Overview of X-Ray Fluorescence Analysis

AMPTEK, INC.
14 Deangelo Drive, Bedford, MA 01730
Ph: +1 781 275 2242 Fax: +1 781 275 3470
sales@amptek.com www.amptek.com

Amptek Inc.
14 Deangelo Drive
Bedford, MA 01730 USA
www.amptek.com

What is X-Ray Fluorescence (XRF)?

- A physical process:

  Emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by high-energy X-rays or gamma rays.

- A technique in analytical chemistry:

  Method to identify elements in a sample and measure their concentrations

  Non-destructive, quick, and simple to carry out.

Physical Process

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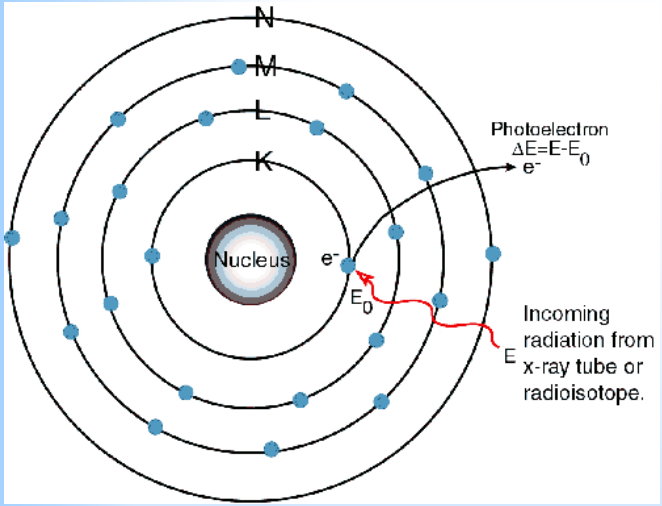

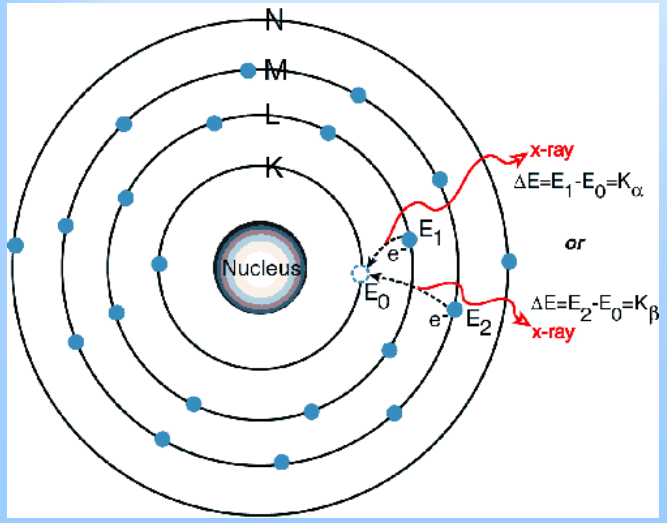

- Incoming radiation hits an atom
- Ejects an electron from an inner shell, creating a vacancy
- An electron from an outer shell "drops down" to fill the vacancy.
- The excited atom emits an X-ray with energy equal to the difference between the levels

$$E_{Xray} = \Delta E = E_K - E_L$$

- Since each element has a unique set of levels, it produces a unique set of "characteristic" X-rays

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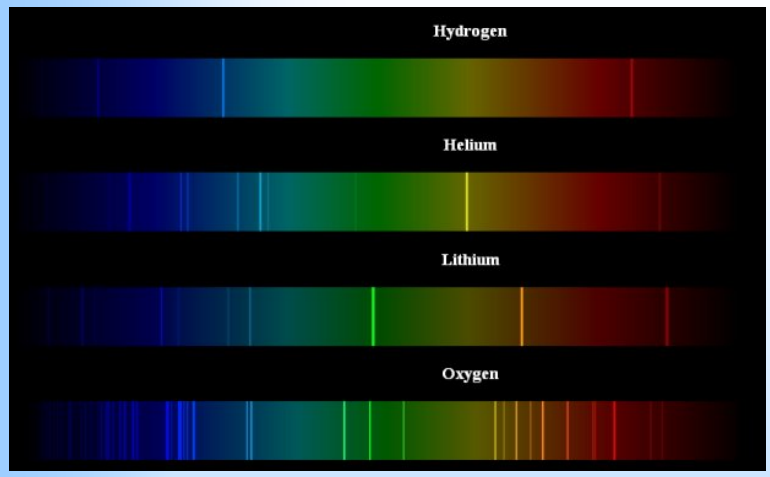

		Fe	Ni	Cu	Zn	Pb
Atomic Levels						
K	1s	7,112	8,333	8,979	9,659	88,005
L_1	2s	845	1,009	1,097	1,196	15,861
L_2	$2p_{1/2}$	720	870	952	1,045	15,200
L_3	$2p_{3/2}$	707	853	933	1,022	13,035
M_1	3s	91	111	122	140	3,851
M_2	$3p_{1/2}$	53	68	77	91	3,554
M_3	$3p_{3/2}$	53	66	75	89	3,066
Characteristic X-Ray Lines						
$K_{\alpha 1}$	$K - L_3$	6,404	7,478	8,048	8,639	74,969
$K_{\alpha 2}$	$K - L_2$	6,391	7,461	8,028	8,616	72,804
$K_{\beta 1}$	$K - M_3$	7,058	8,265	8,905	8,572	84,936
$L_{\alpha 1}$	$L_3 - M_5$	705	852	930	1,012	10,552
$L_{\alpha 2}$	$L_3 - M_4$	705	852	930	1,012	10,450
$L_{\beta 1}$	$L_2 - M_4$	718	869	950	1,035	12,614

- XRF is similar to optical spectroscopy but at higher energy
- Independent of chemical state → **Elemental analysis**

Measurement

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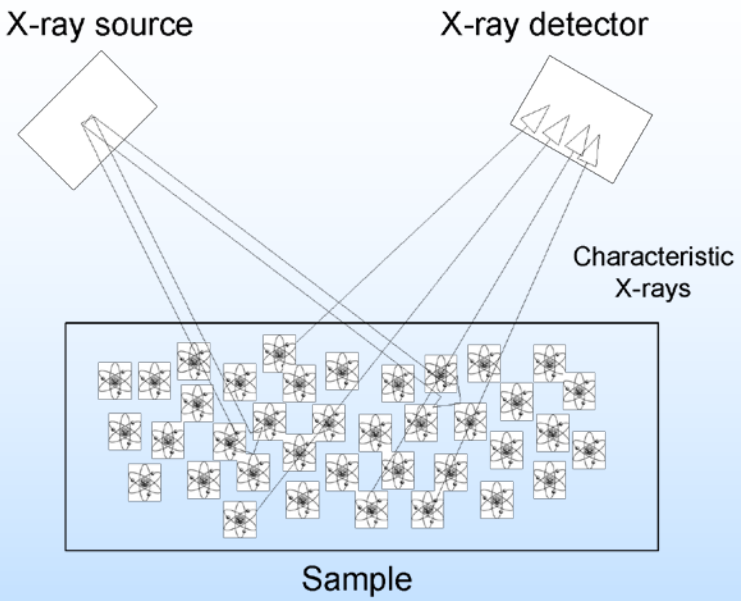

- Intensity of X-ray line proportional to number of atoms → **Quantitative**
- X-rays pass through surface into sample

→ **Nondestructive** and **no sample preparation** is necessary

Best accuracy requires sample preparation

→ **Bulk measurement** rather than only surface

Notion of "bulk" vs "surface" depends on the X-ray energy

Measurement

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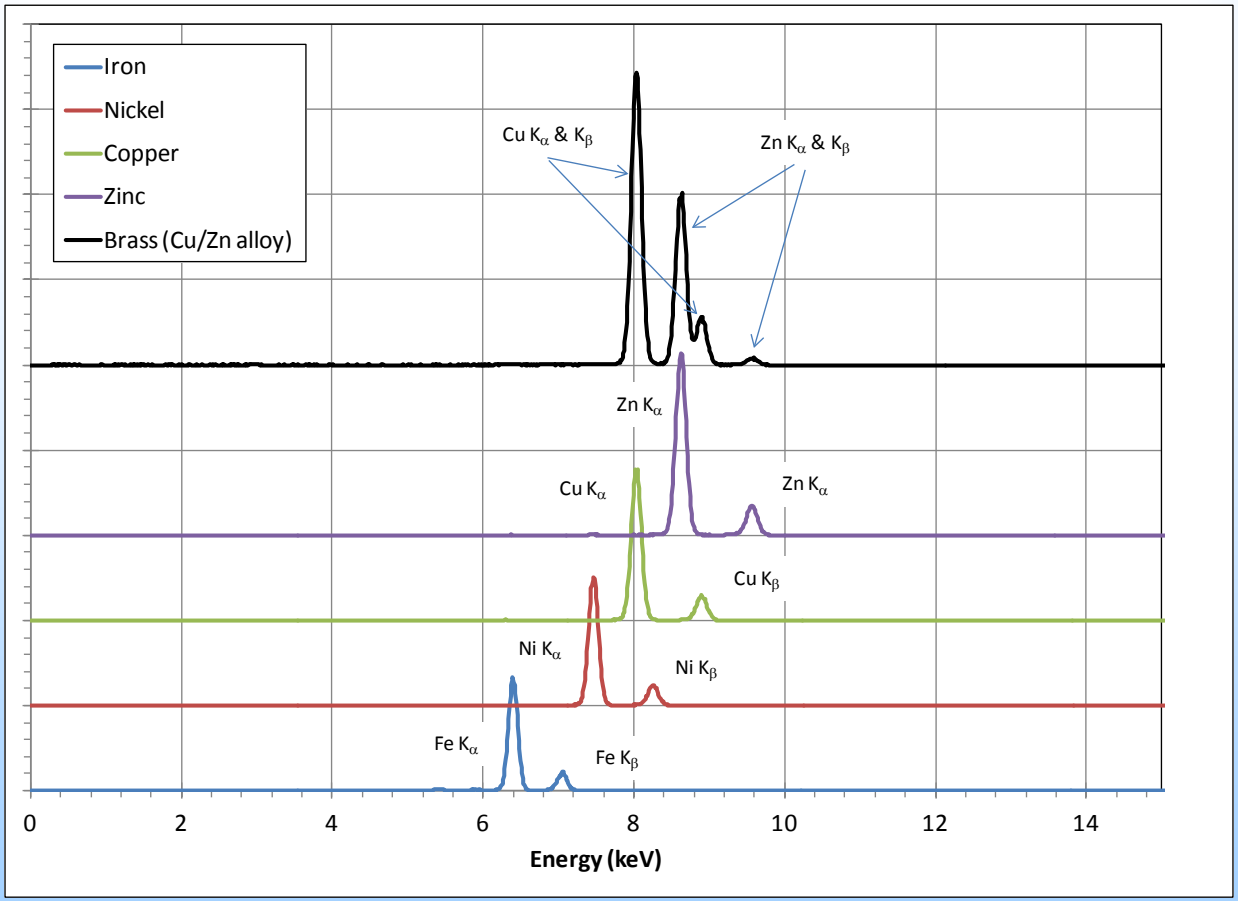

- Presence of Cu and Zn K lines → Elements are in sample (qualitative)
- Intensity of the lines → How much is in sample (quantitative)

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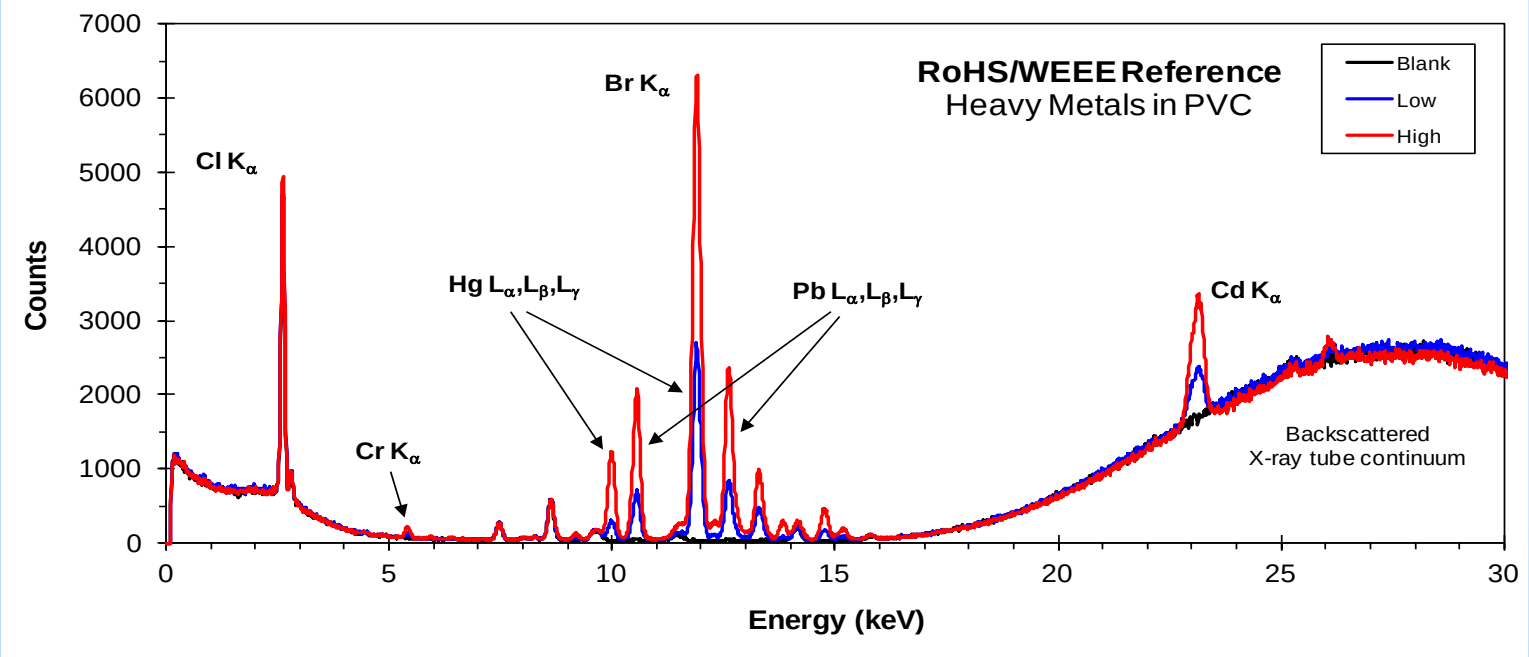

Typical spectrum and results

- Photopeak intensity varies with concentration
- Final result is quantitative concentration

		Certified	XRF
High	Cr	1000 ± 20	895 ± 198
	Br	1100 ± 22	1089 ± 23
	Cd	300 ± 6	264 ± 28
	Hg	1100 ± 22	1050 ± 53
	Pb	1200 ± 24	1184 ± 39
Low	Cr	401 ± 8	388 ± 167
	Br	500 ± 10	487 ± 13
	Cd	100 ± 5	68 ± 13
	Hg	200 ± 5	183 ± 27
	Pb	400 ± 8	398 ± 23
Blank	Cr	0 ± 5	7 ± 40
	Br	0 ± 5	1 ± 2
	Cd	0 ± 5	9 ± 10
	Hg	0 ± 5	0 ± 0
	Pb	0 ± 5	10 ± 9

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What are the main factors limiting XRF?

– Counting variance

- The measurement is based on count discrete X-rays
- Arise from random processes → Inherent statistical variation in number of X-rays
- Percent uncertainty = $1/\sqrt{N}$
  - 100 X-rays detected → 10% precision
  - 1,000 X-rays detected → 3% precision
  - 1,000,000 X-rays → 1000 ppm precision
- Good precision means many X-rays which means high count rates or long times

– Detector response

- Photopeak has some width
- There is always spectral background and overlapping peaks
- Ability to remove these depends on counting variance, energy resolution, and accuracy of software algorithms
- Better energy resolution helps but there are physical and practical limits

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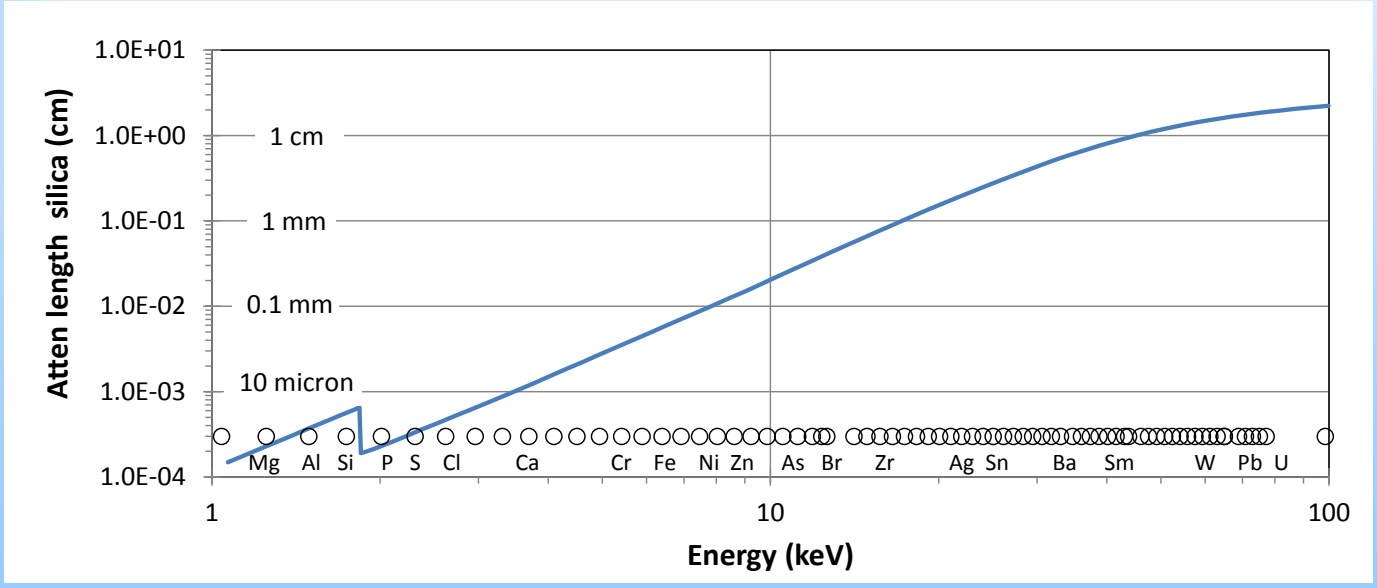
What are the main factors limiting XRF?

- **Attenuation lengths**
  - Penetration depth depends on energy & therefore element
    - In silica, Al X-rays go 3 μm while Sn go 3 mm
  - Response depends on energy/element
  - Sample condition & homogeneity are critical



Measurement FAQ

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- **How accurate is EDXRF?**
  - In the best case, relative accuracy ~ 0.2% (1.00% ± 20 ppm).
    Requires sample prep, a known matrix, good statistics, etc
  - Nondestructive screening, relative accuracy ~ 2% (1.00 ± 0.02%)
    Requires careful optimize and setup, known sample type
  - Quick check on unknown, relative accuracy ~20% (1.0 ± 0.2 %)

- **What is the detection limit for EDXRF?**
  - <1 ppm for prepared samples in a known matrix under good conditions
  - 10 ppm in nondestructive screening with no interfering elements
  - When elements interference or overlap, 1% of other element

- **What elements can be analyzed with EDXRF?**
  - Na to U (down to Be with EDS)
  - Low Z elements (below S) are a challenge
  - Need multiple measurements to cover a wide range of elements

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XRF is one of many methods used in material analysis

Advantages of XRF

- Non-destructive
- No sample preparation
- Fast (seconds to minutes)
- Good precision and accuracy
- Measure Na to U
- Suitable for portable equipment and field use

Disadvantages of XRF

- Limits of detection modest (10 ppm typical)
- Accuracy usually modest (few % relative)
- Difficult to use for lower Z elements

Best results require

- Sample preparation (damaging)
- System optimization
- Matched calibration standards

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XRF Applications

How is XRF used?

Hazardous Material Screening

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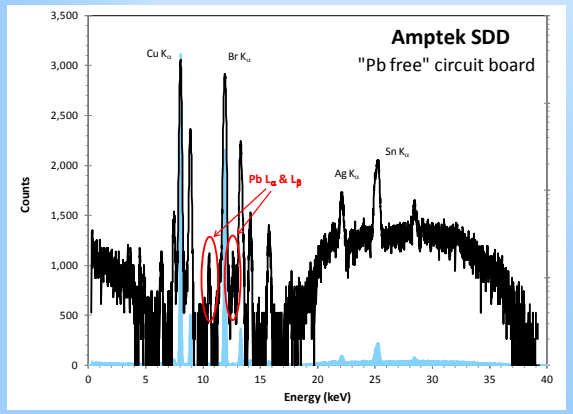
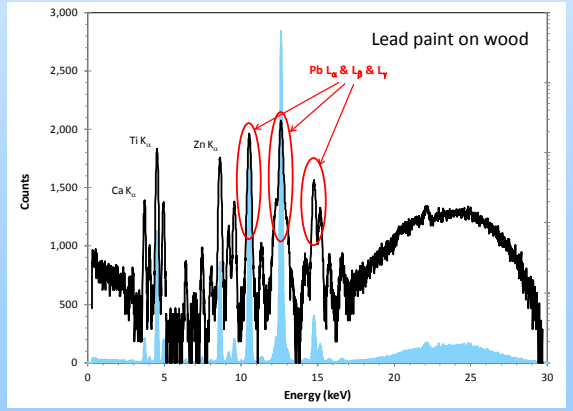
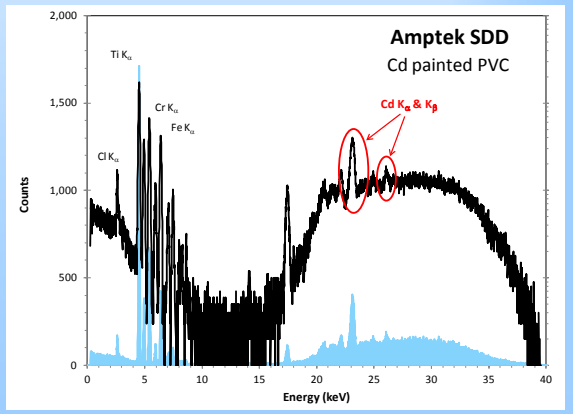
- Is there cadmium on this toy?
- Is there lead in this paint?
- Does this circuit board contain Pb, Cd, or Cr?
- **Nondestructive critical for screening products!**







Metal Alloy Analysis

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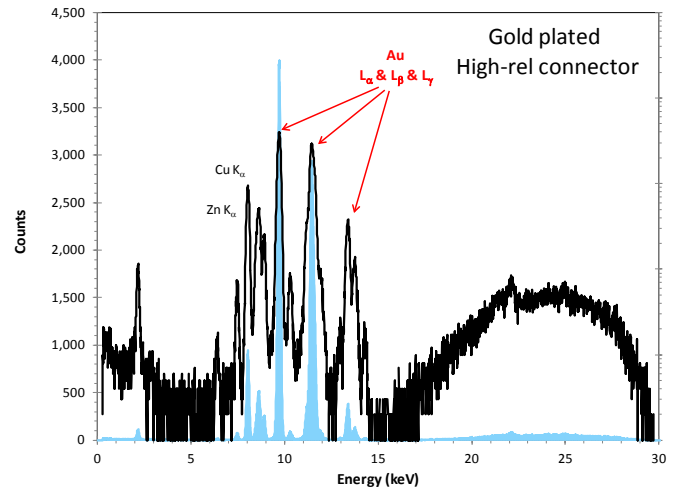
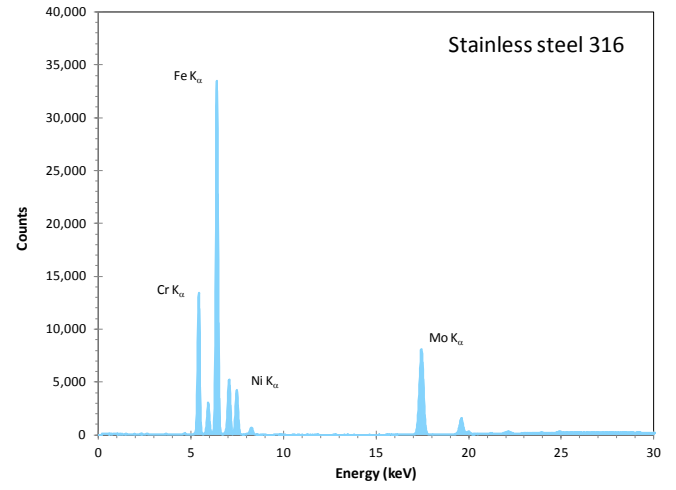
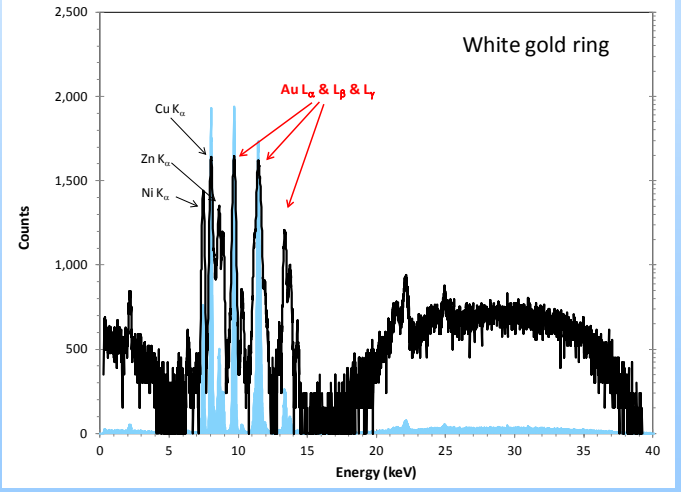
- Are these bolts stainless steel 316?
- Is there Ni in this scrap metal?
- Is there Cd plating on this MILSPEC connector?
- How much Au is in a white gold ring?
- **Speed critical, accuracy moderate**







Art and Archeology

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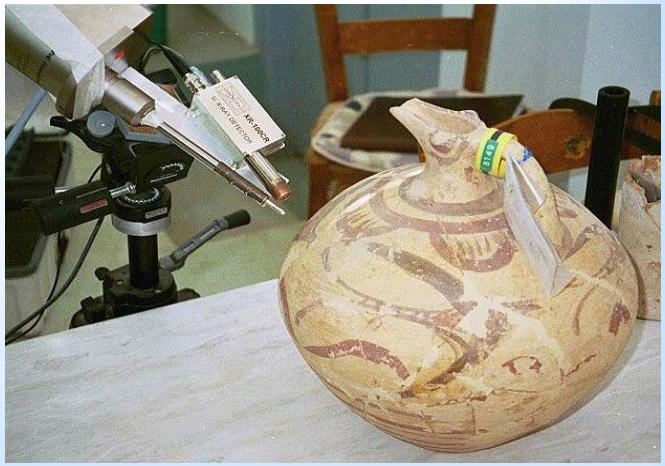
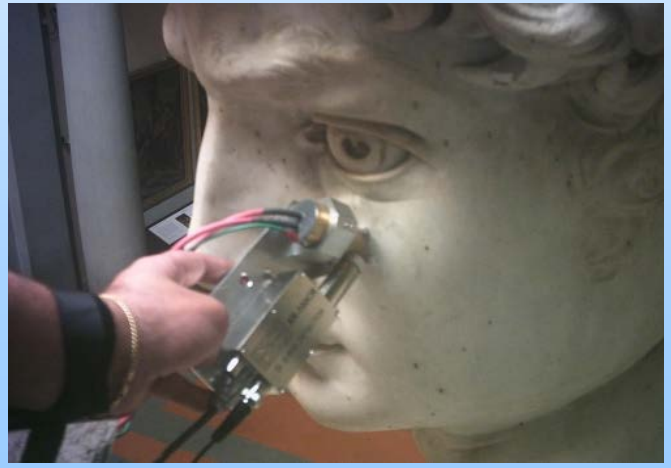
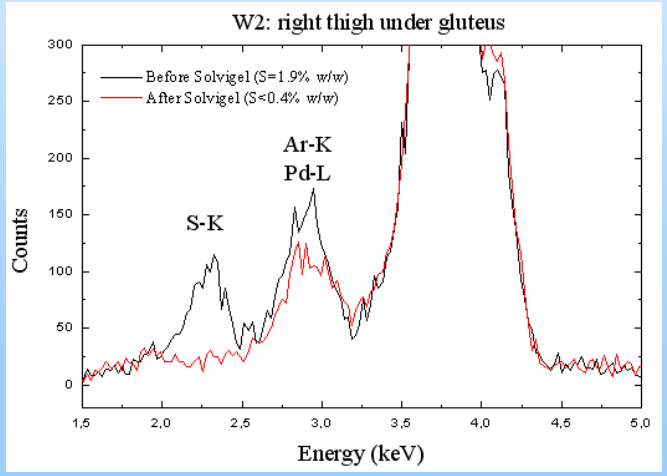
- How did the artist make their paints?
- Is this an ancient or a modern pigment?
- What is the effect of cleaning on the surface of a statue?

- **Nondestructive testing is vital for art!**







Process Control

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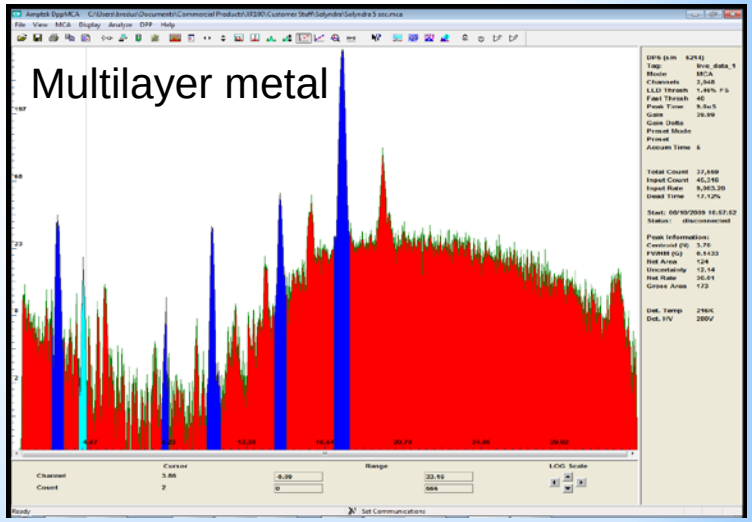
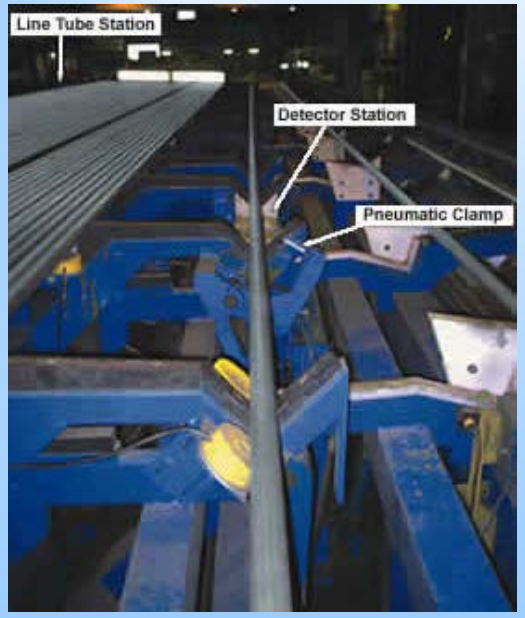
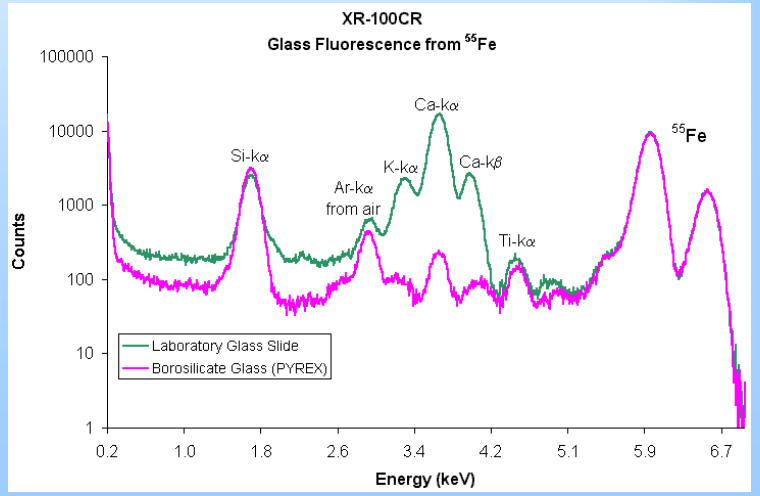
- Is there any change in spectrum?
- Absolute composition not needed but quick, real-time, non-destructive vital.







Field Measurements

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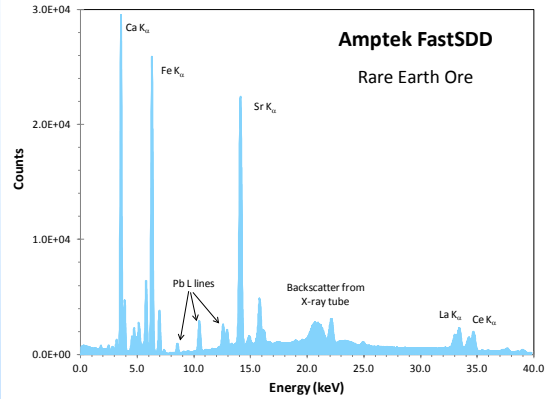
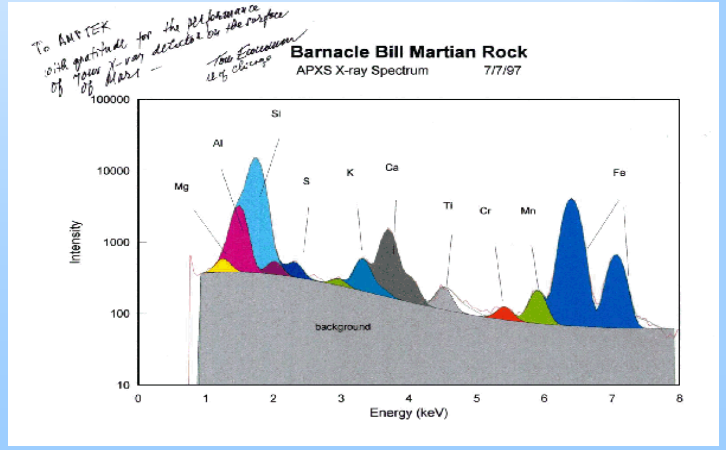
Measuring ores in mines.



Identifying minerals on Mars.

Measuring soil contamination



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Related Analytical Methods

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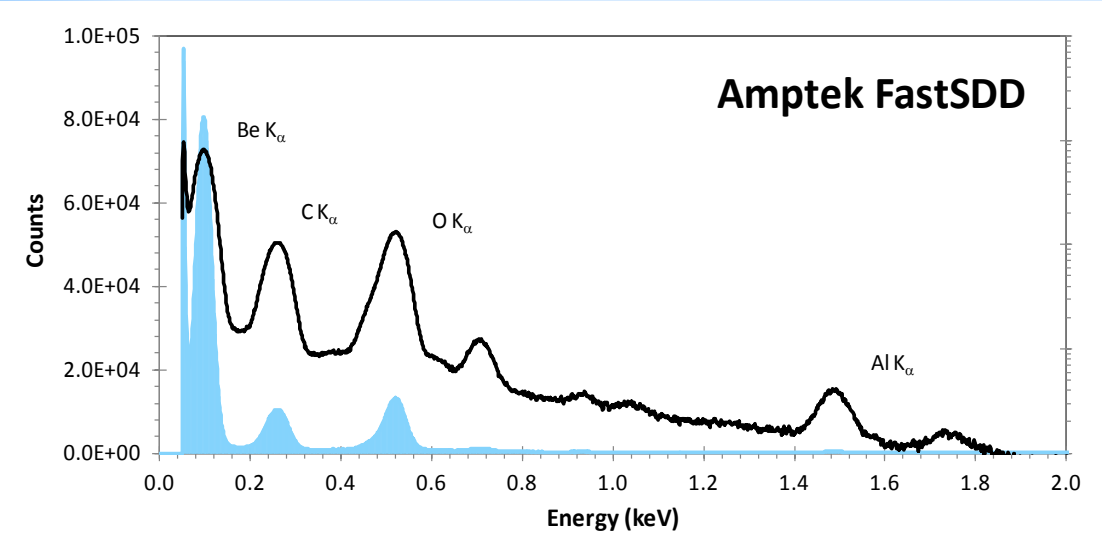
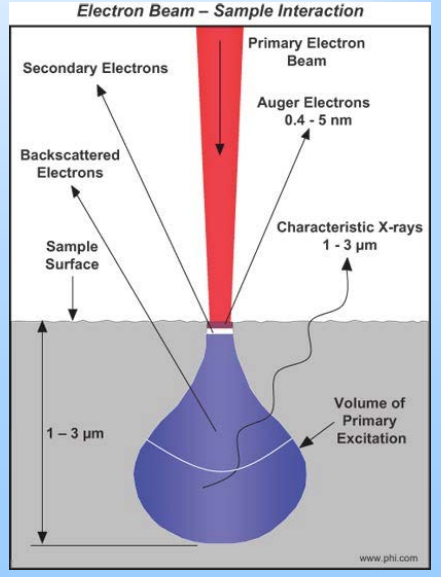
Energy Dispersive X-ray Spectroscopy

- a.k.a. EDS, EDX, XEDS, EDXA
  - Uses electron beam in vacuum chamber to excite the atoms
  - Electrons have short range in matter → Only way to measure lightest elements, down to Be (Z of 4)
  - High spatial resolution (75 um spatial, 1 um in depth)





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Wavelength Dispersive X-ray Spectroscopy (WDXRF)

- Crystal diffractometer disperses the X-ray wavelengths much like a prism disperses visible light.
- X-rays at a particular wavelength (energy) are recorded by a detector.
- It measures only one energy at a time; It obtains a spectrum by sweeping the wavelength over time

- Advantages of WDXRF
  - Much better energy resolution
  - Leads to much better accuracy and detection limits
- Disadvantage of WDXRF
  - Very long time to acquire whole spectrum
  - Requires destructive sample preparation

- Uses similar detectors and signal processors