Wavelength Dispersive X-ray Spectroscopy

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From Oxford Instruments
Outline

- X-ray emission and detection with EDS in the SEM
- Introduction to wavelength dispersive x-ray spectroscopy
- WDS X-ray detection and Spectrometer
- Examples and available detectors and resources at NUANCE
X-ray Generation

Characteristic X-rays

Bremsstrahlung Radiation

Si Kα = 1.740 keV
Fe Kα = 6.405 keV
Electron Beam interacts with sample

X-rays emitted from the sample

Detector converts x-rays to electrical voltage

Elemental analysis is done on electrical signals

EDS
Generating X-Ray Signals

- All x-ray energies measured simultaneously
- Heavier elements = larger continuum
Detection Limits

• Signal must be greater than the background
• Lower than 0.1 wt% (1000 ppm) almost impossible with EDS
• Background is greater in denser materials

Trace Elements

- Remove backgrounds for trace elements
- Improve spectral resolution to separate peak overlaps

Peak Overlaps

Mo L$\alpha$ = 2.29
FWHM of Mn K$\alpha$ = 127 eV
What is Wavelength Dispersive X-ray Spectroscopy?

- X-ray microanalytical technique used in SEM (EPMA)
- Utilizes Bragg’s law of x-ray diffraction (W instead of E)
- Detection limit 10x lower than EDS (0.01 wt%)
- Measures one element at a time with high spectral resolution (2-20 eV)
- Analysis of minor and trace elements and separate peak overlaps
- Point analysis
- Standard based analysis

S Kα = 2.3 keV
Mo Lα = 2.29 keV
X-rays enter the detector

Diffract at crystal of known d

X-rays enter detector and counted

Components
Diffraction Crystals

Bragg's Law

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

- \( \lambda \): wavelength of x-rays
- \( d \): interplanar spacing of crystal
- \( \theta \): angle between the x-rays and lattice planes
- \( n \): an integer

Rowland circle geometry

Si PET Crystal High Angle

Cu LiF Crystal Low Angle

Analyzes one element at a time

NUANCE Northwestern University Atomic and Nanoscale Characterization Experimental Center

Northwestern EXPLORING INNER SPACE
Rowland circle geometry

Analyzes a spot – sample stationary
Johann Crystal

Imperfect Convergence
Low sensitivity and low resolution

R

Johansson Crystal

Perfect Convergence
High sensitivity and high resolution

R
**\( E = 12.396 / \lambda \)**

- **\( E \) = energy (keV)**
- **\( \lambda \) = X-ray wavelength (Å)**

- Multiple crystals needed to span the energy range of elements
- Lattice spacing of the crystal determines energy range
- WD detectors contain many crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>2d (nm)</th>
<th>Energy Range (keV)</th>
<th>Element Range (K Line)</th>
<th>Crystal Geometry Type</th>
<th>Optimized Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM200</td>
<td>19.7</td>
<td>0.07 - 0.22</td>
<td>Be to B</td>
<td>Johann</td>
<td>B</td>
</tr>
<tr>
<td>LSM-80</td>
<td>7.8</td>
<td>0.17 - 0.56</td>
<td>B to O</td>
<td>Johann</td>
<td>C and N</td>
</tr>
<tr>
<td>LSM-60</td>
<td>6.0</td>
<td>0.22 - 0.73</td>
<td>C to F</td>
<td>Johann</td>
<td>O</td>
</tr>
<tr>
<td>TAP</td>
<td>2.575</td>
<td>0.52 - 1.70</td>
<td>O to Al</td>
<td>Johansson</td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>0.8742</td>
<td>1.54 - 4.99</td>
<td>Si to Ti</td>
<td>Johansson</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>0.40267</td>
<td>3.33 – 10.84</td>
<td>Ca to Ge</td>
<td>Johansson</td>
<td></td>
</tr>
</tbody>
</table>
Entrance slit

- **Smaller** – increased spectral resolution
- **Wider** – more x-ray counts
Sealed Proportional Counter (SPC)
- Sealed Xe gas
- Performs best with high Energy X-rays (>Fe Kα)

Flow Proportional Counter (FPC)
- Flowing P-10 (10% CH₄ balance Ar)
- Performs best on low Energy x-rays (<Fe Kα)
The Effect of X-ray Energy Overlaps on the Microanalysis of Chevkinite (Ce, La, Ca, Th)₄(Fe²⁺, Mg)₂(Ti, Fe³⁺)₃Si₄O₂₂ Using SEM EDS-WDS

Lacinska et al., 2021
\[
\frac{C_{\text{unk}}^A}{C_{\text{stan}}^A} \approx \frac{I_{\text{unk}}^A}{I_{\text{stan}}^A} = k_A
\]

\[
C_{A(\text{unk})} = k_A C_{A(\text{stan})}
\]

\[
C_{A(\text{unk})} = k_A \frac{ZAF_{i}^{\text{stan}}}{ZAF_{i}^{\text{unk}}} C_{A(\text{stan})}
\]
Mean Atomic Mass (Z)

- Backscattering – BSE do not generate x-rays
- Stopping power

Absorption (A)

- X-ray traveling through sample has energy \( E_x > E_c \) of element B

Fluorescence (F)

- X-ray traveling through sample has energy \( E_x > E_c \) of element B

Matrix Effects

- Backscattering – BSE do not generate x-rays
- Stopping power

ENiKα = 7.47 kV
FeKα Ec = 7.11 kV

E_{NiKα} = 7.47 kV
FeKα Ec = 7.11 kV
Quantitative WDS (and EDS!)

- Flat
- Homogenous
- Beam stable
- Good standards
  - As much like you sample as possible so they have similar matrix effects
Accelerating Voltage

- Choose appropriate kV
- Typically, >15 kV
- Overvoltage
- Spatial resolution

Probe Current

- If your sample can handle it, a higher probe current = more x-ray counts

Working Distance
Applications

• Materials science
• Metals and alloys
• Geology and petrology
• Aerospace automotives
• Energy generation and storage
• Life sciences
• Semiconductors

<table>
<thead>
<tr>
<th>Published EPMA data</th>
<th>Element wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>Electron microprobe</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td>1σ</td>
</tr>
<tr>
<td>Data collected with AztecWave</td>
<td>Average</td>
</tr>
<tr>
<td>SEM WDS-only</td>
<td>1σ</td>
</tr>
<tr>
<td>SEM EDS+WDS</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td>1σ</td>
</tr>
</tbody>
</table>


From Oxford Instruments

Seddio, 2016
• EDS for major
• WDS for minor

• WDS is a longer analysis, so only use it for trace elements or peak overlap makes it faster!

Example quantitative results obtained for a ref. glass standard with elements <0.2 wt. %:
(Un-normalised analytical totals, oxygen calculated by stoichiometry)

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>As</th>
<th>Ba</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference (wt. %)</td>
<td>46.1</td>
<td>9.44</td>
<td>0.16</td>
<td>1.46</td>
<td>33.22</td>
<td>0.05</td>
<td>1.67</td>
<td>7.64</td>
<td>0.008</td>
<td>0.03</td>
<td>0.02</td>
<td>0.11</td>
<td>99.9</td>
</tr>
<tr>
<td>Technique</td>
<td>Cal.</td>
<td>EDS</td>
<td>WDS</td>
<td>EDS</td>
<td>EDS</td>
<td>WDS</td>
<td>EDS</td>
<td>EDS</td>
<td>WDS</td>
<td>WDS</td>
<td>WDS</td>
<td>WDS</td>
<td>-</td>
</tr>
<tr>
<td>Ave. (wt. %) (4 points)</td>
<td>46.02</td>
<td>8.86</td>
<td>0.154</td>
<td>1.51</td>
<td>33.46</td>
<td>0.033</td>
<td>1.58</td>
<td>7.43</td>
<td>0.008</td>
<td>0.028</td>
<td>0.020</td>
<td>0.085</td>
<td>99.2</td>
</tr>
<tr>
<td>1σ</td>
<td>0.08</td>
<td>0.09</td>
<td>0.004</td>
<td>0.03</td>
<td>0.06</td>
<td>0.002</td>
<td>0.01</td>
<td>0.07</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.011</td>
<td>0.2</td>
</tr>
</tbody>
</table>

From Oxford Instruments
<table>
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<tr>
<th>JEOL JSM 7900F OI Wave 700</th>
<th>Hitachi S-3400 OI Wave 500</th>
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<tr>
<td>LSM-200 Be to B</td>
<td>LSM-80 B to O</td>
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<tr>
<td>LSM-60 C to F</td>
<td>TAP O to Al</td>
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<td>TAP O to Al</td>
<td>PET Si to Ti</td>
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<td>PET Si to Ti</td>
<td>LiF Ca to Ge</td>
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<tr>
<td>LiF Ca to Ge</td>
<td></td>
</tr>
</tbody>
</table>

EPIC has a metals and minerals standard block – it is always better to have a standard like your sample!
Thank you!

Thank you, Rosie Jones from Oxford Instruments

From Oxford Instruments

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