XRF Spectra

Consecutive elements in periodic table

- Plotting only a portion of the XRF spectra of several different elements
- Note periodicity - energy is proportional to $Z^2$ (Moseley’s law)

Periodic Table of XRF Fluorescence Data

Including K and L line energies & detection limits
XRF Energies for Various Elements

Generalizations based on use of field portable analyzers

- **ORGANIC ELEMENTS** (i.e., H, C, N, O) **DO NOT GIVE XRF PEAKS**
  Fluorescence photons from these elements are too low in energy to be transmitted through air and are not efficiently detected using conventional Si-based detectors

- **LOW Z ELEMENTS** (i.e., Cl, Ar, K, Ca) **GIVE ONLY K PEAKS**
  L peaks from these elements are too low in energy (these photons are not transmitted through air and not detected with conventional Si-based detectors)

- **HIGH Z ELEMENTS** (i.e., Ba, Hg, Pb, U) **GIVE ONLY L LINES**
  K peaks from these elements are too high in energy (these electrons have high binding energies and cannot be removed with the limited voltage available in field portable analyzers)

- **MIDDLE Z ELEMENTS** (i.e., Rh through I) **MAY GIVE BOTH K AND L LINES**

XRF – More Detailed Description

Note energy level diagrams are not drawn to scale
Since XRF affects inner shell and not bonding electrons, the XRF spectrum of an element is independent of its chemical form (i.e., spectra of lead, lead arsenate, and tetraethyl lead will ALL show peaks at 10.61 and 12.55 keV).

**K Line Series**

~10% As in Chinese supplement

- L lines not observed (1.28 and 1.32 keV - too low in energy to be excited)
- $K_\alpha$ and $K_\beta$ peak energies are often close together (1.2 keV apart for As)
- K lines observed for low to medium Z elements (i.e., Cl, Fe, As)
- $K_\alpha$ and $K_\beta$ peaks have typical ratio of ~ 5 to 1

**L Line Series**

~10% Pb in imported Mexican tableware
• K lines not observed (75.0 and 94.9 keV - too high in energy to be excited)
• L_α and L_β peak energies are often further apart (2.1 keV apart for Pb)
• L lines observed for high Z elements (i.e., Hg, Pb, Th)
• L_α and L_β peaks have typical ratio of ~ 1 to 1 Pb Lγ line

More Complex XRF Spectrum

Chinese supplement containing 4% As and 2% Hg

• Line overlaps are possible and users must evaluate spectrum to confirm the presence or absence of an element

Effect of Detector Resolution

Spectra of 900 ppm Pb added into Pepto-Bismol
Older Si(PIN) detector

- Resolution ~0.2 keV (FWHM)
- Cannot resolve Pb and Bi peaks

Newer SDD

- Resolution ~0.15 keV (FWHM)
- Can resolve Pb and Bi peaks

Adapted from Bruce Kaiser, Bruker AXS

Artifact Peaks

Arising from X-ray tube source

- Electrons with high kinetic energy (typically 10-50 kV) strike atoms in the X-ray tube source target (typically Rh or Ag) and transfer energy
- The interaction of X-ray source photons with the sample generates several characteristic features in an XRF spectrum which may include the following:
  - Bremsstrahlung
  - Rayleigh peaks
  - Compton peaks

Bremsstrahlung

Continuum/backscatter from cellulose sample
$E_0 = \text{initial energy of electron in X-ray tube source}$

$E_1, E_2 = \text{energy of X-ray}$

- Very broad peak due to backscattering of X-rays from sample to detector that may appear in all XRF spectra
- Maximum energy of this peak limited by kV applied to X-Ray tube, maximum intensity of this peak is $\sim 2/3$ of the applied keV
- More prominent in XRF spectra of less dense samples which scatter more of X-ray source photons back to the detector

**Rayleigh Peaks**

Elastic scattering from metal alloy sample
\[ E_0 = \text{initial energy of X-ray from target element in x-ray tube source} \]
\[ E_1 = \text{energy of X-ray elastically scattered from (typically dense) sample} \]

- Peaks arising from target anode in X-ray tube source (Rh in this case) that may appear in all XRF spectra acquired on that instrument
- No energy is lost in this process so peaks show up at characteristic X-ray energies (Rh \( \text{L}_\alpha \) and \( \text{L}_\beta \) at 20.22 and 22.72 keV in this case)
- Typically observed in spectra of dense samples as weak peaks (due to increased absorption of X-ray source photons by sample)

**Compton Peaks**

Inelastic scattering from cellulose sample
\[ E_0 = \text{initial energy of X-ray from target element in x-ray tube source} \]
\[ E_1 = \text{energy of X-ray inelastically scattered from (typically non-dense) sample} \]

- Peaks arising from target element in X-ray tube (again, Rh in this case) that may appear in all XRF spectra acquired on that instrument.
- Some energy is lost in this process so peaks show up at energies slightly less than characteristic X-ray tube target energies.
- Typically observed in spectra of low density samples as fairly intense peaks (note these peaks are wider than Rayleigh peaks).

**Artifact Peaks**

Arising from detection process

- The interaction of X-ray fluorescence photons from the sample with the detector can generate several different...
types of artifact peaks in an XRF spectrum which may include the following:

- Sum peaks
- Escape peaks

**Sum Peaks**

Example from analysis of Fe sample

![Diagram showing sum peaks](image)

**Fe Kα peak**
6.40 keV

**Fe sum peak**
12.80 keV
• Artifact peak due to the arrival of 2 photons at the detector at exactly the same time (i.e., $K_\alpha + K_\alpha, K_\alpha + K_\beta$)
• More prominent in XRF spectra that have high concentrations of an element
• Can be reduced by keeping count rates low

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**Escape Peaks**

Example from analysis of Pb sample

![Diagram of escape peaks](image)

- Artifact peak due to the absorption of some of the energy of a photon by Si atoms in the detector ($E_{\text{observed}} = E_{\text{incident}} - E_{\text{Si}}$ where $E_{\text{Si}} = 1.74$ keV)
- More prominent in XRF spectra that have high concentrations of an element and for lower Z elements
- Can be reduced by keeping count rates low
Artifact Peaks Due to Blank Media

- May observe peaks due to contaminants in XRF cups, Mylar film, and matrix
- In this case, the cellulose matrix is highly pure and the peaks are due to trace elements in the XRF analyzer window and detector materials
- This can complicate interpretation (false positives)

Summary of Factors That Complicate Interpretation of XRF Spectra

Elements in the sample may produce 2 or more lines

- Kα, Kβ, Lα, Lβ, (we use simplified nomenclature and discussed only α and β lines)
- Lγ, Lα1, Lβ1, Lβ2 (can also have α1 and α2 lines, β1 and β2 lines, γ lines, etc.)

Peak overlaps arising from the presence of multiple elements in the sample and limited detector resolution

Peaks from X-ray source

- Bremsstrahlung (more prominent in less dense samples)
- Rayleigh peaks from X-ray source target (typically Ag Lα, Lβ)
- Compton peaks from X-ray source target (typically at energies < Ag Lα, Lβ)

Sum peaks (two X-ray photons arriving at the detector at the same time)

- \( E = Kα + Kα \)
- \( E = Kα + Kβ \)

Escape peaks (Si in the detector absorbing some of the energy from a X-ray)

- \( E = Kα - Kα \) for Si (where Si line energy = 1.74 keV)
- \( E = Lα - Kα \) for Si
Other artifact peaks

- Product packaging, XRF cup, Mylar film, (measure what you want to measure)
- Contaminants on XRF window or trace levels of elements in XRF window or detector materials (analyze blanks to confirm source of these artifacts)