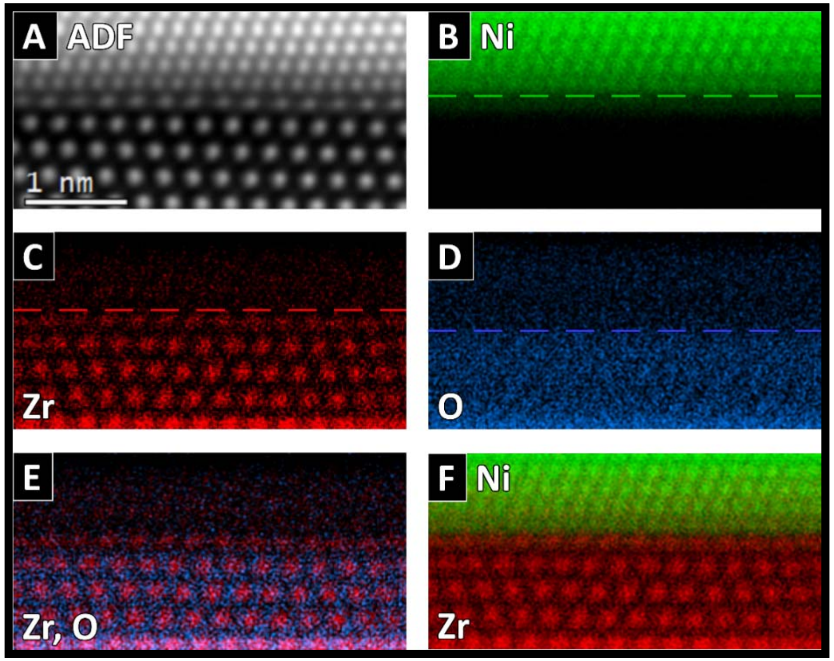
(A) Energy Dispersive Spectroscopy (EDS) & (B) its Application Towards Understanding Thermodynamic Transitions at Interfaces



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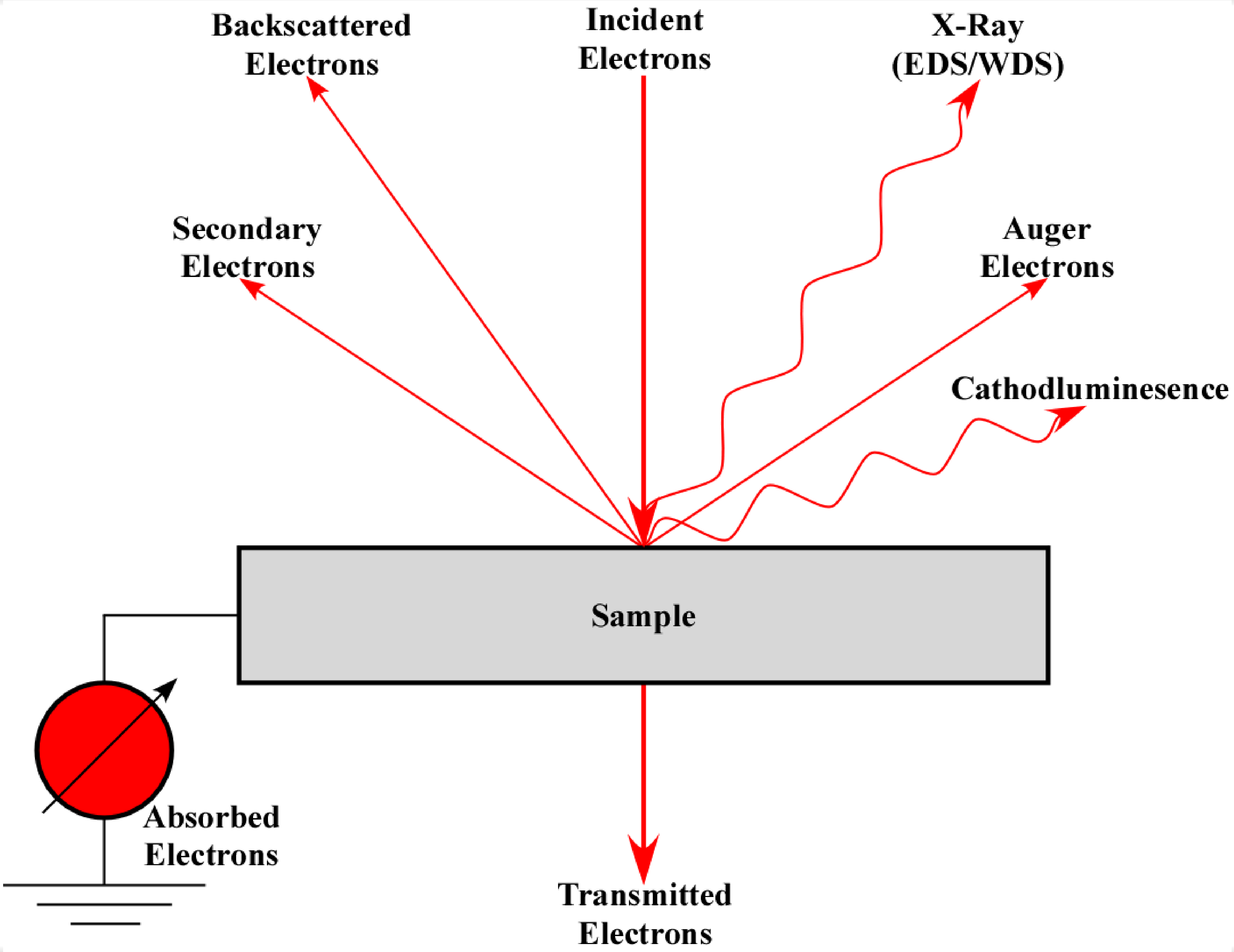
Energy Dispersive Spectroscopy (EDS)

- **Basic principles of the method;**
- **Going quantitative;**
- **Detectors;**
- **Practical approaches.**



Backscattered Electrons

Incident Electrons

X-Ray (EDS/WDS)

Secondary Electrons

Auger Electrons

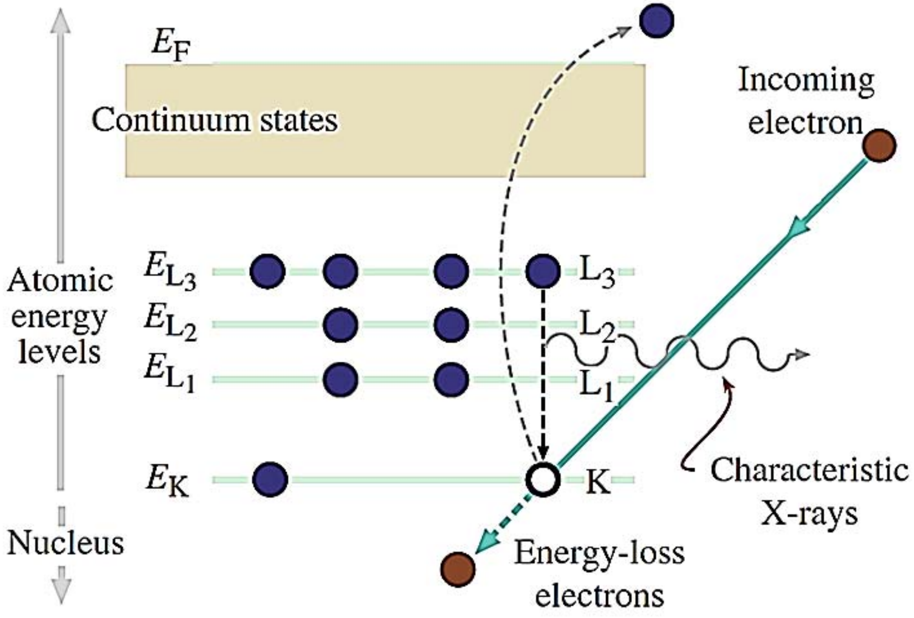
Cathodluminesence

Sample

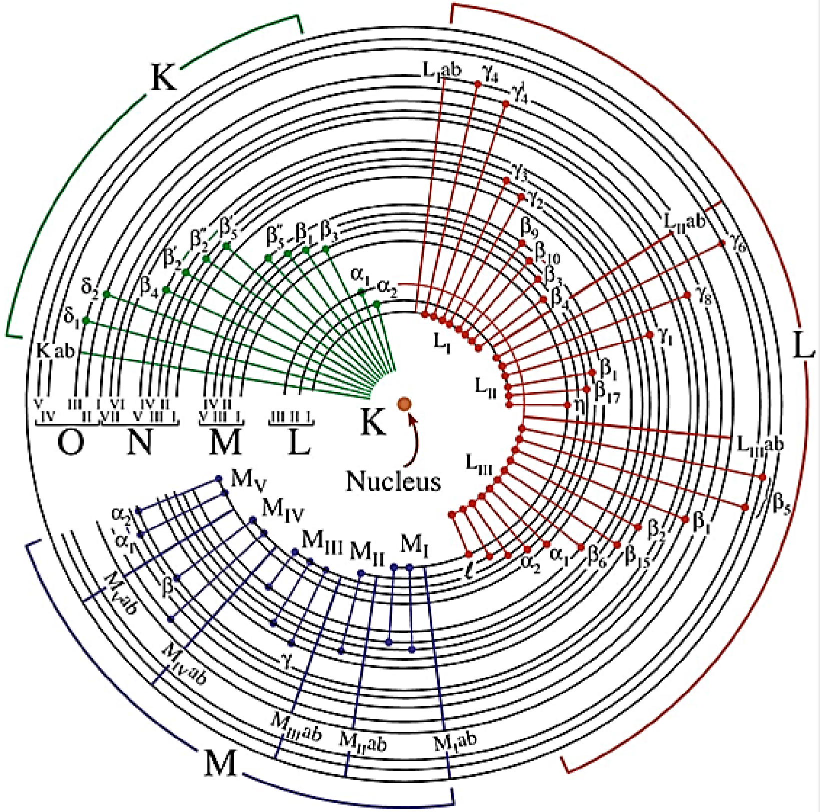
Absorbed Electrons

Transmitted Electrons

Inelastic Scattering => X-ray Emission



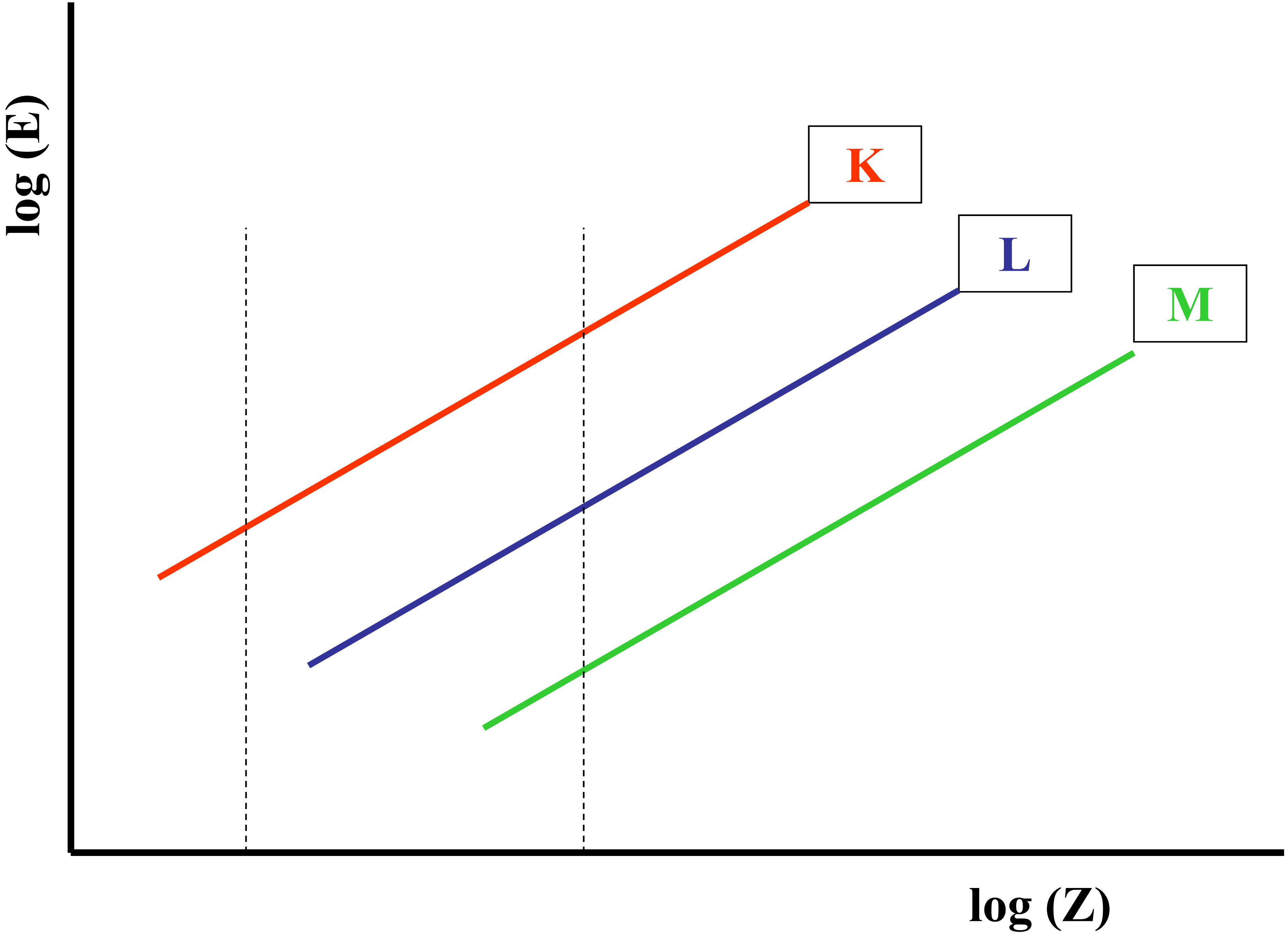
The ionization process



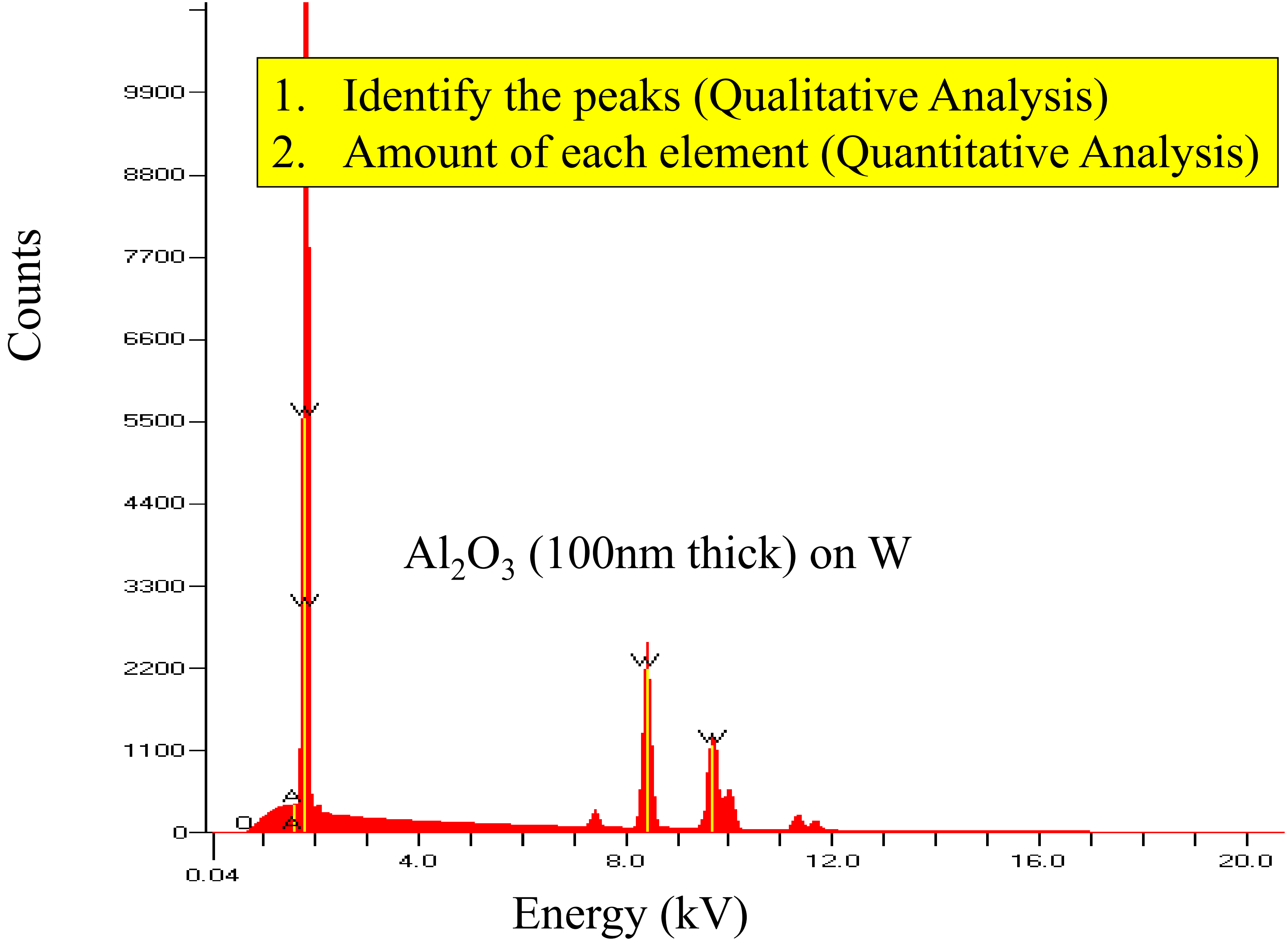
The complete range of possible electron transitions that give rise to K, L, and M characteristic X-rays.

W&C page 55-56

X-ray Spectra

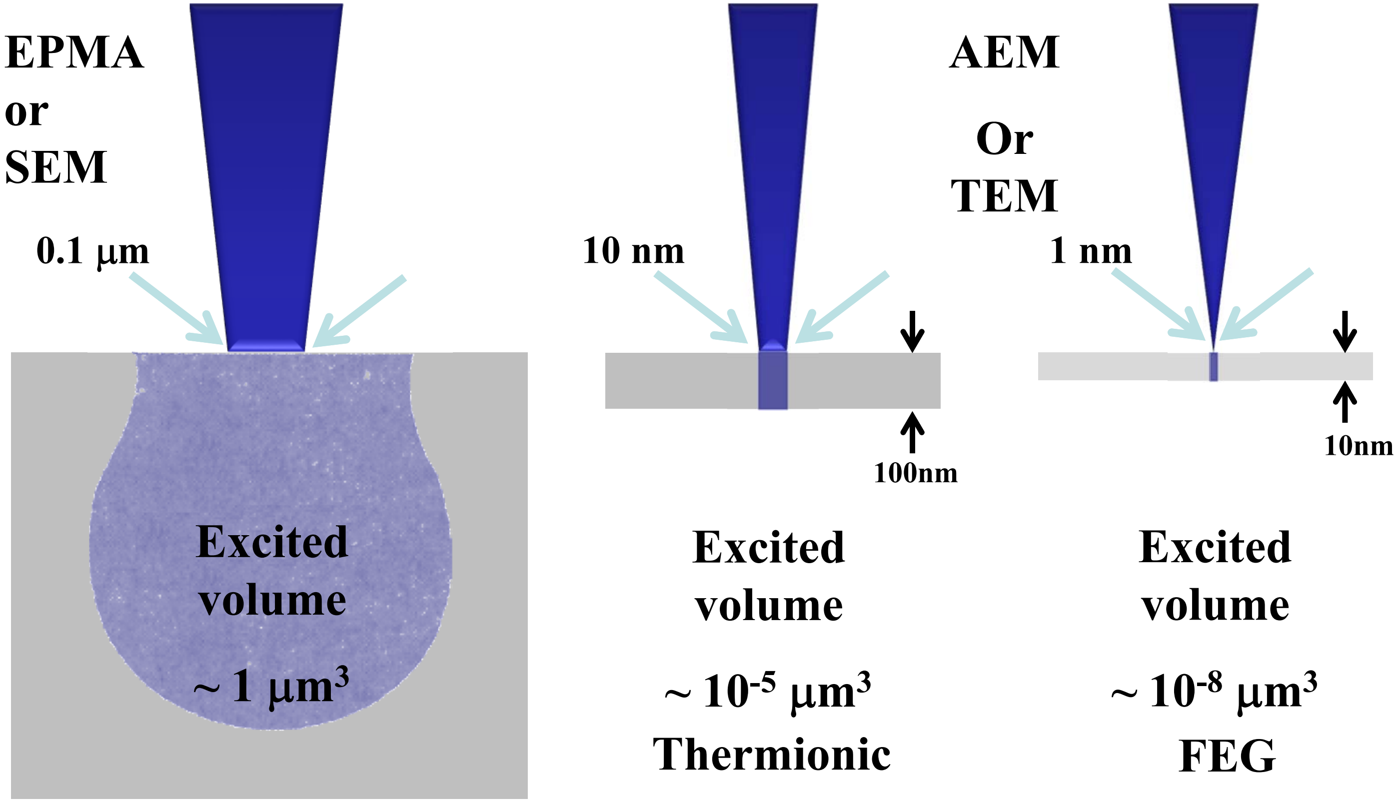


1. Identify the peaks (Qualitative Analysis)
2. Amount of each element (Quantitative Analysis)



Al_2O_3 (100nm thick) on W

Interaction Volume and Resolution



EPMA
or
SEM

0.1 µm

Excited volume

$\sim 1\ \mu m^3$

10 nm

100nm

Excited volume

$\sim 10^{-5}\ \mu m^3$

Thermionic source

AEM

Or
TEM

1 nm

10nm

Excited volume

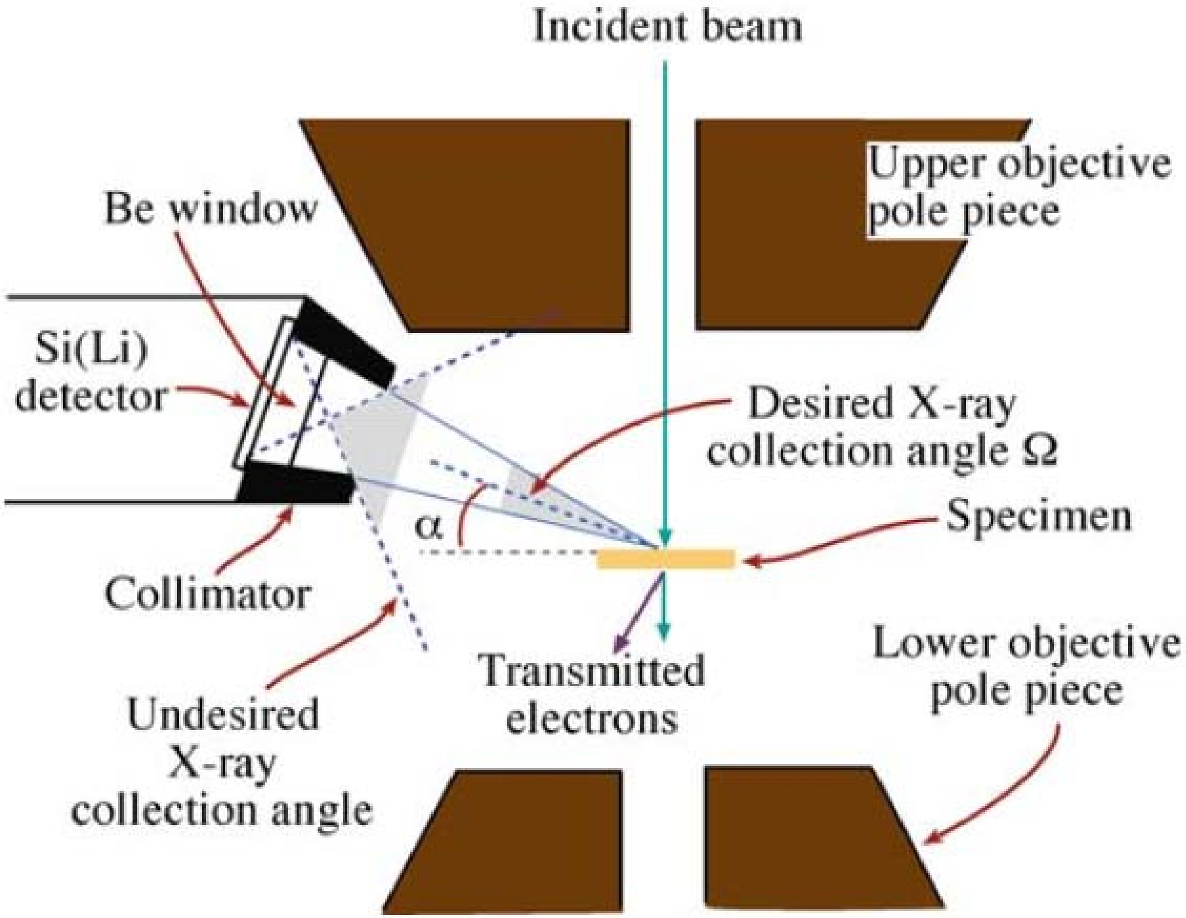
$\sim 10^{-8}\ \mu m^3$

FEG source

EDS & TEM

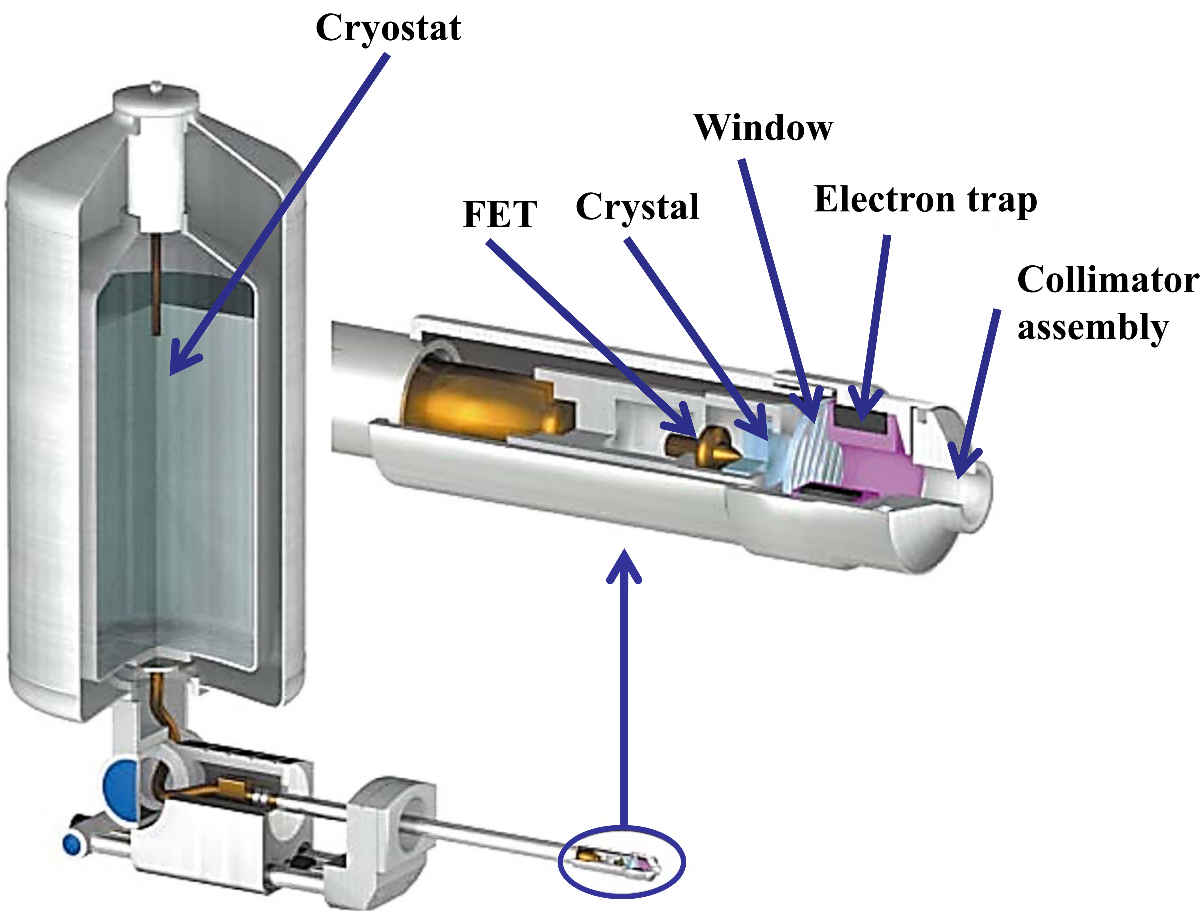
α = take-off angle

Ω = collection angle

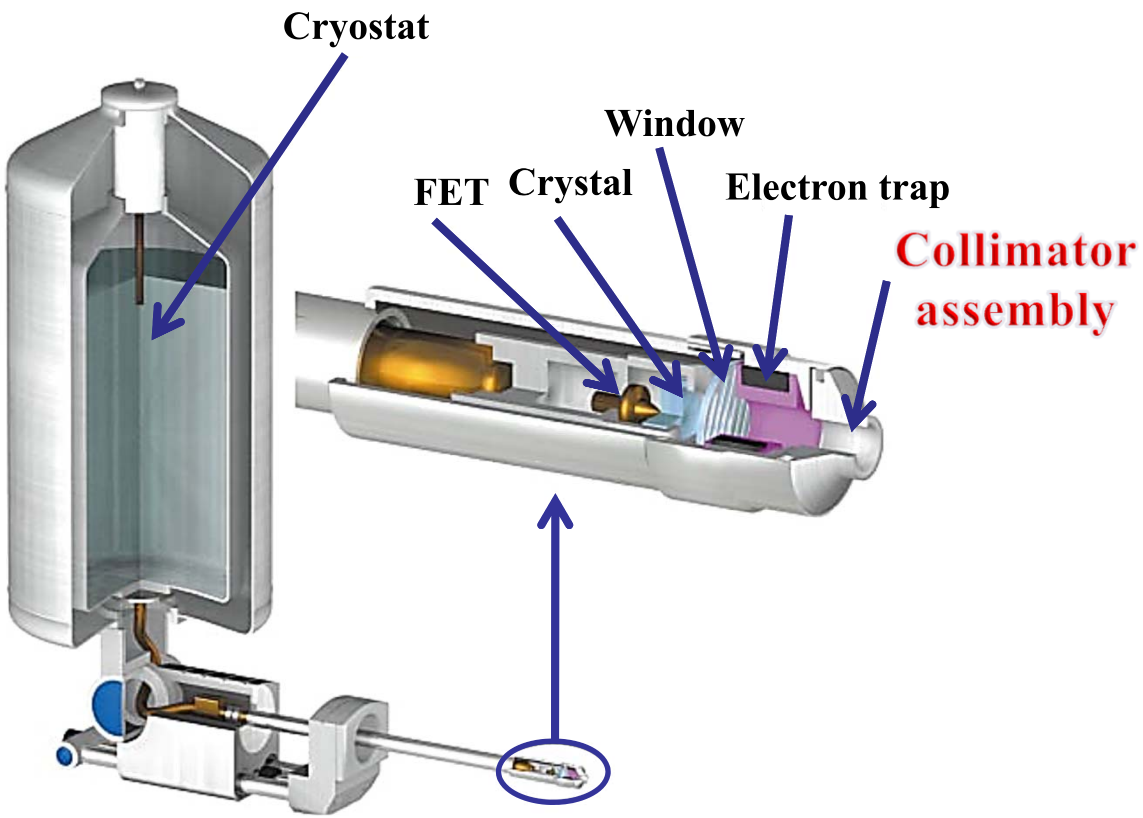


The detector can 'see' X-rays from regions other than the beam-specimen interaction volume over the (relatively large) undesired collection angle.

EDS Hardware

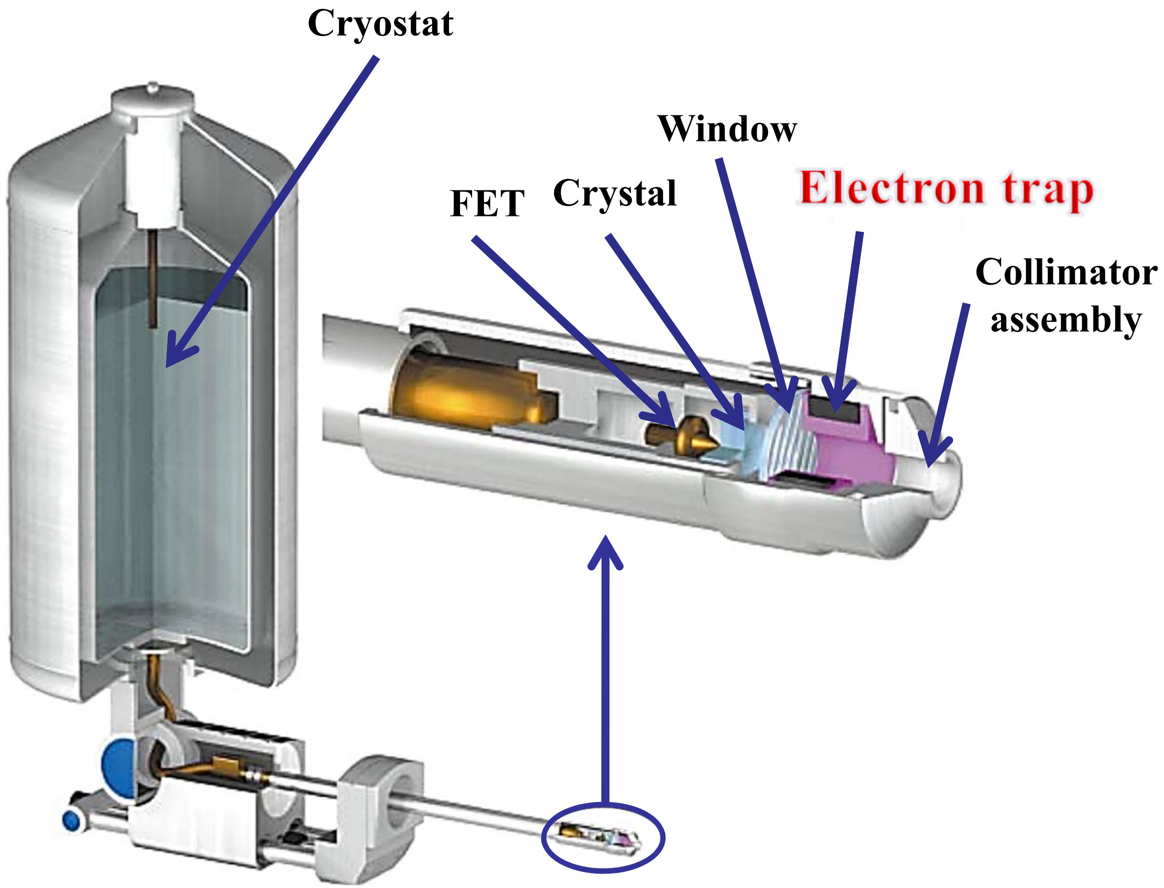


EDS Hardware



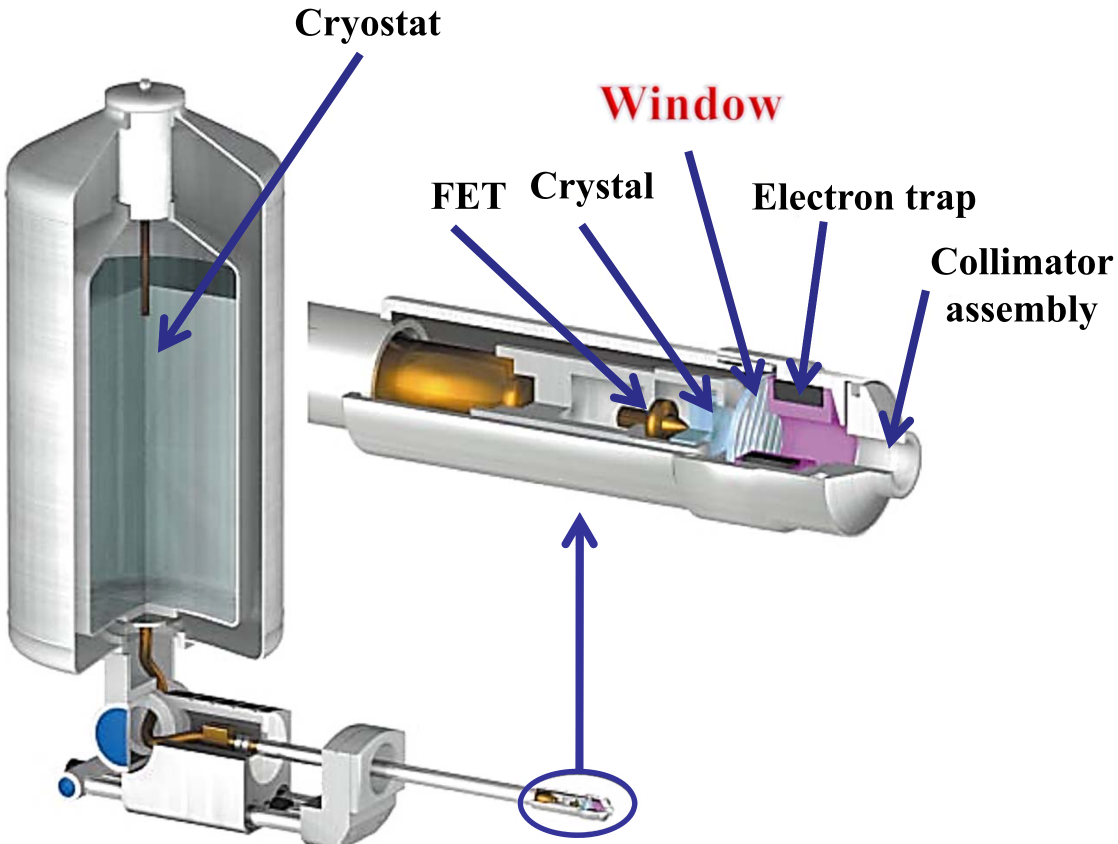
- **Collimator assembly:**
  - Provides a **limiting aperture** through which X-rays must pass to reach the detector.
  - **Limits** stray X-rays from other parts of the microscope chamber.

EDS Hardware



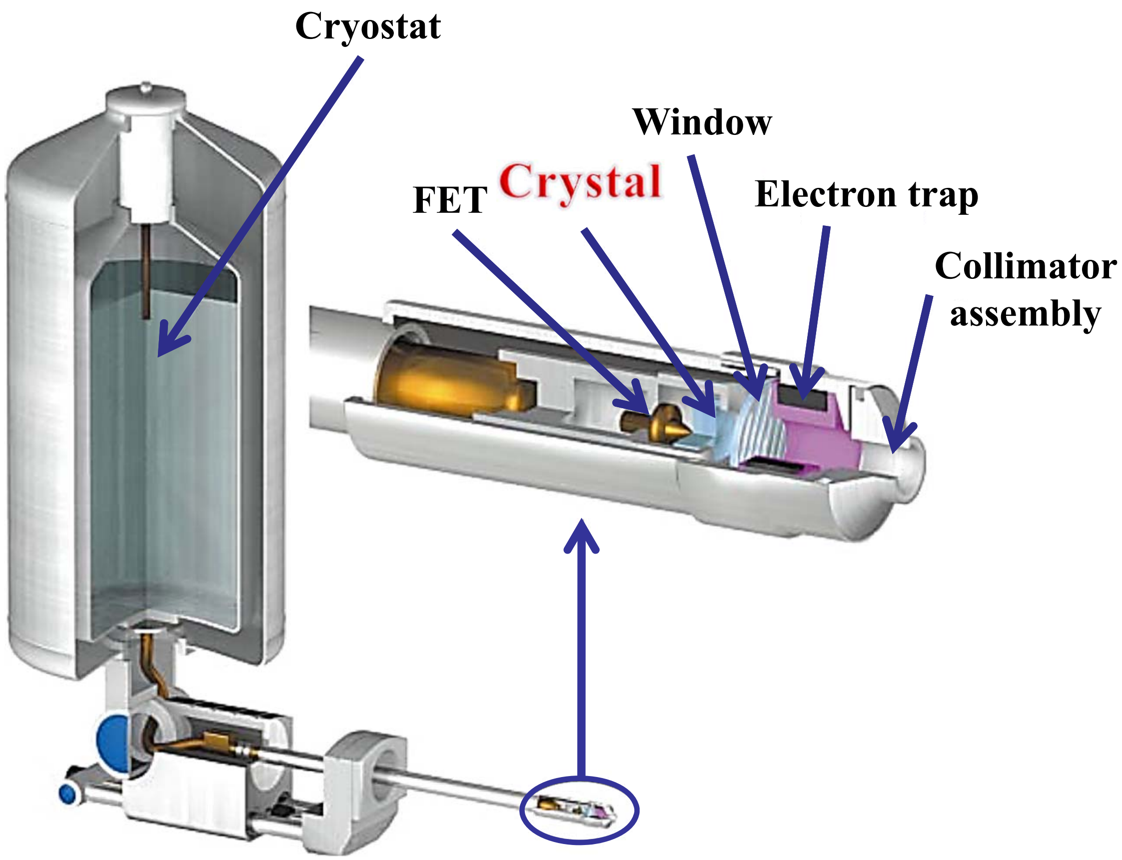
- **Electron trap:**
  - **Electrons that penetrate the detector cause background artifacts** and also overload the measurement chain.
  - A pair of permanent magnets that strongly deflect any passing electrons.
  - **Only required on detectors with thin polymer windows**, as thicker beryllium windows efficiently absorb electrons below 20keV in energy.

EDS Hardware



- **Window:**
  - Provides a barrier to **maintain vacuum within the detector** whilst being as transparent as possible to low energy X-rays.
  - There are two main **types of window materials**:
    1. **Beryllium (Be)** is highly robust, but strongly absorbs low energy X-rays meaning that only elements from sodium (Na) can be detected.
    2. **Polymer-based** thin windows can be made much thinner than Be windows and therefore are transparent to much lower energy X-rays, many allowing detection of X-rays down to 100eV.

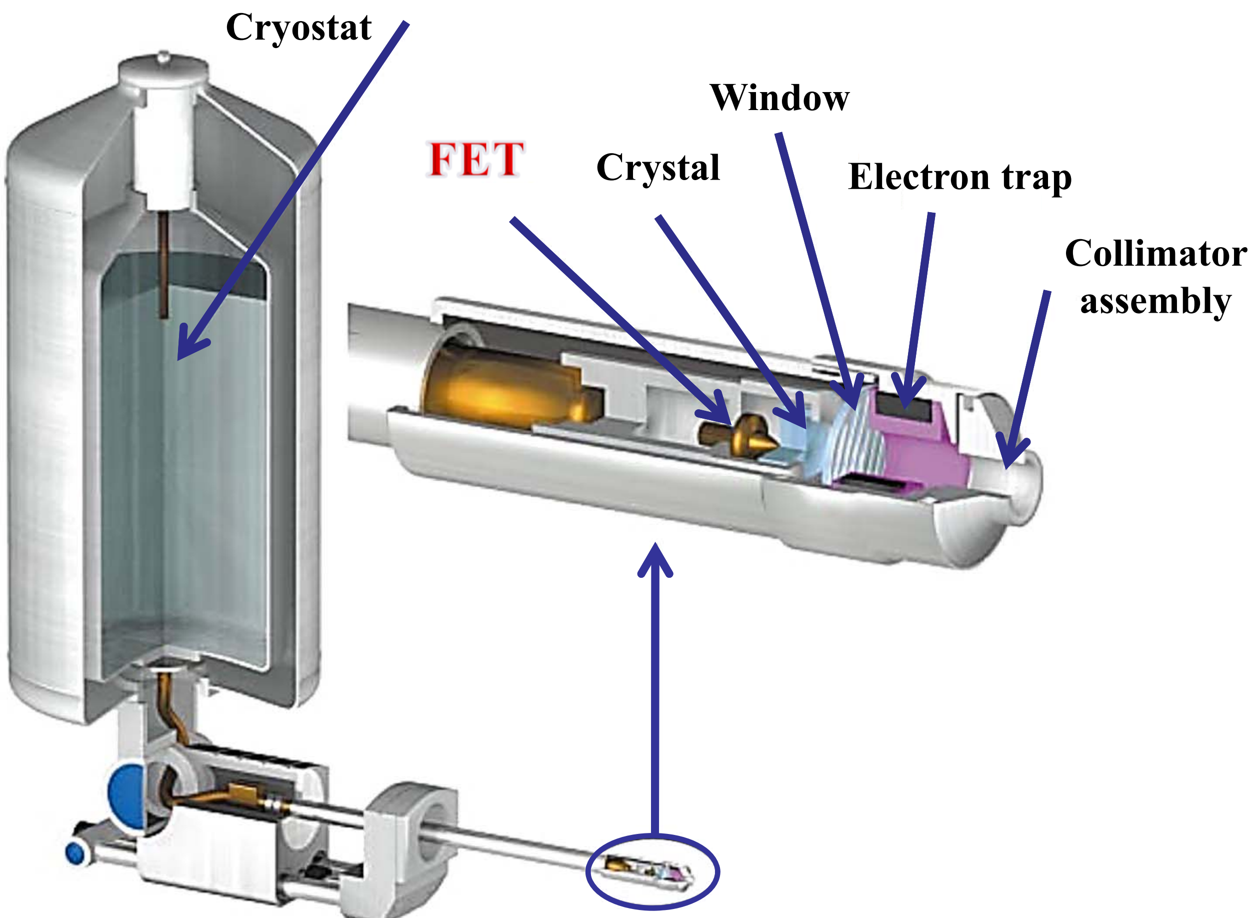
EDS Hardware



- **Crystal:**
  - A semiconductor device that **through the process of ionization converts an X-ray of particular energy into electric charge of proportional size**.

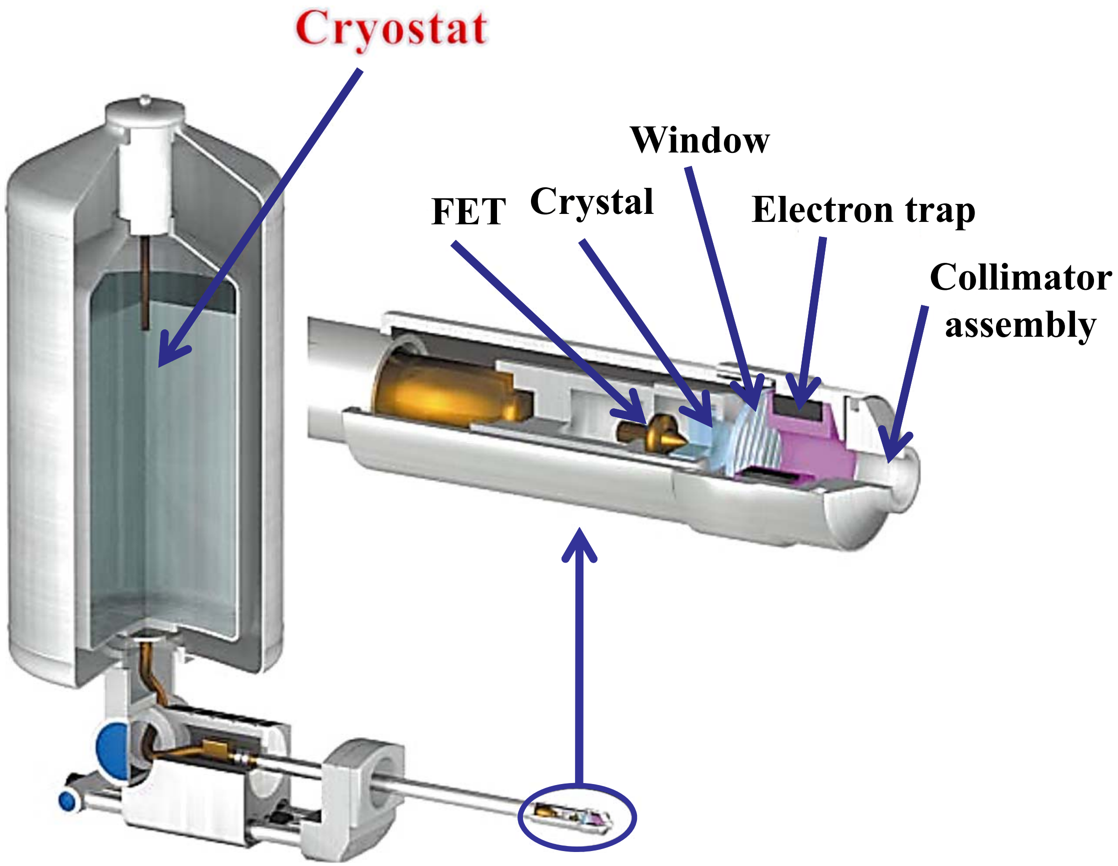
  - Two main materials are used for the detecting crystal:
    1. The most common is **silicon (Si)**, into which is drifted lithium (Li) to compensate for small levels of impurity.
    2. **High purity germanium crystals (HpGe)** are also used.

EDS Hardware



- **FET (Field Effect Transistor):**
  - Positioned just behind the detecting crystal.
  - The 1st stage of the amplification process that measures the charge liberated in the crystal by an incident X-ray and converts it to a voltage output.

EDS Hardware



- **Cryostat:**
  - The charge signals generated by the detector are small and can only be separated from the electronic noise of the detector if **the noise is reduced by cooling the crystal and FET**.
  - **Most EDS detectors work at close to liquid nitrogen temperatures (90K)**, and are cooled using a reservoir of liquid nitrogen held in a dewar.

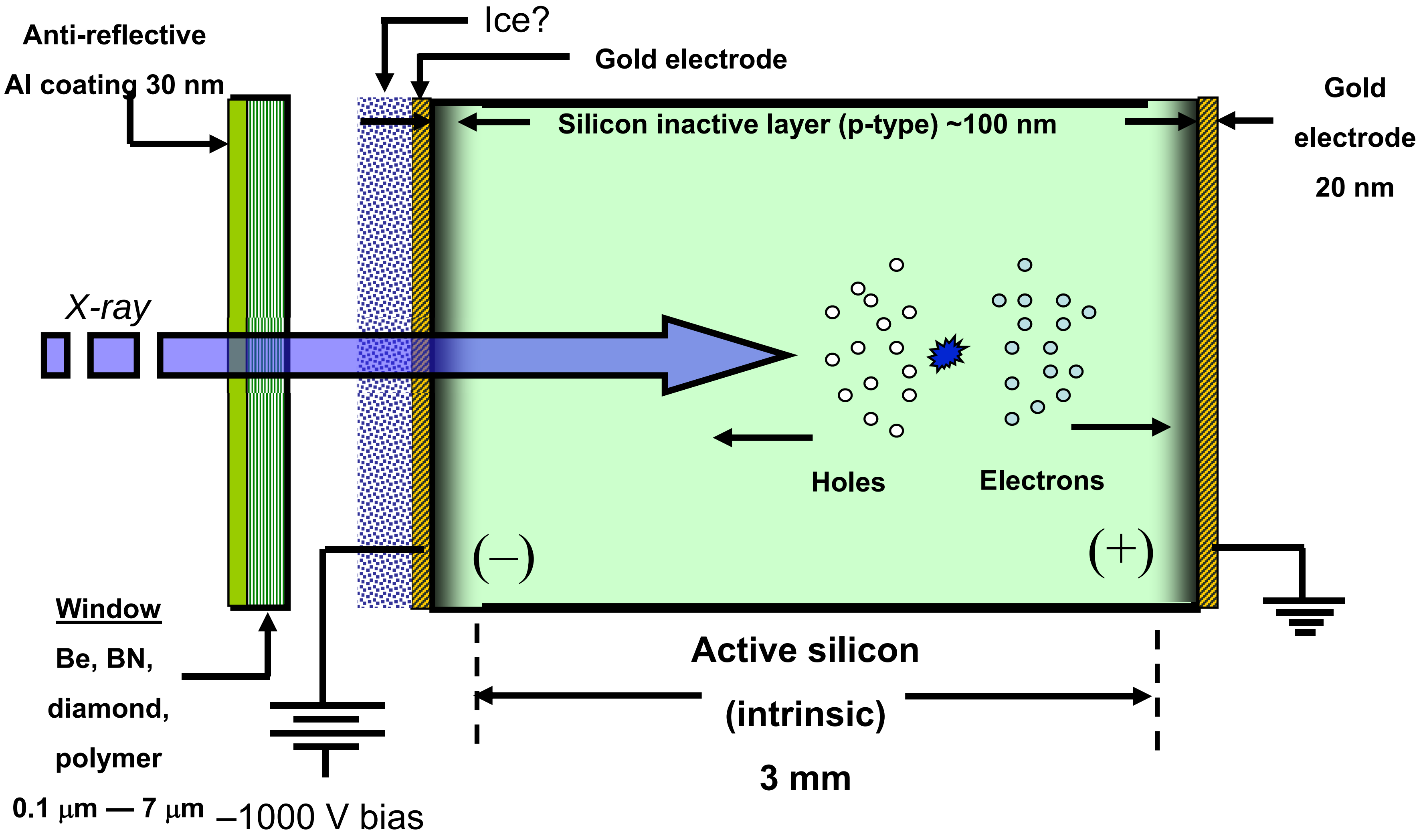
The Detector Concept

- The **EDS detector converts the energy of each individual X-ray into a voltage signal** of proportional size.

- This is achieved through a three stage process:
  1. The **X-ray is converted into a charge by the ionization** of atoms in the semiconductor crystal.
  2. This **charge is converted into the voltage signal by the FET** preamplifier.
  3. The **voltage signal is input into the pulse processor for measurement**. The output from the preamplifier is a voltage 'ramp' where each X-ray appears as a voltage step on the ramp.

- EDS detectors are designed to convert the X-ray energy into the voltage signal as accurately as possible. At the same time **electronic noise must be minimized to allow detection of the lowest X-ray energies**.

Si(Li) EDS Detector



Generation of an electron-hole pair costs 3.8eV in Si. The total number of electron-hole pairs, which defines the current pulse, is defined by the energy of the incident x-ray. So pulse-height analysis is used to analyze the detector response to each incident x-ray, and the energy of the x-ray can be determined.

There are important artifacts which you must be aware of regarding EDS:

Escape peaks occur when an incident photon causes a photo-electron effect to occur in the Si detector, and a Si K x-ray "escapes" from the Si detector. The remaining photon then has an energy of $E_{initial} - E_{Si\ K}$. The energy recorded in the pulse is thus lower by the energy of a Si K x-ray, and a peak in the energy spectrum will appear 1.74 keV below any intense peak. The intensity will be around 0.2% to 2% of the main peak.

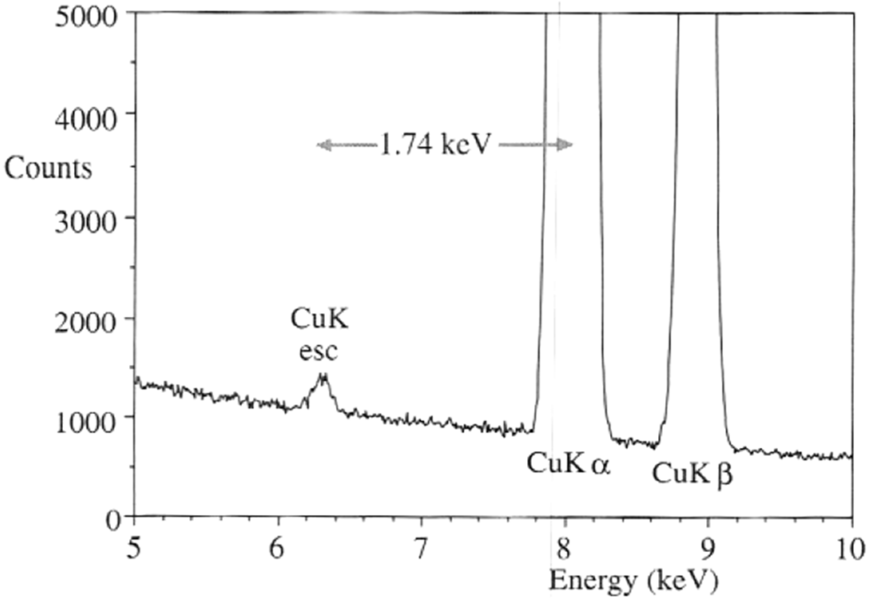


Figure 32.13. The escape peak in a spectrum from pure Cu, 1.74 keV below the Cu K_α peak. The intense K_α peak is truncated because it is ~50–100 times more intense than the escape peak.

Sum peaks appear when 2 X-rays arrive at the same time, and the electronics cannot distinguish them from one single X-ray. This will appear as a peak at double the energy of a strong (intense) peak. This happens for high count rates and thus high dead times.

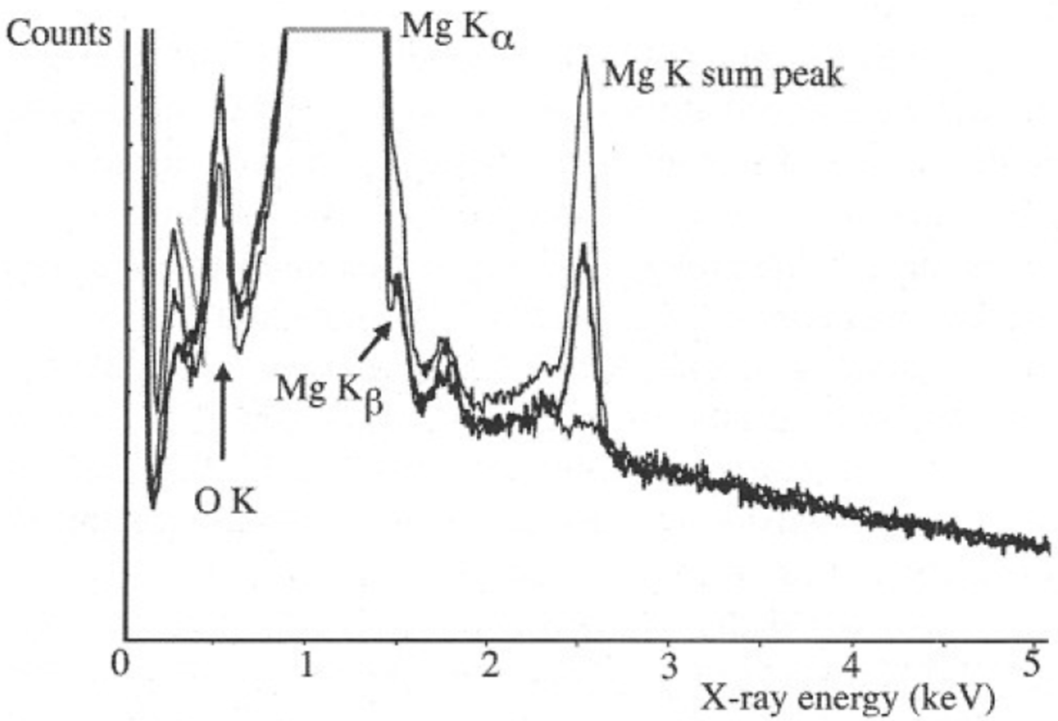


Figure 32.15. The Mg sum (coincidence) peak at various dead times; upper trace 70% dead time, middle trace 47%, lower trace 14%. The artifact is absent at 14% dead time.

There are many possible sources of *stray radiation* in a SEM (or TEM), including the chamber, the detector, and sample holders. Stray radiation originates from backscattered electrons and/or fluorescence.

The *internal fluorescence* peak is due to fluorescence of the Si dead-layer in front of the active part of the Si(Li) detector. A small Si peak appears even when no Si is present in the sample.

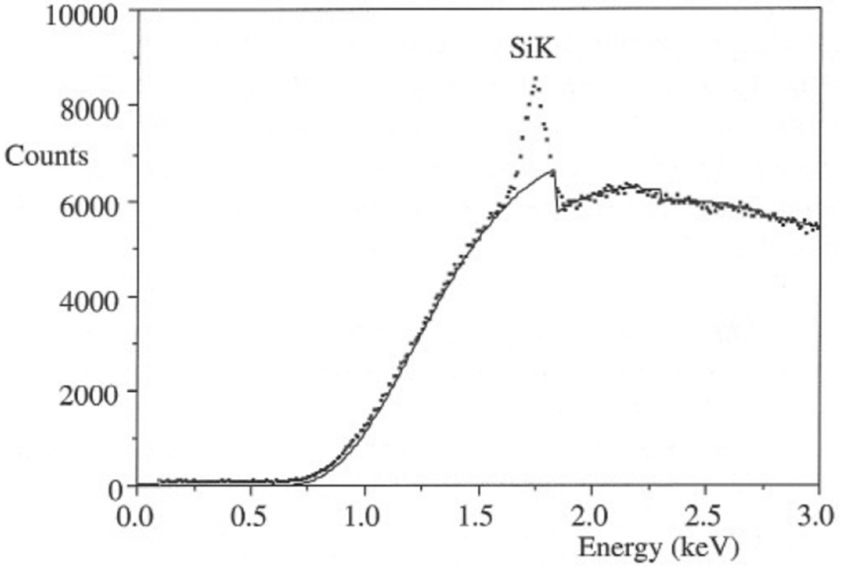


Figure 32.14. The Si internal fluorescence peak in a spectrum from pure C obtained with a Si(Li) detector. The ideal spectrum is fitted as a continuous line which exhibits the Si K absorption edge only.

Castaing’s Original Approach

To conduct quantitative analysis Castaing (1951) introduced the concept of a ratio (k_A) of the characteristic x-ray intensity in a specimen (I_{spec}) and in a reference standard (I_{stan}):

$$k_A = \frac{I^A_{spec}}{I^A_{\mathrm{stan}}}$$

Such that:

$$k_A = f\left(c_A\right)$$

This assumed that the number of ionization events (dn) from a particular atomic shell was produced by a single electron travelling a distance dx. The number of ionization events will be proportional to the number of atoms in a layer of thickness dx and inversely proportional to the area over which the atoms are distributed.

$$\left(dn\right)_{stnd} = Q\left[\left(\frac{N\rho}{A}\right)a \cdot dx\right]\frac{1}{a}$$

Where the bracketed term is the number of atoms in area a and thickness dx, N is Avagadro’s number, ρ is the density, and A is the atomic weight. Q is the ionization cross-section with units of area.

We can rewrite this as:

$$(dn)_{stnd} = \left(\frac{N\rho}{A}\right)\frac{Q}{\left(dE/dx\right)}dE$$

The original deceleration function from Williams (1932) was that:

$$-dE/dx = const \cdot \left(c/v\right)^{1.4} \rho$$

Where c is the velocity of light, and v is the velocity of the electron. So:

$$(dn)_{stnd} = -\left(\frac{N}{A}\right)\left(\frac{c}{v}\right)^{1.4} const \cdot Q \cdot dE$$

Castaing ignored backscattering and wrote:

$$n_{stnd} = -\int_{E_0}^{E_c}\left(\frac{N}{A}\right)\left(\frac{c}{v}\right)^{1.4} const \cdot Q \cdot dE$$

Where E_0 is the energy of the incident electron and E_c is the minimum energy required to ionize the electronic shell of interest (or critical excitation energy).

Both Q and v are functions of the electron energy, so:

$$n_{stnd} = -\frac{const}{A}\int_{E_0}^{E_c} f_A(E)\cdot dE$$

Where f_A(E) depends only on the characteristic of the pure element A. So the number of ionization events from element A produced by an electron travelling in a multi-element sample containing A in mass concentration c_A is:

$$n_{stnd} = -c_A\frac{const}{A}\int_{E_0}^{E_c} f_A(E)\cdot dE$$

Thus:

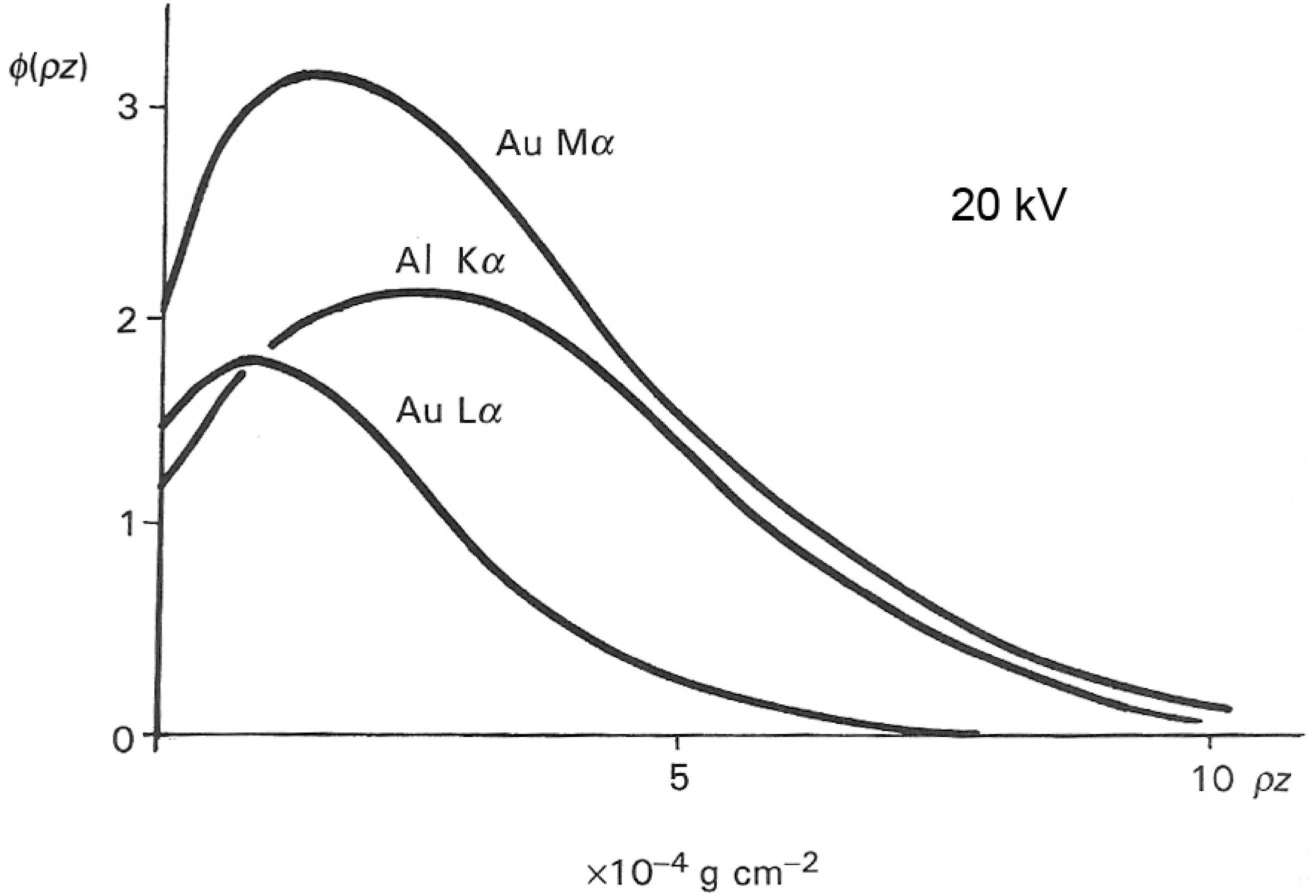
$$\frac{n_{spec}}{n_{stnd}} = c_A$$

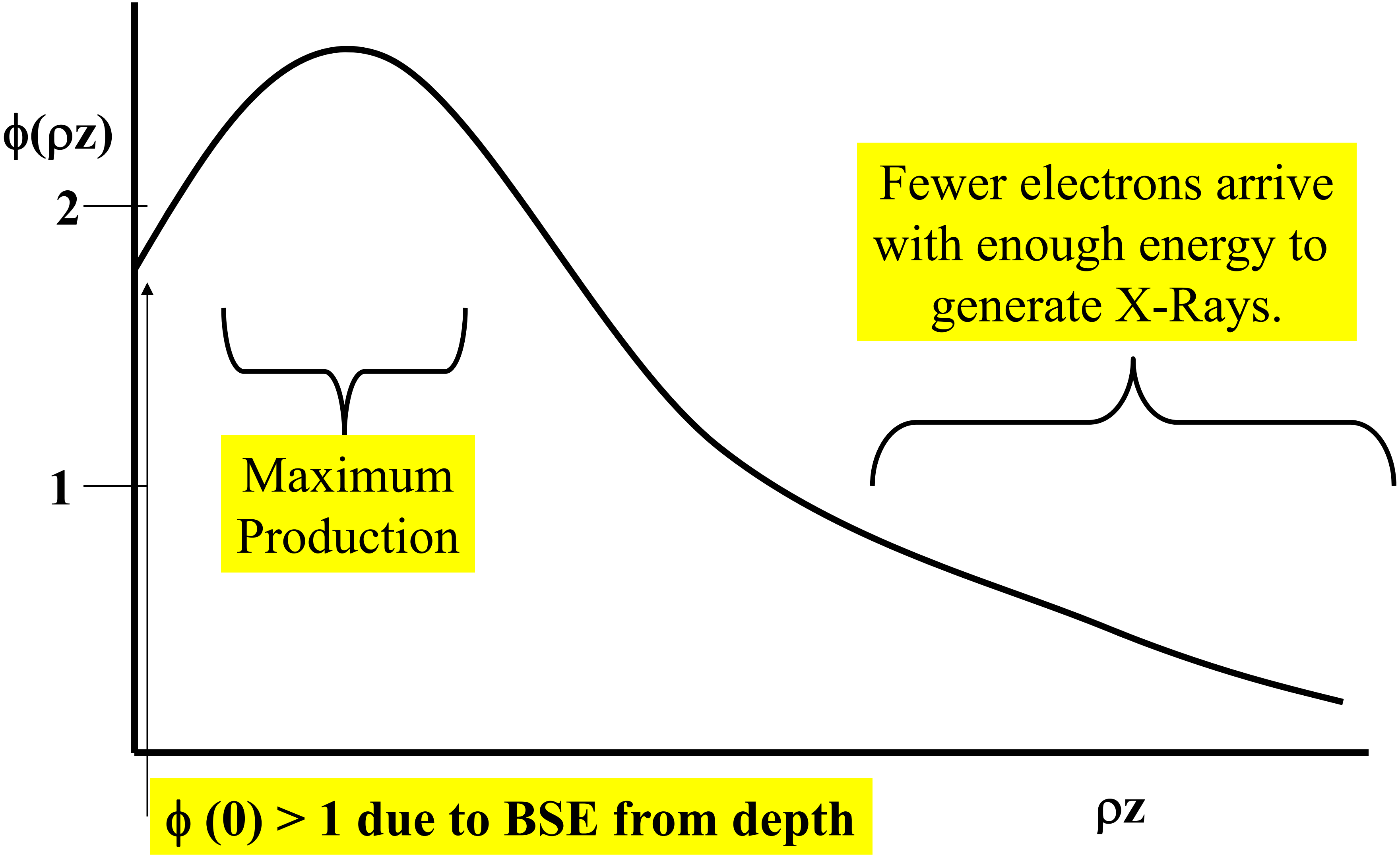
And if absorption is ignored n is directly proportional to the x-ray intensity I. So Castaing's first approximation is:

$$\boxed{\frac{n_{spec}}{n_{stnd}} = \frac{I_{spec}}{I_{stnd}} = k_A = c_A}$$

This approach ignored absorption of the x-rays by the sample itself, which can be very important for a multi-component sample. It also ignored BSE which escape the sample (and therefore do not contribute), and florescence of x-rays.

Since there was no real function for Q, Castaing attempted to measure the way in which the intensity of x-rays ($\phi(\rho z)$) was distributed with mass-depth (ρz) in a sample.





Maximum Production

Fewer electrons arrive with enough energy to generate X-Rays.

φ (0) > 1 due to BSE from depth

Absorption (SEM)

The amount of absorption, dI, experienced by a monochromatic beam of x-rays of intensity I, when passing through a material of thickness dx is given by:

$$\frac{dI}{I} = -\mu dx$$

Where μ is the linear absorption coefficient. Integrating and rearranging:

$$I = I_0 \exp\left[-\left(\frac{\mu}{\rho}\right)\rho x\right]$$

Where μ/ρ is the mass absorption coefficient. For compound specimens containing element A and element B, we can assume the radiation first passes through A:

$$I^A = I_0 \exp\left[-\left(\frac{\mu}{\rho}\right)^A (\rho x)^A\right]$$

And then through material B:

$$I^{AB} = I_0 \exp\left[-\left(\frac{\mu}{\rho}\right)^A (\rho x)^A - \left(\frac{\mu}{\rho}\right)^B (\rho x)^B\right]$$

Physical Basis of Quantitative Analysis

Writing:

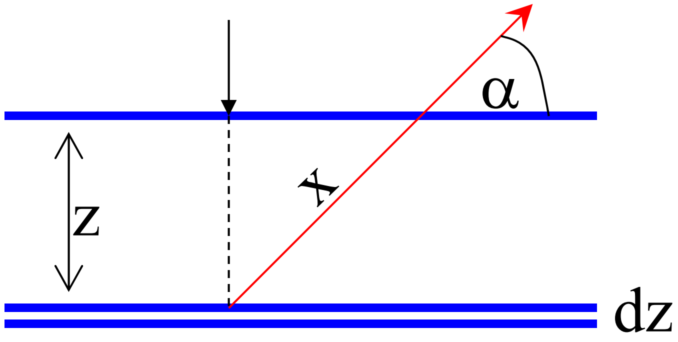
$$(\rho x)^A = c^A (\rho x)^{Total}$$

So:

$$I^{AB} = I_0 \exp\left[-(\rho x)^{Total}\left(c_A\left(\frac{\mu}{\rho}\right)^A + c_B\left(\frac{\mu}{\rho}\right)^B\right)\right] = I_0 \exp\left[-(\rho x)^{Total}\sum c_i\left(\frac{\mu}{\rho}\right)_i\right]$$

And μ/ρ for a compound is: $\sum c_i \left({}^{\mu}\!/_{\rho}\right)_i$

For analysis we need to consider the intensity of x-rays which emerge from the sample and reach the detector, which will be at a specific 'take-off' angle.



$$I = I_0 \exp\left[-\left({}^{\mu}\!/_{\rho}\right)\rho x\right]$$

$$x = \frac{z}{\sin(\alpha)}$$

cosec(x)=1/sin(x)

$$\boxed{I = I_0 \exp\left[-\left({}^{\mu}\!/_{\rho}\right)\frac{\rho z}{\sin(\alpha)}\right]}$$

Physical Basis of Quantitative Analysis…continued

If we consider the x-ray intensity generated in an element dρz at depth z below the surface as given by ϕ(ρz)dρz, the fraction emerging at an angle α from the surface is:

$$dI = \phi(\rho z)\exp\left[-\left(\mu/\rho\right)\rho z \cdot \operatorname{cosec}(\alpha)\right]d\rho z$$

cosec(x)=1/sin(x)

And the total ***emerging*** intensity is:

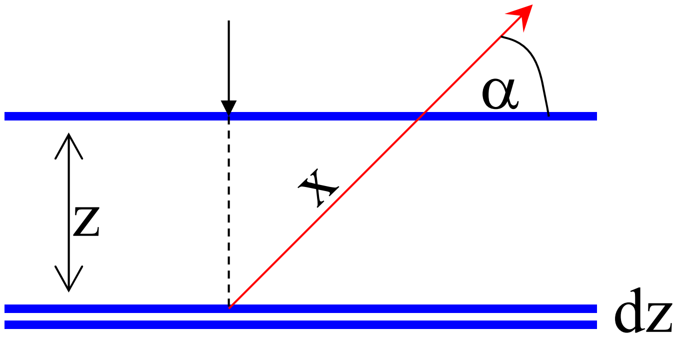
$$I = \int_0^\infty \phi(\rho z)\exp\left[-\left(\mu/\rho\right)\rho z \cdot \operatorname{cosec}(\alpha)\right]d\rho z$$

Since the total intensity ***generated*** is:

$$\int_0^\infty \phi(\rho z)\, d\rho z$$

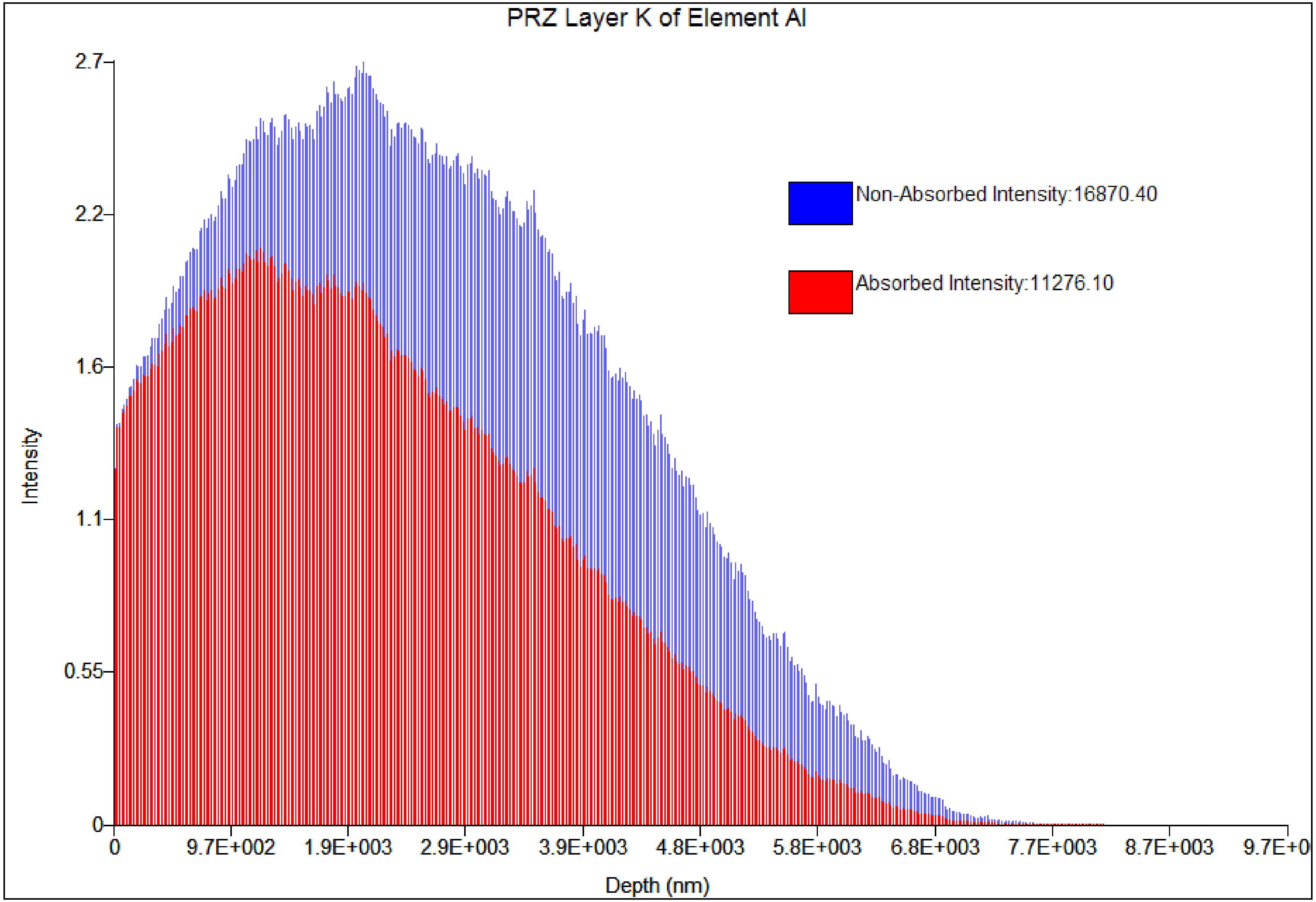
The absorption factor may be defined as:

$$\boxed{f(\chi) = \frac{\int_0^\infty \phi(\rho z)\exp\left[-\left(\mu/\rho\right)\rho z \cdot \operatorname{cosec}(\alpha)\right]d\rho z}{\int_0^\infty \phi(\rho z)\, d\rho z}}$$



$$\chi = \left(\mu/\rho\right)\cdot \operatorname{cosec}(\alpha)$$

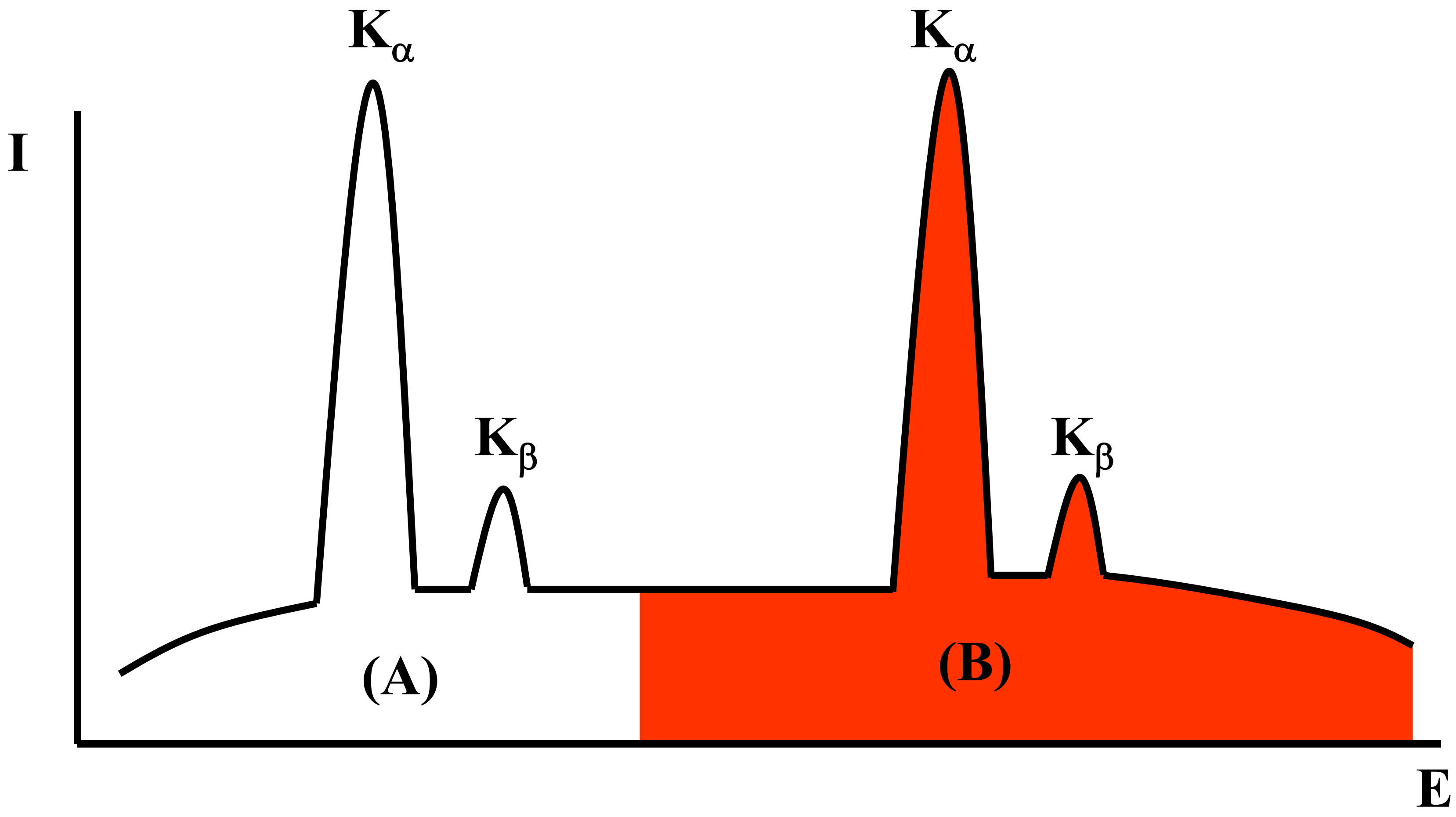
Physical Basis of Quantitative Analysis…continued



Absorption for x-rays in Al generated using a 30 kV beam.

Fluorescence (SEM)

X-Rays may generate secondary X-Rays!



X-Rays from (B) fluoresces (A).

The volume for fluorescence is larger than for primary X-Rays.

Quantitative Microanalysis

We now continue with Castaing's original approach:

$$\frac{n_{spec}}{n_{stnd}} = \frac{I_{spec}}{I_{stnd}} = k_A = c_A$$

But take into account the generation of x-rays as a function of depth, their absorption, and fluorescence. Consider and binary specimen containing elements A and B, where the mass concentration of A is to be measured by reference to a standard consisting of pure A. The intensity of the primary x-ray emission is:

$$I = \phi(\Delta\rho z)\int_0^\infty \phi(\rho z)\exp[-\chi\rho z]\,d\rho z$$

Where $\phi(\Delta\rho z)$ corresponds to the emission from an isolated thin film of **mass thickness** **$\Delta\rho z$**. The total emitted x-ray intensity including fluorescence is:

$$I = \phi(\Delta\rho z)\int_0^\infty \phi(\rho z)\exp[-\chi\rho z]\,d\rho z\,(1+\gamma+\delta)$$

Where γ is the ratio of the intensity of fluorescence emission to the primary characteristic x-ray emission, and δ is the corresponding ratio for continuum fluorescence contribution.

Quantitative Microanalysis…continued

We can rewrite this as:

$$I = \phi(\Delta\rho z)\int_0^\infty \phi(\rho z)\,d\rho z \cdot f(\chi)\cdot(1+\gamma+\delta)$$

where

$$f(\chi) = \frac{\int_0^\infty \phi(\rho z)\exp[-\chi\rho z]\,d\rho z}{\int_0^\infty \phi(\rho z)\,d\rho z}$$

$$\chi = \left(\mu/\rho\right)\cdot\operatorname{cosec}(\alpha)$$

The ratio of x-ray intensities (A radiation) emitted from specimen AB and standard A is then:

$$\frac{I_A^{AB}}{I_A^{A}} = \frac{\phi(\Delta\rho z)_A^{AB}}{\phi(\Delta\rho z)_A^{A}}\,\frac{\left[\int_0^\infty \phi(\rho z)\,d\rho z\right]_A^{AB}}{\left[\int_0^\infty \phi(\rho z)\,d\rho z\right]_A^{A}}\,\frac{f(\chi)_A^{AB}\cdot(1+\gamma+\delta)_A^{AB}}{f(\chi)_A^{A}\cdot(1+\gamma+\delta)_A^{A}}$$

Quantitative Microanalysis…continued

We have already stated that:

$$c_A = \frac{\phi(\Delta\rho z)_A^{AB}}{\phi(\Delta\rho z)_A^{A}}$$

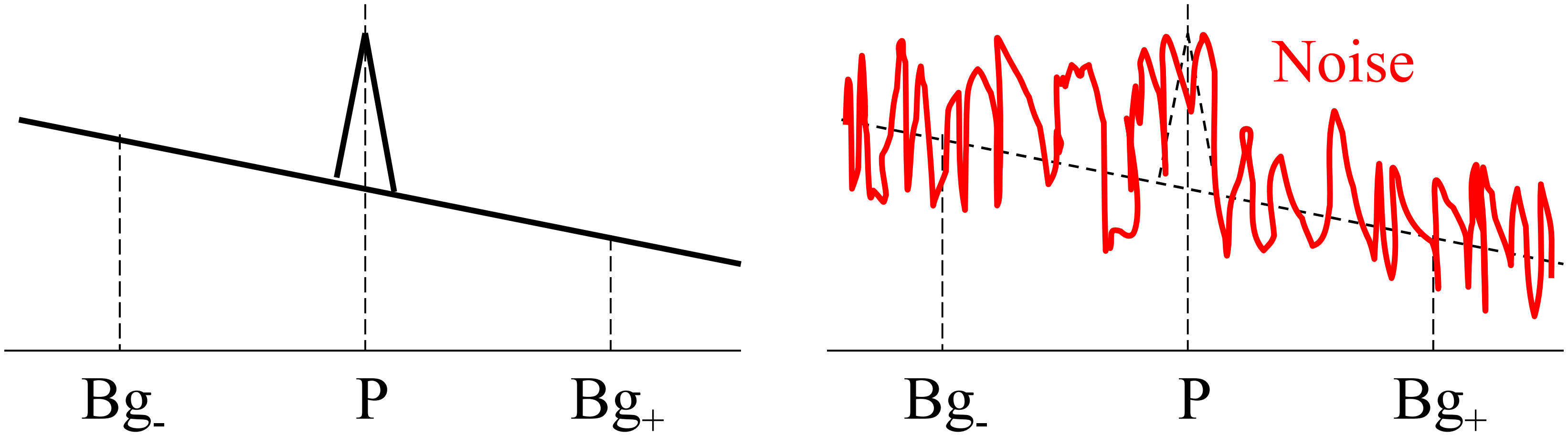
So:

$$\boxed{\frac{I_A^{AB}}{I_A^{A}} = c_A \underbrace{\frac{\left[\int_0^{\infty} \phi(\rho z)\, d\rho z\right]_A^{AB}}{\left[\int_0^{\infty} \phi(\rho z)\, d\rho z\right]_A^{A}} \frac{f(\chi)_A^{AB} \cdot (1+\gamma+\delta)_A^{AB}}{f(\chi)_A^{A} \cdot (1+\gamma+\delta)_A^{A}}}_{\mathbf{Z} \qquad \mathbf{A} \qquad \mathbf{F}}}$$

The terms within the ZAF correction depend on c_A, so an iterative numerical procedure is required to solve for c_A.

Years of work by many groups have provided analytical expressions for all the terms above, which can be incorporated into a relatively simple computer program. Details: *Quantitative Electron-Probe Microanalysis, by V.D. Scott, G. Love, and S.J.B. Reed.*

Detection Limits



P – peak, Bg - background

$$I_P - I_{Bg} \geq 0$$

For 95 % ⇩ confident probability

$$\boxed{I_P - I_{Bg} \geq 2\sqrt{2} \cdot \sigma(I_{Bg})}$$

Detection Limits

$$I_{\lim,0.95} = 2\sqrt{2} \cdot \sigma(I_{Bg}) = \frac{2\sqrt{2}\sqrt{I_{Bg}}}{\sqrt{m\tau}},$$

where m is a number of measurements,

τ is a duration of a single measurement.

$$\Downarrow$$

$$\boxed{C_{\lim,0.95} = g_{ZAF} \cdot C_{std} \cdot \frac{I_{\lim,0.95}}{I_{std}} = g_{ZAF} \cdot C_{std} \cdot \frac{2\sqrt{2}\sqrt{I_{Bg}}}{\sqrt{m\tau} \cdot I_{std}},}$$

where C_{std} is the content of the element of interest in the standard,

I_{std} is the intensity of the element of interest measured from the standard,

g_{ZAF} is the correction factor **(1/ZAF)**.

Thin Film EDS (TEM)

(Cliff-Lorimer Analysis)

We start with Castaing's original starting point:

$$\frac{C_i}{C_i^{stnd}} = k\frac{I_i}{I_i^{stnd}}$$

Where k now includes ZAF.

For TEM samples which are thin, to a first approximation the "A" and "F" factors can be ignored, assuming that absorption and fluorescence are negligible. Thus the basis for the technique is to rewrite Castaing's first equation for two elements in a binary system

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B} \qquad C_A + C_B = 100\%$$

Where k_{AB} is the Cliff-Lorimer factor (which is NOT a constant). This can be extended to ternary (and higher order systems) using:

$$\frac{C_B}{C_C} = k_{BC}\frac{I_B}{I_C} \qquad C_A + C_B + C_C = 1$$

$$k_{AB} = \frac{k_{AC}}{k_{BC}}$$

Cliff-Lorimer Analysis…continued

k_{AB} can be experimentally determined if you have a thin specimen, and collect I_A and I_B. The following precautions should be taken into account:

- The standard should be well characterized and based on a single phase;
- The standard must be thin enough that absorption and fluorescence can be ignored;
- No changes in chemical composition came from the thinning process;
- The thin sample must be stable under the electron beam (measure the concentration as a function of time under the beam and ensure no changes).

Values of k_{AB} can be calculated, but with problems of accuracy (~20% error).

Cliff-Lorimer Analysis…continued

Thicker TEM specimens, or analysis of light elements (such as oxygen or nitrogen) require that absorption be taken into account. This can be done in a manner similar to bulk EDS by defining k_{AB} as the sensitivity factor for a specimen thickness of t=0, and an effective sensititivity factor k_{AB}* where

$$k^*_{AB} = k_{AB}\left(ACF\right)$$

Where ACF is the absorption correction factor:

$$ACF = \frac{\int_0^t \left\{ \phi_B\left(\rho t\right) \exp\left(-\left({}^{\mu}\!/\!{}_{\rho} \right)_B \left({}^{\rho t}\!/\!{}_{\sin\alpha} \right) \right) \right\} d\left(\rho t\right)}{\int_0^t \left\{ \phi_A\left(\rho t\right) \exp\left(-\left({}^{\mu}\!/\!{}_{\rho} \right)_A \left({}^{\rho t}\!/\!{}_{\sin\alpha} \right) \right) \right\} d\left(\rho t\right)}$$

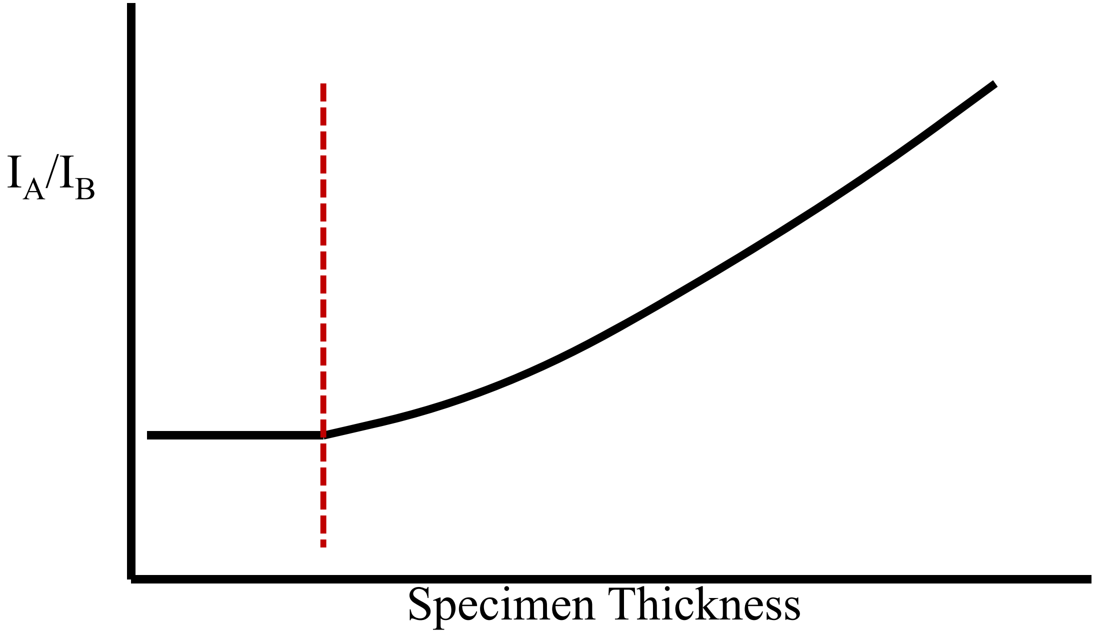
$$\left({}^{\mu}\!/\!{}_{\rho} \right)_A^{spec} = \sum_i \left(\frac{C_i \mu}{\rho} \right)_{i,A}$$

Cliff-Lorimer Analysis…continued

While for bulk specimens ϕ(ρt) varies as a function of depth, for TEM samples less than ~300nm ϕ(ρt) can be estimated as constant and equal to 1. This yields:

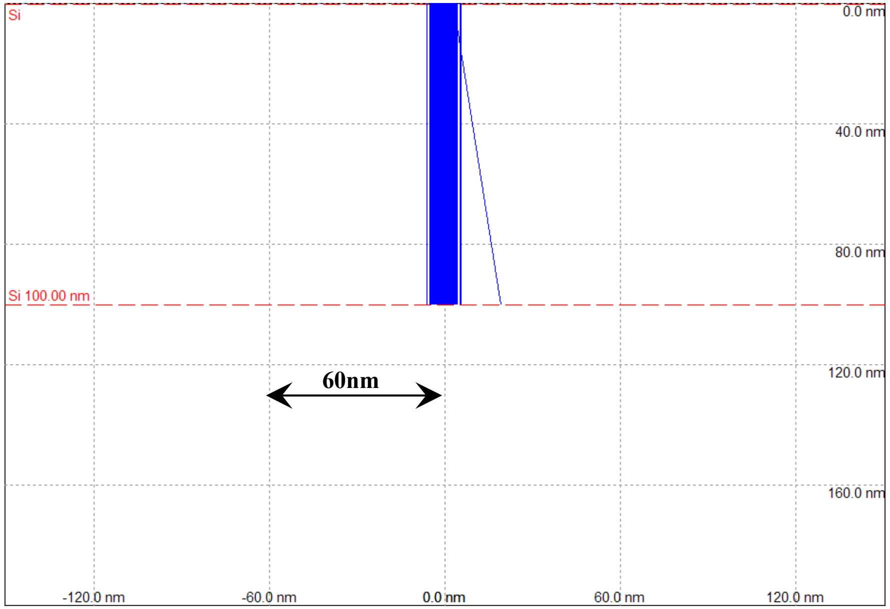
$$ACF = \left(\frac{\left. \frac{\mu}{\rho} \right]_{spec}^{A}}{\left. \frac{\mu}{\rho} \right]_{spec}^{B}} \right) \left(\frac{1 - \exp\left[- \left. \frac{\mu}{\rho} \right]_{spec}^{B} \frac{\rho t}{\sin \alpha} \right]}{1 - \exp\left[- \left. \frac{\mu}{\rho} \right]_{spec}^{A} \frac{\rho t}{\sin \alpha} \right]} \right)$$

So we still (*usually*) need to know ρ and t for our specimen.

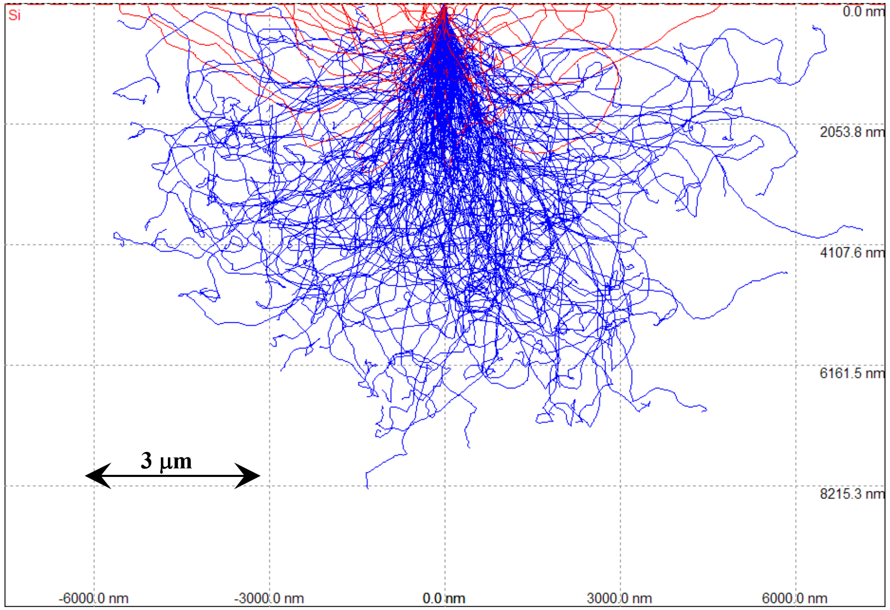


H. Meltzman, Y. Kauffmann, P. Thangadurai, M. Drozdov, M. Baram, D. Brandon and W. D. Kaplan, *An experimental method for calibration of the plasmon mean free path*, Journal of Microscopy, 236 [3]: 165-173, 2009.

Spatial Resolution & Thin Film EDS (TEM)



10nm beam at 300kV in a 100nm thick Si TEM specimen.



10nm incident beam at 30kV in a thick Si specimen.

Spatial Resolution & Thin Film EDS (TEM)

While results and theories differ in minor aspects, there is a general consensus that the beam spreading (b) is governed by the beam energy (E_0), the foil thickness (t) and density (ρ). A good approximation is the single-scattering model:

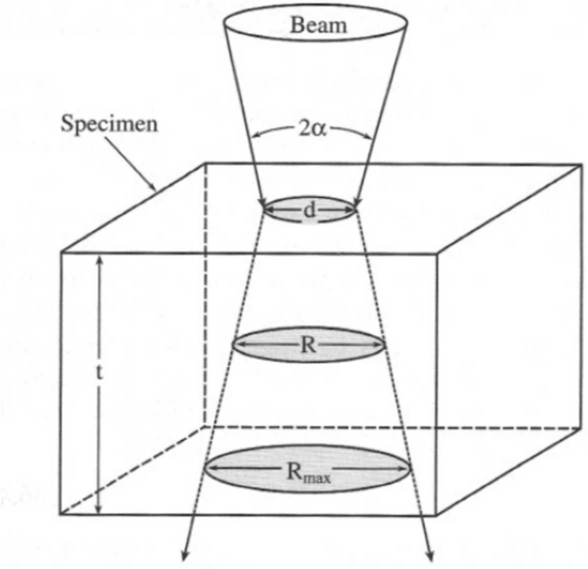
$$b = 7.21x10^5 \frac{Z}{E_0}\left(\frac{\rho}{A}\right)^{\frac{1}{2}} t^{\frac{3}{2}}$$

Where b and t are in cm, ρ is in g/cm^3 and E_0 is in eV. Combining b with the initial beam diameter d, the maximum diameter at the exit face of the specimen is:

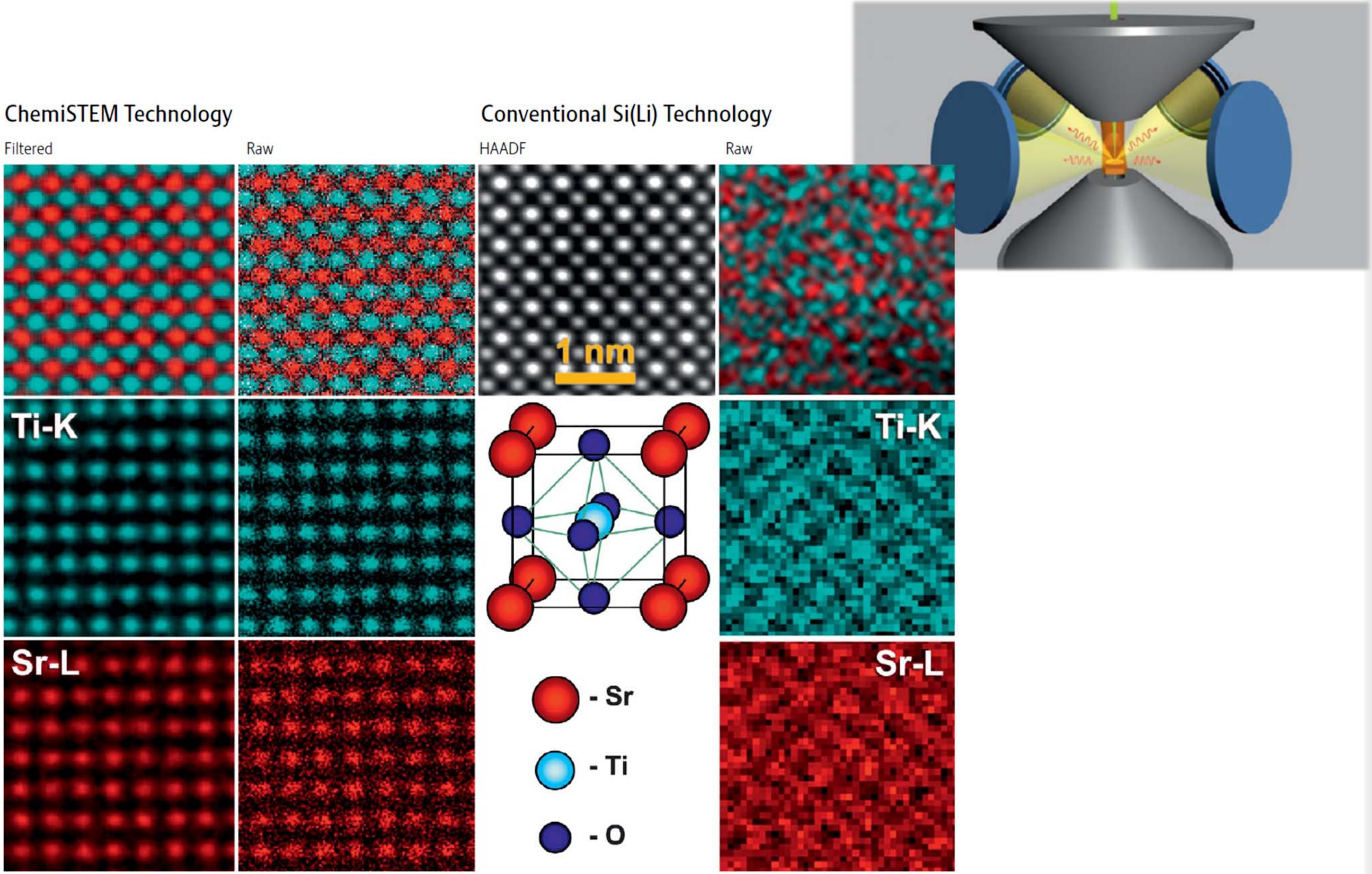
$$R_{\max} = \sqrt{b^2 + d^2}$$

A less conservative value, which is more representative of the total volume of interaction, and the value now accepted is:

$$R = \frac{d + R_{\max}}{2}$$

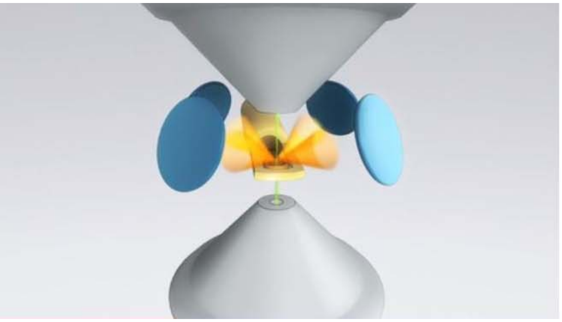


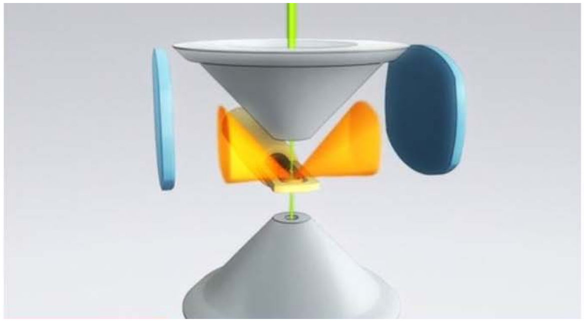
EDS Detectors



http://www.fei.com/uploadedFiles/Documents/Content/07102654_FEI_BROCH_ATOMIC_EDX_4A.pdf

EDS Detectors

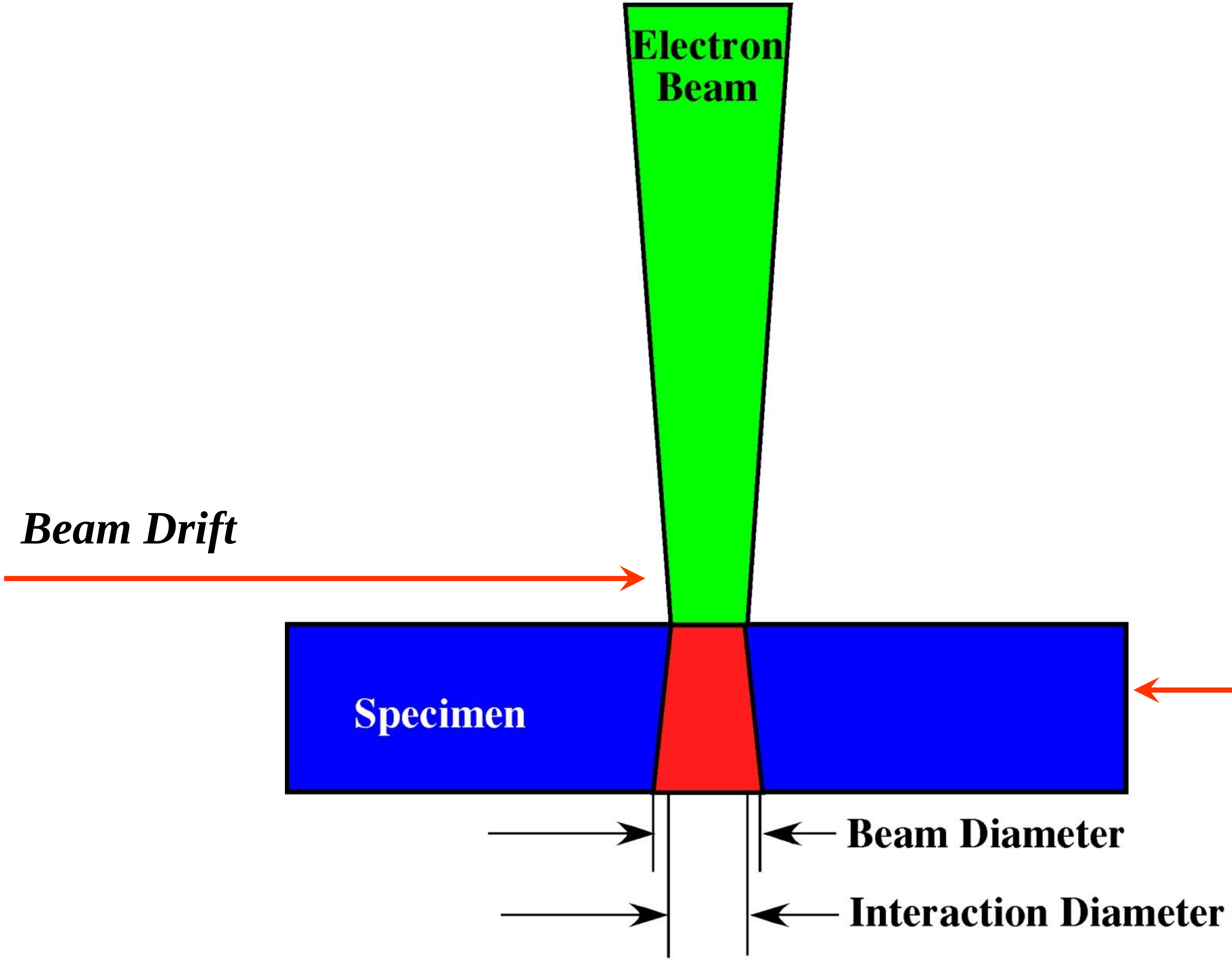




	Super-X	**Dual-X**
Effective Solid Angle (srad)	0.7	***1.76***
Detector efficiency on Si_3N_4 kcps/nA	22	50
Energy Resolution C-K (eV)	< 65 (@ 10kcps)	< 50 (@ 10kcps)
Energy Resolution Mn-K (eV)	130.5 (10kcps) 131 (100kcps)	126 (10kcps) 130 (100kcps)
Spurious Peaks Fe-K/ Ni-K (%)	0.23	1.4

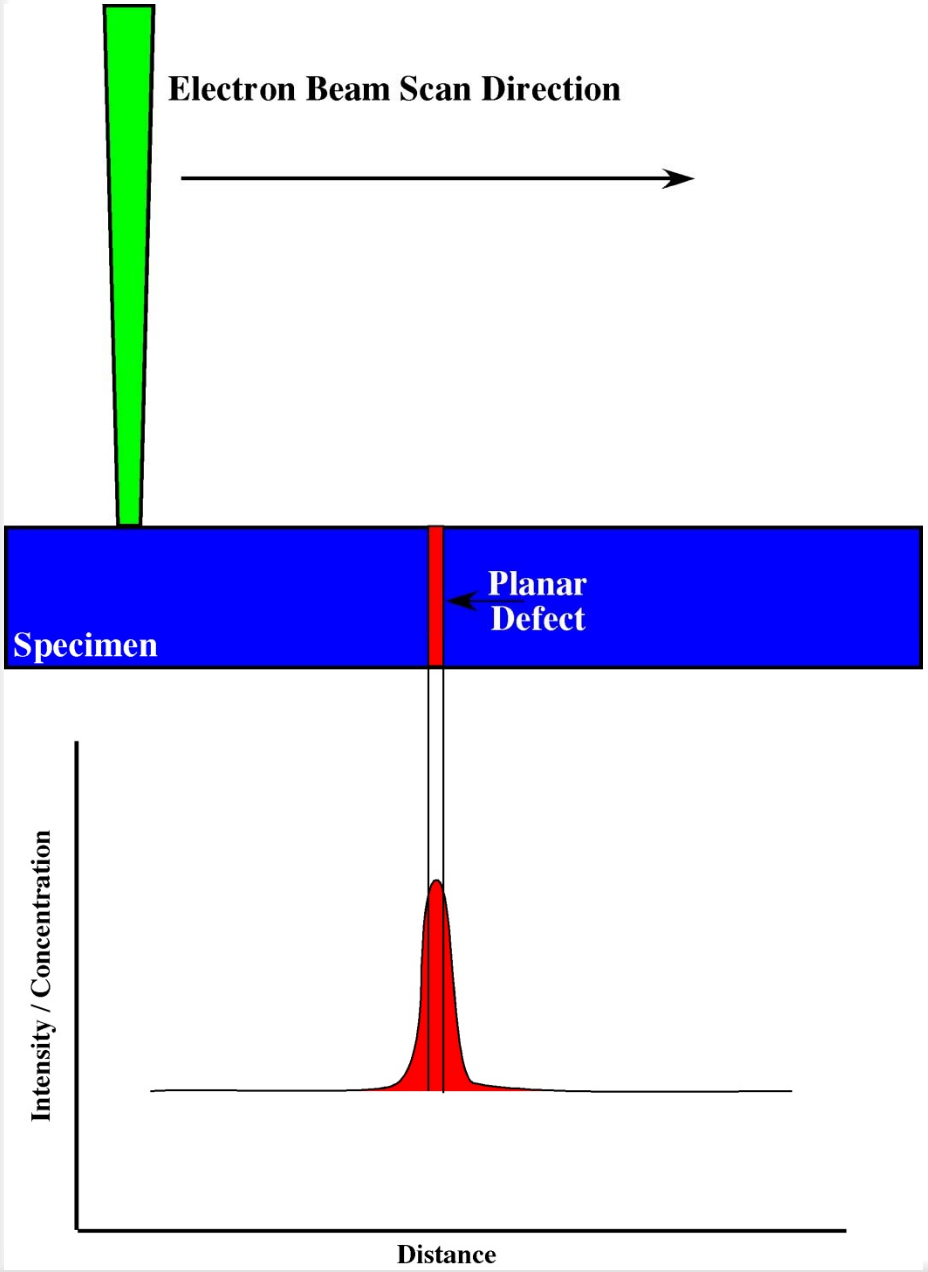
https://www.fei.com/products/tem/themis-z-for-materials-science/

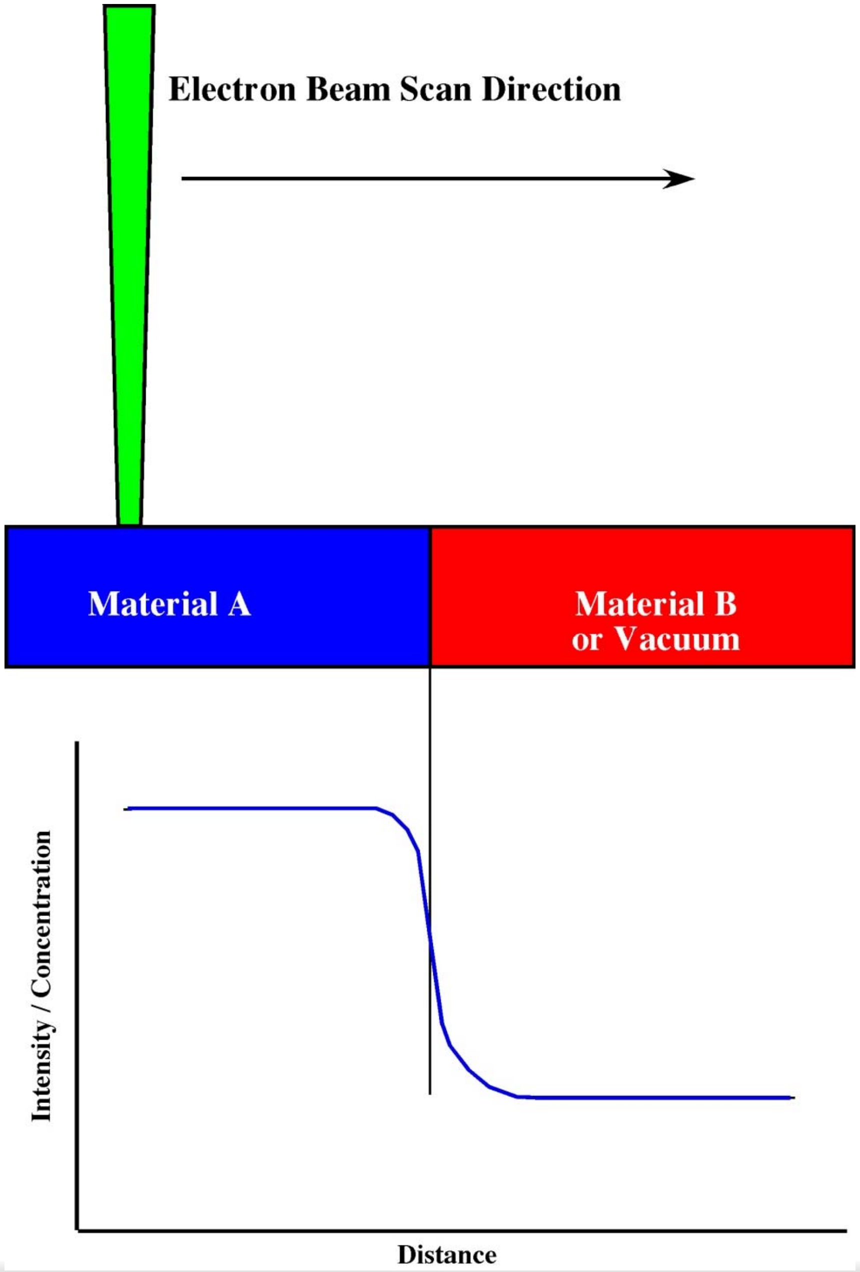
EDS: Can we do it in TEM? **NO**!



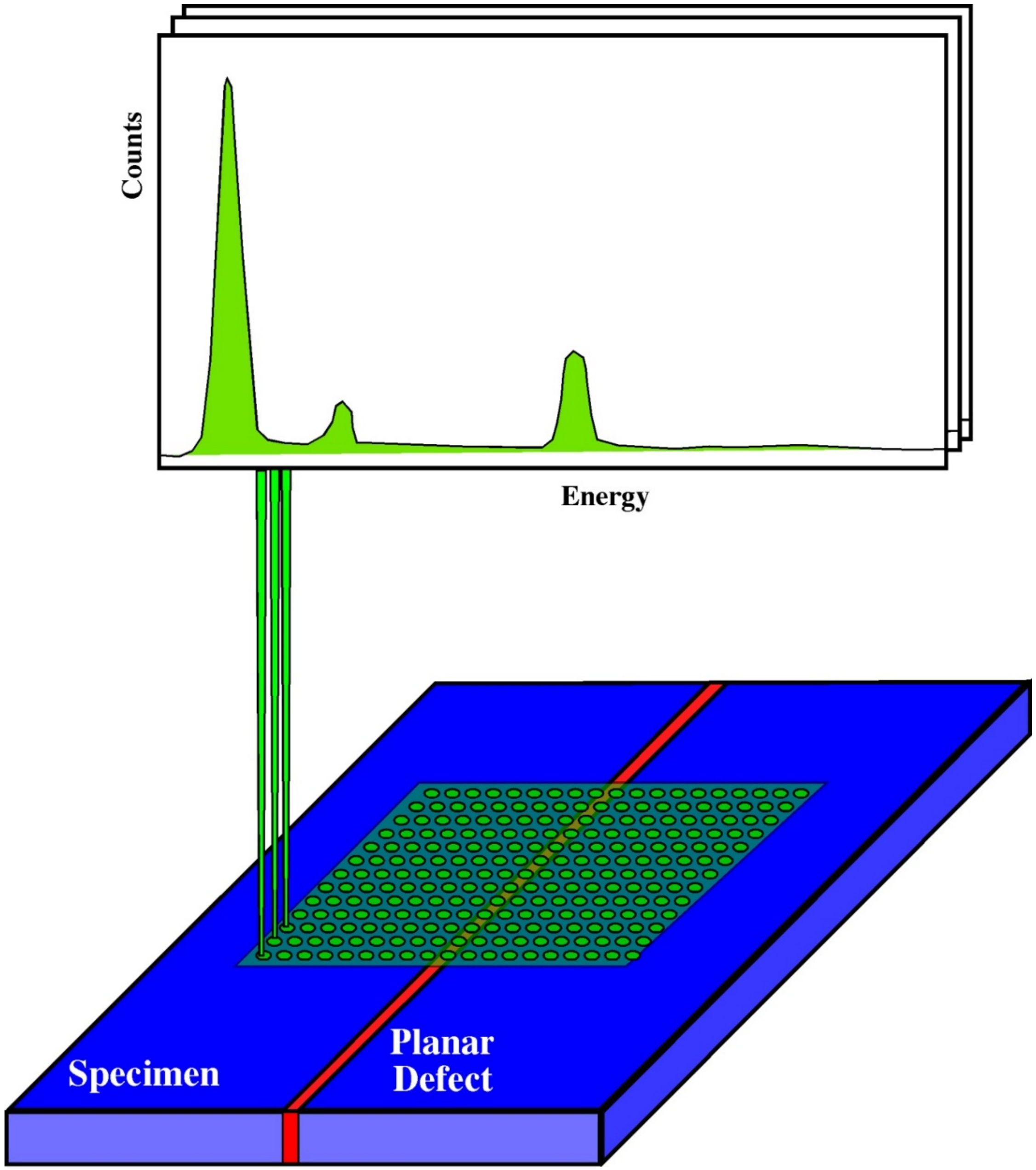
Good enough for conventional work, but not for nano or interfaces.

Solution: STEM line-scans with a known probe size

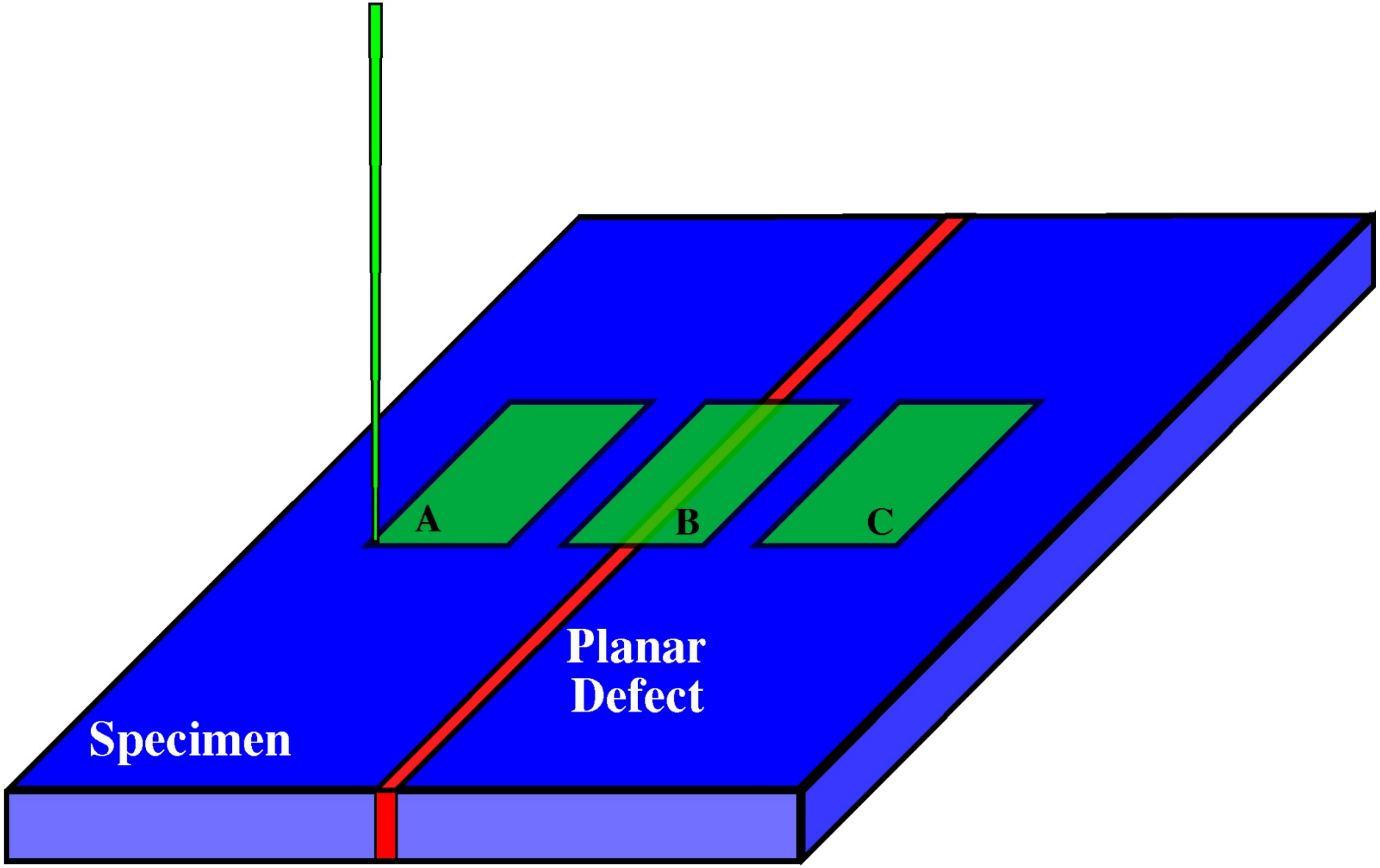




Solution: STEM spectral maps



Solution: STEM spacial difference technique



$$I_{\text{interface}} = I_B - I_A - I_C$$

Summary

- **Basic principles of the method;**
- **Detectors;**
- **Going quantitative;**
- **Practical approaches**

- **After the break: -> interfaces**

THANK YOU !