Understanding X-rays: The electromagnetic spectrum

**Equation:**

\[ E = h \nu = \frac{hc}{\lambda} \]

where,

- \( E \): energy,
- \( h \): Planck's constant,
- \( \nu \): frequency
- \( c \): speed of light in vacuum,
- \( \lambda \): wavelength

**Equation:**

\[ E\lambda = hc = 1.2398 \]

if the units are keV and nm

**Equation:**

\[ E (\text{keV}) = \frac{hc}{\lambda (\text{nm})} = 1.2398/\lambda (\text{nm}) \] or,

\[ \lambda (\text{nm}) = \frac{hc}{E} = 1.2398/E (\text{keV}) \]

**Example:**

- \( \lambda_{\text{BeK}\alpha} = 11.27 \text{ nm} \);
  Hence, \( E_{\text{BeK}\alpha} = 1.2398/11.27 = 0.11 \text{ keV} \)

- \( E_{\text{UL}\alpha} = 13.61 \text{ keV} \);
  Hence, \( \lambda_{\text{UL}\alpha} = 1.2398/13.61 = 0.09 \text{ nm} \)
X-ray production in the EPMA

X-rays are generated by inelastic scattering of the beam electrons by sample atoms

- **Characteristic X-rays: inner shell interactions**
- **Bremmstrahlung (continuum) X-rays: outer and inner shell interactions**
Characteristic X-ray generation

*Inner shell ionization through inelastic scattering*

followed by electron transition from an outer shell to the inner shell
Condition for ionization: Overvoltage

**Overvoltage,** $U = \frac{E}{E_c}, > 1$

$E$: electron beam energy

$E_c$: critical excitation energy, ionization energy

of the shell in target atom

Best analytical condition, $U=5$

![Graph showing inner shell ionization](image-url)
X-ray energies

<table>
<thead>
<tr>
<th>Shell (energy level)</th>
<th>Electron transition</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>N&lt;sub&gt;VII&lt;/sub&gt;</td>
<td></td>
<td></td>
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<tr>
<td>N&lt;sub&gt;IV&lt;/sub&gt;</td>
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<td>N&lt;sub&gt;I&lt;/sub&gt;</td>
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<tr>
<td>M&lt;sub&gt;V&lt;/sub&gt;</td>
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<tr>
<td>M&lt;sub&gt;III&lt;/sub&gt;</td>
<td></td>
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<tr>
<td>M&lt;sub&gt;I&lt;/sub&gt;</td>
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<tr>
<td>L&lt;sub&gt;III&lt;/sub&gt;</td>
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<tr>
<td>L&lt;sub&gt;II&lt;/sub&gt;</td>
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<td>L&lt;sub&gt;I&lt;/sub&gt;</td>
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<tr>
<td>K&lt;sub&gt;I&lt;/sub&gt;</td>
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</tbody>
</table>

**X-ray**

- **K<sub>α</sub>**: L<sub>II+III</sub> to K<sub>I</sub>  
  \[ E_{K\alpha} = E_{c(K_I)} - E_{c(L_{II+III})} \]

- **K<sub>β</sub>**: M<sub>III</sub> to K<sub>I</sub>  
  \[ E_{K\beta} = E_{c(K_I)} - E_{c(M_{III})} \]

- **L<sub>α</sub>**: M<sub>IV+V</sub> to L<sub>III</sub>  
  \[ E_{L\alpha} = E_{c(L_{III})} - E_{c(M_{IV+V})} \]

- **M<sub>α</sub>**: N<sub>VII</sub> to M<sub>V</sub>  
  \[ E_{M\alpha} = E_{c(M_V)} - E_{c(N_{VII})} \]
Characteristic X-ray energy and critical excitation energy

To calculate $E_{c(K)}$:

Start

Rearrange

Substitute $E_{c(L)} = E_{L\alpha} + E_{c(L)}$

Substitute $E_{c(M)} = E_{M\alpha} + E_{c(M)}$

Therefore,

$$E_{K\alpha} = E_{c(K)} - E_{c(L)}$$

$$E_{c(K)} = E_{K\alpha} + E_{c(L)}$$

$$E_{c(K)} = E_{K\alpha} + (E_{L\alpha} + E_{c(M)})$$

$$E_{c(K)} = E_{K\alpha} + E_{L\alpha} + (E_{M\alpha} + E_{c(N)})$$

$$E_{c(K)} \approx E_{K\alpha} + E_{L\alpha} + E_{M\alpha}$$

The energy required to generate $UK\alpha$ must be $> E_{c(K)}$

so the overvoltage $> 1$

$$E_{c(K)} = 98.4 + 13.6 + 3.2$$

$\approx 115.2$ keV

Required energy $> 115.2$ keV

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Required energy $> 115.2$ keV
Maximum x-ray production depth (range)

\[ R_{\text{x-ray}} = 0.033(E^{1.7} - E_{c}^{1.7}) \frac{A}{\rho Z} \]

(Castaing’s formula)

- \( R_{\text{x-ray}} \): x-ray range (maximum depth)
- \( E \): electron beam energy
- \( E_{c} \): critical excitation energy of target atomic shell
- \( A \): atomic weight
- \( \rho \): density
- \( Z \): atomic number
Maximum x-ray production depth (range)

Characteristic X-ray range increases with increasing $E$, and decreasing $\rho$ and $\rho Z$.
The characteristic x-ray range is always less than the electron range.
X-ray depth-distribution: the $\phi(\rho z)$ function

$\phi(\rho z)$ at depth $z = \text{intensity from depth ‘z’ divided by } \phi(\Delta \rho z)$

where, $\rho = \text{density}$, $z = \text{depth}$,
and $\phi(\Delta \rho z) = \text{intensity from a free standing layer of thickness ‘}\Delta z’$
Continuum X-ray generation

Produced by deceleration of beam electrons in the electrostatic field of target atoms

Energy lost by beam electrons is converted to x-ray

(Maximum energy of continuum x-rays = electron beam energy)
Continuum X-rays: background intensity

Low-Z sample
(Ca-Fe poor)
Low background

High-Z sample
(Ca-Fe rich)
High background

Increases with sample atomic number
Wavelength Dispersive Spectrometer (WDS)
Wavelength Dispersive Spectrometer (WDS)

**Bragg’s Law:**

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

- \( n \): order of diffraction
- \( \lambda \): wavelength of X-ray
- \( d \): lattice spacing in diffracting crystal
- \( \theta \): angle of incidence or diffraction

**“L-value”:**

\[ L = n\lambda \frac{R}{d} \]

- \( \theta \): angle of incidence or diffraction
- \( L \): distance between sample and crystal
- \( R \): radius of focusing (Rowland) circle

\[ \sin \theta = \frac{L}{2R} \]

\( \theta \): angle of incidence or diffraction

\( L \): distance between sample and crystal

\( R \): radius of focusing (Rowland) circle
Incidence or Diffraction angle

\[ n\lambda_1 = 2d \sin \theta_1 \]

\[ n\lambda_2 = 2d \sin \theta_2 \]

With a different incidence angle, a different wavelength is diffracted
(for the same order of diffraction, \( n \))
First and second order diffractions

If the incidence angle changes so that \( \sin \theta_2 = 2 \sin \theta_1 \), the 2\(^{nd}\) order diffraction of the same wavelength occurs

\((\text{path } ABC = 1\lambda; \text{ path } DEF = 2 \times ABC = 2\lambda)\)

In WDS: since \( L = 2R \sin \theta \), L-value for the second order diffraction is doubled; \( L_2 = 2L_1 \)
Example 1.

Si Kα

Energy, $E = 1.74$ keV

$$\lambda \text{ (nm)} = \frac{1.2398}{E \text{ (keV)}}$$

Wavelength, $\lambda = \frac{1.2398}{1.74} = 0.7125$ nm

$$L \text{ (mm)} = n \lambda \text{ (nm)} \frac{R \text{ (mm)}}{d \text{ (nm)}}$$

For $n = 1$, $R = 140$, and $d_{\text{TAP}} = 1.2879$,

$$L_{\text{TAP}} = 1 \times 0.7125 \times \frac{140}{1.2879} = 77.45 \text{ mm}$$

Example 2.

U Mα

Energy, $E = 3.17$ keV

$$\lambda \text{ (nm)} = \frac{1.2398}{E \text{ (keV)}}$$

Wavelength, $\lambda = \frac{1.2398}{3.17} = 0.3911$ nm

$$L \text{ (mm)} = n \lambda \text{ (nm)} \frac{R \text{ (mm)}}{d \text{ (nm)}}$$

For $n = 1$, $R = 140$, and $d_{\text{PET}} = 0.4371$,

$$L_{\text{PET}} = 1 \times 0.3911 \times \frac{140}{0.4371} = 125.27 \text{ mm}$$
WDS operation: changing the L-value

Changing the L-value from $L_1$ to $L_2$ changes the incidence angle from $\theta_1$ to $\theta_2$ so that a different wavelength $\lambda_2$ is diffracted.

Radius of focusing circle (R) remains constant

\[
\begin{align*}
n\lambda_1 &= 2d \sin \theta_1 \\
L_1 &= n\lambda_1 \cdot R/d \\
n\lambda_2 &= 2d \sin \theta_2 \\
L_2 &= n\lambda_2 \cdot R/d
\end{align*}
\]
Theoretical limits of spectrometer movement

For a spectrometer with $R = 140$ mm, $L = 2R \sin \theta$

Theoretical limits:
$2R \geq L \geq 0$ at $90^\circ \geq \theta \geq 0^\circ$

$280$ mm $\geq L \geq 0$ mm

$L = 280$ mm $\theta = 90^\circ$
$L = 210$ mm $\theta = 48.6^\circ$
$L = 140$ mm $\theta = 30^\circ$
$L = 70$ mm $\theta = 14.5^\circ$
$L = 0$ mm $\theta = 0^\circ$

Note $\theta$ changes faster between 280-140 mm than between 140-0 mm
Spectrometer movement

Theoretical limits

sample
Actual limits of spectrometer movement

For a spectrometer with $R = 140$ mm,

Actual limits: $60$ mm $\leq L \leq 260$ mm; $12.4^\circ \leq \theta \leq 68.2^\circ$

Typically, $72.5$ mm $\leq L \leq 229.5$ mm; $15^\circ \leq \theta \leq 55^\circ$

Recall $\sin \theta = \frac{L}{2R}$, so $L = 2R \sin \theta$ and $\theta = \sin^{-1}\left(\frac{L}{2R}\right)$
2d of x-ray diffractors

For \( n=1, \theta = 15 \) to \( 55^\circ \) (\( L = 73 \) to 230 mm), and \( R = 140 \) mm, a crystal can diffract \( \sim 0.52d < \lambda < 1.64d \)

[recall, \( L = n\lambda \frac{R}{d} \), i.e., \( \lambda = \frac{L}{nRd} \)]

### Crystal lattices

<table>
<thead>
<tr>
<th></th>
<th>2d (nm)</th>
<th>6</th>
<th>14</th>
<th>22</th>
<th>30</th>
<th>38</th>
<th>46</th>
<th>54</th>
<th>62</th>
<th>70</th>
<th>78</th>
<th>86</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAP</td>
<td>2.576</td>
<td>2.26</td>
<td>0.62</td>
<td>2.16</td>
<td>0.57</td>
<td>2.33</td>
<td>0.58</td>
<td>6.38</td>
<td>63.0</td>
<td>L (mm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAPH</td>
<td>2.576</td>
<td>256.6</td>
<td>67.4</td>
<td>234.8</td>
<td>62.0</td>
<td>253.3</td>
<td>63.0</td>
<td>L (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>0.8742</td>
<td>13Al</td>
<td>24Cr</td>
<td>36Kr</td>
<td>66Tb</td>
<td>70Yb</td>
<td>L (mm)</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>PETH</td>
<td>0.8742</td>
<td>13Al</td>
<td>24Cr</td>
<td>36Kr</td>
<td>66Tb</td>
<td>70Yb</td>
<td>L (mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIF</td>
<td>0.4027</td>
<td>19K</td>
<td>27Rb</td>
<td>48Cd</td>
<td>79Au</td>
<td>L (mm)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LIFH</td>
<td>0.4027</td>
<td>20Ca</td>
<td>31Ga</td>
<td>50Sn</td>
<td>79Au</td>
<td>L (mm)</td>
<td></td>
<td></td>
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</tbody>
</table>

### Layered structures

* \( \lambda_{BeK\alpha} = 11.27 \) nm; so BeK\( \alpha \) can be diffracted only by diffractors with \( 2d > 11.27 \) nm
  * e.g., with LDE3H (at \( L = 157.8 \) mm), and LDEB and LDEBH (at \( L = 217.6 \) mm)
Spectral resolution

![Diagram showing the concept of Full-Width Half-Maximum (FWHM)]
Curved diffracting crystals

Peak resolution with fully focusing Johansson-type crystal: FWHM ~10 eV

Some defocusing in Johan-type, but resolution is not compromised
X-ray focusing ellipsoid
WDS vs. EDS spectral resolution

Peak resolution with WDS (FWHM ~10 eV) is an order of magnitude better than with EDS (FWHM ~150 eV)
WDS detector: Proportional counter

Flow counter:
- P-10 gas (90% Argon + 10% methane quenching agent)
- Polypropylene window

Sealed counter:
- Xenon gas
- Beryllium window

- Incoming x-ray ionizes a gas atom that sets up a chain of ionizations in the gas. The signal is thus amplified by the gas itself.
- Pulse voltage generated is proportional to the voltage in the collection wire under normal operating wire conditions.

Tungsten collection wire at 1-3 kV voltage
Normal operation: 1600-1850 V
Signal amplification

Typical voltage range in the proportional counter region for a W wire: 1600-1850 V

The amplification factor is proportional to the voltage in the collection wire in the proportional counter region.
Quantum efficiency of counter gas

- **Argon:** long wavelength (low energy) detection

- **Xenon:** short wavelength (high energy) detection

Highest when the incoming X-ray is least absorbed by the gas.

Decreases when the X-ray is absorbed by ionizing an inner shell of the gas atom, generating ArKα or XeLα.

Lowest when $E_{X\text{-ray}}$ is slightly higher than the $E_c(Ar\text{-K-shell})$ or $E_c(Xe\text{-L-shell})$ absorption edges.

- **Argon:** long wavelength (low energy) detection
- **Xenon:** short wavelength (high energy) detection
Proportional counter setup: Pulse Height Analysis

A Single Channel Analyzer (SCA) can be set to allow only x-ray voltage pulses within $\Delta E$ to pass through.

$\Delta E$ is determined by Pulse Height Analysis (PHA) through an SCA scan.

Baseline and window voltages ($\Delta E$) are set to filter out noise and unwanted signal.

An SCA scan shows the variation in count rate as a small voltage window ($\Delta E$) is moved across the voltage range.

Proportional counter output:
Voltage pulses from noise and x-ray signal.
Pulse voltage in SCA scan

Energy of $\text{SiK}\alpha$ (1.739 keV) is $\sim 1.39$ times the energy of $\text{MgK}\alpha$ (1.253 keV).
If the pulse for $\text{MgK}\alpha$ is at 4 V, the pulse for $\text{SiK}\alpha$ will be at $4 \times 1.39 = 5.56$ V.

Pulse voltage is proportional to energy of the X-ray being detected.
Escape peak in SCA scan

Escape peaks fluoresced by incoming X-ray:
- P-10 counter: ArK$\alpha$
- Xenon counter: XeL$\alpha$

If the pulse for NiK$\alpha$ (7.47 keV) is at 5.20 V,
the XeL$\alpha$ (4.11 keV) escape peak will be at $5.2 \times \left[ \frac{(7.47 - 4.11)}{7.47} \right] = 2.34$ V
Proportional counter window material

- Mylar has lower transmittance than polypropylene, especially for light element x-rays.
- Thin windows are better for light elements.
  - 1 μm thick polypropylene window transmits ~60% of the F Kα.
  - 6 μm thick polypropylene window transmits only ~5% of the F Kα.
Detector slit

- Positioned in front of the proportional counter window
- Cuts off stray x-rays and electrons

<table>
<thead>
<tr>
<th>Open:</th>
<th>LDE</th>
<th>P-10 flow counter</th>
<th>Very light elements (very low E, very long $\lambda$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550-300 $\mu$m:</td>
<td>PET or LIF</td>
<td>Xe sealed counter</td>
<td>Heavy elements (high E, short $\lambda$)</td>
</tr>
<tr>
<td>300 $\mu$m:</td>
<td>TAP</td>
<td>P-10 flow counter</td>
<td>Light elements (low E, long $\lambda$)</td>
</tr>
<tr>
<td>300 $\mu$m with Mylar film:</td>
<td>PET or LIF</td>
<td>P-10 flow counter</td>
<td>Heavy elements (high E, short $\lambda$)</td>
</tr>
</tbody>
</table>
Semi-quantitative analysis
Compositional imaging with X-rays: elemental mapping

• **Beam-rastered image:**
  
  *electron beam rasters over the area to be imaged*

• **Stage-rastered image:**
  
  *electron beam is stationary, stage moves*
Zn-Sn composite

Background image

Zn-rich phase (low Z)

Sn-rich phase (high Z)

Zn x-ray image

Sn x-ray image

S x-ray image
X-ray defocusing in beam-rastered image
Image quality of x-ray maps

Two factors:

- **Image resolution:** number of points measured within the imaged area

- **X-ray Signal:** beam current and counting (dwell) time per point
Simultaneous mapping with different signals

Combined BSE, WDS and EDS X-ray mapping

Combined BSE, CL and X-ray mapping