2. Properties and Production of X-rays
Properties of X-rays

- X-rays – EM energy with wavelength (\( \lambda \)) of about 0.01 to 10 nm
Properties of X-rays

Planck's equation:

\[ E = h \nu \]

where

\[ E = \text{energy of photon (in Joules)} \]
\[ h = \text{Planck’s constant} \quad (6.6252 \times 10^{-34}\ \text{Joule sec}) \]
\[ \nu = \text{frequency (sec}^{-1}) \]

But

\[ \nu = \frac{c}{\lambda} \]

where

\[ c = \text{velocity of light} \quad (3 \times 10^8\ \text{meters / sec}) \]
\[ \lambda = \text{wavelength of photon (meters)} \]

Thus

\[ E = \frac{hc}{\lambda} \ \text{Joules} \]
Properties of X-ray Photons

\[ E = \frac{hc}{\lambda} \text{ Joules (Planck equation)} \]

When \( E \) = energy of photon expressed in keV
and \( \lambda \) = wavelength of photon expressed in nanometers \((10^{-9} \text{ m})\)

then \( E_{(keV)} = \frac{1.241}{\lambda_{(nm)}} \) (after appropriate substitution of "constant" values)
Properties of X-ray Photons

When wavelength ($\lambda$) is expressed in nanometers [nm] ($10^{-9}$ m) then, after appropriate substitution of "constant" values,

$$E_{(keV)} = \frac{1.241}{\lambda_{(nm)}}$$

and when wavelength expressed in Angstroms [Å] ($10^{-10}$ m):

$$E_{(keV)} = \frac{12.41}{\lambda_{(Å)}}$$
Production of X-rays

• X-rays can be created in a couple of ways:
  
  – Naturally found radioactive isotopes (i.e. 109Cd, 57Co, 55Fe) can be used, but give off half-life decay radiation

  – High-energy electrons can be decelerated via collisions so it loses (releases) energy as X-rays (i.e. Bremsstrahlung, or continuum radiation)
Production of X-rays – Tube Schematic

Cathode assembly

(Filament)

Vacuum

Target Anode: e.g. Rh, Mo

Anode assembly

HT (-ve)

HT (+ve)

Filament Voltage

Glass Envelope

Tube Window

X-rays

Cu Backing
Production of X-rays – Tube Schematic

- Oil insulation
- Focal spot
- HT (+ve) supply
- HT (-ve) supply
- Filament supply
- Tube shield
- X-ray tube insert
- Emergent X-rays
Production of X-rays

- Vacuum tube with cathode (-) and anode (+) ends
  - Cathode – wire coiled filament (W)
  - Anode generally Rh, Cu, Mo, W, or Ti, with C backing
  - Filament current (uA) provides electric power
  - Excited filament forms free excited electron cluster; returns to wire after
- High potential difference (kV) applied between cathode and anode
- Attraction causes high speed acceleration of e- to anode
  - Electron beam accelerates towards atomic particles to make X-rays
- Huge energy on collision, cooling prevents destruction
  - High volt tubes - water/oil medium, air/gas for low voltage tubes
- Inefficient: <1% energy goes perpendicular in Be port as X-rays, ~99% heat
- It is aimed at an evacuated sample for XRF analysis
Properties of the Continuum Spectrum

- Brehmstrahlung (continuum, scatter) shown for Rh anode tube. Note changes in shape with varying kV, and notice RhL line (to be discussed in further detail).
- Shows an energy dispersive spectrum, which is used to excite the actual sample.
Properties of the Continuum Spectrum

The “continuum shape”
Kramer’s formula- photon energy

Kramer's formula := (expressed in terms of energy)

\[
I_E \cdot dE = k' \cdot i \cdot Z \cdot \left[ \frac{E_o - E}{E} \right] \cdot dE
\]

where

\[
I_E \cdot dE = \text{intensity of continuum for energy range } E \text{ to } E + dE
\]

\[
k' = \text{proportionality constant}
\]

\[
i = \text{electron (tube) current } [\mu A]
\]

\[
Z = \text{atomic number of target material}
\]

\[
E_o = \text{maximum energy of bombarding electrons}
\]

\[
\equiv \text{applied tube voltage } [V_0]
\]
Properties of the Continuum Spectrum

• The continuum (or scatter, or Brehmstrahlung) IS NOT a product of actual XRF, but X-rays BEFORE it strikes the sample

• Essentially a baseline measurement of:
  – Brehmstrahlung distribution
  – Transmission characteristics of focusing optic/collimator

• SW needs a scatter spectrum saved to take into consideration the characteristics of your system’s optics for quantitative routines (i.e. FP)

• PM Lab Exercise
  – Looking at the X-ray tube and hardware
  – Observing differences in scatter spectra between different kV, uA, optics
Interaction of X-rays with Matter

\[ I_0(E_0) \]

Sample (Z)

\[ \text{Characteristic line production} \]
\[ E_Z < E_o \]

\[ \text{Photoelectrons} \]

\[ E_{\text{coherent}} = E_o \]

Coherent Scatter [i.e. Elastic, Rayleigh]

\[ E_{\text{incoherent}} < E_o \]

Incoherent Scatter [i.e. Inelastic, Compton]

Absorption phenomena \( \tau \)

Scatter phenomena \( \sigma \)
Basic Atomic Structure - Bohr’s Model

**Nucleus (+ve)**

**Electron energy levels (or “shells”)**

**Orbiting Electrons (-ve)**

**Principle (or Group) quantum numbers (n)**

*where maximum electrons/shell = 2n^2*
Bohr’s Model

- Electrons move in closed orbits around nucleus (most stable state at all times)

- Various possible major orbits called “energy levels” or “shells” (n) where n=1 for innermost (K shell), n=2 for the next (L shell) etc.

- Brehmstrahlung radiation absorbed by sample. X-rays emitted when electrons “jump” orbits

- Energies
  a) potential
  b) binding $\rightarrow$ Absorption Edge Energy

- Critical excitation potential are both a function of atomic number (Z)

- Can be more than one energy level per shell
  - maximum $n^\circ$: $K=1$, $L=3$, $M=5$, $N=7$
1. Incoming “energy-particle” with an energy \( E=hn \) > binding energy of the “K-electron” with which it is on a collision course
1. The “ejected K-electron” has been moved to a higher potential-energy level or even completely away from the atom.

2. Expended or greatly reduced energy “energy-particle” ($E' = h\nu'$).

Electron vacancy i.e. “ionised” K shell.
3. An electron transfers from the L-shell to fill the vacancy created in the K-shell TO BE STABLE, but arrives with excess “potential” energy…

…an “ionised” L-shell is a natural by-product
4. The transferred electron’s excess “potential” energy \([E_L - E_K]\) is converted to a “Ka” X-ray photon.
5. An electron transfers from the M-shell to fill the vacancy created in the K-shell, **AGAIN TO REACH STABILITY**, but arrives with an even greater excess “potential” energy…

... and in the process producing an “ionised” M-shell
6. The transferred electron’s excess “potential” energy \([E_M - E_K]\) is converted to a “Kβ” X-ray photon
7. The emergent “Ka” X-ray photon is “photo-electrically” absorbed (typically within the L-shell) before it has the chance to escape the atom.
8. The energy absorbed by the L-electron is usually sufficient to expel it from the atom. The net result “observed” from outside the atom is the production of “Auger” electrons and not characteristic photons.
XRF – Transition Nomenclature

- Kα₁
- Kα₂
- Kβ₁
- Kβ₂
- Kβ₃

- Lα₁
- Lα₂
- Lβ₁

- M
- L
- K

- 1s
- 2s
- 2p
- 3s
- 3p
- 3d
## XRF – Examples of Elemental Transitions

<table>
<thead>
<tr>
<th>Line</th>
<th>Transition</th>
<th>Energy (keV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siegbahn</td>
<td>IUPAC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K\alpha_1$</td>
<td>K - L3</td>
<td>2p - 1s</td>
<td>8.044</td>
</tr>
<tr>
<td>$K\alpha_2$</td>
<td>K - L2</td>
<td>2p - 1s</td>
<td>8.026</td>
</tr>
<tr>
<td>$K\beta_1$</td>
<td>K - M3</td>
<td>3p - 1s</td>
<td>8.904</td>
</tr>
<tr>
<td>$K\beta_3$</td>
<td>K - M2</td>
<td>3p - 1s</td>
<td>ditto</td>
</tr>
<tr>
<td>$K$ edge</td>
<td></td>
<td></td>
<td>8.993</td>
</tr>
<tr>
<td>$L\alpha_1$</td>
<td>L3 - M5</td>
<td>3d - 2p</td>
<td>0.932</td>
</tr>
<tr>
<td>$L\beta_1$</td>
<td>L2 - M4</td>
<td>3d - 2p</td>
<td>0.952</td>
</tr>
<tr>
<td>$L_1$ edge</td>
<td></td>
<td></td>
<td>1.060</td>
</tr>
</tbody>
</table>

The detector counts photons at each energy (keV), creating a Gaussian distribution → final EDXRF spectrum. The more a particular element, the more photons it emits, and the higher elemental peak (Gaussian curve).
XRF – Examples of Elemental Transitions

Characteristic-line energy & At.Nº (Z)

An example of typical characteristic spectral lines in EDXRF
XRF – Elemental Transition Concepts

• Why can we not see every transition lines on the EDXRF spectrum?
  – The energy resolution of the detector is unable to separate the lines

• Why does the space between the Kα and Kβ lines increase as atomic number (Z) increases?
  – As Z increases, protons in the nucleus create a stronger binding energy to its K-shell electrons, and the L and M shell electrons are less bound. Therefore, energy difference between Kα and Kβ increases with Z.

  – For that same reason, as Z increases, you can see more specific lines (i.e. you can see Mo(Kβ₁) and Mo(Kβ₂), whereas in Ca(K), you cannot).
Absorption Edges

• DEFINITION:
  - Minimum amount of energy required for an element to eject an electron from its core orbital to create a vacancy
  - Therefore, the incoming energy must equal or exceed the binding energy
  - Each elements’ absorption of energy is quantitatively represented by the Mass Attenuation Coefficient ($\mu$), generally represented as MASS/UNIT AREA.

• Example: Ni(Ka) and Ni(Kb) peak shown
  - Absorption edge for Ni(K) is 8.3328keV
Absorption Edges - Basics

1. **Effect of tube voltage and its “continuum” distribution on the excitation of Mo(K) spectra in Mo atoms present in a specimen** [Tube voltage = 15kV]
   → **NO Mo(K) PEAK YET!**
Absorption Edges - Basics

 Incident spectrum $V_0 = 20\text{kV}$

Mo(K) edge

No incident spectral energy $> \text{MoK abs edge}$

2. [Tube voltage = 20kV]
Just at the absorption edge

→ No Mo(K) peak yet!
Absorption Edges - Basics

Portion of incident continuum with energy > MoK absorption edge

3. [Tube voltage = 30kV] Mo(K) peak appears, but not in the optimal excitation region of the continuum spectrum.

→ Peak detected!
Absorption Edges - Basics

4. [Tube voltage = 40kV] Mo(K) peak is now in the optimal excitation region of continuum

⇒ PEAK AT OPTIMAL SENSITIVITY!
As you approach Fe(K) edge at 7.11 keV, that energy gets less and less absorbed by sample due to increased transmission.
Absorption Edges – Thin Films

At the Fe(K) edge, all incoming energy is now consumed in ejecting the K-shell electron, causing a huge spike in energy attenuation.
Beyond Fe(K) edge, as energy continues to increase, X-ray transmission through the sample increases as X-rays become more penetrating, decreasing absorption.
Absorption Edges – Ex. Mo

The diagram illustrates the mass absorption coefficient ($\mu$) as a function of the energy of absorbed photons (keV). It shows the K-absorption edge and L-absorption edges for the absorbing element Mo. The x-axis represents the energy of absorbed photons, ranging from 0 to 30 keV, while the y-axis represents the mass absorption coefficient ranging from 0 to 2000. There is a notable peak at the K-absorption edge, indicating a significant increase in absorption coefficient at this energy level. The graph also notes that there is no data in certain regions, marked as 'no data'.
Absorption Edges – Ex. Fe, Mo

energy of absorbed photon (keV)

mass absorption coefficient (µ)

- red: absorbing element = Fe
- blue: absorbing element = Mo
Absorption Edges – Ex. Cr, Fe, Ni

- CrKα
- FeKα
- NiKα energy

- absorbing element = Cr
- absorbing element = Fe
- absorbing element = Ni

mass absorption coefficient

energy of absorbed photon [KeV]
Matrix mass absorption coefficient $\mu_{matrix}$

$$\mu_{matrix}(E) = \sum_i \left( \omega_i \times \mu_i(E) \right)$$

where

$\mu_{matrix}(E)$ = matrix mass abs coeff for analyte photon - energy $E$

$\omega_i$ = weight fraction of individual matrix element $i$

and

$\mu_i(E)$ = mass abs coeff of element $i$ for analyte photon - energy $E$
Absorption Edges - MACs

Matrix mass absorption coefficient $\mu_{\text{matrix}}$

For alloy composition: 10% Cr; 10% Fe; 80% Ni

$$\left( \mu_{\text{matrix}} \right)_{\text{CrKa}} = \sum (\omega_{\text{Cr}} \mu_{\text{Cr}}(\text{CrKa}) + \omega_{\text{Fe}} \mu_{\text{Fe}}(\text{CrKa}) + \omega_{\text{Ni}} \mu_{\text{Ni}}(\text{CrKa}))$$

$$= (0.1 \times 90) + (0.1 \times 115) + (0.8 \times 146)$$
$$= 9 + 11.5 + 116.8$$
$$= 137.3$$
Important Formulas – MOSELEY’S LAW

\[ \sqrt{\nu} = a[Z - \sigma] \]

but \[ \nu = \frac{c}{\lambda} \]

hence \[ E = a'[Z - \sigma]^2 \]
i.e. \[ E \propto Z^2 \]

where \( \nu, c, \lambda \) & \( E \) = frequency, velocity, wavelength or energy of emitted analyte

\( a, a' \) = constants of proportionality

\( Z \) = atomic number of emitting atom

\( \sigma \) = electronic“ screening” constant

where \( \sigma \approx 1 \) for K - series & \( \approx 7.4 \) for L - series
Why does this phenomenon occur?
- As Z increases, protons, neutrons, electrons, and orbital layers increase
- More protons creates a stronger binding force on the electrons
- Higher binding energy requires more energy to eject inner K-shell electron
- Additional orbitals (L and M series) require less energy to eject due to weaker binding energies
Important Formulas – FLUORESCENT YIELD

Fluorescent yield \( (\omega) \) = \( \frac{N^o \text{ of emitted photons (for a given series)}}{\text{Total } N^o \text{ of incident photons absorbed}} \)

For the K-series \( \omega_K = \frac{bZ^4}{1 + bZ^4} \)

where \( b = \text{Stephenson's constant} (\approx 1.126 \times 10^{-6}) \)
and \( Z = \text{atomic number} \)
Important Formulas – FLUORESCENT YIELD

Fluorescent yield

Emitted Auger-electron region

Emitted X-ray photon region

Range normally covered by K-lines

K-series

Atomic Nº (Z)

Important Formulas – FLUORESCENT YIELD

Fluorescent yield

Emitted Auger-electron region

Emitted X-ray photon region

Range normally covered by K-lines

K-series

Atomic Nº (Z)
Important Formulas – FLUORESCENT YIELD

Fluorescent yield ($\omega$)

L-series

Emitted Auger-electron region

Range normally covered by L-lines

Atomic N° (Z)
The intensity of characteristic X-ray spectral lines generated in a specimen from incident X-ray tube continuum is related to:

\[ I_{\text{characteristic}} = k \cdot i \cdot (V_o - V_c)^n \]

where
- \( k \) = a proportionality constant
- \( i \) = X-ray tube electron-current (e.g. \( \mu A \))
- \( V_o \) = applied (i.e. the "operating") tube potential (kV)
- \( V_c \) = "critical excitation potential" [\( \equiv \) binding energy] (keV)
- \( n \) = a constant with a value \( \approx 1.6 \) for K-series
Uniform Excitation of Characteristic Lines Over the Required Range

Under “direct excitation” conditions in EDXRF, the following tube voltage setting will provide, to a first approximation, uniform excitation over the element range of interest:

\[
\text{applied tube } kV \approx V_{C(low)} + \frac{3}{2} V_{C(high)}
\]

where:

- \(V_{C(low)}\) = "critical potential" equivalent of the lowest-energy analyte’s absorption edge
- \(V_{C(high)}\) = "critical potential" equivalent of the highest-energy analyte’s absorption edge
Important Formulas – BEER-LAMBERT LAW

Sample (Z)

$I_0(E_0)$

$E_{\text{coherent}} = E_0$

Coherent Scatter [i.e. Elastic, Rayleigh]

$E_{\text{incoherent}} < E_0$

Incoherent Scatter [i.e. Inelastic, Compton]

Characteristic line production

$E_Z < E_0$

Photoelectrons

$I(E_0)$

Absorption phenomena $\tau$

Scatter phenomena $\sigma$

Coherent Scatter [i.e. Elastic, Rayleigh]

Incoherent Scatter [i.e. Inelastic, Compton]
Important Formulas – BEER-LAMBERT LAW

Beer-Lambert Law
(for absorption & transmission of X-rays)

\[ I = I_o e^{-\mu \rho x} \]

where

- \( I_o \) = incident (original) intensity
- \( I \) = transmitted intensity
- \( \mu \) = mass absorption coefficient (cm \(^2\)/gm)
- \( \rho \) = density (gms/cm \(^3\))
- \( x \) = thickness (cm)
Critical Penetration Depth of XRF

“Analysis-” (aka “critical-”) depth for XRF

Critical depth “d” is defined as the distance below a sample surface at which “excited” X-ray photons emergent in the direction of the measuring system suffer 99% absorption over their pathlength “x” within the sample.
Analysis Depths of XRF – ex. Steel

Typical “analysis” depths in a steel matrix
Analysis Depths of XRF – Glass

“Analysis” depths in silica glass (linear scale)

- Na
- Si
- Ca
- Fe
- Sr

Depth in microns:
- 6
- 22
- 47
- 226
- 2316
Capabilities of Micro-XRF

- Two closest reference points
  - 1. **Bulk XRF** – Non-focused X-ray beam, large analytical area
  - 2. **SEM/EDS** – Electron beam source

- What makes it “Micro”?
  - Unlike bulk XRF, the X-rays are focused through a glass capillary to generate a beam diameter as low as 30 µm
Micro-XRF vs. SEM-EDS

• Non-destructive: No beam damage or coating of sample

• Minimal Sample Preparation:
  – conductivity not required
  – sample shape can be irregular

• Improved sensitivity: 10x or better (vs. SEM-EDS)
• Navigation by Optical Microscope
• Low Vacuum (~ 300 mTorr) or No Vacuum (Air) → liquids, loose particles
• X-rays are more penetrating (microns to millimeters)
• More appropriate than SEM for larger scale features, for both maps and single points
XRF Advantages – SEM-EDS vs. μ-EDXRF

SEM_EDS spectrum
(SUTW detector)

EDXRF spectrum
(10um Be window detector)

Si
(common line to both spectra)

ec1-1 glass
spectra collected at 20kV

XRF Advantages – SEM-EDS vs. μ-EDXRF

SEM_EDS spectrum
(SUTW detector)

EDXRF spectrum
(10um Be window detector)

XRF Advantages – SEM-EDS vs. μ-EDXRF

SEM_EDS spectrum
(SUTW detector)

EDXRF spectrum
(10um Be window detector)

XRF Advantages – SEM-EDS vs. μ-EDXRF

SEM_EDS spectrum
(SUTW detector)

EDXRF spectrum
(10um Be window detector)

XRF Advantages – SEM-EDS vs. μ-EDXRF

SEM_EDS spectrum
(SUTW detector)

EDXRF spectrum
(10um Be window detector)
XRF Advantages – SEM-EDS vs. µ-EDXRF

(O, Na, Mg, Al, Si, C, K, Ca, Ti, Cr, Mn, Fe)

Si (spectra normalised to this peak)

CaKα

CaKβ

RhL (scattered tube lines)

ec1-1 glass spectra collected at 20kV
Micro-XRF Sensitivity

Lower Limit of Detection
Glasses, Oxides

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>50</td>
</tr>
<tr>
<td>V</td>
<td>40</td>
</tr>
<tr>
<td>Cr</td>
<td>30</td>
</tr>
<tr>
<td>Mn</td>
<td>30</td>
</tr>
<tr>
<td>Fe</td>
<td>25</td>
</tr>
<tr>
<td>Ni</td>
<td>25</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
</tr>
<tr>
<td>Zn</td>
<td>20</td>
</tr>
<tr>
<td>Pb</td>
<td>30</td>
</tr>
<tr>
<td>Rb</td>
<td>15</td>
</tr>
<tr>
<td>Sr</td>
<td>15</td>
</tr>
</tbody>
</table>

Lower Limit of Detection
SS Alloy

<table>
<thead>
<tr>
<th>Element</th>
<th>MicroXRF</th>
<th>EDX</th>
<th>Element</th>
<th>MicroXRF</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>100</td>
<td>1000</td>
<td>Cu</td>
<td>20</td>
<td>1000</td>
</tr>
<tr>
<td>Cr</td>
<td>80</td>
<td>800</td>
<td>Zn</td>
<td>20</td>
<td>1000</td>
</tr>
<tr>
<td>Mn</td>
<td>50</td>
<td>800</td>
<td>Mo</td>
<td>20</td>
<td>2000</td>
</tr>
<tr>
<td>Fe</td>
<td>40</td>
<td>800</td>
<td>Sn</td>
<td>25</td>
<td>4000</td>
</tr>
<tr>
<td>Ni</td>
<td>30</td>
<td>900</td>
<td>Pb</td>
<td>20</td>
<td>5000</td>
</tr>
</tbody>
</table>
Analytical Factors to Consider

• Targets’ character. spectra affected by e-beam intensity

• Atomic Number of Target (Z) – effects intensity

• Filament Current (0-1000uA)
  – Filament supplies e-, thus a stronger filament current = more energy, more free e- creates a stronger beam, which emits more powerful X-rays on collision.

• Tube Voltage (0-50kV)
  – Increasing tube voltage creates stronger “pull” on free electrons, increasing speed of electrons to target, results in X-rays with greater energy (keV)

• Spot/Focal Size (µm-mm)
  – Smaller spot size condenses focal diameter of the e-beam, increasing brilliance

• Time
  – Controls specified duration of exposure, how long tube radiates