Echantillons Stratifiés : Méthode et Limites

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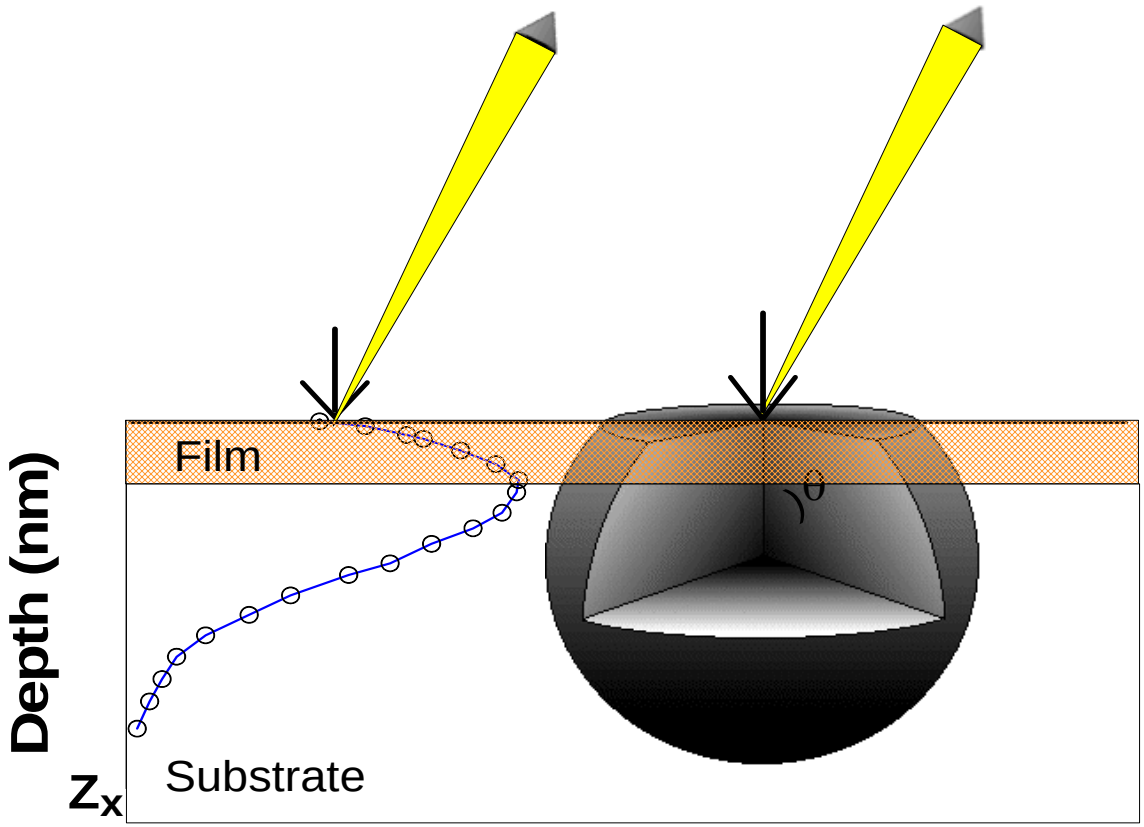
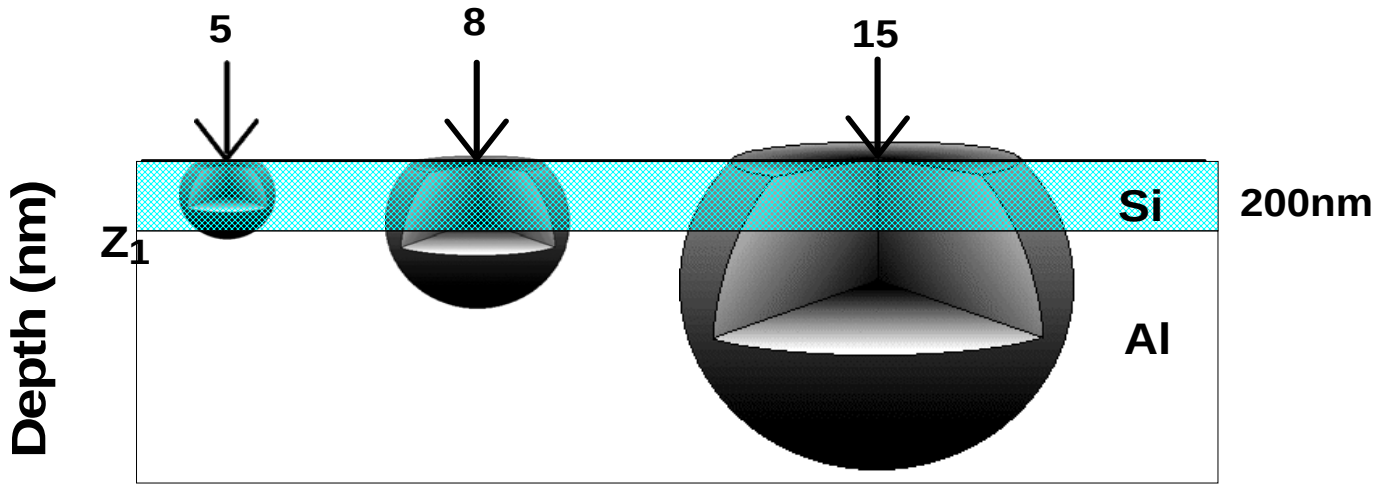
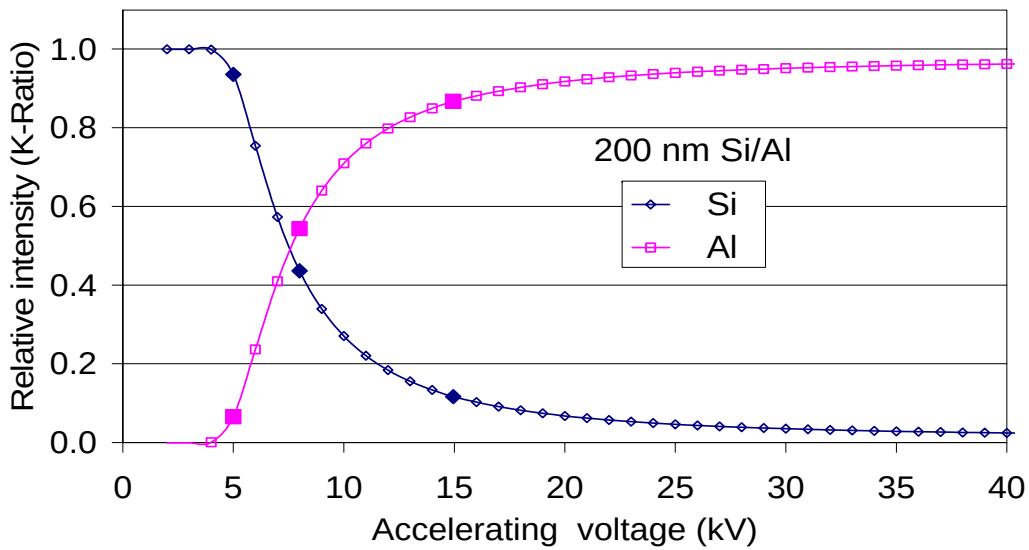
Université Montpellier II

Thin Film Quantification: Principle

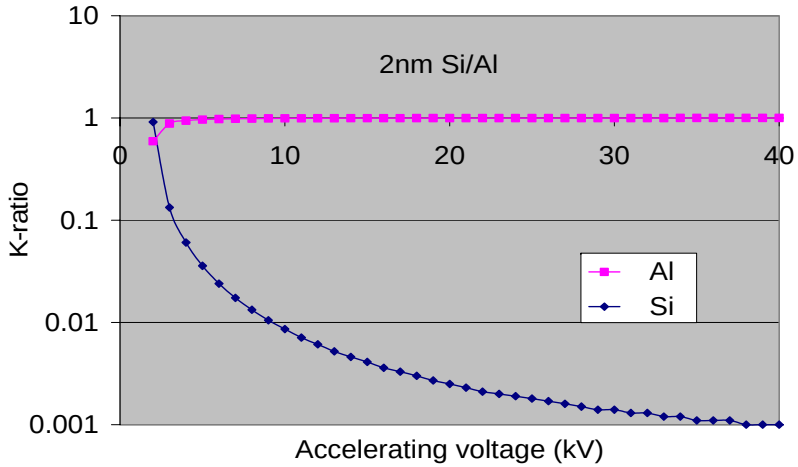


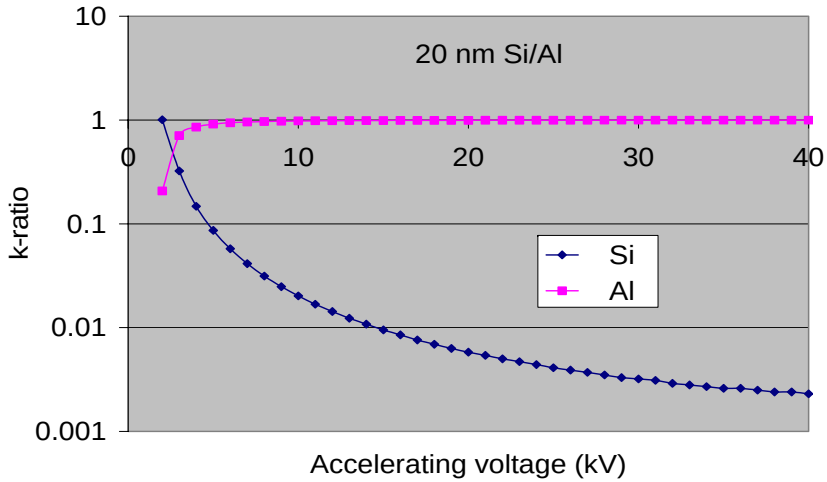
Thin Film Quantification: Principle

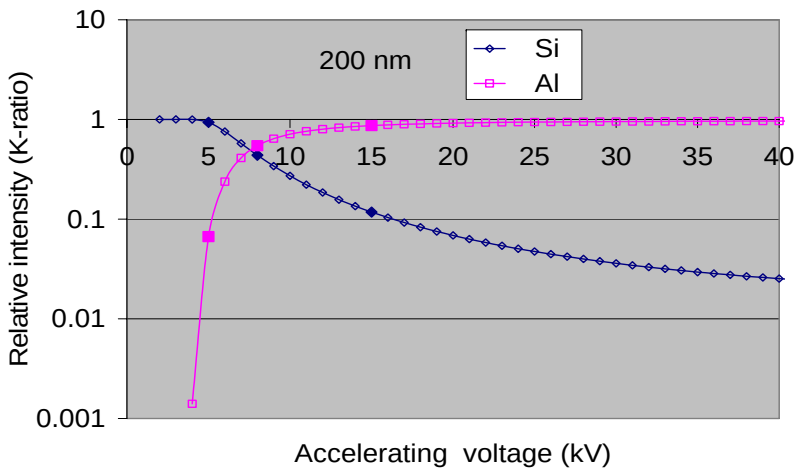


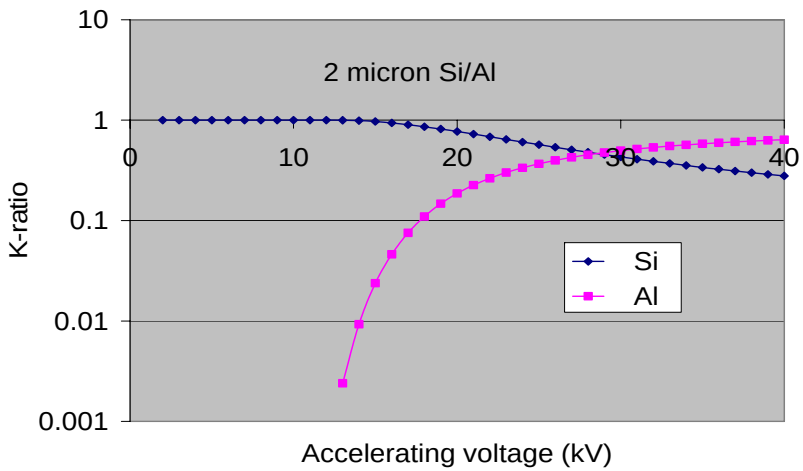


Thin Film Quantification: Range

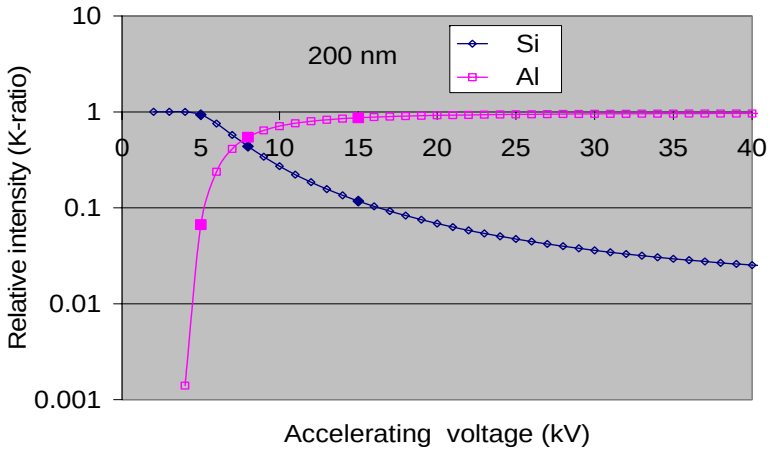


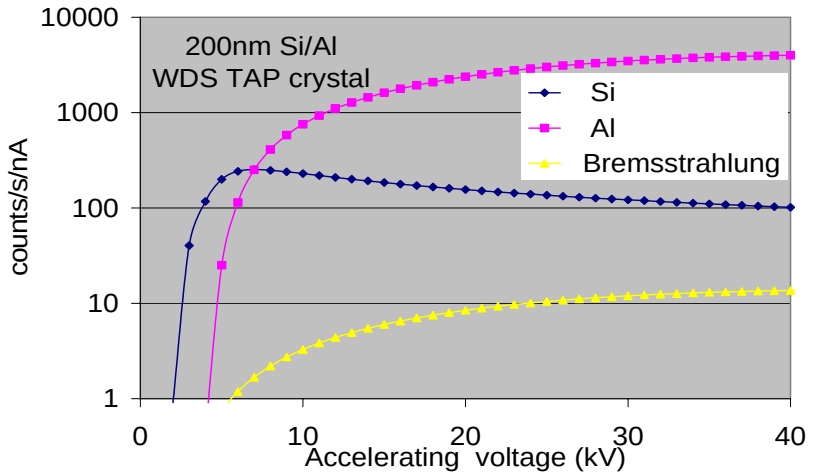


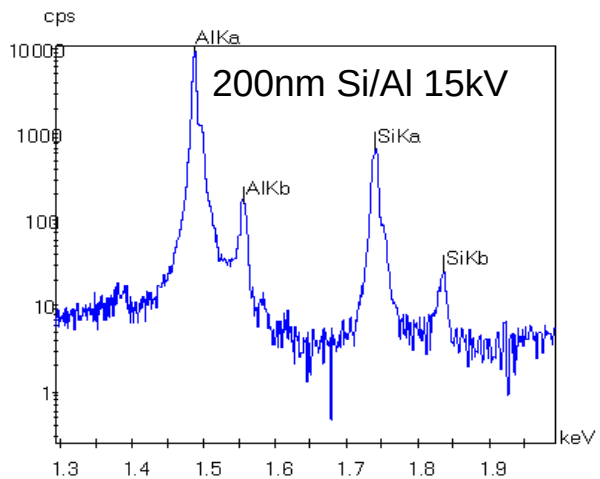


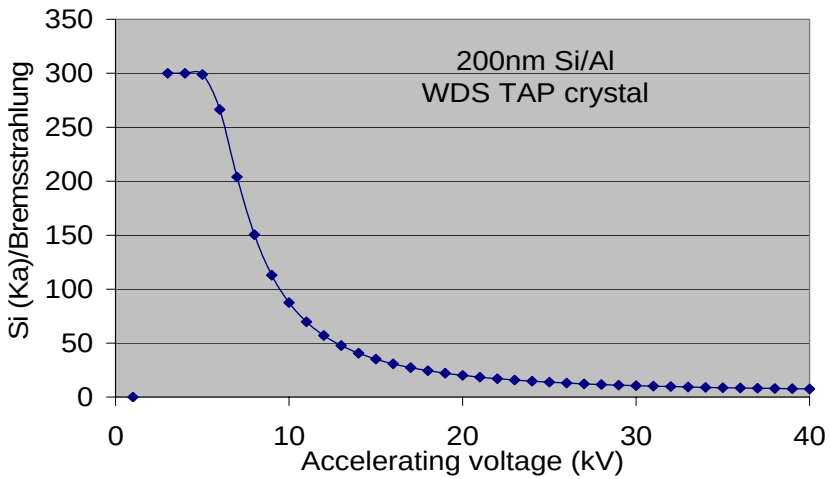


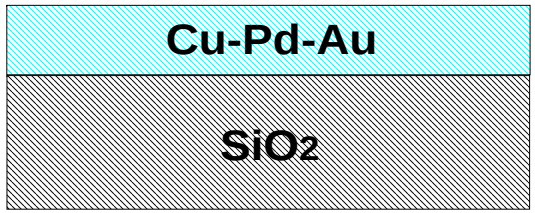
Thin Film Quantification: Experimental Conditions











Comparison of composition (in weight) and film thicknesses (in mg/cm²) relative to Cu-Pd-Au films on SiO_2 obtained by Rutherford backscattering spectroscopy (RBS), Monte Carlo simulation, X-film procedure (1995), and PAP procedure (1990). The experimental measurements, RBS, and Monte Carlo are from Murata et al. (1984). The X-ray takeoff angle is 52.5° , and the accelerating voltage 20keV.

		Murata										
Sample		Measured		RBS		Monte Carlo		X-Film			PAP	
	Element	K-ratio		Comp	mg/cm²	Comp	mg/cm²	Comp	mg/cm²		Comp	mg/cm²
	Cu	0.1910	Kα	0.319		0.302		0.317			0.317	
A	Pd	0.1570	Lα	0.347	0.282	0.354	0.275	0.349	0.274	3%	0.350	0.278
	Au	0.1570	Mα	0.334		0.344		0.334			0.333	
	Cu	0.3010	Kα	0.607		0.590		0.604			0.605	
B	Pd	0.0766	Lα	0.198	0.235	0.209	0.230	0.203	0.233	3%	0.204	0.229
	Au	0.0718	Mα	0.195		0.201		0.193			0.193	
	Cu	0.1140	Kα	0.212		0.201		0.210				
C	Pd	0.2430	Lα	0.576	0.229	0.583	0.251	0.579	0.246	8%		
	Au	0.0900	Mα	0.212		0.216		0.211				

Accuracy of Thin Film Quantification by EPMA

The Accuracy of Analysis Depends of:

- Quantification Procedure
- Sample Characteristic
- Instrument
- Experimental Parameters
- Measurement Quality

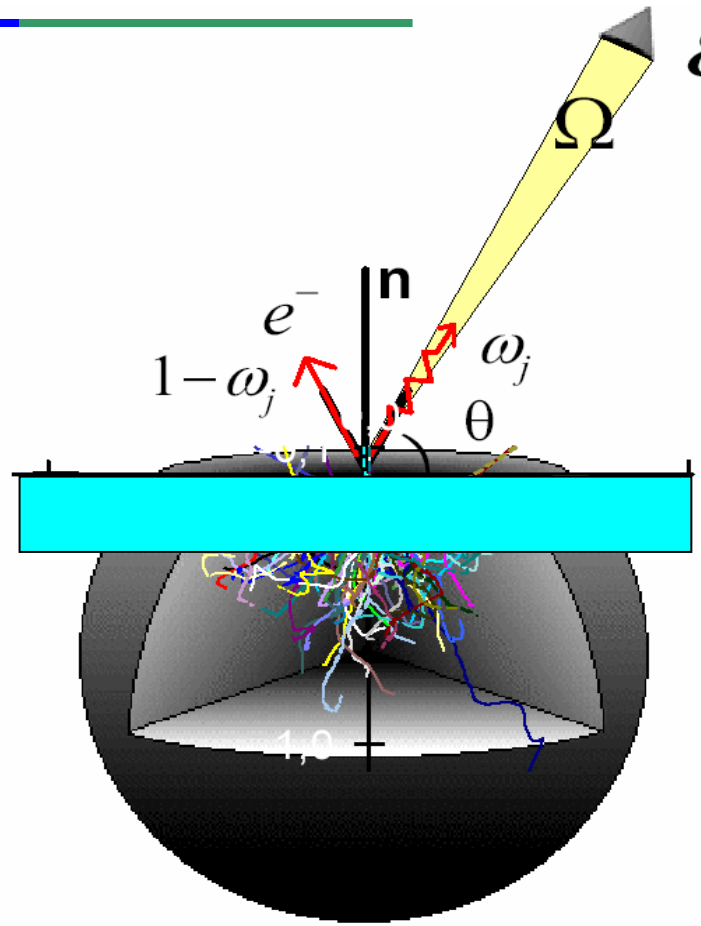
Thin Film Quantification by EPMA is not Only a Problem of Quantification Procedure, but Depends of All these Factors

Quantification ➔Intensity Calculation

$$I_{mes-f} = C_{Af}.\frac{N_o}{A}.n.\frac{\Omega}{4\pi}\varepsilon.\frac{1}{\cos\alpha}.\omega_j P_{nl}.(1+T_{CK}).Q_l^A(E_o).\int_0^{\rho z f}\phi(\rho z).\exp(\chi\rho z).d\rho z\left[1+\left(\sum f_c + f_{FC}\right)_f + \left(\sum f_c + f_{FC}\right)_S\right]$$

$$\phi(\rho z) = f\left(E_o, E_j, \alpha, \rho z_f, \sum C_{if}, \sum C_{is}, \rho z\right)$$

$$\chi = \mu/\rho \cos ec(\theta)$$

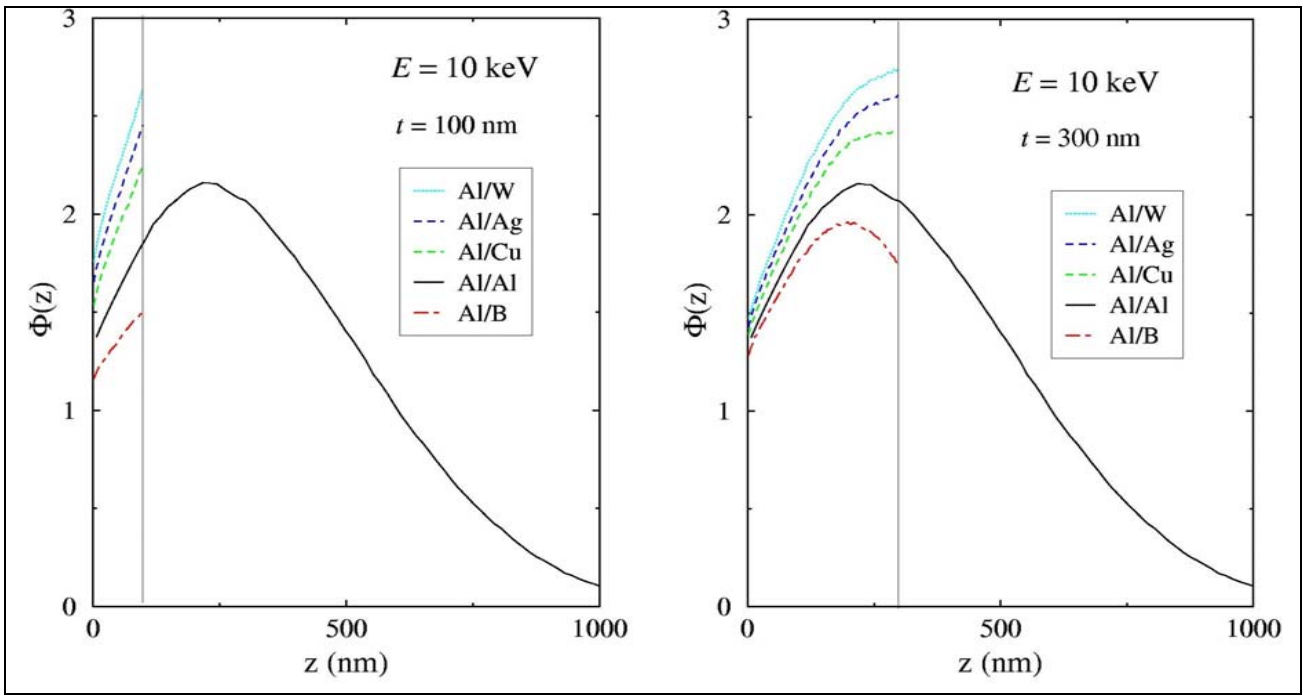


$$P_{nl} = \frac{K_\alpha}{K_\alpha + K_\beta}$$

Intensity Calculation

Monte Carlo Simulation.

- Very efficient and flexible, but the accuracy depends of the quality of the code and the cross sections used.
- Very time consuming ➔ in practice analytical models are used because the quantification requires an iterative procedure.

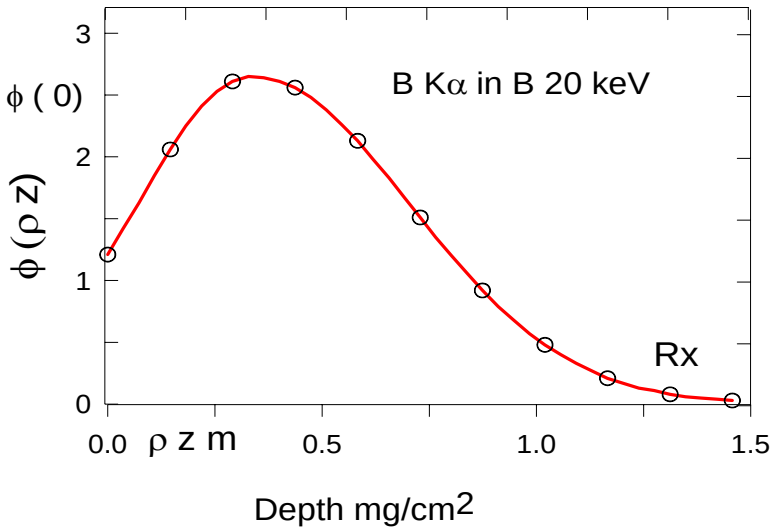


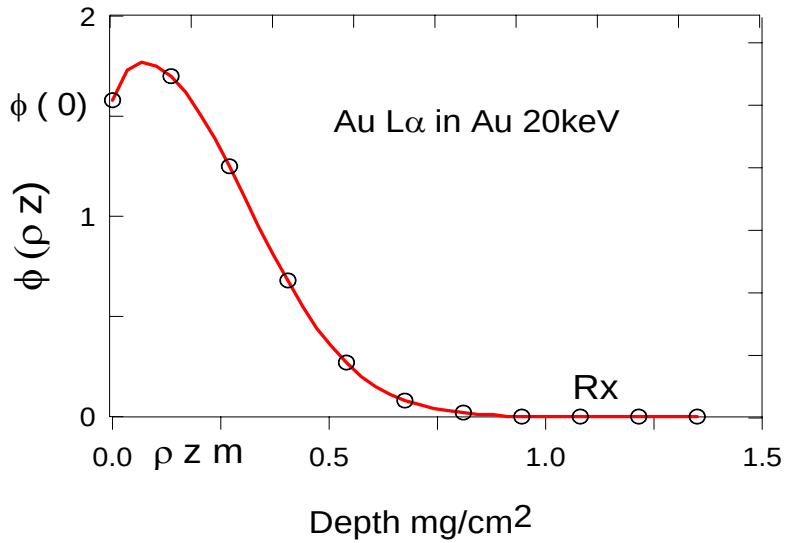
PENELOPE; Llovet et al. *mikrochim. Acta 13 (1995)*

Intensity Calculation

Analytical $\phi(\rho z)$ models

Bulk Sample $\phi(\rho z) = f\left(E_o, E_j, \alpha, \sum C_i, \rho z\right)$





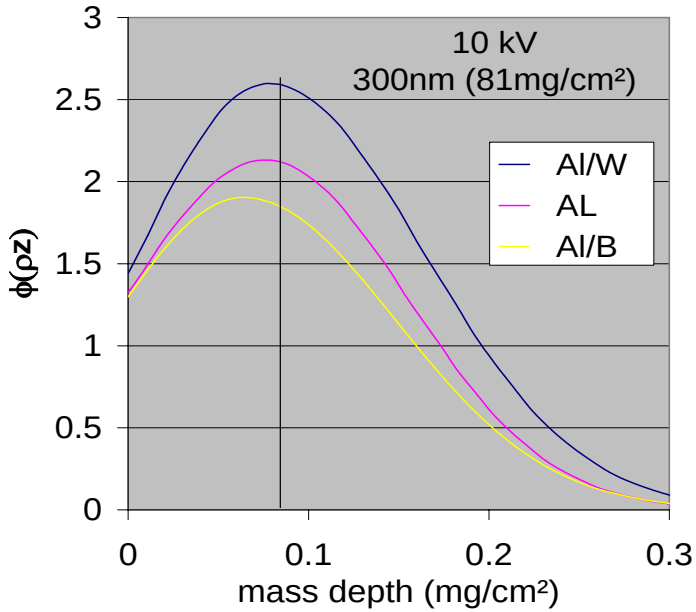
$$\phi(\rho z) = f\left(\rho z, \phi(0), \rho z_m, R_X, \ldots\right)$$

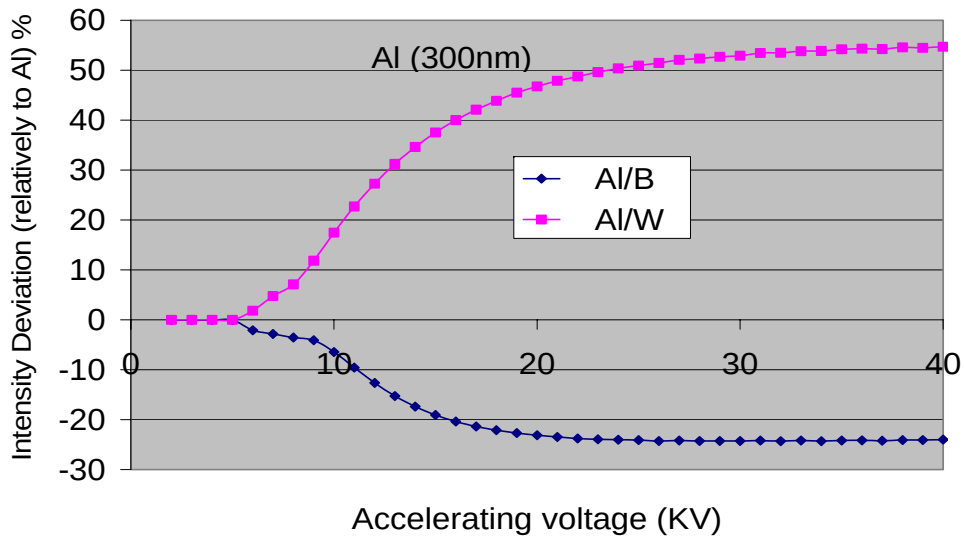
$$\left|\begin{array}{l} \phi(0) = f\left(\rho z, E_o, E_j, \alpha, \sum C_i\right) \\ \rho z_m = f\left(\rho z, E_o, E_j, \alpha, \sum C_i\right) \\ R_X = f\left(\rho z, E_o, E_j, \alpha, \sum C_i\right) \end{array}\right.$$

Intensity Calculation

Analytical $\phi(\rho z)$ models

Thin film $\phi(\rho z) = f\left(E_o, E_j, \alpha, \rho z_f, \sum C_{if}, \sum C_{is}, \rho z\right)$

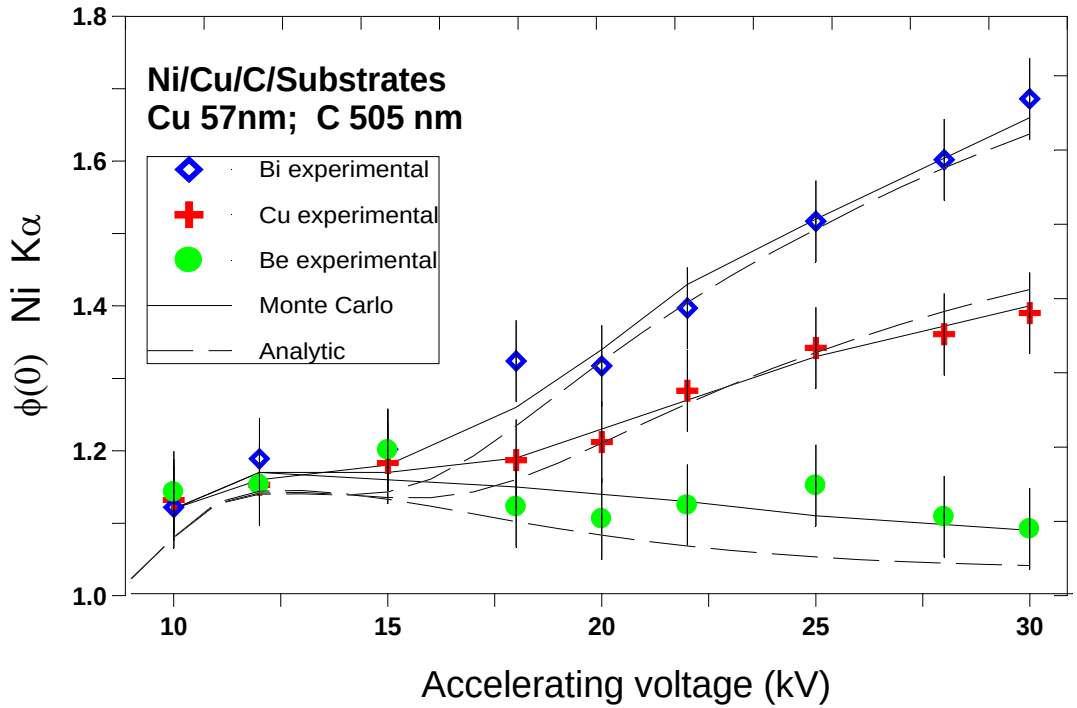


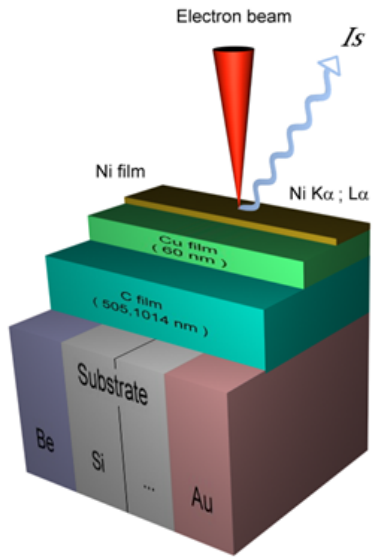


$$\phi(\rho z) = f\left(\rho z, \phi(0), \rho z_m, R_X, \ldots\right)$$

$$\begin{aligned}
\phi(0) &= f\left(E_o, E_j, \alpha, \rho z_f, \sum C_{if}, \sum C_{is}, \rho z\right) \\
\rho z_m &= f\left(E_o, E_j, \alpha, \rho z_f, \sum C_{if}, \sum C_{is}, \rho z\right) \\
R_X &= f\left(E_o, E_j, \alpha, \rho z_f, \sum C_{if}, \sum C_{is}, \rho z\right)
\end{aligned}$$

Example: $\phi(0)$ Thin Film Calculation

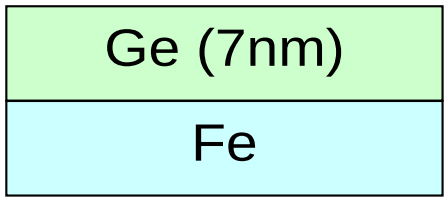




$$\Phi_{F_N/S}(0) \equiv \Phi_{(F_N+S)}(0)$$
$$= [\Phi_{F_N}(0) - \Phi_S(0)] \tanh(As + Bs^2)$$
$$+ \Phi_S(0)$$

Merlet et al. *X-Ray Spectrom,* **33** (2004)

Test: Thickness Accuracy



- Extremely simple case ➔ to check some basis parameters of thin film quantification.
- Pure element film ➔ to check the thickness deviation with the accelerating voltage.
- Accurate measurements.

Advantages:

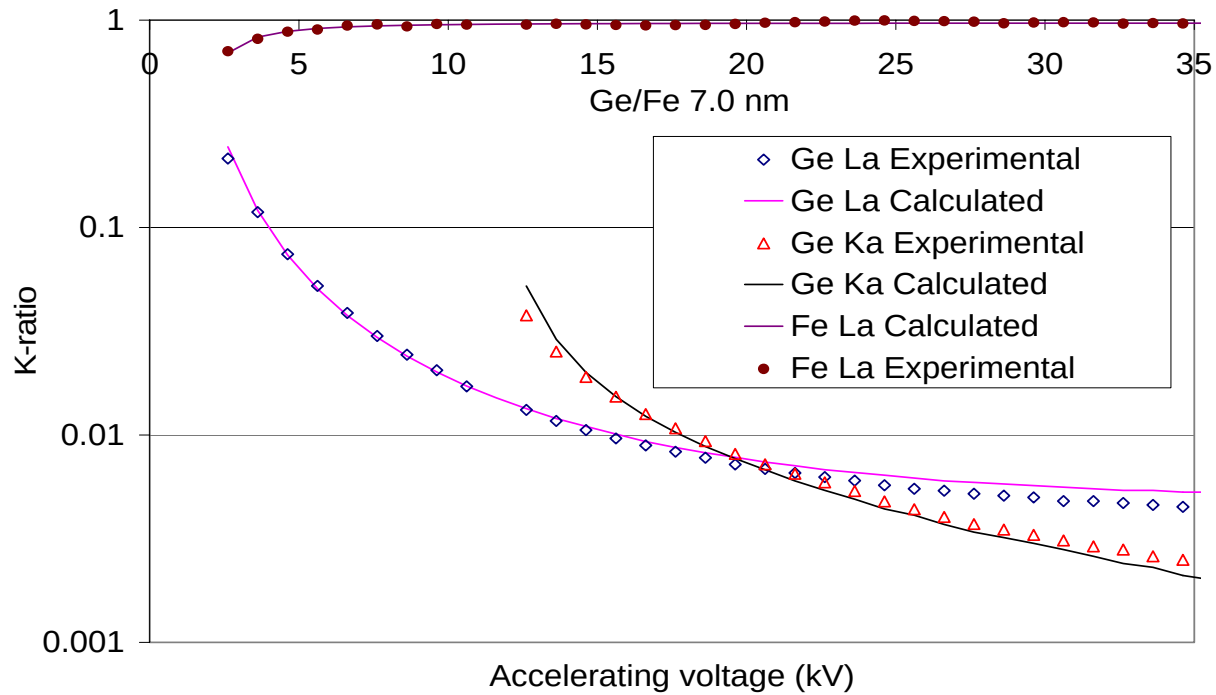
- Kα and Lα lines ➔ 2 databases to validate the method.
- Atomic number of Ge and Fe close➔ substrate effect reduced.
- Low thickness ➔ to scan a large range of the x-ray depth distribution model.
- No characteristic fluorescence by x-ray lines of the substrates.
- No interferences from the substrate

Inconvenient:

- Low intensity of the film.

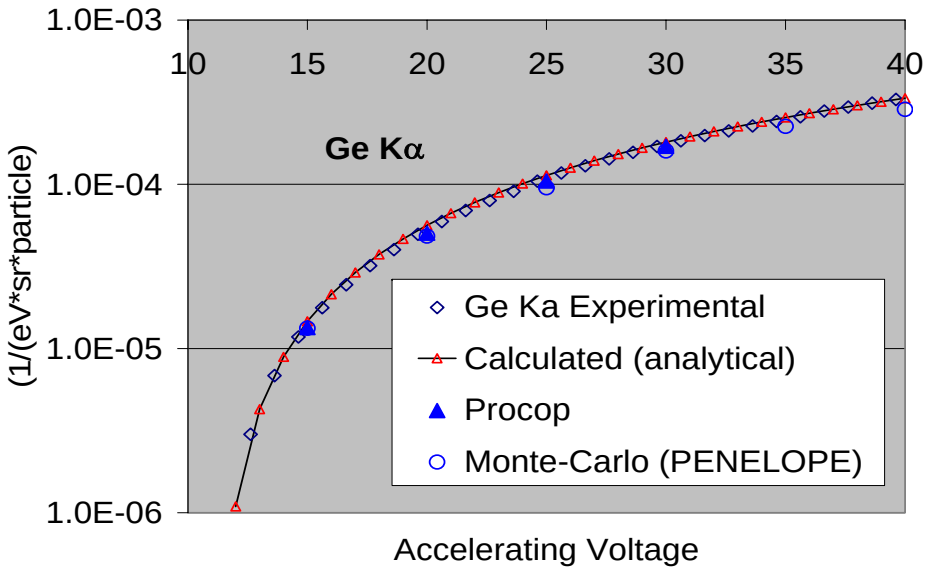
Results

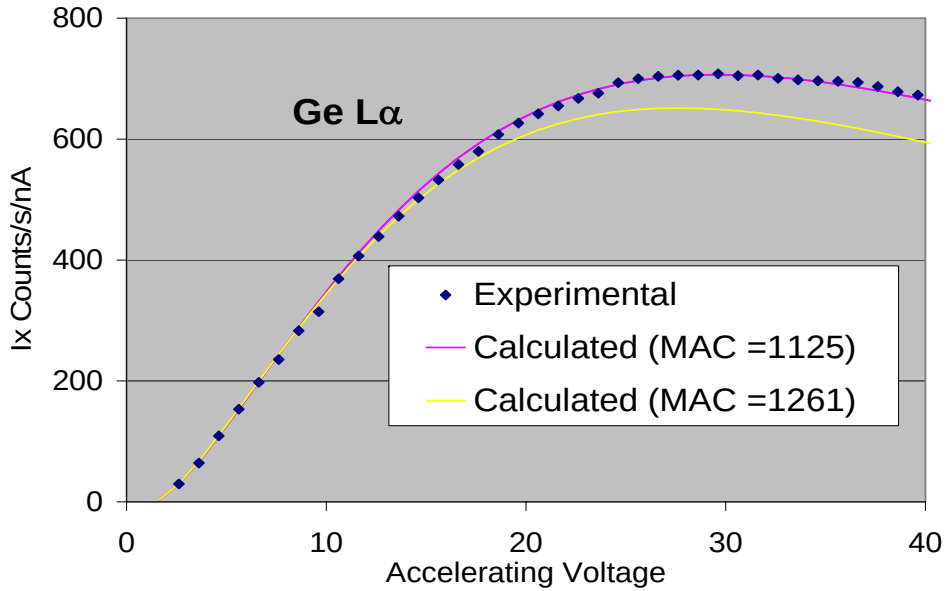
Ge/Fe 7.0nm



- The agreement of the thickness between the Lα and the Kα x-ray lines ~ 4%.

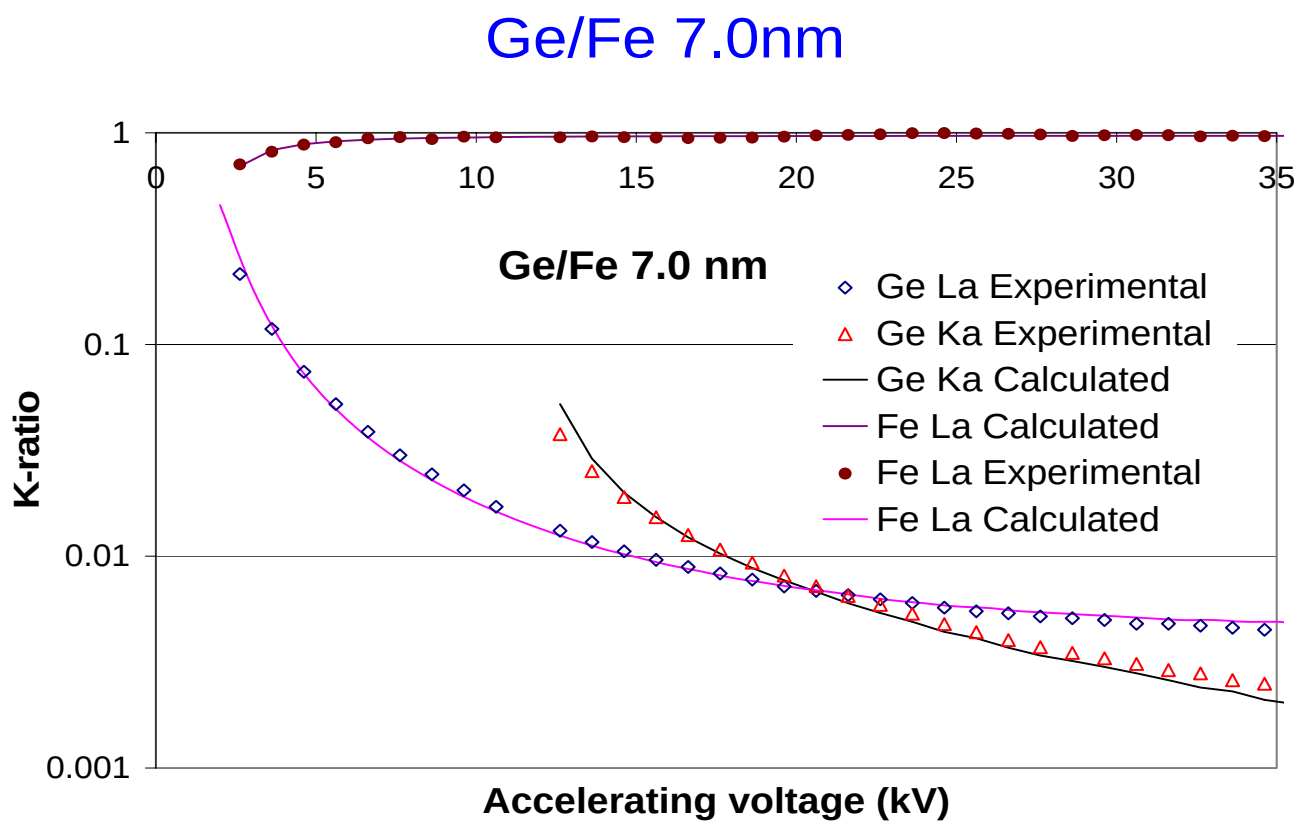
Intensity of Bulk Standard





- Uncertainty of Mass absorption coefficient used in analytical code.

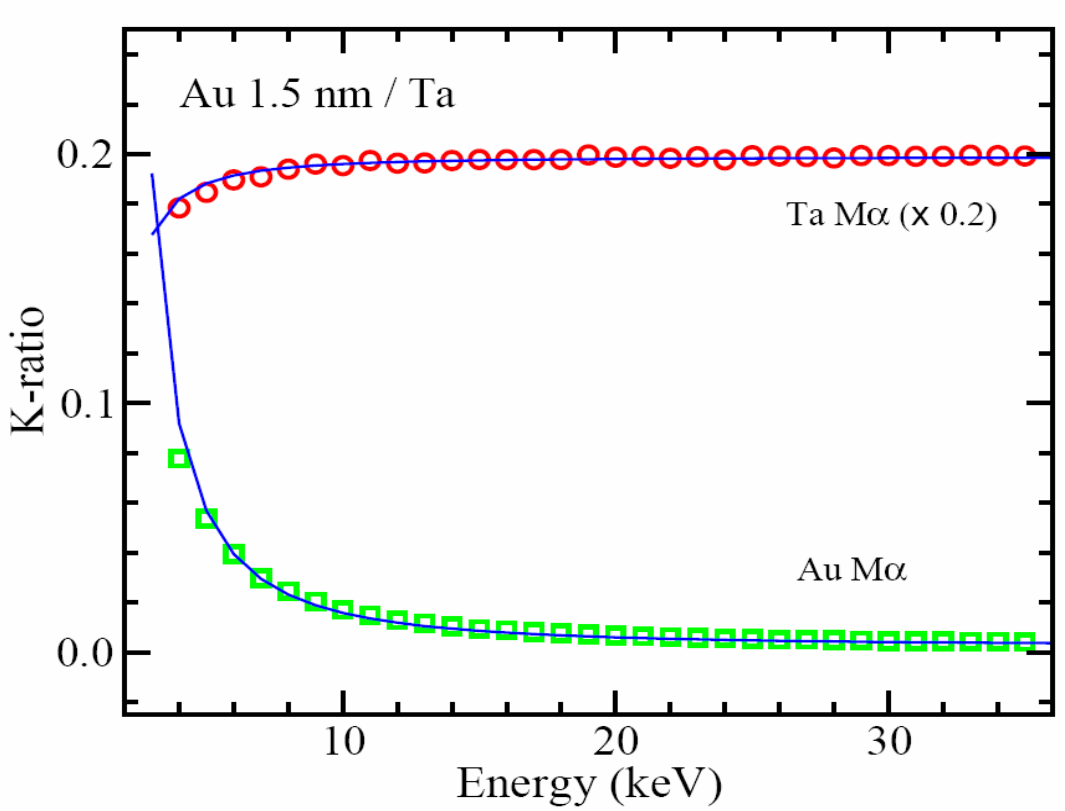
Results

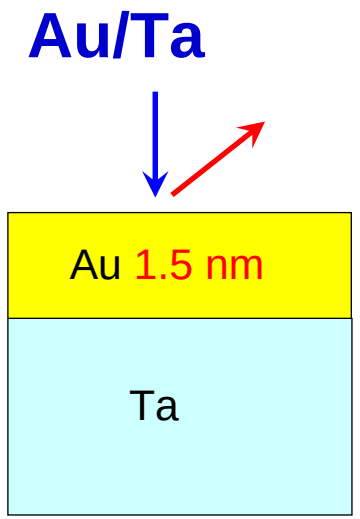


- The agreement of the thickness between the Lα and the Kα x-ray lines is about 2%.

Thickness Accuracy: Example

Measurements were done at a large number of beam voltages to check the consistency of the calculation: σ =1.5%.





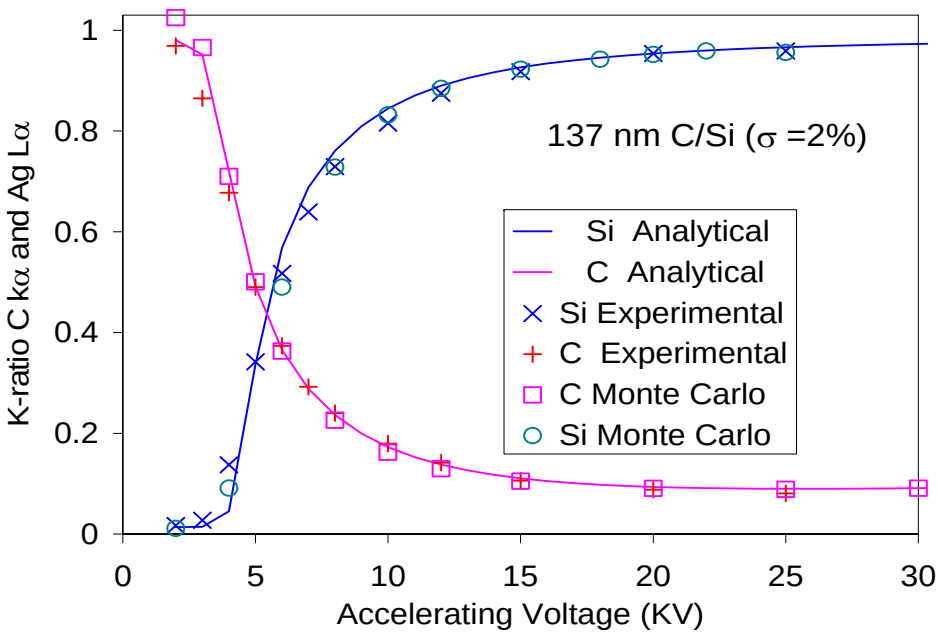
Unknown:
film thickness

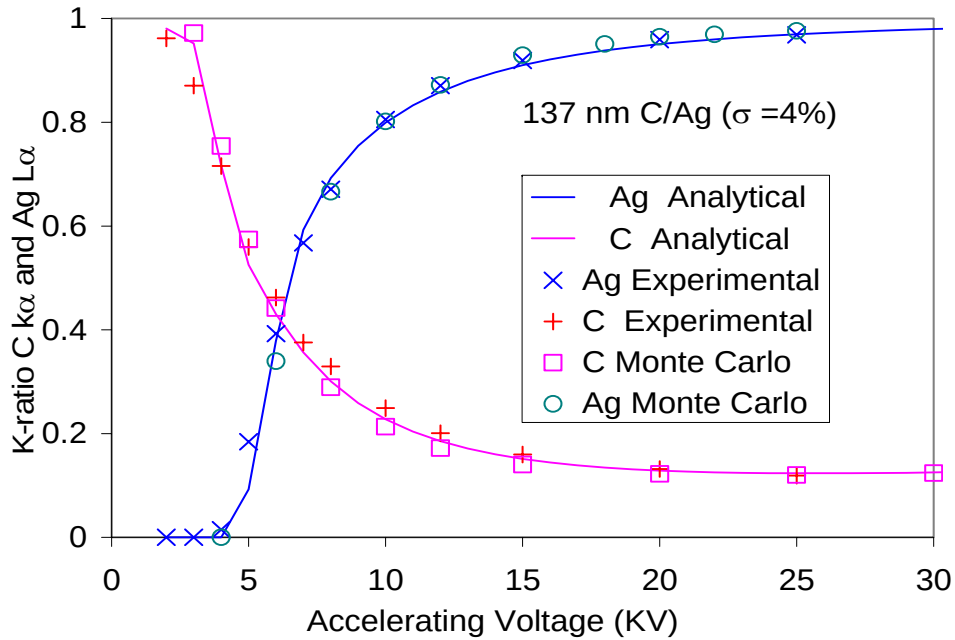
Symbols: experimental data Continuous lines: X-FILM

Test: Substrate Effect

C (137nm)

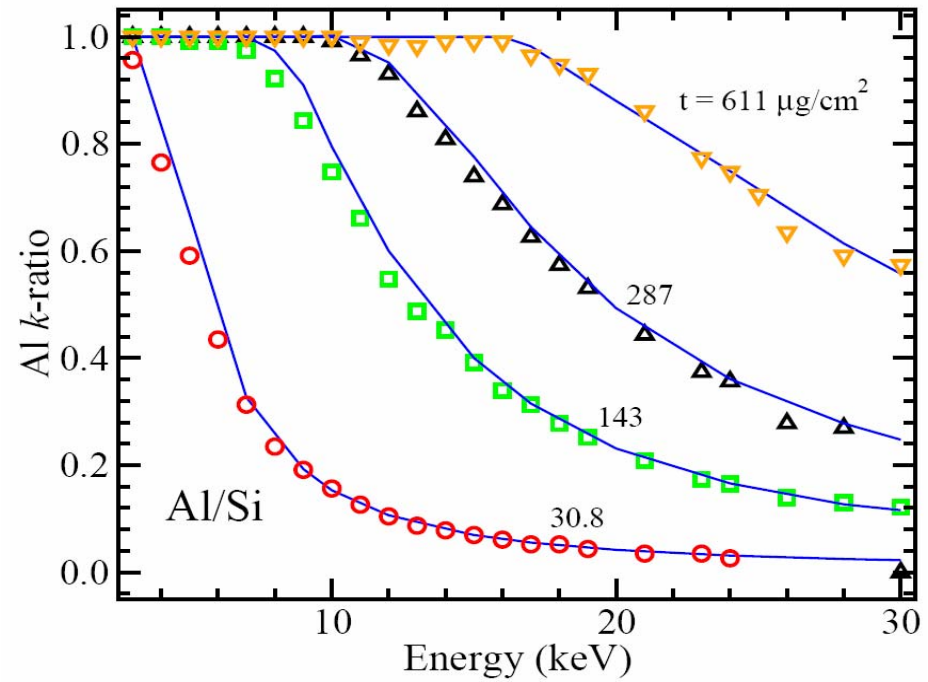
Si ; Ag



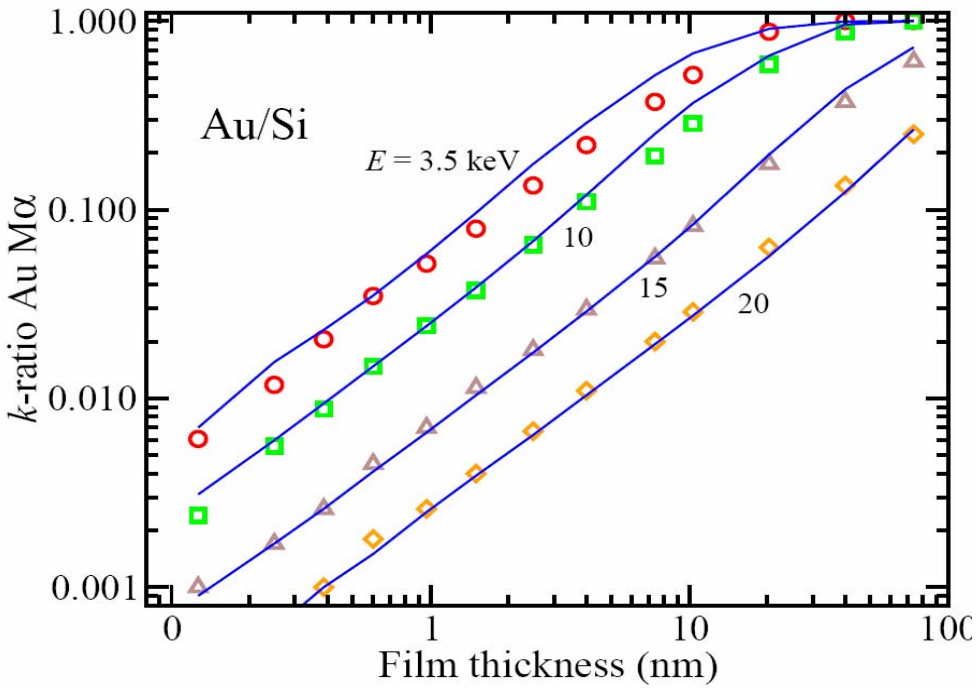


Thickness Accuracy: Example

Al k-ratio from Al/Si



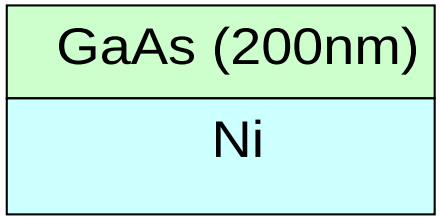
Au k-ratio from Au/Si

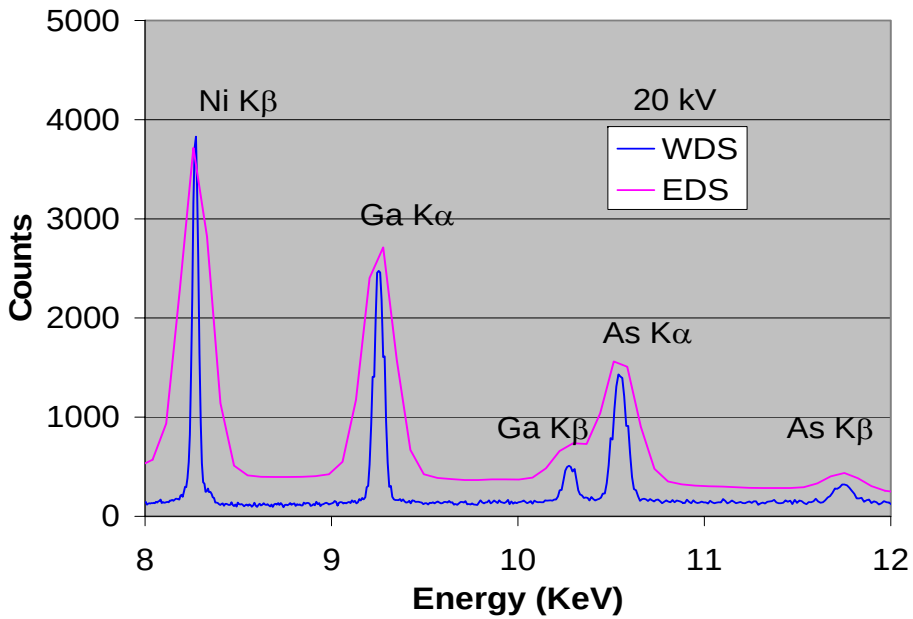


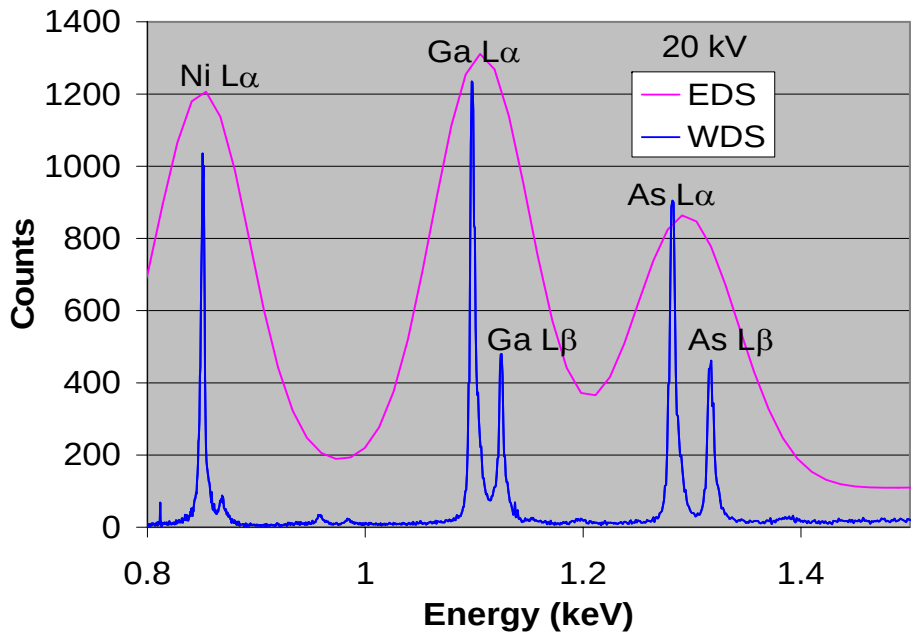
Simbols: experimental data from Reuter *et al* (1978) and Murata *et al.* (1983)
Continuous lines: predictions of X-FILM

Good agreement over the range of measured energies and thickness, except at very low energies (3.5 keV)

Concentration Accuracy

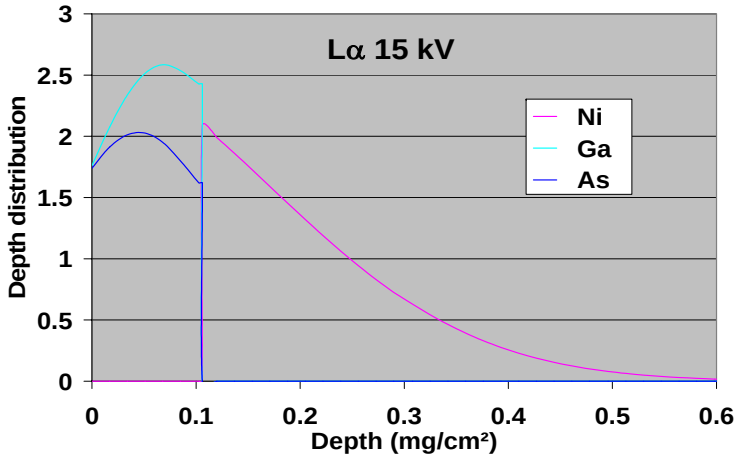


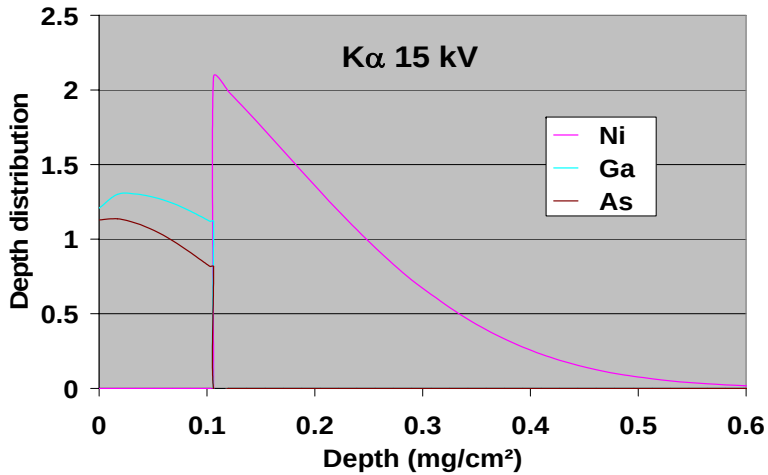


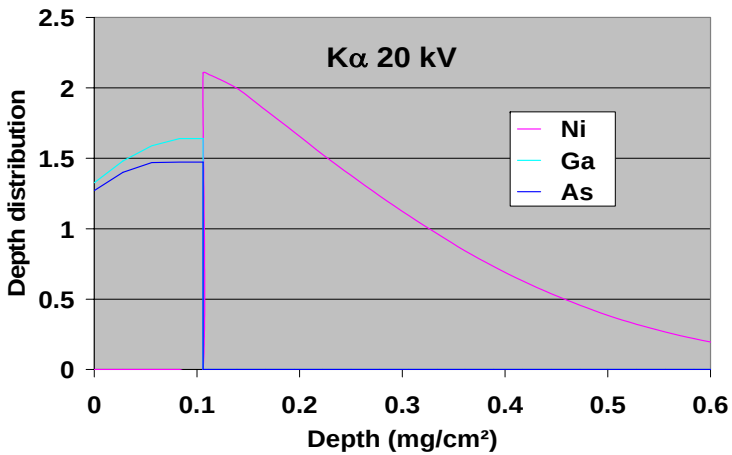


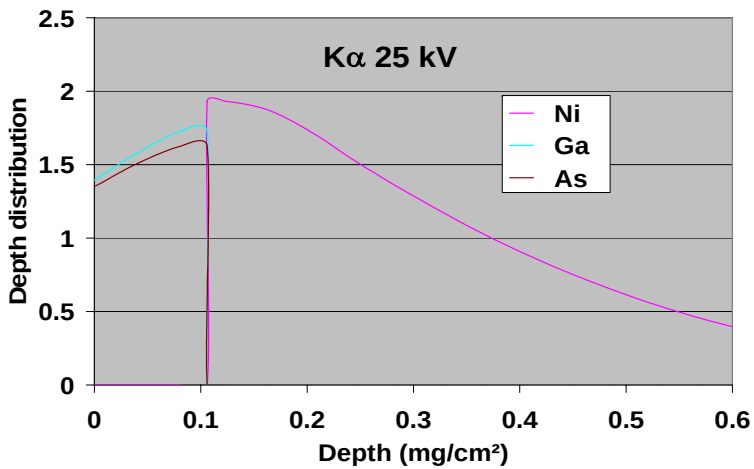
Test: Concentration

GaAs (200nm)/Ni





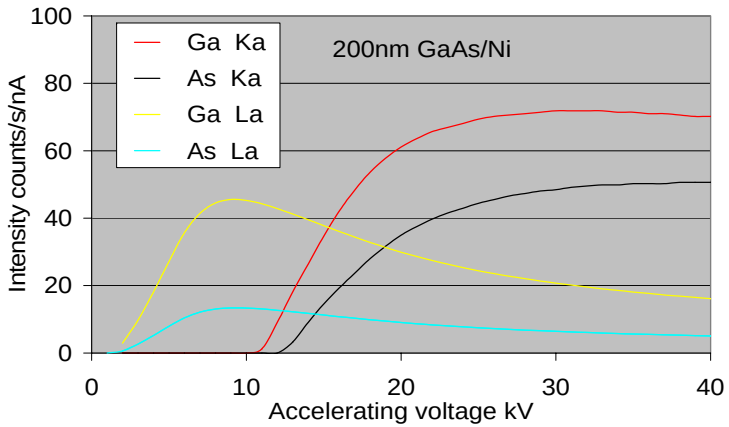


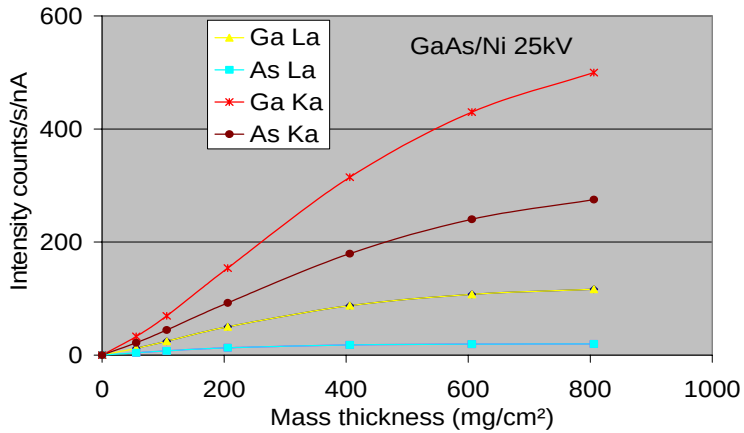


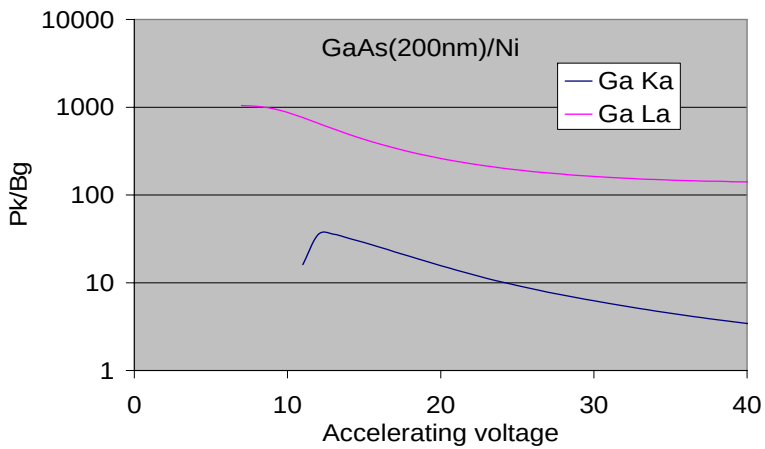
Test: Concentration

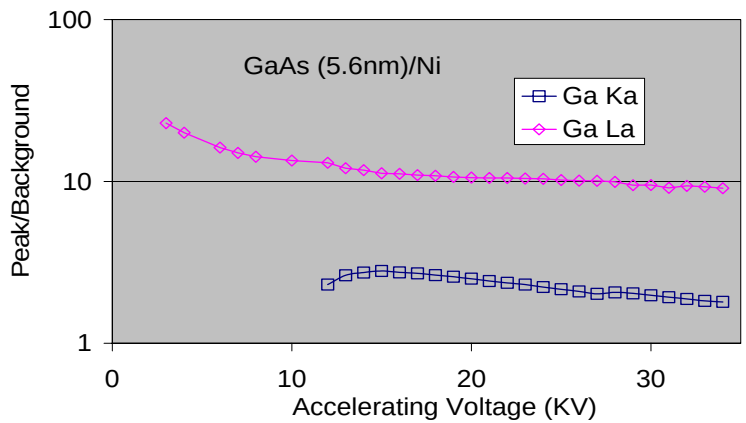
Example: GaAs/Ni

Lα or Kα lines?
Accelerating Voltage?

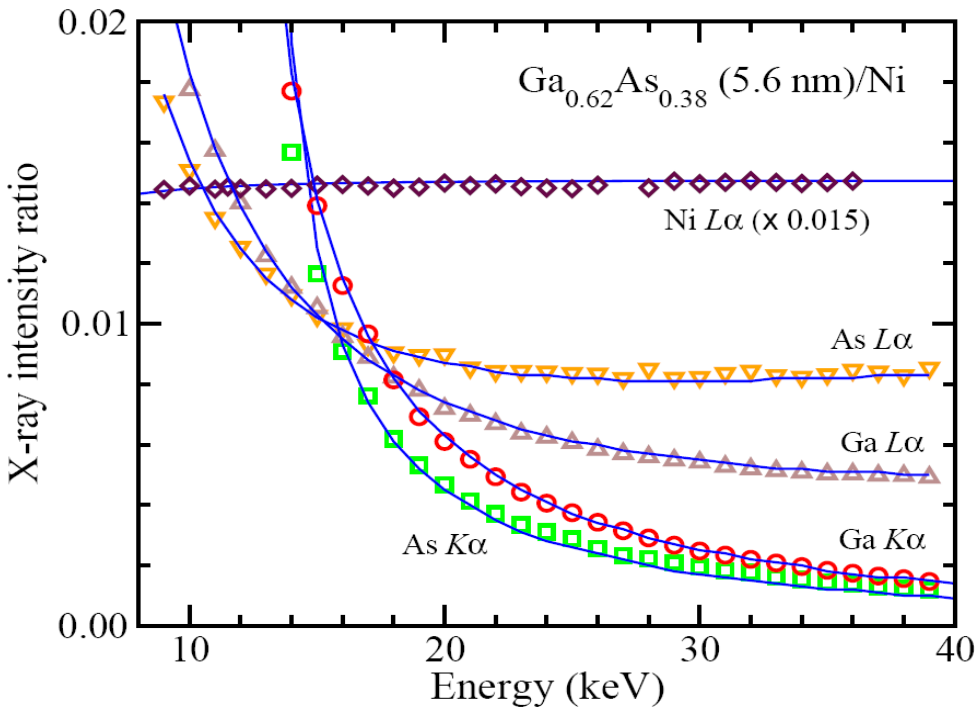




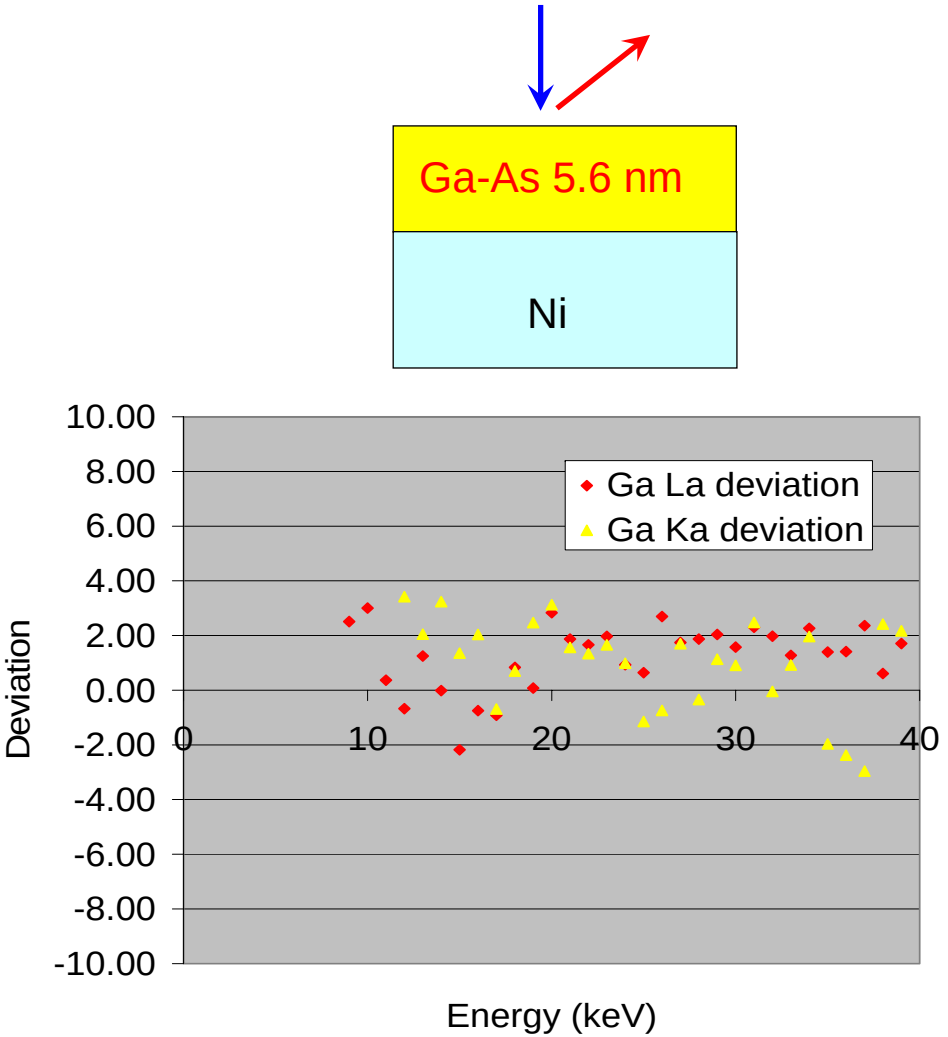




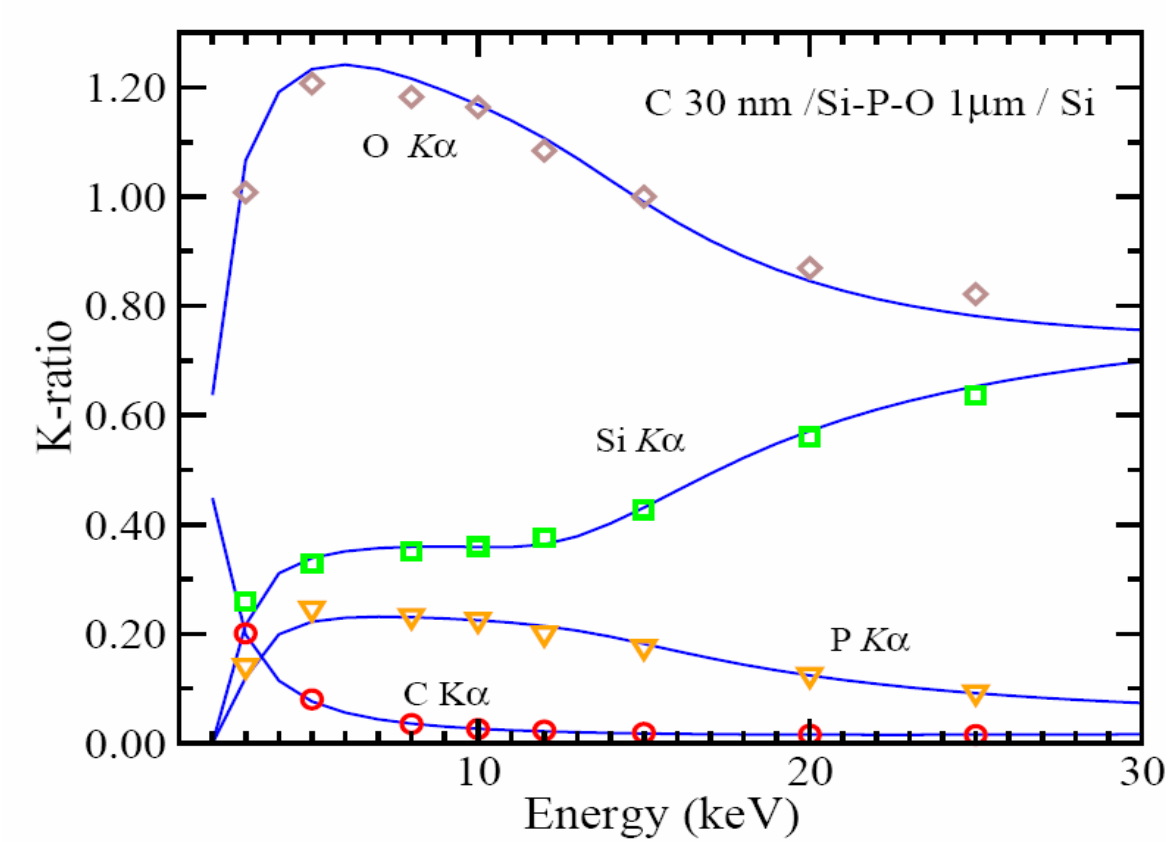
Test: Concentration



Symbols: experimental data; Curves: analytical model
(Merlet et al. physical review A 2006)



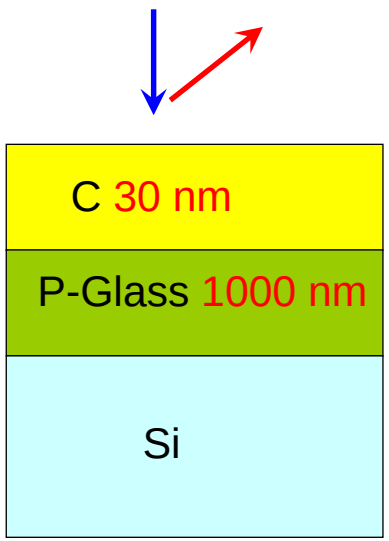
Concentration: Example



Symbols: experimental data Continuous lines: X-FILM

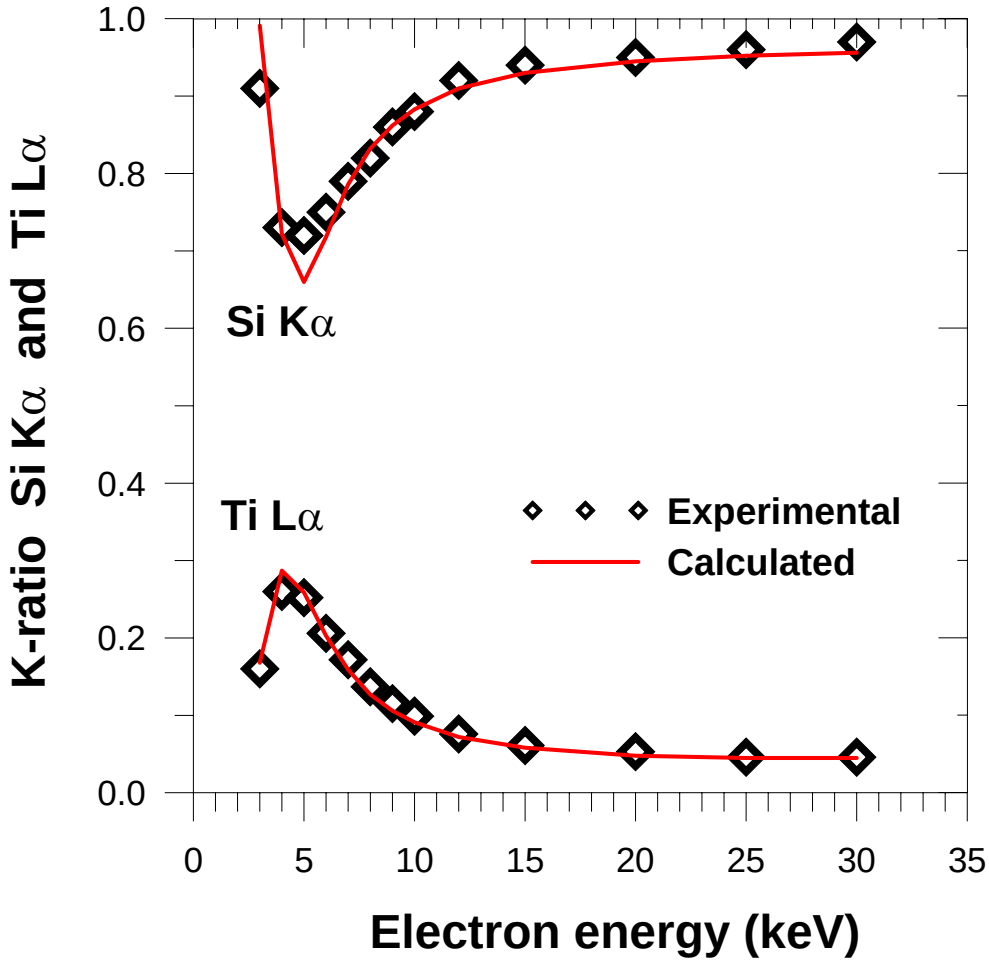
C/P-Glass/Si

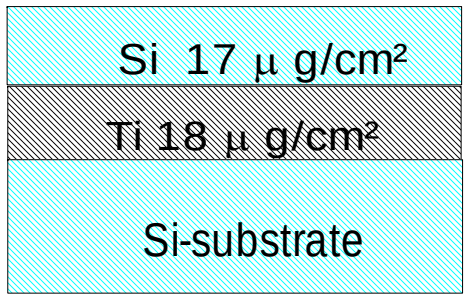
Unknown: thicknesses and glass composition



Good agreement over all the range of measured beam energies

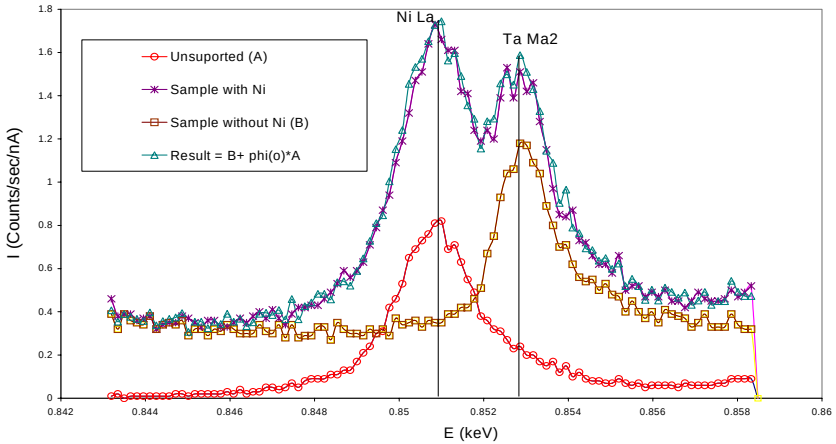
Buried Layer



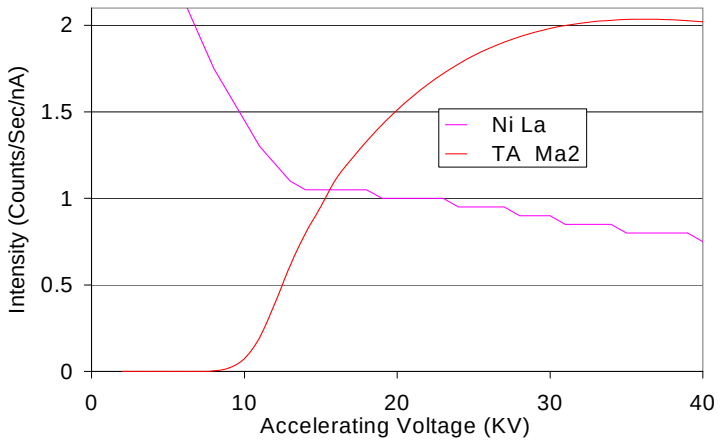


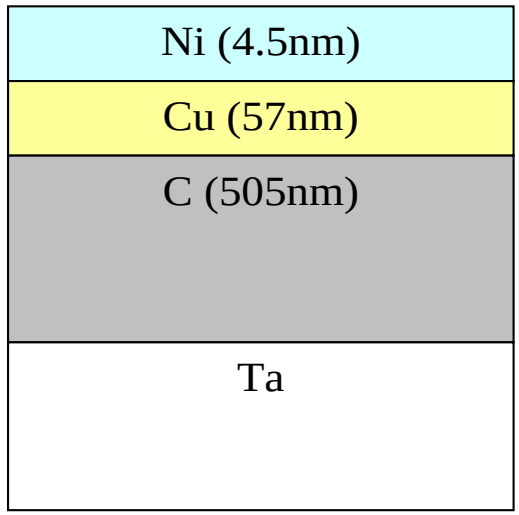
Experimental K-ratio of Bastin et al., and calculated K-ratio by X-FILM as a function of electron energy for a Si-Ti-Si sample.

Practical Aspect: Overlap

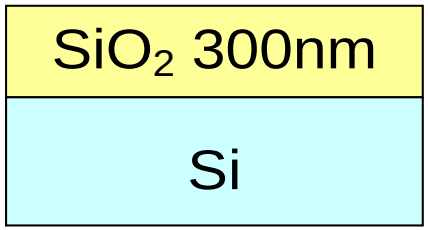


WDS Spectrum with PHA

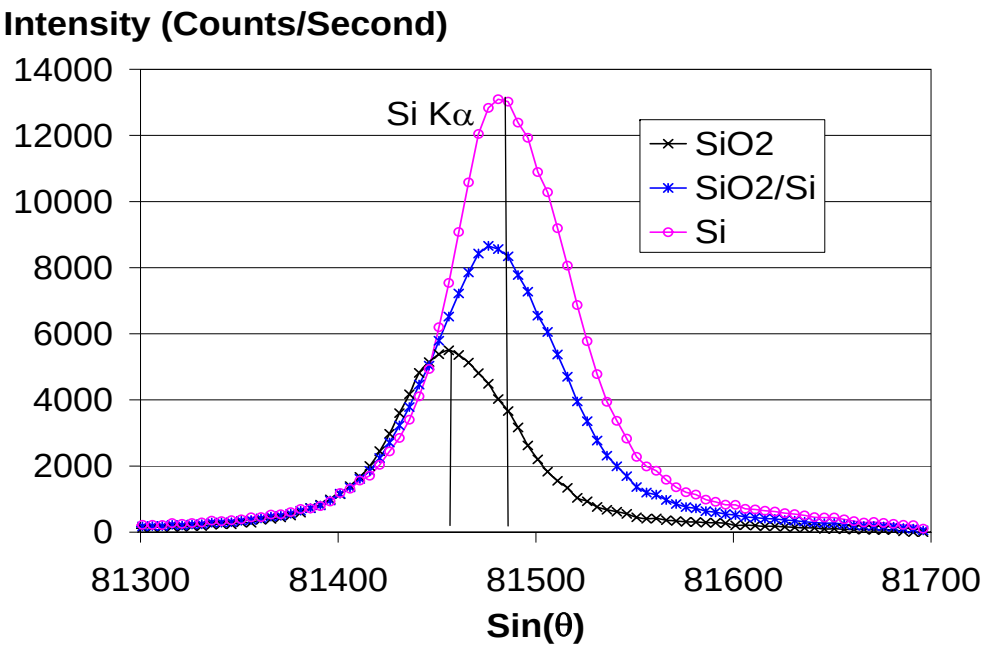


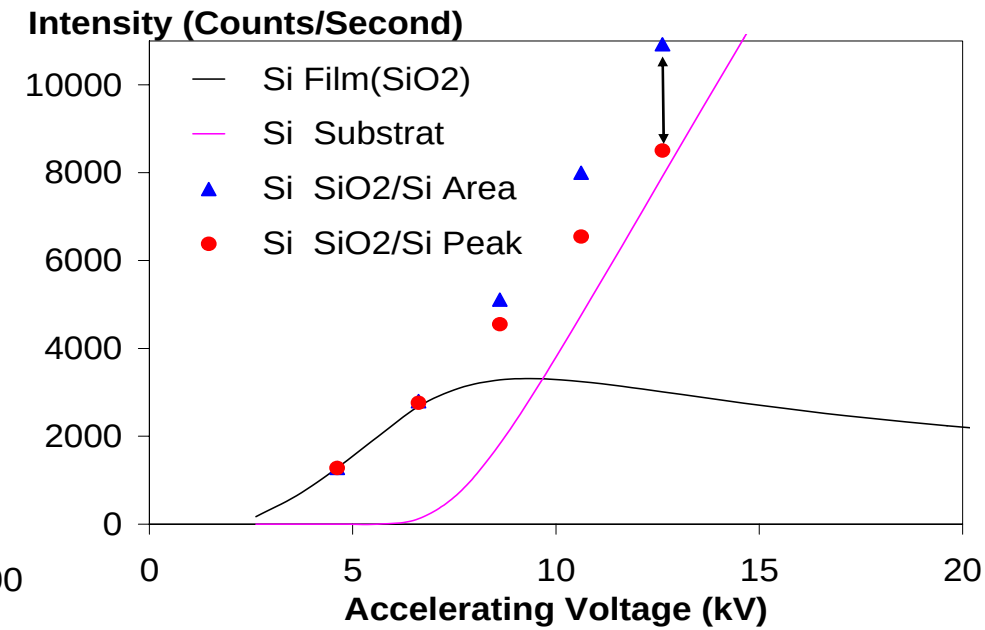


Practical Aspect: Chemical Effect



➔ WDS: Integral Peak Measurement





Capability in Multilayer Procedure

Sample Factors

- Number of Layers
- Elements in a Layer
- Thickness & Position of Layers
- Homogeneity of Layers
- Concentration Level
- Conductivity & Sample Stability
- Surface Roughness & Porosity
- Chemical Bonding
- ……

Instrument Parameters

- Beam Voltage Accuracy +
- Current Stability & Accuracy
- X-ray Detector (Resolution & Sensitivity)
- Vacuum +
- Takeoff Angle
- ……

Quantification Procedure

- Layer Hypothesis
- Quantification Procedure +
- Atomic Parameters +
- Standards
- Overlap Subtraction +
- Artifacts +
- Fluorescence +
- ……

Analytical Conditions

- X-ray Lines +
- Accelerating Voltage +
- Current
- Counting Time (Statistic)
- Background Subtraction & Calculation +
- Crystal Analyzer (WDS)
- …….

Conclusion I

Sample	Difficulty	Uncertainty	
		Concentration	Thickness
Ti-Al-Mg Si	Easy	1-2%	2-5%
Ti-Al-Mg Fe-Cu Si	Easy	1-2% (1 Layer) 3-4% (2 Layer)	2-4% 5%
Si-O Si	Difficult Graphical Simulation Trial & Error Approach	> 2%	>5%
Si-O Si-C-O Si	Extremely Difficult Graphical Simulation Trial & Error Approach	>5% >5%	>10% >10%

Conclusion II

- The analysis of thin film by EPMA is an efficient technique.
- For the easy cases, we can obtain the concentrations of the film with an accuracy similar to bulk sample.
- For the thickness we can obtain an accuracy between 2 to 5 %.
- The technique has large advantage but requires people expert in EPMA because this technique requires a high level of quality for the measurement, the structure hypothesis and the experimental conditions.