

Joint ICTP-IAEA School on Novel Experimental Methodologies for Synchrotron  
Radiation Applications in Nano-science and Environmental Monitoring

# Quantitative XRF Analysis

## algorithms and their practical use

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# Content

- Quantitative analysis
- Relation between intensity and concentration
- Consequences of this relation
- The fundamental parameter method
- Calibration curves
- Dealing with detection limits
- Some final remarks

# Quantitative analysis in XRF

The NET intensity of the characteristic x-ray lines is proportional to the concentration

NET = background corrected  
and interference free

Use mainly Ka or La lines of elements

## Quantitative results

major elements (conc. range 100% - 5%)  
uncertainty of < 1% relative  
i.e. 23.40 +/- 0.12 % Cu (0.5 % relative error)  
minor elements (conc. range 5% - 0.1%)  
uncertainty of 5% relative  
trace elements (<0.1%)  
uncertainty of >5 %

## Semi-quantitative results

uncertainties between 5 and 30% relative

## Qualitative results

presence/absence of elements

Only with  
homogeneous samples

The real situation in  
many XRF applications

The reality for the  
analysis of culturale  
heritage samples

# The fundamental parameter relation

Derivation of the relation between concentration  
and X-ray measured intensity:  
the Sherman equation

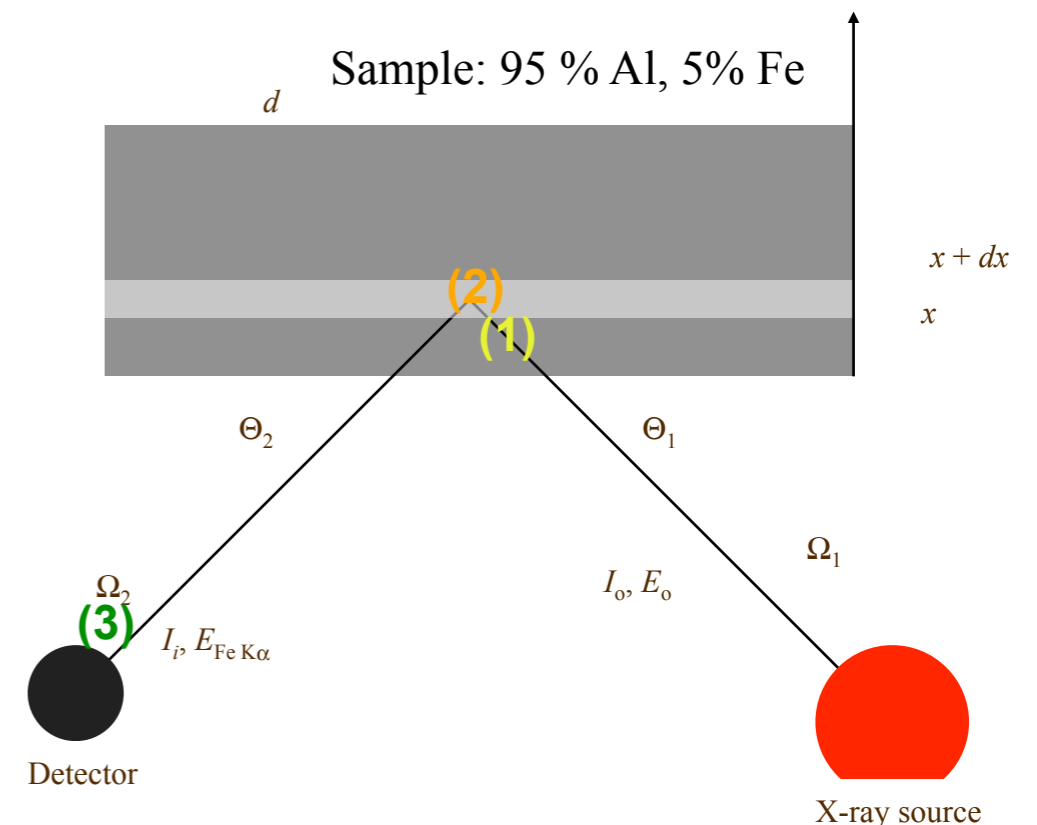
# 3.1 The fundamental parameter relation

Derivation of the relation between Concentration and X-ray measured intensity:  
the Sherman equation

Mono-energetic excitation  
Sample 95% Al, 5% Fe

The measured intensity (cps) of the Fe K $\alpha$  x-rays depend on...

- (1) How many primary x-ray reach the sample at a certain depth
- (2) How many Fe K-vacancies are produced and how many of them cause the emission of K $\alpha$  photons
- (3) How many of those Fe K $\alpha$  photons can leave the sample and get detected



# 1) Number of primary x-ray that reach at depth $x$ :

Path traveled:

$$l = \frac{x}{\sin\Theta_1}$$

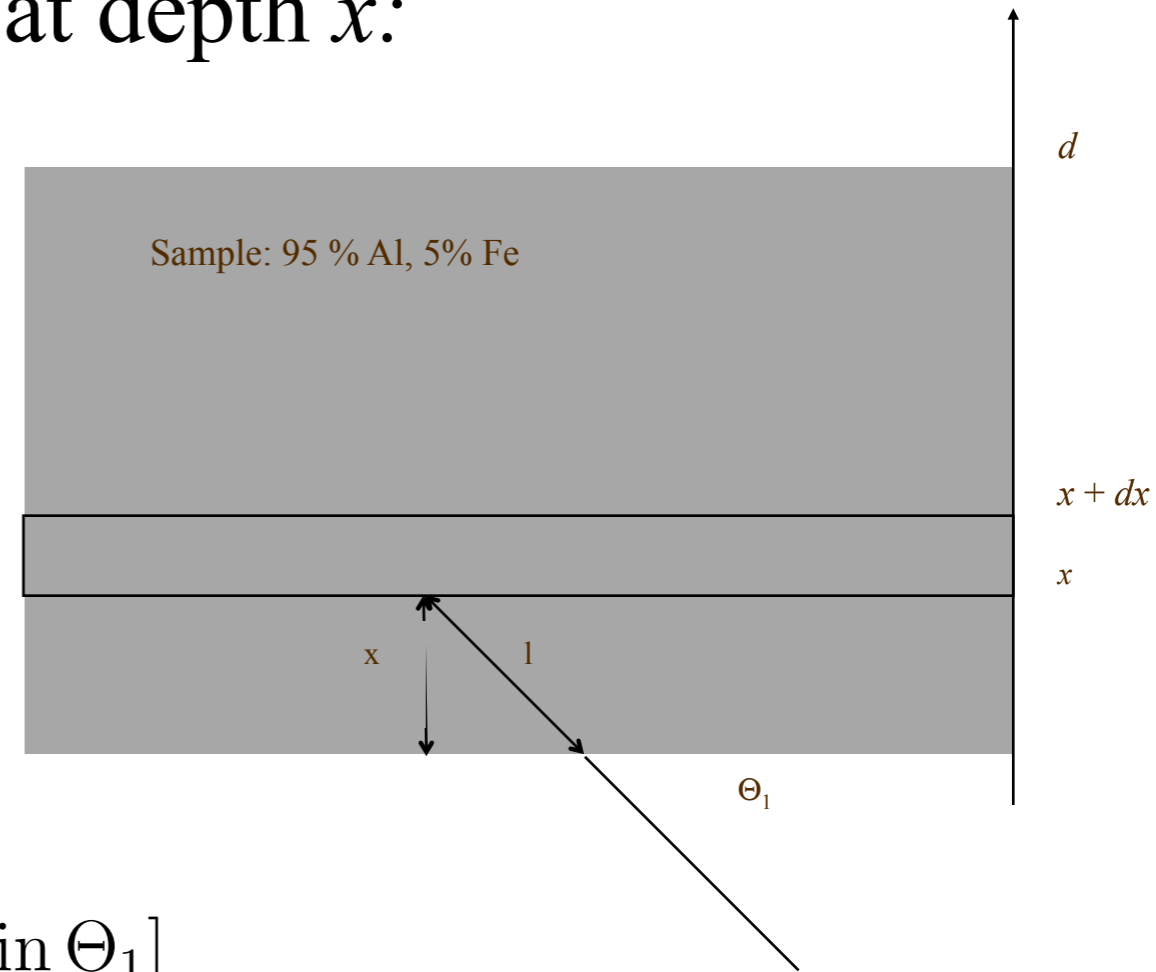
X-ray intensity impinging on depth  $x$ :

$$I_x = I_0(E_0) \exp[-\mu_M(E_0)\rho_M x / \sin \Theta_1]$$

$\rho_M$  density of the sample (matrix)

$\mu_M(E_0)$  mass att. coeff. of the matrix for the primary radiation

$$\mu_M(E_0) = \sum_{j=1}^n w_j \mu_j(E_0) = 0.95 \times \mu_{Al}(E_0) + 0.05 \times \mu_{Fe}(E_0)$$



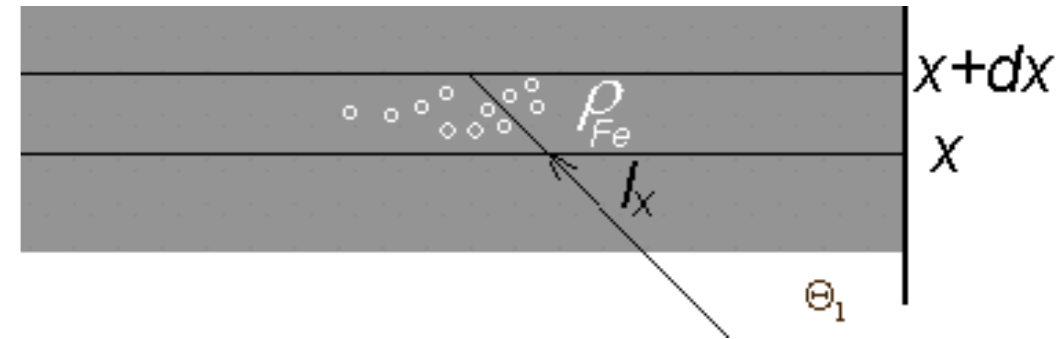
## 2) Number of Fe $K\alpha$ photons emitted from $dx$ :

Number of Fe vacancies created in the layer  $dx$  at depth  $x$

$$\tau_{\text{Fe}}(E_0) \rho \frac{dx}{\sin \Theta_1} I_x$$

$\rho_{\text{Fe}}$  - "density" of Fe, gram Fe per  $\text{cm}^3$  [ $\text{g}/\text{cm}^3$ ]

$\tau_{\text{Fe}}(E_0)$  – fraction of photons that are absorbed and create vacancies in any shell  
photo-electric mass absorption coefficient of Fe [ $\text{cm}^2/\text{g}$ ]



x Fraction of K shell vacancies:  $\tau_{K,Fe}(E_0) = \tau_{Fe}(E_0) \times \left(1 - \frac{1}{J_K}\right)$  ( $J_K$  - K-edge jump ratio of Fe)

x Fraction emitted as K photons:  $\times \omega_K$  ( $\omega_K$  - K-shell fluorescence yield of Fe)

x Fraction emitted as  $K\alpha$  photons:  $\times f_{K\alpha}$  ( $f_{K\alpha}$  -  $K\alpha$  to total K ( $K\alpha + K\beta$ ) ratio)



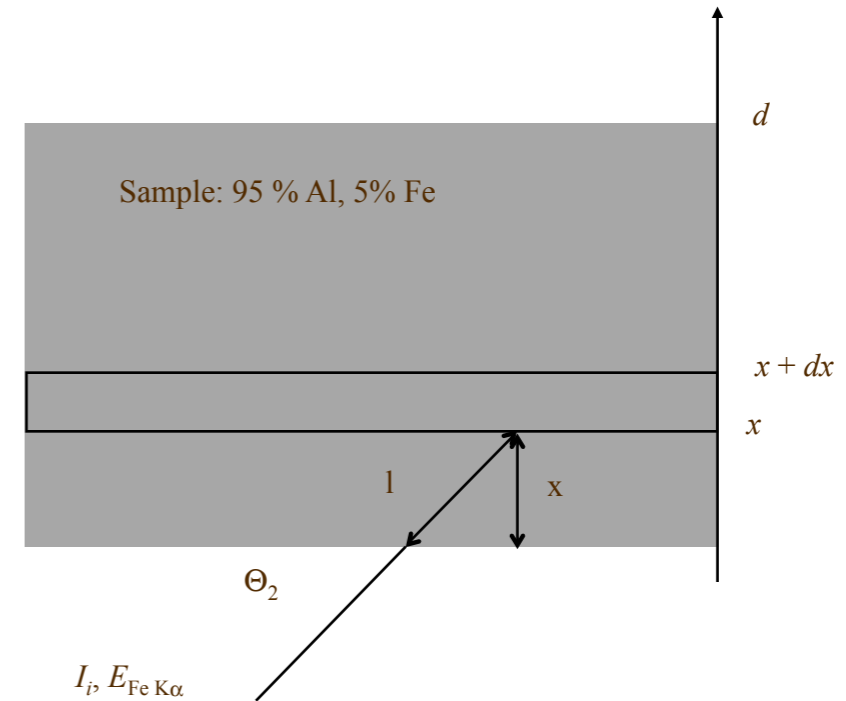
$$dI_{\text{Fe}} = f_{K\alpha} \omega_K \left(1 - \frac{1}{J_K}\right) \tau_{\text{Fe}}(E_0) \rho_{\text{Fe}} \frac{dx}{\sin \Theta_1} I_x$$



### 3) Number of Fe K $\alpha$ that reach the detector

Path traveled:

$$l = \frac{x}{\sin\Theta_2}$$



× Attenuation of Fe K $\alpha$  x-ray from layer at depth  $x$ :

$$\exp[-\mu_M(E_{Fe K\alpha})\rho_M x / \sin \Theta_2]$$

$\mu_M(E_{Fe K\alpha})$  mass att. coeff. of the matrix for Fe K $\alpha$

× Fraction viewed by the detector:  $\frac{\Omega_2}{4\pi}$

× Attenuation in air path, detector windows...  $\epsilon(E_{Fe K\alpha})$  (detector efficiency)



$$dI_{Fe K\alpha} = \frac{\Omega_2}{4\pi} \epsilon(E_{Fe K\alpha}) \exp[-\mu_M(E_{Fe K\alpha})\rho_M x / \sin \Theta_2] dI_{Fe}$$

Combination of the 3 terms

$$dI_{\text{Fe}K\alpha} = \frac{\Omega_2}{4\pi} \epsilon(E_{\text{Fe}K\alpha}) \exp[-\mu_M(E_{\text{Fe}K\alpha})\rho_M x / \sin \Theta_2] dI_{\text{Fe}}$$

$$dI_{\text{Fe}} = f_{K\alpha} \omega_K \left(1 - \frac{1}{J_K}\right) \tau_{\text{Fe}}(E_0) \rho_{\text{Fe}} \frac{dx}{\sin \Theta_1} I_x$$

$$I_x = I_0(E_0) \exp[-\mu_M(E_0)\rho_M x / \sin \Theta_1]$$

Define  $K_{\text{Fe}} = f_{K\alpha} \omega_K \left(1 - \frac{1}{J_K}\right)$  “fundamental” constants

$$G = \frac{\Omega_2}{4\pi \sin \Theta_1} \quad \text{geometrie factor}$$

$$\chi_M(E_{\text{Fe}K\alpha}, E_0) = \frac{\mu_M(E_{\text{Fe}K\alpha})}{\sin \Theta_2} + \frac{\mu_M(E_0)}{\sin \Theta_1} \quad \text{absorption term}$$

detected intensity of Fe K $\alpha$  from a layer  $dx$  at depth  $x$

$$dI_{\text{Fe}K\alpha} dx = G \epsilon(E_{\text{Fe}K\alpha}) K_{\text{Fe}} \rho_{\text{Fe}} \tau_{\text{Fe}}(E_0) \exp[-\chi_M(E_{\text{Fe}K\alpha}, E_0)\rho_M x] dx I_0$$

Intensity from the entire sample: integration over thickness  $d$

$$I_{\text{Fe}K\alpha} = G\epsilon(E_{\text{Fe}K\alpha})K_{\text{Fe}}\rho_{\text{Fe}}\tau_{\text{Fe}}(E_0)I_0 \int_{x=0}^{x=d} \exp[-\chi_M\rho_M x] dx$$

$$I_{\text{Fe}K\alpha} = G\epsilon(E_{\text{Fe}K\alpha})K_{\text{Fe}}\rho_{\text{Fe}}\tau_{\text{Fe}}(E_0)I_0 \left. \frac{\exp[-\chi_M\rho_M x]}{\chi_M\rho_M} \right|_d^0$$

$$I_{\text{Fe}K\alpha} = G\epsilon(E_{\text{Fe}K\alpha})K_{\text{Fe}}\rho_{\text{Fe}}\tau_{\text{Fe}}(E_0)I_0 \left[ \frac{1 - e^{(-\chi_M\rho_M d)}}{\chi_M\rho_M} \right]$$

but  $\rho_{\text{Fe}}/\rho_M = w_{\text{Fe}}$  weight fraction of Fe in the sample

Relation between intensity of the  $K\alpha$  line and weight fraction of element  $i$  for mono-energetic excitation of a sample of thickness  $d$

$$I_i = G\epsilon(E_i)K_i w_i \tau_i(E_0) \frac{1 - e^{-\chi_M(E_i, E_0)\rho_M d}}{\chi_M(E_i, E_0)} I_0$$

Or if we consider the sample as “infinitely” thick

$$I_i = G\epsilon(E_i)K_i w_i \tau_i(E_0) \frac{1}{\chi_M(E_i, E_0)} I_0$$

# Consequences of this relation

Define the “sensitivity” for element  $i$

$$S_i = \epsilon(E_i) K_i \tau_i(E_0)$$

sensitivity depends on the photo-electric cross section, thus of the excitation energy ( $E_0$ )

The absorption term is

$$\chi = \frac{\mu_M(E_i)}{\sin \theta_2} + \frac{\mu_M(E_0)}{\sin \theta_2}$$

Intensity of element  $i$  having a weight fraction  $w_i$

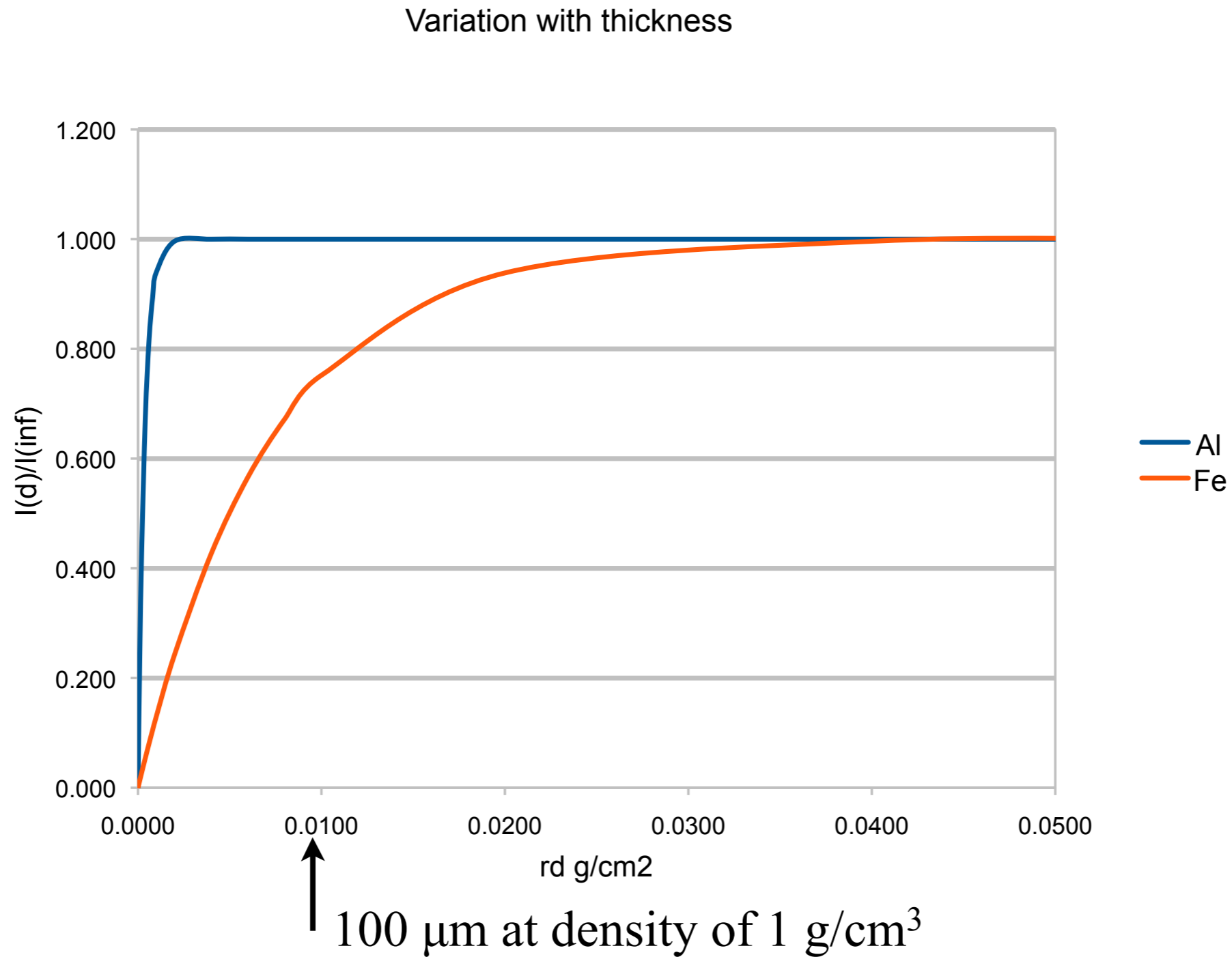
for a “intermediate thick” sample

$$I_i = I_0 G S_i w_i \frac{1 - \exp(-\chi \rho d)}{\chi}$$

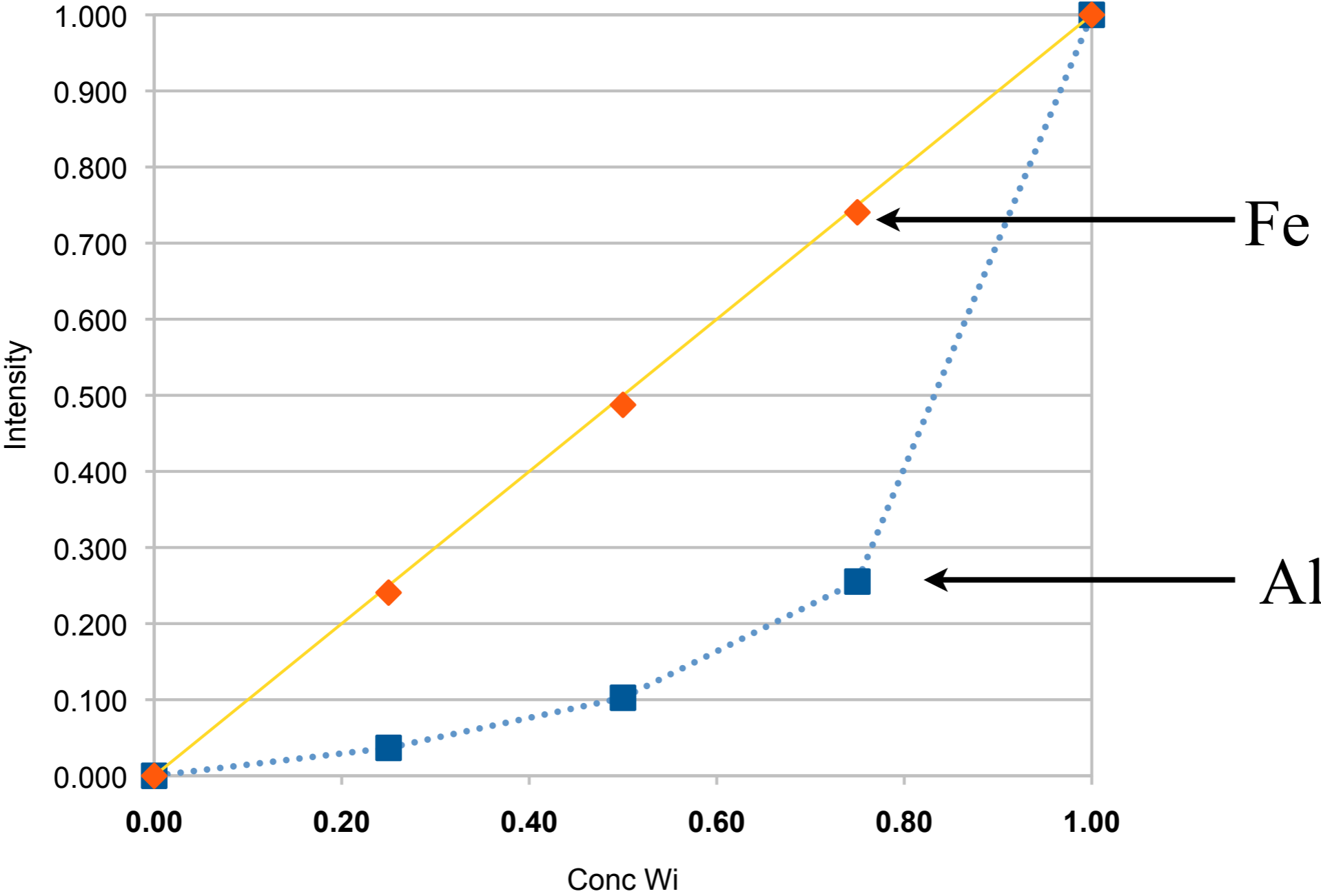
for a “infinity thick” sample

$$I_i = I_0 G S_i w_i \frac{1}{\chi}$$

Depth of analysis is small  
and depends on the element analyzed



The relation between is not necessary linear  
and depends on the element and the matrix  
if the absorption is nearly constant linear calibration lines can be used



# The fundamental parameter method

## Standardless FP method

All elements in the sample give characteristic lines in the spectrum

Set of  $n$  equation with  $n+1$  unknowns  $I_0G$ ,  $w_i$

$$I_{\text{Al}} = I_0G S_{\text{Al}} w_{\text{Al}} \frac{1}{\chi_{\text{Al}}}$$
$$I_{\text{Fe}} = I_0G S_{\text{Fe}} w_{\text{Fe}} \frac{1}{\chi_{\text{Fe}}}$$

With

$$\chi_{\text{Al}} = \frac{w_{\text{Al}} \mu_{\text{Al}}(E_{\text{Al}}) + w_{\text{Fe}} \mu_{\text{Fe}}(E_{\text{Al}})}{\sin \theta_2} + \frac{w_{\text{Al}} \mu_{\text{Al}}(E_0) + w_{\text{Fe}} \mu_{\text{Fe}}(E_0)}{\sin \theta_1}$$
$$\chi_{\text{Fe}} = \frac{w_{\text{Al}} \mu_{\text{Al}}(E_{\text{Fe}}) + w_{\text{Fe}} \mu_{\text{Fe}}(E_{\text{Fe}})}{\sin \theta_2} + \frac{w_{\text{Al}} \mu_{\text{Al}}(E_0) + w_{\text{Fe}} \mu_{\text{Fe}}(E_0)}{\sin \theta_1}$$

Need one more equation  $w_{\text{Al}} + w_{\text{Fe}} = 1$

Can be solved iteratively

**Table 3:** Results obtained on NIST 1108 Naval Brass CRM

Line	Compound	Estim. Conc.	Stdev	Certified value
Mn-Ka	Mn	470ppm	90ppm	0.025%
Ni-Ka	Ni	<219.8 ppm		0.033%
Fe-Ka	Fe	670ppm	70ppm	0.05%
Cu-Ka	Cu	66.9%	0.1%	64.95%
Zn-Ka	Zn	32.92%	0.07%	34.43%

**Table 4:** Results obtained on NIST 1156 Steel CRM

Line	Compound	Estim. Conc.	Stdev	Certified value
Mo-Ka	Mo	2.86%	0.01%	3.1%
Cu-Ka	Cu	0.11%	0.02%	0.025%
Fe-Ka	Fe	70.7%	0.2%	69.7%
Ni-Ka	Ni	17.8%	0.1%	19.0%
Cr-Ka	Cr	0.22%	0.02%	0.2%
Mn-Ka	Mn	0.27%	0.03%	0.21%
Co-Ka	Co	7.82%	0.07%	7.3%
Ti-Ka	Ti	0.25%	0.05%	0.21%



## Standard FP method

use at least one standard to determine  $I_0G$

No normalisation  $\sum w_i=1$ , check for correctness possible

## Problem with FP method

concentration of **ALL** elements must be estimated to do the absorption correction  $\chi$

- Metals
  - often ok for metals
- Geological material (stone, sediments, pottery...)
  - contains oxygen
  - from stoichiometry  $Al_2O_3$ ,  $CaO$ ,  $Fe_2O_3$  ( $FeO$ ?)
- Organic material
  - Missing C, O, N

# Calibration curves

If the matrix remains more or less constant then the absorption term  $\chi$  remains also constant

$$I_i = I_0 G S_i w_i \frac{1}{\chi}$$

or

$$I_i = b_1 \times w_i$$

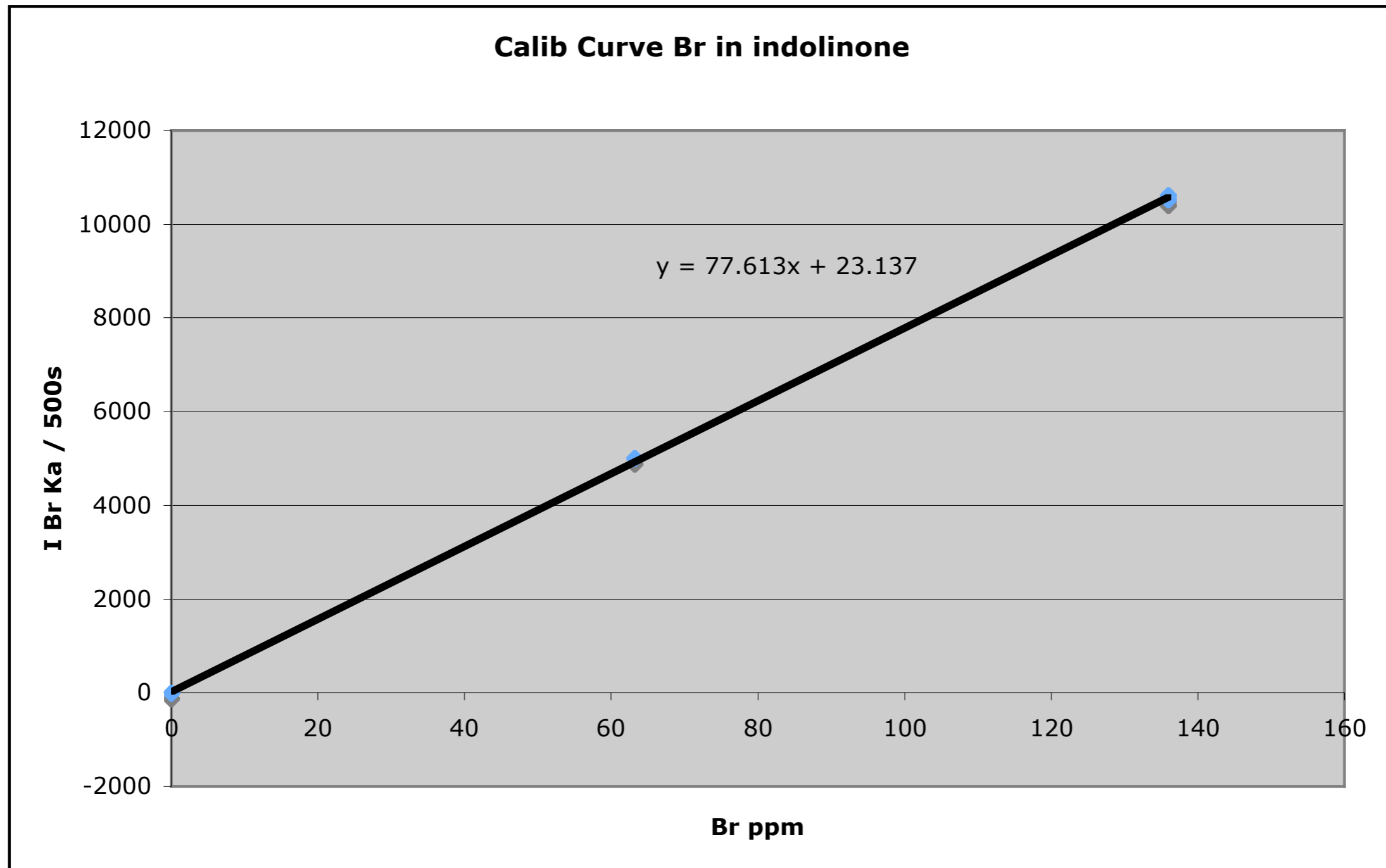
or better

$$I_i = b_0 + b_1 \times w_i$$

Straight line equation  $y = b_0 + b_1 \times x$

Works for e.g. organic material  
Concentration range is always limited

Standards and unknown must be measured under the same conditions  
and intensities corrected for measuring time and tube current



# Calibration using the incoherent scattered radiation

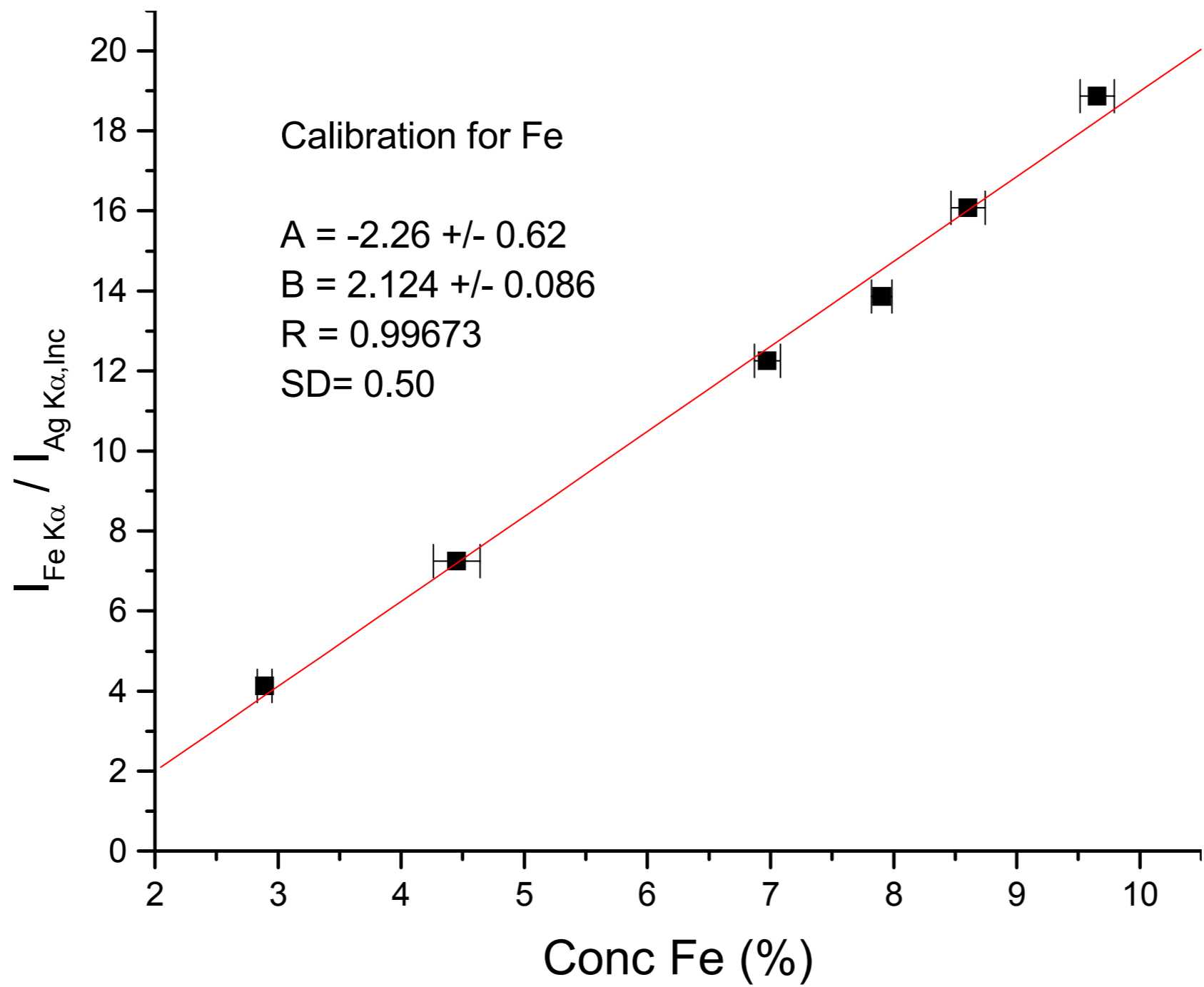
As the matrix changes also the amount of Compton scattering changes.  
Normalising with the intensity of the Compton peak helps

$$\frac{I_i}{I_{Inc}} = b_0 + b_1 w_i$$

Useful for quantitative analysis of geological material

# Composition of geological standards used for calibration

Z	Elem	Units	BCR-2	BIR-1	BHVO-2	DNC-1	NIST 2711	BCR 145	Soil 5
8	O	%	45.0	43.9	44.7	44.00	51.5		
11	Na	%	2.34	1.35	1.65	1.40	1.14		1.92
12	Mg	%	2.17	5.85	4.36	6.11	1.05		1.5
13	Al	%	7.1	8.20	7.14	9.70	6.53		8.19
14	Si	%	25.3	22.42	23.33	22.04	30.44		33
15	P	%	0.153	0.0092	0.118	0.03	0.086		0.11
16	S	%					0.306		
19	K	%	1.49	0.025	0.432	0.194	2.45		1.86
20	Ca	%	5.09	9.51	8.15	8.21	2.88		2.2
21	Sc	ppm	33	44	32	31	9		14.8
22	Ti	%	1.35	0.576	1.64	0.288	0.306		0.47
23	V	ppm	416	310	317	148.00	81.6		151
24	Cr	ppm	18	370	280	270.00	47	313	28.9
25	Mn	ppm	1520	1355	1290	1162	638	156	852
26	Fe	%	9.7	7.90	8.60	6.97	2.89		4.45
27	Co	ppm	37	52	45	57	10	5.61	14.8
28	Ni	ppm		170	119	247	20.6	247	3
29	Cu	ppm	19	125	127	100.0	114	696	77.1
30	Zn	ppm	127	70	103	70.0	350.4	2122	368
31	Ga	ppm	23	16	21.7	15	15		18.4
33	As	ppm		0.44		0.12	105		93.9
37	Rb	ppm	48		9.8	4.50	110		138
38	Sr	ppm	346	110	389	144.0	245.3		330
39	Y	ppm	37	16	26	18.0	25		21
40	Zr	ppm	188	18	172	38	230		221
42	Mo	ppm	248				1.6		1.7
48	Cd	ppm						3.5	
56	Ba	ppm	683	7	130	118	726		562
80	Hg	ppm					6.25	2.01	0.79
82	Pb	ppm	11	3			1162	286	129
90	Th	ppm			1.2		14		11.3
92	U	ppm					2.6		3.15



# Thin films

Basic equation: 
$$I_i = I_0 G S_i w_i \frac{1 - \exp(-\chi \rho d)}{\chi}$$

$\chi \rho d \leq 1$  approximation (Taylor expansion)  $\exp(-\chi \rho d) = 1 - \chi \rho d$

$$\Rightarrow I_i = I_0 G S_i w_i \frac{\chi \rho d}{\chi} = I_0 G S_i w_i \rho d$$

What is  $w_i \rho d$  ?

Dimension is  $\text{g/cm}^2$   
areal concentration

OK

If we know the area

If we analyse the same area for standards and unknowns

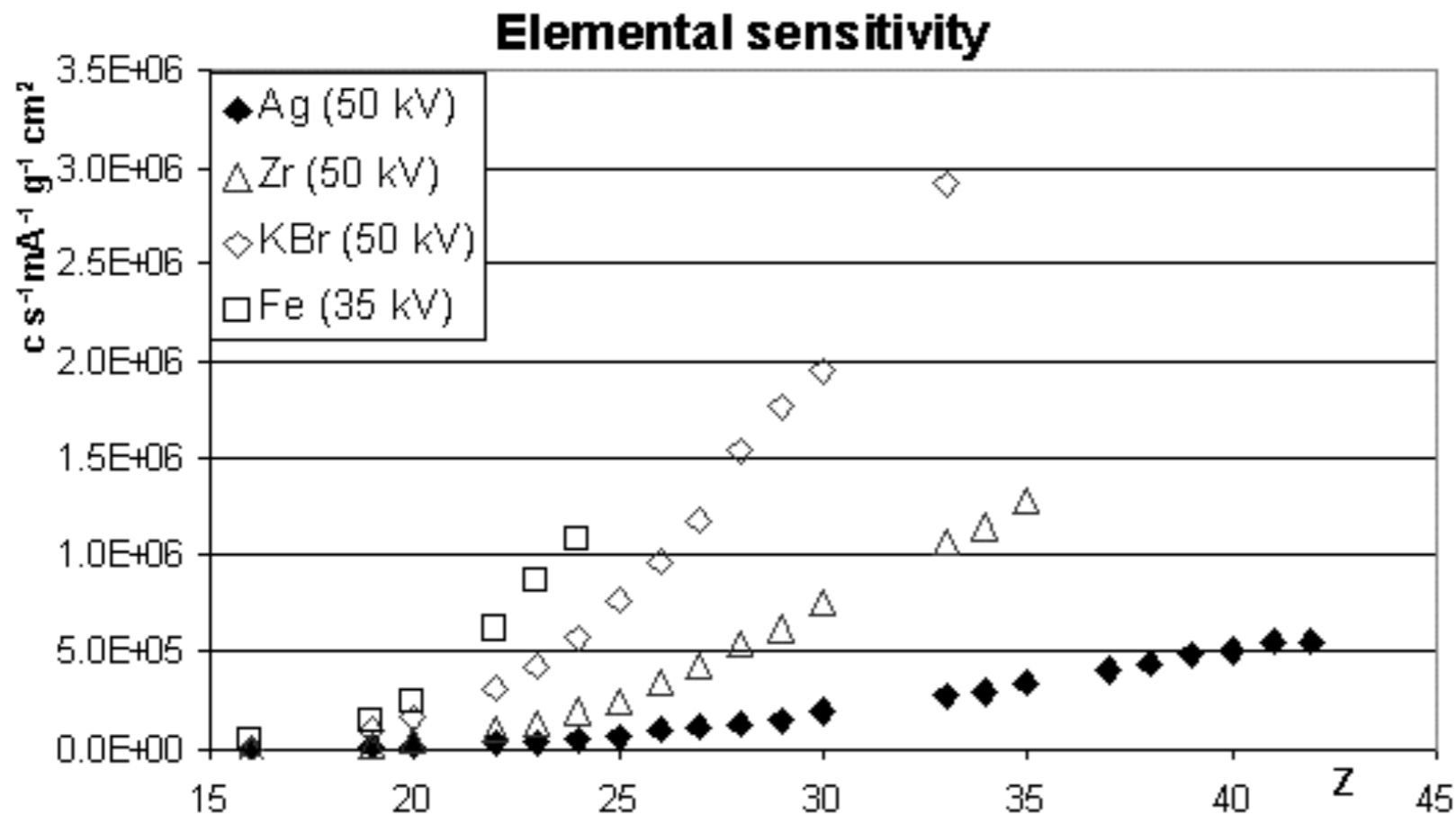
How do we determine the “sensitivity”  $S_i$  for each element  $i$  ?

$$I_i = I_0 G S_i w_i \rho d$$

Analysing thin film standards with known “areal concentration”

e.g. MicroMatter standards

Fe 45.6 ng/cm<sup>2</sup>



Elemental sensitivity  $S_i$  varies smoothly with  $Z$  for a given excitation (allows to interpolate, e.g. fitting a polynomial)



# Dealing with detection limits

To decide after the analysis if a compound is really (95%) present

$$L_C = 3\sqrt{N_B}$$

After spectrum evaluation:

For each element of interest we obtain the net peak data ( $R$ ) and a reliable estimate of the uncertainty ( $s$ )

$$R \pm s$$

IF:

$R > 3 \times s$  report concentration based on  $R$  and uncertainty  
(based on  $s$ )

$-3 \times s \leq R \leq 3 \times s$  report detection limit based on  $R = 3xs$

$R \leq -3 \times s$  revise your data processing!!!

# Detection limits in XRF: practical

And what about blanks???

$$L_C = k_C \sigma_{bl}$$

Instrumental blanks:

- spurious peaks from fluorescence of excitation chamber
- lines from x-ray tube
- ...

Sample blanks:

- elements present in sample support (filters for the analysis of aerosol particles)
- elements introduced during sample preparation (fused sample)
- ...

Need to establish very accurately (n=30):

- the value of this blank contribution  $\mu_{bl}$   
(to subtract from the measured count rate or concentration)
- and the standard deviation  $\sigma_{bl}$   
(to add to the expression of the detection limit)

$$L_C = k_C \sqrt{\sigma_{Blank}^2 + \sigma_{Background}^2}$$

## Detection limits in XRF: example

Analysis of aerosol material collected on a membrane filter

Measurement time 1000s

	V	Fe	Br
Sensitivity Cnts.s	1.31	2.98	8.76
Net peak area Cnts/1000s	110 ± 60	7440 ± 136	198 ± 37
Instrument blank Cnts/1000s	-	200 ± 20	-
Sample blank Cnts/1000s	-	-	73 ± 60

	V	Fe	Br
Sensitivity Cnts.s	1.31	2.98	8.76
Net peak area Cnts/1000s	110 ± 60	7440 ± 136	198 ± 37
Instrument blank Cnts/1000s	-	200 ± 20	-
Sample blank Cnts/1000s	-	-	73 ± 60

Vanadium: 110 cnts < 3\*60 => peak not significant

$$DL = 180/1.31/1000 = 0.1374$$

$$V < 0.1 \mu\text{g}$$

Iron: 7440 >> 3\*136 => peak significant

7440 >> 3\*(136<sup>2</sup> + 20<sup>2</sup>) => signal is from aerosol

$$Fe = (7440-200)/2.98/1000 = 2.4295 \mu\text{g}$$

$$s = \sqrt{(136^2 + 20^2)}/2.98/1000 = 0.0461 \mu\text{g}$$

$$Fe = 2.430 \pm 0.046 \mu\text{g}$$

Bromine: 198 cnts > 3\*37 => peak significant

198 cnts < 3\*\sqrt{(37<sup>2</sup> + 60<sup>2</sup>)} = 211 => maybe signal from filter

$$DL = 211/8.76/1000 = 0.0241 \mu\text{g}$$

$$Br < 0.02 \mu\text{g}$$

# Some final remarks

Be careful!!!!

We use often intensity ratio's rather than concentrations

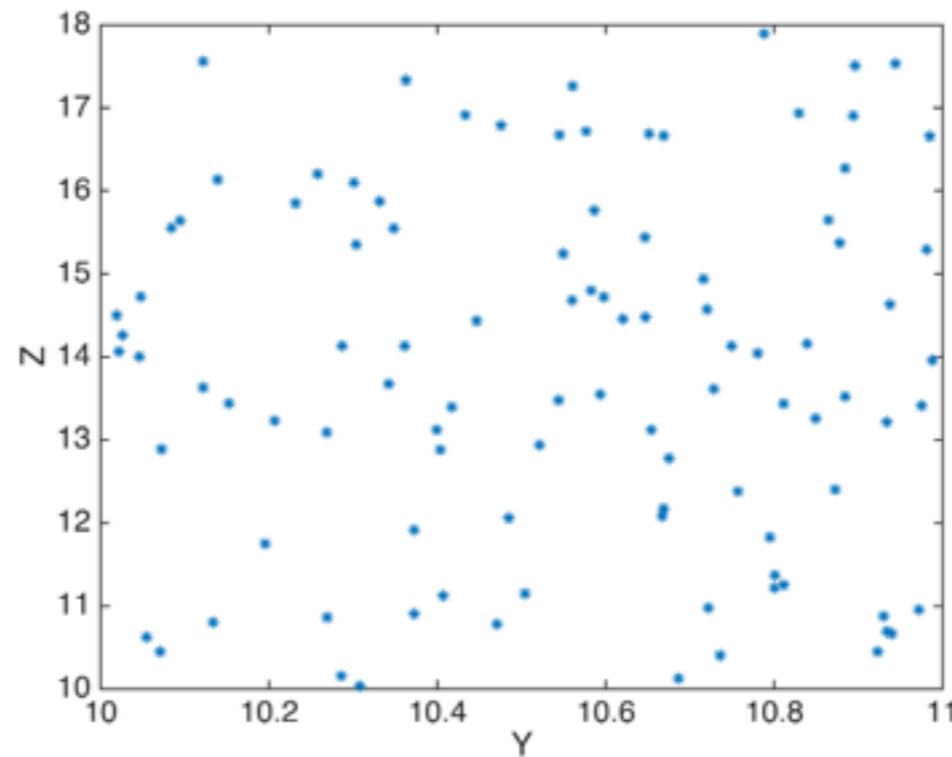
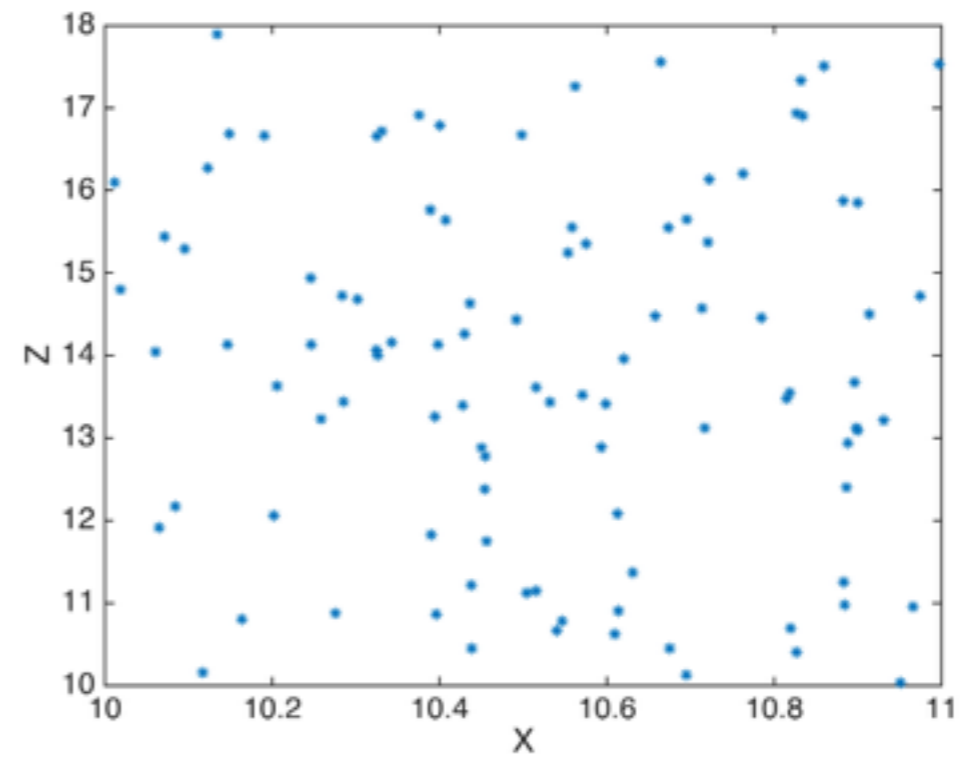
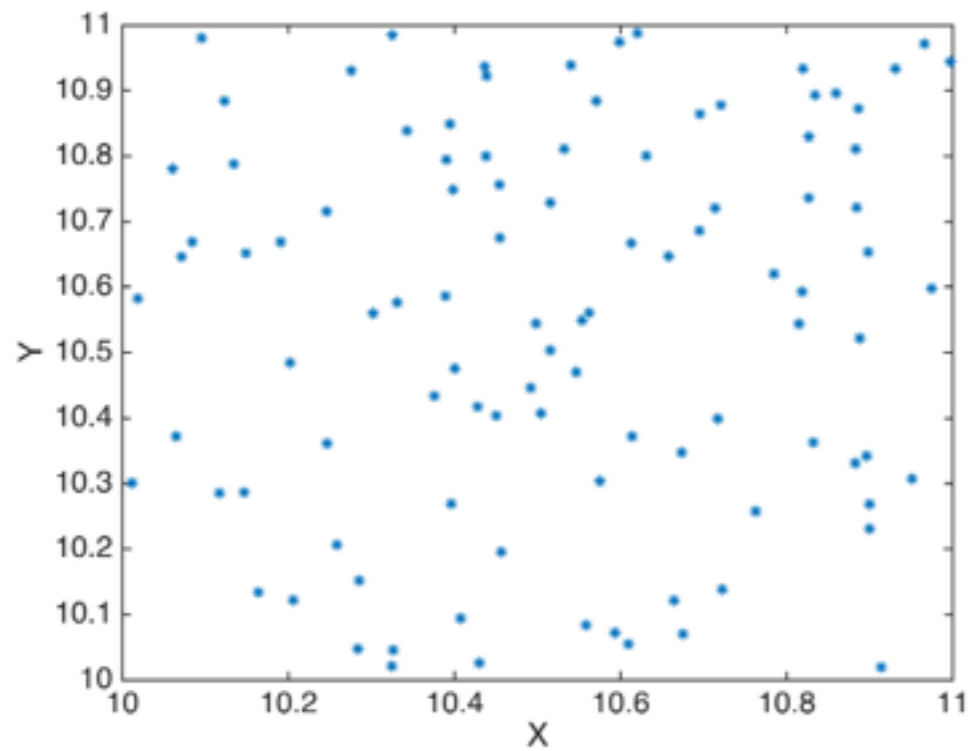
We often normalise intensities to 100 %

Also for “real” concentrations we have  $\sum \text{Element Conc.} = 100 \%$

Beware of the consequences!!!

Three random variables  $X$ ,  $Y$  and  $Z$

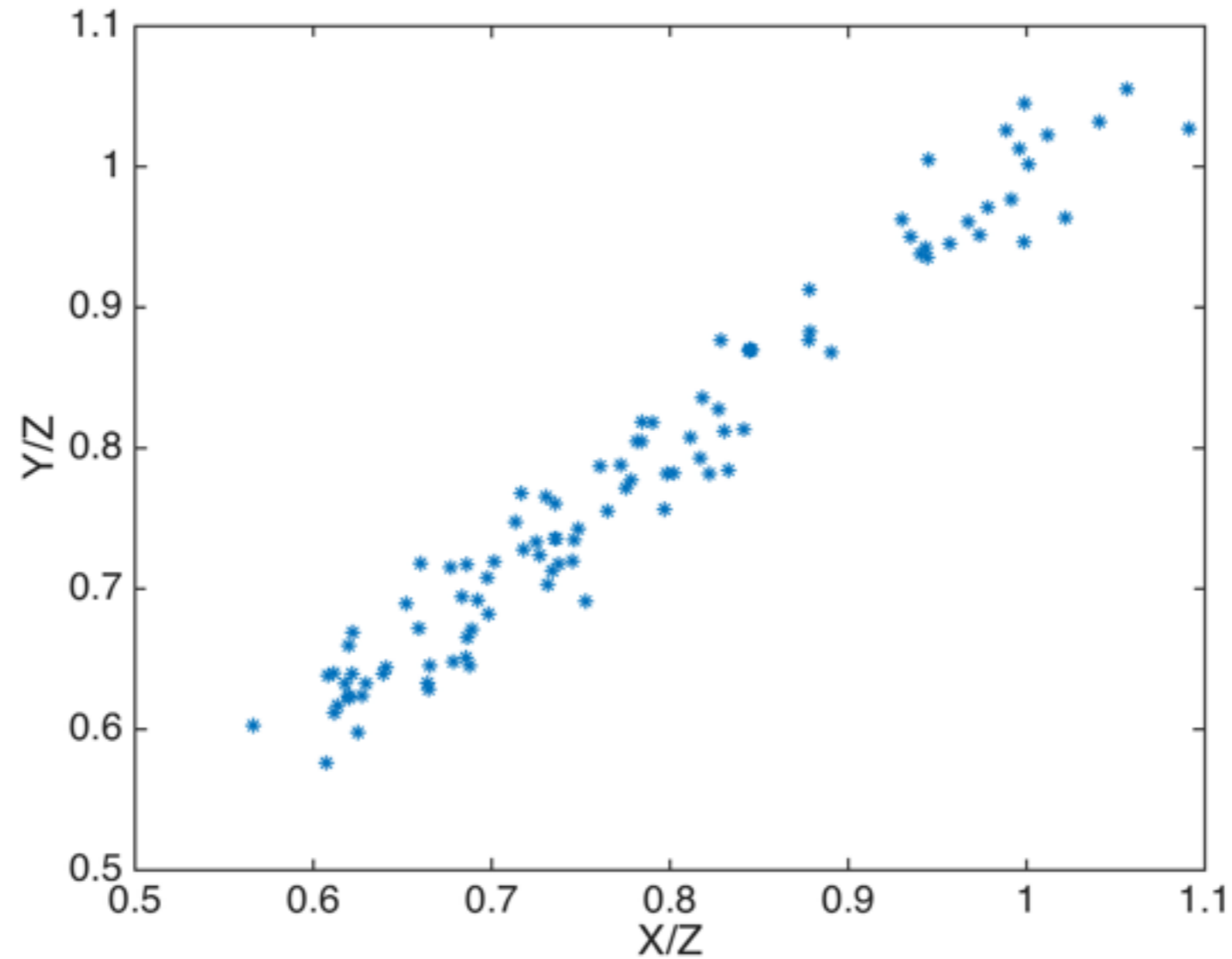
(let's say x-ray intensities of three elements)



They have nothing to do with each other.  
They are uncorrelated

Normalise with  $Z$

i.e. study the ratio's  $X/Z$  en  $Y/Z$



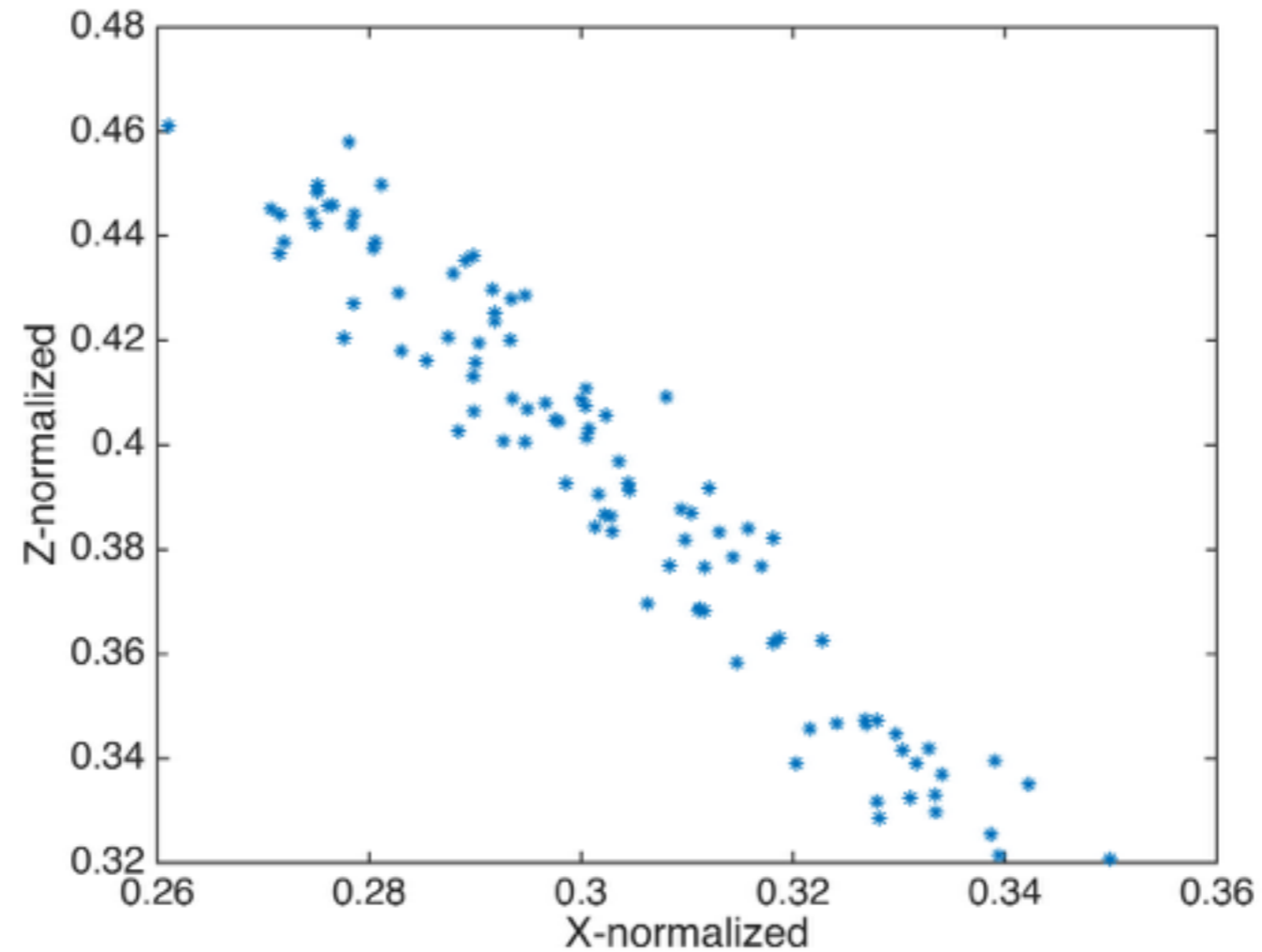
What do you get?

Nonsense!!!

spurious correlation

Or, normalise to the sum  $S = X + Y + Z$

i.e. study the ratio's  $X/S$ ,  $Y/S$  en  $Z/S$



What do you get?

Nonsense!!!

Closure



Once again

Thanks for your attention