EPMA Quantitative analysis

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

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

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

Matrix (ZAF) corrections

Z : atomic number correction

for lost signal due to elastic (back-scattering) and inelastic (energy loss) scattering of the beam electrons that diminish x-ray generation

A : absorption correction

for lost signal due to absorption of x-rays within the sample

F : fluorescence correction

for excess signal due to secondary x-rays generated by primary, higher energy x-rays within the sample (that are absorbed while causing ionizations)

Atomic number (Z) correction

$$\boxed{Z_i \approx \frac{\dfrac{R_i}{S_i}}{\dfrac{R_i^*}{S_i^*}}}$$

* sample

$\boldsymbol{R}$: Electron backscattering factor

$$\frac{\text{x - rays actually generated}}{\text{x - rays would be generated if there were no backscattering}}$$

R approaches 1 at low atomic numbers

$\boldsymbol{S}$: Electron stopping power

$$-\frac{\text{energy lost by beam electron with distance traveled, } dE/ds}{\text{density, } \rho}$$

Z, a function of E_0 and composition

Duncumb-Reed-Yakowitz method:

$R_i = \Sigma\ C_j R_{ij}$

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

$R'_1 = 8.73\text{x}10^{-3}\ U^3 - 0.1669\ U^2 + 0.9662\ U + 0.4523$

$R'_2 = 2.703\text{x}10^{-3}\ U^3 - 5.182\text{x}10^{-2}\ U^2 + 0.302\ U - 0.1836$

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

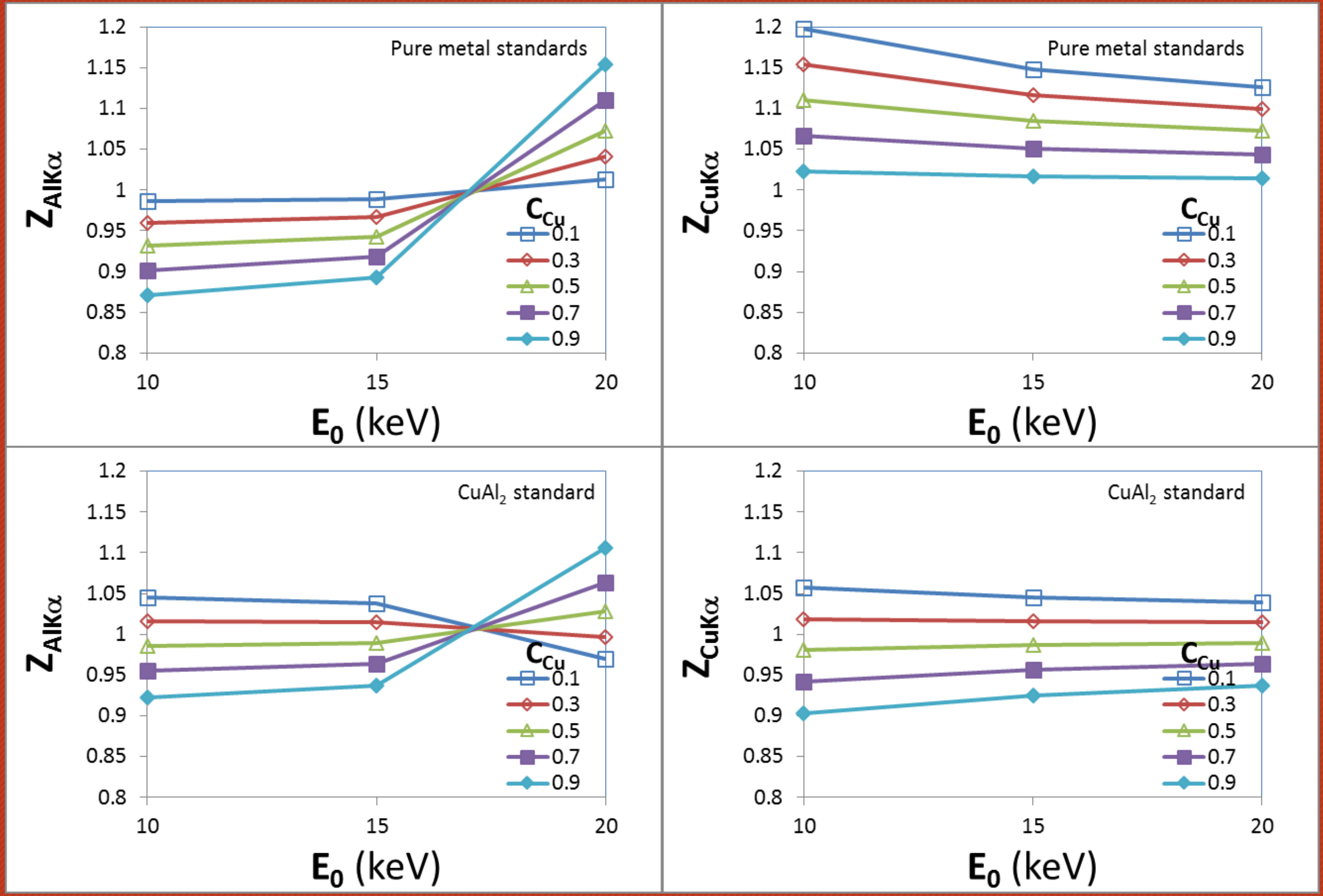
$S_i = \Sigma\ C_j S_{ij}$

$S_{ij} = (\text{const})\ [(2Z_j/A_j)/(E_0+E_c)]\ln[583(E_0+E_c)/J_j]$

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

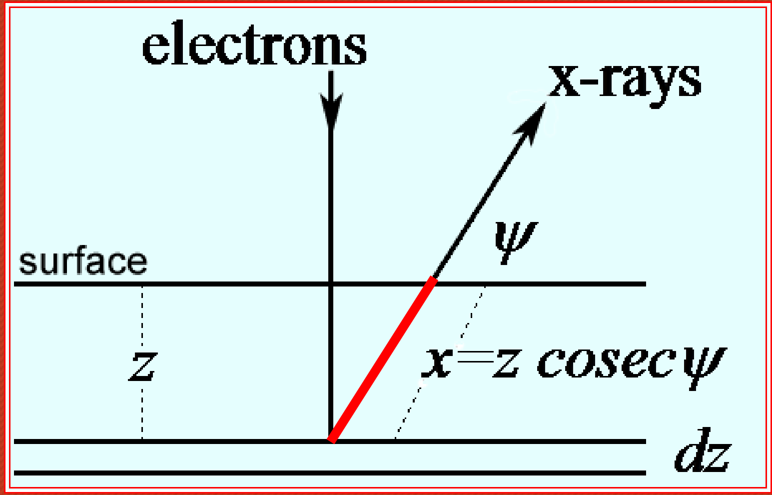
$J\ (\text{eV}) = 9.76Z + 58.82Z^{-0.19}$

Z, a function of E_0 and composition



Al-Cu alloy

X-ray absorption



$$I = I_0 \exp^{-\left({}^{\mu}/_{\rho}\right)(\rho x)}$$
$$= I_0 \exp^{-\left({}^{\mu}/_{\rho}\right)(\rho z\ cosec\ \psi)}$$

I : Intensity emitted

I_0 : Intensity generated

${}^{\mu}/_{\rho}$: mass absorption coefficient

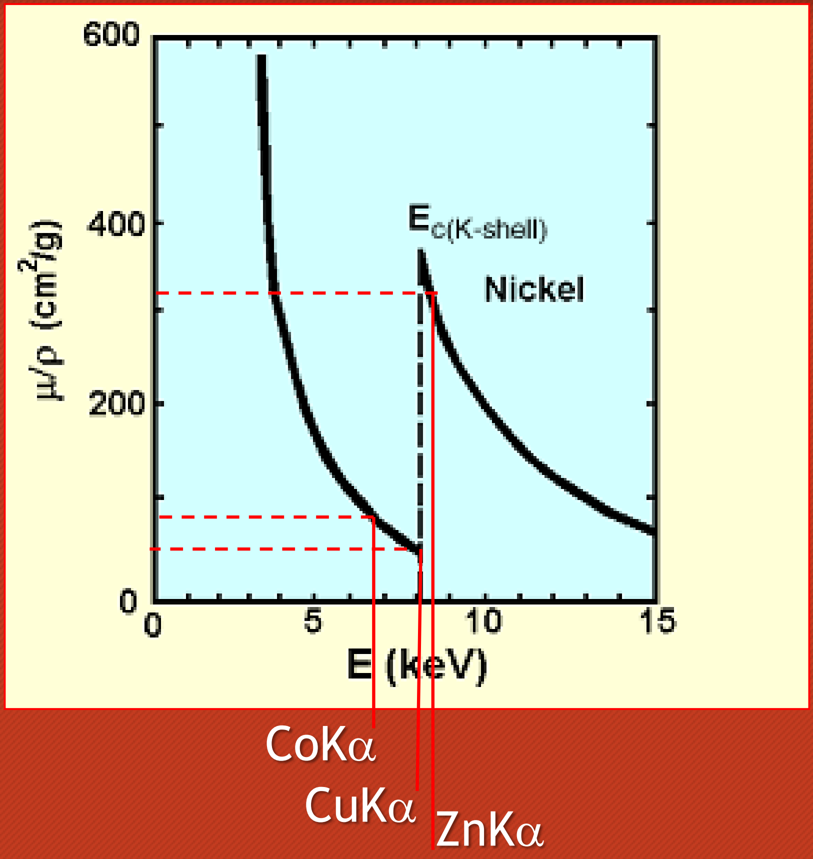
ρ : density

z : depth

ψ : take-off angle

Mass absorption coefficient, $\left(\mu/\rho\right)_{absorber}^{x-ray}$

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



Sharply increases at the critical excitation energy of Ni K-shell, $E_{c(Ni\ K\text{-}shell)}$

Any x-ray with a slightly higher energy than $E_{c(Ni\ K\text{-}shell)}$ *(e.g., ZnK*α*) is efficiently absorbed as it ionizes the Ni K-shell and generates (fluoresces) the NiK*α

Absorption (A) correction

$$\boxed{A_i = \frac{f(\chi_i)}{f(\chi_i)^*}}$$

* sample

Absorption function,

$$f(\chi_i) = I_{i(emitted)}/I_{i(generated)}$$

A, a function of E_0, ψ and composition

Philibert method:

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

where,

$$\chi_i = \left(\mu/\rho\right)^{i\_x-ray}_{specimen} \text{ cosec } \psi$$

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

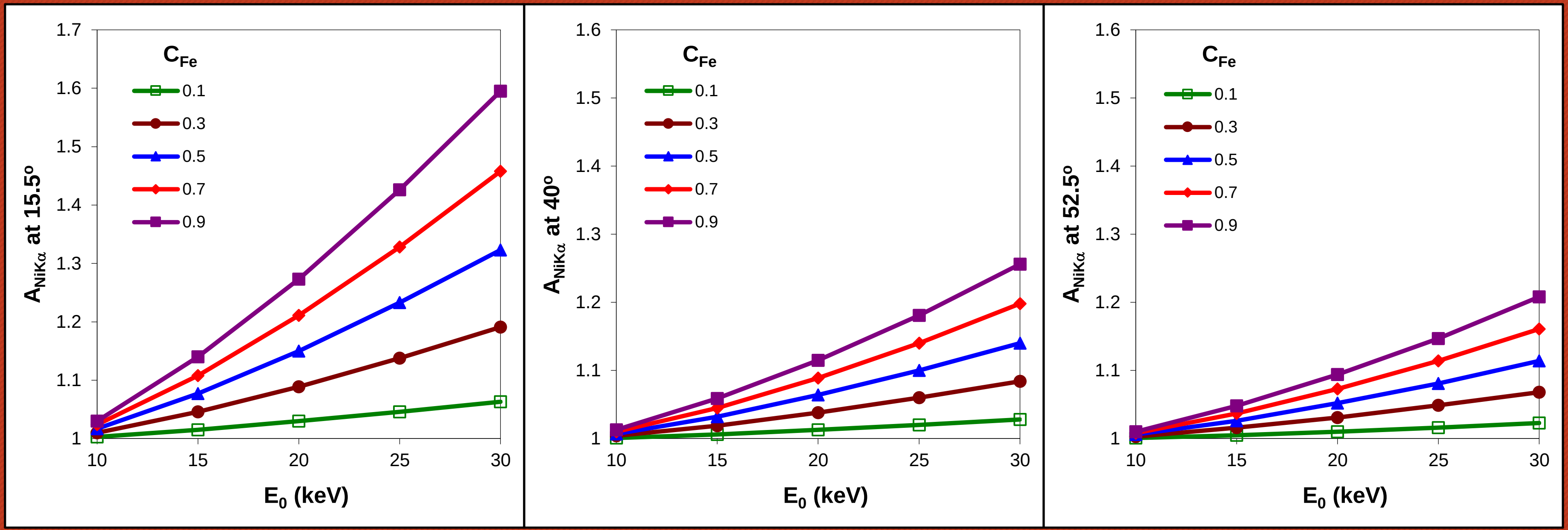
$$\sigma_i = 4.5\text{x}10^5 \;/\; (E_0{}^{1.65}\text{-}E_{i(c)}{}^{1.65})$$

For compounds:

$$h_i = \sum_j h_j C_j$$

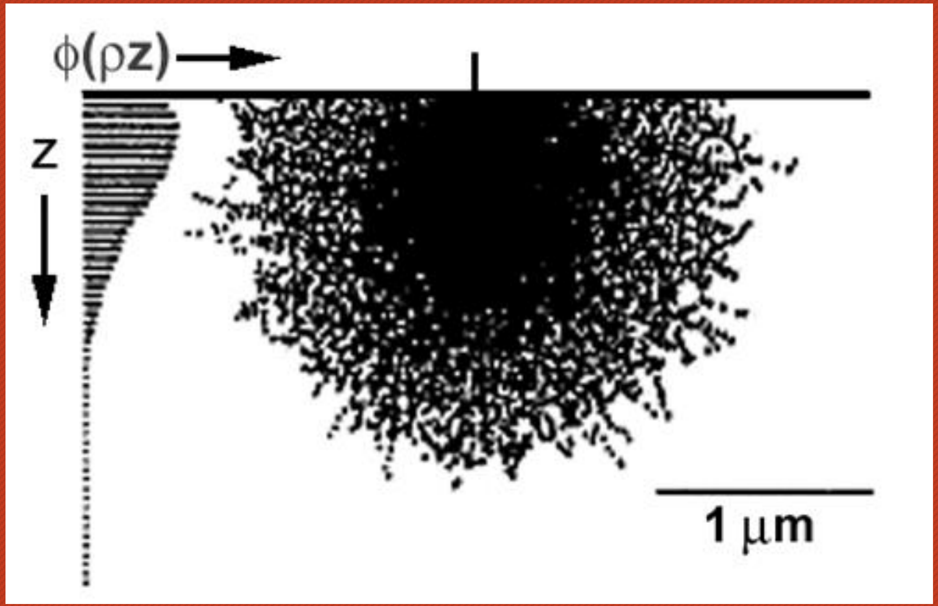
$$\left(\mu/\rho\right)^{i\_x-ray}_{specimen} = \sum_j \left(\mu/\rho\right)^{i\_x-ray}_{element\ 'j'} C_j$$

A, a function of E_0, ψ and composition



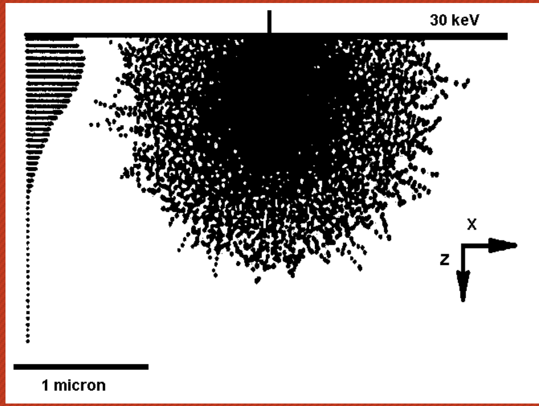
$A_{NiK\alpha}$ in Fe-Ni alloy

Depth-distribution of generated X-rays: the $\phi(\rho z)$ function



$$\phi(\rho z) \text{ at depth z} = \frac{\text{x - ray intensity from a layer of thickness dz at depth z}}{\phi(\Delta\rho z), \text{ x - ray intensity from a free - standing layer of thickness dz}}$$

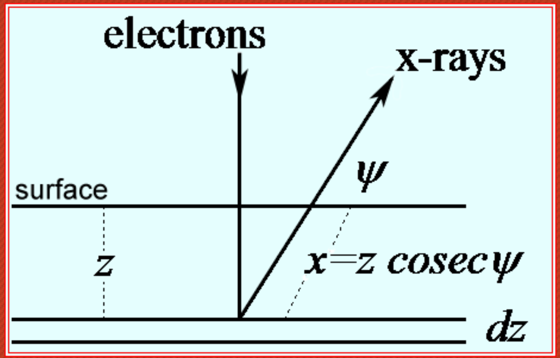
Total X-ray intensity: generated vs. emitted



Total generated intensity

$$I_{gen} = \phi(\Delta\rho z)\int_0^\infty \phi(\rho z)d(\rho z)$$

Total emitted intensity



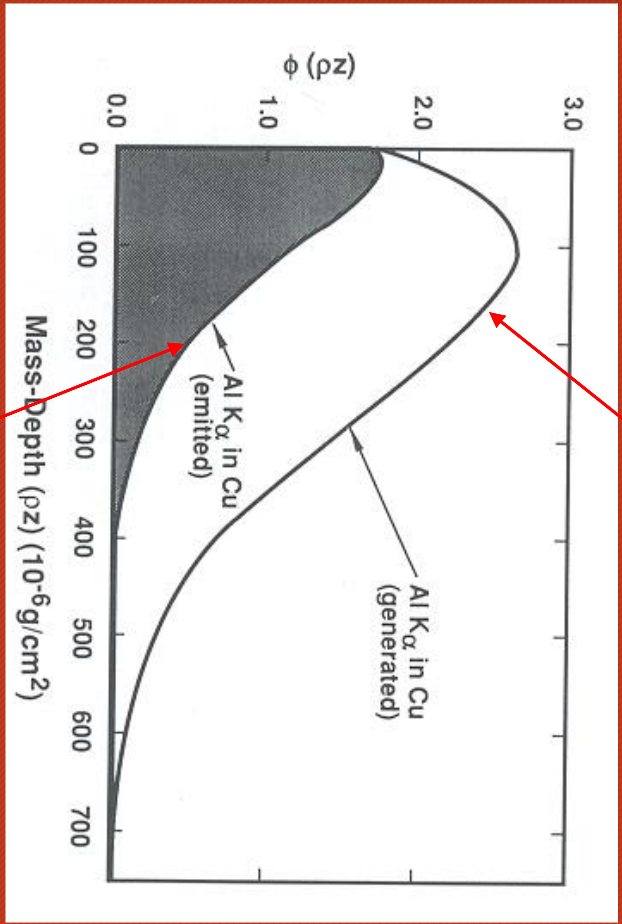
$$I_{emit} = I_{gen}\exp^{-(\mu/\rho)\rho\, z\mathrm{cosec}\psi}$$

$$= \phi(\Delta\rho z)\int_0^\infty \phi(\rho z)\exp^{-\chi\rho z}d(\rho z)$$

where, $\chi = (\mu/\rho)\mathrm{cosec}\psi$

Total X-ray intensity: generated vs. emitted

Emitted Intensity curve



Generated Intensity curve

AlKα is efficiently absorbed by Cu in Al-Cu alloy

$\phi(\rho z)$ matrix correction

Combined atomic number and absorption corrections

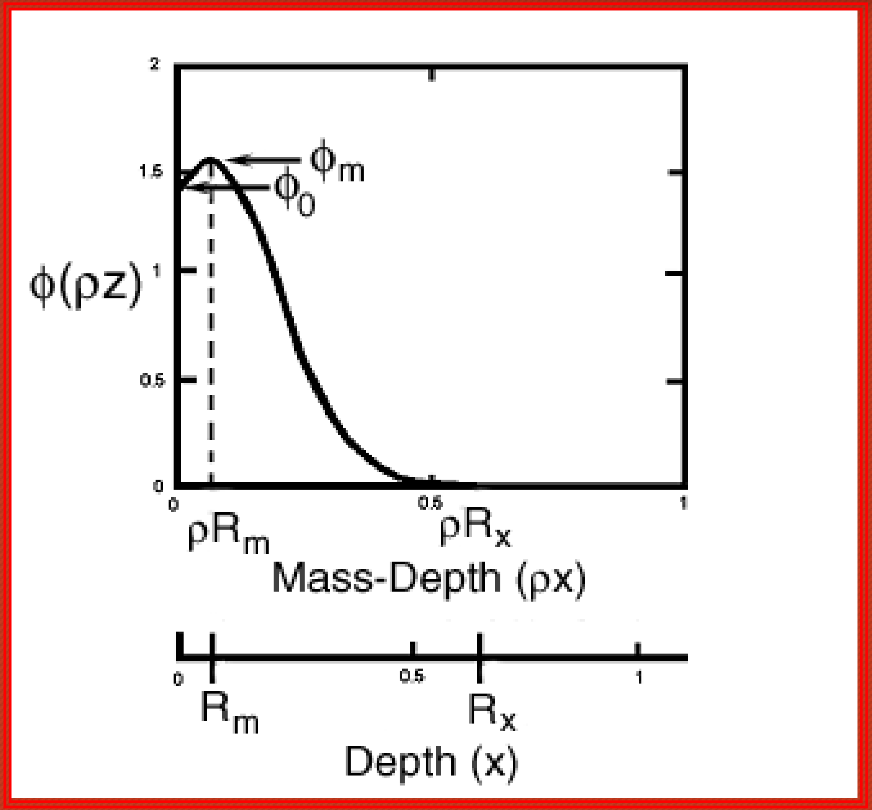
Ratio of emitted intensities in standard (I_{emit}) to sample (I^{*}_{emit})

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

$$I^{*}_{emit} = \phi(\Delta\rho z)\int_0^{\infty}\phi^{*}(\rho z)\exp^{-\chi^{*}\rho z}d(\rho z)$$

$$\boxed{\mathbf{Z_iA_i} = \frac{\int_0^{\infty}\phi_i(\rho z)\exp^{-\chi_i\rho z}d(\rho z)}{\int_0^{\infty}\phi_i^{*}(\rho z)\exp^{-\chi_i^{*}\rho z}d(\rho z)}}$$

$\phi(\rho z)$ matrix correction



ϕ_0 : the value of $\phi(\rho z)$ at $\rho z=0$

R_m : *the depth at which $\phi(\rho z)$ is maximum (ϕ_m)*

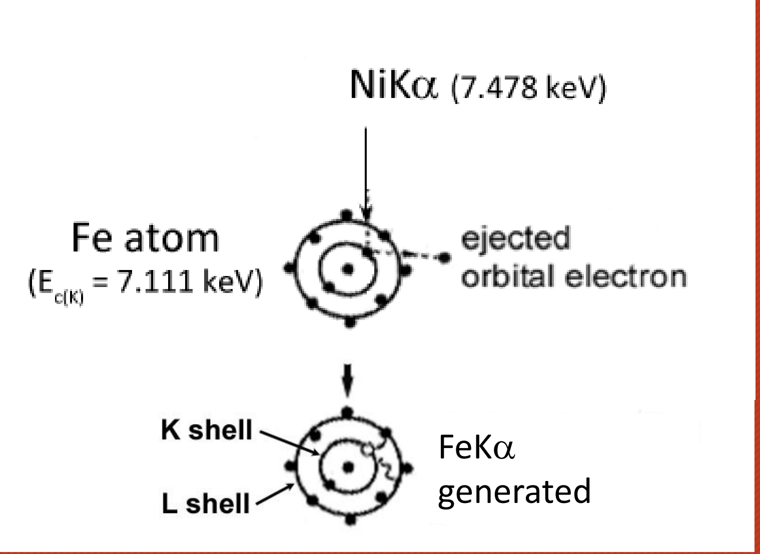
R_x : *the maximum depth of X-ray production (X-ray range)*

Z_iA_i is modeled in terms of ϕ_0, R_m, R_x, and the integral of the $\phi(\rho z)$ function (Pouchou and Pichoir: PAP method)

X-ray fluorescence

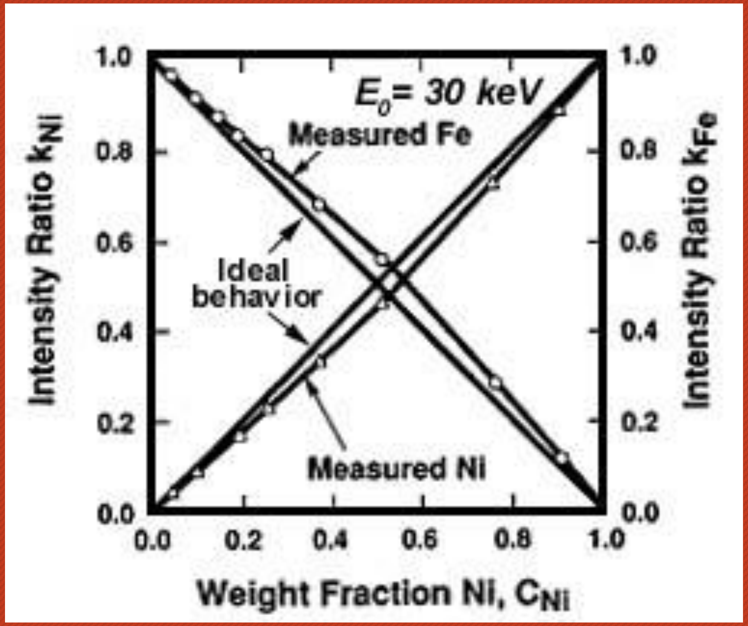
A consequence of X-ray absorption when

$E_{absorbed\ X\text{-}ray} > E_{c(absorber\ shell)}$



- NiKα is absorbed by Fe atom
- FeKα is fluoresced

X-ray fluorescence



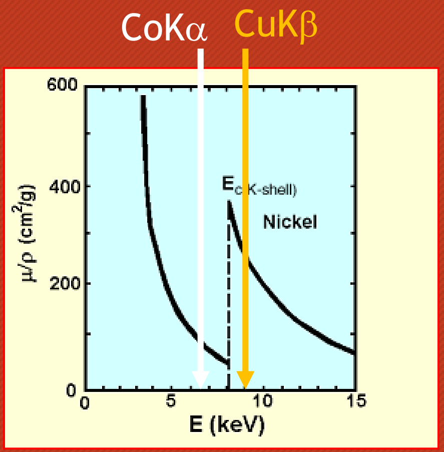
- NiKα is absorbed by Fe atom
- FeKα is fluoresced

X-ray fluorescence

Absorber (Atomic No.)	$E_{K\alpha}$ (keV)	$E_{K\beta}$ (keV)	$E_{c(K)}$ (keV)	$\left(\mu/\rho\right)^{NiK\alpha}_{Absorber}$ (cm^2/g)
Mn(25)*	5.895	6.492	**6.537**	**344**
Fe(26)*	6.4	7.059	**7.111**	**380**
Co(27)	6.925	7.649	7.709	53
Ni(28)	**7.472**	8.265	8.331	59
Cu(29)	8.041	8.907	8.98	65.5

* NiKα fluoresces MnKα,Kβ and FeKα,Kβ

Element Kα,Kβ	Radiation causing fluorescence
Mn	FeKβ, CoKα, CoKβ, NiKα, NiKβ, CuKα, CuKβ
Fe	CoKβ, NiKα, NiKβ, CuKα, CuKβ
Co	NiKβ, CuKα, CuKβ
Ni	CuKβ
Cu	none



Characteristic fluorescence (F) correction

$$F_i = \frac{\left(1 + \sum_j \left\{\frac{I_{ij}^f}{I_i}\right\}\right)}{\left(1 + \sum_j \left\{\frac{I_{ij}^f}{I_i}\right\}\right)^*}$$

* sample

I^f_{ij} : x-ray intensity of element '*i*' fluoresced by element '*j*'

I_i : x-ray intensity of element '*i*' generated by electron beam

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

F, a function of E_0 and composition

Castaing-Reed method:

$$\frac{I_{ij}^{f}}{I_i} = C_j Y_0 Y_1 Y_2 Y_3 P_{ij}$$

$$Y_0 = 0.5\left[\frac{r_i - 1}{r_i}\right]\left[\omega_j \frac{A_i}{A_j}\right]$$

where, ω_j : fluorescent yield

$$Y_1 = \left[\frac{U_j - 1}{U_i - 1}\right]^{1.67} \qquad Y_2 = \frac{\left(\mu/\rho\right)^{j\_x-ray}_{element"i"}}{\left(\mu/\rho\right)^{j\_x-ray}_{specimen}}$$

$$Y_3 = \frac{\ln(1+u)}{u} + \frac{\ln(1+v)}{v}$$

where, $u = \left[\frac{\left(\mu/\rho\right)^{i\_x-ray}_{specimen}}{\left(\mu/\rho\right)^{j\_x-ray}_{specimen}}\right] \text{cosec}\,\psi$

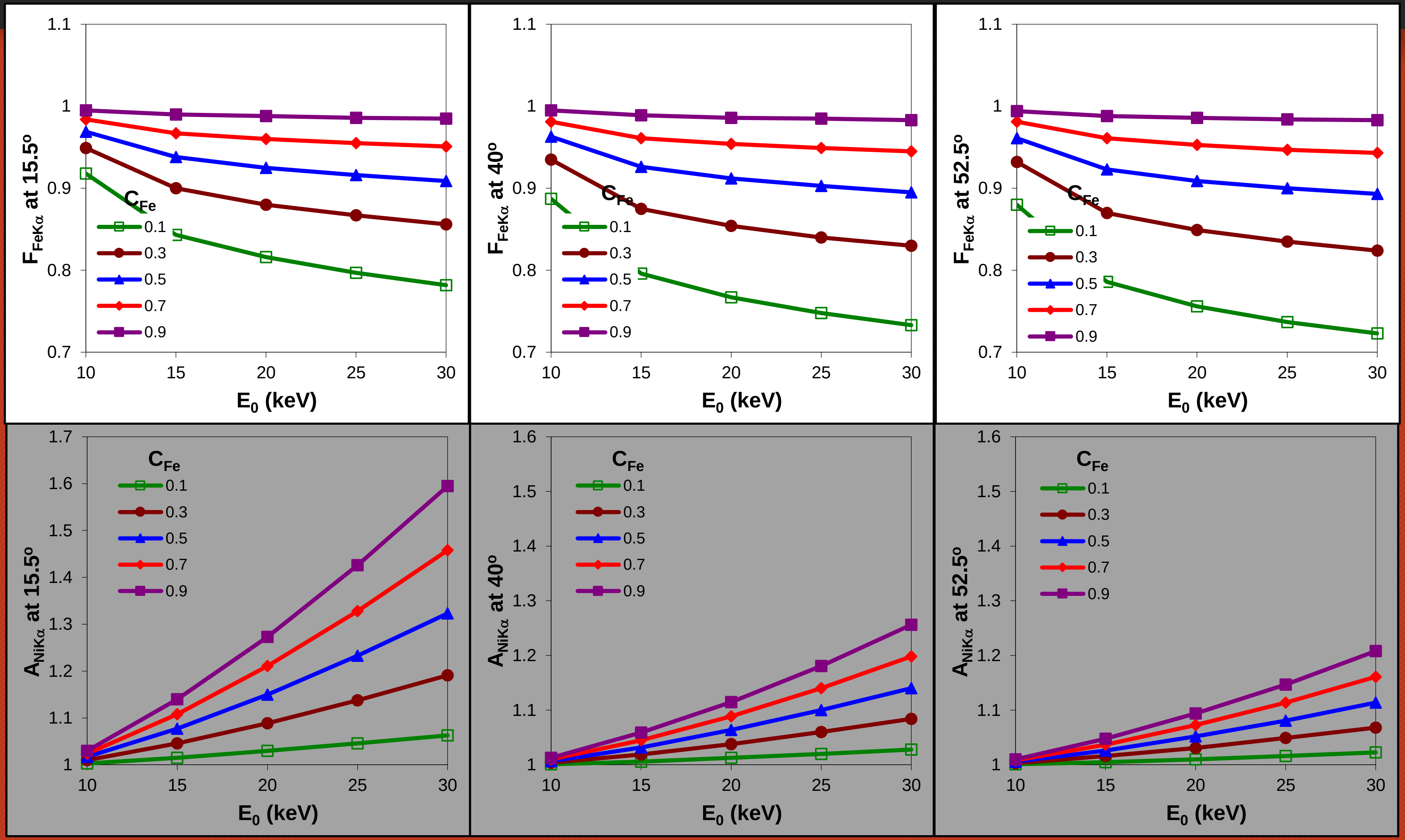
and $v = \frac{3.3 \text{ x } 10^5}{\left[(E_0^{\ 1.65} - E_c^{\ 1.65})\left(\mu/\rho\right)^{j\_x-ray}_{specimen}\right]}$

P_{ij} = 1 for K fluorescing K; 4.76 for K fluorescing L; 0.24 for L fluorescing K

F, a function of E_0 and composition

$F_{FeK\alpha}$

$A_{NiK\alpha}$



Fe-Ni alloy

Matrix correction flowchart

$k \dashrightarrow ZAF_1 \dashrightarrow C_1 \; (= C_{std}k * ZAF_1)$

$C_1 \dashrightarrow ZAF_2 \dashrightarrow C_2 \; (= C_{std}k * ZAF_2)$ (if $C_2 = C_1$, stop here)

$C_2 \dashrightarrow ZAF_3 \dashrightarrow C_3 \; (= C_{std}k * ZAF_3)$ (if $C_3 = C_2$, stop here)

and so on….