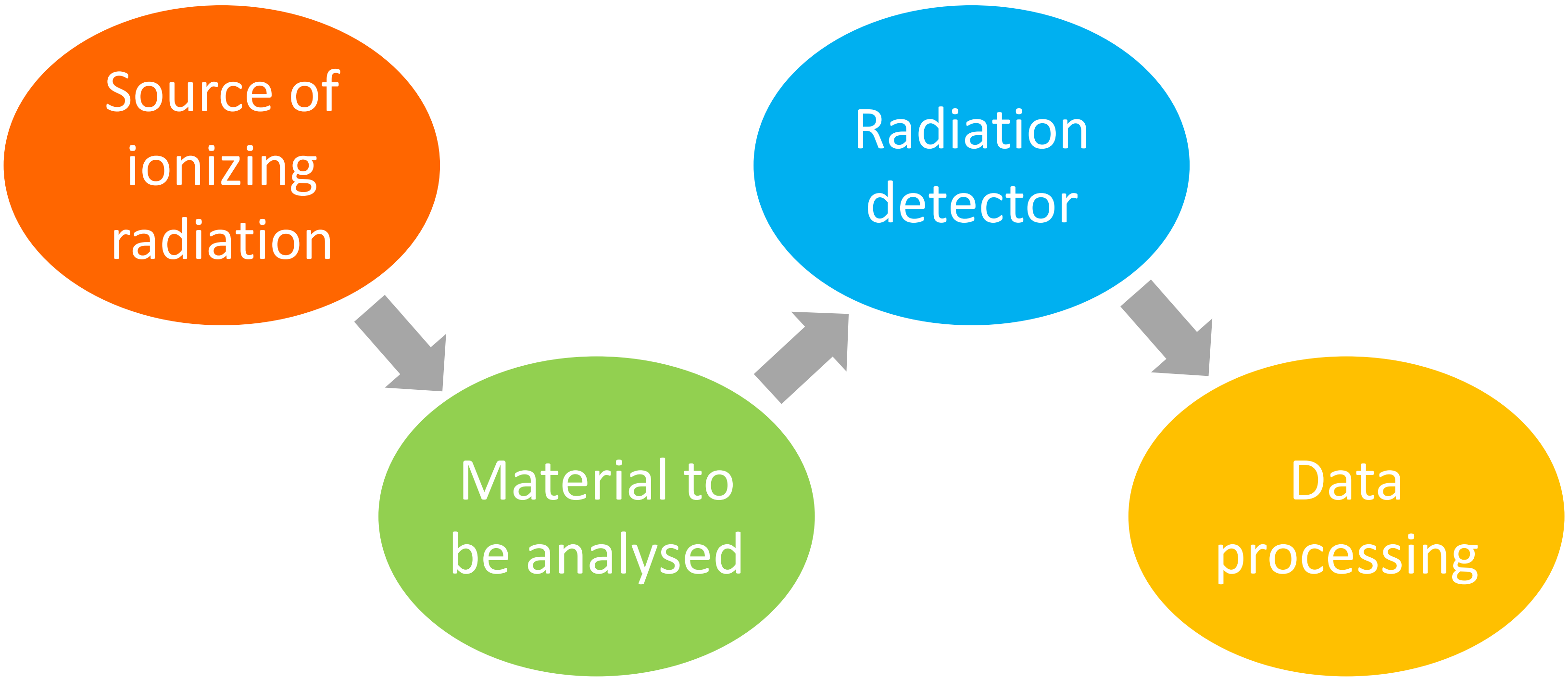
X-Ray Fluorescence analysis

Alessandro Migliori

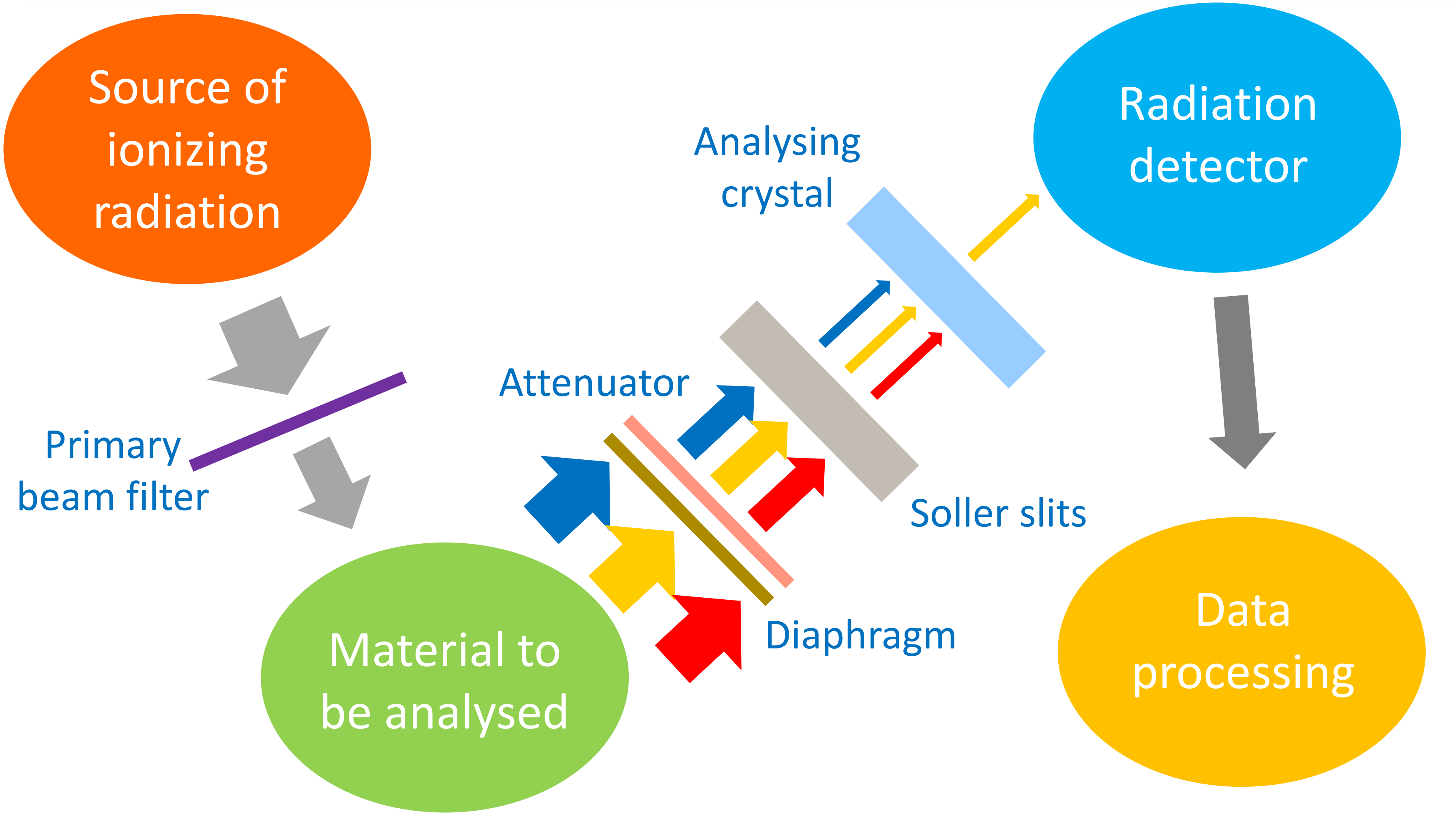
October 27, 2023

❑ Elements in XRF

X-ray fluorescence (XRF) spectroscopy works similarly



Elements in WD-XRF



Outline

- Photoelectric effect and emission of characteristic X-rays
- Excitation sources
- Detectors
- Signal processing
- Geometric arrangement
- Software for spectrum deconvolution

❑ Interaction of X-rays with matter

X-rays can interact with the atoms of the material in two different ways:

- **Photoelectric effect**: Primary X-ray radiation can ionise atoms of the material. The X-ray is absorbed in this process
- **Scattering**:
  - ✓ **Elastic/coherent scattering** (**Rayleigh**): no energy loss after collision with electrons. The Rayleigh effect is present when electrons are strongly bound (inner atomic electrons)
  - ✓ **Inelastic/Incoherent scattering** (**Compton**): energy loss after collision with electrons. The Compton effect is present when electrons are loosely bound (outer, less bound electrons)

❑ Photoelectric effect

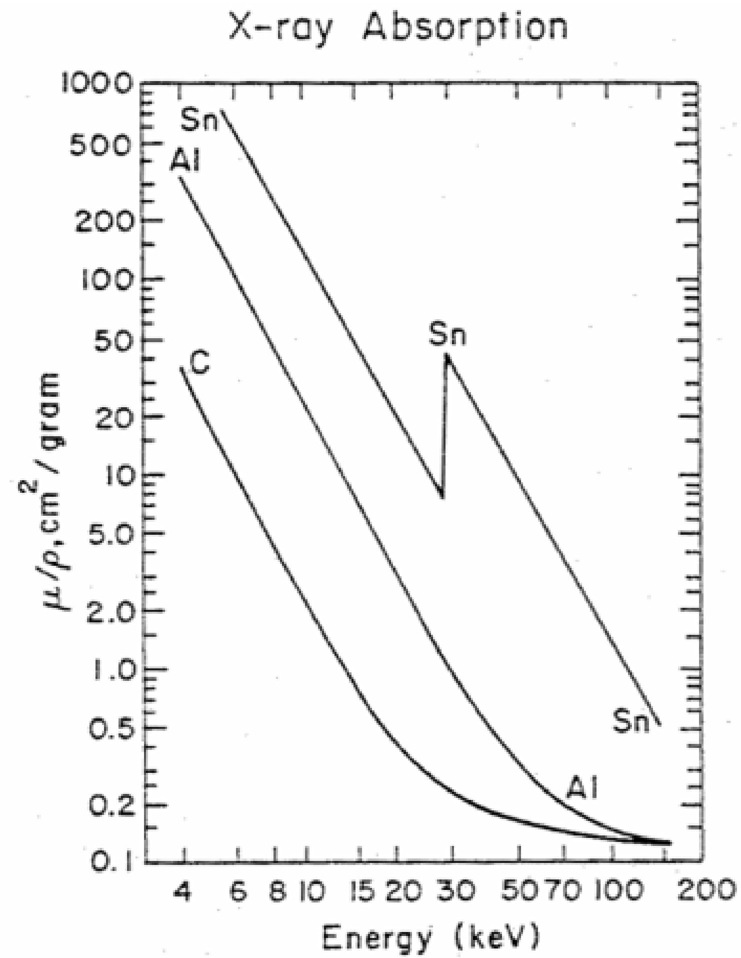
Primary X-ray radiation can ionise atoms of the material to be analysed

This phenomenon is called ***Photoelectric effect***

Cross section of the PE depends strongly on *Z* of the material and on the energy of the X-ray

$$\sigma_{Ph} \propto \frac{Z^n}{E_X^{3.5}} \qquad n = 3 \div 4$$

To maximize the ionization probability, the energy of the X-ray should be higher than the binding energy but as close as possible to it



X-Ray Fluorescence

Incident photon Energy E_0 should be adequate to ionize the atomic bound electrons **→ E_0 ≥ inner shell binding energy**

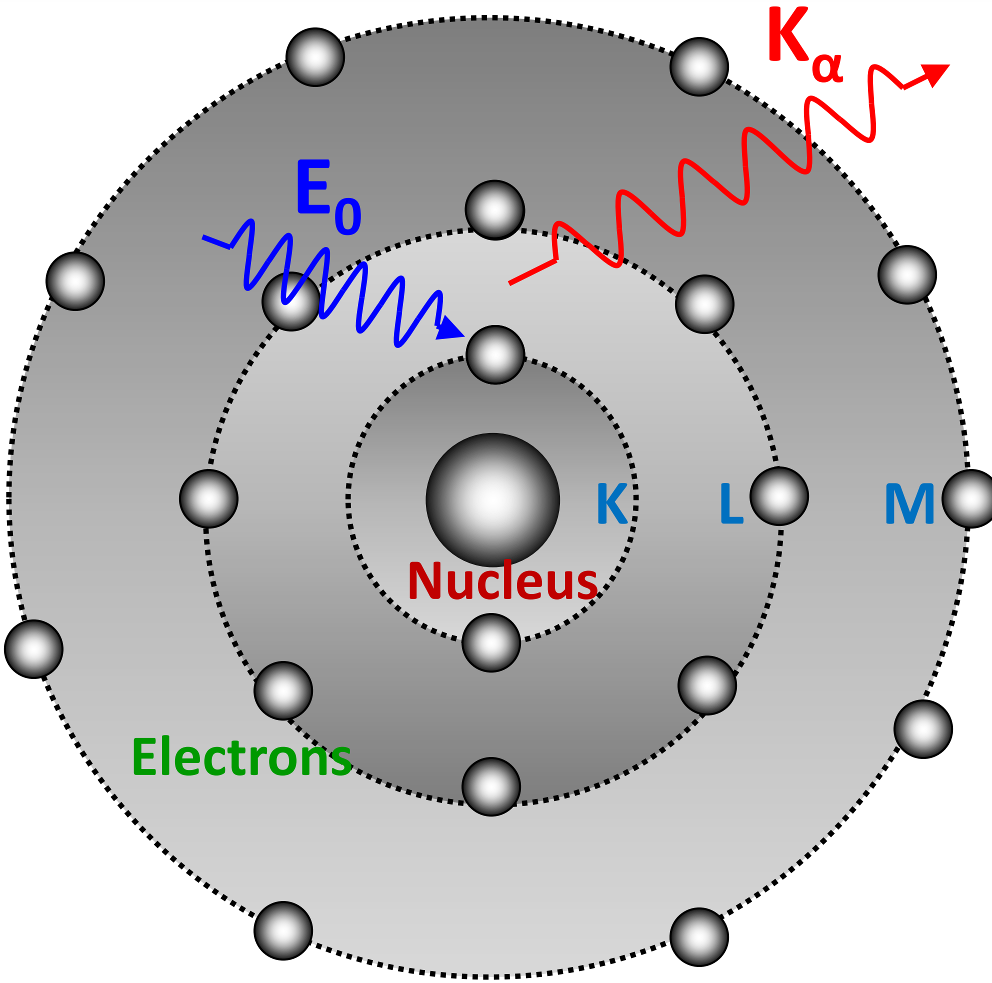
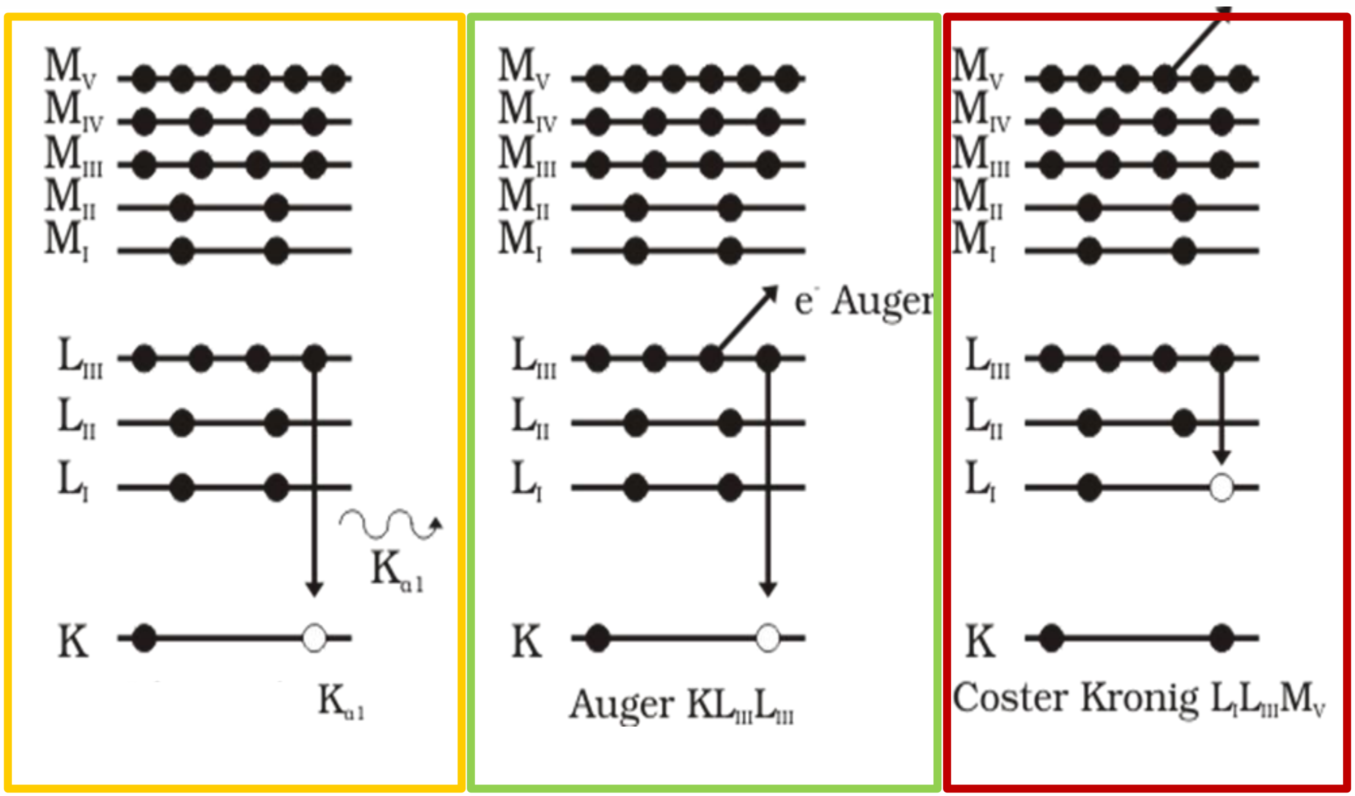


Photo-Ionization of atomic bound electrons (K, L, M) (**Photoelectric absorption**)

Electronic transition and emission of element **→ characteristic fluorescence** radiation

Fluorescence X-ray emission is **isotropic**

❑ De-excitation: Fluorescence/Auger



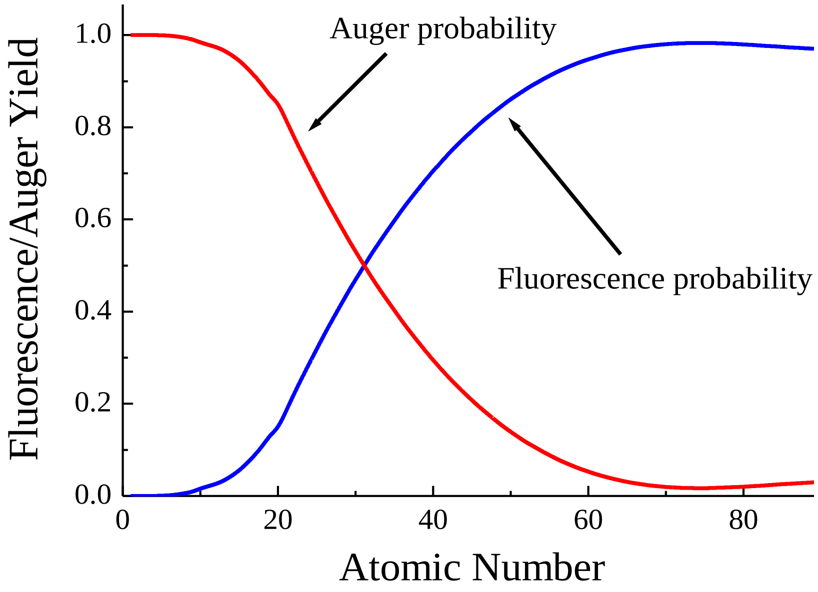
Emission of characteristic X-ray

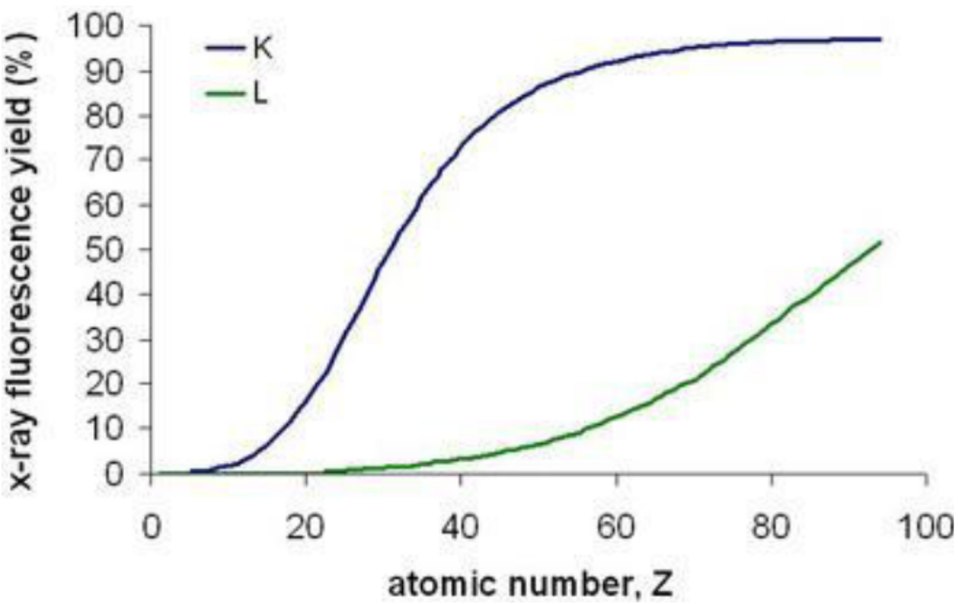
Emission of electron (vacancy filled by electron from different shell)

Emission of electron (vacancy filled by electron from the same shell)

❑ Fluorescence yield

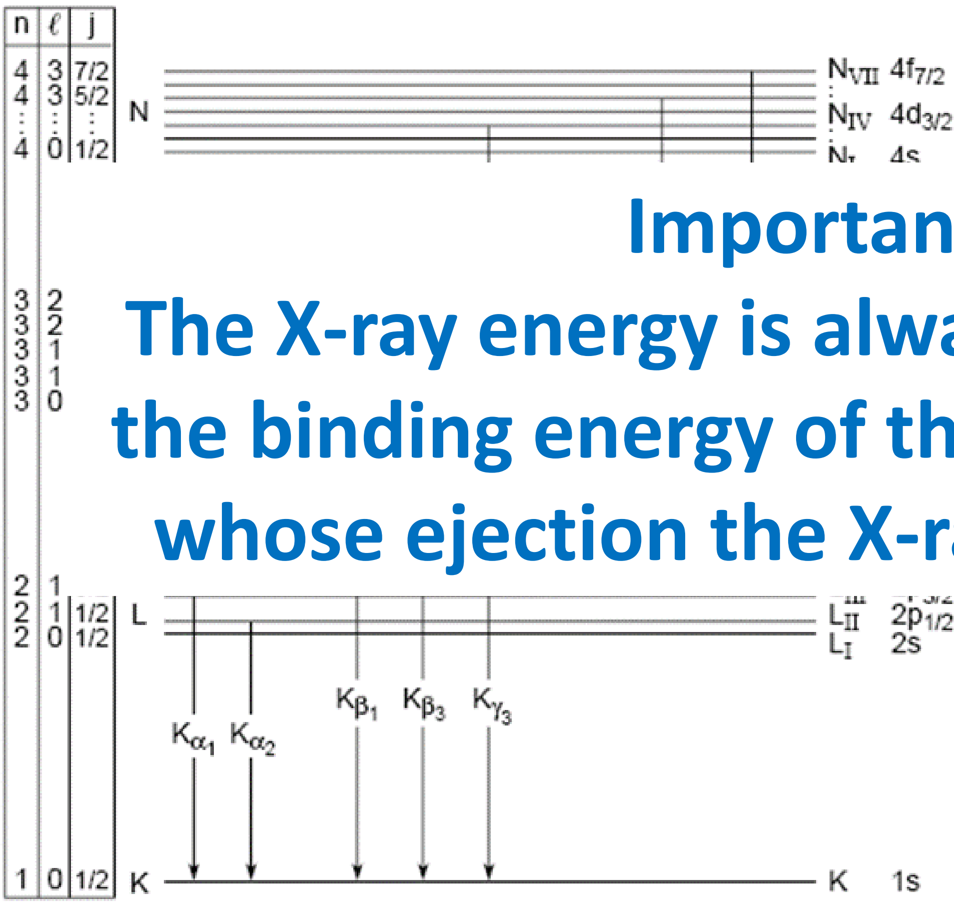
The fluorescence yield is given by the **ratio of the emitted fluorescence photons over the number of the created holes**. The competing process is the **emission of Auger electrons** as the atom returns to its ground state





For low Z the Auger electron emission is dominant

Emission of characteristic X-rays



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

Important!

The X-ray energy is always smaller than the binding energy of the electron, after whose ejection the X-ray was emitted

$\mathbf{K_{\beta}}$: $K\text{-}M_2 + K\text{-}M_3$

$\mathbf{L_{\alpha}}$: $L_3\text{-}M_4 + L_3\text{-}M_5$

$\mathbf{L_{\beta 1}}$: $L_2\text{-}M_4$

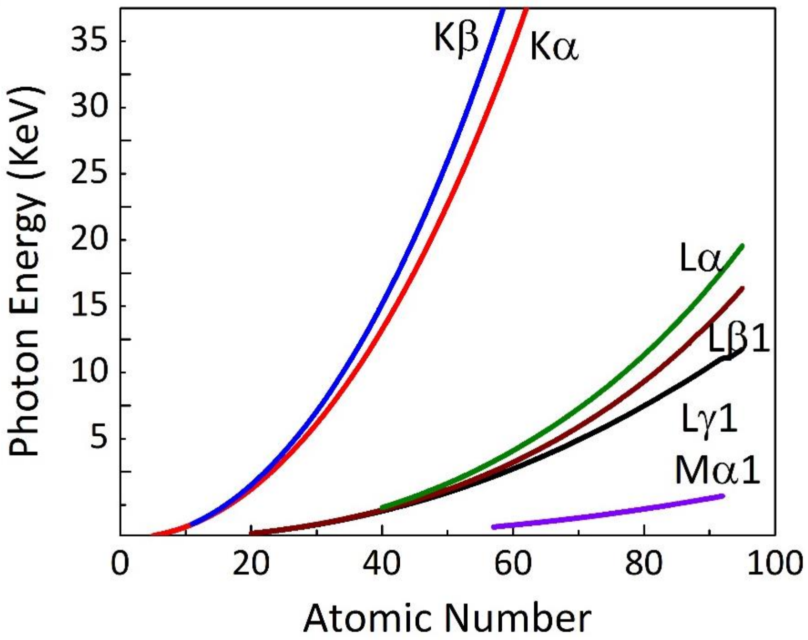
$\mathbf{L_{\beta 2}}$: $L_3\text{-}N_5$

X-ray energies

Moseley's law

$$E = h \cdot A \cdot R \cdot (Z - b)^2$$

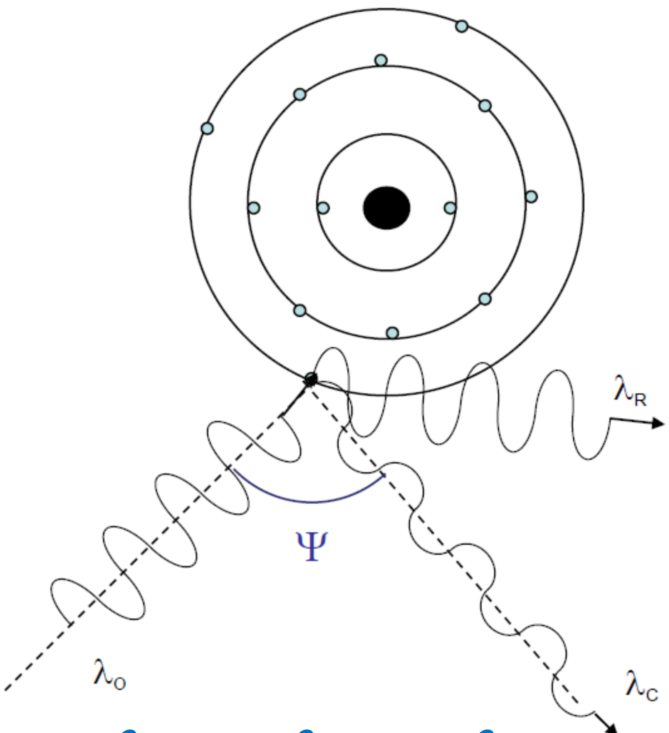
h = Planck constant
R = Rydberg frequency
Z = atomic number
A = 3/4 for K_α, 5/36 for L_α
b = 1 for K_α, 7.4 for L_α



K_α	E [eV] ≈ 10.20 · $(Z - 1)^2$	$E_{Fe\text{-}K\alpha} \approx 6380$ eV
L_α	E [eV] ≈ 1.89 · $(Z - 7.4)^2$	$E_{Pb\text{-}L\alpha} \approx 10520$ eV

X-ray spectroscopy within the energy range 1÷30 keV offers in principle the possibility to detect all the periodic table elements (Z > 10) through their K, L or even M series of emission lines

❑ X-ray scattering



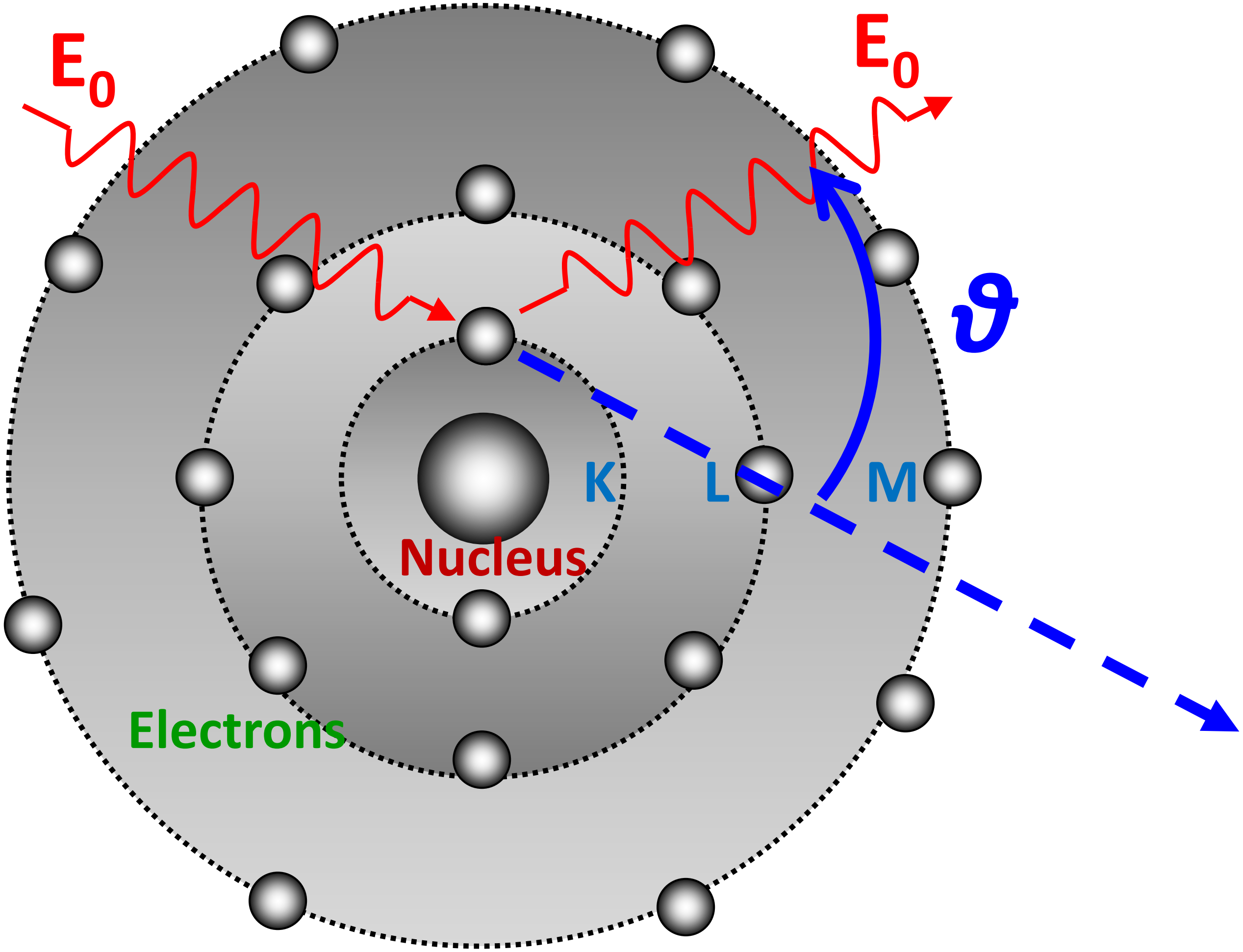
$$\lambda_C > \lambda_R = \lambda_0$$

Elastic/coherent scattering (Rayleigh):
no energy loss after collision with electrons. The Rayleigh effect is present when electrons are strongly bound.
Rayleigh is more intense for high *Z* (= heavy) matrices

Inelastic/Incoherent scattering (Compton):
energy loss after collision with electrons. The Compton effect is present when electrons are loosely bound.
Compton is more intense for low *Z* (= light) matrices

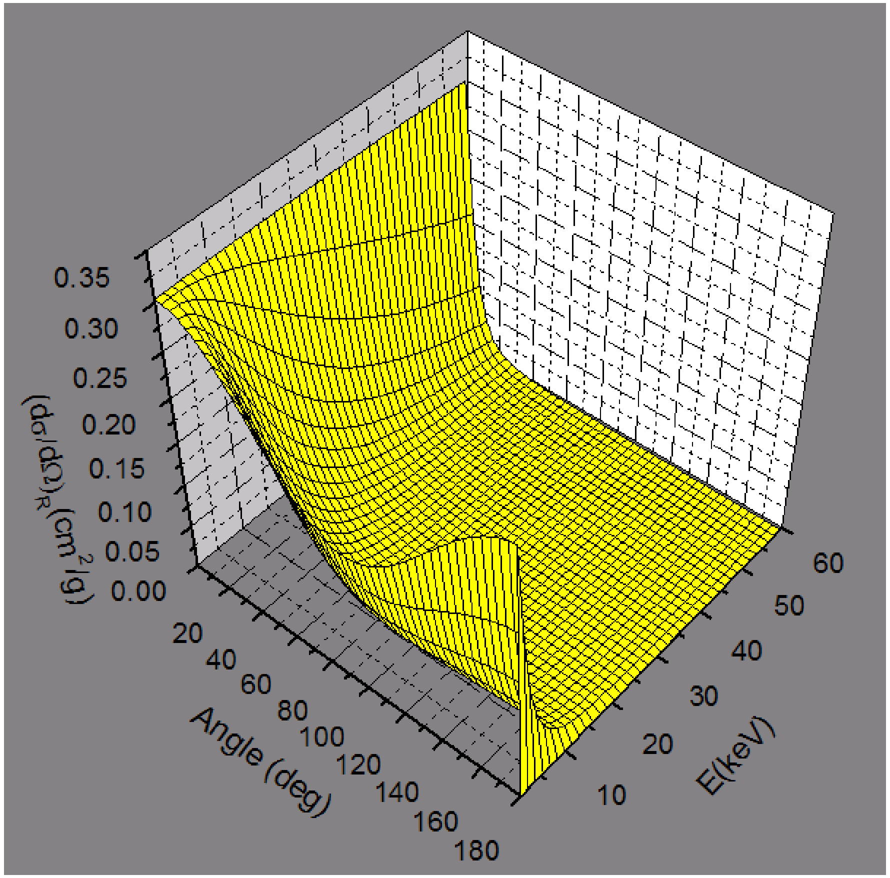
Rayleigh scattering

Incident photon
Energy E_0

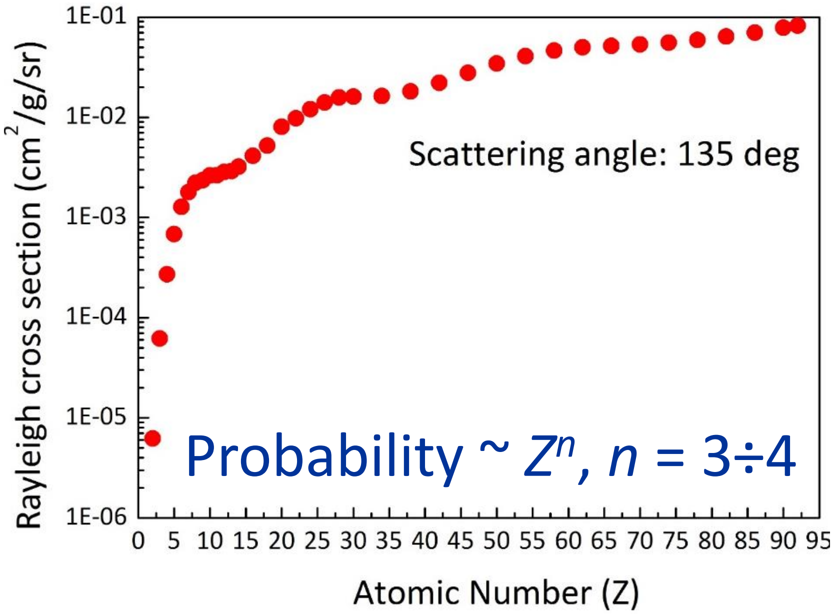


***$E_i = E_0$* : Coherent (Rayleigh)**
It occurs mostly with inner atomic electrons

❑ Rayleigh scattering



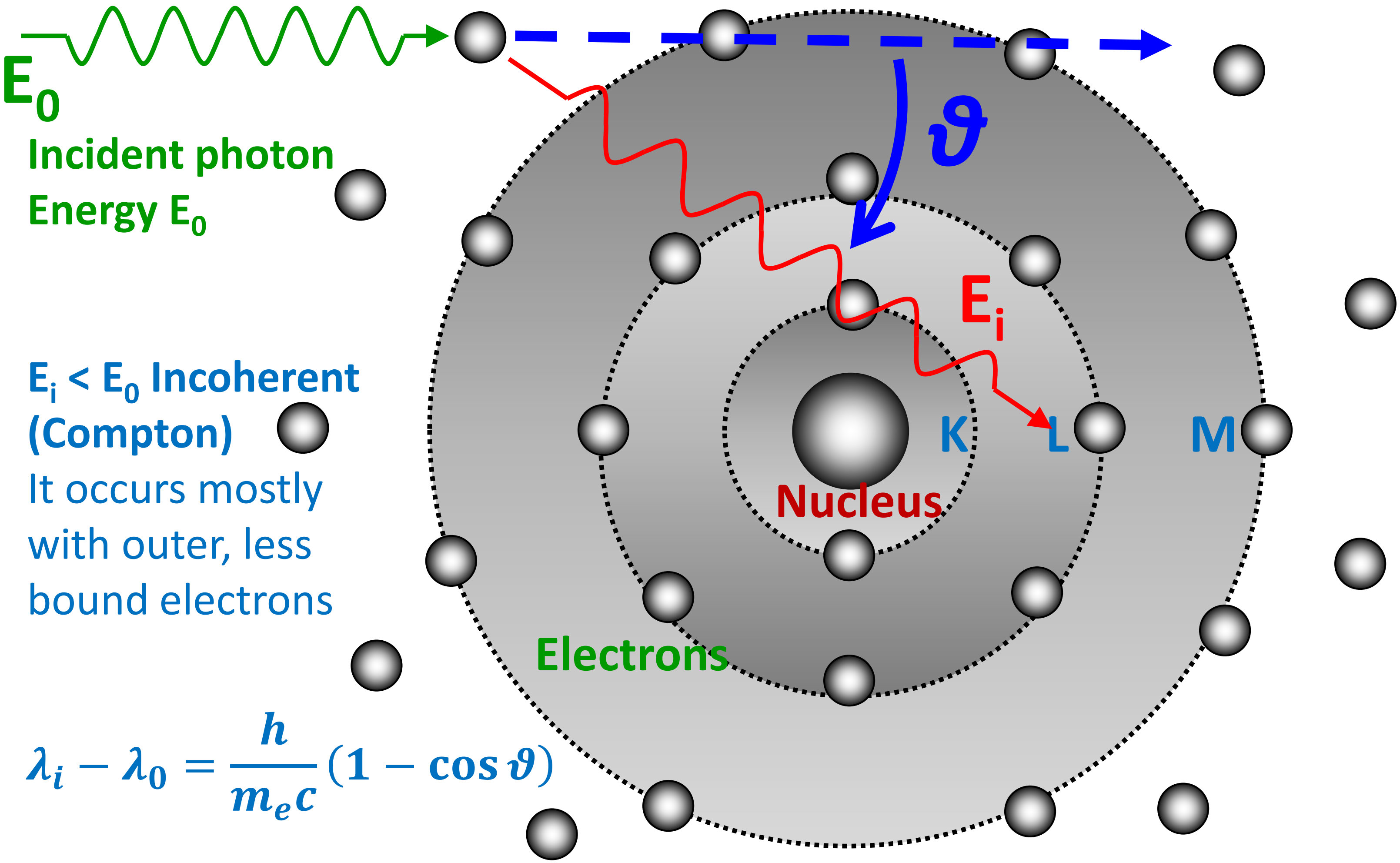
Compound	(%)
Al_2O_3	16
SiO_2	57
CaO	13
Fe_2O_3	14



Probability ~ Z^n, n = 3÷4

Scattering Rayleigh is **anisotropic**

❑ Compton scattering

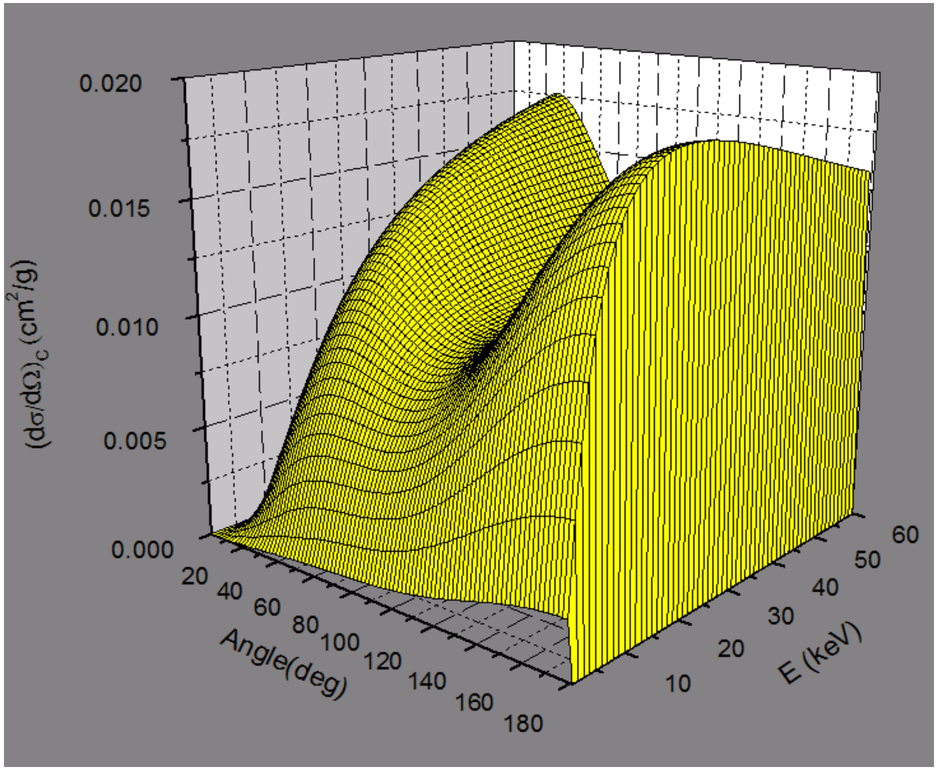


Incident photon
Energy E_0

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

$$\lambda_i - \lambda_0 = \frac{h}{m_e c}(1 - \cos\vartheta)$$

Compton scattering



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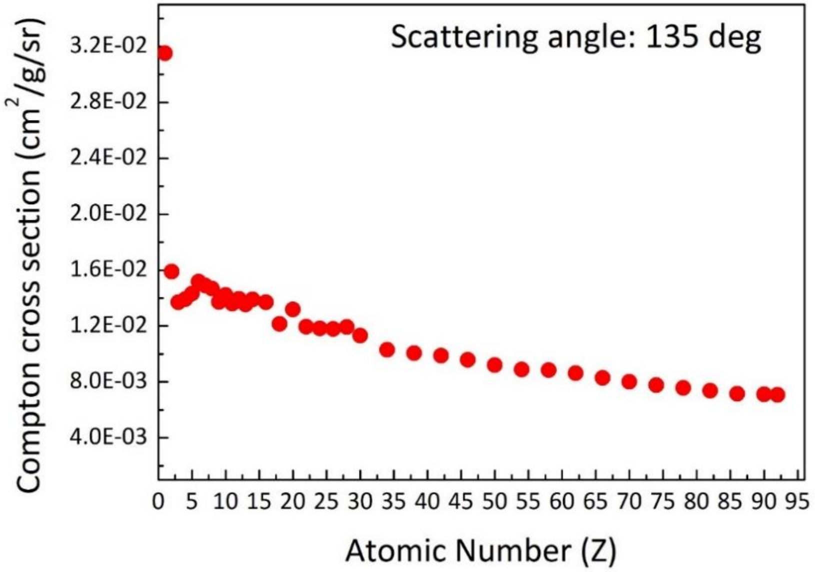


Scattering Compton is **anisotropic**

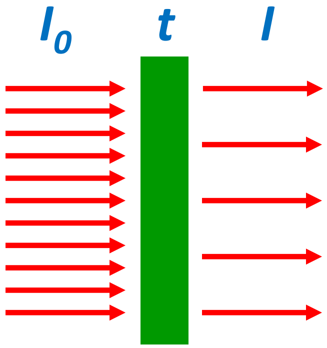
❑ Linear attenuation coefficient μ

Attenuation of photons by a thin layer of thickness *dt* is described by

$$dI = I \cdot \mu \cdot dt$$

where *I* is the number of photons per unit area and unit time (photon flux) of which *dI* are attenuated while penetrating the layer of a material characterized by the (**total, linear**) **attenuation coefficient** μ. This is equivalent to

$$I = I_0 \cdot e^{-\mu \cdot t}$$



I and I_0 are the photon fluxes behind and in front of the absorber, respectively, and *t* is the thickness. μ is a function not only of the material (atomic number *Z*) but also of the photon energy *E*

❑ Mass attenuation coefficient μ_m

$$\mu = \mu_m \cdot \rho$$

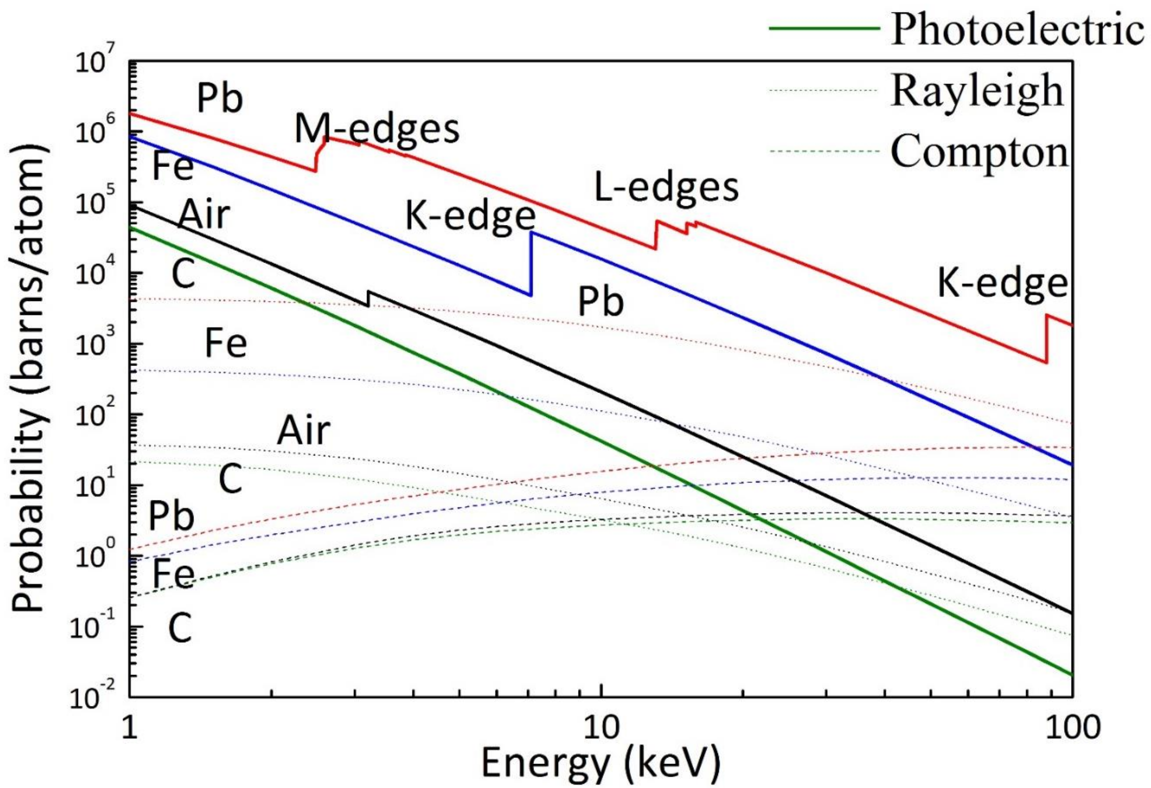
the total mass attenuation coefficient μ_m don't depend on the density ρ of the material.

The coefficient μ_m summarizes all possible photon interactions

$$\mu_m = \tau_m + \sigma_m$$

where $\boldsymbol{\tau_m}$ describes the photo absorption and $\boldsymbol{\sigma_m = \sigma_{coh} + \sigma_{inc}}$ are the contributions by coherent and incoherent scattering, respectively.

Both kinds of scattering contribute much less than the photo absorption to the total $\boldsymbol{\mu_m}$



❑ Mass attenuation coefficient μ_m

the mass attenuation coefficient of a material that is composed of several elements, with weight fractions w_i , is

$$\mu_m = \sum_i w_i \cdot \mu_m^i$$

Use of mass attenuation coefficients suggests replacing the thickness by the **area-related mass** $m = M/A$ (mass M per unit area A) and rewriting the attenuation law as

$$I = I_0 \cdot e^{-\mu_m \cdot m}$$

$t \cdot \rho = M/A$, in **grams/cm²**

Sources of ionizing radiation

- Radioisotopes (α, γ, x-rays)
- X-Ray Tubes
- Electrons (SEM)
- Charged particles (accelerators)
- Synchrotron radiation

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- **Radioisotopes (α, γ, x-rays)**
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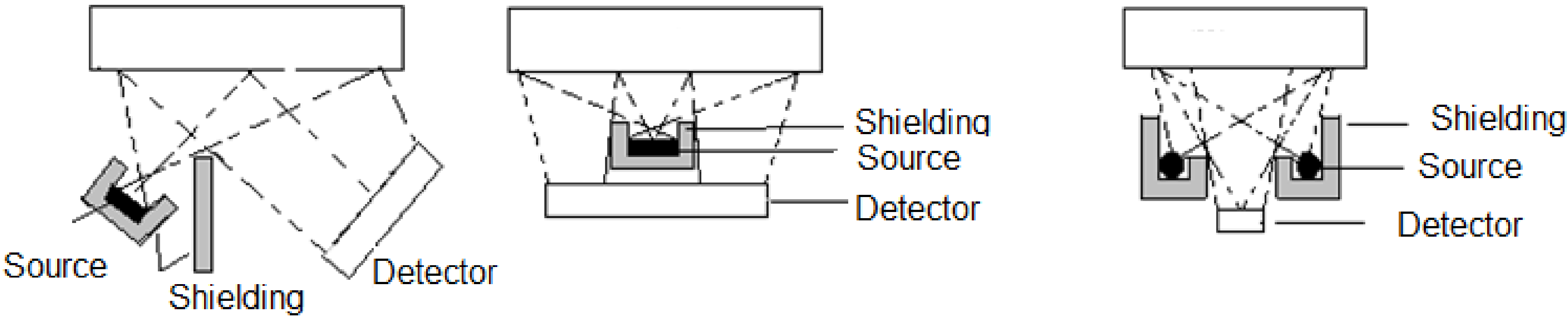
❑ Radiation sources

Main arrangements for source excitation



Disk shaped sources

Annular sources

Slide modified from an original lecture from Prof. Pierre Van Espen, University of Antwerp

Radioisotopes

Isotope	^{55}Fe	^{244}Cm	^{109}Cd	^{241}Am	^{57}Co
Energy (keV)	5.9	14.3, 18.3	22.1, 88	59.5	122
Elements (K-lines)	Al-V	Ti-Br	Fe-Mo	Ru-Er	Ba-U
Elements (L-lines)	Br-I	I-Pb	Yb-Pu	None	None

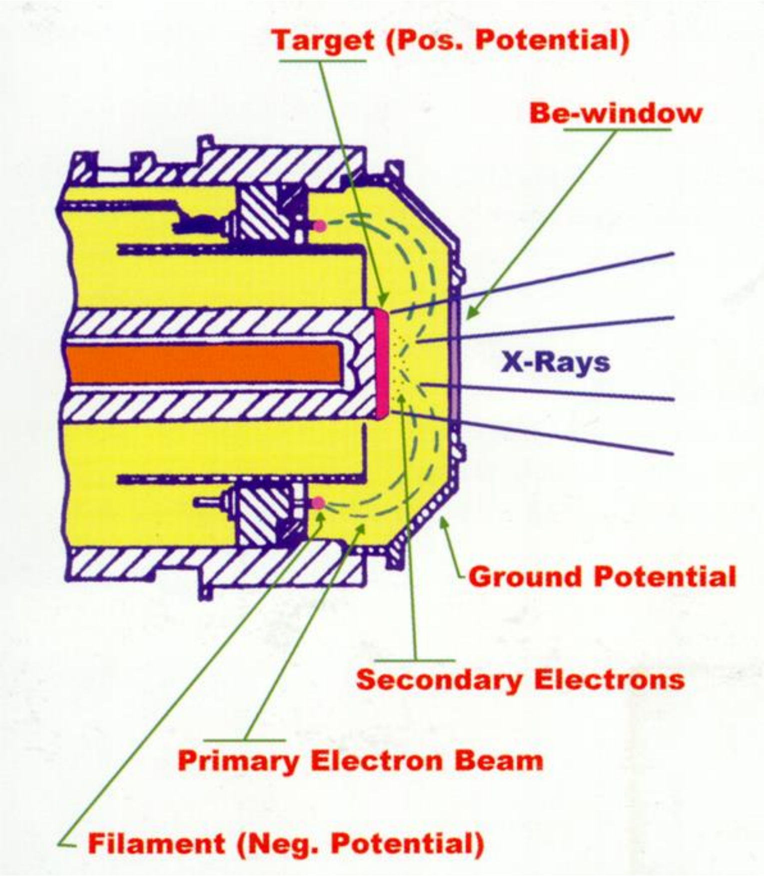
While isotopes have fallen out of favor they are still useful for many gauging applications

❑ RI: advantages and limitations

- Pro´s
  - Compact, simple construction
  - Portability
  - Monochromatic excitation
  - Low cost

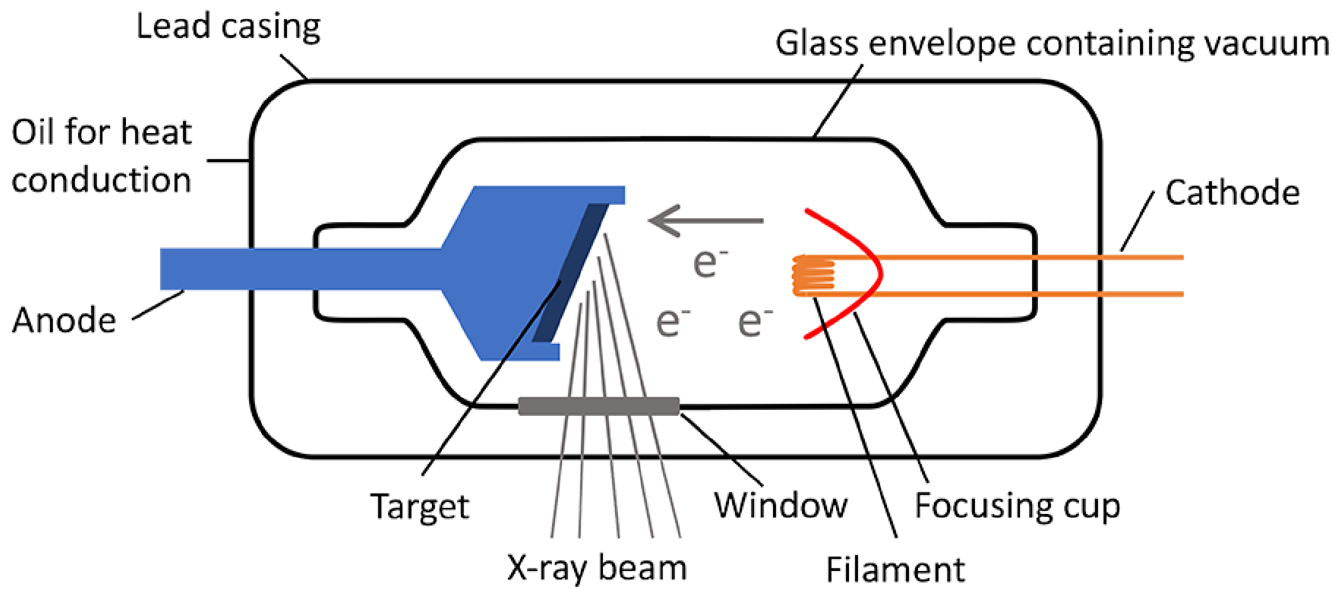
- Con´s
  - Change in flux due to radioactive decay
  - Constant radiation exposure
  - Non-tunable energy

❑ End window X-ray tube



- The filament (**cathode**) is heated and releases electrons
- The target (**anode**) is positively charged creating a difference in potential
- The electrons are accelerated and travel from the cathode to the anode, where they are decelerated

❑ Side window X-ray tube



- Voltage and anode selection determines optimal source excitation and which elements can be excited
- More power = higher sensitivity

❑ Optimization of excitation spectrum

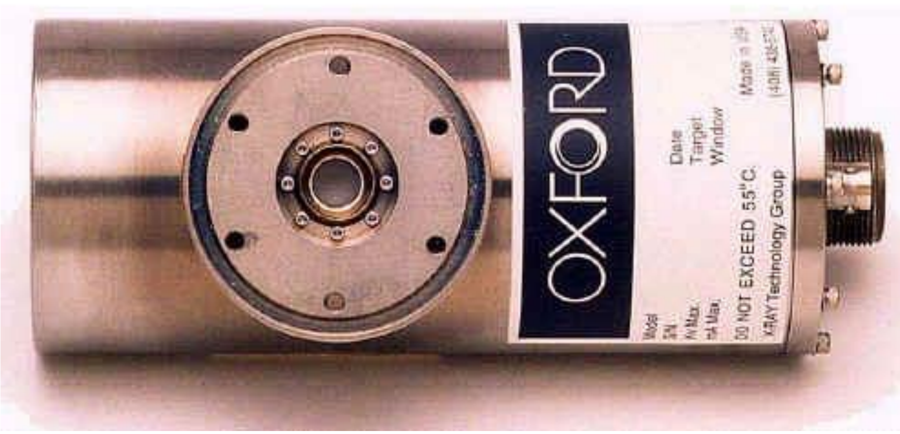
X-ray tube optimization

- Anode material
- High voltage
- Current
- Incident/Exit angle
- Type and thickness of tube window
- Side/End window tube
- Incident beam aperture diameter and distance

Power consumption

❑ X-ray tubes

Oxford Model: XTF5011



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

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

❑ X-ray tube parameters

- Exit window material: **Beryllium 30÷1000 µm thick**
- Anode selection determines **optimal source excitation**
- Tube power: combination of high voltage (kV) and electron current (mA). According to the binding energies of elements of interest:
  - ✓ **High energy: high kV (low mA)**
  - ✓ **Low energy: low kV (high mA)**
- Cooling by internal and/or external water circuit
  - ✓ 50÷1000 W: air cooled or only internal water for anode
  - ✓ 2.4÷4 kW: cooling anode and tube housing by external cooling water from heat exchanger

Type	Target Material	Grounding	Window Thickness	Max. load	Cooling water
Side-window	W, Cr, Mo, Au, etc.	Anode	1000µm, 300µm (Cr)	2.4 - 3kW	Tap water
End-window	Rh, Pd, etc.	Cathode	127 - 30µm	0.05 - 4kW	Deionized water

Important concepts

- **Electronvolt** (**eV**): is the amount of energy gained (or lost) by an elementary charge (electron/proton) moving across an electric potential difference of 1 V
- When a charged particle is accelerated (decelerated), **it emits electromagnetic radiation** (**Larmor's equation**)
- **Binding energy** (eV → keV): is the amount of energy required to free electrons from their atomic shells (it is also know as ionisation energy)

Origin of X-rays in the X-ray tube

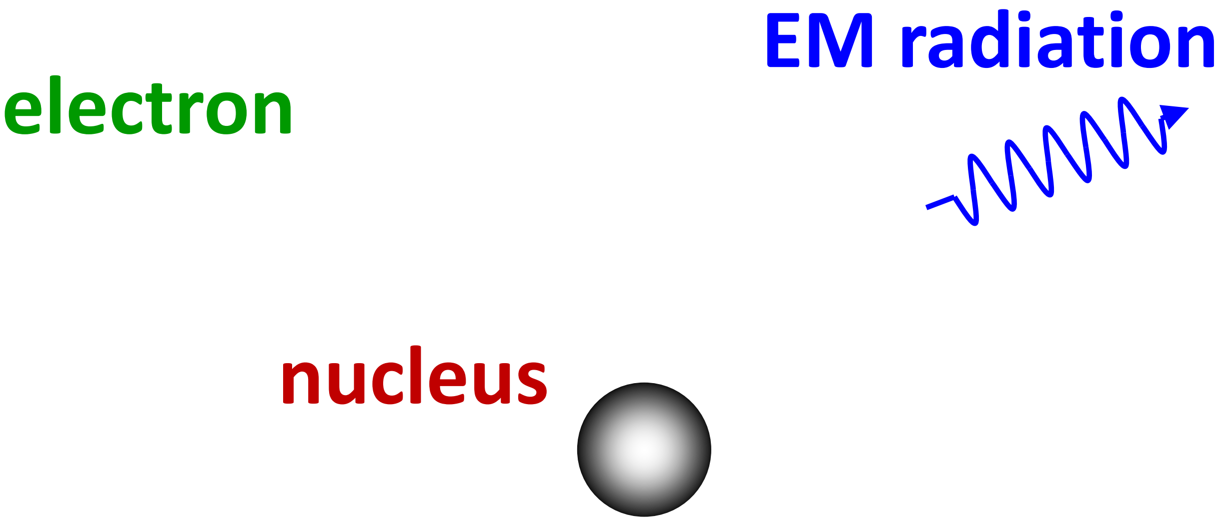
X-rays originate from the interaction of high energy electrons with the atoms of the anode material

The spectrum of an X-ray tube shows two types of X-ray radiation:

- **Bremsstrahlung**: Continuous radiation or white radiation
- **Characteristic radiation**: Unique energies of anode element

Both types of radiation depend on the anode material

❑ Bremsstrahlung



Comes from the German words *bremsen* (braking) and *Strahlung* (radiation)

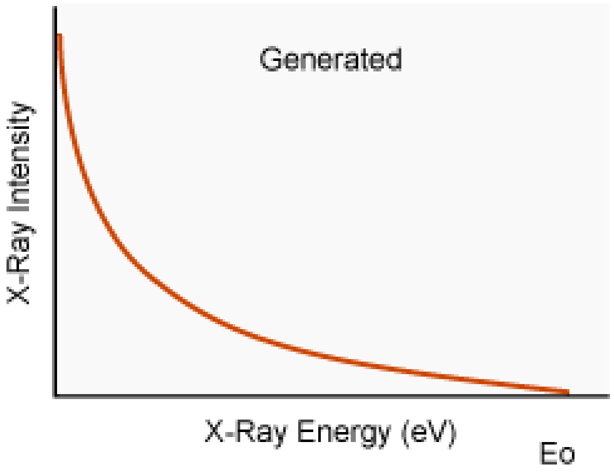
It is electromagnetic radiation that occurs as a charged particle (like an electron) is decelerated around the nucleus of an atom. The range of changes in velocity is large and therefore **there is a broad range of energies being released**

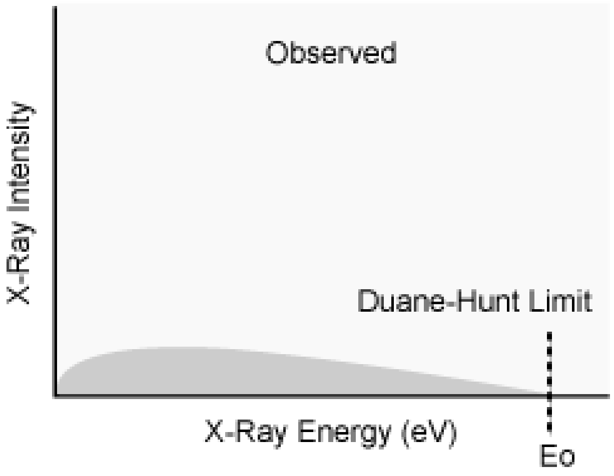
❑ Properties of Bremsstrahlung

Kramers' law (distribution of Bremsstrahlung intensity with wavelength)

$$I(E) = KiZ\left[\frac{E_0 - E}{E}\right]$$

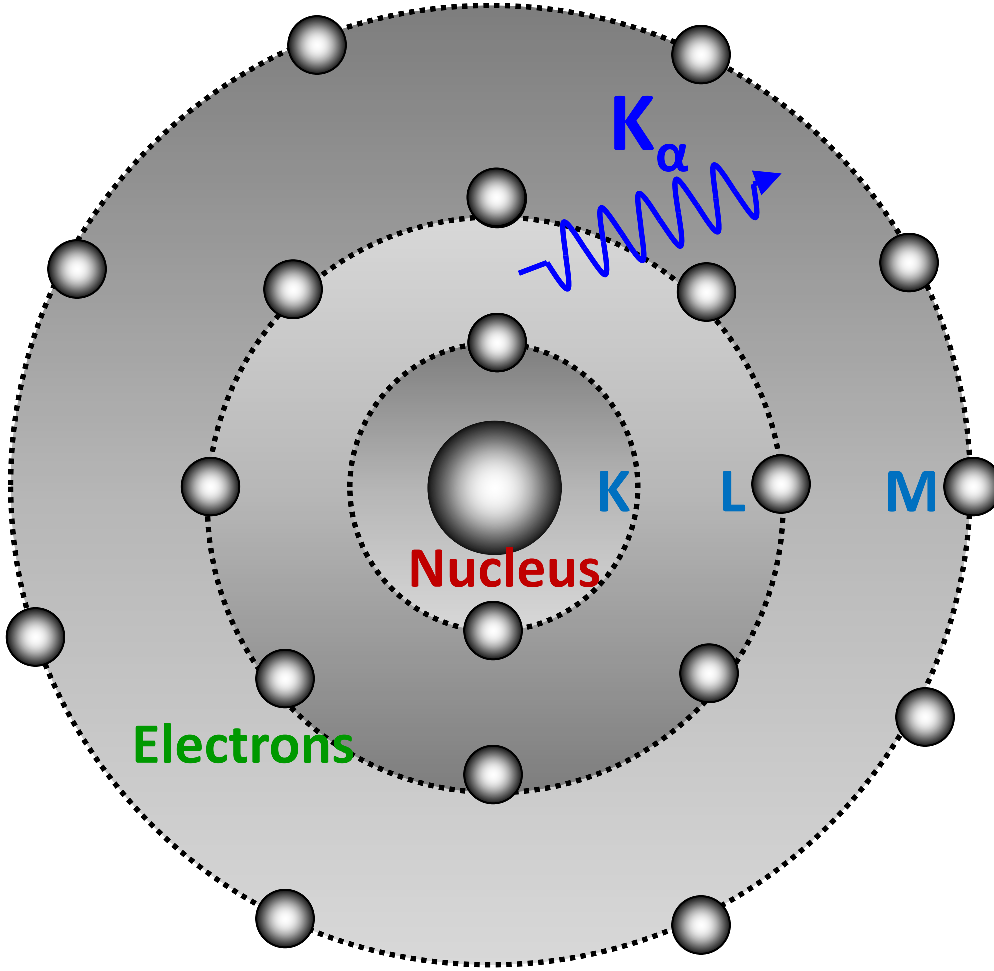
K = constant
i = current (mA)
Z = atomic number of anode material





Emission of characteristic radiation

electron



Accelerated electrons in the tube can remove electrons from the shells of the anode's atoms

Electronic transition and emission of element → **characteristic fluorescence** radiation (unique for that element)

Primary radiation from X-ray tube

Characte	
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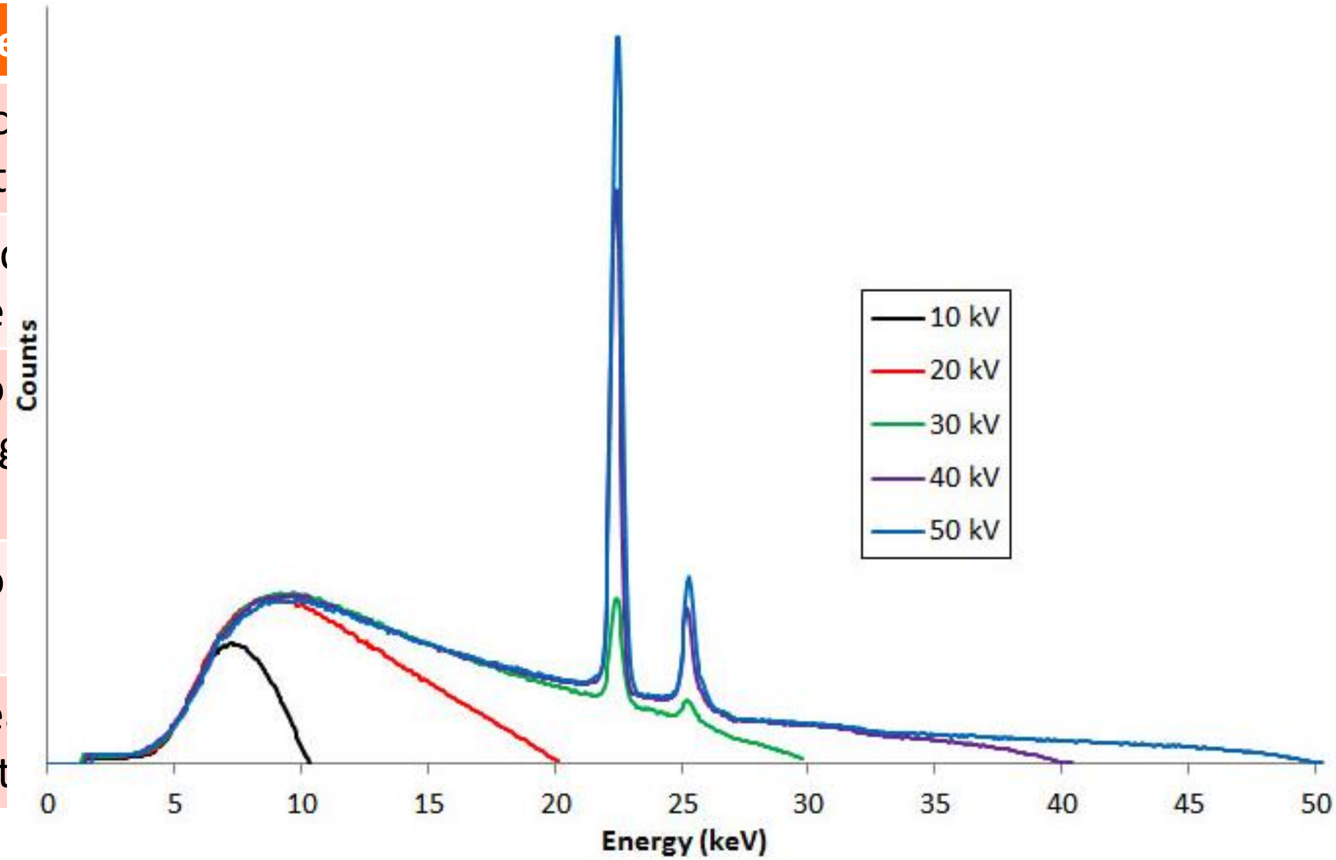
Bombar shell ele	th atom
Radiatio dropping	n of f the
Radiatio	nge of
X-ray be of target	be



❑ X-ray tube: advantages and limitations

- Pro´s
  - Different anode materials available
  - Tunable energy by selecting HV
  - Low power tubes can be even portable
  - Not constant radiation exposure (on/off)
  - Possibility to use modifyiing devices
- Con´s
  - Require of power generator
  - For power 600 W cooling system is required
  - Limited life time (~ 3000 hrs)

Primary X-ray beam modifiers

Energy selection:

- Filters
- Monochromators
- Secondary targets

Spatial:

- Collimators
- X-ray optics devices
- Fresnel zone plates
- KB mirror
- …

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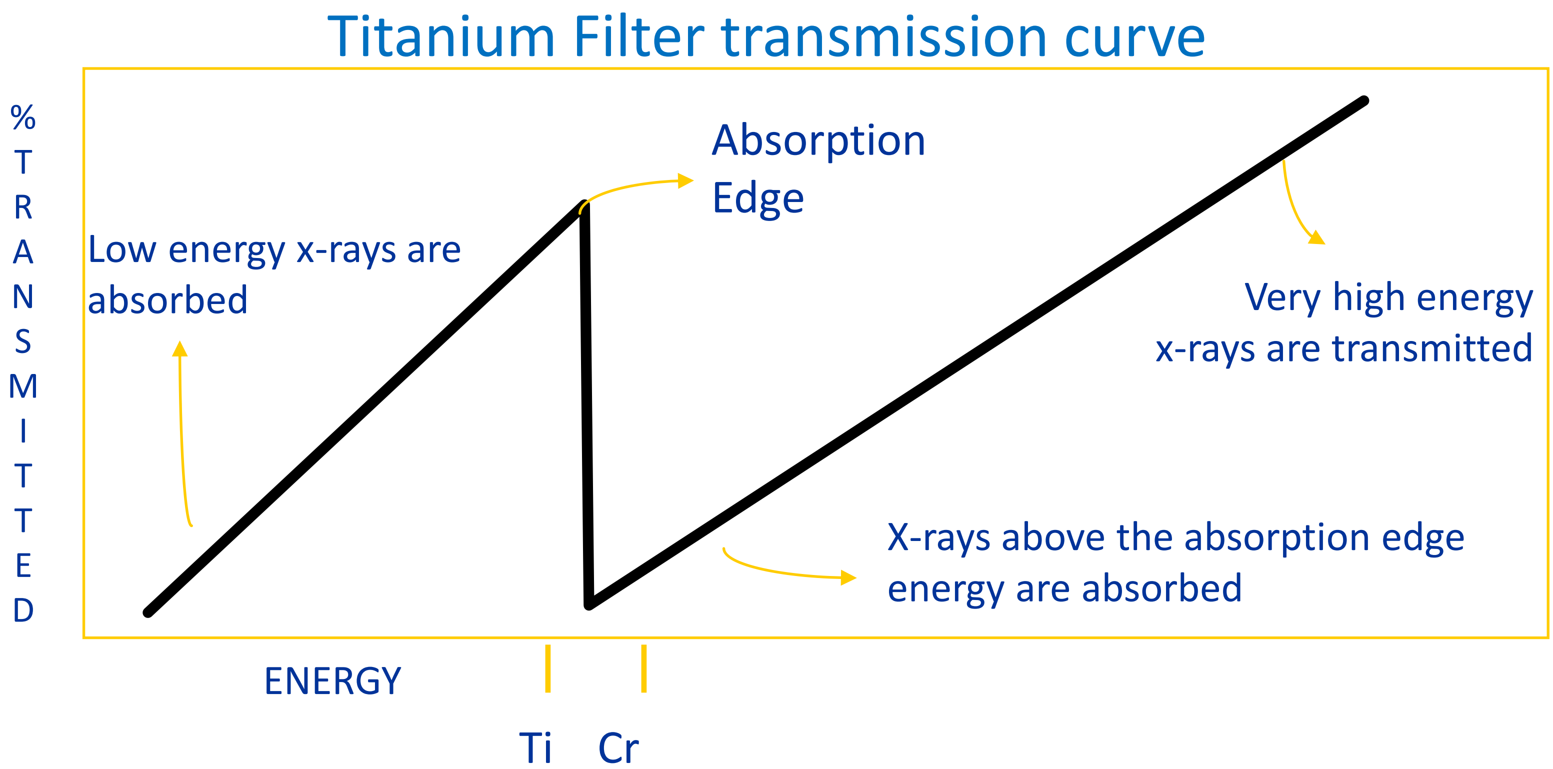
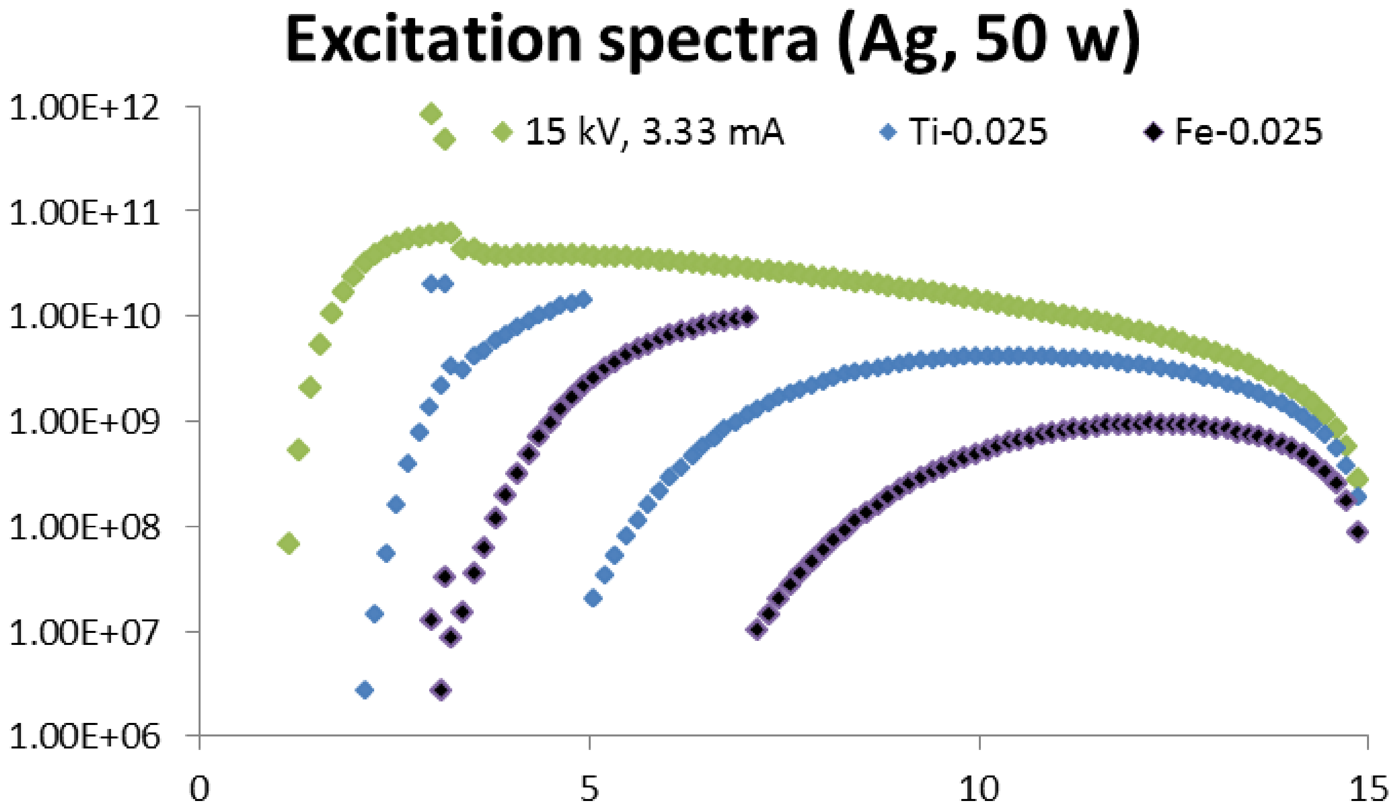
Absorption filters



The transmission curve shows the parts of the source spectrum that are transmitted and those that are absorbed

❑ Absorption filters



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- **Secondary targets**

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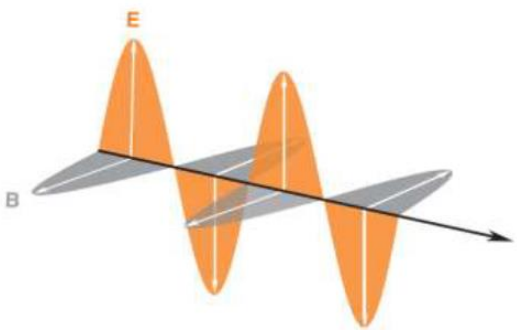
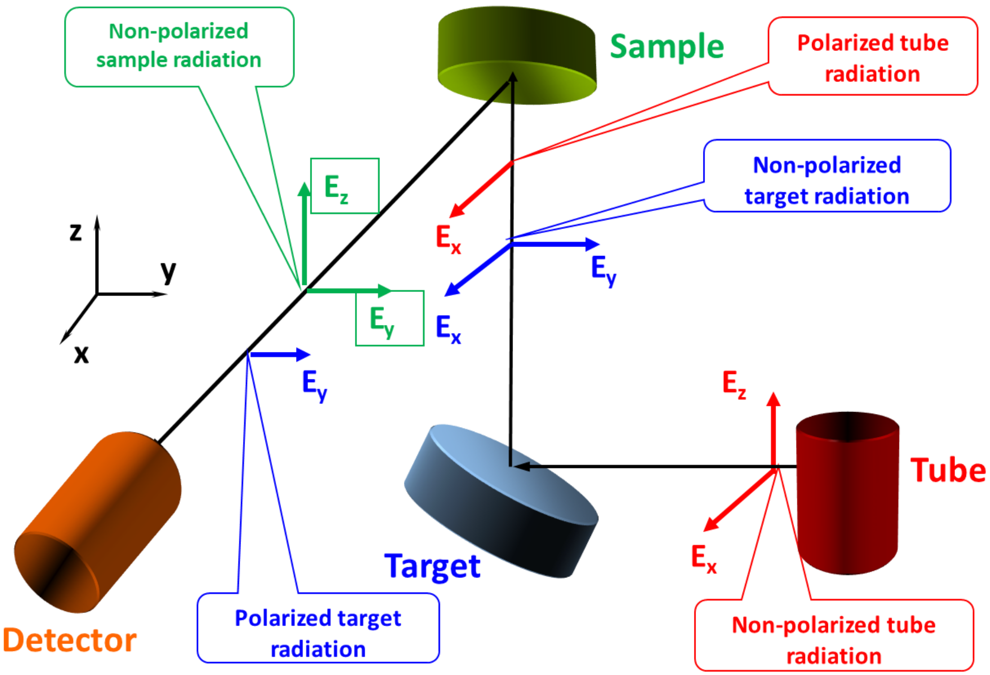
❑ Secondary targets

Courtesy from
Dr. Charalampos Zarkadas, Malvern Panalytical



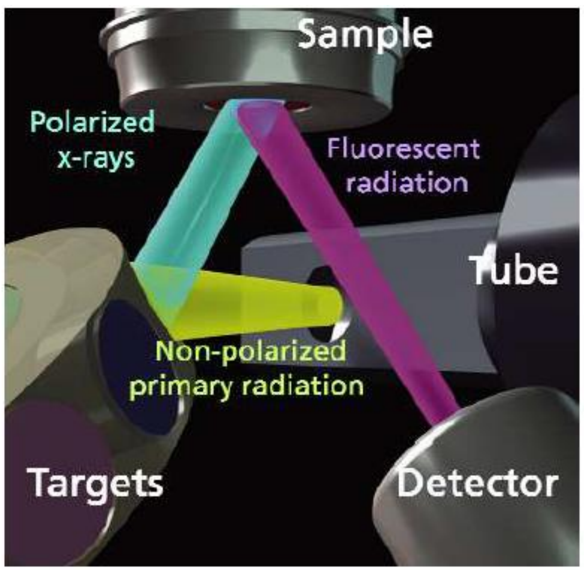


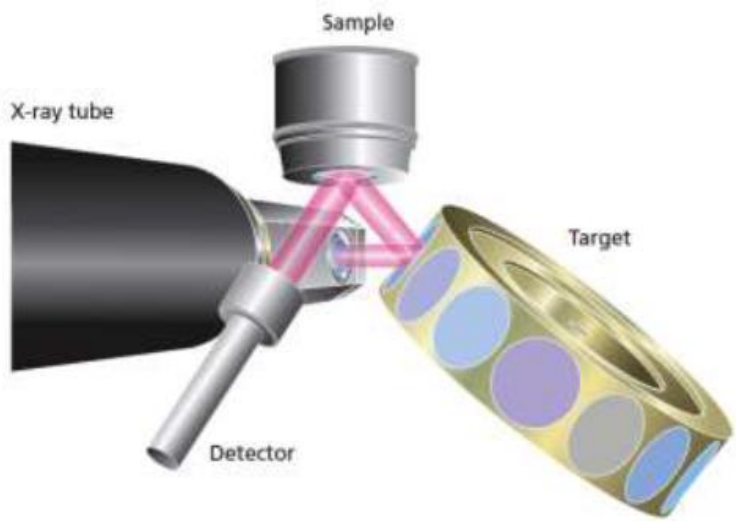
3D optics and various polarization states:

1) Non-polarized primary radiation from X-ray tube to target
2) Non-polarized target fluorescence radiation to the sample + Polarized scattered X-ray tube radiation behind the target
3) Sample fluorescence radiation into from the detector + Polarized scattered target fluorescence radiation + **Vanishing scattered radiation from the X-ray tube**

❑ Secondary targets

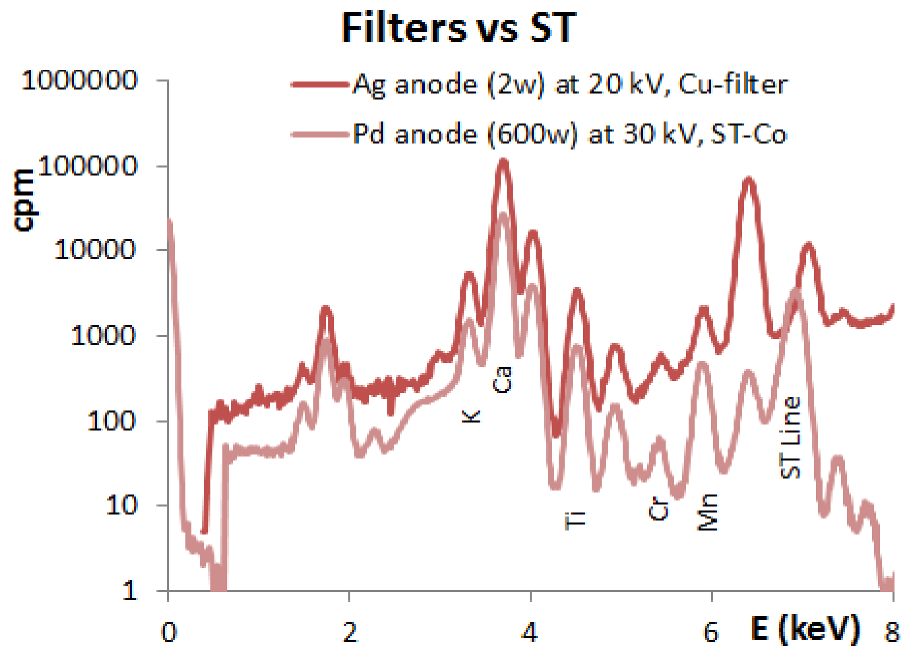
Using more secondary targets, it is possible to excite elements of interest with lines above the respective absorption edges, optimized sensitivities can therefore be achieved





Reproduced from Epsilon 5 specifications sheet (Malvern Panalytical)

❑ Comparison ST vs Direct or filtered



Improved fluorescence and lower background

The characteristic fluorescence of the anode source is used to excite the sample, with the lowest possible background intensity.

It requires almost 100x the flux of filter methods but gives superior results.

Primary X-ray beam modifiers

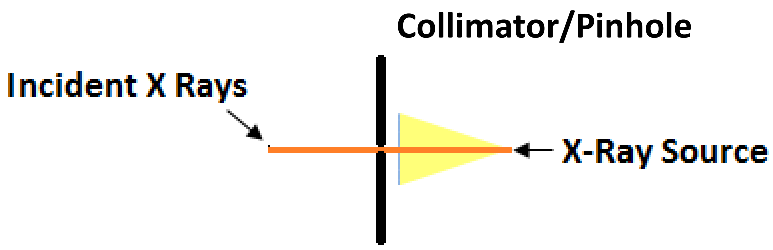
Energy selection:

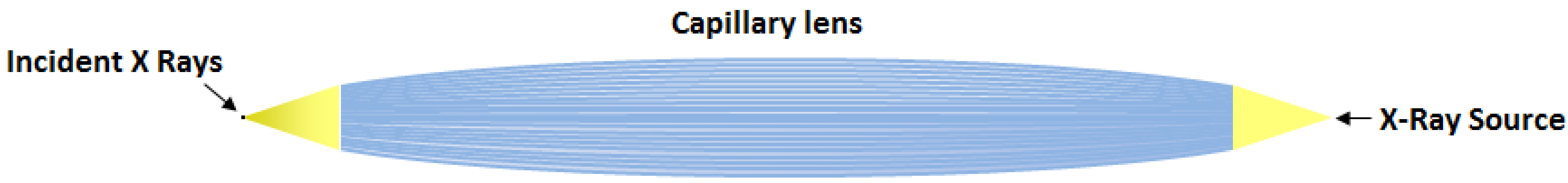
- Filters
- Monochromators
- Secondary targets

Spatial:

- **Collimators**
- **X-ray optics devices**
- Fresnel zone plates
- KB mirror
- …

❑ Polycapillary lens vs Pinhole



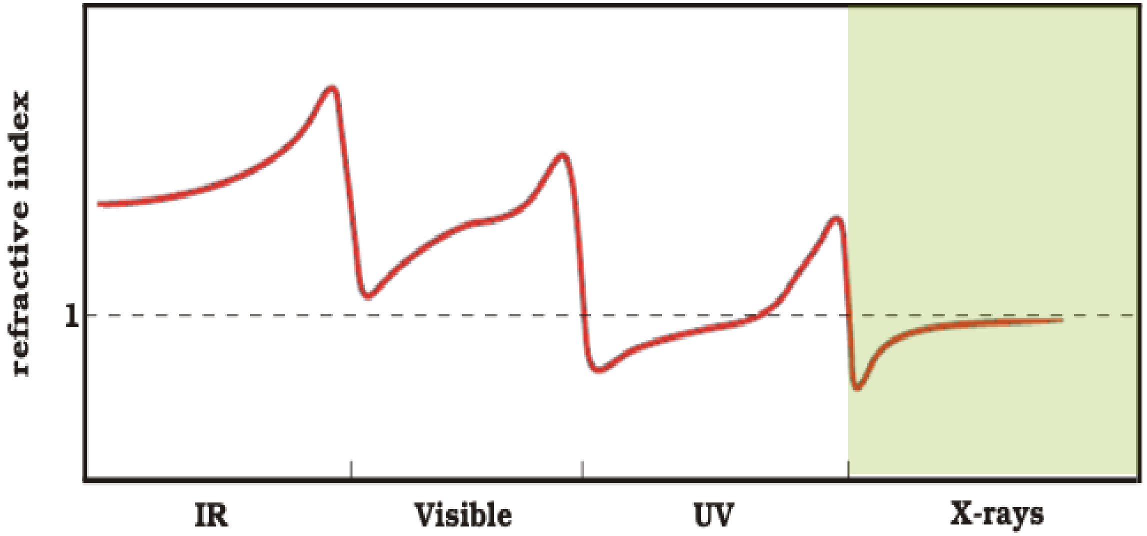


Spot size ~ 15÷20 μm

Gain in intensity: 300x

❑ X-ray Optics

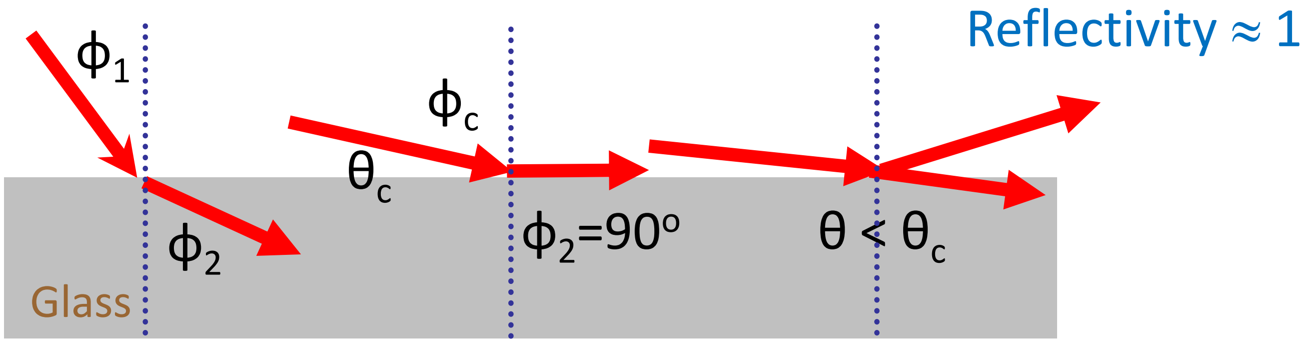
Refractive index: $\boldsymbol{n = \frac{c}{u_p}}$



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

β = Attenuation term
δ = Phase term

X-ray total reflection

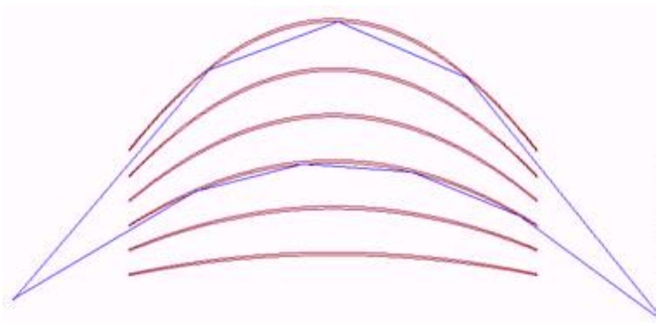


Snell Law

$$\sin\phi_2 = \frac{\sin\phi_1}{n} \Rightarrow \phi_2 > \phi_1$$

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

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

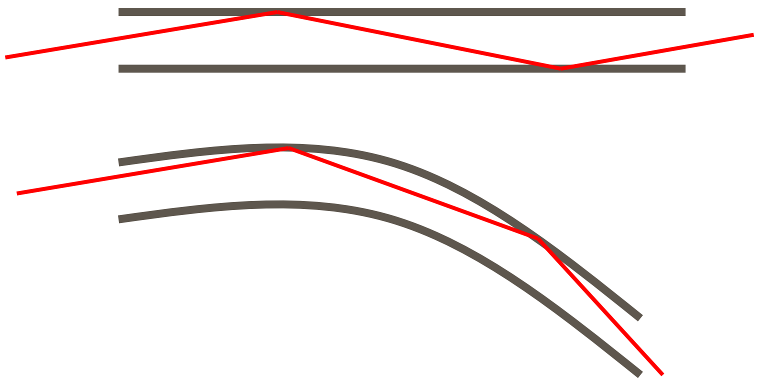


Z: Atomic number

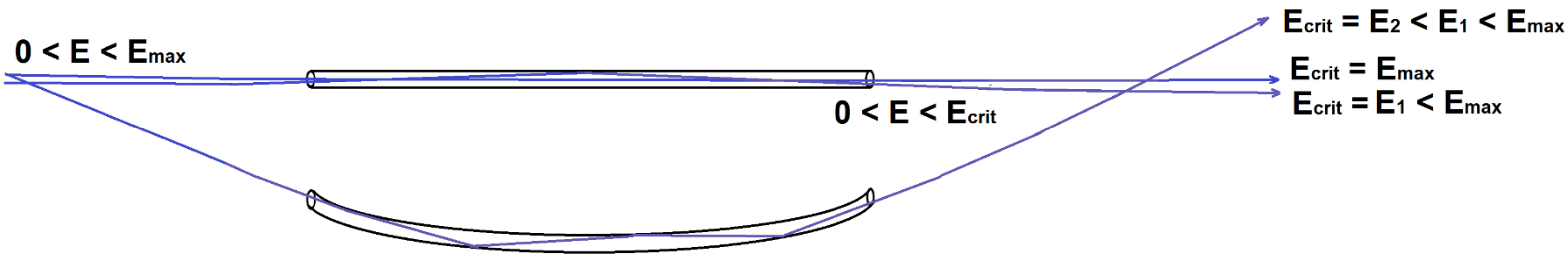
A: Atomic mass

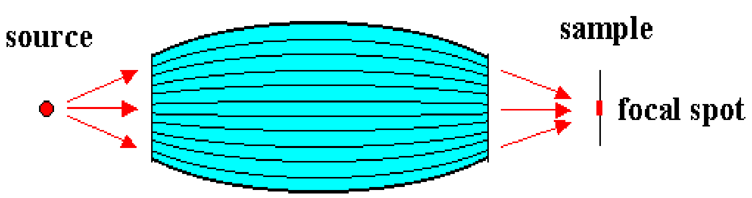
ρ: Density

Glass capillaries



Multiple reflections in a straight glass capillary



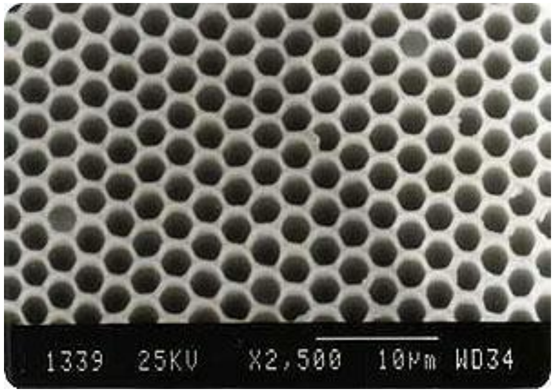


Focusing X-rays by thousands of individual capillaries

Polycapillary lenses

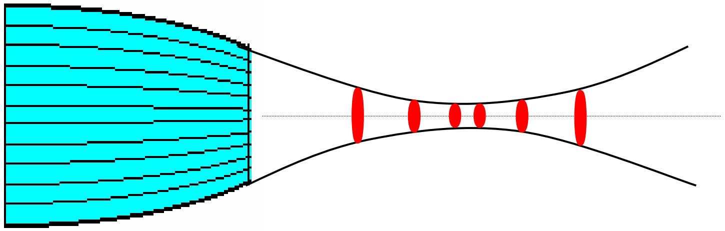
Bundles of thousands glass mono-capillaries in certain arrangements can be used for:

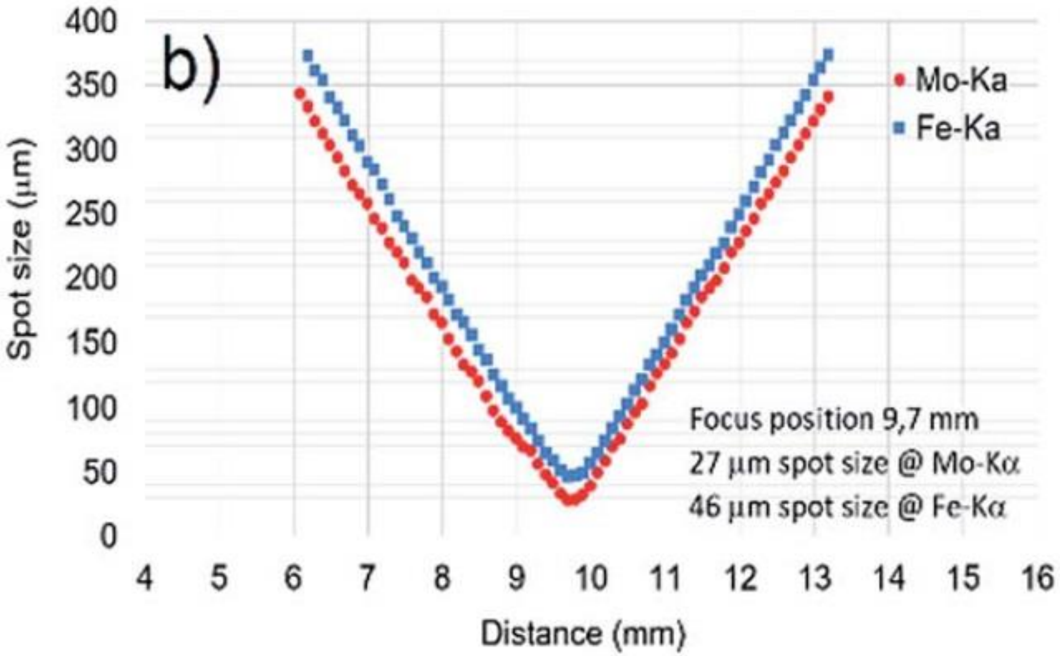
- **Directing**
- **Focusing**
- **Parallelizing**



❑ Polycapillary lenses

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

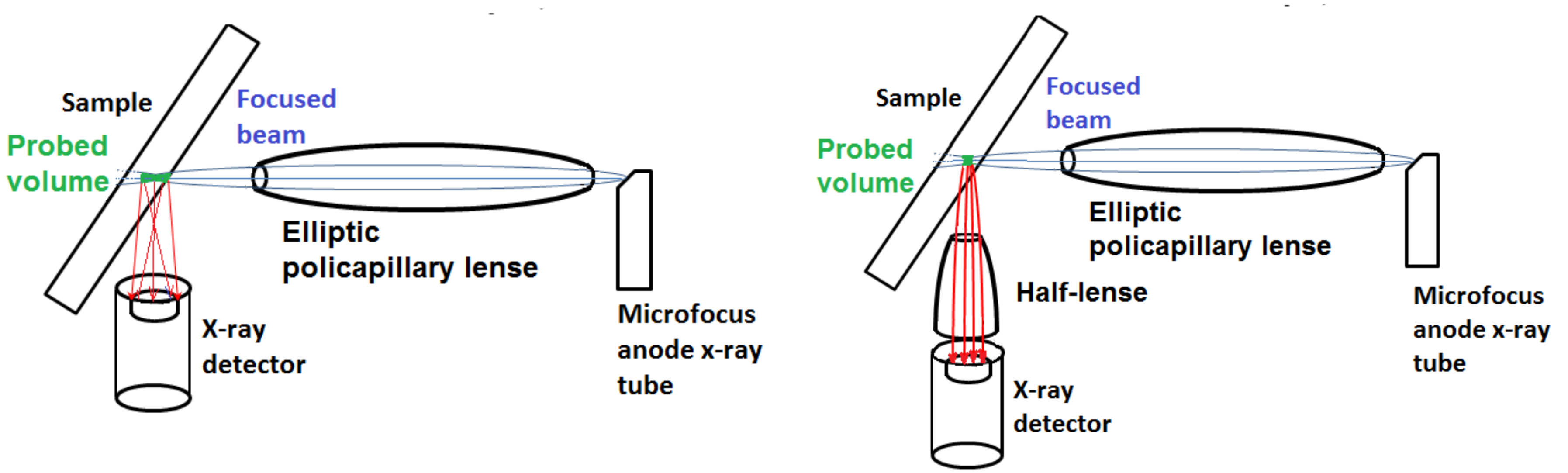




F. P. Romano et al., JAAS 2017,
DOI: 10.1039/c6ja00439c

❑ Polycapillary lenses

Polycapillary lenses can be used for micro-XRF scanning applications
In combination with conical lens the inspected volume can be restricted in depth, thus allowing 3D scanning of samples



❑ Main configurations of XRF spectrometers

- **Non-dispersive instruments**
  The characteristic radiation is filtered and measured by one or several detection channels/measurement condition, optimized for detection of one element

- **WDXRF**
  The characteristic radiation emitted by the sample is separated by wavelengths (in multiple channels or sequentially by scan) by using an arrangement of x-ray collimators and diffracting crystals bringing selected wavelength photons to a detector

- **EDXRF**
  The characteristic radiation is measured with a detector capable of producing a signal of amplitude proportional to the energy of the incident photon

Detectors

- Proportional Counters
- Scintillation Detectors
- Si(Li)
- LEGe
- PIN Diode
- SDD
- CCD, CMOS cameras
- CZT, other

Poor energy resolution
WDXRF

Improved energy resolution
EDXRF

❑ Detectors

- Proportional Counters
- Scintillation Detectors
- **Si(Li)**
- **LEGe**
- **PIN Diode**
- **SDD**
- CCD, CMOS cameras
- CZT, other

Main features of detectors

- **Intrinsic Efficiency**

  Ratio of photons that produce a signal to the total number of photons that reach the detector. Depends on energy of the photon, attenuation in detector entrance window and detector absorption

- **Energy resolution**

  Capability to differentiate close by amplitude (energy) signals

- **Charge collection time**

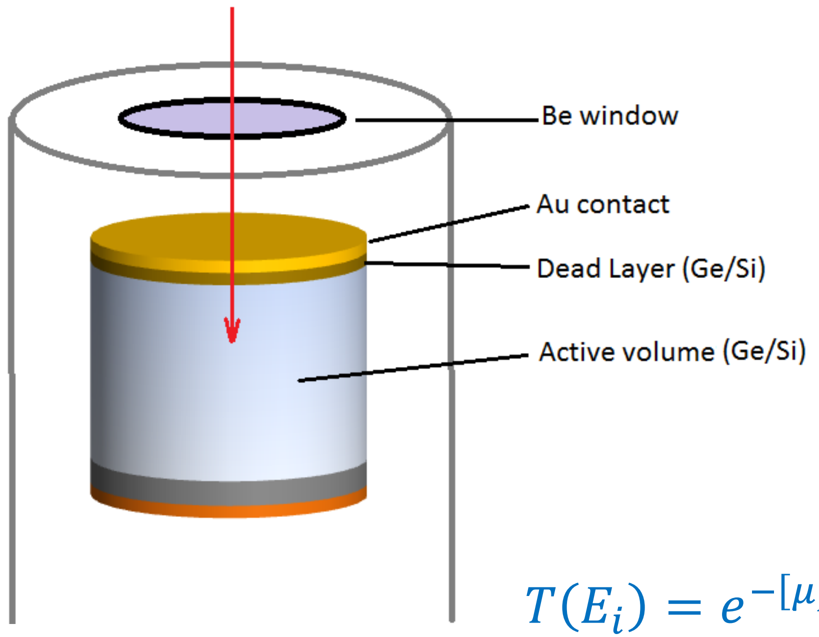
  Time required to collect charge. Depends on the drift velocity of the charge carriers

Main features of detectors

Detector	Energy Range (keV)	Energy resolution at 5.89 keV (ΔE/E, %)	Charge collection time (µs)
Proportional Counter	0.2 - 50	15	0.2
Scintillation NaI(Tl)	3 - 10000	40	0.25
Avalanche photodiode	0.1 - 50	20	0.001
Semiconductor Si(Li), SDD, HPGe	1 - 10000	3	0.5 - 15
CCD	0.1 - 70	3	1

Intrinsic Efficiency

T: Fraction of X-rays that is transmitted through the entrance layers
D: Fraction of X-rays that is detected in the sensitive volume

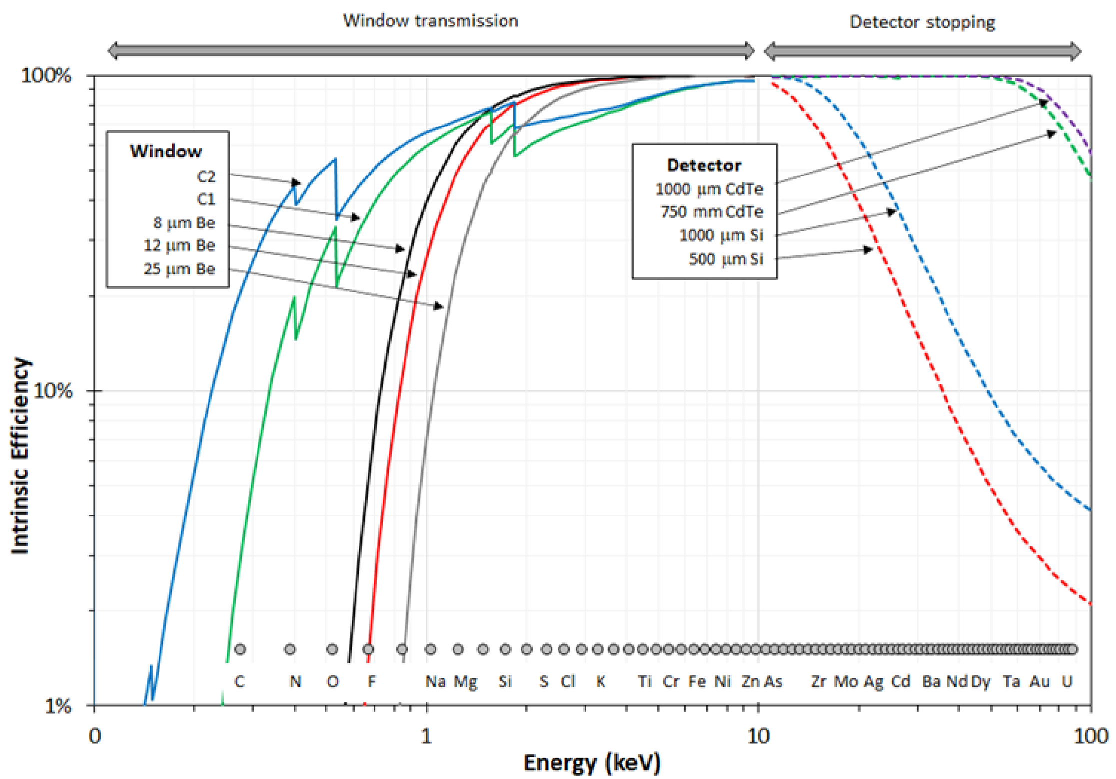


$$\boldsymbol{\varepsilon(E_i) = T(E_i)\ D(E_i)}$$

$$D(E_i) = \frac{1 - e^{-[\mu_{Si}(E_i)\rho_{Si}X_{Si}]}}{\mu_{Si}(E_i)\rho_{Si}}$$

$$T(E_i) = e^{-[\mu_{Be}(E_i)\rho_{Be}X_{Be}+\mu_{Au}(E_i)\rho_{Au}X_{Au}+\mu_{Si}(E_i)\rho_{Si}X_{Si}]}$$

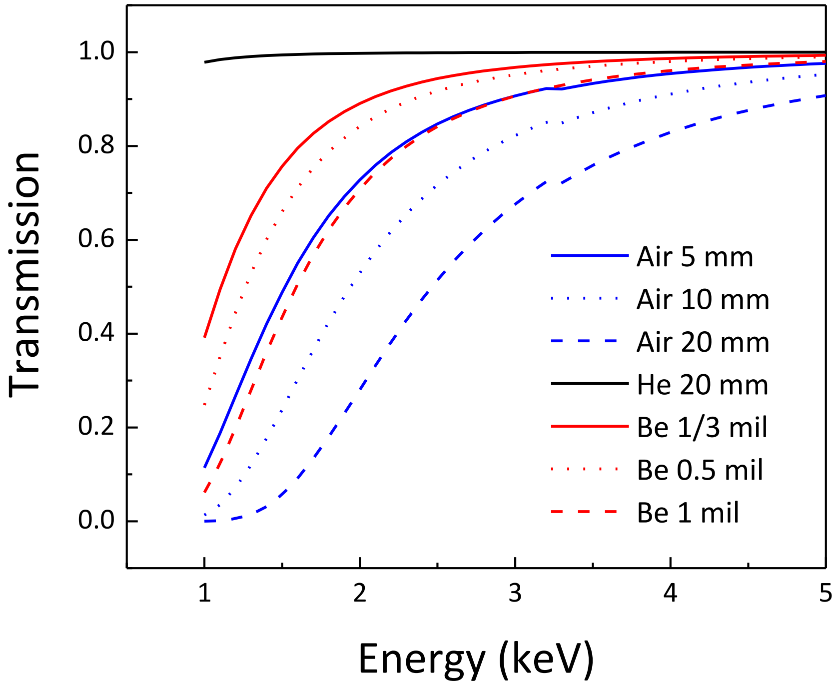
❑ Efficiencies of different detectors

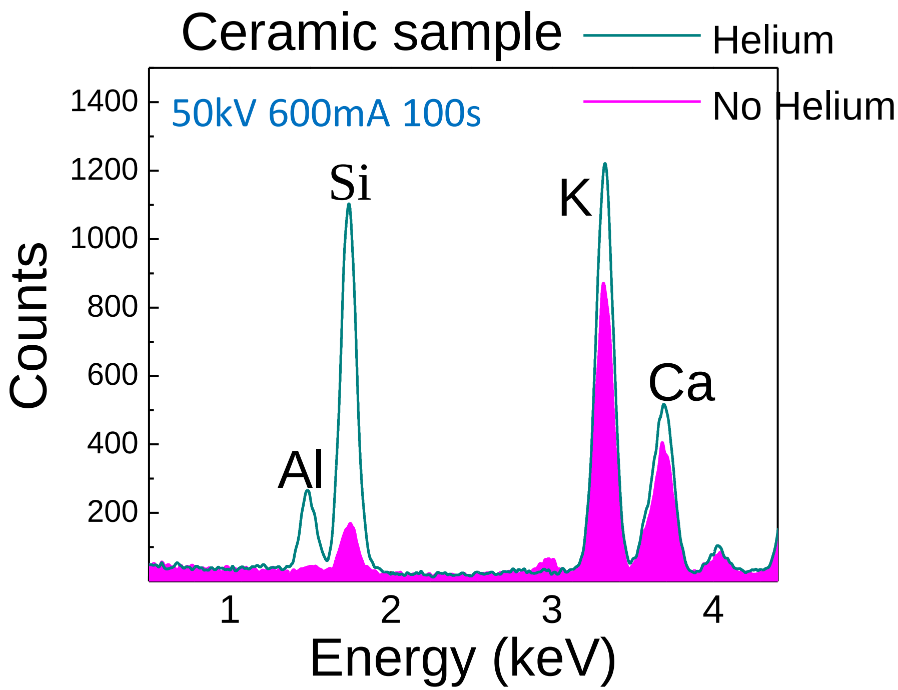


Comparison of different detector's efficiency from AMPTEK
https://www.amptek.com/products/x-ray-detectors/fastsdd-x-ray-detectors-for-xrf-eds/fastsdd-silicon-drift-detector

❑ "Light" elements (Na, Mg, Al, Si)

Vacuum atmosphere or **He flushing** is required in the x-rays path between sample and detector





The improvement in the intensity of Al-K and Si-K characteristic X-ray lines is significant, 22 and 7.3 times respectively

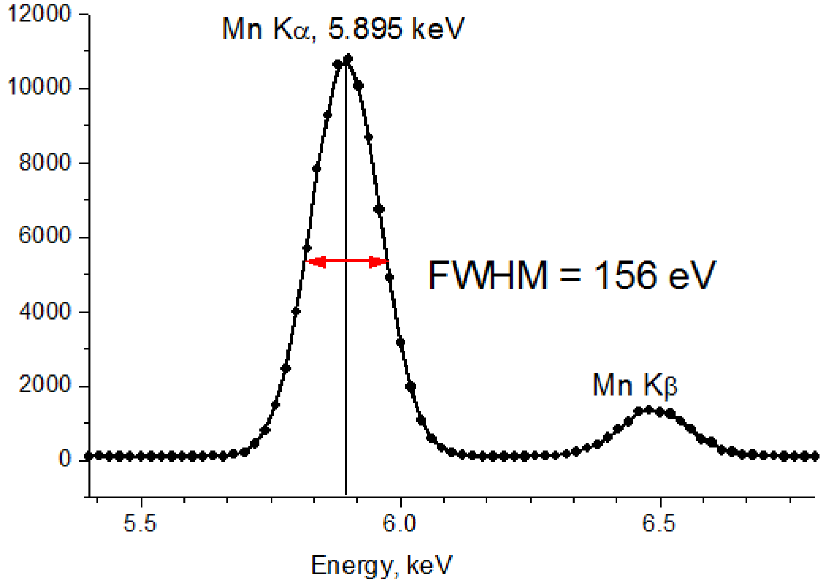
Energy resolution

Full Width at Half Maximum (FWHM) of a peak

$$FWHM^2_{Peak} = FWHM^2_{Noise} + FWHM^2_{Stat}$$

Electronic noise

Statistical fluctuation in number of charge carriers



(Modified from an original lecture by Prof. P. Van Espen, AXES, University of Antwerp)

$$FWHM_{Stat} = 2.3548\sqrt{\varepsilon F E}$$

ε = Energy to create e-h pair

F = Fano factor (~0.114)

E = X-ray energy

Mn-K_α, E = 5895 eV

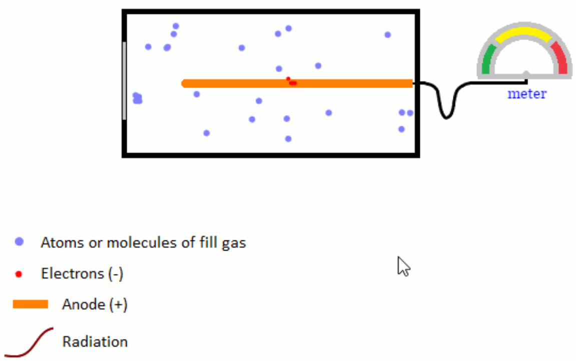
$FWHM_{Stat}$ ~ 120 eV

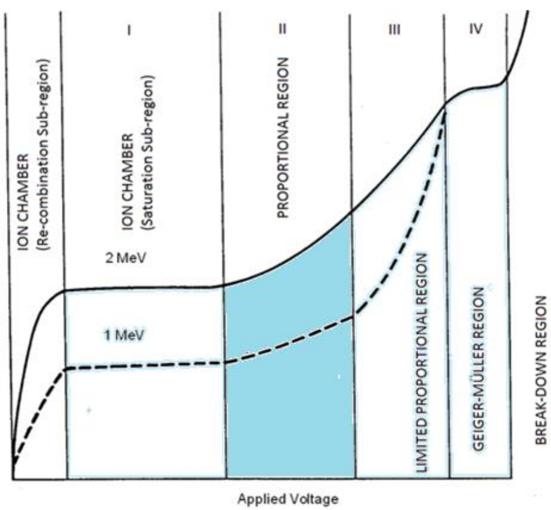
$FWHM_{Noise}$ ~ 100 eV

$\rightarrow$ **$FWHM_{Peak}$ ~ 156 eV**

❑ Gas detectors: Proportional counters

- Gas detectors: Chamber filled with a gas (often noble gases) and voltage plates known as electrodes
- X-rays can ionize the gas, but mostly interact with the cathode and knock out electrons, which further ionize the gas





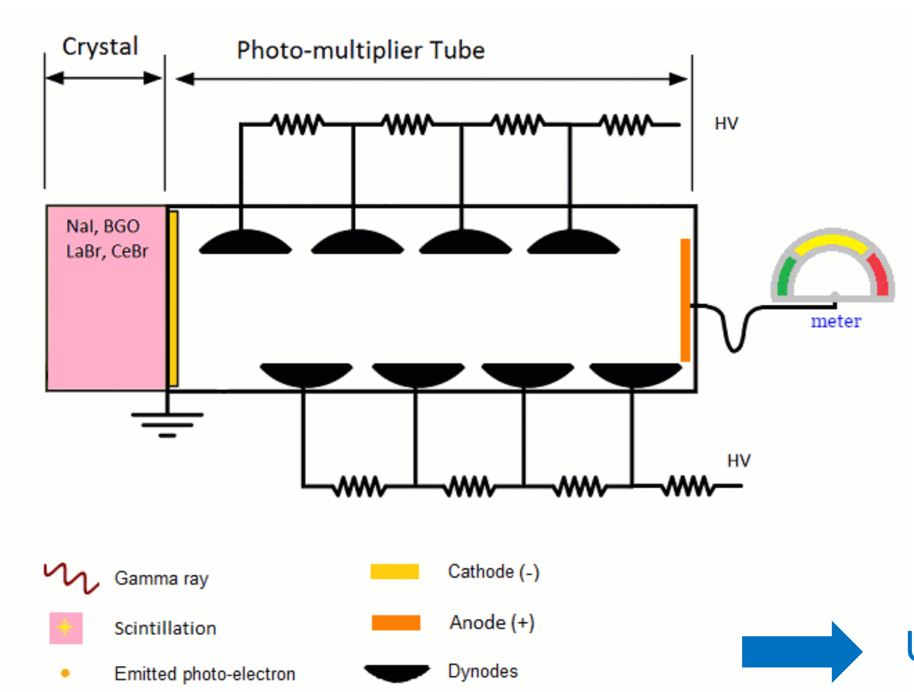
Detector	Energy resolution	Effect used for detection
Ionization chamber (recomb)	Poor	Voltage is low, only primary Ionization of the gas and collection of charge
Ionization chamber (saturation)	None	Multiple Ionization of the gas and collection of charge, number of ions collected is not proportional to energy deposited by the charged particle tracks-> dose rate
Proportional counters	Limited ~ 15 %	High voltage is chosen as to have an intensity of the sparks (amount of charge collected) proportional to the incident energy. Multiplication of charge is linear with energy of photon
Geiger Müller counters	None	Progressive growth of ionization in a strong electric field between the anode and the cathode Charge multiplication in avalanches

- Typical gas: P-10 (Ar+Methane);
- Efficiency > 90 %
- Energy resolution ~ 15 %
- Charge collection ~ 0.2 ms

→ Used in WDXRF to detect energies below 6 keV

❑ Scintillation detectors

- Photons or particles produce a spark of light, which intensity is proportional to the energy deposited
- Light spark impinges into a metal plate and produces the ejection of electrons (inverse photo-effect)
- Electrons are accelerated to the next plate (dynode) and multiply the effect of ejection of electrons
- The electron cloud is furtherly multiplied and finally collected as a pulse of charge



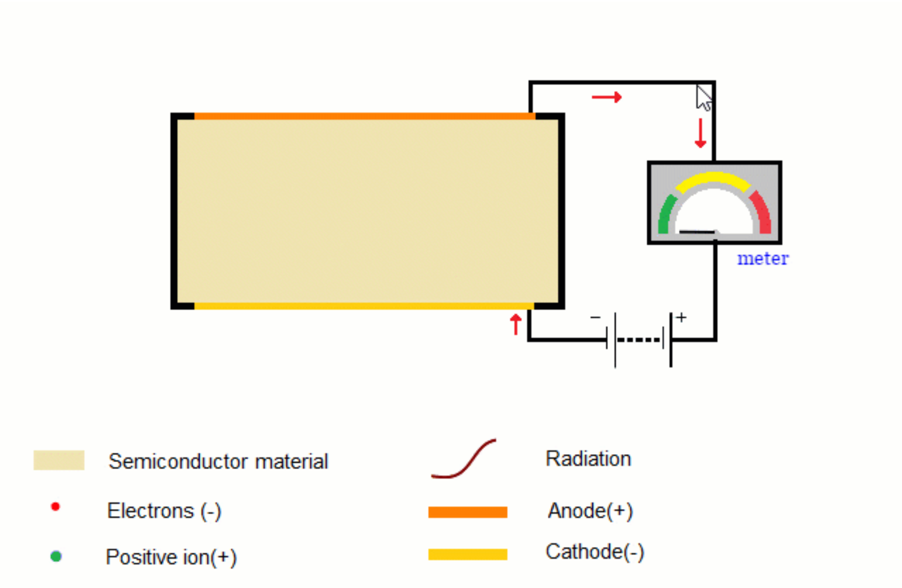
- Typical scintillator: NaI(Tl)
- Efficiency > 90 % (for E > 5 keV)
- Energy resolution ~ 40 %
- Charge collection ~ 0.25 ms

The poor energy resolution is due to several contributions:
- Statistical variations in electron production at the crystal,
- Non-uniform reflectivity of the reflecting covering of the crystal
- Non uniformity of photocathode and/or PMT sensitivity
- Statistical variations in electron production at the photocathode
- Statistical variations in dynode multiplication
- Electrical noise and high voltage fluctuations

➡ Used in WDXRF to detect energies > 6 keV

Semiconductor detectors

- X-rays produce **electron-hole pairs**, whose number is **proportional** to the energy of the radiation (average energy to produce an electron/hole pair is 3.6eV for Si and 2.9eV for Ge)
- Electrons and holes are collected from the depleted active region to the electrodes, where they result in a **pulse** that can be further **amplified** and finally **measured**
- This pulse carries information about the energy of the original incident radiation. The number of such pulses per unit time also gives information about the intensity of the radiation



- Typical detectors: Si(Li), LEGe, SDD
- Efficiency > depending on window and thickness
- Energy resolution ~ 3 %
- Charge collection ~ 5-20 μs

Charge collection time

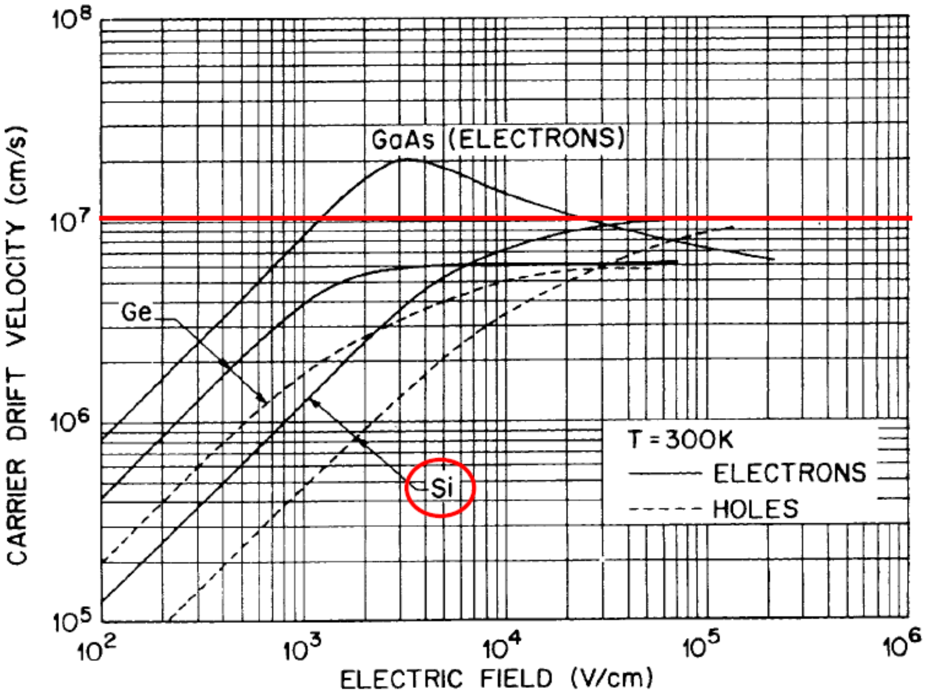
The local velocity of a charge carrier is given by

$$v(x) = \mu \cdot E(x)$$

μ = mobility

In Si at 300 K (valid at low fields $E < 10^4$ V/cm)

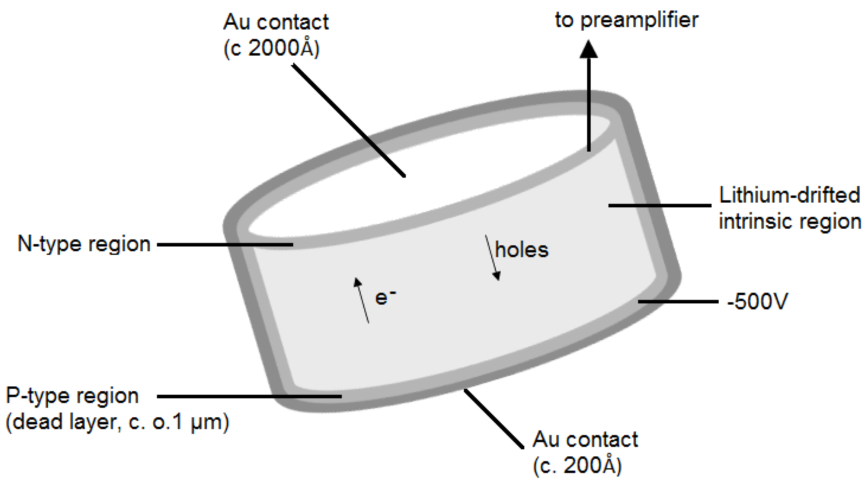
μ(electrons) = 1350 cm^2/Vs
μ(holes) = 480 cm^2/Vs



The mobility is growing up to about 10^4 V/cm
At high fields ($E > 10^5$ V/cm) constant drift velocity ~ 10^7 cm/s

❑ Silicon Lithium detectors - Si(Li)

Using the purest Si the depleted region has thickness of maximum 2 mm. Using the process of Li “drifting“, it is possible to create a “compensated“ region where the concentrations of donors and acceptors are almost exactly balanced on thicknesses up to 10 mm. In tis region the material has almost the same behaviour on instrinsic Si.

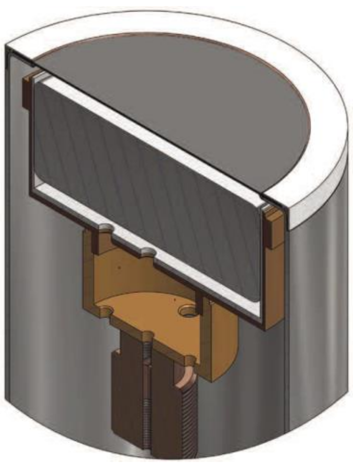


- Energy resolution ~ 140 – 170 eV (Mn-Ka)
- Charge collection ~ 10 µs
- Input capability ~ 10^5 photons/sec

Photo Credit: Mirion Technologies
https://www.canberra.com/fr/produits/detectors/si-li-detectors.html

❑ Low-energy Ge detectors - LEGe

Ge crystal can have a depleted, sensitive thickness of centimeters, and therefore (thanks also to the higher Z) can be used for detection of high-energy X-rays. They are called high-purity Ge detectors (HPGe) because they can be used as detectors without any doping. The major drawback of Ge detectors is that they must be cooled to liquid nitrogen temperatures to produce spectroscopic data.

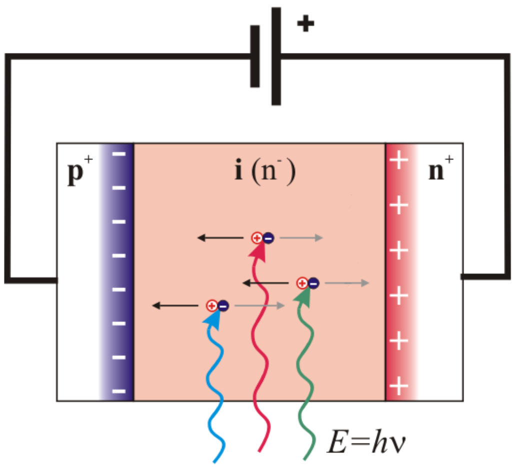


- Energy resolution ~ 140 – 170 eV (Mn-Ka)
- Charge collection ~ 10 µs
- Input capability ~ 10^5 photons/sec

Photo Credit: Mirion Technologies
https://www.canberra.com/fr/produits/detectors/germanium-detectors.html

❑ Si-PIN detectors

A PIN diode (p-type, intrinsic, n-type diode) is a diode with a wide undoped intrinsic semiconductor region between a p-type semiconductor and an n-type semiconductor. The depletion region exists almost completely within the intrinsic region, which has a constant width (or almost constant) regardless of disturbances applied to the diode.

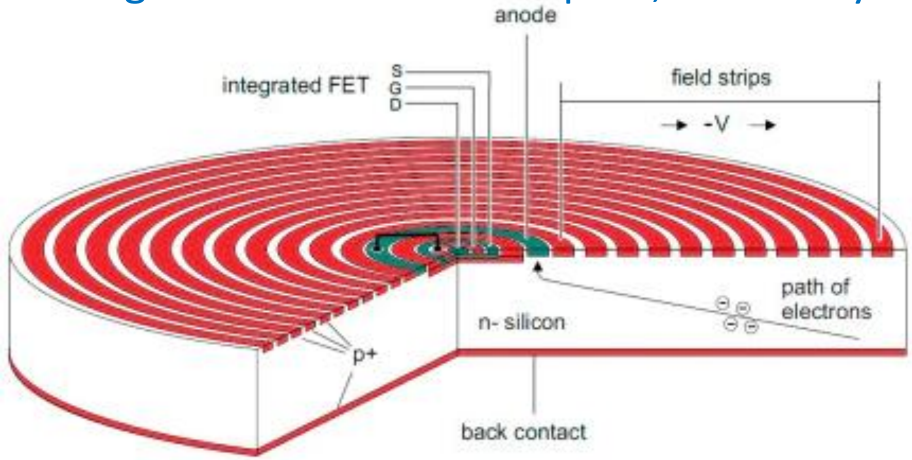


- Energy resolution ~ 170 – 190 eV (Mn-Ka)
- Charge collection ~ 10 µs
- Input capability ~ 10^5 photons/sec

Image reproduced from http://www.jowil.de/Semester8/Optoelectronics.pdf

❑ Silicon drift detectors - SDD

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. For SDDs faster counting is enabled and higher leakage current can be accepted, drastically reducing the need for cooling.

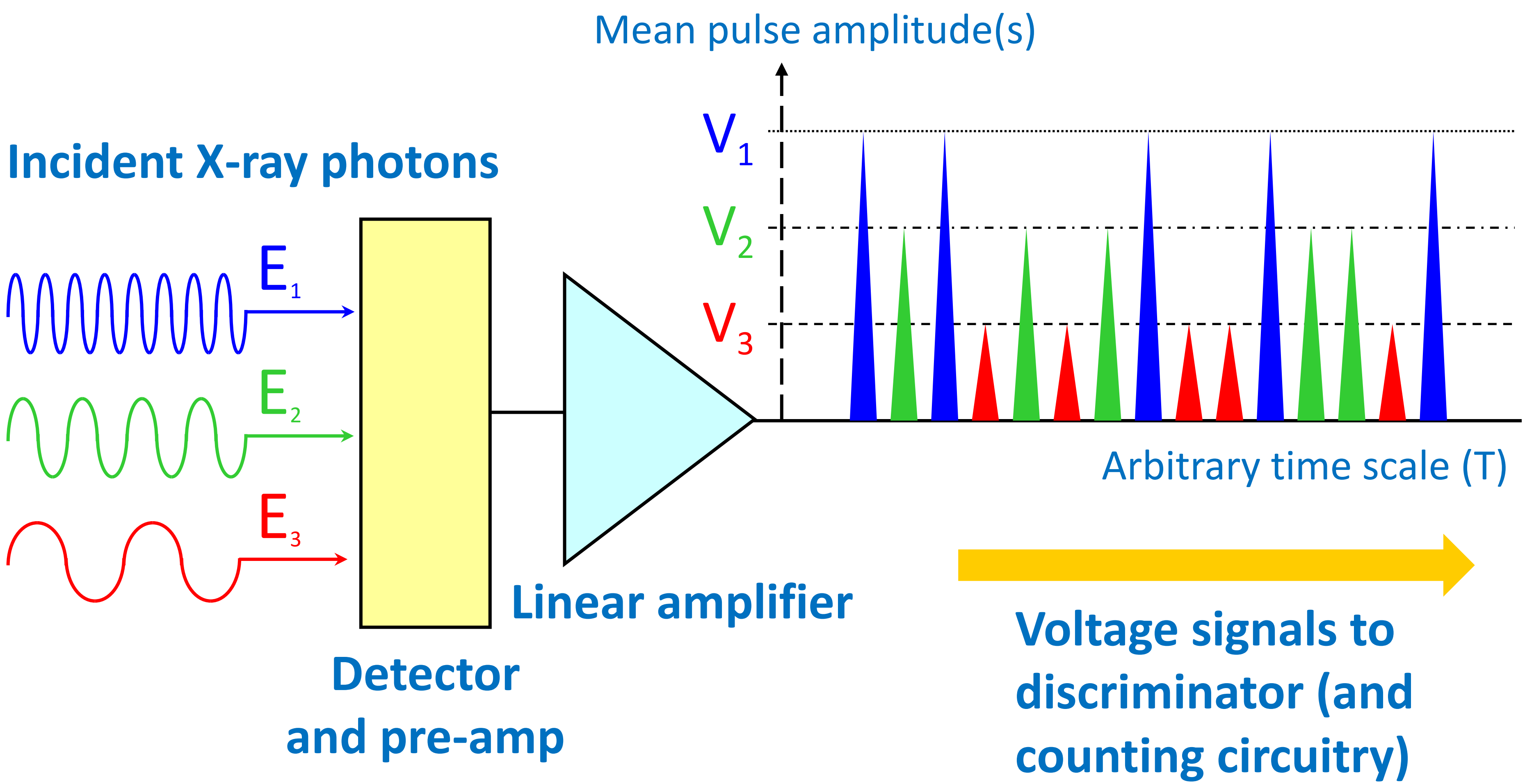


- Energy resolution ~ 130 – 150 eV (Mn-Ka)
- Charge collection ~ 1 ms
- Input capability ~ 10^6 photons/sec

https://tools.thermofisher.com/content/sfs/brochures/TN52342_E_0512M_SiliconDrift_H.pdf

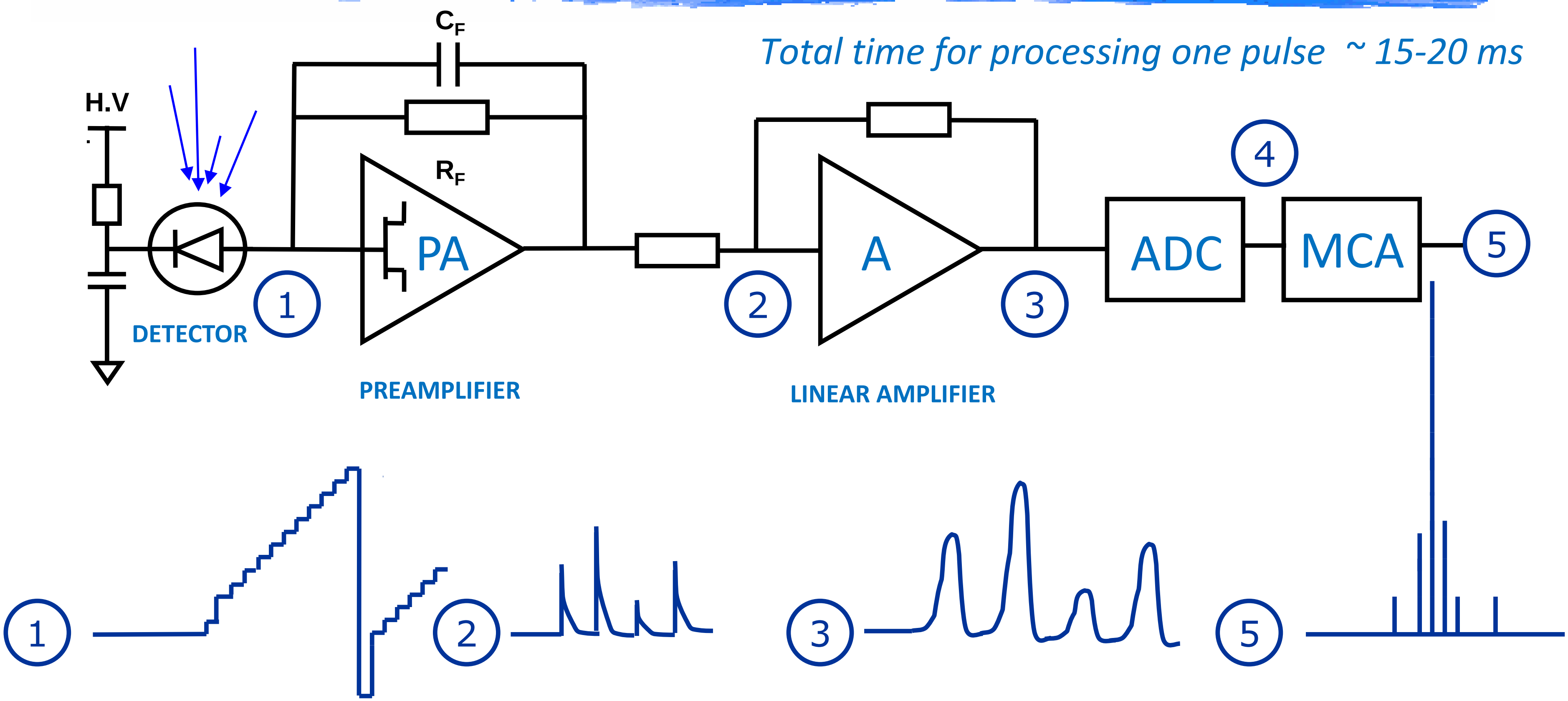
Detector photograph reproduced from https://www.rayspec.co.uk/x-ray-detectors/silicon-drift-detectors/xrf/

❑ Signal processing



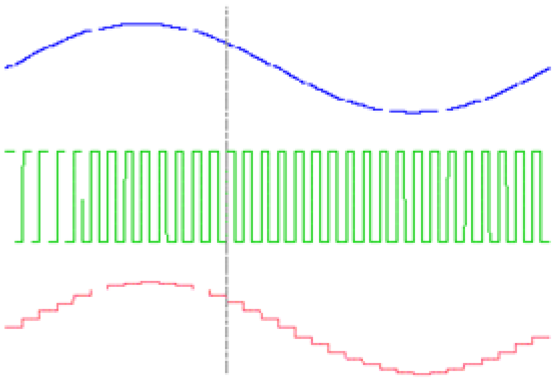
❑ Analog signal processing

Total time for processing one pulse ~ 15-20 ms



[illegible] channel in the multichannel analyzer (MCA).

❑ Digital signal processing



Analog signals

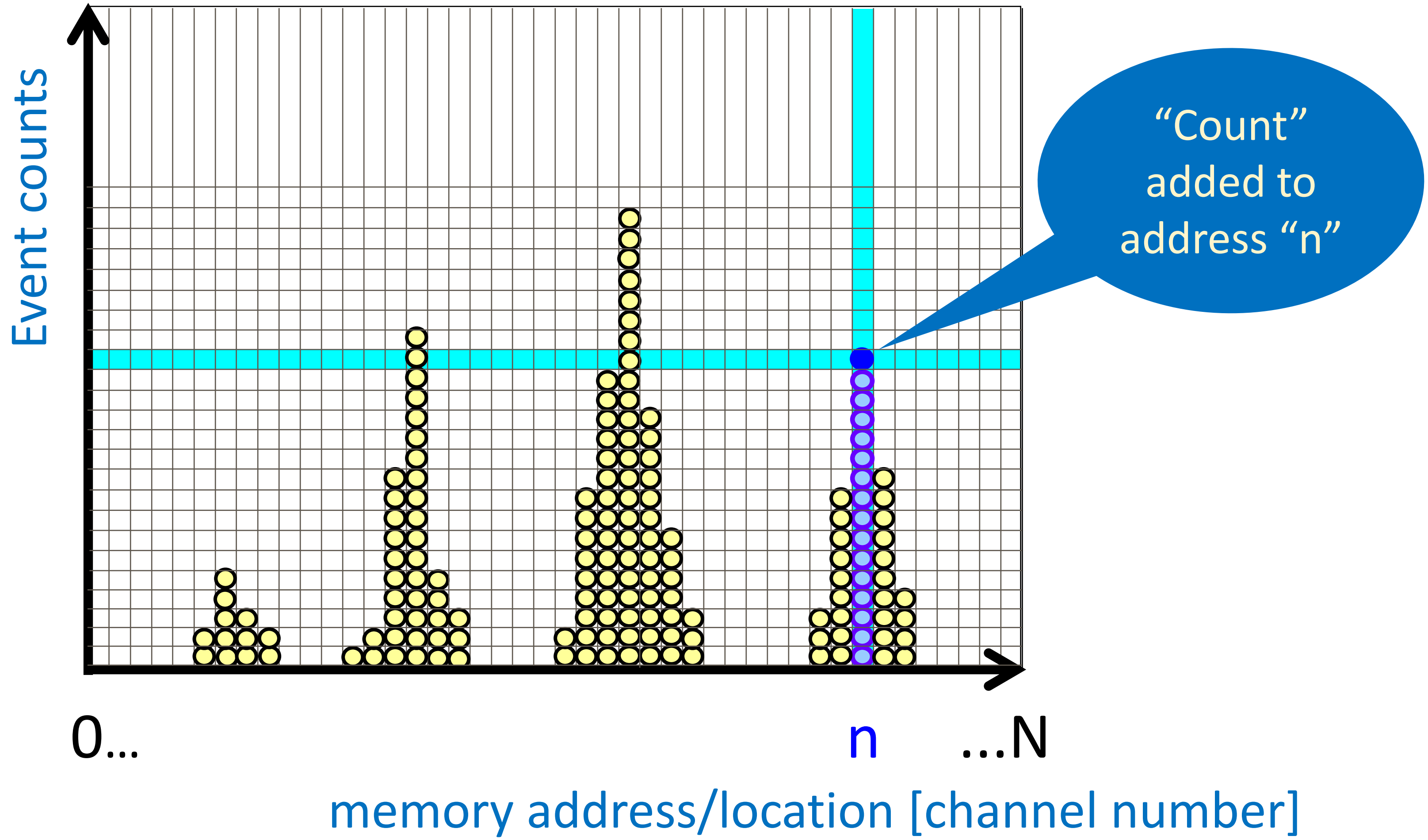
are measured against an internal HF clock

and sampled

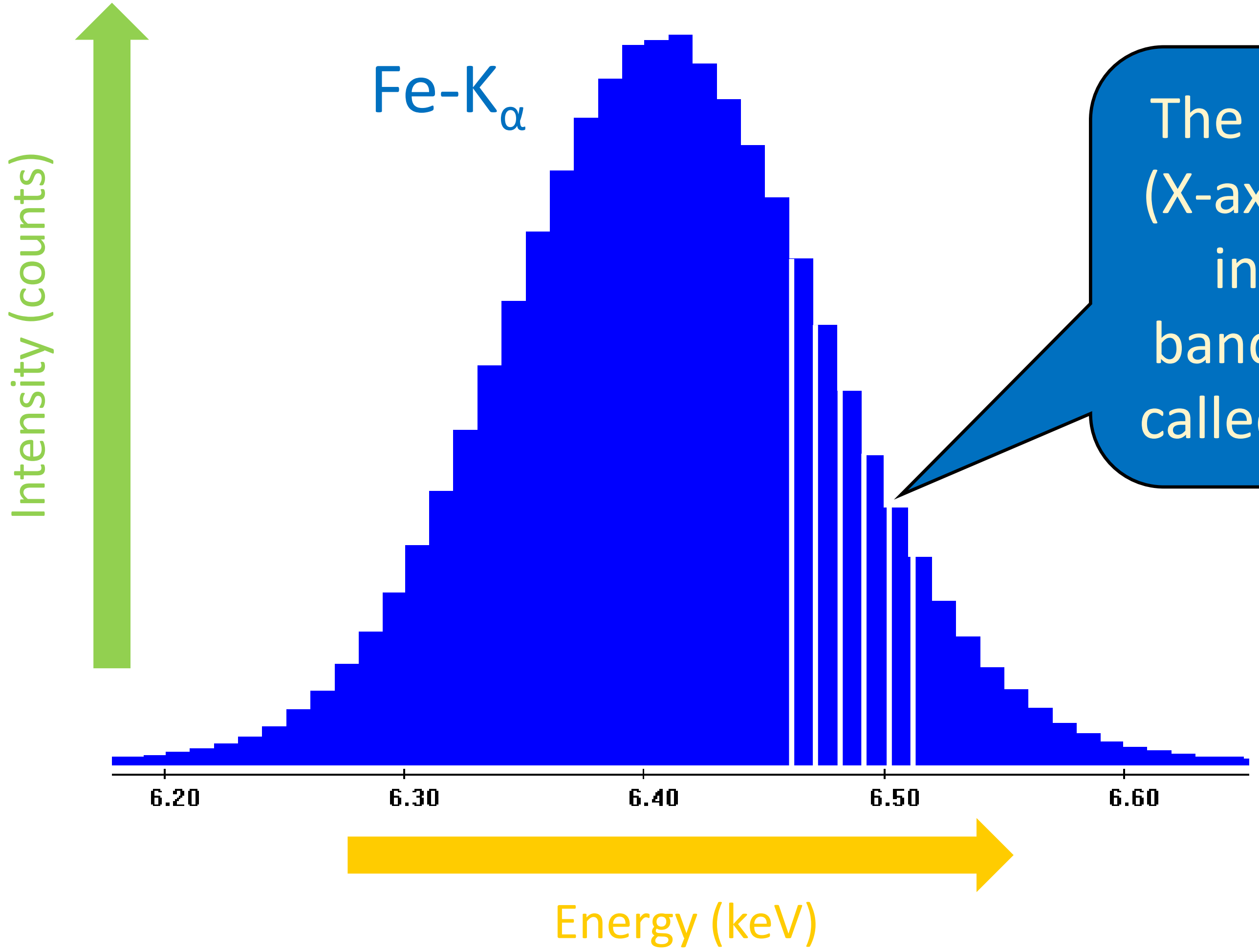
signal in | Fast discrimination | DSP | Evaluation of height | Shaping

Total time for processing one pulse ~ 15-20 ns

❑ Multichannel analyzer



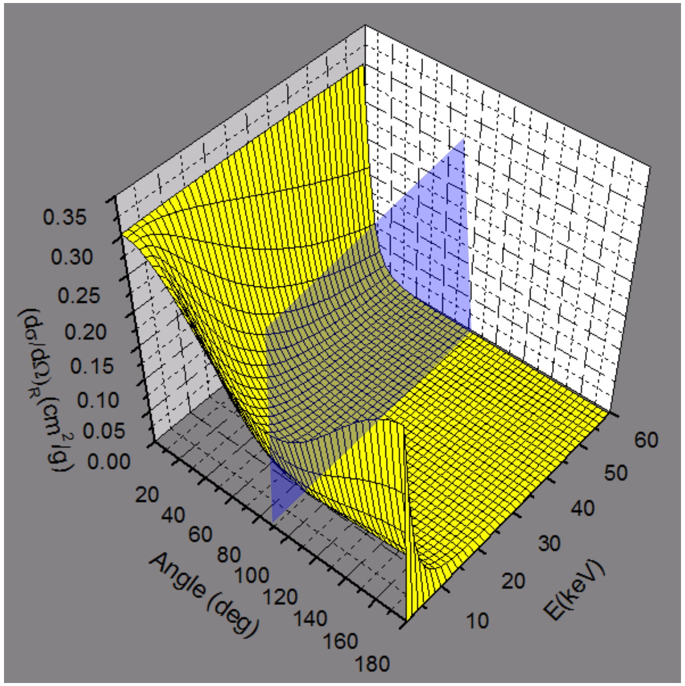
Construction of EDXRF spectrum



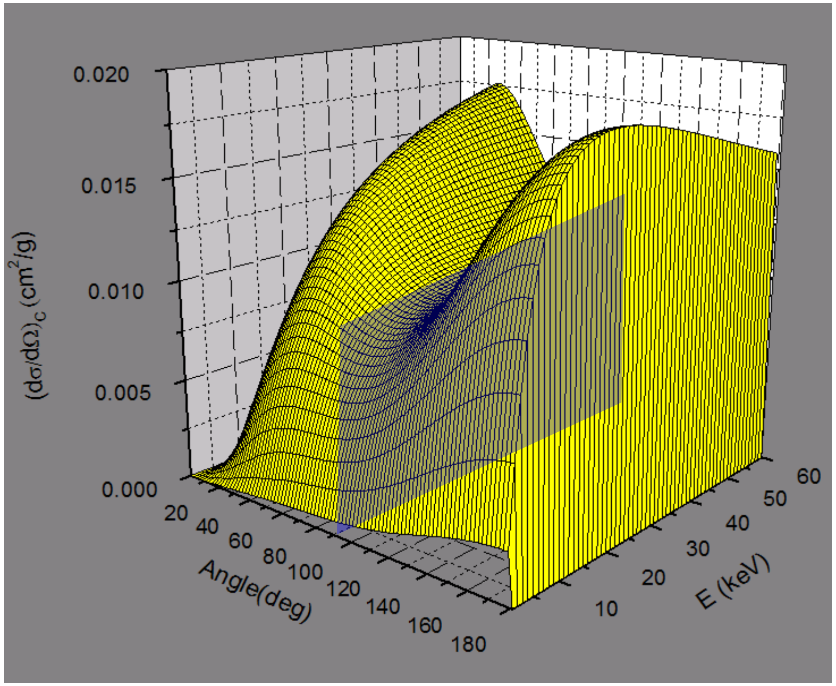
The energy scale (X-axis) is divided into narrow bands of energy, called “**channels**”

❑ Geometry arrangement

Maximize the detection of x-ray emission while minimizing the detection of the primary radiation scattered at the sample



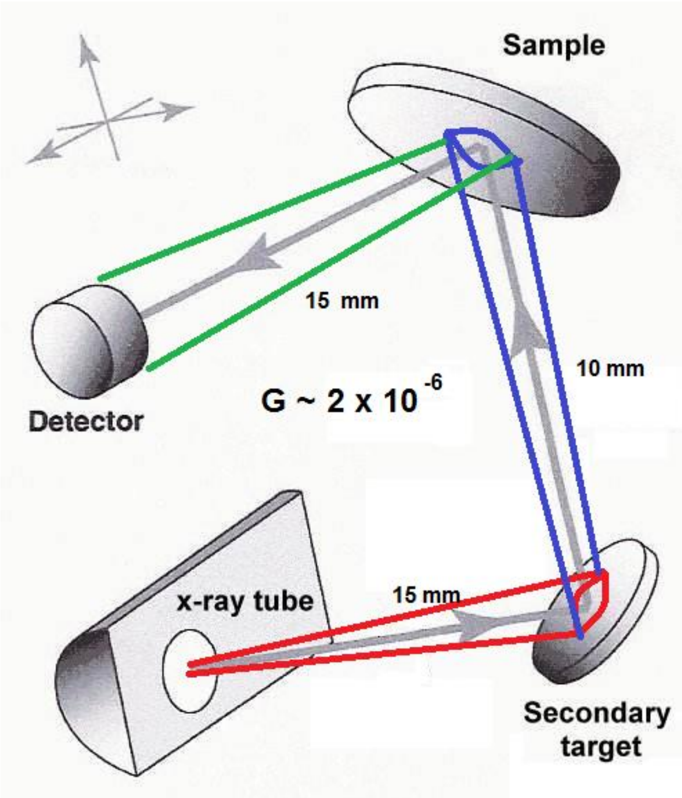
Coherent scattering

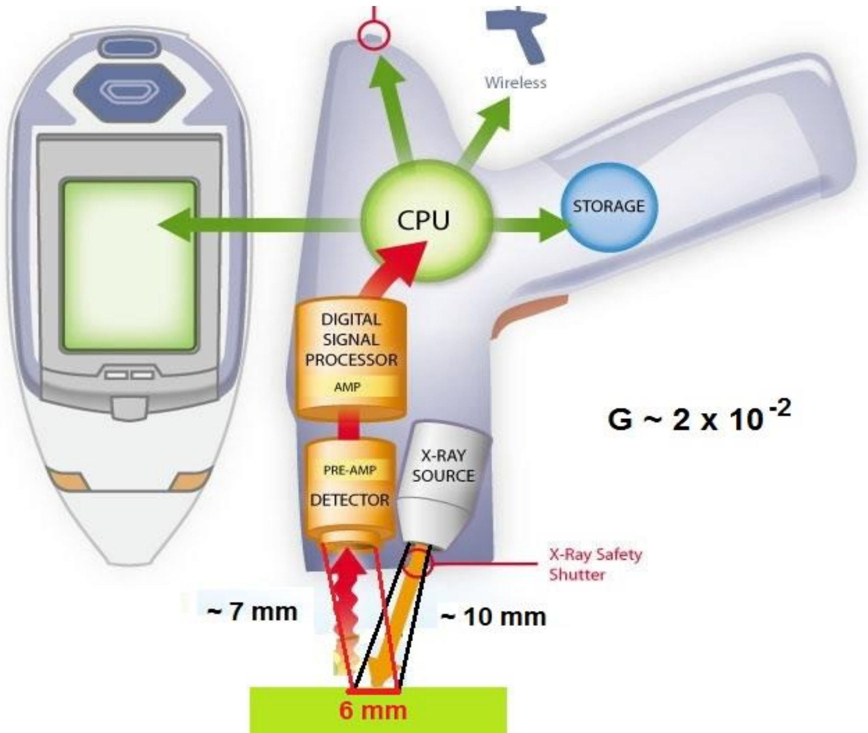


Incoherent scattering

Geometry arrangement

$$\varepsilon_{abs} = G \cdot \varepsilon(E)$$





Modelling a peak

Peak described by a Gaussian

$$\chi^2 = \sum_{1}^{n} [y(i) - y_i]^2$$

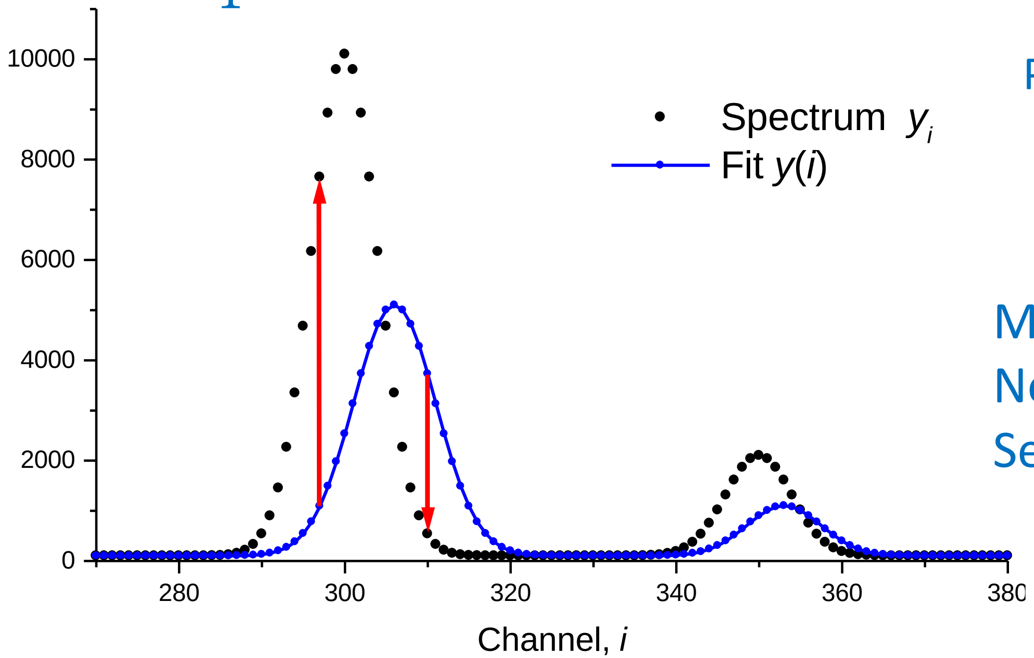
Continuum

Peak position

$$y(i) = b + H \cdot exp\left[\frac{(x_i - x_p)^2}{2\sigma^2}\right]$$

Peak height

Peak width

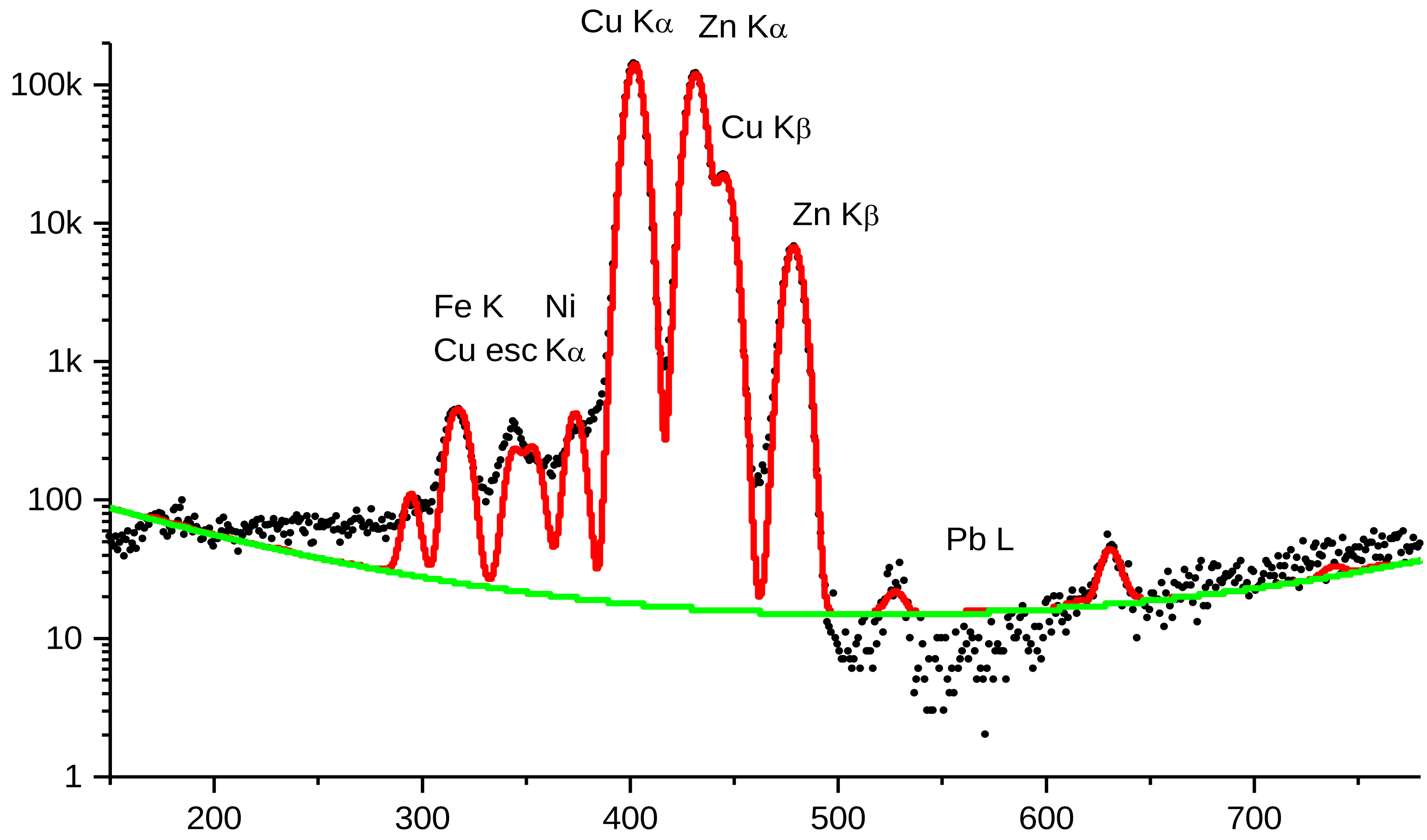


Minimum:

No direct analytical solution

Search χ^2 for minimum

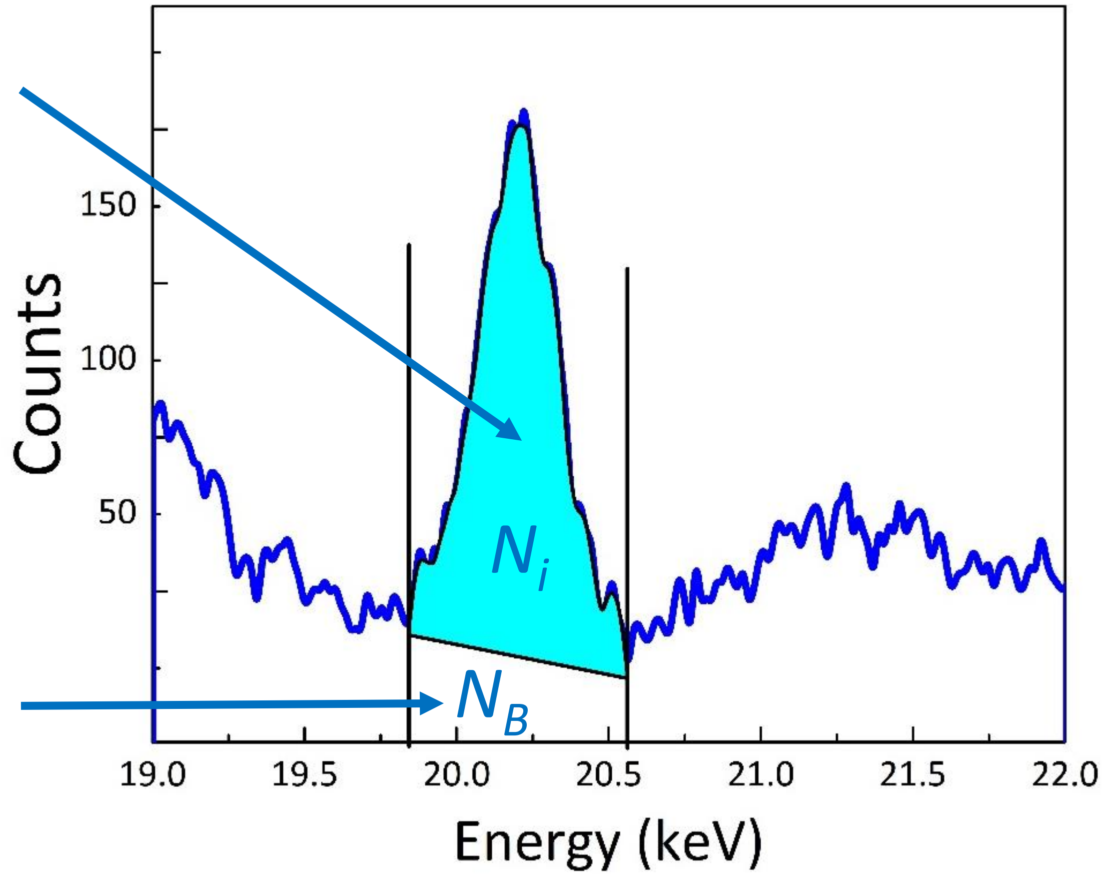
❑ The need for advanced peak model



❑ Spectral background

I_i = Fluorescence intensity (cps)

I_B = Background intensity (cps)



Spectrum deconvolution

$$P(i, E_{jk}) = G(i, E_{jk}) + f_S S(i, E_{jk}) + f_T T(i, E_{jk})$$

Gaussian:

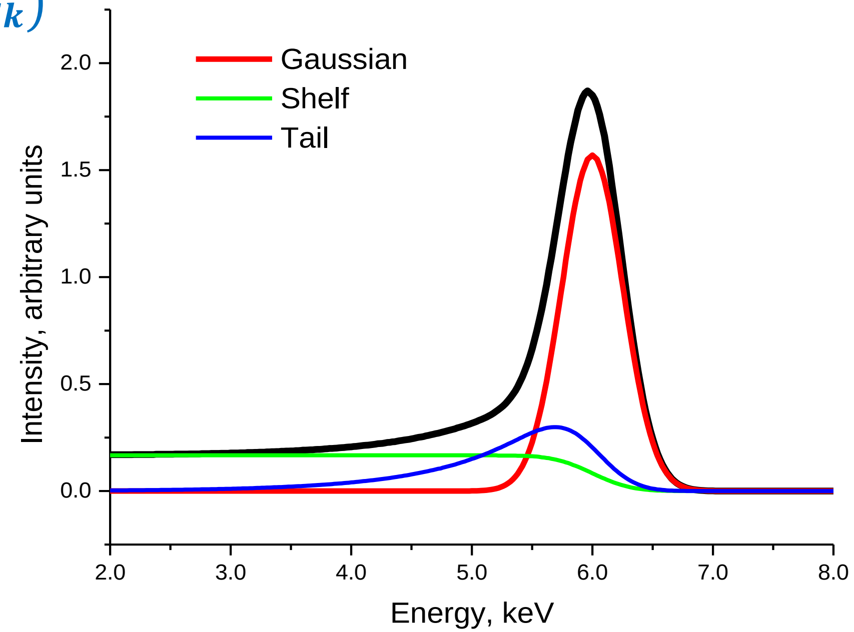
$$G(i, E_{jk}) = \frac{Gain}{S_{jk}\sqrt{2\pi}} exp\left[-\frac{(E_i - E_{jk})^2}{2S_{jk}^2}\right]$$

Step:

$$S(i, E_{jk}) = \frac{Gain}{2E_{jk}} erfc\left[\frac{E(i) - E_{jk}}{\sqrt{2}\sigma}\right]$$

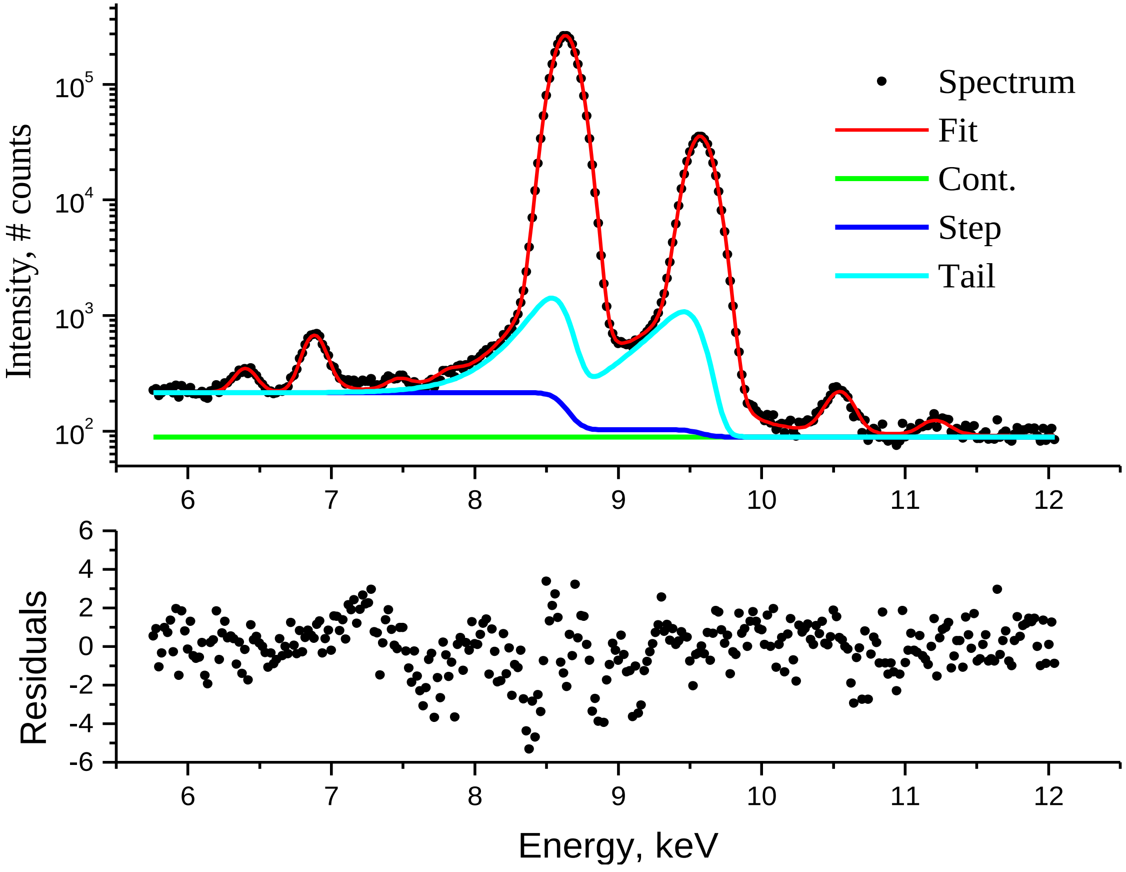
Tail:

$$T(i, E_{jk}) = \frac{Gain}{2\gamma\sigma exp\left[-\frac{1}{2\gamma^2}\right]} exp\left[\frac{E(i) - E_{jk}}{\gamma\sigma}\right] erfc\left[\frac{E(i) - E_{jk}}{\sqrt{2}\sigma} + \frac{1}{\sqrt{2}\gamma}\right]$$



❑ Determination of parameters

Fit of pure metal foils spectra



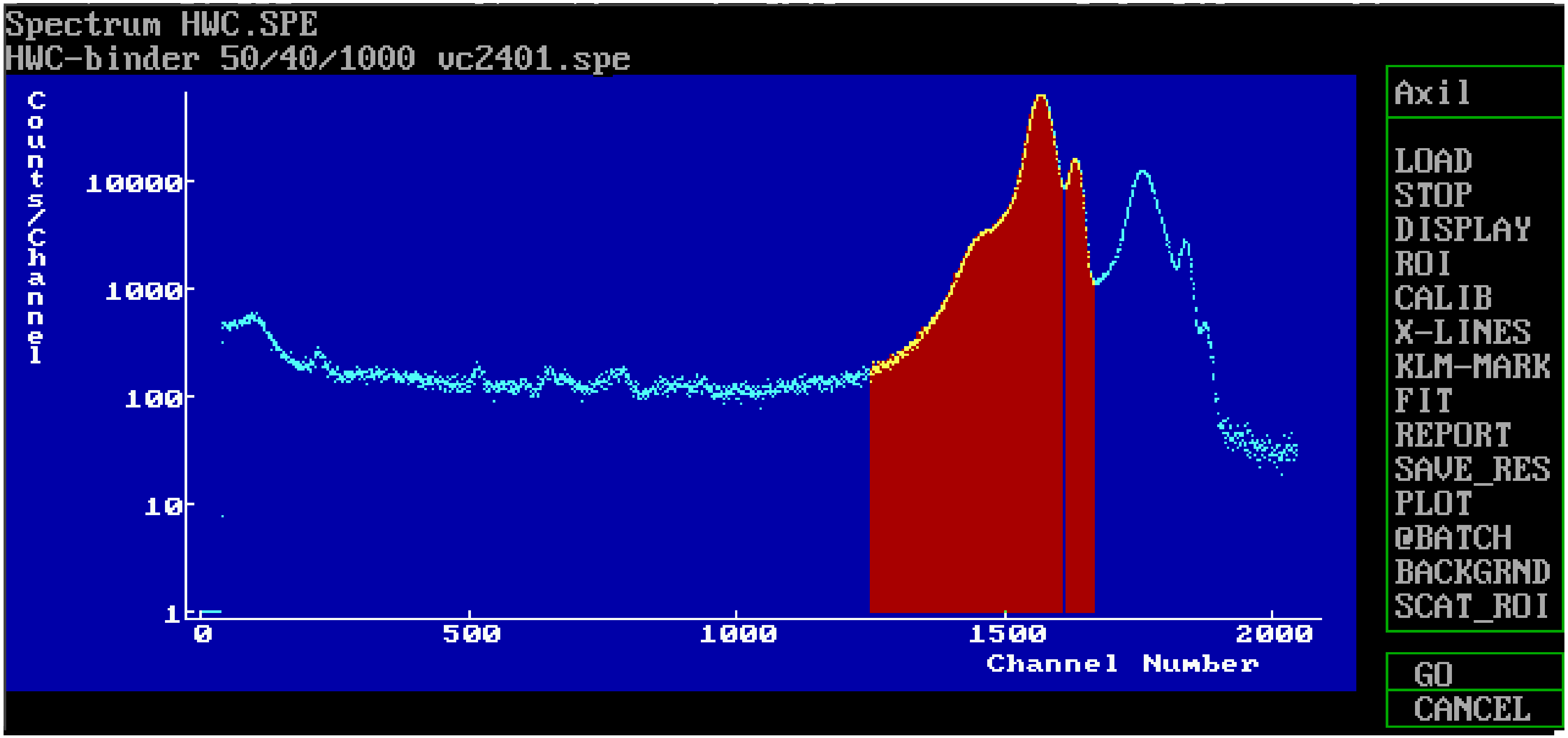
❑ Software for spectrum deconvolution

	QXAS	WinQXAS	PyMCA	WinAxil	bAxil
Released by	IAEA	IAEA	ESRF	Canberra	BrightSpec
Availability	Free upon request	Free upon request	Free download	$$$$	$$$$
Operating Environment	DOS [(a)]	Win 95	Win 10	Win 95-XP	Win 10
Multiple ROIs[(b)]	No	Yes	No	No	No
Scatter peaks fit	Basic models	Basic models	No	Advanced	Advanced
Spectrum format conversion	Old formats *.asc (ASCII) *.spe (QXAS)	*.asc (ASCII) *.spe (QXAS)	Different options	Multiple Canberra & Ortec, *.asc, *.spe	*.asc, *.spe, *.spc, *.txt, *.csv, *.mps, *.xml, *axml
Batch run	Yes	No	Yes	Yes	Yes
Quantitative tools	Multiple	Elemental sensitivity	Fund. Par.	Elemental sensitivity Fund. Par.	No

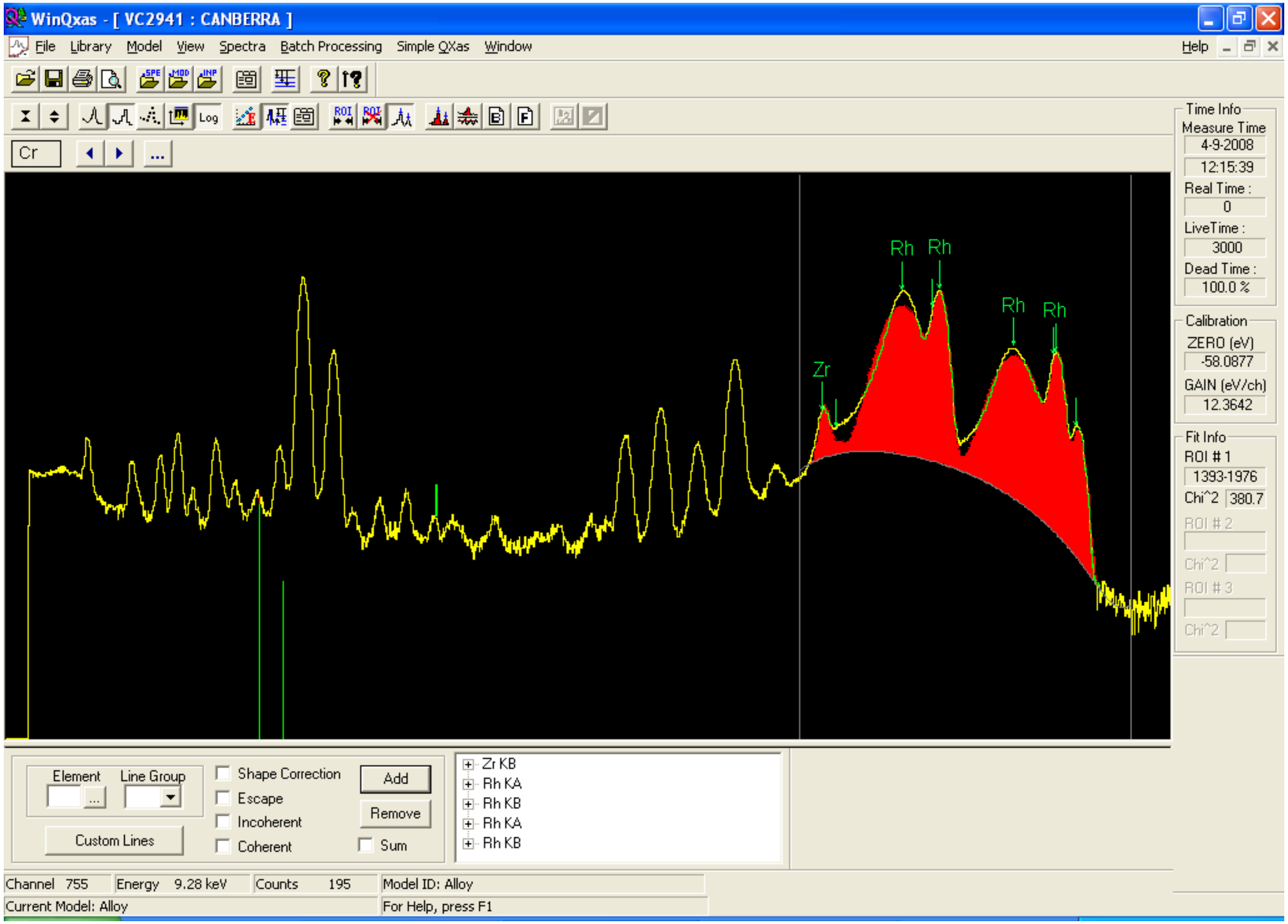
(a) Possibility of running on DOS Box for Windows

(b) Capable of selecting multiple Region of Interest for fitting

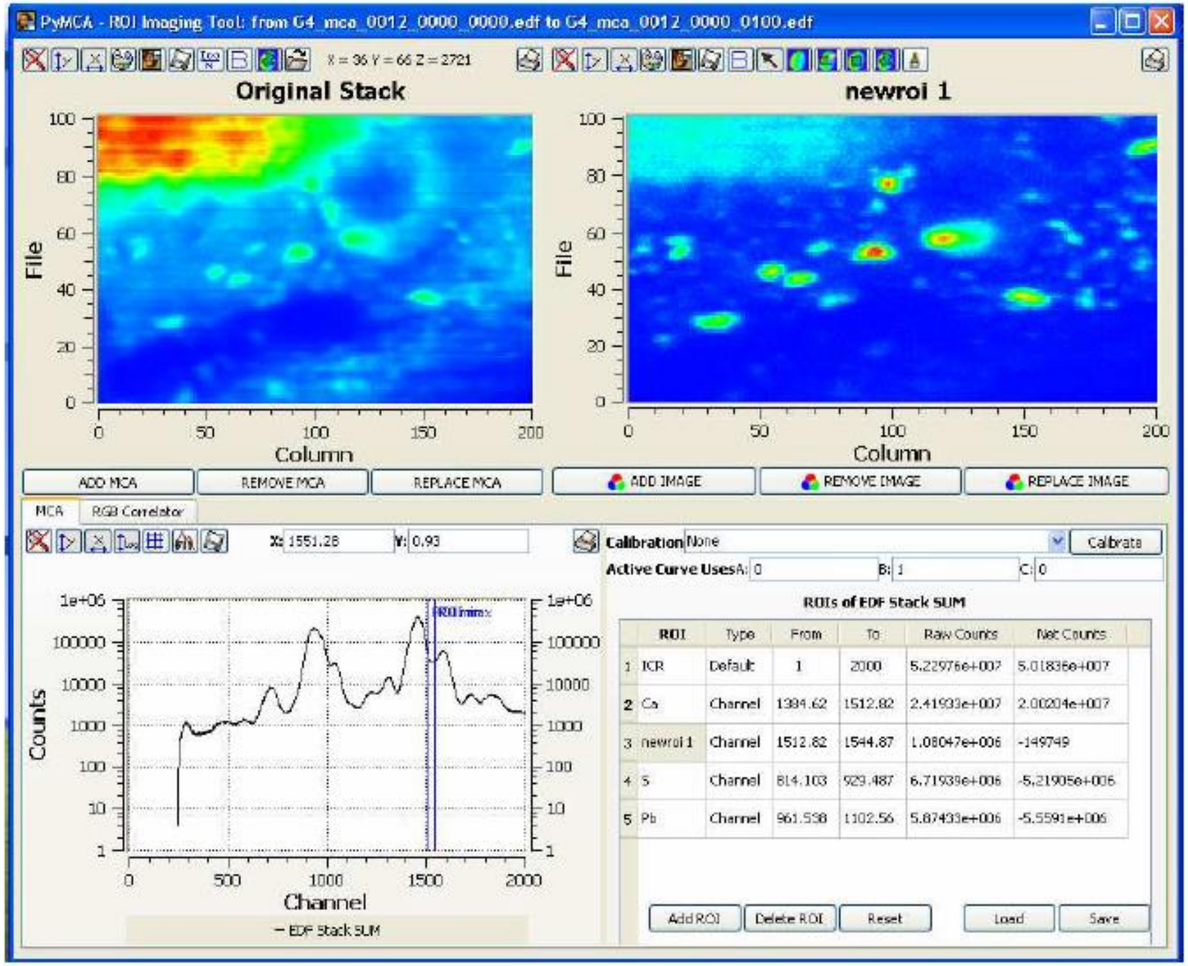
❑ AXIL-DOS (IAEA, free)



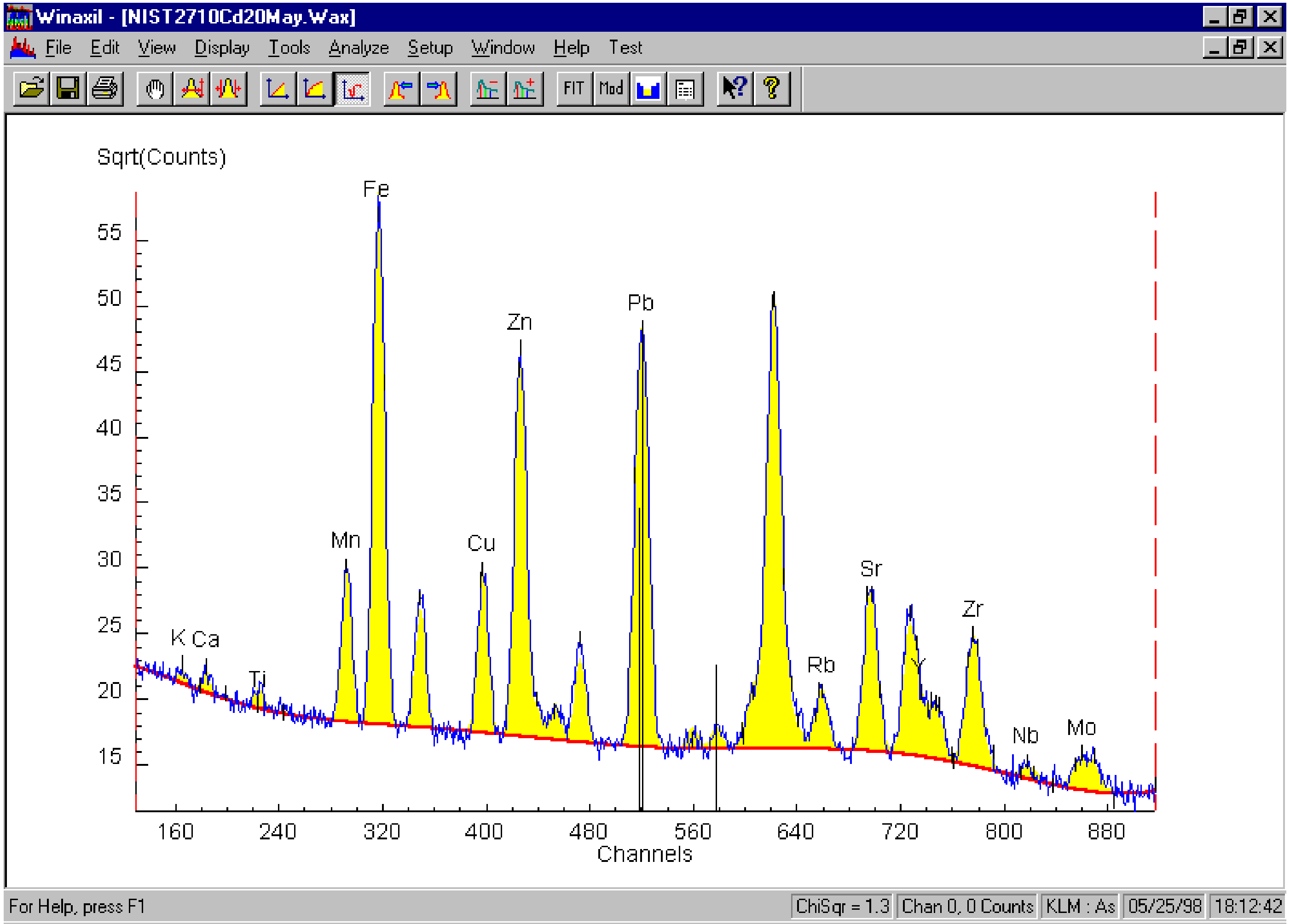
❑ Win QXAS (IAEA, free)



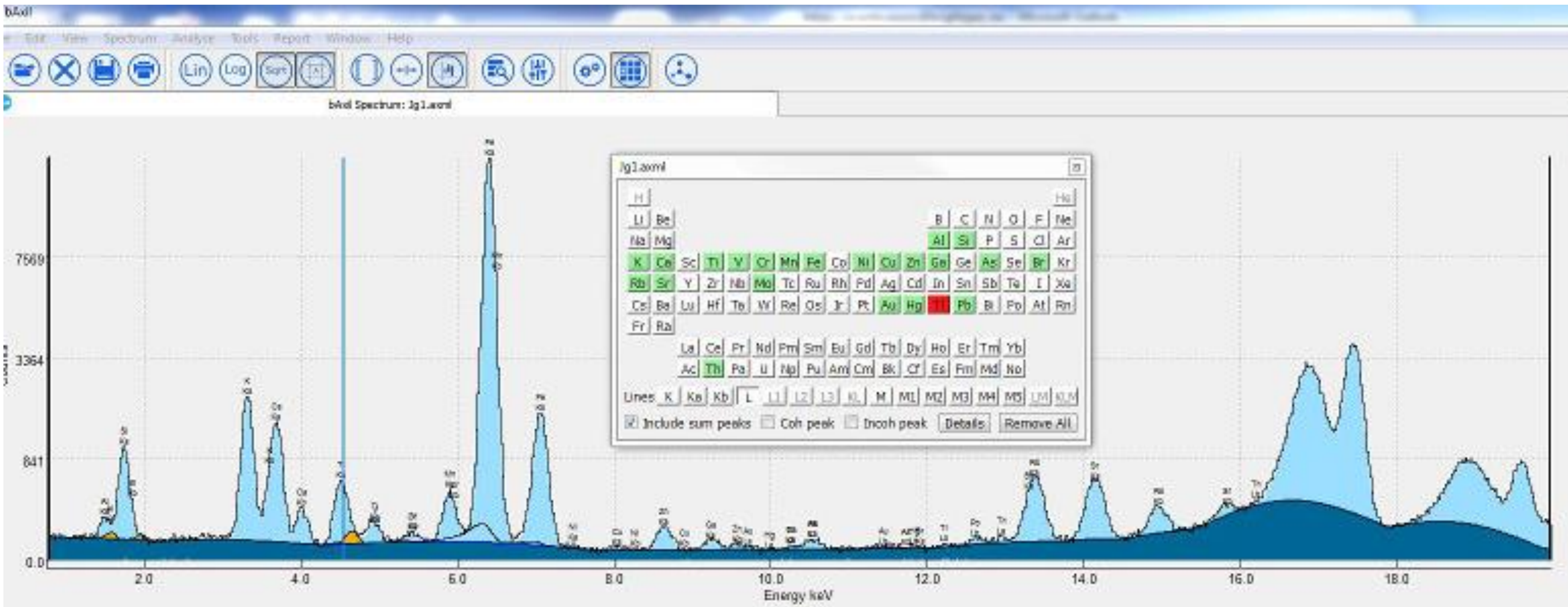
❑ PyMCA (ESRF, free)



❑ WinAxil (Canberra)



❑ bAxil (BrightSpec)



Thanks for your attention!