EDXRF User Training

4. Spectral Artifacts and Other Spectral Issues
Absorption and Scatter Phenomena

Absorber \((Z)\)

Coherent [elastic] (Rayleigh)
\[\lambda_{\text{coherent}} = \lambda_o\]

Incoherent [inelastic] (Compton)
\[\lambda_{\text{incoherent}} \neq \lambda_o\]

Characteristic line production
\[\lambda_Z > \lambda_o\]

Photoelectrons

Absorption phenomena \(\tau\)

Scatter phenomena \(\sigma\)
1. Scattered X-rays – Rayleigh (Coherent)

Electromagnetic radiation (emr) of frequency $n_0$ (energy $E_0$) incident upon “tightly-bound” electron or atom

“Electron/atom” oscillates at same frequency as incident emr and itself re-radiates (“scatters”) at the same frequency/energy

$\mathbf{n_R = n_0}$

$\mathbf{E_R = E_0}$
1. Scattered X-rays - Compton (Incoherent)

An energy loss occurs by the incident photon during its "collision" with the "loosely bound" electron.

Incoherent / Compton / Inelastic scattering

\[ E_c = \frac{E_o}{1 + [0.00196(1 - \cos \phi)] \cdot E_o} \]

(Where \( E \) expressed in keV)

Incident photon (energy \( E_o \))

Compton scattered photon (lower energy \( E_c \))

Photon scatter angle \( \phi \)

Path of recoiling electron
1. Scattered X-rays – Compton Energy Change

An energy loss occurs by the incident photon ($\lambda_o$) during its interaction with the “loosely bound” electron.

$\lambda_c - \lambda_o = 0.00243(1 - \cos \phi)$

(where $\lambda$ expressed in nm)
1. Scattered X-rays – Spectrum Tube Lines

X-ray tube: Rh anode
Sample: Plexiglas
Detector: Si(Li)
Standard optics

RhKa incoherent scatter
RhKa coherent scatter
RhL (coherent scatter)
RhKb incoherent scatter
RhKb coherent scatter
1. Scattered X-rays – Spectrum Tube Lines

Plexiglas
Rh anode tube
Scatter angle 90°
Applied kV = 30

- RhKα incoherently scattered “Compton”
- RhKα coherent “Rayleigh” scatter
- RhKβ incoherently scattered “Compton”
- RhKβ coherent “Rayleigh” scatter
- RhLα,β coherent “Rayleigh” scatter

“Compton” shift

keV
Illustrating “Compton (Incoherent) shift”

- Scatter angle 90°
- Tube voltage 30kV
- Plexiglas scatter sample
- Rh anode tube

Compton shift
1. Scattered X-rays – Rhodium Tube Lines

- **Compton scattered RhKa**
  - Incoherent
  - Inelastic
  - Energy loss

- **Rayleigh scattered RhKa**
  - Coherent
  - Elastic
  - No energy loss

- **Compton scattered RhKb**

- **Rayleigh scattered RhKb**
2. Bragg Diffraction Peaks

Conditions for Bragg Diffraction

incident wave-front “AD”

emergent wave-front “DC”

path length difference $= AB + BC$

$= n\lambda$
2. Bragg Diffraction Peaks

Bragg’s Law

\[ n\lambda = 2d \sin \theta \]

where

- \( \lambda \) = wavelength of incident beam (nm)
- \( d \) = interatomic spacing of diffraction planes (nm)
- \( \theta \) = incident (and emergent) angles wrt diff planes
- \( n \) = an integer, normally called the "order" number
2. Bragg Diffraction Peaks

Bragg-angle dispersive XRD

\[ \lambda = 2d \sin \theta \]

\[ d = \frac{\lambda}{2} \cdot \frac{1}{\sin \theta} \]

\[ d = \frac{k}{\sin \theta} \]  
(fixed wavelength - XRD)
2. Bragg Diffraction Peaks

Energy-Dispersive XRD

\[ 2d \sin \theta = \lambda \]

\[ \frac{1}{2d} \cdot \frac{1}{\sin \theta} = \frac{1}{\lambda} \equiv E \]

\[ d \propto \frac{1}{2 \sin \theta} \cdot \frac{1}{E} \]

\[ d = \frac{k'}{E} \quad \text{(fixed angle - XRD)} \]
2. Bragg Diffraction Peaks

Diffraction of Primary Radiation
(extreme situation)

Diffraction peak coincides with Rh Lb

Sample moved slightly between measurements

Aluminium sheet
Rh anode tube
Polycapillary
2. Bragg Diffraction Peaks

Diffraction of Primary Radiation
(effect of tube anode)

Aluminium sheet
Polycapillary

Rh anode tube
Mo anode tube

1.00  2.00  3.00  4.00  5.00  6.00  7.00  8.00  9.00
keV
2. Bragg Diffraction Peaks

- Solutions
  - Rotation of sample
  - Software deletion routine
  - Primary beam filters
  - Lower µA
Effect of sample rotation #1

Require to measure Ti, Cr & Fe in corundum
2. Bragg Diffraction Peaks - Rotation

Effect of sample rotation #2

Require to measure Ti, Cr & Fe in corundum

Regions of interest for:
- Ti
- Cr
- Fe

AlKα
3. Spectral Interference

- Without any correction, overlapping elemental peaks (spectral interference) can cause misleading intensities

- Each peak has Region of Interest (ROI) – *See next slide for image*
  - ROI is an energy range within an elemental peak
  - Photon counts within this energy range contribute to that element’s intensity
  - Any counts outside the ROI is not included in the element’s intensity
  - Generally the ROI is expressed as a factor of the FWHM (ex. 1.2x FWHM)

- If two elements’ ROI overlap, it becomes difficult to determine which element that photon count belongs to
3. Spectral Interference

The ROI defines the energy range (number of channels) to be considered contributory to the intensity of an analyte peak. The **gross** peak intensity is the **sum** of the “raw” counts in the individual channels.
3. Spectral Interference

\[
\begin{array}{ccccccc}
Z (K\alpha) &=& 15 & 25,26 & 33 & 38 & 40 & 42 \\
Z (L\alpha) &=& 40 & & 82 & & & \\
\end{array}
\]
3. Spectral Interference

Example 1 - Kb/Ka overlap, DZ=1

MnKα
Z=25

FeKα
Z=26

MnKβ

FeKβ

5.5                                     6.0                                      6.5                                      7.0                                      7.5
keV
3. Spectral Interference

Example 2 - Kb/Ka overlap, DZ=2

- SrKα, Z=38
- ZrKα, Z=40
- PbLγ1
- PbLγ3
- SrKβ1,3
- SrKβ2
- ZrKβ1,3
- MoKα, Z=42

Graph showing spectral interference with keV values on the x-axis.
3. Spectral Interference

Example 3 - K/L series overlap, $\Delta Z \sim 50$
3. Spectral Interference

Example 4 - K/L series overlap, $\Delta Z=25$

![Graph showing spectral interference]

- $P K_\alpha$
- $Z=15$
- $ZrL\alpha, \beta, \gamma$
- $Z=40$
3. Spectral Interference

Peak deconvolution - Fe in the presence of Mn

FeKa is overlapped by MnKb
3. Spectral Interference

Peak deconvolution - Fe in the presence of Mn

The ROI for FeKa showing asymmetry due to overlapping MnKb
3. Spectral Interference

Peak deconvolution - Fe in the presence of Mn

The generated profile for MnKb assuming a known a/b intensity ratio.
3. Spectral Interference

Peak deconvolution - Fe in the presence of Mn

The resultant FeKa ROI after subtraction of MnKb

Subtracted MnKb profile
3. Spectral Interference

Gas proportional counter

Solid state LN$_2$ cooled Si(Li) detector

Resolution = 18%
FWHM = 1060eV

Resolution = 2.7%
FWHM = 160eV

Mn(Ka+Kb)

FeKa

MnKb

FeKb
3. Spectral Interference

Regions of K-series spectral overlap.

\[ K_\beta \text{ for element } Z \]

overlaps

\[ K_\alpha \text{ for element } (Z+n) \]

\( n = 1 \)
\( n = 2 \)
\( n = 3 \)
3. Spectral Interference

Spectral interference (MoL$\alpha$/SK$\alpha$)
3. Spectral Interference

Spectral interference (BaLα/TiKα & VKα/TiKβ/BaLβ)
3. Spectral Interference

• Solutions:

  – Use NET intensity mode
    • Subtracts background levels and deconvolutes peaks

  – Use Peak Fit tool (based on Halographic Peak Deconvolution) to identify correct peak ID list:
    • Uses theoretical peak ratios (i.e. Ka to Kb)
    • Calculated peak intensities
    • Atomic parameters of sample
    • Hardware parameters (i.e. detector resolution)
    • Can also use SUBTRACT Deconvolution

  – Use higher detector time constant to improve peak resolution

  – For quantitative analysis of samples with interference, use calibration standards
4. Sum Peaks

- Definition: Photon counts are processed by the detector ONE EVENT AT A TIME. However, sometimes the detector will process two photon counts at once.
- Occurs most when there is high dead-time (high µA)
- Occurs most with a few common, predictable permutations

- Solutions:
  - Use lower tube current to lower sum peak height
  - Software cannot delete sum peaks, but it can identify theoretical locations of possible sum peaks with a marker
4. Sum Peaks – Example Cu(K)

Cu(K) sum peak doublet
5. Escape Peaks

- The detector is made of a Silicon chip
- If an element’s incoming photon (i.e. Cu(K) at 8.04keV) is greater in energy than the Si binding energy (1.74keV), than that photon is capable of exciting and fluorescing the Si.
- As a result, 1.74keV of the Cu photon energy is consumed in ejecting the Si electron
- The resulting Cu photon now has:
  - \( 8.04\text{keV} - 1.74\text{keV} = 6.3\text{keV} \)
- The photon will not be placed at the Cu peak, but at 6.3keV.
- If the count-rate is high, there will be a peak formed at ~6.3keV.

- SOLUTION: Software can identify and subtracting escape peaks
5. Escape Peaks – Example Cu(K)

Cu(K) escape peak
6. Absorption and Enhancement

• If there are at least 2 elements in a sample and:
  – The element of higher energy lies *near & above* the absorption edge of the lower energy element, it the energy from the higher element can be attenuated and used to fluoresce the other element

• The result is the *higher energy element is absorbed*

• The *lower energy is enhanced*

• **SOLUTION:**
  – To get the most accurate quantitative data, proper corrections should be done by creating a calibration model using standards
6. Absorption and Enhancement – Ex. Steel

[Image of a graph showing X-ray peaks for various elements in a steel sample.]

[Graph details include peaks labeled FeKα, CuKα, ZnKα, etc., along the x-axis with corresponding intensity values on the y-axis.]
## 6. Absorption and Enhancement – MAC’s

### Table of Mass Absorption Coefficients (\(\mu\))

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Radiation being absorbed</th>
<th>CrK(\alpha)</th>
<th>FeK(\alpha)</th>
<th>NiK(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>0.2291</td>
<td>0.1937</td>
<td>0.1659</td>
</tr>
<tr>
<td></td>
<td>keV</td>
<td>5.42</td>
<td>6.41</td>
<td>7.48</td>
</tr>
<tr>
<td>Cr</td>
<td>90</td>
<td>445</td>
<td>316</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>115</td>
<td>71</td>
<td>397</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>146</td>
<td>90</td>
<td>61</td>
<td></td>
</tr>
</tbody>
</table>
### 6. Absorption and Enhancement

Examples of change in matrix absorption with changing composition

<table>
<thead>
<tr>
<th>Composition #1</th>
<th>Case for CrKα (when Cr constant)</th>
<th>Case for FeKα (when Fe constant)</th>
<th>Case for NiKα (when Ni constant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>wt % (μ) CrKα</td>
<td>wt % (μ) FeKα</td>
<td>wt % (μ) NiKα</td>
</tr>
<tr>
<td>Cr</td>
<td>10% 9.0 80% 356.0 10% 31.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>10% 11.5 10% 7.1 80% 317.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>80% 116.8 10% 9.0 10% 6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ matrix</td>
<td>137.3</td>
<td>372.1</td>
<td>355.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition #2</th>
<th>Case for CrKα (when Cr constant)</th>
<th>Case for FeKα (when Fe constant)</th>
<th>Case for NiKα (when Ni constant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>10% 9.0 10% 44.5 80% 252.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>80% 92.0 10% 7.1 10% 39.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>10% 14.6 80% 72.0 10% 6.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ matrix</td>
<td>115.6</td>
<td>123.6</td>
<td>298.6</td>
</tr>
</tbody>
</table>

μ matrix (comp 1 / 2) 1.19 3.01 1.19
Spectral Issues - Summary

- Tube Scatter
- Sum Peaks
- Escape Peaks
- Overlaps
- Absorption / Enhancement