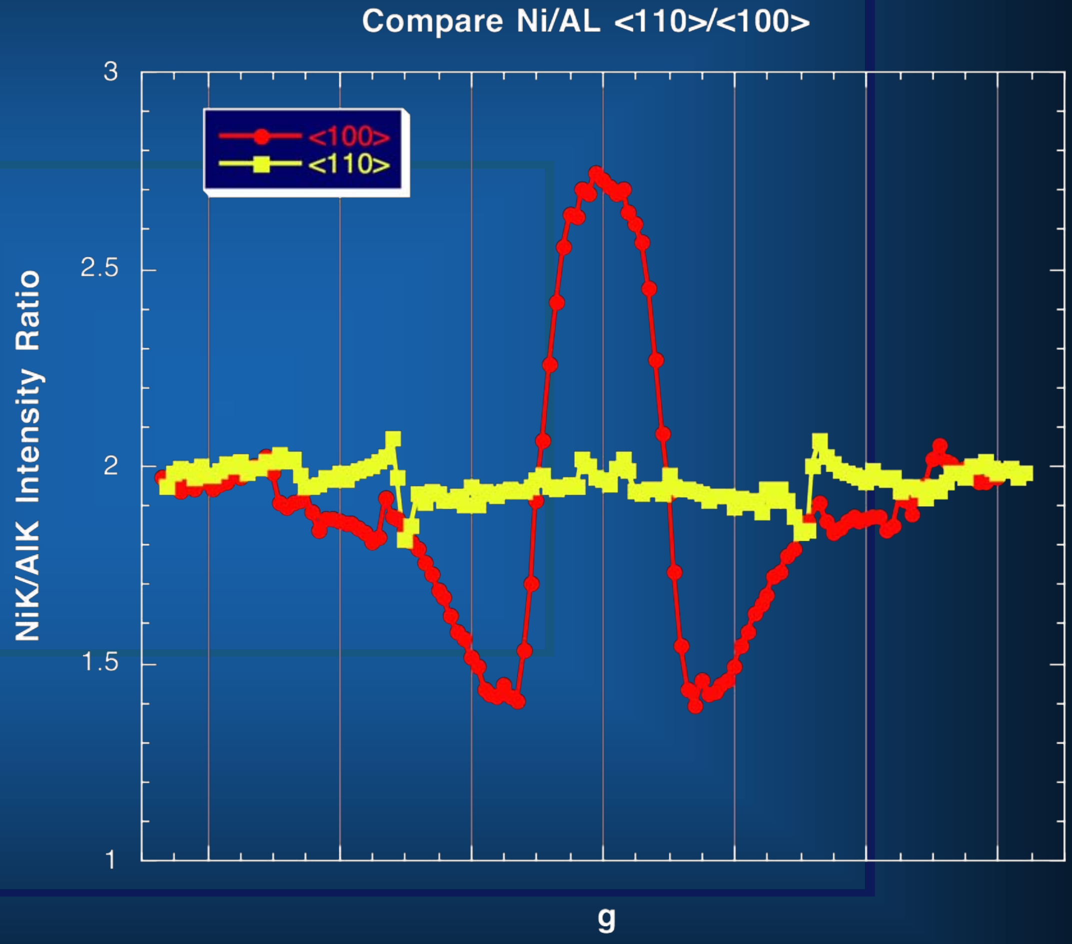


Orientation Dependance in Homogeneous Alloys

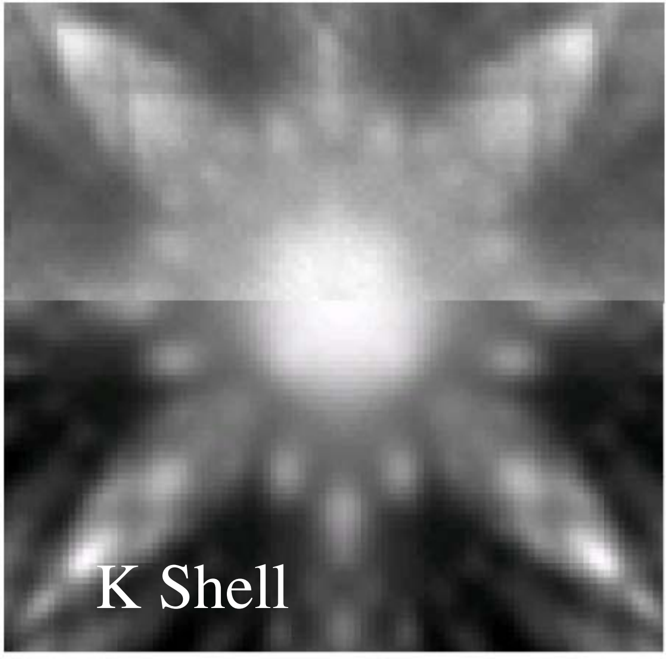


Applications in Ordered Systems





HARECXS - Mo K/L Shell

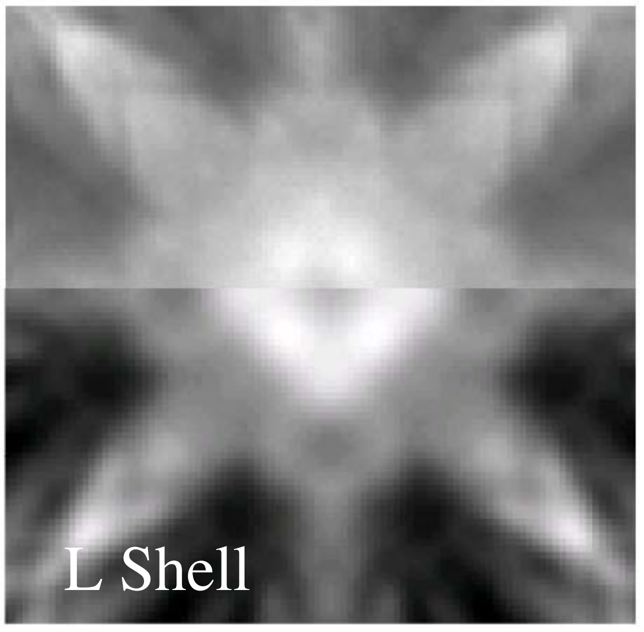


Expt

Calculated

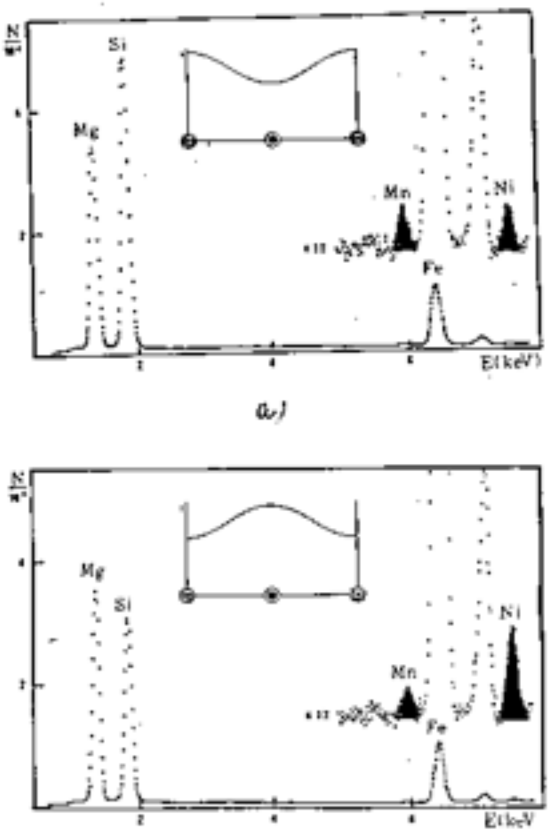
Expt

Calculated



with M. Oxley, L. Allen - Melbourne

ALCHEMI
Atom Location by CHanneling EMIssion
Tafto & Spence - Science 1982

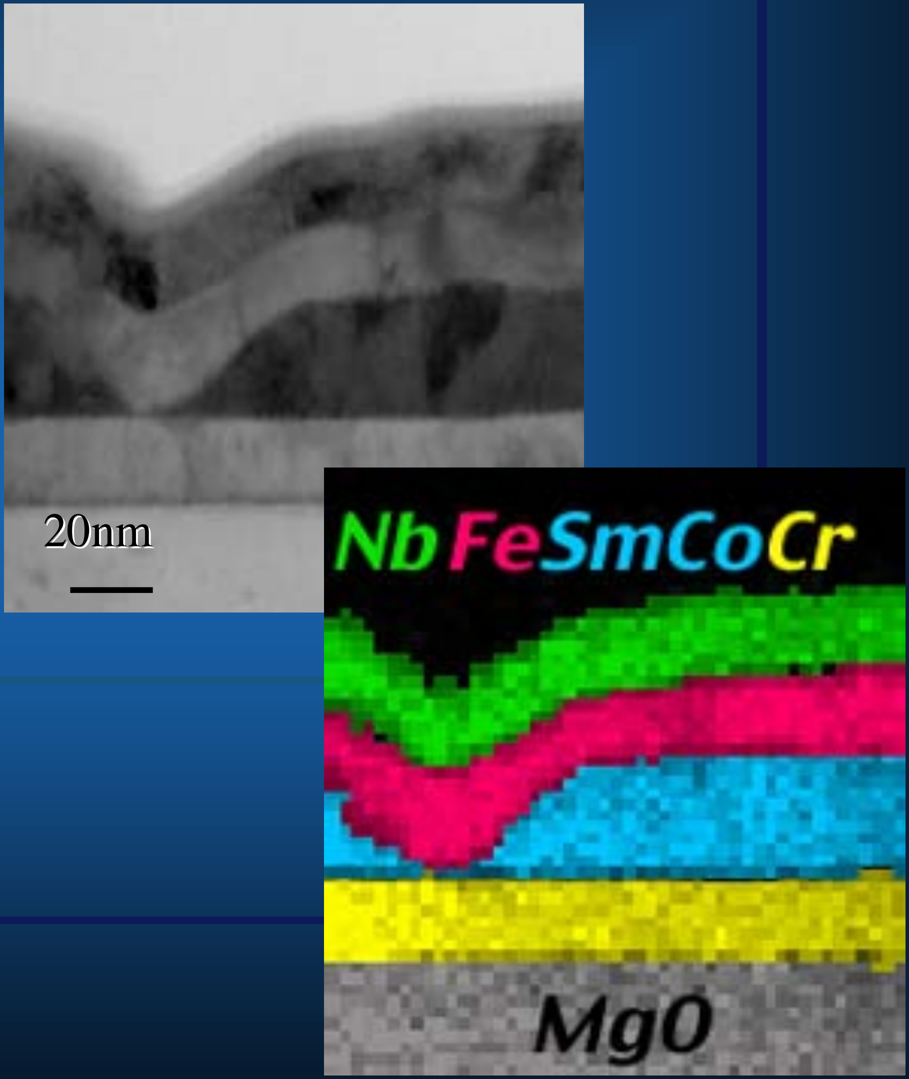


$(Mg_{0.90}Fe_{0.10}Ni_{0.004}Mn_{.002})_2SiO_4$

Note: Mn prefers Si Sites and Ni prefers Mg Sites

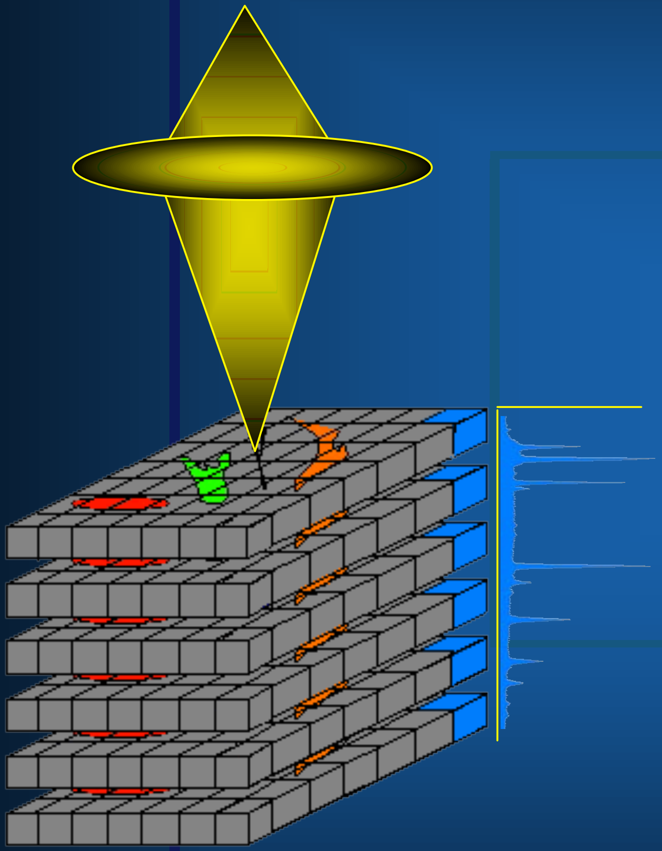
Spectral Imaging

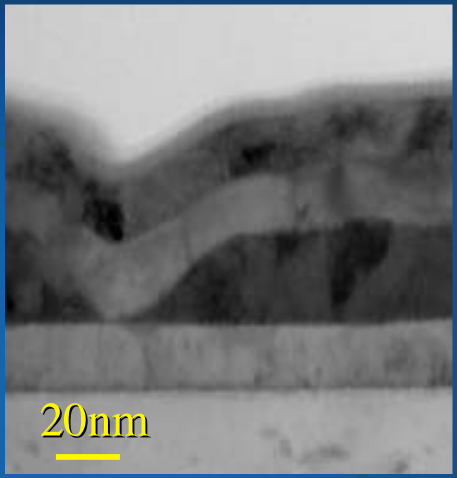
FEI Tecnai F20

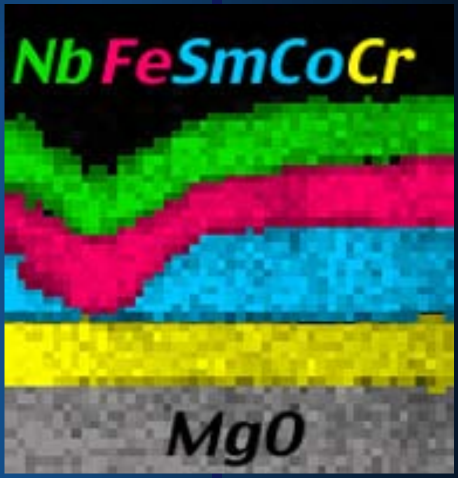


How much data is generated in PRD Expt's

Compare with Spectrum Imaging

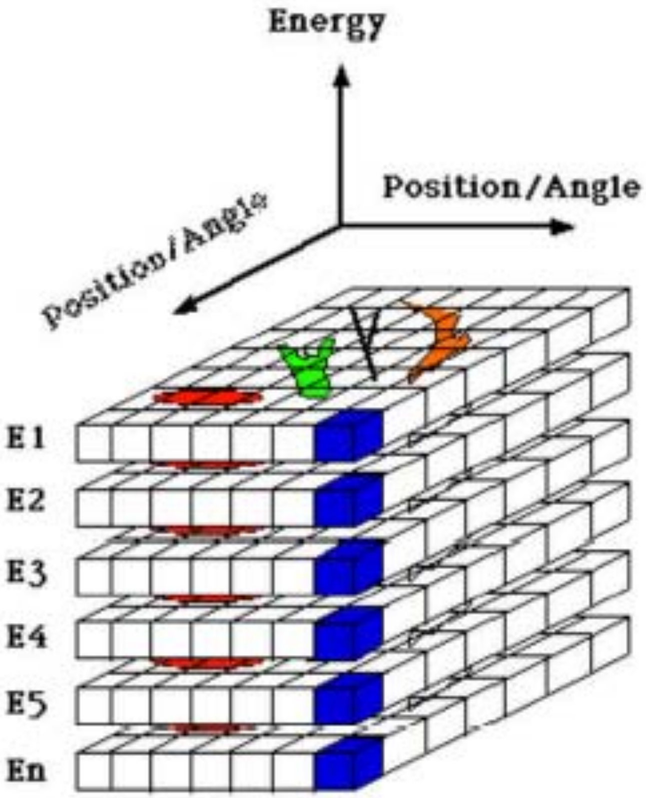


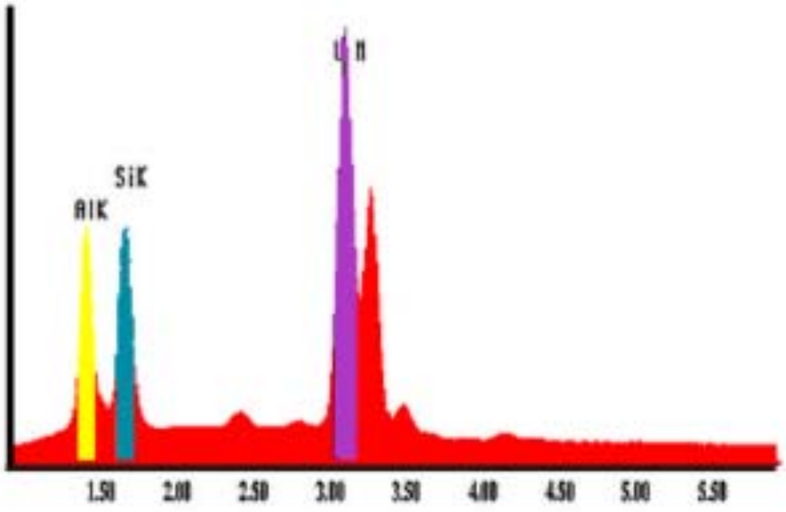


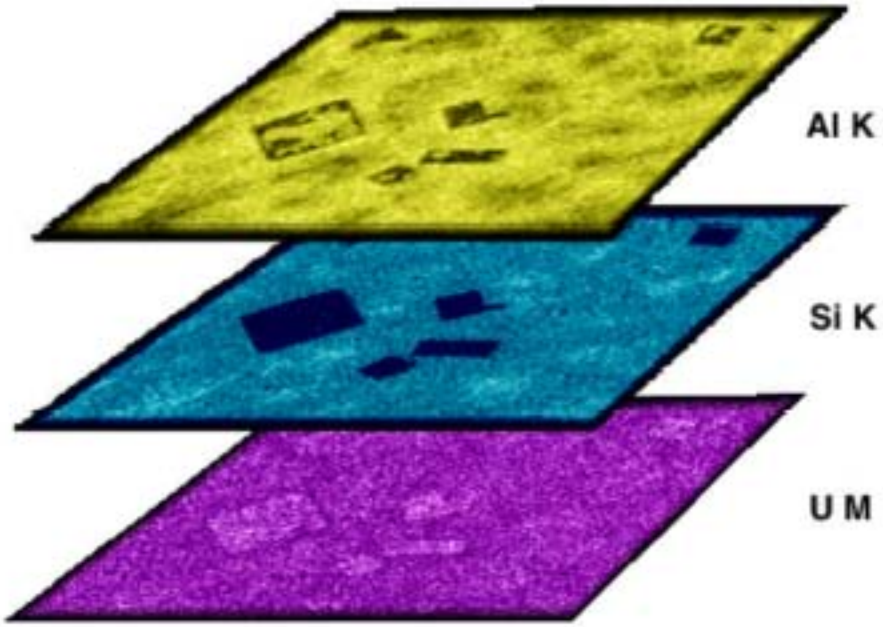


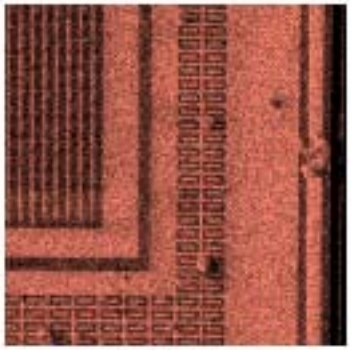
XY E	128^2	256^2	512^2	1024^2
256	4M	16M	67M	262M
512	8M	32M	134M	524M
1024	16M	64M	268M	1G

Spectrum Imaging

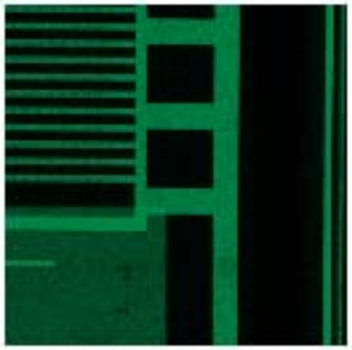




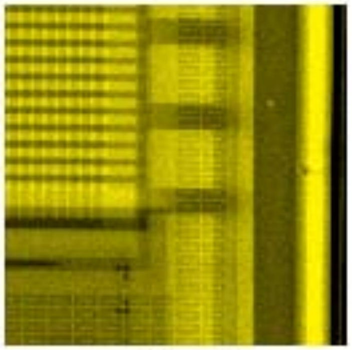




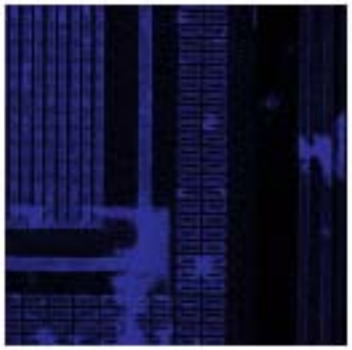
O + Low Energy



Aluminium



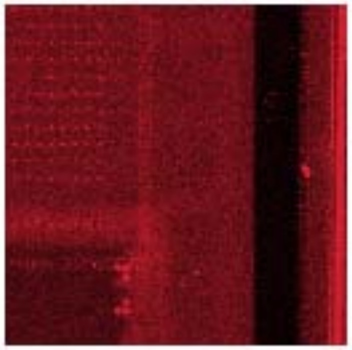
Silicon



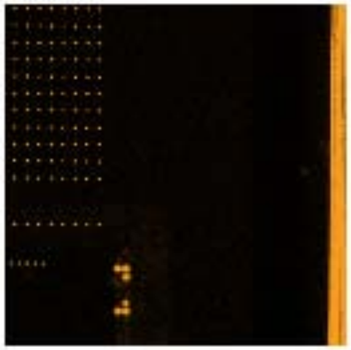
Potassium

Titanium

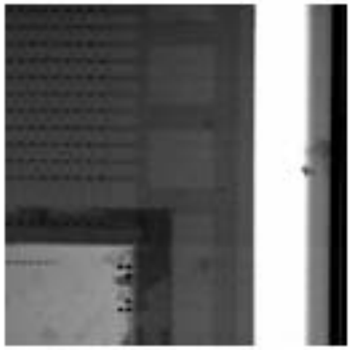
Cobalt



Iron

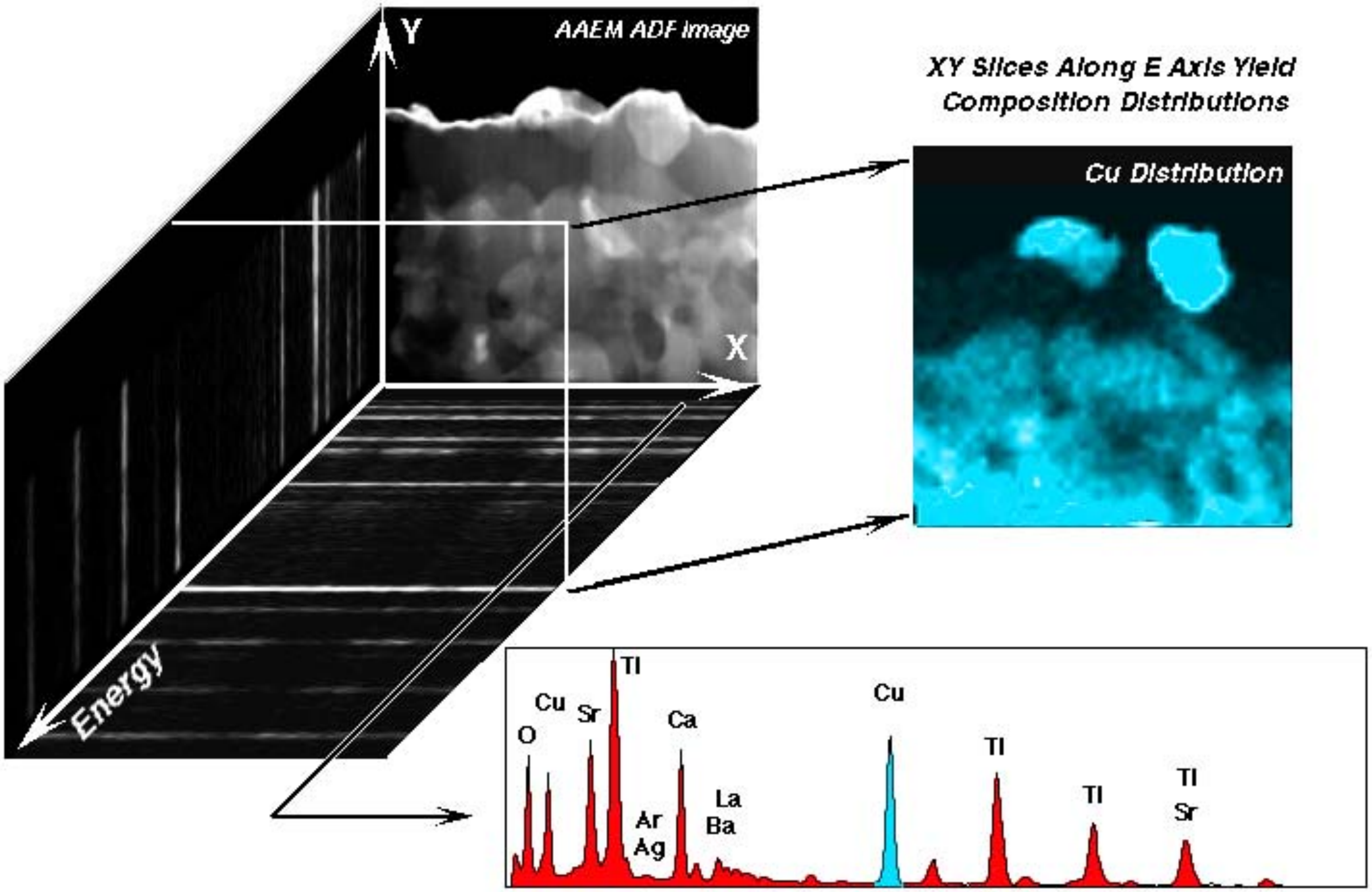


Tungsten



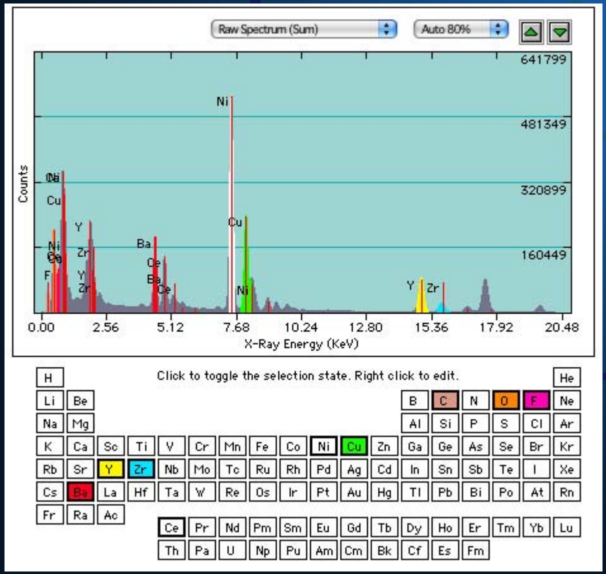
Electron Image

Three Dimensional Spectrum Imaging Profiles Using the ANL AAEM System

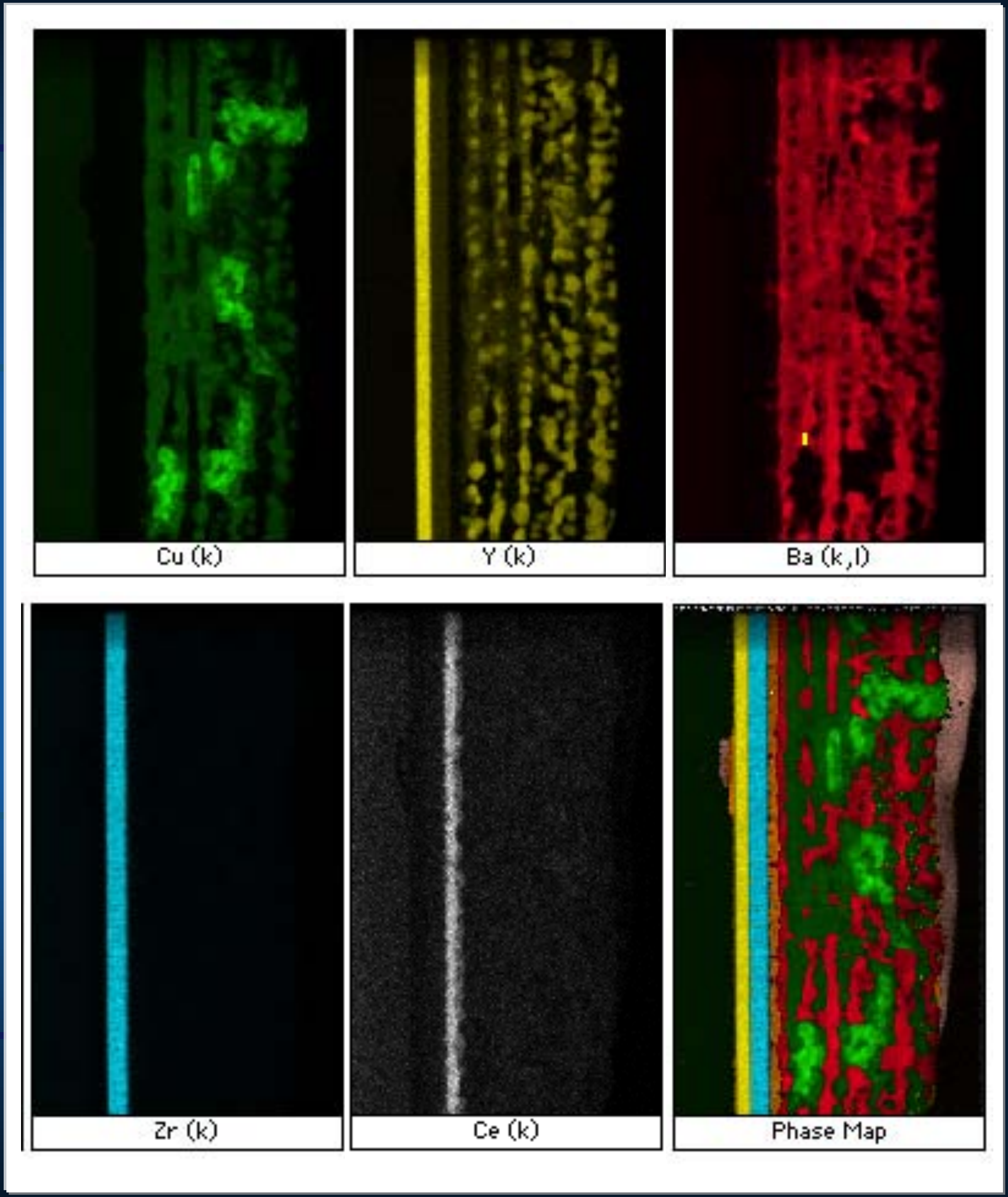


XY Slices Along E Axis Yield Composition Distributions

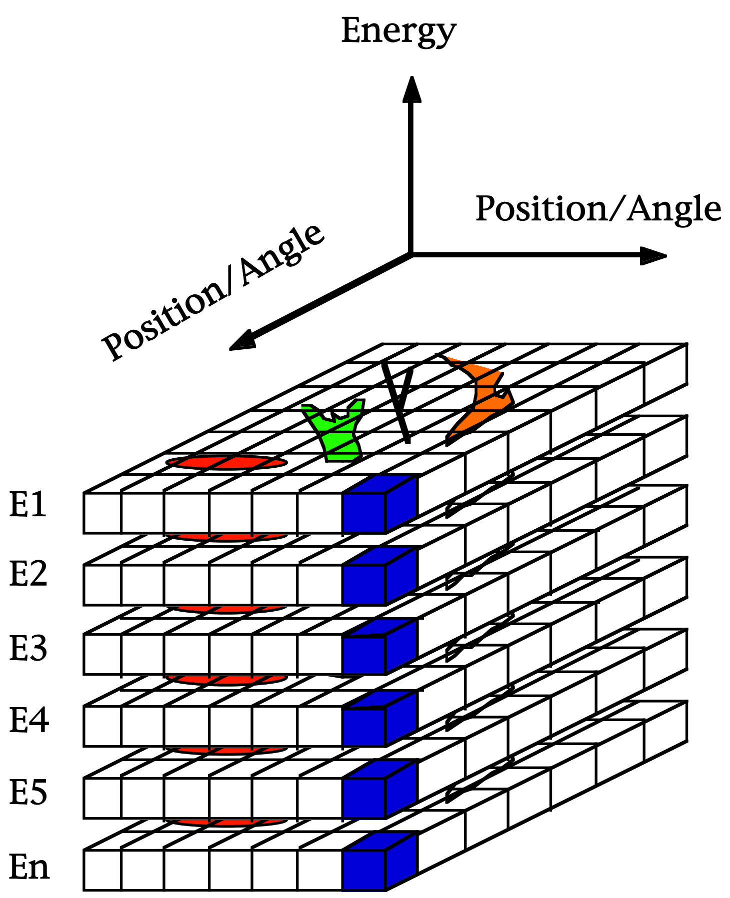
Line Scans along the Energy Axis Yield Complete Spectral Profiles



Click to toggle the selection state. Right click to edit.



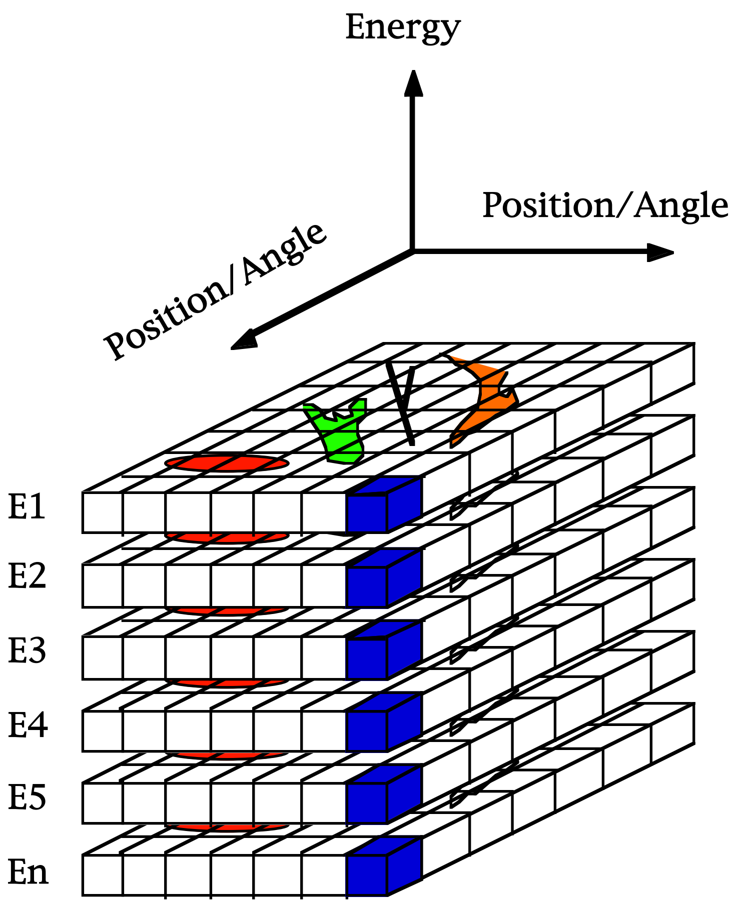
Spectrum Imaging allows for Off-line Projections/Summations Operations



Spectrum Imaging

But it requires massive data strorage

XY E	128^2	256^2	512^2	1024^2
256	4 M	16 M	67 M	262 M
512	8 M	32 M	134 M	524 M
1024	16 M	64 M	268 M	1 G



Spectrum Imaging

XY t	128^2	256^2	512^2	1024^2
1µs	16 ms	65 ms	0.26 s	1.05 s
1ms	16 s	65 s	4.4 min	17.5 min
1 s	~4.5 hrs	~18 hrs	~3 days	~12 days
1 min	~11 days	~1.5 mnths	~ 6 mnths	~2 yrs