XRF in Cultural Heritage

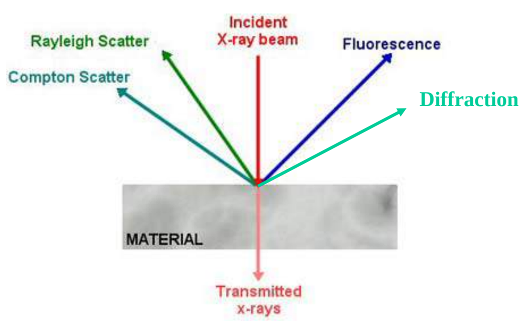
17 November 2016

Lynn Lee
Getty Conservation Institute

Overview

- Fundamentals of X-ray fluorescence spectrometry
- Qualitative analysis of EDXRF
  - Advantages and disadvantages
  - Handheld vs. micro-XRF vs. macro-XRF
- Tips and tricks
- Case studies

Interaction of X-rays with Material



XRF: Interpretation of Results

- Elemental composition
- Approximate relative concentration*

Limitations:
- No conclusive information on phase of analyte
- No conclusive information on oxidation state of analyte

*Nonhomogeneous samples with air-path XRF

Cabinet-based XRF vs. Air-path XRF

- Major element analysis 1 -100% concentration range
- Trace element analysis down to 5 – 10 ppm level
- Semi-quantitative analysis
  - Fundamental Principles (FP) based methods are approximately comparative as matrix specific calibrated methods

Courtesy of Maggi Loubser

Cabinet-based XRF vs. Air-path XRF

- Major element analysis 1 -100% concentration range
- Trace element analysis down to 5 – 10 ppm level
- Semi-quantitative analysis
  - Fundamental Principles (FP) based methods are approximately comparative as matrix specific calibrated methods

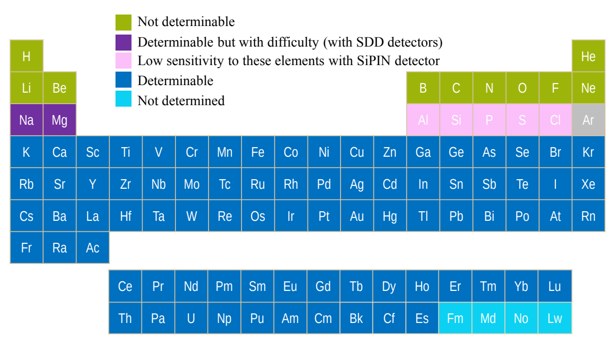
- Determine elemental composition magnesium (Mg) to uranium (U)
- Fast, real time results: on-the-spot elemental composition analysis
- Non-destructive
- Little to no sample prep – point & shoot
- Hand-held and portable

Courtesy of Maggi Loubser

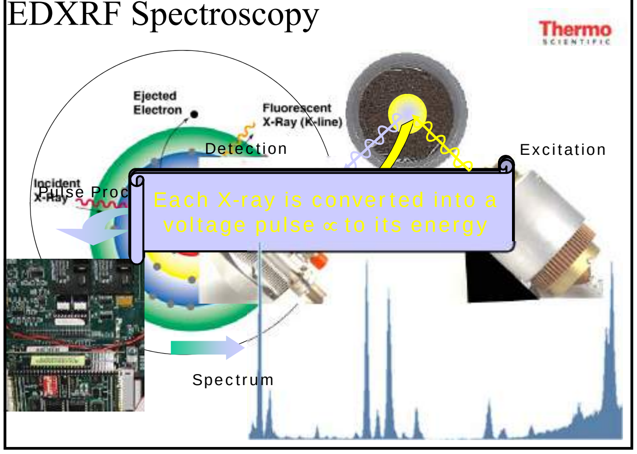
Limitations of Air-path XRF

- Matrix effects
- Physical effects
- Light elements unable to be analysed: H, He, Li, Be, B, C, N, O, F
- Attenuation of low energy photons in air: Al difficult; Mg not possible
- Limited penetration depth (depth from which photon escapes) in sample
  - Element and energy specific
- Resolution dependent on detector

Air-path energy-dispersive XRF



EDXRF Spectroscopy



Characteristic Line Spectrum

- Atoms in the anode (target) are bombarded by high speed electrons

Characteristic Line Spectrum

- Atoms in the anode (target) are bombarded by high speed electrons
- These electrons expel an electron from the K shell if they have enough energy

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)

Characteristic Line Spectrum

- Atoms in the anode (target) are bombarded by high speed electrons
- These electrons expel an electron from the K shell if they have enough energy
- The vacancy created is filled by an electron from a higher shell
  - These transitions occur from higher to lower energy states, and the energy difference is emitted as an x-ray photon

Characteristic Line Spectrum

- Atoms in the anode (target) are bombarded by high speed electrons
- These electrons expel an electron from the K shell if they have enough energy
- The vacancy created is filled by an electron from a higher shell
  - These transitions occur from higher to lower energy states, and the energy difference is emitted as an x-ray photon
- The **excitation potential** is the minimum tube potential required to expel an electron from a specified electron shell to create an electron vacancy in that shell

Excitation Potential

- Minimum X-ray tube operating potential (kV) that can excite characteristic lines in the tube target *or* the sample
- Each element has as many excitation potentials as it has electron orbitals or energy levels
- Excitation potentials increase with atomic number *Z*

Absorption Edges: Important in excitation by X-rays

- An ABSORPTION EDGE is the *maximum wavelength* (the minimum X-ray energy, which is the excitation potential) that can expel an electron from a specified electron level in an atom.
- *Absorption Edges*, expressed as wavelengths (Å or nm), correspond to *Excitation Potentials*, expressed as energy (kV).
- For each element there is *one* K absorption edge, *three* L absorption edges, and *five* M absorption edges.

Excitation Potential

Excitation Potential (kV)		
Rh K	=	23.2
Rh L_{III}	=	3.0
Rh M_V	=	0.3072

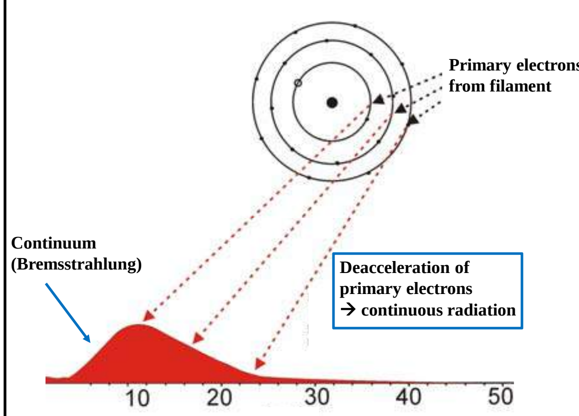
Excitation Potential vs. Absorption Edge

Excitation Potential (kV)						Absorption Edge (Å)
Rh K	=	23.2	≡	$\frac{12.4}{23.2}$	=	0.53
Rh L_{III}	=	3.0	≡	$\frac{12.4}{3.0}$	=	4.13
Rh M_V	=	0.3072	≡	$\frac{12.4}{0.3072}$	=	40.36

Excitation by X-rays

- ONLY X-rays with wavelengths shorter than a specific absorption edge (or greater than a specific binding energy) can excite the characteristic lines corresponding to that edge.
- The closer an exciting wavelength is to an absorption edge the more strongly it is absorbed, and therefore the more efficiently it excites the characteristic lines.
- The most efficient wavelength for exciting a specific line is a wavelength just shorter than the corresponding absorption edge (energy just above the binding energy)

G11



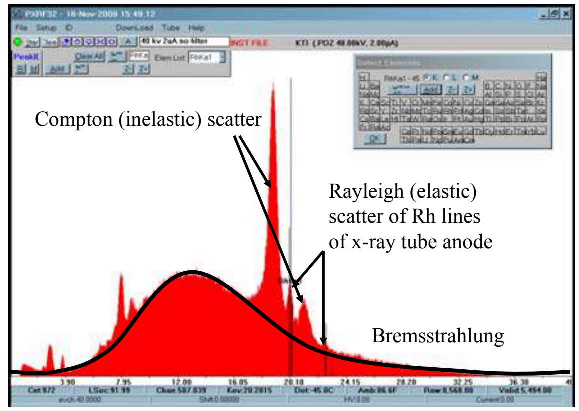
Courtesy of Maggi Loubser

Slide 20

G11 GCI 11, 11/6/2016

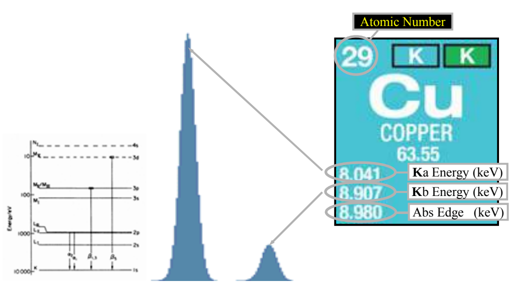
Rayleigh and Compton Scattering

- Rayleigh (elastic) scattering
  - Incident radiation scattered by sample atoms without losing any energy.
  - Rayleigh lines = characteristic energies of x-ray tube target
- Compton (inelastic) scattering
  - Incident radiation scattered by sample atom with some loss in energy.

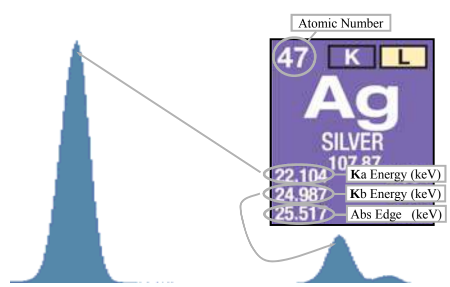


Courtesy of Alexander Seyfarth

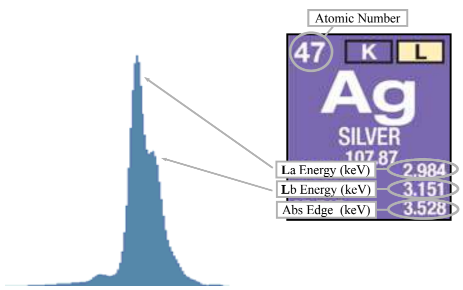
X-ray Emission: Copper



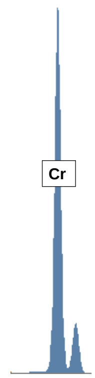
X-ray Emission: Silver (K-lines)



X-ray Emission: Silver (L-Lines)



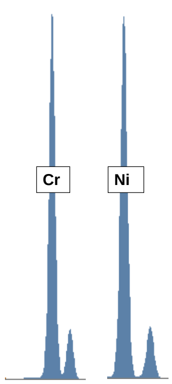
EDXRF spectrum: Pure elements



Most have several peaks

→ **Cr has 2 peaks**

EDXRF spectrum: Pure elements

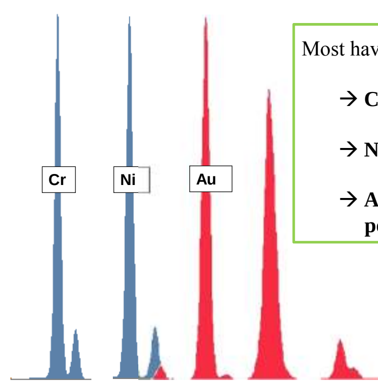


Most have several peaks

→ **Cr has 2 peaks**

→ **Ni has 2 peaks**

EDXRF spectrum: Pure elements



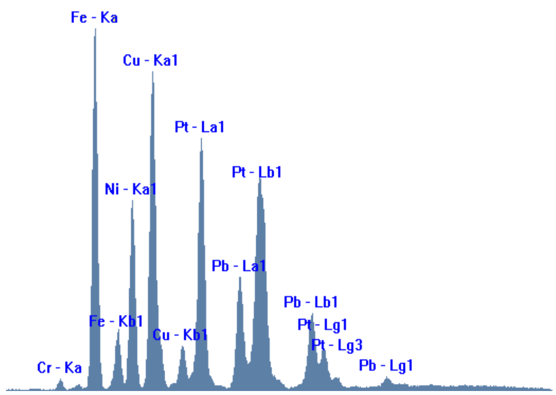
Most have several peaks

→ **Cr has 2 peaks**

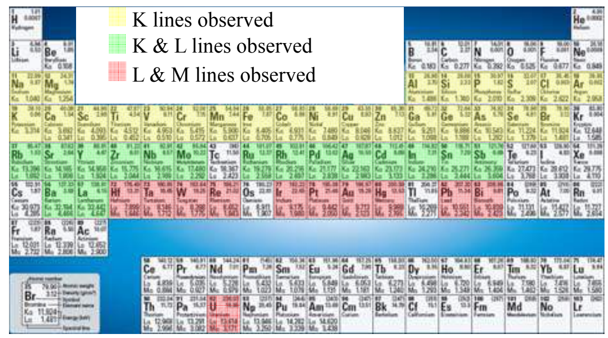
→ **Ni has 2 peaks**

→ **Au has more than 3 peaks**

EDXRF spectrum: Platnium ore



X-ray line families of relevance



Adjustable Parameters

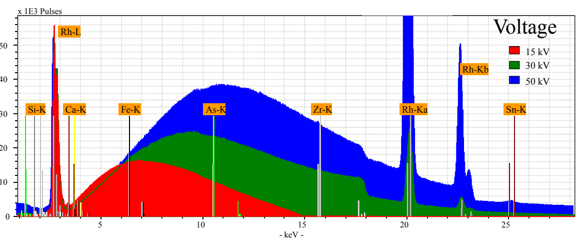
X-ray source target	Determines shape of continuous excitation spectrum and x-ray lines available for excitation (only adjustable if x-ray tube is interchangeable)
Collimation	Determines area of excitation (spot size on sample)
Voltage	Determines the highest energy that a photon coming from the tube can have
Current	Proportional to the number of photons produced in the x-ray tube
Filter	changes the excitation spectrum
Atmosphere (vacuum / He)	reduces the absorption of low energy photons air, improves detection of elements lines < 3 keV
Time	

Excitation Source

- Most common tube targets
  - Mo, Rh for general use
  - W for heavy elements
  - Cu, Cr, Ag for light elements
- W target for heavy elements
  - 2 to 5 times larger peak areas for K-line elements > 20 keV

Change in Excitation (kV)

- Voltage setting determines excitation energy



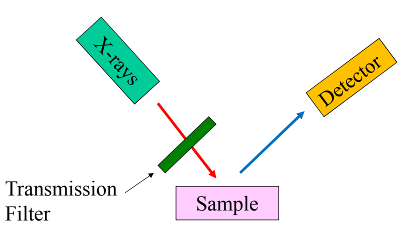
General voltage and current tips

- Low kV, high μA for light(er) element analysis
- High kV, high μA for heavy element analysis
- (kV x μA) needs to stay BELOW the max rating of the instrument
  → $40\ kV \times 8\ \mu A = 4 \times 10^{4}\ V \times 8 \times 10^{-6}\ A = 32 \times 10^{-2}\ W = 0.32\ W$

Filters: Changing the excitation spectrum

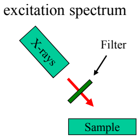
Metal films placed between the sample and the X-ray source to change the excitation spectrum

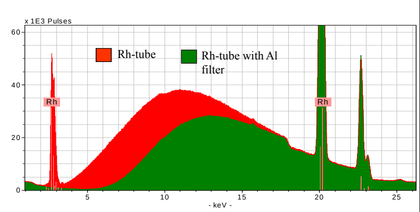
- to suppress undesired parts of the excitation spectrum
- to reduce background coming from backscattered primary radiation



Filters: Changing the excitation spectrum

Filters are metal films placed between the sample and the X-ray source to change the excitation spectrum





Courtesy of Alexander Seyfarth

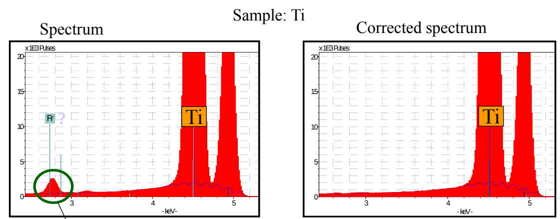
Artifacts in spectrum due to detector

- Escape peaks → incident x-ray photon excites Si Ka1 escapes the detector before being reabsorbed

  Measured energy of element will be reduced by **1.740 keV** (energy of the escaped Si Ka1 x-ray**)**

- Sum peaks → pile up of electrons at detector due to high current

Escape peaks



Ti Ka 4.512 keV
Si Ka 1.7398 keV
Escape peak 2.77 keV
Escape peak = 4.5 keV-1.74 keV

Courtesy of Bruker

Escape peaks and spectral overlaps

Elements lower in atomic number then Si (14) cannot have an escape peak from the EDX unit, ex. Mg and Al

Escape peaks and spectral overlaps

Elements lower in atomic number then Si (14) cannot have an escape peak from the EDX unit, ex. Mg and Al

Ca escape peak

Ca Ka	3.69 keV
Si Ka	1.74 keV
Escape peak	1.95 keV
P Ka	2.01 keV

Relevant when trying to determine whether phosphorous is present along with calcium (ex: to indicate use of bone black)

Escape peaks and spectral overlaps

Elements lower in atomic number then Si (14) cannot have an escape peak from the EDX unit, ex. Mg and Al

Ca escape peak

Ca Ka	3.69 keV
Si Ka	1.74 keV
Escape peak	1.95 keV
P Ka	2.01 keV

Relevant when trying to determine whether phosphorous is present along with calcium (ex: to indicate use of bone black)

Cu escape peak

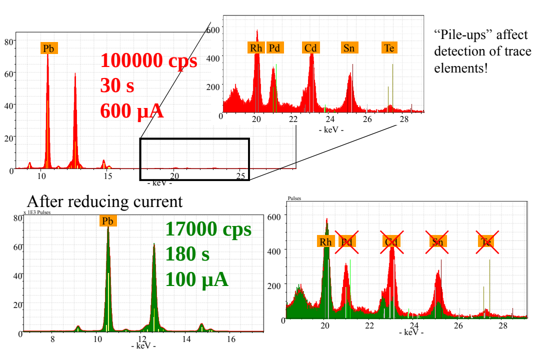
Cu Ka	8.05 keV
Si Ka	1.74 keV
Escape peak	6.31 keV
Fe Ka	6.40 keV

Relevant when analyzing copper alloys and trying to determine if alloy contains low levels of iron.

Artifacts in spectrum due to detector

- Sum peaks → pile up of electrons at detector due to high current

Sum Peaks (Pile-Ups)



Pb sum peaks and spectral overlaps

Pb La and Lb sum peaks		
Pb La + Pb La	21.0 keV	Pd Ka = 21.2 keV
Pb La + Pb Lb	23.1 keV	Cd Ka = 23.2 keV
Pb Lb + Pb Lb	25.2 keV	Sn Ka = 25.2 keV

Relevance:

- Detection of low intensity tin peaks in the presence of intense lead L lines (study of bronzes, detection of lead-tin yellow pigment, etc.).
- Detection of low intensity cadmium lines in the presence of intense lead L lines (detection of cadmium yellow or cadmium red in the presence of lead white).

Interference with Instrumentation

- Equipment and instrument contribution
  - Incident radiation may excite instrument components and their characteristic x-ray lines may be detected in the spectrum
- Possible contributors:
  - Collimators, lens components, detector can, window material, etc.

Interactions in the Sample

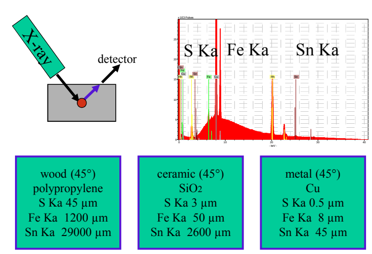
- Scattering of incident radiation
  - Rayleigh (elastic) scattering
  - Compton (inelastic) scattering
  - Bragg scattering (diffraction peaks)
- Matrix effects: Relating to how X-rays interact with matter
  - Absorption
  - Enhancement

Absorption and Enhancement

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

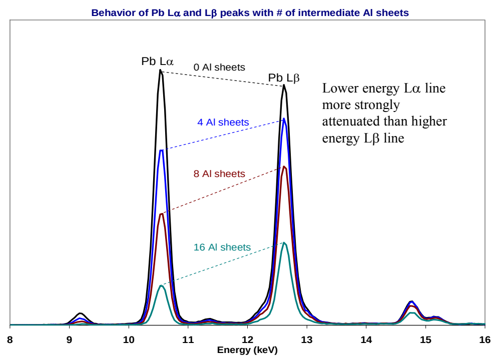
Absorption

- Absorption: responsible for the information depth
  - depth from which a photon produced within the sample can leave the sample and reach the detector



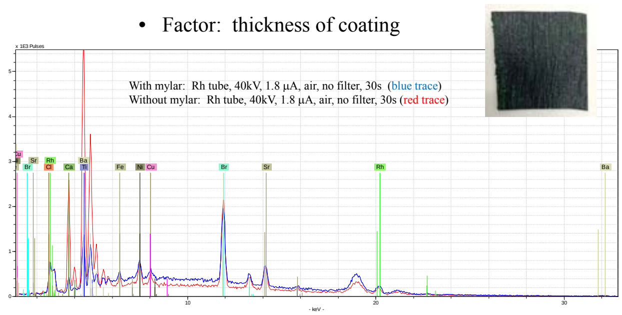
Courtesy of Alexander Seyfarth

Visualizing absorption



Top coat layer: Simulated varnish layer

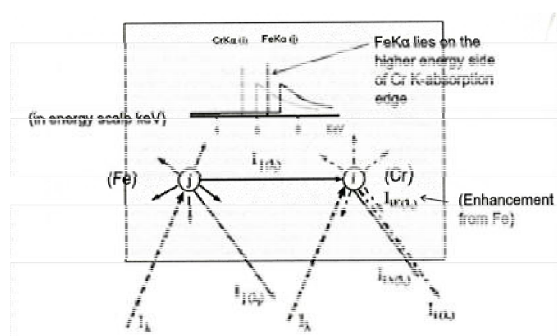
- Factor: thickness of coating



Enhancement

- Fluorescence from one or more matrix elements have sufficient energy to excite (induce) fluorescence in another element in the matrix
- Observe more analyte fluorescene than would normally be excited by X-ray tube radiation
- Enhancement may or may not occur; Absorption always occur

Enhancement

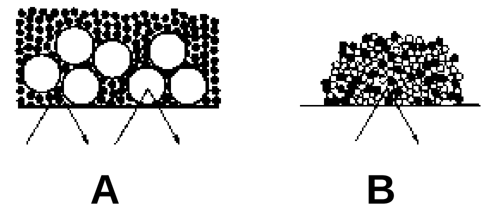


$$I_{I(\lambda_i)} = I_{IA(\lambda_i)} + I_{IE(\lambda_i)}$$

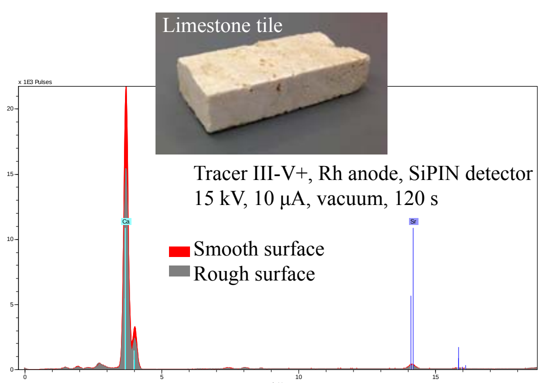
Physical factors that influence XRF spectra

- Particle size effects
- Surface roughness
- Impact of air-gap
- Sampling prep for nonhomogenous samples

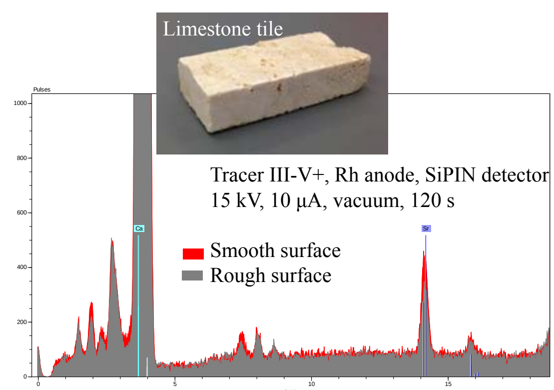
Particle Size



Example of surface roughness

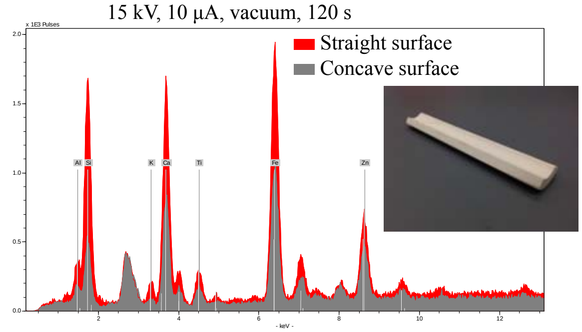


Example of surface roughness



Example of air gap impact

Tracer III-V+, Rh anode, SiPIN detector
15 kV, 10 µA, vacuum, 120 s



Sample Prep: Complexity of heterogeneous samples

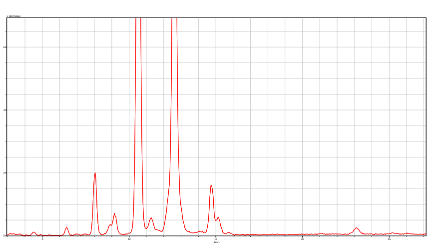
Limestone spots vs. homogenised pressed briquette

%	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	LE	Ba
LStone 1	2.24	1.84	4.96	0.07	0.06	0.61	30.3	0.07	0.38	0.47	51.1	7.8
LStone 2	2.13	1.66	12.1	ND	0.11	ND	23.8	0.07	0.66	0.5	51.1	7.77
LStone 3	2.28	1.45	4.34	0.1	0.05	0.47	32.2	0.07	0.38	0.36	50.3	7.94
LStone 4	ND	1.54	4.35	0.08	0.04	0.4	36	0.08	0.37	0.29	48.4	8.36
LStone 5	ND	1.28	3.54	0.08	0.06	0.3	35.1	0.07	0.41	0.2	50.5	8.35
LStone 6	1.79	1.29	3.69	0.08	0.1	0.32	33.8	0.07	0.42	0.22	50	8.16
Average	**2.11**	**1.51**	**5.50**	**0.08**	**0.07**	**0.42**	**31.89**	**0.07**	**0.44**	**0.34**	**50.23**	**8.06**
pressed pellet	3.05	1.35	4.51	0.07	0.01	0.52	36.1	0.07	0.39	0.34	45.8	7.73

Courtesy of Maggi Loubser

Sample Prep: Complexity of heterogeneous samples

Christ Child (96.SD.18), JPGM



Pb → possibly under layer containing lead white and/or red lead
Hg→ possibly vermilion
Cu → blue/green drapery (azurite, malachite, verdigris, PB15, PG 7)
Fe → possibly Mars Red, red ochre or blue/green drapery (Prussian blue)

Considerations for cultural heritage samples

Pros

- \+ *In situ* analysis in galleries, outdoors
- \+ Access hard to reach areas
- \+ Spot size appropriate for reliable analysis of homogeneous materials, i.e., metals
- \+ Flexible positioning

Cons

- Non-interchangable anodes (interferences, e.g., Rh/Ag)
- May not be able to reach recessed areas
- May probe subsurface
- Larg(ish) spot size (4-6 mm)
- Difficult to position accurately
- Cannot contact surface

Courtesy of Karen Trentelman

Micro-XRF: A complement to handheld XRF

Bruker Artax micro-XRF spectrometer – small spot size (65 mm – 2 mm), can scan areas up to 50 x 50 mm

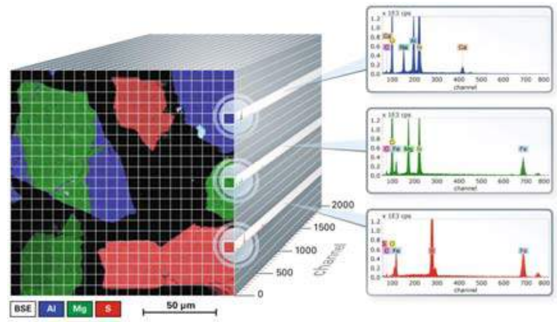
Pros

+ polycapillary optics can probe features <100 µm
+ relatively easy to move and position (camera)
+ line and area mapping capability

Cons

- not easily transportable
- geometric constraints

Macro-XRF scanner: Individual elemental maps



Courtesy of Roald Tagle

Case Study: Rembrandt's *An Old Man in Military Costume*

Rembrandt's *An Old Man In Military Costume*
78.PB.246
J. Paul Getty Museum

Trentelman, K., et. al., Applied Physics A, **121**, 801-11 (2015)

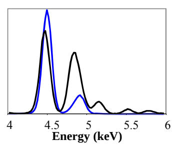
Case Study: Rembrandt's *An Old Man in Military Costume*

Rembrandt's *An Old Man In Military Costume*
78.PB.246
J. Paul Getty Museum

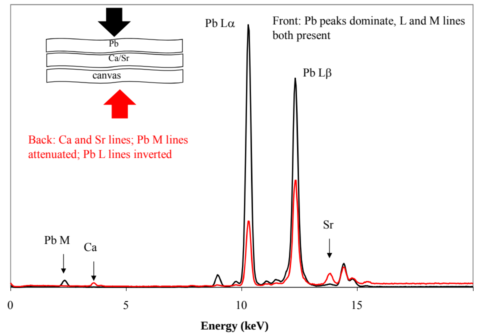
Trentelman, K., et. al., Applied Physics A, **121**, 801-11 (2015)

Common interferences

- Inhomogeneous samples
- Substrate
- Area of interest smaller than aperture (6mm)
- Shielding from varnish/dirt/patina on surface
- Rough or complex surface shapes
- Contamination on window
- Overlap of peaks (e.g. Pb/As or Ba/Ti)
- Sum / escape peaks



Layered samples



Summary

- Problem definition: is XRF appropriate?
- Operating parameter selection
- Spectral interpretation
- Impact of instrument components on results
- Inference of compounds from elements
- Reporting data and results
- Going beyond XRF to find answers
  - Complementary techniques, e.g. Raman and XRD

XRF Boot Camp for Conservators

- 4 days of lectures and hands-on exercise modules illustrating fundamental concepts and practical considerations
- Group projects with museum objects and presentations

http://getty.edu/conservation/our_projects/education/xrf/