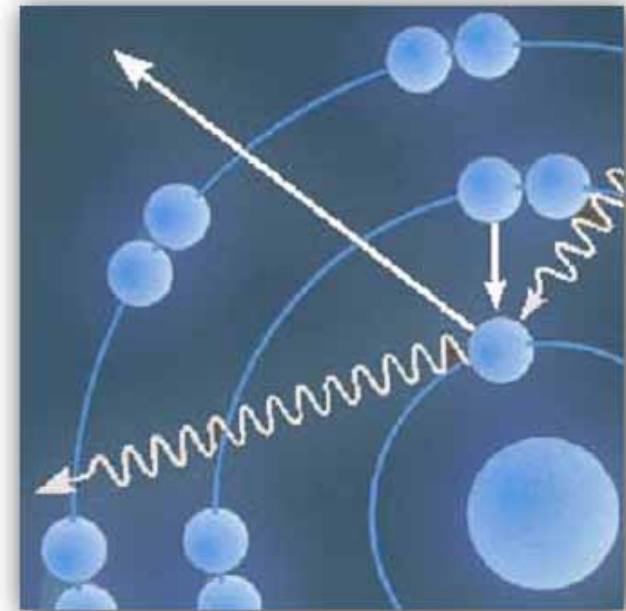


Introduction to the QuanX

Energy-Dispersive X-ray Fluorescence Spectrometry

Theory
Introduction



Overview: Theory Presentation



- Basic overview
- History of X-ray spectrometry
- Atomic Structure and XRF
- Properties of X-rays
- Source – sample interaction
- EDXRF instrumentation
- X-ray detection process
- Analysis considerations
- Review of statistics

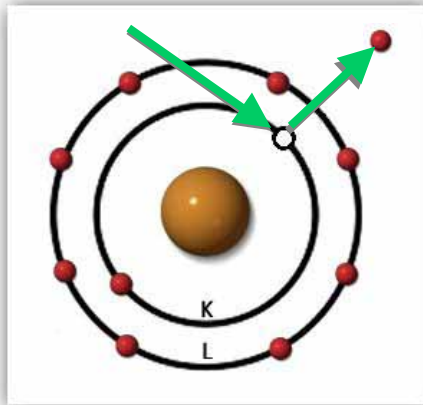
The slide features a dark blue header bar at the top. On the left side, there is a decorative graphic of white, curved lines that resemble a wireframe or a stylized wave pattern. The main content area is white and contains a central graphic of a blue-bordered rectangle with a yellowish-beige center, which has a 3D effect as if it's a sign on a stand. The text "EDXRF Basic Overview" is centered within this sign in a bold, black, sans-serif font. At the bottom of the slide, there is a black horizontal bar containing the "Thermo NORAN" logo in red and white text.

EDXRF Basic Overview

Thermo NORAN

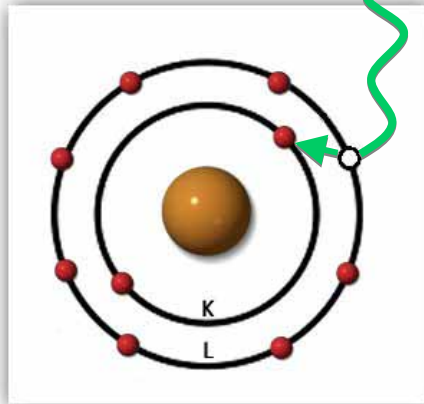
Source - Sample Interaction

X-Ray Fluorescence

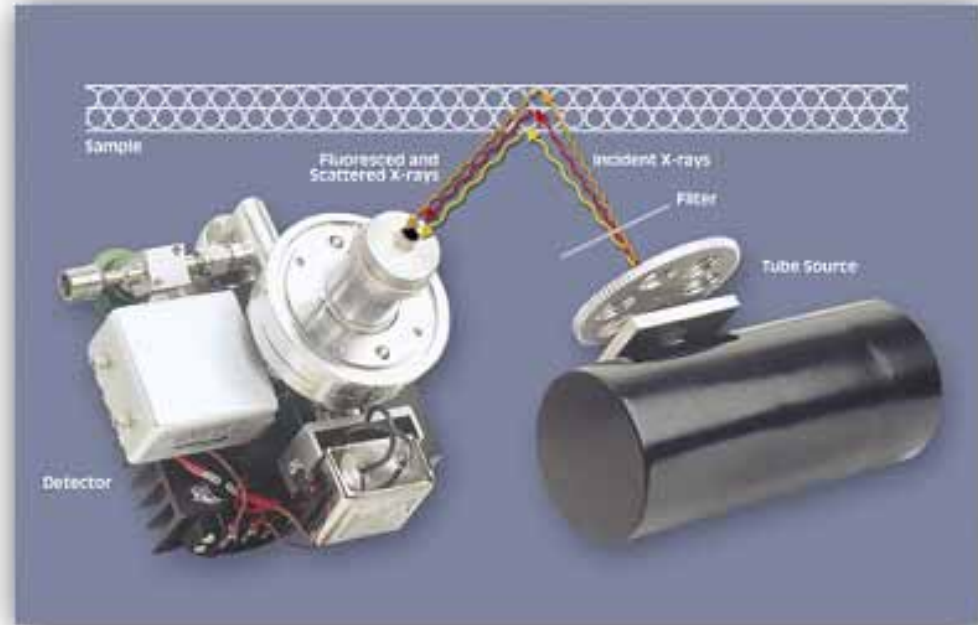


An Incoming x-ray photon strikes an electron, the electron breaks free and leaves the atom.

x-ray photon



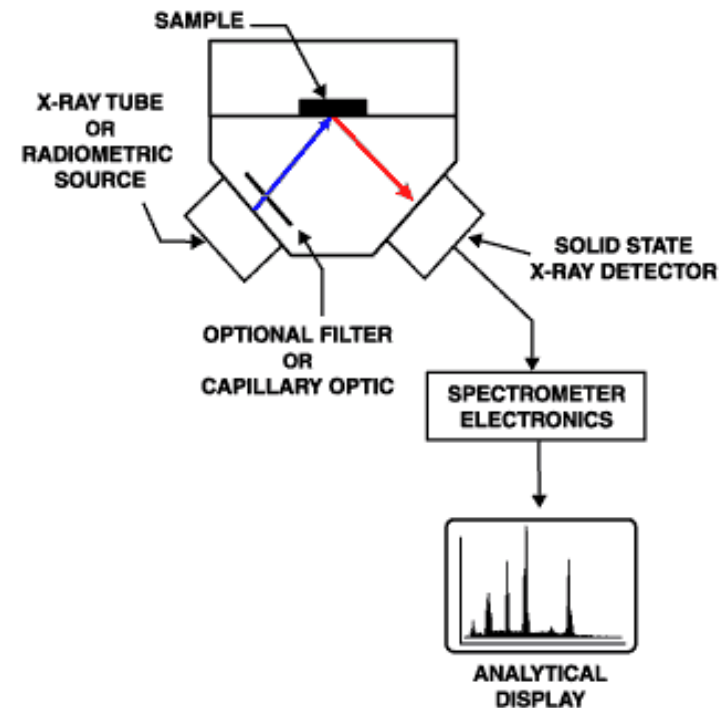
An electron from a higher energy replaces the electron, the electron releases energy (fluoresces) as it drops in the form of an x-ray photon.



EDXRF Basic Overview

What happens in XRF analysis?

- **Atoms within the sample are excited by a stream of x-rays.**
- **Excited atoms return to ground state by emitting x-rays.**
- **The detector and multi-channel analyzer collect x-ray energy pulses as counts in a spectrum.**
- **Elements from Na to U on the Periodic Table can be detected.**
- **Peak intensities are related to element concentration.**



Properties of X-Rays

The relationship between Energy, Frequency, and Wavelength may be expressed by one formula:

$$E = hF = \frac{hc}{\lambda}$$

E is the **Energy** of the radiation

λ is the **Wavelength** of the radiation

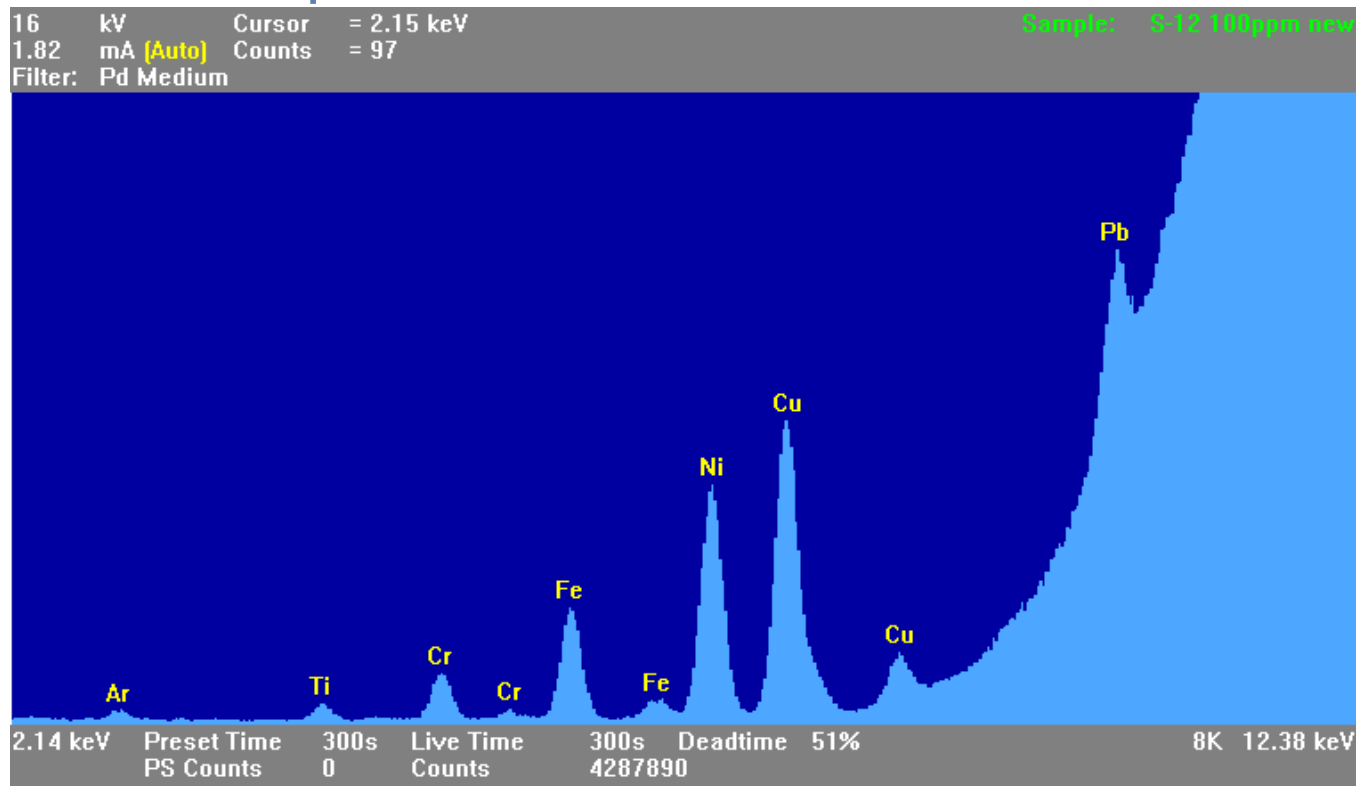
F is the **Frequency** of the radiation

c is the speed of light 3×10^{10} cm/second

h is Planck's constant 4.135×10^{-15} eV-sec = 6.625×10^{-27} erg-sec

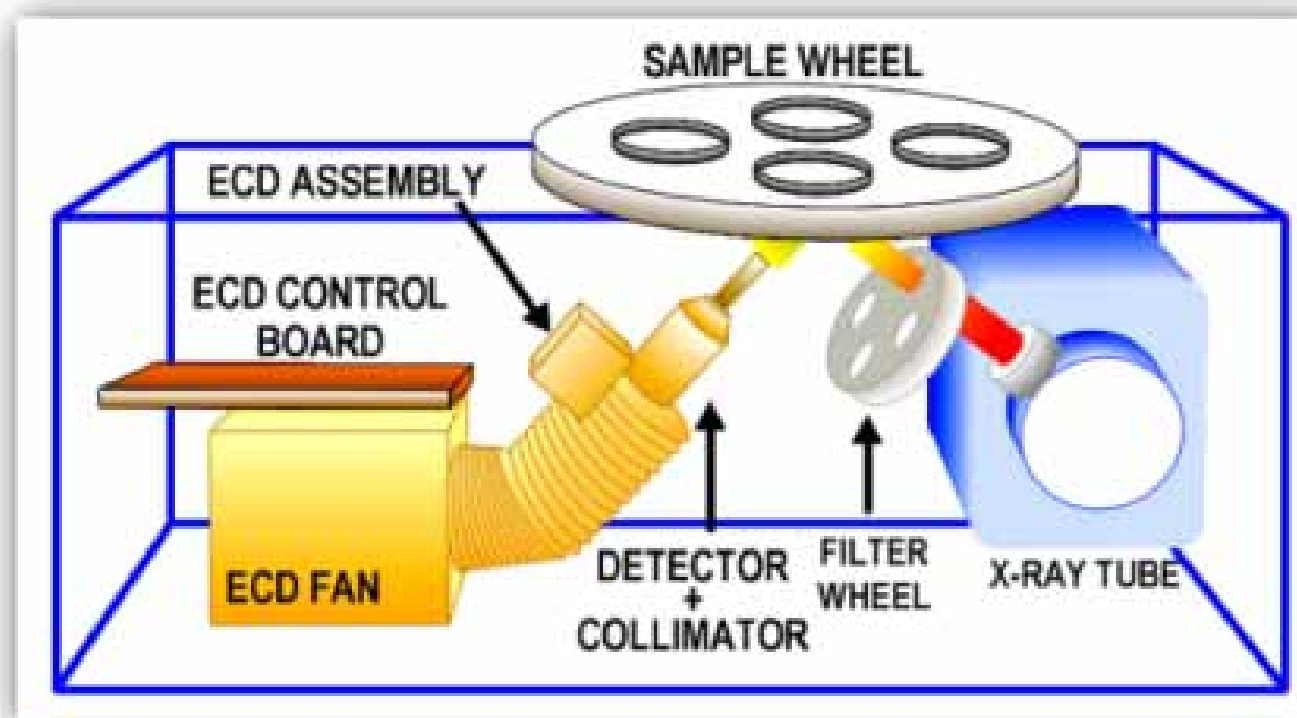
EDXRF Spectrum

Note that the EDXRF spectrum is plotted on an energy scale that is reversed compared to a WDXRF spectrum



EDXRF Instrumentation

Schematic overview



EDXRF Instrumentation

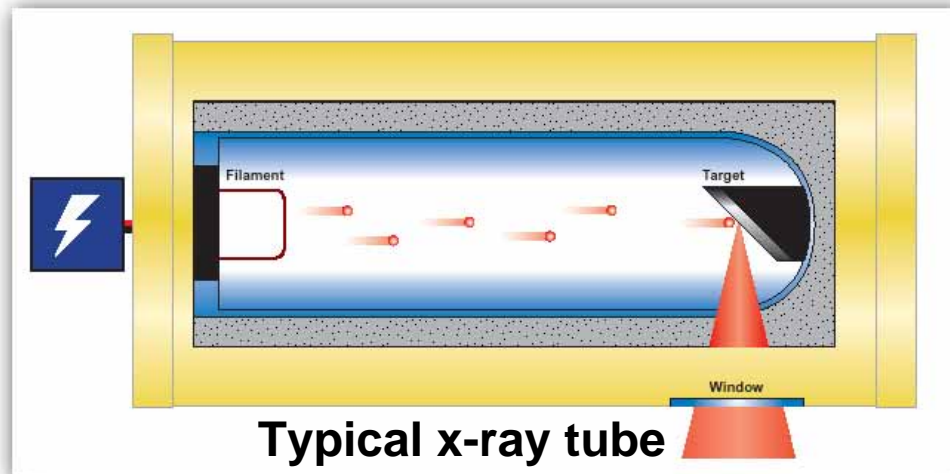
X-Ray excitation sources

➤ Isotopes

- Clean radiation source.
- Monochromatic, low background, easier quantitation.

➤ X-Ray tubes

- More versatile than isotopes.
- Higher flux.
- No decay.
- Produce less background than direct electron sources.
- Better signal to noise ratio.
- 1% of energy is converted into x-rays; the remaining 99% is converted to heat.



EDXRF Instrumentation

Tube Voltage Parameters

Tube Voltage:

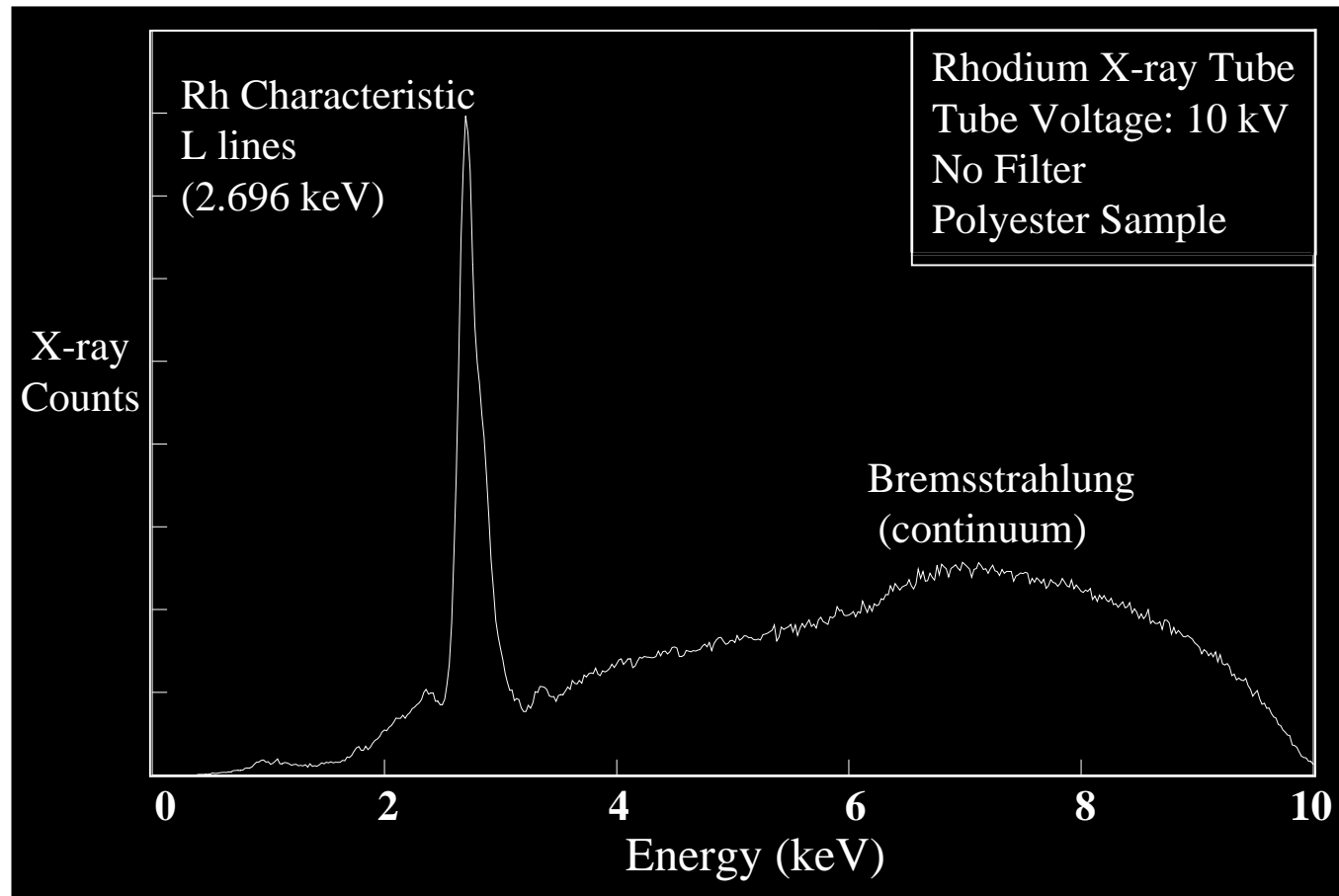
- ✦ **Tube Voltage (kV) = Energy Max (keV)**
- ✦ **Intensity proportional to KV^2**
- ✦ **Set higher than highest absorption edge energy**

Tube Current:

- ✦ **Intensity proportional to mA**
- ✦ **Adjust to 50% Deadtime**

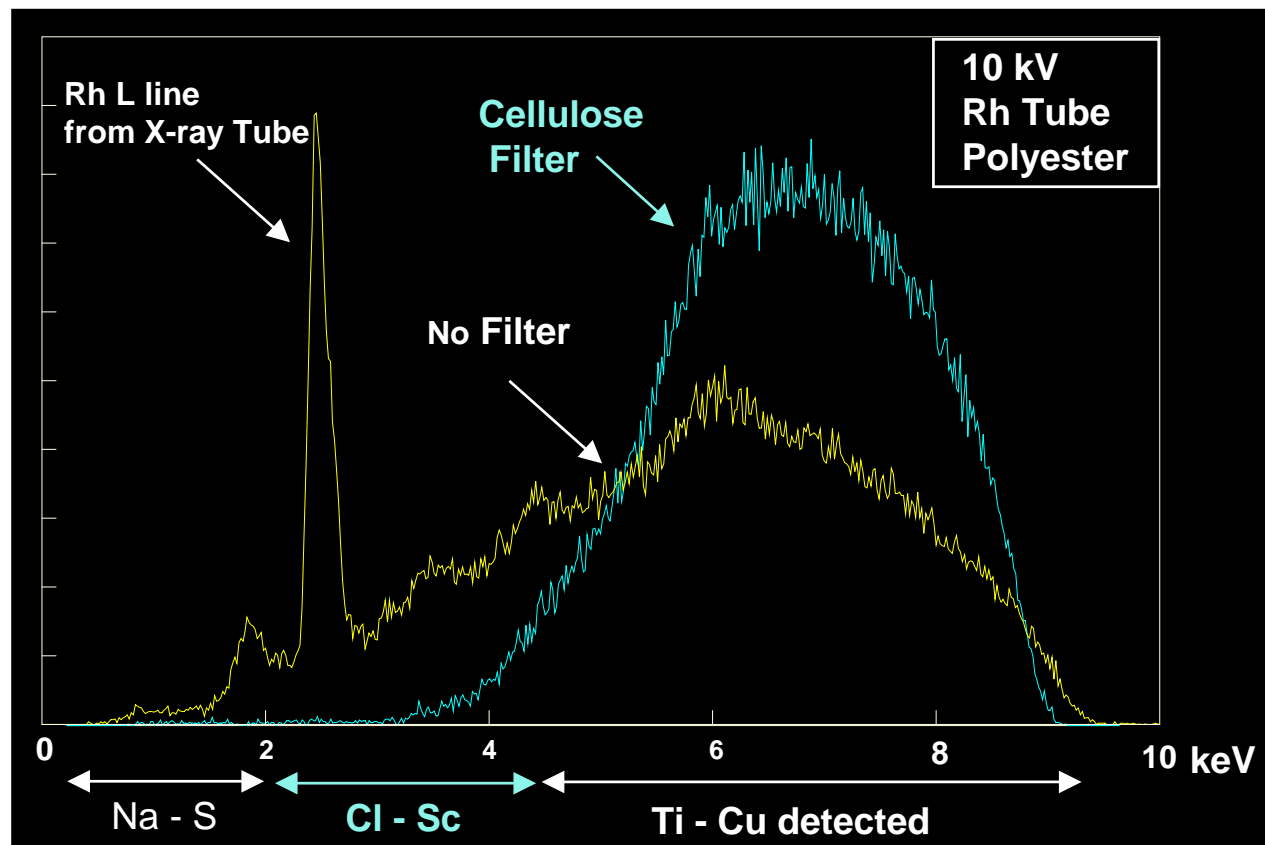
EDXRF Instrumentation

X-ray Tube Output Spectrum



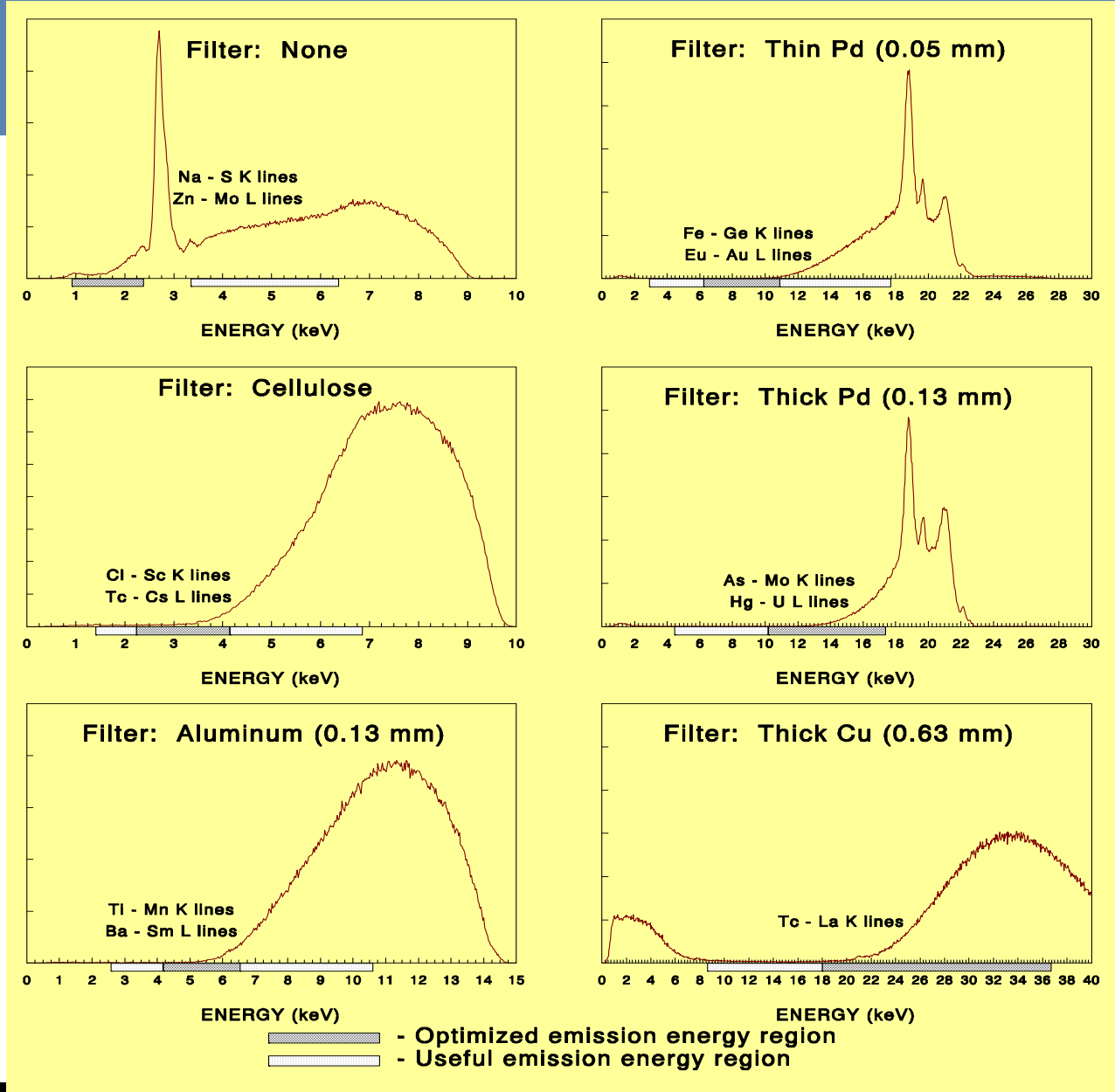
EDXRF Instrumentation

No Filter vs. Cellulose Filter



EDXRF Instrumentation

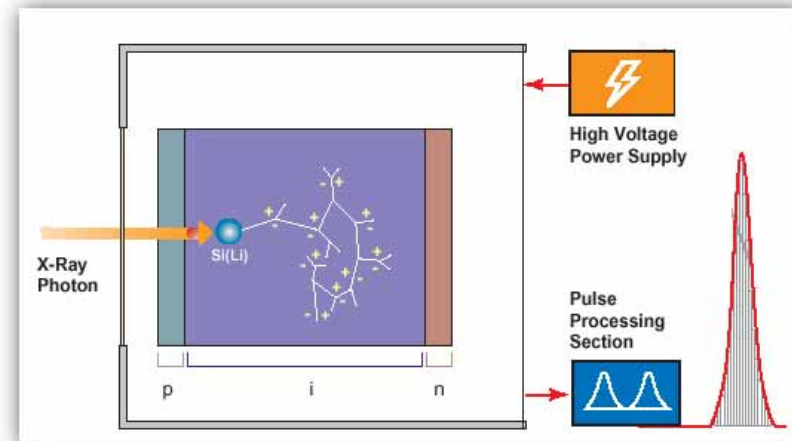
Use of primary beam filter to reduce scatter tube continuum



EDXRF Instrumentation

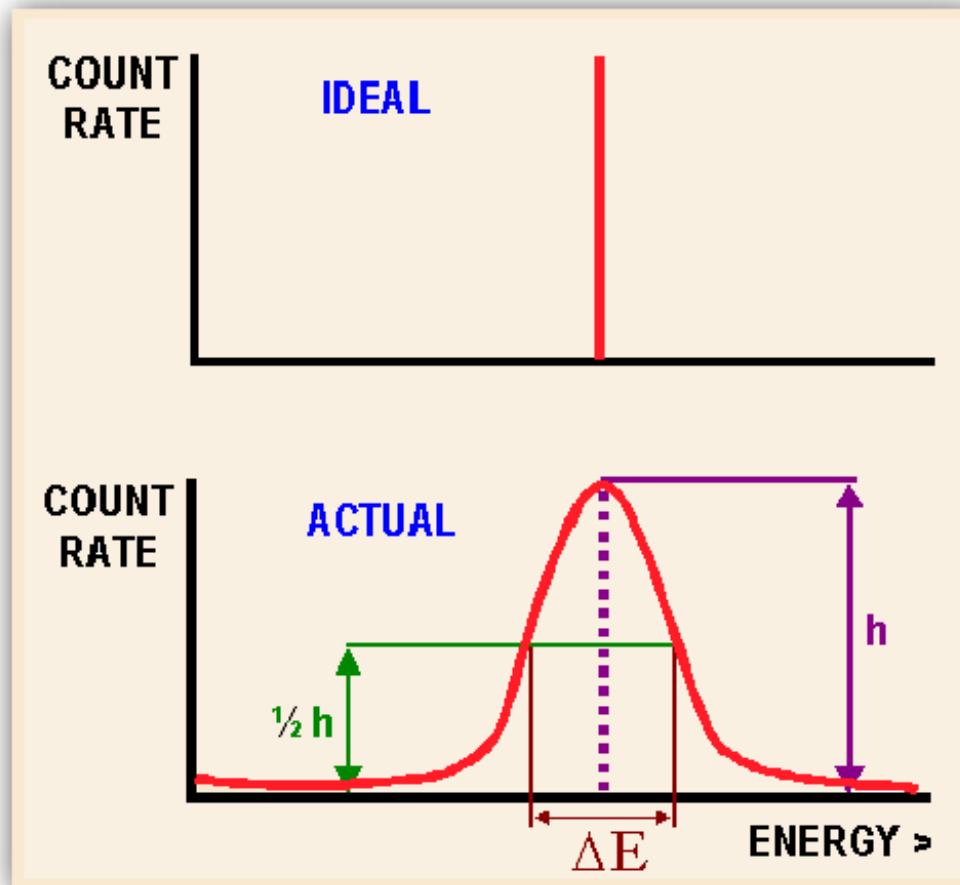
EDS detector characteristics

- Semiconductor
- Electric potential
- Absorbed x-rays result in charge which results in pulse
- FET (field effect transistor) collects charge, integrates to derive voltage pulse
- Liquid Nitrogen or Peltier cooling is used to reduce thermal noise
- Peaks are approximately Gaussian
- Resolution increases with energy



EDXRF Instrumentation

Detector specifications: resolution

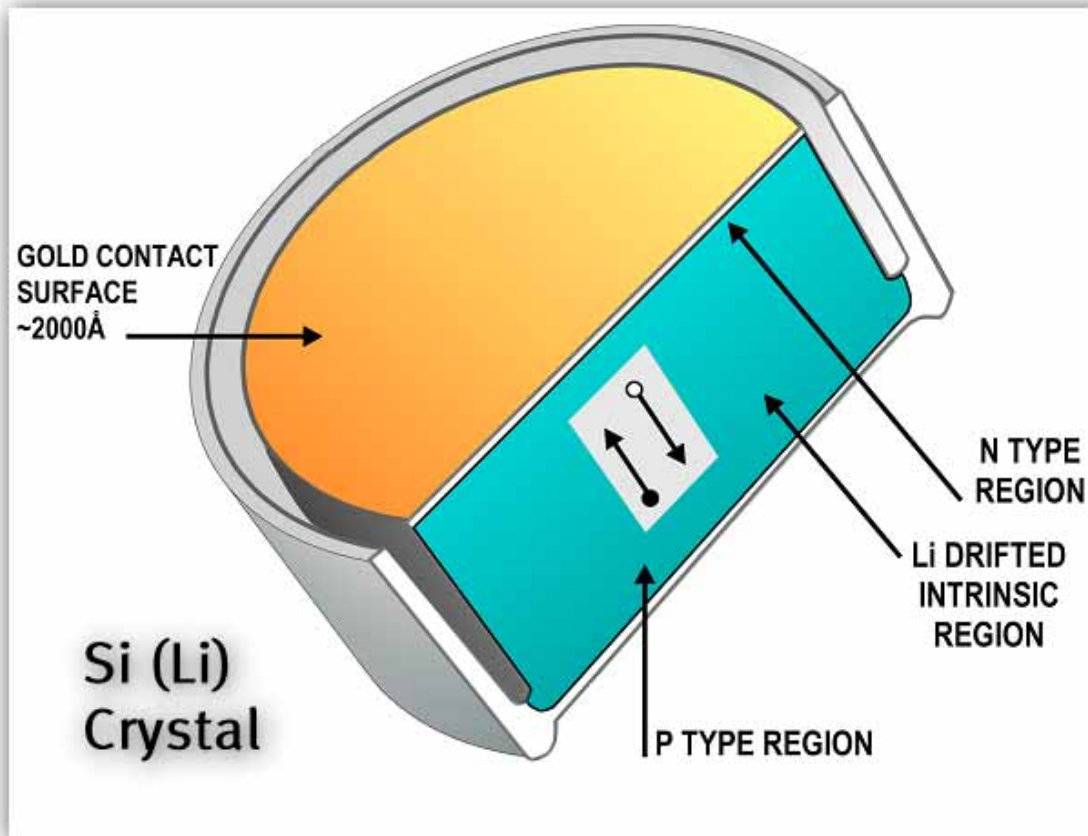


➤ Detectors are evaluated on spectral resolution.

➤ Full width half maximum (FWHM) at Mn is the industry standard.

EDXRF Instrumentation

Lithium drifted Silicon detector



Pell (1960) added Li at elevated temperatures at reverse bias and created the Si(Li) crystal

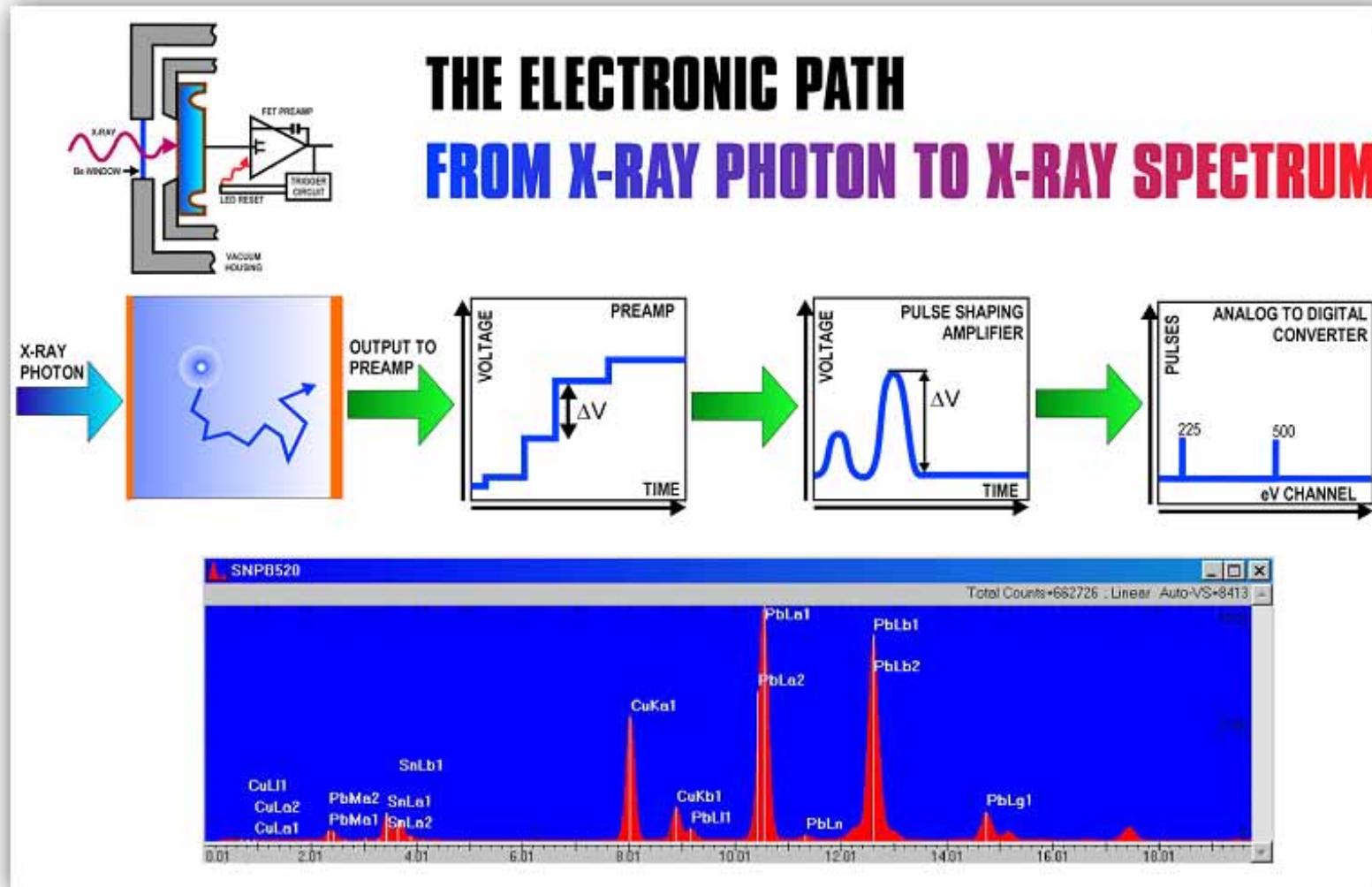
- Intrinsic semiconductors will not conduct current in an applied electric field unless it absorbs energy causing electrons to be promoted to the conduction band.



X-ray Detection Process

Thermo NORAN

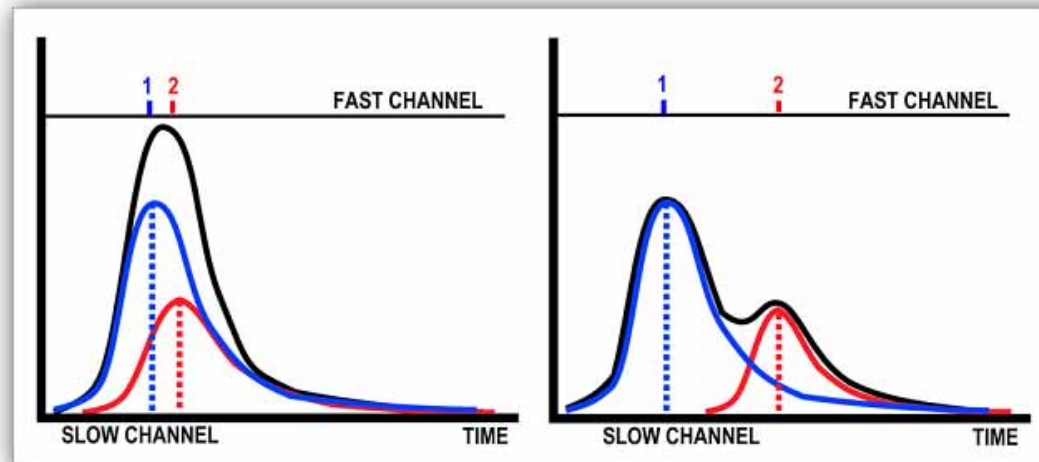
X-Ray Detection Process



X-Ray Detection Process

Pulse pile up rejection

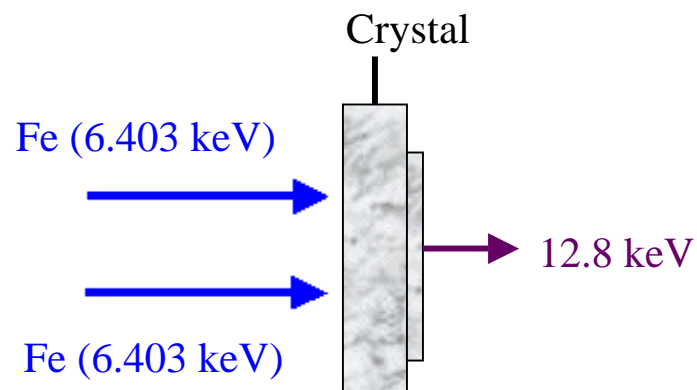
- **Leading edge pile up** occurs when two pulses arrive in the processor at the same time and the event peaks are too close to each other chronologically to be distinguished.
- **Trailing edge pile up** occurs when event peaks are separated sufficiently to allow the second event to be rejected.



X-Ray Detection Process

Spectral artifacts: sum peaks

Iron sum peak example:



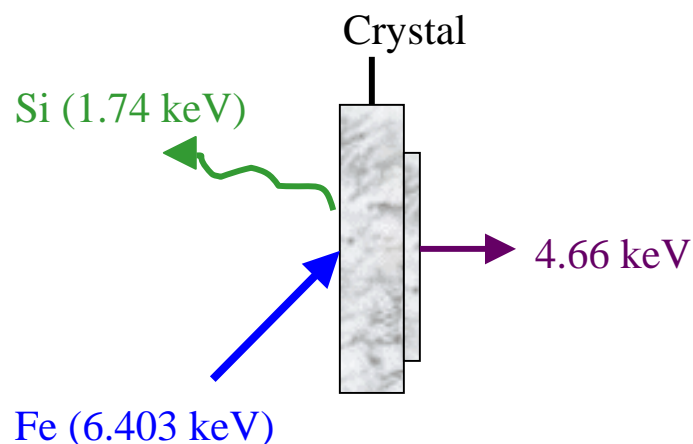
$$\text{Sum Peak} = \text{Fe} + \text{Fe}$$

- Arise when 2 or more x-rays enter the detector crystal at exactly the same time.
- Made up of integer multiples of the parent peak.
- Can be reduced by keeping count rates low, generally lower than 30% deadtime.

X-Ray Detection Process

Spectral artifacts: escape peaks

Iron escape peak example:



$$\text{Escape Peak} = \text{Fe} - \text{Si}$$

- Occurs when the detector crystal emits a Si x-ray that results in a loss of energy equal to the Si photon energy.
- This is a function of the incoming X-ray energy and detector to sample geometry.
- Can be modeled and accounted for in software.

X-Ray Detection Process

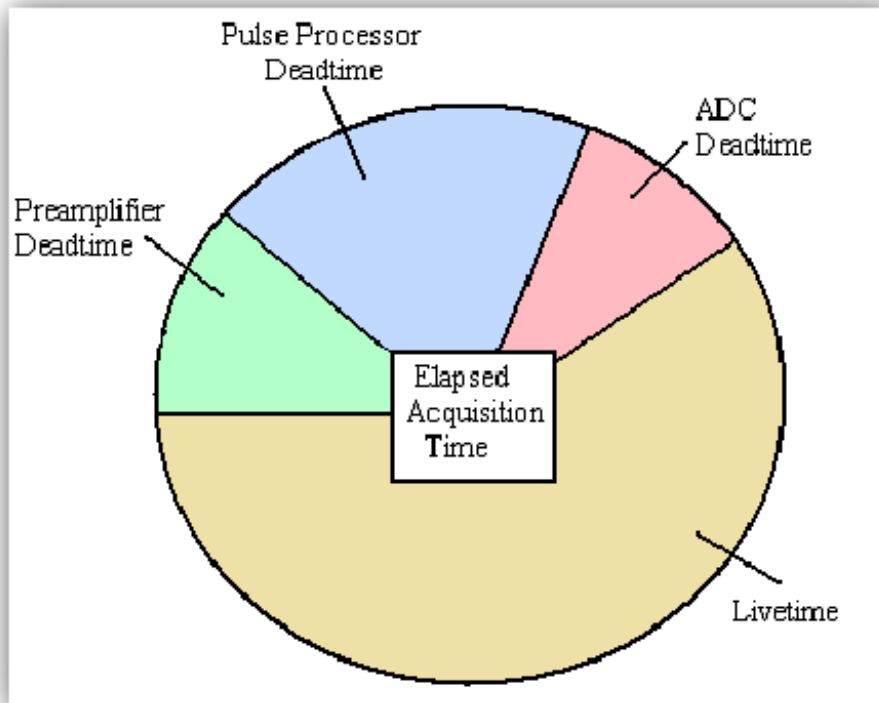
Spectrum artifacts

- **Escape peaks at 1.74 KeV below parent peak**
- **Sum peaks at double the value of major peak or at combined values of any large peaks**
- **Argon peaks (eliminated by vacuum)**
- **Compton and Rayleigh Scatter peaks from from tube characteristic lines**
- **Scatter from tube. e.a.: trace of Cu (eliminated by filters)**



X-Ray Detection Process

Deadtime



Livetime + Deadtime = Total Acquisition Time

➤ A measure of the period of time in which the system is unable to accept another signal for processing

Causes of Dead Time include:

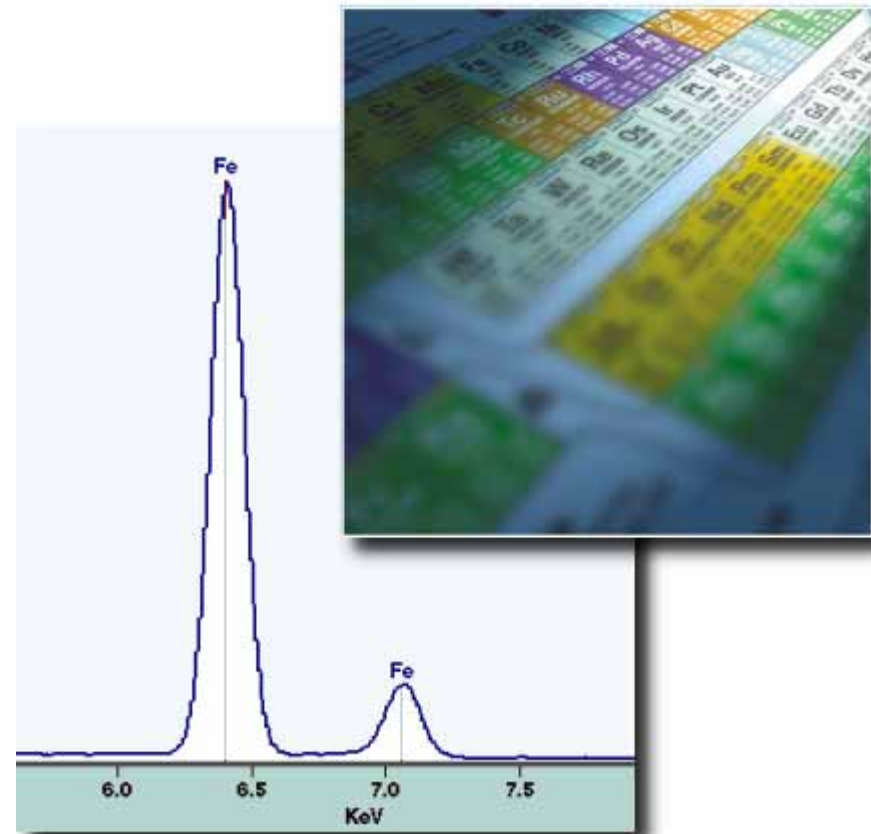
- Peak pile-up rejection circuitry.
- The FET reset process.
- The signal conversion process.
- The ADC / MCS analysis process time.

Influenced by incoming count rate and pulse processor rate (time constant).

X-Ray Detection Process

Deadtime adjustments: general rules

- **Target deadtime is 50%**
- **Best working range is between 40% to 60%**
Provides best accuracy.
- **Maximum dead time should be less than 65%**





Analysis Considerations

Analysis Considerations

Analysis complicating factors



- Multiple lines in spectrum and peak overlaps
- Resolution broadening by detector/amplifier
- X-Rays absorbed differently (enhancement, absorption, fluorescence); peak heights vary
- Sample matrix
- Background

Analysis Considerations

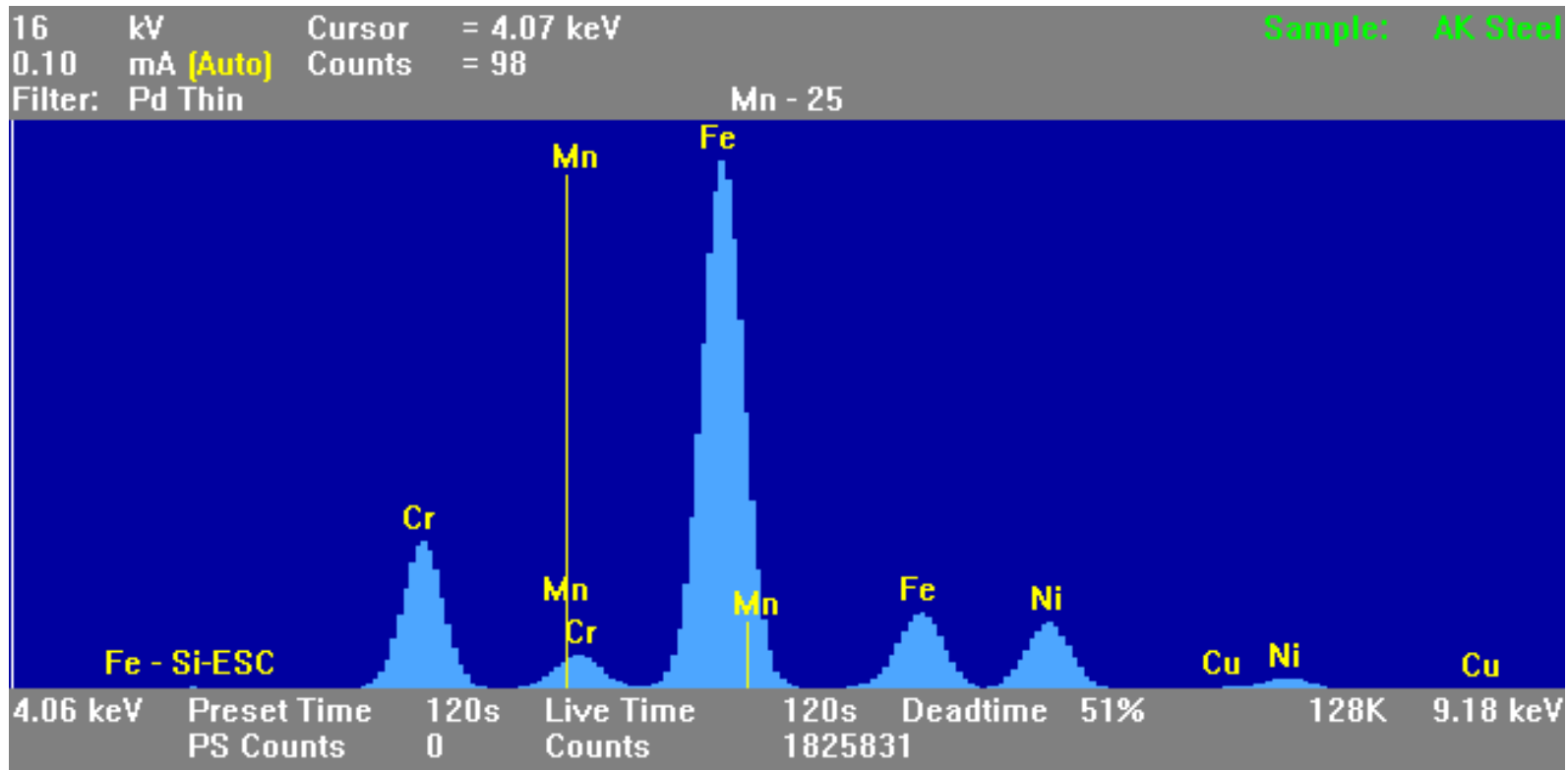
Common peak overlaps



<u>Element</u>	<u>Overlap</u>
Ti Kb	V Ka
V Kb	Cr Ka
Cr Kb	Mn Ka
Mn Kb	Fe Ka
Fe Kb	Co Ka
Pb Ma	S Ka, Mo La
Pb La	As Ka
Si Ka	W, Ta Ma
Ba La	Ti Ka
Br La	Al Ka

Analysis Considerations

Peak overlaps



Analysis Considerations

Vacuum, air, helium flush

- **Atomic number 20 and greater**
 - Analyze in air to reduce light element sensitivity
 - Argon peak may be present
- **Atomic number 20 and lower**
 - Analyze in vacuum; reduces air scattering and significantly improves light element sensitivity
 - Removes Argon peak
- **Liquid Samples Atomic number 20 and lower**
 - Never use vacuum
 - Use helium flush for elements below atomic number 22 and to remove argon peaks
 - Will cause scatter of light elements, especially Al
- **Powder samples**
 - May use vacuum if special sample cup or film is used

Review of Statistics

Evaluating intensity: counting error

- The confidence in the accuracy of our estimate can be no greater than the width of the Poisson distribution.

The **standard deviation** of a Poisson distribution is: $\sigma = \sqrt{\bar{n}}$

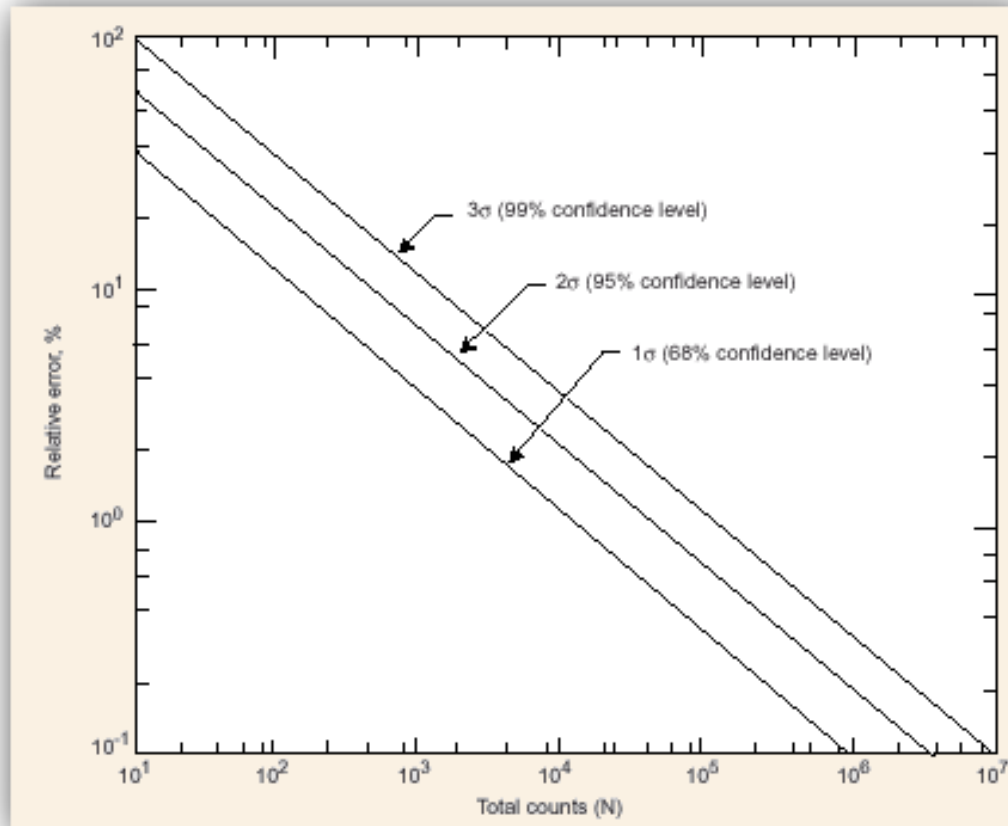
The **relative standard deviation** for a Poisson distributions is: $\varepsilon = \frac{1\sigma}{\sqrt{\bar{n}}}$

where \bar{n} = number of counts

Relative error can also be expressed at higher levels of confidence by substituting 2σ or 3σ for σ in the equation for relative standard deviation.

Review of Statistics

Evaluating Precision



If we have a peak comprising of 100 individual x-ray counts, the counting error is expected to be:

$$\varepsilon = \frac{1\sigma}{\sqrt{n}} = \frac{1}{10} \text{ or } 10\%$$

If we have a peak comprising of 10,000 individual x-ray counts, the counting error is expected to be:

$$\varepsilon = \frac{1}{100} \text{ or } 1\%$$

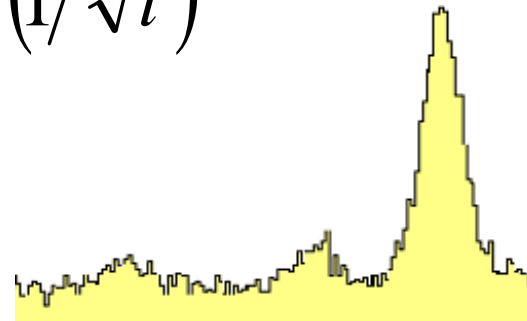
- For 99% (3 σ) confidence level, a peak count of 100 yields $\pm 30\%$ error.
- For 99% (3 σ) confidence level, a peak count of 10,000 yields $\pm 3\%$ error.

Review of Statistics

Minimum detection limits

➤ In EDXRF, we are often asked to determine the MDL (or LLD - Lower Limit of Detection). This parameter is concerned with the intensity of the X-ray signal above the background signal. This value is calculated using the formula:

$$MDL = C \cdot 3 \cdot \left(\sqrt{B} / P \right) \cdot \left(1 / \sqrt{t} \right)$$



Detection Limits

Detection Limits Example

The LLDs for EDXRF are sometimes limited high count rate of scatter or elements that are not of interest.

Use of the High count rate setting can sometimes improve LLDs

