QXAS Calibration options for quantitative analysis

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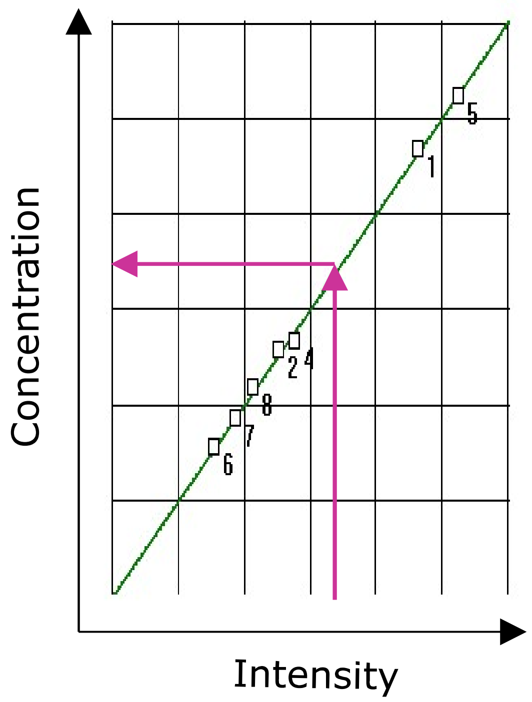
Outline:

- Fundamentals Analytical basis
  - A reference method
  - Derivation of Shermann-Nikina equation
- Main options for quantitative analysis
  - Radioisotopes
  - X-ray tubes
- QXAS options
  - Filters
  - Optical elements
- Concluding remarks

A Reference method:



XRF is a reference method, standards are required for both, calibration procedure and to assess the quality of the quantitative results.

Standards are measured, intensities obtained, and certain calibration (intensities vs. concentration) is established.

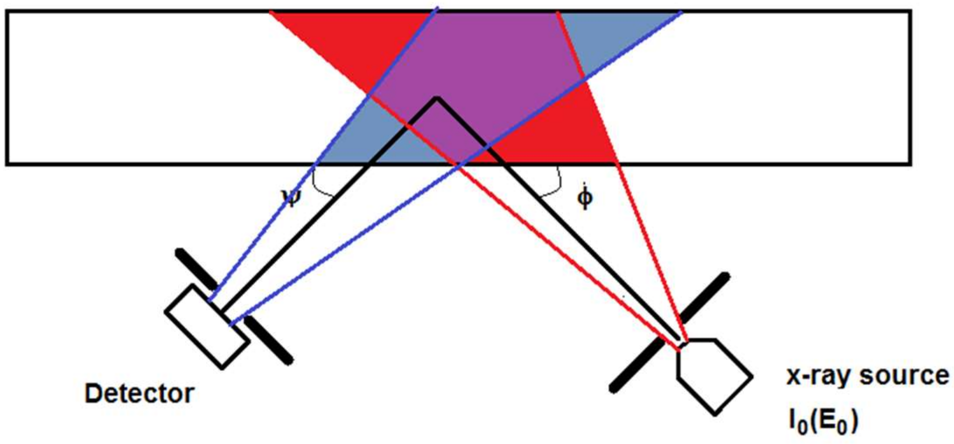
Commercial XRF instruments usually compare the spectral intensities of unknown samples to those of known standards.

Being a Reference method means:

- Geometry arrangements, instrument operational parameters and sample preparation followed during method implementation/calibration must be maintained!
- Samples deviating by nature or with concentrations outside the calibration range from those assumed for a given calibration cannot be analyzed.

The theroetical relationship (Shermann-Nikina): Assumptions

- Sample surface is flat and larger than the area visible by detector
- Average effective angles are assumed for excitation (ϕ) and detection (φ)
- The elements are homogenously distributed through the sample
- The energy distribition and intensity of the excitation radiation remains unchanged
- The geometry allocation does not change



The theroetical relationship (Shermann-Nikina): Assumptions

$$I_i = \varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} G K_i A(E_0, E_i) R_i(E_0, E_j) I_0(E_0) dE_0$$

$K_i = \frac{J_K^i - 1}{J_K^i} \omega_K^i f_{K_\alpha}^i \tau i(E0)$ contains all the fundamental parameters for specific K-line of element i

$A_S(E_0, E_i) = \frac{1 - e^{-\chi_S(E_0,E_i)\rho X}}{\chi_S(E_0, E_i)}$ takes into account the attenuation of both excitation and fluorescent radiation in the sample

$R_i(E_0, E_j)$ Considers the enhancement of x-ray production of element *i* by the characteristic of other major elements *j* present in the sample and having characteristic energies larger than absorption edge of element *i*

$I_0(E_0)$ Is the probability distribution by energies of the excitation radiation

$\varepsilon(E_i)$ Is the efficiency of the detector for energy E_i

G Is the overall effective solid angle

Demostration available at http://www.nsil-pt.com/xrs
Soon available at elearning.iaea.org

The theroetical relationship: Limitations

$$I_i = \varepsilon(E_i) w_i \int_{E>E_i^{ab}}^{E_{max}} G K_i A(E_0, E_i) R_i (E_0, E_j) I_0(E_0) dE_0$$

- It is a non-linear (on w_i) dependence, since…

$$A(E_0, E_i) = \frac{[1 - \exp(-\chi_i \rho_S x)]}{\chi_i}$$

➡ attenuation within the sample depends on the sample effective attenuation χ_i coefficient and on sample aerial density $\rho_S x$ (mass per unit area, gcm^{-2}]

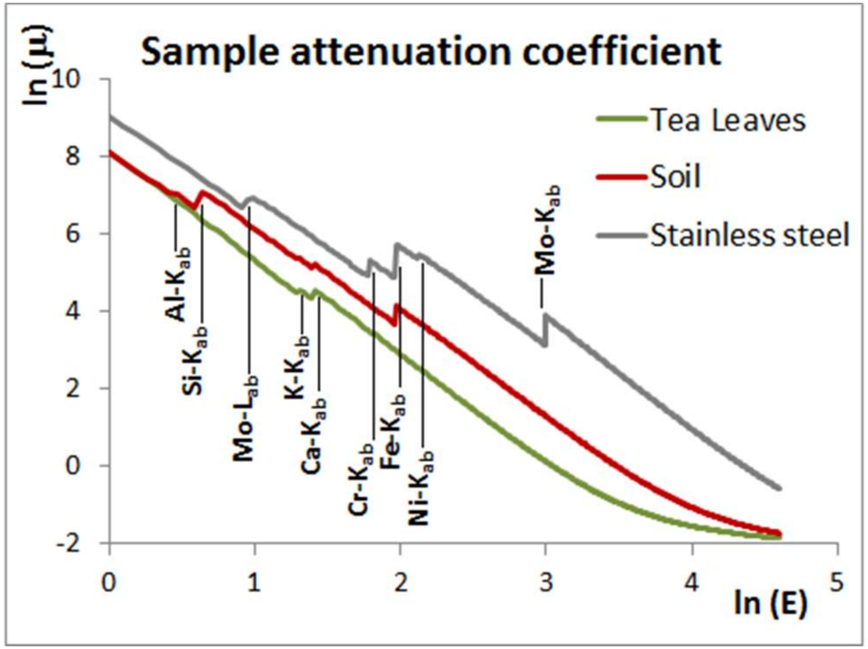
⇨ $$\chi_i = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_i)}{\sin\phi} = ????$$

The theroetical relationship: Limitations

$$I_i = \varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} G K_i A(E_0, E_i) R_i(E_0, E_j) I_0(E_0) dE_0$$

$$\mu_S(E_0) = \sum_j w_j \mu_j(E_0)$$

Depends on all major constituents, which are not known a priori



Attenuation correction

$$A(E_0, E_i) = \frac{[1 - \exp(-\chi_i \rho_S x)]}{\chi_i}$$

- cannot be evaluated in the more general case, since…

$$\mu_S(E) = \sum_j w_j \mu_j(E)$$

We cannot measure the characteristic radiation from all w_j since $I_j = 0$

-> either $K_i = f_K \times \omega_K \times \left(1 - \frac{1}{J_K}\right) \times \tau_i(E_0)$ or

$$\omega_K = 0 \forall E_0 < E_i^{ab,K}$$

-> $\varepsilon(E_i) = 0$

Enhancement effects

$$I_i = \varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} G K_i A(E_0, E_i) R_i(E_0, E_j) I_0(E_0) dE_0$$

$$R_i(E_0, E_j) = \left(1 + \sum_j w_j S_{i,j}\right)$$

enhancement effects are difficult to estimate, and also require of knowledge on elemental composition

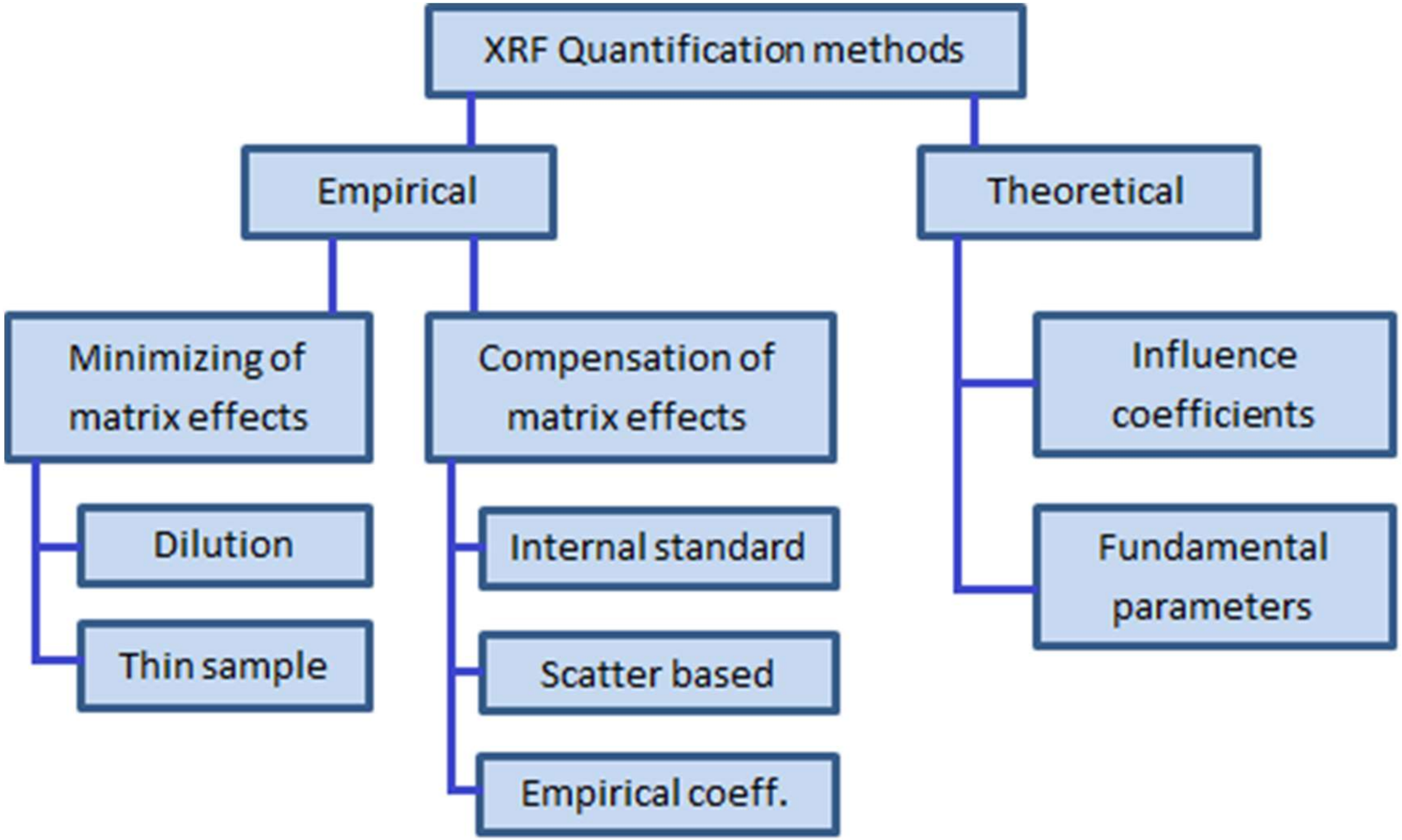
$$R_i(E_0, E_j) > 1 \quad \left| \begin{array}{l} w_j > 0.01 \\ E_j > E_i^{ab} \end{array} \right.$$

$$S_{i,j} = \frac{1}{2} K_j \tau_j(E_0) \frac{\tau_i(E_j)}{\tau_i(E_0)} \frac{\chi(E_0, E_i)}{1 - e^{-\chi s(E_0, E_i)\rho X}} D_{i,j}$$

$$D_{i,j} = \int_0^{\frac{\pi}{2}} \tan(\Theta) \left[\frac{1 - e^{-\chi_1(E_i, E_j)\rho X}}{\chi_1(E_i, E_j)\chi_2(E_0, E_j)} - \frac{1 - e^{-\chi(E_0, E_i)\rho X}}{\chi(E_0, E_i)\chi_2(E_0, E_j)} \right] d\theta + \int_{\frac{\pi}{2}}^{\pi} \tan(\Theta) \left[\frac{e^{-\chi_2(E_0, E_j)\rho X} - e^{-\chi(E_0, E_i)\rho X}}{\chi_1(E_i, E_j)\chi_2(E_0, E_j)} - \frac{1 - e^{-\chi(E_0, E_i)\rho X}}{\chi(E_0, E_i)\chi_2(E_0, E_j)} \right] d\theta$$

$$\chi(E_0, E_i) = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_i)}{\sin\psi} \quad \chi_1(E_i, E_j) = \frac{\mu_S(E_i)}{\sin\psi} + \frac{\mu_S(E_j)}{\cos\theta} \quad \chi_2(E_0, E_j) = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_j)}{\cos\theta}$$

Common approaches for quantification



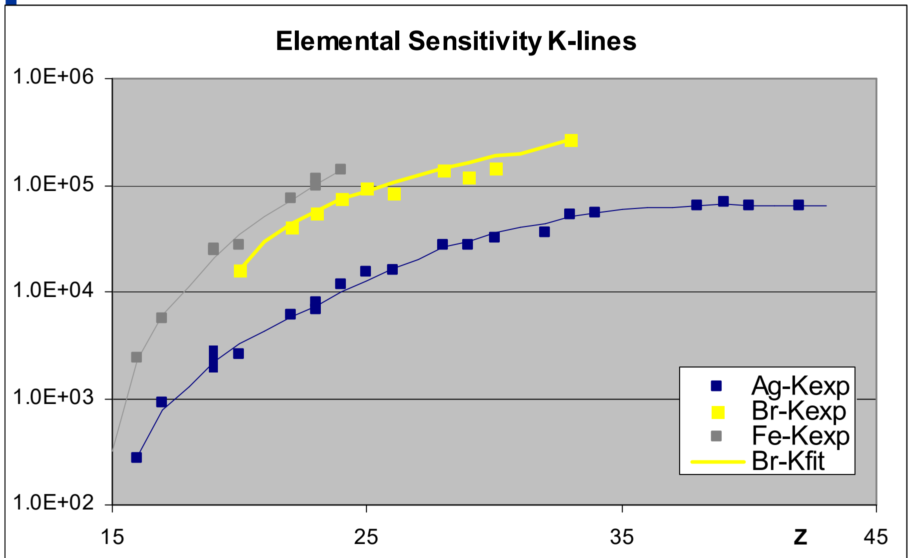
Instrumental calibration

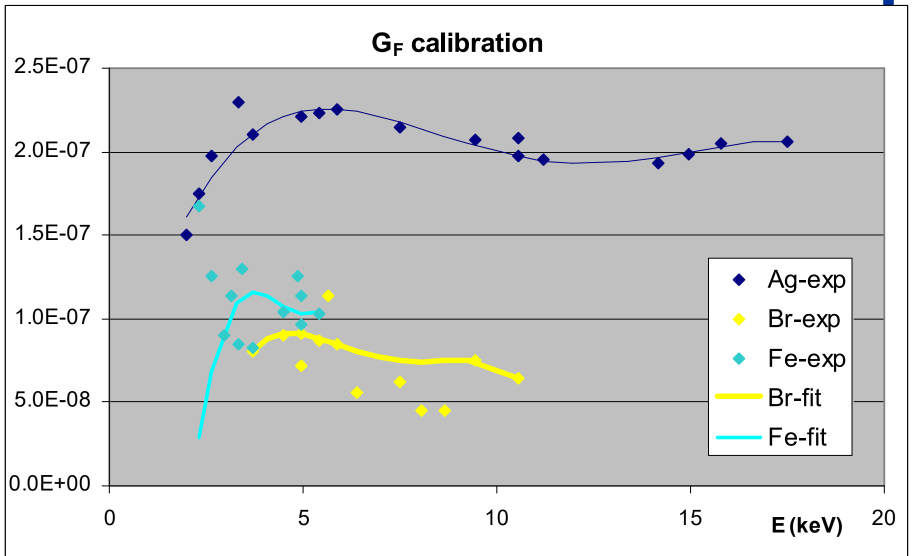
$$I_i = \varepsilon(E_i) w_i \int_{E>E_i^{ab}}^{E_{max}} G K_i A(E_0, E_i) R_i(E_0, E_j) I_0(E_0) dE_0$$

- Instrumental sensitivity
- Fundamental parameters

$$\frac{I_i}{w_i A(E_0, E_i)} = G\varepsilon(E_i) \int_{E>E_i^{ab}}^{E_{max}} K_i I_0(E_0) dE_0 = S_i$$

$$\frac{I_i}{w_i \varepsilon(E_i) \int_{E>E_i^{ab}}^{E_{max}} K_i A(E_0, E_i) I_0(E_0) dE_0} = G$$

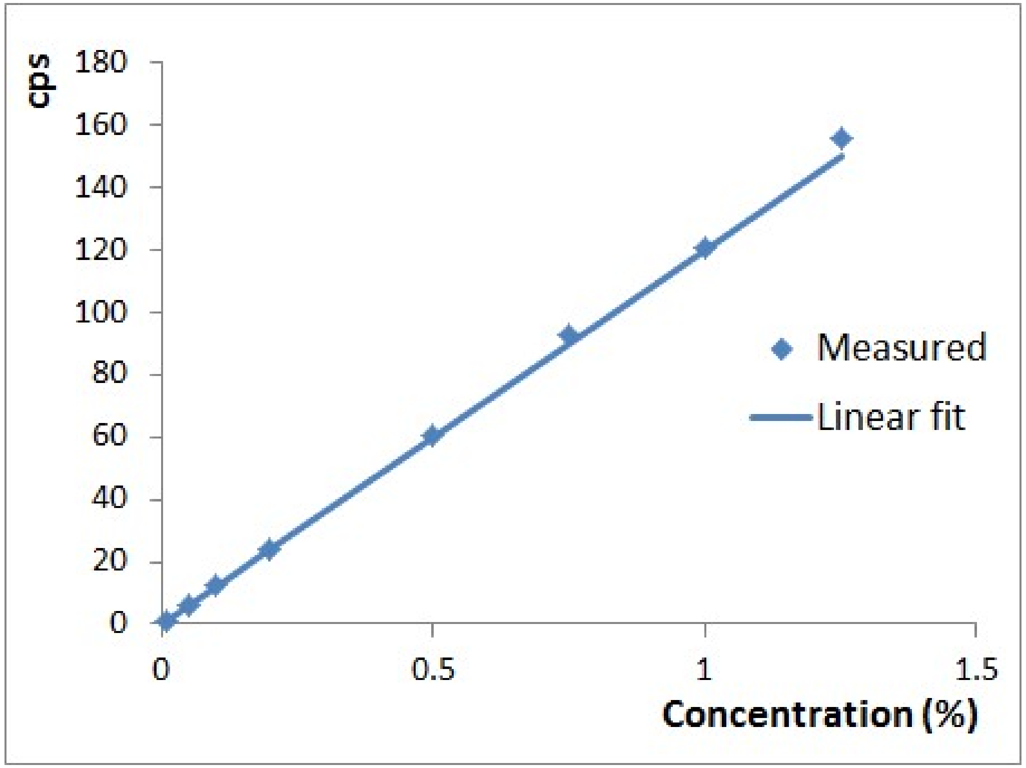




Strong dilution of the sample

Dilution with binder or fusing agent (1:10)

- Matrix is that of the diluting agent
- Loss of effective sensitivity

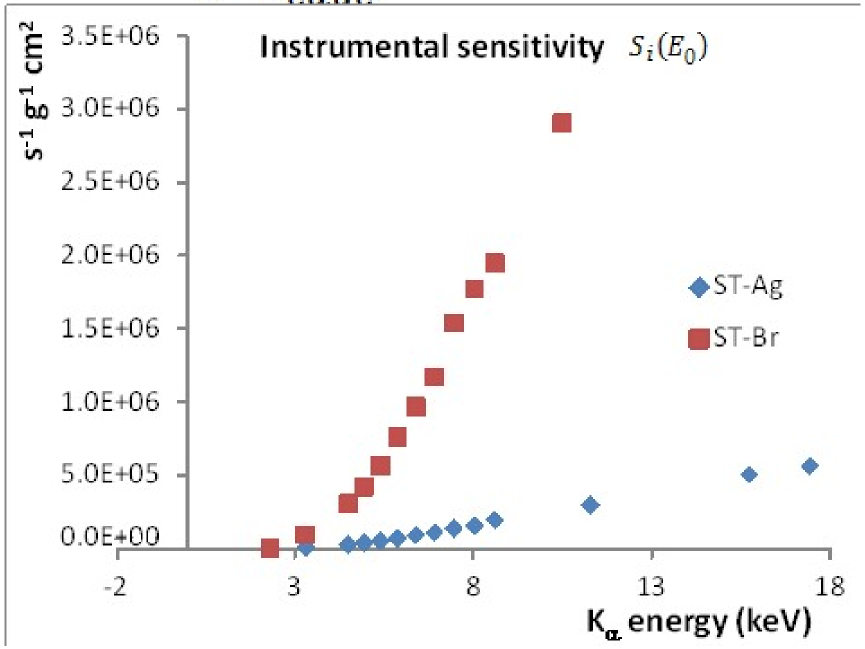


Thin sample

$$\chi_i(E_0, E_i)\rho_S x \le 0.1$$

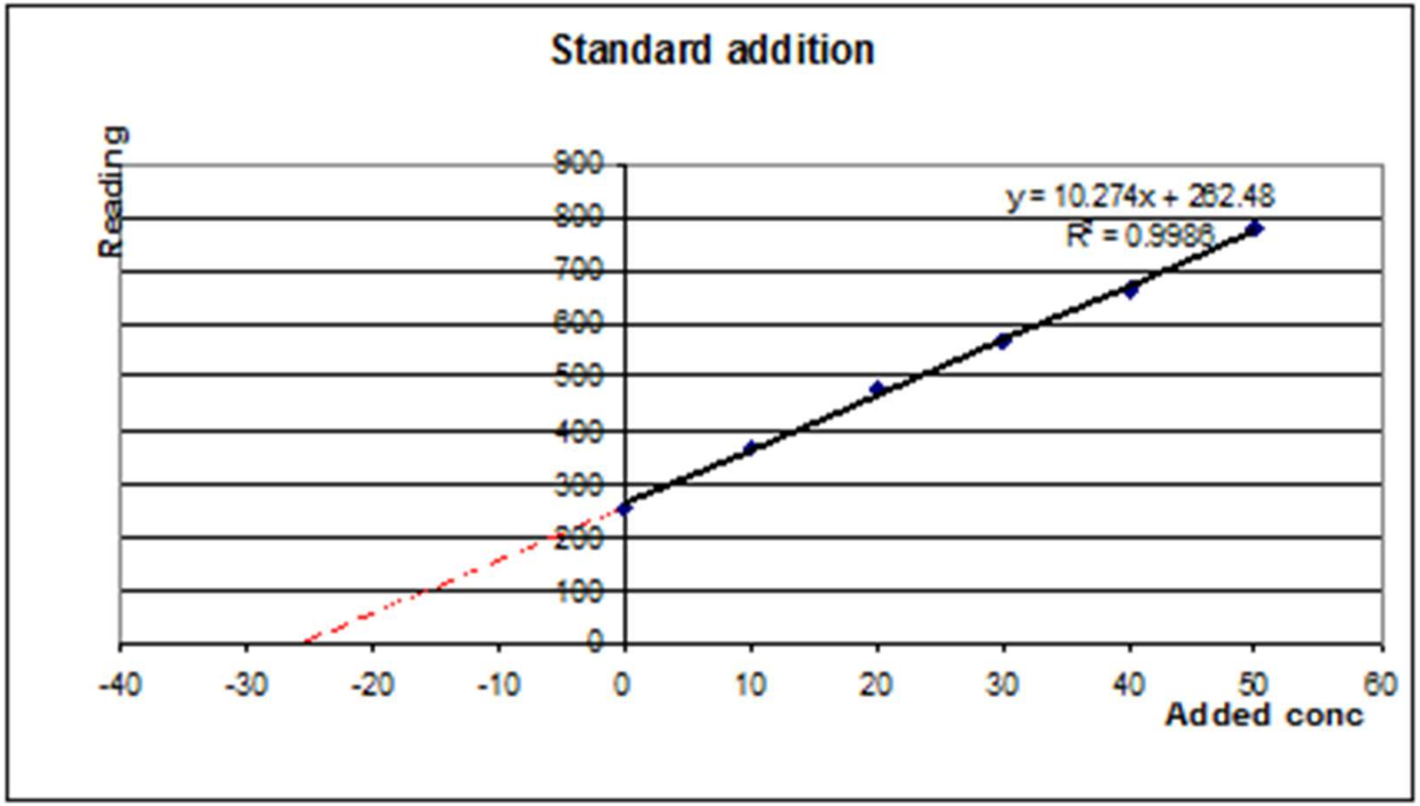
$$A(E_0, E_i) = \frac{[1 - \exp(-\chi_i \rho_S x)]}{\chi_i} \approx \frac{[1 - (1 - \chi_i \rho_S x)]}{\chi_i} \approx \rho_S x$$

$$S_i(E_0) = \frac{I_D(E_i)}{\rho_i X} = G\varepsilon(E_i) K_i T_{env}(E_i) \int_{E=E_{edge}^K}^{E_{max}} \tau_i(E_0) I_1(E_0) dE_0$$



External standard addition

Adding small aliquots of the element (at trace concentration)



Thin sample + Internal standard: TXRF

$$I_i = \varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} G K_i A(E_0, E_i) R_i(E_0, E_j) I_0(E_0) dE_0$$

$$\chi_i(E_0, E_i) \rho_S x \leq 0.1$$

$$I_i = \varepsilon(E_i) w_i G K_i \rho_S x I_0(E_0) = \rho_i x \varepsilon(E_i) G K_i I_0(E_0)$$

$$\frac{I_i}{I_{st}} = \frac{\varepsilon(E_i)}{\varepsilon(E_{st})} \frac{w_i}{w_{st}} \frac{G}{G} \frac{K_i}{K_{st}} \frac{\rho_S x I_0(E_0)}{\rho_S x I_0(E_0)}$$

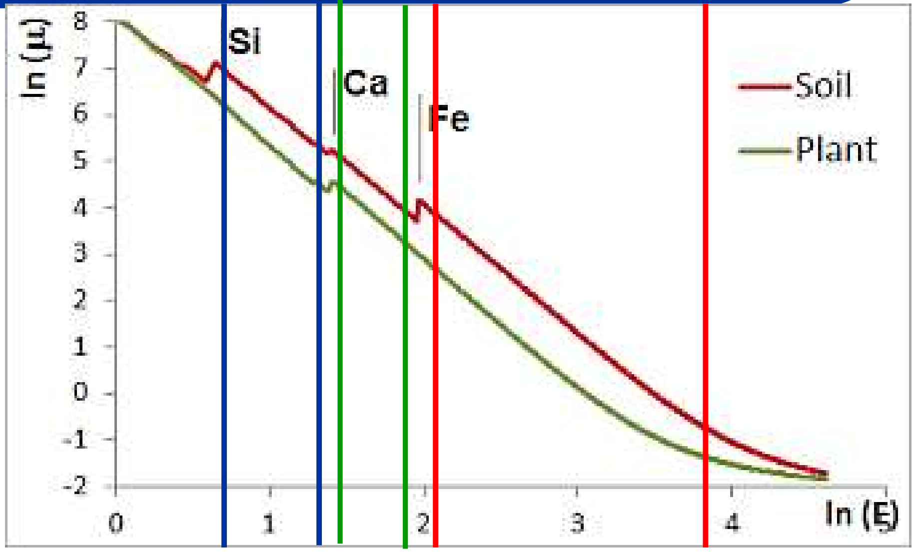
$$w_i = \frac{I_i}{I_{st}} \frac{\varepsilon(E_{st})}{\varepsilon(E_i)} \frac{K_{st}}{K_i} w_{st} = \frac{I_i}{I_{st}} \frac{S_{st}}{S_i} w_{st}$$

Assumptions for scatter normalization:

1) For all *i* elements with

$$E_i > E_j^{ab} \begin{bmatrix} w_j > 0.01 \\ Z_j = \max \end{bmatrix}$$

$$\ln[\mu_S(E_i)] = a \ln(E_i) + b$$



2) Sample can be considered as 'infinitely thick'

$$\chi(E_0, E_i)\rho_S x \to \infty$$

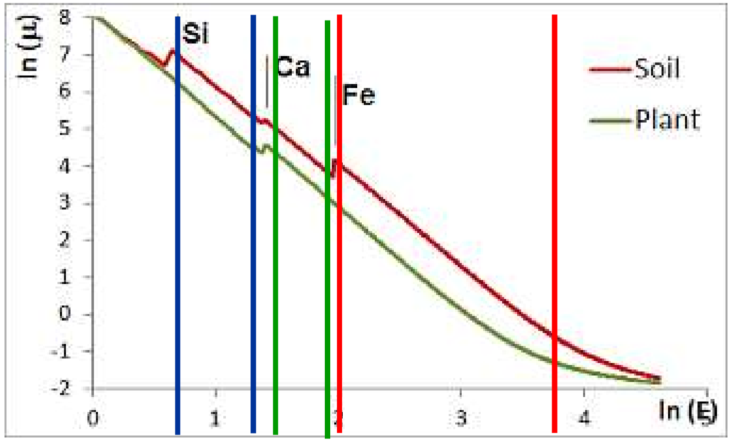
$$A(E_0, E_i) \to \frac{[1 - \exp(-\infty)]}{\chi_i} \approx \frac{[1-0]}{\chi_i} = \frac{1}{\chi_i}$$

$$I_i = G\varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} K_i \frac{R_i(E_0, E_j)}{\chi(E_0, E_i)} I_0(E_0) dE_0 = G\varepsilon(E_i) w_i \int_{E > E_i^{ab}}^{E_{\max}} \frac{K_i}{\chi(E_0, E_i)} I_0(E_0) dE_0$$

How to transform the dependence...

$$I_i = G\varepsilon(E_i) w_i \int_{E>E_i^{ab}}^{E_{max}} \frac{K_i}{\chi(E_0, E_i)} I_0(E_0) dE_0$$

$$\chi(E_0, E_i) = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_i)}{\sin\psi} \Rightarrow \frac{1}{\chi_S(E_0, E_i)} = \frac{\sin\psi \sin\varphi}{\mu_S(E_i)\sin\varphi + \mu_S(E_0)\sin\psi}$$



we can express the value of any $\mu_s(E_i)$ as function of $\mu_s(E_0)$!

$$a = \frac{\ln[\mu_S(E_0)] - \ln[\mu_S(E_i)]}{\ln[E_0] - \ln[E_i]} = \frac{\ln\left[\frac{\mu_S(E_0)}{\mu_S(E_i)}\right]}{\ln\left[\frac{E_0}{E_i}\right]}$$

$$a \times \ln\left[\frac{E_0}{E_i}\right] = \ln\left[\frac{\mu_S(E_0)}{\mu_S(E_i)}\right]$$

$$\ln\left[\left(\frac{E_0}{E_i}\right)^a\right] = \ln\left[\frac{\mu_S(E_0)}{\mu_S(E_i)}\right] \Rightarrow$$

$$\ln(a) - \ln(b) = \ln(\frac{a}{b}), \quad c \times \ln(a) = \ln(a^c)$$

$$\frac{\mu_S(E_i)}{\mu_S(E_0)} = \left(\frac{E_i}{E_0}\right)^a$$

Transforming further the dependence:

$$I_i = G\varepsilon(E_i)w_i \int_{E>E_i^{ab}}^{E_{\max}} \frac{K_i}{\chi(E_0, E_i)} I_0(E_0)dE_0$$

$$\chi(E_0, E_i) = \frac{\mu_S(E_0)}{\sin\varphi} + \frac{\mu_S(E_i)}{\sin\psi} \Rightarrow \frac{1}{\chi_S(E_0, E_i)} = \frac{\sin\psi\sin\varphi}{\mu_S(E_i)\sin\varphi + \mu_S(E_0)\sin\psi}$$

$$\frac{\mu_S(E_i)}{\mu_S(E_0)} = \left(\frac{E_i}{E_0}\right)^a \Rightarrow \quad = \frac{\sin\psi\sin\varphi}{\mu_S(E_0)\left(\frac{E_i}{E_0}\right)_a \sin\varphi + \mu_S(E_0)\sin\psi}$$

$$= \frac{\sin\psi\sin\varphi}{\mu_S(E_0)\left[\left(\frac{E_i}{E_0}\right)^a \sin\varphi + \sin\psi\right]}$$

$$\Rightarrow I_i = G\varepsilon(E_i)w_i \int_{E>E_i^{ab}}^{E_{\max}} \frac{K_i \times \sin\varphi\sin\psi}{\mu(E_0)\left[\left(\frac{E_i}{E_0}\right)^a \sin\varphi + \sin\psi\right]} I_0(E_0)dE_0$$

but still we need to know $\mu_s(E_0)$...

How to get rid of depending from $\mu_S(E_0)$?

$$I_i = G\varepsilon(E_i) w_i \int_{E>E_i^{ab}}^{E_{\max}} \frac{K_i \times \sin\varphi \sin\psi}{\mu(E_0)\left[\left(\frac{E_i}{E_0}\right)^a \sin\varphi + \sin\psi\right]} I_0(E_0) dE_0$$

We might use some scatter peak… for instance, for Compton peak:

$$I_C = G_C \varepsilon(E_C) \frac{1}{\chi_C} I(E_0) \sum_j \frac{N_0}{A_j} w_j \sigma_{C,j}$$

where $\sigma_{C,i}$ - Total incoherent scatter cross section

Following the same procedure used before, it can be transformed to:

$$\Rightarrow \quad I_C = \frac{G_C \varepsilon(E_C) \sin\psi \sin\phi}{\mu_S(E_0)\left[\left(\frac{E_C}{E_0}\right)^a \sin\phi + \sin\psi\right]} I(E_0) \sum_j \frac{N_0}{A_j} w_j \sigma_{C,j}$$

Internal standardization using Compton…

$$I_i = G\varepsilon(E_i)w_i \frac{K_i \times \sin\varphi \sin\psi}{\mu(E_0)\left[\left(\frac{E_i}{E_0}\right)^a \sin\varphi + \sin\psi\right]} I_0(E_0)$$

$$I_C = \frac{G_C \varepsilon(E_C)\sin\psi \sin\phi}{\mu_S(E_0)\left[\left(\frac{E_C}{E_0}\right)^a \sin\phi + \sin\psi\right]} I(E_0) \sum_j \frac{N_0}{A_j} w_j \sigma_{C,j}$$

If we use Compton counting as internal standard…

$\frac{I_i}{I_C}$ ⇨ Does not depend on sample matrix!

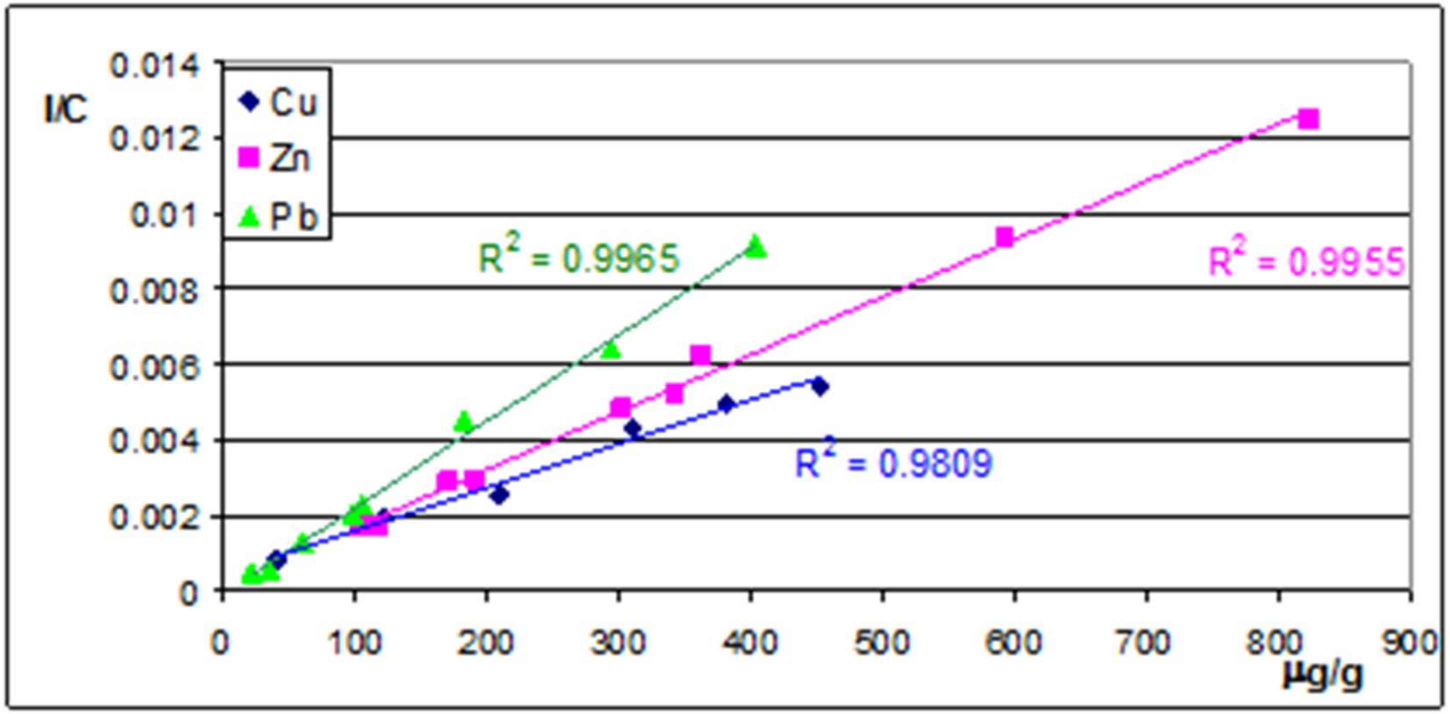
⇨ Does not depend on excitation flux intensity!

$$\frac{I_i}{I_C} = \frac{G}{G_C} \times \frac{\varepsilon(E_i)}{\varepsilon(E_C)} \times \frac{\left(\frac{E_C}{E_0}\right)^a \sin\varphi + \sin\psi}{\left(\frac{E_i}{E_0}\right)^a \sin\varphi + \sin\psi} \times \frac{w_i K_i}{\sum_j \frac{N_0}{A_i} w_j \sigma_{C,j}} \Rightarrow \frac{I_i}{I_C} = a \times w_i + b$$

WOOOOOOOW !!! It IS Linear in regard to w_i

Scatter normalization

Regression of fluorescence intensities normalized to scatter



Theoretical influence coefficients (α)

$$w_i = K_i M_i I_i + B_i \qquad M_i = 1 + \sum_{i \neq j} \alpha_{i,j} w_j$$

$$w_i = \frac{I_i \chi_S(E_0, E_i)}{G\varepsilon(E_i) K_i T_{env}(E_i) \tau_i(E_0) I_1(E_0)}$$

$$\chi_S(E_0, E_i) = w_i \chi_i(E_0, E_i) + \sum_{j \neq 1} w_j \chi_j(E_0, E_i)$$

$$\chi_S(E_0, E_i) = \left(1 - \sum_{j \neq 1} w_j\right) \chi_i(E_0, E_i) + \sum_{j \neq 1} w_j \chi_j(E_0, E_i) = \chi_i(E_0, E_i)\left[1 + \sum_{j \neq 1} \alpha_{i,j} w_j\right]$$

$$\alpha_{i,j} = \frac{\chi_j(E_0, E_i)}{\chi_i(E_0, E_i)}$$

$$w_i = \frac{I_i \chi_i(E_0, E_i)\left[1 + \sum_{j \neq 1} \alpha_{i,j} w_j\right]}{G\varepsilon(E_i) K_i T_{env}(E_i) \tau_i(E_0) I_1(E_0)} = \frac{I_i G\varepsilon(E_i) K_i T_{env}(E_i) \tau_i(E_0) I_1(E_0)\left[1 + \sum_{j \neq 1} \alpha_{i,j} w_j\right]}{I_i^{pure} G\varepsilon(E_i) K_i T_{env}(E_i) \tau_i(E_0) I_1(E_0)}$$

$$= \frac{I_i\left[1 + \sum_{j \neq 1} \alpha_{i,j} w_j\right]}{I_i^{pure}} = R_i \left[1 + \sum_{j \neq 1} \alpha_{i,j} w_j\right] \quad R_i = \frac{I_i}{I_i^{pure}} = w_i$$

It only works for monochromatic excitation!

Empirical influence coefficients (α)

$$\begin{Bmatrix} I_1 = \alpha_1^1 + \cdots + \alpha_1^i + \cdots + \alpha_1^n \\ . \\ . \\ . \\ I_n = \alpha_n^1 + \cdots + \alpha_n^i + \cdots + \alpha_n^n \end{Bmatrix}$$

n x n standards need to be measured to find the alphas!

$$\alpha_i^j = \frac{\Delta_i^j}{\Delta}$$

standards need to cover the expected interval of concentrations!

Fundamental parameters

Calibration:

$$G = \frac{I_i}{w_i \varepsilon(E_i) K_i T_{env}(E_i) \int_{E_i^{abs}}^{E_{max}} \frac{1}{\chi_S(E_0, E_i)} \tau_i(E_0) I_1(E_0) dE_0}$$

Initial guess:

$$w_i^j = \frac{I_i}{G\varepsilon(E_i) K_i T_{env}(E_i) \int_{E_i^{abs}}^{E_{max}} \tau_i(E_0) I_1(E_0) dE_0}$$

Finding the dark matrix:

1. Known
2. From scatter ratio calibration
3. By iterative calculation

$$I_{Sc}^{j,dark} = I_{Sc}^{meas} - G\varepsilon(E_{Sc}) T_{env}(E_{Sc}) \frac{1}{\chi_S(E_0, E_{Sc})} I_1(E_0) \sum \frac{N_0}{A_i} w_i \sigma_i^{Sc}(E_0)$$

$$I_{Inc}^{j,dark} = G\varepsilon(E_{Inc}) T_{env}(E_{Inc}) \frac{1}{\chi_S^j(E_0, E_{Inc})} I_1(E_0) \frac{N_0}{A_j} [w_Z \sigma_Z^{Inc}(E_0) + w_{Z+2} \sigma_{Z+2}^{Inc}(E_0)]$$

$$I_{Coh}^{j,dark} = G\varepsilon(E_0) T_{env}(E_0) \frac{1}{\chi_S^j(E_0, E_0)} I_1(E_0) \frac{N_0}{A_j} [w_Z \sigma_Z^{Coh}(E_0) + w_{Z+2} \sigma_{Z+2}^{Coh}(E_0)]$$

Fundamental parameters

Calibration:

$$G = \frac{I_i}{w_i \varepsilon(E_i) K_i T_{env}(E_i) \int_{E_i^{abs}}^{E_{max}} \frac{1}{\chi_S(E_0, E_i)} \tau_i(E_0) I_1(E_0) dE_0}$$

Initial guess:

$$w_i^j = \frac{I_i}{G \varepsilon(E_i) K_i T_{env}(E_i) \int_{E_i^{abs}}^{E_{max}} \tau_i(E_0) I_1(E_0) dE_0}$$

Finding the dark matrix:

1. Known
2. From scatter ratio calibration
3. By iterative calculation

Iterative calculation of concentrations

$$w_i^{j+1} = \frac{I_i}{G \varepsilon(E_i) K_i T_{env}(E_i) \int_{E_i^{abs}}^{E_{max}} \frac{1}{\chi_S(E_0, E_i)} \tau_i(E_0) I_1(E_0) dE_0}$$

QXAS options:

- Analysis of alloys
  - ☞ Fundamental Parameters (DM = No matrix !)
- Analysis of APM in aerosol filters
  - ☞ Thin sample
- Analysis of liquid samples
  - ☞ TXRF : Thin sample + internal standard
  - ☞ EDXRF: Thin sample (APDC pre-concentration + filtration)
- Analysis of biological (light) matrices
  - ☞ FP (DM from scatter calibration)
- Analysis of soils and sediments
  - ☞ Compton correction (Fe and higher E_i)
  - ☞ Fundamental parameters
    -> If matrix is known (e.g. XRD)
    -> or empirically estimated
    -> or using scatter cross sections

Concluding remarks

QXAS incorporates a rich variety of programs covering almost all possible choice for quantification

- Not user-friendly environment (MSDos).
- Requires installation of DosBox like tools in Windows OS
- Careful attention to diversity of commands

Thanks for your time and attention...