Handheld and portable X-ray Fluorescence spectrometers: Conceptual design, Qualitative analysis, advantages and limitations

Andreas Karydas

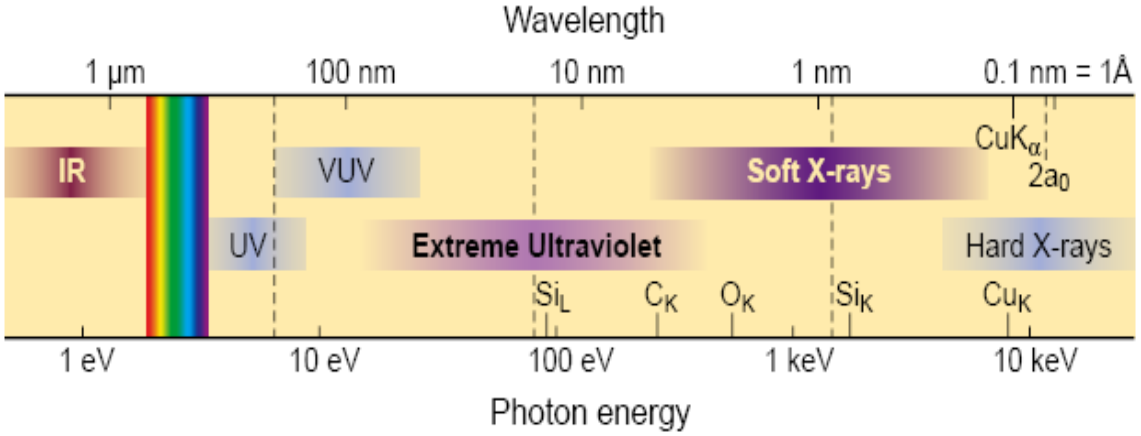
Institute of Nuclear and Particle Physics
NCSR "Demokritos"
Agia Paraskevi
Athenss, Greece

karydas@inp.demokritos.gr

Outline

- Principles of XRF analysis
- Qualitative analysis
- X-ray instrumentation: Sources, Detectors, optics
- Optimization of Hand-held/portable XRF analysis

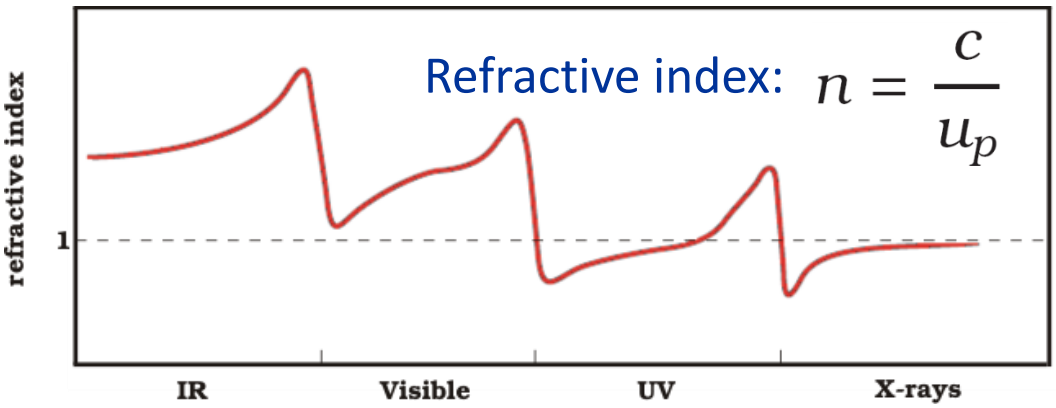
Basic properties of X-rays



X-Ray Regime of Energies - Wavelengths:
0.2 keV - 98 keV
→ 40 Å - 0.13 Å

$$E(keV) = \frac{12.398}{\lambda(\text{Å})}$$

E: energy (keV)
λ : wavelength (Å)

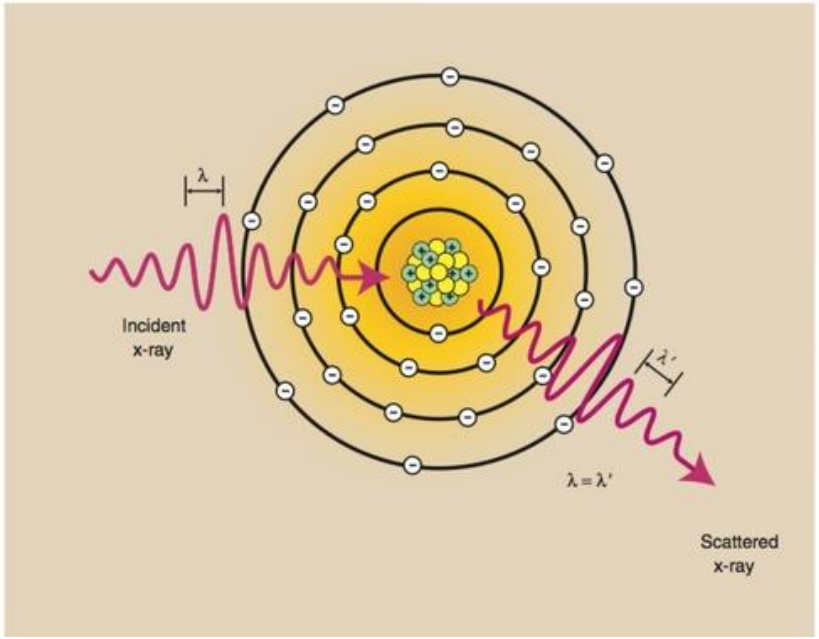


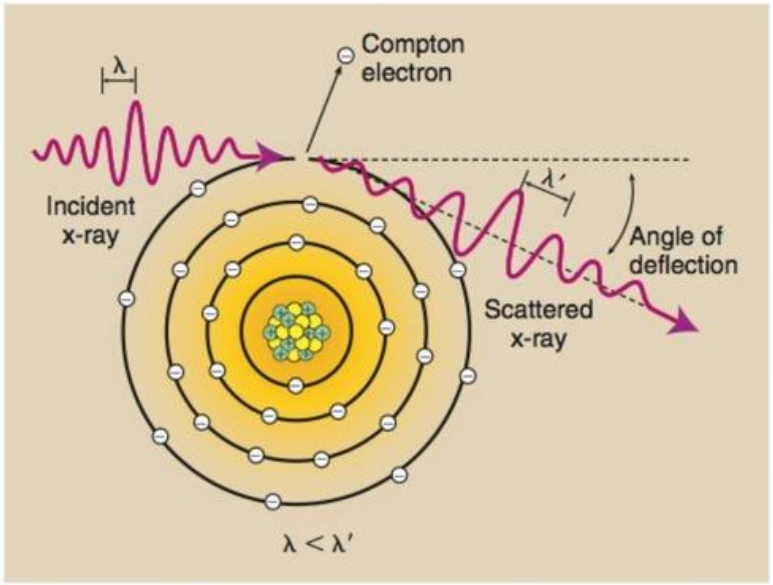
Refractive index: $n = \frac{c}{u_p}$

$$n = 1 - \delta + i\beta$$

$i\beta$ → attenuation term
δ → phase term

X-ray Scattering Interactions with atoms



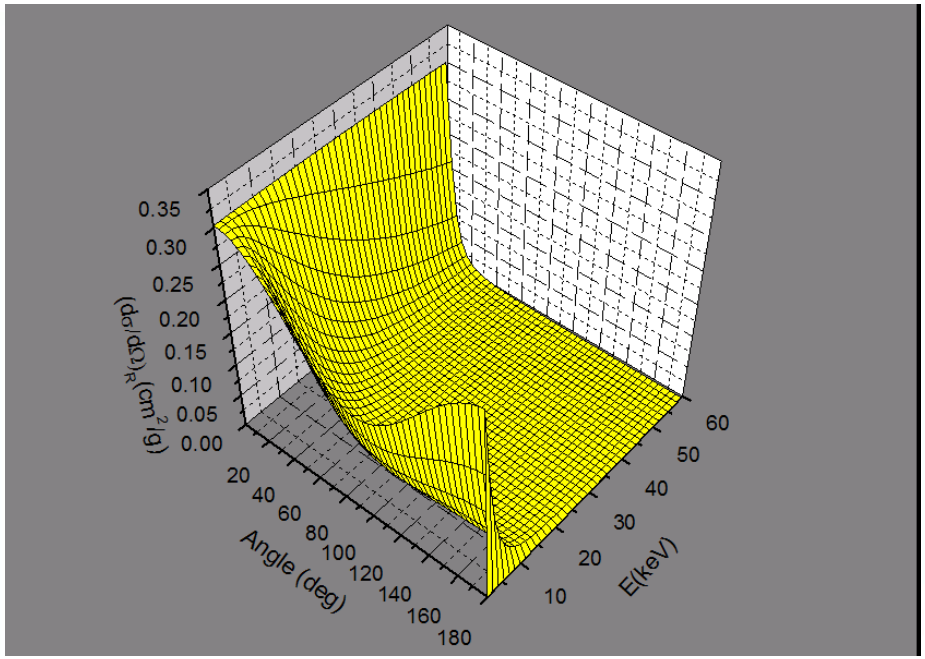


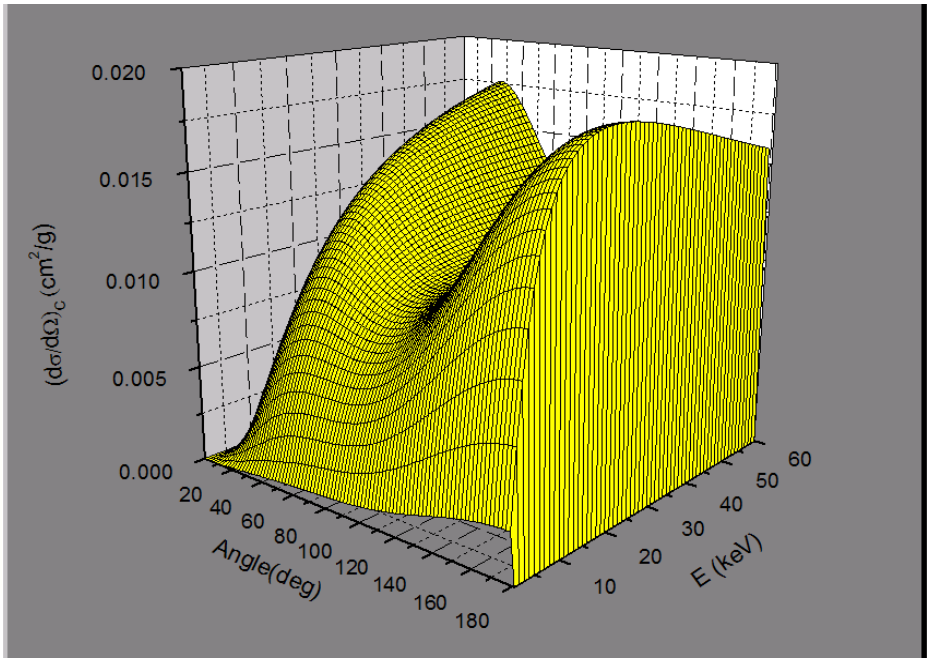
***E_i=E_0* : Coherent (Rayleigh),**
it occurs mostly with inner-shell atomic electrons

$E_i < E_0$: Incoherent (Compton),
it occurs mostly with outer, less bound electrons

E_0>>Binding Energy

X-ray Scattering Interactions with atoms



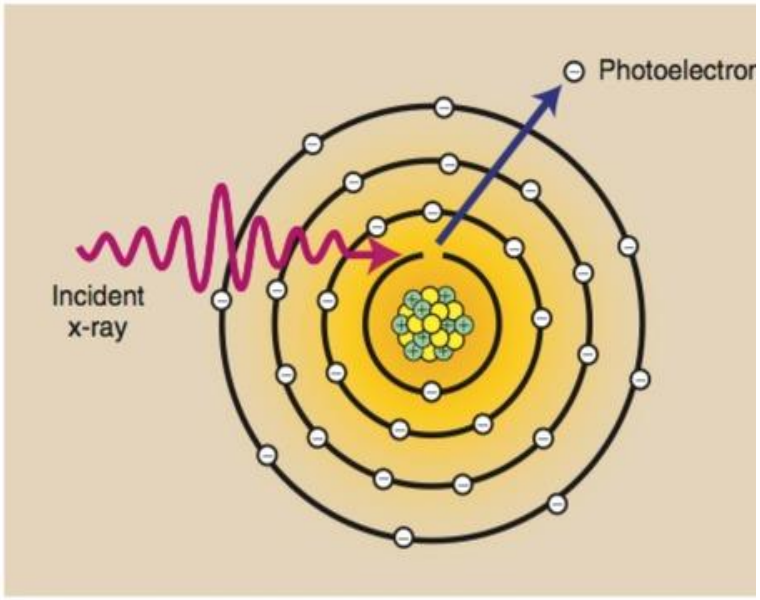


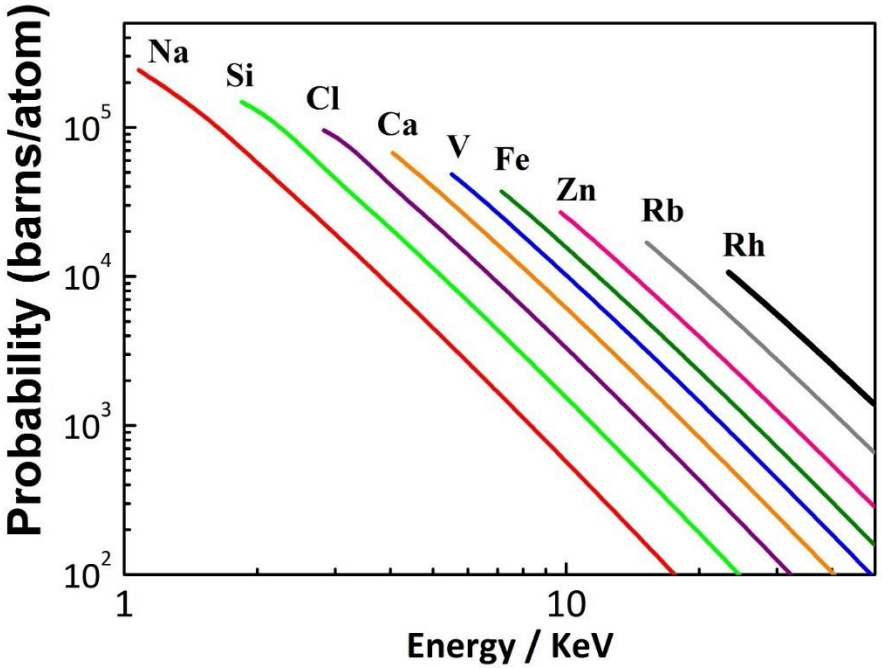
***E_i=E_0* : Coherent (Rayleigh),**
it occurs mostly with inner-shell atomic electrons

$E_i < E_0$: Incoherent (Compton),
it occurs mostly with outer, less bound electrons

E_0>>Binding Energy

Photoelectric interaction





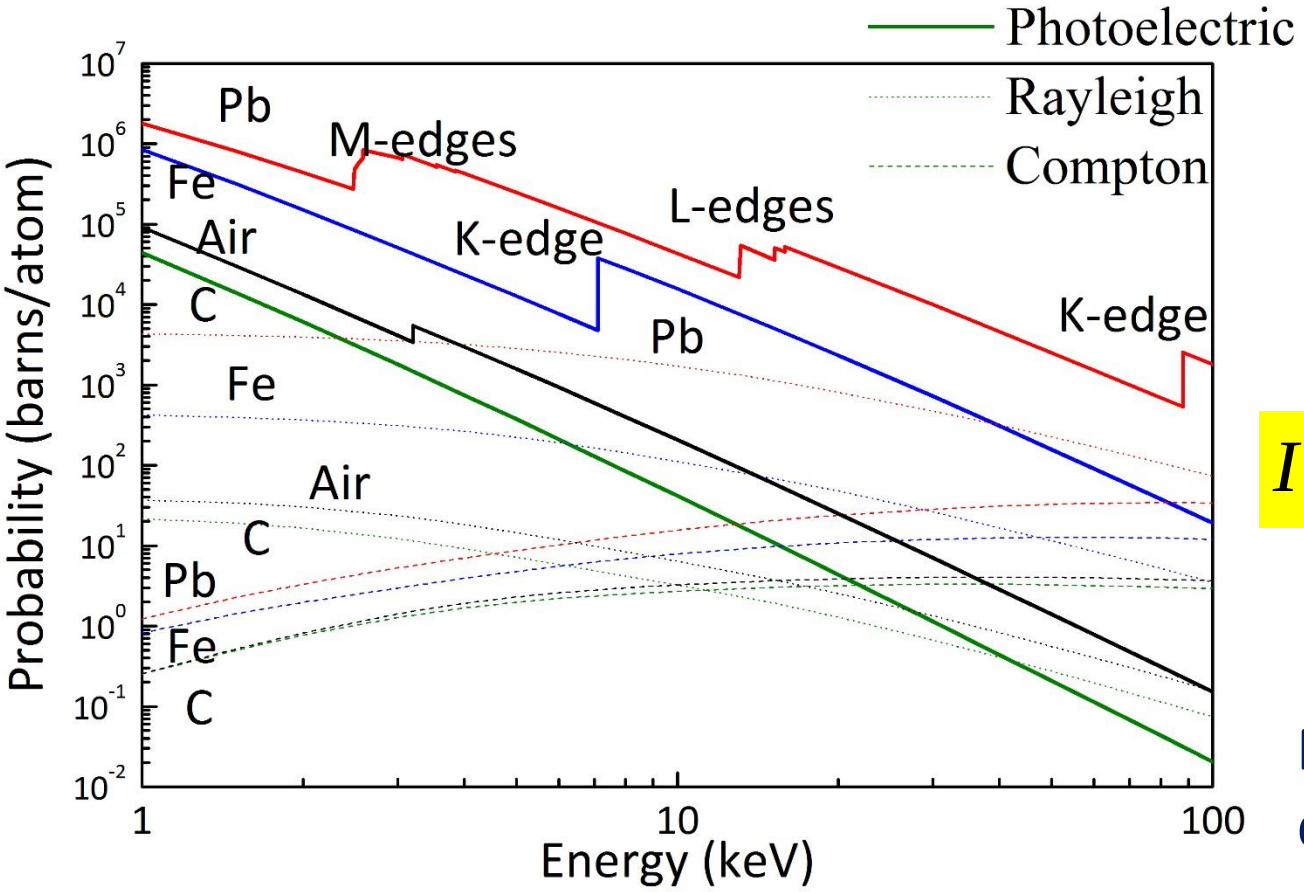
Basic Condition: E_0 >= Binding energy of the inner-shell electron

Photoelectric cross section:

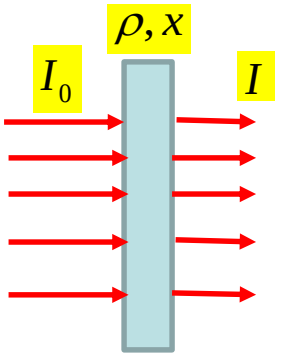
$$\tau \sim E^{-3.5}$$

$$\tau \sim Z^{3\ to\ 4}$$

X-rays interactions with matter



Beer-Lambert law

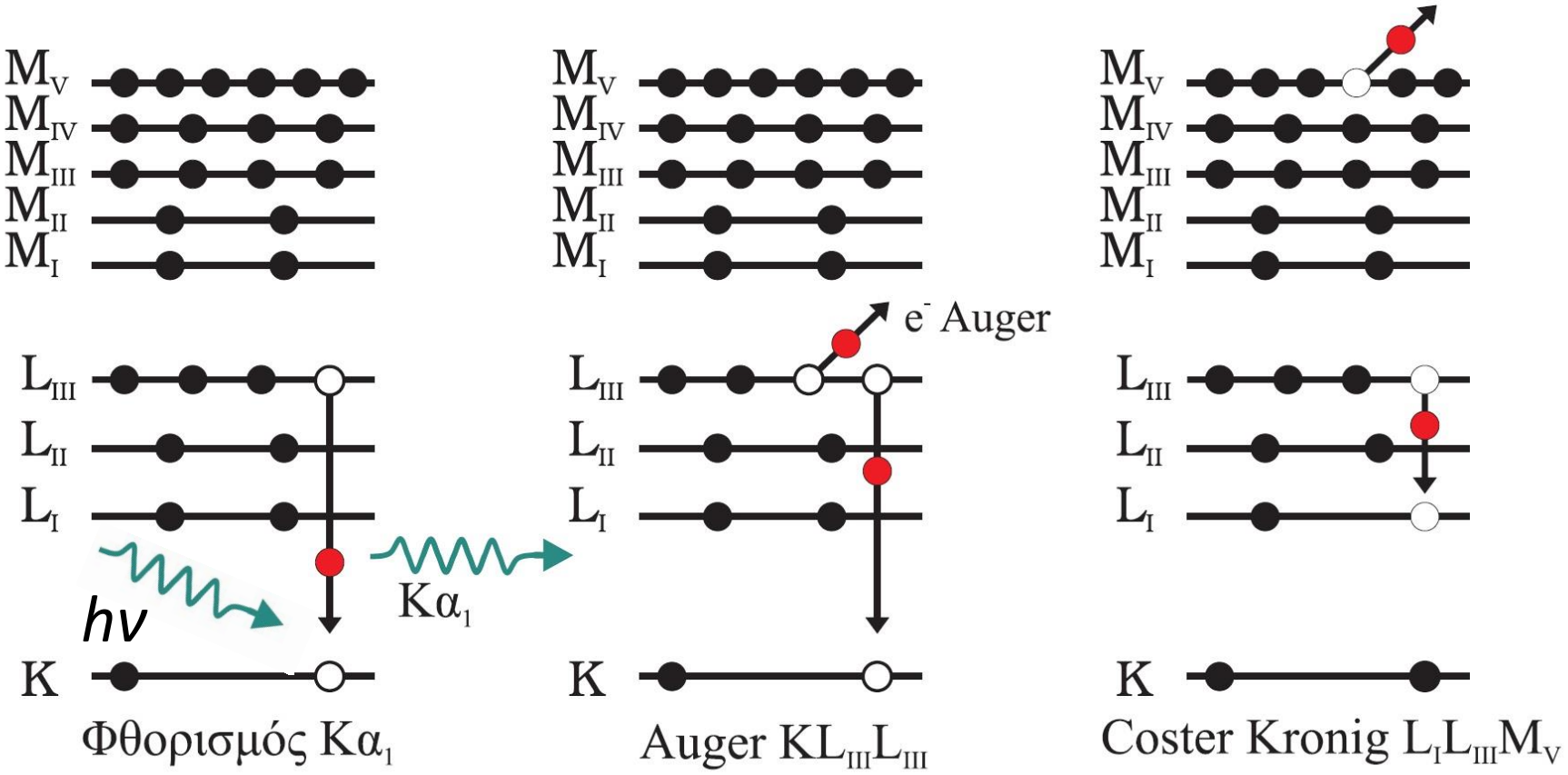


$$I = I_0 \cdot e^{-(\tau+\sigma_R+\sigma_C)\cdot\rho\cdot x}$$

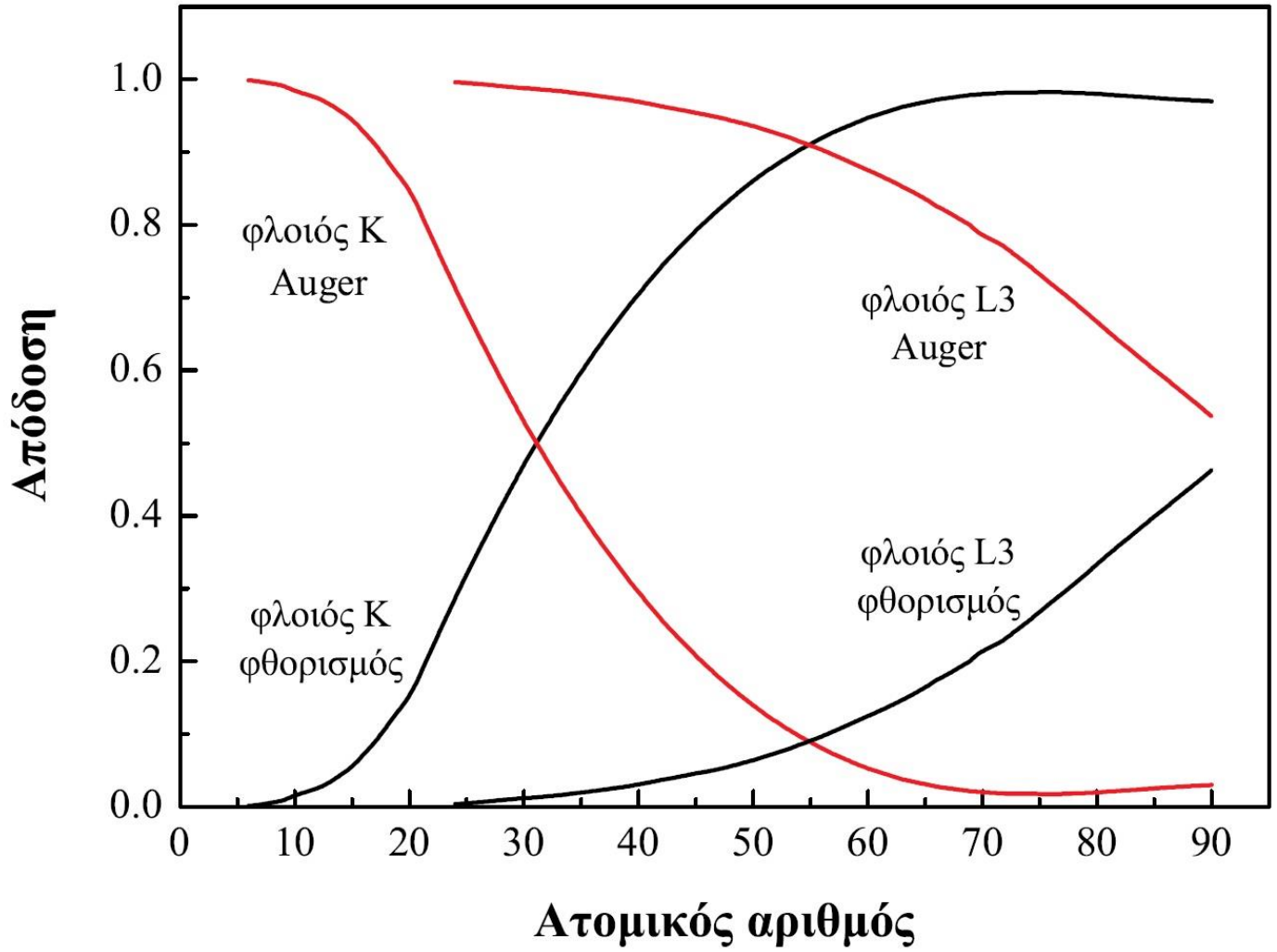
Ratio photo./scat.
≈ **1000 - 10000**

Photoelectric is the dominant process

Atomic Relaxation



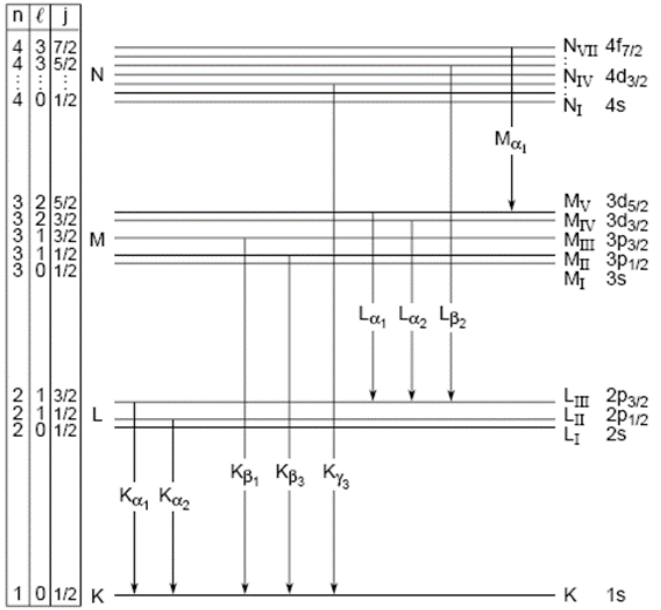
Fluorescence probability



Example: The fluorescence probability for Si is almost 5%, only 5 holes decay through emission of fluorescence K radiation over 100 primary ionizations

Emission of element ‘characteristic’ x-rays

The emission of characteristic X-ray lines follows allowed electronic transitions between specific subshells



Siegbahn/IUPAC notation:

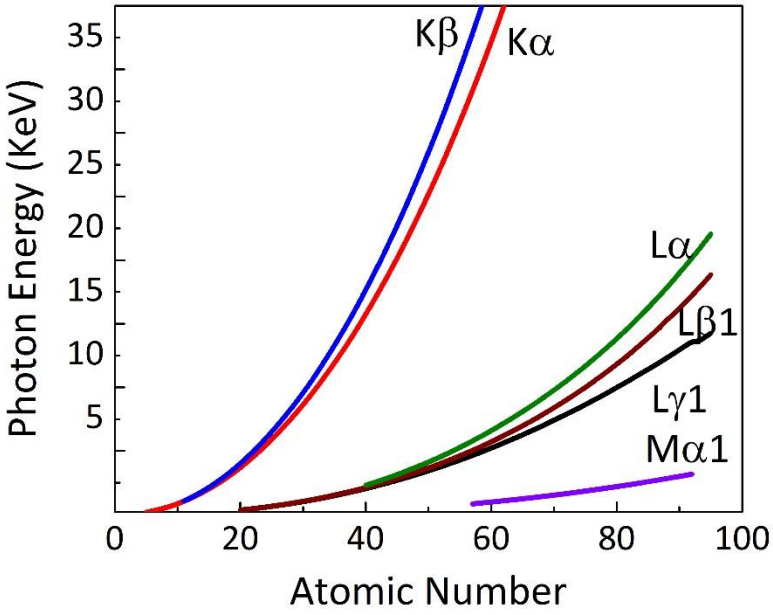
Kα: K-L2+K-L3

Kβ: K-M2+K-M3

Lα: L3-M4+L3-M5

$L\beta_1$: L2-M4

$L\beta_2$: L3-N5



Moseley law: $E_{ij} = k_{ij} \cdot (Z - \sigma_i)^2$

L_{III} to K shell: $E_{K\alpha 1} = U_K - U_{LIII}$

Unique set of emission energies for each element

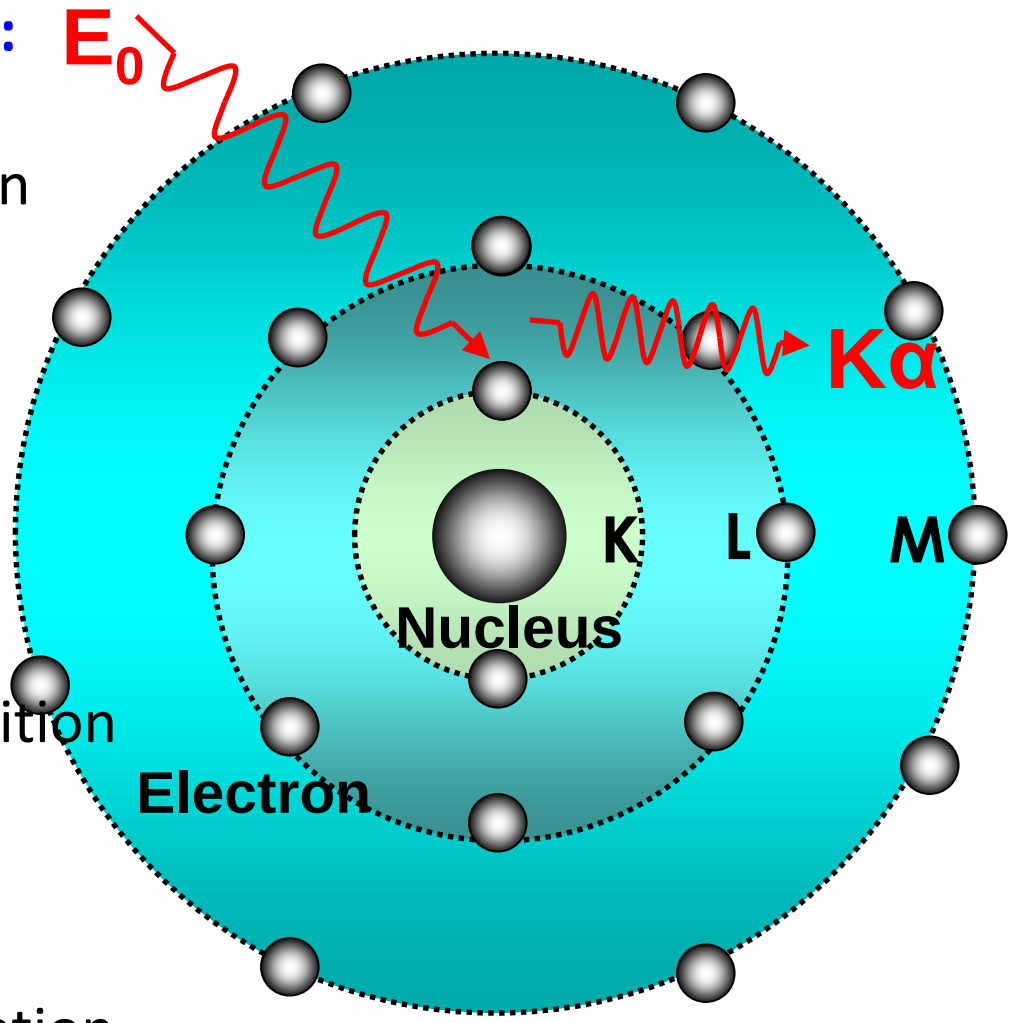
X-ray spectroscopy within the energy range 1-30keV offers in principle the possibility to detect all the periodic table elements through their K, L or even M series of characteristic X-ray lines

Working principle: X-Ray Fluorescence

Working principle:

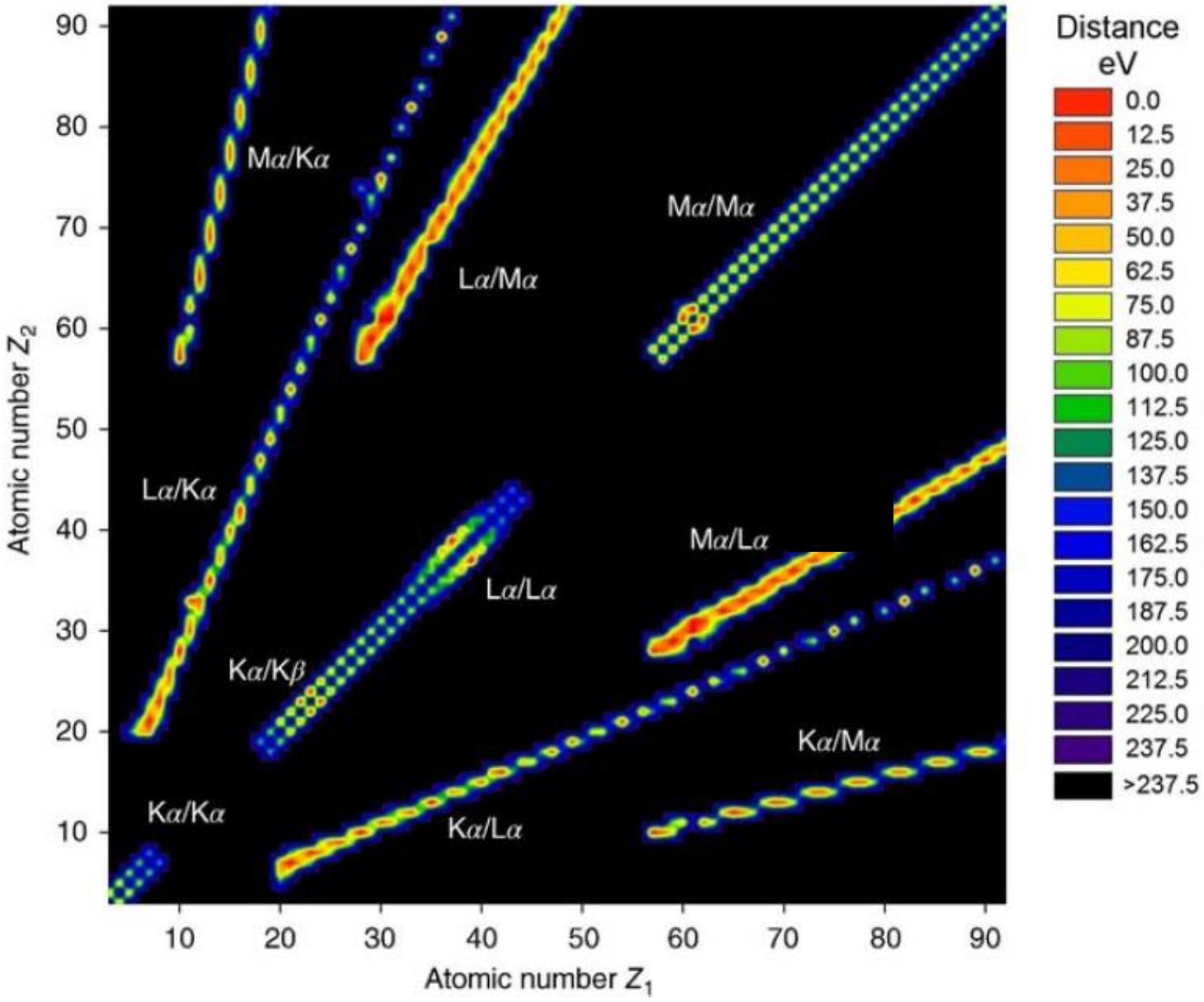
1) Photo-Ionization of **atomic bound electrons** (K, L, M) /**Photoelectric absorption**

2) Electronic transition and emission of element '**characteristic**' **fluorescence** radiation



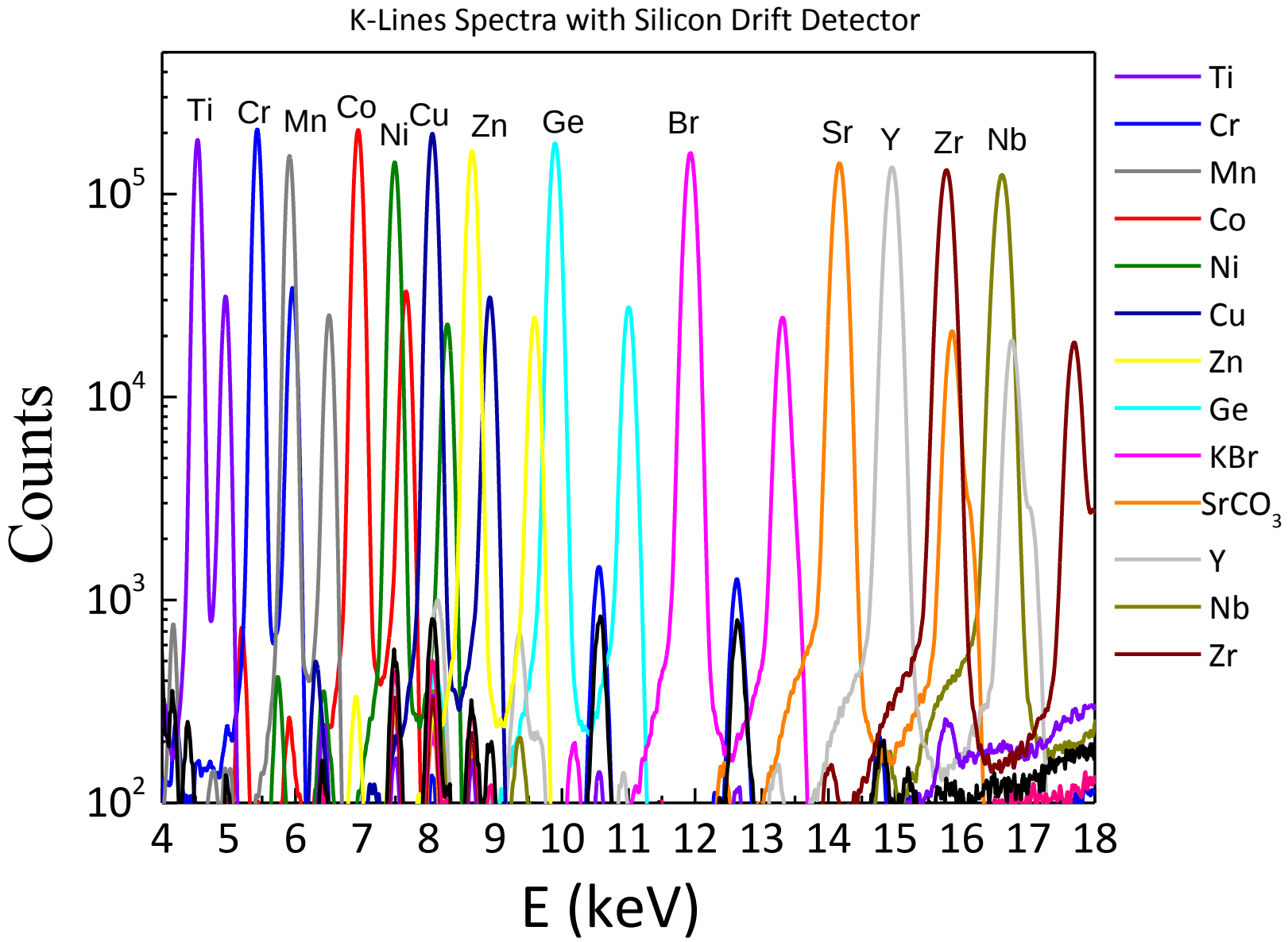
Incident photon Energy E_0 should be adequate to ionize the atomic bound electrons E_0 >= Inner shell binding energy

Spectral interferences in XRF analysis

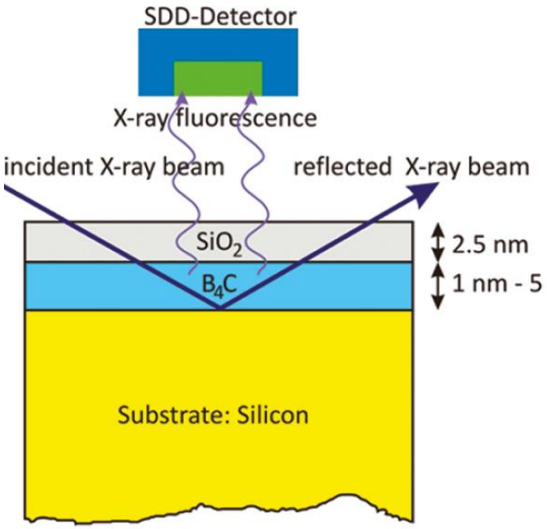


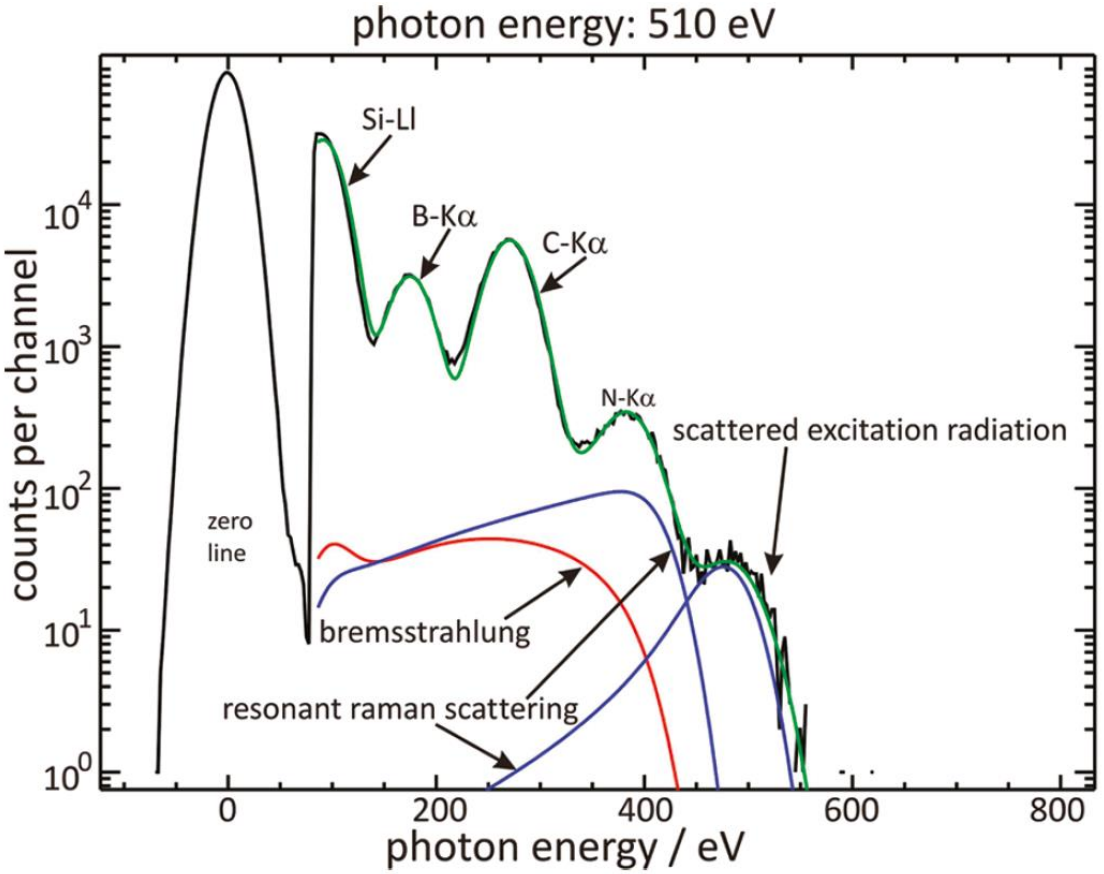
Total-Reflection X-Ray Fluorescence Analysis and Related Methods, and Reinhold Klockenkämper, Alex von Bohlen

XRF multielemental analysis: K-lines



Low Z XRF element analysis (down to Boron)

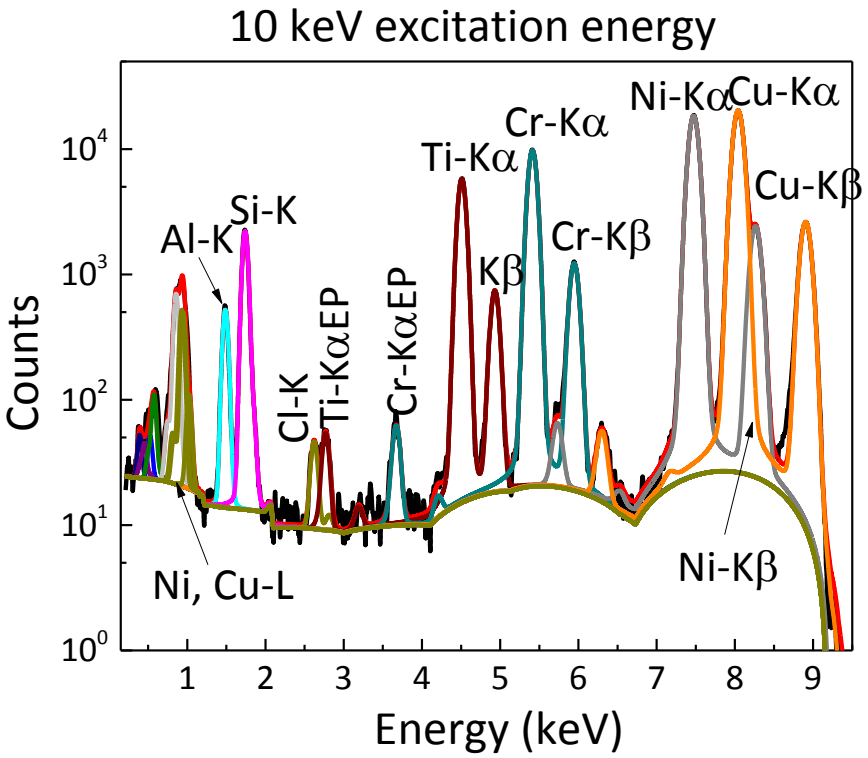


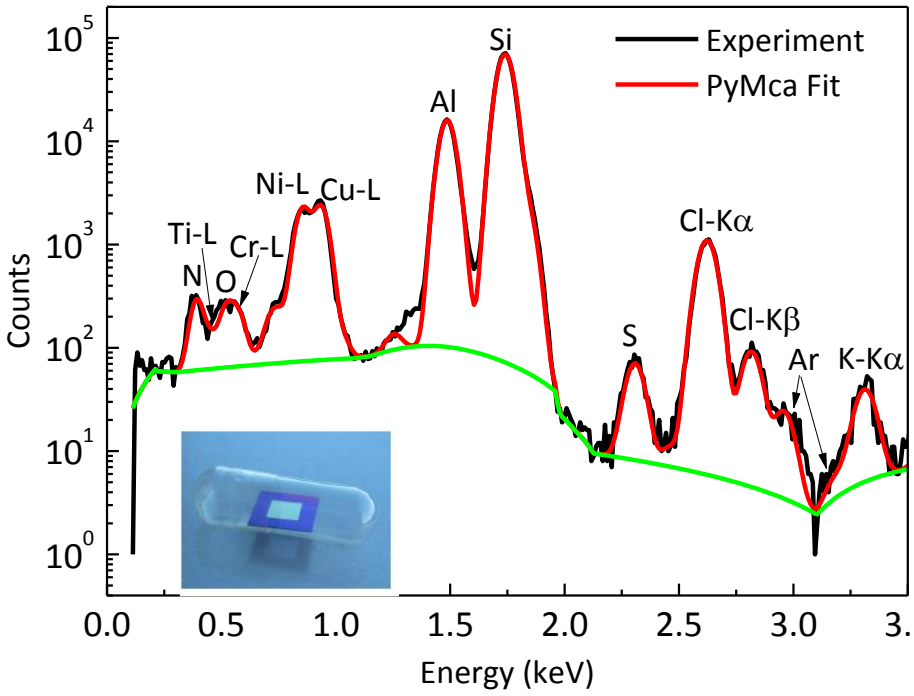


Unterumsberger et al., dx.doi.org/10.1021/ac202074s, Anal. Chem. 2011, 83, 8623–8628

XRF spectra of nano-layered systems

Cr/Al/Ni/Cu/Ti/ onto Si_3N_4 200 nm, each layer about 10 ug/cm^2, ~10-40nm

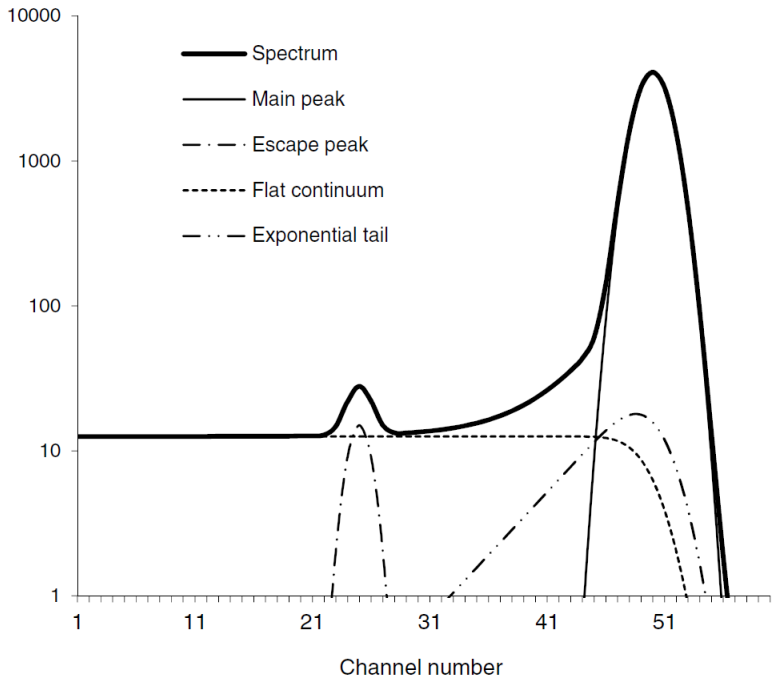


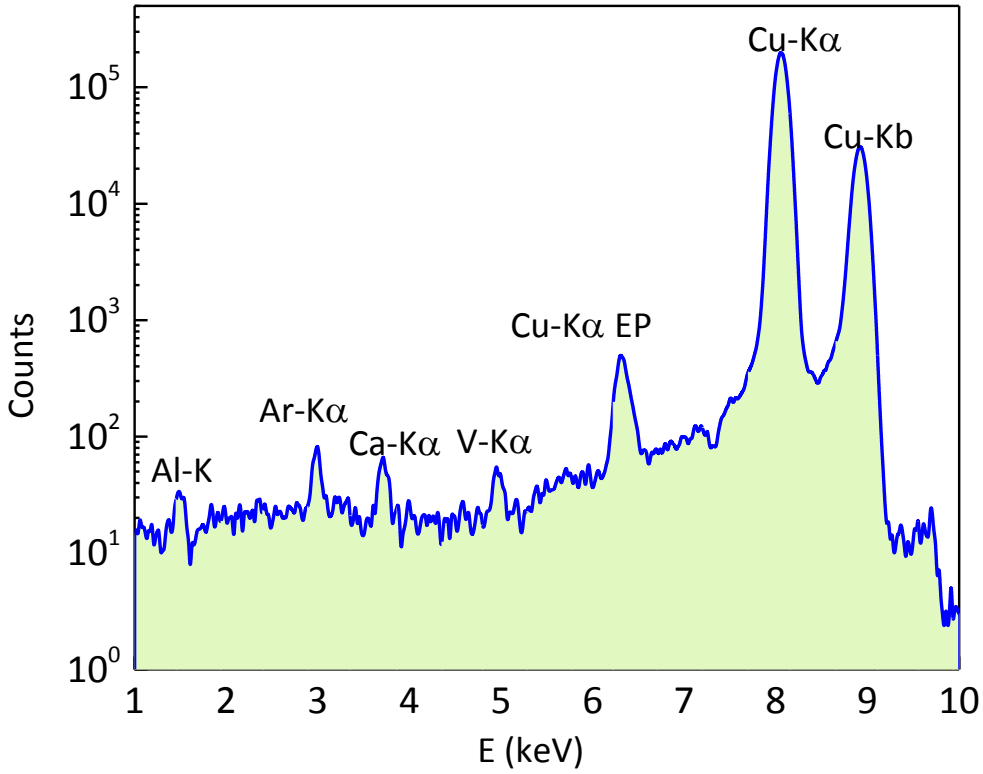


Spectra measured at Elettra Sincrotrone Trieste, XRF beamline

Karydas et al., Journal of Synchrotron Radiation, (2018). 25, 189–203

Detector Response function





Peak shape of characteristic X-ray lines: Gaussians with tails and continuum

XRF Analytical Sensitivity

LoD: Limit of Detection

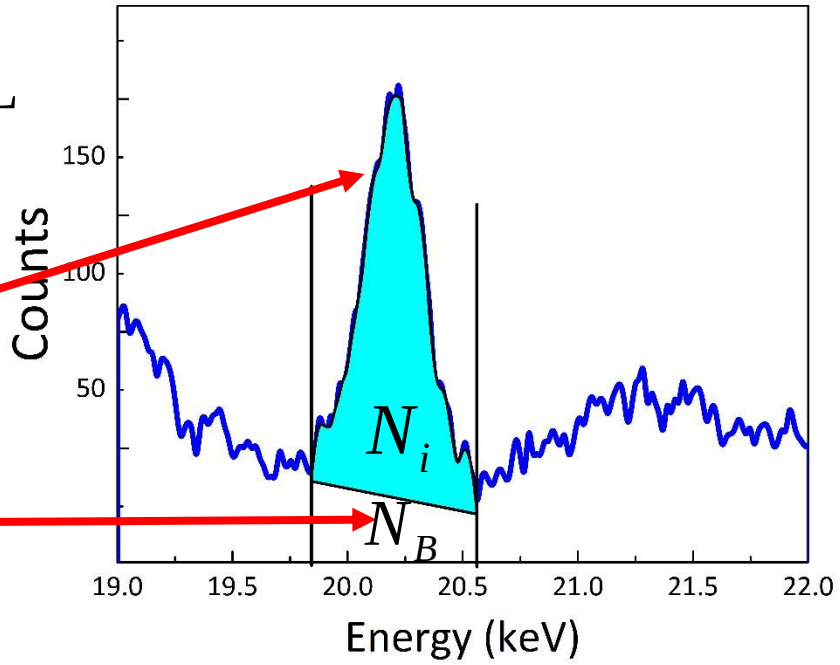
$$(LoD)_i \approx 3 \cdot c_i \cdot \frac{\sigma_i}{N_i} \quad (95\%)\ \text{CL}$$

$$\sigma_i \approx \sqrt{N_B}$$

I_i Fluorescent intensity (cps)

I_B Background intensity (cps)

c_i Analyte concentration



$$(LoD)_i \approx 3 \cdot \frac{\sqrt{I_B / t}}{(I_i / c_i)} \propto \frac{\sqrt{t}}{t}$$

$$LoQ \approx 3.3 \cdot LoD$$

XRF Information depth

Material	X-ray line	D (μm)
Bronze 95% Cu, 5% Sn	Cu-Kα	10
	Sn-Kα	32
Gold 95% Au, 4.5 % Ag, 0.5% Cu	Cu-Kα	1.4
	Au-Lα	2
	Ag-Kα	5
Egyptian Blue 20% + 80% binder	Cu-Kα	270
	Ca-Kα	37
	Si-Kα	6

The information depth depends on:

- the sample matrix composition
- analyte energy
- incident beam energy (spectrum)
- geometry (incident/outgoing angles)

Critical thickness

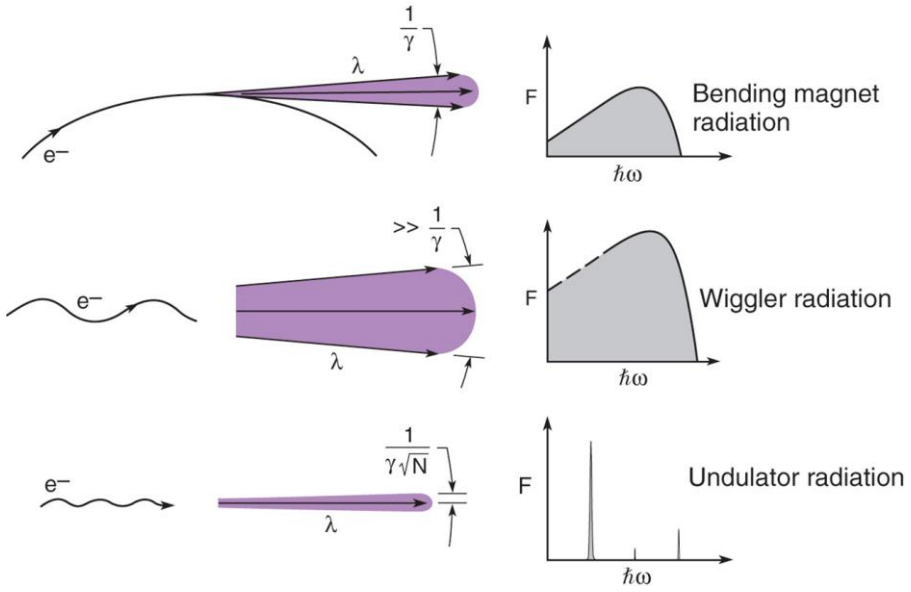
$$D = \frac{1}{\rho \cdot \mu_T(E_i)}$$

$$\mu_T(E_o, E_i) \equiv \mu_s(E_o)/\sin\vartheta_1 + \mu_s(E_i)/\sin\vartheta_2$$

X-ray sources

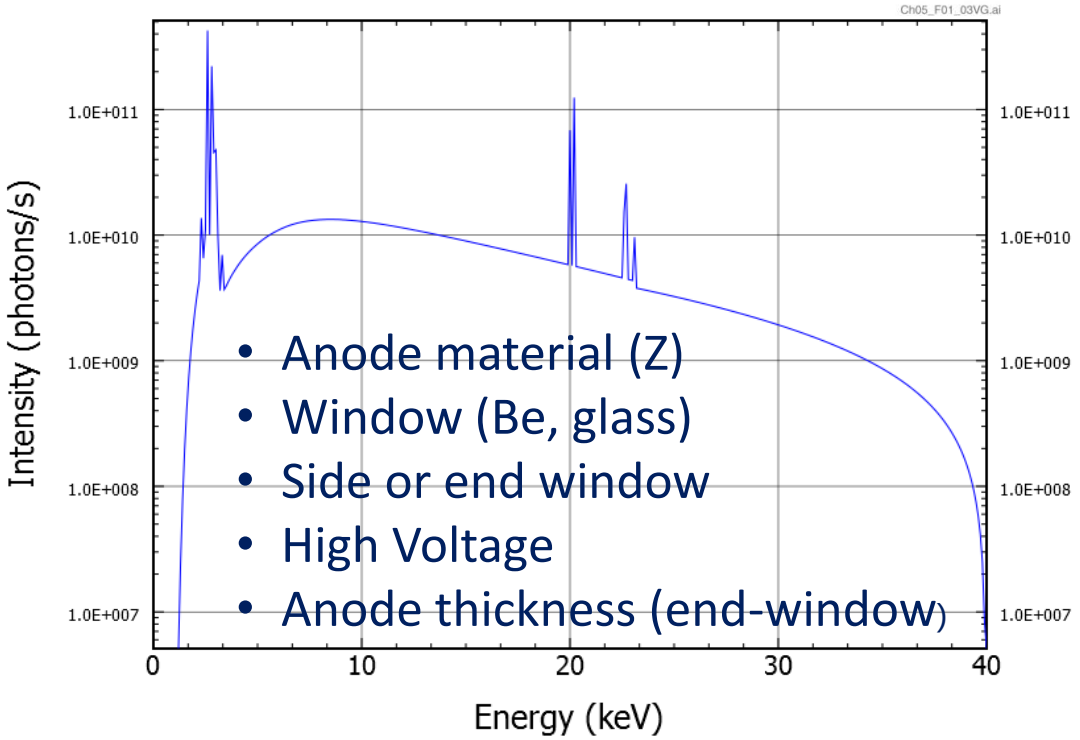
Synchrotron radiation

High brilliance, low divergence, high polarization: Micro/Nano-XRF (< 1µm)

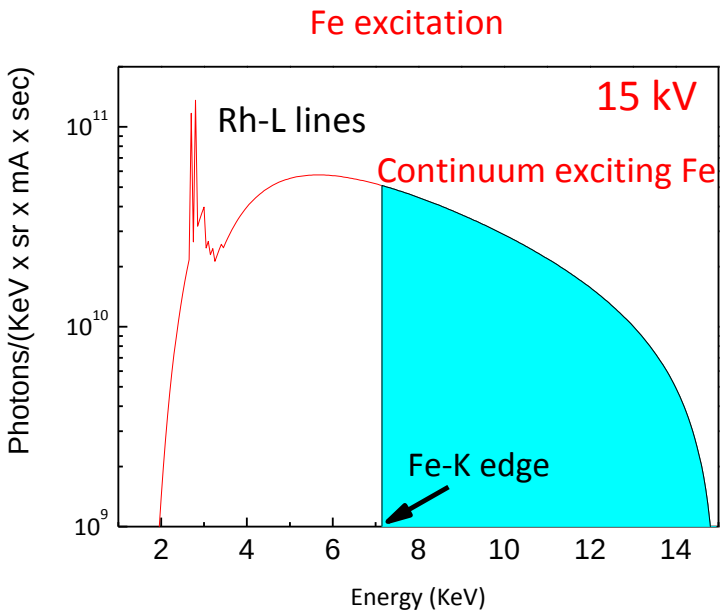


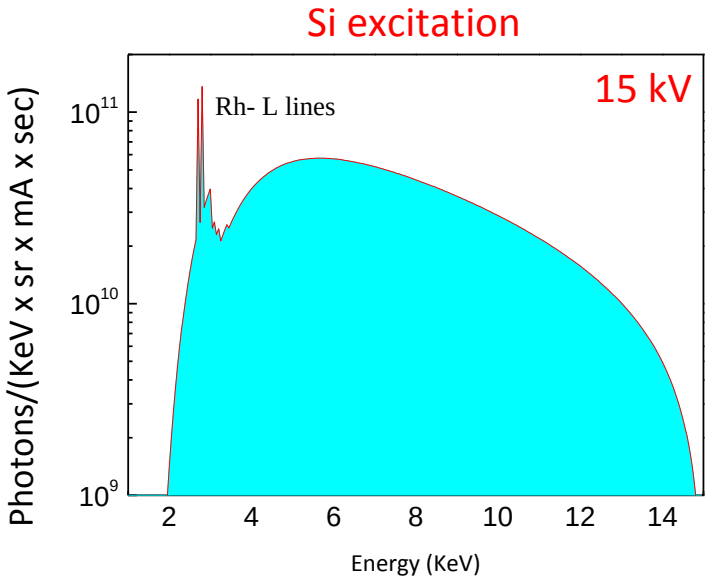
X-ray tubes

- High power (~ kW) diffraction x-ray tubes
- Micro focus (~ 50-100µm) anode size - Brilliance optimised (30-50 W (air cooled)
- Miniature X-ray tubes – geometry optimized (2W-12W, 50kV)

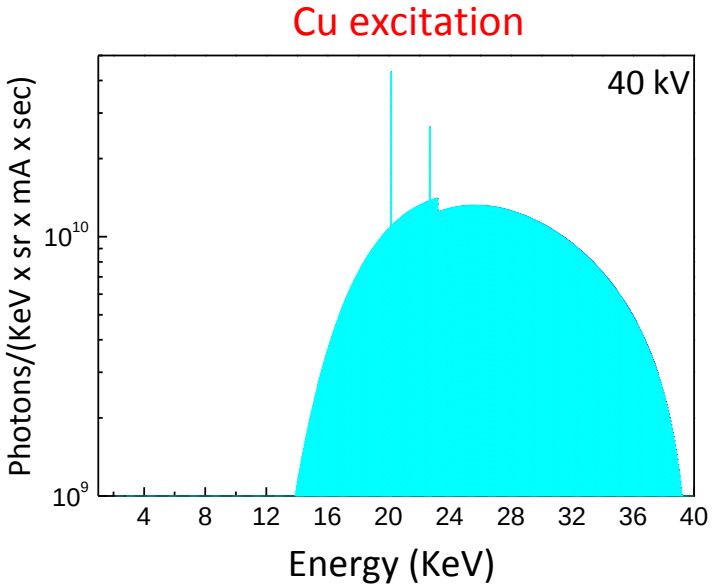


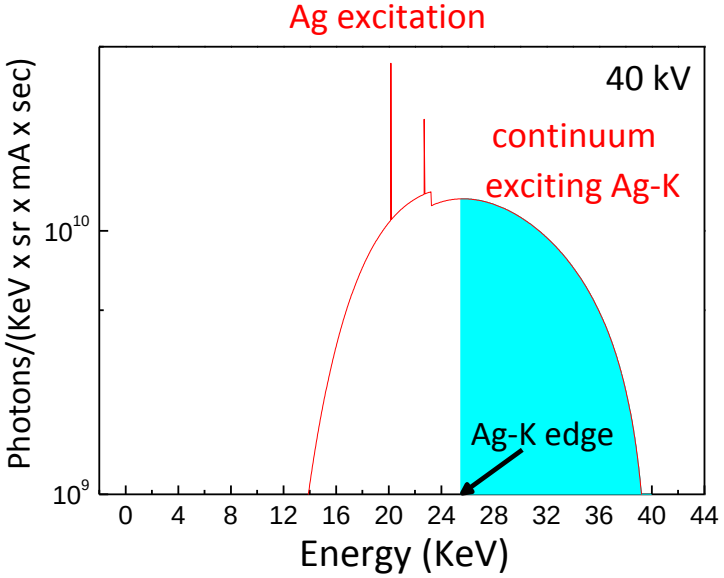
Tube excited XRF analysis





15 kV
Unfiltered

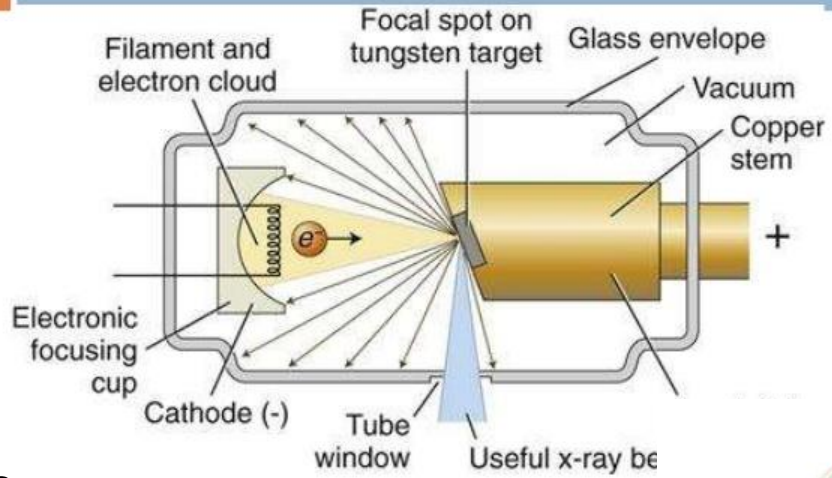




40 kV
Filtered

XRF instrumentation: X-ray Sources-Detectors

Oxford Model: XTF5011

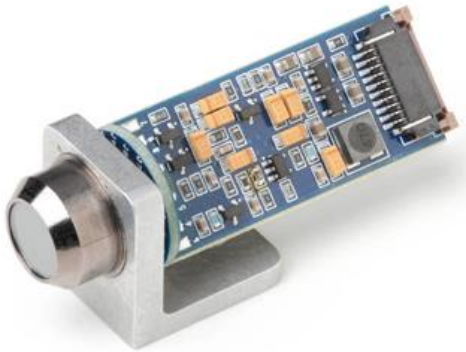


Anode materials: Rh, Ag, Mo
Focus spot size 50-150 µm
Exposure < 0.5 mR/hr

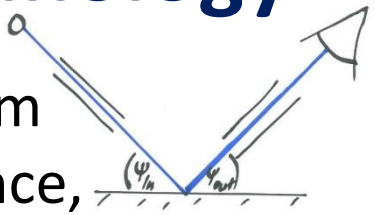
Newton M47, 50kV 10W
X-ray Source, 400 grs

Moxtek end/side window tubes, 10W, 50kV

Miniature X-ray detector



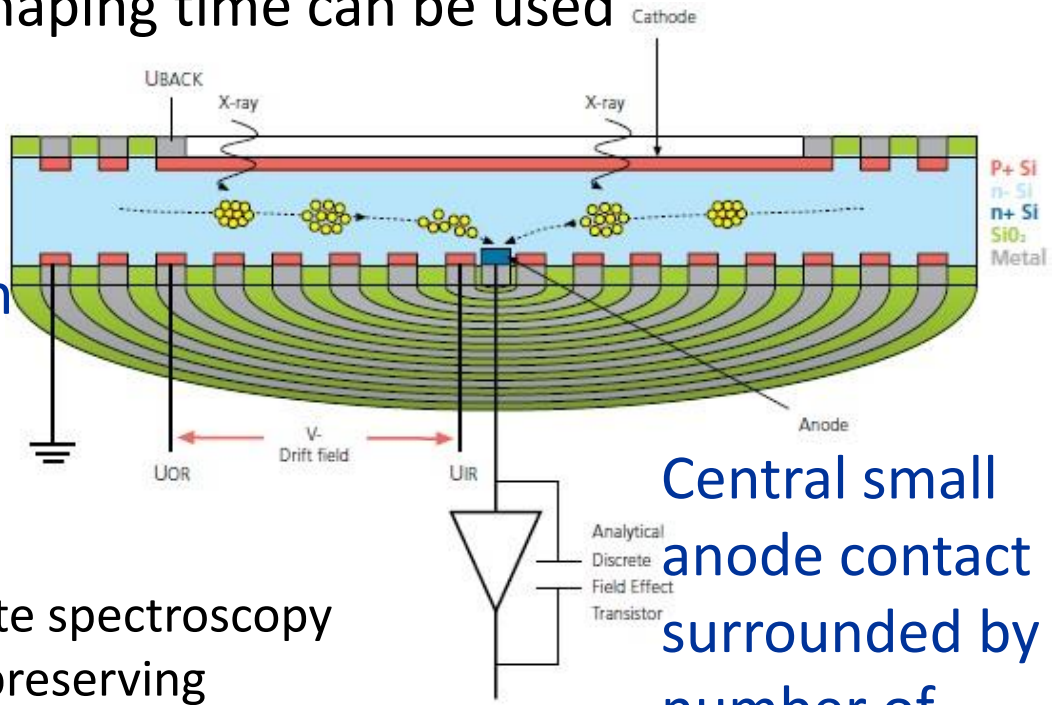
Energy Dispersive Detector's technology



Silicon Drift Detector - Principle: The charge is drifted from a large area into a small read-out node with low capacitance, independent of the active area of the sensor. Thus, the serial noise decreases and shorter shaping time can be used

Two advantages:

1) Faster counting is enabled
2) Higher leakage current can be accepted, drastically reducing the need for cooling



Central small anode contact surrounded by a number of concentric drift electrodes

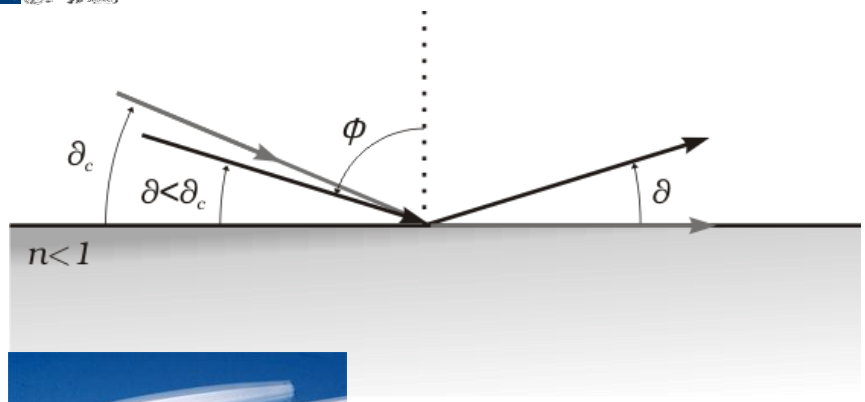
CUBE preamplifier supports high-rate spectroscopy in XRF mapping applications, while preserving enough energy resolution at shorter shaping times. The use of short peaking times further reduces the impact of the detector leakage current on the total noise. Room temperature operation!

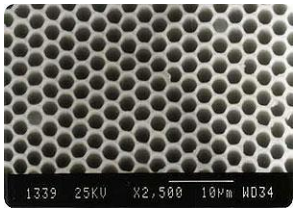
Figure from Oxford Instruments Manual

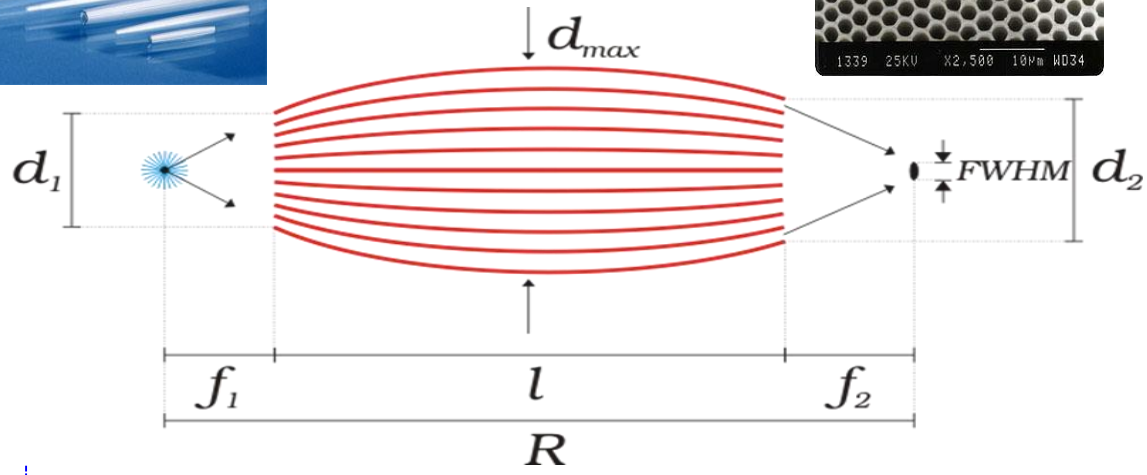
X-ray Optics in XRF analysis: Focusing

$$n \approx 1 - \delta \qquad \vartheta_{crit} = \sqrt{2\delta}$$

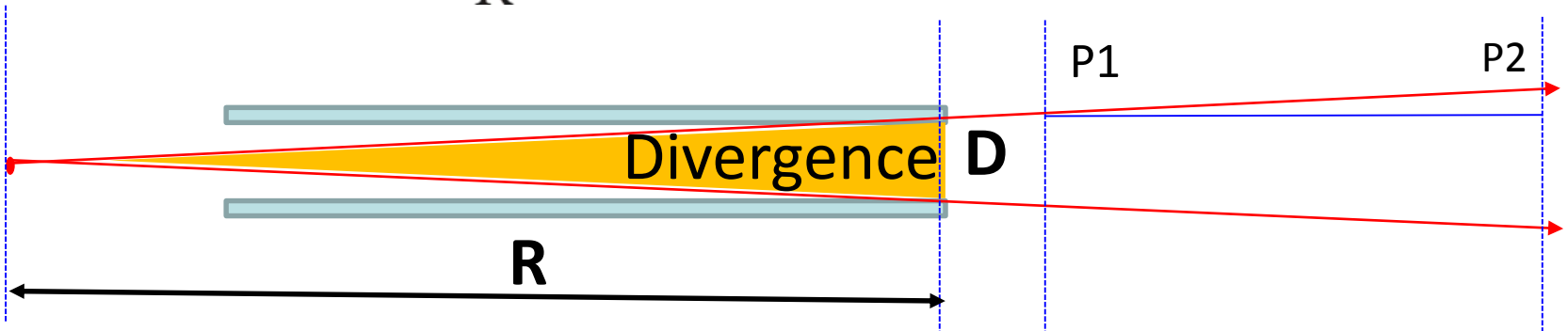
$$\vartheta_{crit}(degrees) \approx \frac{1.651}{E(keV)} \sqrt{\frac{Z}{A}\rho\left(\frac{g}{cm^3}\right)}$$





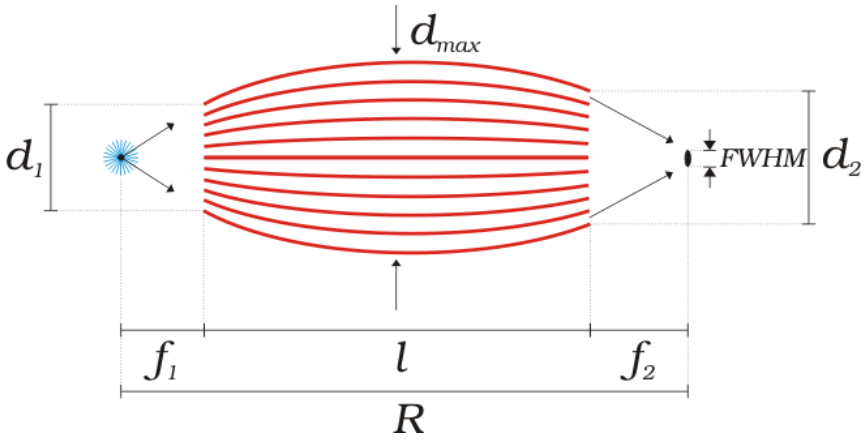


- Polycapillary full lens
- Collimator
- Curved crystals

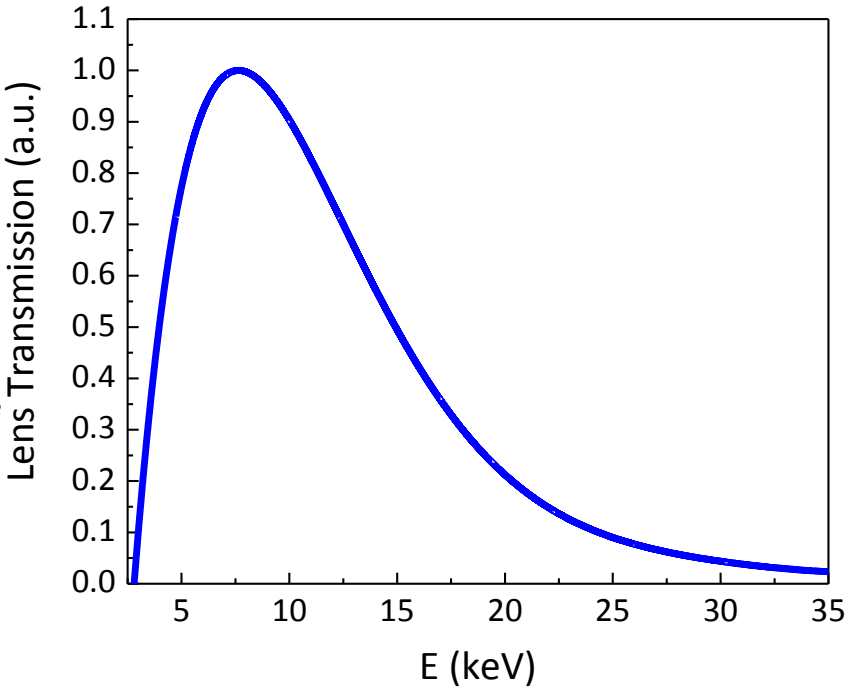


Characteristics of Polycappilary X-ray lenses

- Spot size –FWHM (E)
- Gain Factor – G(E)
- Focal distance



Lens Transmission efficiency

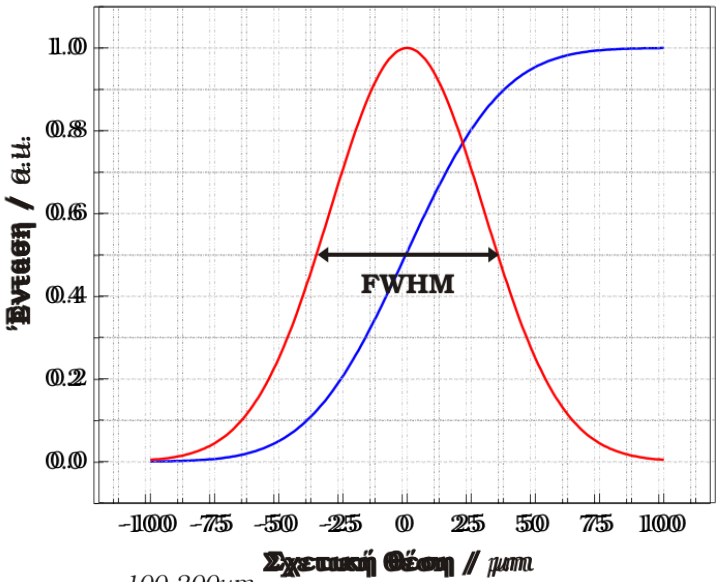


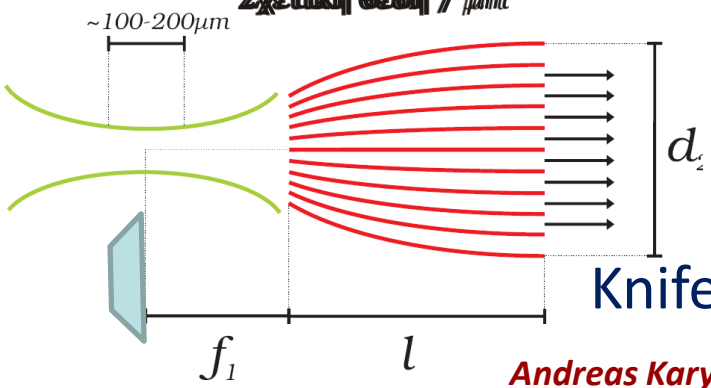
$$G(E) = \frac{\Phi_{lens}}{\Phi_{col}} = \frac{T(E) \cdot d_{in}^2 \cdot R^2}{\left[FWHM(E)\right]^2 \cdot f_1^{\,2}}$$

T(E)=transmission efficiency

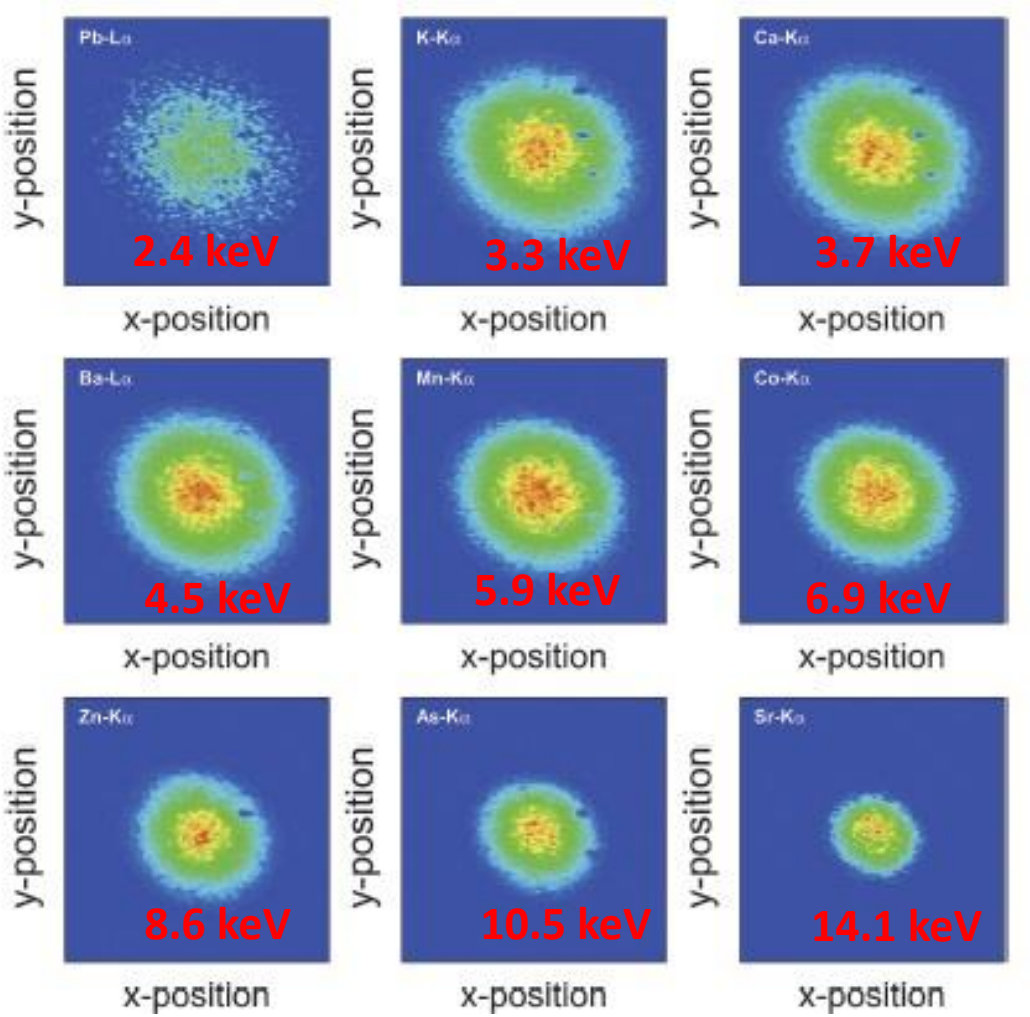
Characteristics of Polycappilary X-ray lenses

- Spot size –FWHM (E)
- Gain Factor – G(E)
- Focal distance



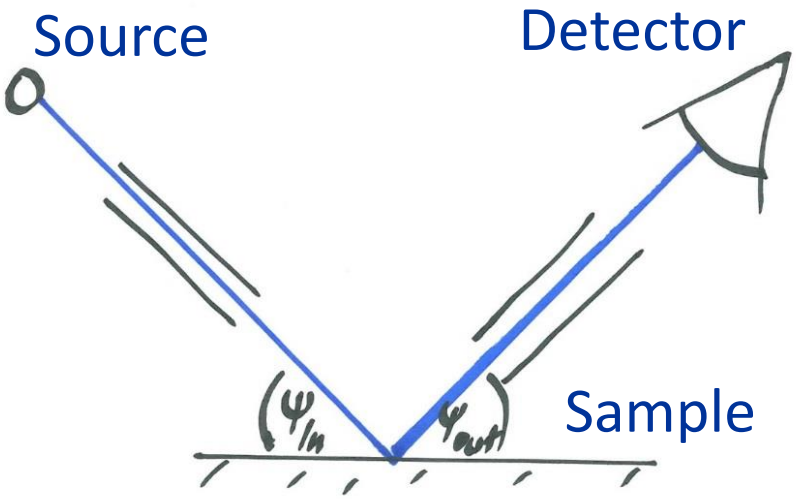


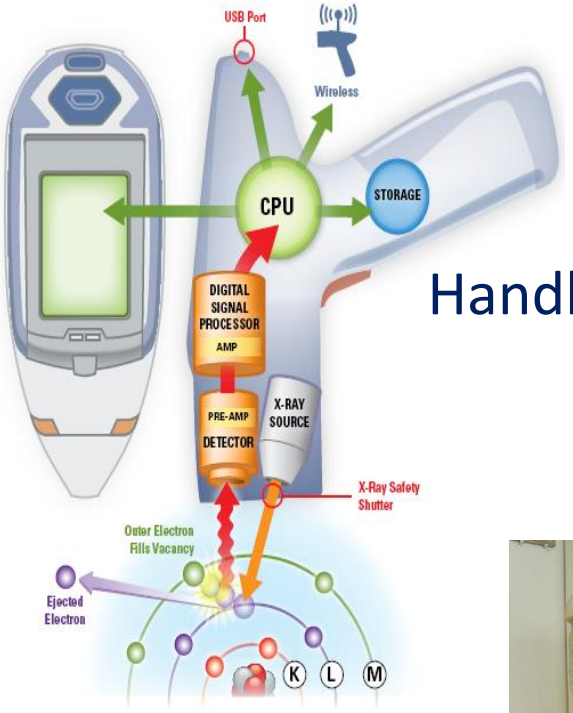
Knife edge scan



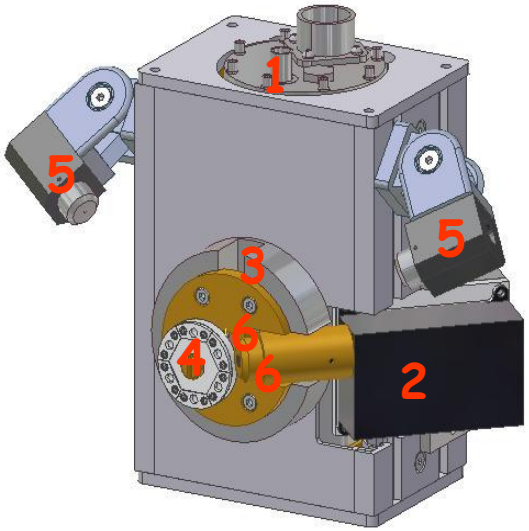
T. Wolff et al, JAAS, 2009 24 669

Portable milli-beam spot XRF spectrometer

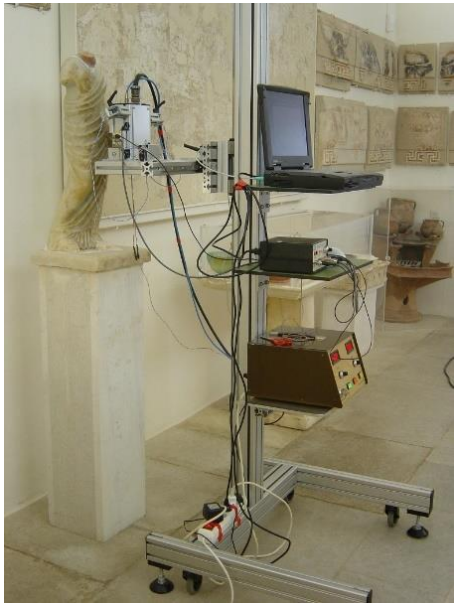




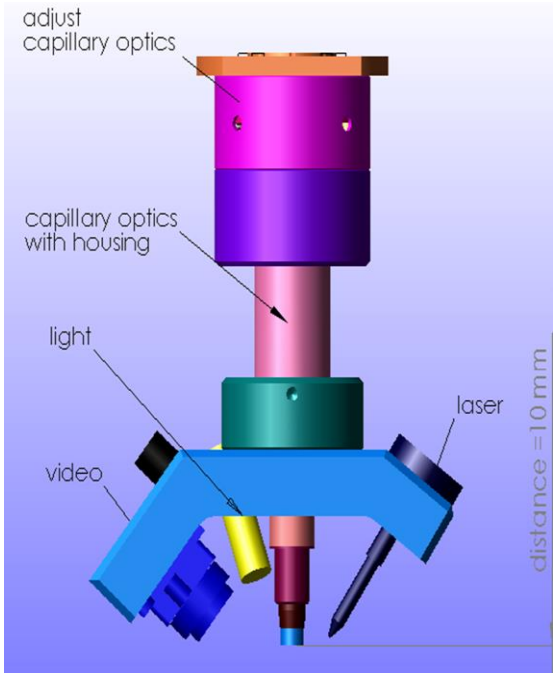
Handheld



1. X-ray source,
2. X-ray detector
3. Beam shutter
4. Rotatable filter wheel
5. Lasers for sample positioning
6. Collimating parts



Portable Micro XRF spectrometer



Customized design of the micro-XRF probe by IFG based on ARTAX model by Bruker-AXS

Fluorescence production: Selective excitation

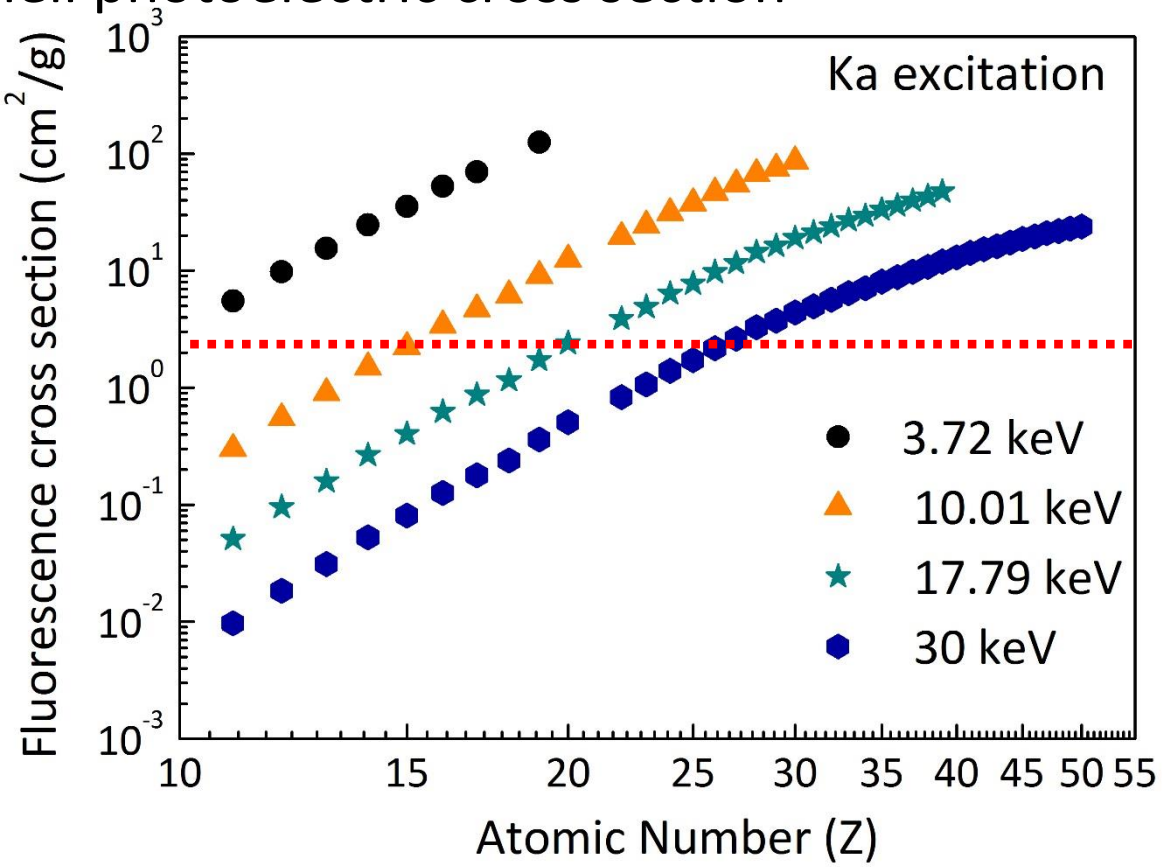
XRF K-shell fluorescence cross section $\sigma_{KX}(E_o)$

$$\sigma_{KX}(E_o) = \tau_K(E_o) \cdot \omega_K \cdot F_{KX}$$

Transition probability for Kα emission

K-shell fluorescence yield

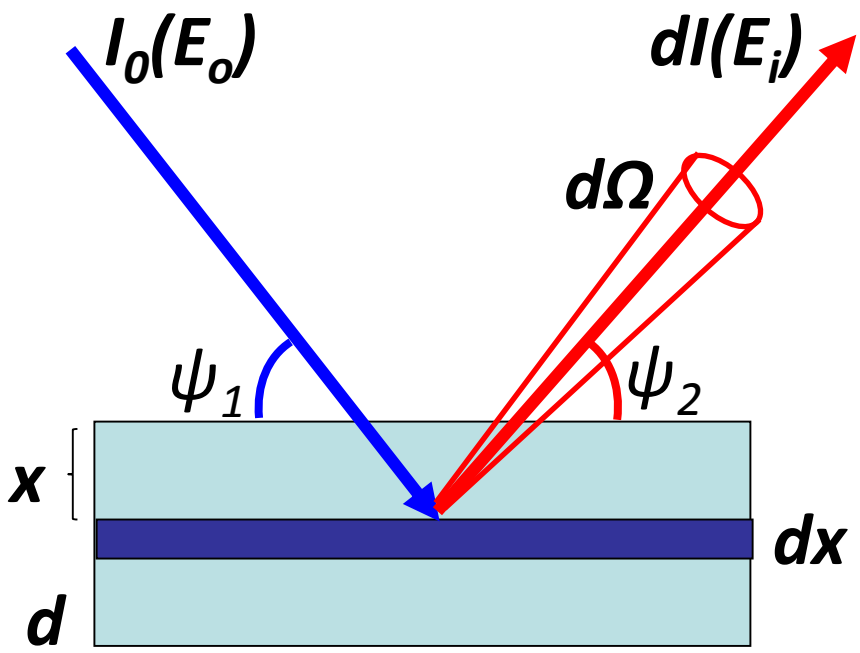
K-shell photoelectric cross section



Optimizing the energy of the exciting beam for maximizing the produced characteristic X-ray intensity

Fluorescence Emission Rate

$$dI_i(E_i) = \underbrace{I_0 \exp\left(-\frac{\mu(E_0)\rho x}{\sin\psi_1}\right)}_{1} \cdot \underbrace{\frac{C_i \tau_{is}(E_0)}{\sin\psi_1}\rho dx}_{2} \underbrace{\omega_{is} R_{is}(E_F)}_{3} \underbrace{\exp\left(-\frac{\mu(E_i)\rho x}{\sin\psi_2}\right)}_{4} \underbrace{\frac{d\Omega}{4\pi}\varepsilon_D(E_i,\Omega)}_{5}$$



1 – Rate of incident photons at depth x

2 – Probability of production of a vacancy in the atomic shell s (s=K, L1, L2, L3, …) of the element *i* across the path $dx/\sin\psi_1$

3 – Probability of emission of a photon of energy E_F of the element i among the family of emitted photons corresponding to transitions to the atomic shell

4 – Transmission of the fluorescent radiation in the outgoing path towards the detector

5 – Overall detection efficiency for E_F photons

Fluorescence Emission Rate: Approximation

Monochromatic excitation, Emission angle, detection efficiency constant within the solid angle

$$I_i(E_i, E_0) = I_0 C_i \omega_{is} R_{is}(E_F) \frac{\tau_{is}(E_0)}{\mu(E_0) + \mu(E_F)\frac{\sin\psi_1}{\sin\psi_2}} \left\{1 - \exp\left[-\left(\frac{\mu(E_0)}{\sin\psi_1} + \frac{\mu(E_i)}{\sin\psi_2}\right)\rho \quad d\right]\right\} \frac{\Omega}{4\pi} \varepsilon_D(E_i)$$

Thick sample: $\rho\, d \gg 1$

$$I_i(E_i, E_0) = \frac{I_0 C_i \omega_{is} R_{is}(E_F) \tau_{is}(E_0)}{\mu(E_0) + \mu(E_F)\frac{\sin\psi_1}{\sin\psi_2}} \left(\frac{\Omega}{4\pi}\right) \varepsilon_D(E_F)$$

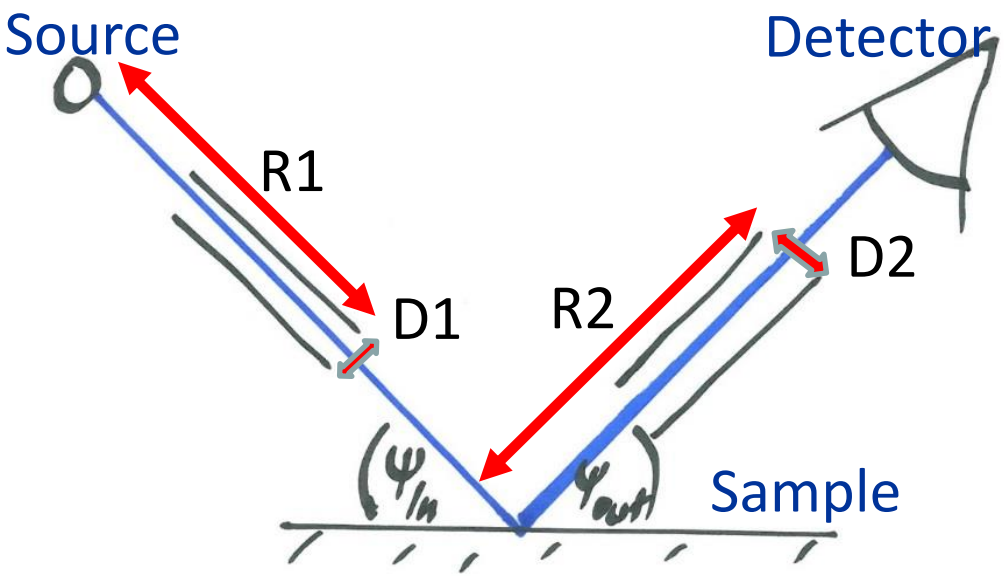
Thin sample: $\rho\, d \ll 1$

$$I_i(E_i, E_0) = \frac{I_o \cdot C_i \cdot R_{is}(E_f) \cdot \tau_{is}(E_O) \cdot \rho d}{sin\psi_1} \left(\frac{\Omega}{4\pi}\right) \varepsilon_D(E_f)$$

AND those elements not detected also contribute to the attenuation within the whole matrix!

Tube excitation: $I_i\,(E_i) = \int_{E=U_{Xi}}^{E=U_o} I(E_i, \mathrm{E})\mathrm{dE}$

Optimization of pXRF analysis



Fluorescence intensity depends on:

- ✓ Tube intensity, optimized spectral distribution for different elements
- ✓ Geometry: $1/R_1^2$, D_1^2, $1/R_2^2$, D_2^2

D_2= diameter of detector crystal or collimator

- ✓ X-ray lens features (micro-XRF, spot size, focal distance, gain)
- ✓ Incident/outgoing sample angles
- ✓ Absorption in air paths, detector windows

Background radiation

- ✓ Set-up geometry (scattering angle)
- ✓ Degree of exciting spectrum monochromaticity – Use of filters
- ✓ Proper collimation of exciting/fluorescence radiation to avoid parasitic lines

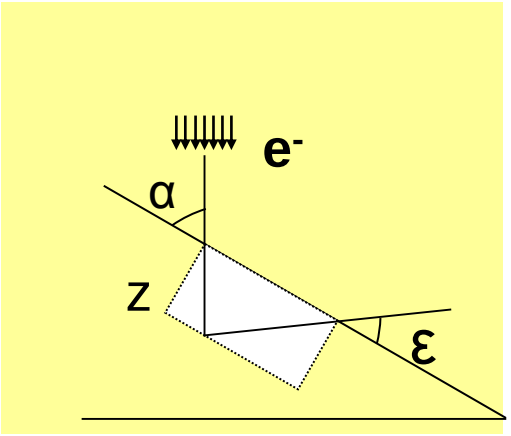
Optimization of excitation spectrum

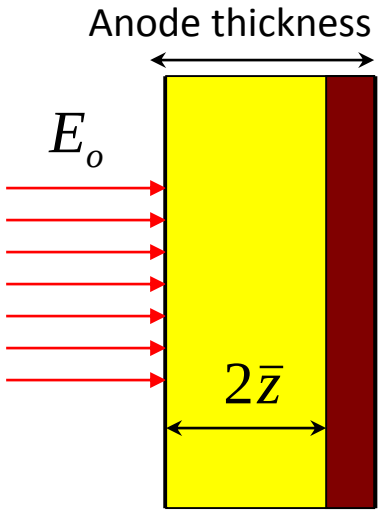
X-ray tube optimization

- Anode material
- High voltage
- Current

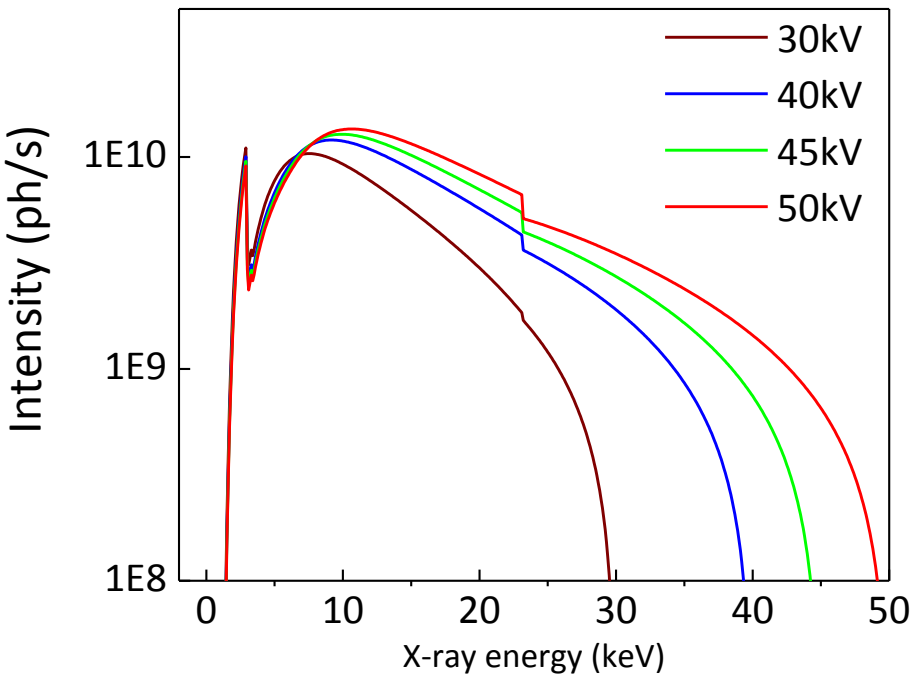
} *Power consumption*

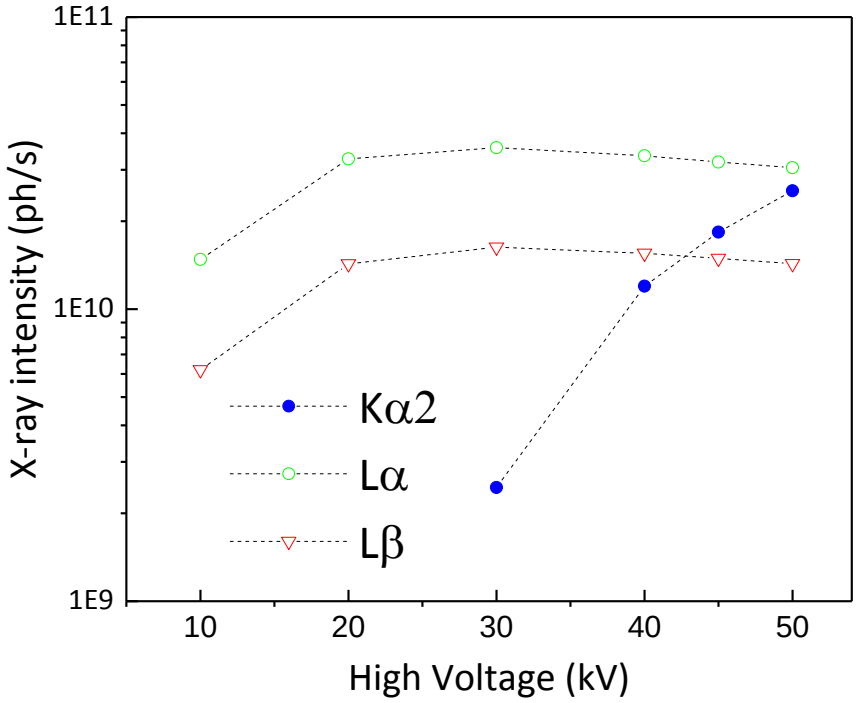
- Incident/Exit angle
- Type and thickness of tube window
- Side/End window tube
- Incident beam aperture diameter and distance





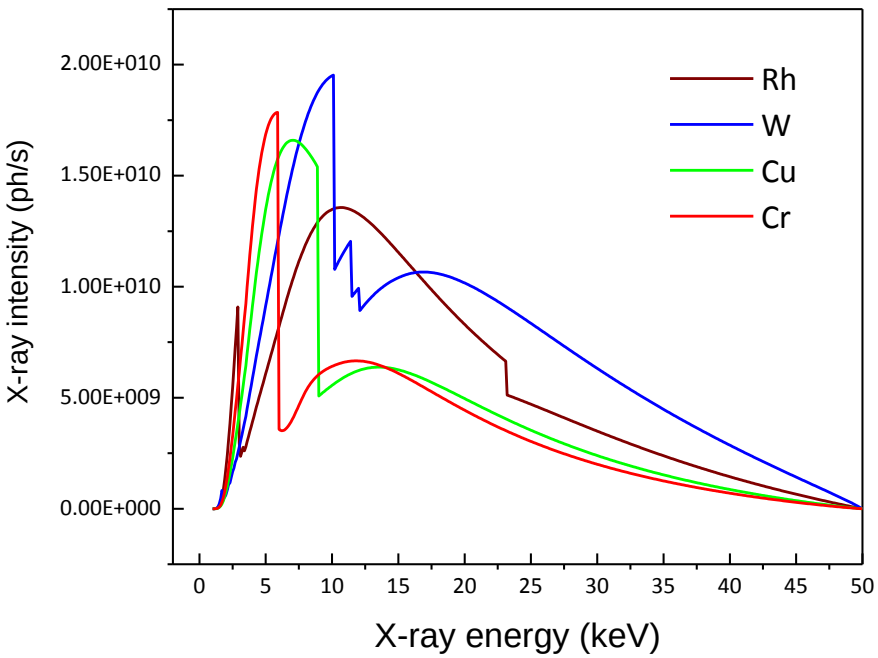
X-ray tube optimization – High Voltage

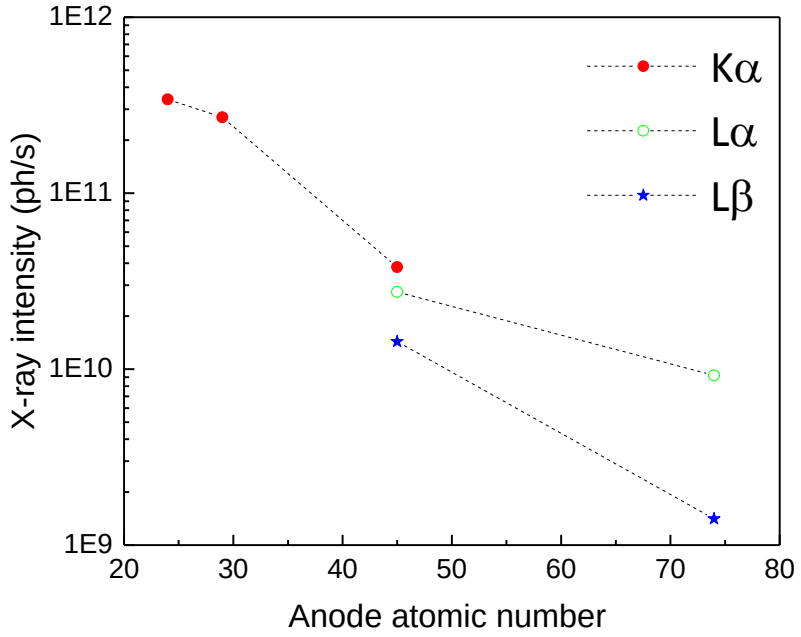




Rh anode, 50kV, side window, standard 78/12

X-ray tube optimization – Anode material

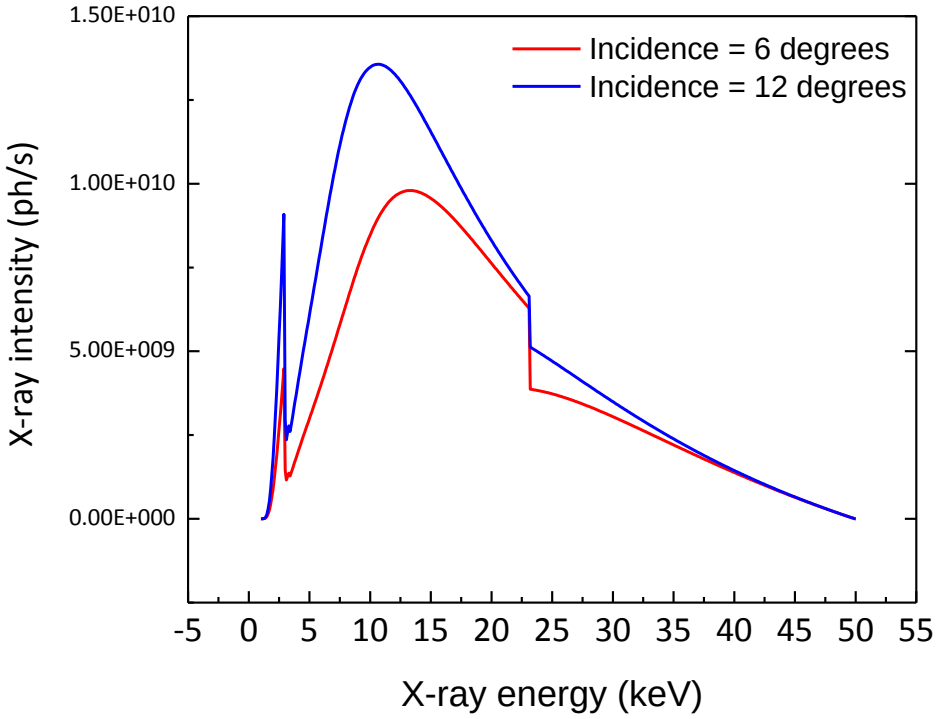


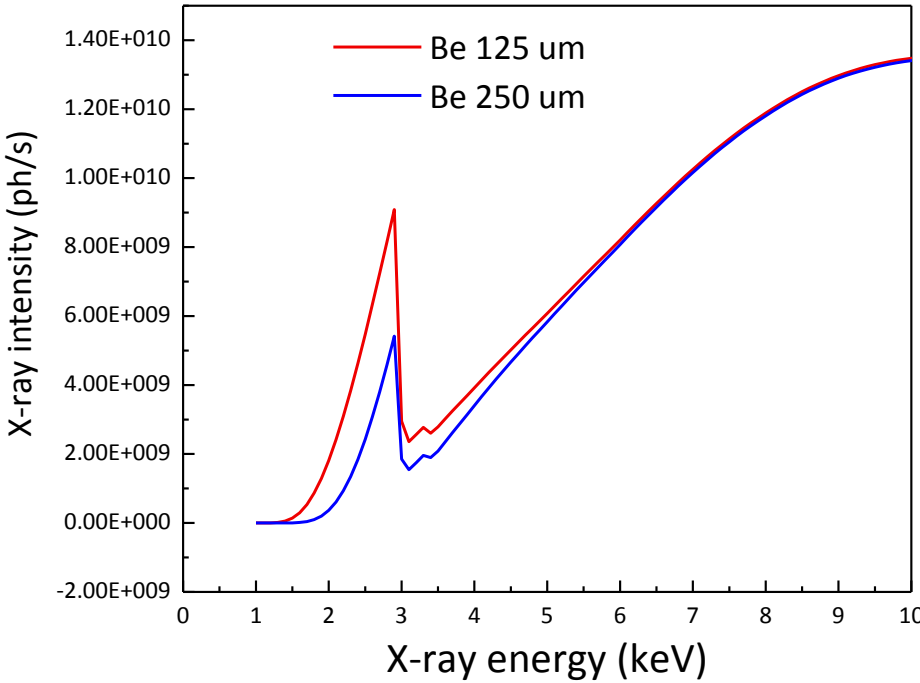


Operation at 50kV, side window

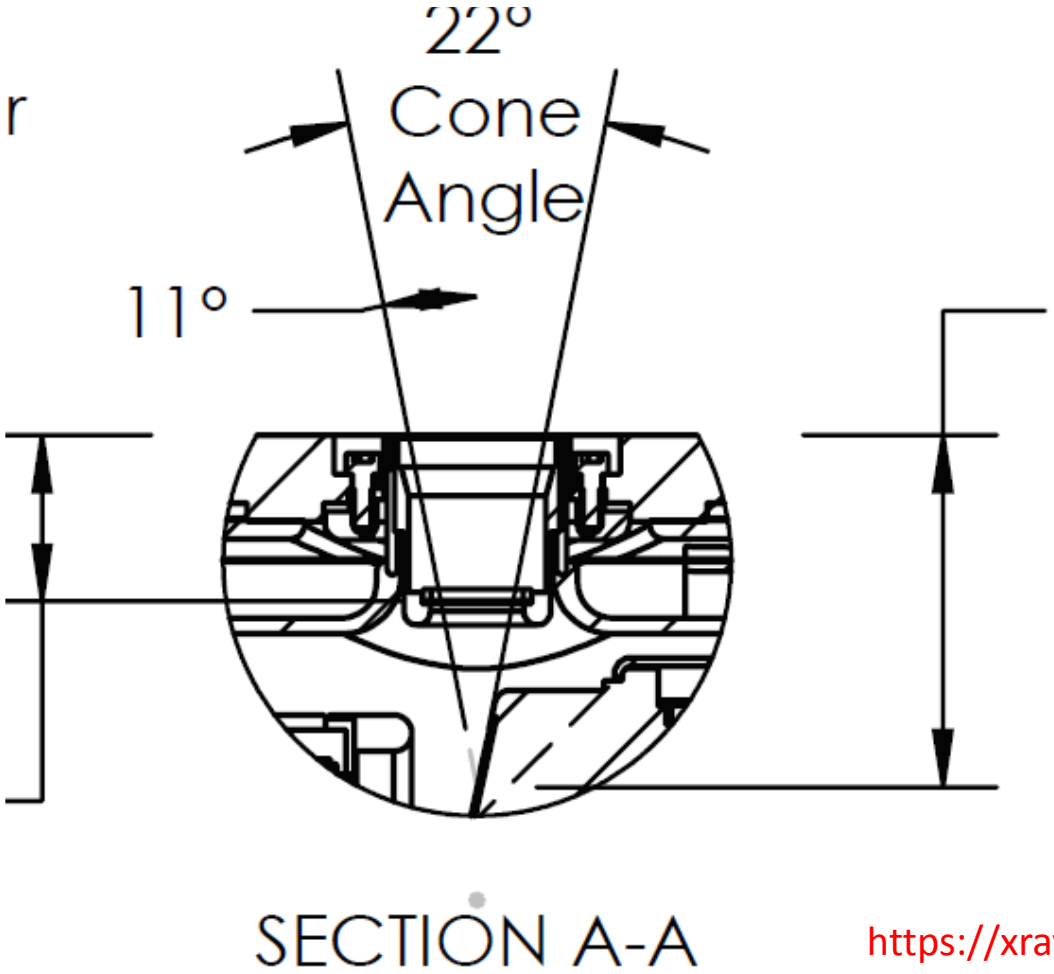
X-ray tube – Incidence angle/Window

Rh anode, 50kV, side window



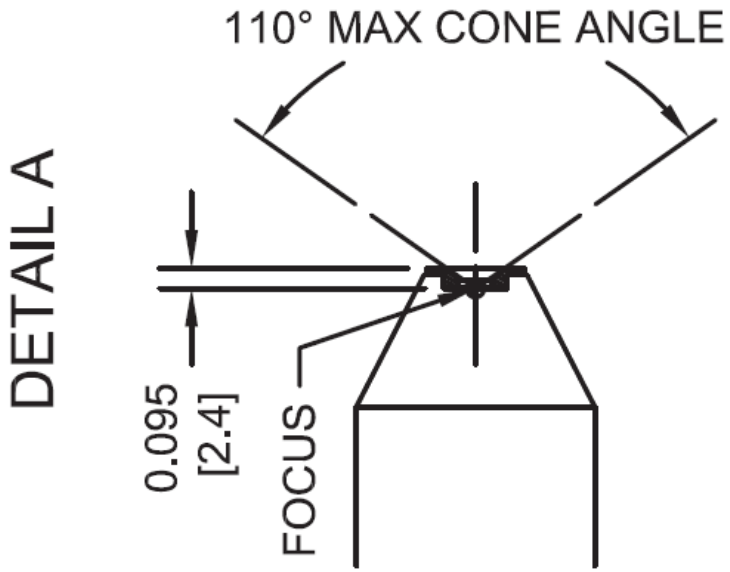


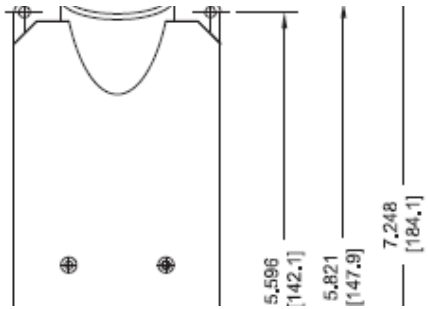
X-ray tube geometry – Side window

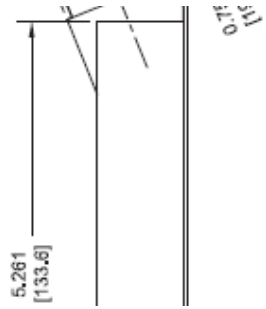


https://xray.oxinst.com/products/x-ray-tubes/

X-ray tube geometry – End window

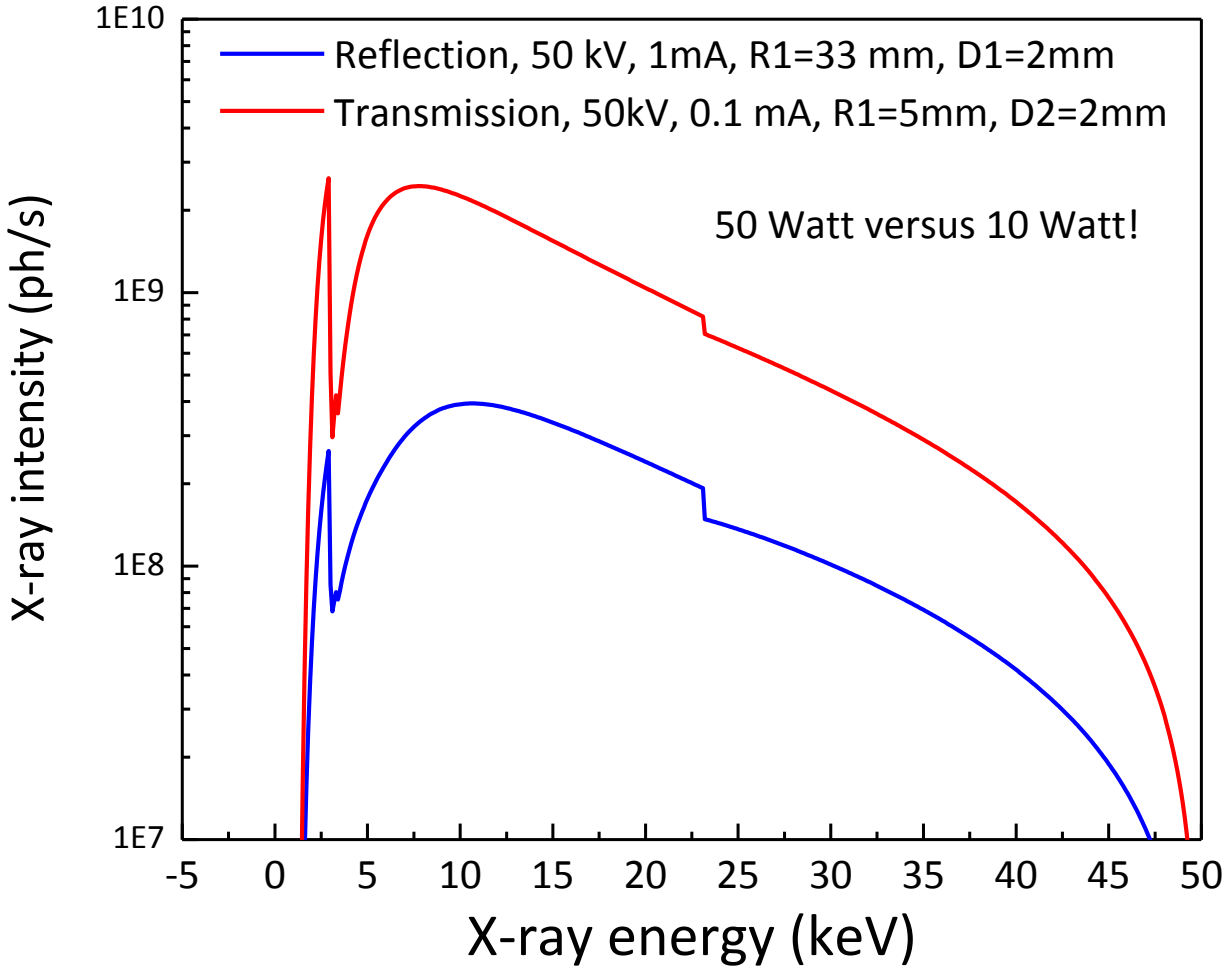






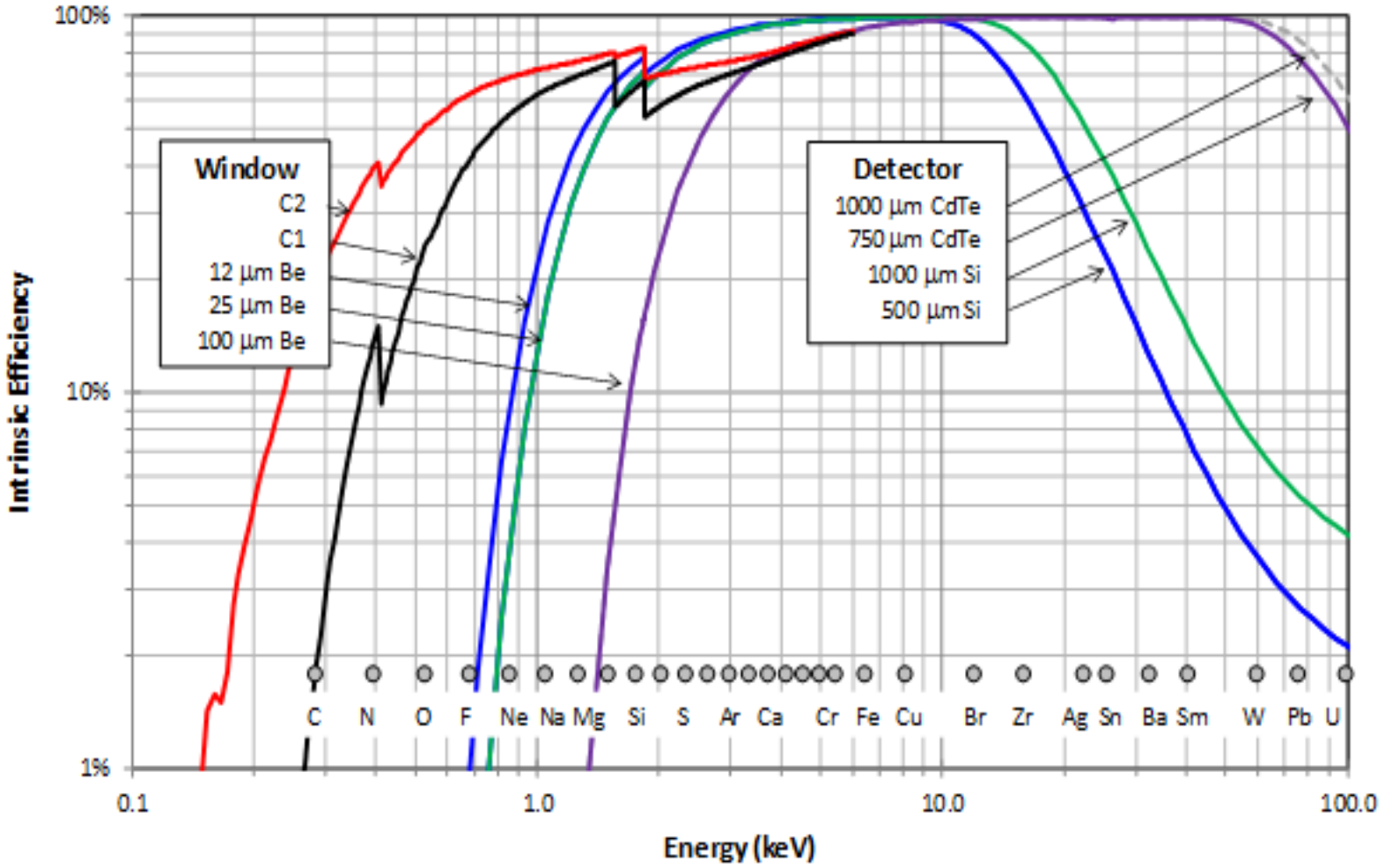
http://www.newtonscientificinc.com/

X-ray tube geometry optimization



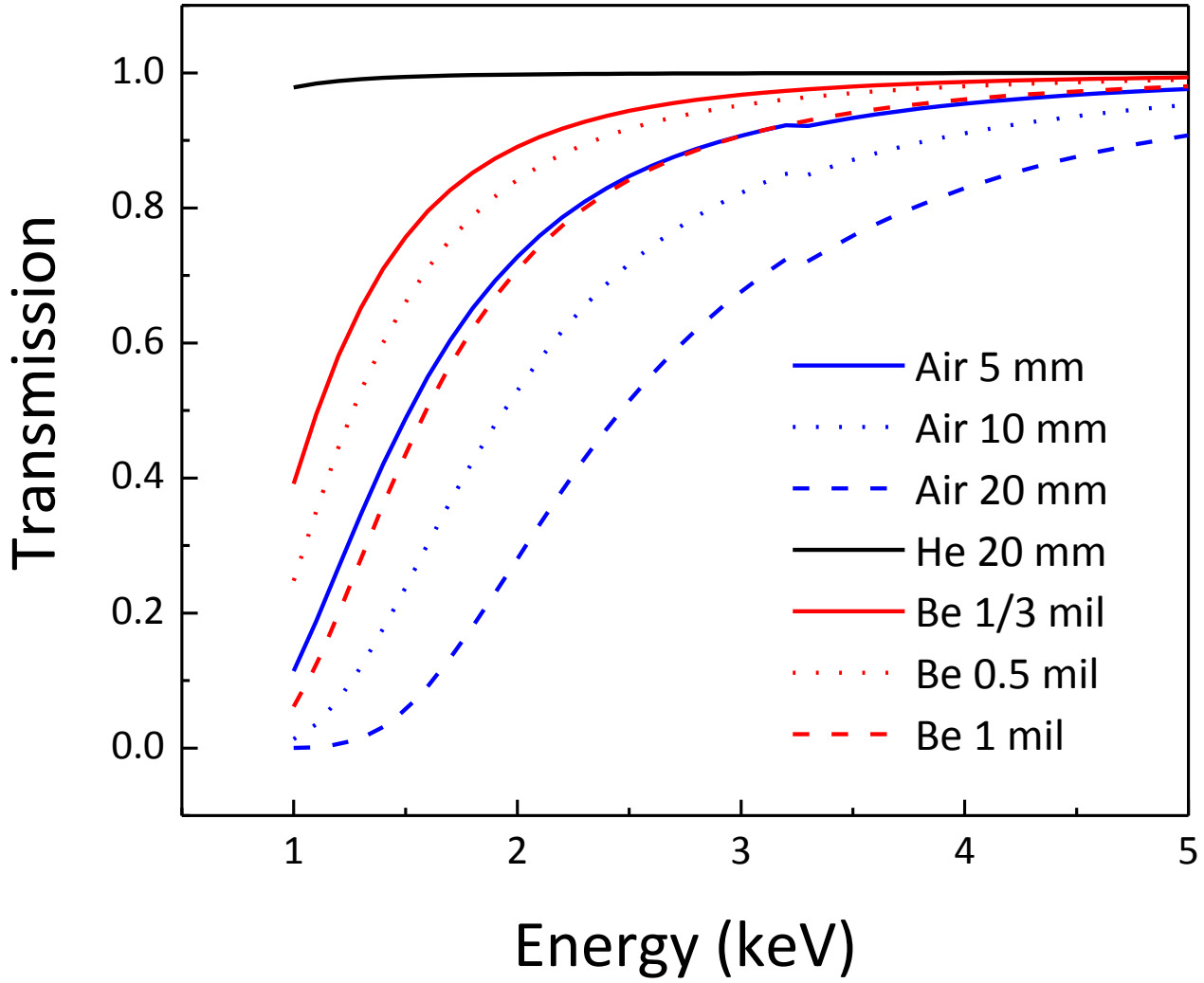
X-ray detectors optimization:

Window/thickness

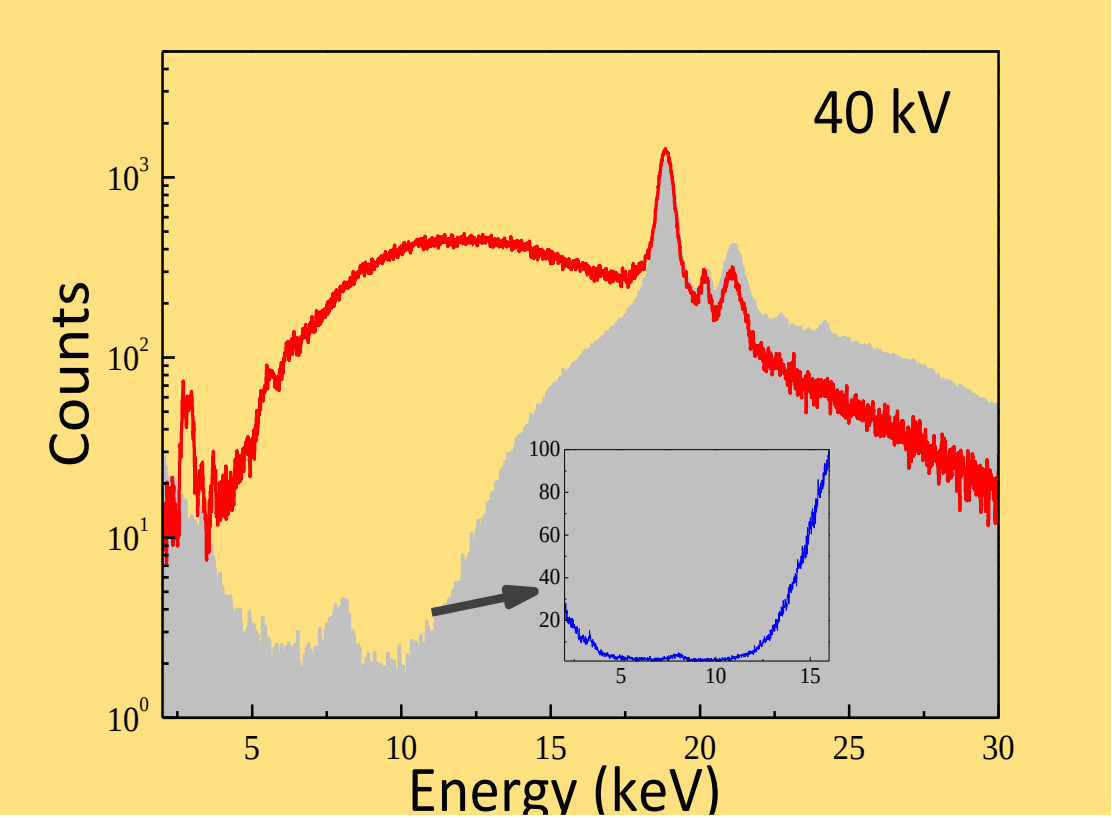


www.Amptek.com

X-ray detection environment



Filter modifier of the exciting beam

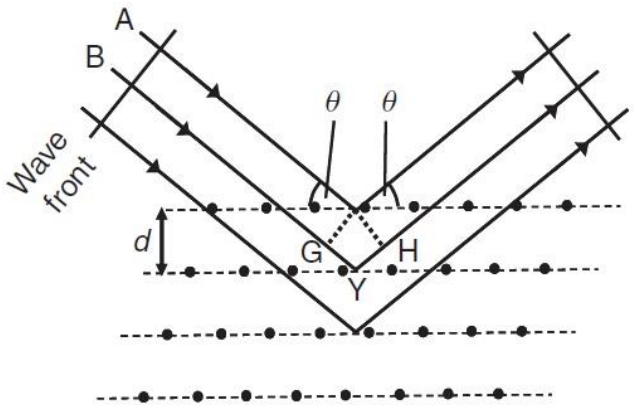


@ 19 keV: 3-4 times

@ 5-15 keV: 10-100 times

Filtered vs Unfiltered excitation: An example

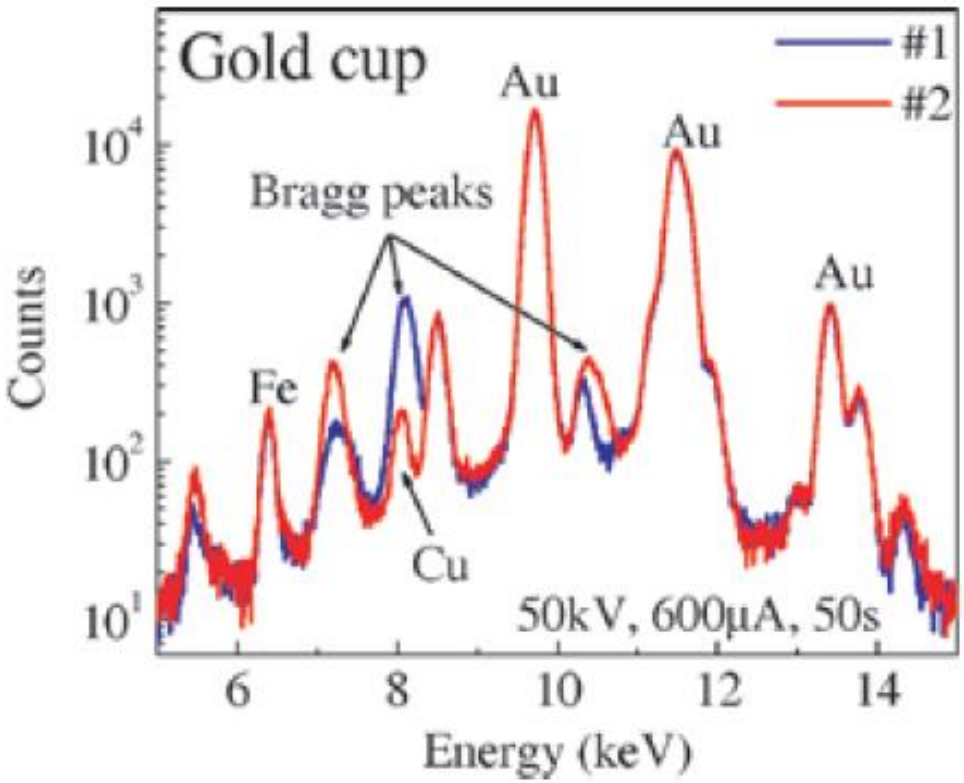
Rh anode tube, 40 kV, low atomic number scatterer



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

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

Bragg's Law



Optimizing Det. collimation: Requirements

The detector collimation ensures:

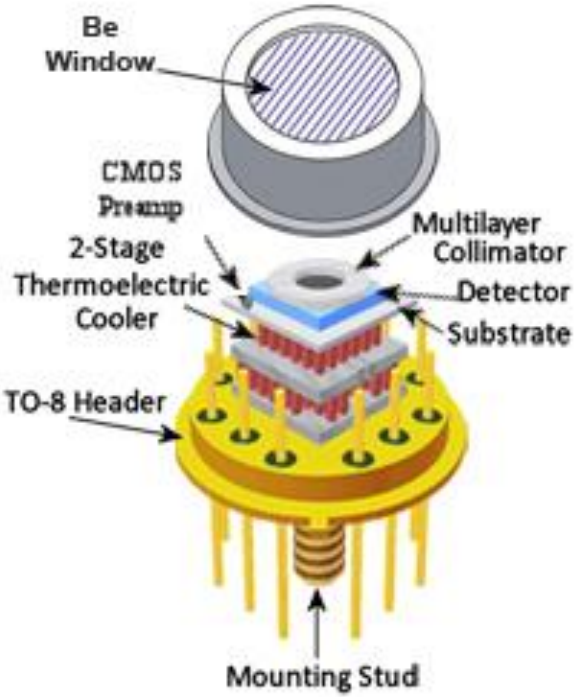
- Detected radiation occurs only from the sample itself

- Same solid angle is defined for low and high energy fluorescent X-ray lines (Fe-Ka, Sn-Ka)

- Blank spectra are free of collimator material X-rays

- Elimination to certain degree of detector materials fluorescence

- Improved P/B ratio by focusing only to central area of the crystal (actual use of part of the crystal effective area)



www.Amptek.com

Thank you for your attention!!!