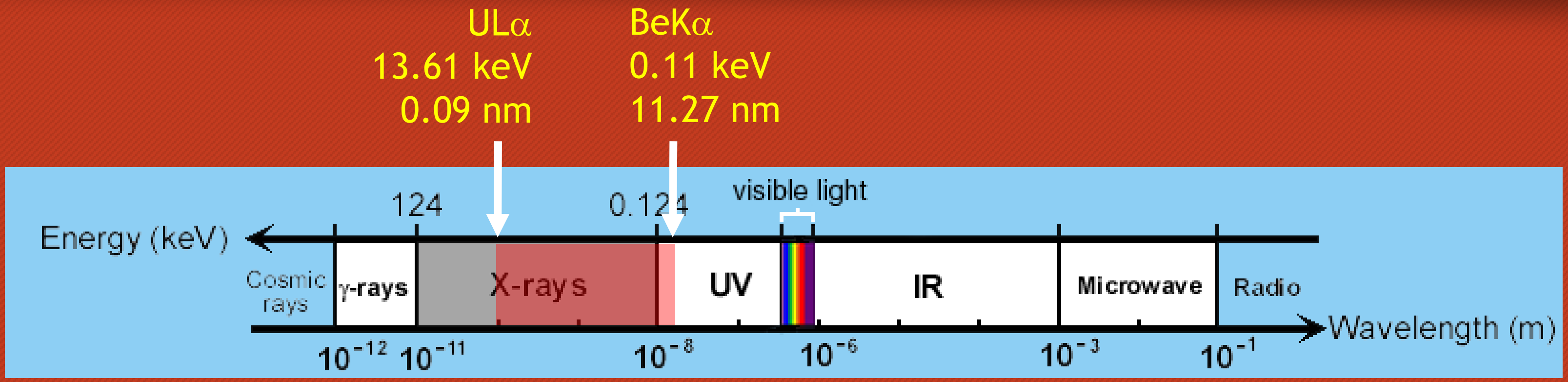
Understanding X-rays: The electromagnetic spectrum



$E = h\nu = h\frac{c}{\lambda}$ where, E : energy, h : Planck's constant, ν : frequency

c : speed of light in vacuum, λ : wavelength

$E\lambda = hc = 1.2398$ *if the units are keV and nm*

E (keV) $= h\frac{c}{\lambda} = 1.2398/\lambda$ (nm) or, λ (nm) $= h\frac{c}{E} = 1.2398/E$ (keV)

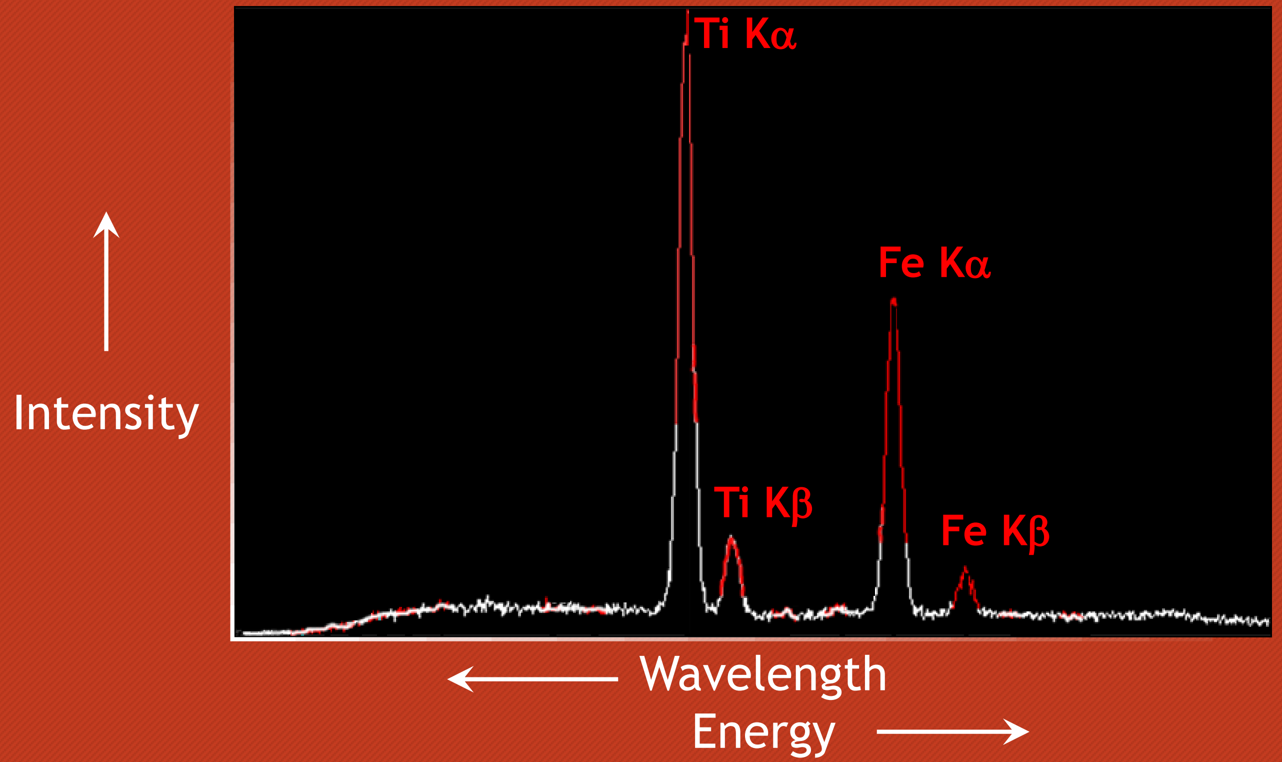
E.g., $\lambda_{BeK\alpha} = 11.27$ nm; Hence, $E_{BeK\alpha} = 1.2398/11.27 = 0.11$ keV

$E_{UL\alpha} = 13.61$ keV; Hence, $\lambda_{UL\alpha} = 1.2398/13.61 = 0.09$ nm

X-ray production in the EPMA

X-rays are generated by inelastic scattering of the beam electrons by sample atoms

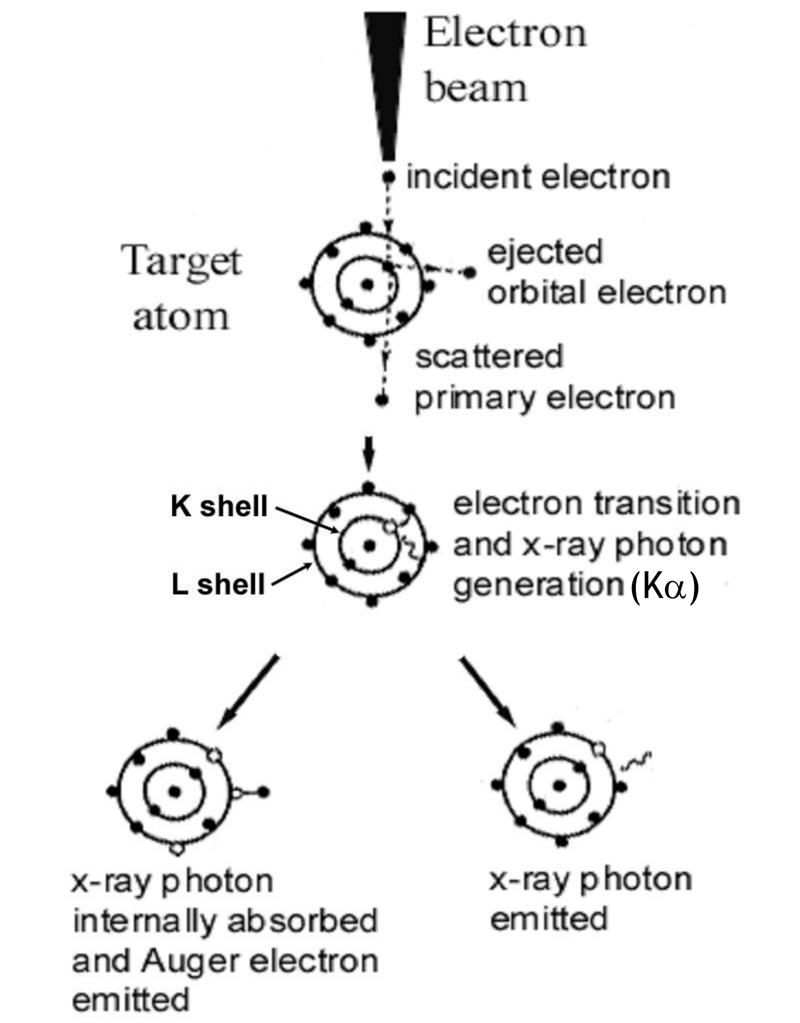
- *Characteristic X-rays: inner shell interactions*
- *Bremmstrahlung (continuum) X-rays: outer and inner shell interactions*



Characteristic X-ray generation

Inner shell ionization through inelastic scattering

followed by electron transition from an outer shell to the inner shell



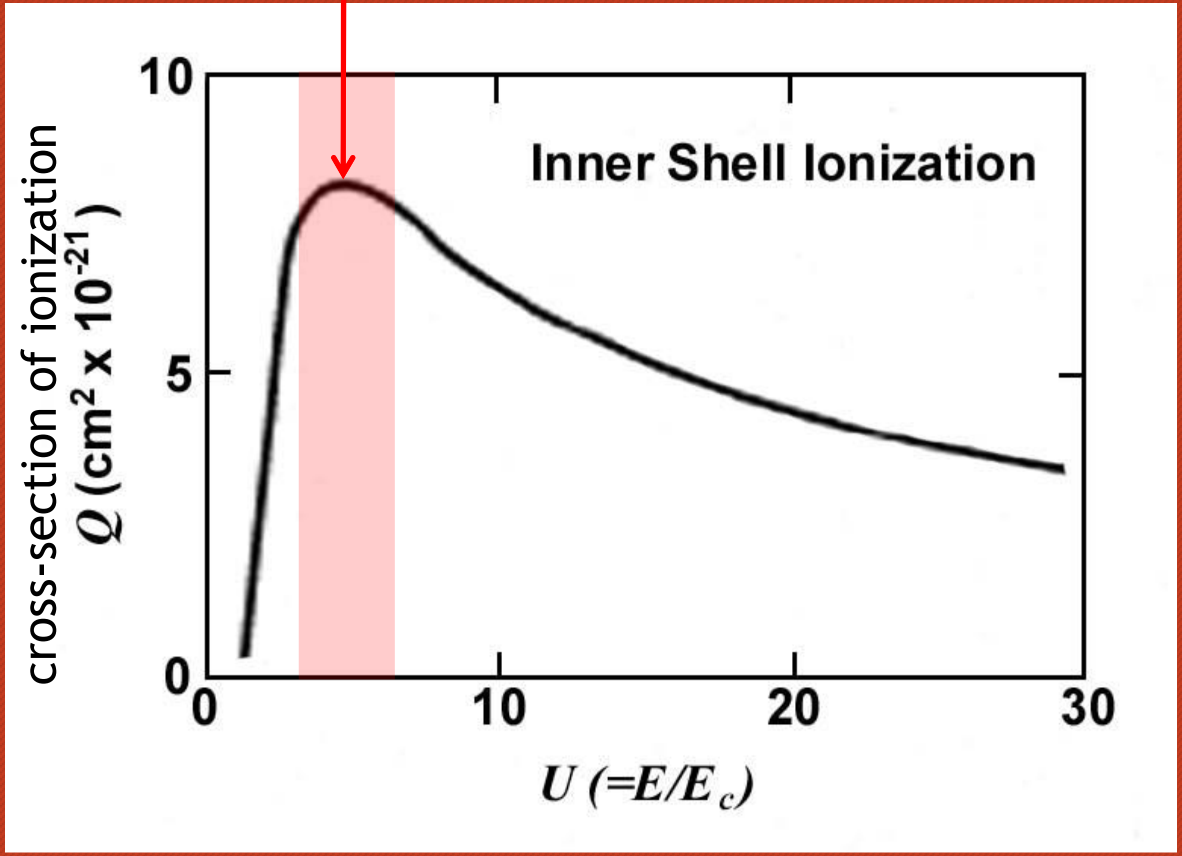
Condition for ionization: Overvoltage

Overvoltage, $U = E/E_c$, > 1

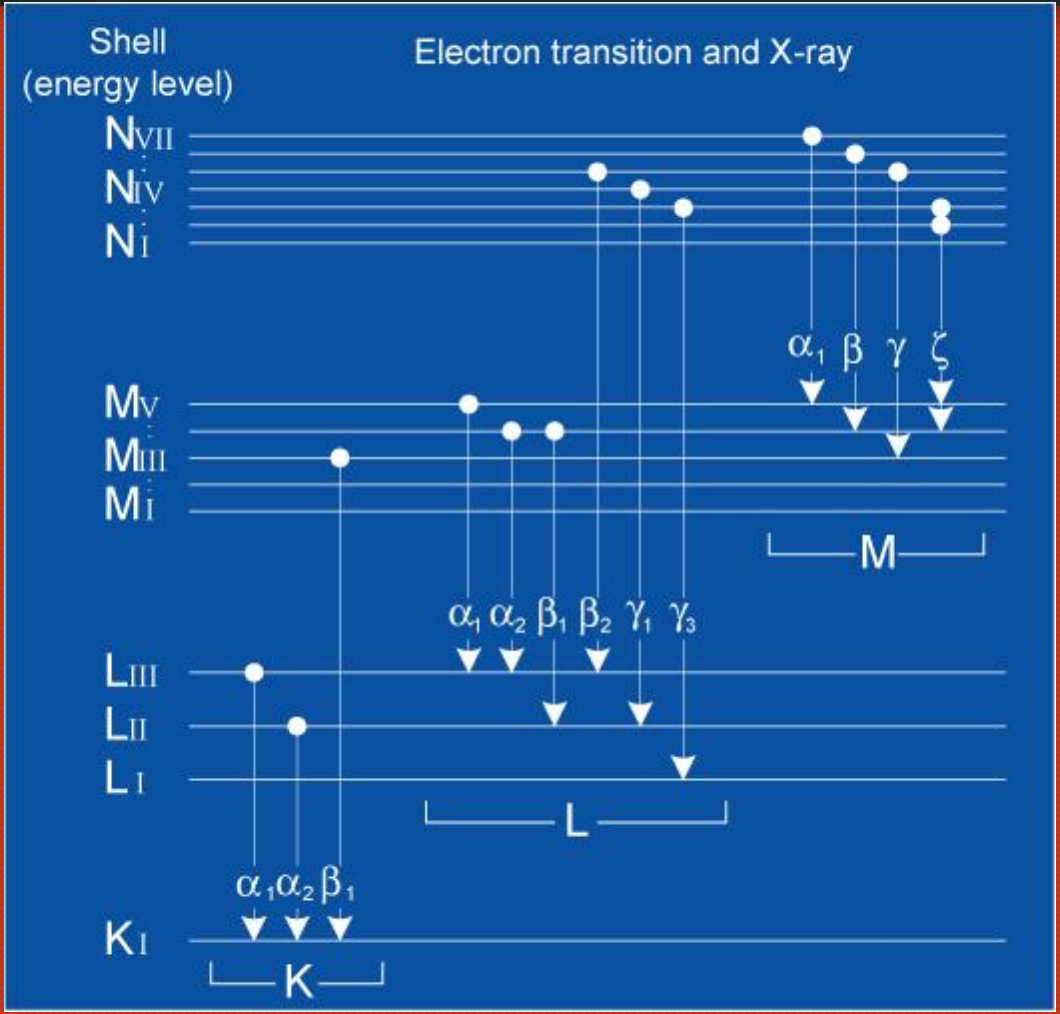
E : electron beam energy

E_c : critical excitation energy,
ionization energy
of the shell in target atom

Best analytical condition, $U \approx 5$

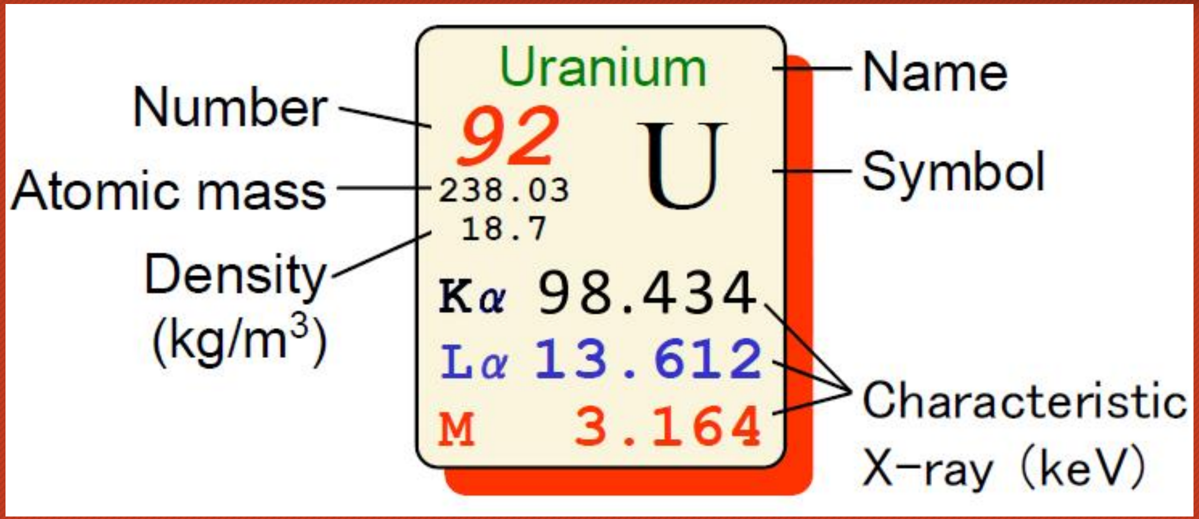


X-ray energies



X-ray	Electron transition	Energy
Kα	L_{II+III} to K_I	$E_{K\alpha} = E_{c(K_I)} - E_{c(L_{II+III})}$
Kβ	M_{III} to K_I	$E_{K\beta} = E_{c(K_I)} - E_{c(M_{III})}$
Lα	M_{IV+V} to L_{III}	$E_{L\alpha} = E_{c(L_{III})} - E_{c(M_{IV+V})}$
Mα	N_{VII} to M_V	$E_{M\alpha} = E_{c(M_V)} - E_{c(N_{VII})}$

Characteristic X-ray energy and critical excitation energy



The energy required to generate UKα *must be* > $E_{c(K)}$ so the overvoltage > 1

$E_{c(K)} \approx 98.4 + 13.6 + 3.2$

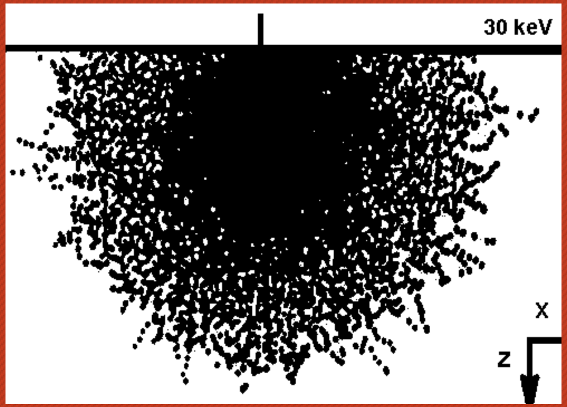
≈ 115.2 keV

Required energy > 115.2 keV

To calculate $E_{c(K)}$:

Start	$E_{K\alpha}$	$= E_{c(K)} - E_{c(L)}$
Rearrange	$E_{c(K)}$	$= E_{K\alpha} + E_{c(L)}$
Substitute $E_{c(L)} = E_{L\alpha} + E_{c(M)}$		$= E_{K\alpha} + (E_{L\alpha} + E_{c(M)})$
Substitute $E_{c(M)} = E_{M\alpha} + E_{c(N)}$		$= E_{K\alpha} + E_{L\alpha} + (E_{M\alpha} + E_{c(N)})$
Therefore,	$E_{c(K)}$	$\approx E_{K\alpha} + E_{L\alpha} + E_{M\alpha}$

Maximum x-ray production depth (range)

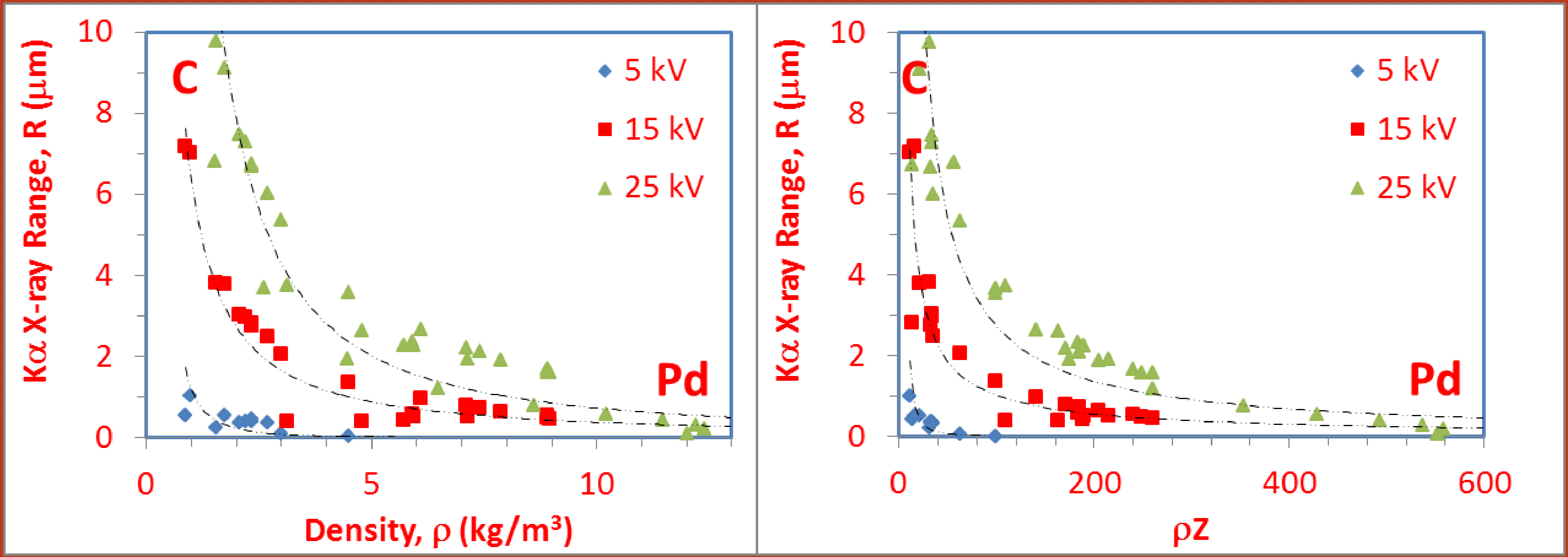


$$R_{X\text{-}ray} = 0.033(E^{1.7} - E_c^{1.7})\frac{A}{\rho Z}$$

(Castaing's formula)

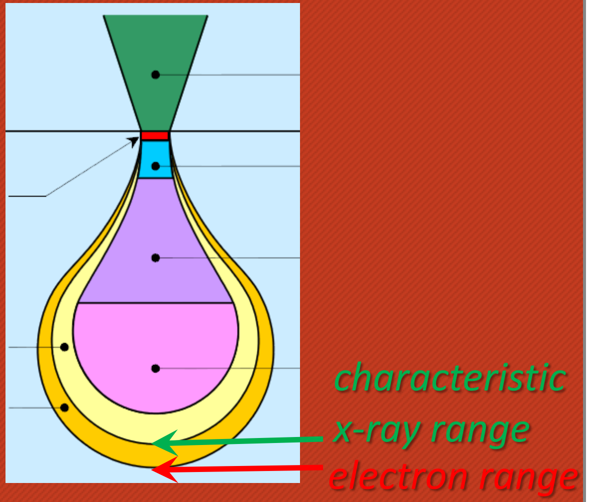
$R_{X\text{-}ray}$ = x-ray range (maximum depth)
E = electron beam energy
E_c = critical excitation energy of target atomic shell
A = atomic weight
ρ = density
Z = atomic number

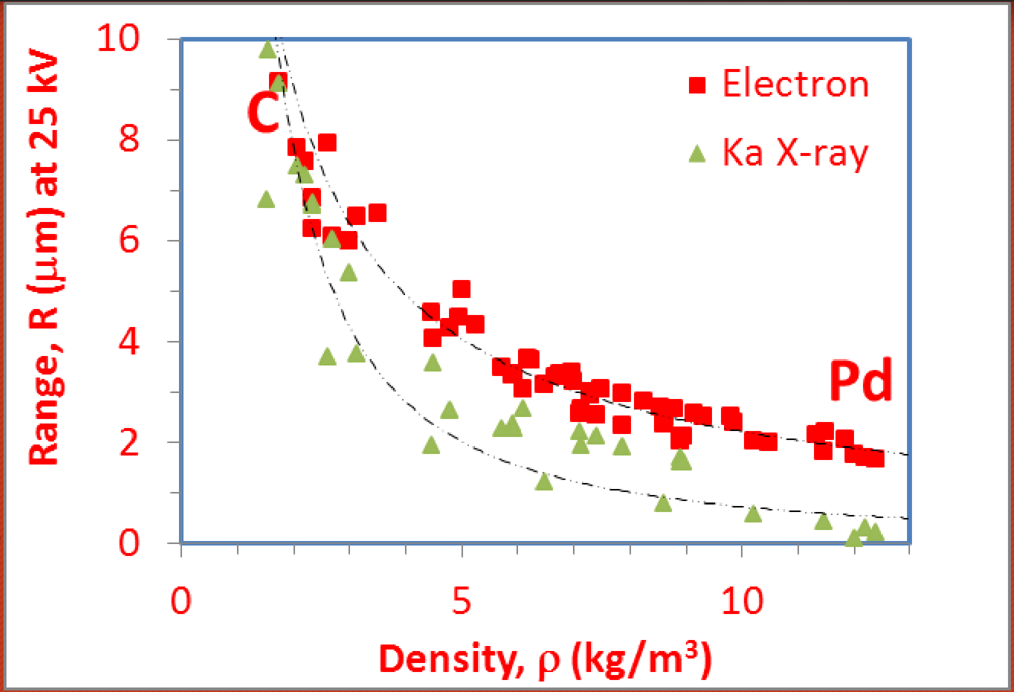
Maximum x-ray production depth (range)



Characteristic X-ray range increases with increasing E, and decreasing ρ and ρZ

Electron range versus X-ray range





$$R_{electron} = 0.0276\,E^{1.67}\frac{A}{\rho Z^{0.889}}$$

$$R_{X\text{-}ray} = 0.033(E^{1.7} - E_c^{1.7})\frac{A}{\rho Z}$$

E = beam energy

E_c = critical excitation energy of sample atomic shell

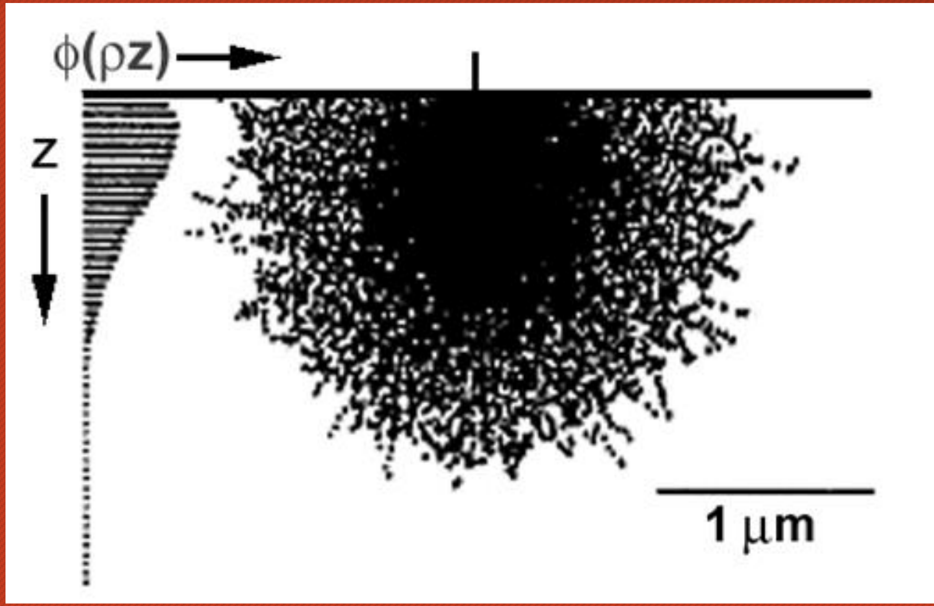
Z = atomic number

A = atomic weight

ρ = density

The characteristic x-ray range is always less than the electron range

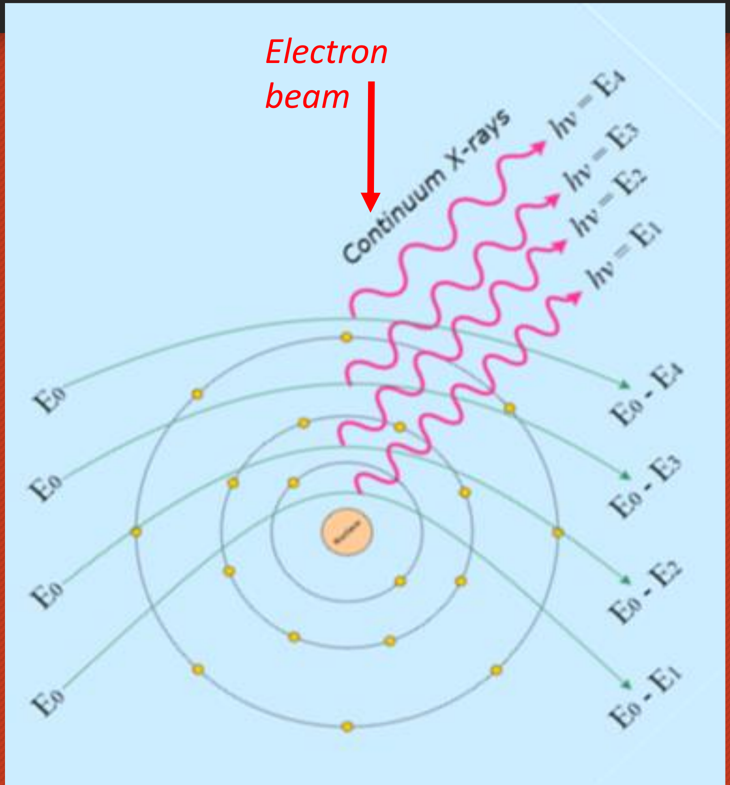
X-ray depth-distribution: the $\phi(\rho z)$ function



$\phi(\rho z)$ at depth z = intensity from depth 'z' divided by $\phi(\Delta\rho z)$

where, ρ = density, z = depth,
and $\phi(\Delta\rho z)$ = intensity from a free standing layer of thickness 'Δz'

Continuum X-ray generation



Produced by deceleration of beam electrons in the electrostatic field of target atoms

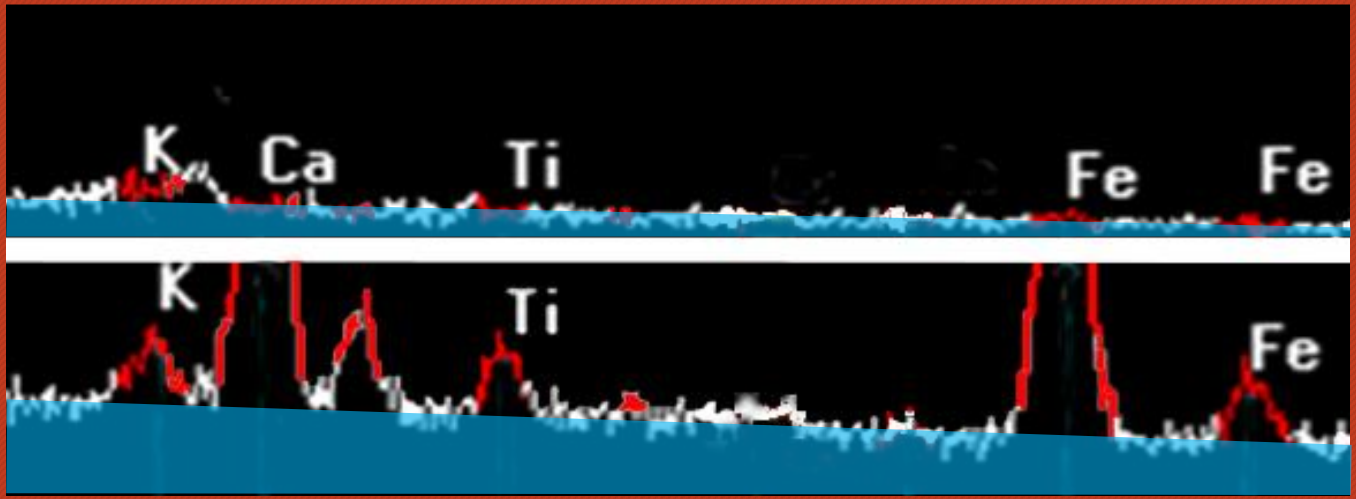
Energy lost by beam electrons is converted to x-ray

(Maximum energy of continuum x-rays = electron beam energy)

Continuum X-rays: background intensity

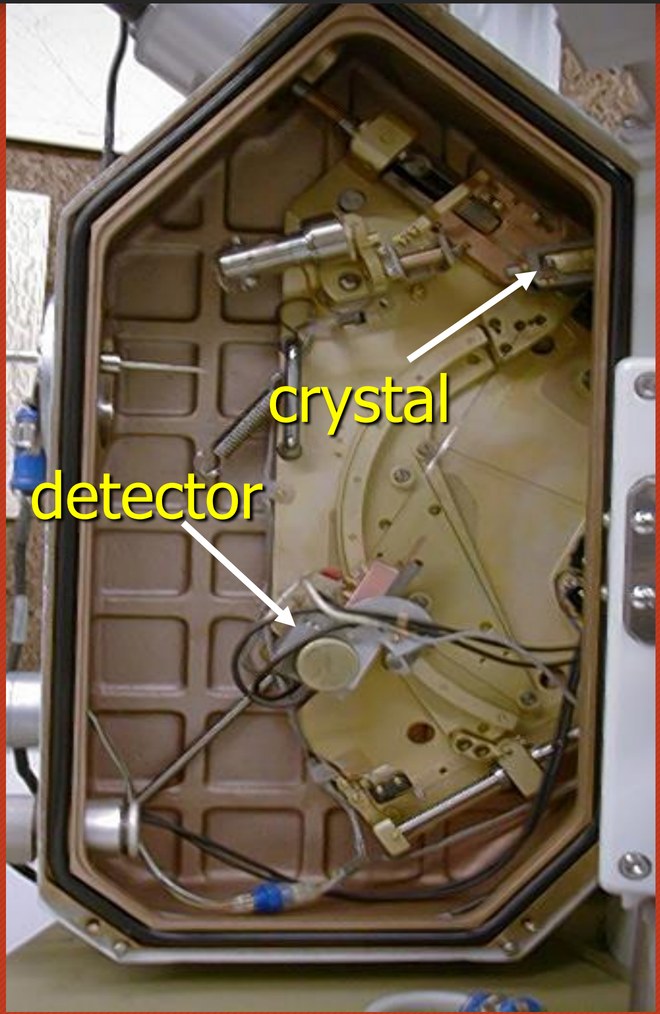
Low-Z sample
(Ca-Fe poor)
Low background

High-Z sample
(Ca-Fe rich)
High background



Increases with sample atomic number

Wavelength Dispersive Spectrometer (WDS)



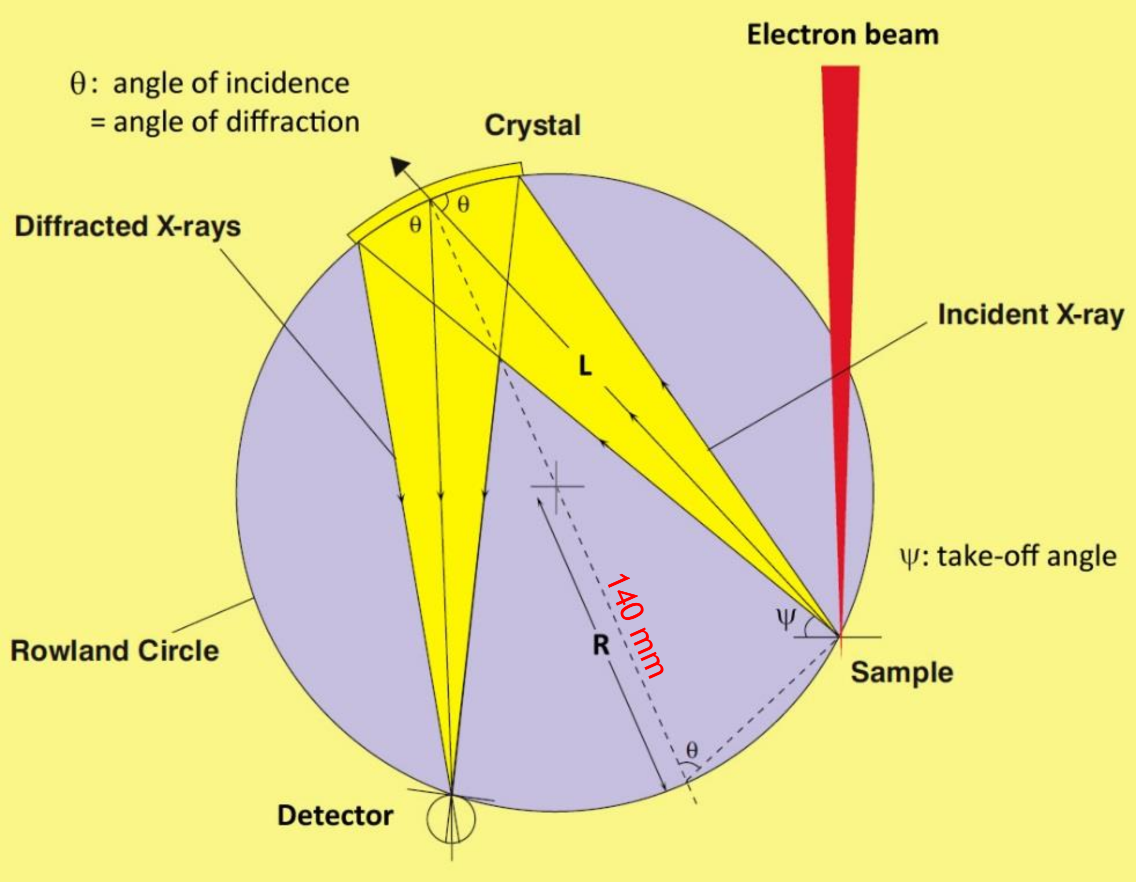
Wavelength Dispersive Spectrometer (WDS)

$$\sin\theta = \frac{L}{2R}$$

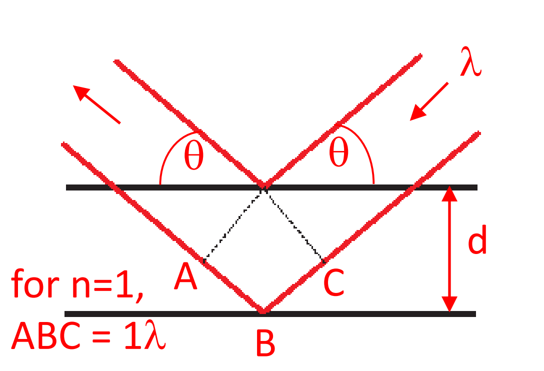
θ: angle of incidence or diffraction

L: distance between sample and crystal

R: radius of focusing (Rowland) circle



"L-value": $L = n\lambda \frac{R}{d}$



Bragg's Law:

$$n\lambda = 2d\sin\theta$$

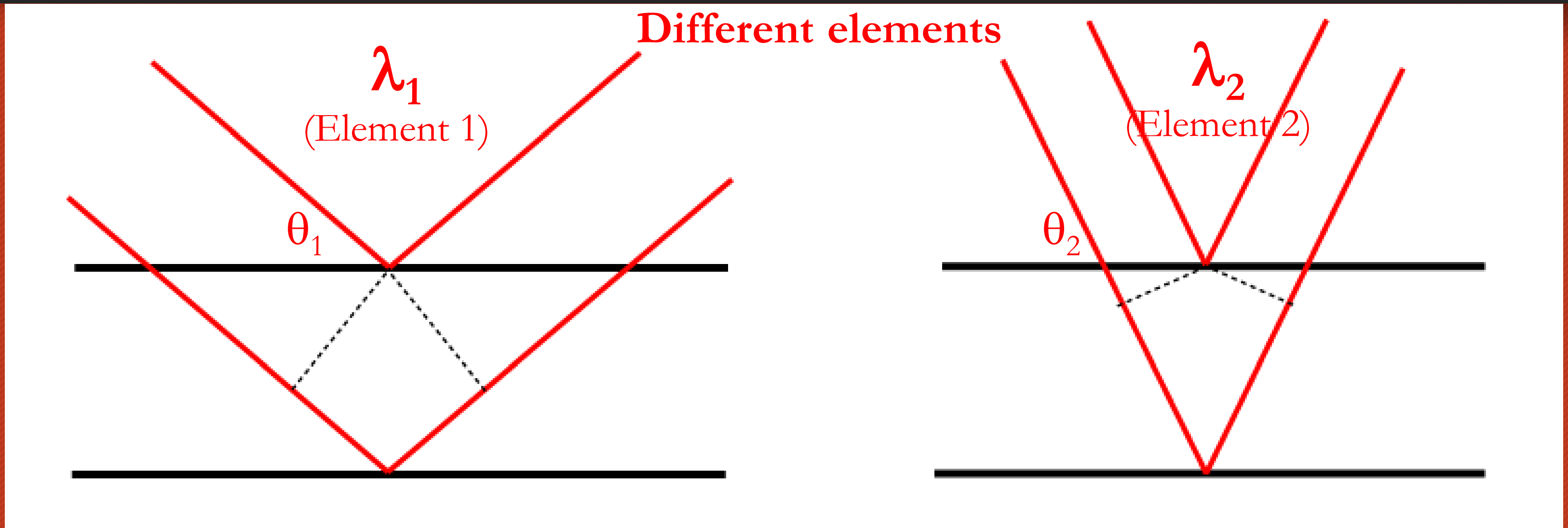
n: order of diffraction

λ: wavelength of X-ray

d: lattice spacing in diffracting crystal

θ: angle of incidence or diffraction

Incidence or Diffraction angle



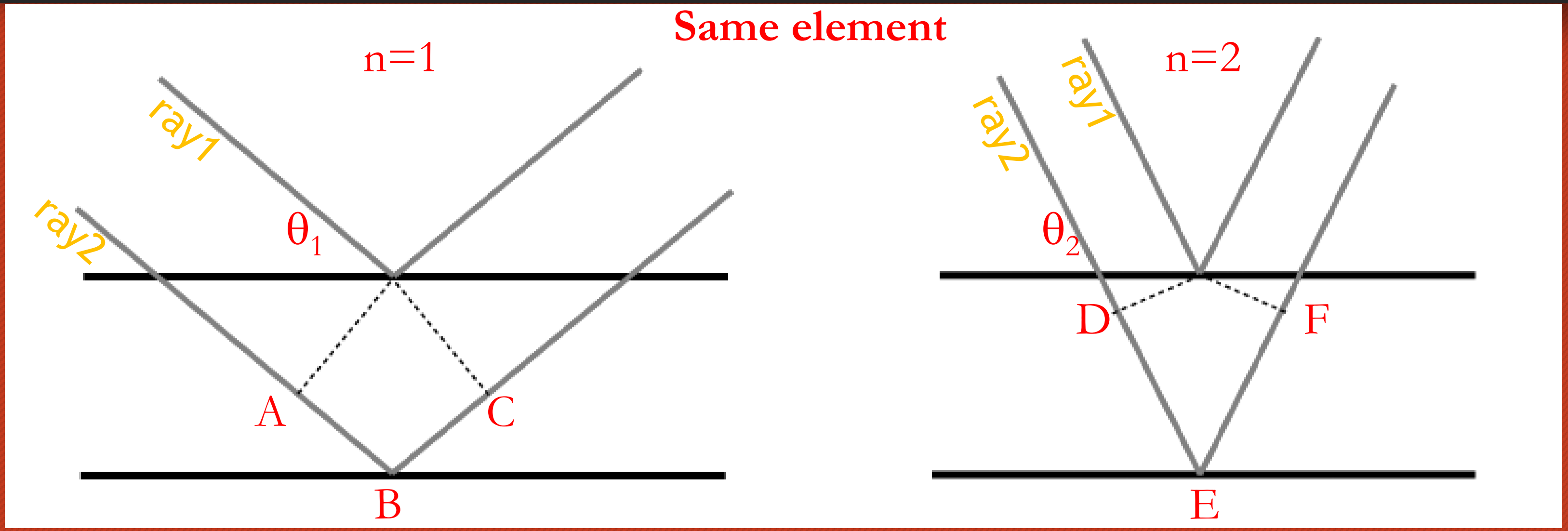
$$n\lambda_1 = 2d \sin\theta_1$$

$$n\lambda_2 = 2d \sin\theta_2$$

With a different incidence angle, a different wavelength is diffracted

(for the same order of diffraction, n)

First and second order diffractions



$1\lambda = 2d \sin\theta_1$ $2\lambda = 2d \sin\theta_2$

If the incidence angle changes so that $\sin\theta_2 = 2\sin\theta_1$, *the* 2nd *order diffraction of the same wavelength occurs*

(path ABC = 1λ; *path* DEF = 2 x ABC = 2λ*)*

In WDS: since $L = 2R \sin\theta$, *L-value for the second order diffraction is doubled;* $L_2 = 2L_1$

L-value

Example 1.

Si Kα

Energy, E = 1.74 keV

$$\lambda \text{ (nm)} = \frac{1.2398}{E \text{ (keV)}}$$

$$\text{Wavelength, } \lambda = \frac{1.2398}{1.74} = 0.7125 \text{ nm}$$

$$L \text{ (mm)} = n \lambda \text{ (nm)} \frac{R \text{ (mm)}}{d \text{ (nm)}}$$

For n =1, R = 140, and d_{TAP} = 1.2879,

$$L_{TAP} = 1 \times 0.7125 \times \frac{140}{1.2879}$$

$$= 77.45 \text{ mm}$$

Example 2.

U Mα

Energy, E = 3.17 keV

$$\lambda \text{ (nm)} = \frac{1.2398}{E \text{ (keV)}}$$

$$\text{Wavelength, } \lambda = \frac{1.2398}{3.17} = 0.3911 \text{ nm}$$

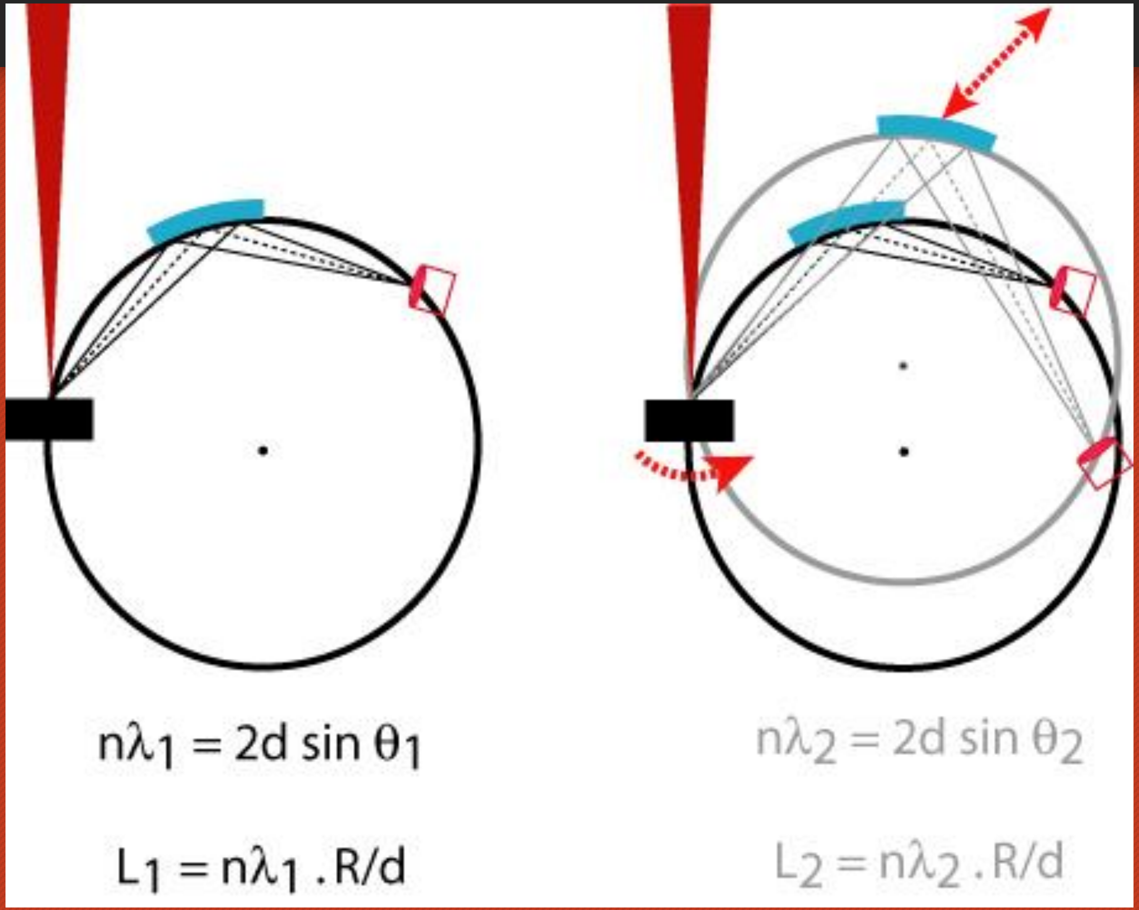
$$L \text{ (mm)} = n \lambda \text{ (nm)} \frac{R \text{ (mm)}}{d \text{ (nm)}}$$

For n=1, R = 140, and d_{PET} = 0.4371,

$$L_{PET} = 1 \times 0.3911 \times \frac{140}{0.4371}$$

$$= 125.27 \text{ mm}$$

WDS operation: changing the L-value



Radius of focusing circle (R) *remains constant*

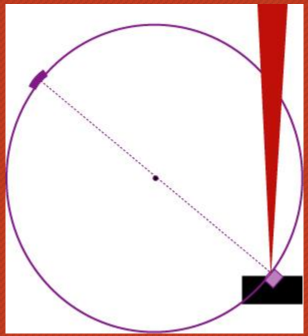
Changing the L-value from **L_1** *to* **L_2** *changes the incidence angle from* θ_1 *to* θ_2

so that a different wavelength λ_2 *is diffracted*

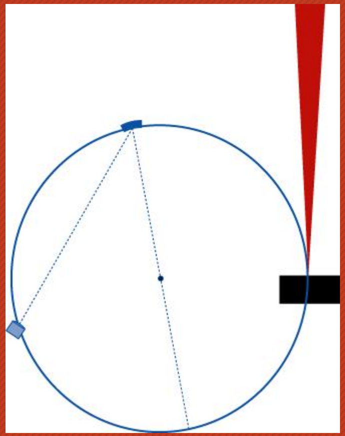
Theoretical limits of spectrometer movement

For a spectrometer with R = 140 mm,

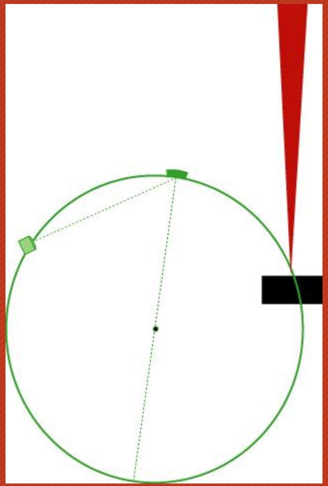
$L = 2R \sin\theta$



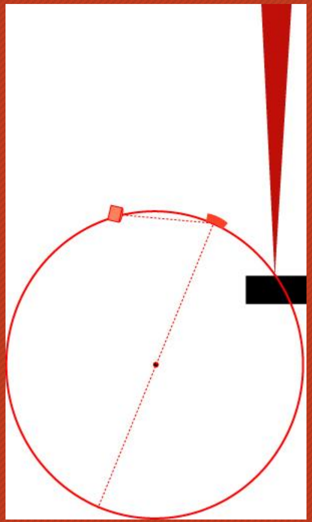
L = 280 mm
$\theta = 90^o$



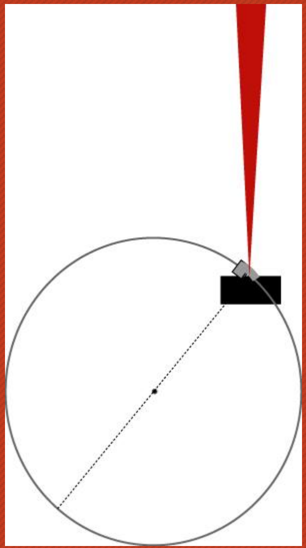
L = 210 mm
$\theta = 48.6^o$



L = 140 mm
$\theta = 30^o$



L = 70 mm
$\theta = 14.5^o$



L = 0 mm
$\theta = 0^o$

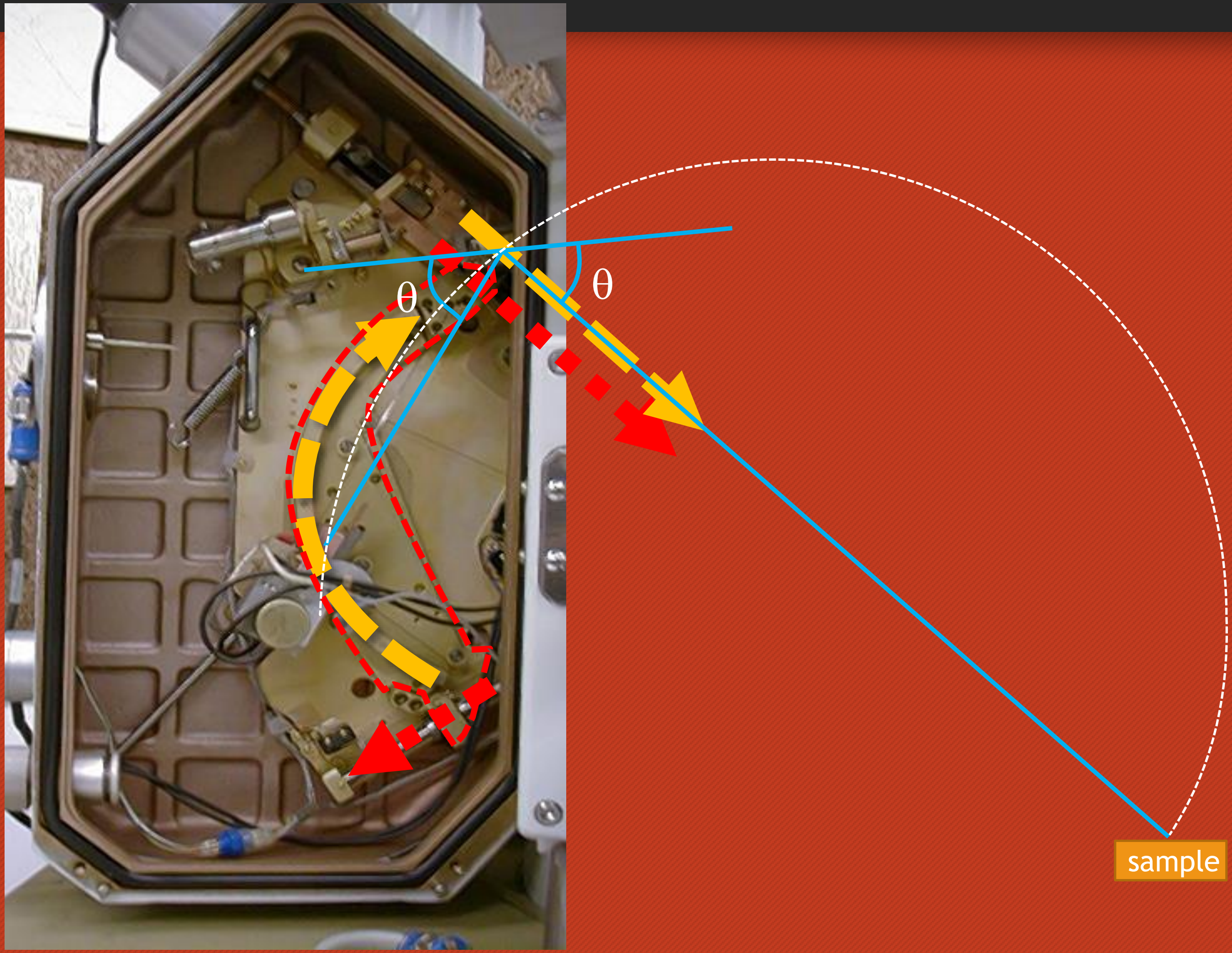
Theoretical limits:

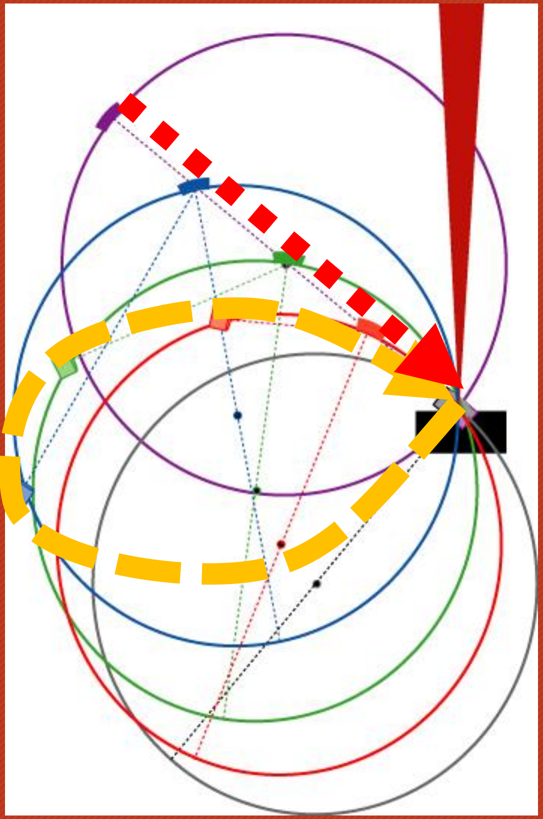
$2R \geq L \geq 0$ at $90^o \geq \theta \geq 0^o$

$280 \text{ mm} \geq L \geq 0 \text{ mm}$

Note θ changes faster between 280-140 mm than between 140-0 mm

Spectrometer movement





Theoretical limits

Actual limits of spectrometer movement

For a spectrometer with R = 140 mm,

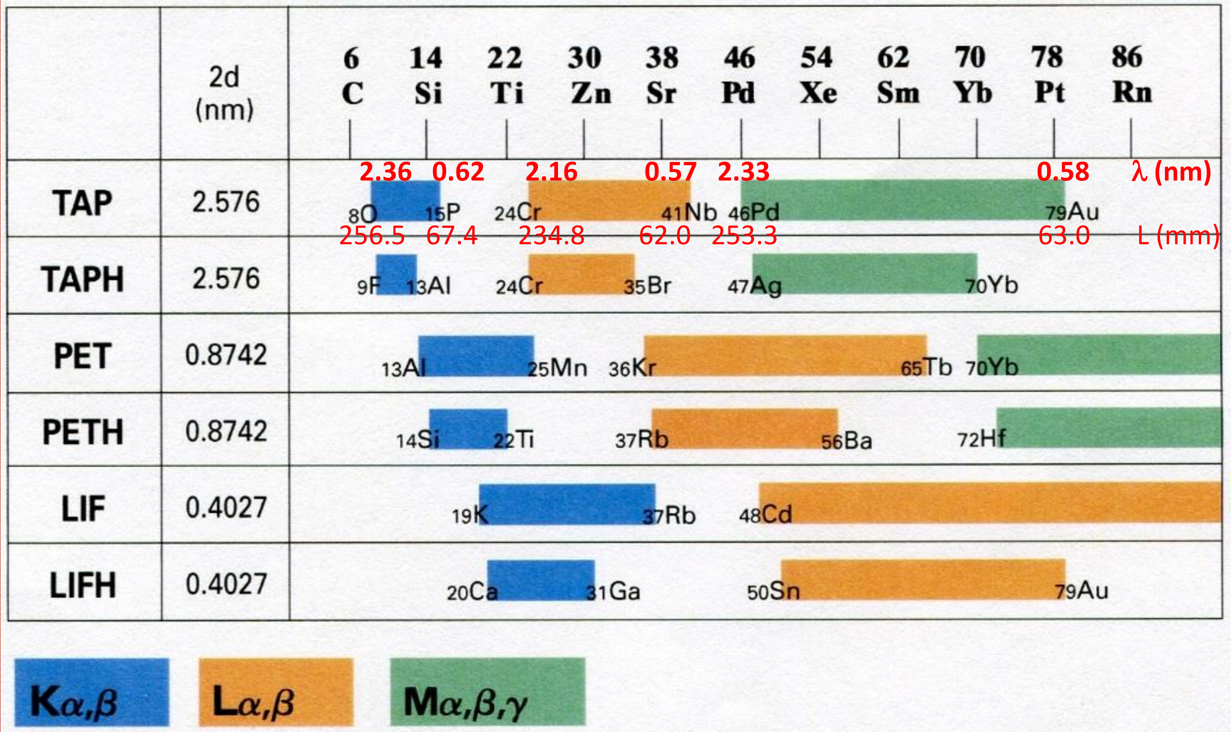
Actual limits: $60 \text{ mm} \leq L \leq 260 \text{ mm}$; $12.4^{o} \leq \theta \leq 68.2^{o}$

Typically, $72.5 \text{ mm} \leq L \leq 229.5 \text{ mm}$; $15^{o} \leq \theta \leq 55^{o}$

Recall $\sin\theta = \frac{L}{2R}$, so $L = 2R\sin\theta$ and $\theta = \sin^{-1}\left(\frac{L}{2R}\right)$

2d of x-ray diffractors

Crystal lattices



For n=1, θ = 15 to 55^o (L = 73 to 230 mm), and R = 140 mm, a crystal can diffract **~ 0.52d < λ < 1.64d**

[recall, $L = n\lambda \frac{R}{d}$, i.e., $\lambda = \frac{L}{nR} d$]

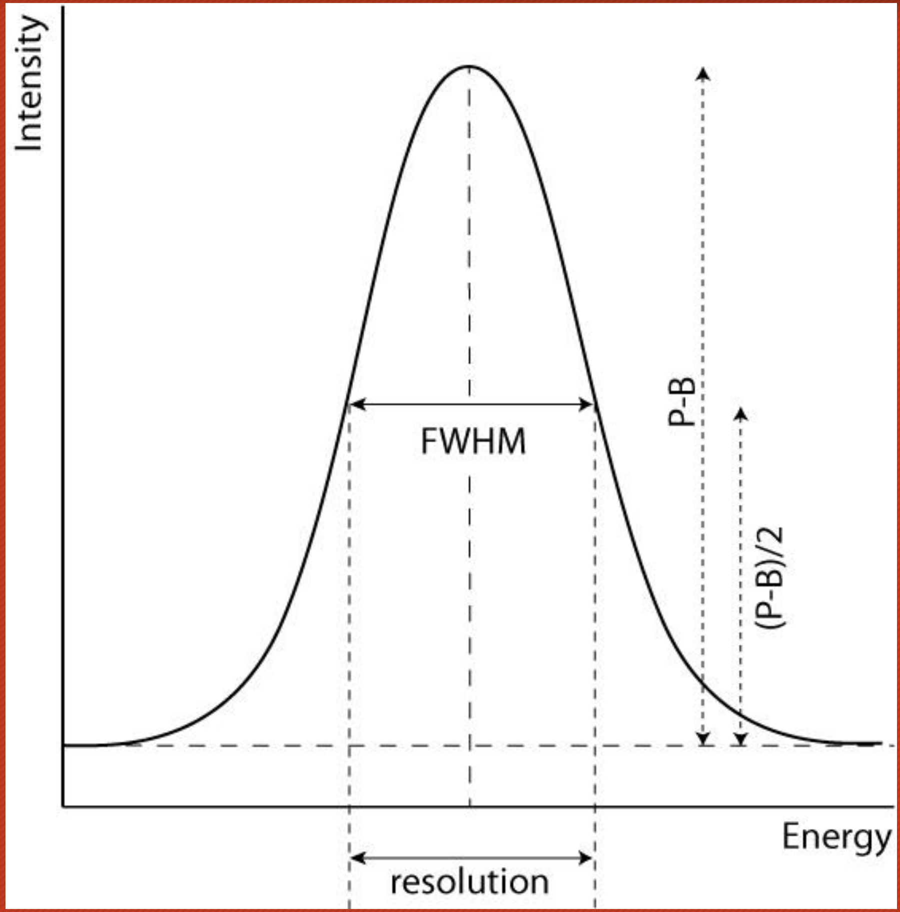
Layered structures

	2d (nm)	Be	B	C	N	O	F
NSTE	Approx.10		○	○	○	○	
LDE1	Approx.6			△	◎	◎	◎
LDE2	Approx.10		◎	◎	◎	○	
LDEB	Approx.14.5	◎	○				
LDE1H	Approx.6			△	◎	◎	
LDE2H	Approx.10		◎	◎			
LDENH	Approx.8			○	◎		
LDE3H	Approx.20	◎	○				
LDE5H	Approx.8			◎	◎		
LDEBH	Approx.14.5	◎	◎				

$\lambda_{BeK\alpha}$ = 11.27 nm; so BeKα can be diffracted only by diffractors with 2d > 11.27 nm

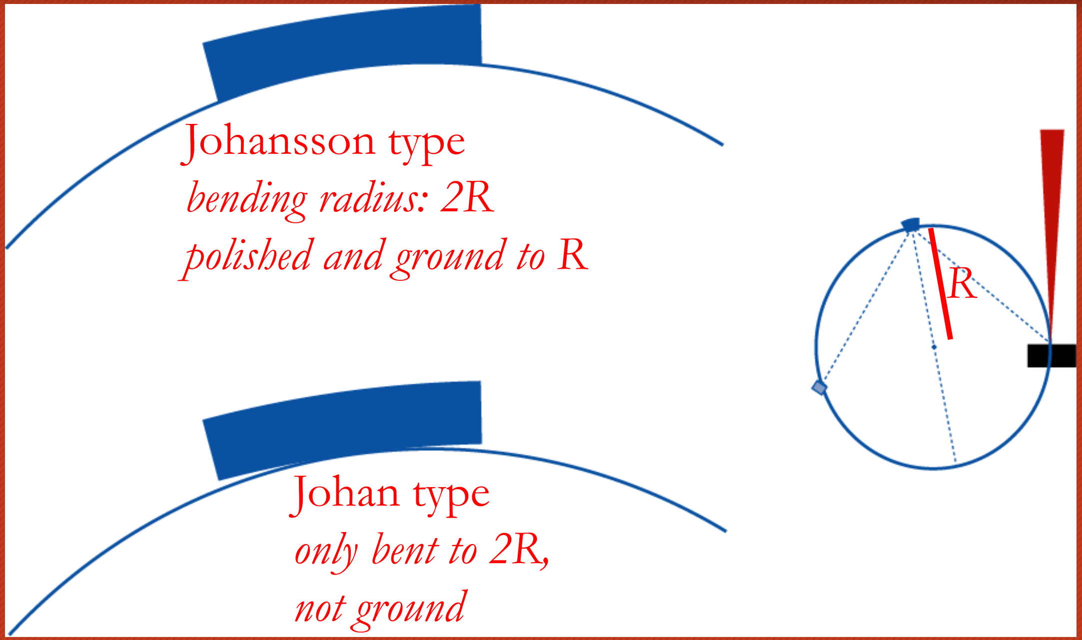
e.g., with LDE3H (at L = 157.8 mm), and LDEB and LDEBH (at L = 217.6 mm)

Spectral resolution



Full-Width Half-Maximum (FWHM)

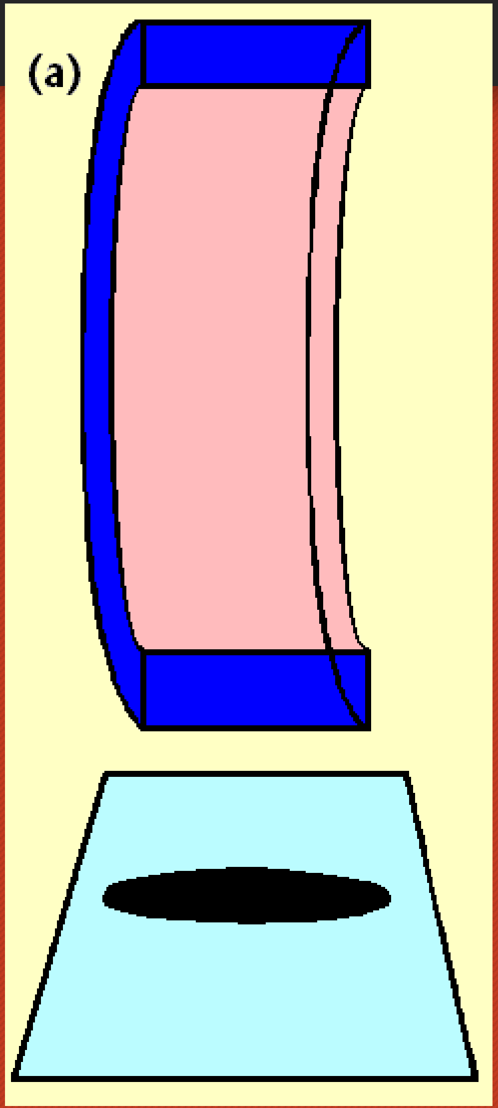
Curved diffracting crystals



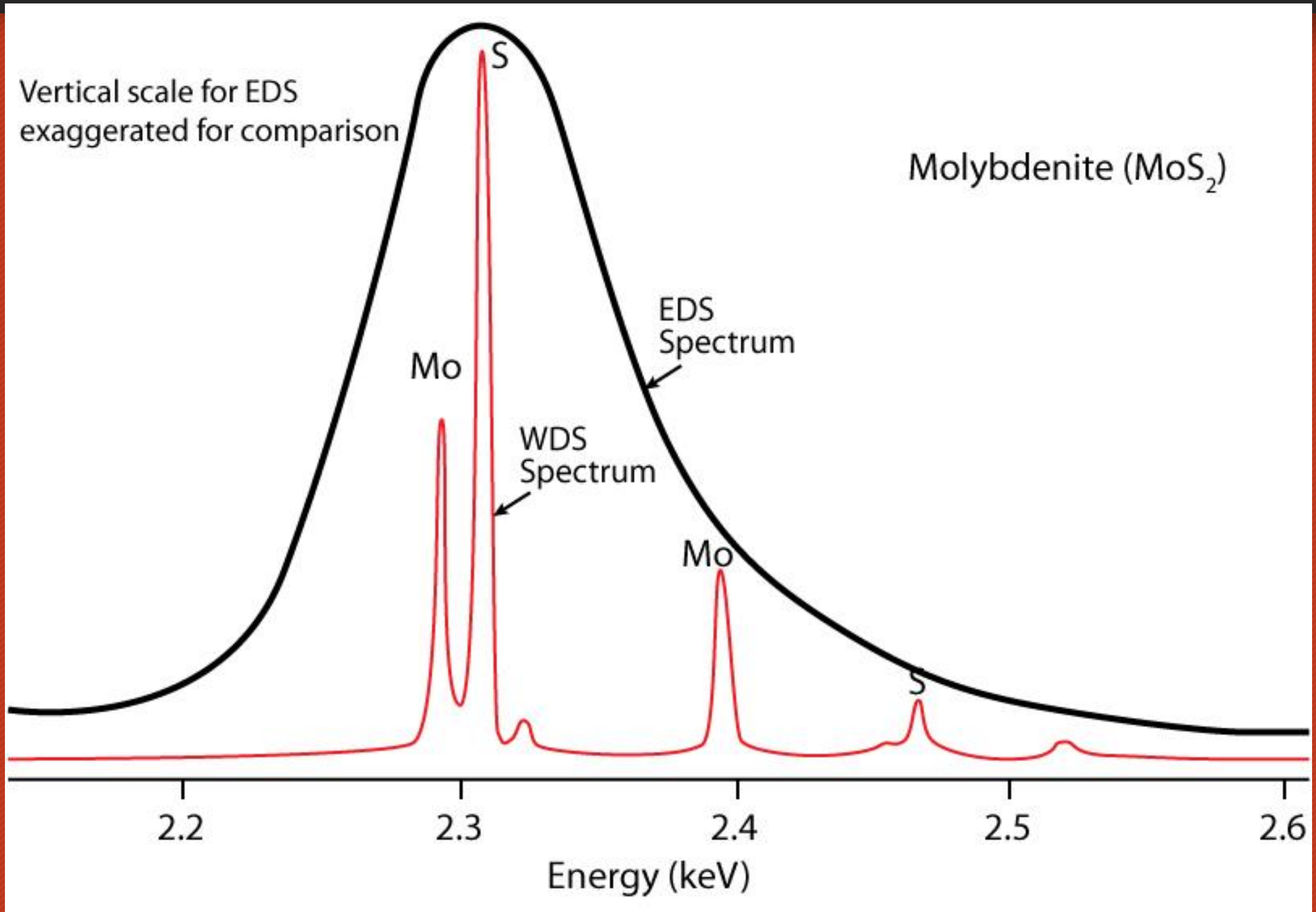
Peak resolution with fully focusing Johansson-type crystal: FWHM ~10 eV

Some defocusing in Johan-type, but resolution is not compromised

X-ray focusing ellipsoid



WDS vs. EDS spectral resolution

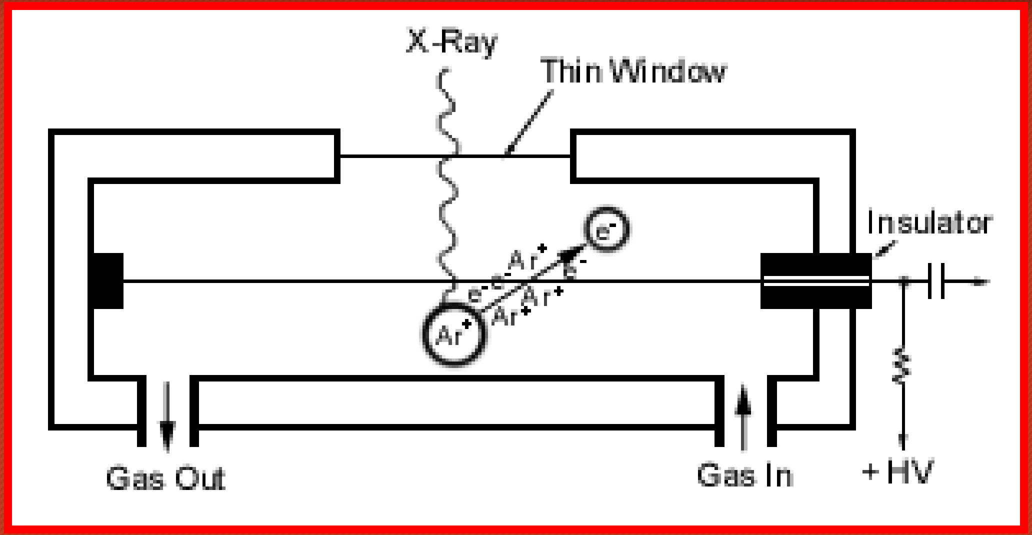


Peak overlaps in EDS spectrum

*Peak resolution with WDS (FWHM **~10 eV**) is an order of magnitude better than with EDS (FWHM **~150 eV**)*

WDS detector: Proportional counter

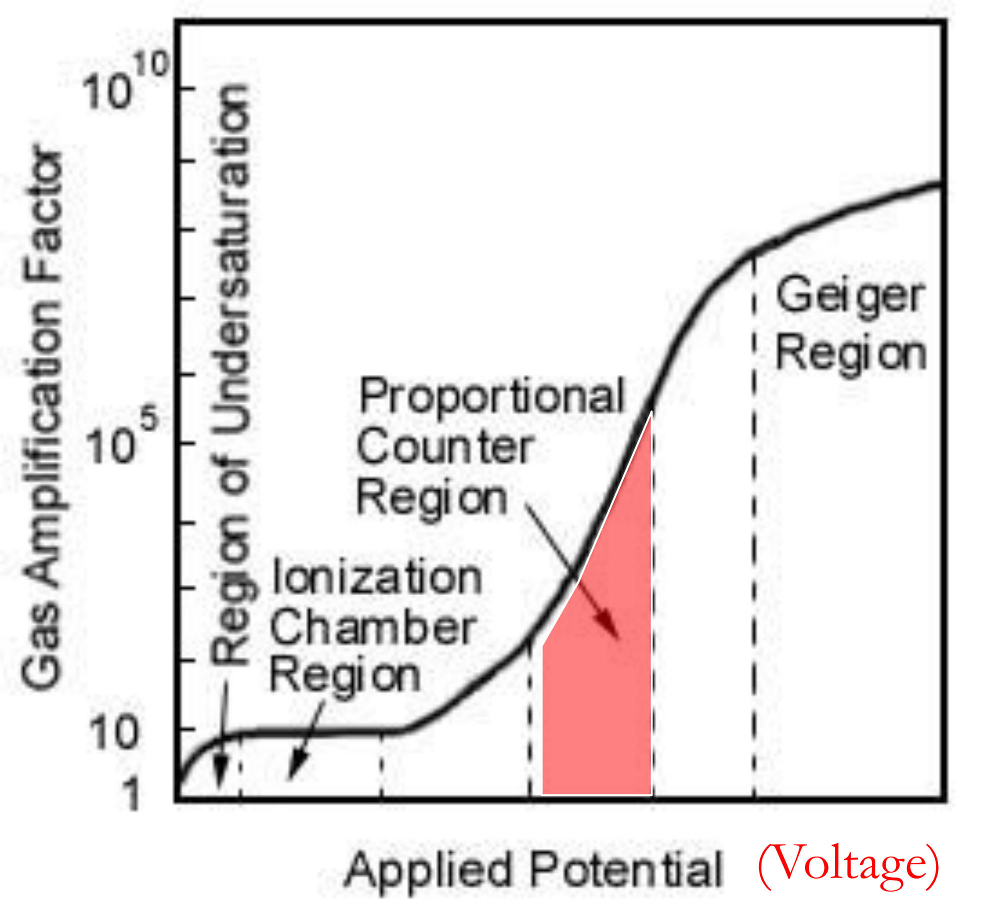
Tungsten collection wire at 1-3 kV voltage
Normal operation: 1600-1850 V



- *Incoming x-ray ionizes a gas atom that sets up a chain of ionizations in the gas. The signal is thus amplified by the gas itself.*
- *Pulse voltage generated is proportional to the voltage in the collection wire under normal operating conditions.*

- *Flow counter:*
  - *P-10 gas (90% Argon + 10% methane quenching agent)*
  - *Polypropylene window*
- *Sealed counter:*
  - *Xenon gas*
  - *Beryllium window*

Signal amplification



Typical voltage range in the proportional counter region for a W wire: 1600-1850 V

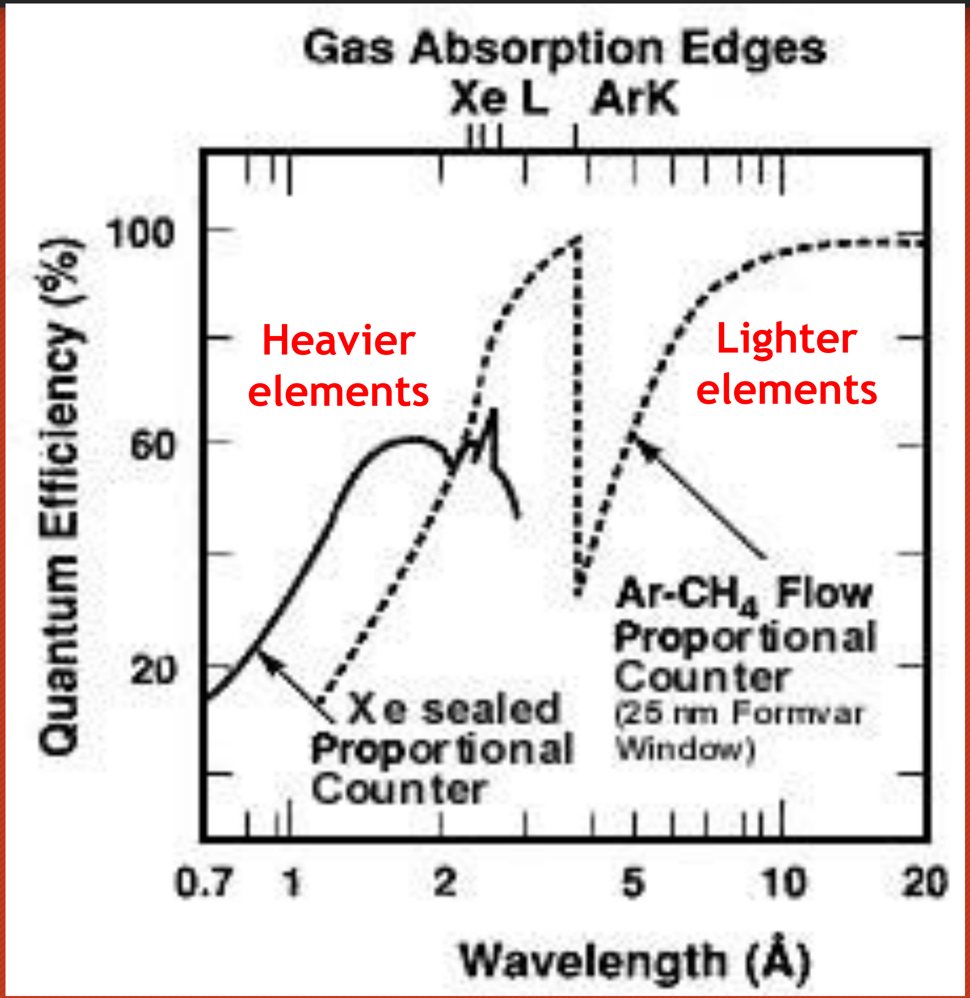
The amplification factor is proportional to the voltage in the collection wire in the proportional counter region

Quantum efficiency of counter gas

Highest when the incoming X-ray is least absorbed by the gas

Decreases when the X-ray is absorbed by ionizing an inner shell of the gas atom, generating ArKα or XeLα

Lowest when $E_{X\text{-}ray}$ is slightly higher than the $E_{c(Ar\ K\text{-}shell)}$ or $E_{c(Xe\ L\text{-}shell)}$ absorption edges

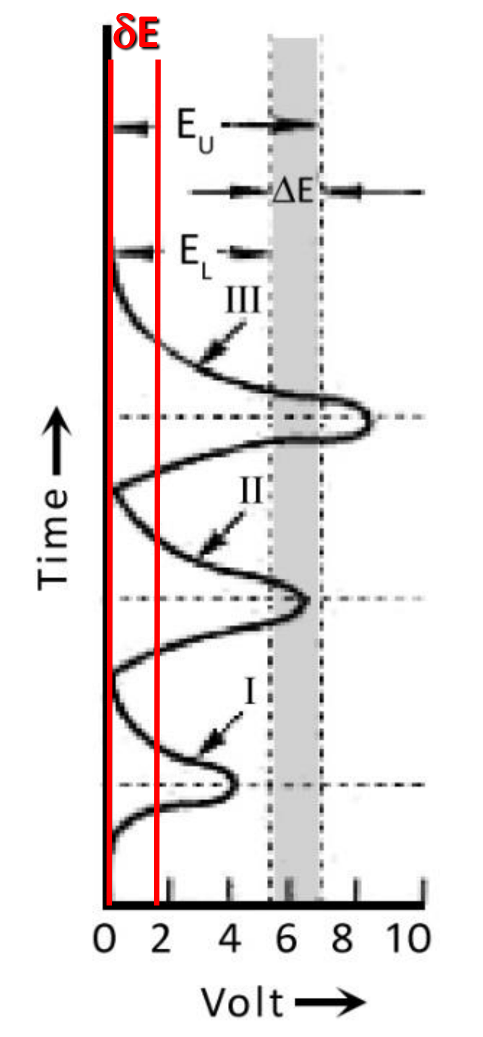


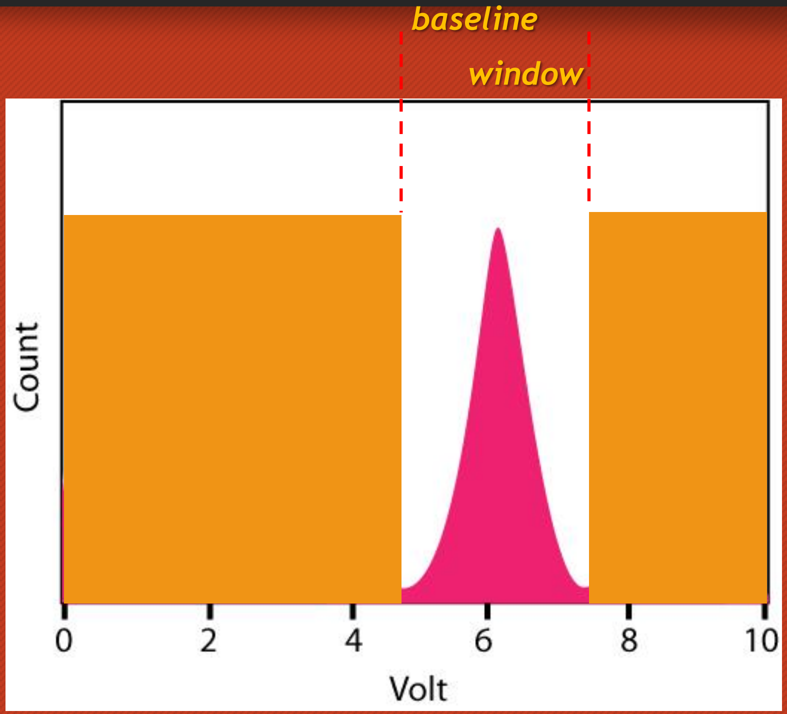
- *Argon: long wavelength (low energy) detection*
- *Xenon: short wavelength (high energy) detection*

Proportional counter setup: Pulse Height Analysis

Proportional counter output:

Voltage pulses from noise and x-ray signal





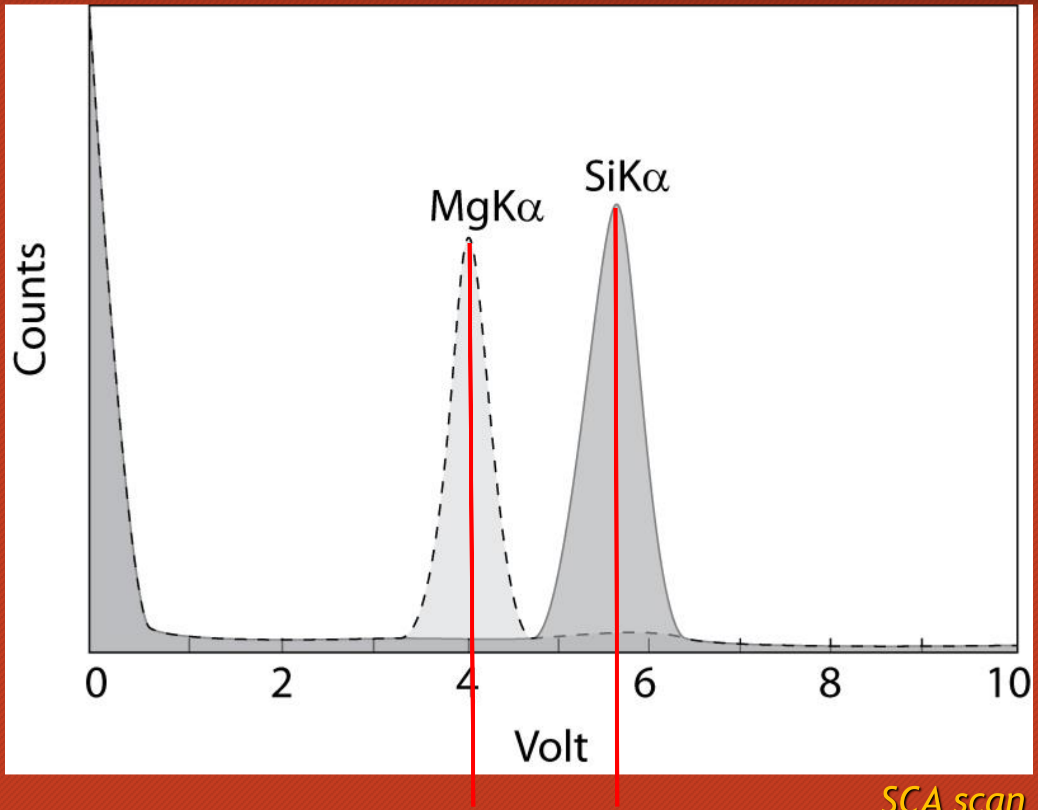
An SCA scan shows the variation in count rate as a small voltage window (δE) is moved across the voltage range

Baseline and window voltages (ΔE) are set to filter out noise and unwanted signal

A Single Channel Analyzer (SCA) can be set to allow only x-ray voltage pulses within ΔE to pass through

ΔE is determined by Pulse Height Analysis (PHA) through an SCA scan

Pulse voltage in SCA scan



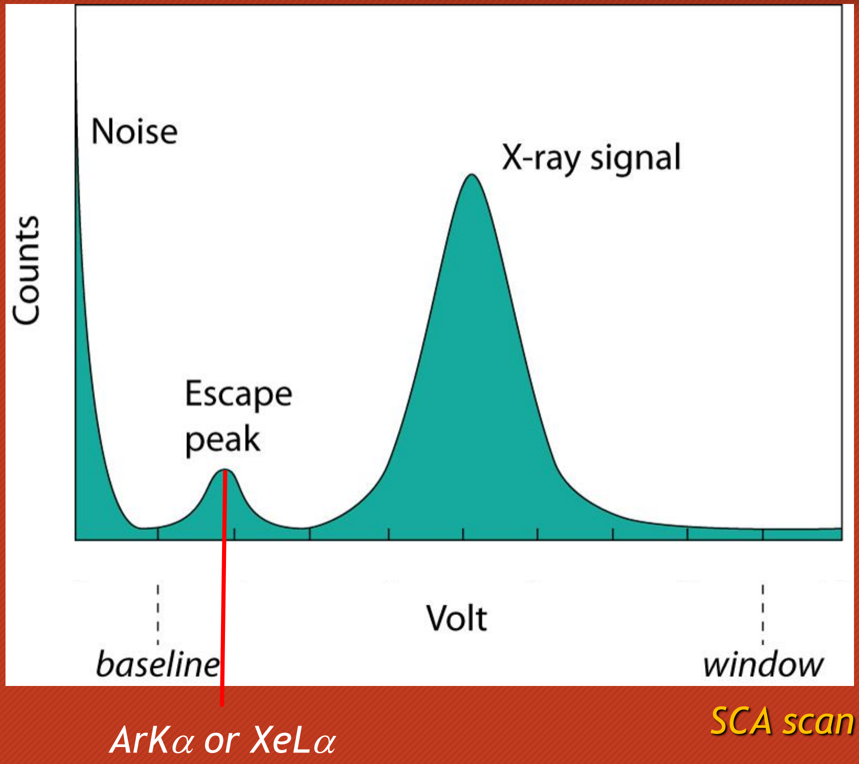
SCA scan

Pulse voltage is proportional to energy of the X-ray being detected

Energy of SiKα (1.739 keV) is ~1.39 times the energy of MgKα (1.253 keV)

If the pulse for MgKα is at 4 V, the pulse for SiKα will be at 4 x 1.39 = 5.56 V

Escape peak in SCA scan



SCA scan

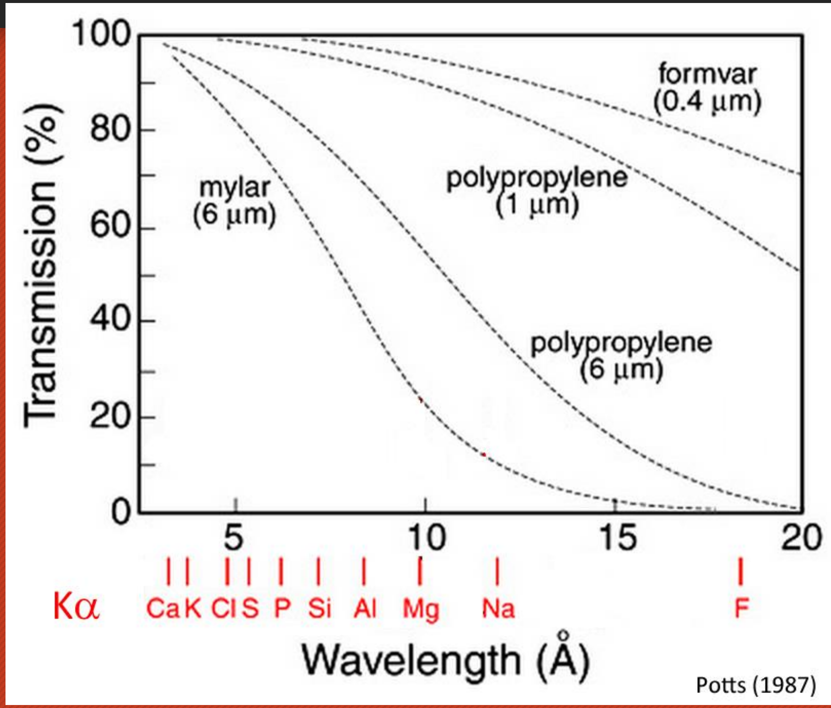
Escape peaks fluoresced by incoming X-ray:

- P-10 counter: ArKα
- Xenon counter: XeLα

If the pulse for NiKα (7.47 keV) is at 5.20 V,

the XeLα (4.11 keV) escape peak will be at 5.2 x [(7.47 - 4.11) / 7.47] = 2.34 V

Proportional counter window material



- *Mylar has lower transmittance than polypropylene, especially for light element x-rays*
- *Thin windows are better for light elements*

1 µm thick polypropylene window transmits ~60% of the F Kα

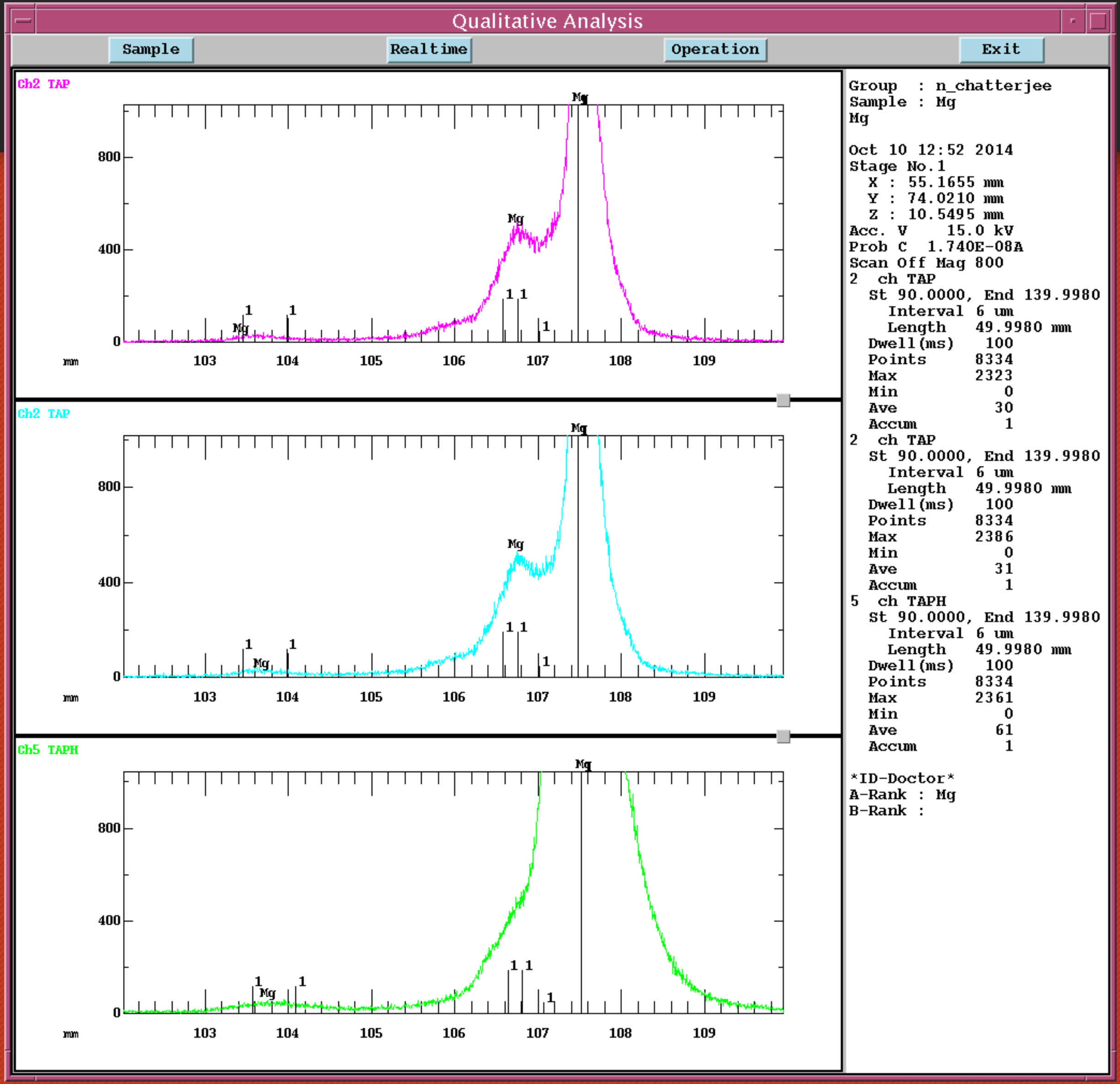
6 µm thick polypropylene window transmits only ~5% of the F Kα

Detector slit

- *Positioned in front of the proportional counter window*
- *Cuts off stray x-rays and electrons*

Open:	*LDE*	*P-10 flow counter*	*Very light elements (very low E, very long λ)*
550-300 μm:	*PET or LIF*	*Xe sealed counter*	*Heavy elements (high E, short λ)*
300 μm:	*TAP*	*P-10 flow counter*	*Light elements (low E, long λ)*
300 μm with Mylar film:	*PET or LIF*	*P-10 flow counter*	*Heavy elements (high E, short λ)*

Semi-quantitative analysis



Compositional imaging with X-rays: elemental mapping

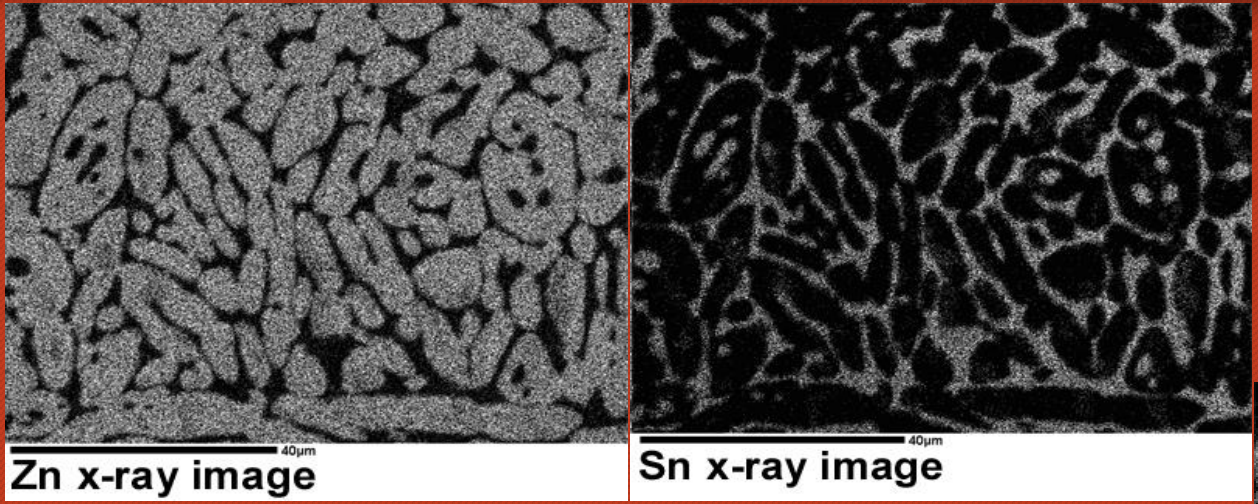
- **Beam-rastered image:**

  electron beam rasters over the area to be imaged

- **Stage-rastered image:**

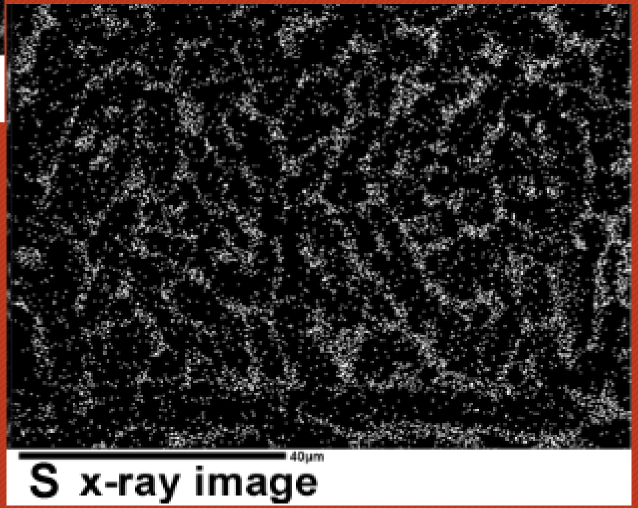
  electron beam is stationary, stage moves

Background in x-ray image



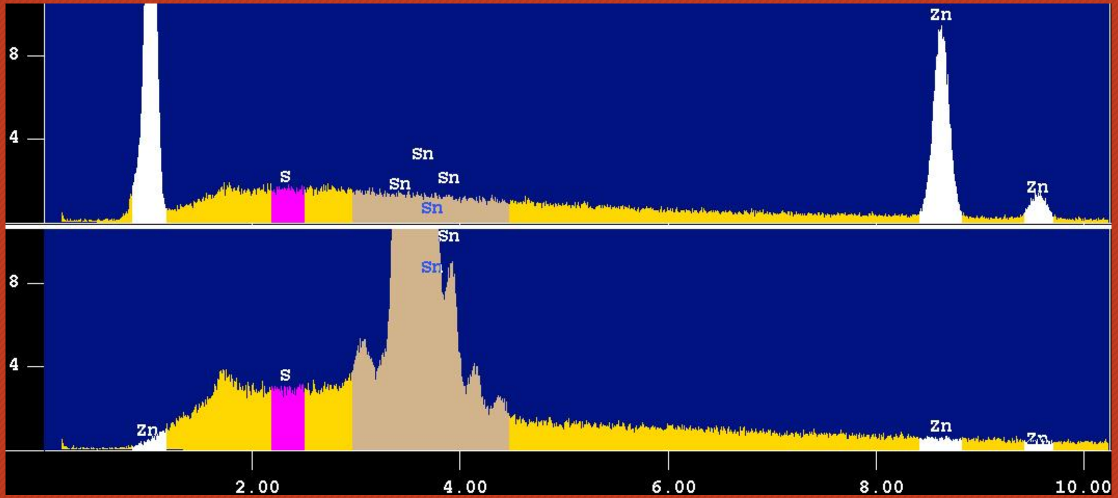
Zn-Sn composite

Background image

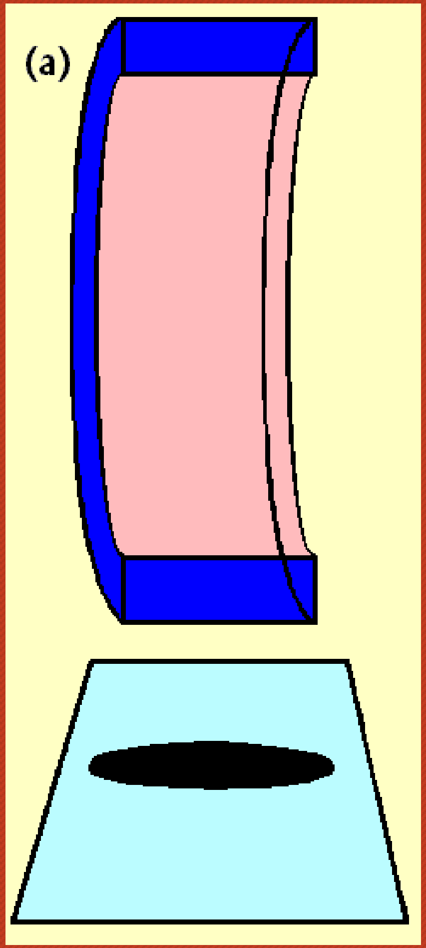


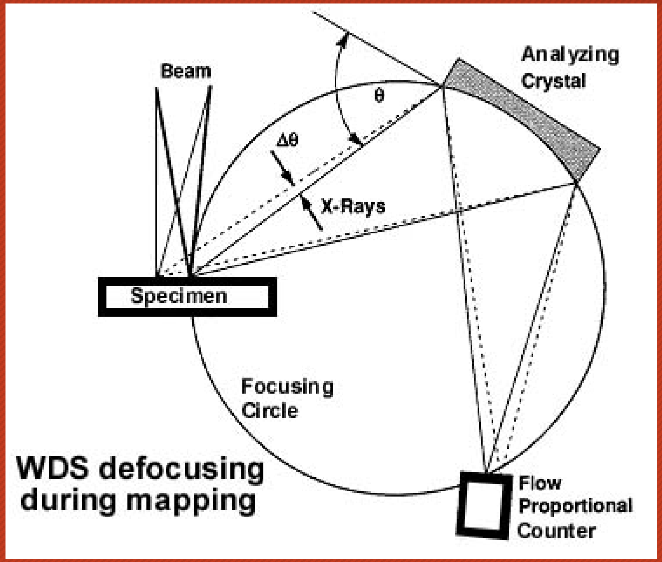
Zn-rich phase
(low Z)

Sn-rich phase
(high Z)



X-ray defocusing in beam-rastered image





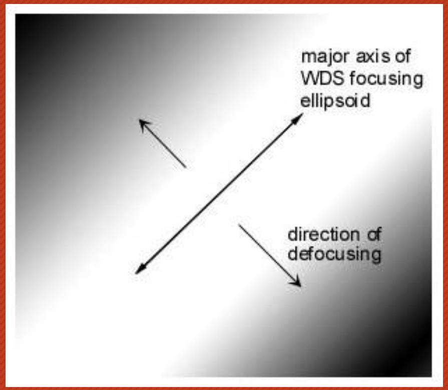


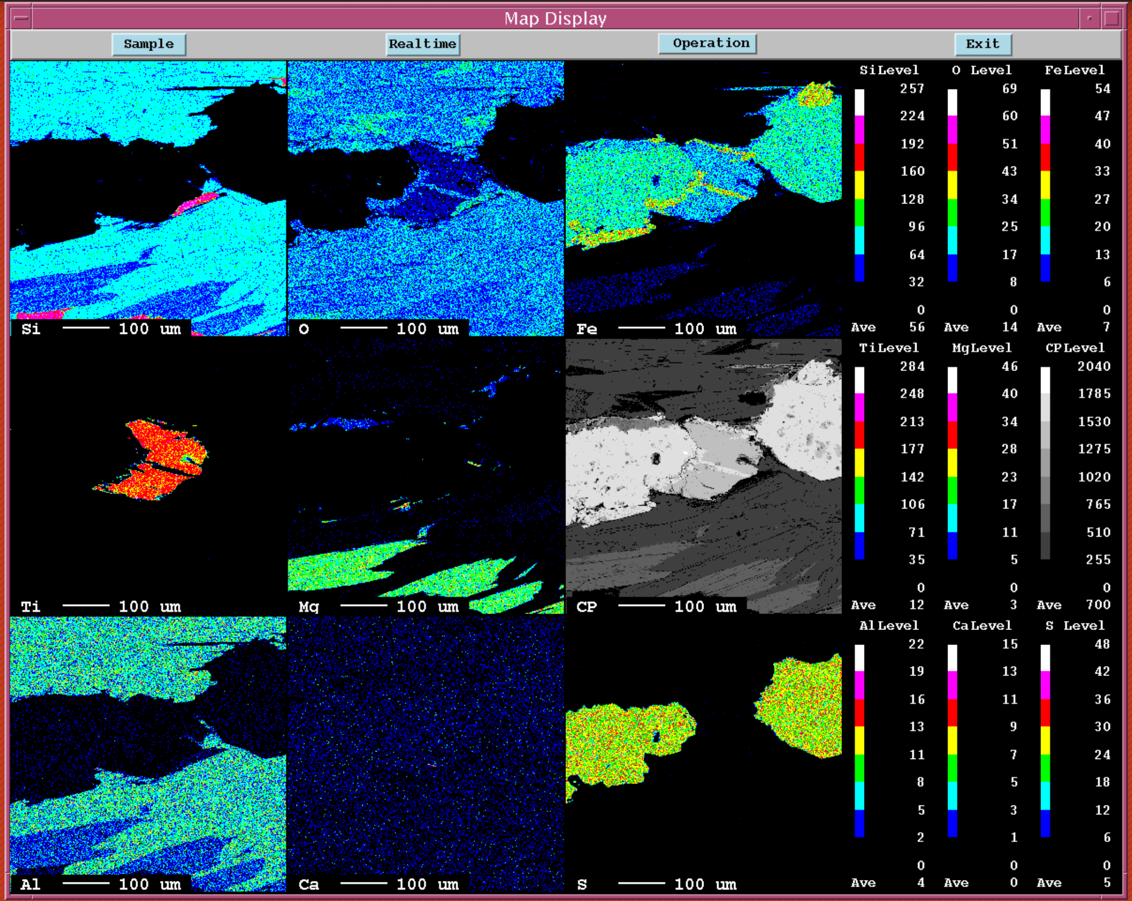
Image quality of x-ray maps

Two factors:

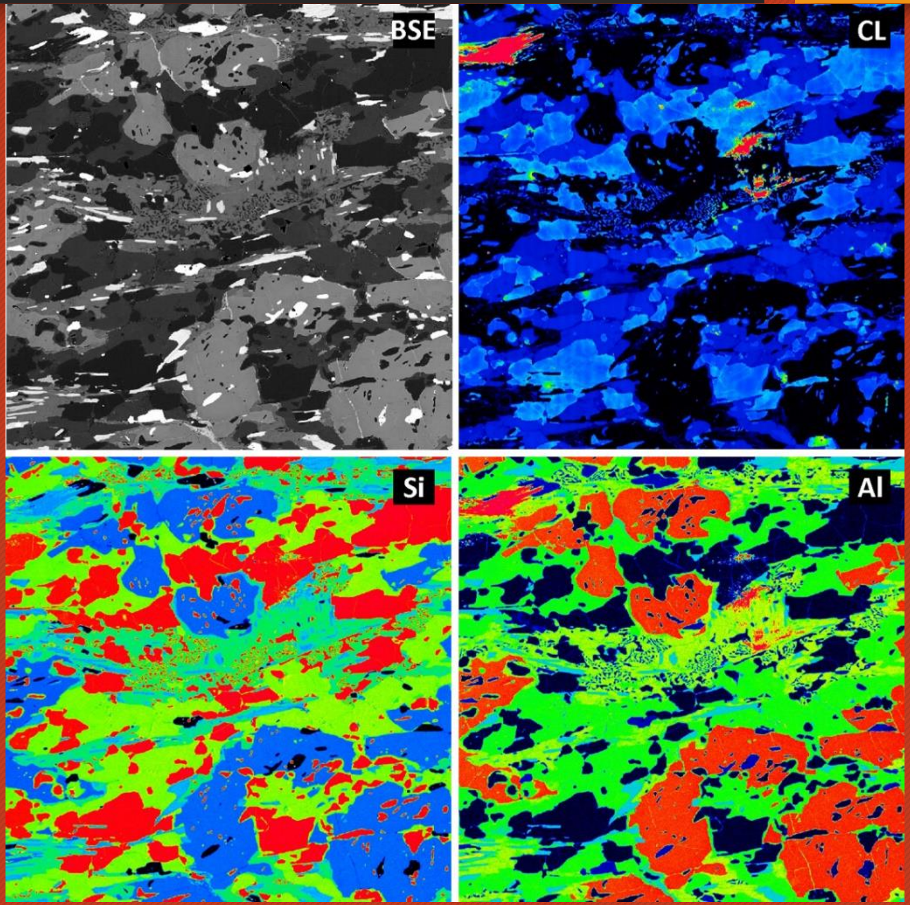
- Image resolution:
  number of points measured within the imaged area

- X-ray Signal:
  beam current and counting (dwell) time per point

Simultanous mapping with different signals



Combined BSE, WDS and EDS X-ray mapping



Combined BSE, CL and X-ray mapping