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XRF SPECTROMETRY

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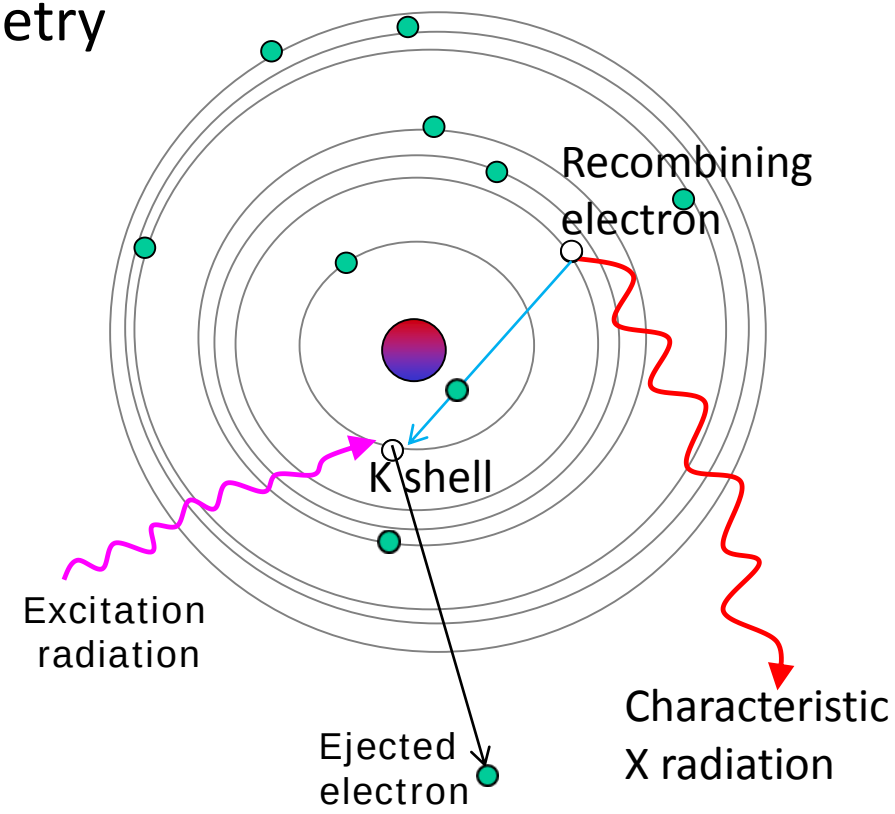
XRF SPECTROMETRY
-Basic principles-

XRF – X-Ray Fluorescence spectrometry

Fluorescence – emission of the energy after excitation

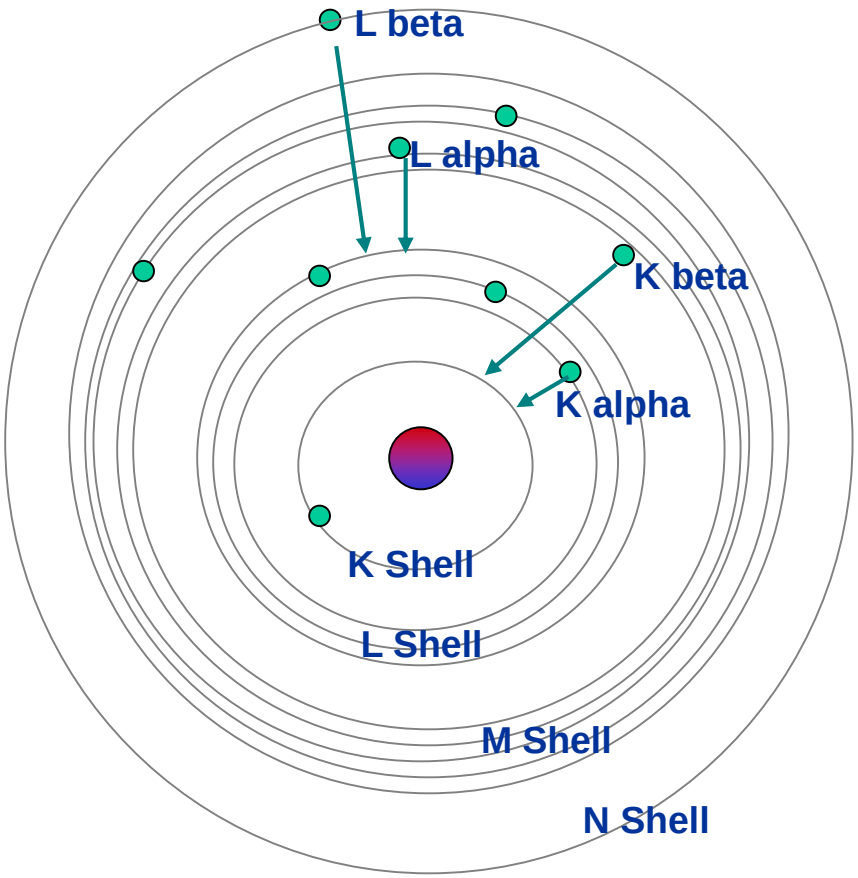
Interaction of excitation radiation with material:

- Excitation radiation (photons or particles);
- Photoelectron apsorption-emission of the characteristic X-Rays;
- *Bremstrahlung* - deceleration radiation;
- Elastic scaterring;
- Non-elastic scatering;
- Auger electrons – competiting process to emission of the characteristic radiation.



All these effects are visible in the XRF spectrum.

XRF SPECTROMETRY
-Basic principles-



K – alfa lines:
Transitions of electrons from L to K shells,
Higher probabilities
The most intensive peaks

K - beta lines:
Transitions of electrons from M to K shells,

L – alfa lines:
Transitions of electrons from M to L shells,

L - beta lines:
Transitions of electrons from N to L shells,

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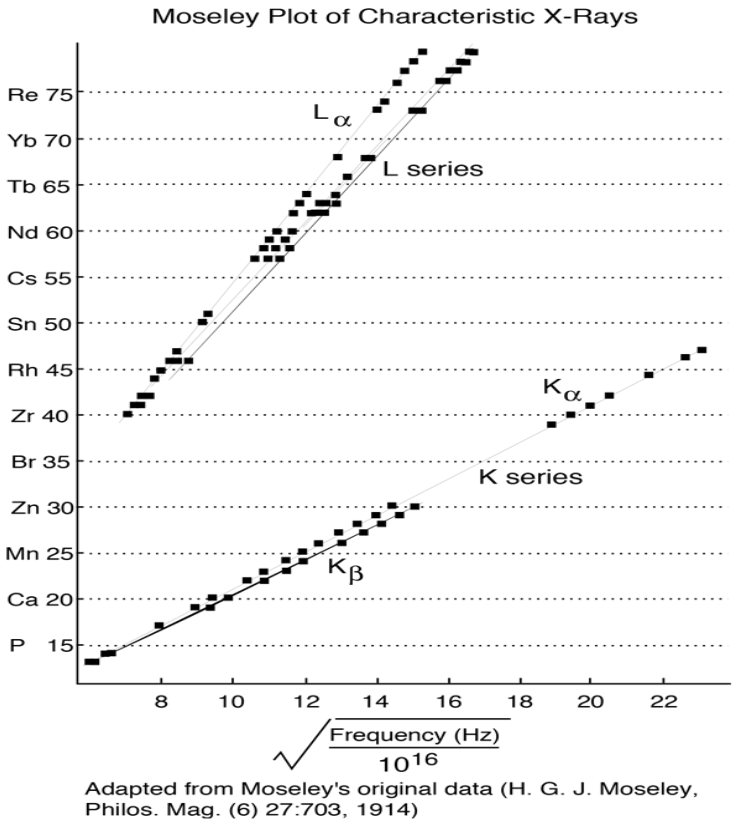
XRF SPECTROMETRY
-Basic principles-



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

There are a strict rules of the inner shells transitions so energy emitted has predicted energies.

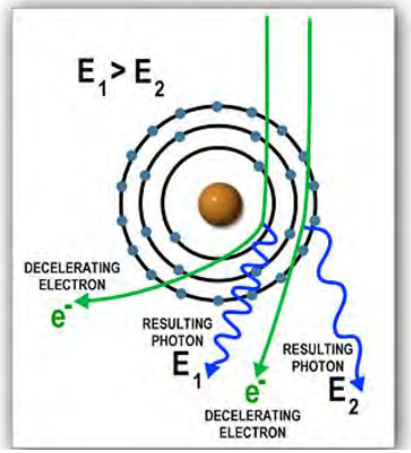
Each element has a specific value of the energy difference between atomic shells.

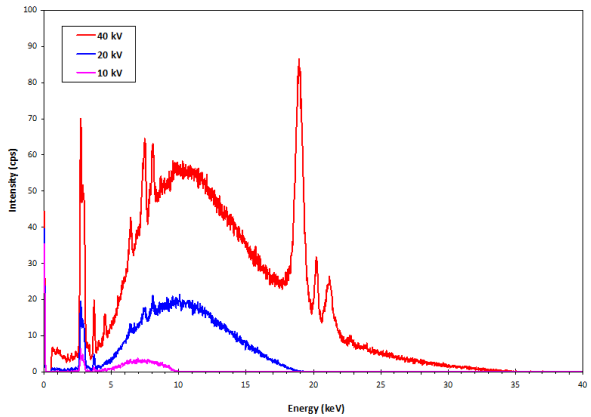
So induced transitions in the inner shells of the each element are followed by emission of the photon radiation with specific and characteristic energy.

According to this, there is no chemical elements with the same energy for the same transition i.e. energy of the emitted photons can be used for element identification.

XRF SPECTROMETRY
-Basic principles-

Bremstrahlung - deceleration or braking radiation;

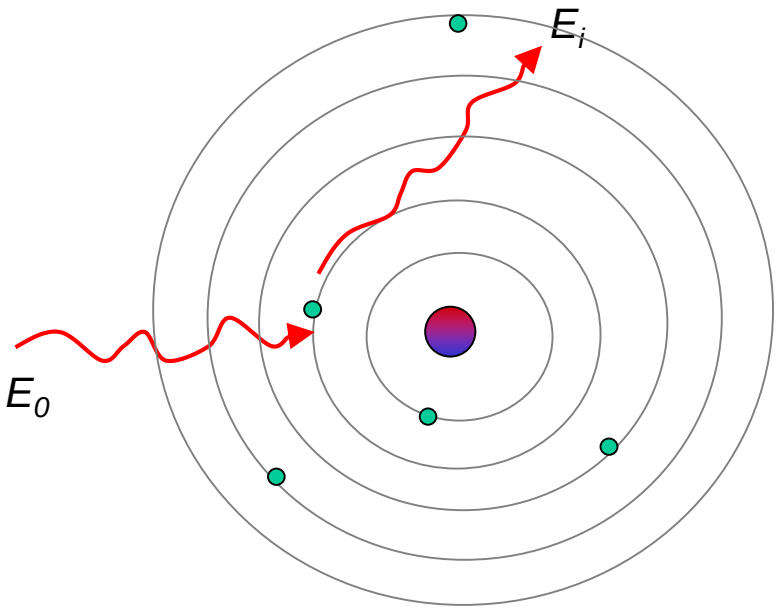


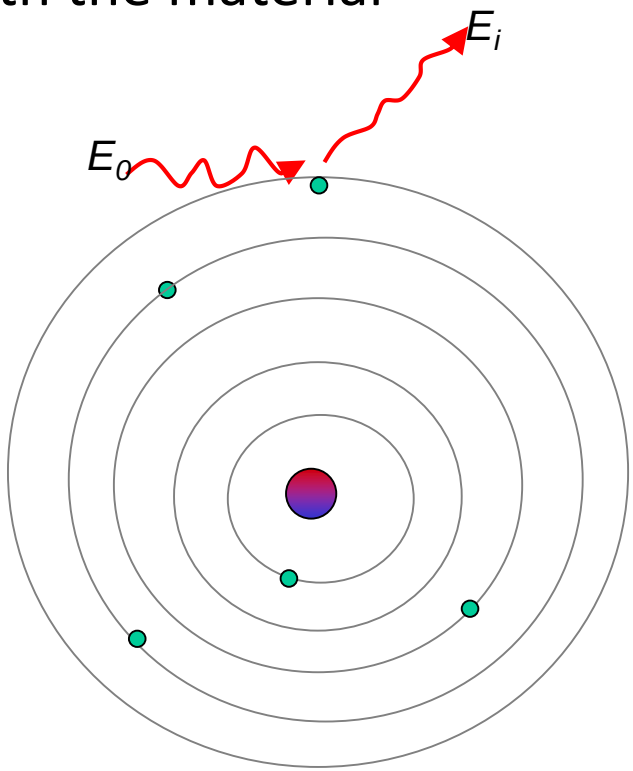


- One of the phenomens of the interaction of charged particles in the viccinity of the other particle with opposite charge.
- In the case of XRF, that is effect of the decelaration of the electrons in the Coulomb field of the atom nucleus in the irradiated material. (X ray tube)
- Continuous photon radiation limited with the energy of the incoming particles (electrons).
- Competing process to the photoelectron apsorption.
- Effect is more prominent with low Z elements since they are characterized with small probability for the photoelectron apsorption.
- Effect is presented just in the case of the excitation with X ray tubes and its intensity depends of the energy of the electrons (voltage).

XRF SPECTROMETRY
-Basic principles-

Scattering of the X rays – interaction with the material



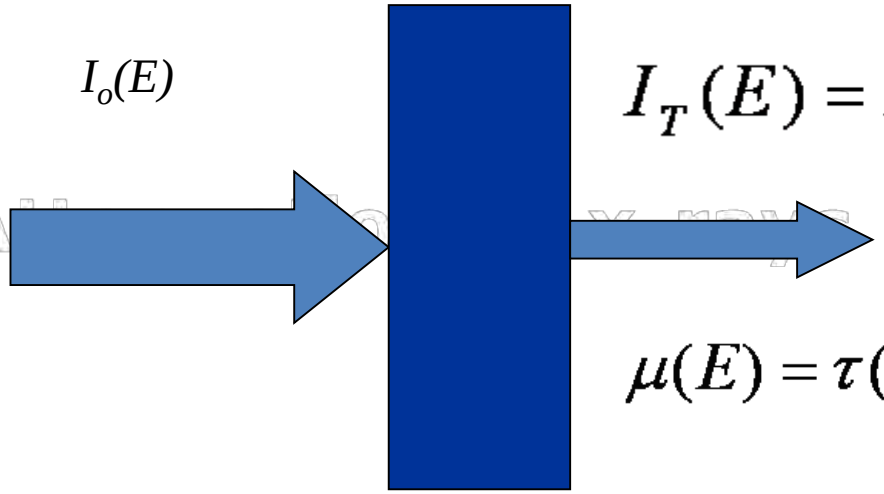


$E_i = E_0$: Elastic (Coherent or Rayleigh) scattering on the inner atomic shells

$E_i < E_0$: Non-elastic (incoherent or Compton) scattering on the the outer atomic shells

XRF SPECTROMETRY
-Basic principles-

Attenuation of x-rays in the material



$$I_T(E) = I_0(E)e^{-\mu(E)\rho d}$$

$$\mu(E) = \tau(E) + \sigma_R(E) + \sigma_C(E)$$

- $\tau(E)$ – photo-electric absorption cross section
- $\sigma_R(E)$ – elastic scattering cross-section
- $\sigma_C(E)$ – inelastic scattering cross-section

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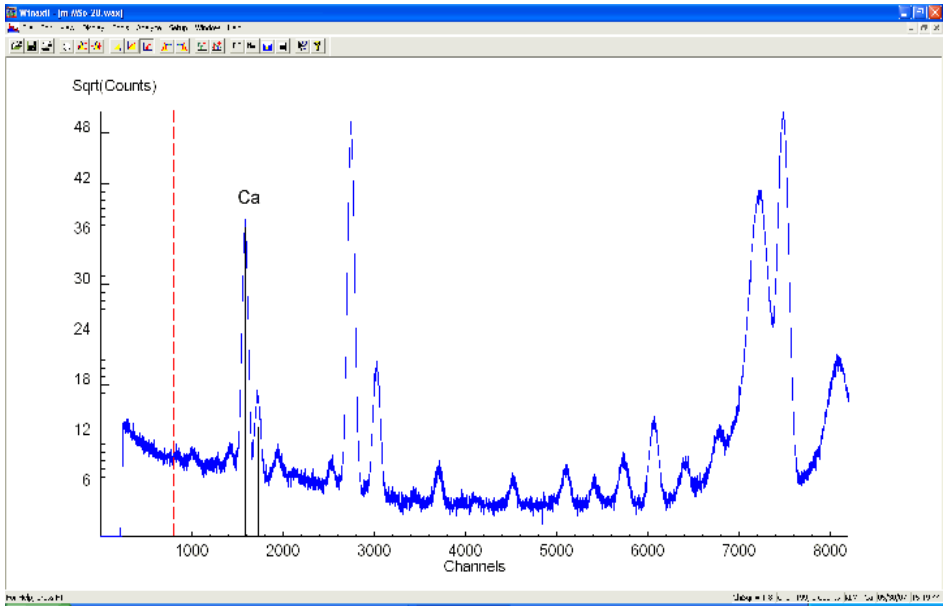
XRF SPECTROMETRY
-Basic principles-

Almost all physical effects of the interactions of radiation with material are visible in XRF spectrum.



EDXRF spectrum

- Continuum radiation-Bremstrahlung
- Characteristic radiation
  - ✓ K, L or M-lines
- Scattered excitation radiation
  - ✓ Coherent
  - ✓ Incoherent
- Sum peaks

  Fe-Kα + Fe-Kα= 12.8 keV
- Escape peaks

  Ca-Ka-1.74keV = 1.95 keV

Combination of the K, L and M lines should be considered for the qualitative analysis as well as the secondary excitation for quantitative analysis

XRF SPECTROMETRY - Types of instrumentation

XRF Instrumentation

TYPES OF THE EXCITATION RADIATION:

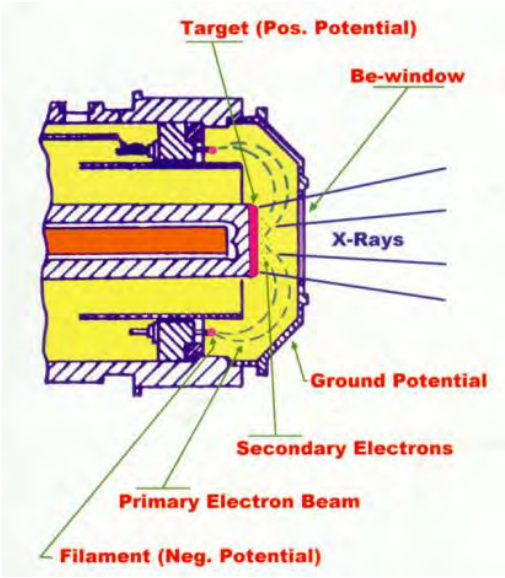
- Radioisotopes – ^{109}Cd, ^{241}Am, ^{55}Fe RIXRF Radioisotope Induced X – Ray Flurescence Spectrometry
- X-RAY TUBES
- Electrons – SEM EDS – Scanning Electron Microscopy – Energy Dispersive Spectrometry
- Synchrotron radiation – PIXE Particle Induced X – Ray Emission Spectrometry

TYPES OF THE DETECTORS:

- Energy Dispersive Instruments
  - Si(Li), Si-PIN, SDD, CZT-CdZnTe
- Wave-length dispersive Instruments
  - Crystal or multilayer detectors
- Non-dispersive Instruments
  - data collection in different detection channels with filters i.e. each channel provides information on one single element.

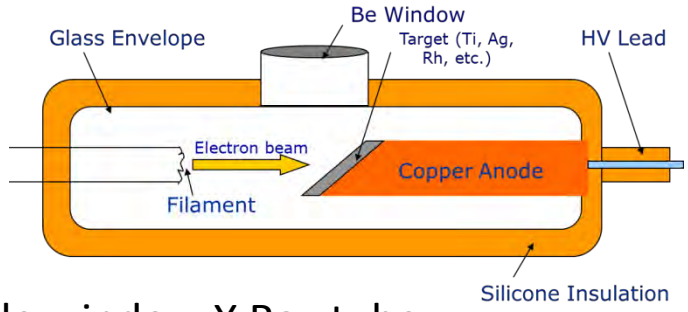
XRF SPECTROMETRY - Types of instrumentation

X RAY TUBES



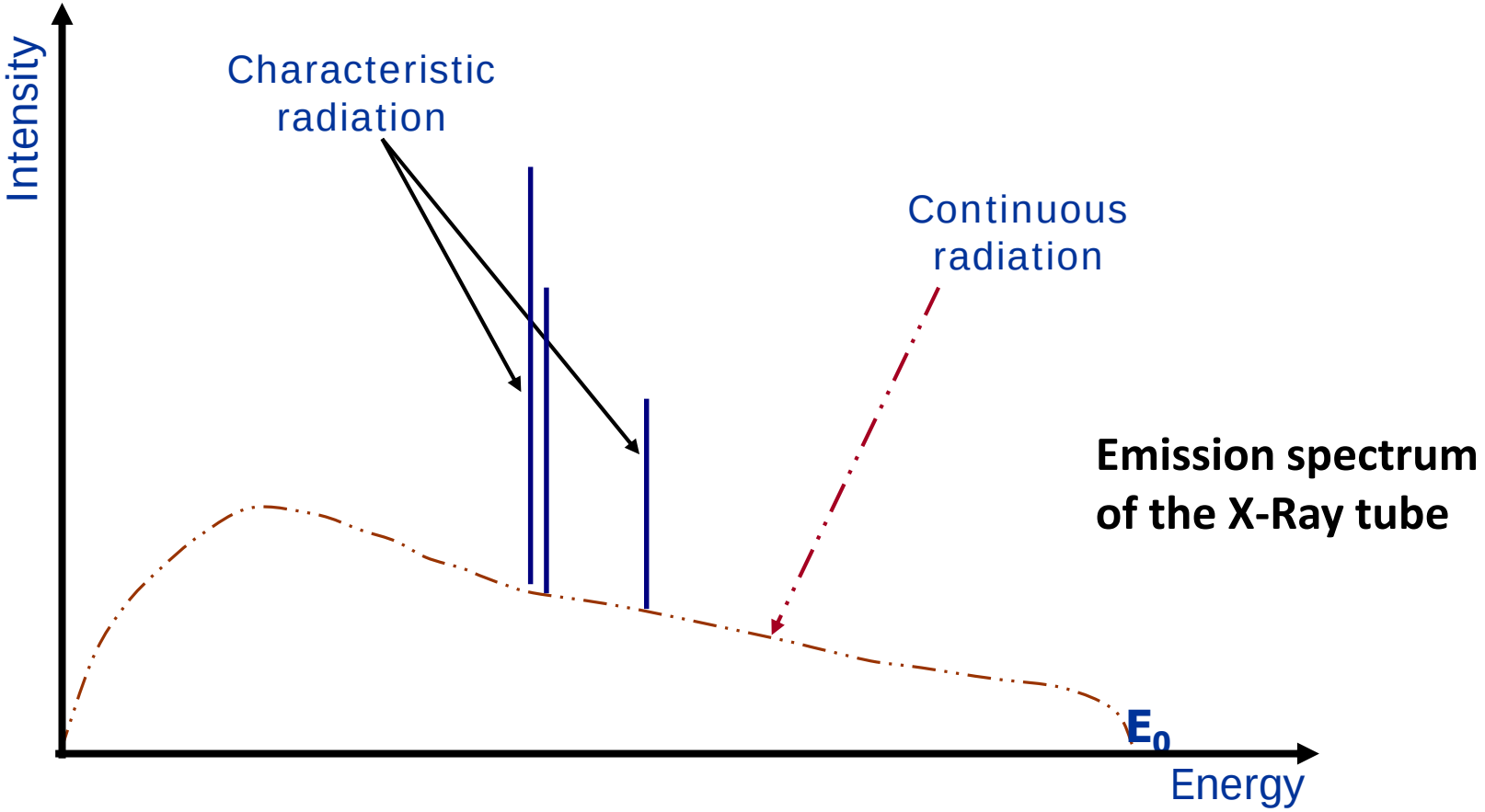
End point X Ray tube

- Electrons from filament (usually made of W) are accelerated to the positive target and, after interaction with anode material, continuous and characteristic radiation are emitted and focused in desired orientation.
- High voltage applied determines energy of the emitted radiation and elements that can be excited in XRF spectrometry.
- More power i.e. higher current applied increases flux of the emitted radiation and improve sensitivity of the analytical procedure.
- Selection of the anode material determines energy of the excitation i.e. optimization of the analytical technique and determines a range of the elements that can be excited. (Mo, Rh, W, Ag, Au, Cu,...)
- Focus of the external X-Ray beam can be achieved with pin-hole collimators (mili beam) or with poly-capilary optics (micro XRF techniques).



Side window X Ray tube

XRF SPECTROMETRY - Types of instrumentation



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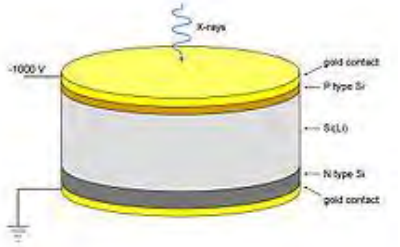
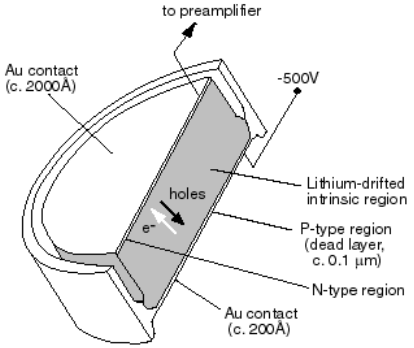
XRF SPECTROMETRY - Types of instrumentation

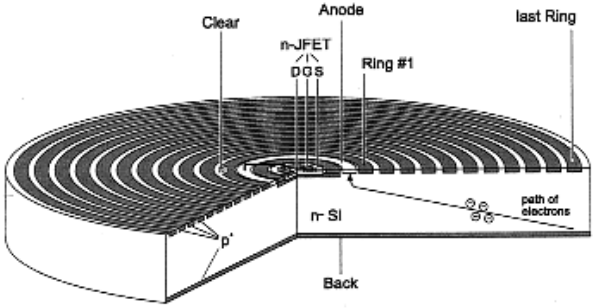
Detectors:
Si(Li);
PIN diode;
Silicon Drift Detectors
CdZnTe – CZT, CdTe
HgI_2



Cooling: LN_2
Window: Beryllium or Polymer
Counts Rates:3,000 – 50,000cps
Resolution: 120-170eV at Mn K_a

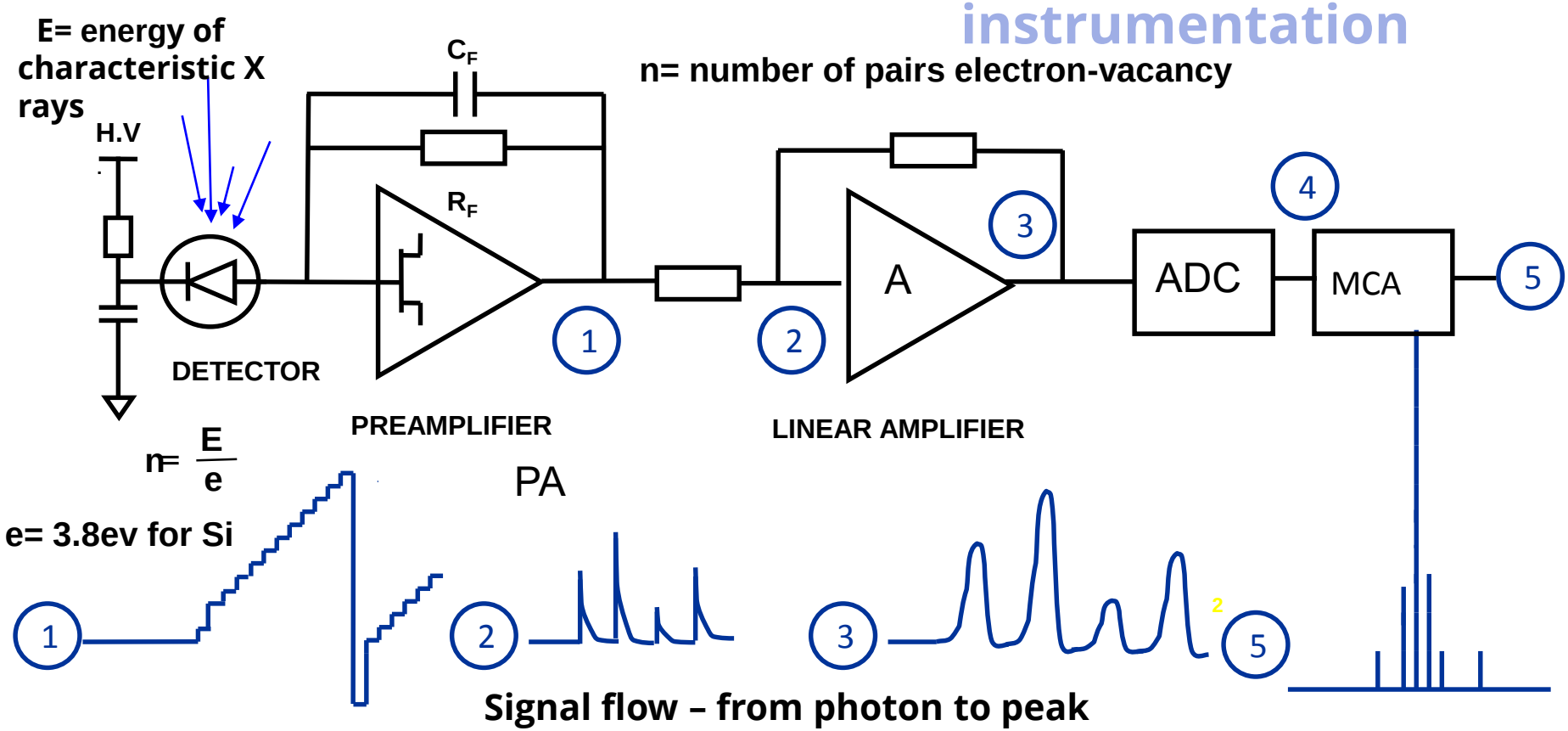


Cooling: Thermoelectrically cooled (Peltier)
Window: Beryllium
Count Rates: 3,000 – 20,000 cps
Resolution: 139eV at Mn K_a



Cooling: Peltier
Window: Beryllium or Polymer
Count Rates; 10,000 – 500,000 cps
Resolution: 125 eV at Mn K_a

XRF SPECTROMETRY - Types of instrumentation

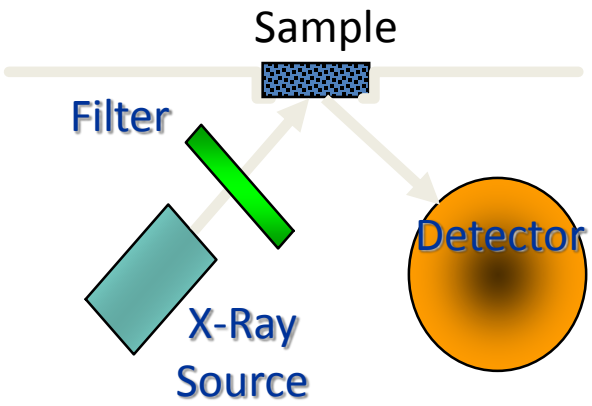


Signal flow – from photon to peak

X-rays that are absorbed in the detector cause a drift of charge inside the detector crystal which is collected by the preamplifier. The current value is proportional to the absorbed energy. An analog to digital converter (ADC) inspects the amplitude of the pulses and determines a digital code value for each. The reception of a pulse having a specific digital code is registered in a channel in the multichannel analyzer (MCA). Intensity of peak is measured by registered pulses.

XRF SPECTROMETRY - Types of instrumentation

Optimization of Excitation Sources - Filtering

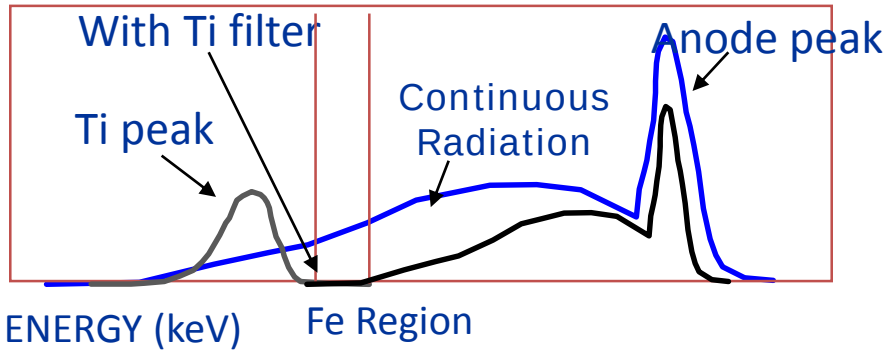


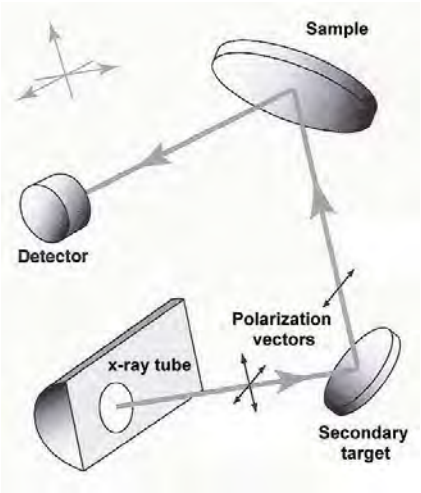
Use of filters enables:

- Background Reduction;
- Improved Fluorescence.

Use of secondary targets enables:

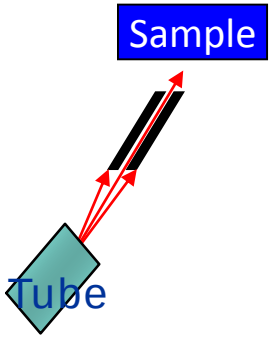
- Low intensities of background radiation
- Selection of the target material determine analytical range

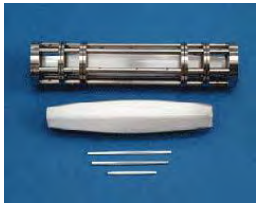




XRF SPECTROMETRY - Types of instrumentation

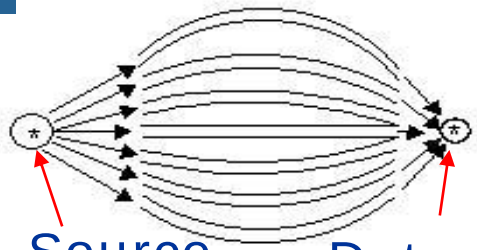
Optimization of Excitation Sources - Focusing





Collimation of the original dimension of the X – Ray beam is necessary step in analytical procedures in order to enable optimized spot size and radiation protection. Collimators are usually circular (pin-hole) or a slit and restrict the size and/or shape of the source beam. Collimator sizes range from 0.1 to several mm.
Major disadvantage - loss of the X –Ray beam intensity.

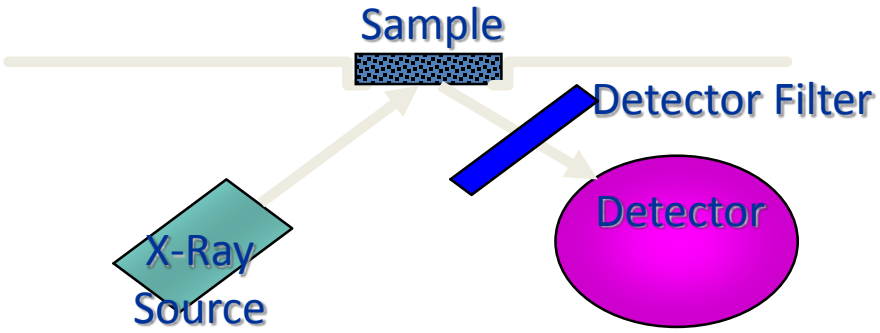
Bragg reflection inside a Capillary



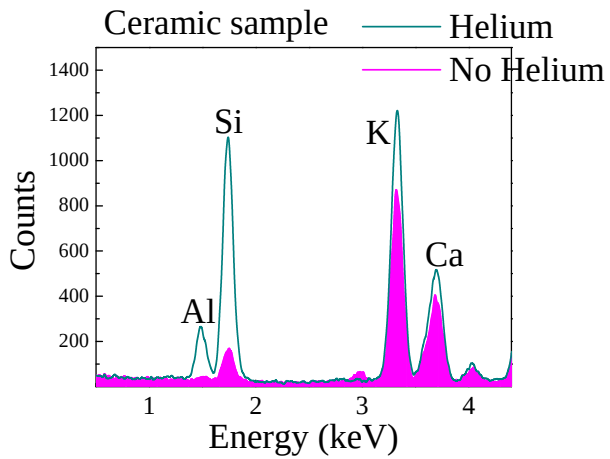
Focusing optics like poly-capillary devices were developed in order to
redirect and focus original beam to a small spot with usually 100 microns dimensions in diameter.

XRF SPECTROMETRY - Types of instrumentation

Optimization of detection process - Filtering



Filters made of proper materials are positioned in the optic path between the sample and detector to filter out unwanted x-ray peaks and background continuous radiation.



The improvement in the intensity of Al-K and Si-K characteristic X-ray lines is significant.

Another approach:
Filtering to remove air from the optical path for detection of characteristic X-Rays:
Helium purging or
Vacuum chambers

XRF SPECTROMETRY - Types of instrumentation

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Experimental set-up optimization

Selection of the parameters

X Ray tubes:

anode material;

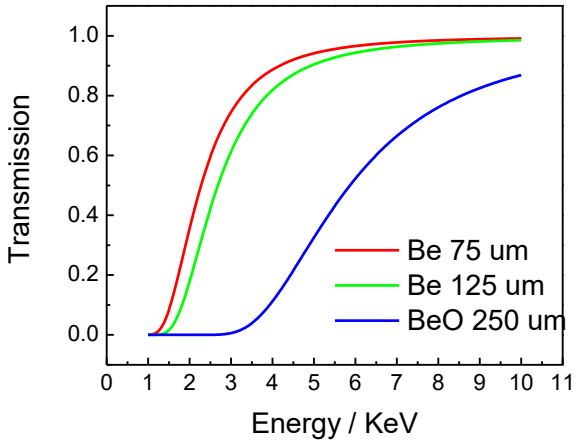
power characteristics: Max voltage and current;

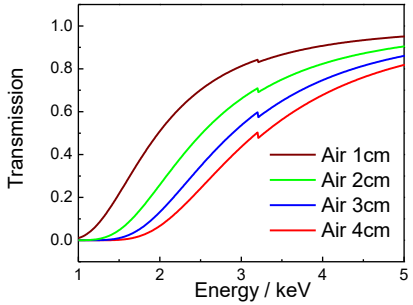
window material and thickness;

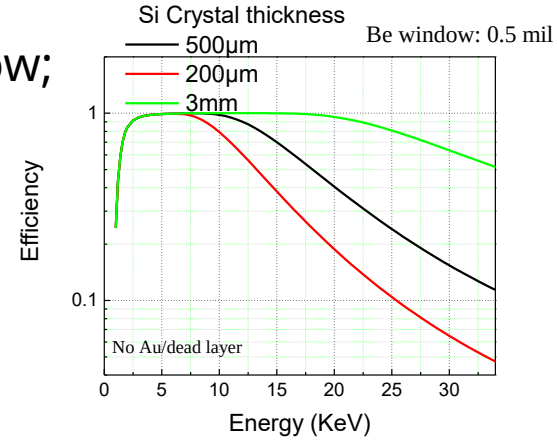
Detectors:

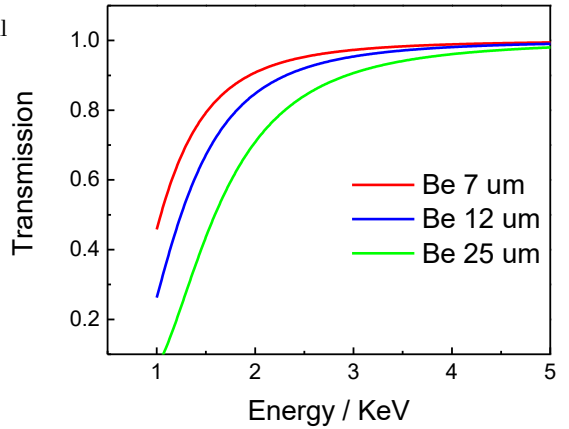
thickness of the Be window;

crystal thickness;









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XRF SPECTROMETRY - Analytical capabilities

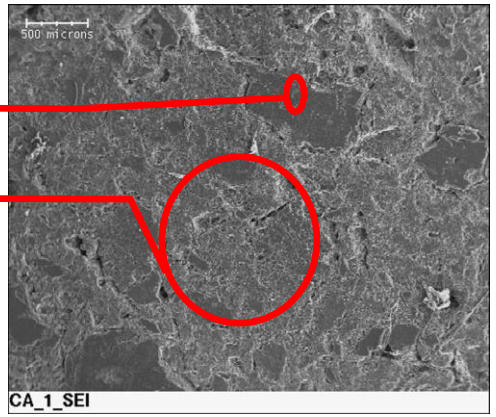
EDXRF spectrometry analytical technique

Advantages:

- Non-invasive or/and Non-destructive;
- Minimal sample preparation;
- Multi-elemental;
- Simple operation;
- Fast data collection enables experimental set up modification in real time ;
- Minimal running costs and affordable price;
- Detection limits in the range of ppm;
- Local and bulk analysis capability depending on the spot size:
  0.02 mm (poly-capillary lenses),
  0.2 mm - 1 mm (pin-hole collimator)
  3-5 mm large area
- For average content a spot size should be larger than sample heterogeneity.

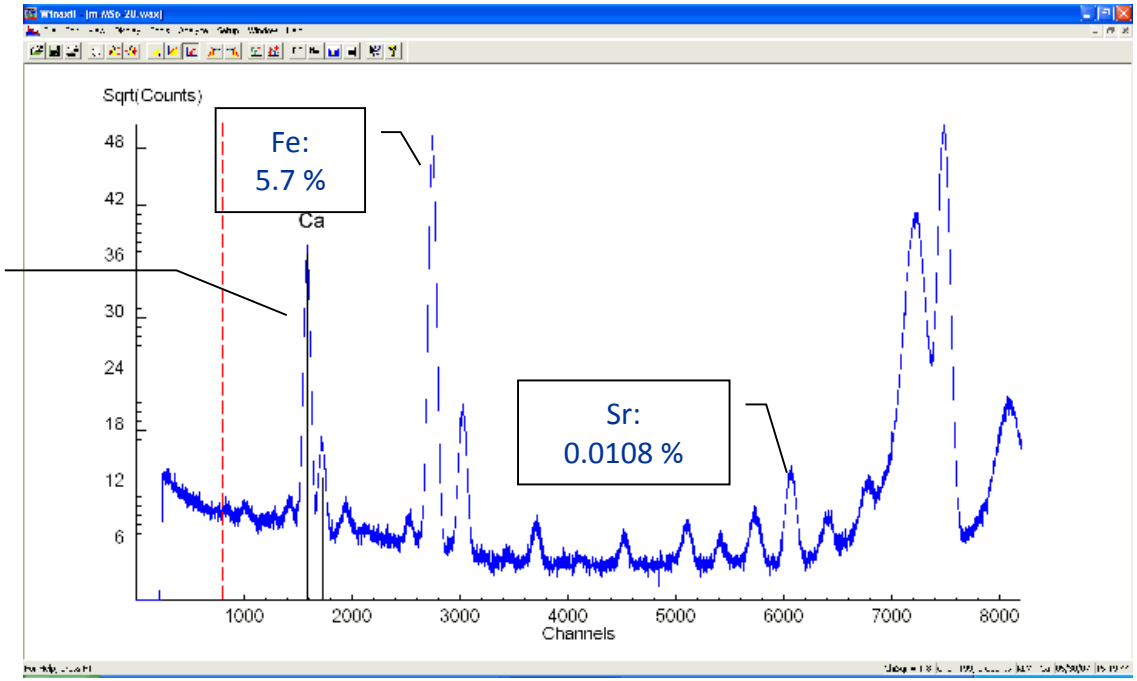
Disadvantages:

- Elemental analysis – no information regarding molecular bonds;
- Surface analysis – small volume;
- Prominent matrix sensitivity;
- Complicated quantitative analysis;
- Low sensitivity for light elements;

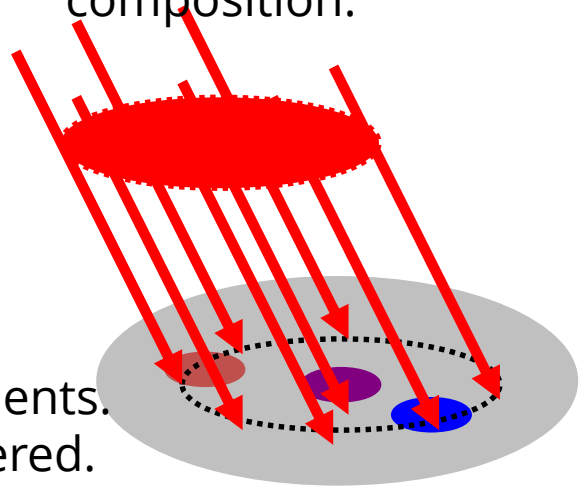


XRF SPECTROMETRY - Analytical capabilities

Interpretation of the XRF spectrum



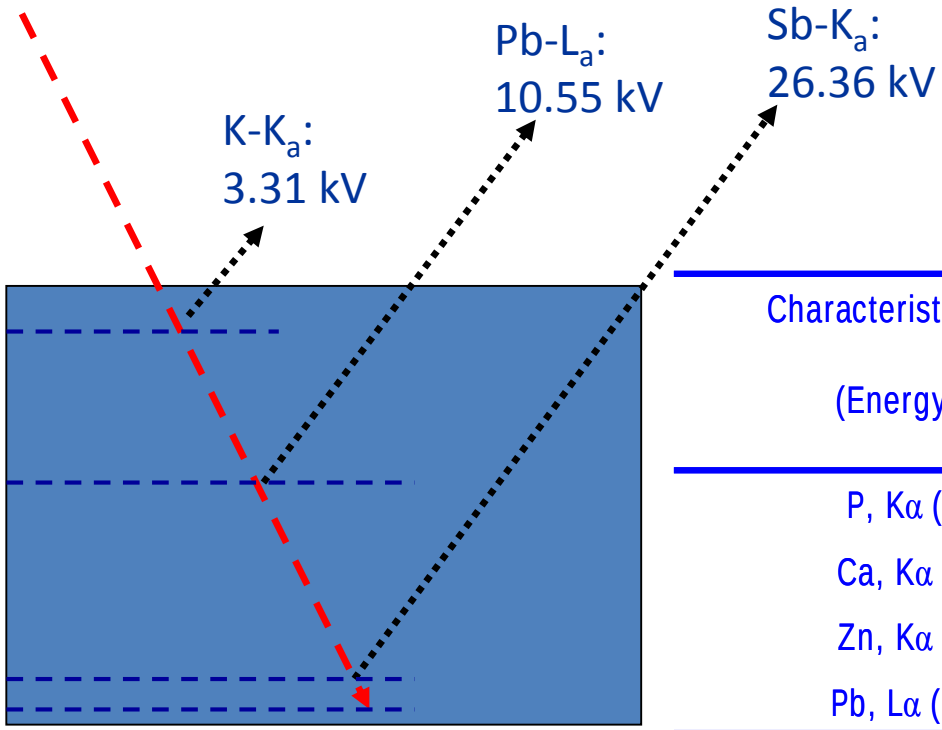
Surface or volume heterogeneity can produce false results regarding elemental composition.



Peak areas can not be compared between elements
Excitation and detection are not the same for all elements.
In same cases, secondary excitation has to be considered.

XRF SPECTROMETRY - Analytical capabilities

- Penetration (excitation) depth depends on sample material and energy of the excitation radiation;
- Information depth is not equal for all detected elements



Characteristic radiation (Energy, keV)	Penetration depth, μm	
	$\vec{Z}=12.5$	$\vec{Z}=15$
P, Kα (2.01)	12	9
Ca, Kα (3.69)	50	32
Zn, Kα (8.62)	540	340
Pb, Lα (10.51)	930	570

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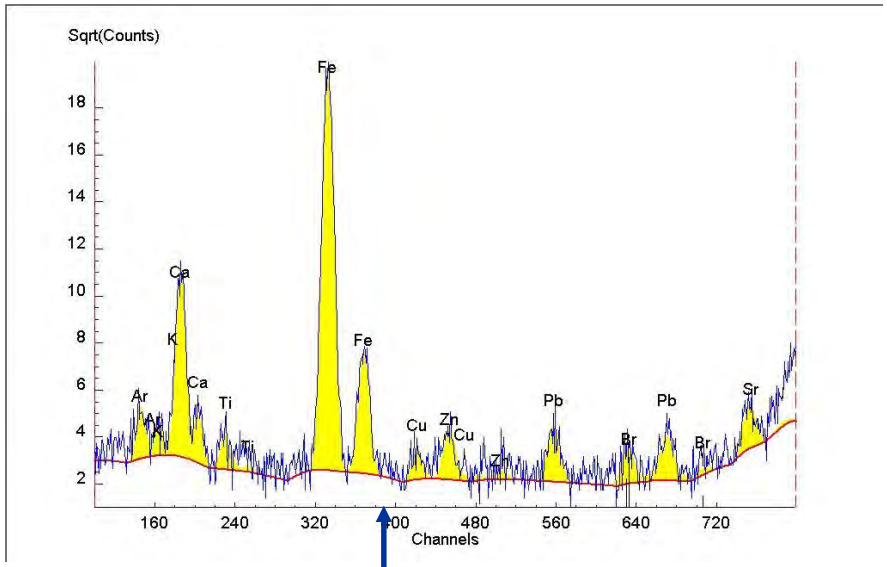
XRF SPECTROMETRY - Analytical capabilities

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

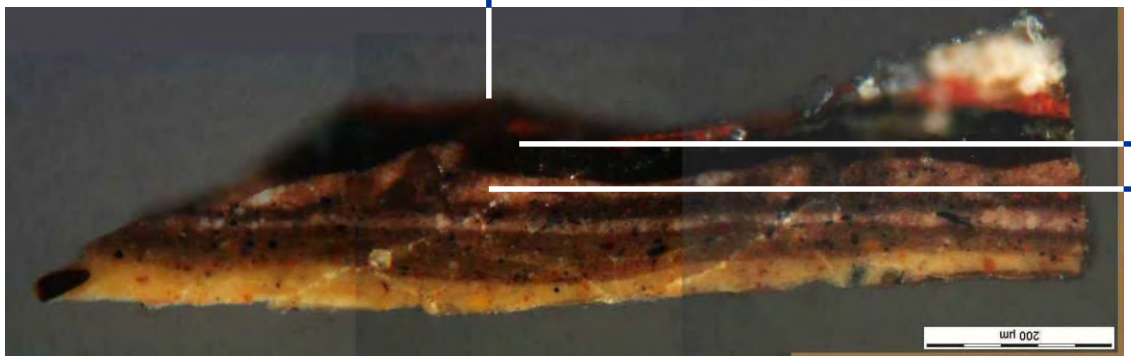
Critical or informational depth- sample volume from which originate 99% of the detected signal i.e. characteristic X-rays.
Information depth is extended from few micrometers up to few hundreds depending on the matrix, energy of the characteristic X-Rays and exciting energy

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

XRF SPECTROMETRY - Analytical capabilities



In the case of the multilayered samples, signals from different layers will superimposed in the one same XRF spectrum so even qualitative analysis can be difficult. Interpretation should include some physical rules in XRF spectrometry.



Black iron oxide (Fe)

Ochre (Ca, Rb, Pb, Sr)

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XRF SPECTROMETRY - Applications

On the basis of analytical capabilities of EDXRF Spectrometry, this analytical technique is applicable for almost all applications:

- **Biology and Medicine (detection of heavy metals in blood and tissues, quantification of Sr and Pb in the bones (in-vivo),...)**
- **Environment (Heavy metals in Atmosphere and water (filters), Marine samples, soils, sediments,...)**
- **Geosciences (analysis of the rocks and sediments, soil cores,...)**
- **Art and Archaeology (paintings, icons, ceramic, ...)**
- **Materials Science (characterization of material)**
- **Forensic science**
- **Industrial applications (ROHS, Sulfur in the fuel, tagging, contamination monitoring,...)**

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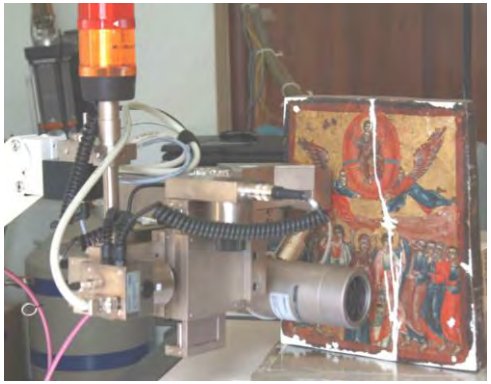
XRF SPECTROMETRY - Applications

https://labs.icahn.mssm.edu/toddlab/bone-lead-test/



Interreg – IPA CBC
Romania - Serbia

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Thank you!