X-ray intensity is proportional to the concentration, $C \propto I$

$$\frac{C_i}{C_{(i)}} \propto \frac{I_i}{I_{(i)}}$$

$C_i, I_i$: concentration and intensity in sample
$C_{(i)}, I_{(i)}$: concentration and intensity in standard

$$\frac{I_i}{I_{(i)}} = k_i \text{ (k - ratio)}$$

$$\frac{C_i}{C_{(i)}} = k_i \cdot [\text{ZAF}]_i$$
Matrix (ZAF) corrections

\textbf{Z}: atomic number correction

*electron back-scattering difference between standard and sample*

\textbf{A}: absorption correction

*absorption of x-ray inside the sample*

\textbf{F}: fluorescence correction

*fluorescence of x-ray due to absorption of a higher energy x-ray inside the sample*
Atomic number \( (Z) \) correction

\[ Z_i \approx \frac{R_i}{S_i} \]

\( R \): Electron backscattering factor

- x-rays actually generated
- x-rays would be generated if there were no backscattering

\( S \): Electron stopping power

- energy lost by beam electron with distance traveled, \( \frac{dE}{ds} \)
- density, \( \rho \)

* sample
**Z, a function of $E_0$ and composition**

**Duncumb-Reed-Yakowitz method:**

\[ R_i = \sum C_j R_{ij} \]

\[ R_{ij} = R'_1 - R'_2 \ln (R'_3 Z_j + 25) \]

\[ R'_1 = 8.73 \times 10^{-3} U^3 - 0.1669 U^2 + 0.9662 U + 0.4523 \]

\[ R'_2 = 2.703 \times 10^{-3} U^3 - 5.182 \times 10^{-2} U^2 + 0.302 U - 0.1836 \]

\[ R'_3 = (0.887 U^3 - 3.44 U^2 + 9.33 U - 6.43)/U^3 \]

\[ S_i = \sum C_j S_{ij} \]

\[ S_{ij} = (\text{const}) \left[ \frac{(2Z_j/A_j)}{(E_0'E_c)} \right] \ln \left( \frac{583(E_0'E_c)}{J_j} \right) \]

where, $E_0$ and $E_c$ are in keV, and $J$ is in eV, and

\[ J \text{ (eV)} = 9.76Z + 58.82Z^{-0.19} \]
Z, a function of $E_0$ and composition

![Graphs showing $Z_{AlK\alpha}$ and $Z_{CuK\alpha}$ as functions of $E_0$ for different compositions of Al-Cu alloys.](image-url)
X-ray absorption

\[ I = I_0 \exp\left(-\frac{\mu}{\rho}(\rho x)\right) \]

\[ = I_0 \exp\left(-\frac{\mu}{\rho}(\rho z \csc \psi)\right) \]

- \( I \): Intensity emitted
- \( I_0 \): Intensity generated
- \( \frac{\mu}{\rho} \): mass absorption coefficient
- \( \rho \): density
- \( z \): depth
- \( \psi \): take-off angle
Mass absorption coefficient, $\left( \frac{\mu}{\rho} \right)_{x-ray \_absorber}$

Variation of $\left( \frac{\mu}{\rho} \right)_{Ni \_x-ray}$ as a function of x-ray energy

![Graph showing variation of mass absorption coefficient as a function of x-ray energy.](image)

Sharp increase at the critical excitation energy of Ni K-shell, $E_{c(Ni \_K-shell)}$

Any x-ray with a slightly higher energy than $E_{c(Ni \_K-shell)}$ (e.g., ZnKα) is efficiently absorbed as it ionizes the Ni K-shell and generates (fluoresces) the NiKα
Absorption (A) correction

Absorption function,

\[ f(\chi_i) = \frac{I_{i\text{(emitted)}}}{I_{i\text{(generated)}}} \]

* sample
A, a function of $E_0$, $\psi$ and composition

**Philibert method:**

$$f(\chi_i) = \left[ \left( 1 + \frac{\chi_i}{\sigma_i} \right) \left( 1 + \frac{h_i}{\sigma_i (1 + h_i)} \right) \right]^{-1}$$

where,

$$\chi_i = \left( \frac{\mu}{\rho} \right)_{\text{x-ray specimen}} \cosec \psi$$

$$h_i = 1.2 A_i / Z_i^2$$

$$\sigma_i = 4.5 \times 10^5 / (E_0^{1.65} - E_{i(c)}^{1.65})$$

For compounds:

$$h_i = \sum_j h_j C_j$$

$$\left( \frac{\mu}{\rho} \right)_{\text{x-ray specimen}} = \sum_j \left( \frac{\mu}{\rho} \right)_{\text{x-ray element } j} C_j$$
A, a function of $E_0$, $\psi$ and composition

$A_{\text{NiK}\alpha}$ in Fe-Ni alloy
Depth-distribution of generated X-rays: the $\phi(\rho z)$ function

\[ \phi(\rho z) \text{ at depth } z = \frac{\text{x-ray intensity from a layer of thickness } dz \text{ at depth } z}{\phi(\Lambda \rho z), \text{x-ray intensity from a free-standing layer of thickness } dz} \]
Total X-ray intensity: generated vs. emitted

**Total generated intensity**

\[ I_{gen} = \phi(\Delta \rho z) \int_{0}^{\infty} \phi(\rho z) d(\rho z) \]

**Total emitted intensity**

\[ I_{emit} = I_{gen} \exp^{-\left(\frac{\mu}{\rho}\right) z \csc \psi} \]

\[ = \phi(\Delta \rho z) \int_{0}^{\infty} \phi(\rho z) \exp^{-\chi \rho z} d(\rho z) \]

where, \( \chi = \left(\frac{\mu}{\rho}\right) \csc \psi \)
Total X-ray intensity: generated vs. emitted

AlKα is efficiently absorbed by Cu in Al-Cu alloy
Combined atomic number and absorption corrections

Ratio of emitted intensities in standard \( I_{\text{emit}} \) to sample \( I_{\text{emit}}^* \)

\[
I_{\text{emit}} = \phi(\Delta \rho z) \int_0^\infty \phi(\rho z) \exp^{-\chi \rho z} d(\rho z)
\]

\[
I_{\text{emit}}^* = \phi(\Delta \rho z) \int_0^\infty \phi^*(\rho z) \exp^{-\chi^* \rho z} d(\rho z)
\]

\[
Z_i A_i = \frac{\int_0^\infty \phi_i(\rho z) \exp^{-\chi_i \rho z} d(\rho z)}{\int_0^\infty \phi_i^*(\rho z) \exp^{-\chi_i^* \rho z} d(\rho z)}
\]
$\phi(\rho z)$ matrix correction

- $\phi_0$: the value of $\phi(\rho z)$ at $\rho z=0$
- $R_m$: the depth at which $\phi(\rho z)$ is maximum ($\phi_m$)
- $R_x$: the maximum depth of X-ray production (X-ray range)

$Z_i A_i$ is modeled in terms of $\phi_0$, $R_m$, $R_x$, and the integral of the $\phi(\rho z)$ function (Pouchou and Pichoir: PAP method)
A consequence of X-ray absorption when $E_{\text{absorbed X-ray}} > E_c(\text{absorber shell})$

- NiKα is absorbed by Fe atom
- FeKα is fluoresced

X-ray fluorescence
X-ray fluorescence

- $\text{NiK}_\alpha$ is absorbed by Fe atom
- $\text{FeK}_\alpha$ is fluoresced
# X-ray fluorescence

<table>
<thead>
<tr>
<th>Absorber</th>
<th>$E_{K\alpha}$ (keV)</th>
<th>$E_{K\beta}$ (keV)</th>
<th>$E_{C(K)}$ (keV)</th>
<th>$\frac{\mu}{\rho}$ NiK$\alpha$ Absorber (cm$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(25)*</td>
<td>5.895</td>
<td>6.492</td>
<td>6.537</td>
<td>344</td>
</tr>
<tr>
<td>Fe(26)*</td>
<td>6.4</td>
<td>7.059</td>
<td>7.111</td>
<td>380</td>
</tr>
<tr>
<td>Co(27)</td>
<td>6.925</td>
<td>7.649</td>
<td>7.709</td>
<td>53</td>
</tr>
<tr>
<td>Ni(28)</td>
<td>7.472</td>
<td>8.265</td>
<td>8.331</td>
<td>59</td>
</tr>
<tr>
<td>Cu(29)</td>
<td>8.041</td>
<td>8.907</td>
<td>8.98</td>
<td>65.5</td>
</tr>
</tbody>
</table>

* NiK$\alpha$ fluoresces MnK$\alpha$, K$\beta$ and FeK$\alpha$, K$\beta$

<table>
<thead>
<tr>
<th>Element</th>
<th>K$\alpha$, K$\beta$</th>
<th>Radiation causing fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td></td>
<td>FeK$\beta$, CoK$\alpha$, CoK$\beta$, NiK$\alpha$, NiK$\beta$, CuK$\alpha$, CuK$\beta$</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>CoK$\beta$, NiK$\alpha$, NiK$\beta$, CuK$\alpha$, CuK$\beta$</td>
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<tr>
<td>Co</td>
<td>NiK$\beta$, CuK$\alpha$, CuK$\beta$</td>
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</tr>
<tr>
<td>Ni</td>
<td>CuK$\beta$</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>
Characteristic fluorescence (F) correction

Fluorescence correction includes the summation of intensities of the element fluoresced by all other elements in the compound.

\[
F_i = \frac{1 + \sum_j \left\{ \frac{I_{ij}^f}{I_i} \right\}}{1 + \sum_j \left\{ \frac{I_{ij}^f}{I_i} \right\}^*}
\]

\( I_{ij}^f \): x-ray intensity of element ‘i’ fluoresced by element ‘j’

\( I_i \): x-ray intensity of element ‘i’ generated by electron beam

* sample
F, a function of $E_0$ and composition

Castaing-Reed method:

\[
\frac{I'_i}{I_i} = C_i Y_0 Y_i Y'_i P_i
\]

\[
Y_0 = 0.5 \left( \frac{r_i - 1}{r_i} \right) e_i \frac{A_i}{A_j}
\]

where, $e_i$ : fluorescent yield

\[
Y_i = \left( \frac{U_j - 1}{U_i - 1} \right)^{1.67}
\]

\[
Y'_i = \left( \frac{\Upsilon_i}{\rho_i} \right)^{1.67} y_{\text{x-ray element} i}
\]

\[
Y'_i = \left( \frac{\Upsilon_i}{\rho_i} \right)^{1.67} y_{\text{x-ray specimen}}
\]

\[
Y_i = \frac{\ln(1 + u)}{u} + \frac{\ln(1 + v)}{v}
\]

where,

\[
u = \sqrt{\left( \frac{\Upsilon_i}{\rho_i} \right)^{1.67} y_{\text{x-ray specimen}}} \csc \psi
\]

\[
v = 3.3 \times 10^5
\]

And

\[
P_i = 1 \text{ for } K \text{ fluorescing } K; \ 4.76 \text{ for } K \text{ fluorescing } L; \ 0.24 \text{ for } L \text{ fluorescing } K
\]
$F$, a function of $E_0$ and composition

$F_{FeK\alpha}$

$A_{NiK\alpha}$

Fe-Ni alloy
Matrix correction flowchart

\[ k \rightarrow ZAF_1 \rightarrow C_1 \ (= C_{std}k \times ZAF_1) \]

\[ C_1 \rightarrow ZAF_2 \rightarrow C_2 \ (= C_{std}k \times ZAF_2) \ (\text{if } C_2 = C_1, \text{ stop here}) \]

\[ C_2 \rightarrow ZAF_3 \rightarrow C_3 \ (= C_{std}k \times ZAF_3) \ (\text{if } C_3 = C_2, \text{ stop here}) \]

and so on....