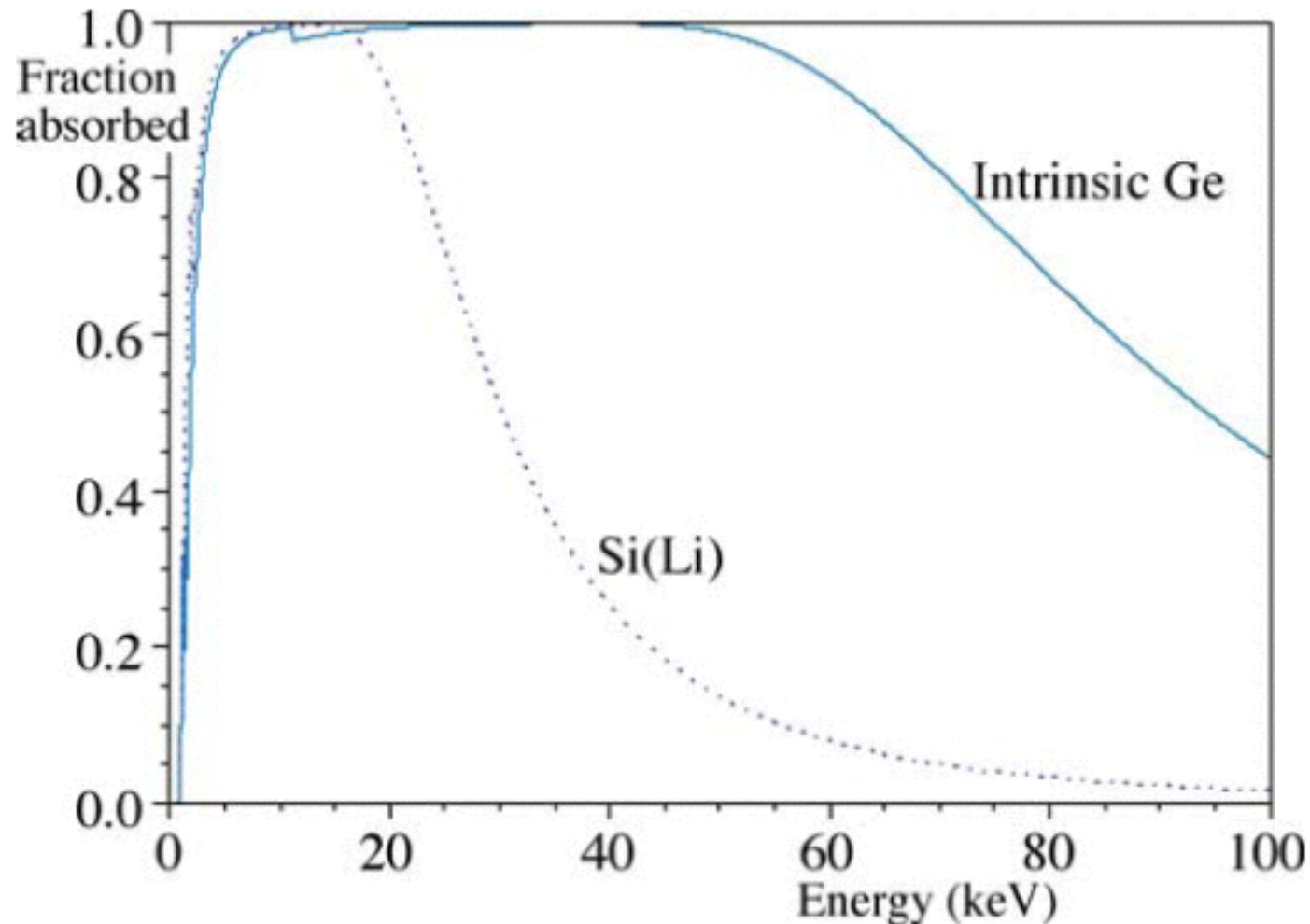# Chapter 10

Practical Application and Quantitative Analysis of EDX spectrometer

High energy efficiency up to 100 keV X-ray energy caculated for Si(Li) and IG dectoe

➢A typical energy range for Si(Li) detector is 20KeV

Intrinsic Germanium Detectors:

The higher purely intrinsic region is easy produced than Si

The intrinsic region (IG) is ~5 mm and can 100% efficient detect Pb Kα ~75keV

The energy for e/h pair of IG is about 2.8 eV, smaller than Si(3.8 eV)

PROTECT YOUR DETECTOR
The intense doses of high-energy electrons or X-rays which can easily be generated in an AEM (e.g., when the beam hits a grid bar) can destroy the Li compensation in a Si(Li) detector, but there is no such problem in an IG crystal.

Dead layer effect:

The p and n regions, at either of the detector, are usually termed "Dead layer"
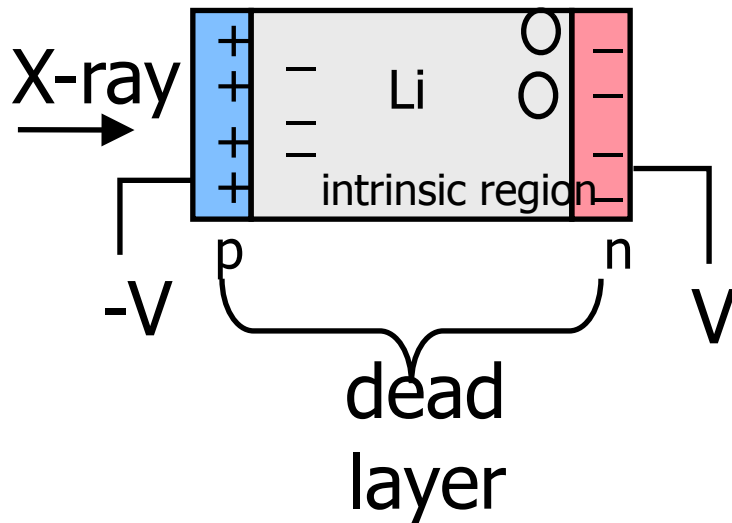
Why use Liquid N_2 cooling ?

X-ray

Li

intrinsic region

p   n

-V   V

dead layer

1. Thermal energy would active electron-hole pair, **giving a noise level**.
2. The Li atoms will diffuse under applied bias, that will **destroy the intrinsic property**.
3. The noise in FET will **mask the signal** from low-energy X-rays.

• The dead layer effect is more clearly at low-Z element.

➢ The display resolution chosen *depends on the number of channels* available. A typical energy range for Si(Li) detector is 20KeV and 2048 channels this gives you a display resolution of 10ev per channel

➢ Define energy resolution R of the detector:
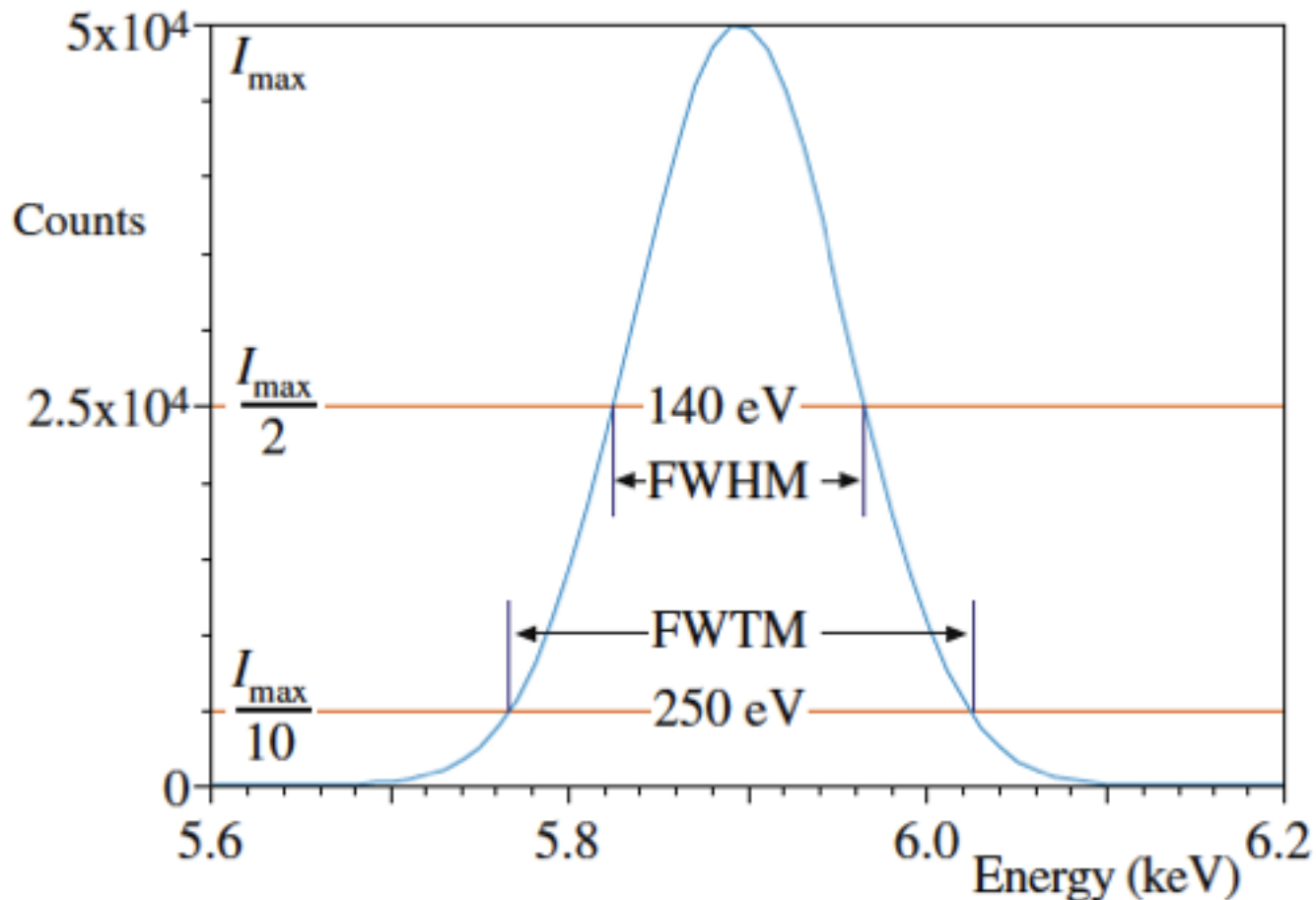
➢   Typically, Si(Li) detector have a resolution of ~140 eV at Mn K_α with the best being 127 eV. The best reported IG resolution is 114 eV.

➢ Because the value of ε is lower for Ge(2.9eV) than for Si (3.8eV), IG detectors have higher resolution than Si(Li). The resolution is also a function of the area of the detector, and the values gives relate to the performance of 10-mm^2

Artifacts Common to EDX System

1. **Escape Peak (signal detection artifacts)**

2. **The internal-fluorescence peak:**

3. **Sum peak:**

4. Post-specimen scattering

Artifacts Common to EDX System

1. Escape Peak (signal detection artifacts)

Because the detector is not a perfect "sink" for all the X-ray energy, it is possible that a small fraction of the energy is lost and not transformed into electron-hole pairs.

ESCAPE PEAK
Si escape peaks appear in the spectrum 1.74 keV below the true characteristic peak position.
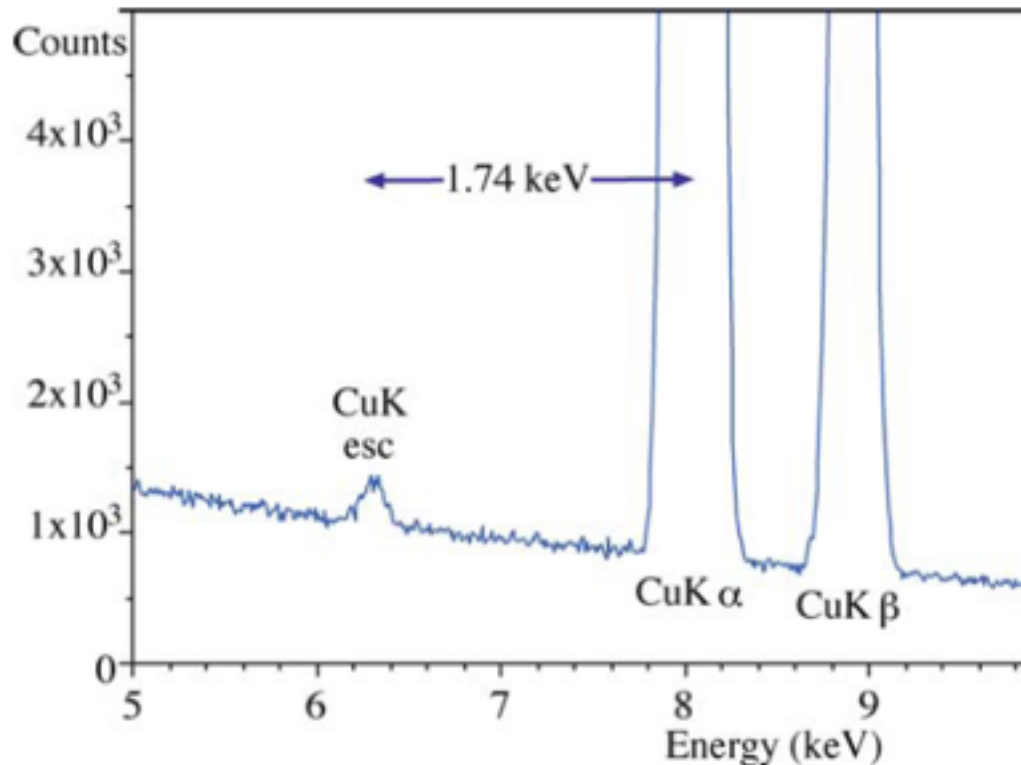
Incoming x-ray phonon fluoresces a Si Kα x-ray (~ 1.74keV) which escapes from the intrinsic region of the detector. The detector then registers an energy of E-1.74eV

Incoming x-ray phonon fluoresces a Si Ka x-ray
(~ 1.74eV) which escapes from the intrinsic region of the detector.
The detector then registers an energy of E-1.74eV
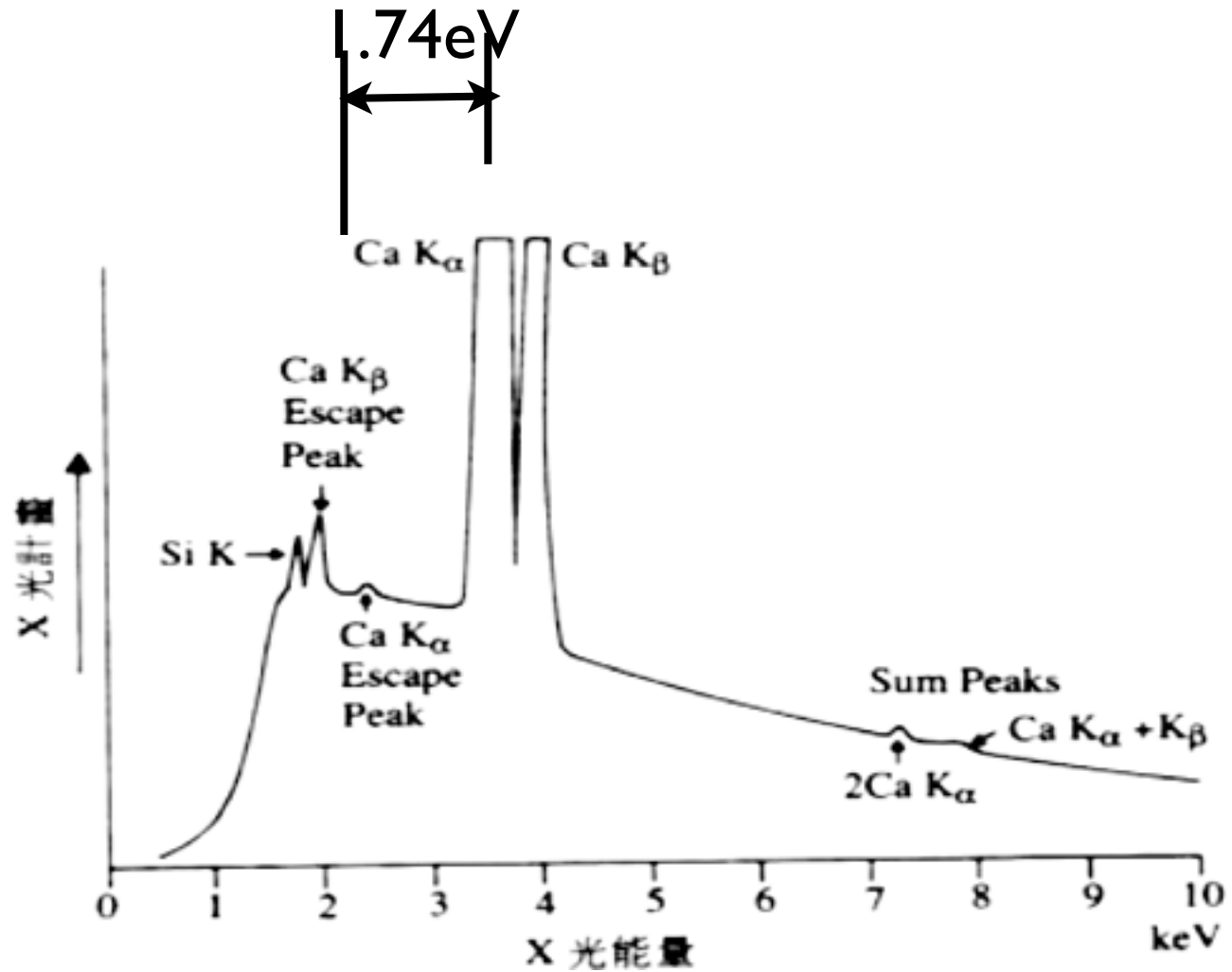
2. The internal-fluorescence peak:

This is a characteristic peak from the Si or Ge in the detector dead layer and enters the intrinsic region of the detector, which registers a small peak in the spectrum. (You will see this in long counting time.)

LONG COUNTING TIMES

A small Si K_α peak will occur in ALL spectra from Si(Li) detectors after long counting times.
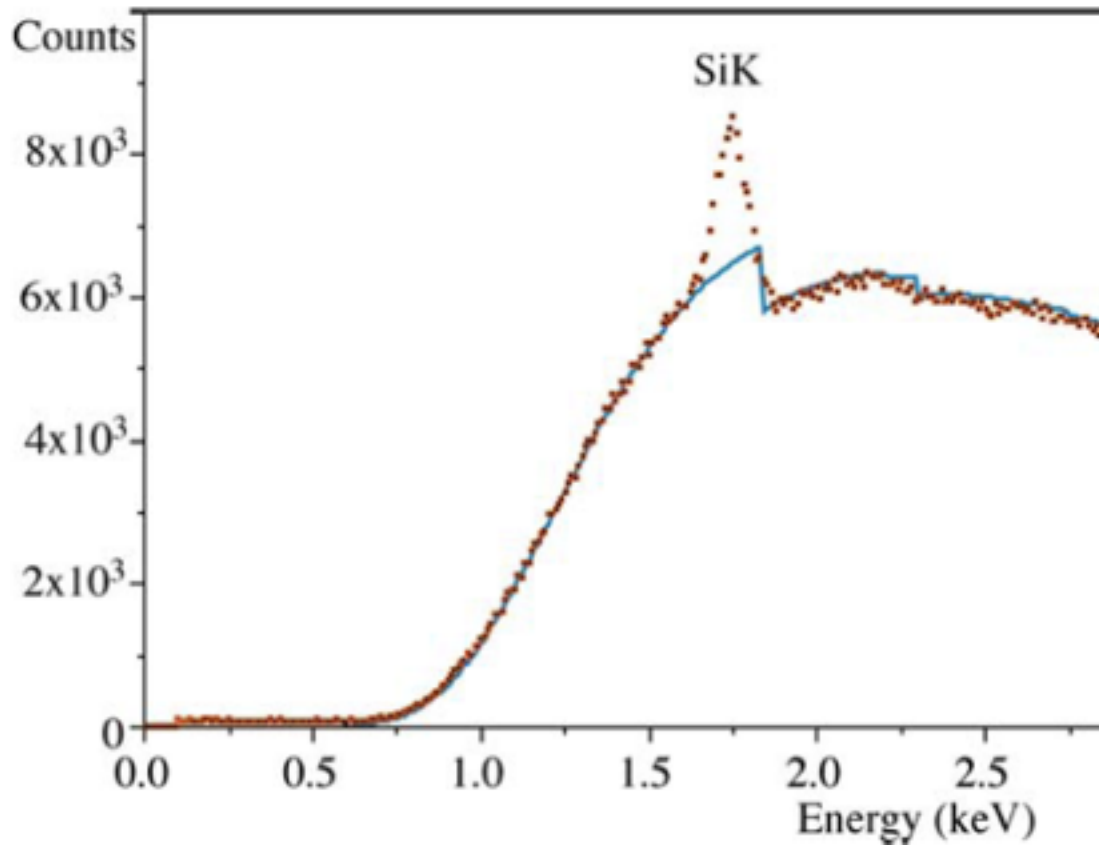
3. Sum peak:

The sum peak arises when the electronics are not fast enough. Two photons enter the detector at almost exactly the same time.
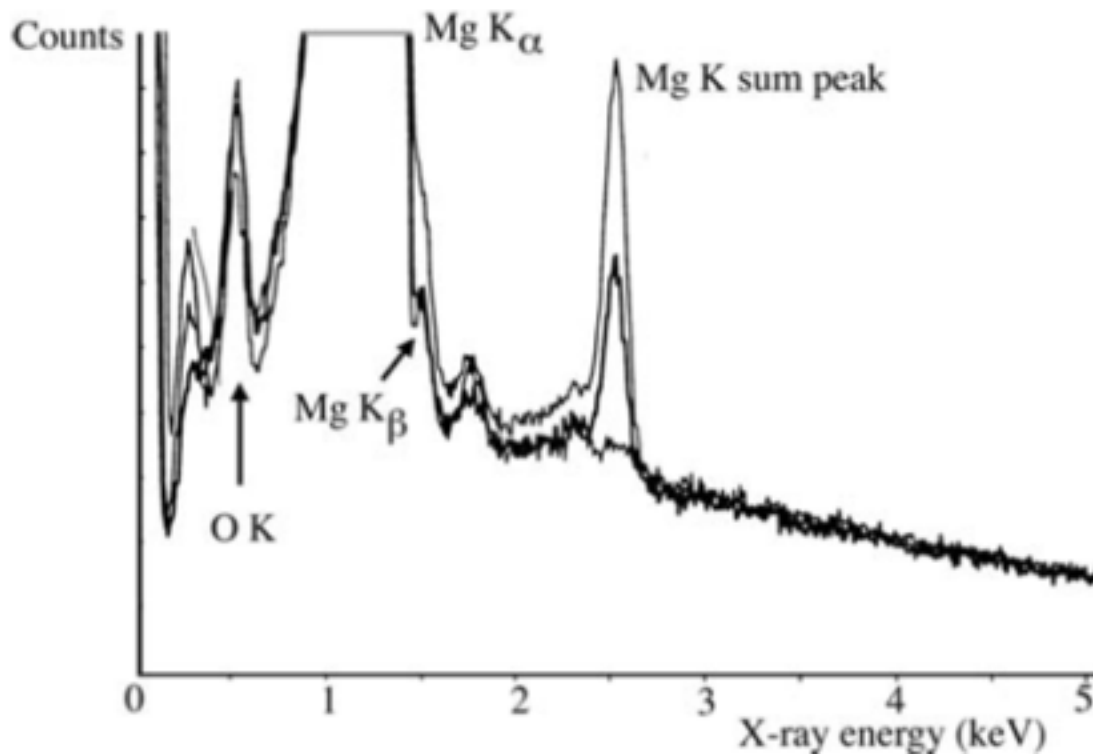
The input count rate is high.
The dead times are excess of about 60%
There are major characteristic peaks in the spectrum

THE SUM PEAK
The sum peak should be invisible if you maintain a reasonable input count rate, typically <10,000 cps, which should give a dead time of <60%.

Counts

Mg K$_\alpha$

Mg K sum peak

Mg K$_\beta$

O K

2x Al Kα=Ar Kα

0   1   2   3   4   5
X-ray energy (keV)

4. Post-specimen scattering

Post-specimen scattering

SPURIOUS X-RAYS
We define **spurious X-rays** as those that come from the specimen but are **not** generated by the electron probe in the chosen analysis region.
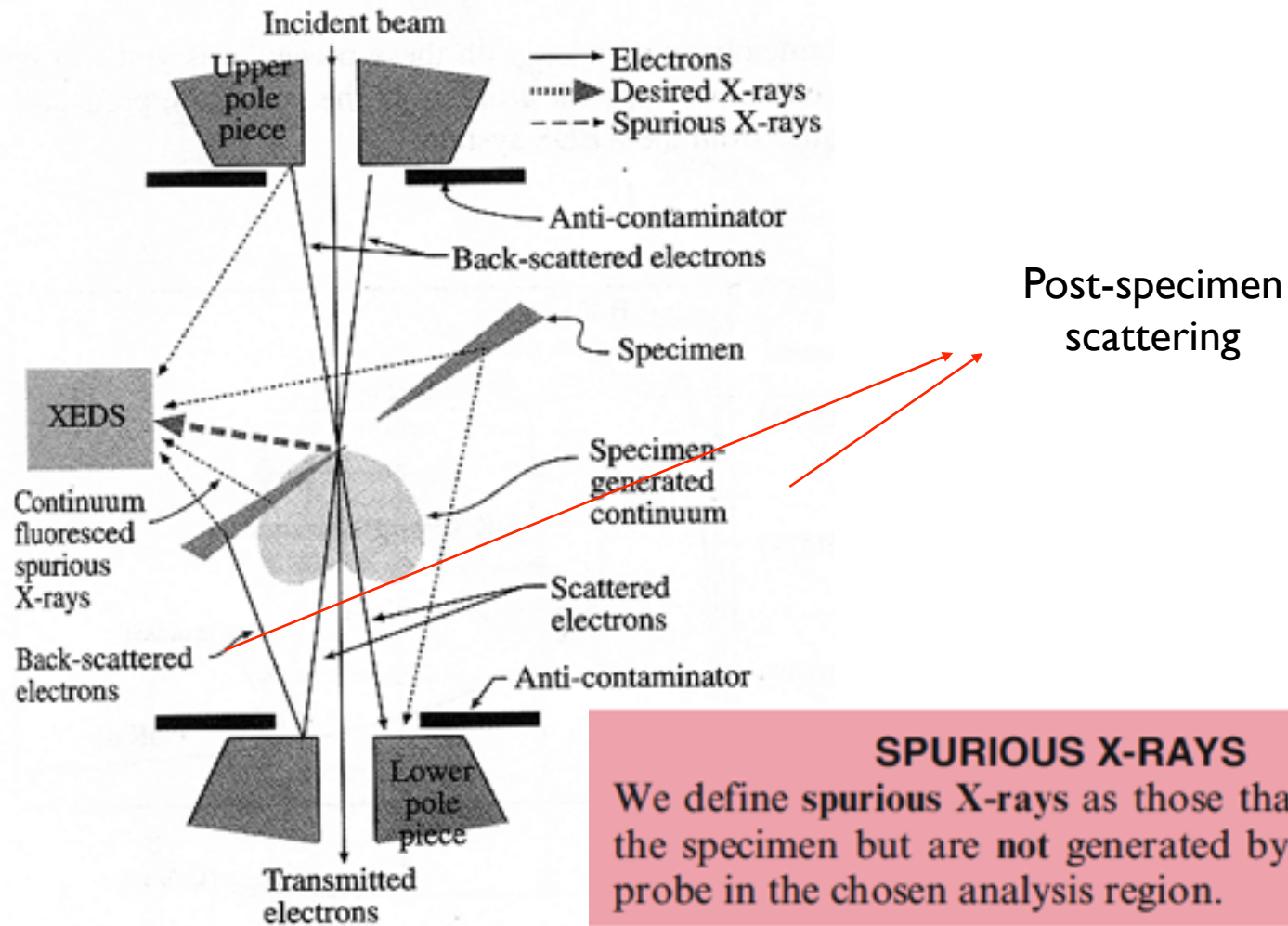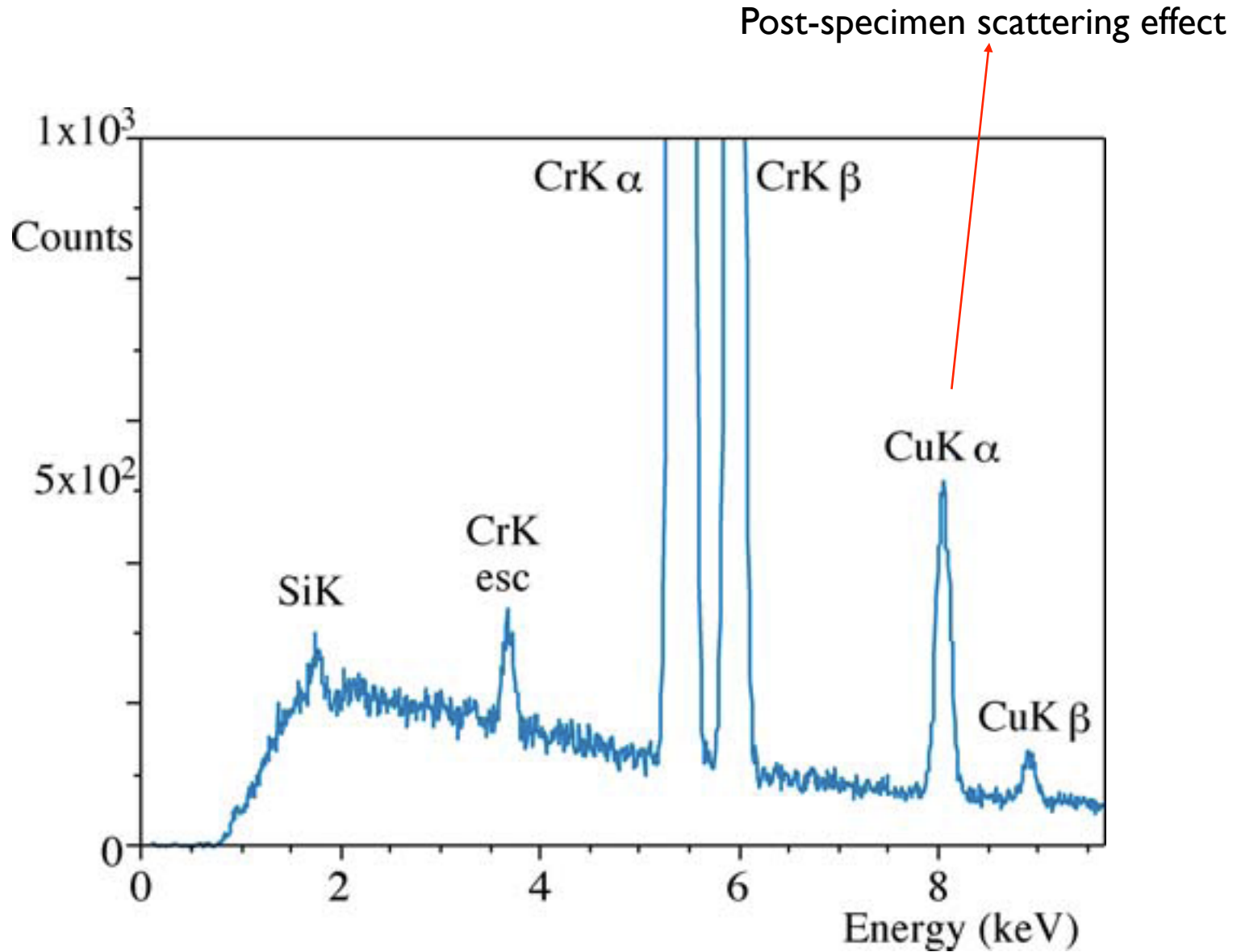
Figure 33.6. Sources of system and spurious X-rays generated whe the primary beam is scattered by a tilted, wedge specimen. Note the BSI which excite X-rays in the stage and elsewhere in the specimen and tl specimen-generated bremsstrahlung which fluoresces X-rays from tl specimen itself, but well away from the region chosen for analysis.

4. Post sample peaks-Cu

4. Post sample peaks-Fe
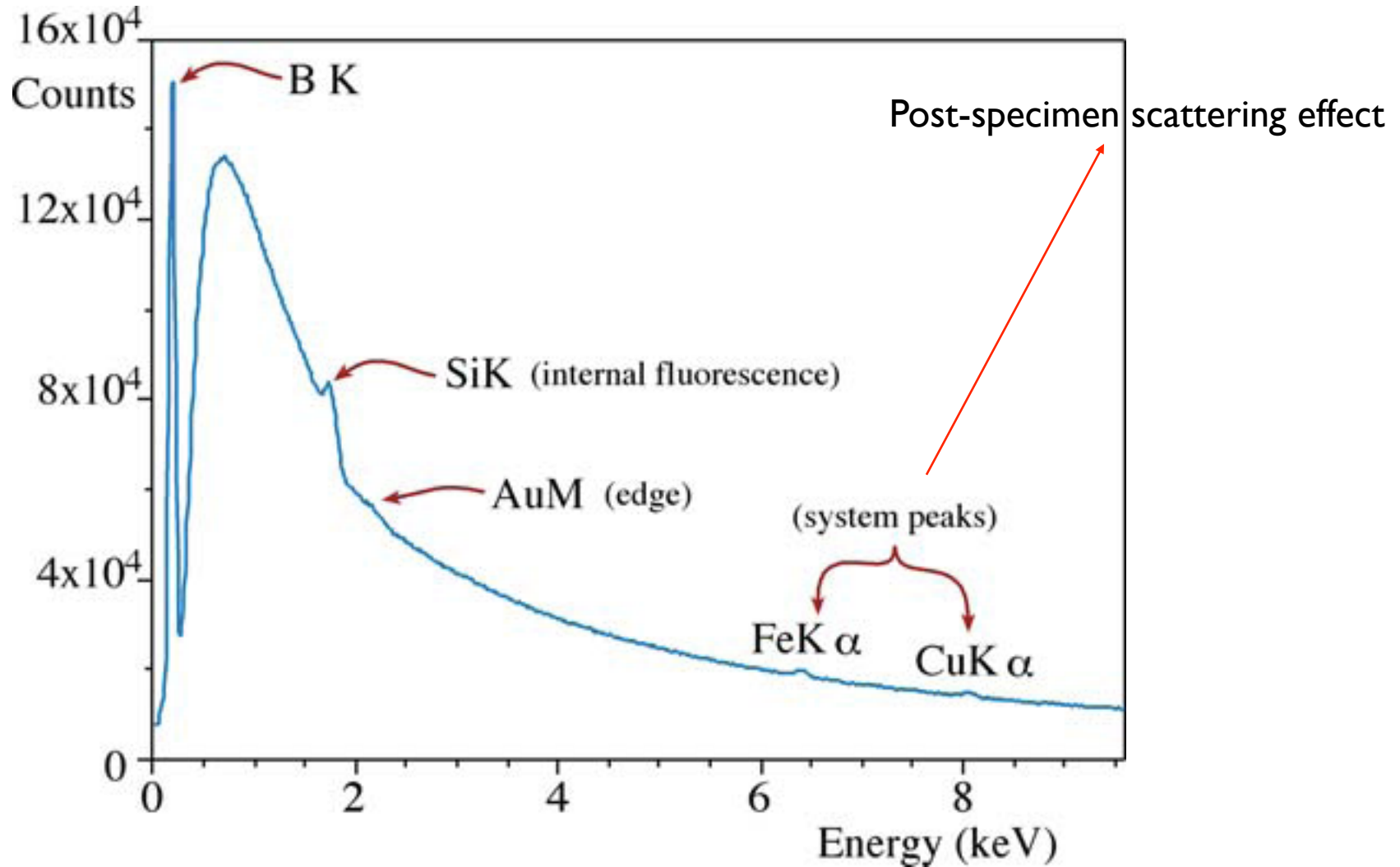
We can summarize the methods used to minimize the effects of post-specimen scattering quite simply:

Always remove the objective diaphragm.

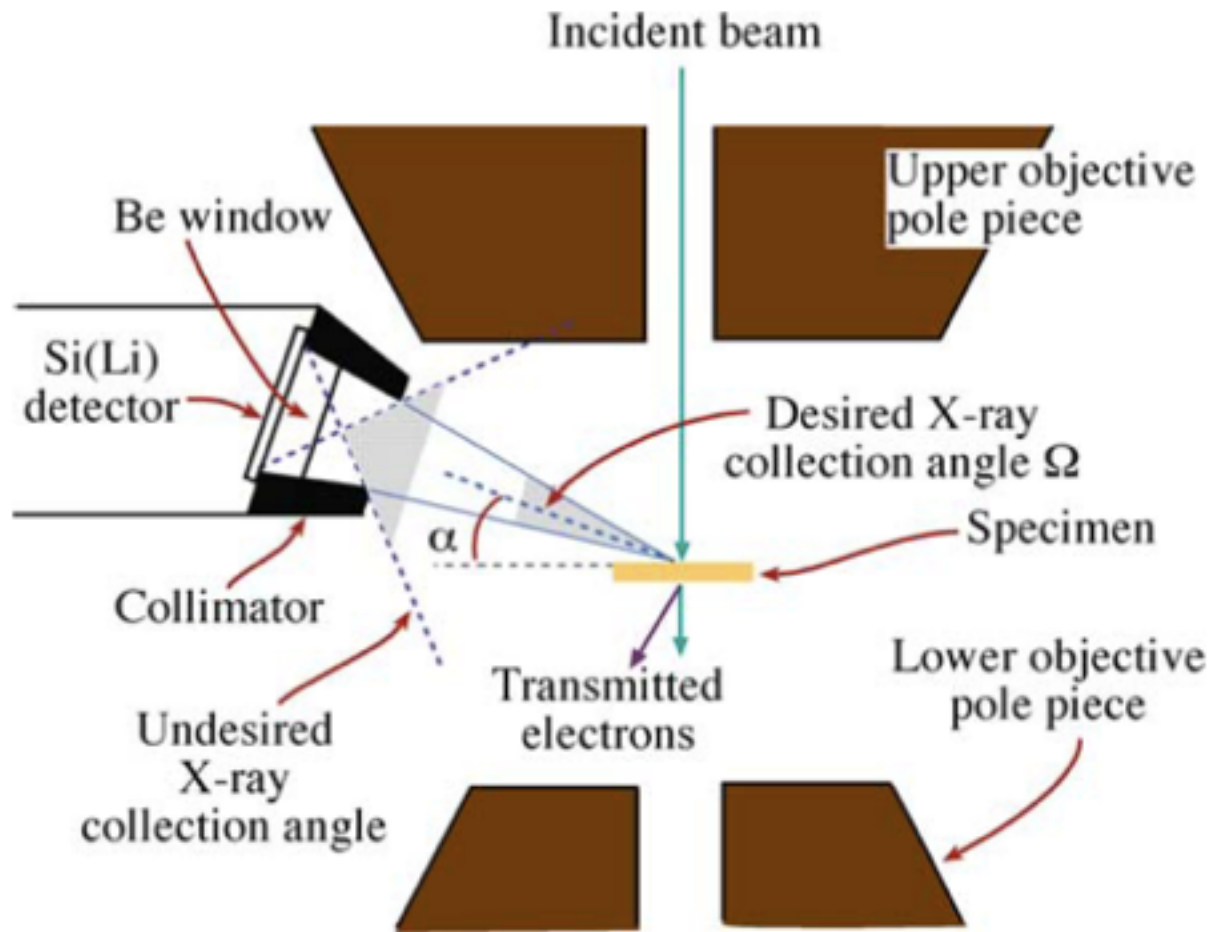Operate as close to zero tilt as possible.

Use a Be specimen holder and Be grids

The XEDS-TEM Interface

➢ *Collection angle* (Ω): the solid angle subtended at the analysis point on the specimen by the active area of the front face of the detector.
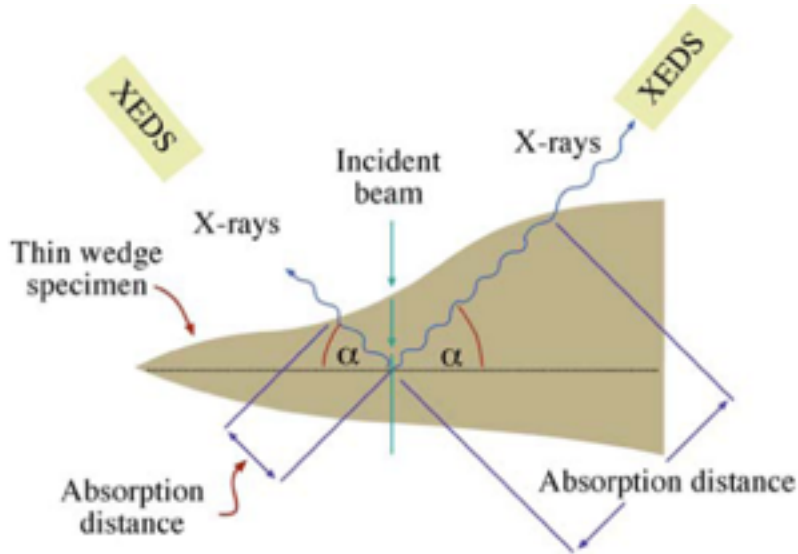
$$\Omega = \frac{A \cos\delta}{S^2}$$

➢ *Take-off angle* (α): the angle between the specimen surface and a line to the center of the detector, (or the angle between the transmitted beam and the line to the detector (90°+ α))

Incident beam

Be window

Si(Li) detector

Collimator

Undesired X-ray collection angle

Upper objective pole piece

Desired X-ray collection angle Ω

Specimen

α

Transmitted electrons

Lower objective pole piece

➢   The value of Ω is the most important parameter in determining the quality of your X-ray microanalysis

(O)   (X)

XEDS

XEDS

Thin wedge specimen

Incident beam

X-rays

X-rays

α   α

Absorption distance

Absorption distance

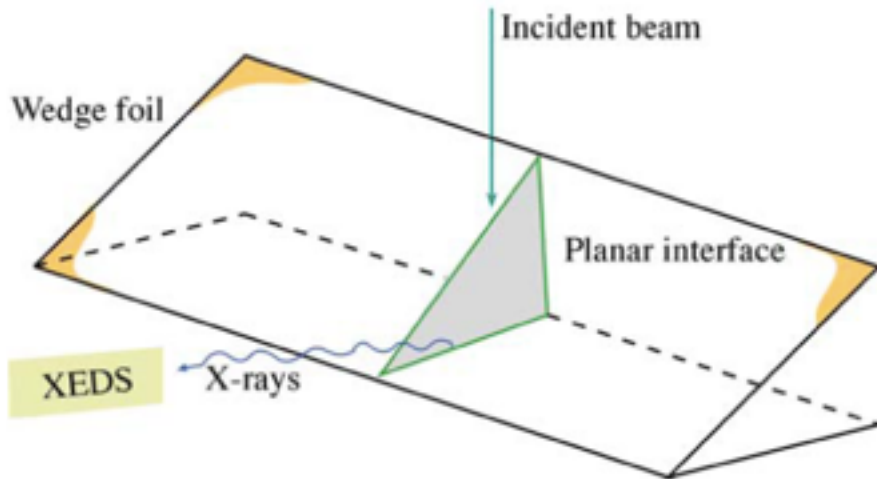(B)

Wedge foil

Incident beam

Planar interface

XEDS   X-rays

➢ Is the detector pointing on axis?

If the detector is not pointing on axis, the map will show an asymmetric intensity distribution.
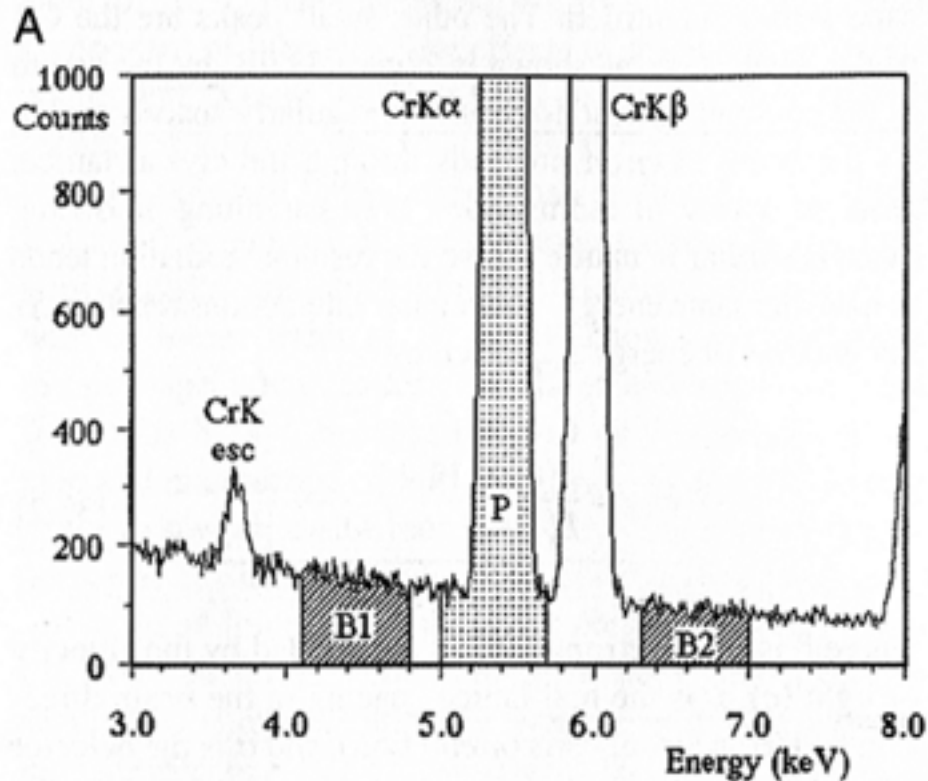
➢ Where is the detector with respect to the image?

Need to orient specimen such that the interface is parallel to the detector axis and the beam.

Peak-to-Background ratio (P/B)

The best test of how well your EDX is interface to your TEM is to measure the peak-to-background (P/B) ratio in a standard specimen (100 nm Cr Film.

Define: integrate the Cr Kα peak intensity from 5.0 keV to 5.7 keV and divide this by the average background intensity in a 10-eV channel

In a well-behaved analytic electron microscope, P/B ratio will increase with increasing keV
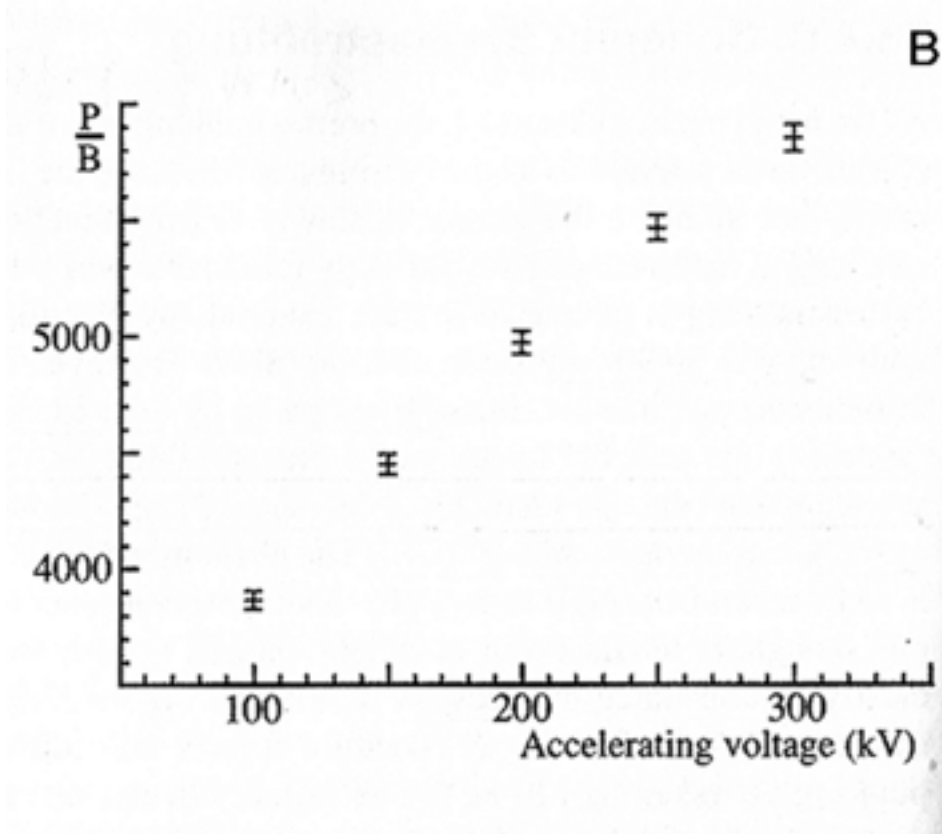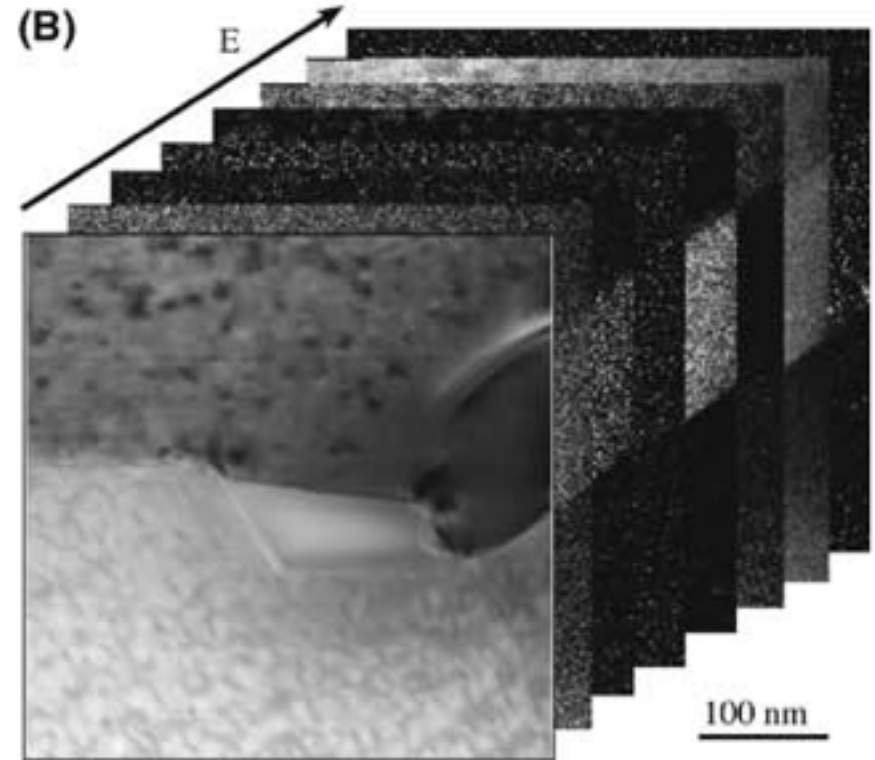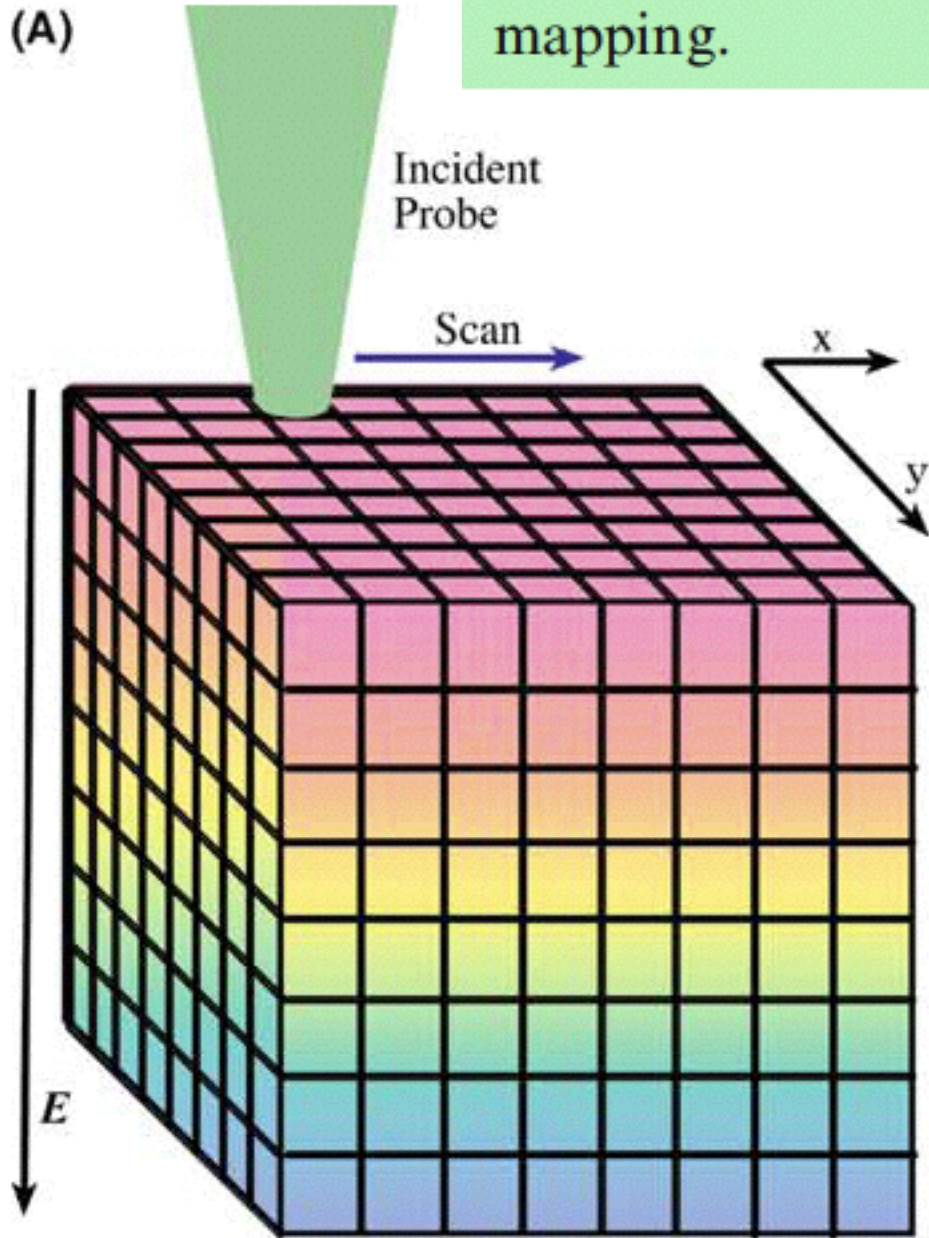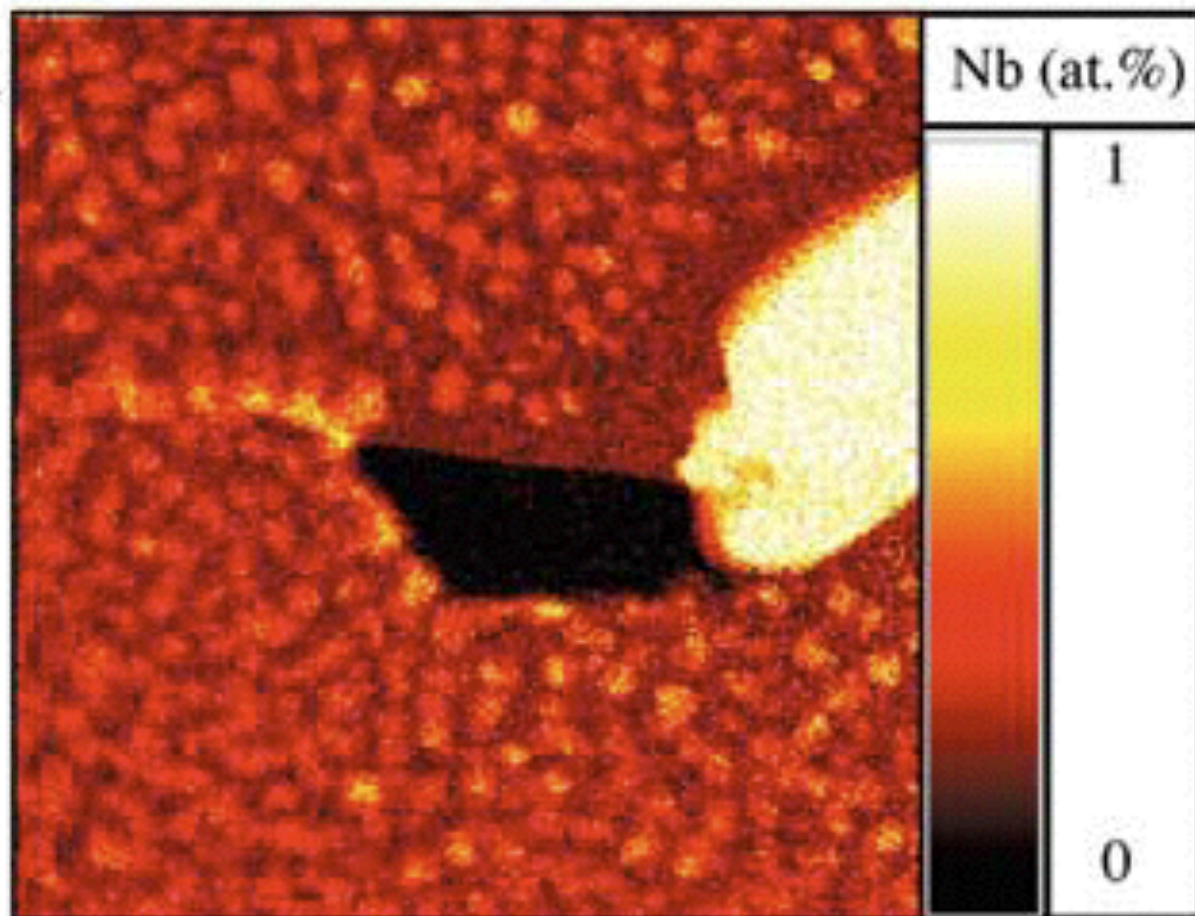

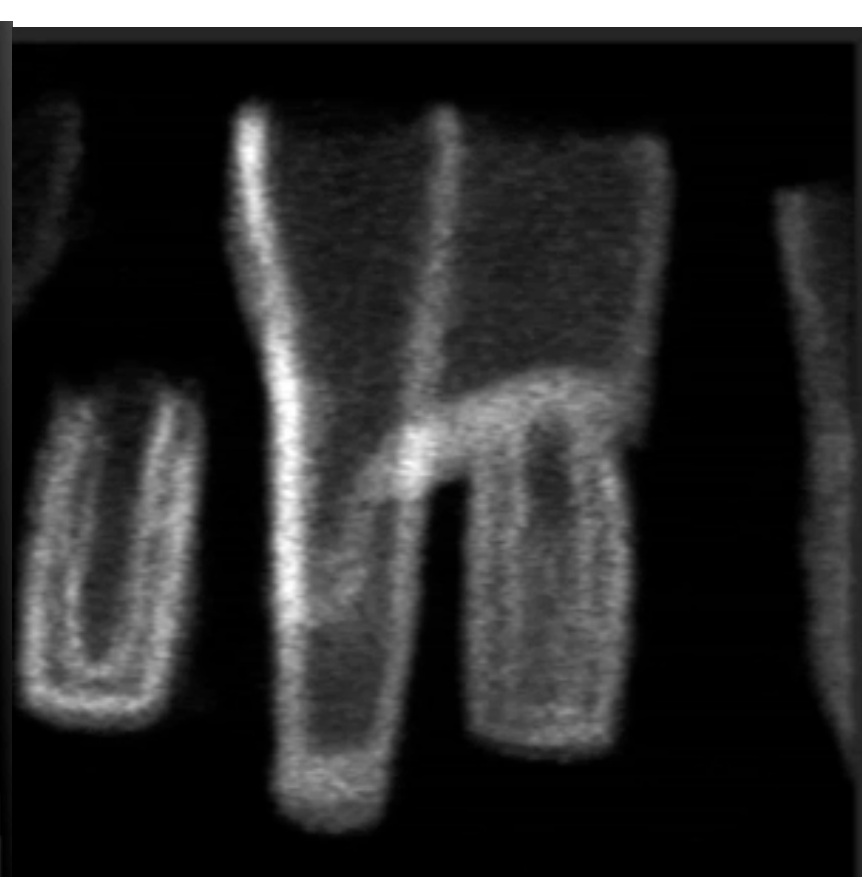P: the degree of scattering

B: the degree of bremsstrahlung

(A)

Incident Probe

Scan

x

y

E

(B)

E

100 nm

(D)
PCA

Nb (at.%)

1

0
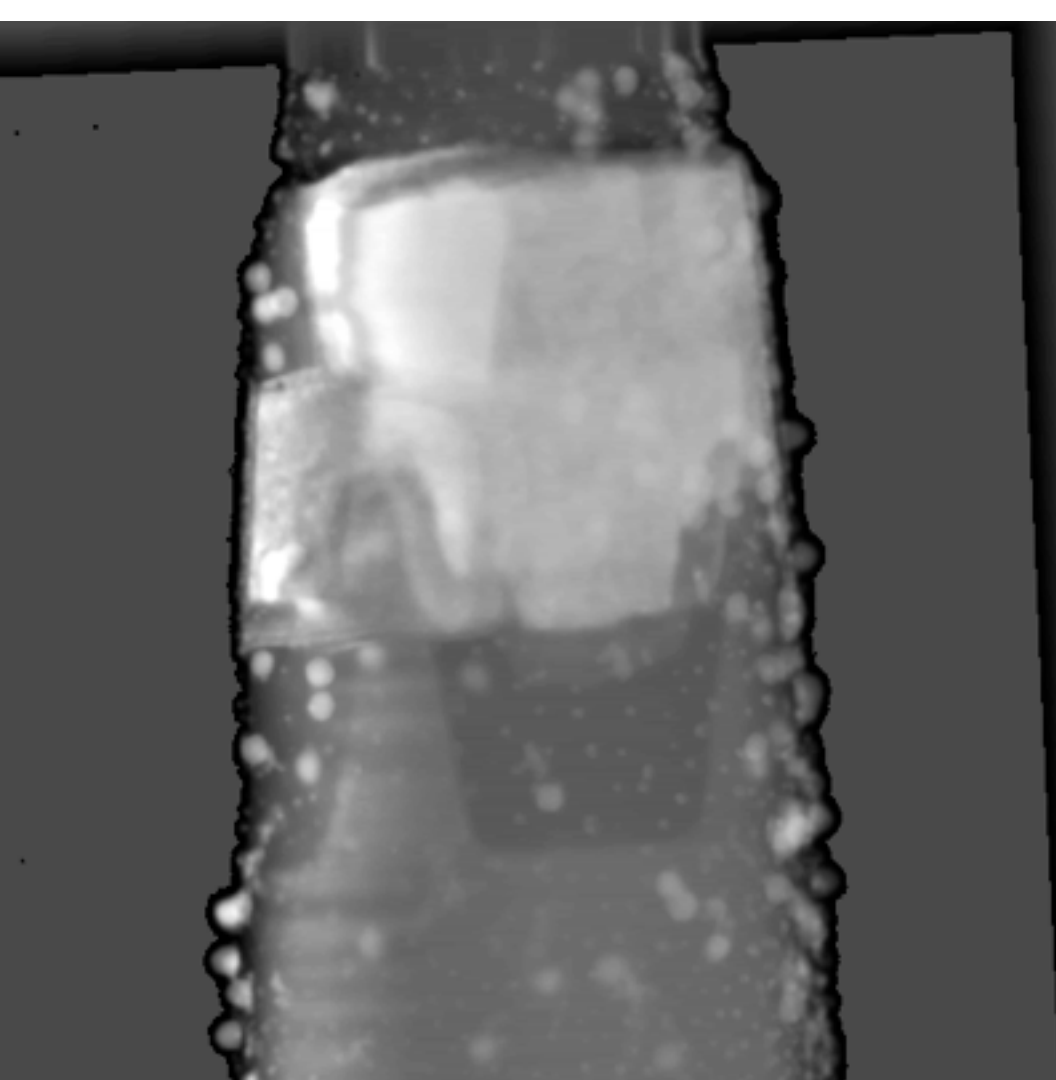
Al at GBs in an electro-migrated specimen of Al-4% Cu. The bright regions are CuAl2 intermetallics

Qualitative X-ray analysis

Spatial resolution: distances measured in nm

Chemical resolution: detectability depending on P/B

Energy resolution: identifying elements by

distinguishing peaks; different eV

Good qualitative analysis requires a large number of X-ray counts in the spectrum
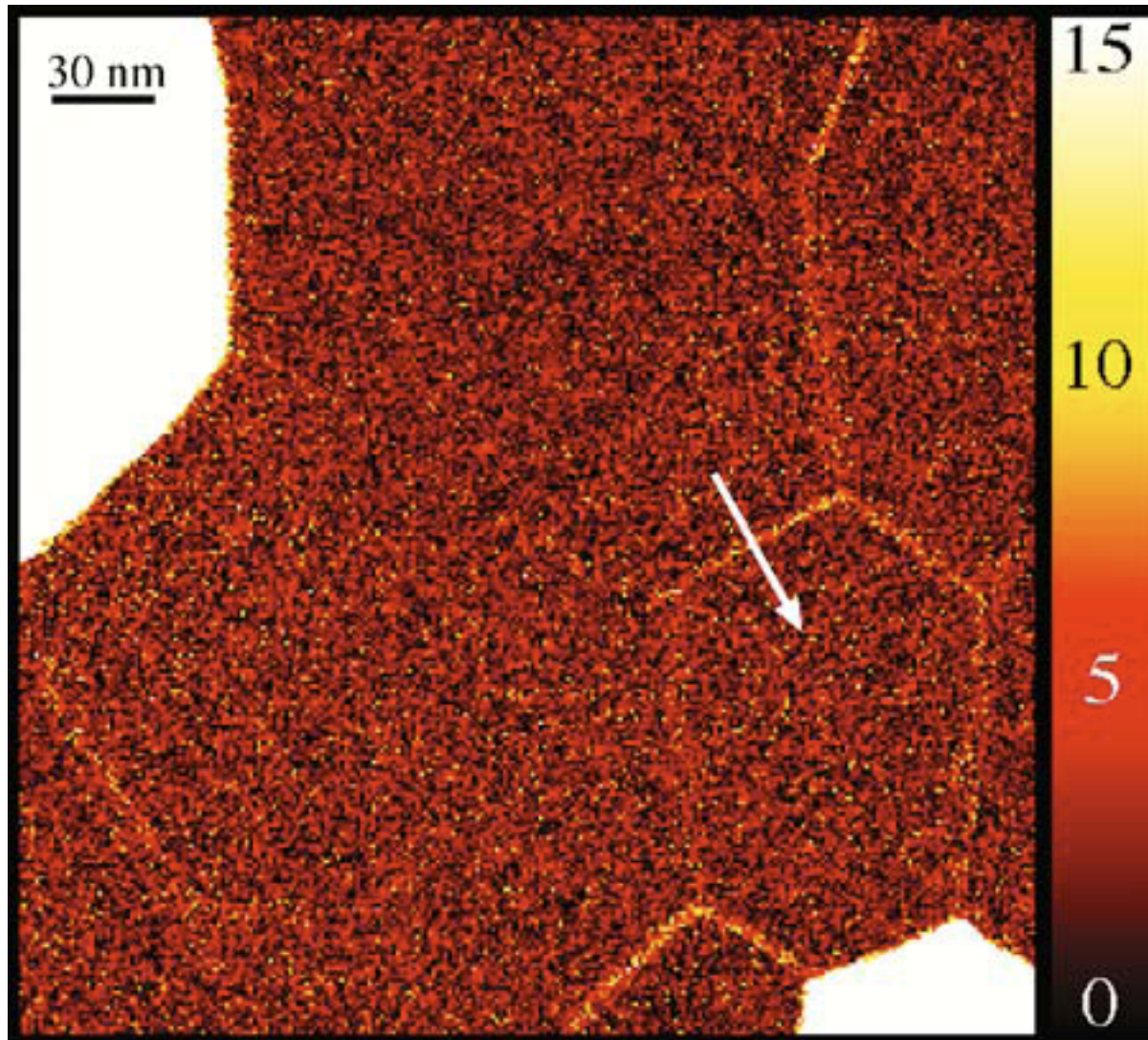
Note: if you have a few weight percent of a *light* element present in the sample, the X-ray may be absorbed within the specimen and so may not be detected.
If your spectrum contains many peaks, and particularly if peak overlap is occurring, then misidentification may occur during such an "autosearch" routine, especially if there is no operator intervention.

Peak Identification

Peak analysis follows these steps:

- Look at the most intense peak and work on down through its family

- Go to next most intense peak not included in previous step and repeat the same step. Then repeat this exercise until all peaks are identified

- Think about pathological overlaps; look for spurious peaks, system peaks, and artifact peaks.

The key to good qualitative analysis is to be suspicious and *to not just seek the peaks you expect*, but to be prepared also to find peaks that don't expect.

The ideal is that you are looking for families of peaks. If a family member is missing your identification may be wrong.

(E)

(F)
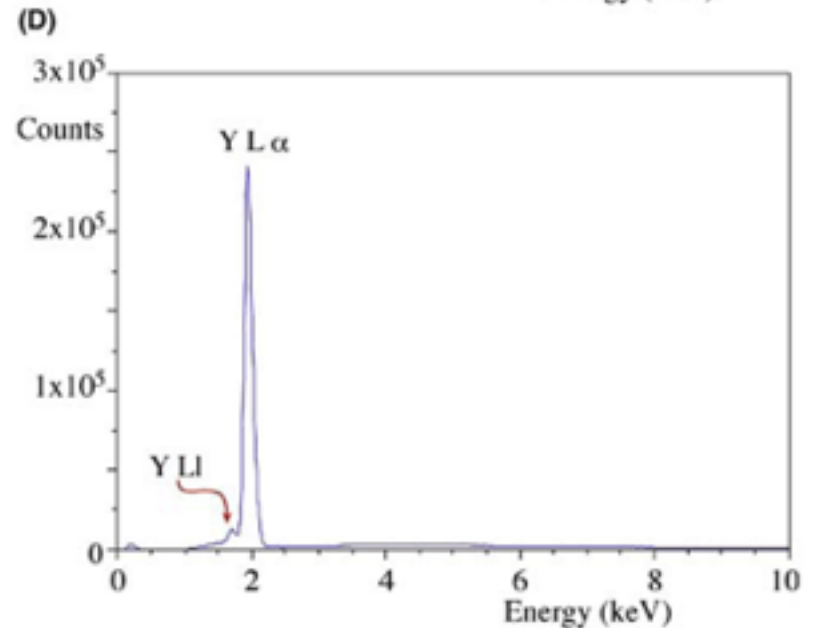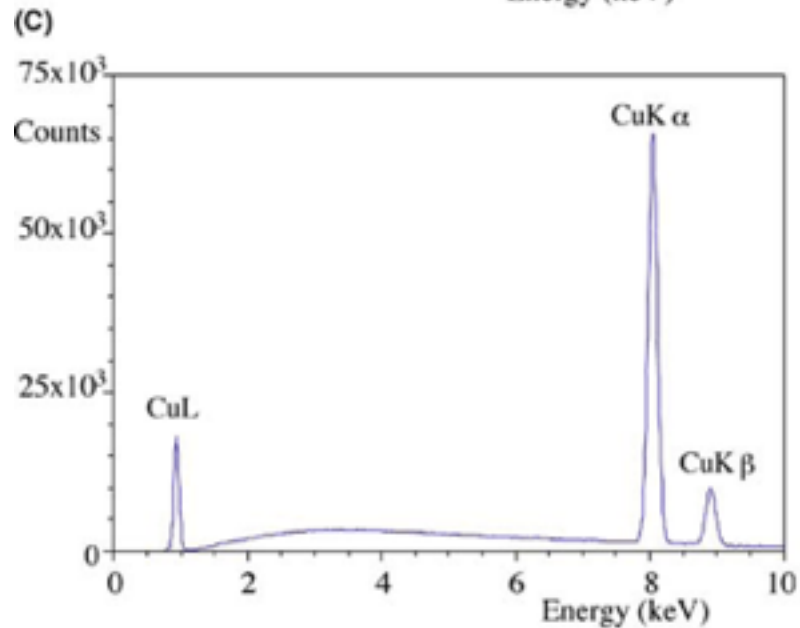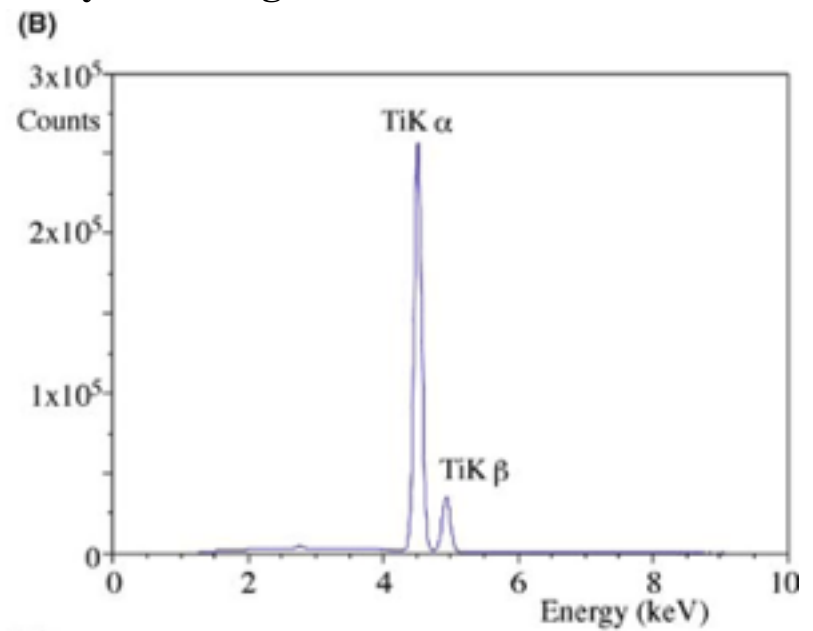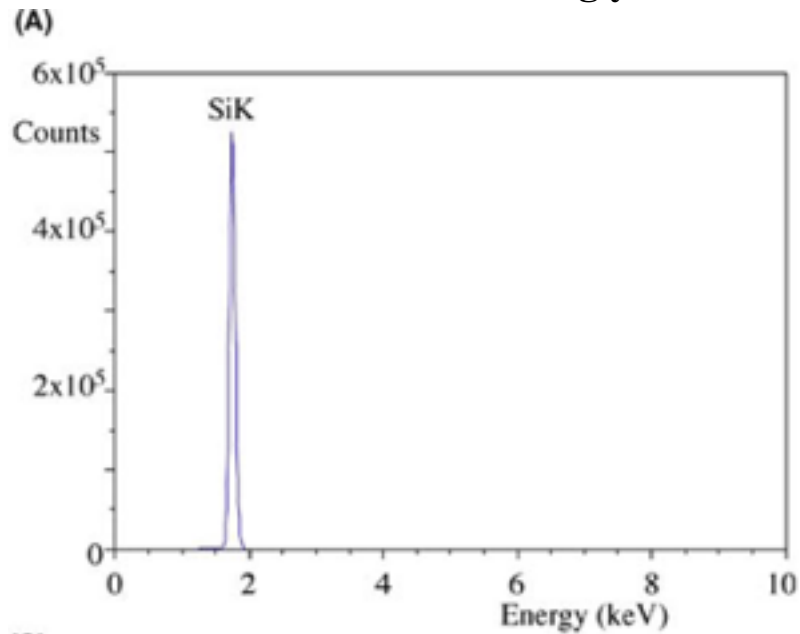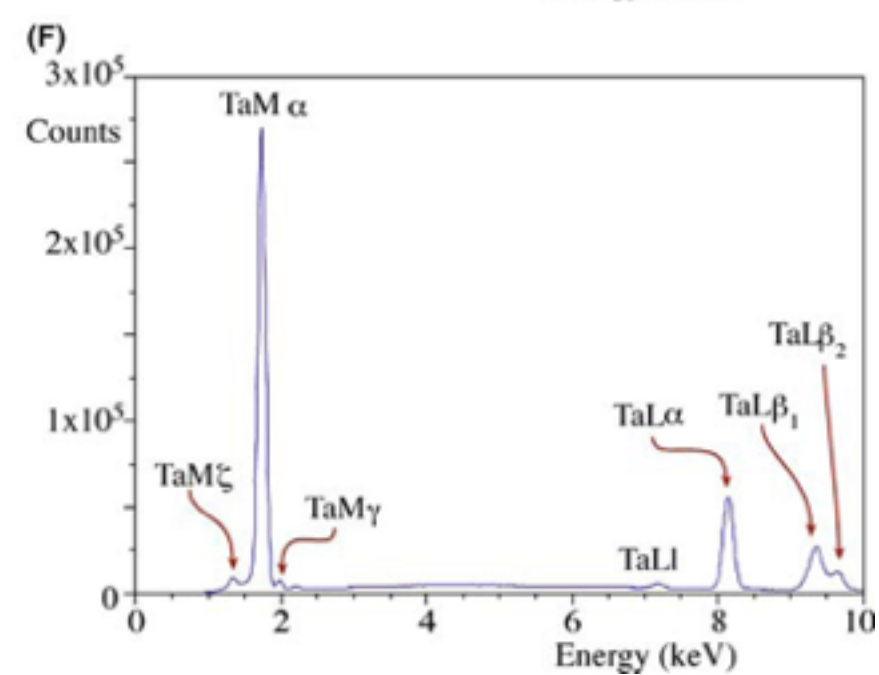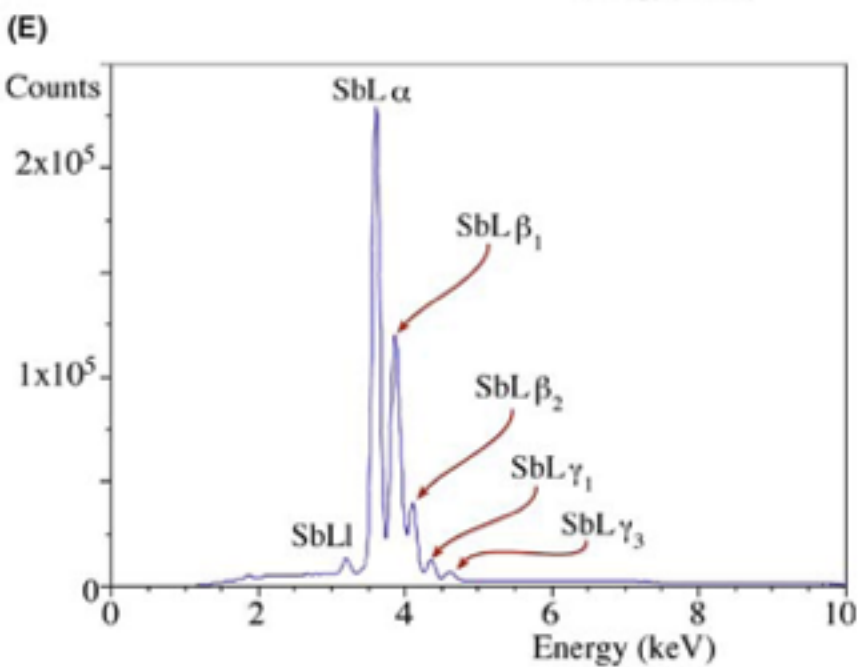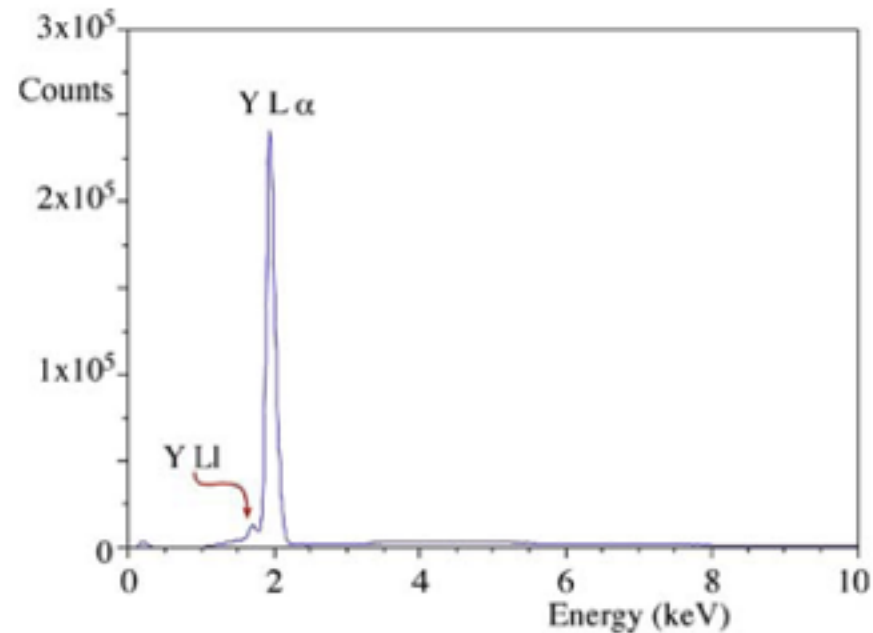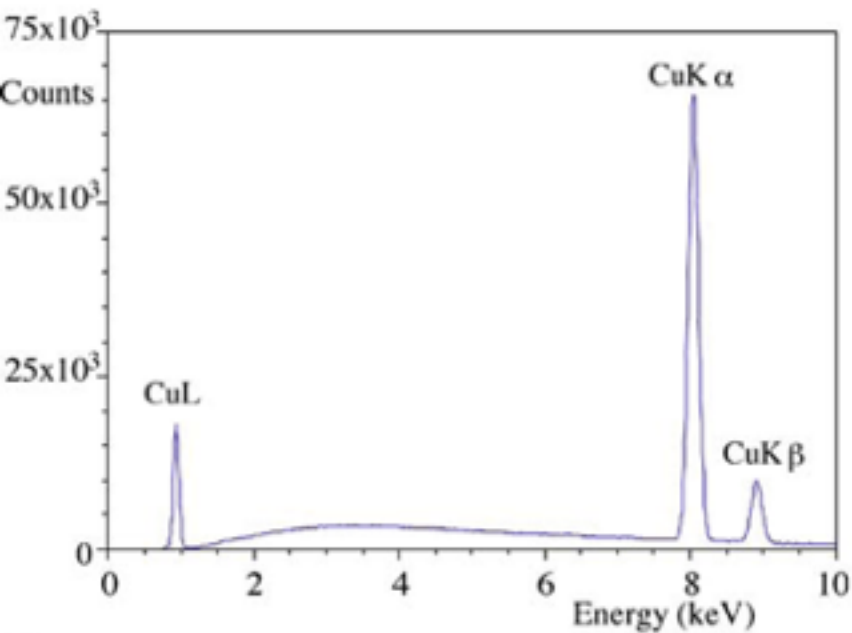
Pathological overlap: when it is impossible to separate two peaks even when you know they are both there

O K:0.52KeV

Cr L : 0.45-0.57KeV

Fe L : 0.72KeV

Example:
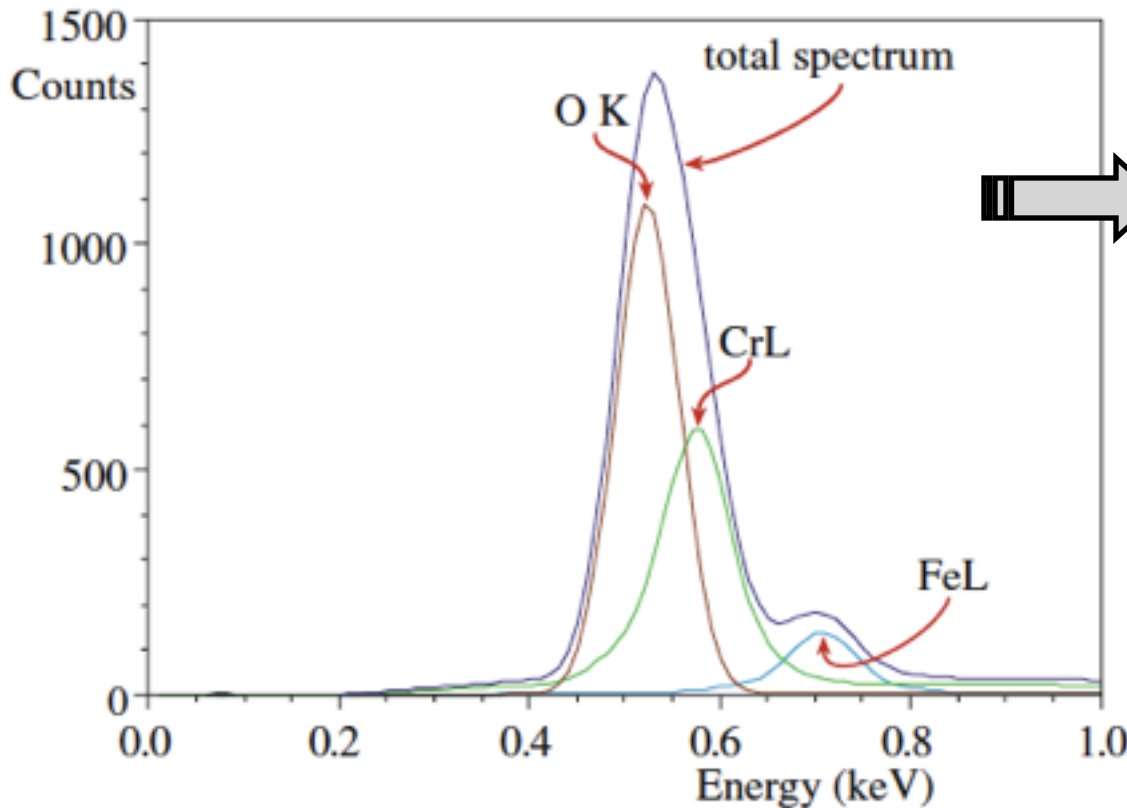
1. Maximize the energy resolution of detector system(large τ)

2. run a peak deconvolution routine

Peak Visibility

Small-intensity fluctuations that you cannot clearly identify as peaks are often present in your spectrum.

A simple statistical criterion(Liebhafsky *et al*. 1972)
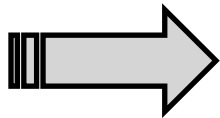
Ascertain if the peak is statistically significant.

or Ascertain if it can be dismissed as random noise

You must count for a long enough time so that the bremsstrahlung intensity is relatively smooth and any peaks are clearly visible, as summarized in following figure
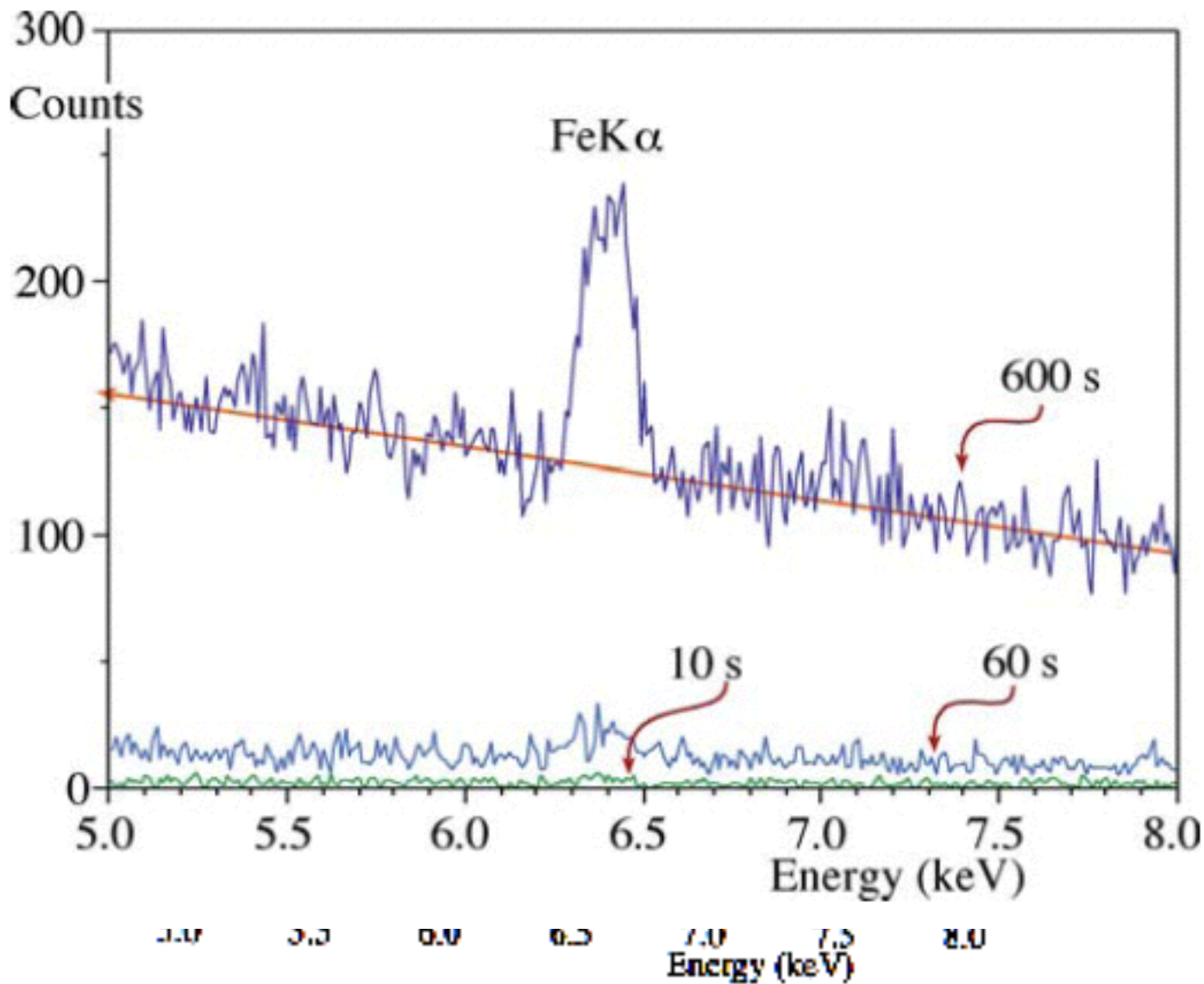
With increasing counting time a clear characteristic Fe Kα peak develops above background in a spectrum from Si-0.2%Fe. This demonstrates the need acquire statistically significant counts before deciding if a small peak is present or absent.

A simple statistical criterion(Liebhafsky *et al*. 1972)

Summarized:

Increase the display gain until the average background intensity is half the total full scale of the display, so the small peaks are more easily observed.

Get the computer to draw a line under the peak to separate the peak and background counts.

Integrate the peak (I_A) and background ($I_A{}^b$) counts over the same number of channels; use FWHM if it can be discerned with any confidence; if not, then the whole peak integral will do.

Quantitative X-ray analysis

ZAF Method :

$C_A + C_B = 100\%$

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B} = (ZAF)\frac{I_A}{I_B}$$

K_{AB} is a sensitivity factor. It is not in fact, a constant, but contribution of comes from three factors:
a) Z: atomic number
b) A: the absorption of X-ray within the sample
c) F: the fluorescence of X-ray within the sample

~ ZAF correction

$$k_{AB} = \frac{(Q\omega a)_B \, A_A}{(Q\omega a)_A \, A_B}$$

A: atomic weight
Q: ionization cross-section
ω: fluorescence yield of characteristic X-ray
a: relative transmission probability

when a K-shell is ionized, the atom will return to the ground state either by emission of K or K.

$$a = \frac{I(K_\alpha)}{I(K_\alpha + K_\beta)}$$

In the thin film case, the contribution from A and F are negligible

$$k_{AB} = \frac{(Q\omega a)_B \, A_A}{(Q\omega a)_A \, A_B} \sim \frac{1}{Z}$$

The Cliff-Lorimer ratio technique:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} = (ZAF) \frac{I_A}{I_B} \sim \frac{1}{Z} \frac{I_A}{I_B}$$

k_{AB} : Cliff-Lorimer factor

K_{AB} can be calculated or can be experimentally determined

Example

A homogenized thin foil of Cu-Mn solid solution was used to determine k_{CuMn}. The sample was first analyzed by EPMA and found to be 96.64 wt.% Cu and 3.36 wt.% Mn. Since our accuracy is increased by collecting many spectra, a total of 30 were accumulated ($n = 30$ in equation 35.13). In a typical spectrum, the Cu K_{α} peak contained 271,500 counts above background and the Mn K_{α} peak contained 10,800 counts. So if we insert these data into the Cliff–Lorimer equation we get

$$\frac{96.64}{3.36} = k_{CuMn} \frac{271,500}{10,800}$$

$$k_{CuMn} = 1.14$$

To determine an error on this value of the k factor, equation 35.12 must be used. The student "t" analysis of the k factors from the other 29 spectra gives an error of ± 0.01 for a 95% confidence limit. This error of about $\pm 1\%$ relative is about the best that can be achieved using the experimental approach to k-factor determination.

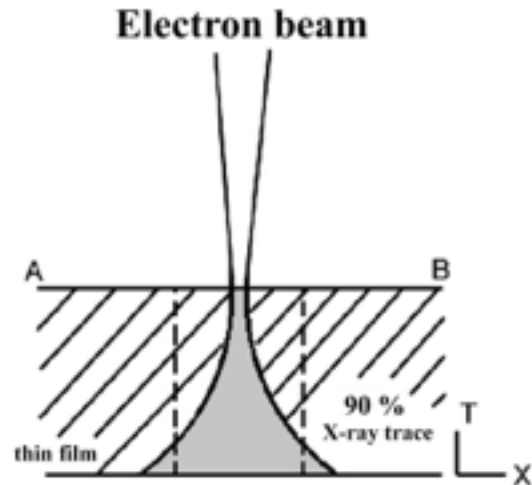### Table 35.1. Experimentally Determined k_{ASi} and k_{AFe} Factors for K_α X-ray Lines[a]

Element (A)	k_{ASi} (1) 100 kV	k_{ASi} (2) 100 kV	k_{ASi} (3) 120 kV	k_{ASi} (4) 80 kV	k_{ASi} (5) 100 kV	k_{ASi} (5) 200 kV	k_{AFe} (6) 120 kV	k_{ASi} (7) 200 kV
Na	5.77	3.2	3.57 ± 0.21	2.8 ± 0.1	2.17	2.42		3.97 ± 2.32
Mg	2.07 ± 0.1	1.6	1.49 ± 0.007	1.7 ± 0.1	1.44	1.43	1.02 ± 0.03	1.81 ± 0.18
Al	1.42 ± 0.1	1.2	1.12 ± 0.03	1.15 ± 0.05			0.86 ± 0.04	1.25 ± 0.16
Si	1.0	1.0	1.0	1.0	1.0	1.0	0.76 ± 0.004	1.00
P			0.99 ± 0.016				0.77 ± 0.005	1.04 ± 0.12
S			1.08 ± 0.05		1.008	0.989	0.83 ± 0.03	1.06 ± 0.12
Cl					0.994	0.964		1.06 ± 0.30
K		1.03	1.12 ± 0.27	1.14 ± 0.1			0.86 ± 0.014	1.21 ± 0.20
Ca	1.0 ± 0.07	1.06	1.15 ± 0.02	1.13 ± 0.07			0.88 ± 0.005	1.05 ± 0.10
Ti	1.08 ± 0.07	1.12	1.12 ± 0.046				0.86 ± 0.02	1.14 ± 0.08
V	1.13 ± 0.07			1.3 ± 0.15				1.16 ± 0.16
Cr	1.17 ± 0.07	1.18	1.46 ± 0.03				0.90 ± 0.006	
Mn	1.22 ± 0.07	1.24	1.34 ± 0.04				1.04 ± 0.025	1.24 ± 0.18
Fe	1.27 ± 0.07	1.30	1.30 ± 0.03	1.48 ± 0.1			1.0	1.35 ± 0.16
Co							0.98 ± 0.06	1.41 ± 0.20
Ni	1.47 ± 0.07	1.48	1.67 ± 0.06				1.07 ± 0.006	
Cu	1.58 ± 0.07	1.60	1.59 ± 0.05		1.72	1.50	1.17 ± 0.03	1.51 ± 0.40
Zn	1.68 ± 0.07				1.74	1.55	1.19 ± 0.04	1.63 ± 0.28
Ge	1.92							1.91 ± 0.54
Zr								3.62 ± 0.56
Nb							2.14 ± 0.06	
Mo	4.3		4.95 ± 0.17				3.8 ± 0.09	
Ag	8.49		12.4 ± 0.63				9.52 ± 0.07	6.26 ± 1.50
Cd	10.6				9.47	6.2		
In								7.99 ± 1.80
Sn	10.6							8.98 ± 1.48
Ba					29.3	17.6		21.6 ± 2.6

Table 35.2. Experimentally Determined k_{ASi} and k_{AFe} Factors for L_α X-ray Lines[a]

Element (A)	k_{ASi} (8) 100 kV	k_{ASi} (5) 100 kV	k_{ASi} (5) 200 kV	k_{ASi} (9) 100 kV	k_{AFe} (6) 120 kV	k_{ASi} (7) 200 kV
Cu		8.76	12.2			
Zn		6.53	6.5			8.09 ± 0.80
Ge						4.22 ± 1.48
As						3.60 ± 0.72
Se						3.47 ± 1.11
Sr					1.21 ± 0.06	
Zr					1.35 ± 0.1	2.85 ± 0.40
Nb					0.9 ± 0.06	
Mo				2.0		
Ag	2.32 ± 0.2				1.18 ± 0.06	2.80 ± 1.19
In					2.21 ± 0.07	2.86 ± 0.71
Cd		2.92	2.75			
Sn	3.07 ± 0.2					
Ba		3.38	2.94			3.36 ± 0.58
Ce				1.4		
Sn	3.1 ± 0.2			1.3		
W	3.11 ± 0.2			1.8		3.97 ± 1.12
Au	4.19 ± 0.2	4.64	3.93		3.1 ± 0.09	4.93 ± 2.03
Pb	5.3 ± 0.2	4.85	4.24	2.8		5.14 ± 0.89

[a]Sources: (1) Cliff and Lorimer (1975), (2) Wood *et al.* (1981), (3) Lorimer *et al.* (1977), (4) McGill and Hubbard (1981), (5) Schreiber and Wims (1981), (6) Wood *et al.* (1984), (7) Sheridan (1989), (8) Goldstein *et al.* (1977), (9) Sprys and Short (1976).

The Interaction Between Electron Beam and Specimen

Electron beam

A

B

90 %
X-ray trace

T

thin film

X

Spatial resolution

1 — 2 — 3 — 4 — 5

Interface

100%

98%

% A in B

0%

1   2   3   4   5
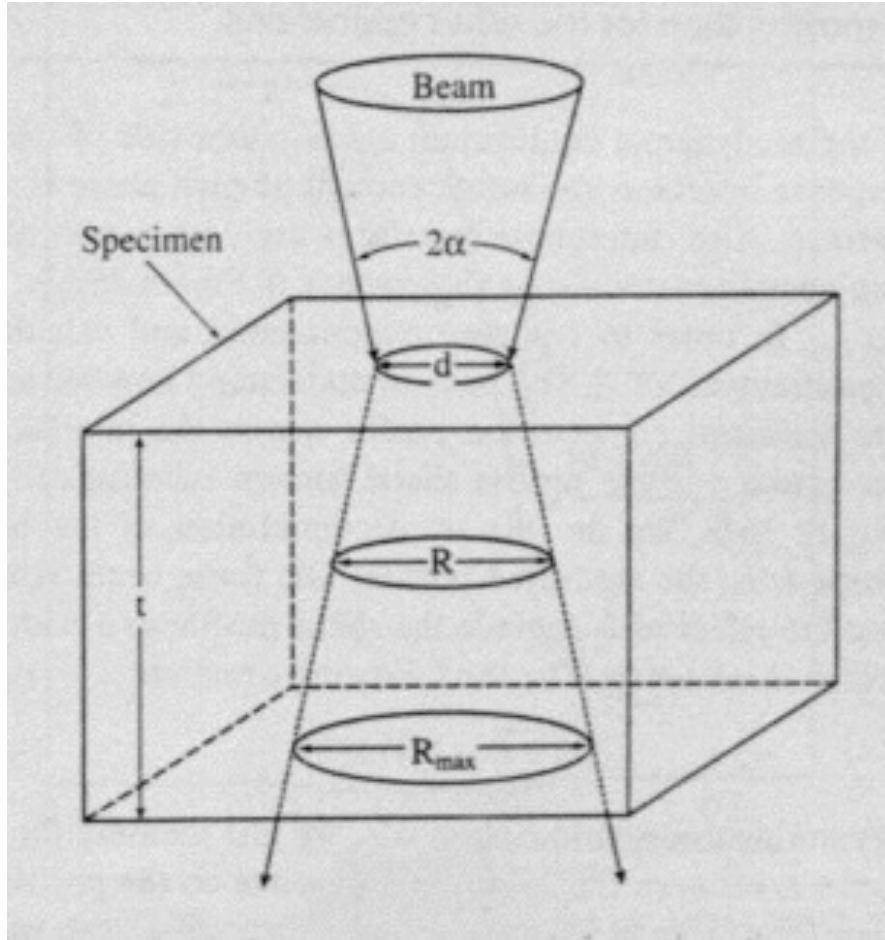
←L→

2%

Distance →
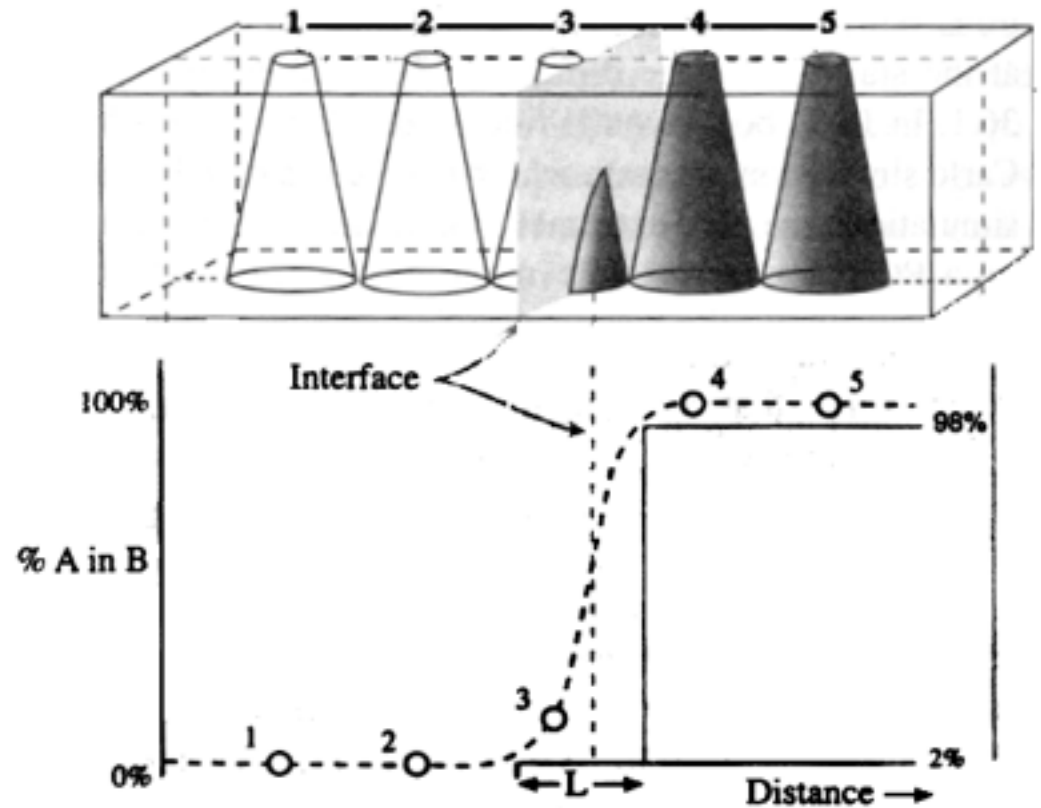
Schematic diagram showing the measured composition profile obtained across a planar interface at which an atomically discrete composition change occurs. The spatial resolution can be related to the extent (L) of the measured profile between the 2% and 98% points.

Monte Carlo simulation for energy and sample thickness
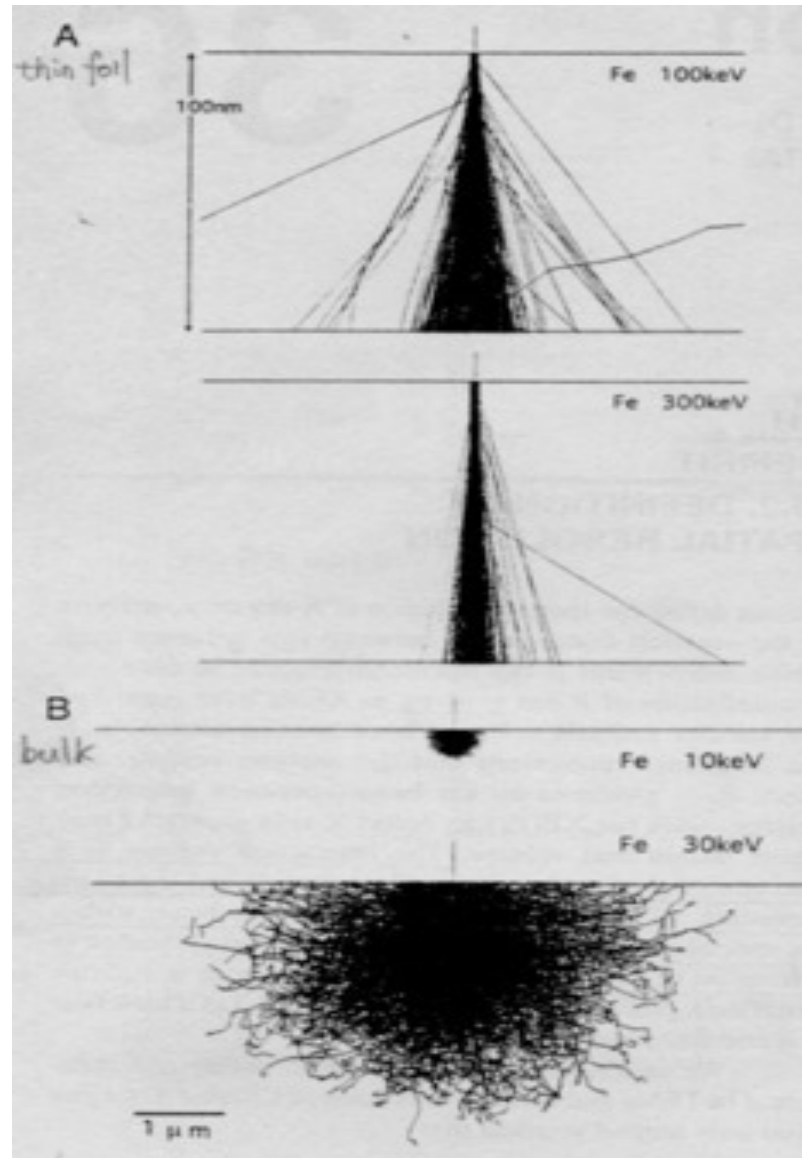
Spatial Resolution (R) of EDX

$$R_{max} = (b^2 + d^2)^{1/2}$$

b: beam broaden spreading

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

EDS (deconvolution)

Supposed the relationship of *the measured composition profile f*, *beam broadening function g* and the *real composition profile h* is given as follows.

$$f = g * h$$

where $*$ represents for the convolution operator.

A Wiener filter [ref] was applied to deconvolute the composition profiles. The "true" compositional distribution h can be obtained from

$$h = IFFT\left(\frac{Conj(G) * F}{G^2 + K} \right)$$

where *IFFT is the inverse Fourier transform operator*, *G, F are the Fourier transforms of f and g*, respectively. *Conj(G) is the conjugate of G and G^2 is multiplication of G with its conjugate*, while *K is a constant which is related to the noise of the signal* [7].
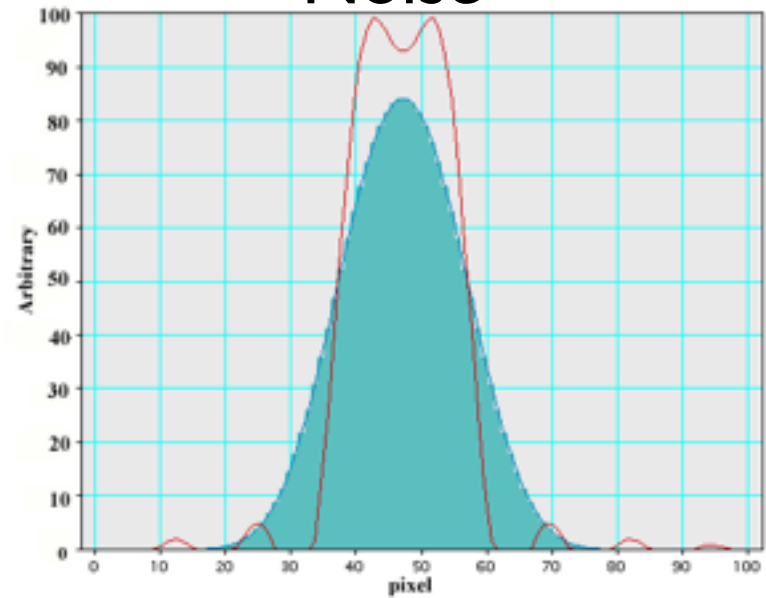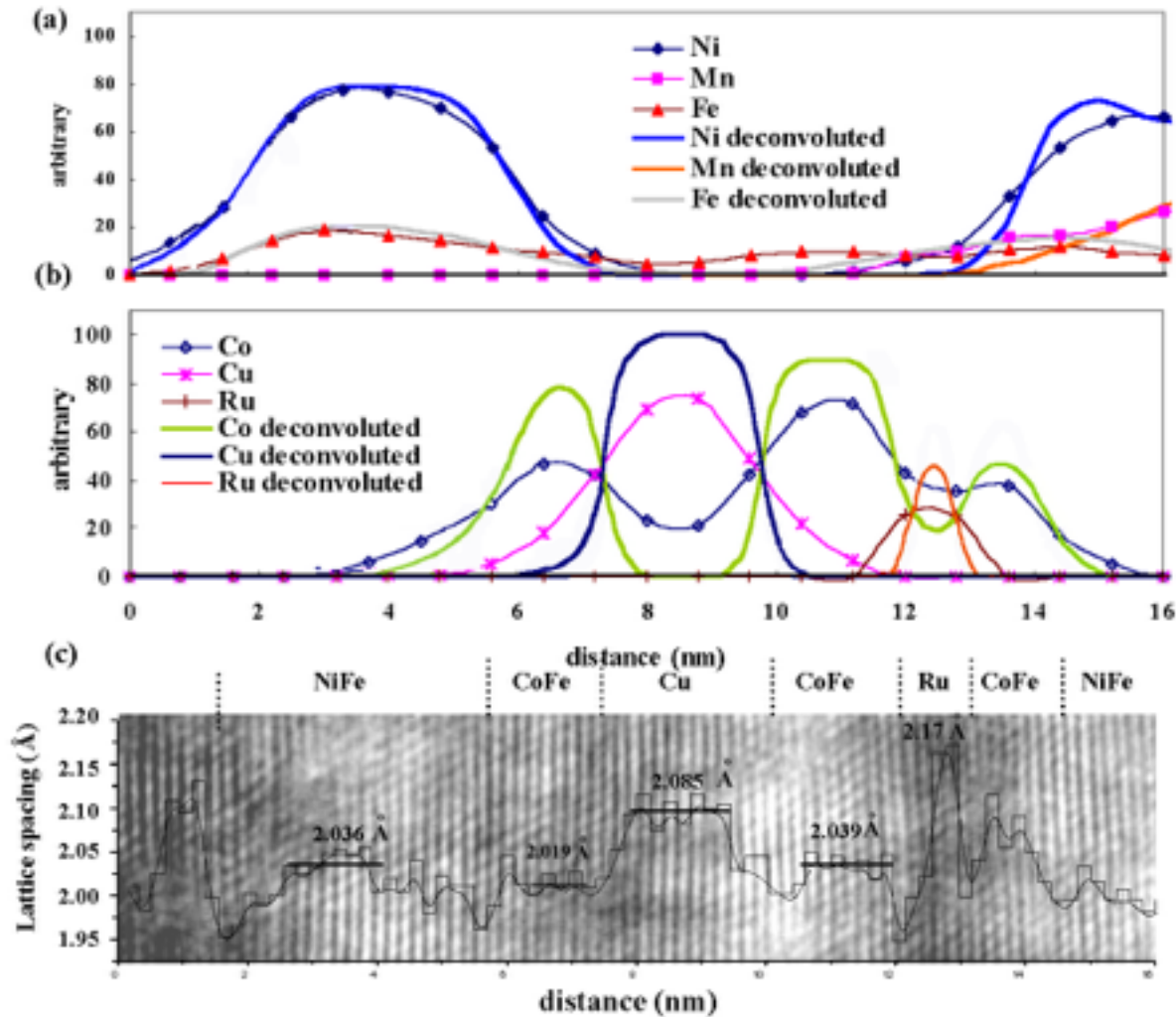
The Selection of K Value

Proper
Noise

Over
Noise

K=1
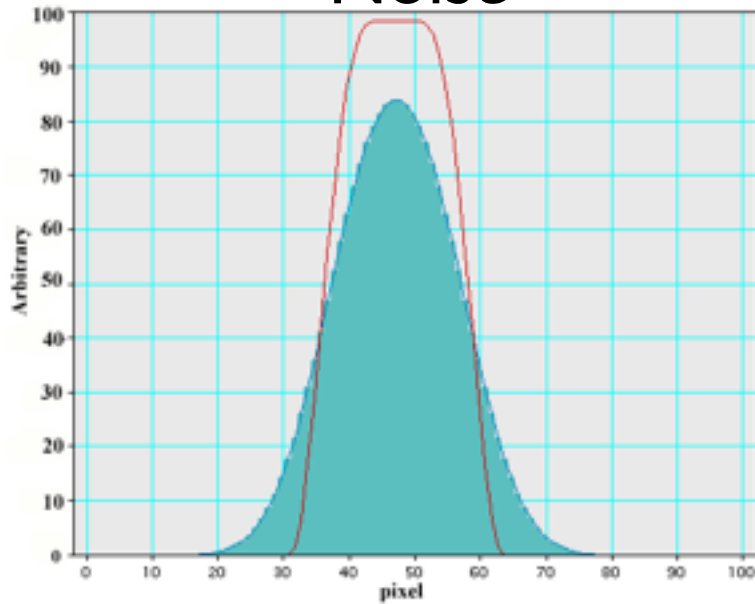
K=0.1

The Comparison of EDX deconvoluted and non-deconvoluted

The End.

Thank You so much!