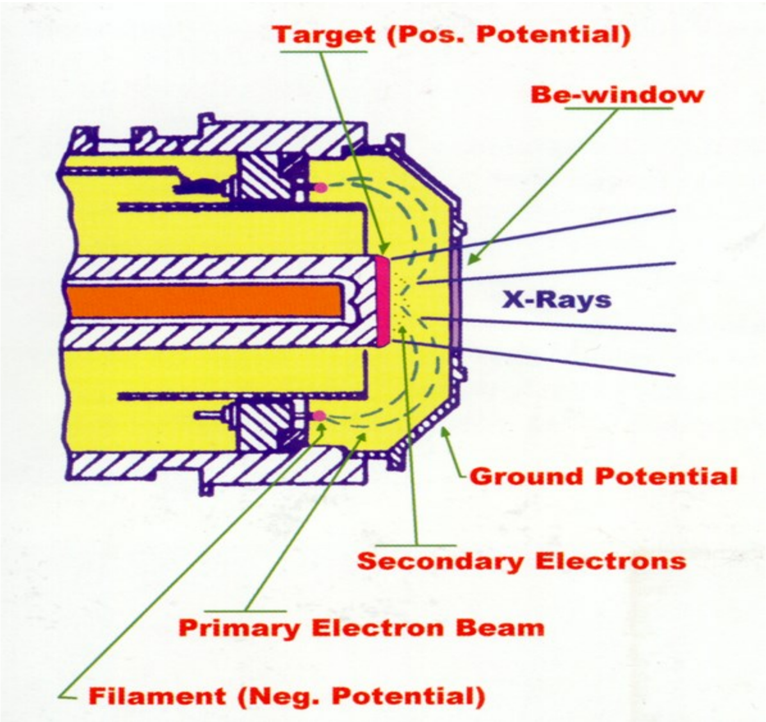
The Hardware

- **Sources**
- **Optics**
- **Filters & Targets**
- **Detectors**

Sources

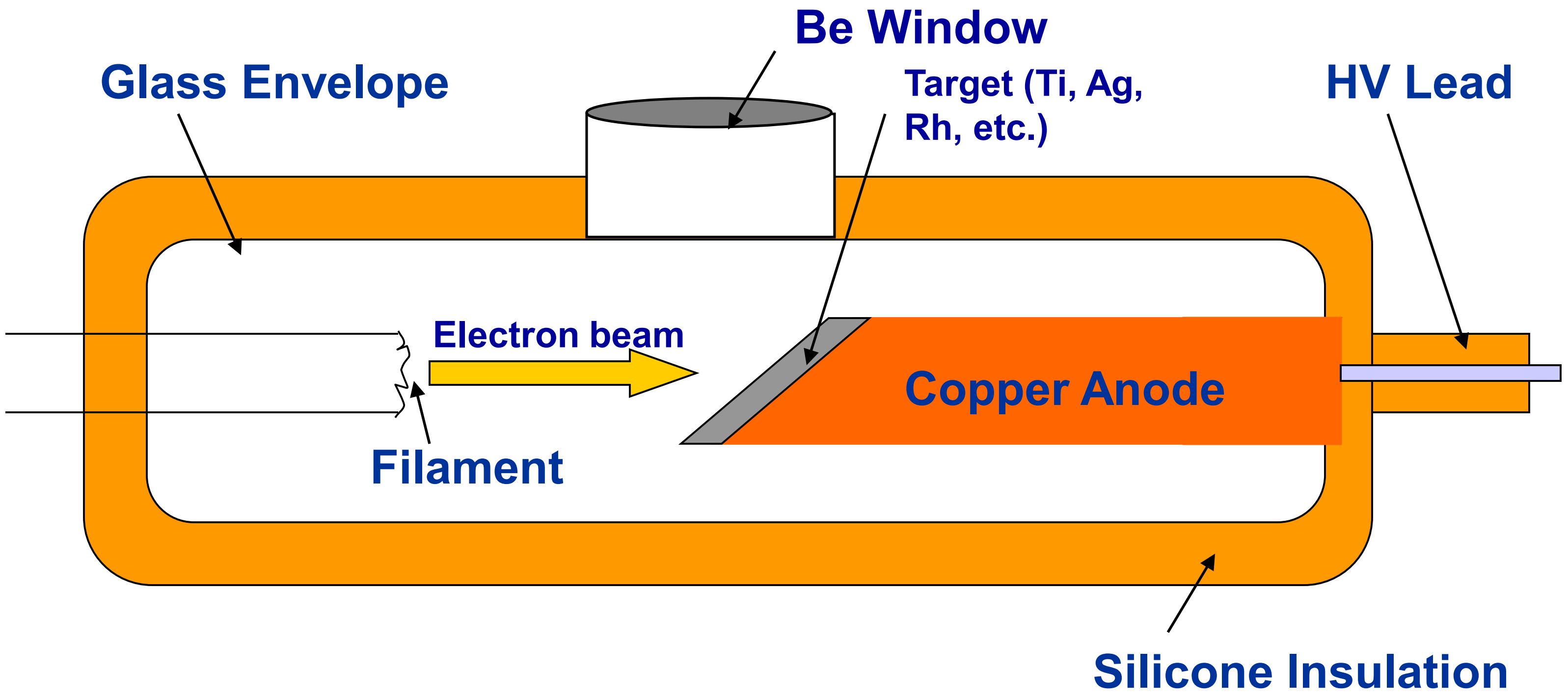
- End Window X-Ray Tubes
- Side Window X-Ray Tubes
- Radioisotopes
- Other Sources
  - Scanning Electron Microscopes
  - Synchrotrons
  - Positron and other particle beams

End Window X-Ray Tube



- X-ray Tubes
  - Voltage determines which elements can be excited.
  - More power = lower detection limits
  - Anode selection determines optimal source excitation (application specific).

Side Window X-Ray Tube



Radioisotopes

Isotope	Fe-55	Cm-244	Cd-109	Am-241	Co-57
Energy (keV)	5.9	14.3, 18.3	22, 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.

Other Sources

Several other radiation sources are capable of exciting material to produce x-ray fluorescence suitable for material analysis.

- **Scanning Electron Microscopes (SEM) – Electron beams excite the sample and produce x-rays. Many SEM’s are equipped with an EDX detector for performing elemental analysis**
- **Synchotrons - These bright light sources are suitable for research and very sophisticated XRF analysis.**
- **Positrons and other Particle Beams – All high energy particles beams ionize materials such that they give off x-rays. PIXE is the most common particle beam technique after SEM.**

Source Modifiers

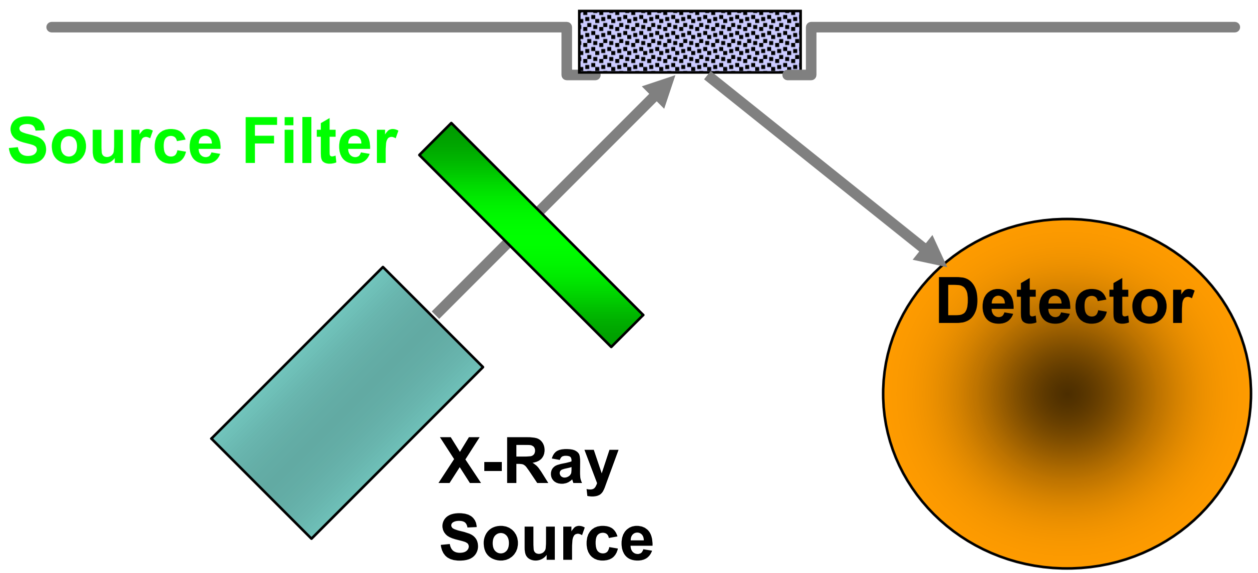
Several Devices are used to modify the shape or intensity of the source spectrum or the beam shape

- **Source Filters**
- **Secondary Targets**
- **Polarizing Targets**
- **Collimators**
- **Focusing Optics**

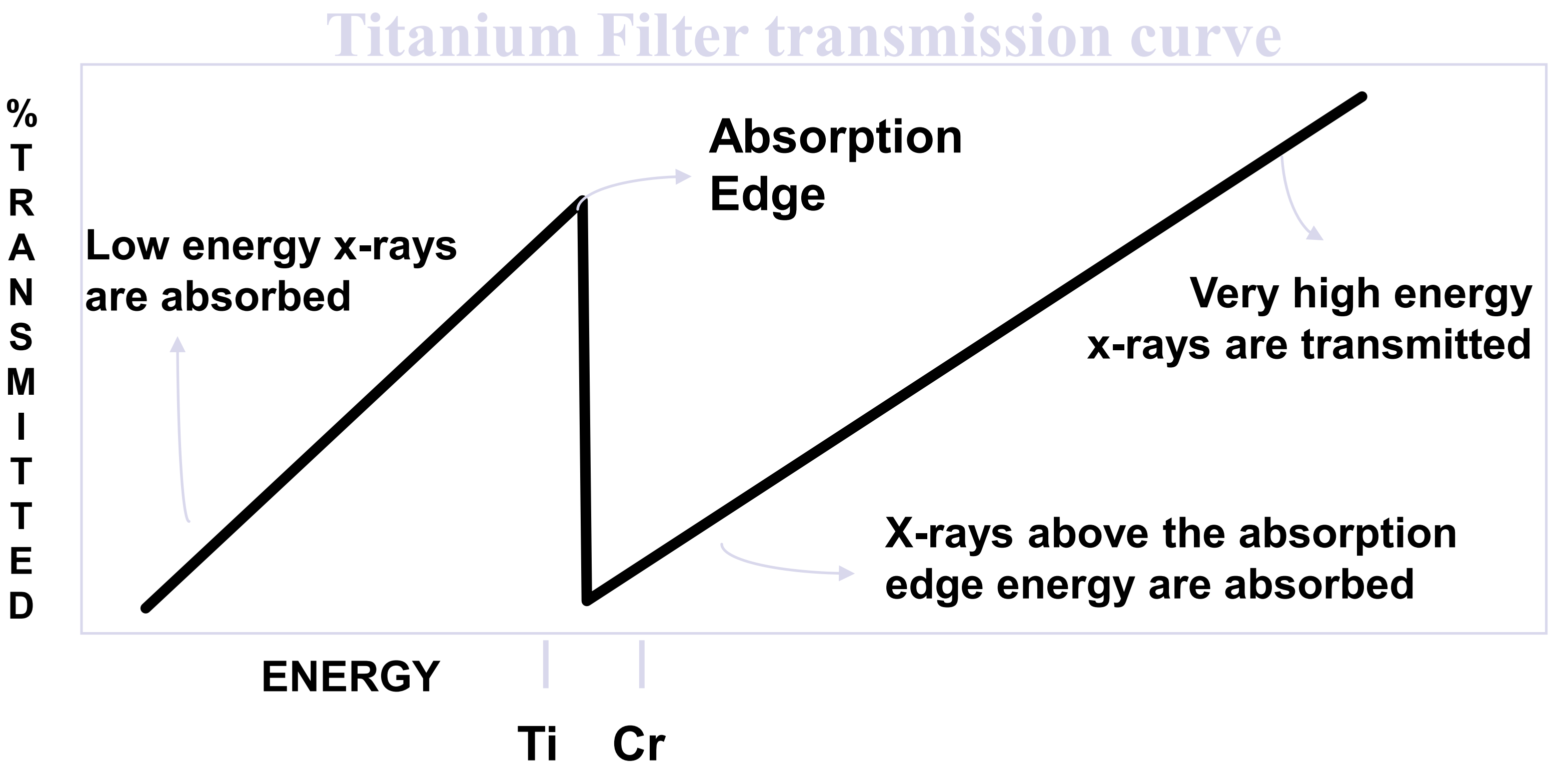
Source Filters

Filters perform one of two functions

- Background Reduction
- Improved Fluorescence



Filter Transmission Curve



Titanium Filter transmission curve

Low energy x-rays are absorbed

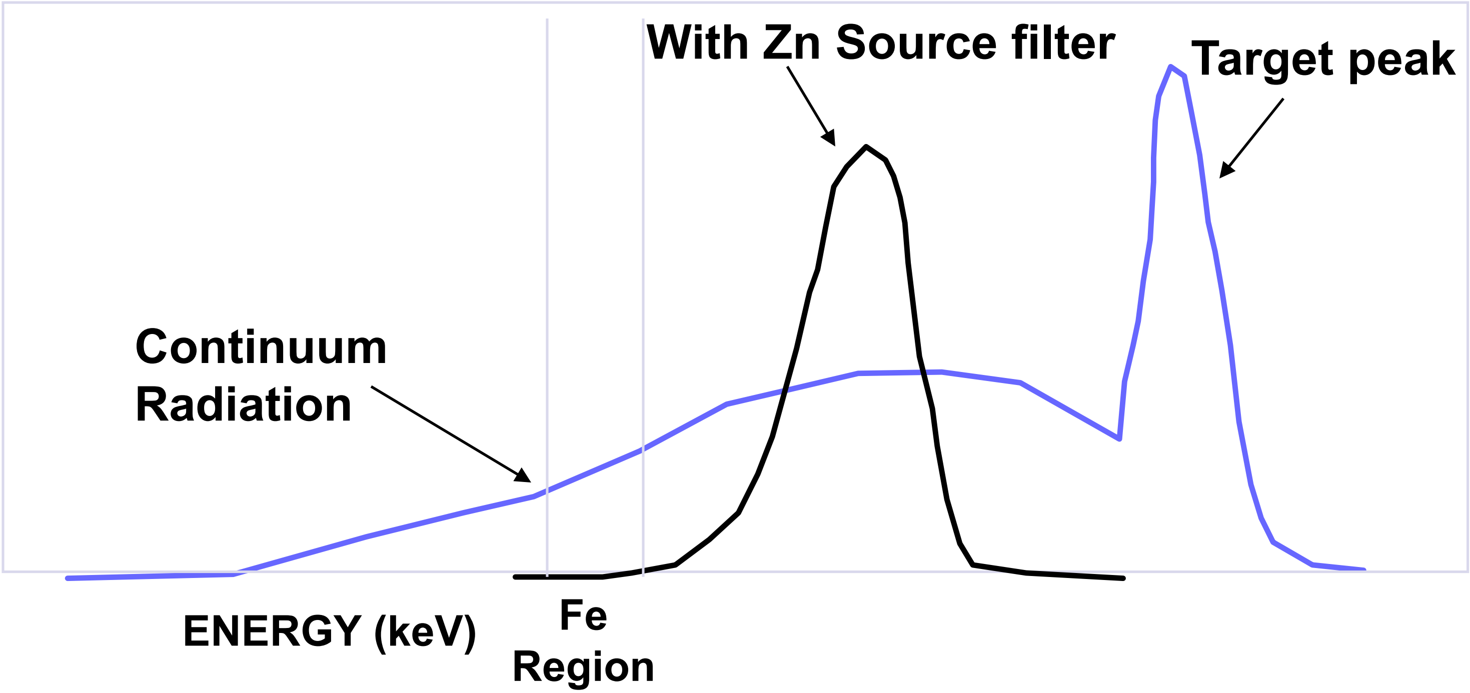
Absorption Edge

Very high energy x-rays are transmitted

X-rays above the absorption edge energy are absorbed

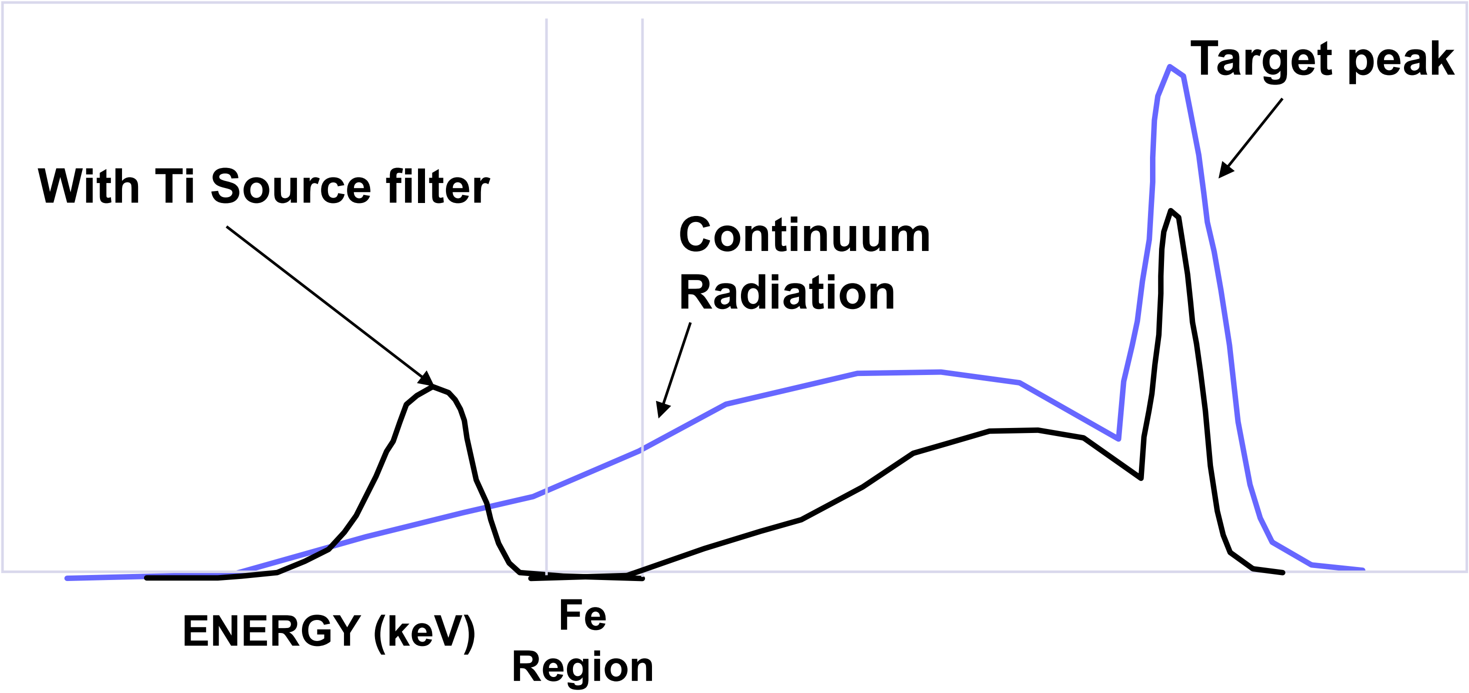
The transmission curve shows the parts of the source spectrum are transmitted and those that are absorbed

Filter Fluorescence Method



The filter fluorescence method decreases the background and improves the fluorescence yield without requiring huge amounts of extra power.

Filter Absorption Method



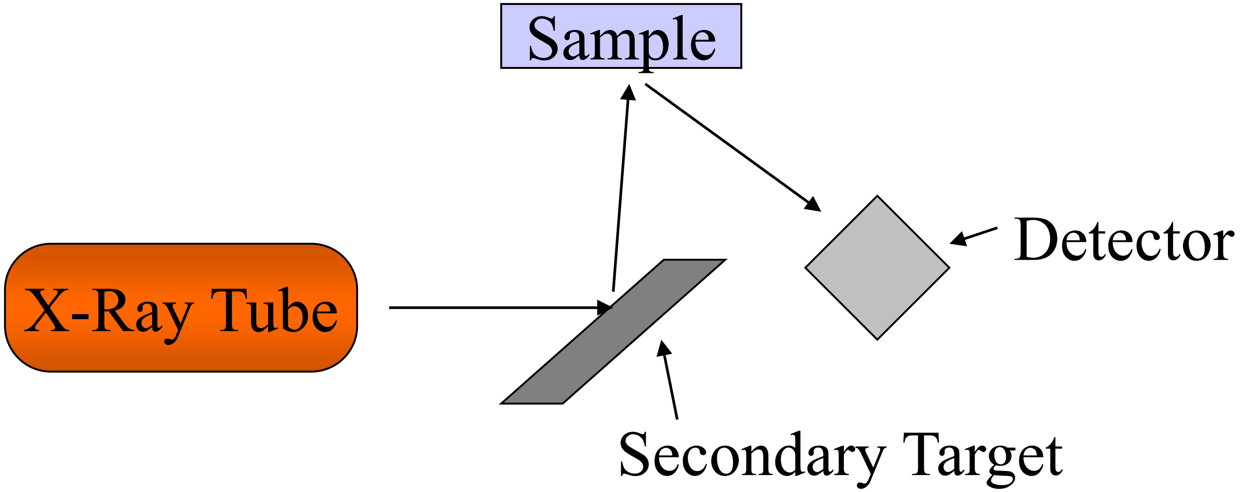
The filter absorption Method decreases the background while maintaining similar excitation efficiency.

Secondary Targets

Improved Fluorescence and lower background
The characteristic fluorescence of the custom line source is used to excite the sample, with the lowest possible background intensity.

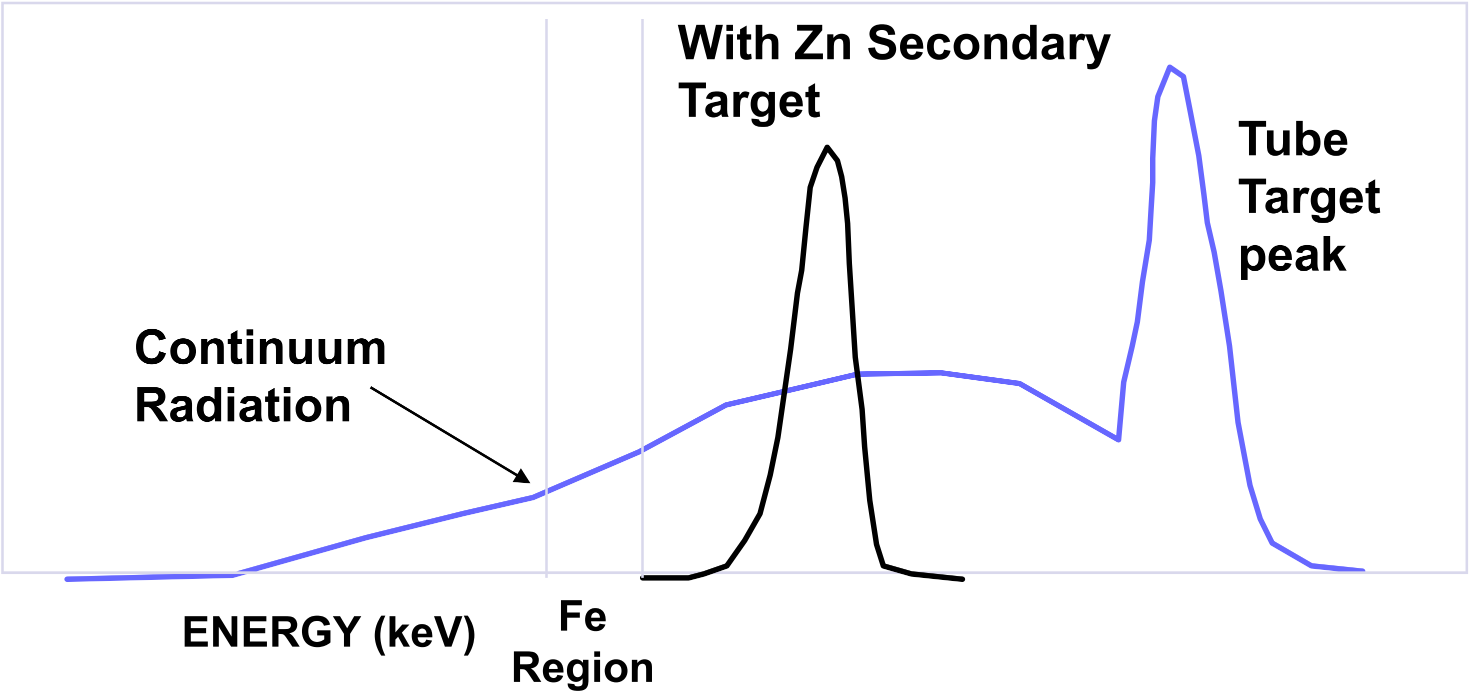
It requires almost 100x the flux of filter methods but gives superior results.

Secondary Targets



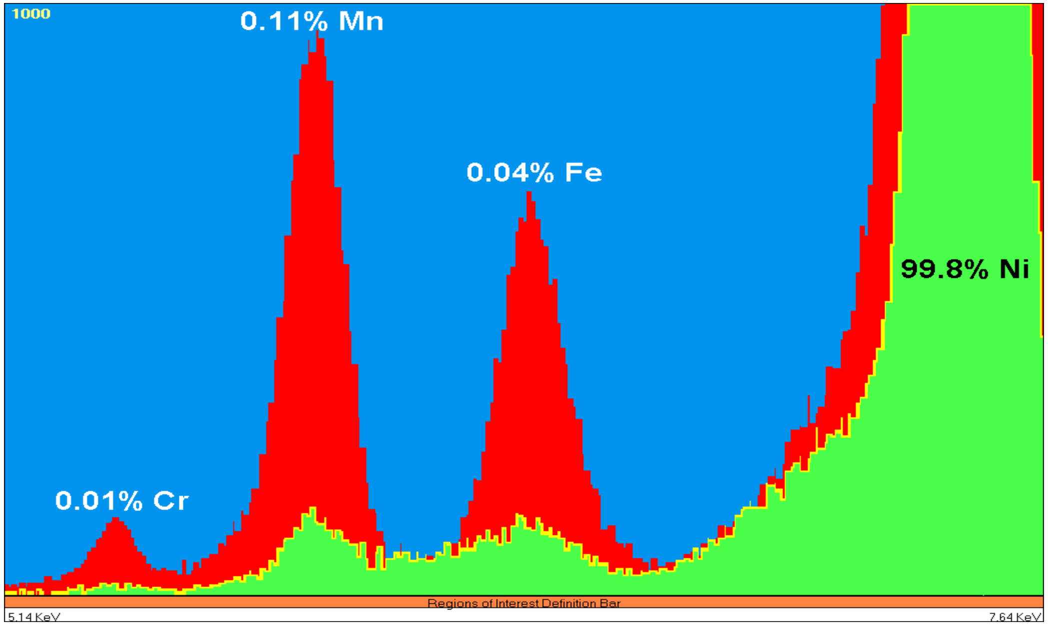
A. The x-ray tube excites the secondary target
B. The Secondary target fluoresces and excites the sample
C. The detector detects x-rays from the sample

Secondary Target Method



Secondary Targets produce a more monochromatic source peak with lower background than with filters

Secondary Target Vs Filter



Comparison of optimized direct-filtered excitation with secondary target excitation for minor elements in Ni-200

Polarizing Target Theory

a) **X-ray are partially polarized whenever they scatter off a surface**

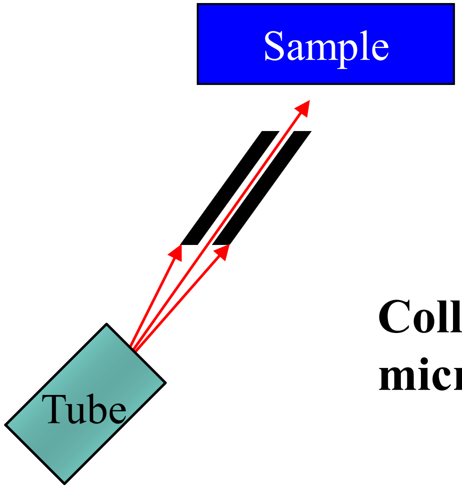
b) **If the sample and polarizer are oriented perpendicular to each other and the x-ray tube is not perpendicular to the target, x-rays from the tube will not reach the detector.**

c) **There are three type of Polarization Targets:**

- **Barkla Scattering Targets - They scatter all source energies to reduce background at the detector.**
- **Secondary Targets - They fluoresce while scattering the source x-rays and perform similarly to other secondary targets.**
- **Diffractive Targets - They are designed to scatter specific energies more efficiently in order to produce a stronger peak at that energy.**

Collimators

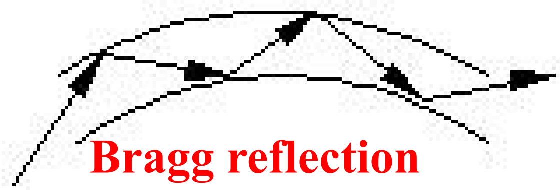
Collimators are usually circular or a slit and restrict the size or shape of the source beam for exciting small areas in either EDXRF or uXRF instruments. They may rely on internal Bragg reflection for improved efficiency.



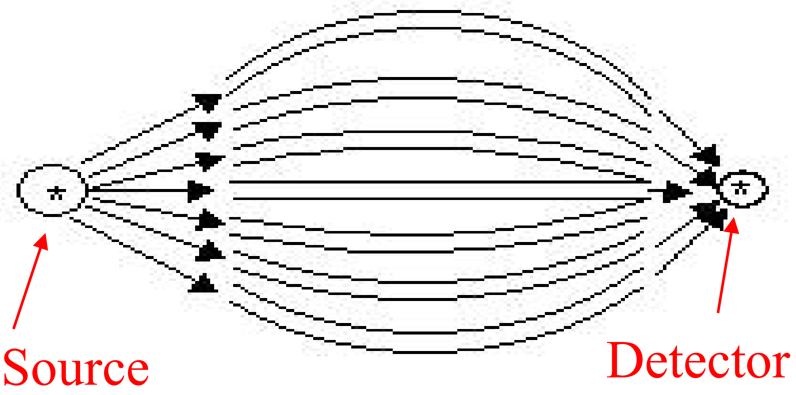
Collimator sizes range from 12 microns to several mm

Focusing Optics

Because simple collimation blocks unwanted x-rays it is a highly inefficient method. Focusing optics like polycapillary devices and other Kumakhov lens devices were developed so that the beam could be redirected and focused on a small spot. Less than 75 um spot sizes are regularly achieved.



Bragg reflection inside a Capillary



Detectors

- Si(Li)
- PIN Diode
- Silicon Drift Detectors
- Proportional Counters
- Scintillation Detectors

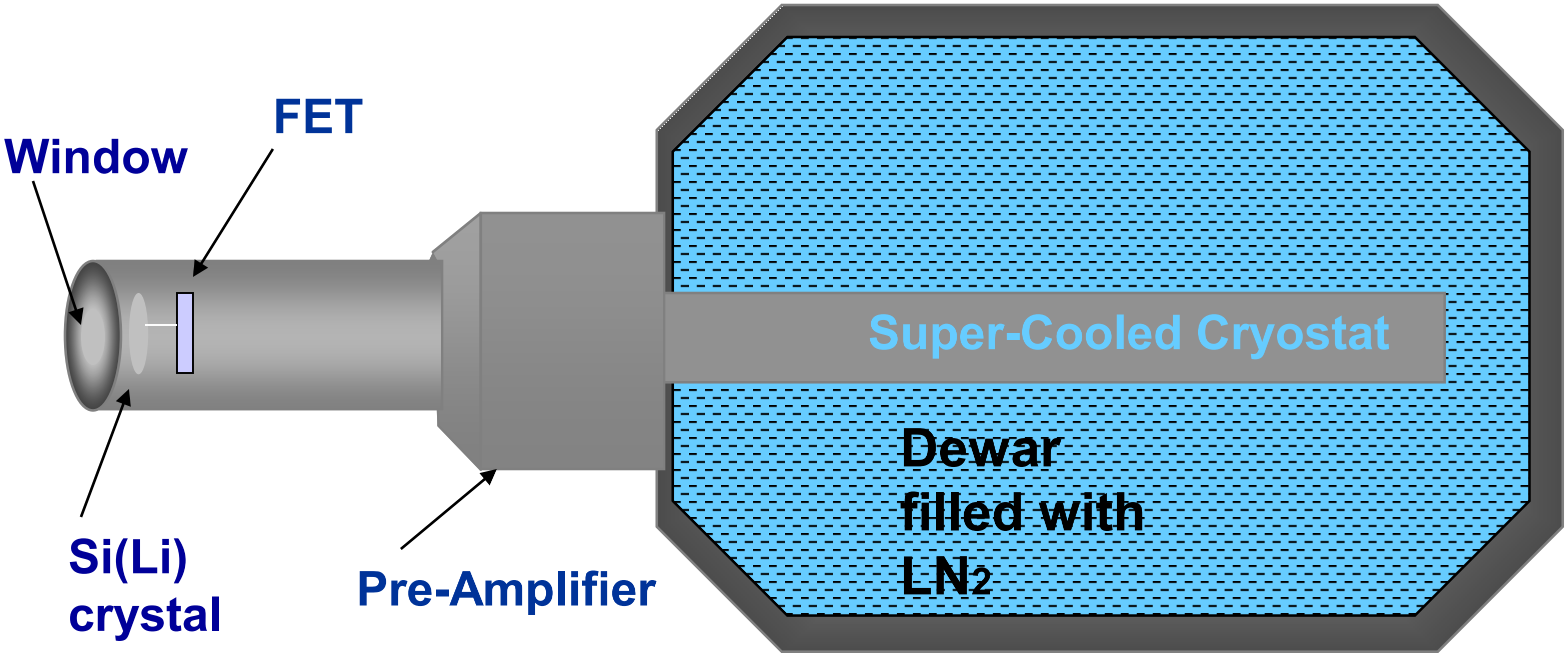
Detector Principles

- A detector is composed of a non-conducting or semi-conducting material between two charged electrodes.
- X-ray radiation ionizes the detector material causing it to become conductive, momentarily.
- The newly freed electrons are accelerated toward the detector anode to produce an output pulse.
- In ionized semiconductor produces electron-hole pairs, the number of pairs produced is proportional to the X-ray photon energy

$$n = \frac{E}{e}$$

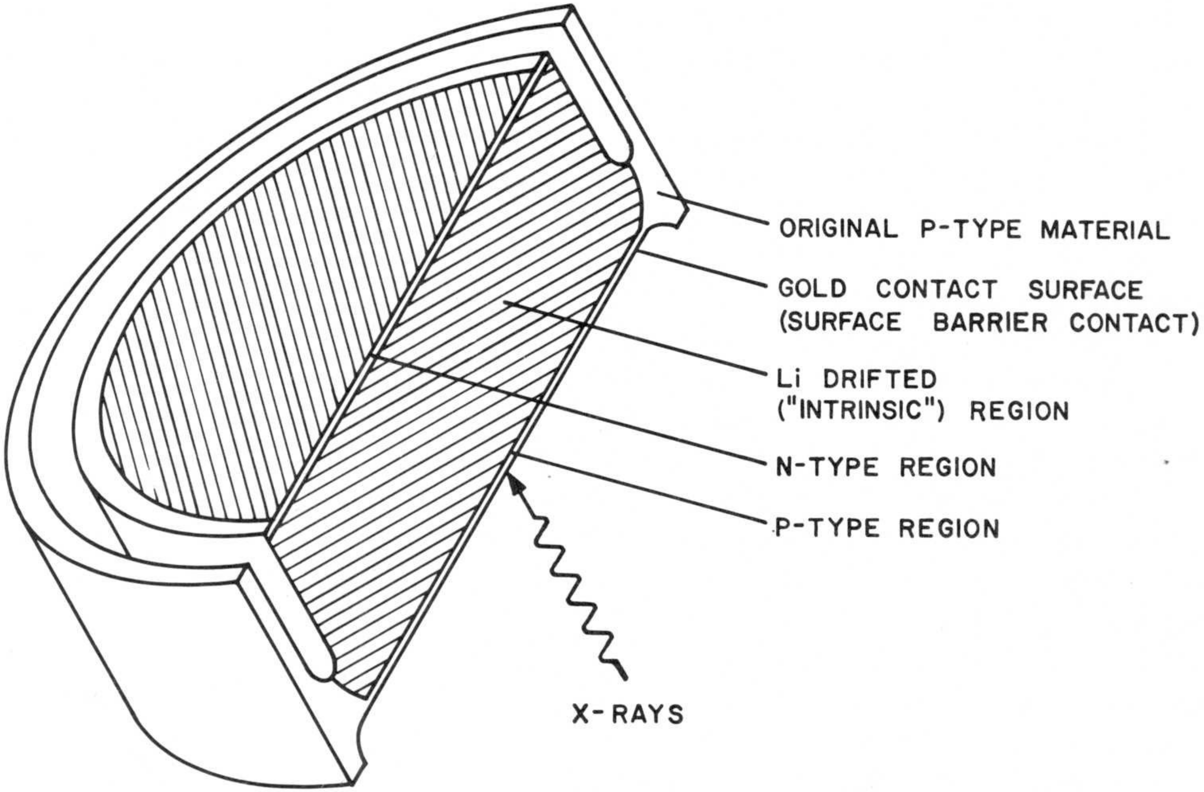
where :
n = number of electron-hole pairs produced
E = X-ray photon energy
e = 3.8ev for Si at LN_2 temperatures

Si(Li) Detector

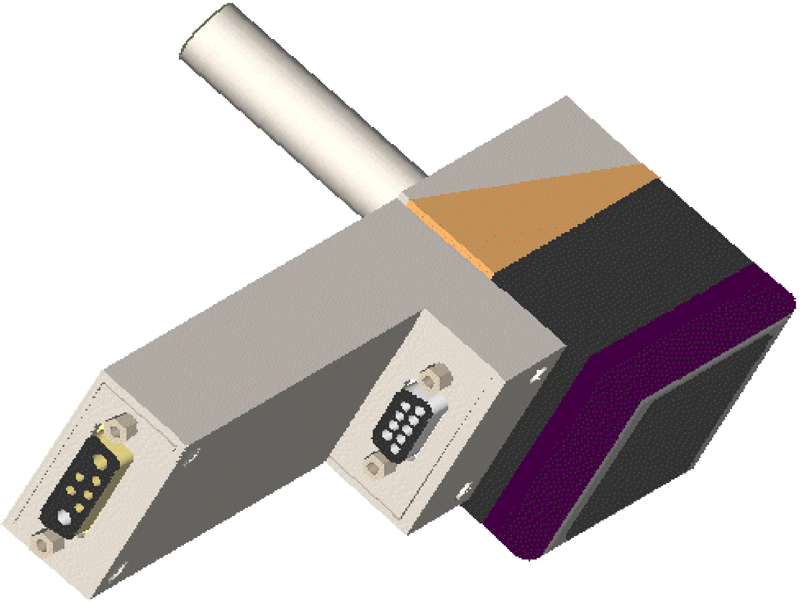


Cooling: LN$_2$ or Peltier
Window: Beryllium or Polymer
Counts Rates: 3,000 – 50,000 cps
Resolution: 120-170 eV at Mn K-alpha

Si(Li) Cross Section

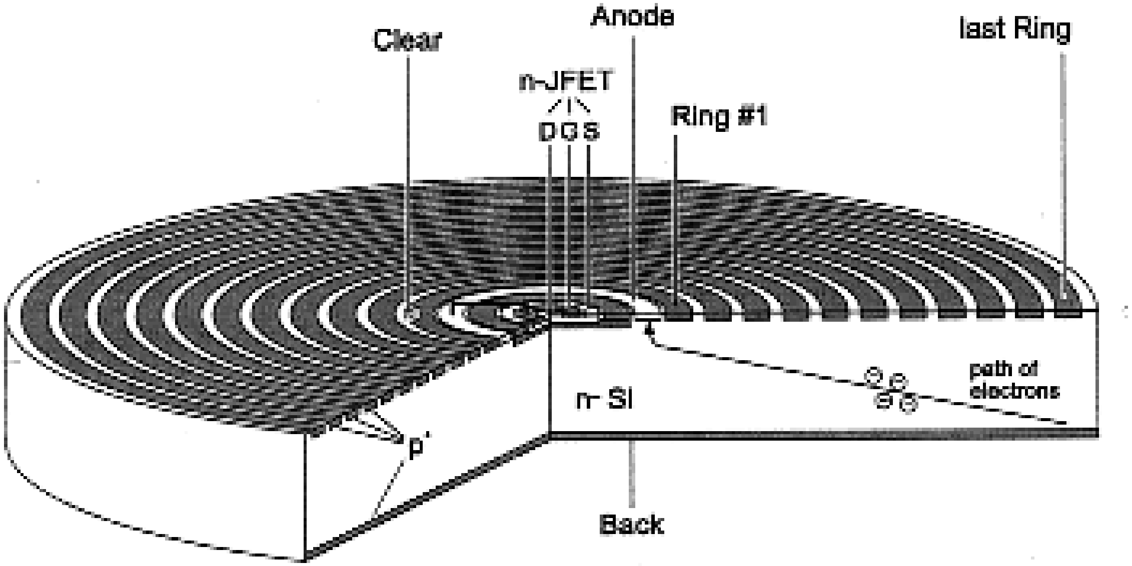


PIN Diode Detector



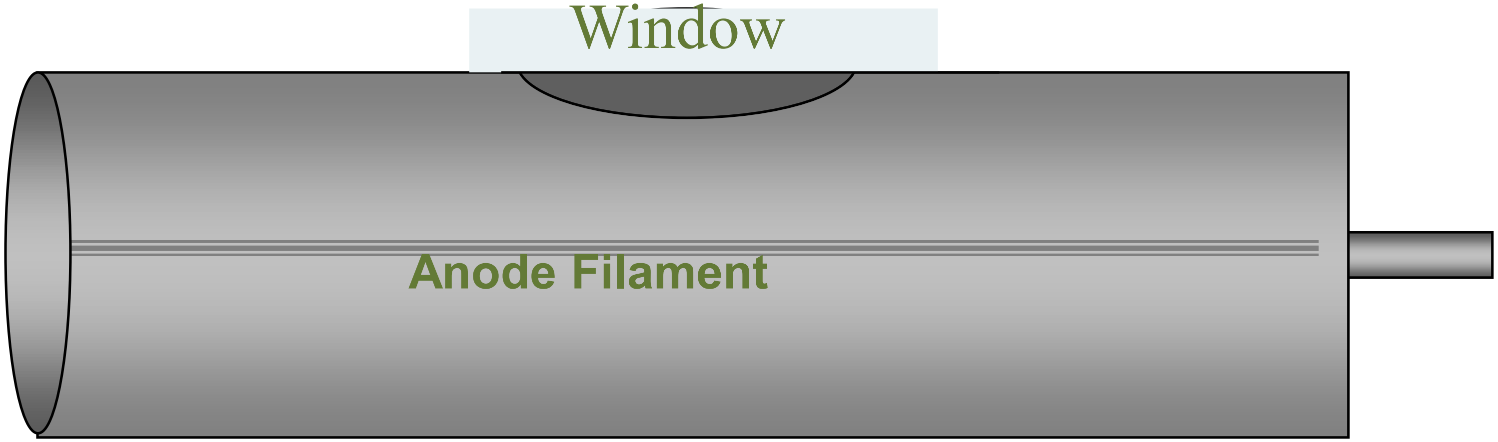
Cooling: Thermoelectrically cooled (Peltier)
Window: Beryllium
Count Rates: 3,000 – 20,000 cps
Resolution: 170-240 eV at Mn k-alpha

Silicon Drift Detector- SDD



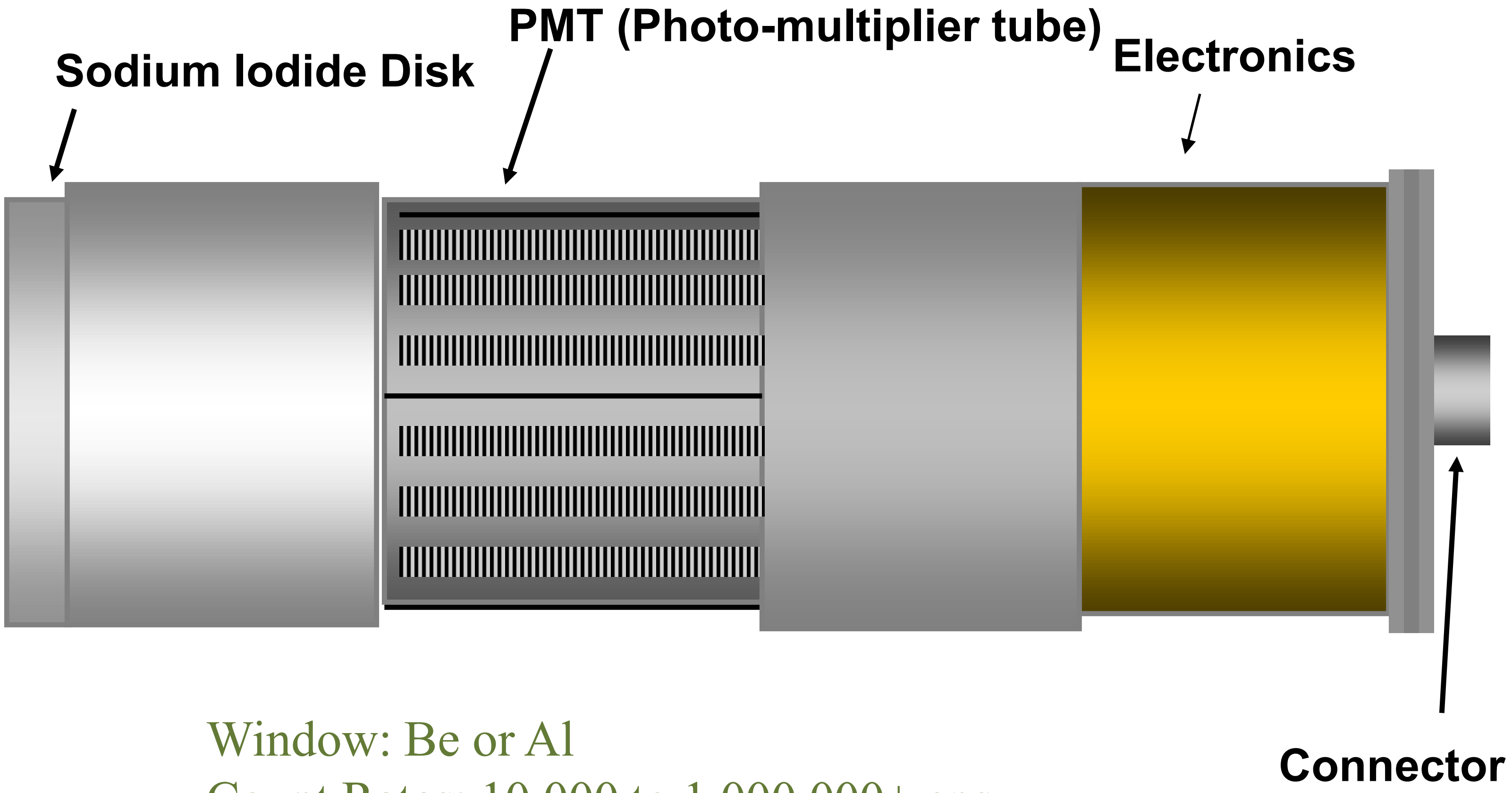
Packaging: Similar to PIN Detector
Cooling: Peltier
Count Rates; 10,000 – 300,000 cps
Resolution: 140-180 eV at Mn K-alpha

Proportional Counter



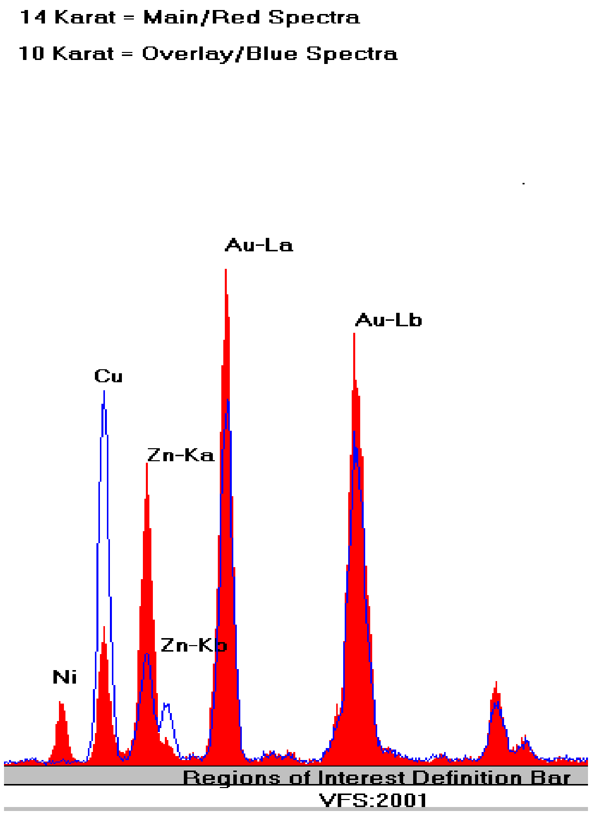
Fill Gases: Neon, Argon, Xenon, Krypton
Pressure: 0.5- 2 ATM
Windows: Be or Polymer
Sealed or Gas Flow Versions
Count Rates EDX: 10,000-40,000 cps WDX: 1,000,000+
Resolution: 500-1000+ eV

Scintillation Detector



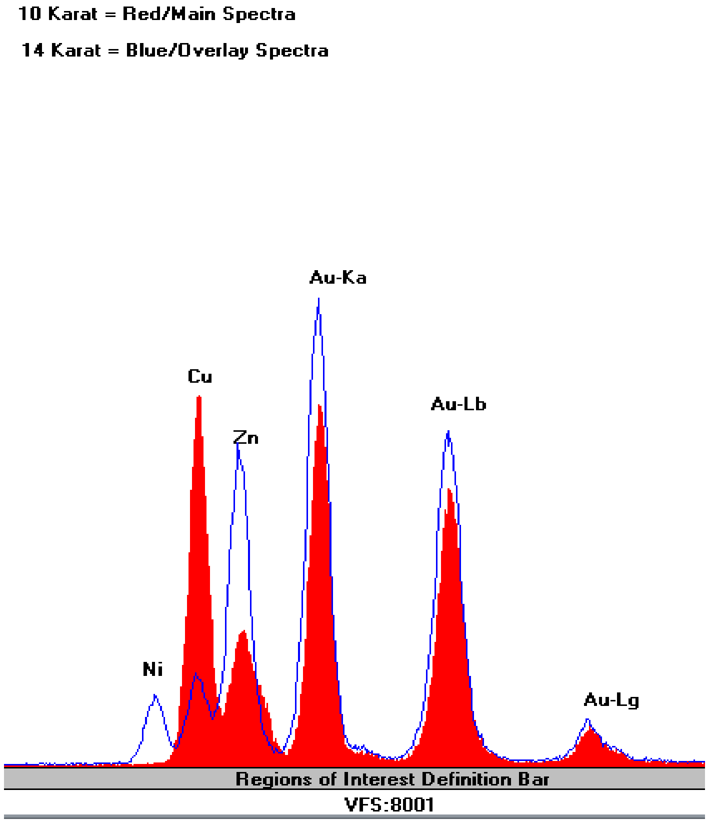
Window: Be or Al
Count Rates: 10,000 to 1,000,000+ cps
Resolution: >1000 eV

Spectral Comparison - Au



Si(Li) Detector

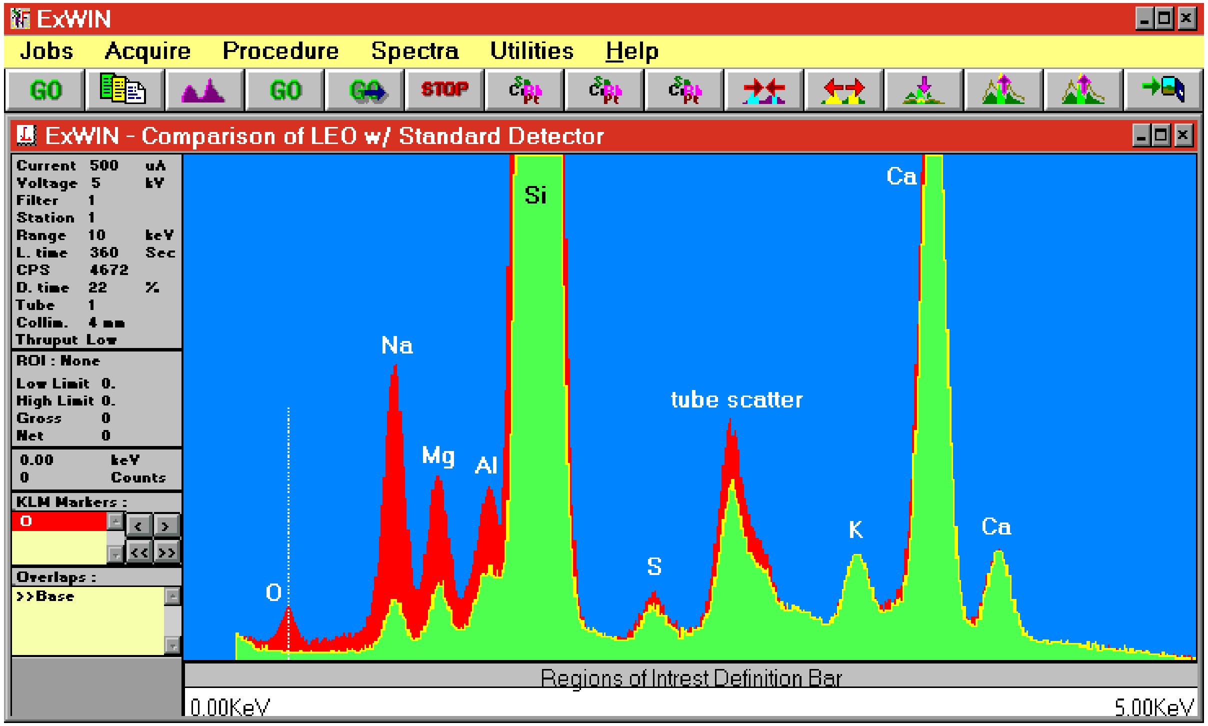
10 vs. 14 Karat



Si PIN Diode Detector

10 vs. 14 Karat

Polymer Detector Windows



Current 500 uA
Voltage 5 kV
Filter 1
Station 1
Range 10 keV
L. time 360 Sec
CPS 4672
D. time 22 %
Tube 1
Collim. 4 mm
Thruput Low

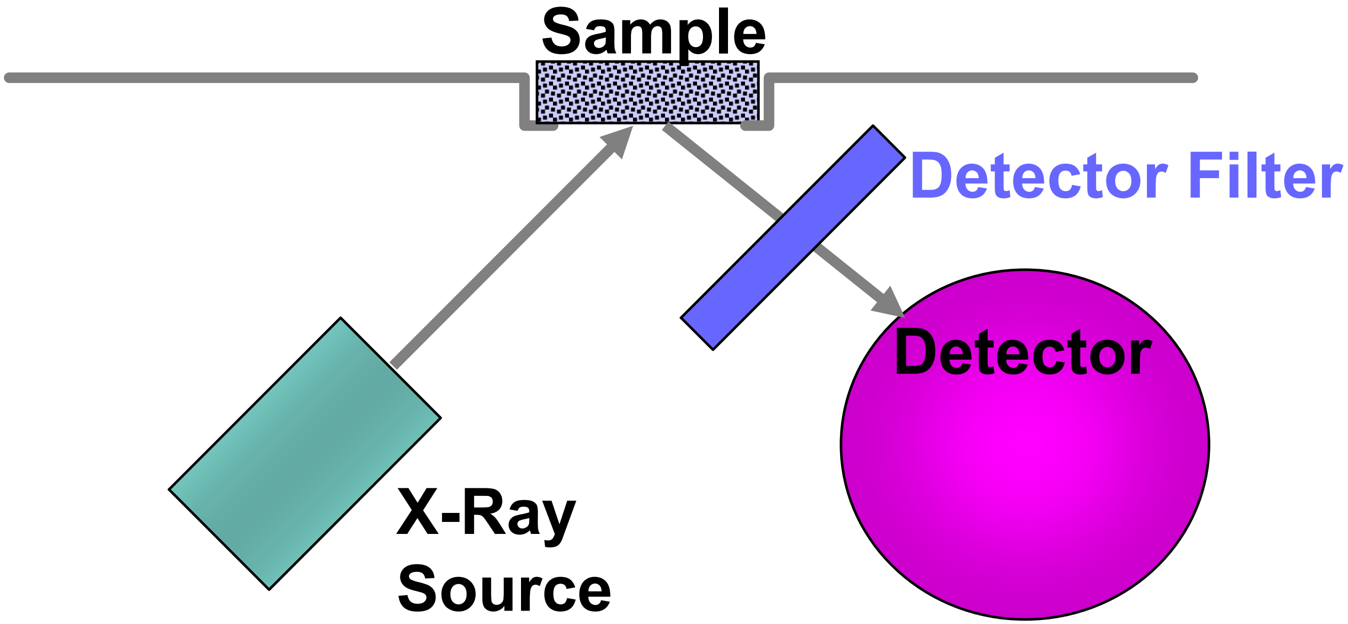
ROI : None
Low Limit 0.
High Limit 0.
Gross 0
Net 0

0.00 keV
0 Counts

- Optional thin polymer windows compared to a standard beryllium windows
- Affords 10x improvement in the MDL for sodium (Na)

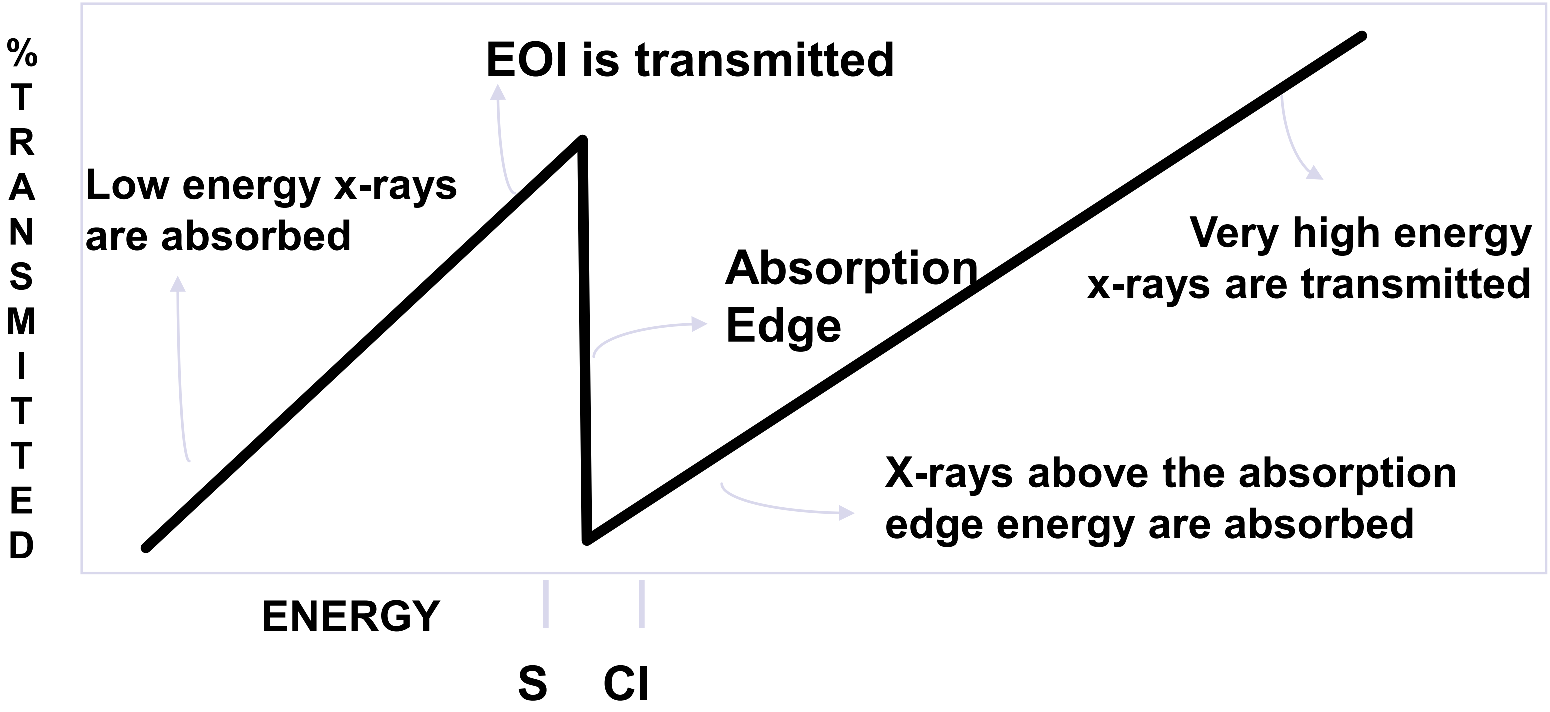
Detector Filters

Filters are positioned between the sample and detector in some EDXRF and NDXRF systems to filter out unwanted x-ray peaks.



Detector Filter Transmission

Niobium Filter Transmission and Absorption



% TRANSMITTED

EOI is transmitted

Low energy x-rays are absorbed

Absorption Edge

Very high energy x-rays are transmitted

X-rays above the absorption edge energy are absorbed

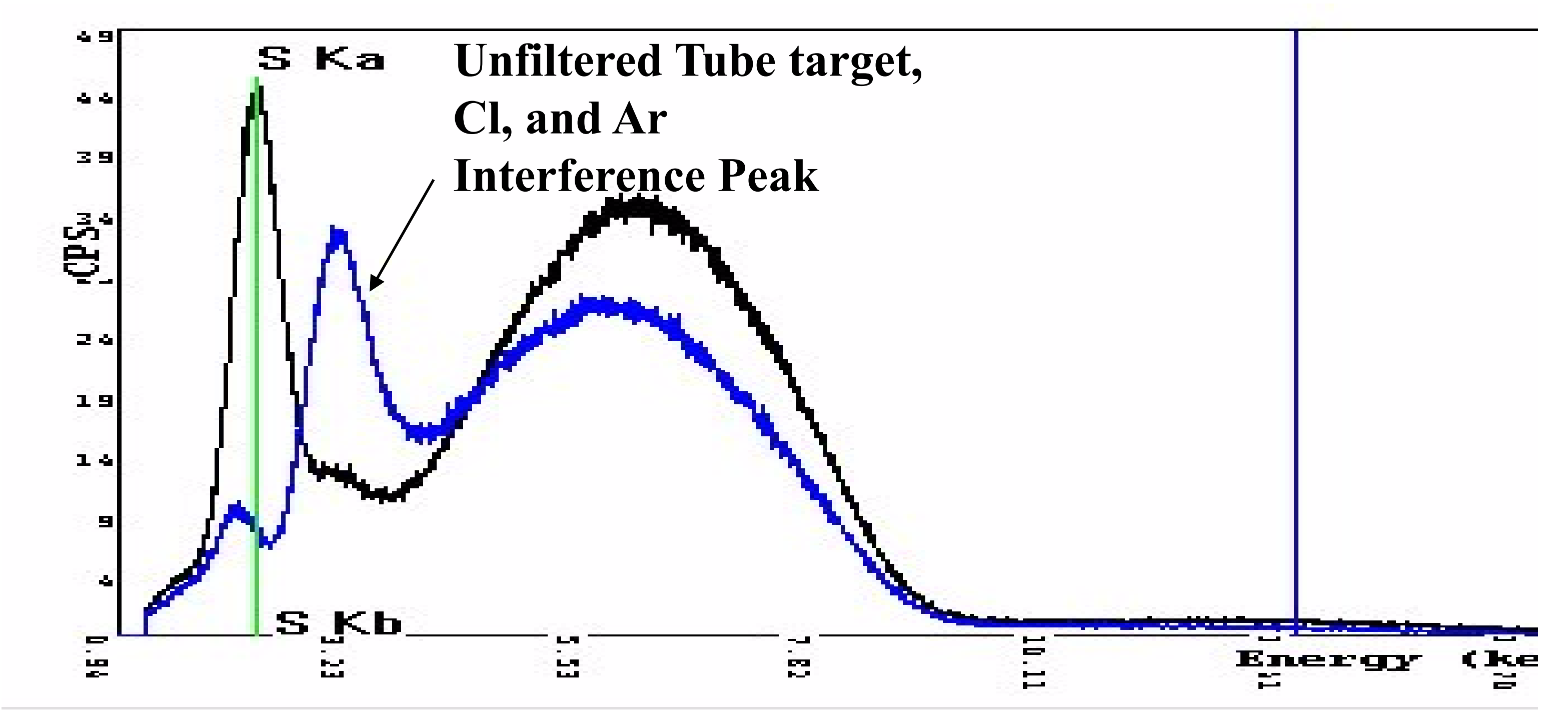
ENERGY

S Cl

A niobium filter absorbs Cl and other higher energy source x-rays while letting S x-rays pass. A detector filter can significantly improve detection limits.

Filter Vs. No Filter

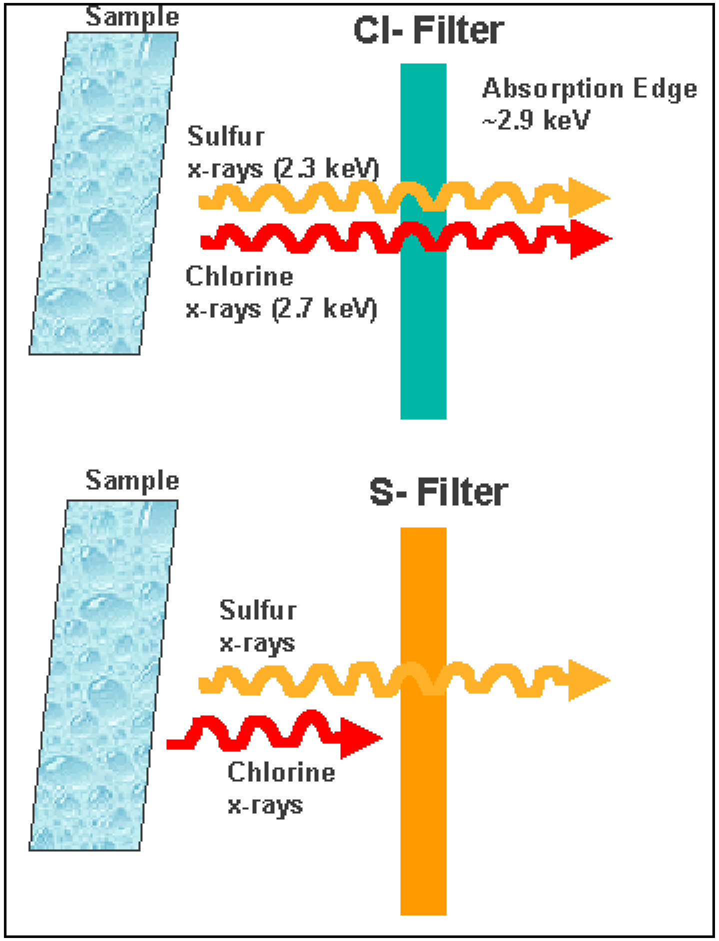
Detector filters can dramatically improve the element of interest intensity, while decreasing the background, but requires 4-10 times more source flux. They are best used with large area detectors that normally do not require much power.



Unfiltered Tube target, Cl, and Ar Interference Peak

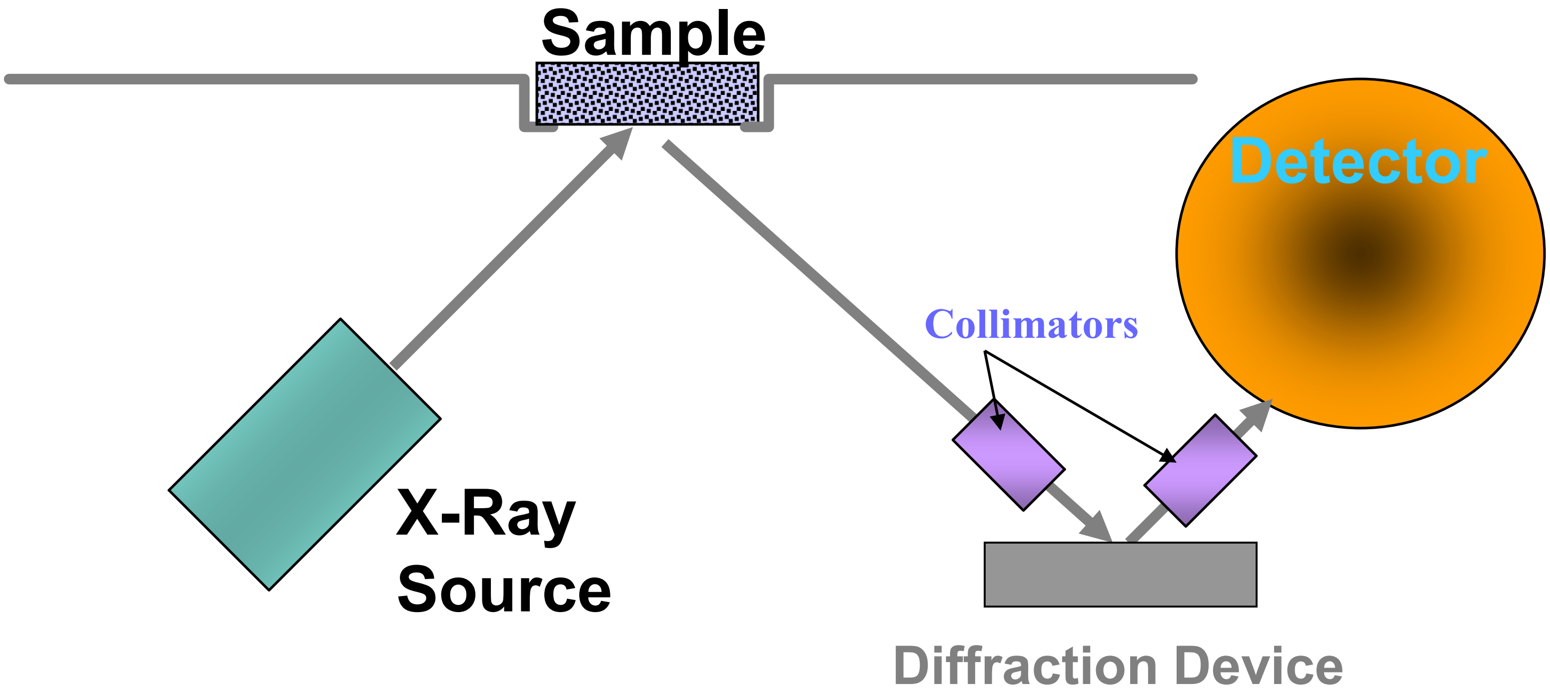
Ross Vs. Hull Filters

- The previous slide was an example of the Hull or simple filter method.
- The Ross method illustrated here for Cl analysis uses intensities through two filters, one transmitting, one absorbing, and the difference is correlated to concentration. This is an NDXRF method since detector resolution is not important.



Wavelength Dispersive XRF

Wavelength Dispersive XRF relies on a diffractive device such as crystal or multilayer to isolate a peak, since the diffracted wavelength is much more intense than other wavelengths that scatter of the device.

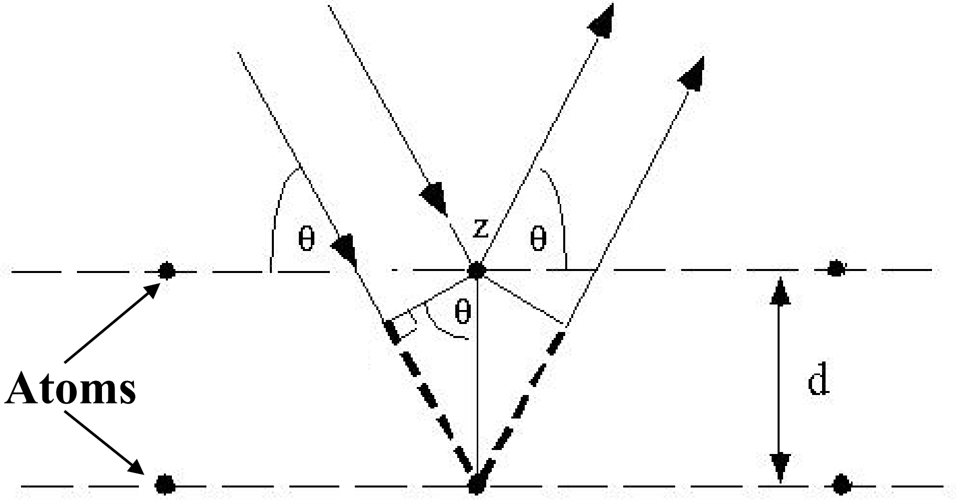


Diffraction

The two most common diffraction devices used in WDX instruments are the crystal and multilayer. Both work according to the following formula.

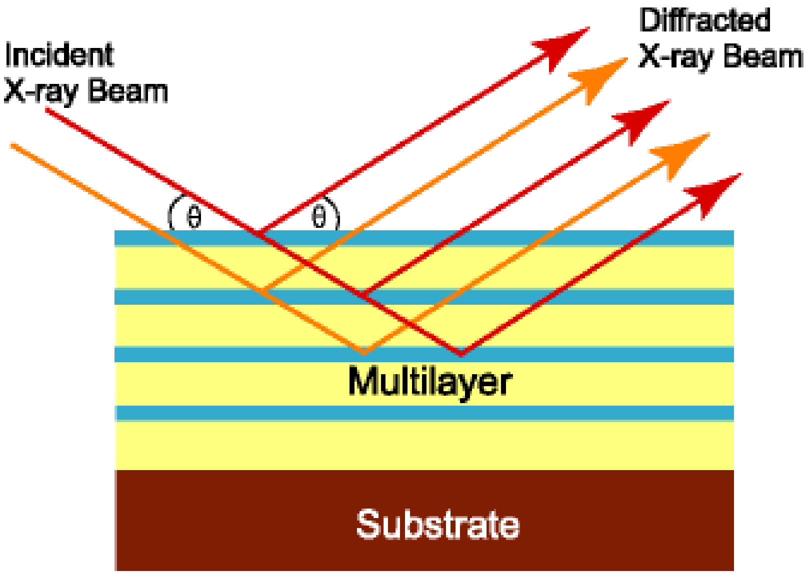
$$n\lambda = 2d\,'\,\sin\theta$$

n = integer
d = crystal lattice or
multilayer spacing
θ = The incident angle
λ = wavelength



Multilayers

While the crystal spacing is based on the natural atomic spacing at a given orientation the multilayer uses a series of thin film layers of dissimilar elements to do the same thing.

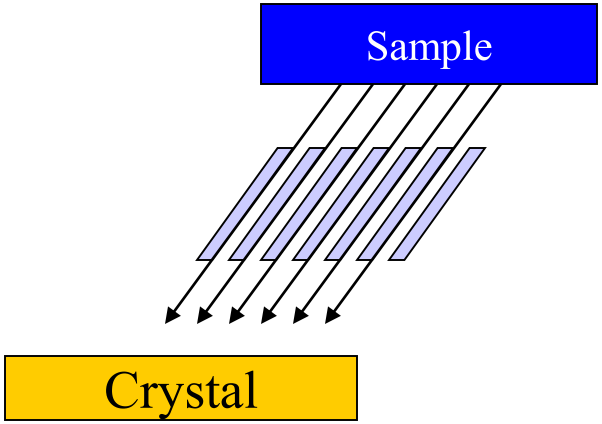


Modern multilayers are more efficient than crystals and can be optimized for specific elements.

Often used for low Z elements.

Soller Collimators

Soller and similar types of collimators are used to prevent beam divergence. The are used in WDXRF to restrict the angles that are allowed to strike the diffraction device, thus improving the effective resolution.



Cooling and Temperature Control

Many WDXRF Instruments use:

- X-Ray Tube Coolers, and

- Thermostatically controlled instrument coolers

The diffraction technique is relatively inefficient and WDX detectors can operate at much higher count rates, so WDX Instruments are typically operated at much higher power than direct excitation EDXRF systems. Diffraction devices are also temperature sensitive.

Chamber Atmosphere

Sample and hardware chambers of any XRF instrument may be filled with air, but because air absorbs low energy x-rays from elements particularly below Ca, Z=20, and Argon sometimes interferes with measurements purges are often used. The two most common purge methods are:

Vacuum - For use with solids or pressed pellets

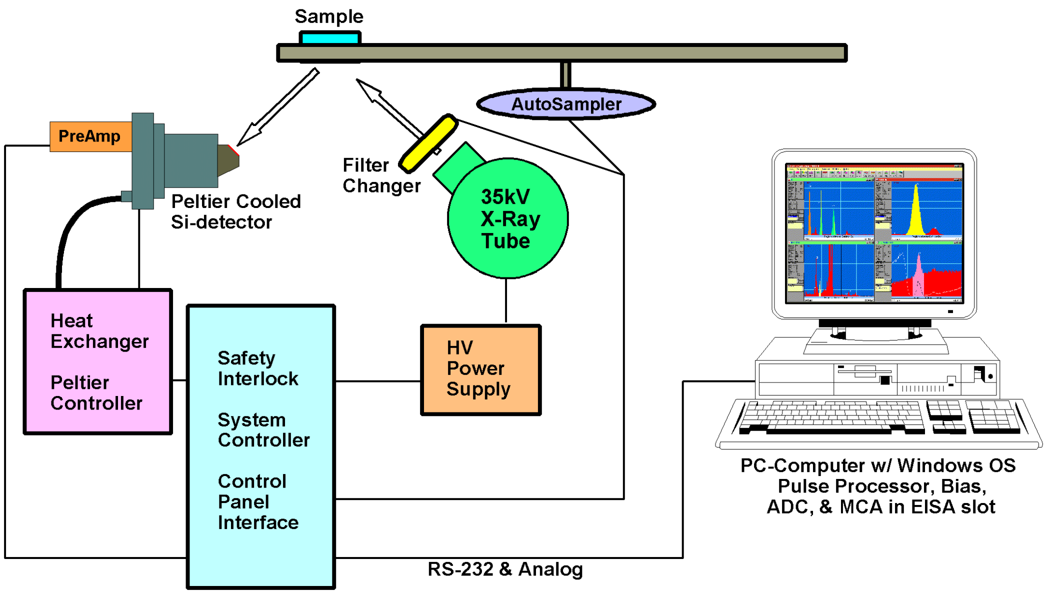
Helium - For use with liquids or powdered materials

Changers and Spinners

Other commonly available sample handling features are sample changers or spinners.

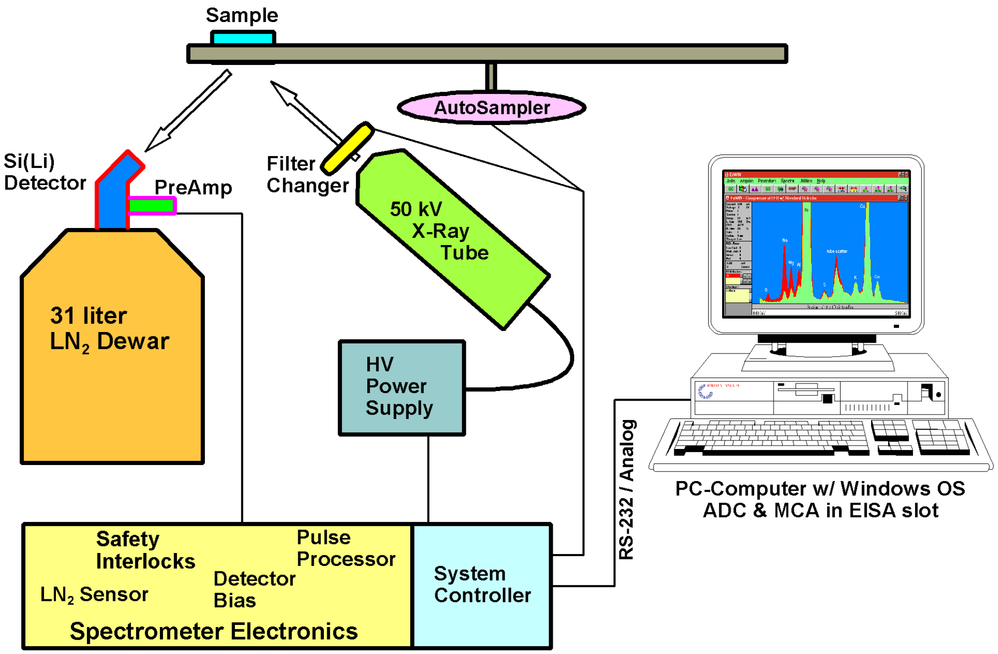
- **Automatic sample changers are usually of the circular or XYZ stage variety and may have hold 6 to 100+ samples**
- **Sample Spinners are used to average out surface features and particle size affects possibly over a larger total surface area.**

Typical PIN Detector Instrument



This configuration is most commonly used in higher end benchtop EDXRF Instruments.

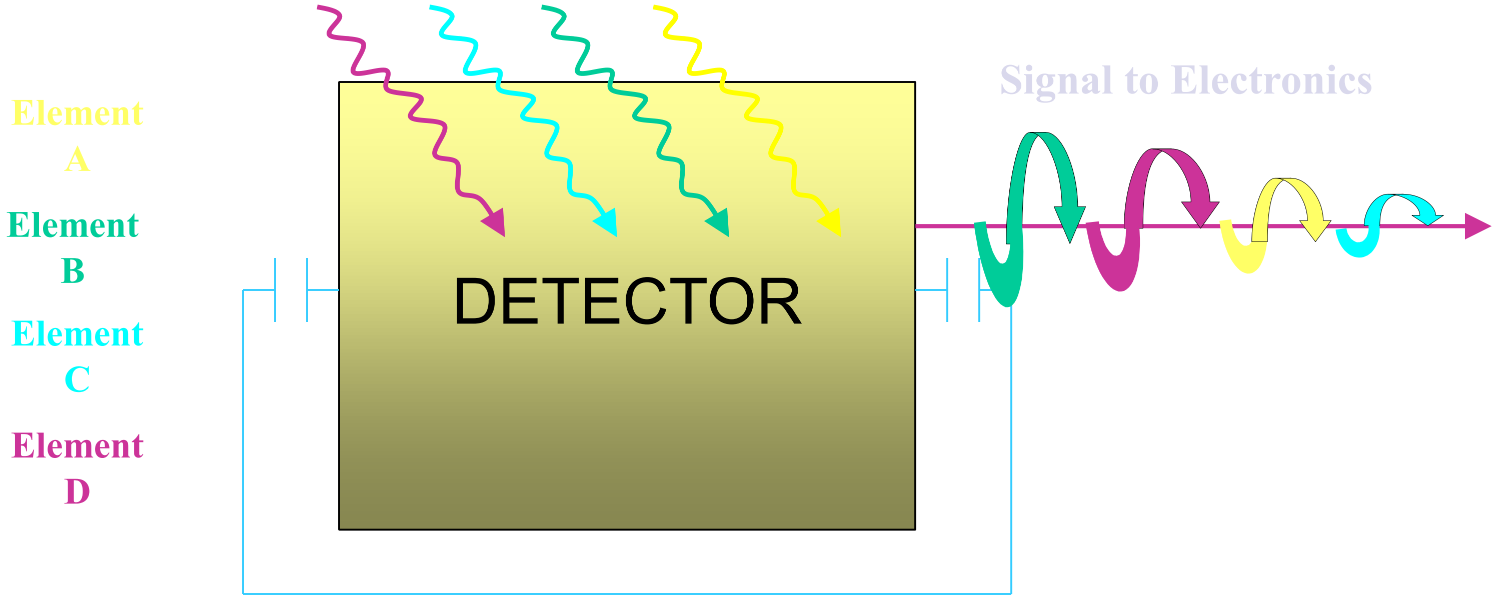
Typical Si(Li) Detector Instrument



This has been historically the most common laboratory grade EDXRF configuration.

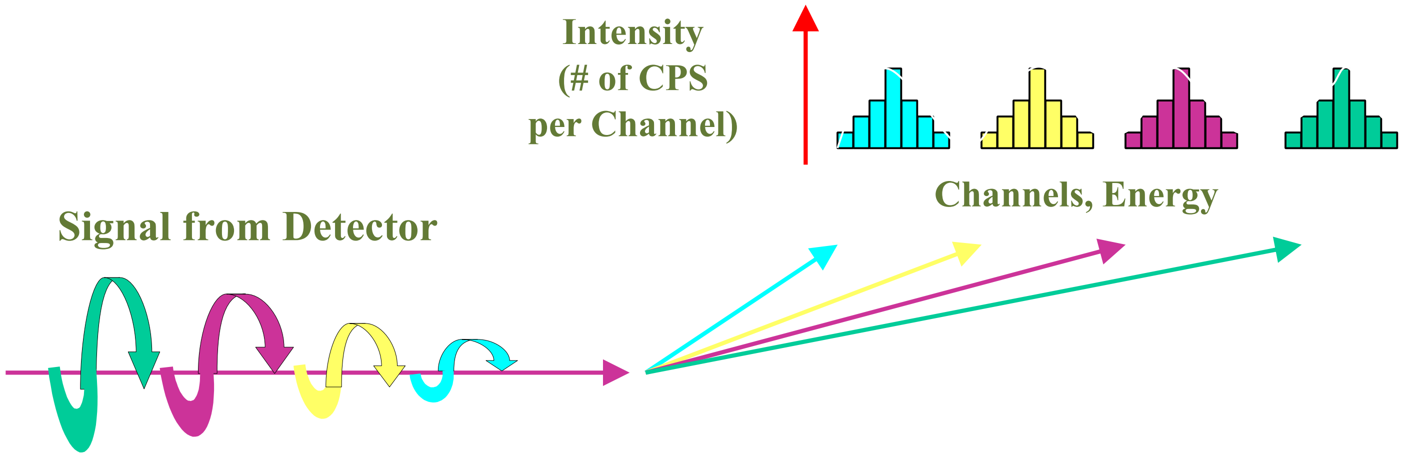
Energy Dispersive Electronics

Fluorescence generates a current in the detector. In a detector intended for energy dispersive XRF, the height of the pulse produced is proportional to the energy of the respective incoming X-ray.



Multi-Channel Analyser

- **Detector current pulses are translated into counts (counts per second, "CPS").**
- **Pulses are segregated into channels according to energy via the MCA (Multi-Channel Analyser).**



WDXRF Pulse Processing

- The WDX method uses the diffraction device and collimators to obtain good resolution, so The detector does not need to be capable of energy discrimination. This simplifies the pulse processing.

- It also means that spectral processing is simplified since intensity subtraction is fundamentally an exercise in background subtraction.

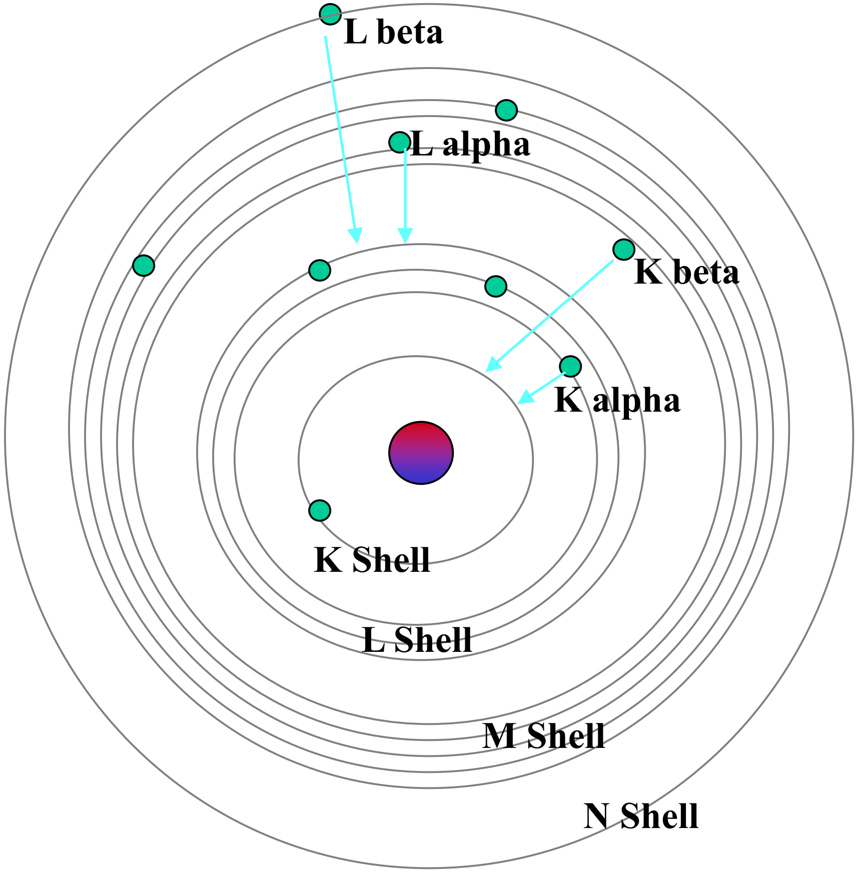
Note: **Some energy discrimination is useful since it allows for rejection of low energy noise and pulses from unwanted higher energy x-rays.**

Evaluating Spectra

In addition to elemental peaks, other peaks appear in the spectra:

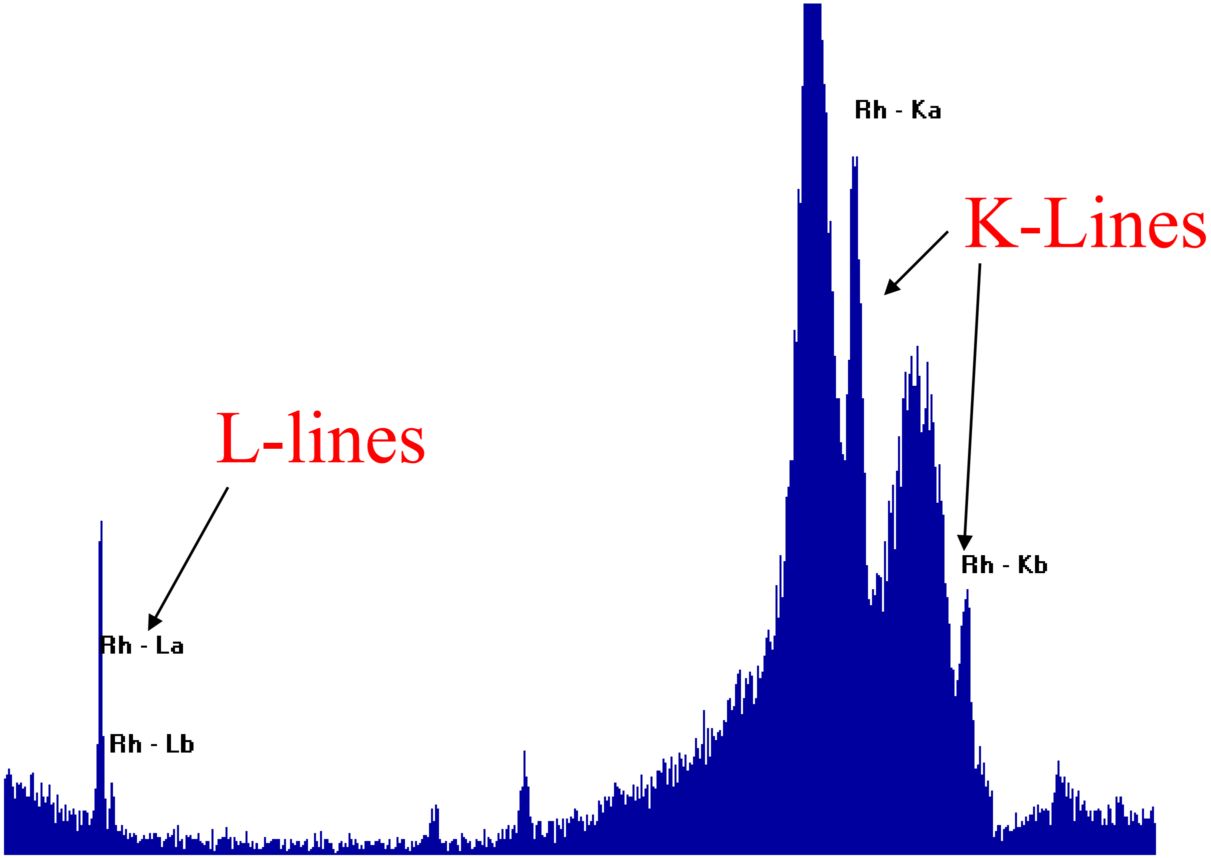
- K & L Spectral Peaks
- Rayleigh Scatter Peaks
- Compton Scatter Peaks
- Escape Peaks
- Sum Peaks
- Bremstrahlung

K & L Spectral Lines



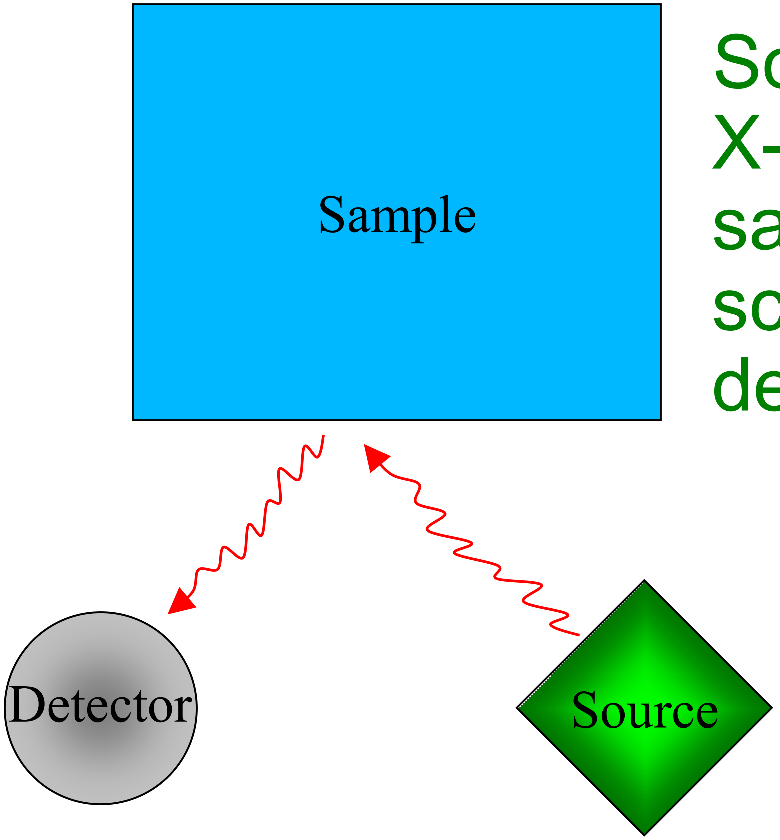
- **K - alpha lines:** L shell e- transition to fill vacancy in K shell. Most frequent transition, hence most intense peak.
- **K - beta lines:** M shell e- transitions to fill vacancy in K shell.
- **L - alpha lines:** M shell e- transition to fill vacancy in L shell.
- **L - beta lines:** N shell e- transition to fill vacancy in L shell.

K & L Spectral Peaks



Rh X-ray Tube

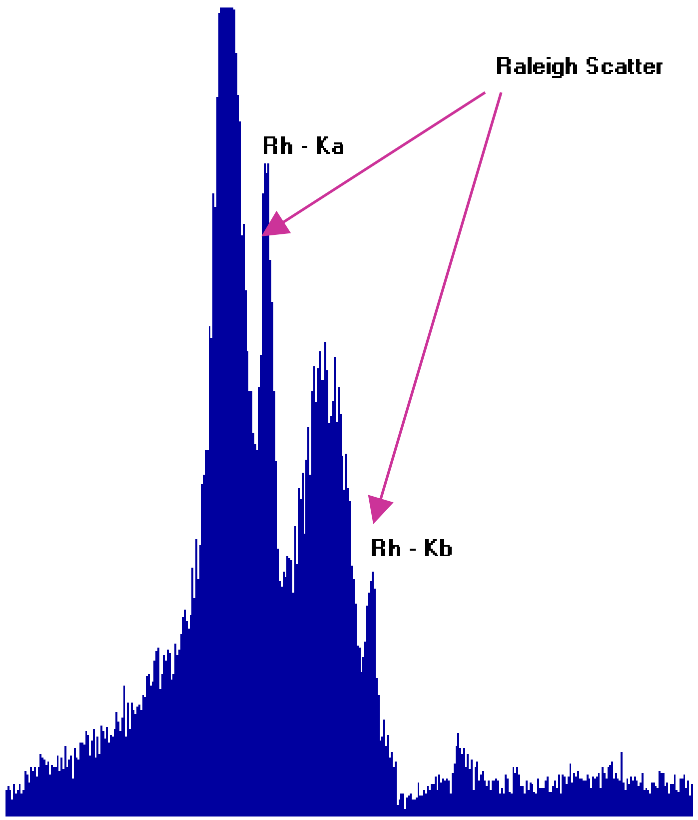
Scatter



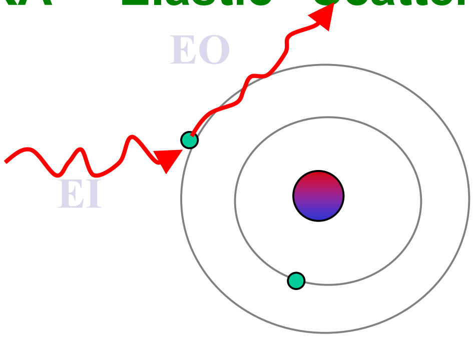
Some of the source X-rays strike the sample and are scattered back at the detector.

Sometimes called "backscatter"

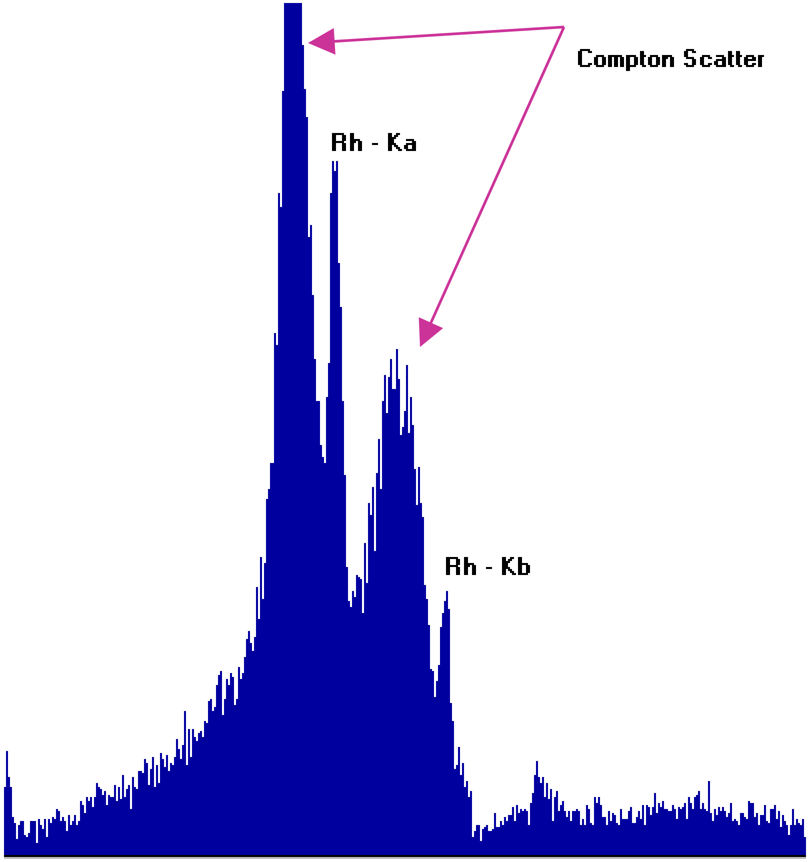
Rayleigh Scatter



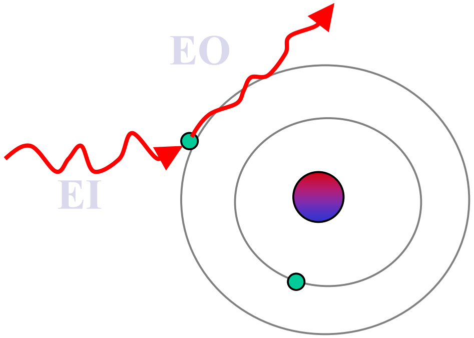
- X-rays from the X-ray tube or target strike atom without promoting fluorescence.
- Energy is not lost in collision. (EI = EO)
- They appear as a source peak in spectra.
- AKA - “Elastic” Scatter



Compton Scatter



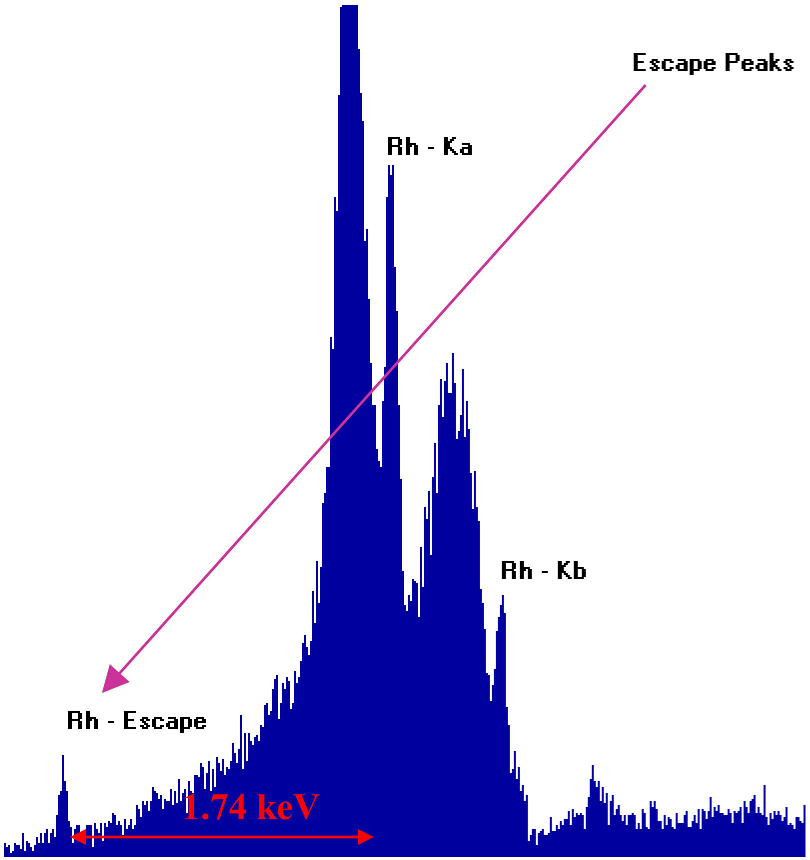
- X-rays from the X-ray tube or target strike atom without promoting fluorescence.
- Energy is lost in collision. (EI > EO)
- Compton scatter appears as a source peak in spectra, slightly less in energy than Rayleigh Scatter.
- AKA - “Inelastic” Scatter



Sum Peaks

- 2 photons strike the detector at the same time.
- The fluorescence is captured by the detector, recognized as 1 photon twice its normal energy.
- A peak appears in spectra, at: 2 X (Element keV).

Escape Peaks

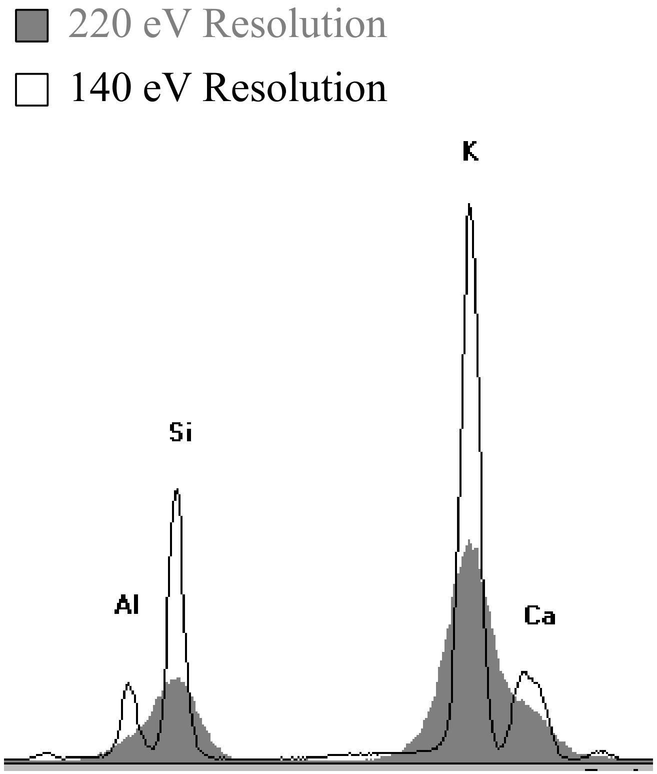


- X-rays strike the sample and promote elemental fluorescence.
- Some Si fluorescence at the surface of the detector escapes, and is not collected by the detector.
- The result is a peak that appears in spectrum, at: Element keV - Si keV (1.74 keV).

Interferences

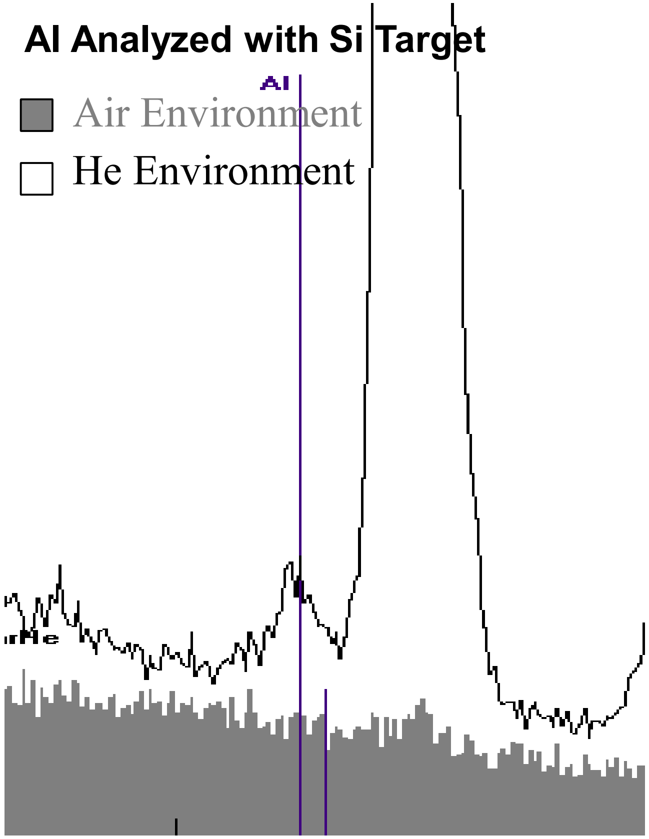
- ❖ **Spectral Interferences**
- ❖ **Environmental Interferences**
- ❖ **Matrix Interferences**

Spectral Interferences



- Spectral interferences are peaks in the spectrum that overlap the spectral peak (region of interest) of the element to be analyzed.
- Examples:
  - K & L line Overlap - S & Mo, Cl & Rh, As & Pb
  - Adjacent Element Overlap - Al & Si, S & Cl, K & Ca...
- Resolution of detector determines extent of overlap.

Environmental Interferences



- Light elements (Na - Cl) emit weak X-rays, easily attenuated by air.
- Solution:
  - Purge instrument with He (less dense than air = less attenuation).
  - Evacuate air from analysis chamber via a vacuum pump.
- Either of these solutions also eliminate interference from Ar (spectral overlap to Cl). Argon (Ar) is a component of air.

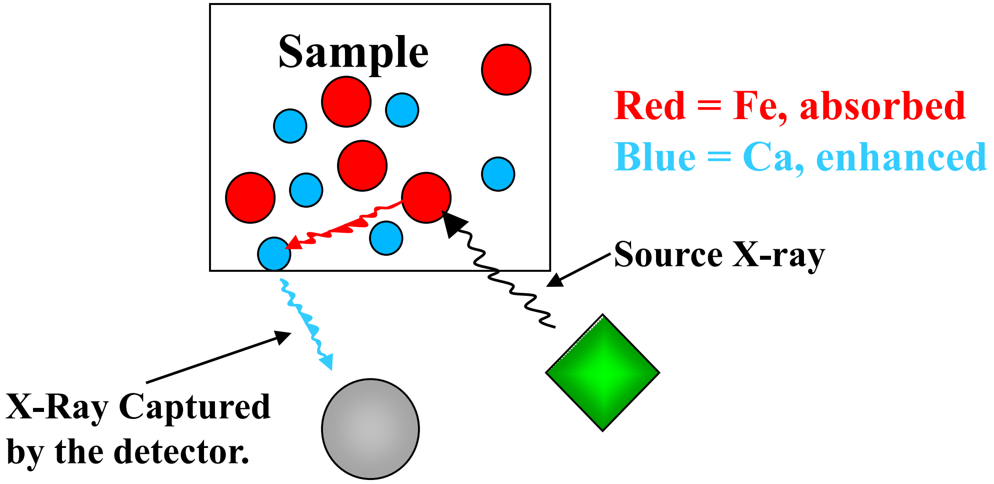
Matrix Interferences

Absorption/Enhancement Effects

- Absorption: Any element can absorb or scatter the fluorescence of the element of interest.
- Enhancement: Characteristic x-rays of one element excite another element in the sample, enhancing its signal.

Influence Coefficients, sometimes called alpha corrections are used to mathematically correct for Matrix Interferences

Absorption-Enhancement Affects



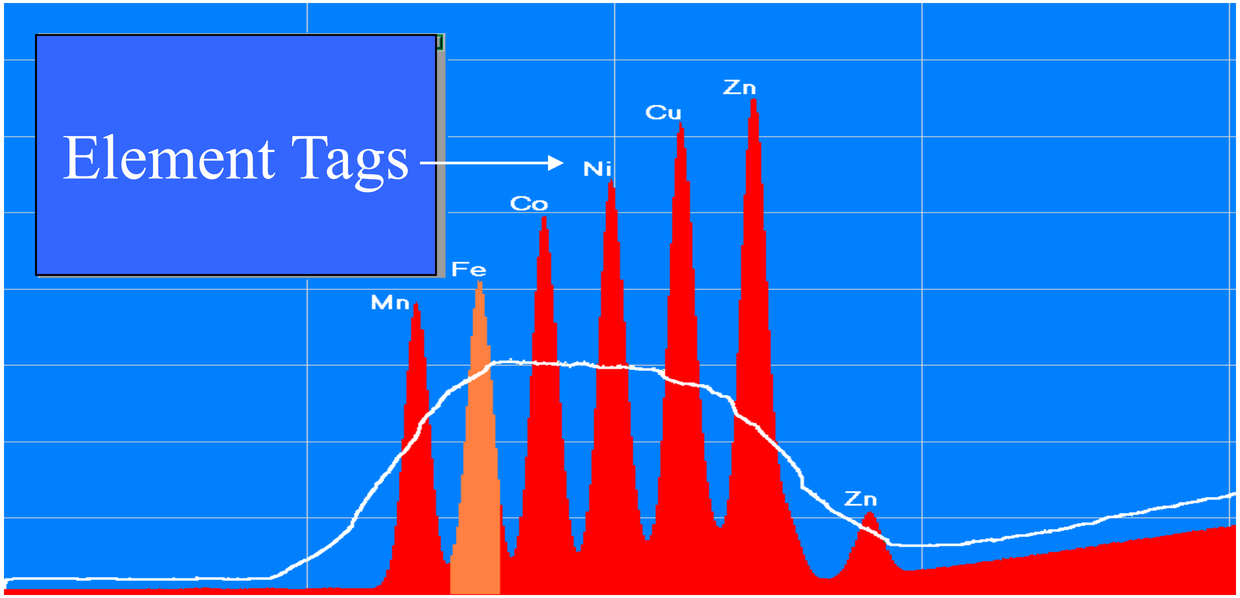
- Incoming source X-ray fluoresces Fe.
- Fe fluorescence is sufficient in energy to fluoresce Ca.
- Ca is detected, Fe is not. Response is proportional to concentrations of each element.

Software

- Qualitative Analysis
- Semi-Quantitative Analysis (SLFP, NBS-GSC.)
- Quantitative Analysis (Multiple intensity Extraction and Regression methods)

Qualitative Scan Peak ID

Automated Peak identification programs are a useful qualitative examination tool



- This spectrum also contrasts the resolution of a PIN diode detector with a proportional counter to illustrate the importance of detector resolution with regard to qualitative analysis.

Semi-Quantitative Analysis

SLFP

Standardless Fundamental Parameters

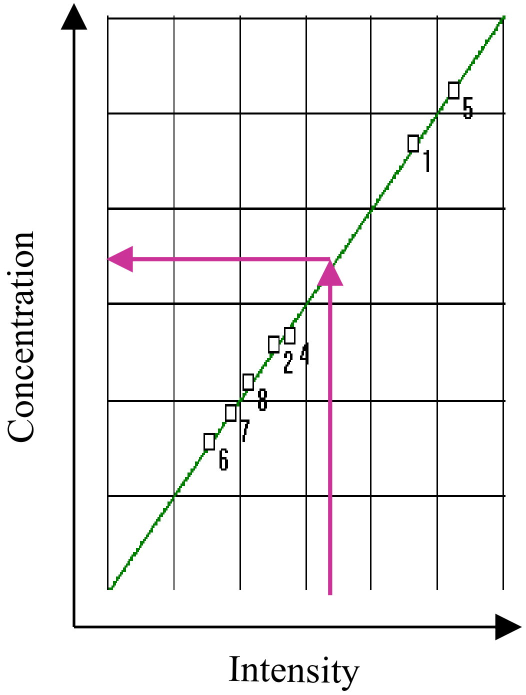
- The algorithm computes both the intensity to concentration relationship and the absorption affects
- Results are typically within 10 - 20 % of actual values.

FP (with Standards)

NBS-GSC, NRLXRF, Uni-Quant, TurboQuant, etc…

- The concentration to intensity relationship is determined with standards, while the FP handles the absorption affects.
- Results are usually within 5 - 10 % of actual values

Quantitative Analysis



XRF is a reference method, standards are required for quantitative results.

Standards are analysed, intensities obtained, and a calibration plot is generated (intensities vs. concentration).

XRF instruments compare the spectral intensities of unknown samples to those of known standards.

Standards

- Standards (such as certified reference materials) are required for Quantitative Analysis.
- Standard concentrations should be known to a better degree of precision and accuracy than is required for the analysis.
- Standards should be of the same matrix as samples to be analyzed.
- Number of standards required for a purely empirical method, $N=(E+1)^2$, N=# of standards, E=# of Elements.
- Standards should vary independently in concentration when empirical absorption corrections are used.

Sample Preparation

Powders:

Grinding (<400 mesh if possible) can minimise scatter affects due to particle size. Additionally, grinding insures that the measurement is more representative of the entire sample, vs. the surface of the sample.

Pressing (hydraulically or manually) compacts more of the sample into the analysis area, and ensures uniform density and better reproducibility..

Solids:

Orient surface patterns in same manner so as minimise scatter affects.

Polishing surfaces will also minimise scatter affects.

Flat samples are optimal for quantitative results.

Liquids:

Samples should be fresh when analysed and analysed with short analysis time - if sample is evaporative.

Sample should not stratify during analysis.

Sample should not contain precipitants/solids, analysis could show settling trends with time.