Radiation interaction with matter and energy dispersive x-ray fluorescence analysis (EDXRF)

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MAUD school 2016
Caen, France
### Radiation – x-rays (photons), neutrons, electrons

#### Wave – particle duality

<table>
<thead>
<tr>
<th>Radiation Type</th>
<th>Planck / Einstein</th>
<th>De Broglie</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-rays (photons)</td>
<td>$E = h \nu$</td>
<td>$\lambda = \frac{h}{p}$</td>
</tr>
</tbody>
</table>

#### Properties

<table>
<thead>
<tr>
<th>Radiation Type</th>
<th>Electromagnetic Radiation</th>
<th>Neutral Particles</th>
<th>Charged Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>x-rays (photons)</td>
<td>0 rest mass $c = \lambda \nu$</td>
<td>$E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m}$</td>
<td>$E_k = eV = \frac{1}{2}mv^2 = \frac{p^2}{2m}$</td>
</tr>
<tr>
<td>neutrons</td>
<td>neutral particles</td>
<td>1.675E-27 kg</td>
<td>$\lambda = \frac{h}{mv}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>939.6 MeV/c2</td>
<td></td>
</tr>
<tr>
<td>electrons</td>
<td>charged particles</td>
<td>9.11E-31 kg</td>
<td>$\lambda = \frac{h}{\sqrt{2meV}} \frac{1}{\sqrt{1 + \frac{eV}{2mc^2}}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>511.0 keV/c2</td>
<td></td>
</tr>
<tr>
<td>Interaction Type</td>
<td>Interaction Partners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------</td>
<td></td>
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</tr>
<tr>
<td>X-rays, Photons</td>
<td>Dipole</td>
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<tr>
<td>Neutrons</td>
<td>Strong force</td>
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<tr>
<td></td>
<td>Magnetic</td>
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<tr>
<td></td>
<td>Neutron capture</td>
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<tr>
<td>Electrons</td>
<td>Coulomb force</td>
<td></td>
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</tbody>
</table>

- Neutrons: Magnetic and Neutron capture interactions result in unpaired electrons and nuclei.
- Electrons: Coulomb force interactions result in electrons and nuclei.
## Radiation – x-rays (photons), neutrons, electrons

<table>
<thead>
<tr>
<th></th>
<th>Energy (keV)</th>
<th>Wavelength (Å)</th>
<th>Velocity (m/s)</th>
<th>Temperature (K)</th>
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<tbody>
<tr>
<td><strong>x-rays</strong></td>
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<tr>
<td><strong>photons</strong></td>
<td></td>
<td></td>
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<tr>
<td>CuKa1</td>
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<td>1.54</td>
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<td>MoKa1</td>
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<tr>
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Radiation – x-rays (photons), neutrons, electrons

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\[ E = h\nu \]

\[ \lambda = \frac{hc}{E} \]
Radiation – attenuation - Beer Lambert law

\[ I(x) = I_0 \exp(-\mu x) \]

Calculated for X-Rays \( E = 17500 \text{eV} \)
Radiation – attenuation - Beer Lambert law

**Beer Lambert Law**

\[ I(x) = I_0 \exp(-\mu x) \]

\[ \mu = \mu_a + \mu_s \]

**Scattering** (elastic, inelastic)

Absorption

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Attenuation X-Rays: microscopic view

- Photoelectric absorption
- Elastic (Rayleigh) Scattering
- Inelastic (Compton) Scattering
X-Rays cross section magnitude

\[ I(x) = I_0 \exp(-\mu x) \]
\[ \mu = \sigma_c + \sigma_i + \tau \]

Data from:
H. Ebel, R. Svagera, M. F. Ebel, A. Shaltout and J. H. Hubbell,
Numerical description of photoelectric absorption coefficients for fundamental parameter programs,
X-Rays

Radiation interaction with matter and EDXRF – MAUD school 2016 – Giancarlo Pepponi
Atomic binding energies, electron energy levels

Absorption edges
Electron energy levels
Shells

<table>
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<tr>
<th>shell</th>
<th>n</th>
<th>l</th>
<th>j</th>
<th>spin sign</th>
<th>max number of electrons</th>
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<td>1.5</td>
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<td>0.5</td>
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<th>energy_eV</th>
<th>jump</th>
<th>level_width_eV</th>
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</table>

www.txrf.org/xraydata

www.txrf.org/xraydata

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Secondary effects – fluorescence vs Auger

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data from:
M. O. Krause,
X-Ray Fluorescence – characteristic lines

Siegbahn = Manne Siegbahn (swedish physicist)
Nobel Prize in Physics in 1924
IUPAC = International Union of Pure and Applied Chemistry

<table>
<thead>
<tr>
<th>Siegbahn</th>
<th>IUPAC</th>
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<tr>
<td>$K\alpha_1$</td>
<td>K-L3</td>
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<tr>
<td>$K\alpha_2$</td>
<td>K-L2</td>
</tr>
<tr>
<td>$K\beta_1$</td>
<td>K-M3</td>
</tr>
<tr>
<td>$K\beta_2$</td>
<td>K-N2,N3</td>
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<tr>
<td>$K\beta_3$</td>
<td>K-M2</td>
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<td>$L\alpha_1$</td>
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<td>$L\alpha_2$</td>
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<td>$L\beta_1$</td>
<td>L2-M4</td>
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<td>$L\beta_2$</td>
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<td>$L\beta_3$</td>
<td>L1-M3</td>
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<td>$L\beta_4$</td>
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Germanium

<table>
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<tr>
<th>Line</th>
<th>Energy [keV]</th>
<th>Probability</th>
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<td>$K\alpha_1$</td>
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</table>
Electrons interaction with matter


http://serc.carleton.edu/research_education/geochemsheets/electroninteractions.html
Inner shell ionization cross section: x-rays vs electrons
Neutrons interaction with matter

Fig. 12.2 Various categories of neutron interactions. The letters separated by commas in the parentheses show the incoming and outgoing particles.

http://www.uio.no/studier/emner/matnat/fys/FYS-KJM4710/h14/timeplan/neutron_chapter.pdf
Cross section: x-rays vs neutrons

https://www.psi.ch/niag/comparison-to-x-ray
## Cross section: x-rays vs neutrons

### Attenuation coefficients for thermal neutrons [cm⁻¹]

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<th>2a</th>
<th>3b</th>
<th>4b</th>
<th>5b</th>
<th>6b</th>
<th>7b</th>
<th>8</th>
<th>1b</th>
<th>2b</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
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<td>1.46</td>
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### Attenuation coefficients for X-ray [cm⁻¹] (150kV)

| H  | 0.02 |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Li | 0.06 | Be | 0.22 |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Na | 0.13 |    | 0.24 |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| K  | 0.14 | Ca | 0.26 | Sc | 0.48 | Ti | 0.73 | V  | 1.04 | Cr | 1.29 | Mn | 1.32 | Fe | 1.57 | Co | 1.78 | Ni | 1.96 | Cu | 1.97 | Zn | 1.64 | Ga | 1.42 | Ge | 1.33 | As | 1.50 | Se | 1.23 | Br | 0.90 | Kr | 0.17 |
| Rb | 0.47 | Sr | 1.61 | Y  | 1.61 | Zr | 1.60 | Nb | 1.04 | Mo | 1.04 | Tc | 1.61 | Ru | 1.61 | Rh | 1.61 | Pd | 1.61 | Ag | 1.61 | Cd | 1.61 | In | 1.61 | Sn | 1.61 | Sb | 1.61 | Te | 1.61 | I  | 0.43 |
| Cs | 1.42 | Ba | 2.73 | La | 5.04 | Hf | 19.70 | Ta | 25.47 | W  | 30.49 | Re | 34.47 | Os | 37.92 | Ir | 39.01 | Pt | 38.61 | Au | 35.94 | Hg | 25.88 | Ti | 23.23 | Pb | 22.81 | Bi | 20.28 | Po | 20.22 | At | 9.77 |

### Lanthanides

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<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
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### Actinides

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<td>Md</td>
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</table>

[https://www.psi.ch/niag/comparison-to-x-ray](https://www.psi.ch/niag/comparison-to-x-ray)
Neutron cross section

Scattering (full line) and absorption (dotted) cross sections of light element commonly used as neutron moderators, reflectors and absorbers, the data was obtained from database NEA NENDF/B-VII.1 using JANIS software

https://en.wikipedia.org/wiki/Neutron_cross_section
Scattering - Differential cross section

\[
\frac{d\sigma}{d\Omega} = d\theta d\phi
\]

http://www.physics.csbsju.edu/QM/square.17.html
X-Rays - Differential cross section – elastic scattering

elastic scattering at MoKa1

elastic scattering at CuKa1

270°
θ angle / deg

θ angle / deg
X-Rays - Differential cross section – inelastic scattering

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Electrons - Differential elastic cross section

Data from: http://www.ioffe.rssi.ru/ES/Elastic/
X-ray differential elastic cross section and the form factor

\[
\frac{d\sigma_{el}}{d\Omega} = \frac{d\sigma_T}{d\Omega} |F(x, Z)|^2
\]

Thomson cross section

\[
\frac{d\sigma_T}{d\Omega} = \frac{r_0^2}{2} (1 + \cos^2 \theta)
\]

Atomic form factor (atomic scattering factor)

\[
F(x, Z) = \frac{\sin \frac{\theta}{2}}{\frac{2}{\lambda}}
\]

Variable related to the momentum transfer

\[
F(x, Z) = 4\pi \int_0^{\infty} r^2 \rho(r, Z) \frac{\sin(4\pi xr)}{4\pi xr} dr
\]
X-ray differential elastic cross section and the form factor

... but actually there is a further dependence on energy ...

\[
f = f^0(x, Z) + f'(E, Z) + if''(E, Z)
\]

\[
F(x, Z) = 4\pi \int_0^\infty r^2 \rho(r, Z) \frac{\sin(4\pi xr)}{4\pi xr} dr
\]

- \(f''\) photoelectric absorption
- \(f'\) corrections for photoabsorption (Kramers-Kronig dispersion)
- relativistic effects, nuclear scattering

Diffraction (structure factor)

\[
F(h, k, l) = \sum_j f_j e^{-M_j} e^{2\pi i(hx_j + ky_j + lz_j)}
\]
X-ray differential elastic cross section and the form factor

forward scattering factors \((x = \theta = q = 0)\)

\[ f = f(0, Z, E) = f_1 + if_2 \]
\[ f_2 = f'' \]
\[ f_1 = f^0 \left( x = 0 \right) + f' \]

\(f_1\) and \(f_2\) are directly related to the index of refraction (reflection, refraction, XRR)

\[ n = 1 - \frac{1}{2\pi} Nr_0 \lambda^2 (f_1 + if_2) \]
\[ n = 1 - \delta - i\beta \]

\[ \mu_a = 2r_0 \lambda f_2 \]

\[ \delta = \frac{1}{2\pi} Nr_0 \lambda^2 f_1 \]
\[ \beta = \frac{1}{2\pi} Nr_0 \lambda^2 f_2 \]
X-ray differential inelastic cross section (Compton)

\[
\frac{d\sigma_i}{d\Omega} = \frac{d\sigma_{KN}}{d\Omega} S(q, Z)
\]

\[
\frac{d\sigma_{KN}}{d\Omega} = \frac{r_0^2}{2} P(\theta, E)
\]

\[
P(\theta, E) = \frac{1}{(1 + \alpha(1 - \cos \theta))^2} \left[ 1 + \cos^2 \theta + \frac{\alpha^2(1 - \cos \theta)^2}{1 + \alpha(1 - \cos \theta)} \right]
\]

\[
\alpha = \frac{E}{m_0 c^2}
\]

\[
S(q, Z) = \int_{\varepsilon > 0} \left| F_{\varepsilon}(q, Z) \right|^2
\]

Inelastic scattering function

\[
F_{\varepsilon}(\vec{q}, Z) = \sum_{n=1}^{Z} \left\langle \Psi_{\varepsilon} \left| \exp(i\vec{q} \cdot \vec{r}_n) \right| \Psi_0 \right\rangle
\]

Form factor elastic scattering

\[
F(\vec{q}, Z) = \sum_{n=1}^{Z} \left\langle \Psi_0 \left| \exp(i\vec{q} \cdot \vec{r}_n) \right| \Psi_0 \right\rangle
\]
In a spectrum the Compton peak is broader due to the angle dependence (in the accepted solid angle there are different scattering angles) and due to Doppler broadening.
X-Ray Absorption near edge fine structure

The X-ray Absorption Fine Structure (XAFS) of an iron foil

L-edges
2s and 2p -> cont.

K-edges
1s -> cont.

Different phenomena for:
- ‘free’ atoms
- molecules
- condensed systems
**X-Ray Absorption near edge fine structure**

- **Core electron**
  - unoccupied levels
  - \( E_{\text{ph}} \sim E_b \)
  - \( \Rightarrow \) Edge fine structure (XANES or NEXAFS)

- **Core electron**
  - continuum
  - outgoing wavefunction
  - \( E_{\text{ph}} > E_b \)

- **Extended fine structure (EXAFS)**

Interference:
- incoming wavefunction
- Backscattering from neighbouring atoms
Energy Dispersive X-Ray Fluorescence analysis (EDXRF)

Radiation interaction with matter and EDXRF – MAUD school 2016 – Giancarlo Pepponi
X-Ray Fluorescence analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
<th>Uncertainty</th>
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<tbody>
<tr>
<td>Ca</td>
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<td>0,500</td>
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<tr>
<td>Cr</td>
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<td>Fe</td>
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<td>Ni</td>
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<tr>
<td>Cu</td>
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<td>0,146</td>
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<td>Zn</td>
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<td>0,136</td>
</tr>
<tr>
<td>Ga</td>
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<td>0</td>
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<tr>
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<td>Ag</td>
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<td>2,160</td>
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<tr>
<td>Cd</td>
<td>56,722</td>
<td>2,398</td>
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</tbody>
</table>

Radiation interaction with matter and EDXRF – MAUD school 2016 – Giancarlo Pepponi
X-Ray Fluorescence analysis

Radiation interaction with matter and EDXRF – MAUD school 2016 – Giancarlo Pepponi

 photon energy [keV]

counts/channel

Kα
Kβ
Lα
Lβ
M

Zn
Cu
Ni
Co
Fe
Mn
Cr
K
Ca
Ba
Ba
Tl, Pb, Bi
Al
Si
Sr
Cd
Ag
Ba
K Ca

W Lβ scatter
X-Ray Fluorescence analysis

Multielement sample
10 ng Cd
W white spectrum
monochromatised at about 33 keV
load: 45 kV 20 mA; 500s

W white spectrum scattered radiation
X-Ray line families

Sr-K lines

<table>
<thead>
<tr>
<th>Siegbahn</th>
<th>IUPAC</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Kα₁</td>
<td>K-L3</td>
<td>Lα₁</td>
<td>L3-M5</td>
</tr>
<tr>
<td>Kα₂</td>
<td>K-L2</td>
<td>Lα₂</td>
<td>L3-M4</td>
</tr>
<tr>
<td>Kβ₁</td>
<td>K-M3</td>
<td>Lβ₁</td>
<td>L2-M4</td>
</tr>
<tr>
<td>Kβ₂</td>
<td>K-N2,N3</td>
<td>Lβ₂</td>
<td>L3-N5</td>
</tr>
<tr>
<td>Kβ₃</td>
<td>K-M2</td>
<td>Lβ₃</td>
<td>L1-M3</td>
</tr>
<tr>
<td></td>
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<td>Lβ₄</td>
<td>L1-M2</td>
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</table>
X-Ray line families

Pb L-lines

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Sr-K lines

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</table>
Modelling the response function of energy dispersive X-ray spectrometers with silicon detectors
F. Scholze, and M. Procop
Detector artefacts / ‘environmental’ artefacts

- Escape peak
- Sum / pile up peaks
- Ar
X-Ray Fluorescence – intensity - Sherman equation

\[ I_0 \ G_0 \ G_1 \]

generational factors and primary flux form the element independent proportionality constant

\[
dI_{\zeta jk} \propto e^{-\mu_s, E_0 \frac{z}{\sin \phi_i}} \ W_{\zeta} \left( \frac{\tau_j}{\rho} \right) \ \zeta E_0 \ \rho_s \ dz \\
\cdot \ \omega_{\zeta j} \ P_{\zeta jk} \ e^{-\mu_s, E_{\zeta jk} \frac{z}{\sin \phi_f}} \ \epsilon E_{\zeta jk}
\]

1. attenuation to depth \( z \)
2. photoelectric absorption in layer \( dz \)
3. fluorescence yield
4. transition probability (relative intensity of lines in shell)
5. attenuation to the detector
6. detector efficiency
X-Ray Fluorescence – intensity - Sherman equation

\[ dI_{\zeta jk} \propto e^{-\mu_{\zeta},E_0 \frac{z}{\sin \phi_i}} W_\zeta \left( \frac{T_j}{\rho} \right) \rho_s dz \cdot \omega_{\zeta j} \rho_{\zeta jk} e^{-\mu_{\zeta},E_{\zeta jk} \frac{z}{\sin \phi_f}} \epsilon_{E_{\zeta jk}} \]

- attenuation to depth z
- photoelectric absorption in layer dz
- fluorescence yield
- transition probability (relative intensity of lines in shell)
- attenuation to the detector
- detector efficiency

Integration over thickness

\[ I_{\zeta jk \text{ layer}} \propto W_\zeta \left( \frac{T_j}{\rho} \right) \rho_s \omega_{\zeta j} \rho_{\zeta jk} \cdot \frac{1 - e^{-\frac{\mu_{\zeta},E_{\zeta jk}}{\sin \phi_f} - \frac{\mu_{\zeta},E_{\zeta jk}}{\sin \phi_i} T}}{\frac{\mu_{\zeta},E_{\zeta jk}}{\sin \phi_f} + \frac{\mu_{\zeta},E_{\zeta jk}}{\sin \phi_i}} \]

geometrical factors and primary flux form the element independent proportionality constant
X-Ray Fluorescence – intensity - Sherman equation

\[ I_{\xi,j,k} = I_0 \ G \ S_{\xi,j,k} \ \rho_s \ W_\zeta \int_{E_{edge}}^{E_{max}} \int_0^t \exp \left[ - \left( \frac{\mu_{s,E_0}}{\sin \phi_i} + \frac{\mu_{s,E_{\xi,j,k}}}{\sin \phi_f} \right) z \right] \ dz \ dE \]

Monochromatic

\[ I_{\xi,j,k} = I_0 \ G \ S_{\xi,j,k} \ \rho_s \ W_\zeta \int_0^t \exp \left[ - \left( \frac{\mu_{s,E_0}}{\sin \phi_i} + \frac{\mu_{s,E_{\xi,j,k}}}{\sin \phi_f} \right) z \right] \ dz \]

\[ 1 - \exp \left[ - \left( \frac{\mu_{s,E_0}}{\sin \phi_i} + \frac{\mu_{s,E_{\xi,j,k}}}{\sin \phi_f} \right) t \right] \]

\[ \left( \frac{\mu}{\rho} \right)_{sample} = \sum_\zeta W_\zeta \left( \frac{\mu}{\rho} \right)_\zeta \]
Fluorescence enhancement, secondary fluorescence

Incident photon → Photoelectron → Fluorescence photon

Cascade photon

Secondary fluorescence photon
Fluorescence enhancement, secondary fluorescence

J. Appl. Phys. 75, 2026 (1994); http://dx.doi.org/10.1063/1.356303 (3 pages)

Molecular beam epitaxial growth of single domain ZnSe on Ge

L. K. Li, Y. Wang, M. Jurkovic, and W. I. Wang

200 nm of ZnSe on Ge

Radiation interaction with matter and EDXRF – MAUD school 2016 – Giancarlo Pepponi
Fluorescence enhancement, secondary fluorescence

GaAs

![Graph showing x-ray intensity versus energy for Ga, As, and GaAs]
Fluorescence enhancement, secondary fluorescence

GaAs solution deposited on silicon – Cascade – No Secondary Fluo

GaAs Wafer – No Cascade – No Secondary Fluo

GaAs Wafer – Cascade – Secondary Fluo
Data analysis XRD vs XRF

XRD : Rietveld
XRF : Fundamental parameters method
In MAUD:
the XRD definitions are obviously followed, since they are contain more information:

from the XRD definition you can derive the XRF one, not the other way around.
Instrumental parameters

XRF: energy, intensity fraction
XRD: wavelength, intensity fraction

\[ \lambda = \frac{hc}{E} \quad \lambda(\text{Å}) = \frac{12.3984}{E(\text{eV})} \]

In MAUD:
One or multiple wavelengths can be indicated with intensity fraction

Integration over different energies/wavelengths done numerically
Primary radiation – x-ray tube

Tube spectrum and filtered spectrum automatically calculated in MAUD
Primary radiation – x-ray tube

Tube spectrum and filtered spectrum automatically calculated in MAUD
Primary radiation – x-ray tube

XRF and XRD signals related to different part of the X-ray primary beam
In MAUD: defined separately, hence taken into account
X-Ray Fluorescence – intensity - Sherman equation

\[
I_{\zeta jk} \propto \int_{E_{\text{edge}}}^{E_{\text{max}}} W_{\zeta} \left( \frac{\tau_j}{\rho} \right) \zeta_E \rho_s \omega_{\zeta j} \rho_{\zeta j} \cdot
\]

\[
1 - e^{-\left( \frac{\mu_s E \zeta j k}{\sin \phi_f} + \frac{\mu_s E}{\sin \phi_i} \right) T}
\]

\[
\frac{\mu_s E \zeta j k}{\sin \phi_f} + \frac{\mu_s E}{\sin \phi_i}
\]

\[
dE
\]
Grain size effect in XRF

\[ F_i = \frac{1 - \exp \left[ - \left( \mu_f^*(E_0) \csc \psi_1 + \mu_f^*(E_i) \csc \psi_2 \right) a_r \right]}{\left( \mu_f^*(E_0) \csc \psi_1 + \mu_f^*(E_i) \csc \psi_2 \right) a_r} \]

\( \mu^* \) = linear absorption coefficient

\( a_r \) = radiometric particle diameter

\( a \) = geometric particle diameter

Similar to Brindley correction, but not quite the same:
In Maud? Work in progress
Grain size effect in XRF

overcome by sample preparation: fused beads
1050 deg C + lithium tetraborate (LiT or Li₂B₄O₇) and lithium metaborate (LiM or LiBO₂)
(commonly used in various proportions)
Thank you for your attention!