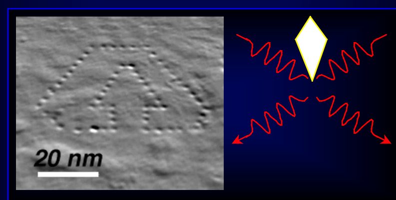
Introduction to XEDS



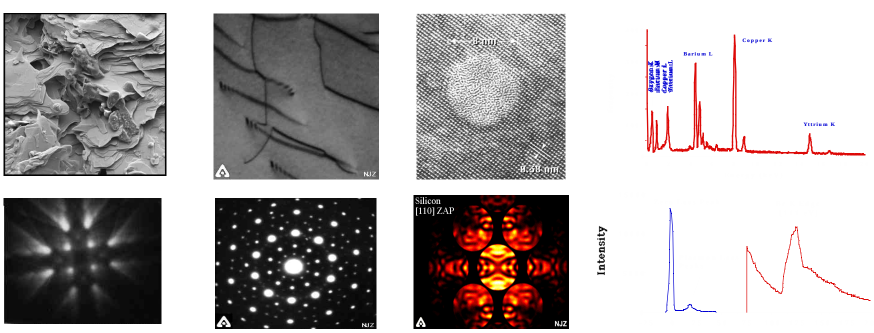
Nestor J. Zaluzec

zaluzec@microscopy.com

zaluzec@aaem.amc.anl.gov

MicroCharacterization via Electron Microscopy

SEM	TEM - STEM - HREM	AEM
Scanning Electron Microscopy	Transmission - Scanning Transmission - High Resolution Electron Microscopy	Analytical Electron Microscopy



Morphology, Crystallography, Elemental , Chemical , Electronic Structure

Brief Review of X-ray Generation

Instrumentation: Detector Systems

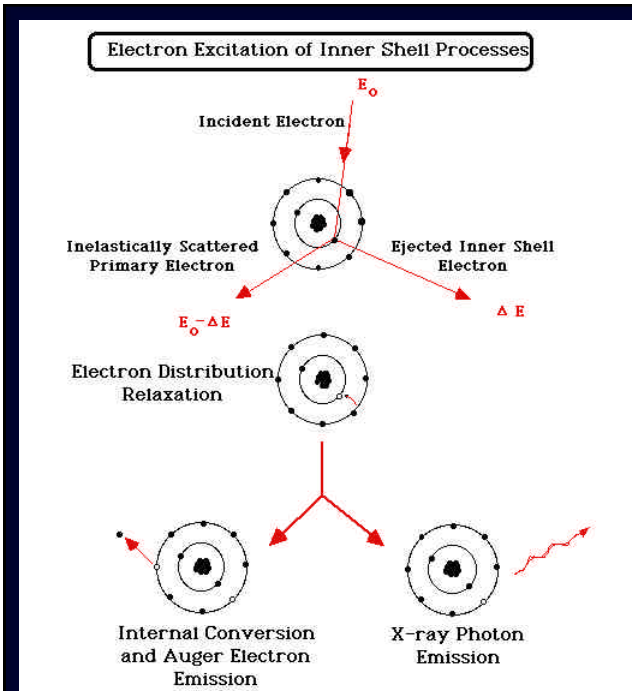
Instrumentation: EM Systems

Data Analysis and Quantification:

Additional Topics

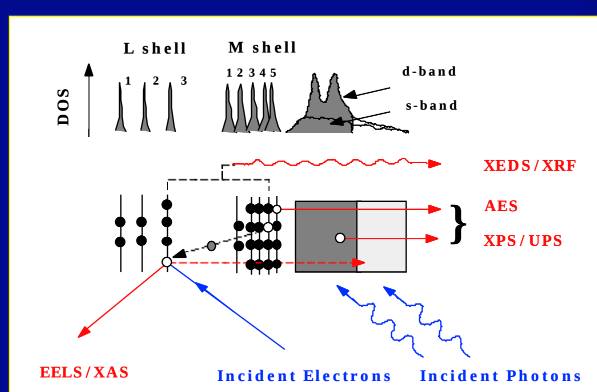
Brief Review of X-ray Generation

Electron Excitation of Inner Shell & Continuum Processes
Characteristic and Bremsstrahlung Emission
Spectral Shapes
Notation of Lines



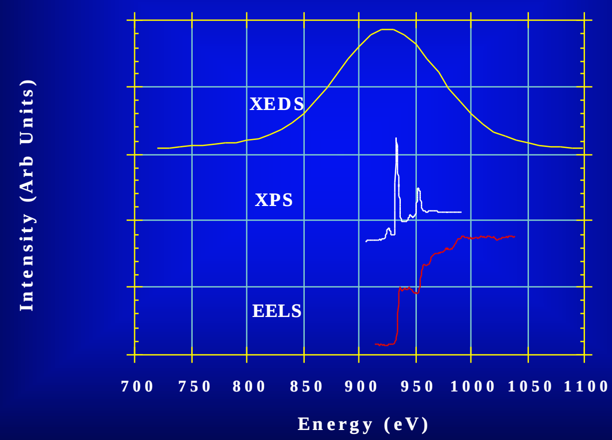
The Emission Process:

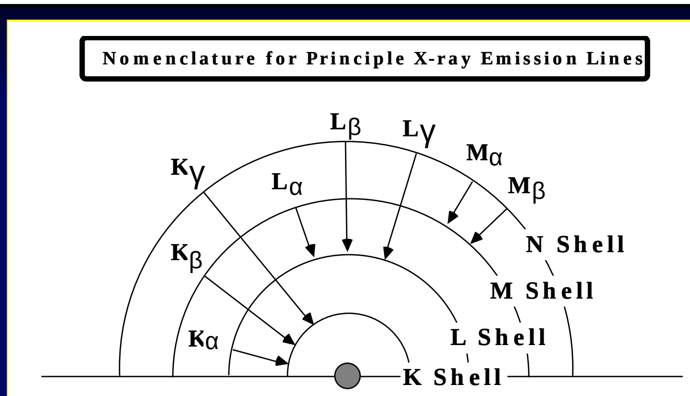
1-Excitation,
2-Relaxation,
3-Emission



Schematic Diagram Illustrating Sources of Inelastic Scattering Signals

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.

$E(K\alpha) = E_K - E_L$ $E(K\beta) = E_K - E_M$

X-ray line energies are unique.

$E_0 > E_x$ to "excite the E_xth family of lines"

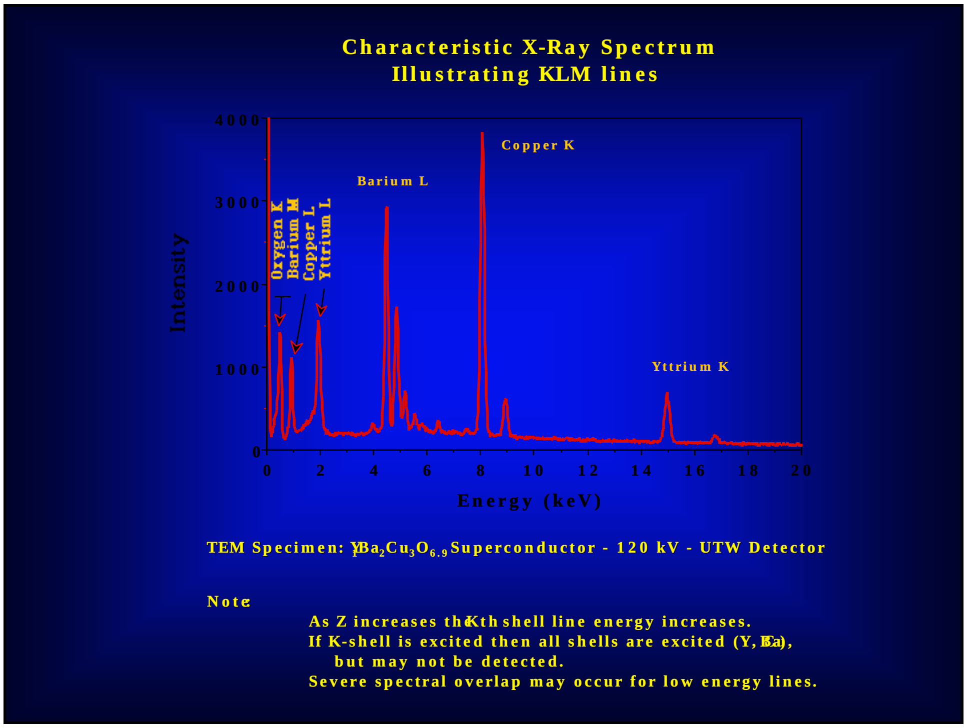
Nomenclature for X-ray Lines

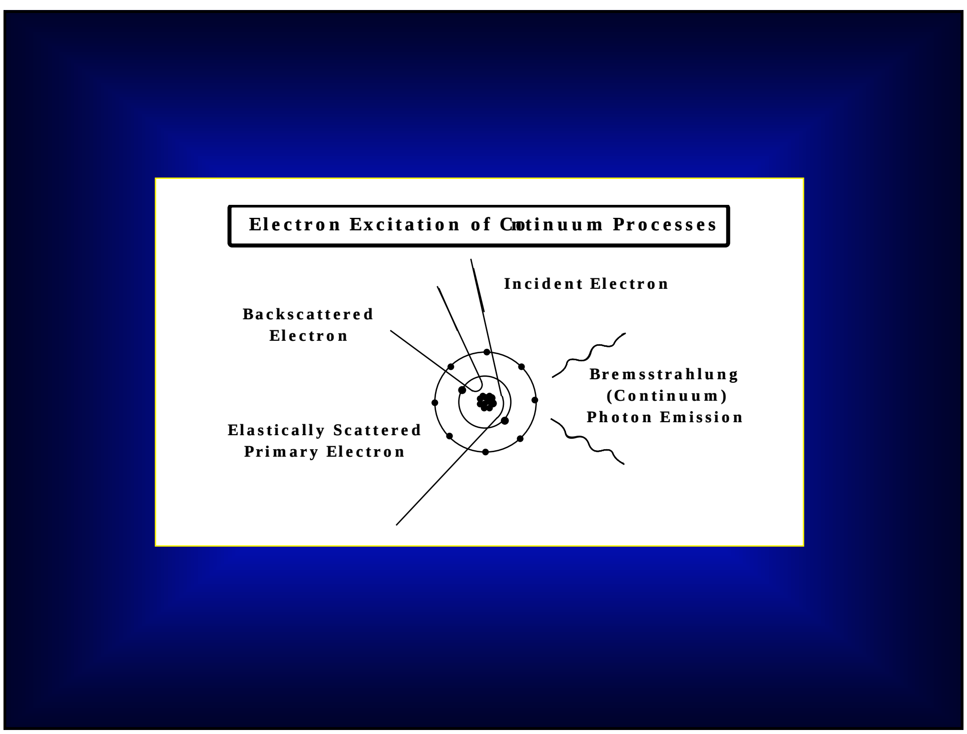
X-ray Transition Selection Rules:
(Principle Quantum Numbers)

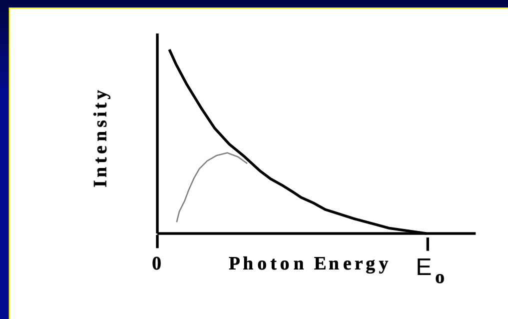
Shell	n	l	j	Rule
K	1	0	1/2	
L	2	0,1	1/2, 3/2	$\Delta n > 0$
M	3	0,1,2	1/2, 3/2, 5/2	$\Delta l = +1, -1$
N	4	0,1,2,3	1/2, 3/2, 5/2, 7/2	$\Delta j = +1, 0, -1$

Relative Intensities of Major X-ray Lines

$K_{\alpha1}$ = 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	


Characteristic X-Ray Spectrum
Illustrating KLM lines
Intensity
Energy (keV)
0
1000
2000
3000
4000
0
2
4
6
8
10
12
14
16
18
20
Oxygen K
Barium M
Copper L
Yttrium L
Barium L
Copper K
Yttrium K
TEM Specimen: YBa2Cu3O6.9 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, Ba),
but may not be detected.
Severe spectral overlap may occur for low energy lines.


Electron Excitation of Continuum Processes
Incident Electron
Backscattered
Electron
Bremsstrahlung
(Continuum)
Photon Emission
Elastically Scattered
Primary Electron



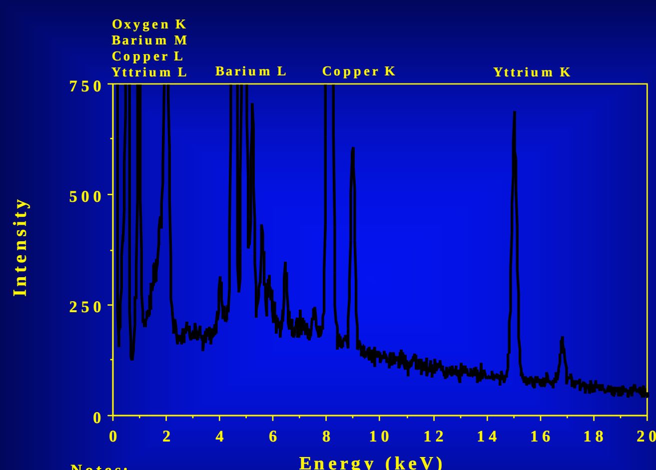
Energy Range - Continuous Distribution

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

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

$$I \sim i_0 Z (E_0 - E)/E$$

Electron Excitation of Continuum (Background) Intensity



Notes:

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 (micro-calorimeters) Detectors
- Multichannel Analyzers

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

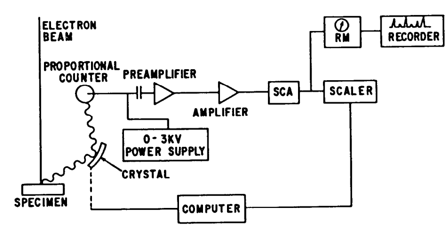
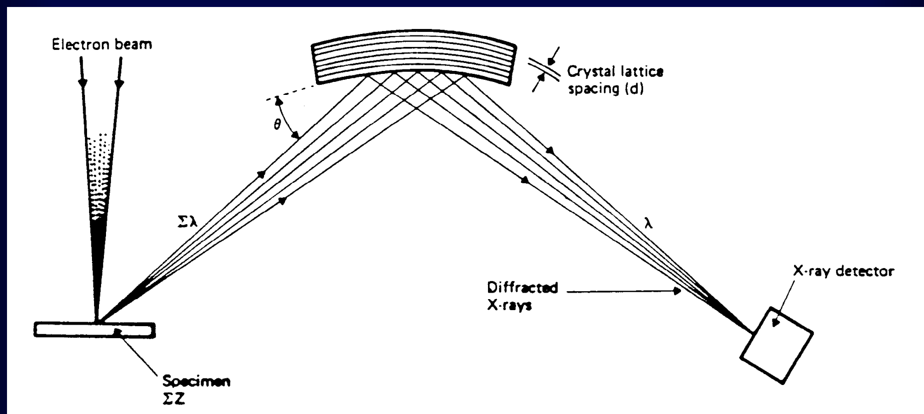


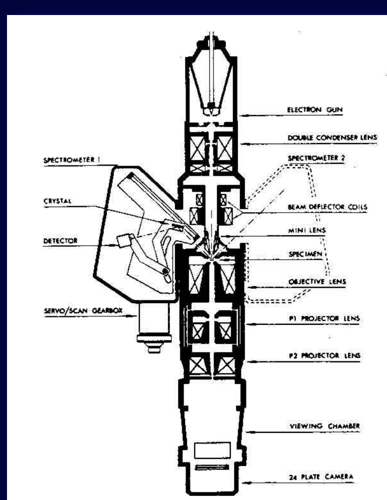
FIGURE 1. Basic components of a crystal diffraction spectrometer system.

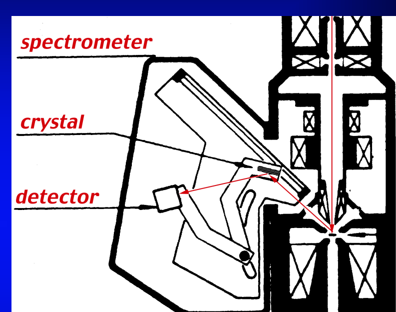


Operation of a Crystal Spectrometer Using Braggs' Law

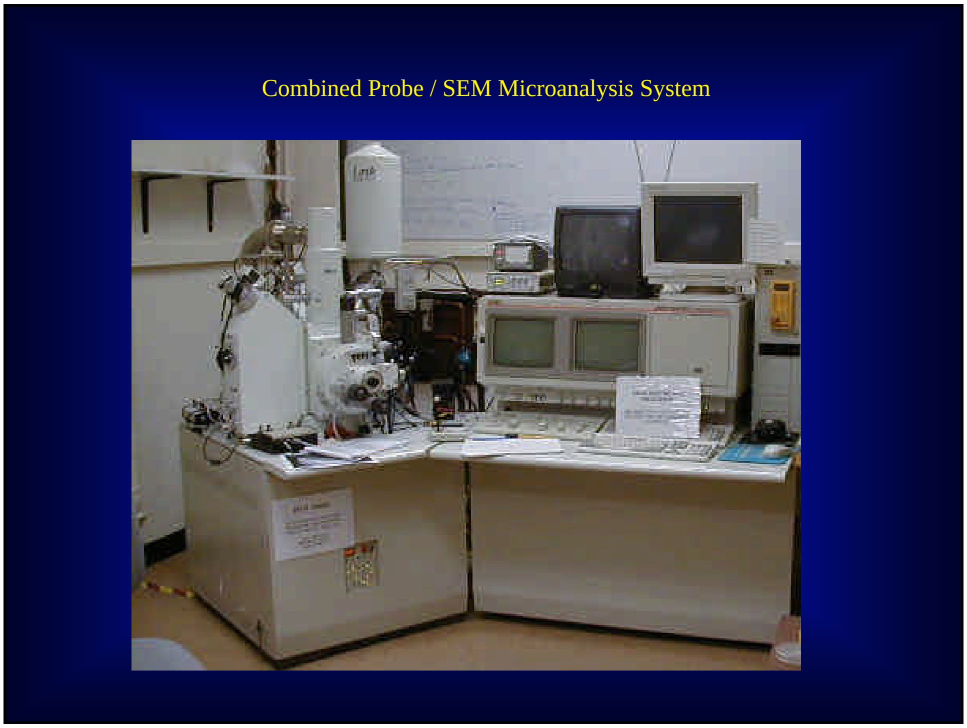
$$\lambda = 2\,\mathbf{d}\ \mathbf{sin}(\theta)$$

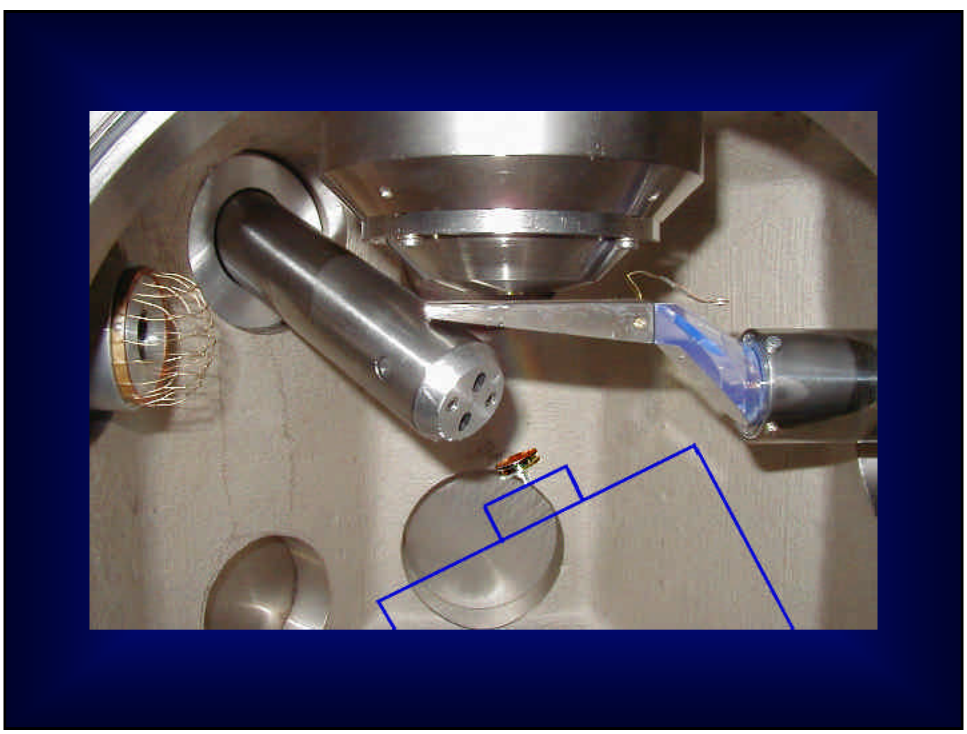
$$\lambda = 12.398\,[\text{Å}] / E\ [\mathbf{keV}]$$





Installation of a Crystal Spectrometer in a TEM - EMMA-4 System


Combined Probe / SEM Microanalysis System



Energy Dispersive Spectrometers: (Solid State Detector)

Operates on Energy Deposition Principle

Simple, Nearly Operator Independent
Large Solid Angles (0.05-0.3 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

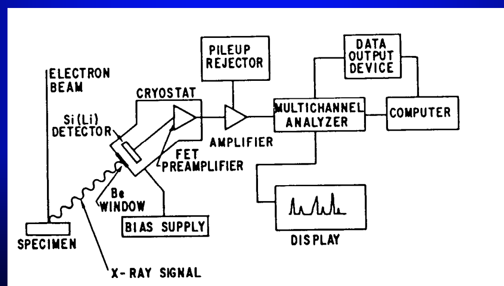
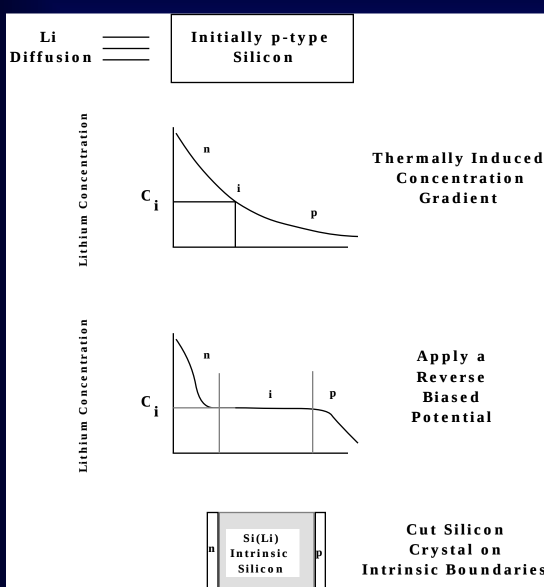


FIGURE 10. Operating schematic of a Si(Li) detector system.



•P-type Silicon high conductivity due to impurities (usually Boron); Lithium acts as a compensating dopant neutralizing the Si giving it a high resisitivity

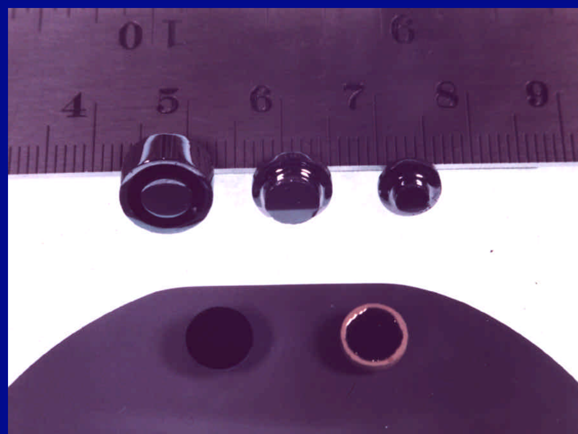
• Radiation deposits energy in the Si(Li) lattice & creates free electron-hole pairs in the crystal @ 1 electron-hole pair/3.8 eV of deposited energy @ 77K.

• Intrinsic semiconducting Si allows both electrons & holes to become mobile under application of a potential bias across the crystal

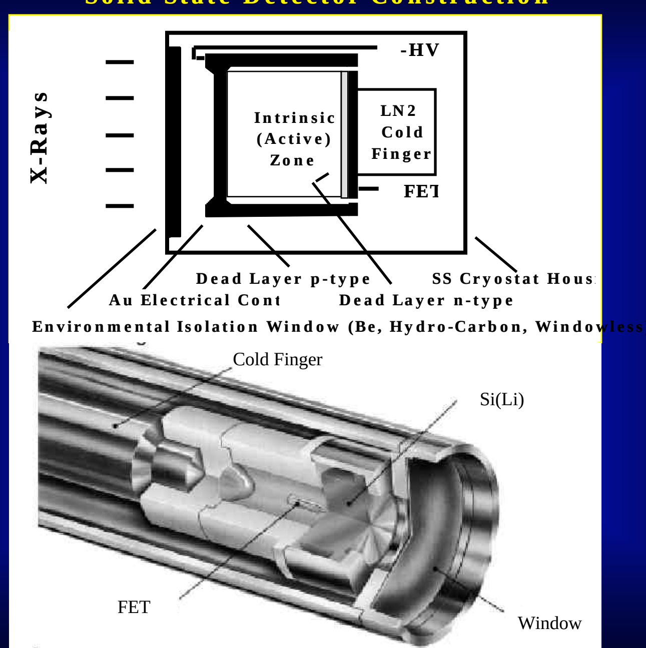
Properties of Intrinsic Silicon

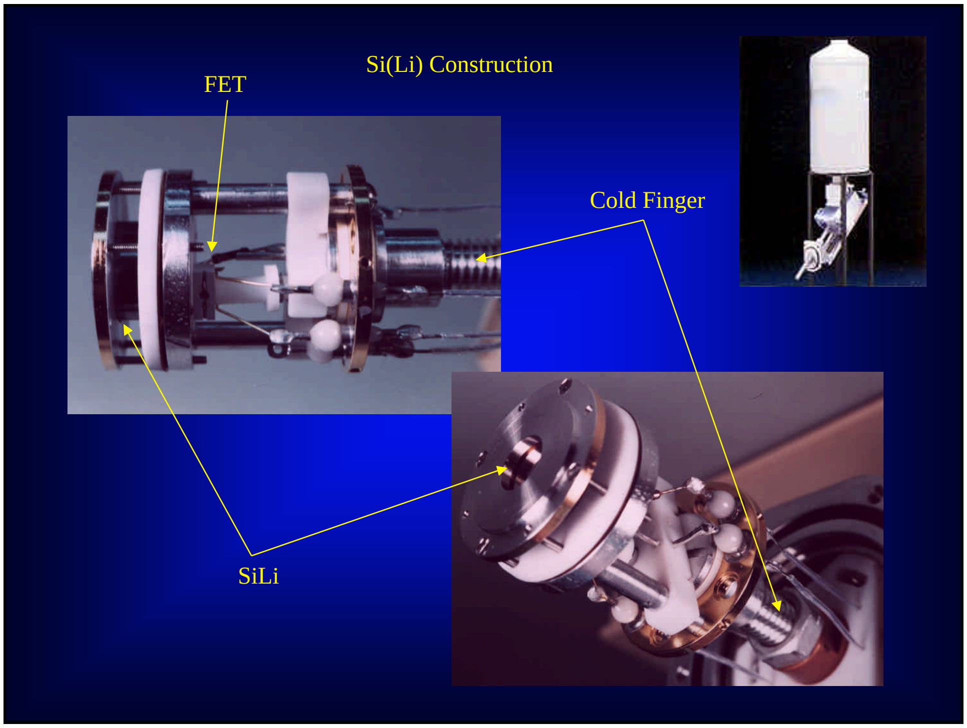
Attaching HV electrodes to the two surfaces the Si(Li) crystal will act similiar to a capacitor with free charges developing on the electrical contacts. Charge developed in the crystal is N = E/ε (E= x-ray Energy, ε = 3.8eV/e-h pair) i.e. ==> 10 kV X-ray produces ~2630 electrons = 4.2 x 10 -16 Coulombs.

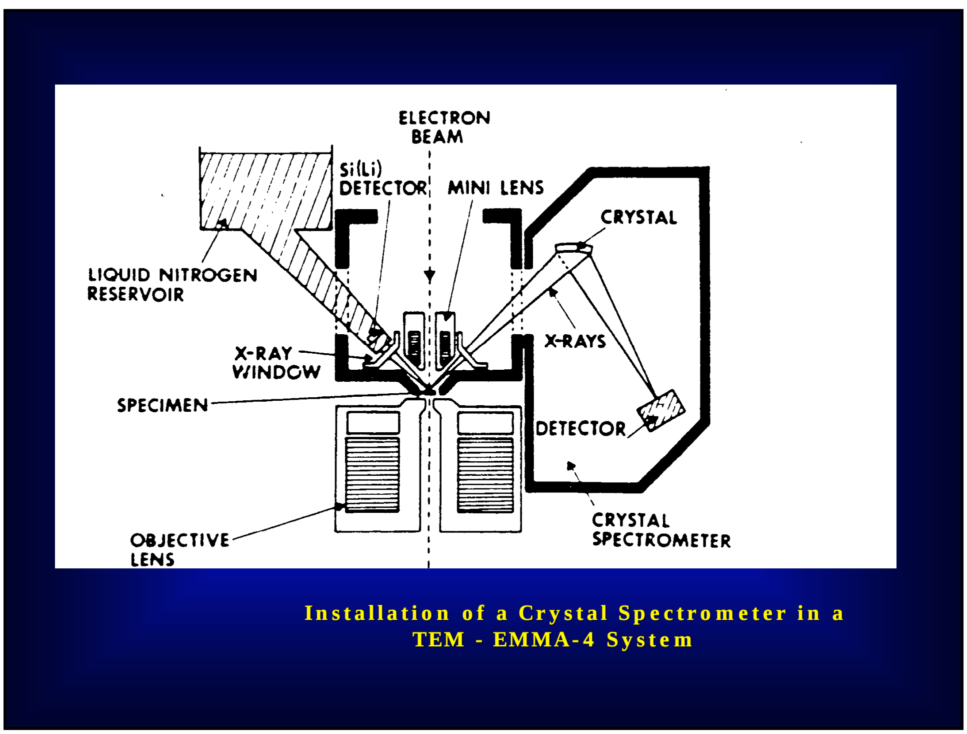
Fabrication of Si(Li) Crystals

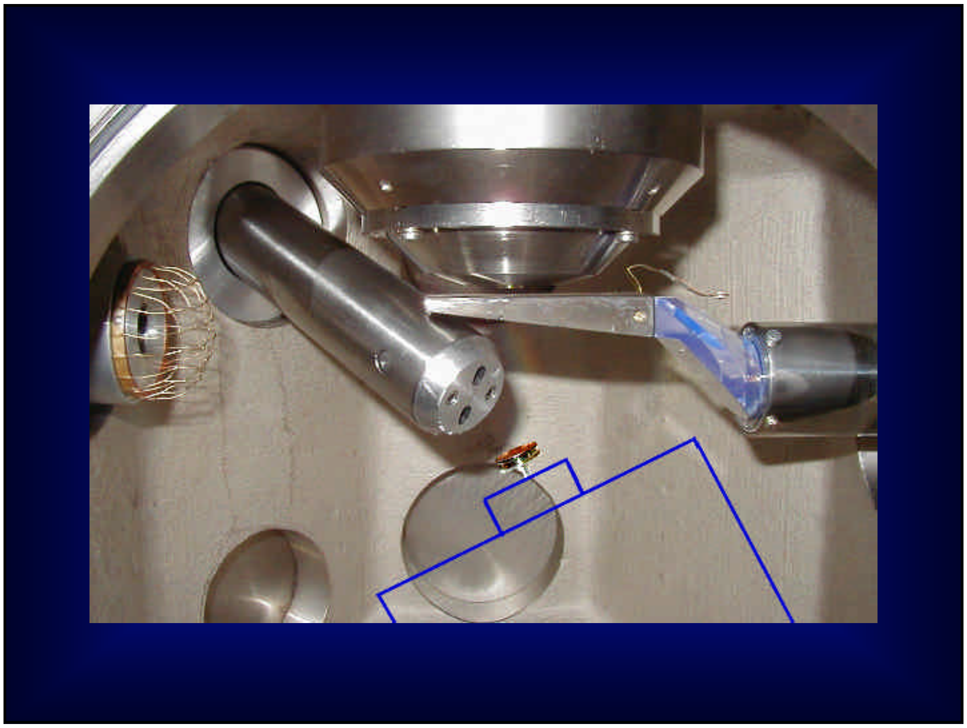


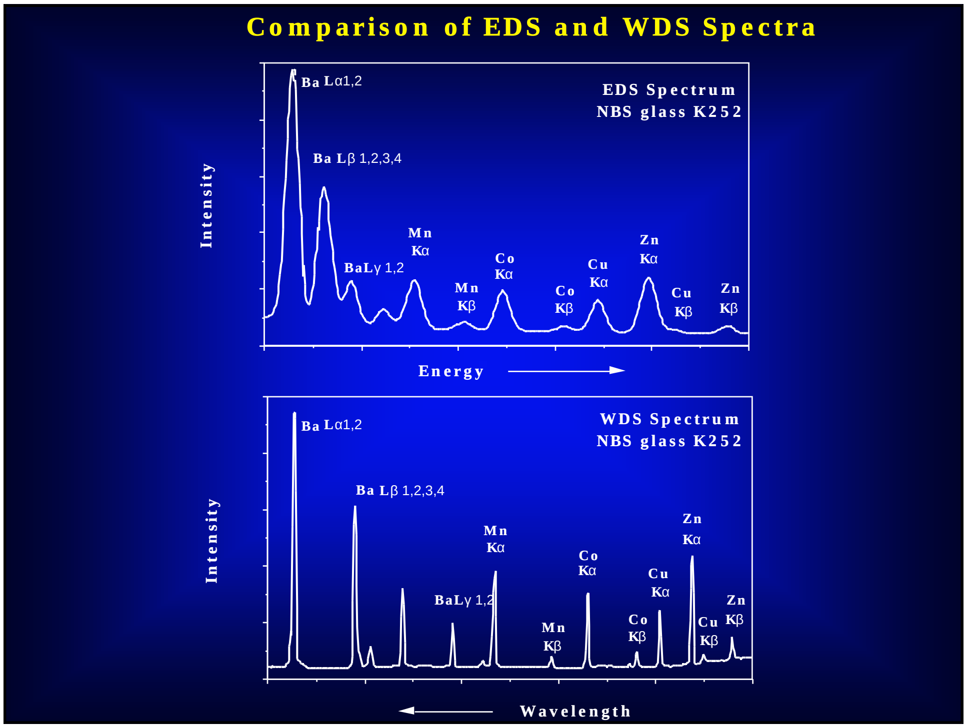
Solid State Detector Construction




Si(Li) Construction
FET
Cold Finger
SiLi


ELECTRON
BEAM
Si(Li)
DETECTOR
MINI LENS
CRYSTAL
LIQUID NITROGEN
RESERVOIR
X-RAYS
X-RAY
WINDOW
SPECIMEN
DETECTOR
OBJECTIVE
LENS
CRYSTAL
SPECTROMETER
Installation of a Crystal Spectrometer in a
TEM - EMMA-4 System





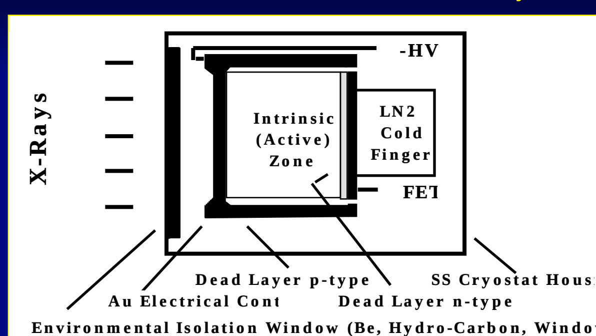
Comparison of EDS and WDS Spectra
EDS Spectrum
NBS glass K252
Ba Lα1,2
Ba Lβ 1,2,3,4
BaLγ 1,2
Mn Kα
Mn Kβ
Co Kα
Co Kβ
Cu Kα
Cu Kβ
Zn Kα
Zn Kβ
Intensity
Energy
WDS Spectrum
NBS glass K252
Ba Lα1,2
Ba Lβ 1,2,3,4
BaLγ 1,2
Mn Kα
Mn Kβ
Co Kα
Co Kβ
Cu Kα
Cu Kβ
Zn Kα
Zn Kβ
Intensity
Wavelength

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 % (3-15 keV)
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	Negligible	Important
Operation	Skilled (?)	Novice

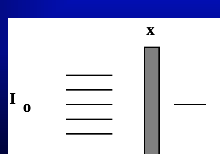
* Values depend on definition, specimen, and operating conditions

Solid State Detector Efficiency



Relative Detection Efficiency

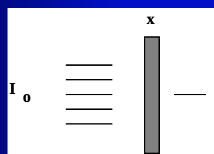
Solid State Detectors Si(Li) or Instrinsic (High Purity) Ge
Using a simple absorption model define the relative detector efficiency ε(E) by the following procedure:



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

Relative Detection Efficiency

Solid State Detectors Si(Li) or Instrinsic (High Purity) Ge
Using a simple absorption model define the relative detector efficiency $\varepsilon(E)$ by the following procedure:



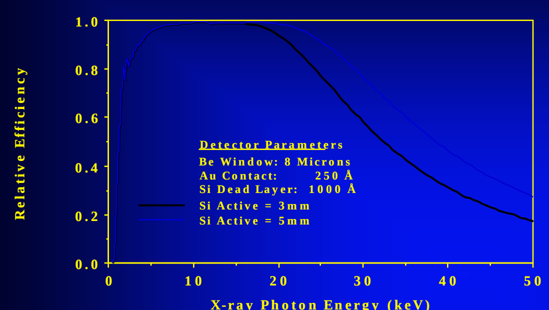
$$I_T = I_o \exp(-\mu x) = I_o \exp\left(-\left[\frac{\mu}{\rho}\right]\rho\, x\right)$$

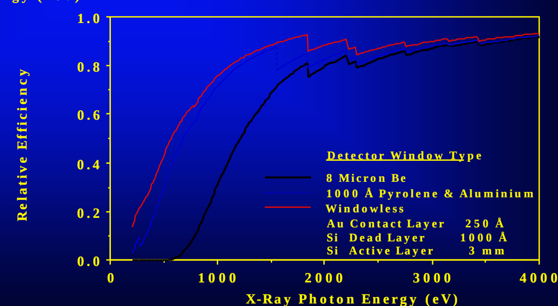
$$\varepsilon(E) = \frac{I_A * I_T}{I_o} = \exp\left(\sum_{i}^{HC/Be/Au/DL} -\left(\frac{\mu(E)}{\rho}\right)_i * \rho_i * t_i\right) * \left\{1 - \exp\left(-\left(\frac{\mu(E)}{\rho}\right)_j * \rho_j * t_j\right)\right\}$$

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

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

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

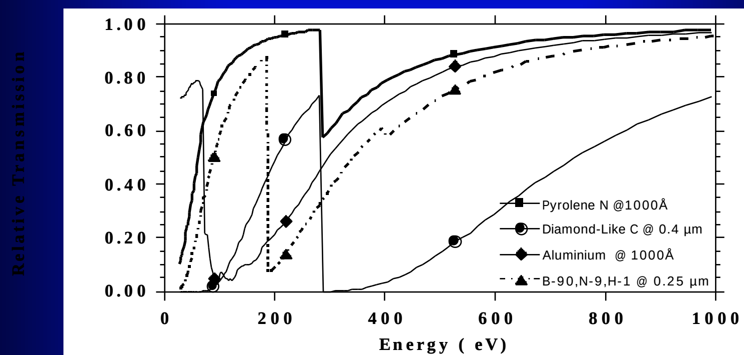




Relative Transmission Efficiency

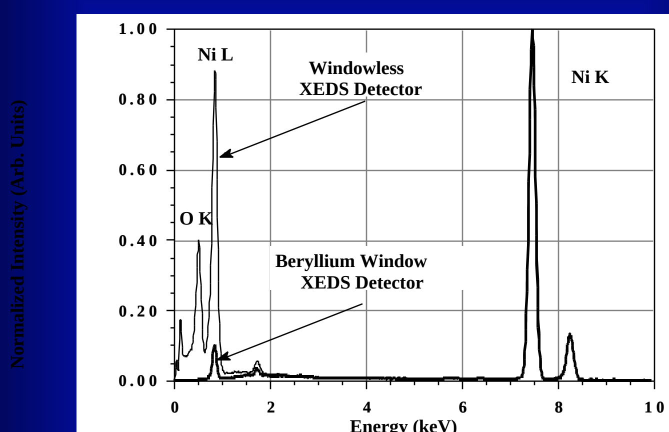
$$\varepsilon(E) = \frac{I_T}{I_o} = \exp\left(\sum_{i}^{Window} -\left(\frac{\mu(E)}{\rho}\right)_i \cdot \rho_i \cdot t_i \right)$$

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



Note the Variation in transmission characteristics by Window Type. Not all UltraThin Windows are Equivalent!!! For example Detection of Nitrogen using a Diamond window is virtually impossible.

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 K line (7.48 keV)

Windowlessvs. Conventional Detectors

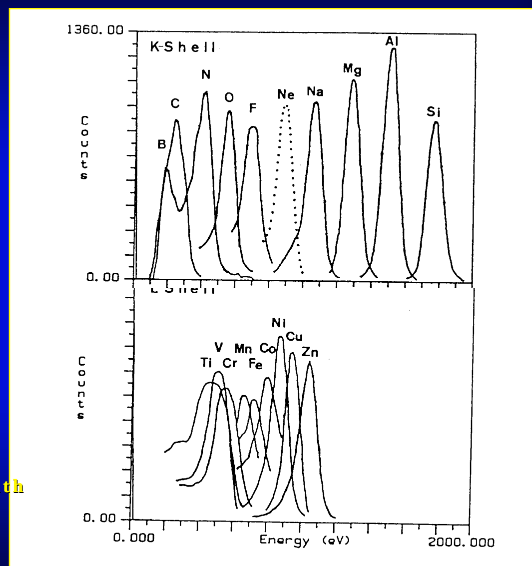
K Shell Spectra using
Windowless Detector

Boron -> Silicon

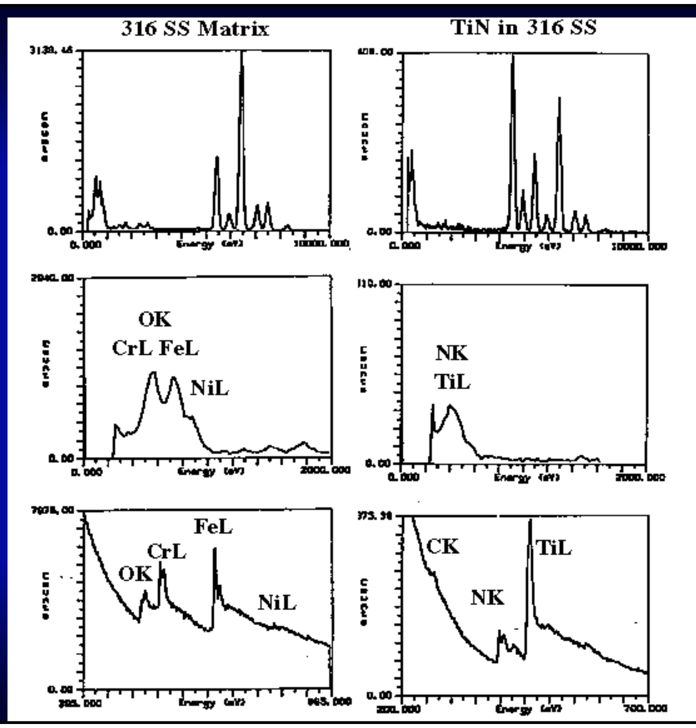
L Shell Spectra Using
Windowless Detector

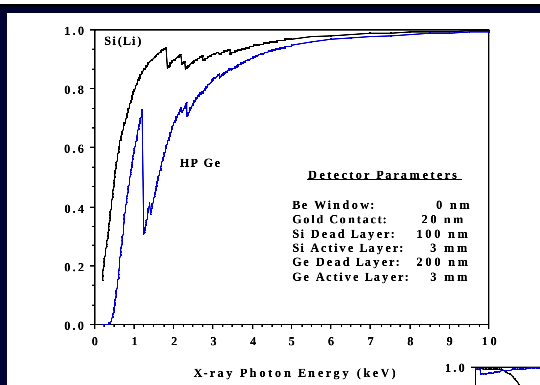
Titanium ->Zinc

Note Potential Overlaps with
K shell Lines

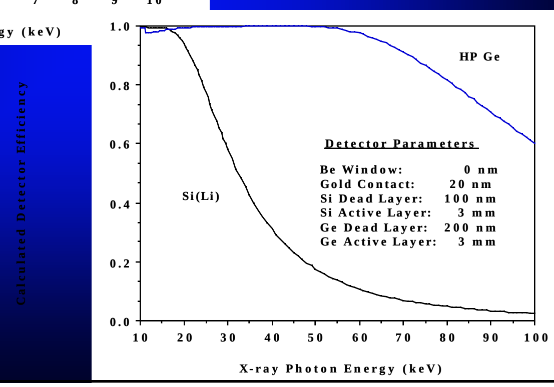


Comparision
Light
Element
Spectroscopy
Resolution
XEDS vs EELS

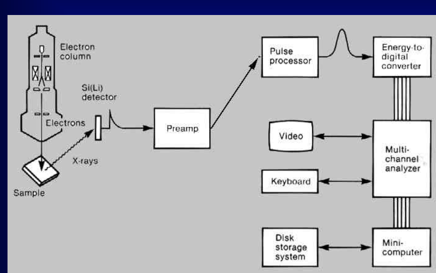


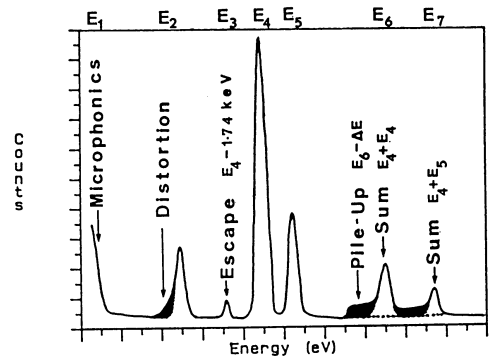


Calculated Efficiency
Si(Li) andHPGe
Windowless Systems



The Multi-Channel Analyzer





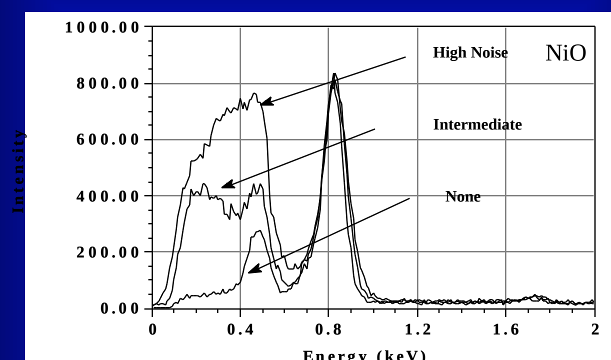
$$\text{Resolution} = \text{FWHM} = \sqrt{\text{Noise}^2 + 2.35^2 \varepsilon F E}$$

ε = 3.8eV (in Si) / 2.9eV (in Ge)
F = Fano Factor ~ 0.1
E = X-ray Energy
Noise = Electronic Noise (mainly in the FET)

Nominal FWHM Values in Modern Si(Li) Detectors:

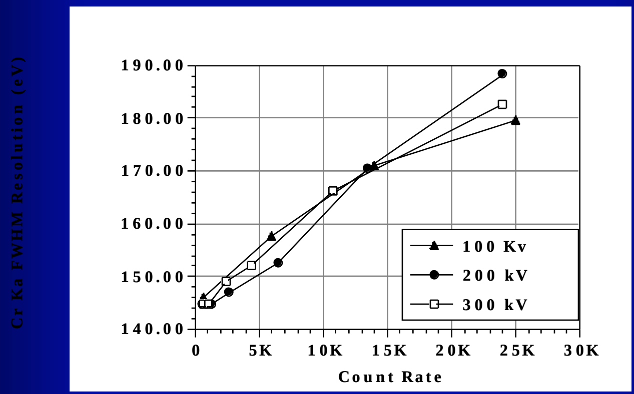
O Kα (0.52keV)	= 80 to 100eV
Mn Kα (5.9keV)	= 130 to 160eV
Mo Kα (17.5keV)	= 190 to 230eV

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



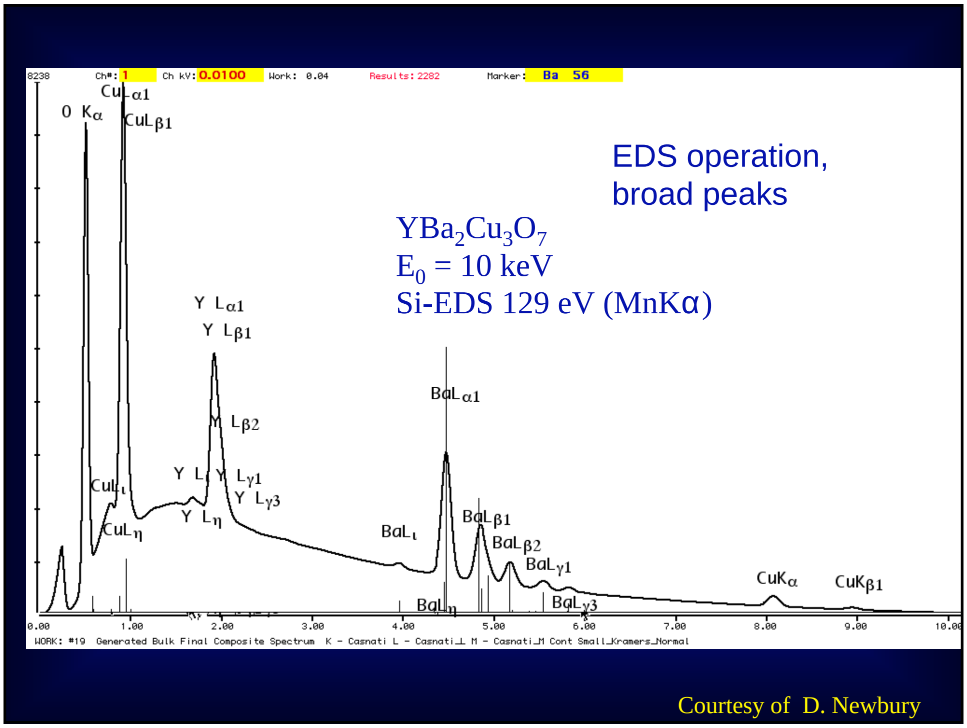
WL & UTW detectors are particuliarly sensitive to low energy noise and microphonics. Observe the changes in the spectra

Resolution Loss with Count Rate

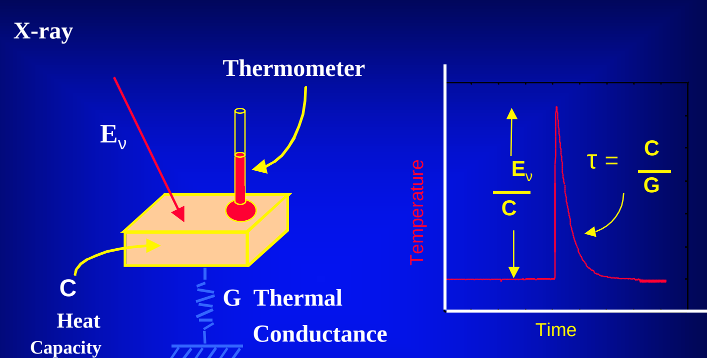


SuperConductor Detectors

Courtesy of D. Newbury



NIST - Microcalorimetry Approach to EDS

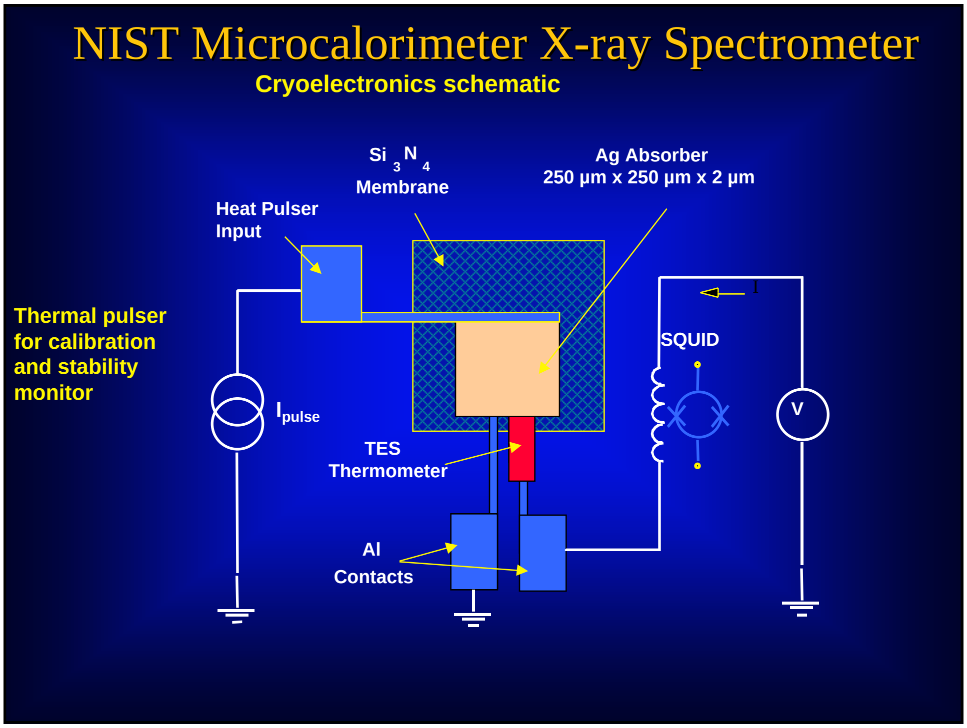


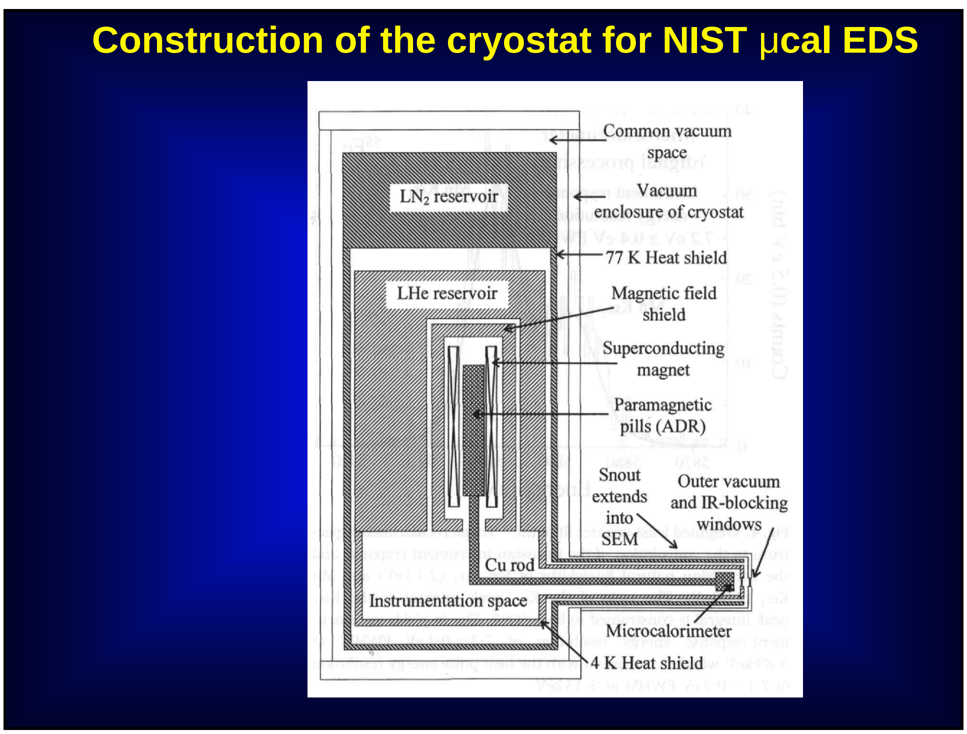
$\Delta E_{FWHM} = 2.36\sqrt{kT^2C}$

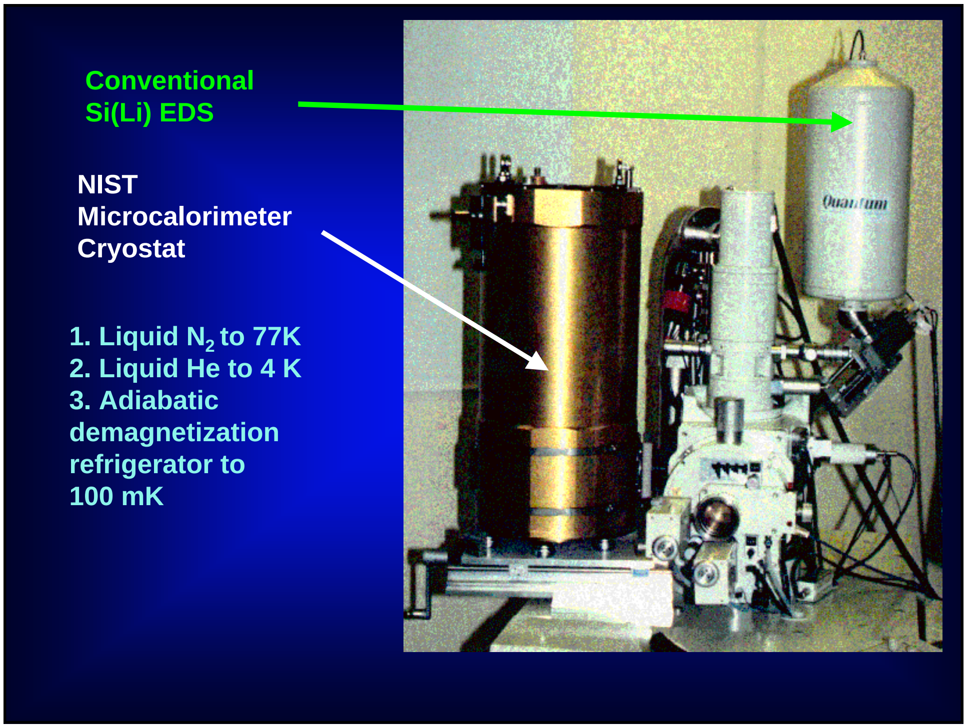
Need heat capacity C to be small:

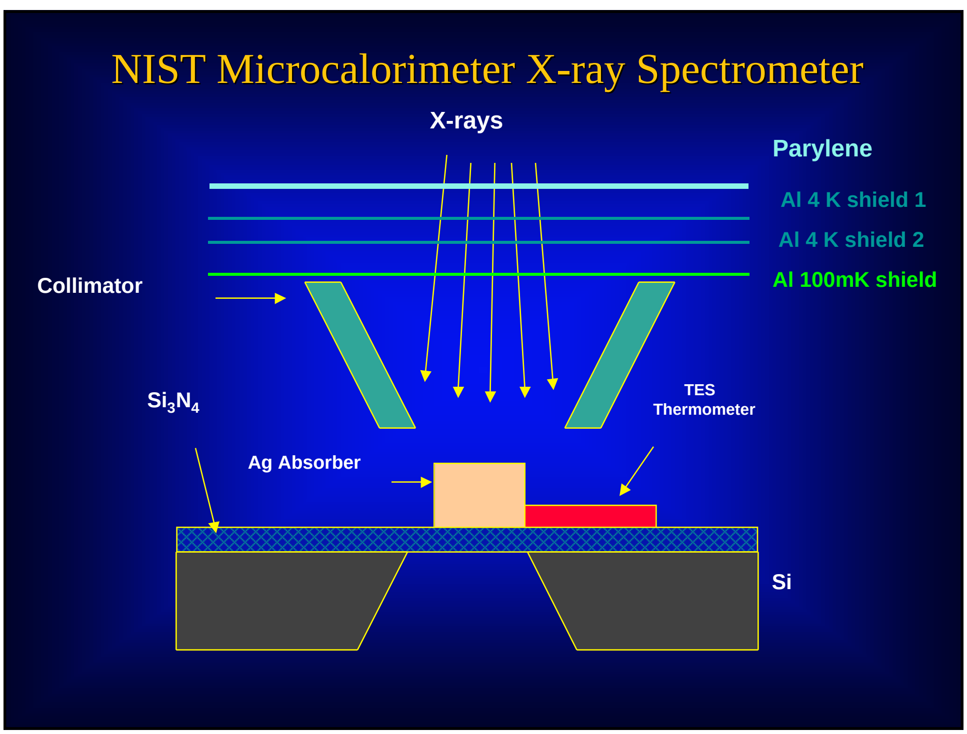
1. Low temperature of operation
2. Small absorber volume
3. Insulators and superconductors

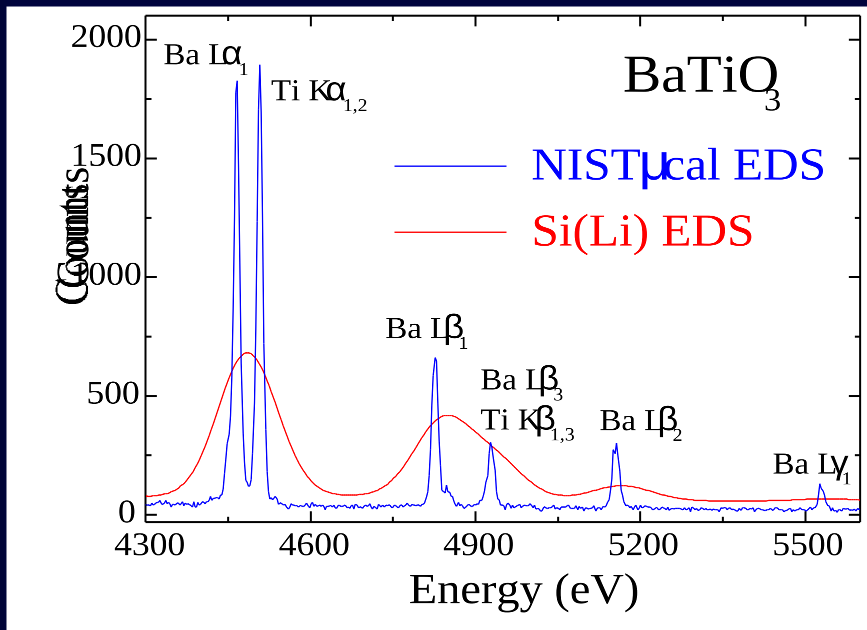
For area ~ mm^2, thickness ~ few μm ΔE_{FWHM} ~ few eV at T = 100 mK


NIST Microcalorimeter X-ray Spectrometer
Cryoelectronics schematic
Si 3 N 4
Membrane
Ag Absorber
250 µm x 250 µm x 2 µm
Heat Pulser
Input
Thermal pulser
for calibration
and stability
monitor
I
SQUID
Ipulse
V
TES
Thermometer
Al
Contacts


Construction of the cryostat for NIST µcal EDS
Common vacuum
space
LN2 reservoir
Vacuum
enclosure of cryostat
77 K Heat shield
LHe reservoir
Magnetic field
shield
Superconducting
magnet
Paramagnetic
pills (ADR)
Snout
extends
into
SEM
Outer vacuum
and IR-blocking
windows
Cu rod
Instrumentation space
Microcalorimeter
4 K Heat shield


Conventional
Si(Li) EDS
NIST
Microcalorimeter
Cryostat
1. Liquid N_2 to 77K
2. Liquid He to 4 K
3. Adiabatic
demagnetization
refrigerator to
100 mK
Quantum

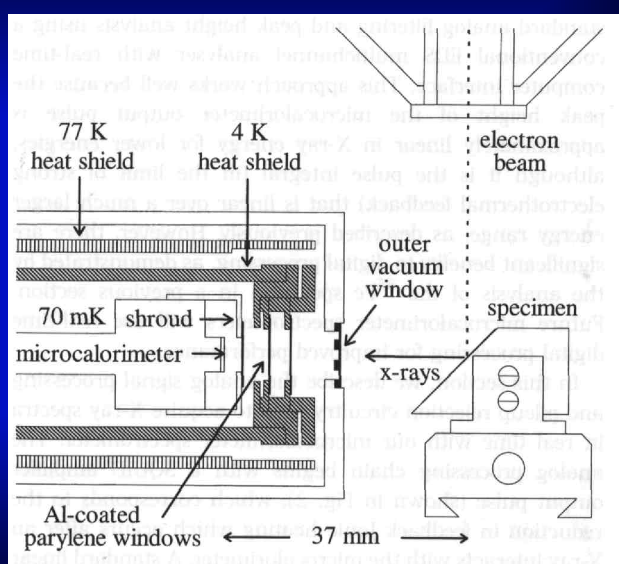

NIST Microcalorimeter X-ray Spectrometer
X-rays
Parylene
Al 4 K shield 1
Al 4 K shield 2
Al 100mK shield
Collimator
Si_3N_4
TES
Thermometer
Ag Absorber
Si



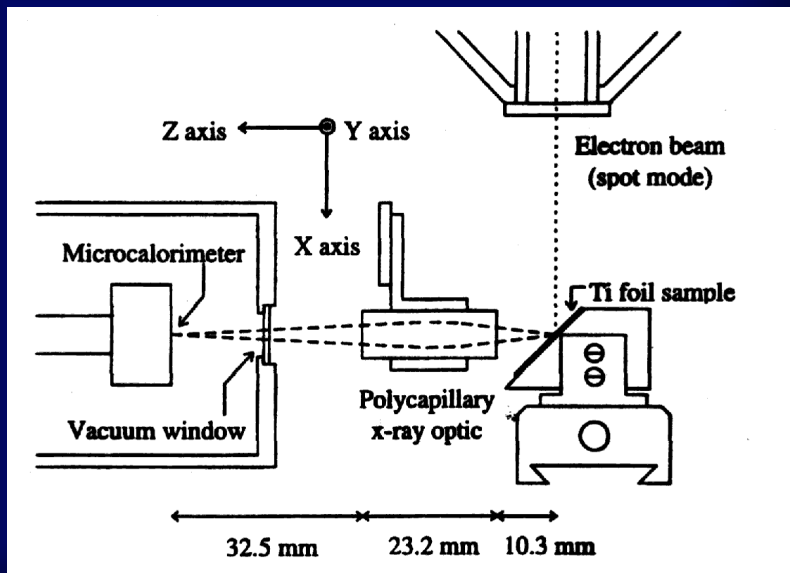
Solid angle limitations

Detector 0.5x0.5 mm at 37 mm
$\Omega = A/r^2 =$ 0.00018 sr

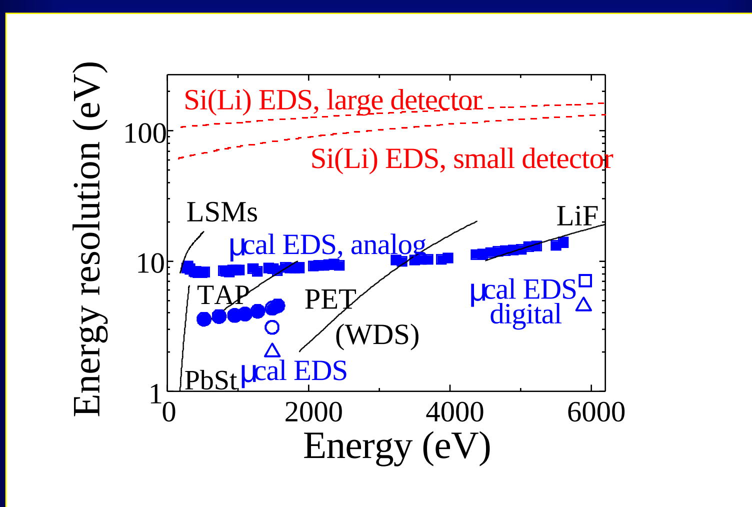
Obviously, This is a very small solid angle detector!



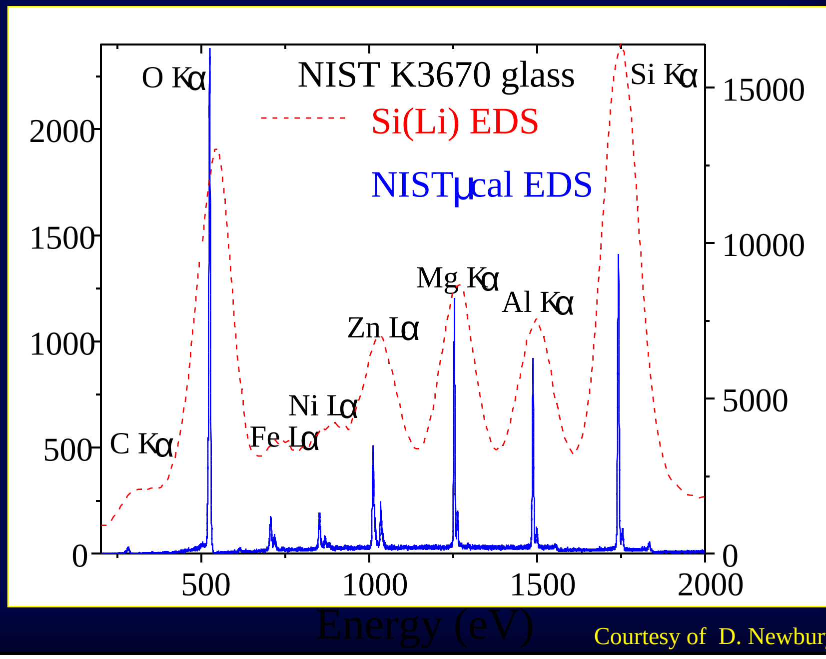
Use of Polycapillary X-ray Optic to Increase Ω



Energy Resolution



Low Photon Energy NIST Microcalorimeter

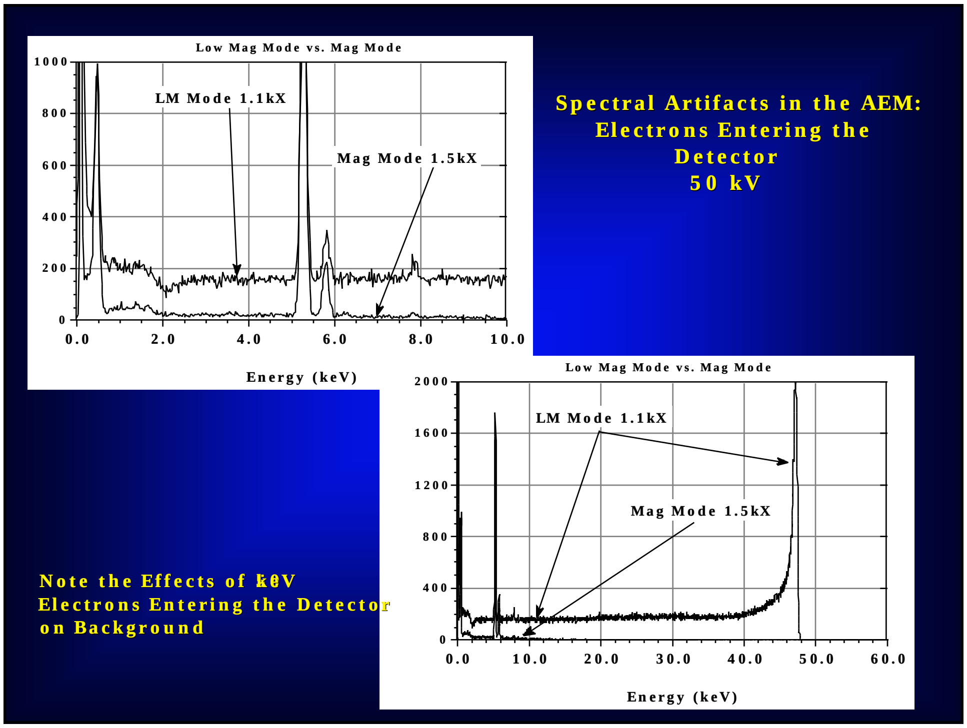


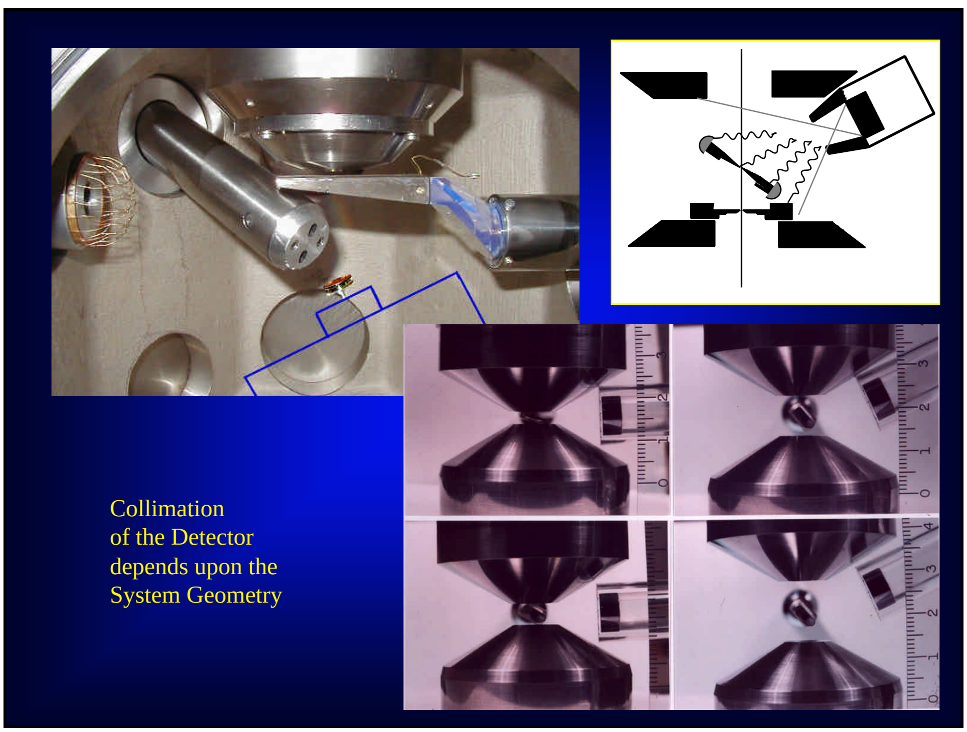
Courtesy of D. Newbury

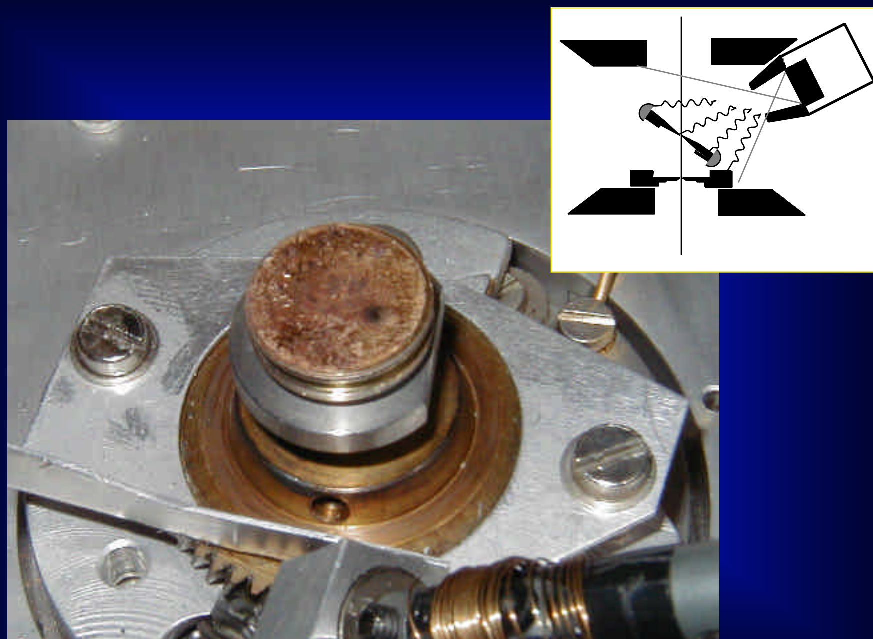
Instrumentation: SEM Systems

The SEM as a system
Spectral Artifacts in the SEM
- Systems Peaks
- Artifacts

Specimen Contamination & Preparation
Optimizing Experimental Conditions

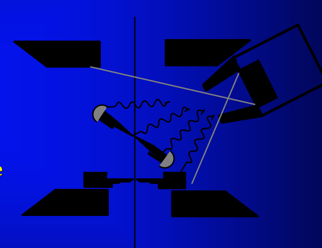

Low Mag Mode vs. Mag Mode
LM Mode 1.1kX
Mag Mode 1.5kX
Energy (keV)
Low Mag Mode vs. Mag Mode
LM Mode 1.1kX
Mag Mode 1.5kX
Energy (keV)
Spectral Artifacts in the AEM:
Electrons Entering the
Detector
50 kV
Note the Effects of keV
Electrons Entering the Detector
on Background


Collimation
of the Detector
depends upon the
System Geometry



Detector/Specimen Geometry

Subtending Solid Angle



Collection Solid Angle

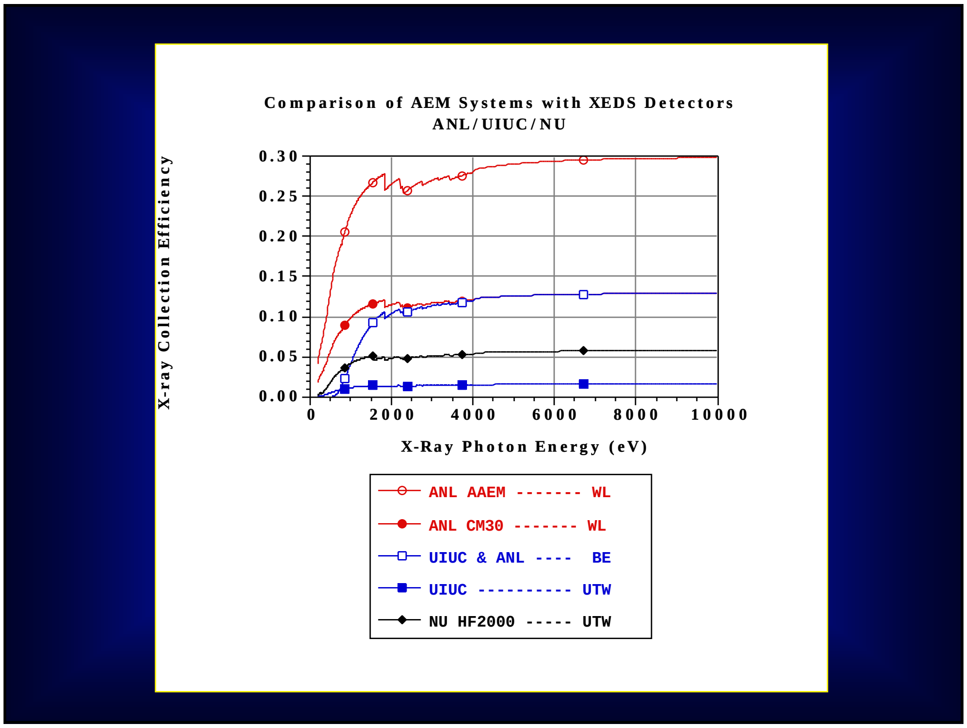
ω = A/R^2 = 0.3 - 0.001sR

A = Detector Active Area

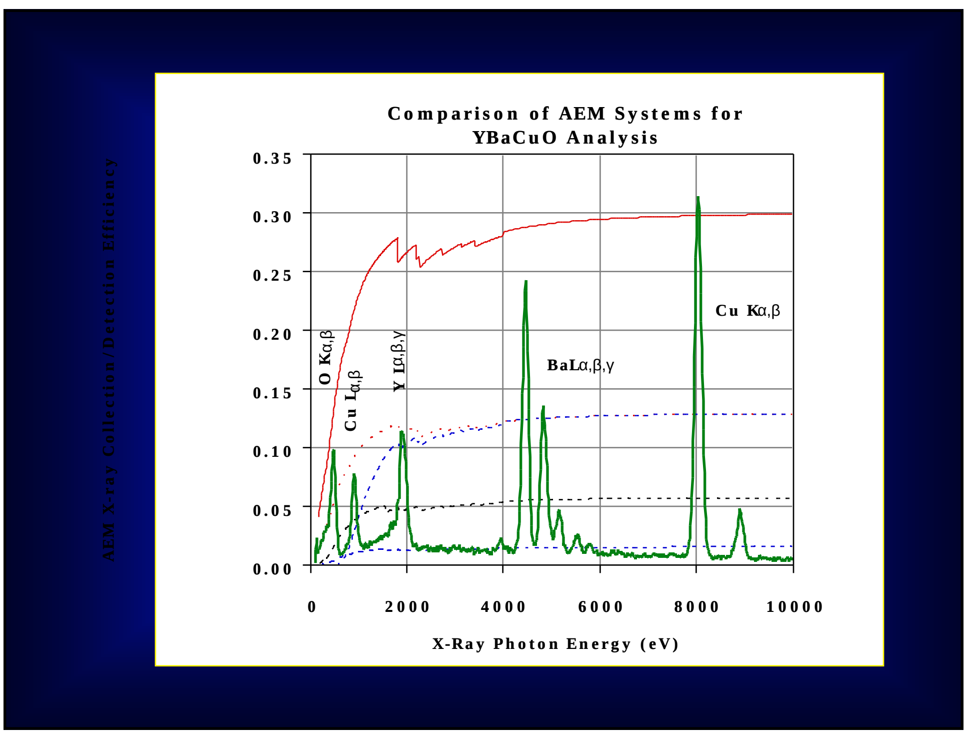
= 10-30 mm2

R = Crystal to Specimen Distance

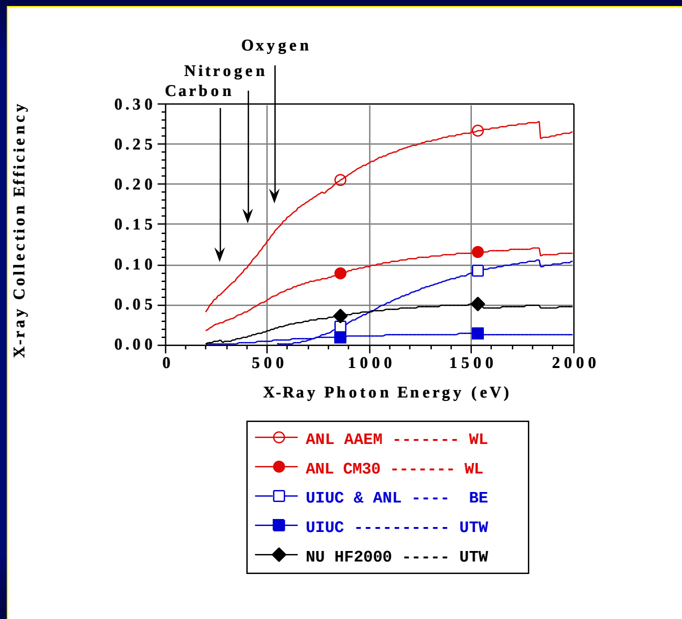
= 10 -> ?? mm



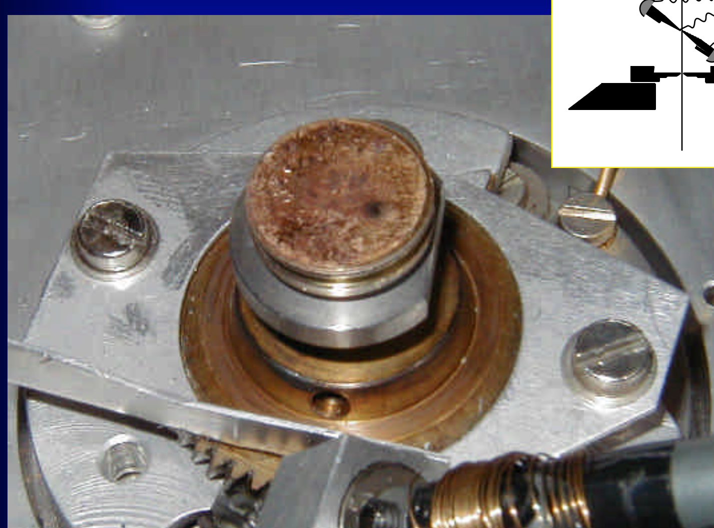
Comparison of AEM Systems with XEDS Detectors
ANL/UIUC/NU
X-ray Collection Efficiency
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2000
4000
6000
8000
10000
X-Ray Photon Energy (eV)
ANL AAEM ------- WL
ANL CM30 ------- WL
UIUC & ANL ---- BE
UIUC ---------- UTW
NU HF2000 ----- UTW

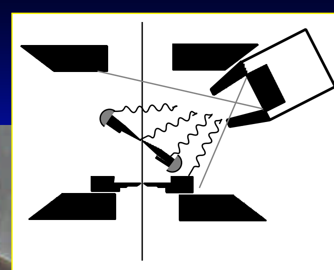


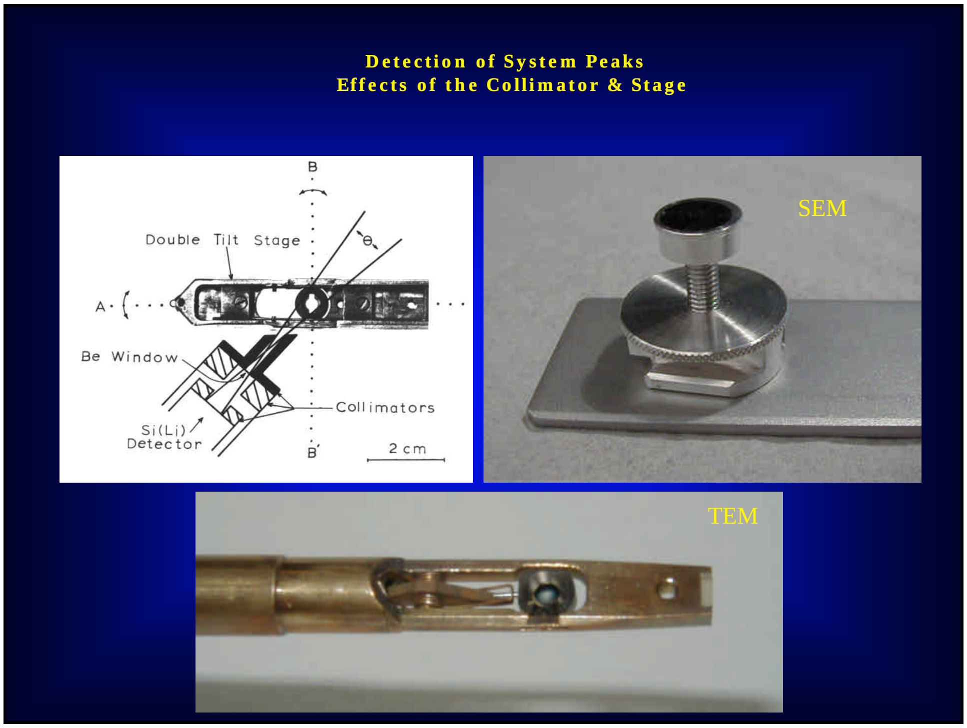
Comparison of AEM Systems for
YBaCuO Analysis
AEM X-ray Collection/Detection Efficiency
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
O Kα,β
Cu Lα,β
Y Lα,β,γ
BaLα,β,γ
Cu Kα,β
0
2000
4000
6000
8000
10000
X-Ray Photon Energy (eV)

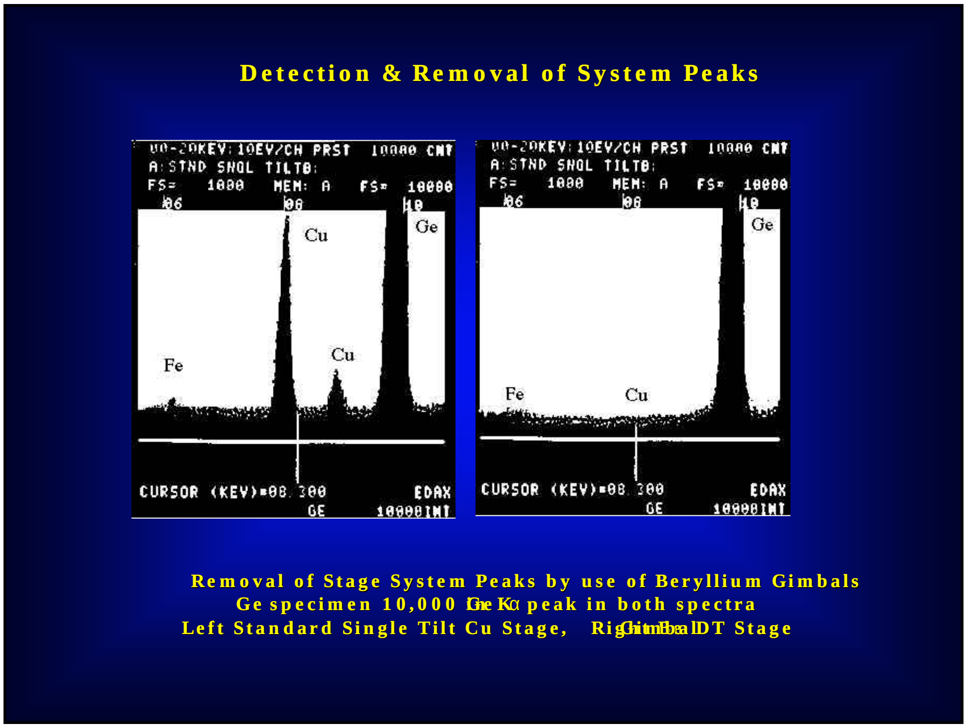


Oxygen
Nitrogen
Carbon
X-ray Collection Efficiency
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
500
1000
1500
2000
X-Ray Photon Energy (eV)
ANL AAEM ------- WL
ANL CM30 ------- WL
UIUC & ANL ---- BE
UIUC ---------- UTW
NU HF2000 ----- UTW






Detection of System Peaks
Effects of the Collimator & Stage
B
Double Tilt Stage
θ
A
Be Window
Collimators
Si(Li)
Detector
B′
2 cm
SEM
TEM


Detection & Removal of System Peaks
00-20KEV:10EV/CH PRST 10000 CNT
A:STND SNGL TILTB:
FS= 1000 MEM: A FS= 10000
Cu
Ge
Fe
Cu
CURSOR (KEV)=08.300 EDAX
GE 10000INT
00-20KEV:10EV/CH PRST 10000 CNT
A:STND SNGL TILTB:
FS= 1000 MEM: A FS= 10000
Ge
Fe
Cu
CURSOR (KEV)=08.300 EDAX
GE 10000INT
Removal of Stage System Peaks by use of Beryllium Gimbals
Ge specimen 10,000 Ge Kα peak in both spectra
Left Standard Single Tilt Cu Stage, Right Be Gimbal DT Stage

4

Reactive Gas Plasma Processing Applications to Analytical Electron Microscopy

Example:

- **The figure at the right shows the resu 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 immedi vicinity of the electron probe. The an of the contamination is a function of time spent at each location. Here the was varied from 15 - 300 seconds.**

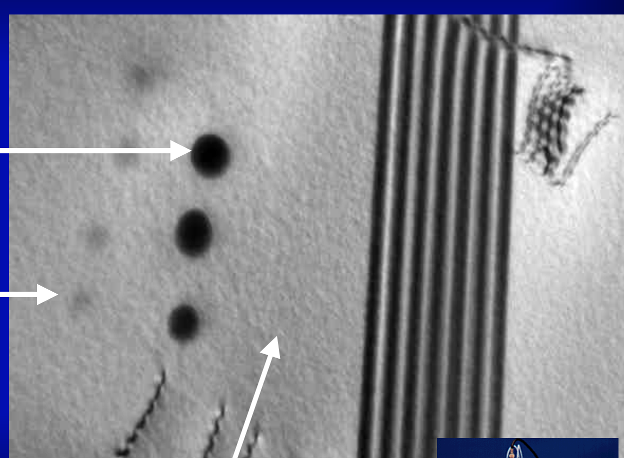
9

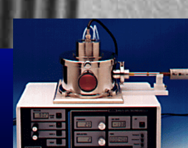
Comparision Results on Electropolished 304 SS

•Untreated Specimen

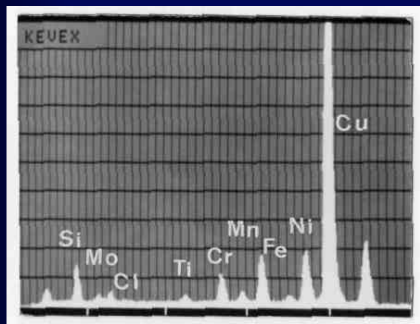
•After 5 minutes Argon Processing

•After 5 minutes of additional Oxygen Processing

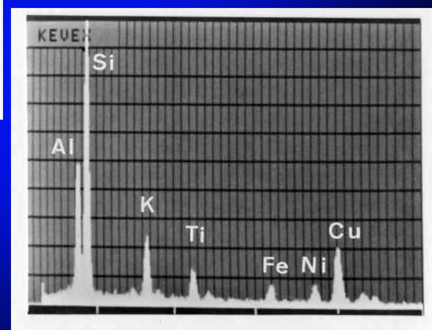




Specimen Contamination Effects



Electropolishing leaves residual Cl on surface



Ion Milling leaves redeposited Fe, Ni, Cu from SS Holder & Cu Washer

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

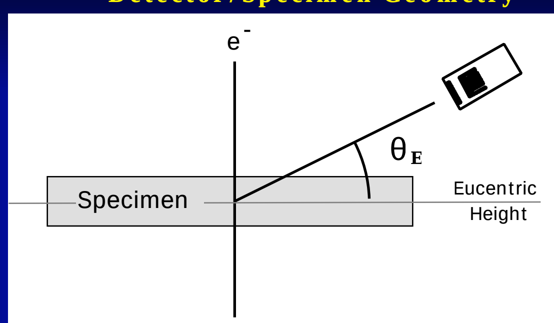
Choice of Electron Source
- Spatial Resolution
- Tungsten Hairpin
- LaB_6
- Field Emission

Radiative Partition Function (Γ) Governs the Relative Intensities

Nominal Values (Varies slowly with Atomic Number)

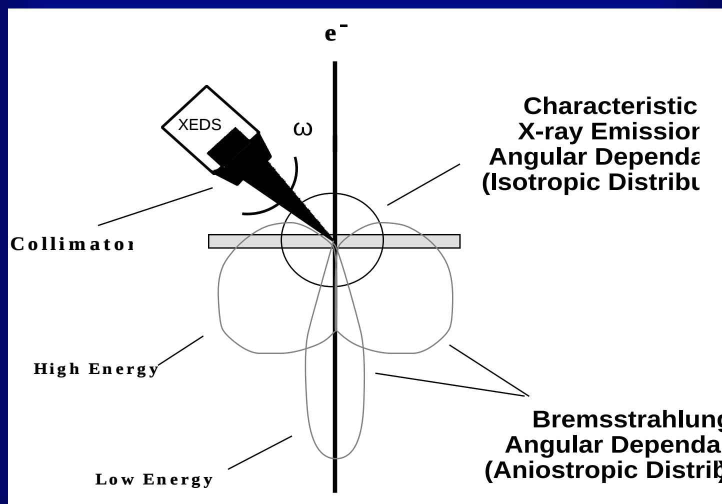
K Shell	L Shell	M Shell
$K_{\alpha1}$ = 100	$L_{\alpha1}$ = 100	$M_{\alpha1,2}$ = 100
$K_{\alpha2}$ = 50	$L_{\alpha2}$ = 50	M_{β} = 60
$K_{\beta1}$ = 15-30	$L_{\beta1}$ = 50	
$K_{\beta2}$ = 1-10	$L_{\beta2}$ = 20	
$K_{\beta3}$ = 6-15	$L_{\beta3}$ = 1-6	
	$L_{\beta4}$ = 3-5	
	$L_{\gamma1}$ = 1-10	
	$L_{\gamma3}$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

Detector/Specimen Geometry



Designation	Elevation Angle θ_E	Azimuthal Angle θ_A
Low	0°	45°
	0°	90°
Intermediate	15-30°	90°
High	68-72°	0°

Detector/Specimen Geometry



X-ray Production = Cross-section * electrons

Maximizing The Signal

$$\eta = \text{Probe current} = \frac{(\pi d_o \alpha_o)^2 \mathcal{B}}{4}$$

$$\mathcal{B} = \text{Brightness} = \left(\frac{J_c}{\pi k T}\right) eV_r$$

$$V_r = \text{Relativistic Voltage} = V_o\left(1+\frac{eV_o}{[\ 2m_oc^2\ ]}\right)$$

$$V_o(\ 1+ 9.785 \times 10^{-7} V_o)$$

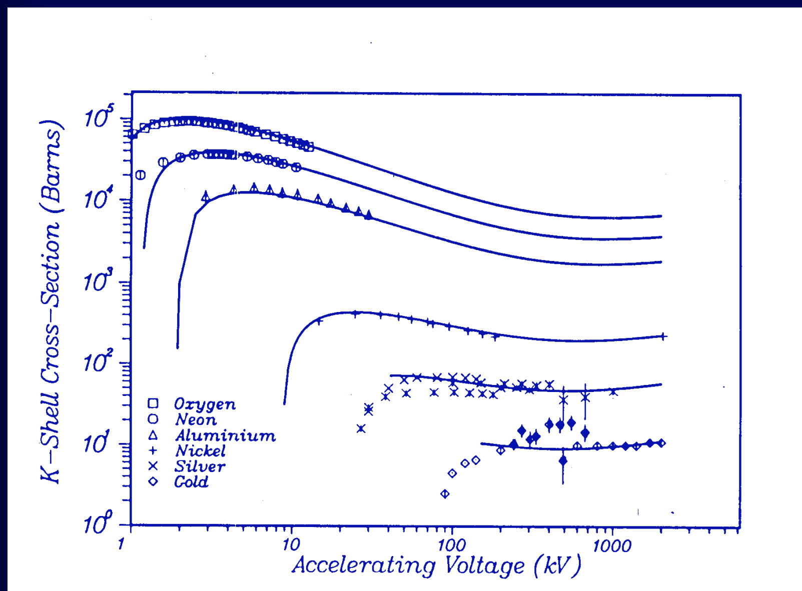
Non-Relativistic Cross-section Model

$$Q_K = \frac{a_K * b_K *\{\ \ln\ (c_K * \frac{E_o}{E_c})\}}{E_o\ E_c}$$

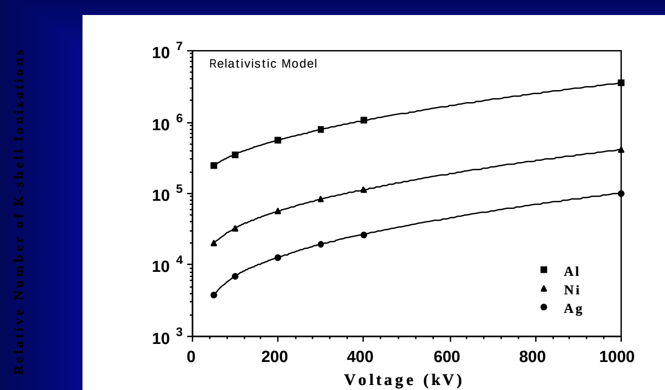
Relativistic Cross-section Model

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

$$T_o = 1/2\ m_o c^2 \beta^2, \text{ where } \beta = v/c$$



Effects on Intensity with Accelerating Voltage for constant Probe size parameters



$$I = Q * \eta$$

For identical probe diameters one has higher x-ray production at higher voltage due to the increase in beam current.
Alternatively, one can achieve the same statistical intensity for smaller probes at higher

Minimium Detectable Mass

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

Minimum Mass Fraction

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

k, k^* = Constants

P_x = Characteristic Signal from element X

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

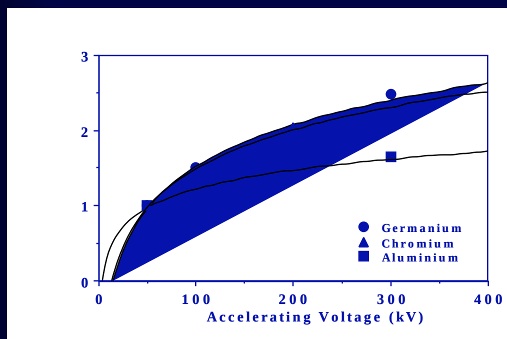
I_o = Incident electron flux

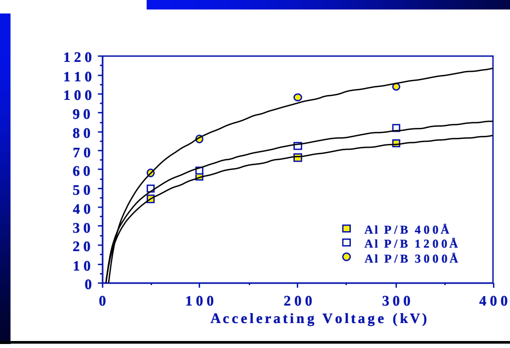
J_o = Incident electron current density

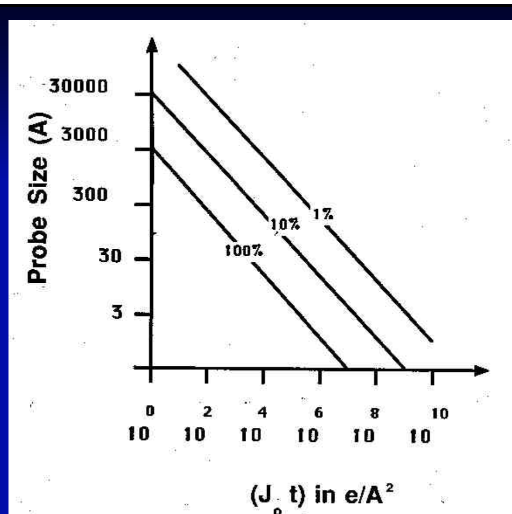
d_o = Probe diameter

= Analysis time

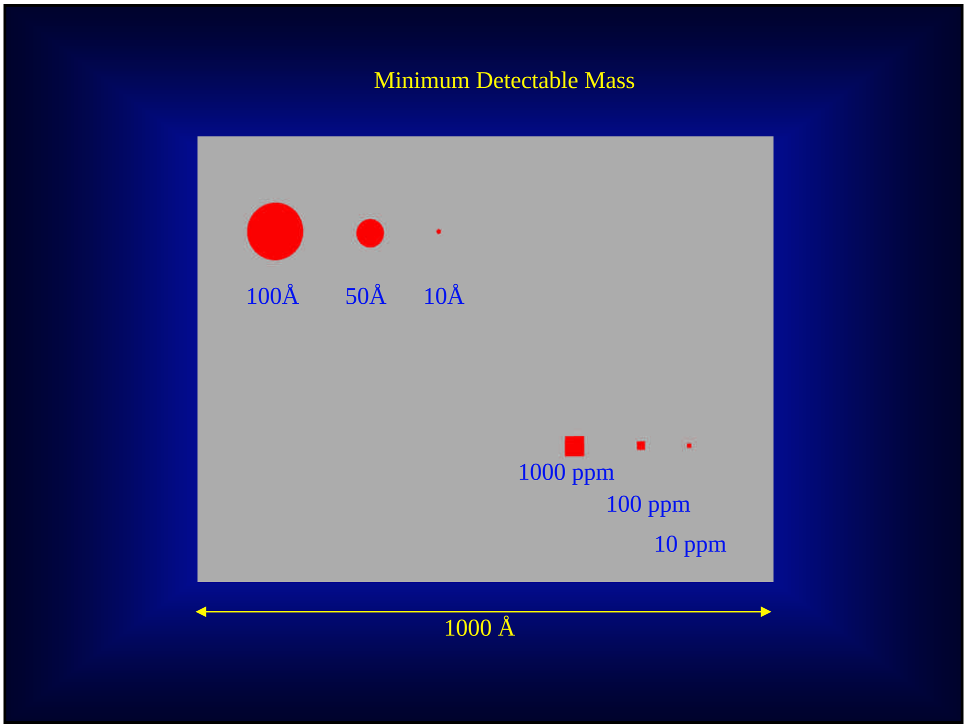
Experimental Peak/Background Variation with Voltage

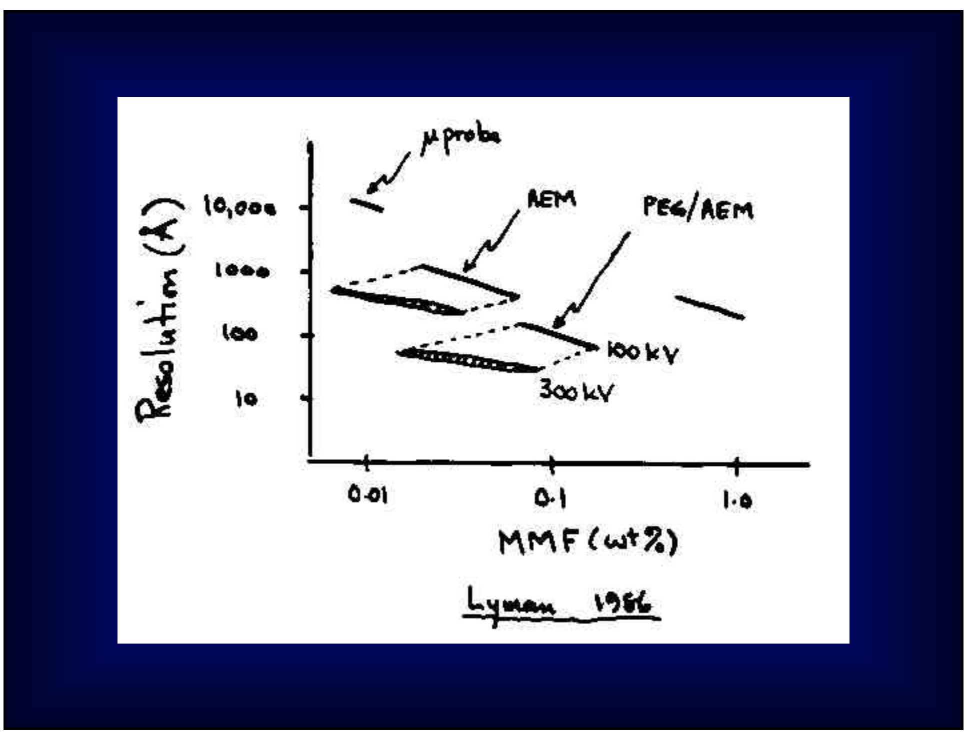




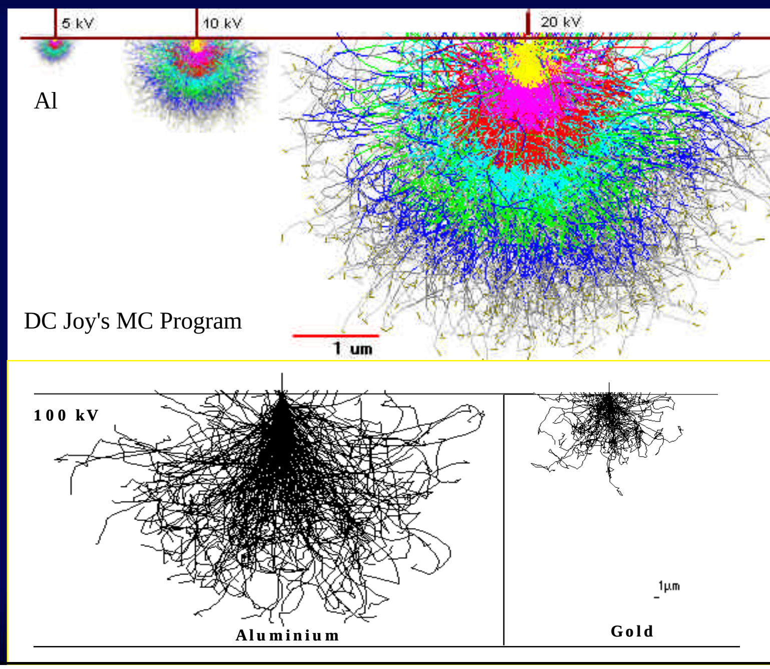


$$d_o = \frac{k}{MMF}\left[\frac{1}{P_x (P/B)_x J_e t}\right]^{1/2}$$

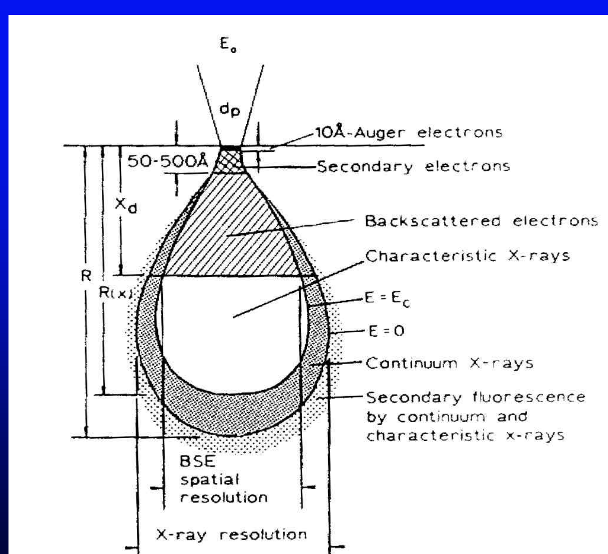

Minimum Detectable Mass
100Å
50Å
10Å
1000 ppm
100 ppm
10 ppm
1000 Å

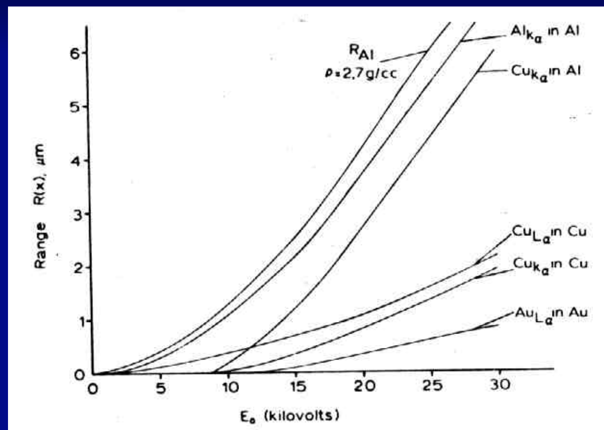

μprobe
AEM
PEG/AEM
10,000
1000
100
10
Resolution (Å)
100 kV
300 kV
0.01
0.1
1.0
MMF (wt%)
Lyman 1986

Spatial Resolution /Beam Spreading Monte Carlo Calculations



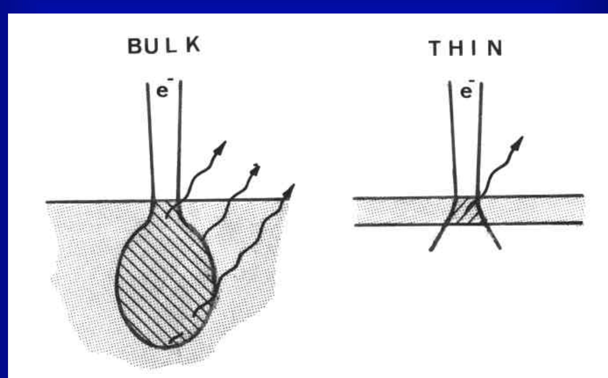
Depth Distribution

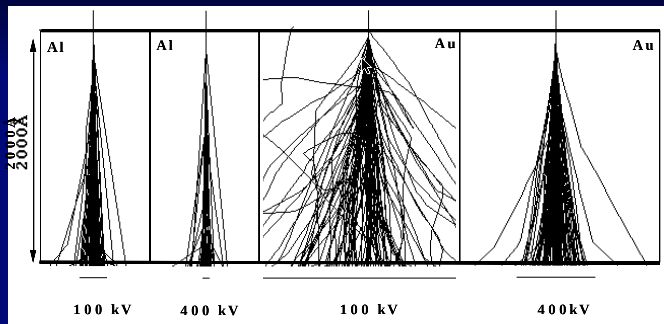




Goldstein

R [μm] = 0.231 (Eo[kV] $^{1.5}$ - Ec[kV] $^{1.5}$) / ρ [gm/cm^3] (**Reed**)





Monte Carlo Calculations of(Newbury &Myklebust-1979)

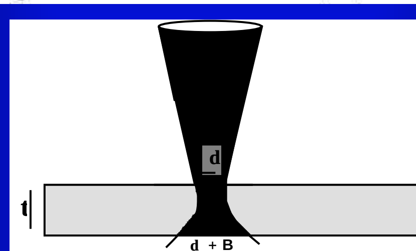
Element	Z	Thickness 10nm	50nm	100nm	500nm
Carbon	6	0.22	1.9	4.1	33.0
Aluminium	13	0.41	3.0	7.6	66.4
Copper	29	0.78	5.8	17.5	244.0
Gold	79	1.71	15.0	52.2	1725.0

Analytic Formulation (Elastic Scattering - Goldstein etal 1977)

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

b= Beam Broadening [cm]
E_0= Accelerating Voltage [kV]
A= Atomic Weight

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

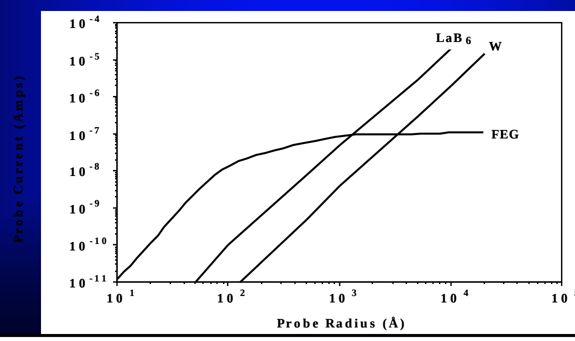


Element	Z	10nm	50nm	100nm	500nm
Carbon	6	0.16	1.8	5.13	57.4
Aluminium	13	0.26	1.9	8.12	90.9
Copper	29	0.68	7.6	21.4	*
Gold	79	15.5	17.3	*	*

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

Comparison of Electron Sources

Type		Brightness β/V_o $A/cm^2/sr/eV$	Source Size (µm)	Energy Spread (eV)	Noise	Stability	Cohereny	Vacuum (Torr)
Thermonic	Hairpin	1	50	2-3	Low	Good	Low	$<10^{-4}$
	Pointed	5	10			Fair	Moderate	$<10^{-5}$
LaB_6	Poly Crystal	10-30	10	~1	Low	Good	Moderate	$<10^{-6}$
	Single Crystal	20-50	5					
Field Emission	Thermal Assist	100-500	<100Å	~.5	Fair	Moderate	High	$<10^{-8}$
	Cold	100-1000		<.25		Fair		$<10^{-10}$

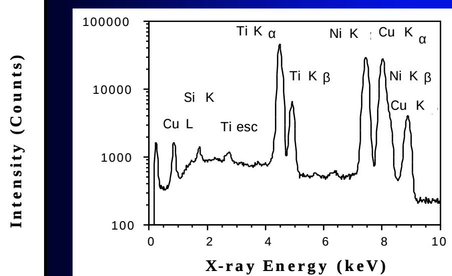


Data Analysis and Quantification:

Spectral Processing
Quantification Methods

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

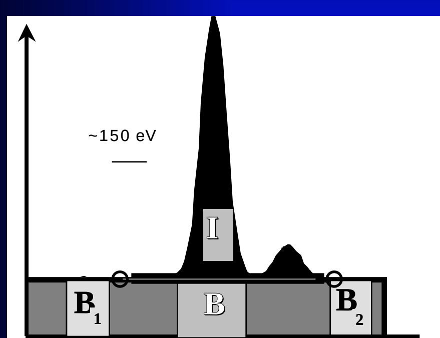
Deconvolution: Fourier Method for Resolution Enhancement

Background Modeling

Simple - Linear and/or Polynomial Interpolation

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

Spectral Processing : XEDS
Simple Data Reduction



$$B \approx B_1 + B_2$$

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

Recall that for a Gaussian Peak

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

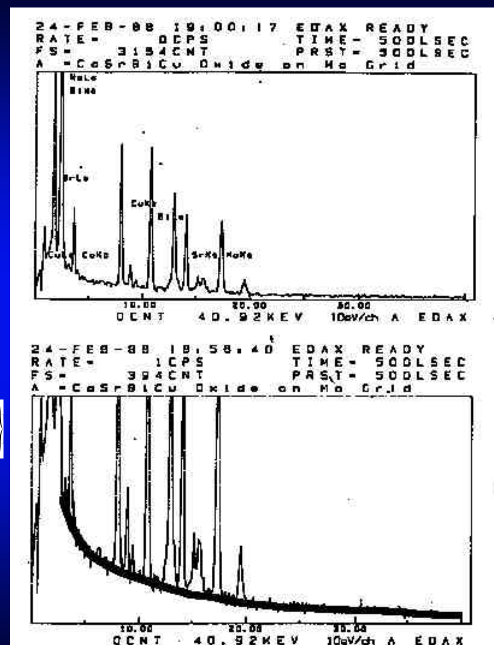
Hence for the ratio of Intensities

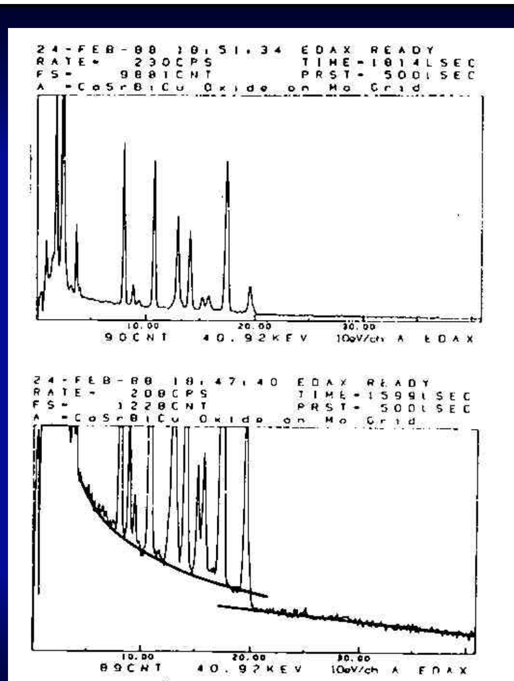
$$\frac{I_1}{I_2} = \frac{\sigma_1 * A_1}{\sigma_2 * A_2} \neq \frac{A_1}{A_2}$$

Spectral Processing : XEDS

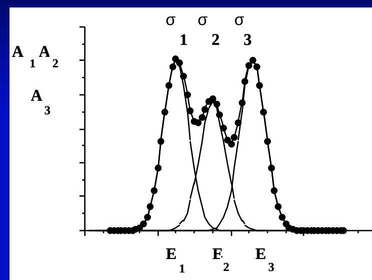
Background Modeling : Power Law/Parametric Fits

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





Spectral Processing : XEDS
Curve Fitting : Linear Modeling



Let

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

then

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

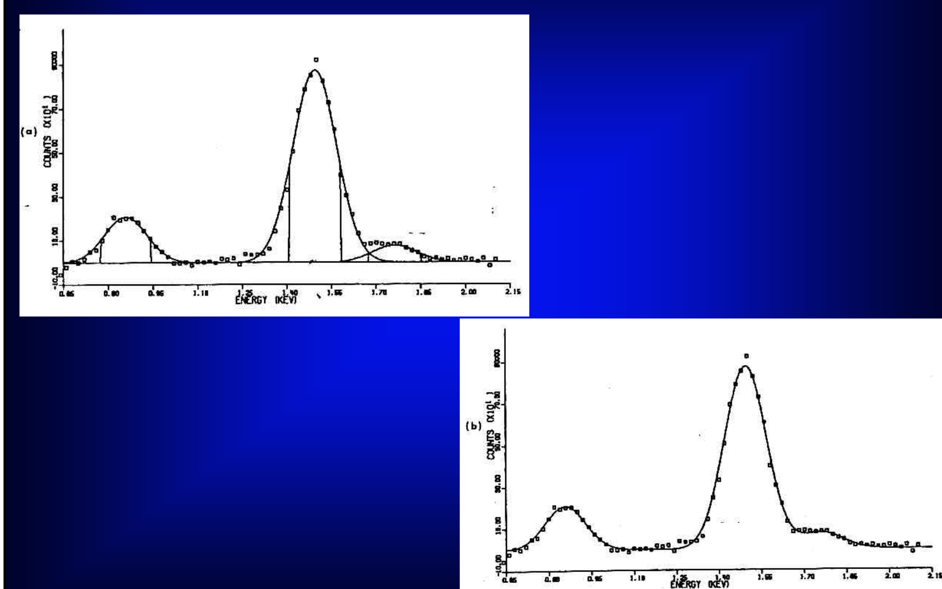
Using simple matrix algebra solve for A

•Fast and simple procedure

•Presumes operator knows all elements present

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

Spectral Processing : XEDS
Curve Fitting : Linear Modeling



Spectral Processing : XEDS
Curve Fitting : Non- Linear Modeling

Calculate and Minimize χ^2

$$\chi^2 = \sum_{k=1}^{M} \left(\sum_{i=1}^{N} \frac{(y_i - Y_k)^2}{y_i^2} \right) \quad \text{with } Y_k = A_k \exp\left(\frac{-(E_i - E_k)^2}{2\sigma^2(E_k)} \right)$$

and y_i = raw data

$\chi 2$ is minimized by searching (E, A) parameter space

Pattern Search

- Sequential method: mechanical iteration of each parameter until a local minmimum is found.
- Simplex method: simultaneous variation of all parameters.

Gradient Search

- Evaluate

Multiple Least Squares with Derivitive Reference

- Linearization of the above problem
  E---> E + δE σ--> $\sigma + \delta\sigma$

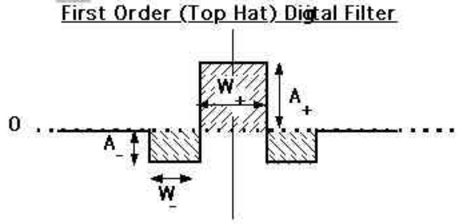
$$I'(E) = I(E) - \delta E \frac{\delta I(E)}{\delta E} + \left(\sigma\delta\sigma + \frac{(\delta E)^2}{2}\right) \frac{\delta^2 I(E)}{\delta E^2}$$

Spectral Processing : XEDS
Digital Filtering

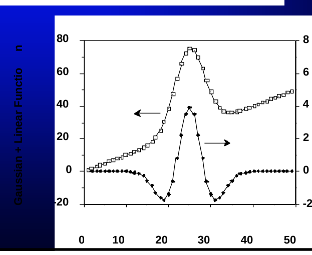
Background Suppression by Mathematical modeling
- Replace Data by new spectra formed by the following linear operation.

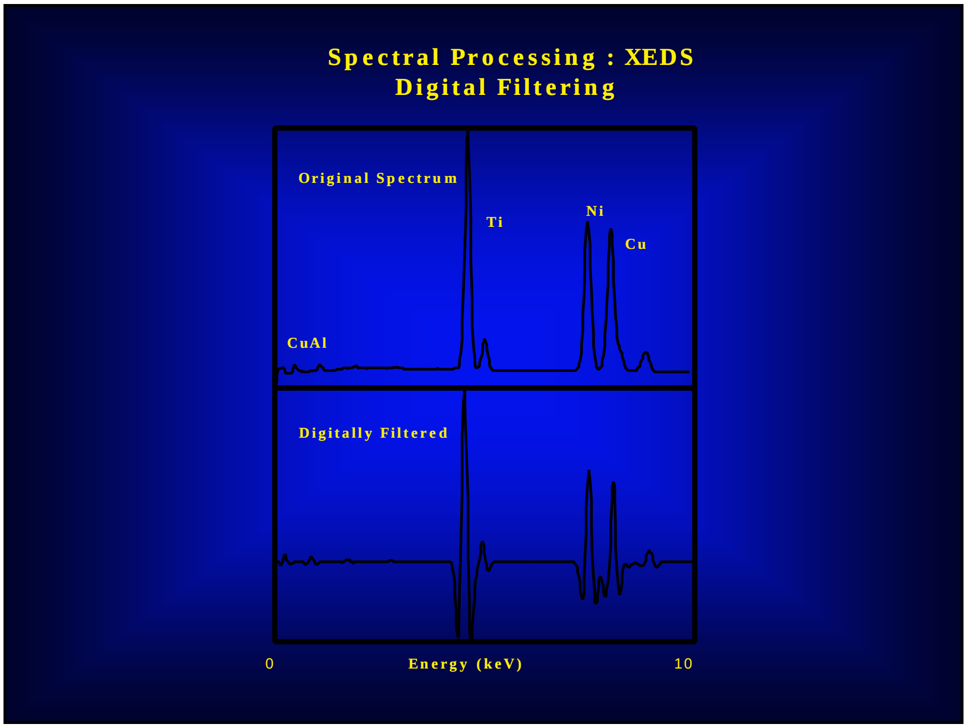
$$G(x_i) = [F(x_{+1}) - 2^*\left(\frac{W_-}{W_+}\right)^* F(x_0) + F(x_{-1})] \quad \text{where } F(x_j) = \Sigma f(x_j)$$

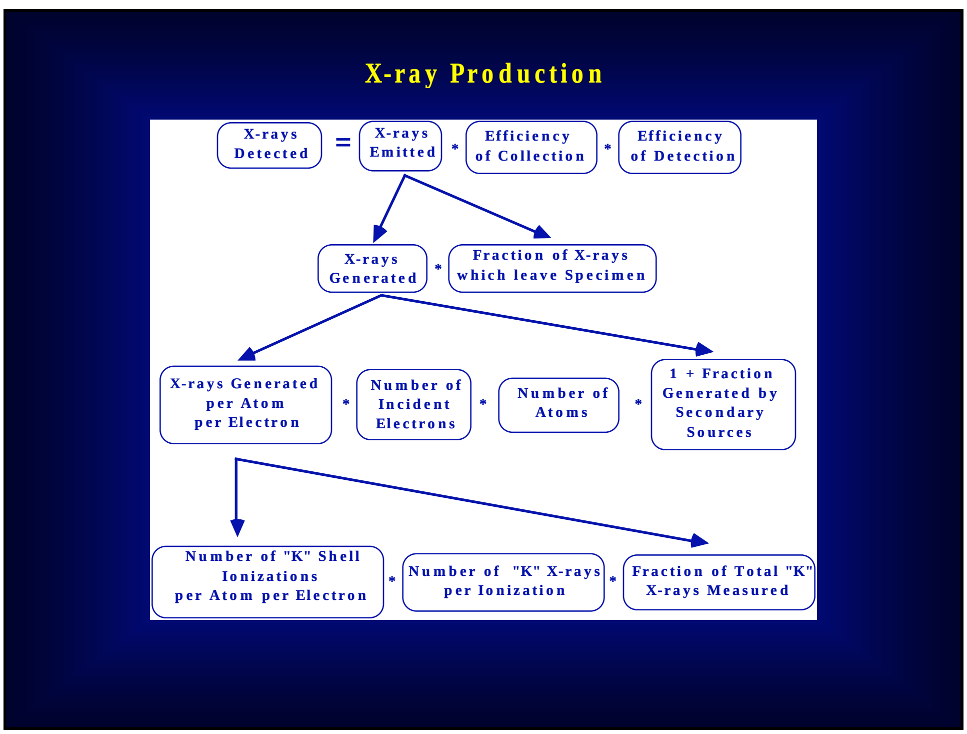
First Order (Top Hat) Digital Filter



Operator independent
Introduces severe spectral distortion




Spectral Processing : XEDS
Digital Filtering
Original Spectrum
Ti
Ni
Cu
CuAl
Digitally Filtered
0
Energy (keV)
10


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

X-ray Production

$$I_A^{K\alpha} = \Gamma_A \omega_A \left\{ \int_{Ec}^{E} \frac{\sigma_A(E,Z)}{S_A} \right\} \{R_A\} \{f(\chi)\} \{F_A\} C_A \left\{ \frac{N_o \rho}{W_A} \right\} \{\eta_o \varepsilon_A \Omega\}$$

I_A	=	Measured x-ray intensity per unit area
σ	=	K^{th}-shell ionization cross-section
ω	=	K^{th}-shell fluorescence yield
Γ	=	K^{th}-shell radiative partition function
R	=	Backscatter Correction Term
S	=	Electron Stopping Power
$f(\chi)$	=	Absorption Correction Term
F	=	Fluorescence Correction Term
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

Quantification Procedures - Matrix Corrections

Empirical Models

Assume that each element linearly influences the x-ray intensity of each other element. Produce a table of coefficients to correct for inter-element effects

ZAF Corrections

Matrix effects are grouped into 3 categories and calculated
Z - Atomic Number, A- Absorption, F - Fluroescence
Deviations from Linearity (I vs C) are corrected by multiplicative terms

Phi-Rho-Z $\varphi(\rho z)$

Model the depth distribution of electron scattering and combine stopping power and absorption corrections

Monte Carlo

Individual electron trajectories simulated in a computer used mainly to simulate scattering and to formulate analytical equations for ZAF and $\varphi(\rho z)$ methods or treat special geometries.

Quantitative Analysis using XEDS 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:

$$\frac{I_U^{K\alpha}}{I_S^{K\alpha}} = \frac{\Gamma_U \omega_U \left\{ \int_{Ec}^{E} \frac{\sigma_U(E,Z)}{S_U} \right\} \{R_U\}\{f(\chi)\}\{F_U\} C_U \left\{ \frac{N_o \rho_U}{W_U} \right\} \{\eta_o^U \varepsilon_U \Omega\}}{\Gamma_S \omega_S \left\{ \int_{Ec}^{E} \frac{\sigma_S(E,Z)}{S_S} \right\} \{R_S\}\{f(\chi)\}\{F_S\} C_S \left\{ \frac{N_o \rho_S}{W_S} \right\} \{\eta_o^S \varepsilon_S \Omega\}}$$

$$\frac{I_U^{K\alpha}}{I_S^{K\alpha}} = \frac{\left\{ \int_{Ec}^{E} \frac{\sigma_U(E,Z)}{S_U} \right\} \{R_U\}\{f(\chi)\}\{F_U\}\{\rho_U\}\{\eta_o^U\} C_U}{\left\{ \int_{Ec}^{E} \frac{\sigma_S(E,Z)}{S_S} \right\} \{R_S\}\{f(\chi)\}\{F_S\}\{\rho_S\}\{\eta_o^S\} C_S}$$

$$\frac{I_U^{K\alpha}}{I_S^{K\alpha}} = \{K_Z\} \cdot \{K_A\} \cdot \{K_F\} \cdot \frac{\{\eta_o^U\}}{\{\eta_o^S\}} \cdot \frac{C_U}{C_S}$$

These equations state 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 correction terms and the beam current ratio.

Determining the k Factors

Experimental Measurements

Prepare standards of known composition
then measure relative intensities and solve explicitly
for the 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 k factor measurements,
then fit the AEM parameters to best match the data.
Extrapolate to systems where measurements and/or
standards do not exist.

Quantitative Analysis using XEDS
Standardless Method

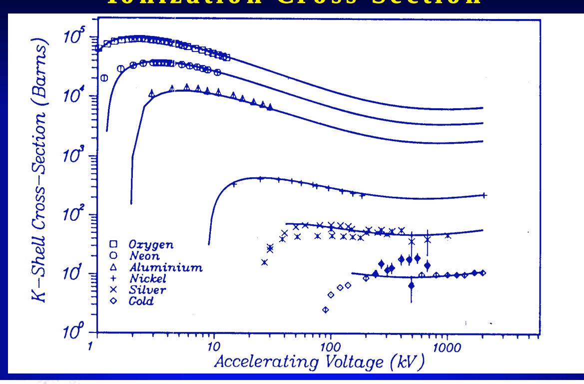
Invoke the Intensity Ratio Method, but now consider the ratio of the different x-ray lines from the same specimen:

$$\frac{I_A^{K\alpha}}{I_B^{K\alpha}} = \frac{\Gamma_A \omega_A \left\{ \int_{Ec}^{E} \frac{\sigma_A(E,Z)}{S_A} \right\} \{R_A\} \{f(\chi)\} \{F_A\} C_A \left\{ \frac{N_o \rho}{W_A} \right\} \{\eta_o \varepsilon_A \Omega\}}{\Gamma_B \omega_B \left\{ \int_{Ec}^{E} \frac{\sigma_B(E,Z)}{S_B} \right\} \{R_B\} \{f(\chi)\} \{F_B\} C_B \left\{ \frac{N_o \rho}{W_B} \right\} \{\eta_o \varepsilon_B \Omega\}}$$

$$\frac{I_A^{K\alpha}}{I_B^{K\alpha}} = \frac{\Gamma_A \omega_A \left\{ \int_{Ec}^{E} \frac{\sigma_A(E,Z)}{S_A} \right\} \{R_A\}\{f(\chi)\}\{F_A\} \left\{ \frac{1}{W_A} \right\} \{\varepsilon_A\} C_A}{\Gamma_B \omega_B \left\{ \int_{Ec}^{E} \frac{\sigma_B(E,Z)}{S_B} \right\} \{R_B\}\{f(\chi)\}\{F_B\} \left\{ \frac{1}{W_B} \right\} \{\varepsilon_B\} C_B}$$

$$\frac{I_A^{K\alpha}}{I_B^{K\alpha}} = \left\{K_Z^{AB}\right\} \cdot \left\{K_A^{AB}\right\} \cdot \left\{K_F^{AB}\right\} \cdot \frac{\{\varepsilon_A\}}{\{\varepsilon_B\}} \cdot \frac{C_A}{C_B}$$

Ionization Cross-Section



For K Shells

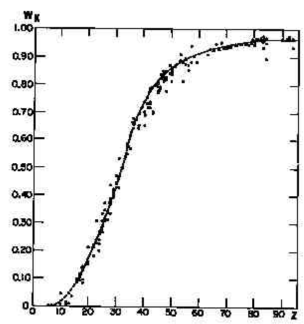
$$Q_K = \frac{a_K * b_K * \{ \ln (c_K * \frac{T_o}{E_c}) - \ln(1-\beta^2) - \beta^2 \}}{T_o * E_c}$$

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

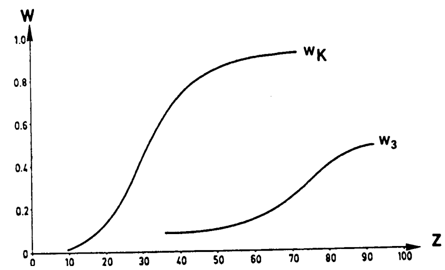
For L Shells

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

X-ray Fluorescence Yield has Systematic Variation With Atomic Number



ω_K shell

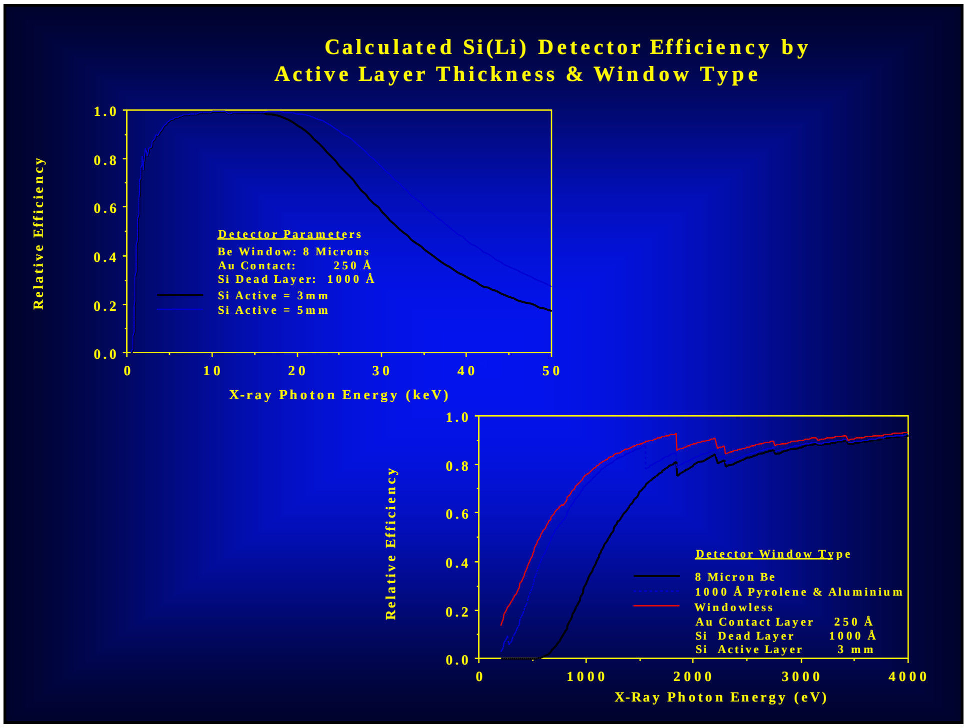


ω_K vs ω_L shell

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	



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

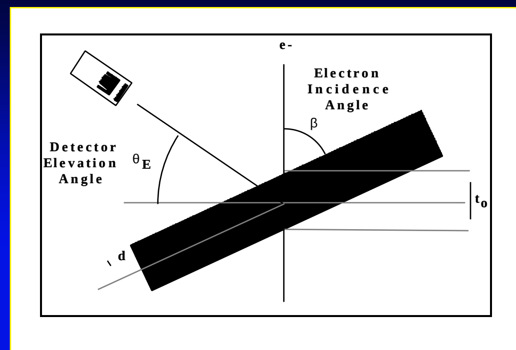
ω(L) - Krause, J. Phys. Chem. Ref. Data (1974) Vol 8, p.307

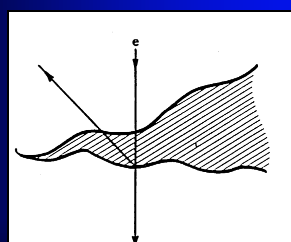
σ(Eo) - Inokuti, Rev. Mod. Physics, 43, No. 3, 297 (1971)
- Goldstein etal, SEM 1, 315, (1977)
- Chapman etal, X-ray Spectrometry, 12,153,(1983)
- Rez, X-ray Spectrometry, 13, 55, (1984)
- Egerton, Ultramicroscopy, 4, 169, (1969)
- Zaluzec, AEM-1984, San Fran. Press. 279, (1984)

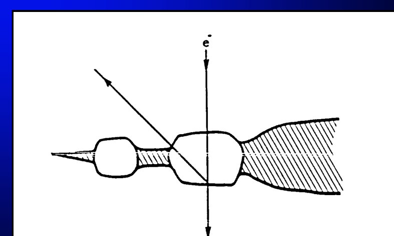
ε (E) - Use mass absorption coefficients from:
-Thinh and Leroux; X-ray Spect. (1979), 8, p. 963
-Henke and Ebsiu, Adv. in X-ray Analysis,17, (1974)
-Holton and Zaluzec, AEM-1984, San Fran Press,353,(1984)

X-Ray Absorption Correction

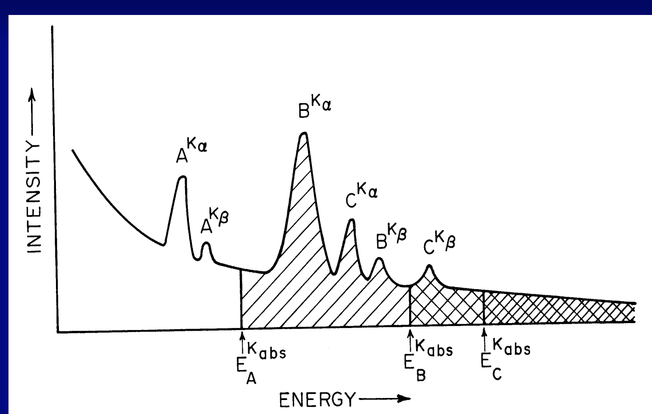
Path Length Out of the sample is the critical parameter







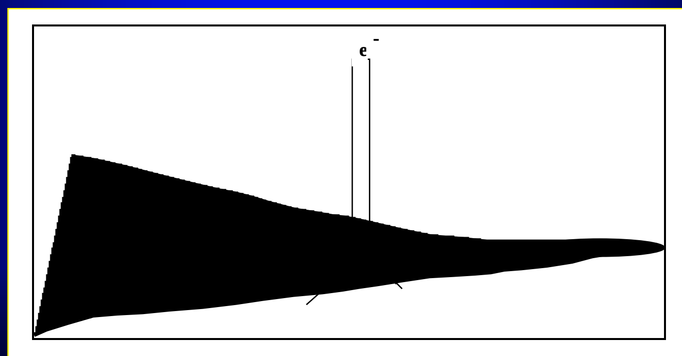
X-ray Fluorescence Correction
Both Characteristic and Continuum X-rays

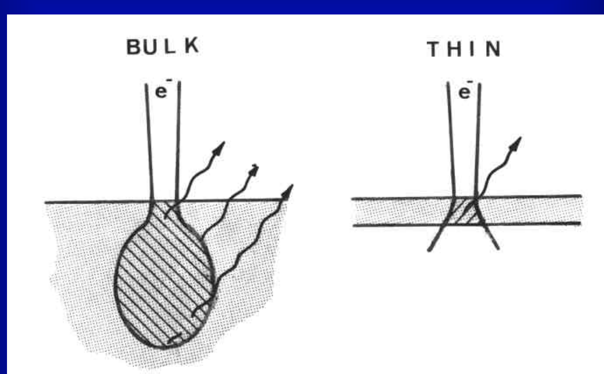


$$I_A^{\text{Measured}} = I_A^{\text{Electron}} + I_A^{\text{XRF by B}}$$

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.





Quantitative Analysis using XEDS

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	=	K^{th}-shell ionization cross-section
ω	=	K^{th}-shell fluorescence yield
Γ	=	K^{th}-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

Quantitative Analysis using XEDS
Standardless Method

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

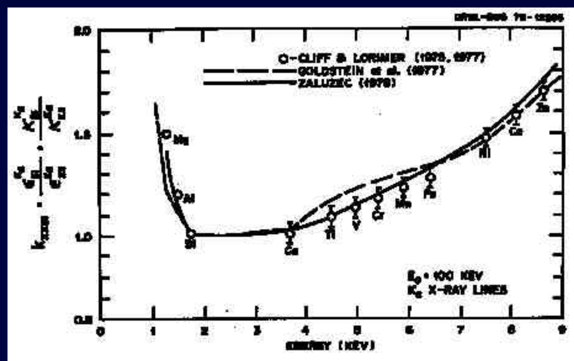
$$\frac{I_A}{I_B} = \frac{\kappa_A\ \varepsilon_A\ C_A}{\kappa_B\ \varepsilon_B\ C_B} = k_{AB}^{-1}\frac{C_A}{C_B}$$

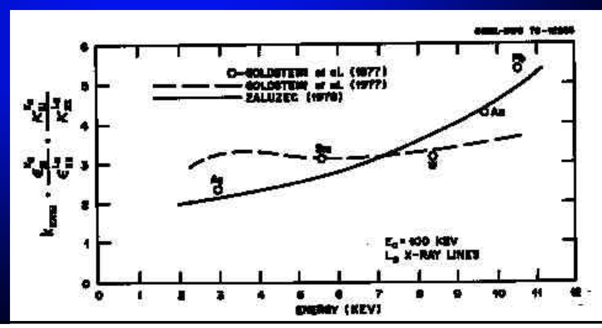
$$\kappa_A = \frac{\sigma_A\omega_A\Gamma_A}{W_A}$$

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

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 k_A/k_B is a true physical constant and is independant of the AEM system. The ratio of e_A/e_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.**





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**:

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

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

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**

Advantages

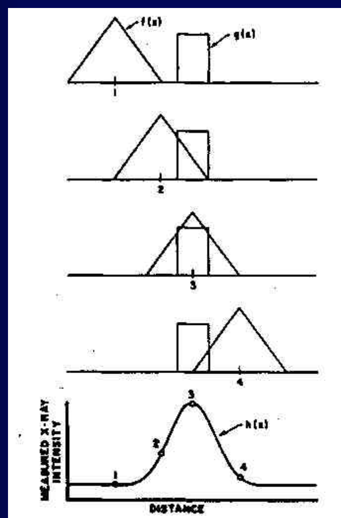
Standard may be a pure element.
The closer the standard is to the unknown material the smaller the correction and higher the accuracy.

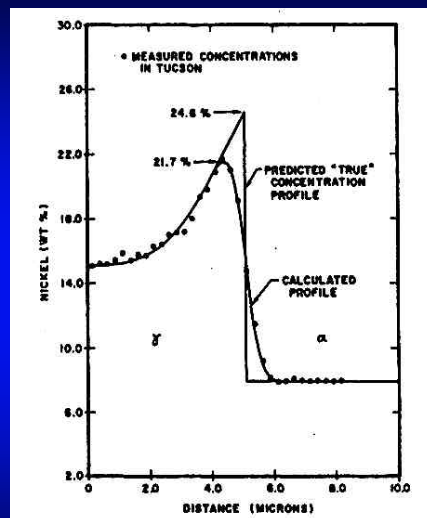
Disadvantages

Effects of surface films can be critical
Must have a standard for each element to be analyzed

Additional Topics

Heterogeneous Specimens
Composition Profiles
Mapping
ESEM
Electron Channelling





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

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

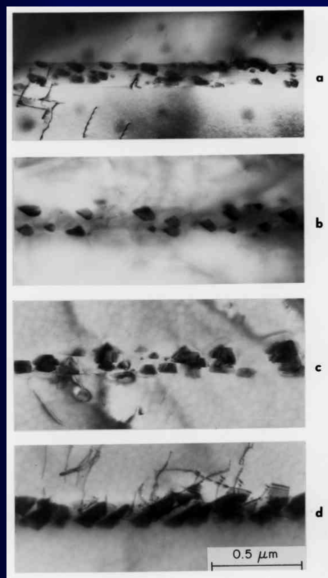
* = Convolution operator

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



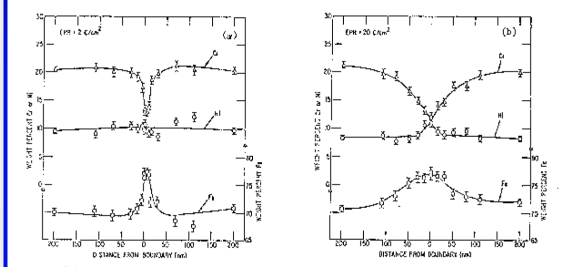
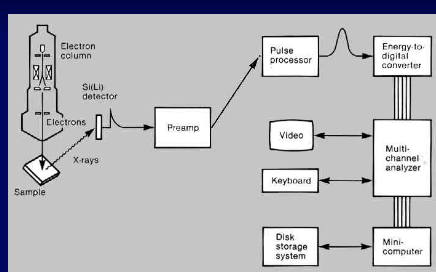
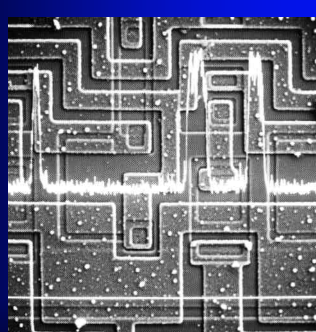


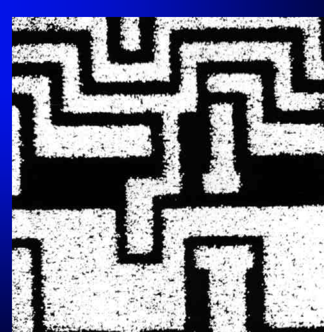
Fig. 9. Typical Concentration Profiles for Chromium, Nickel, and Iron Across a Grain Boundary of Type 304 SS CERT Specimens Sensitized to EPR Values of (a) 2 and (b) 20 C/cm^2 as Determined by Energy Dispersive X-ray Analyses with a JEOL 100 CX Electron Microscope Equipped for STEM Operation. The error bars represent the uncertainties associated with the counting statistics only.



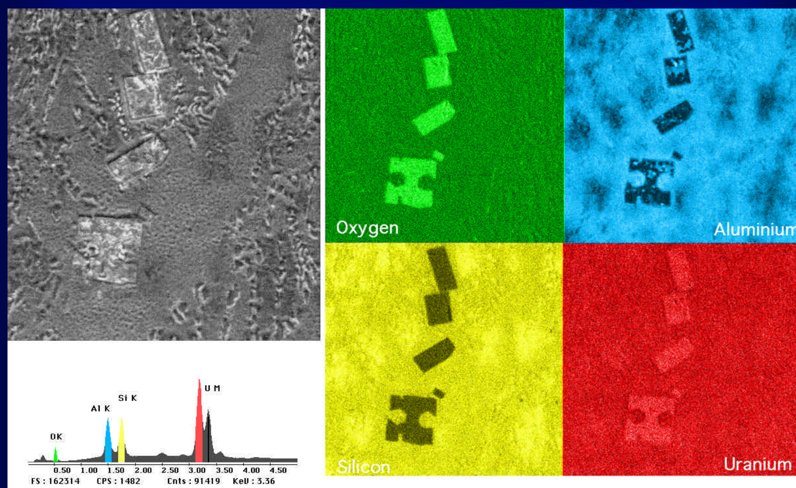
Analog "Dot" Maps

Good for Major Species
Overlaps can prohibit mapping
Low Conc. very difficult

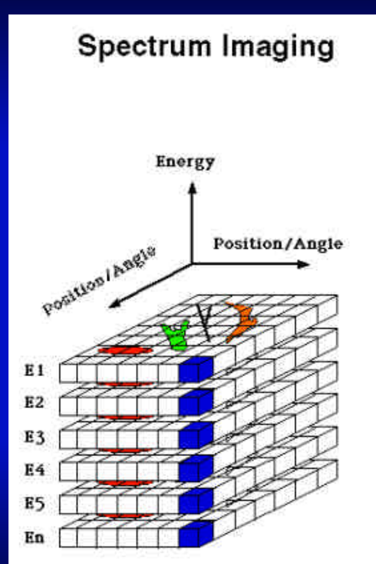


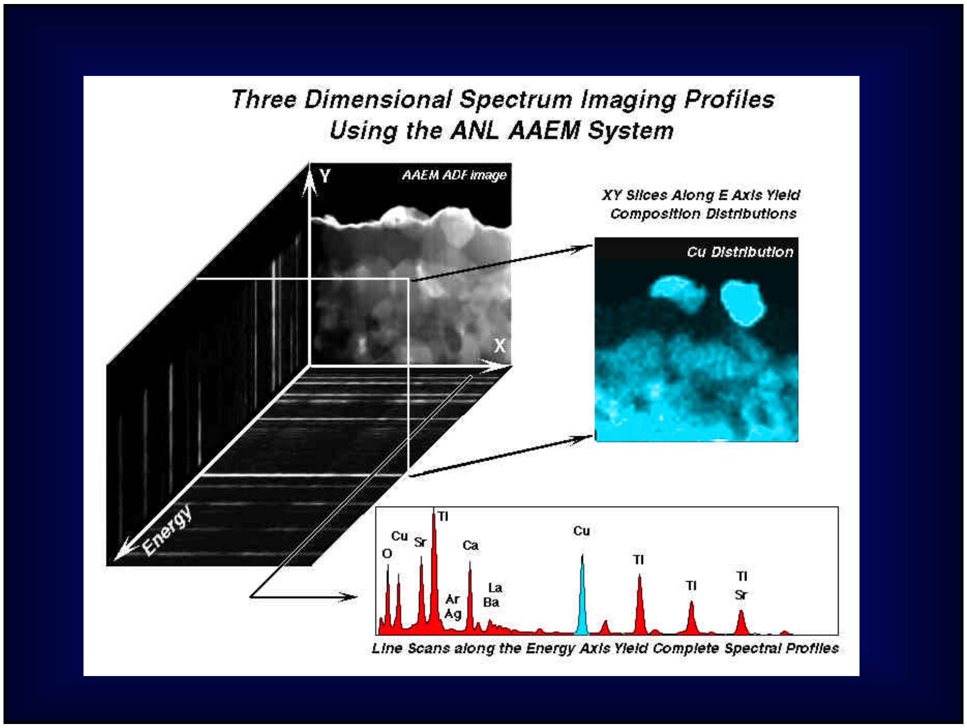


Digital Mapping

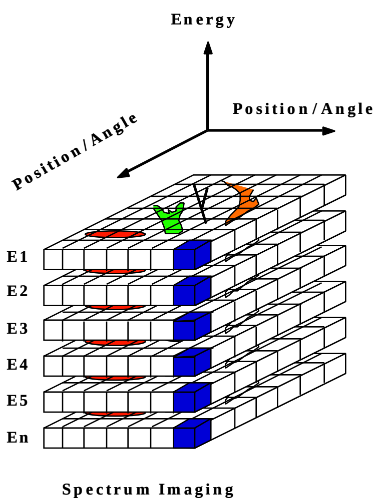


Computationally Mediated - Spectral Imaging





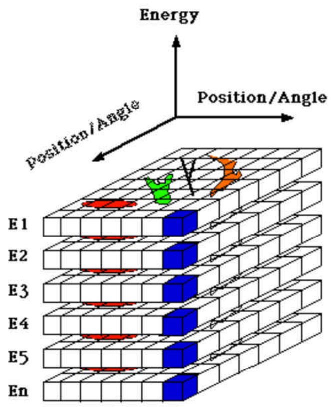
Spectrum Imaging allows for Off-line Projections/Summations Operations

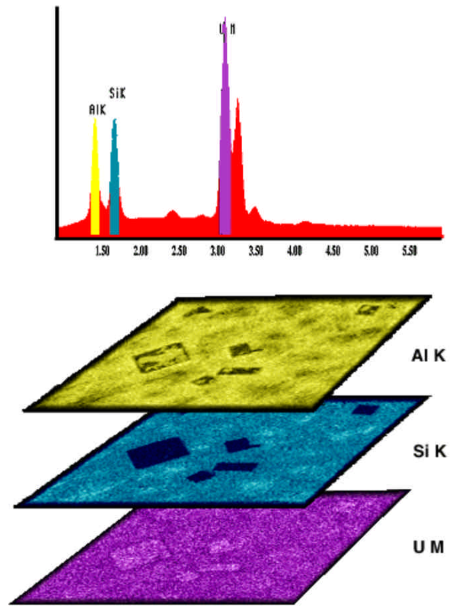


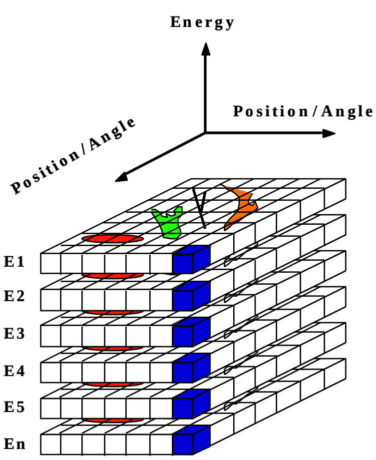
But it requires massive data strorage

E \ XY	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







Spectrum Imaging

t \ XY	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

X-RAY MICROANALYSIS IN
ENVIRONMENTAL / VARIABLE PRESSURE
SEM

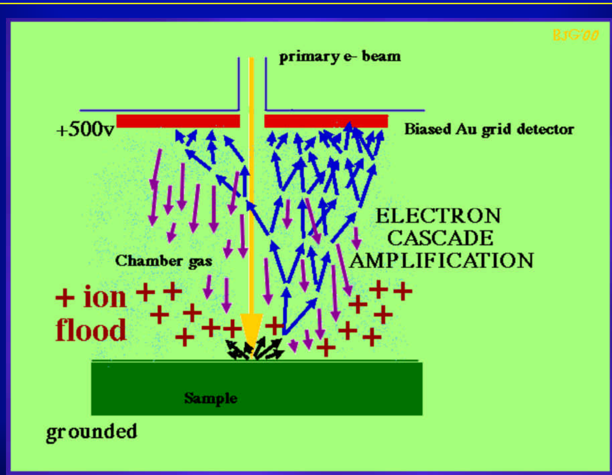
Courtesy of B.J. Griffin

VPSEM/ESEM allow examination of a wide range of untreated samples because:

• Conventional wisdom suggests that charge neutralisation for poor and non-conductive materials through gas-electron interaction is effective

Early work states that this neutralisation occurs with Ar chamber pressures of only 0.1 torr - BSEI stability (Nickel and Robinson, 1979)

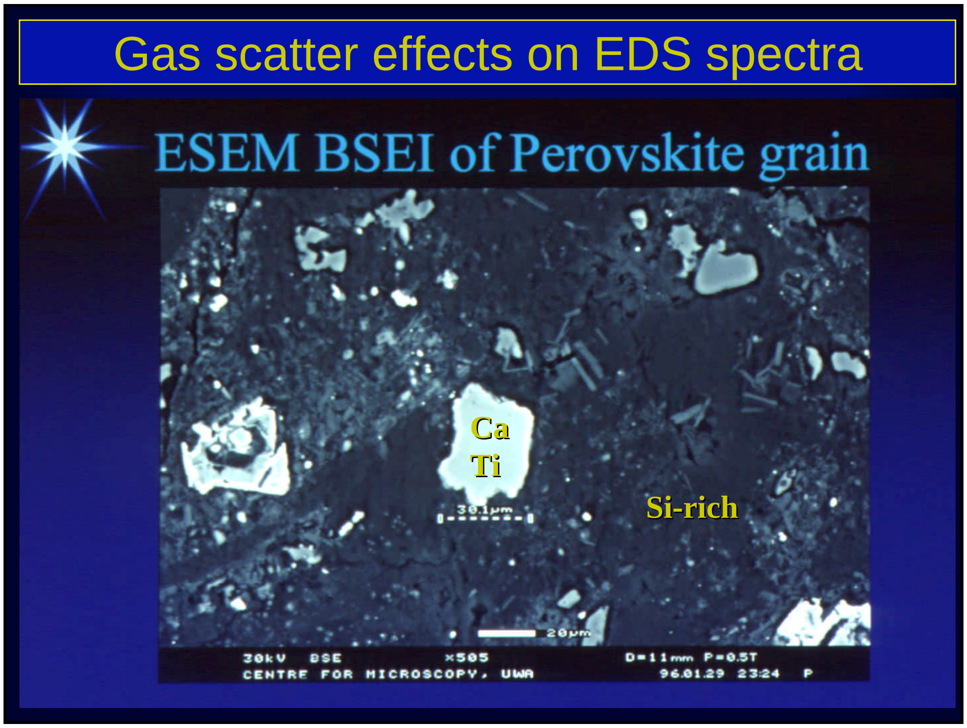
Conventional/current 'SE' detection in conventional and variable pressure (VP) SEM

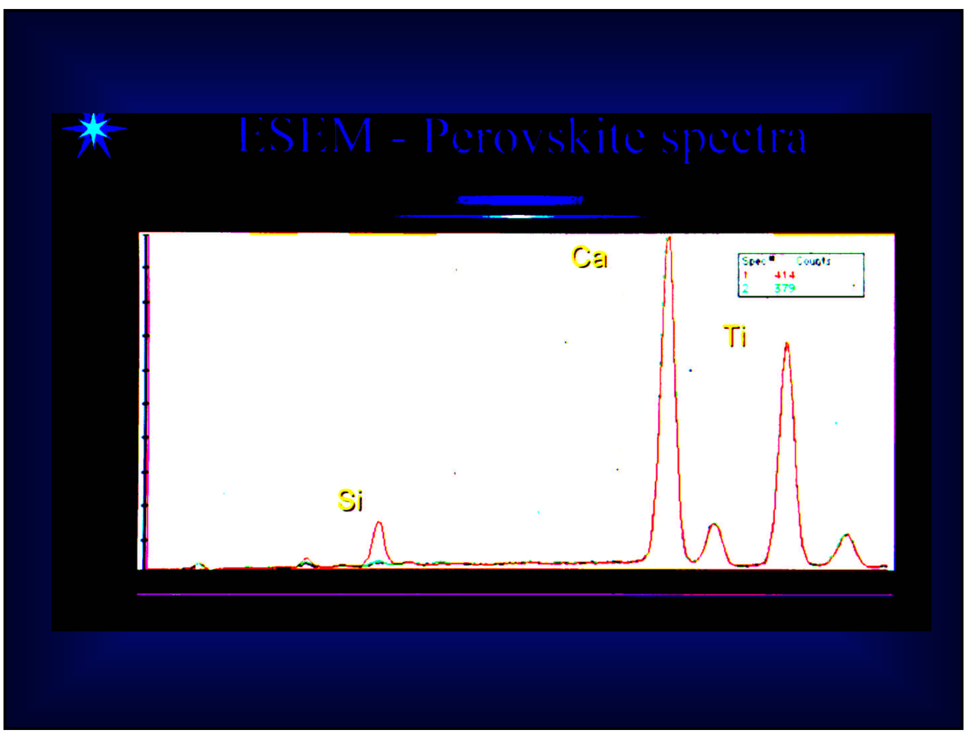


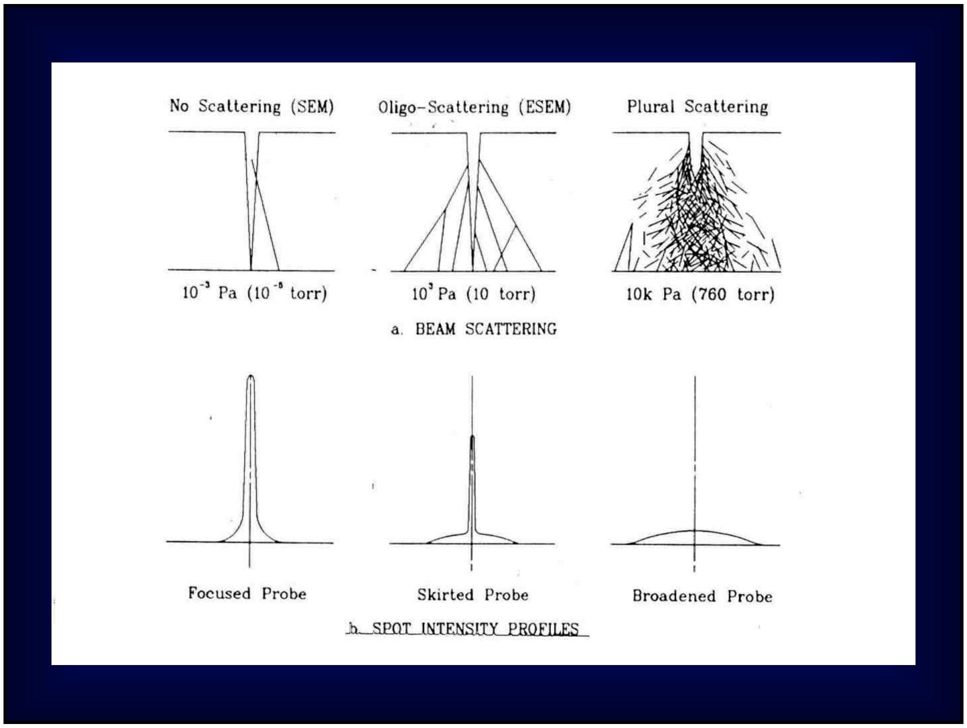
KNOWN COMPROMISES

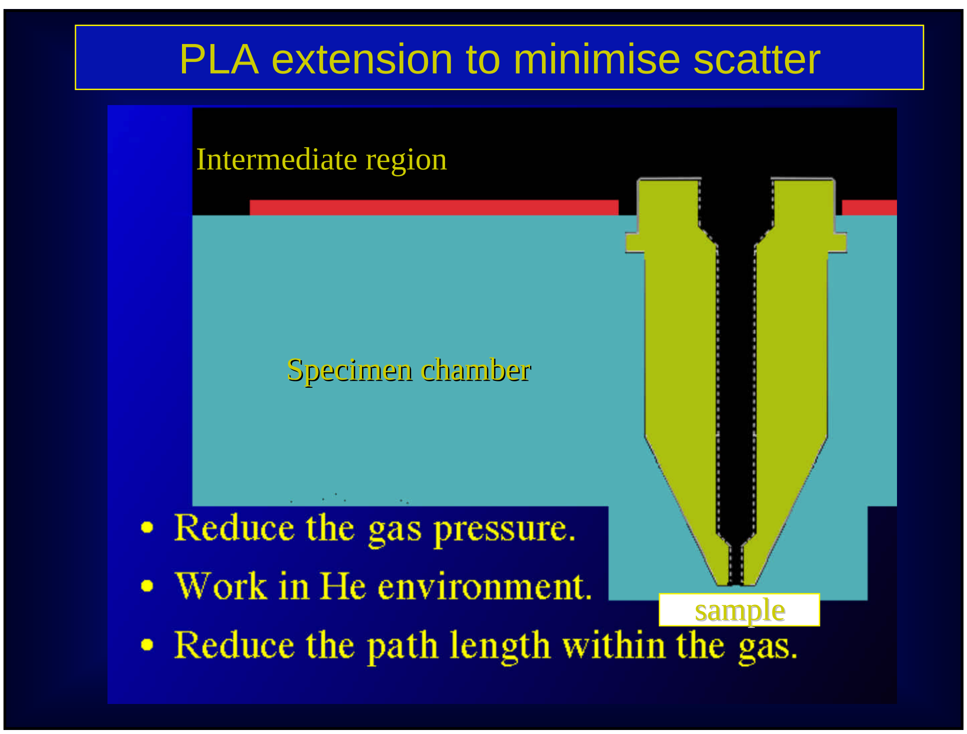
- **Gas-electron interactions radially scatter the primary electrons away from the intended landing point = f(gas, pressure, path length & Eo)**
- **Primary beam current cannot be directly measured and it fluctuates with pressure**

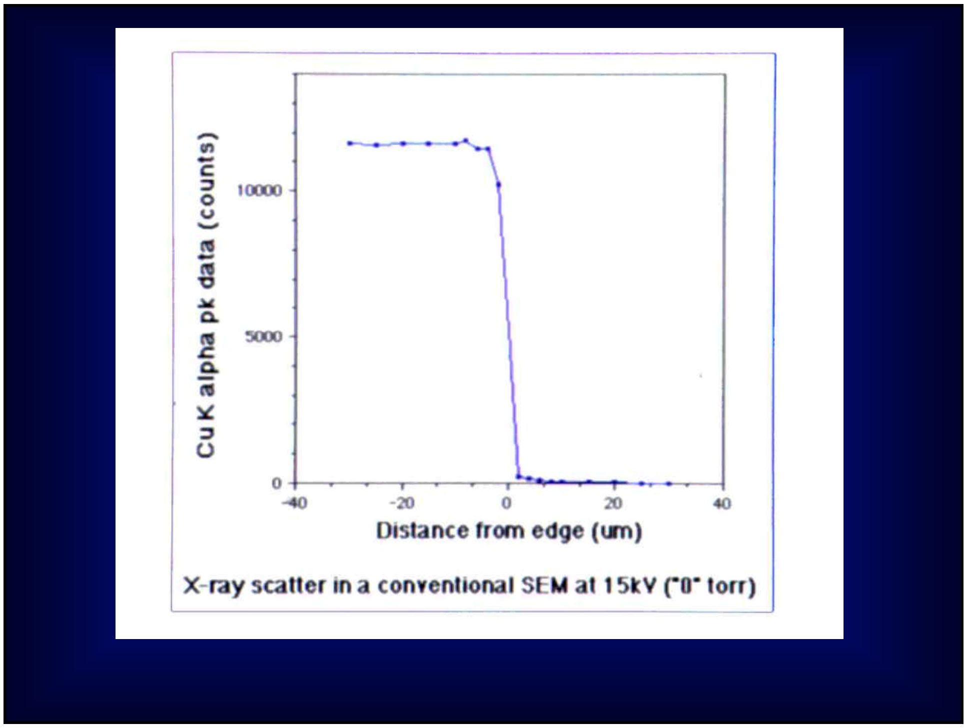
X-ray maps are diffuse & point analyses need normalisation

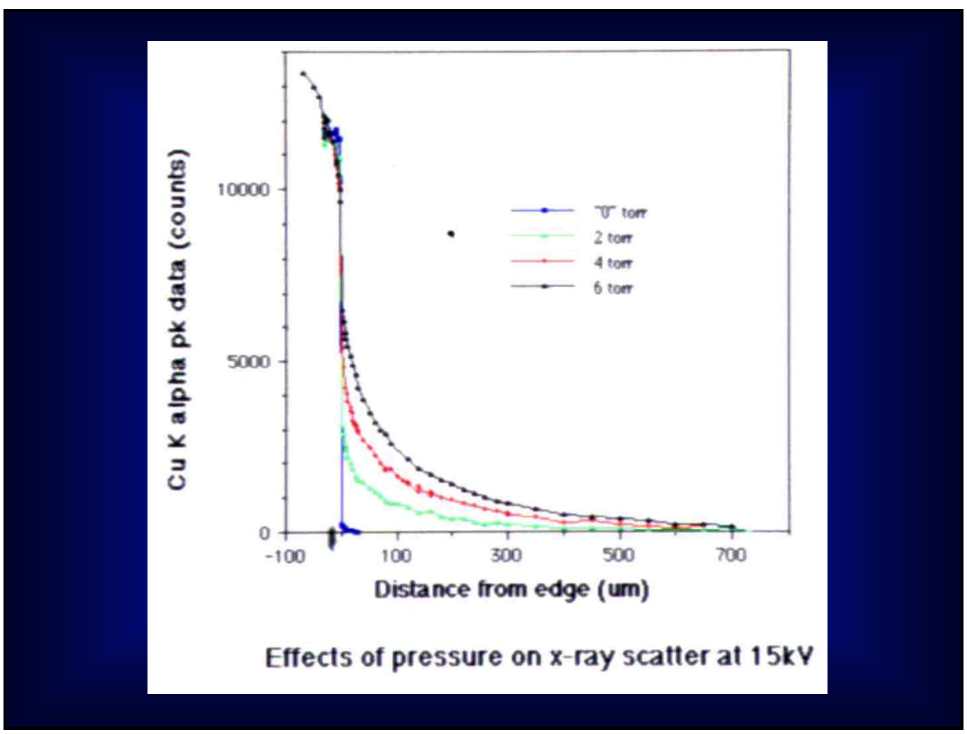

Gas scatter effects on EDS spectra
ESEM BSEI of Perovskite grain
Ca
Ti
Si-rich
30.1µm
20µm
30kV BSE x505
CENTRE FOR MICROSCOPY, UWA
D=11mm P=0.5T
96.01.29 23:24 P

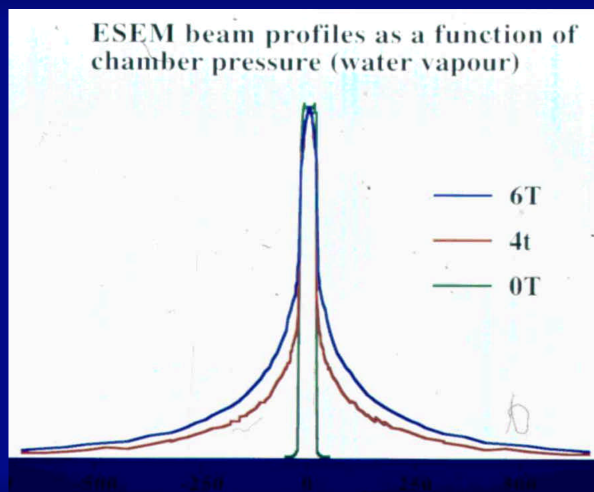

ESEM - Perovskite spectra
Ca
Ti
Si
Spec Counts
1 414
2 379

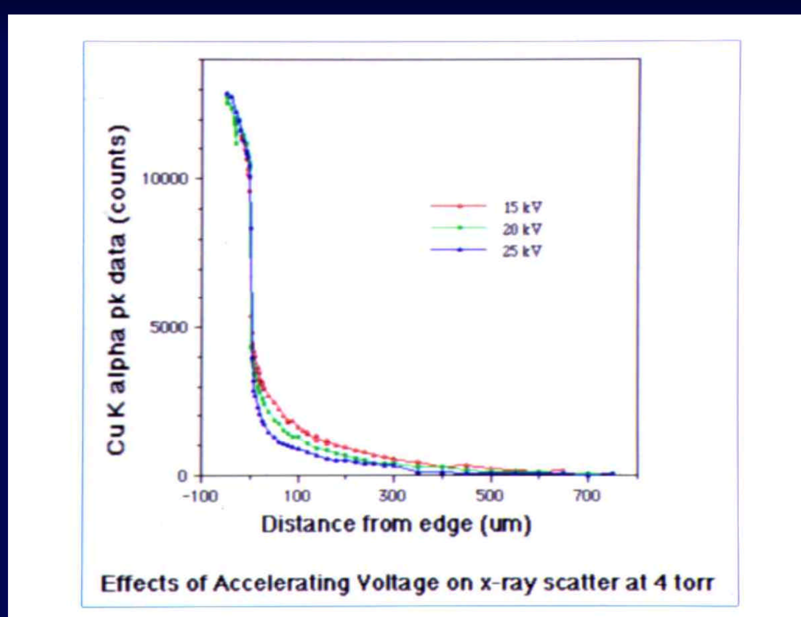

No Scattering (SEM)
Oligo-Scattering (ESEM)
Plural Scattering
10^{-3} Pa (10^{-5} torr)
10^3 Pa (10 torr)
10k Pa (760 torr)
a. BEAM SCATTERING
Focused Probe
Skirted Probe
Broadened Probe
b. SPOT INTENSITY PROFILES

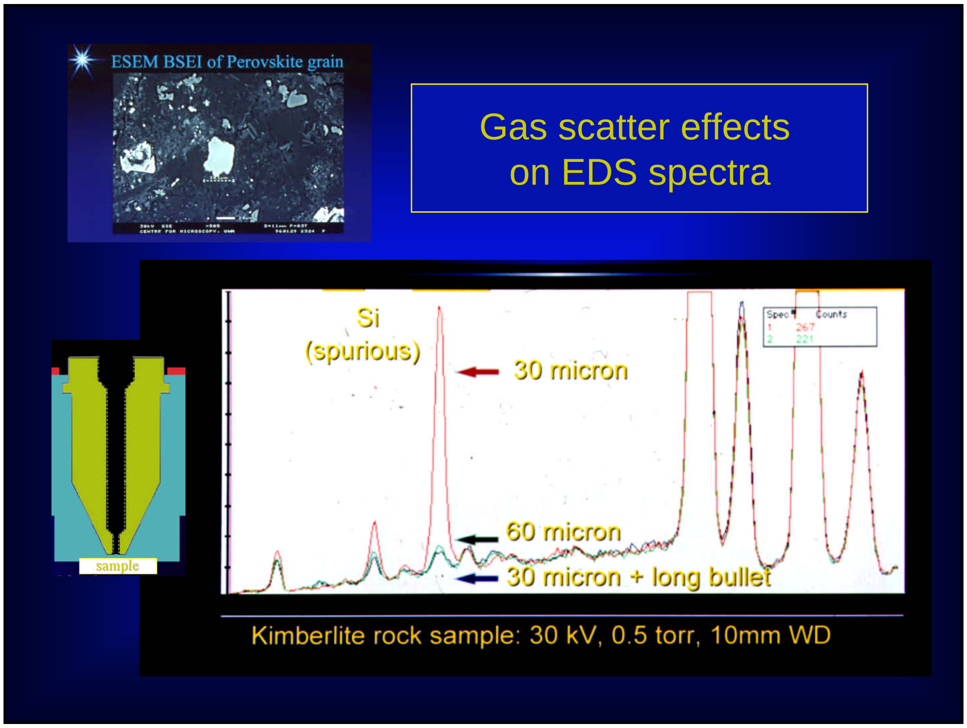

PLA extension to minimise scatter
Intermediate region
Specimen chamber
• Reduce the gas pressure.
• Work in He environment.
sample
• Reduce the path length within the gas.

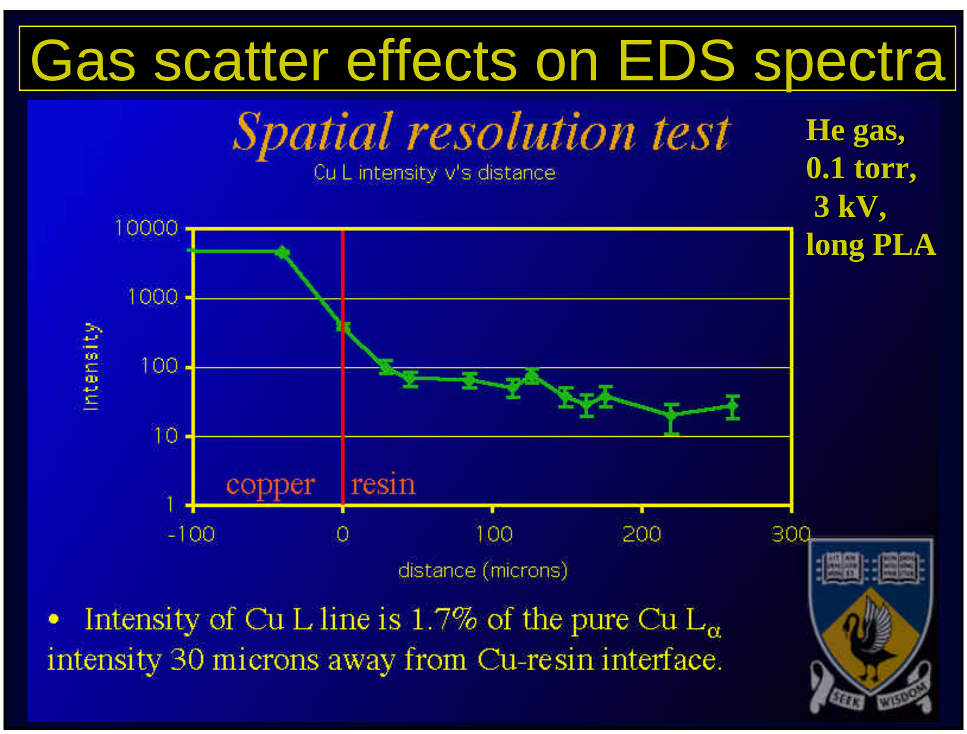

Cu K alpha pk data (counts)
10000
5000
0
-40
-20
0
20
40
Distance from edge (um)
X-ray scatter in a conventional SEM at 15kV ("0" torr)


Cu K alpha pk data (counts)
10000
5000
0
-100
100
300
500
700
"0" torr
2 torr
4 torr
6 torr
Distance from edge (um)
Effects of pressure on x-ray scatter at 15kV


ESEM beam profiles as a function of chamber pressure (water vapour)
6T
4t
0T


Cu K alpha pk data (counts)
10000
5000
0
-100
100
300
500
700
Distance from edge (um)
15 kV
20 kV
25 kV
Effects of Accelerating Voltage on x-ray scatter at 4 torr


ESEM BSEI of Perovskite grain
Gas scatter effects on EDS spectra
Si (spurious)
30 micron
60 micron
30 micron + long bullet
sample
Kimberlite rock sample: 30 kV, 0.5 torr, 10mm WD

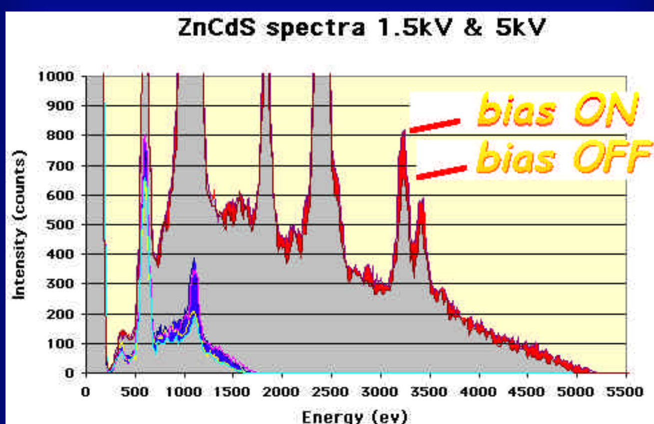

Gas scatter effects on EDS spectra
Spatial resolution test
Cu L intensity v's distance
He gas, 0.1 torr, 3 kV, long PLA
Intensity
10000
1000
100
10
1
-100
0
100
200
300
distance (microns)
copper
resin
• Intensity of Cu L line is 1.7% of the pure Cu L_α intensity 30 microns away from Cu-resin interface.
SEEK WISDOM

Other factors compromising EDS quantitation

POTENTIAL EFFECTS ON THE ACCELERATING VOLTAGE due to:

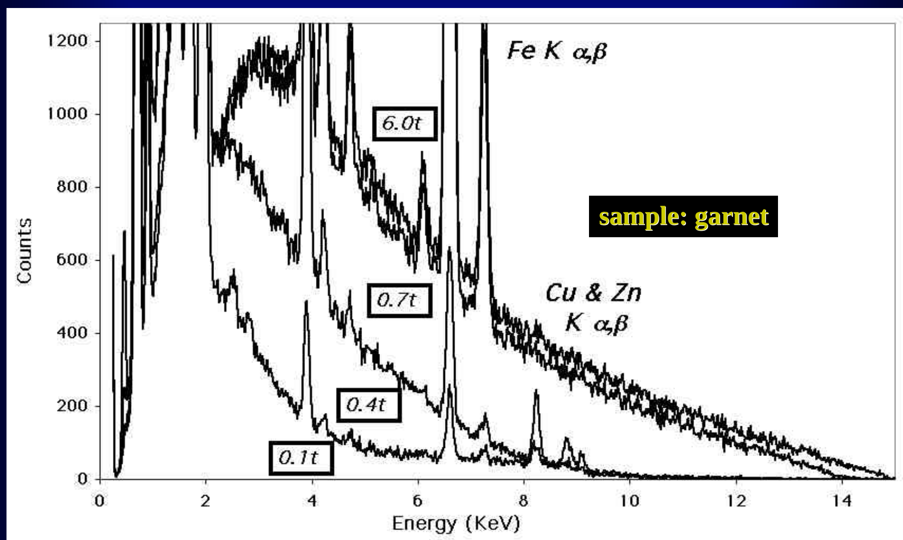
- **increase in landing energy of the primary beam**
  ie secondary acceleration
  - by positive surface or 'space' charge
- decrease in landing energy of the primary beam as a result of incomplete charge neutralisation or charge implantation in the sample

Positive 'space' charge



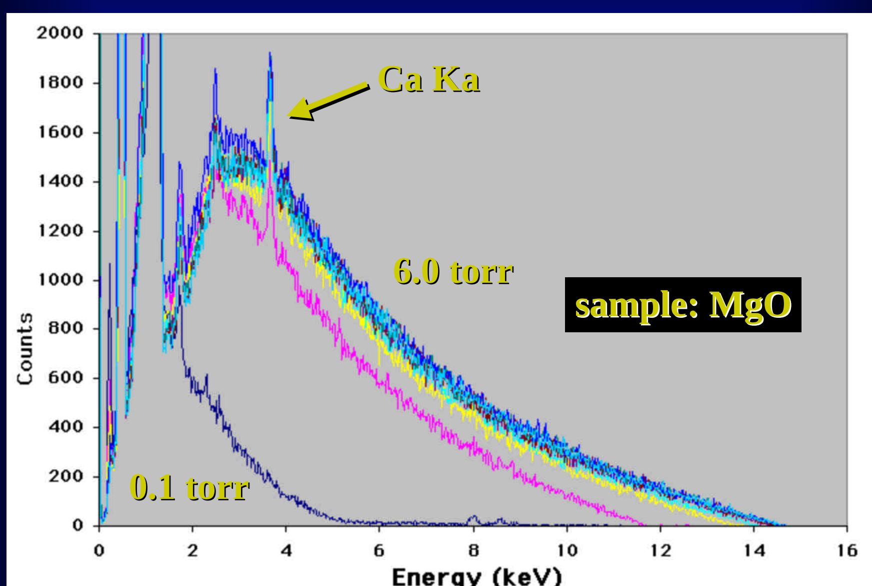
Effects on low kV EDS spectra of increases in electron landing energy as a function of ESD bias
- "floating" conductive sample

Charging/Pressure effects on EDS spectra



Spectra collected at 15 kV, 11mm gpl, H2O, 100 sec & "3000" cps

Charging/Pressure effects on EDS spectra



Effects of varying pressure on EDS spectra

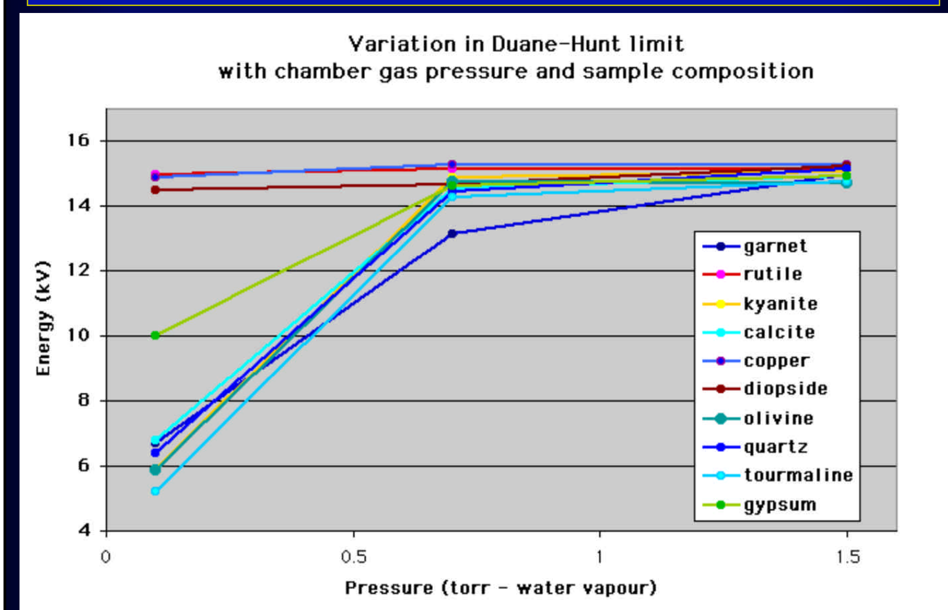
- EDS spectra vary with chamber pressure

- Duane-Hunt limit changes and indicates a negative charging of the sample

- sample charging effects are present even at moderate chamber pressures

- electrostatic mirror formation at low pressure - results in addition of high E x-rays from chamber components imposed on low "Eo" sample spectrum

D-H limit variat'n with composition



Summary - charging effects

These data support earlier work and confirm that:

• poorly conductive samples charge NEGATIVELY in VPSEM/ESEM under most routine conditions

• reducing the gas path length does not avoid the problem

• the gaseous secondary electron detector bias is a factor in the degree of charging experienced

• sample composition is a major factor in the degree of charging experienced - this is extendable to sample size and analysis point location

Implications for quant. microanalysis

• beam dose must be kept constant and monitored - to avoid temporal effects

• standards MUST have similar conductive properties to the unknowns - otherwise electron landing energies will differ and incorrect matrix corrections applied

• the Duane-Hunt limit should always be monitored

• moderate to high pressures should be used and extended PLA to minimise scattering effects

• the Bremstrahlung-based correction procedure may need reconsideration

Conclusions - EDS in VPSEM/ESEM

- a wide range of factors can significantly affect EDS x-ray spectra collected in VPSEM/ESEM
- charging effects are seen up to ~ 2.0 torr and extreme caution must be used in collection and interpretation of this type of data
- charging effects vary with sample composition
- applications exist where the VPSEM/ESEM have unique microanalytical strengths
- quantitative microanalysis at conventional / acceptable levels remains difficult at present

http://tpm.amc.anl.gov/Lectures/XEDS-Apr2001.pdf
(not until Monday)

Zaluzec@aaem.amc.anl.gov
Zaluzec@microscopy.com