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BRUKER NANO ANALYTICS' CULTURAL HERITAGE WEBINAR SERIES 2022

Handheld XRF in Cultural Heritage Studies

I. Back to basics – Taking control of Your Path to Meaningful Compositional Information

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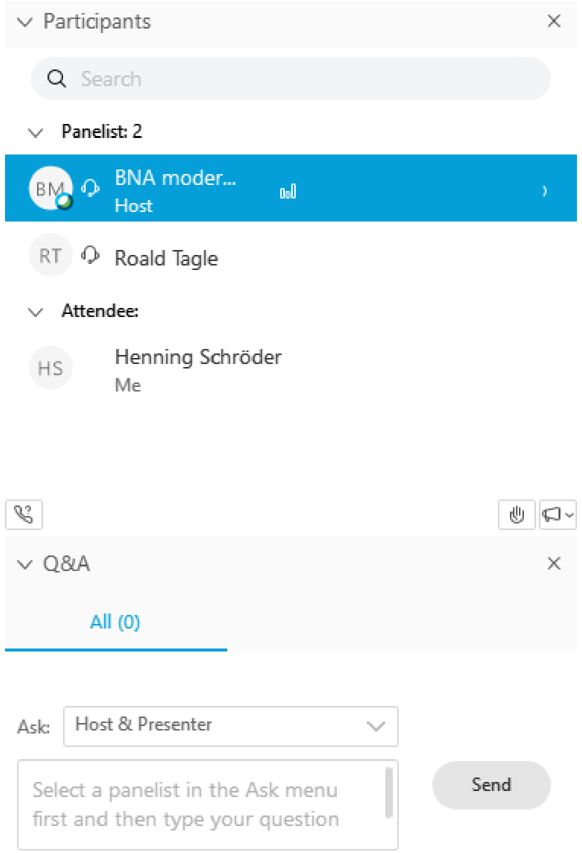
Art & Conservation Webinar Series
Handheld XRF in Cultural Heritage Studies

If you have questions during this webinar,
please **type your questions**, thoughts, or comments in the **Q&A box** and **press Send**.

We ask for your understanding if we do not have time to discuss all comments and questions within the session.

Any unanswered questions or comments will be answered and discussed by e-mail or in another WebEx session.



Handheld XRF in Cultural Heritage Studies
Webinar Series

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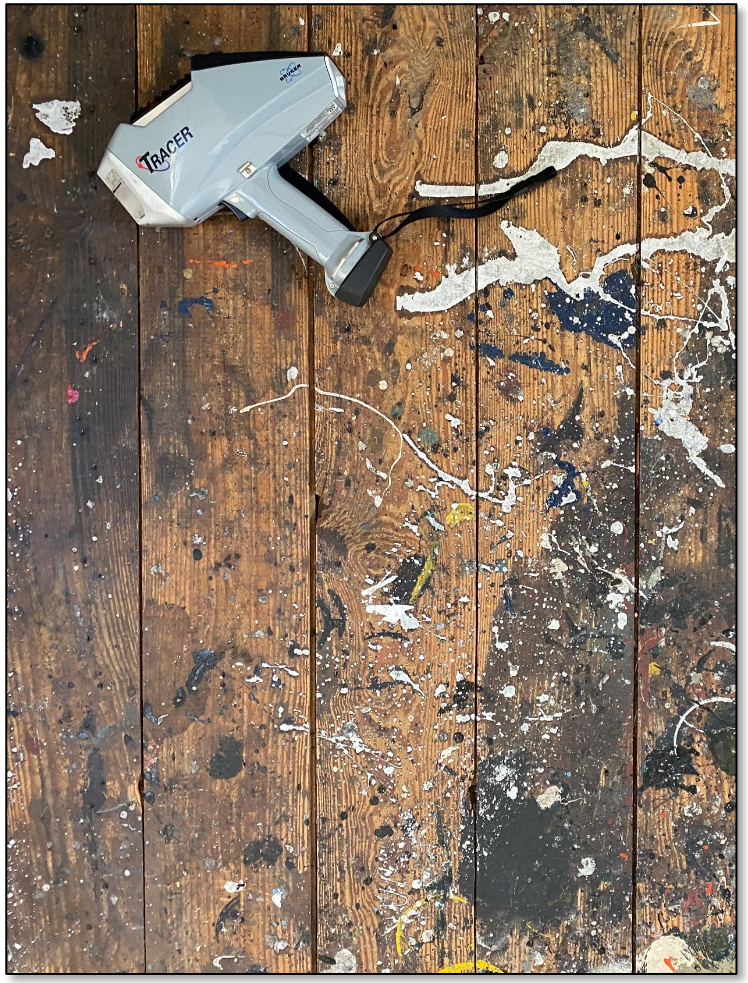
- Three webinars specifically addressing use of handheld-XRF, presented as part of the ongoing series on elemental analysis in Cultural Heritage Studies
  - I. Back to basics - taking control of your path to meaningful information
  - II. Approaches to challenging measurements - Paintings, pigments and objects
  - III. Quantitative data - what do the numbers mean?

- Other webinars in the series: collaboration with our colleagues at Bruker Optics, where we will demonstrate the benefits of integrating elemental and spectroscopic techniques



Back to basics with Handheld XRF
Our speakers

Maggi Loubser
Programme Manager – Tangible Heritage Conservation
University of Pretoria

Dr. Nigel Kelly
Senior Market Applications Scientist
Bruker Nano Analytics

Back to basics with Handheld XRF
Presentation Outline

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Back to basics with Handheld XRF
Why?

"Just because you can aim and shoot and get numbers, it does not mean the numbers mean anything!"

Back to basics with Handheld XRF
XRF is a mature technique

WDXRF ~1964 vintage

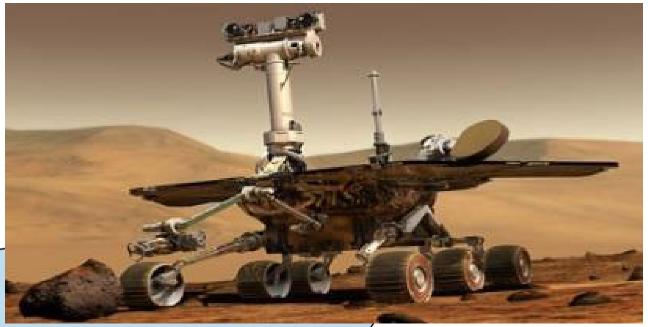
~1960 first WDXRF

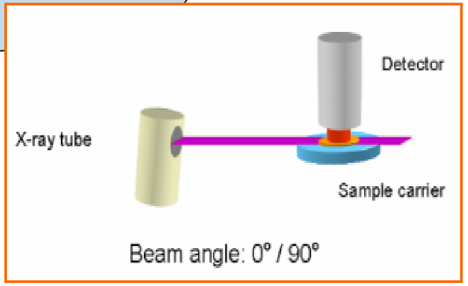
~1990 Laboratory based WDXRF with PC control

Bench top EDXRF and WDXRF

Handheld XRF

XRF on the Mars Rover





Total Reflection XRF (TXRF)

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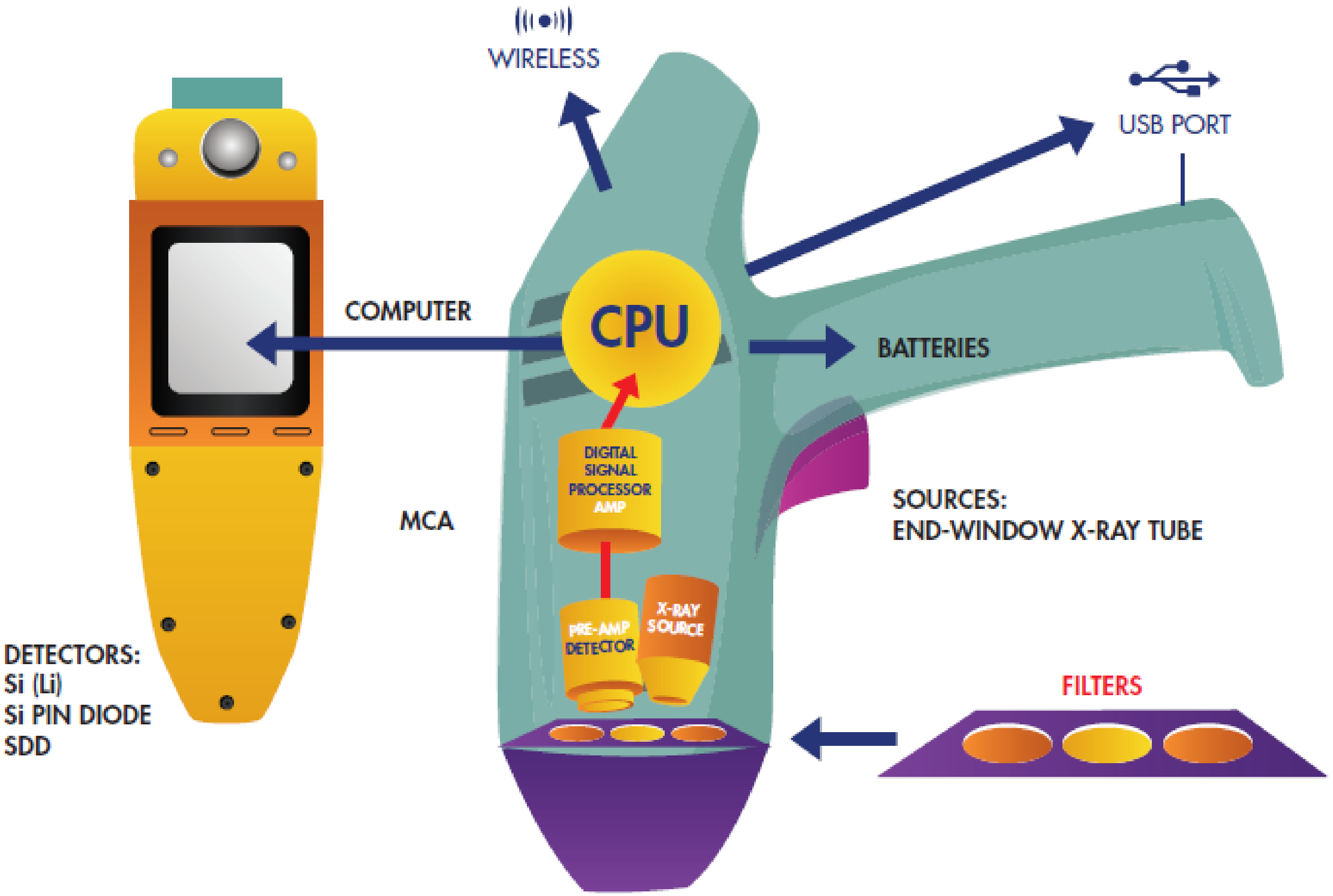
HANDHELD XRF IN CULTURAL HERITAGE STUDIES

Back to basics in Handheld XRF
Anatomy of a Spectrometer

Knowing your handheld XRF
Anatomy of a spectrometer



Knowing your handheld XRF
Anatomy of a spectrometer

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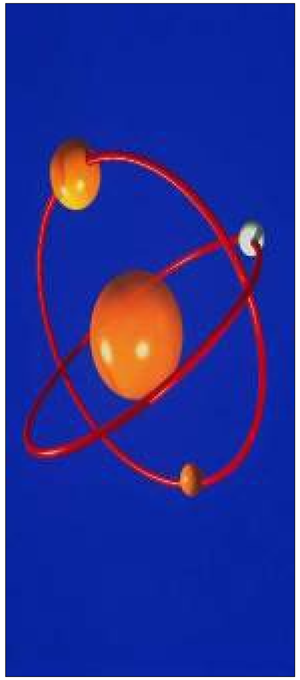
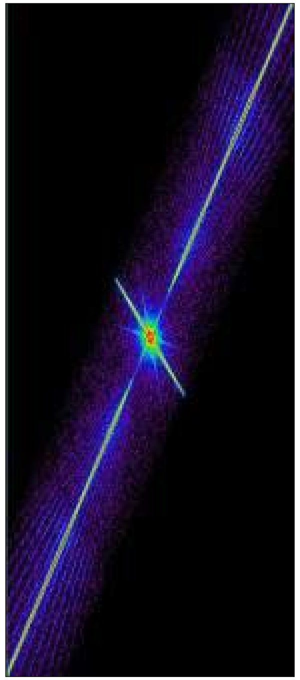
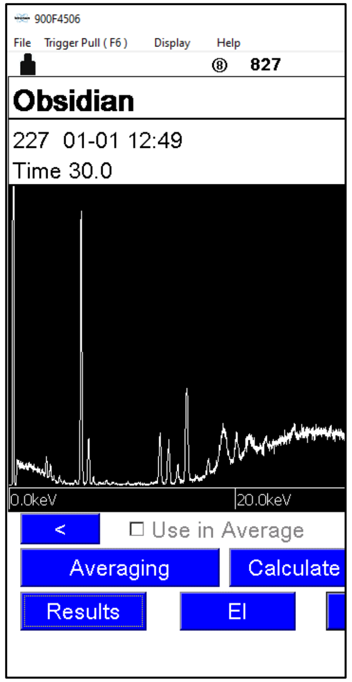
Excitation Source



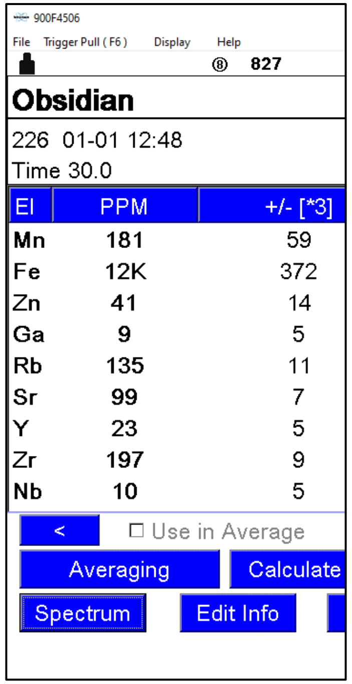
Ionizes Atoms



Energy Emission



Spectral Capture



Test Results

The process – in 5 steps

Knowing your handheld XRF
Anatomy of a spectrometer

Excitation Source	Ionizes Atoms	Energy Emission	Spectral Capture	Test Results

Atoms in a sample are excited by a beam of primary X-rays

Knowing your handheld XRF
Anatomy of a spectrometer

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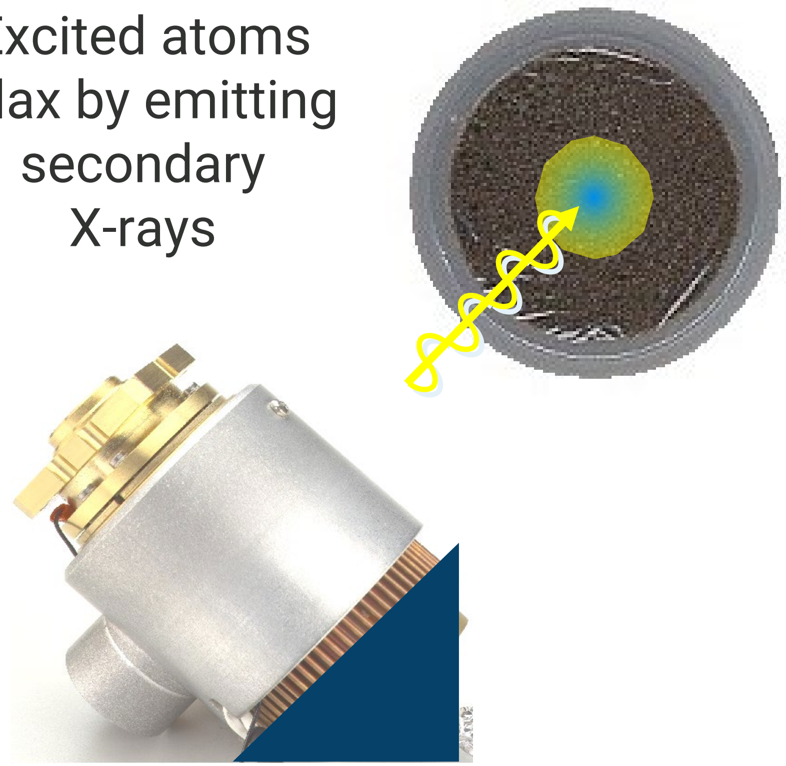
Excitation Source | Ionizes Atoms | Energy Emission | Spectral Capture | Test Results

Excited atoms relax by emitting secondary X-rays



Knowing your handheld XRF
Anatomy of a spectrometer

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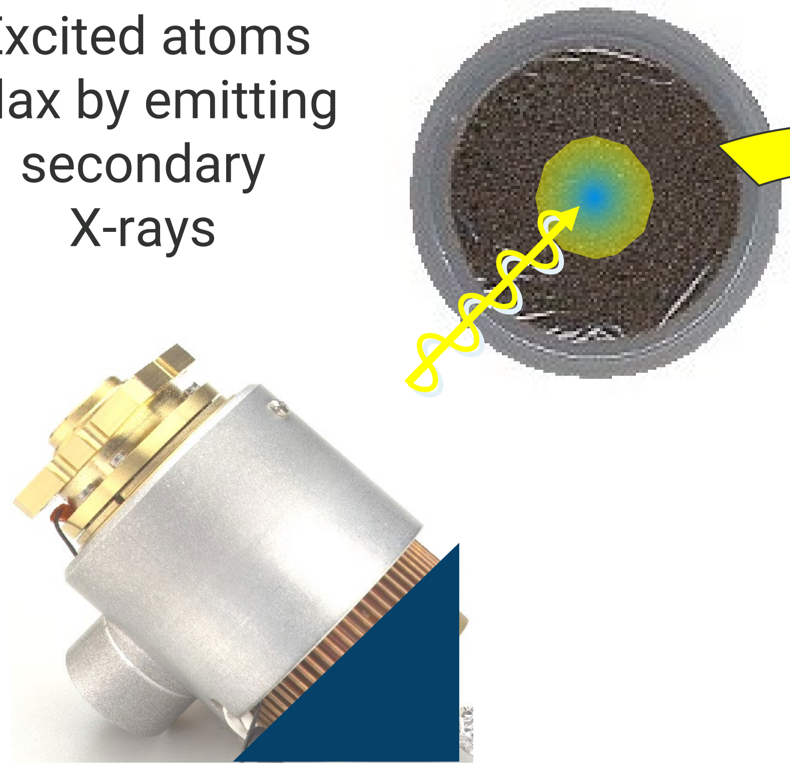
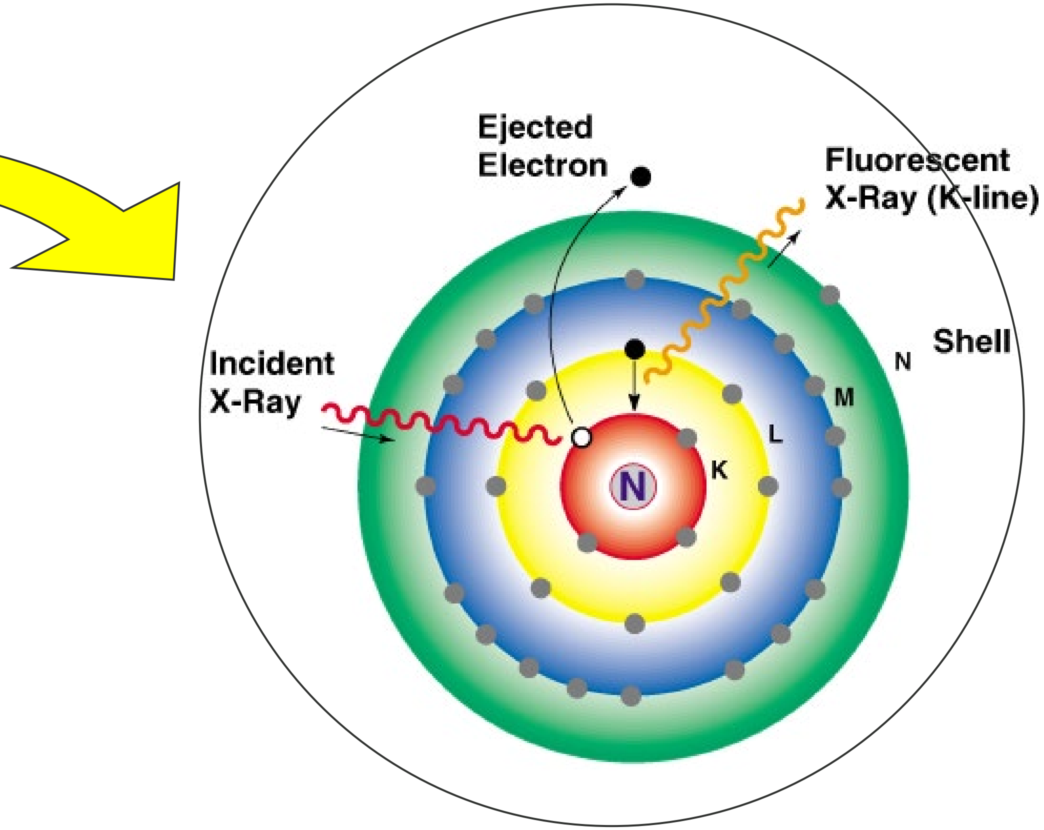
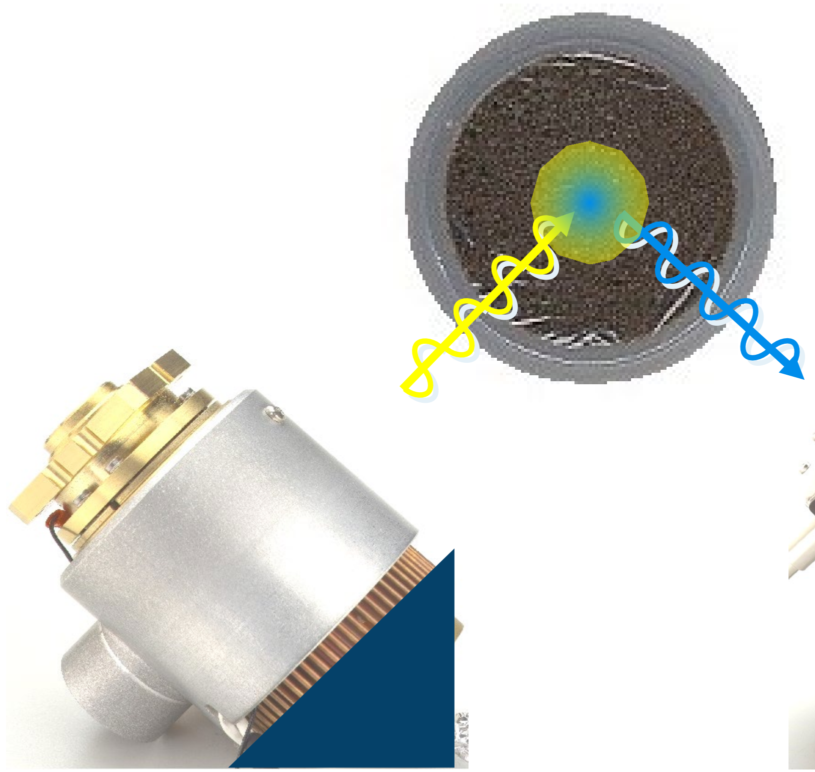


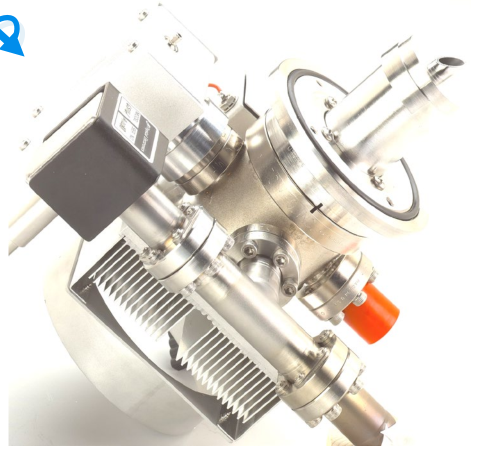


Knowing your handheld XRF
Anatomy of a spectrometer

Excitation Source → Ionizes Atoms → **Energy Emission** → **Spectral Capture** → Test Results



The emitted X-rays are collected by the detector



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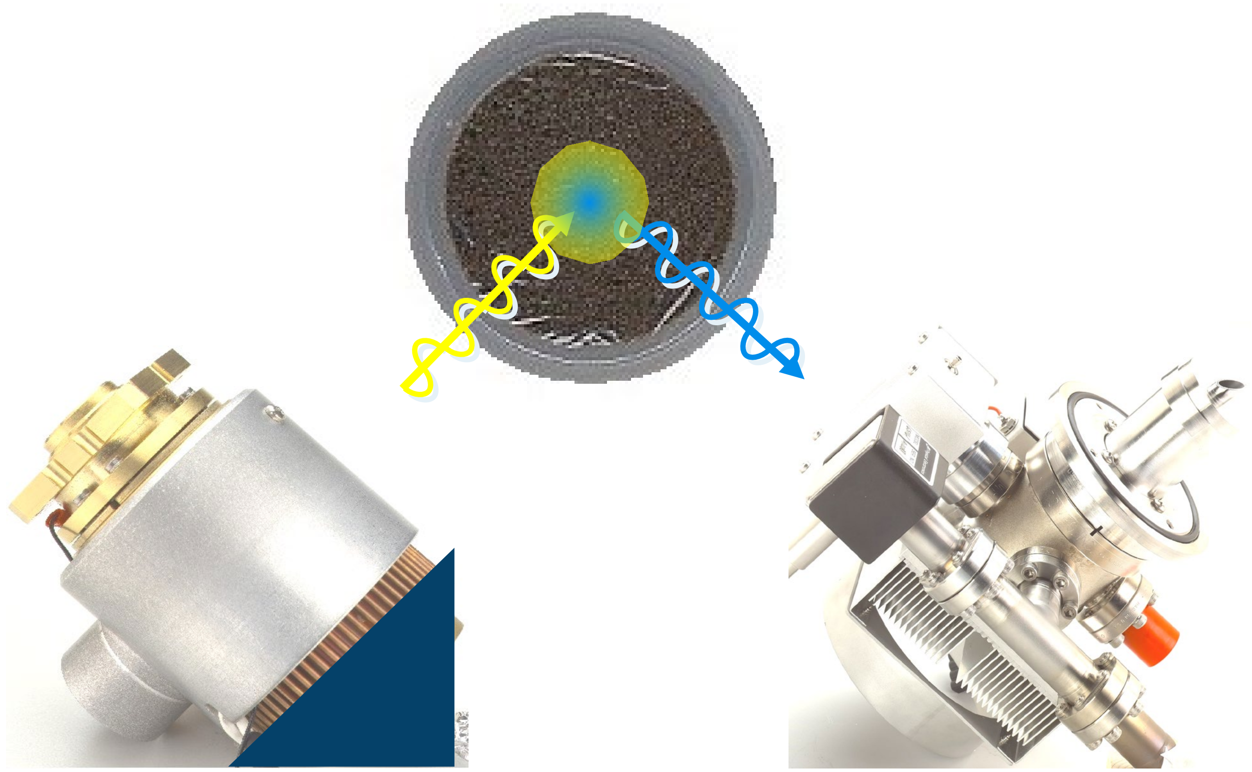
Knowing your handheld XRF
Anatomy of a spectrometer

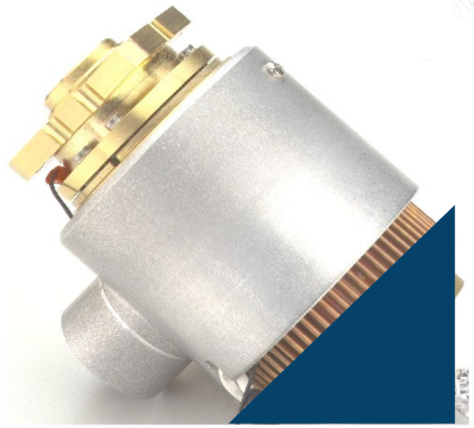
Excitation Source	Ionizes Atoms	Energy Emission	Spectral Capture	Test Results

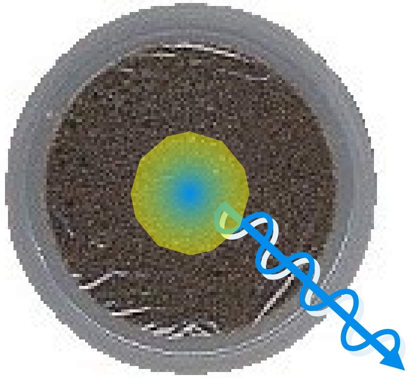


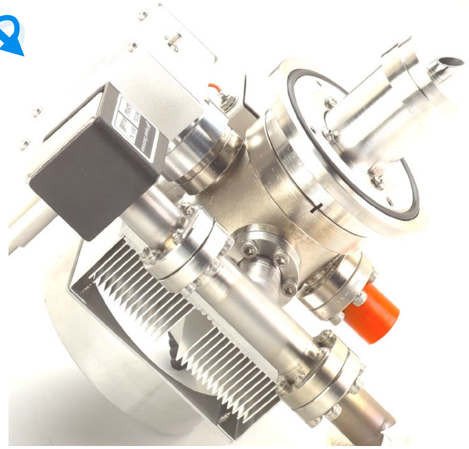
Each X-ray is converted into a voltage pulse $\propto$ to its energy

Knowing your handheld XRF
Anatomy of a spectrometer

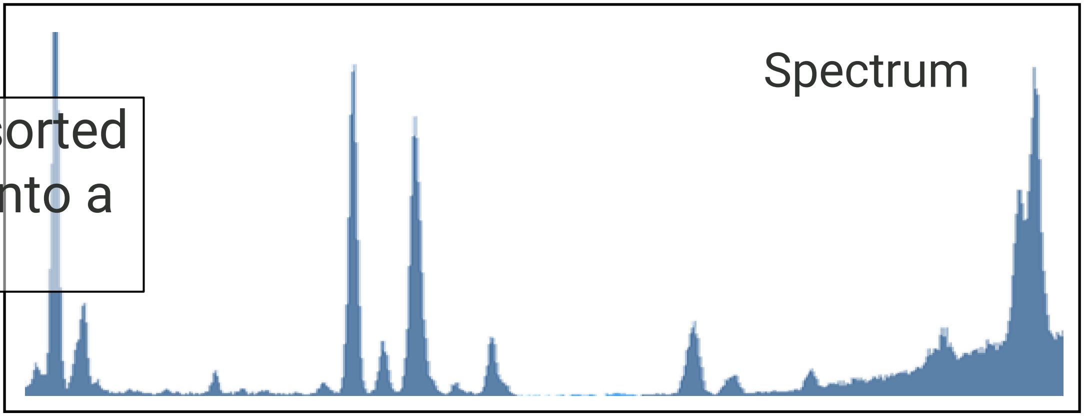
Excitation Source → Ionizes Atoms → Energy Emission → Spectral Capture → Test Results







The pulses are sorted and combined into a spectrum



Knowing your handheld XRF
Anatomy of a spectrometer

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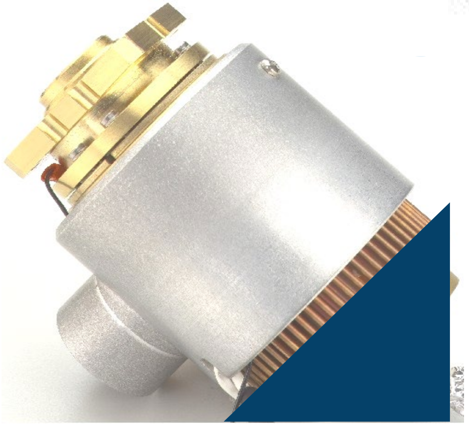
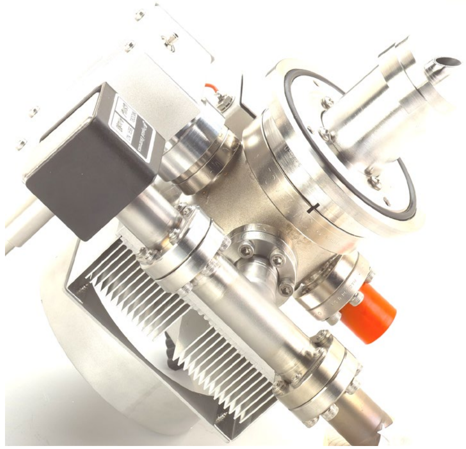
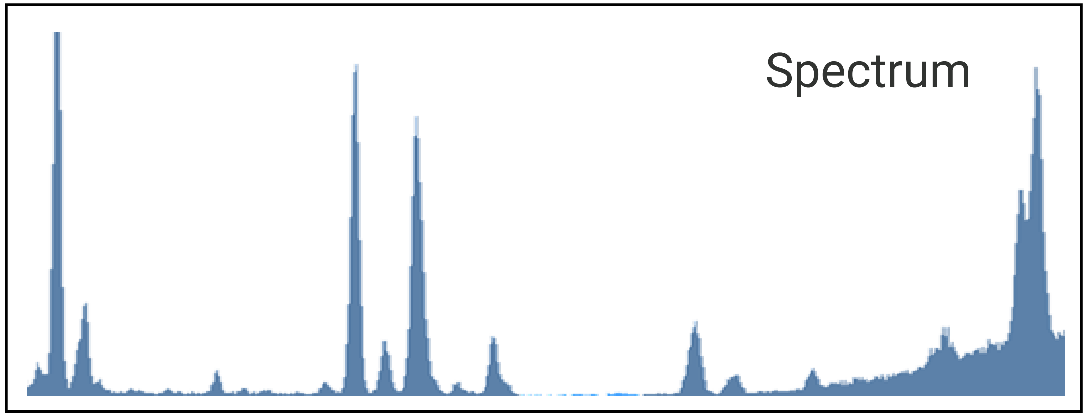
Excitation Source | Ionizes Atoms | Energy Emission | Spectral Capture | **Test Results**







Results

Element	Concentration		Std. Dev.	Peak (cps)
Unknown				
SiO_2	34.8	%	0.1	3830
Fe	6.82	%	0.05	670
Zn	23.83	%	0.05	6680
Ba	2.41	%	0.01	1246
Pb	5.78	%	0.03	1196

Peak intensities may be related to concentration, thickness or other factors

HANDHELD XRF IN CULTURAL HERITAGE STUDIES

Back to basics in Handheld XRF

Generation of X-rays

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Generation of X-rays & Excitation Potentials
What are X-rays?

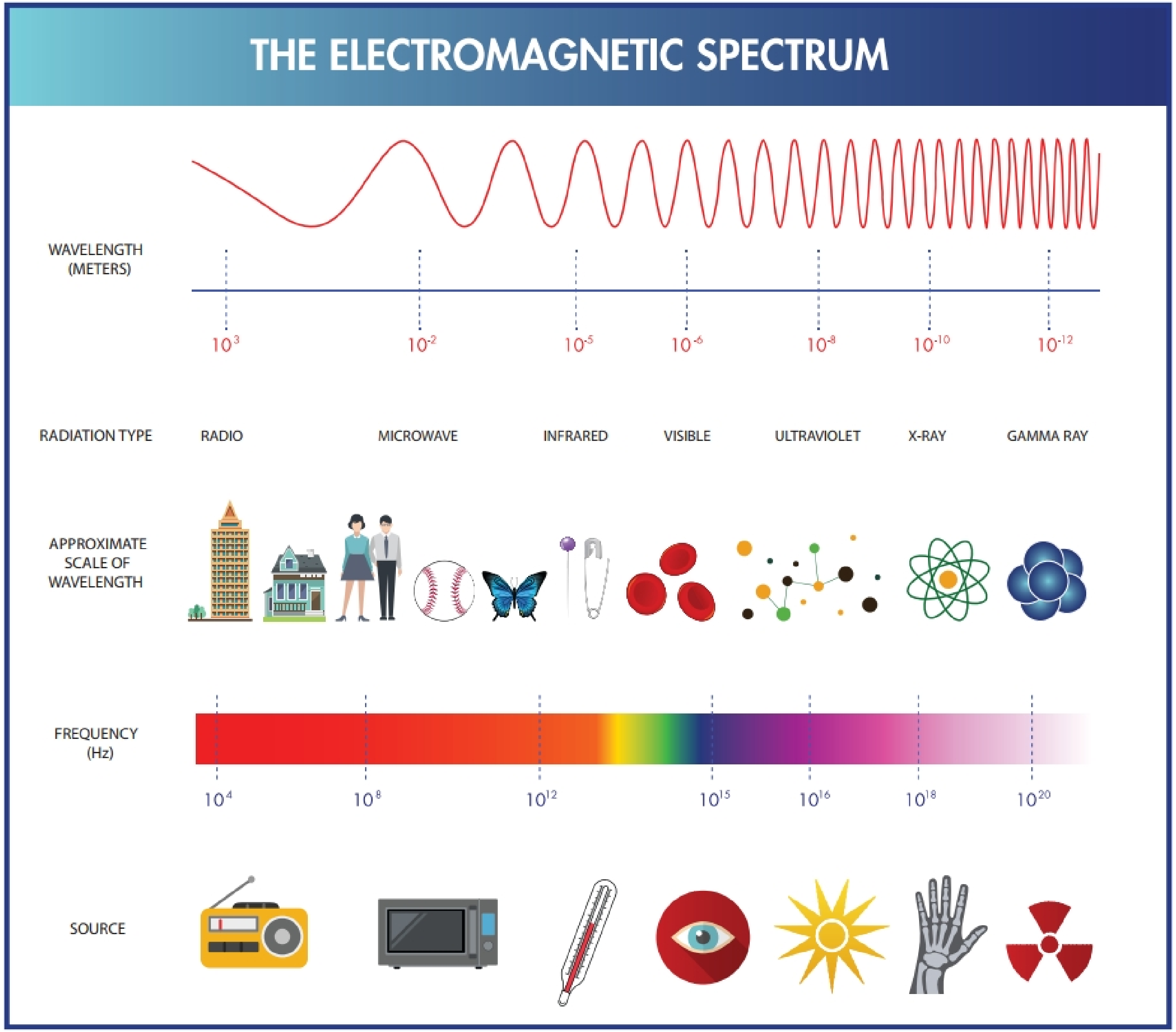
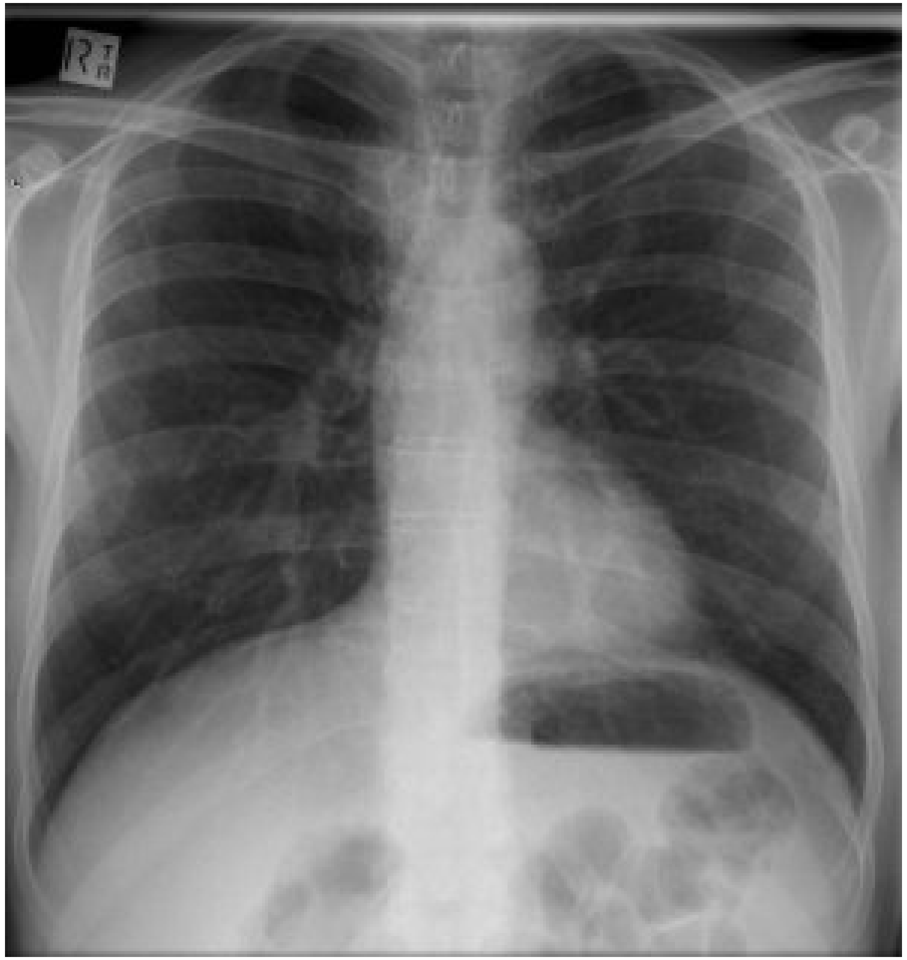


Image from: Anikó Bezur, Lynn Lee, Maggi Loubser, and Karen Trentelman, 2020. Handheld XRF in Cultural Heritage: A Practical Workbook for Conservators. Getty Conservation Institute. ISBN 1937433625

Generation of X-rays & Excitation Potentials
What are X-rays?

- The same X-rays used in medical diagnostics
- The difference – energies used are a lot lower when used on humans
  - *we do not want to excite our atoms!*



- If a spectrometer is added and not just the contrast film, can measure
  - Ca and P (from bones)
  - Fe (from Hemoglobin in blood)

Generation of X-rays & Excitation Potentials
Properties of X-rays

Binding energy of an electron

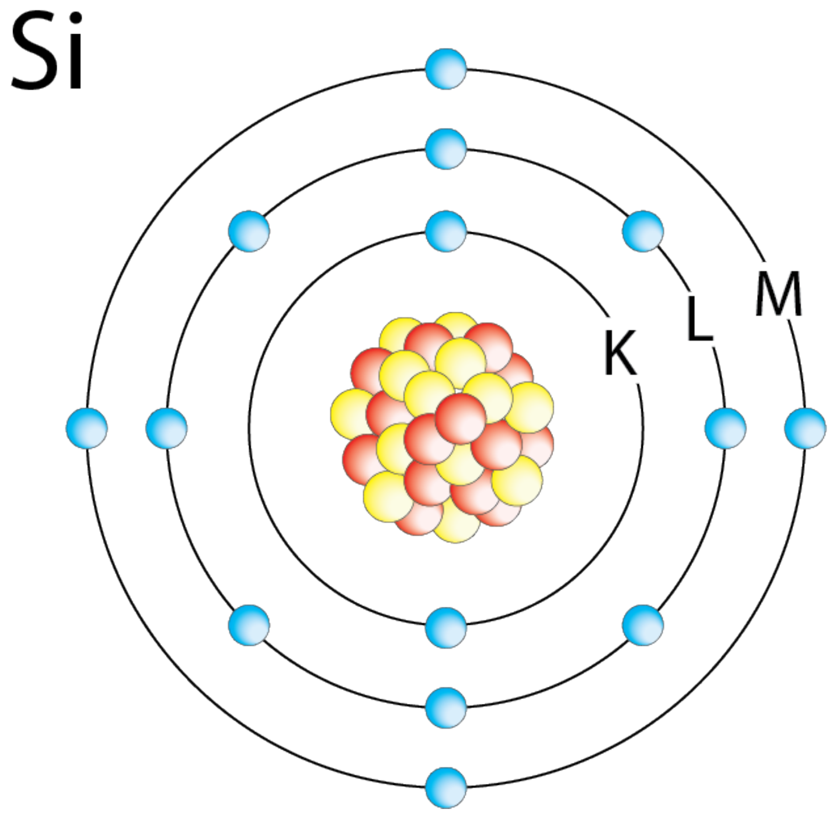
- The binding energy is the minimum X-ray energy required to expel an electron from a given atom sub-shell (K,L,M shell).
- The basic unit of binding energy is the kiloelectron volt (keV).
- The binding energy has the same numerical value as the *Excitation Potential* (units of kV)

Wavelength of an X-ray photon

- Units of measurement:
  - Angström unit (Å) or nanometers (nm)

1 Å = 10^{-10} m

10 Å = 1 nm



Generation of X-rays & Excitation Potentials
Properties of X-rays

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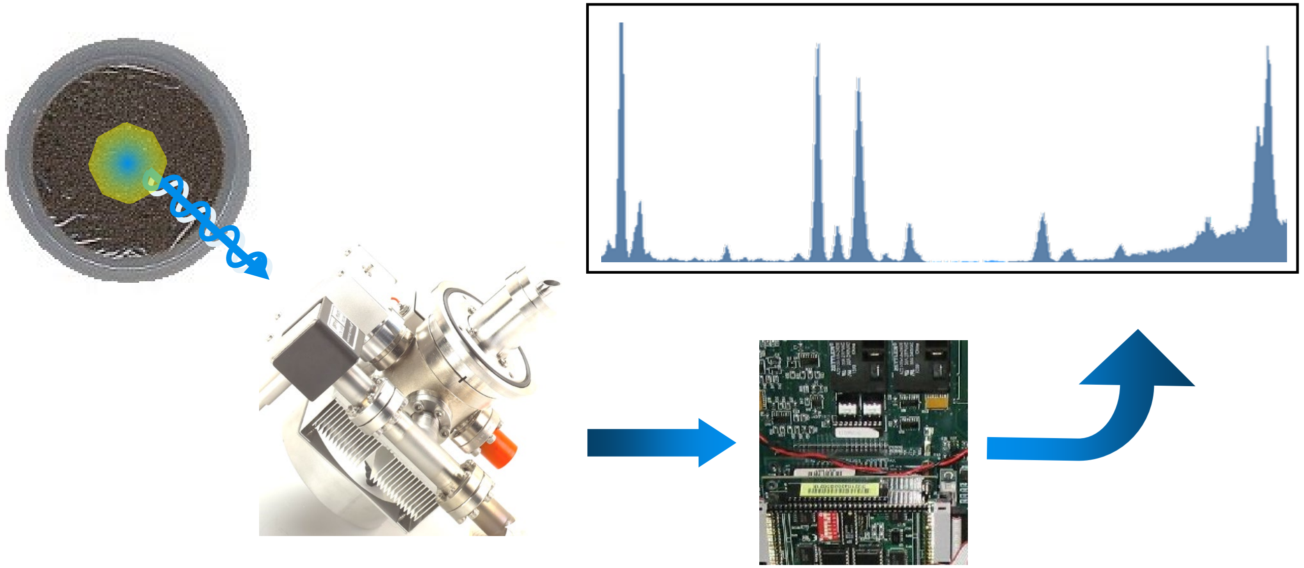
Intensities of X-rays

- Measured based on the amount if ionization they cause
- This occurs in a detector where the ionization results in electron pair formation that can produce a pulse
- X-ray intensity is reported as the number of counts measured per unit of time,
  - e.g., counts per second (cps)

    kilocounts per second (kcps)



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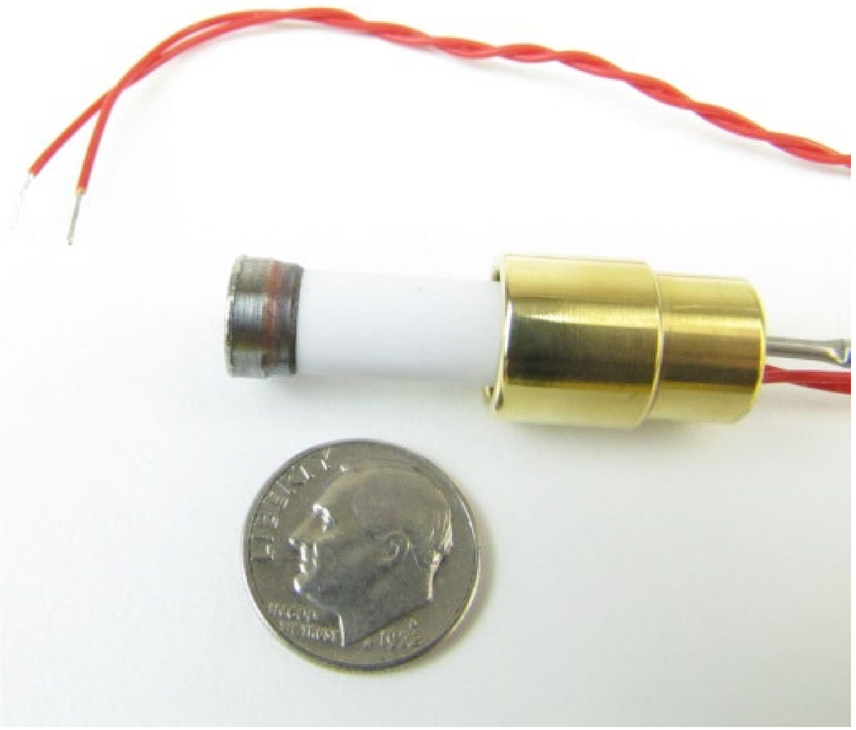
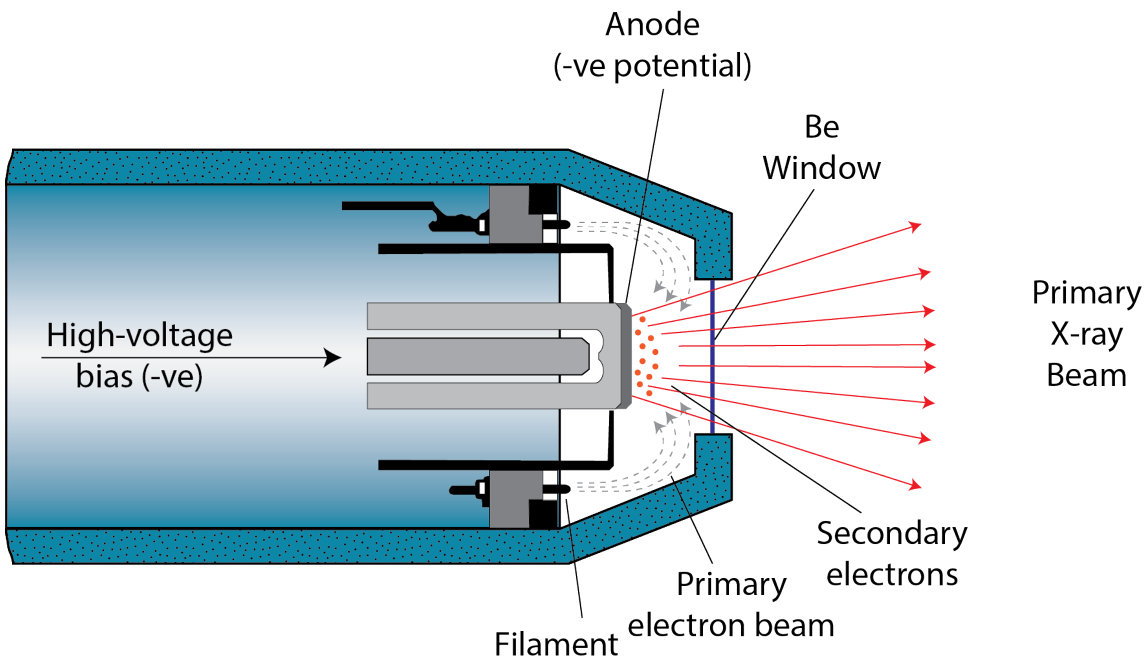
Generation of X-rays & Excitation Potentials
How do we generate primary X-rays?

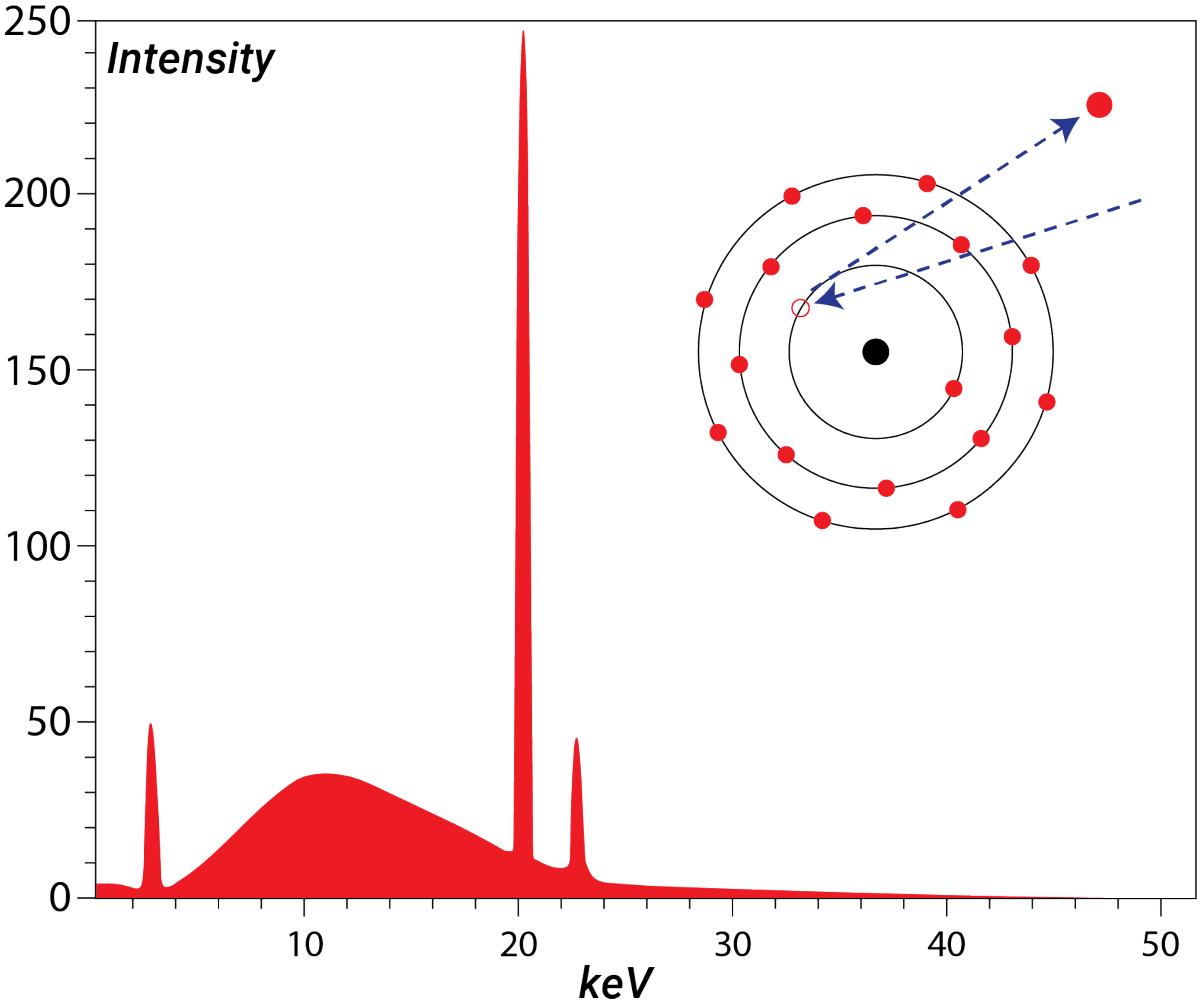
- Example of a miniature X-ray tube





Generation of X-rays & Excitation Potentials
How do we generate primary X-rays in the X-ray Tube?

- Generating X-rays / photons
  - Electrons from the source filament displace inner shell electrons
  - Vacancy created is filled by other electron shells
  - This transition to replace the vacancy produces characteristic X-rays (photons)
  - The transition event determines the energy (and label) of the X-ray line
    - e.g.,
      - L to K = Kα
      - M to K = Kβ
      - M to L = Lα



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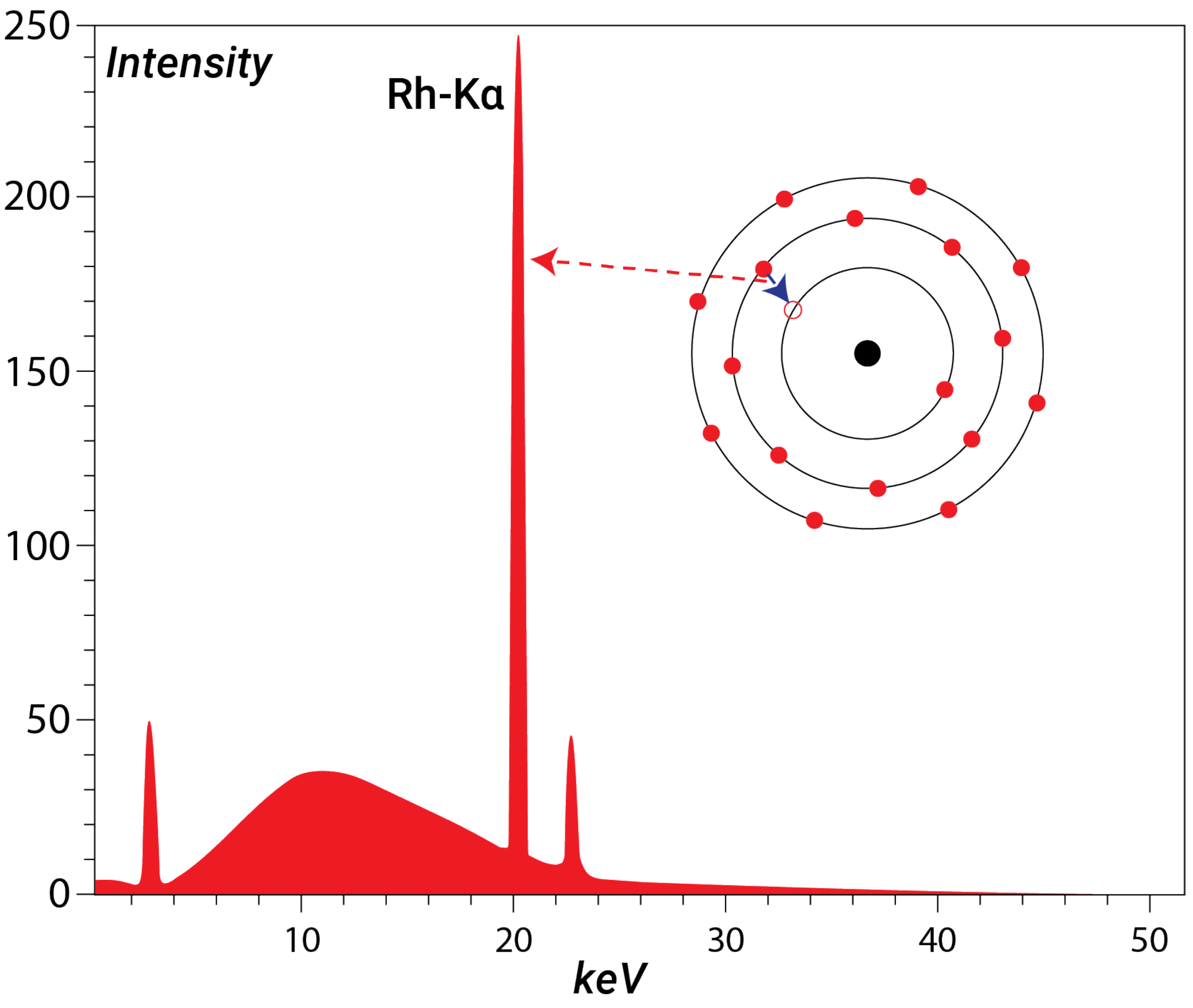

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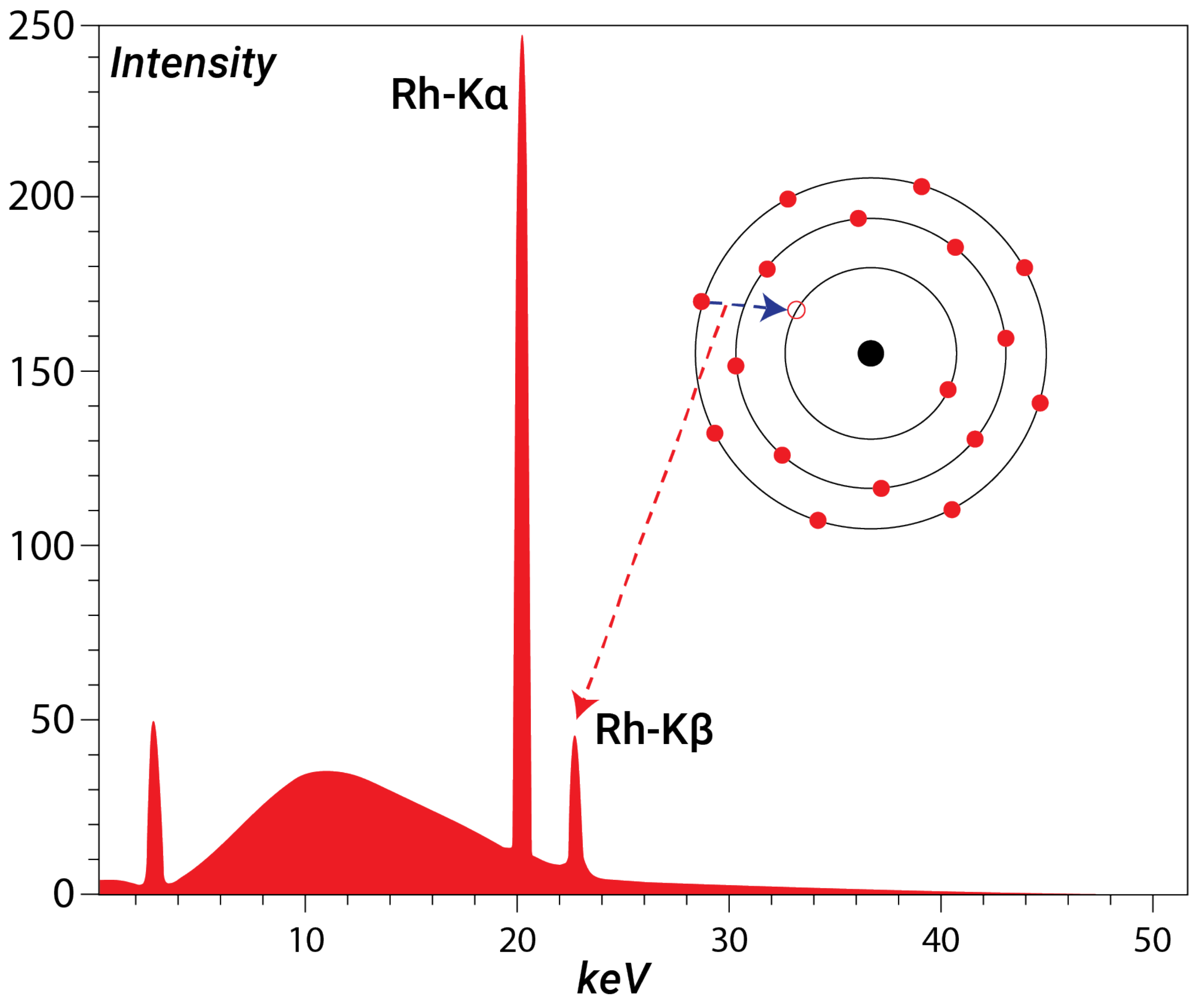

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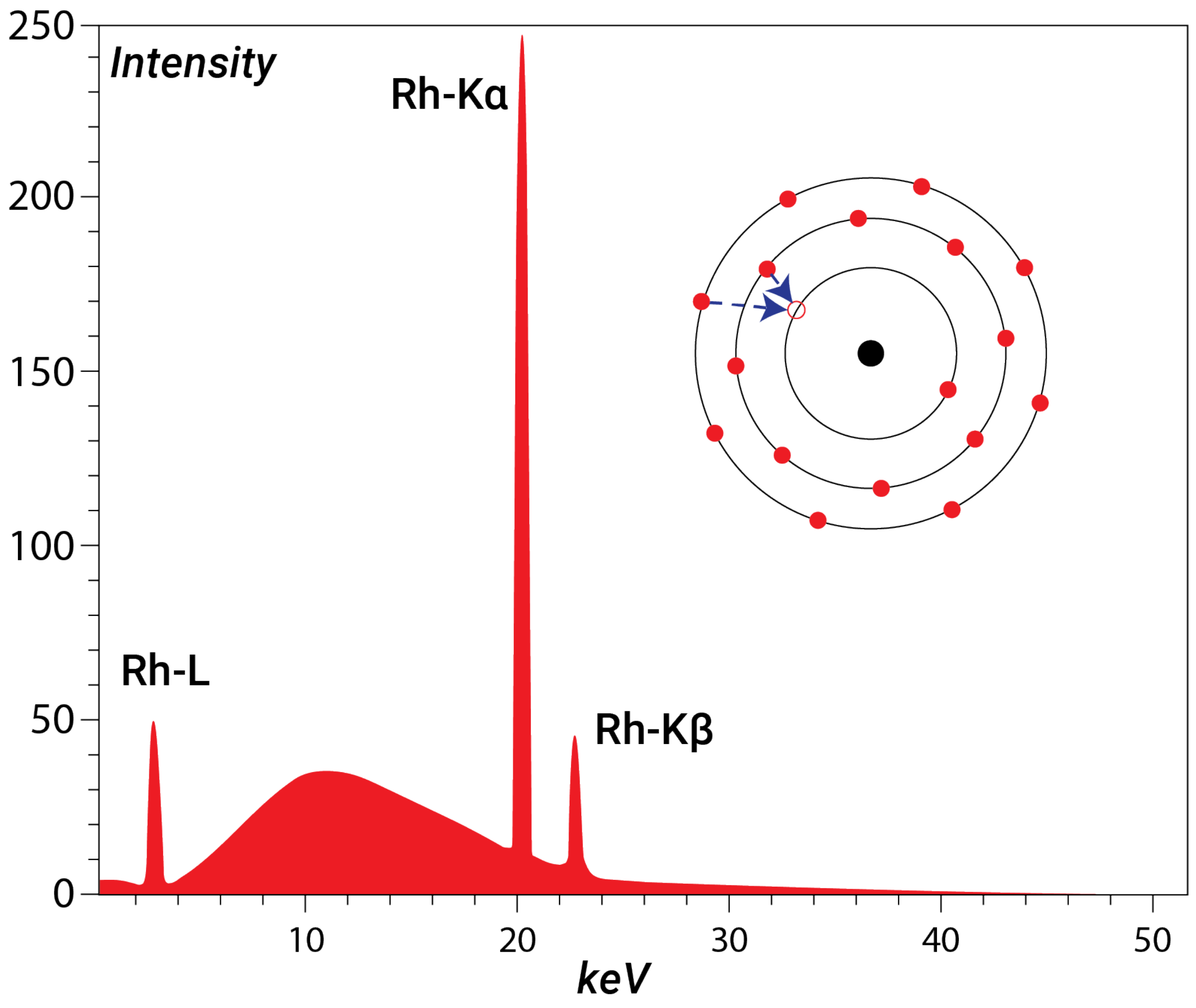
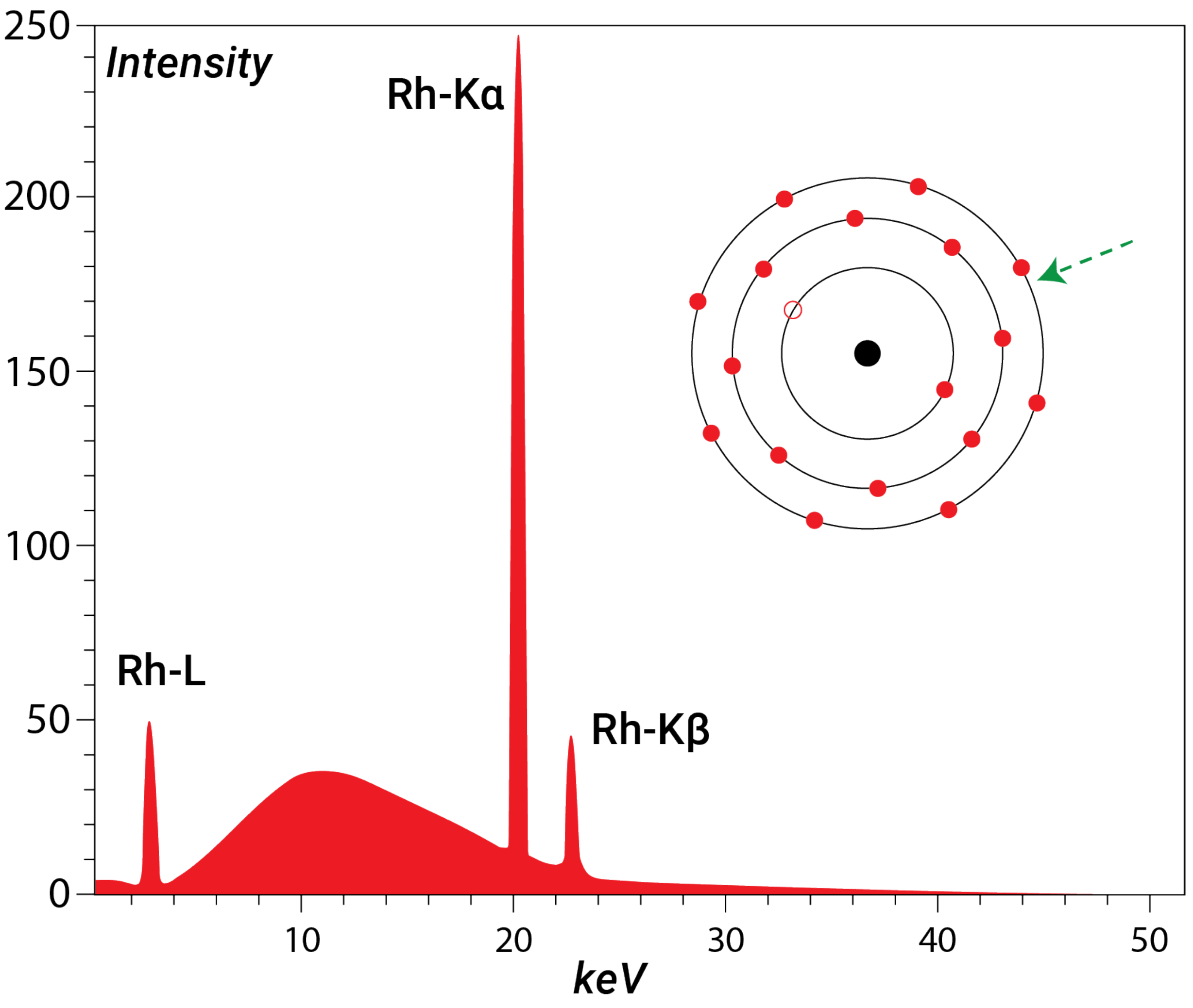


Generation of X-rays & Excitation Potentials
How do we generate primary X-rays in the X-ray Tube?

- The X-ray continuum
- Deceleration of primary electrons by an atom's electron field produces white or continuous radiation (Bremsstrahlung)



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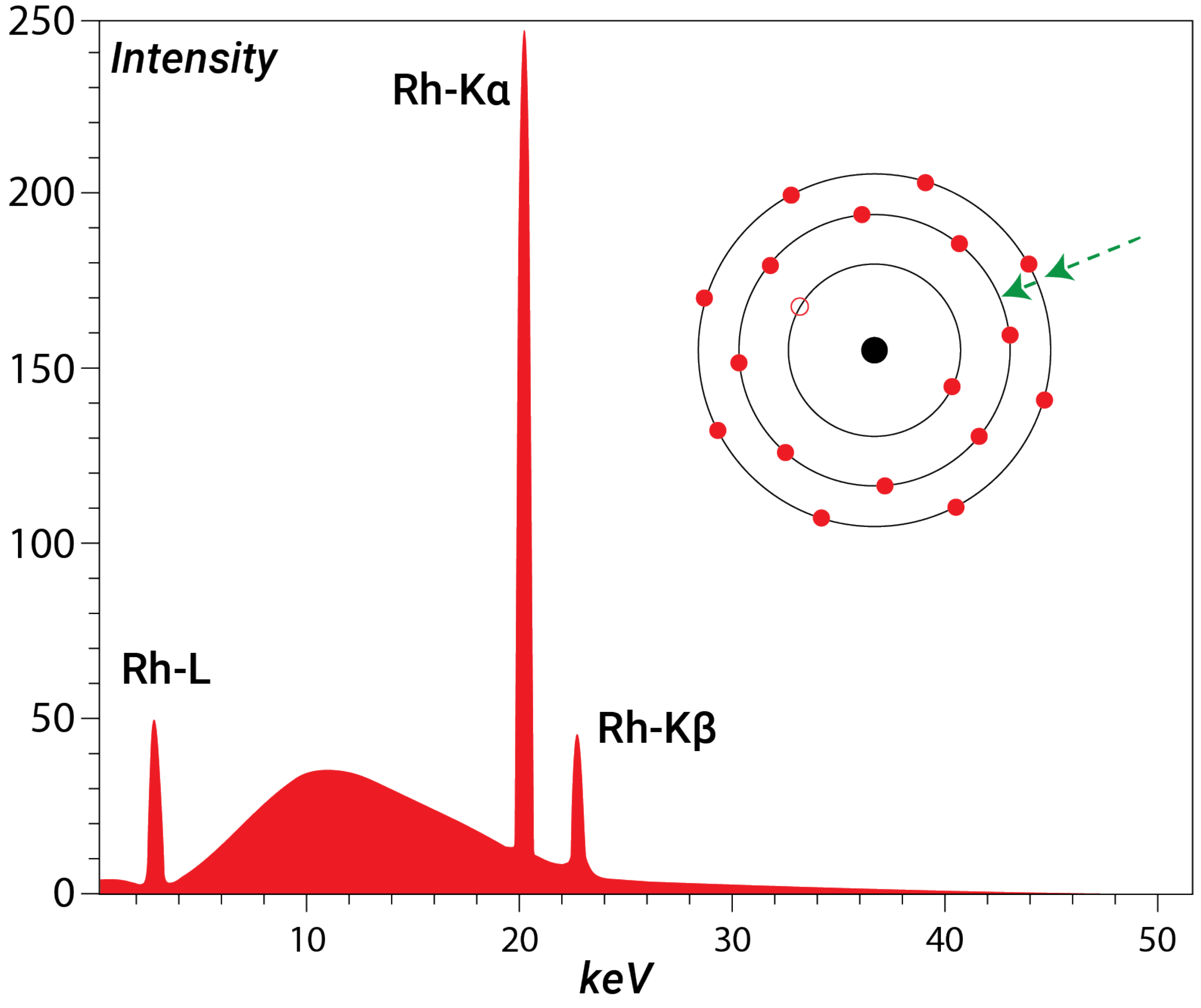

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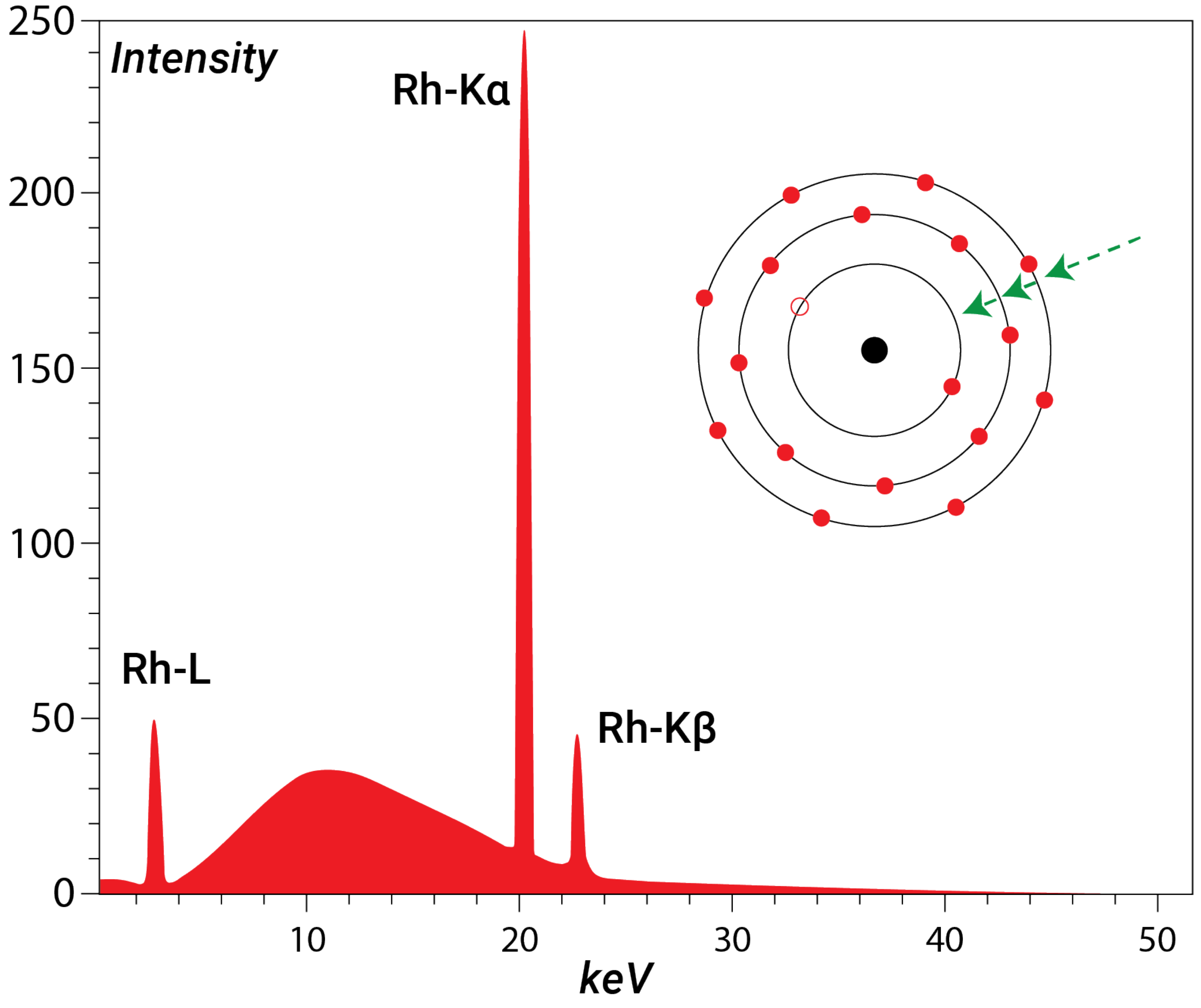

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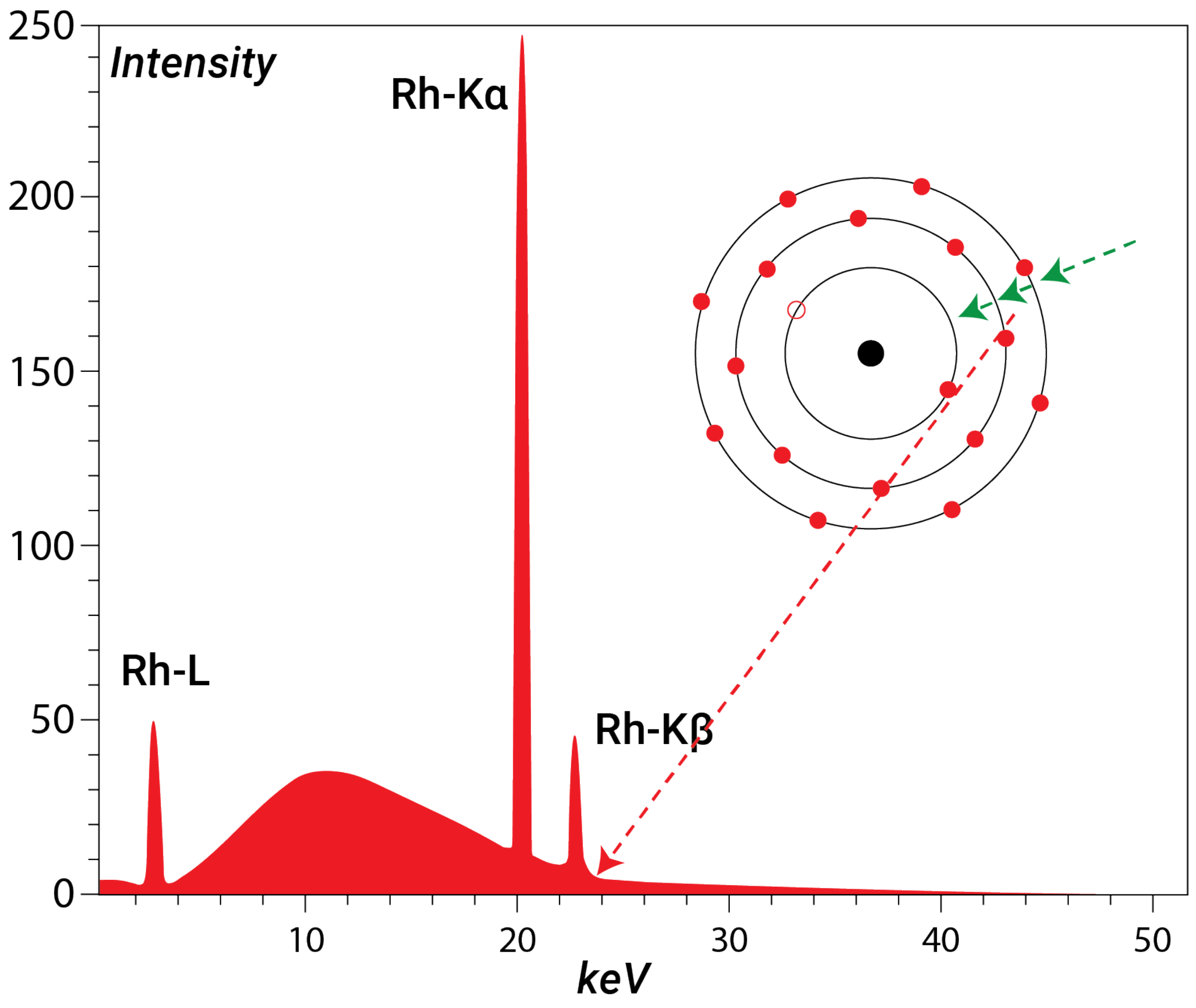

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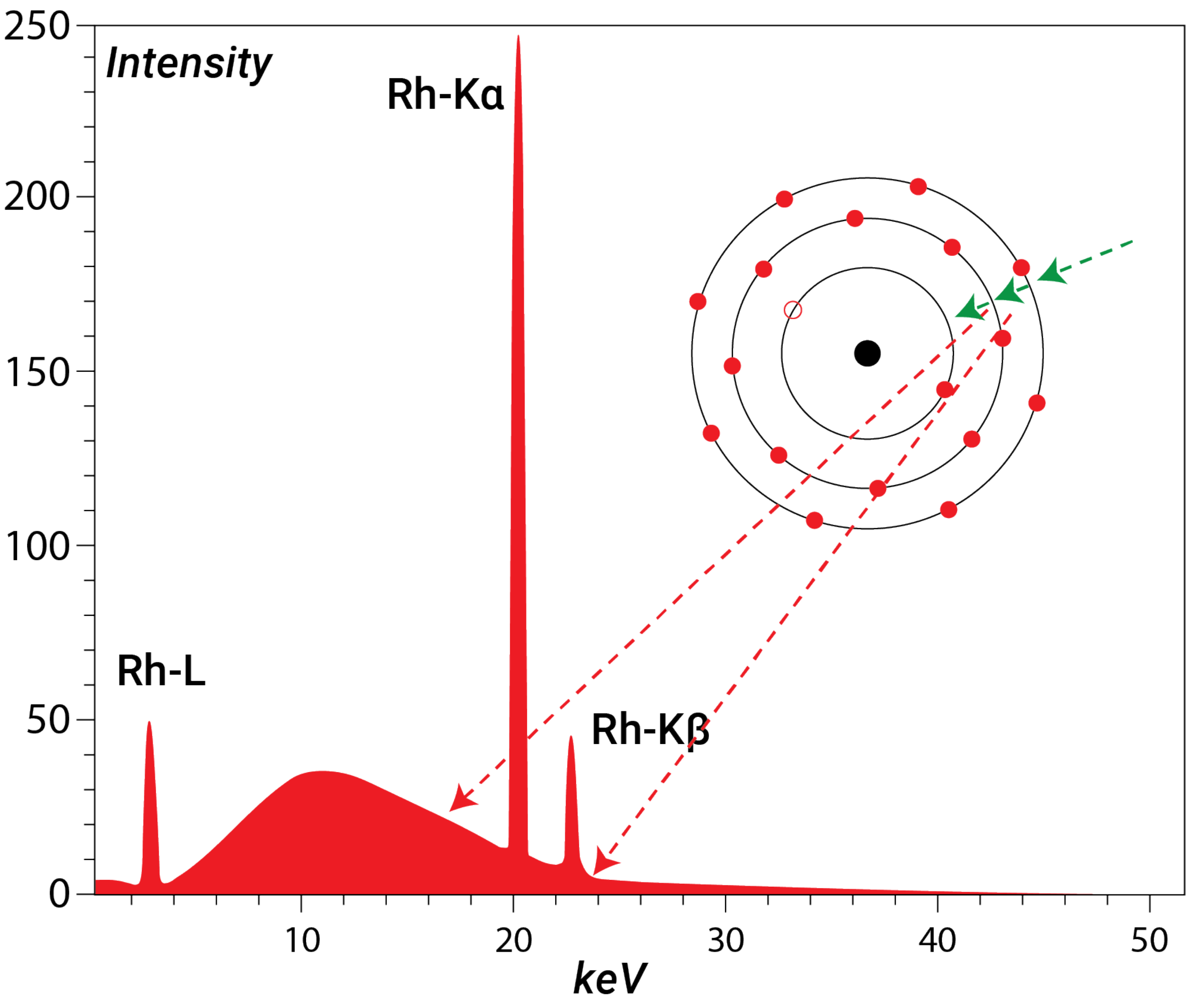

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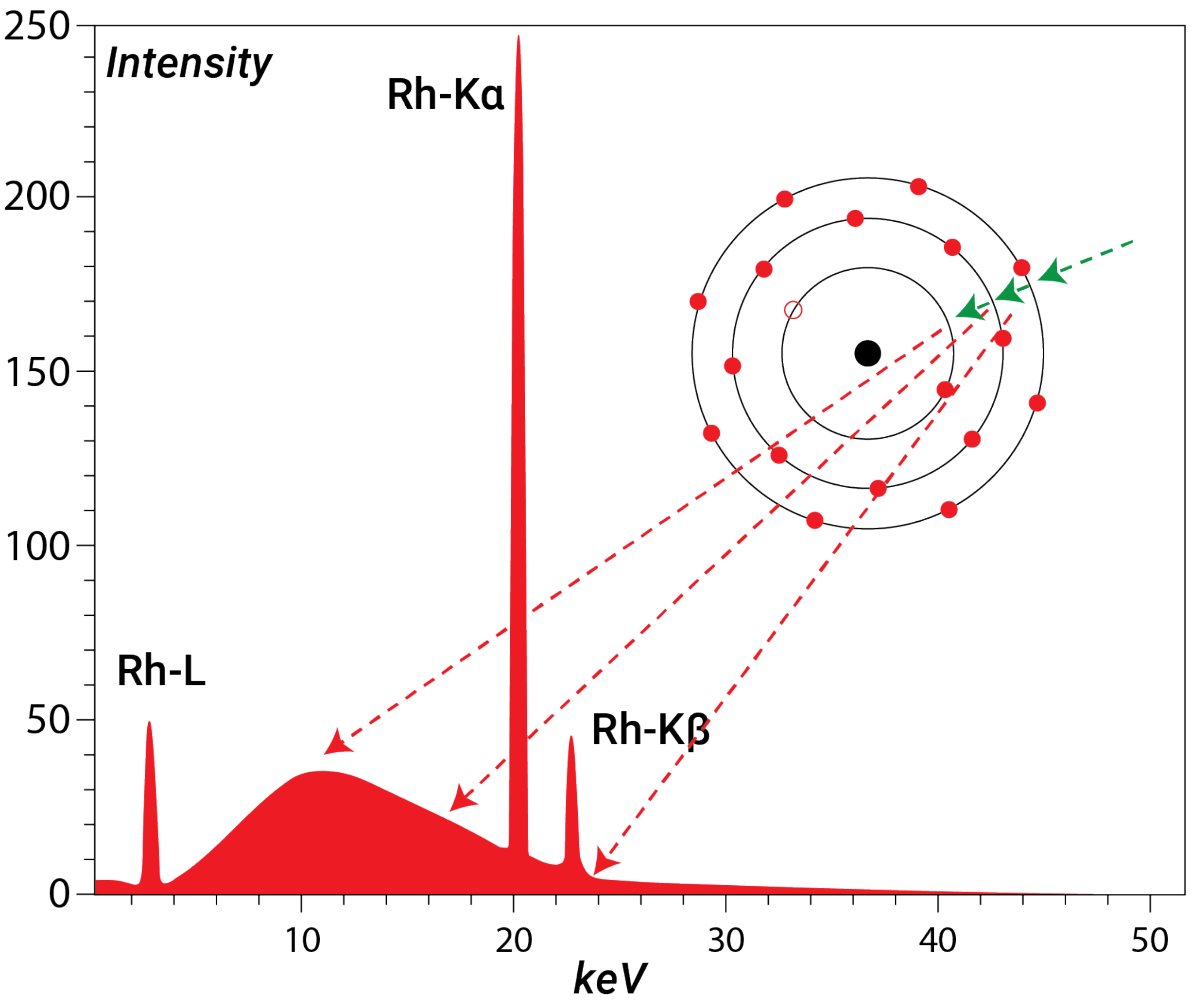
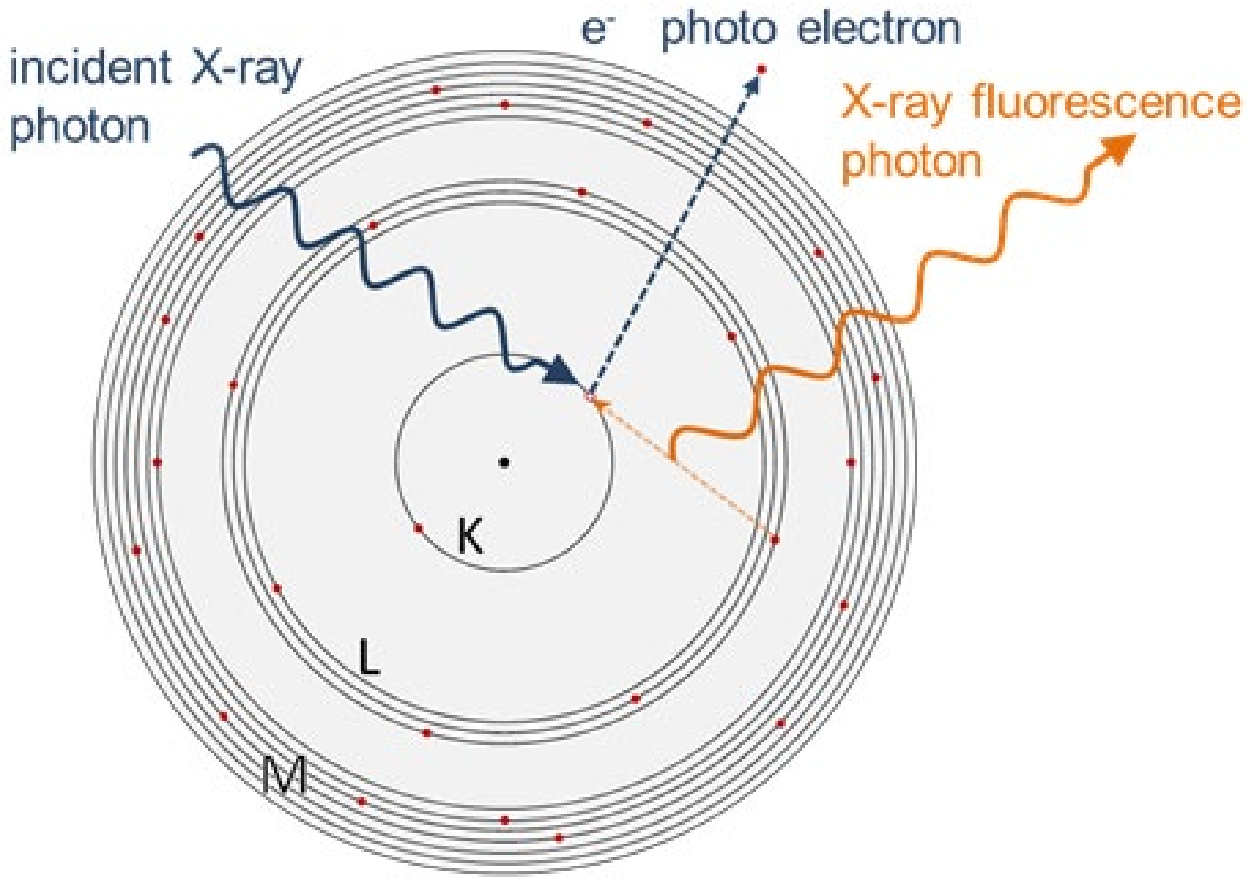


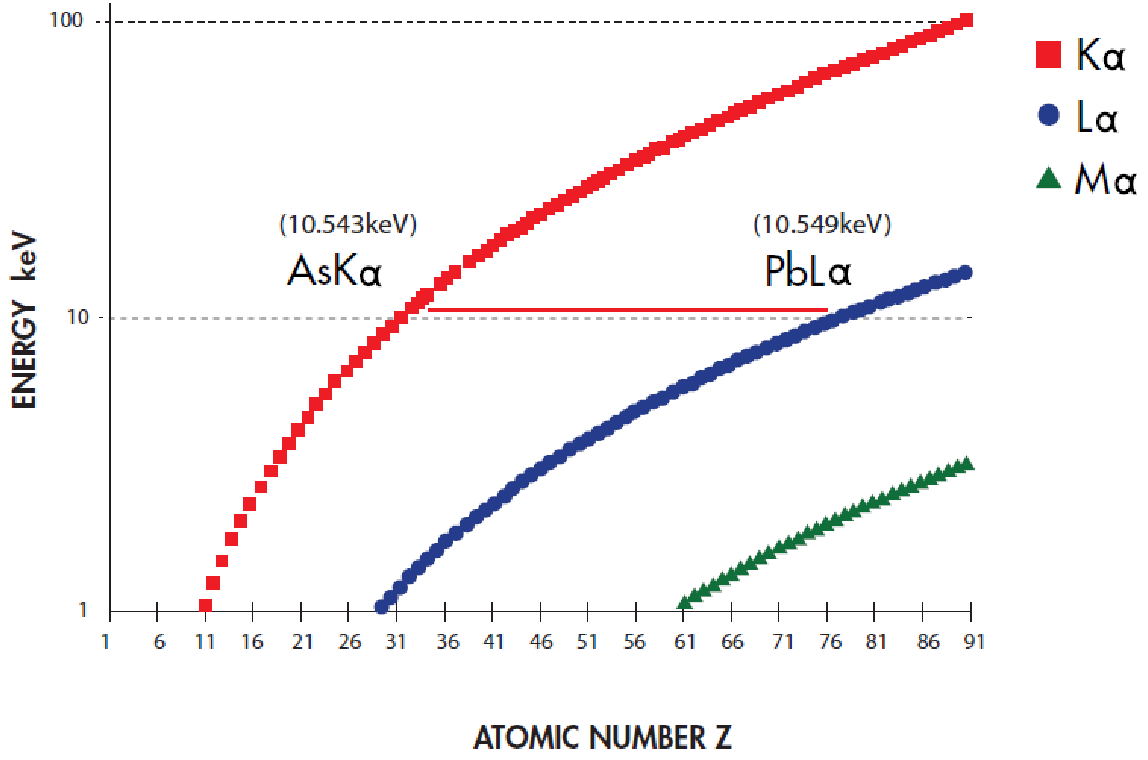
Generation of X-rays & Excitation Potentials
Generating secondary X-rays in a sample

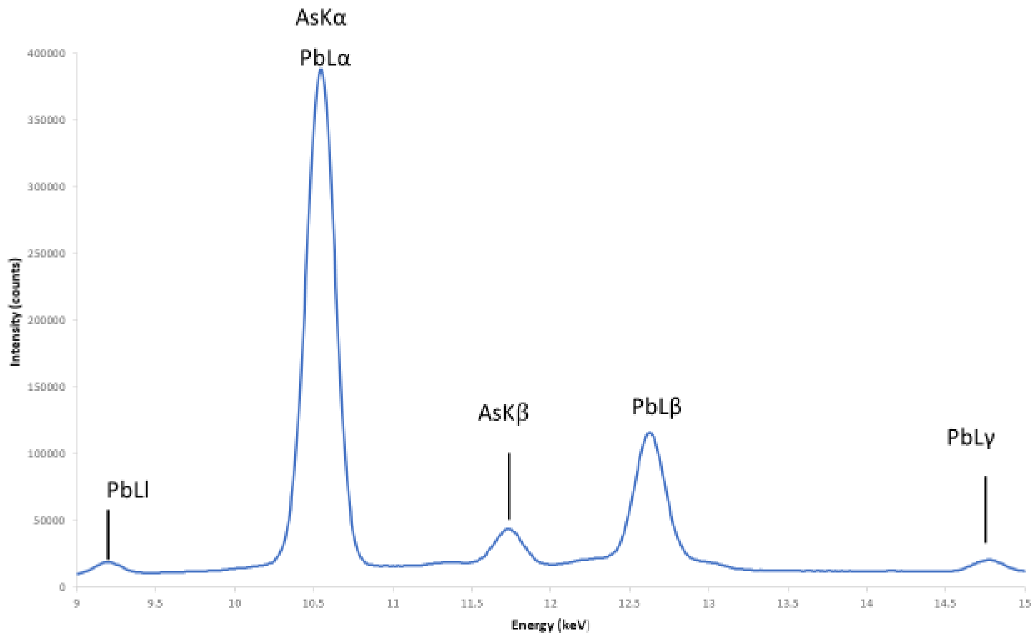
- Similar process to generating primary X-rays
  - X-ray (photon) expels the inner core electron to start the process, instead of an electron
  - We now have a complex array of different atoms instead of a single composition target



Generation of X-rays & Excitation Potentials
X-ray emission energy vs Atomic number (Z)

Moseley's Law - Relationship in practical terms





HANDHELD XRF IN CULTURAL HERITAGE STUDIES

Back to basics in Handheld XRF
Modulation of primary X-rays – volts, current, filters

Modulation of X-rays – volts, current, filters
What controls the generation of characteristic X-rays from the sample?

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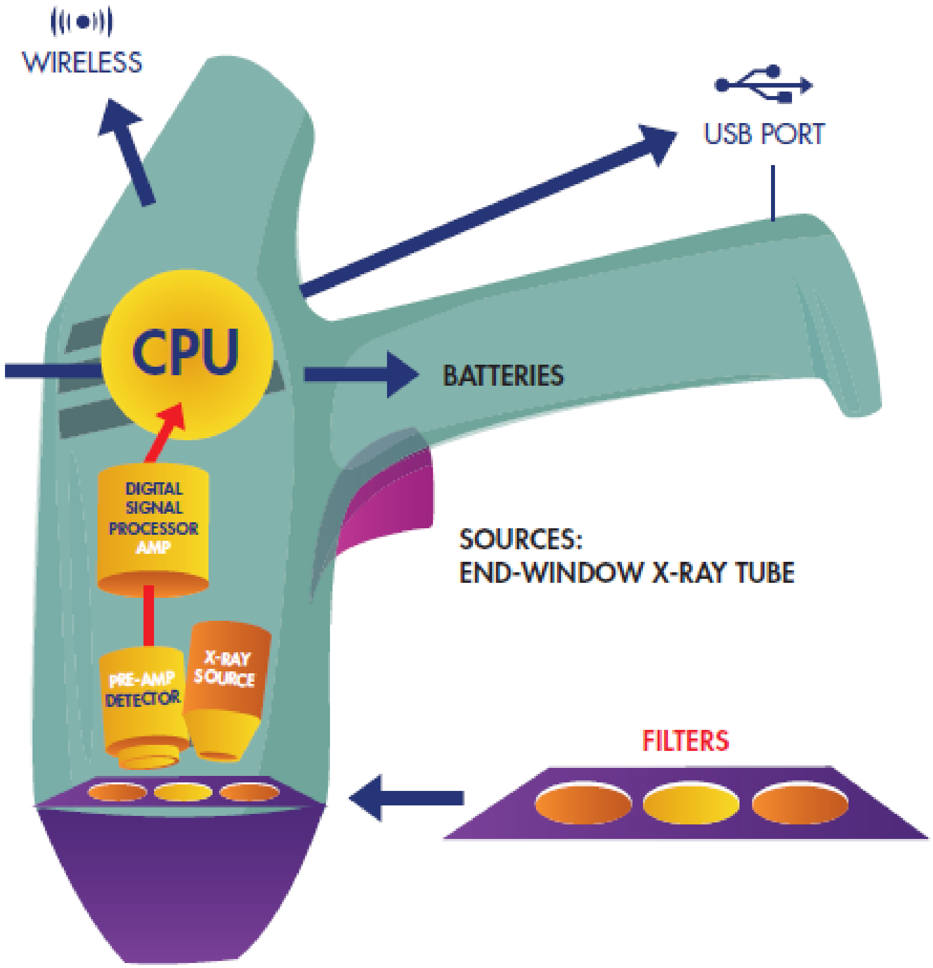
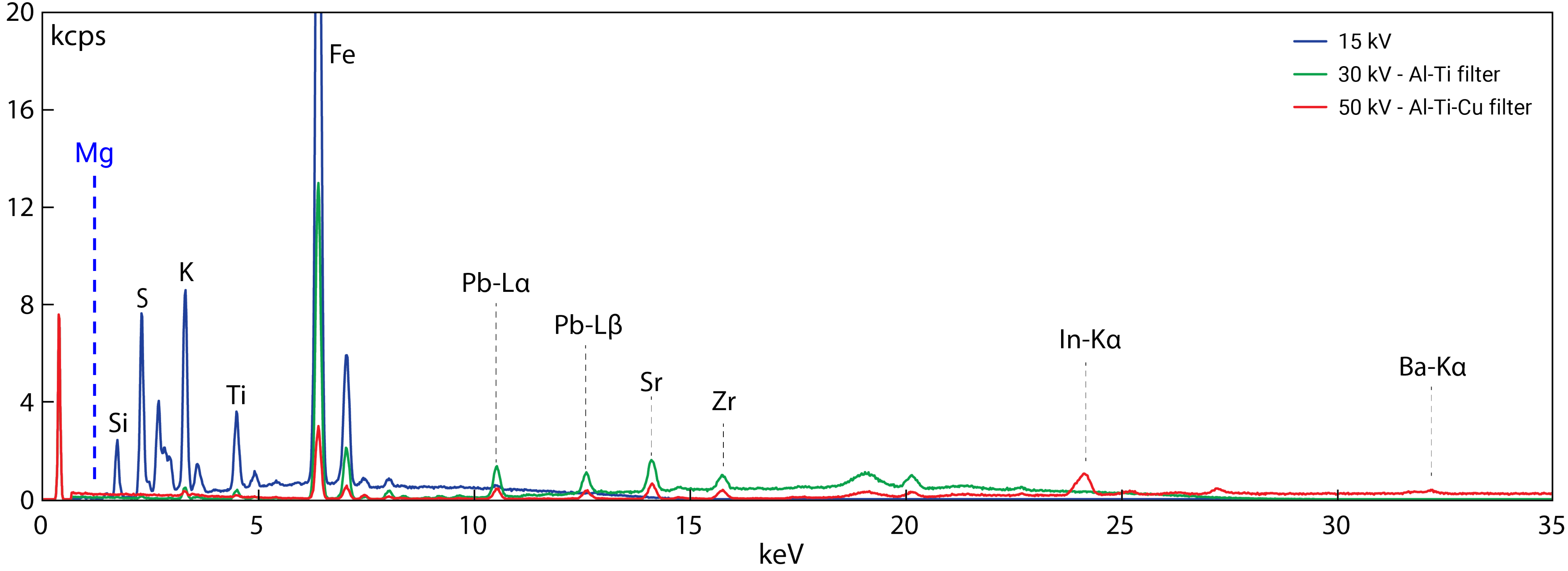


- Three ways to modulate the primary X-ray source to influence the response from the sample (as observed in the spectrum)
  - Voltage (kV)
  - Current (µA)
  - Primary beam filters

Modulation of X-rays – volts, current, filters
Range of measurable X-rays (HH-XRF)

Typical

- Mg-Kα (1.254 keV)
  - medium, detector dependent
- Ba-Kα (32.196 keV)



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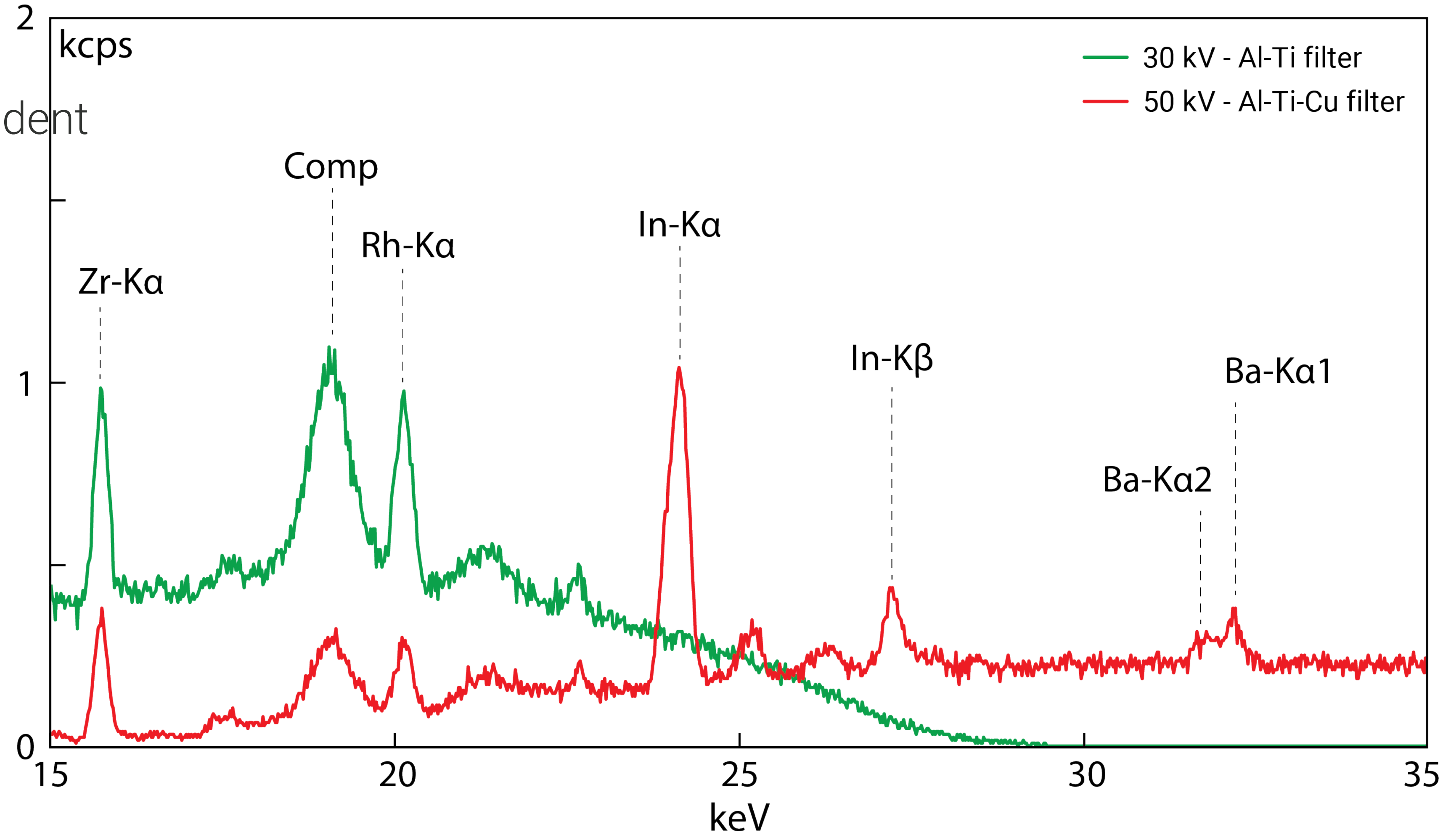

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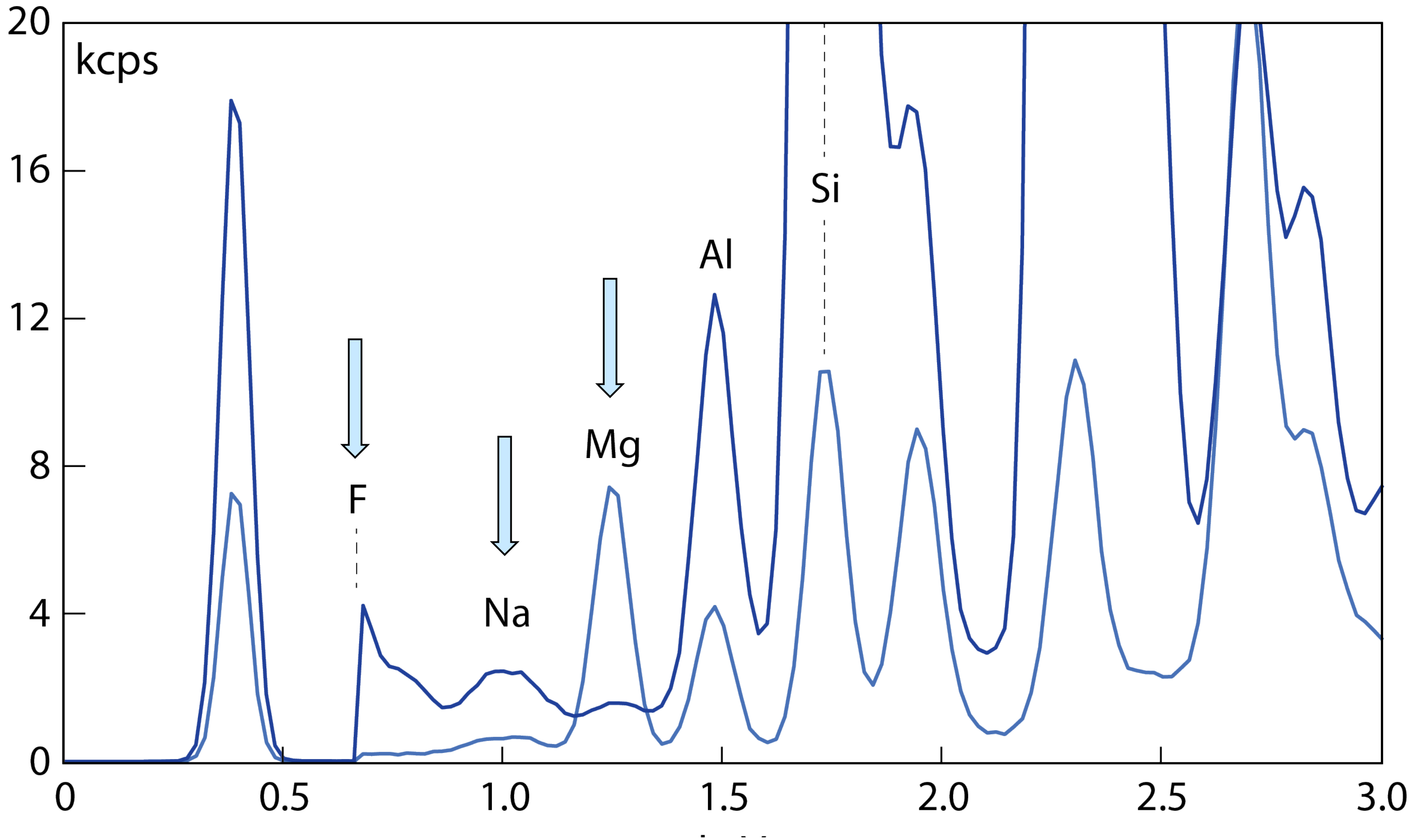
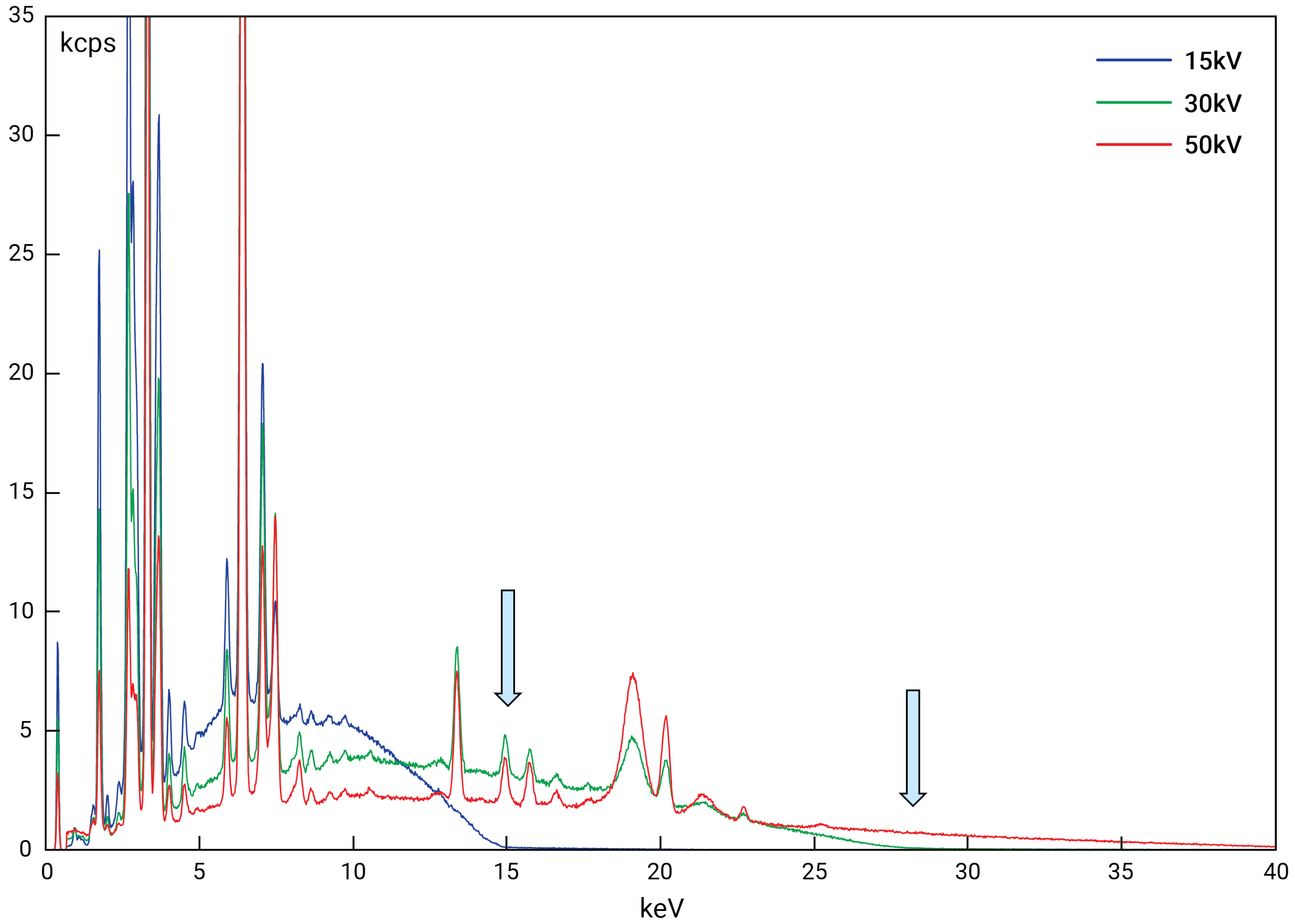
Possible

- Na-Kα (1.040 keV)
- F-Kα (0.677 keV)
  - *Requires enhanced transmission using He-flush +/- graphene detector)*
- The biggest limiting factor is escape depth from sample for these low energies



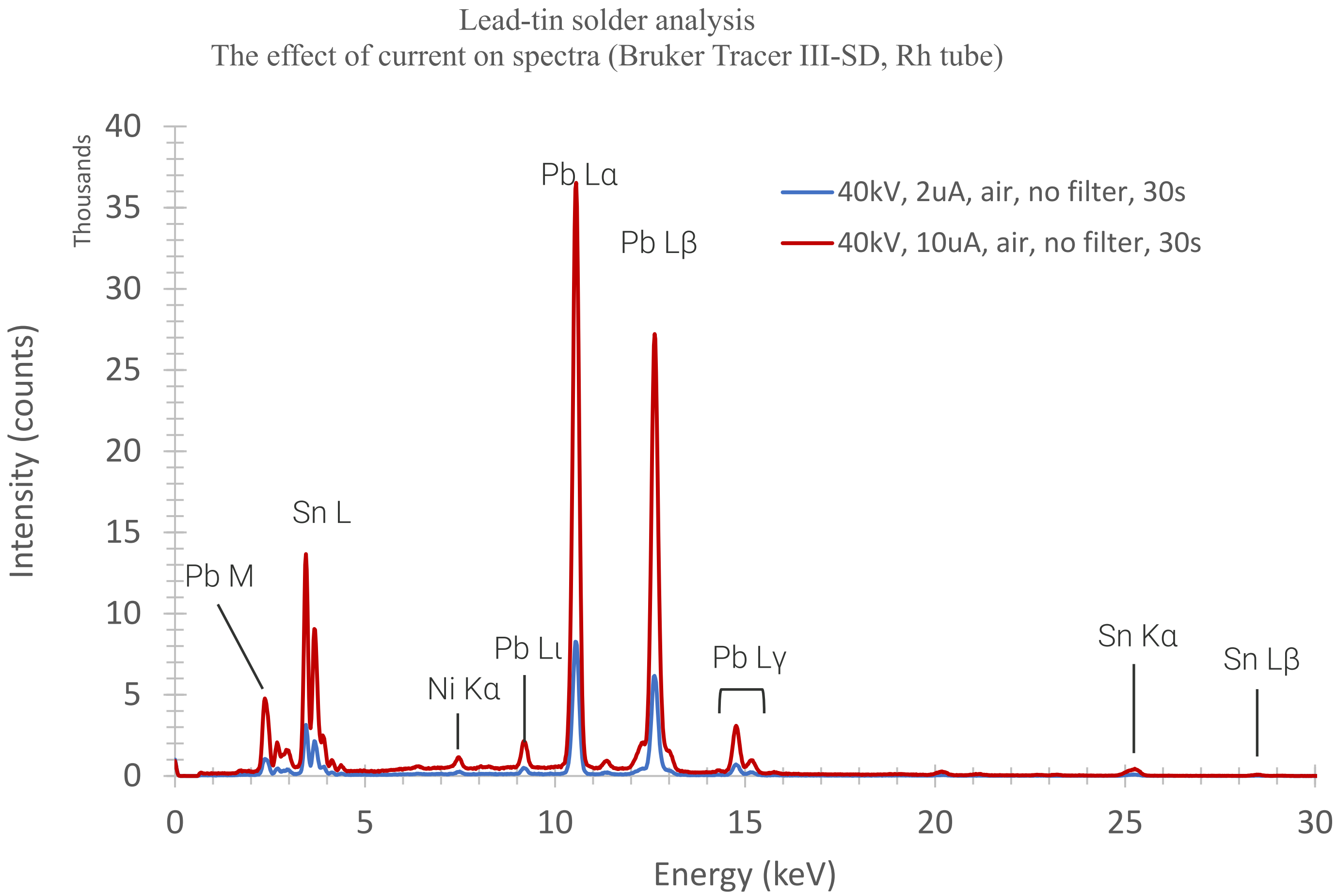
Modulation of X-rays – volts, current, filters
Using voltage to modulate excitation



- Voltage applied to the generation of X-rays influences
  - Ability to excite X-rays from different shells in atoms
  - Resulting shape of the X-ray continuum due to Bremsstrahlung

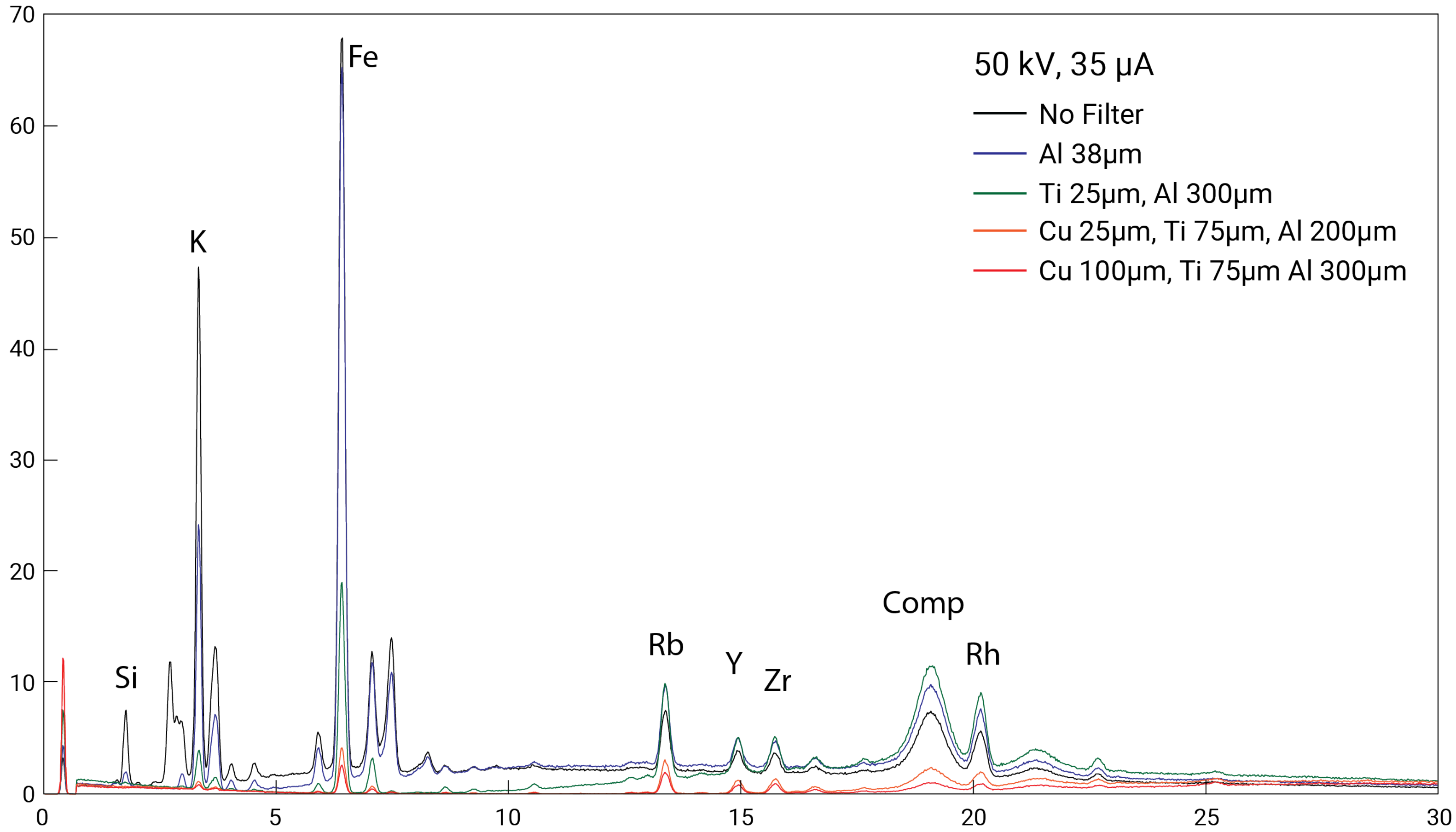
Modulation of X-rays – volts, current, filters
Using current to modulate excitation

- Current influences the number of photons that are generated from the sample
  - Higher current = higher counts
- Maximum current will depend on X-ray tube wattage
- Current used balances highest count rate without overwhelming the detector (deadtime)



Modulation of X-rays – volts, current, filters
Using filters to modulate excitation

- Filters – thin metal sheets placed between the primary beam and the sample
  - Influence the energy "shape" of the primary beam by attenuating lower energy X-rays
- Used to reduce
  - Local background
  - Diffraction peaks and other artifacts
  - Saturation of detector



HANDHELD XRF IN CULTURAL HERITAGE STUDIES

Back to basics in Handheld XRF
The spectrum: Detection of X-rays, artifacts

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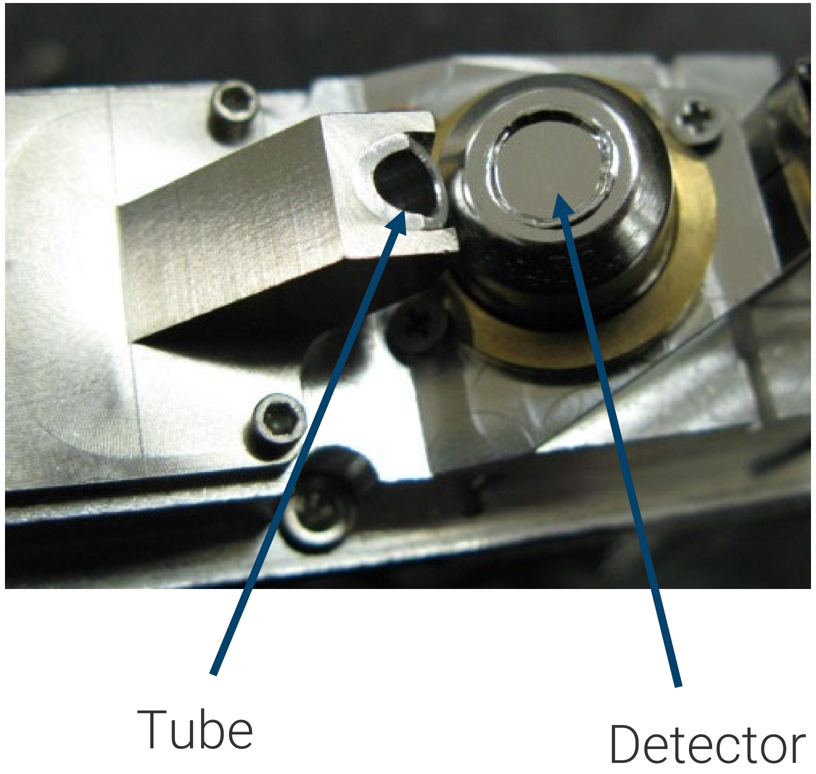
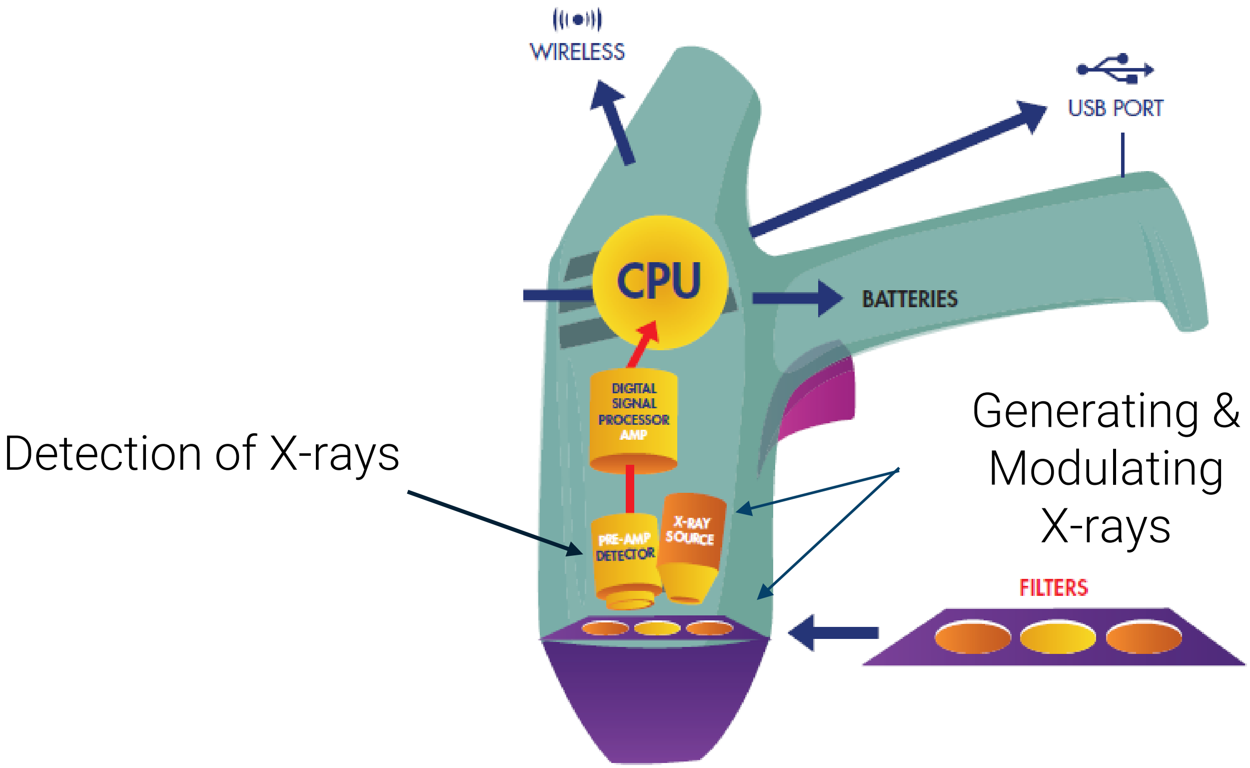
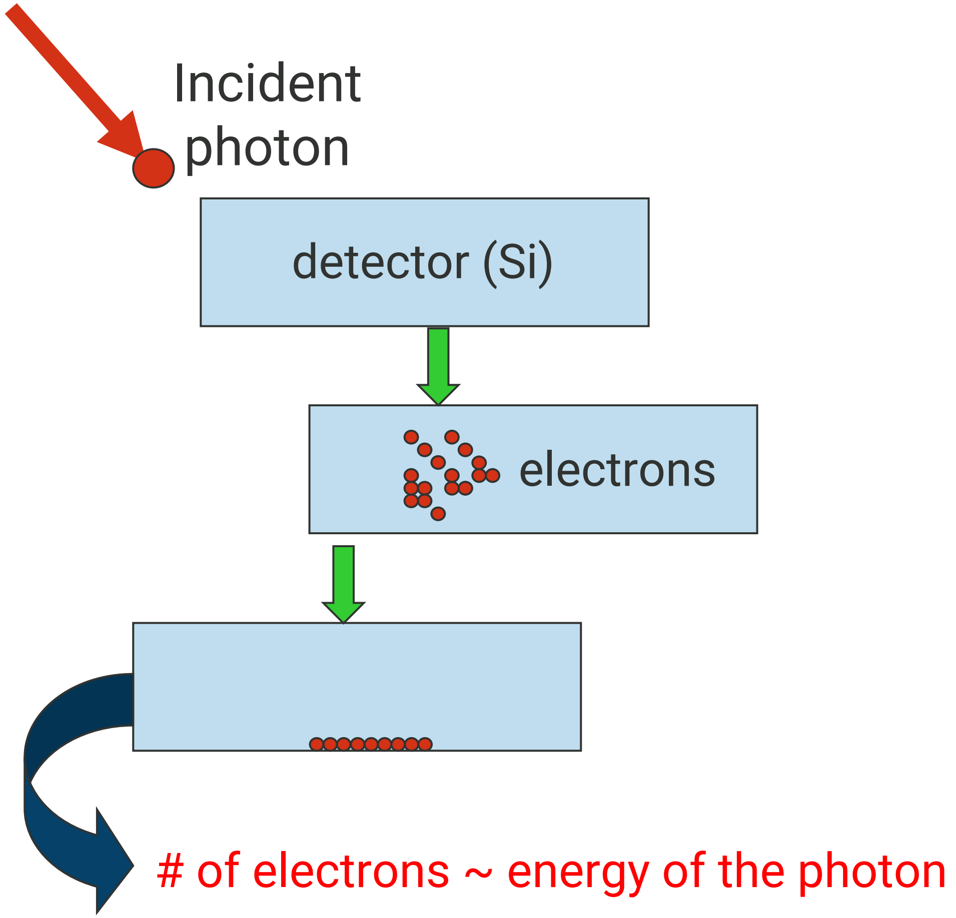
The spectrum: Detection of X-rays, artifacts
The X-ray detector

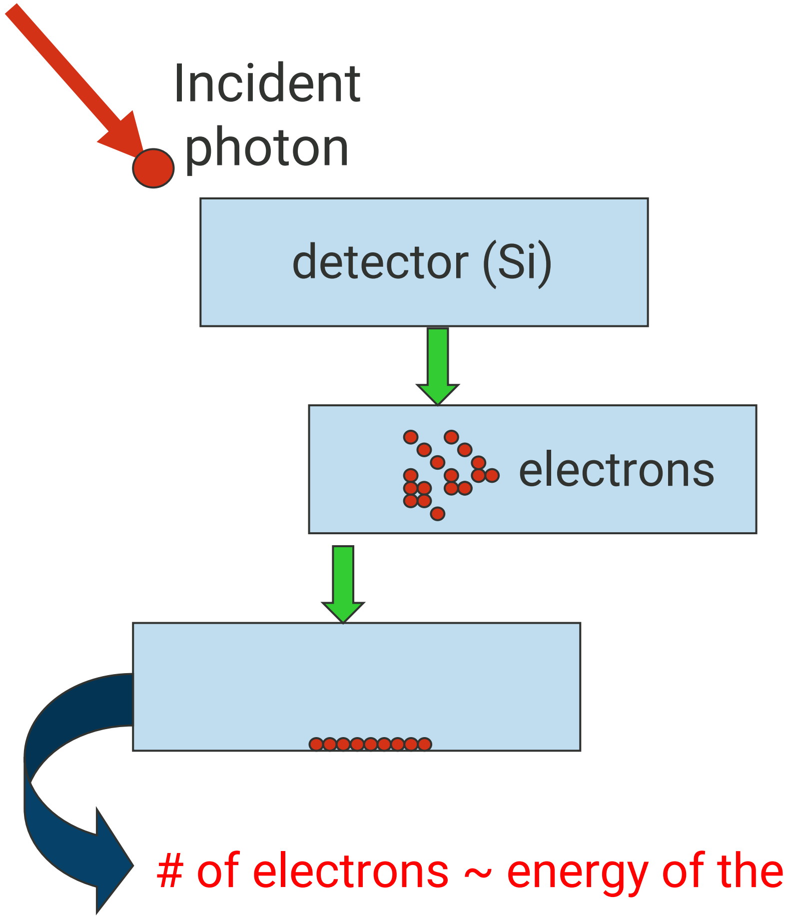




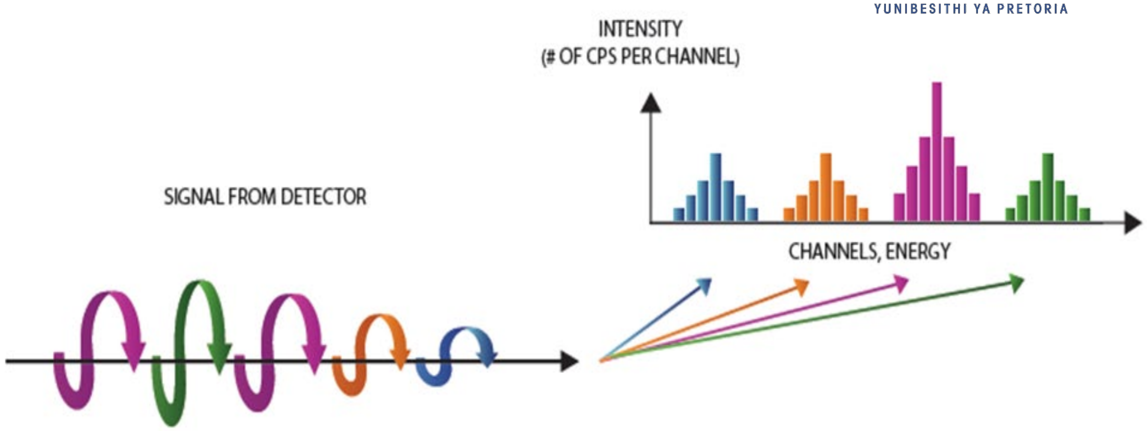
The spectrum: Detection of X-rays, artifacts
The X-ray detector



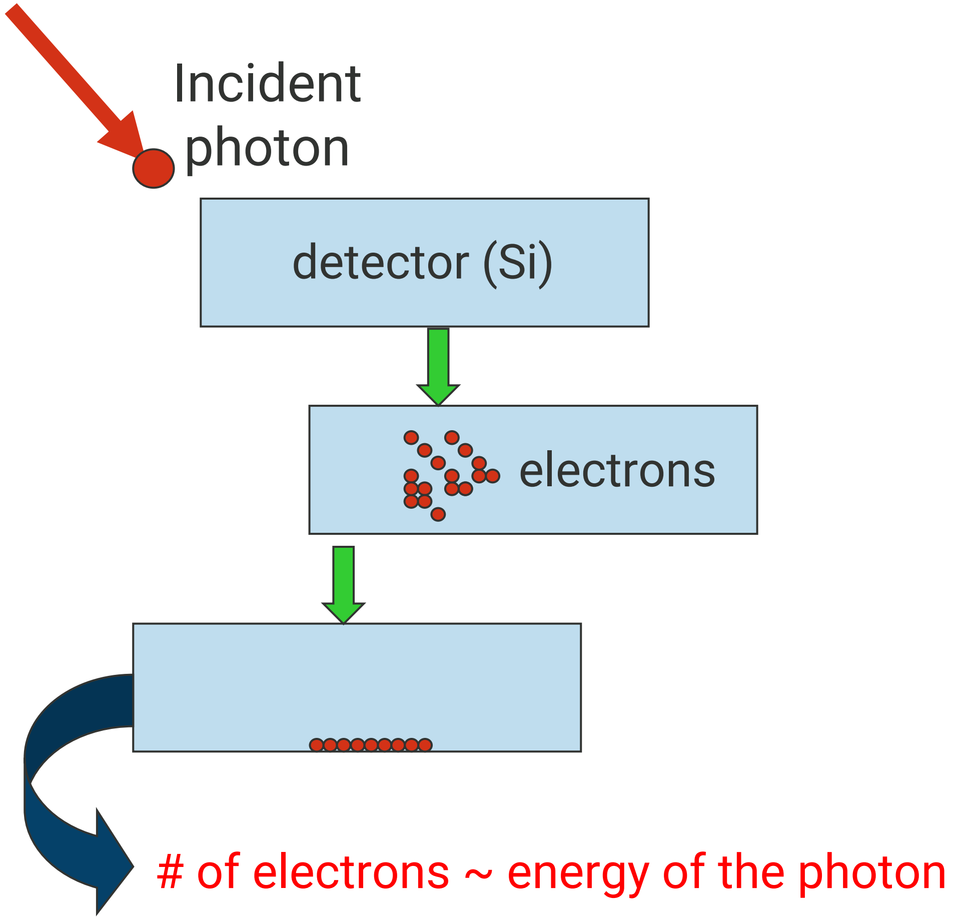
The spectrum: Detection of X-rays, artifacts
The X-ray detector

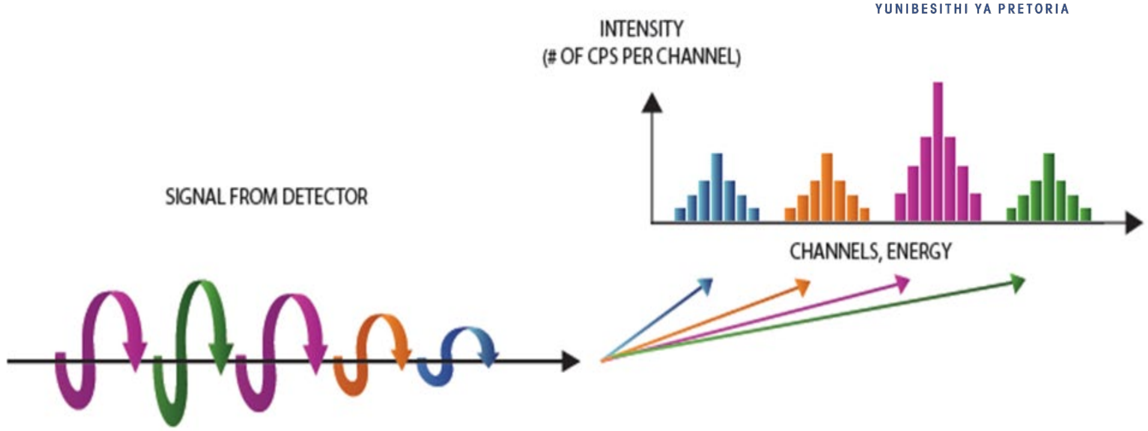


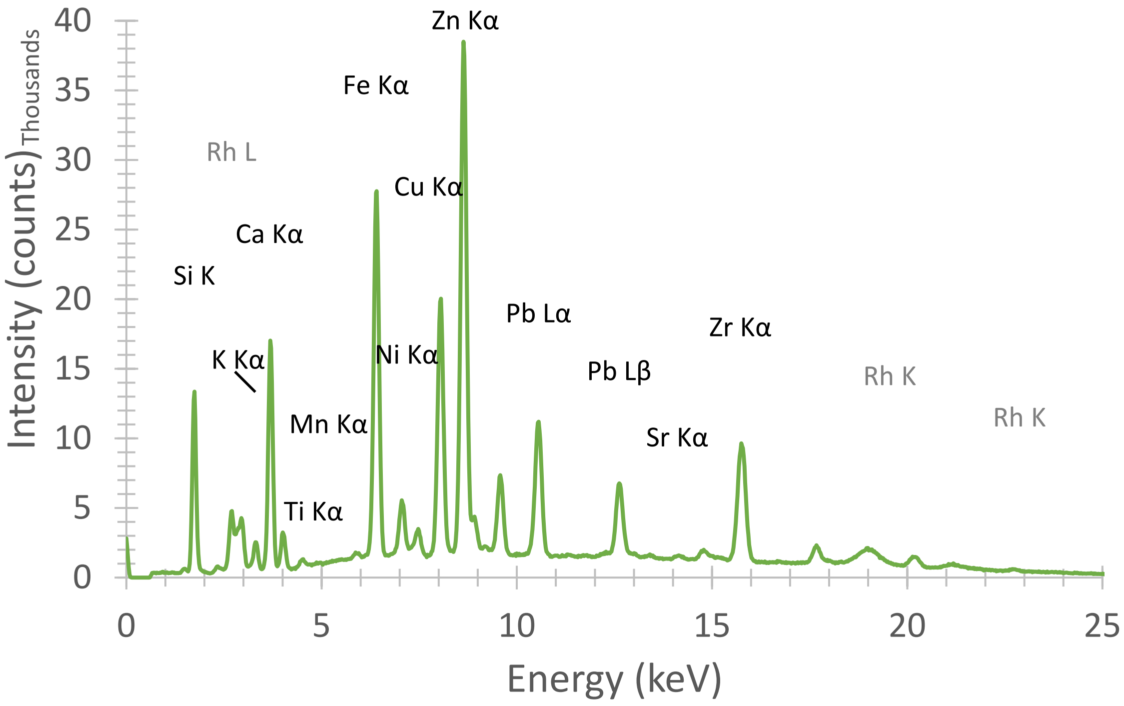
# of electrons ~ energy of the photon



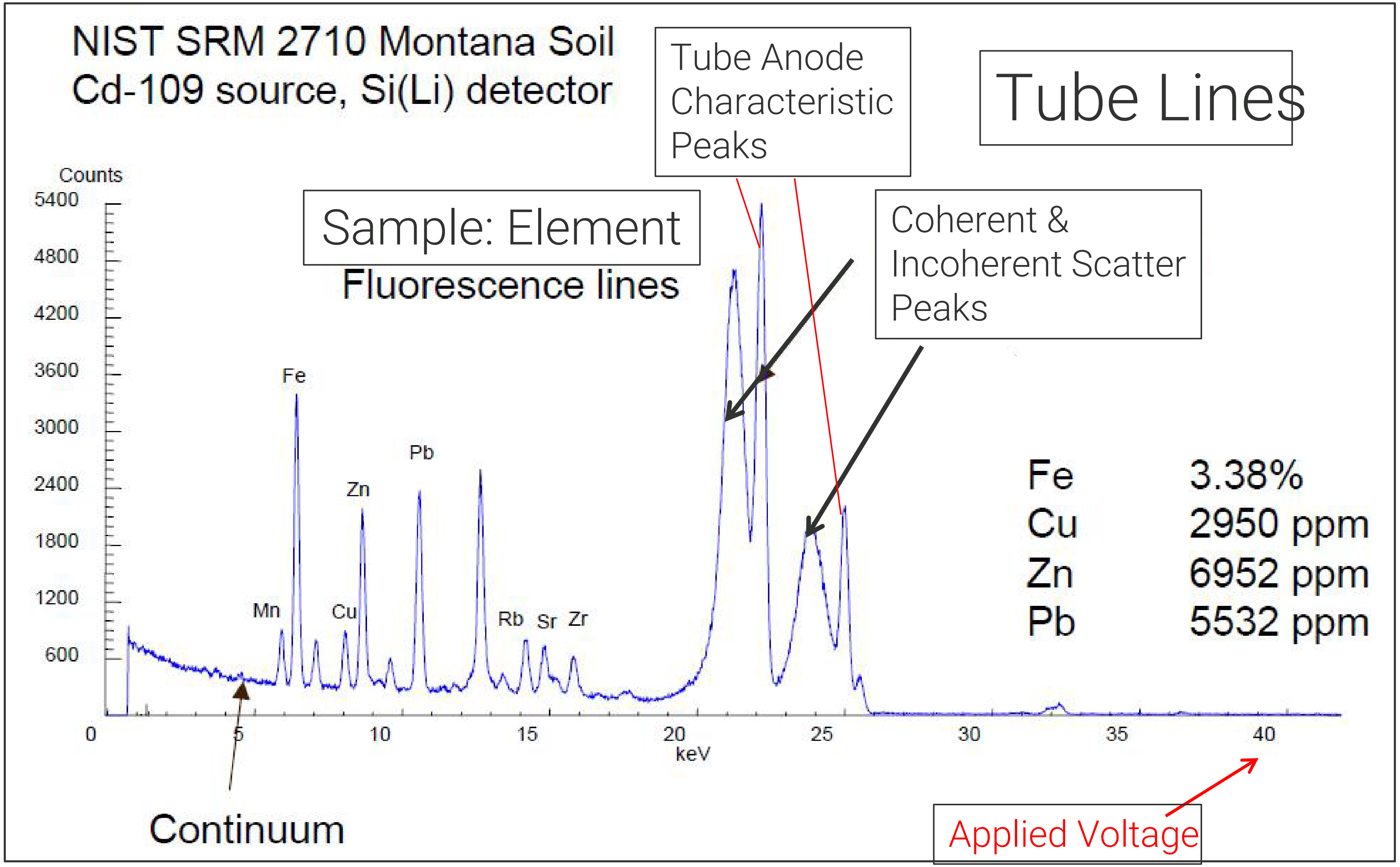
The spectrum: Detection of X-rays, artifacts
The X-ray detector







The spectrum: Detection of X-rays, artifacts
The spectrum we see



The spectrum: Detection of X-rays, artifacts
Artifacts in detection

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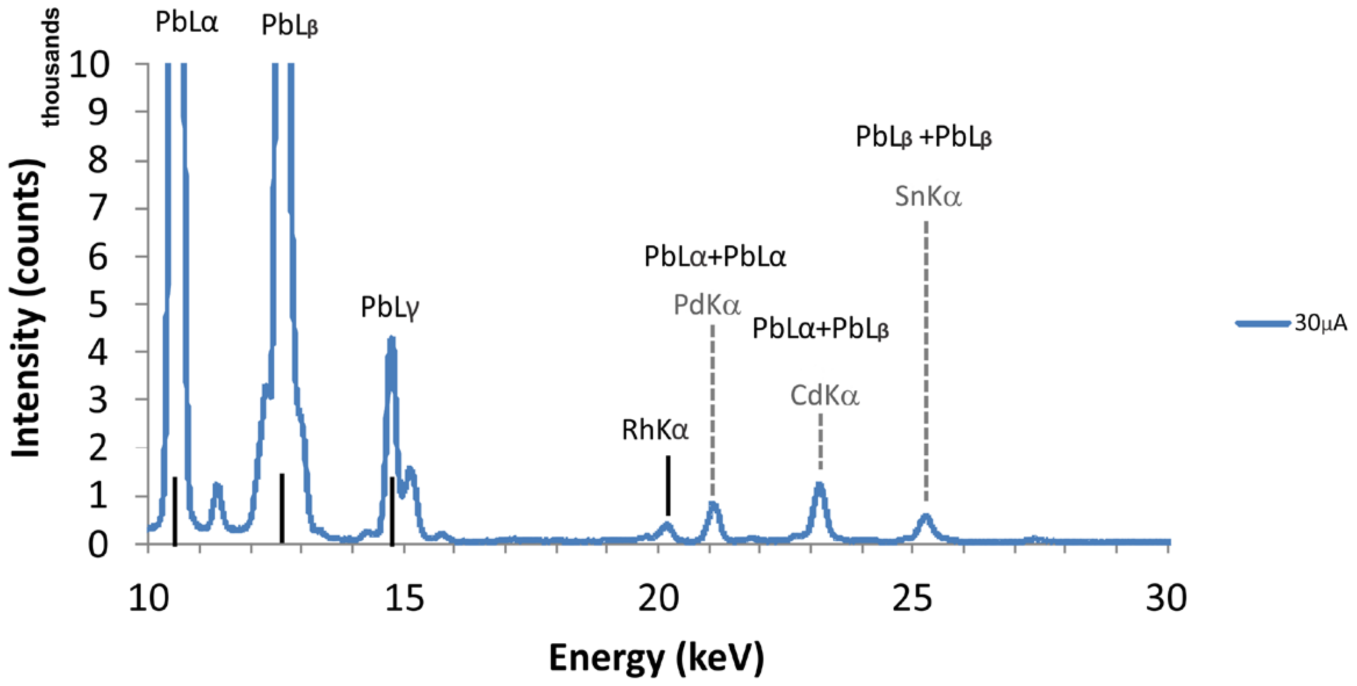
Sum peaks

- Occur at very-high count rates when multiple photons reach the detector closer together in time than can be separated by the processing electronics
  - e.g., two photons hit the detector simultaneously
  - puts out a voltage pulse proportional to the sum of the energy from both photons

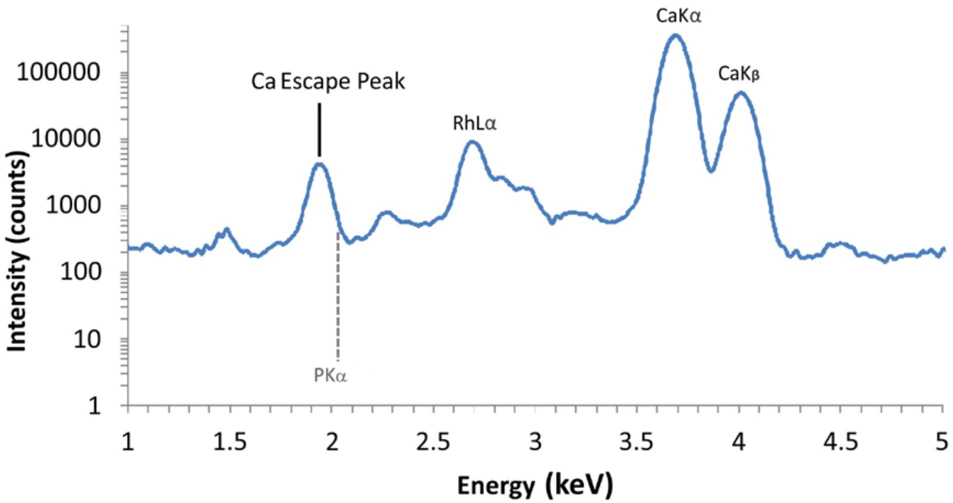


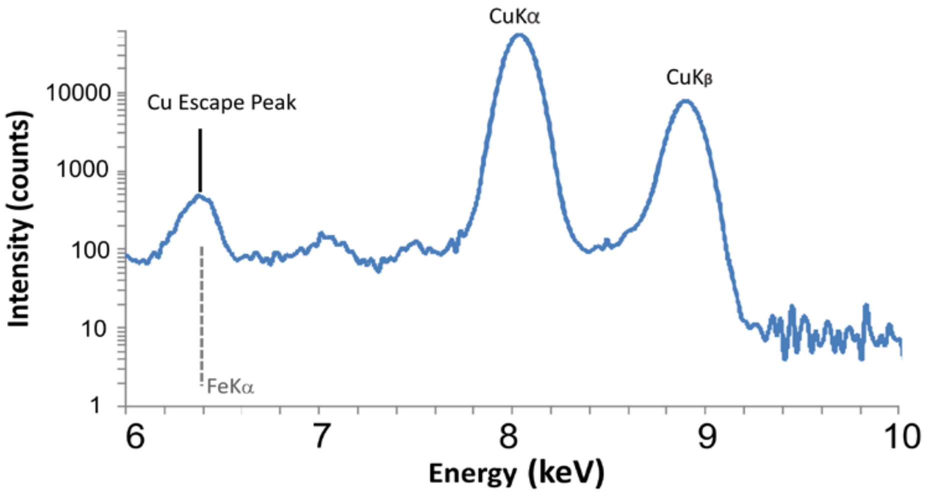
Element	Sum Peaks	Energy (keV)	Coincidence Peak (keV)	
Pb L lines	Pb Lα + Pb Lα	21.10	Pd Kα	21.19
	Pb Lα + Pb Lβ	23.16	Cd Kα	23.16
	Pb Lβ + Pb Lβ	25.27	Sn Kα	26.25

The spectrum: Detection of X-rays, artifacts
Artifacts in detection

Escape peaks

- When fluorescent X-rays from a sample hit the Si atoms in the detector
  - Si Kα fluorescence photon is generated if the X-rays have an energy greater than the excitation potential of Si (1.84 keV)
- Si Kα photon may be reabsorbed by the detector. Occasionally, it "escapes."
  - the energy of the incoming X-ray photon is reduced by the amount of energy lost to the escaped Si Kα photon (1.74 keV)
  - Ca Kα (3.69 keV) would have an escape peak at 3.69–1.74 = 1.95 keV





The spectrum: Detection of X-rays, artifacts
Overlapping peaks in the spectrum

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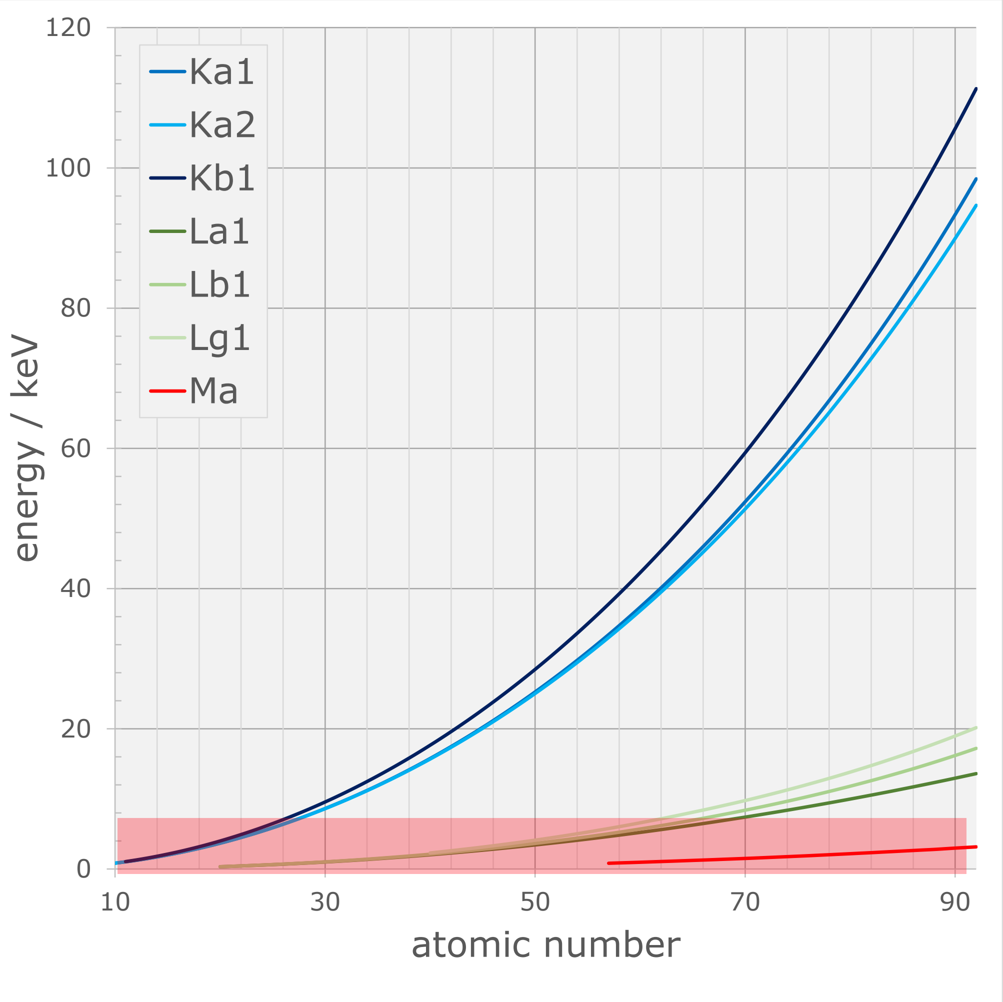
- Overlaps are present whether we like it or not!
  - Close spacing of X-ray lines at low energies (Moseley's law)
  - Similar energies from different X-ray lines

	Kα	Kβ		Lα	Lβ		Mα	Mβ
S	2.309	2.465	Mo	2.292	2.394	Pb	2.342	2.444
Ti	4.512	4.933	Ba	4.466	4.828			
V	4.953	5.428						
As	10.543	11.726	Pb	10.551	12.614			



- Strategies
  - Chose appropriate X-ray lines (e.g., Kb over Ka)
  - Deconvolution

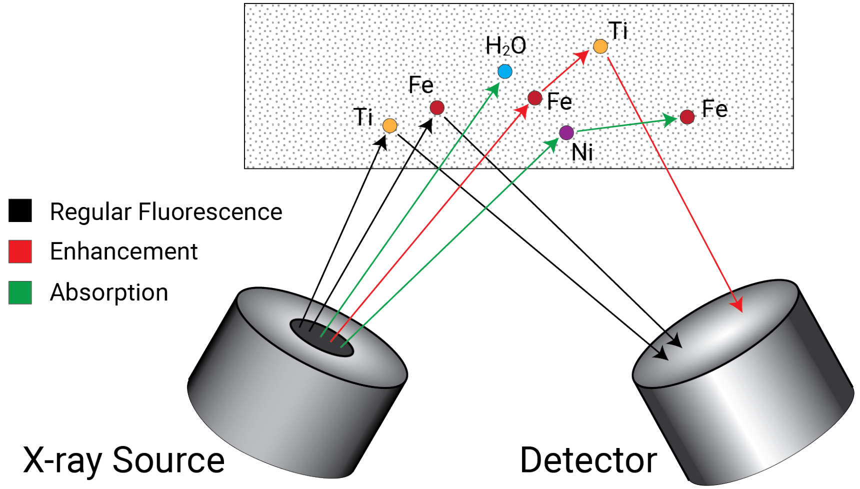
HANDHELD XRF IN CULTURAL HERITAGE STUDIES

Back to basics in Handheld XRF

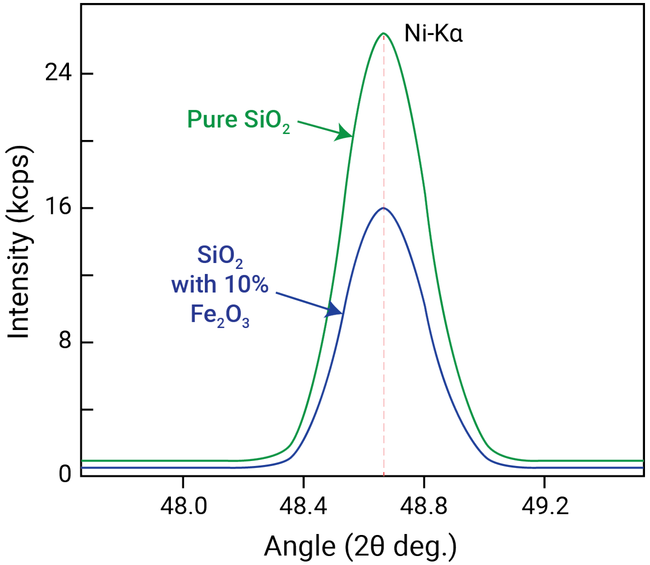
Other contributions to the result

Other contributions to the result
Matrix effects

- Relative intensity across the spectrum is subject to the sample matrix
  - i.e., what happens to the excited photon while it travels out of the sample to the detector.
    - Inter-element effects
    - Absorption
    - Enhancement



Matrix	Ni-Kα (kcps)	Mass Absorp. Coeff. (λ cm^2/g)
SiO_2	26.46	37.55
10% Fe_2O_3 90% SiO_2	16.05	58.63



Other contributions to the result
Non-matrix factors

- **Sample thickness**
- **Surface topography and the impact of an air-gap**
- **Feature size**
- Moisture
- Sample cups - films
- Chemical effects
- Mineralogical effects

Other contributions to the result
Non-matrix factors

- **Sample thickness**
- Surface topography and the impact of an air-gap
- Feature size
- Moisture
- Sample cups - films
- Chemical effects
- Mineralogical effects

- What is my sampling depth using XRF?
  - Penetration Depth - how deep do primary X-rays transmit into the sample?
    - kV /mA (excitation potential of anode of X-ray tube)
    - density of the sample
  - Escape (Information) Depth - from how deep in the sample is X-ray fluorescence can be detected?
    - energy of the fluorescence radiation
    - composition / density of the sample
      - *depth within the sample from which up to 99% (or 99.9%) of the signal for an element from an infinitely thick sample can be obtained*

Other contributions to the result
Non-matrix factors

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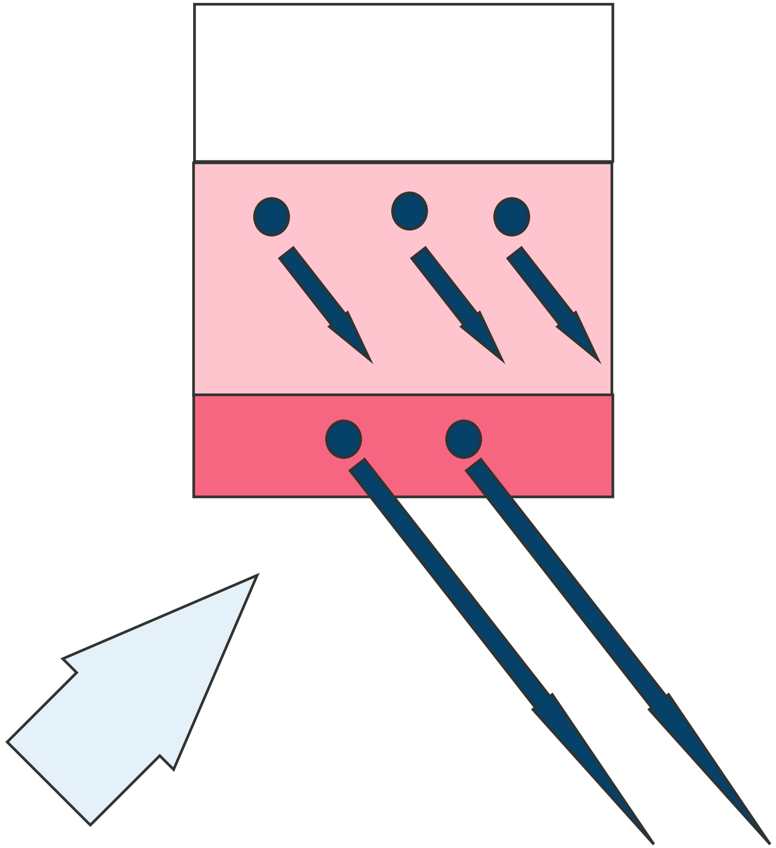

For infinitely thick samples

- No excitation of the inner parts of the sample
- An intermediate part can be excited, but the fluorescence radiation is absorbed within the sample
- The detectable fluorescence radiation comes from the parts close to the surface

Other contributions to the result
Non-matrix factors

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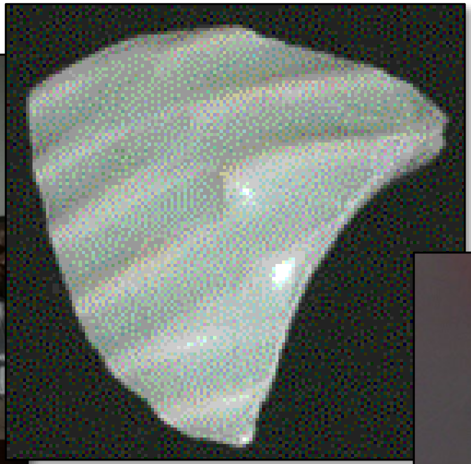
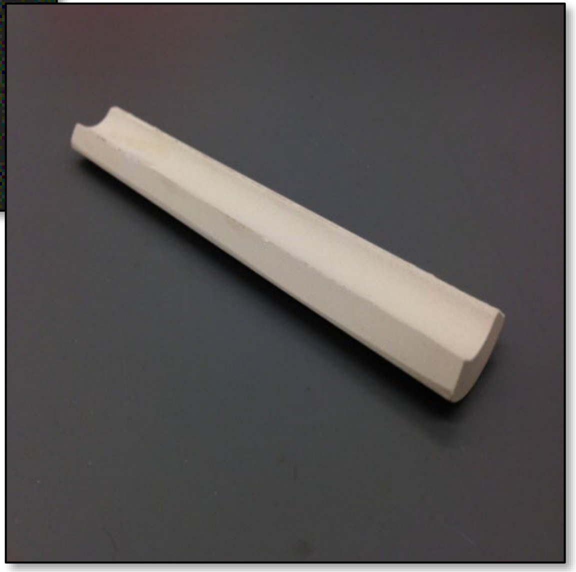
- Sample thickness
- **Surface topography and the impact of an air-gap**
- Feature size
- Moisture
- Sample cups - films
- Chemical effects
- Mineralogical effects

- Air Gap
  - Pronounced topography on the sample surface increases the distance between the sample and detector

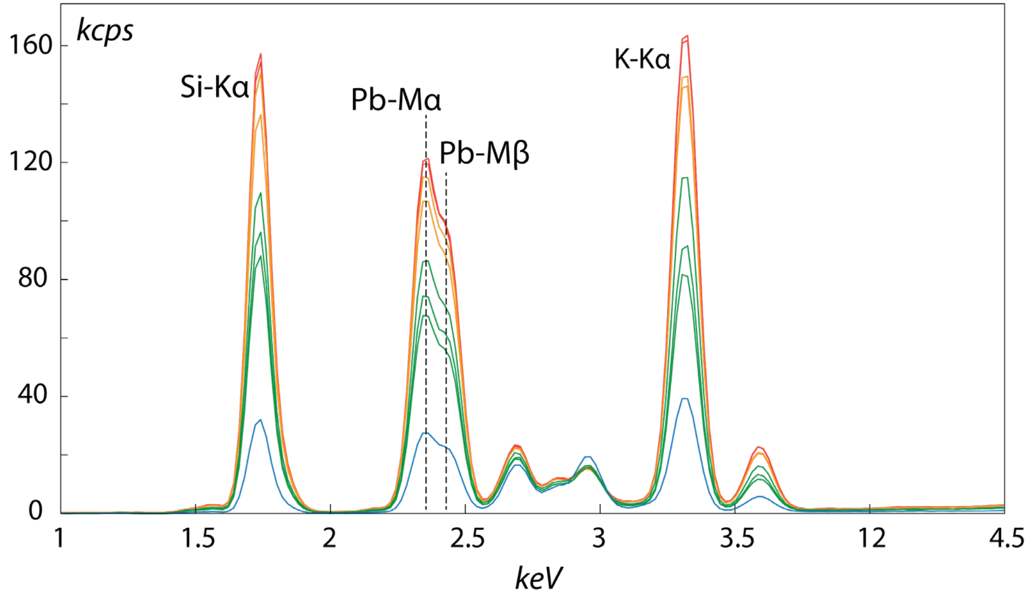


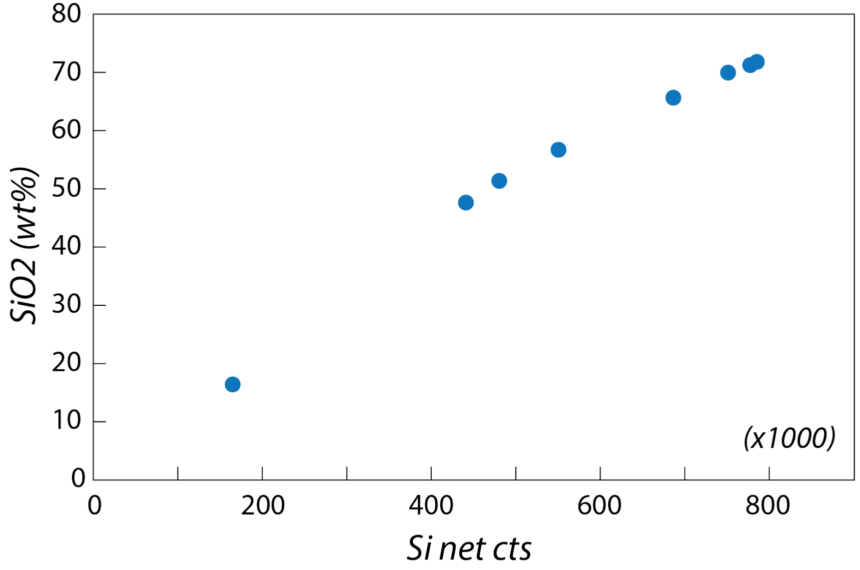


Other contributions to the result
Non-matrix factors

- Sample thickness
- **Surface topography and the impact of an air-gap**
- Feature size
- Moisture
- Sample cups - films
- Chemical effects
- Mineralogical effects

- Air Gap

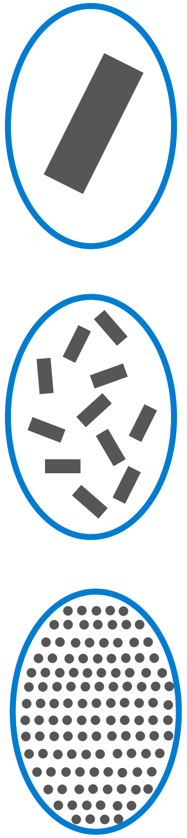




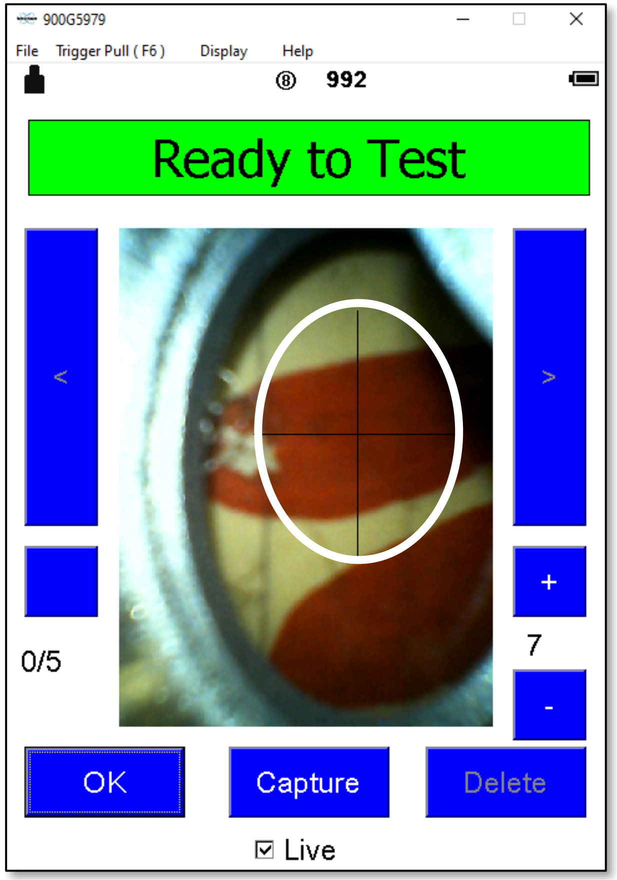
Other contributions to the result
Non-matrix factors

- Sample thickness
- Surface topography and the impact of an air-gap
- **Feature size**
- Moisture
- Sample cups - films
- Chemical effects
- Mineralogical effects

- Beam size vs Analytical target



8mm collimator



Painted wood fishing lure
(Indiana State Museum Collection)

Handheld XRF in Cultural Heritage Studies
Summary

- For handheld XRF - a point and shoot technique will not result in meaningful information

- Measurements taken without thought to the underlying technique will result in weak results, or at worst, erroneous data

- Understanding of the instrument, how it operates, and how it interacts with the sample creates a powerful approach to investigation of cultural heritage materials

To learn more about practical usage of HH-XRF in cultural heritage work

Download from the Getty website here:

https://gty.art/3a7Mjaa

Innovation with Integrity