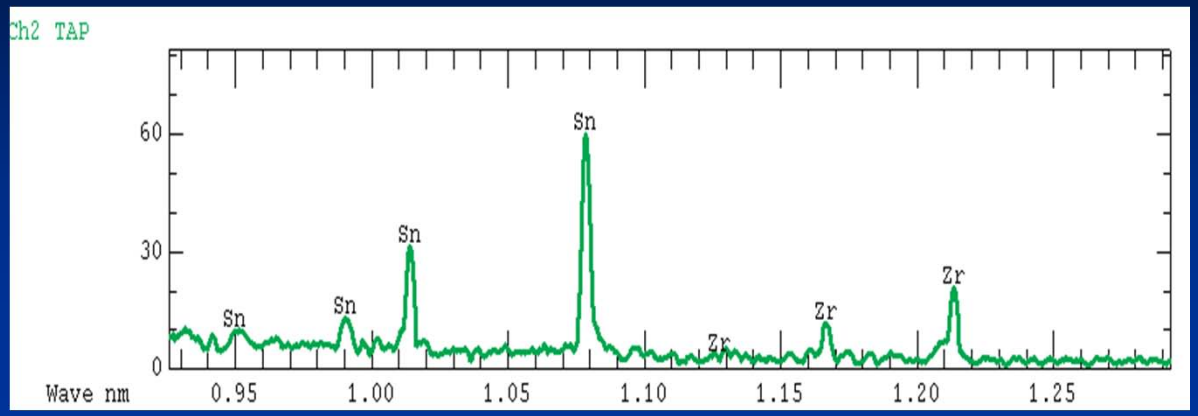
EPMA: Quantitative analysis



WDS spectrum:
Intensity is proportional to concentration

$$\frac{C_i}{C_{(i)}} \propto \frac{I_i}{I_{(i)}} \qquad where, \qquad \frac{I_i}{I_{(i)}} = k_i$$

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

C_i and $C_{(i)}$: concentration of element "i" in sample and standard

I_i and $I_{(i)}$: measured X-ray intensities of element "i" in sample and standard

k_i : k-ratio of element "i" **ZAF** *: matrix corrections*

Matrix (ZAF) corrections

Z : *atomic number correction*

A : *absorption correction*

F : *fluorescence correction*

Atomic number (Z) correction

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

* ***sample***

$R = \Sigma\, C_j R_j$

[R = #X-ray photons generated / #photons if there were no back-scatter]

$S = \Sigma\, C_j S_j$

[$S = -(1/\rho)(dE/ds)$, stopping power]

Z, a function of E_0 and composition

Duncumb-Reed-Yakowitz method:

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

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

$$R'_1 = 8.73\text{x}10^{-3} U^3 - 0.1669 U^2 + 0.9662 U + 0.4523$$
$$R'_2 = 2.703\text{x}10^{-3} U^3 - 5.182\text{x}10^{-2} U^2 + 0.302 U - 0.1836$$
$$R'_3 = (0.887 U^3 - 3.44 U^2 + 9.33 U - 6.43)/U^3$$

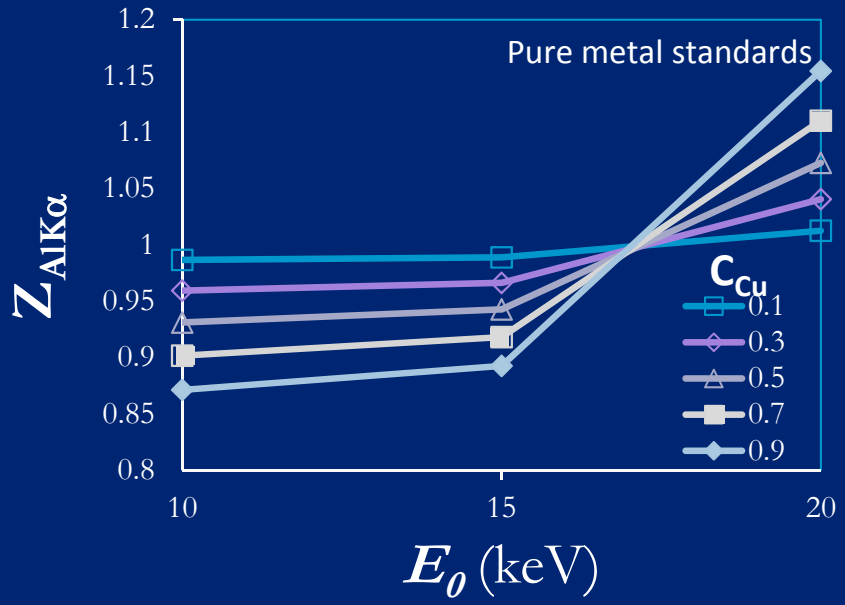
$$S_i = \Sigma_j C_j S_{ij}$$

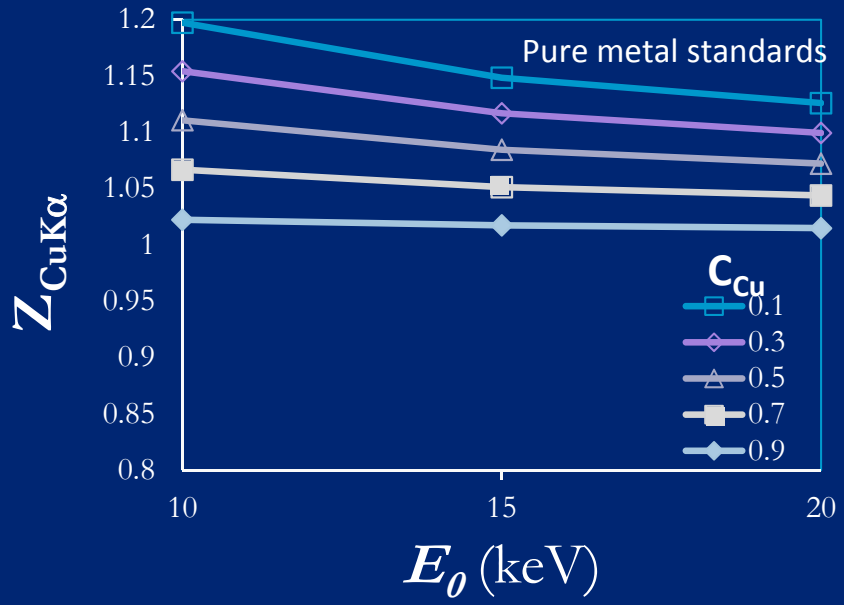
$$S_{ij} = (\text{const}) [(2Z_j/A_j)/(E_0+E_c)] \ln[583(E_0+E_c)/J_j]$$

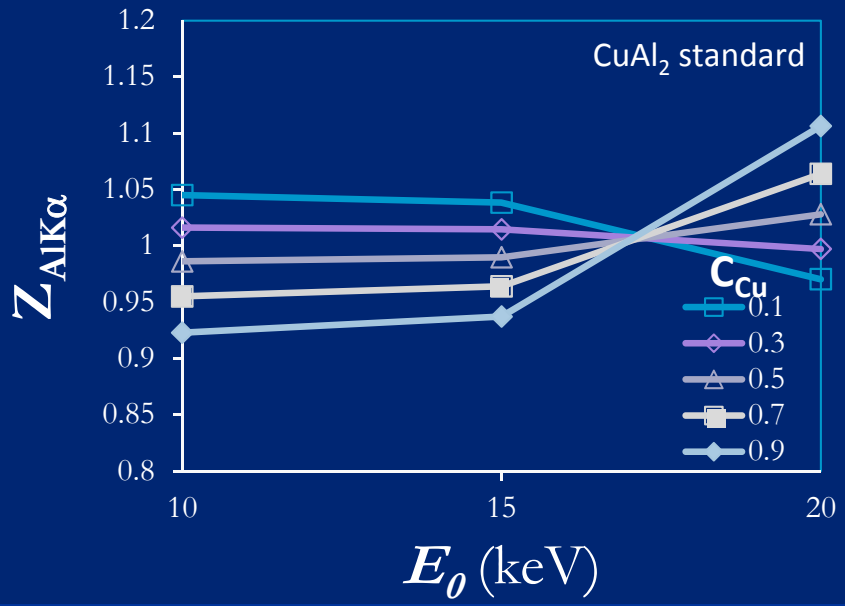
where, J (keV) $= (9.76Z + 58.82Z^{-0.19})\text{x}10^{-3}$

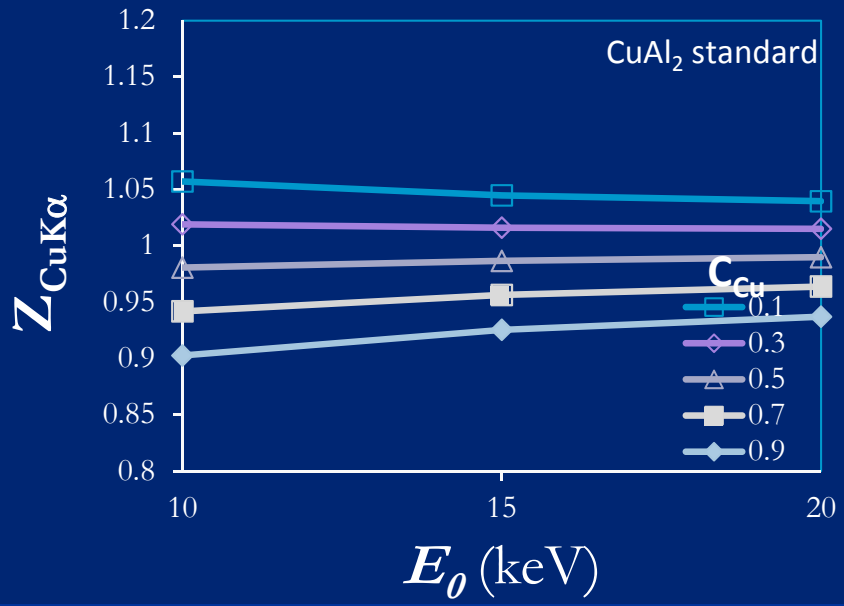
Z, a function of E_0 and composition

Al-Cu alloy

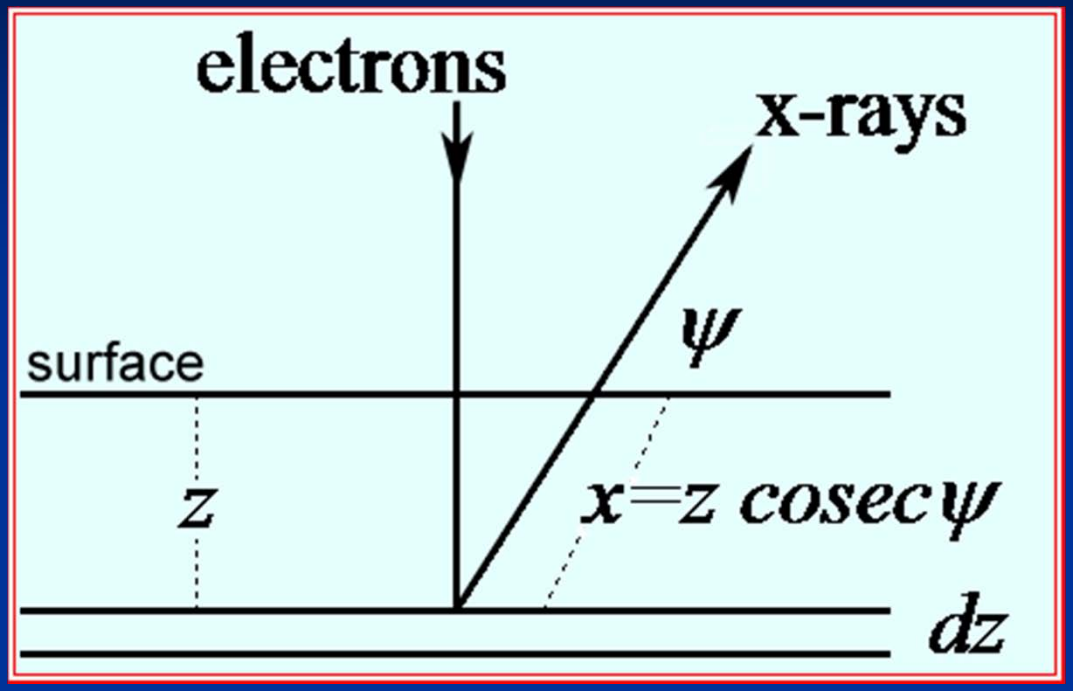








X-ray absorption



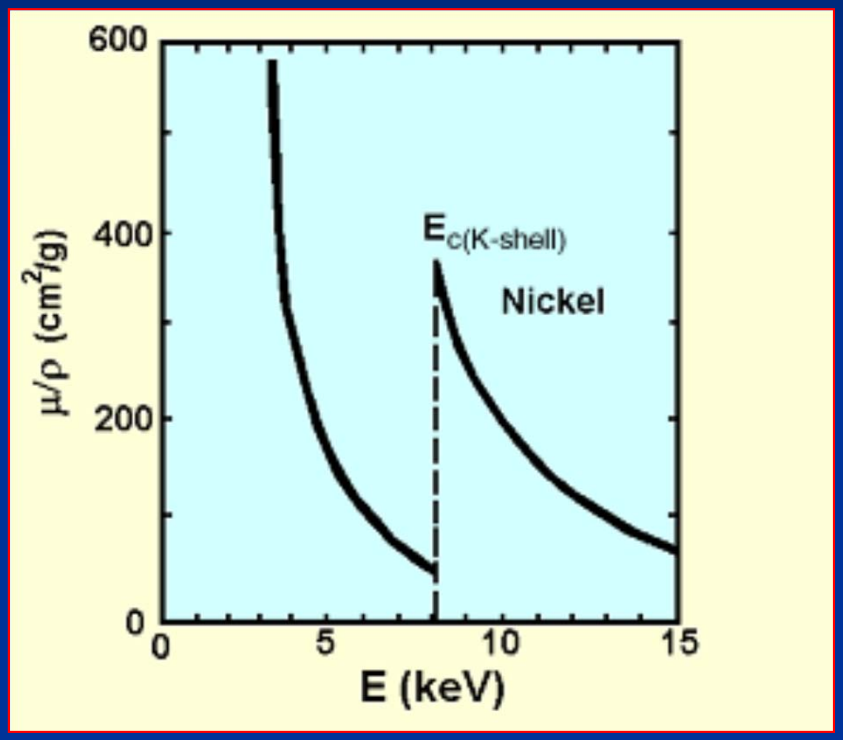
$$I = I_0 \exp^{-(\mu/\rho)(\rho x)} = I_0 \exp^{-(\mu/\rho)(\rho z \, cosec\psi)}$$

I: Intensity emitted; I_0*: Intensity generated*

μ/ρ*: mass absorption coefficient*

ρ*: density;* z*: depth;* ψ*: take-off angle*

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



A function of energy being absorbed

	Energy (keV)	$E_{c(K\ shell)}$ (keV)	$\left(\mu/\rho\right)^{energy}_{Ni}$ (cm^2/g)
CoKα	6.925		53
NiKα	7.472	**8.331**	60
CuKα	8.041		49
ZnKα	**8.632**		**311**

ZnKα is absorbed by Ni

For compounds,

$$\left(\frac{\mu}{\rho}\right)^{energy}_{compound} = \sum_j \left(\frac{\mu}{\rho}\right)^{energy}_{element\ 'j'} C_j$$

Absorption (A) correction

$$\mathbf{A}_i = \frac{f(\chi_i)}{f(\chi_i)^*}$$

* ***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,

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

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

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

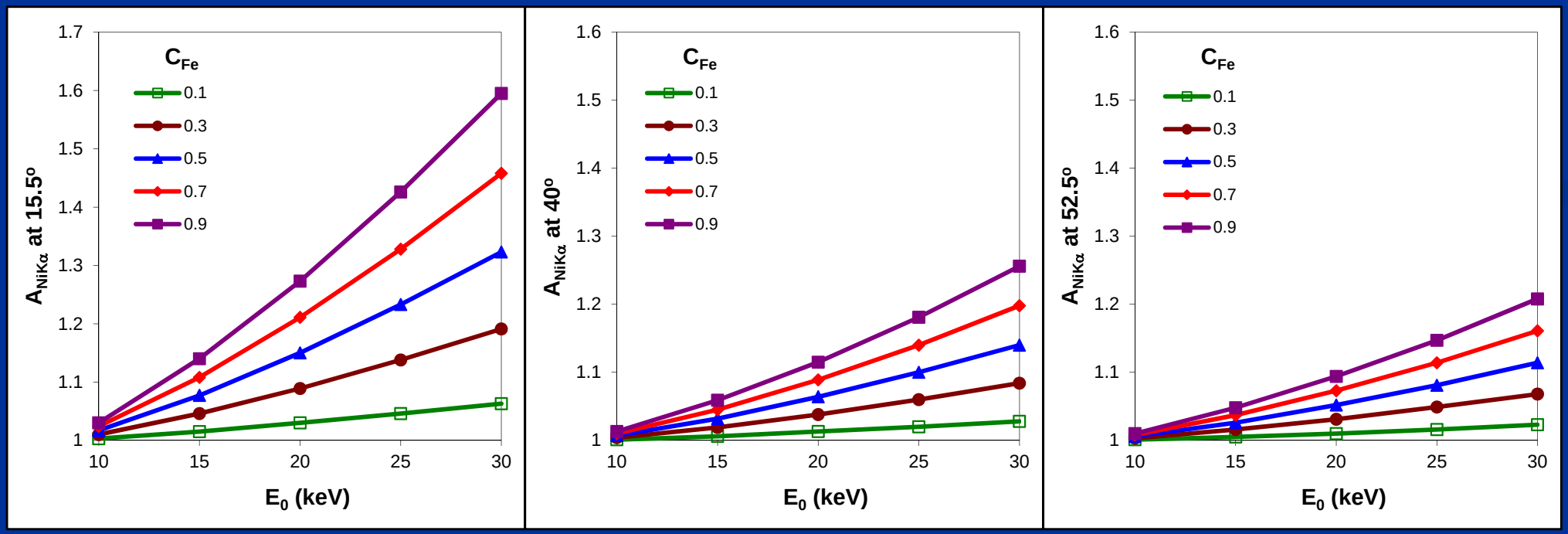
For compounds:

$$h_i = \sum_j h_j C_j$$

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

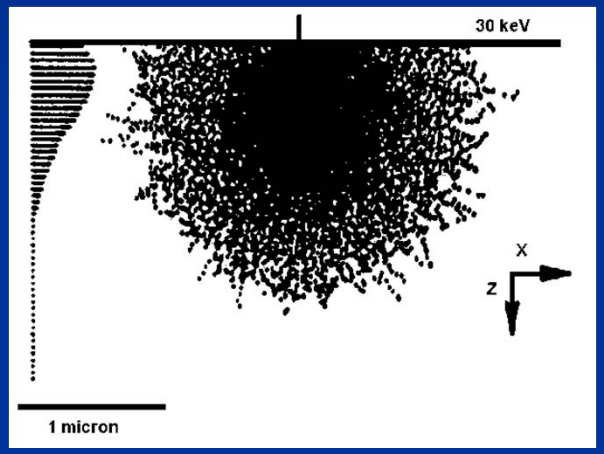
A, a function of E_0, ψ and composition

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



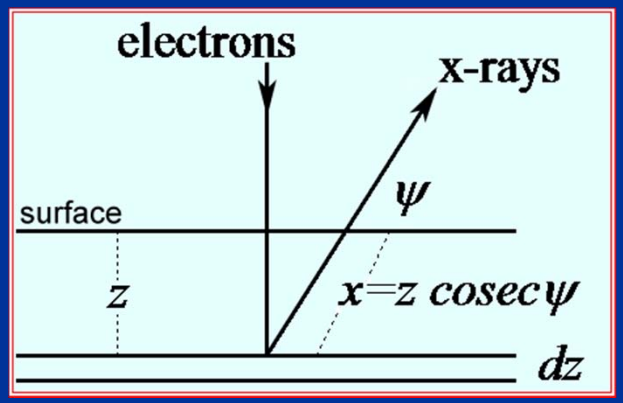
Total X-ray intensity: generated versus emitted

Generated intensity



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

Emitted intensity

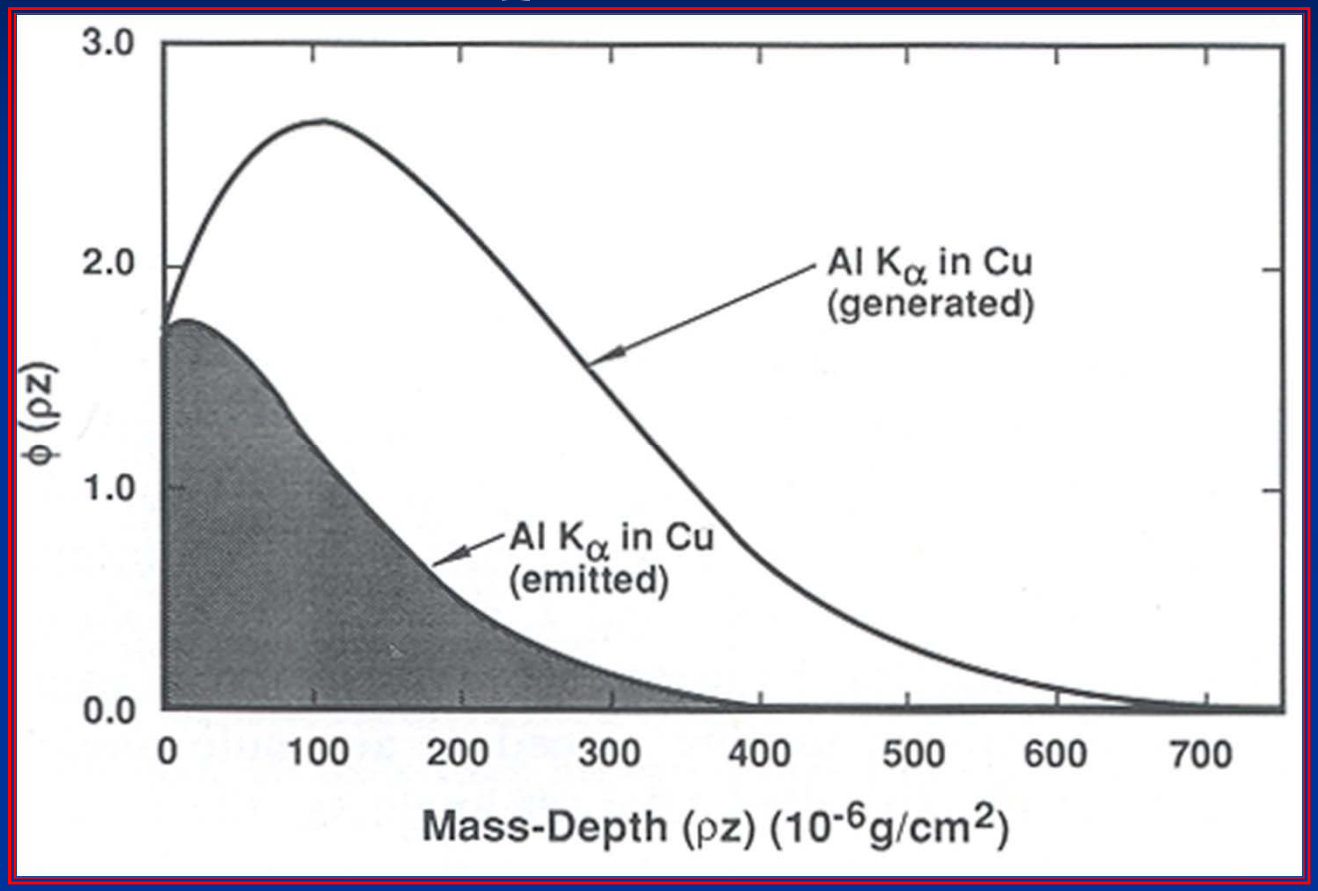


$$I_{emit} = I_{gen}\exp^{-\chi\rho z}$$

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

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

Generated and emitted X-ray intensity variation with depth: AlKα in Al-Cu alloy



Effect of matrix (mainly Cu) on the emitted intensity of **AlKα**, which is highly absorbed in **Cu**;

$$\left(\mu/\rho\right)_{Cu}^{AlK\alpha} = 4837.5\ cm^2/g$$

$\phi(\rho z)$ matrix correction

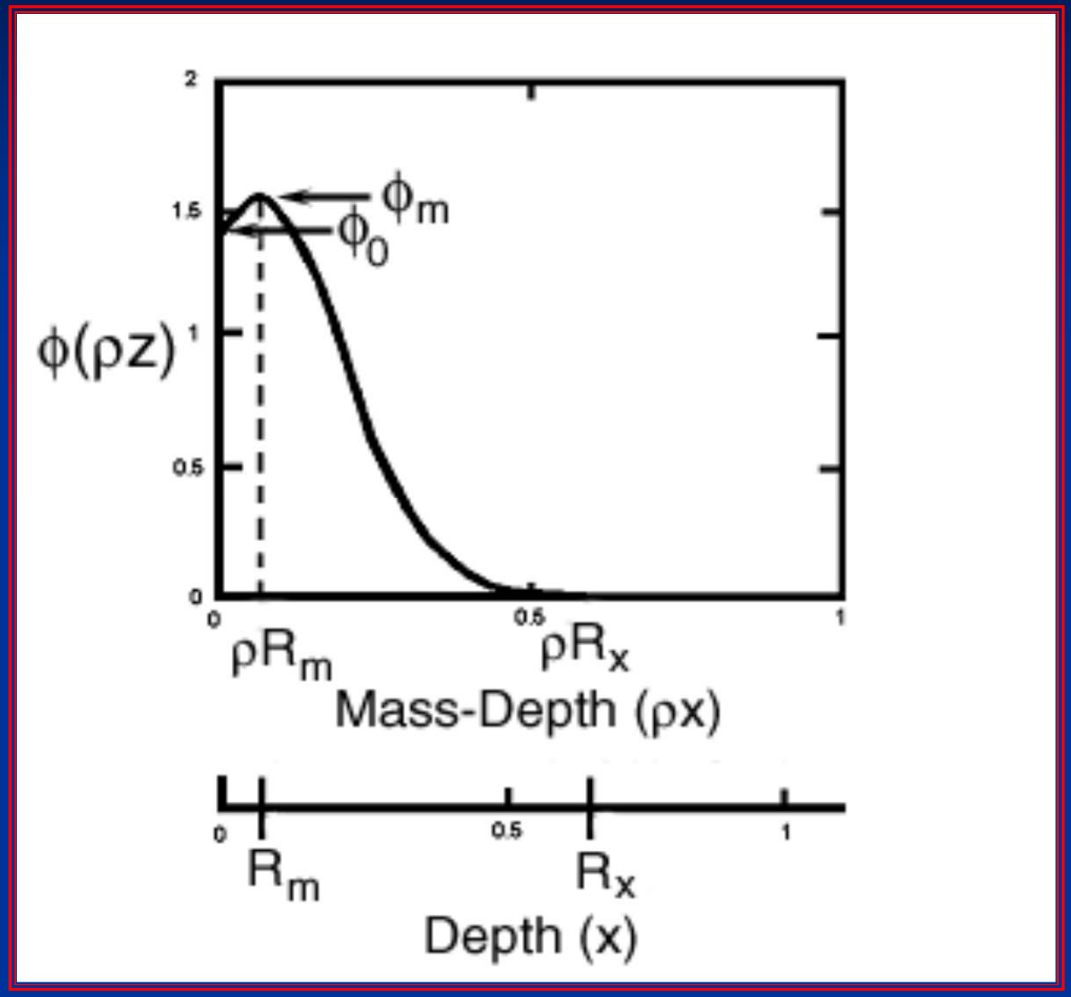
The combined atomic number and absorption corrections is the ratio of emitted intensities in standard (I_{emit}) to sample (I^{*}_{emit})

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

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

$$\mathbf{Z}_i\mathbf{A}_i = \frac{\int_0^\infty \phi_i(\rho z)\exp^{-\chi_i\rho z}\, d(\rho z)}{\int_0^\infty \phi_i^{*}(\rho z)\exp^{-\chi_i\rho z}\, d(\rho z)}$$

$\phi(\rho z)$ matrix correction



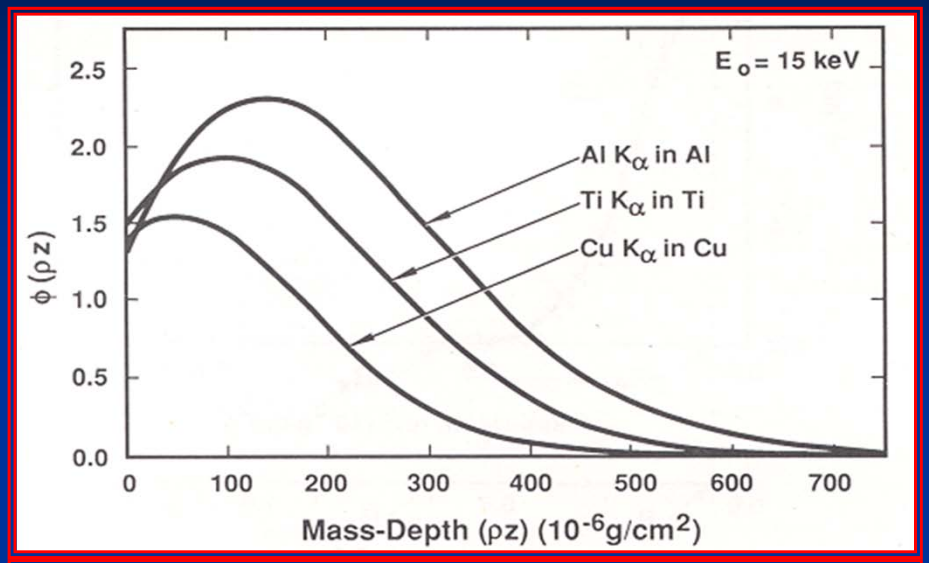
ϕ_0 : *the value of* $\phi(\rho z)$ *at* $\rho z=0$

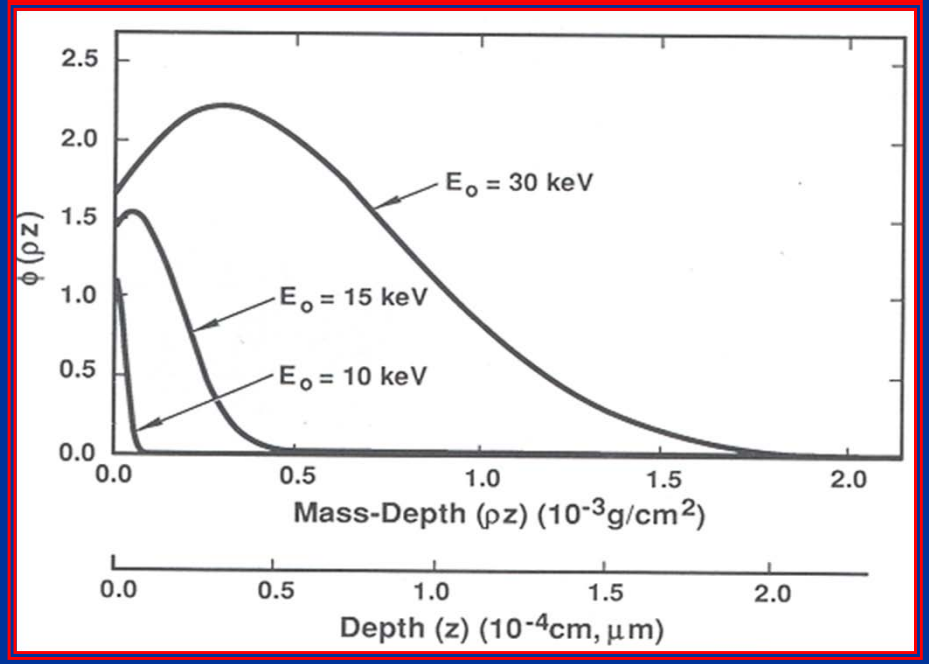
R_m : *the depth at which* $\phi(\rho z)$ *is maximum* (ϕ_m)

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)

$\phi(\rho z)$ dependence on Z and E_0





- R_m *and* R_x
  - *decrease with increase in atomic number,* Z
  - *increase with beam energy,* E_0
- $\phi(0)$ *increases with beam energy,* E_0

X-ray fluorescence

A consequence of X-ray absorption when

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

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 Mn and Fe

Element	**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

$$\mathbf{F}_i = \frac{\left(1+\sum_j \left\{I_{ij}^f / I_i\right\}\right)}{\left(1+\sum_j \left\{I_{ij}^f / I_i\right\}\right)^*}$$

* ***sample***

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

I_i : intensity of X-ray *"i"* generated by electron beam

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

F, a function of E_0 and composition

Castaing-Reed method:

$I\,f_{ij} / I_i = C_j Y_0 Y_1 Y_2 Y_3 P_{ij}$

$Y_0 = 0.5[(r_i\text{-}1)/r_i][\omega_j A_i/A_j]$

ω_j : fluorescent yield

$Y_1 = [(U_j\text{-}1)/(U_i\text{-}1)]^{1.67}$

$Y_2 = (\mu/\rho)^j{}_i/(\mu/\rho)^j{}_{spec}$

$Y_3 = [\ln(1+u)]/u + [\ln(1+v)]/v$

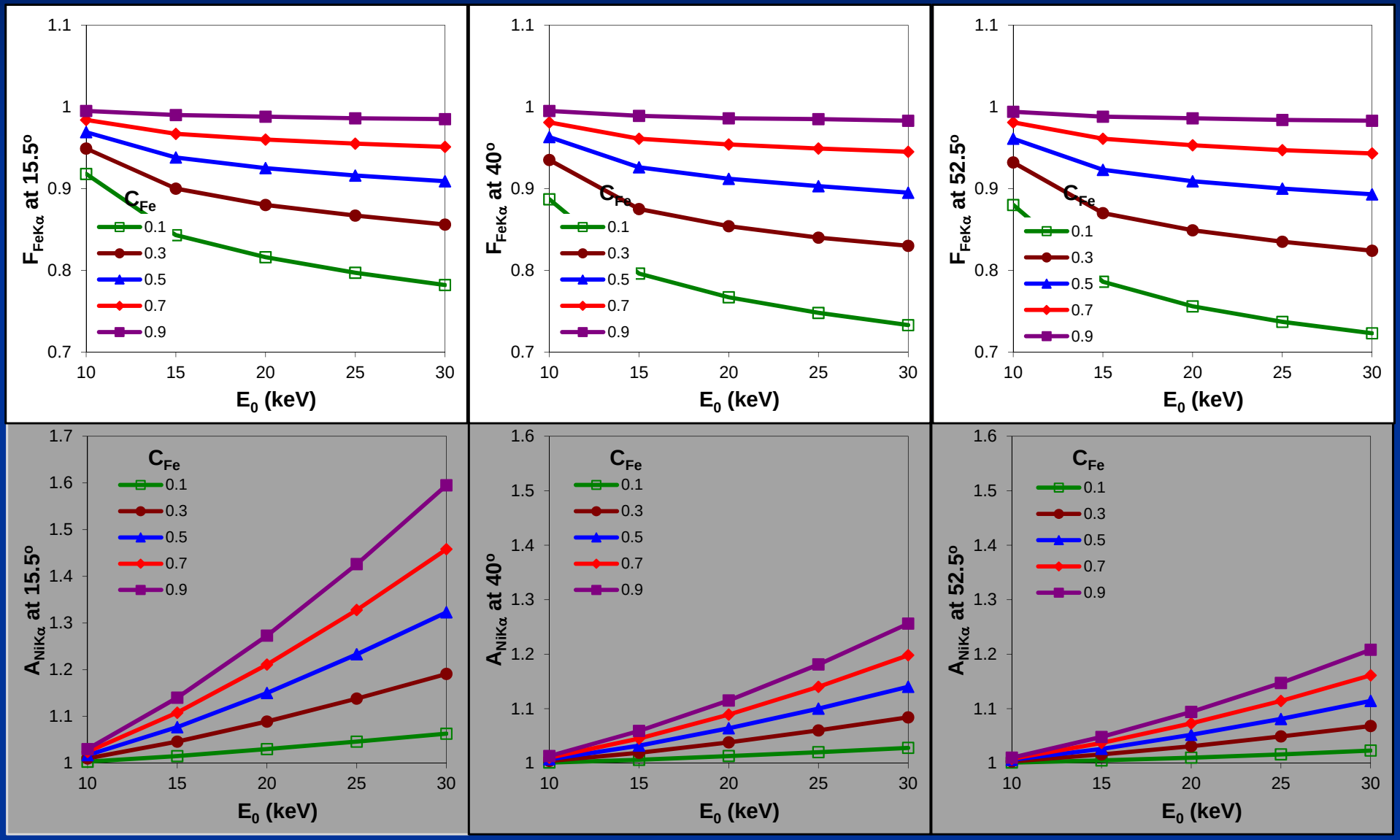
$u = [(\mu/\rho)^i{}_{spec}/(\mu/\rho)^j{}_{spec}]$ cosec ψ

$v = 3.3\text{x}10^5/[(E_0{}^{1.65}\text{-}E_c{}^{1.65})(\mu/\rho)^j{}_{spec}]$

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

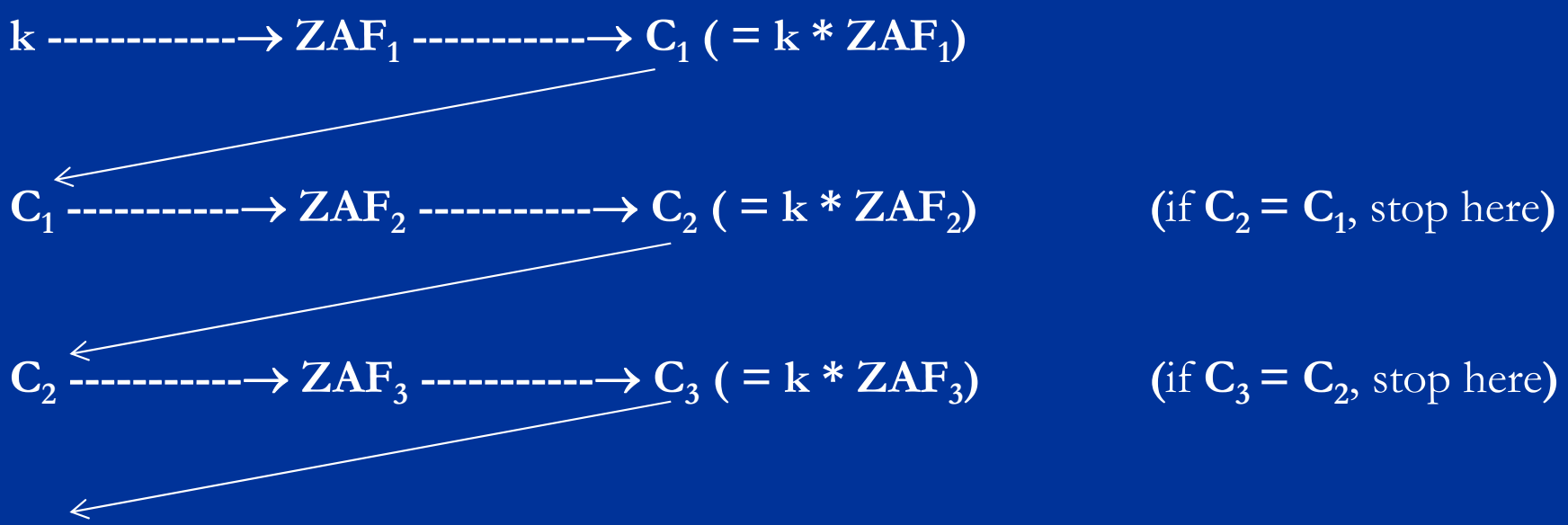
$F_{FeK\alpha}$ in Fe-Ni alloy



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

Matrix correction flowchart

Concentrations are calculated through an iterative procedure:



12.141 Electron Microprobe Analysis

January (IAP) 2012