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**

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**XRF – More Detailed Description**

Note energy level diagrams are not drawn to scale

![XRF Energy Level Diagram](www.niton.com/images/fluorescence.png)
Since \textit{XRF affects inner shell and not bonding electrons}, the XRF spectrum of an element is \textit{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)

\textbf{K Line Series}

\textasciitilde 10\% As in Chinese supplement

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

\textbf{L Line Series}

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

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**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 L_\alpha and 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)

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**Compton Peaks**

Inelastic scattering from cellulose sample
$E_0$ = initial energy of X-ray from target element in x-ray tube source
$E_1$ = 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
• 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

- 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
- K\textsubscript{α}, K\textsubscript{β}, L\textsubscript{α}, L\textsubscript{β}, (we use simplified nomenclature and discussed only α and β lines)
- L\textsubscript{γ}, L\textsubscript{α1}, L\textsubscript{β1}, L\textsubscript{β2} (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 L\textsubscript{α}, L\textsubscript{β})
- Compton peaks from X-ray source target (typically at energies < Ag L\textsubscript{α}, L\textsubscript{β})

Sum peaks (two X-ray photons arriving at the detector at the same time)
- E = K\textsubscript{α} + K\textsubscript{α}
- E = K\textsubscript{α} + K\textsubscript{β}

Escape peaks (Si in the detector absorbing some of the energy from a X-ray)
- E = K\textsubscript{α} – K\textsubscript{α} for Si (where Si line energy = 1.74 keV)
- E = L\textsubscript{α} – K\textsubscript{α} 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)