
Modern Thin Film Analysis by Electron Probe K-ratio Measurements

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Thin film analyses

- What's the point?
 - Determining thickness and composition of layers (multilayers) on substrate.

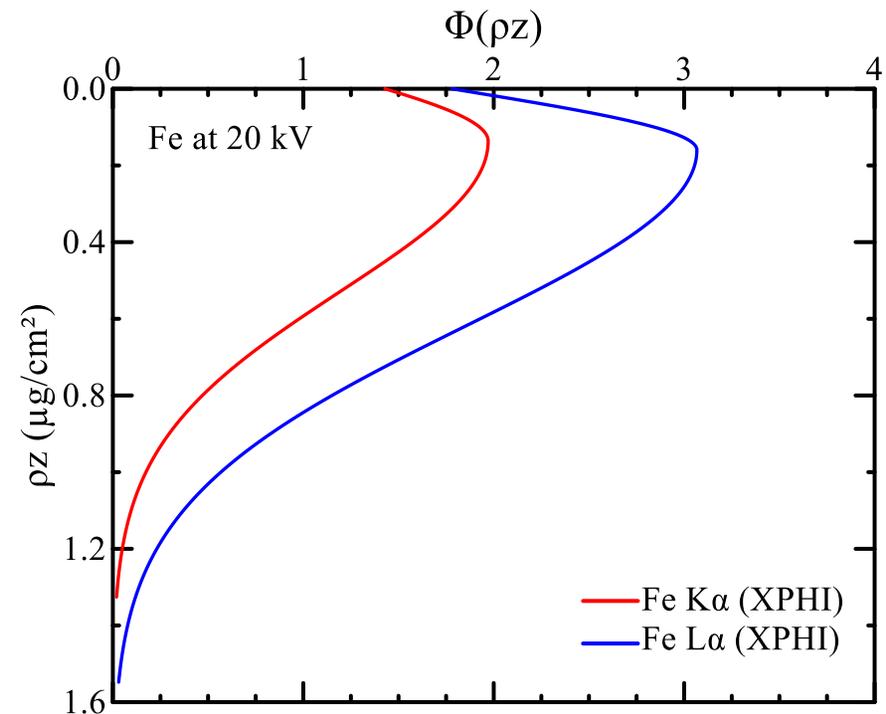
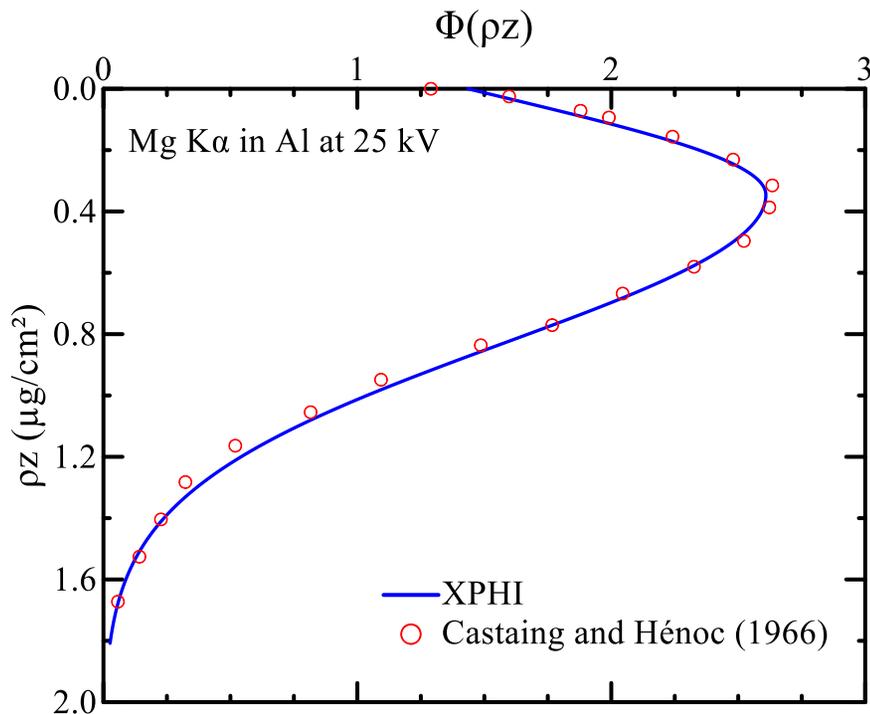


EPMA quantification methods were designed for bulk homogeneous materials (not 10-100 nm thin layers).

- What are the issues for thin films?
- How to perform thin film analysis?
- How precise/accurate are such analyses?

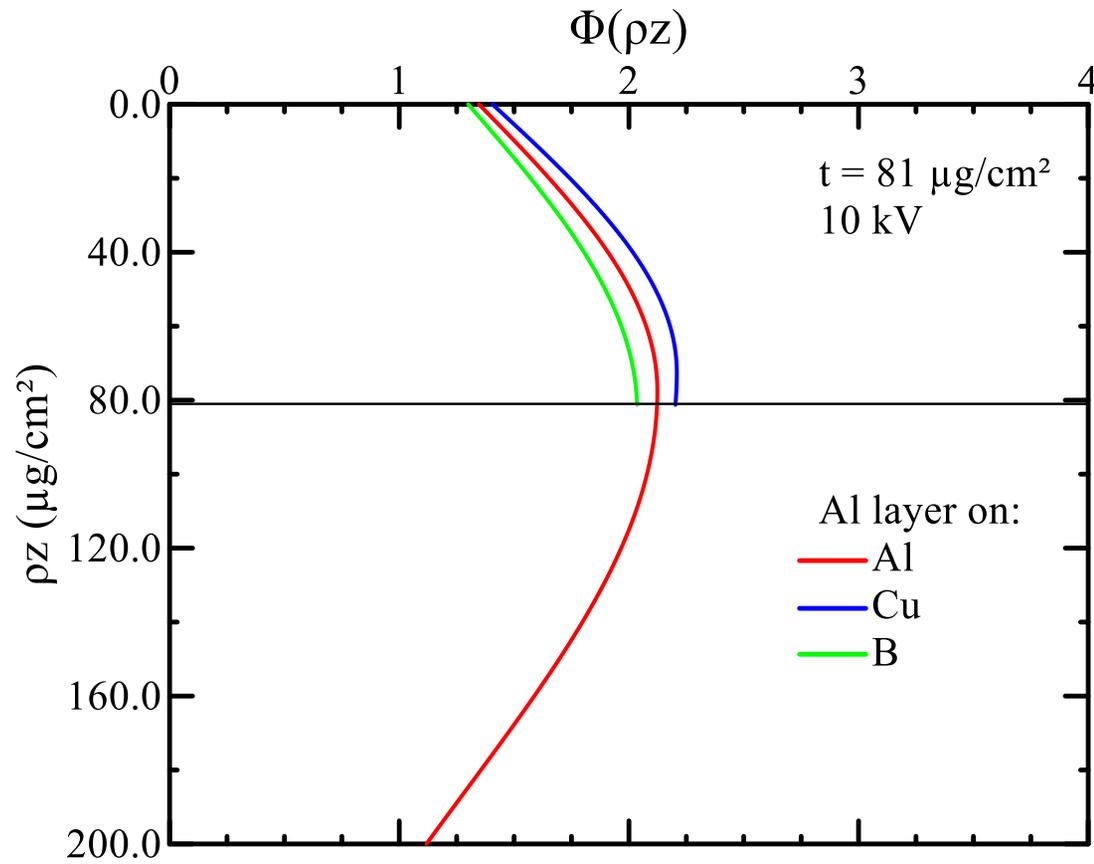
Phi-rho-z for bulk materials

- Transformation of k-ratios into elemental composition
 - matrix-correction procedures
 - assume homogeneous composition
- Phi-rho-z procedure (PAP, XPP, XPHI, ...)
 - realistic description of the ionization depth distribution
 - different for each element and each characteristic X-ray



Phi-rho-z for thin film

- Phi-rho-z model adapted to thin films
 - ponderation function for PAP
 - weighting procedure of phi-rho-z parameters for XPHI



Phi-rho-z for thin film

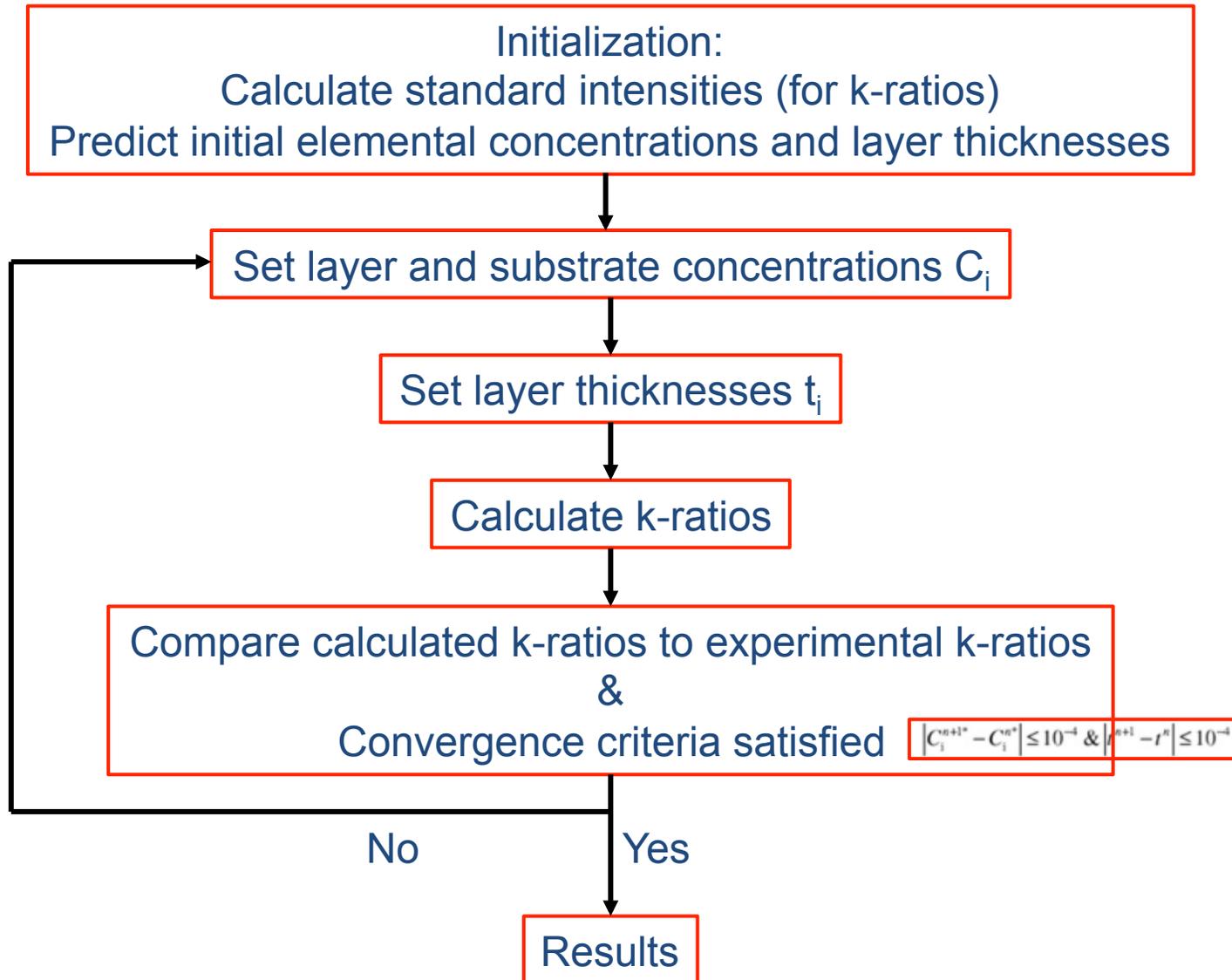
- Integration of the $\phi(\rho z)$ to calculate total emitted X-ray intensity for a given layer

$$I_i = A C_i \int_{\rho z_1}^{\rho z_2} \Phi_i(\rho z) e^{-\mu/\rho \rho z / \sin \theta} d\rho z$$

- → Repeat for all layers and for the substrate
- → Calculate theoretical k-ratios
- → Iteration on composition and film thickness to match experimental k-ratios

Phi-rho-z for thin film

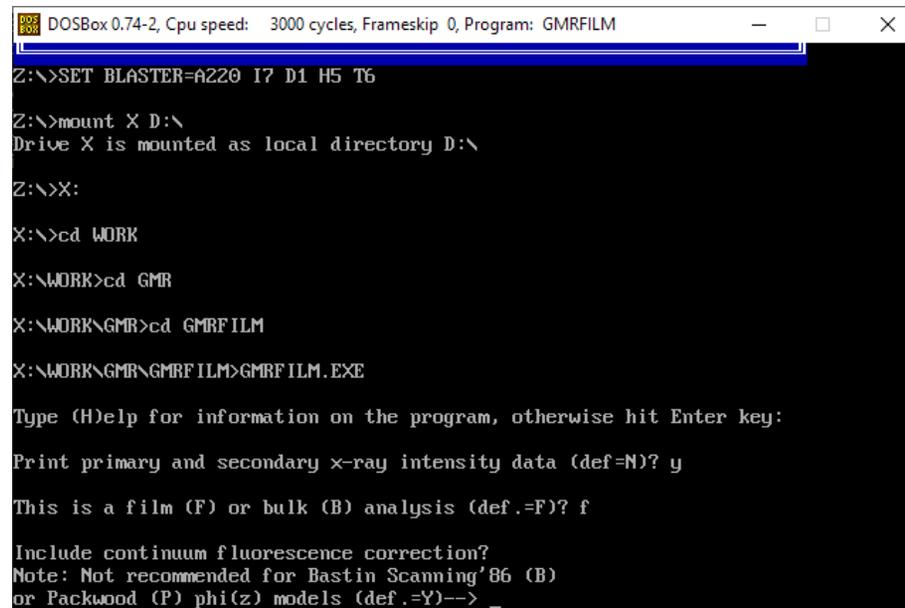
- → Iteration until convergence



Current thin film analysis programs

- STRATAGEM (Pouchou and Pichoir) \$\$
- XFILM (Merlet) \$?
- LayerProbe (Oxford Instruments) \$\$
- GMRFilm (Waldo, GMR)
 - Free program
 - But old, requires DOS, input by command prompt

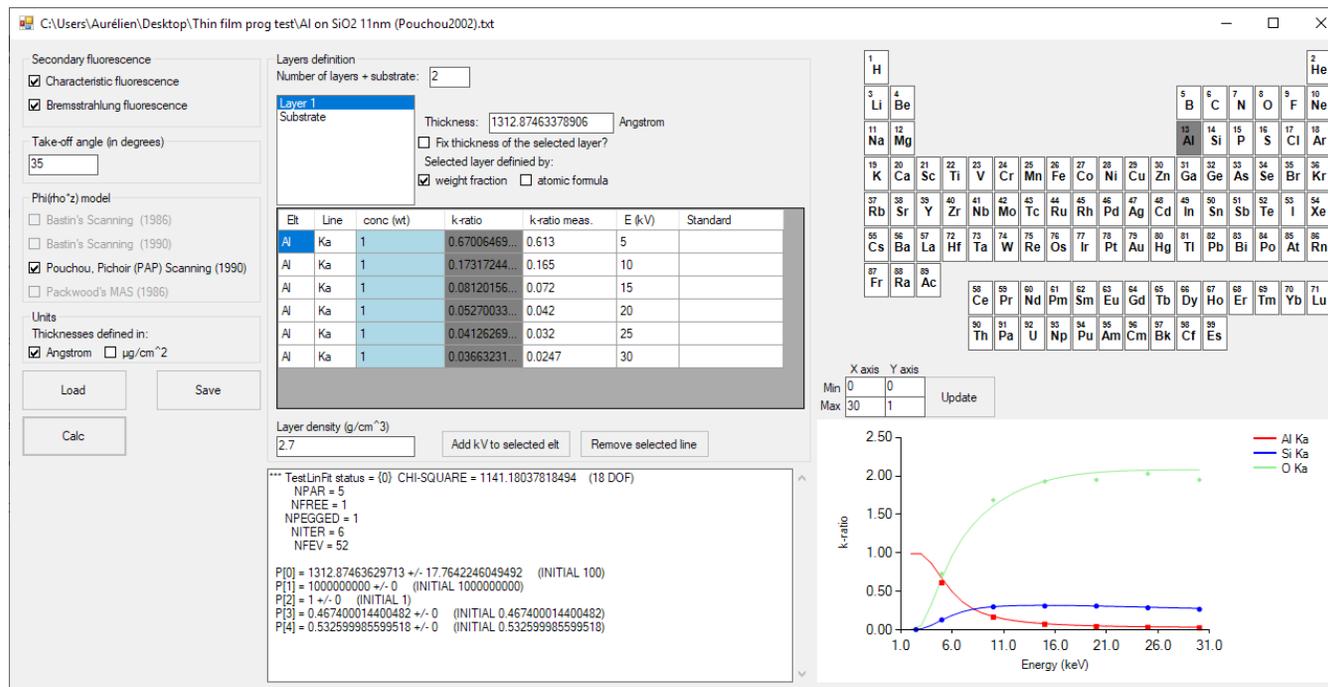
Not easy to use for
large set of data



```
DOSBox 0.74-2, Cpu speed: 3000 cycles, Frameskip 0, Program: GMRFILM
Z:\>SET BLASTER=A220 I7 D1 H5 T6
Z:\>mount X D:\
Drive X is mounted as local directory D:\
Z:\>X:
X:\>cd WORK
X:\WORK>cd GMR
X:\WORK\GMR>cd GMRFILM
X:\WORK\GMR\GMRFILM>GMRFILM.EXE
Type (H)elp for information on the program, otherwise hit Enter key:
Print primary and secondary x-ray intensity data (def=N)? y
This is a film (F) or bulk (B) analysis (def.=F)? f
Include continuum fluorescence correction?
Note: Not recommended for Bastin Scanning'86 (B)
or Packwood (P) phi(z) models (def.=Y)--> _
```

BadgerFilm

- Development of a thin film analysis program
 - User-friendly graphical interface
 - Powerful non-linear fitting algorithm (converge even for far starting conditions)
 - Implementation of the PAP algorithm
 - Elements up to Einsteinium (Z=99)
 - Free (and code available on request)



X-ray Intensities

- 3 “kind” of X-ray intensities to consider

1) Characteristic X-ray intensity generated by primary electrons

Secondary fluorescence:

2) X-ray intensity generated by Characteristic X-rays

3) X-ray intensity generated by Bremsstrahlung

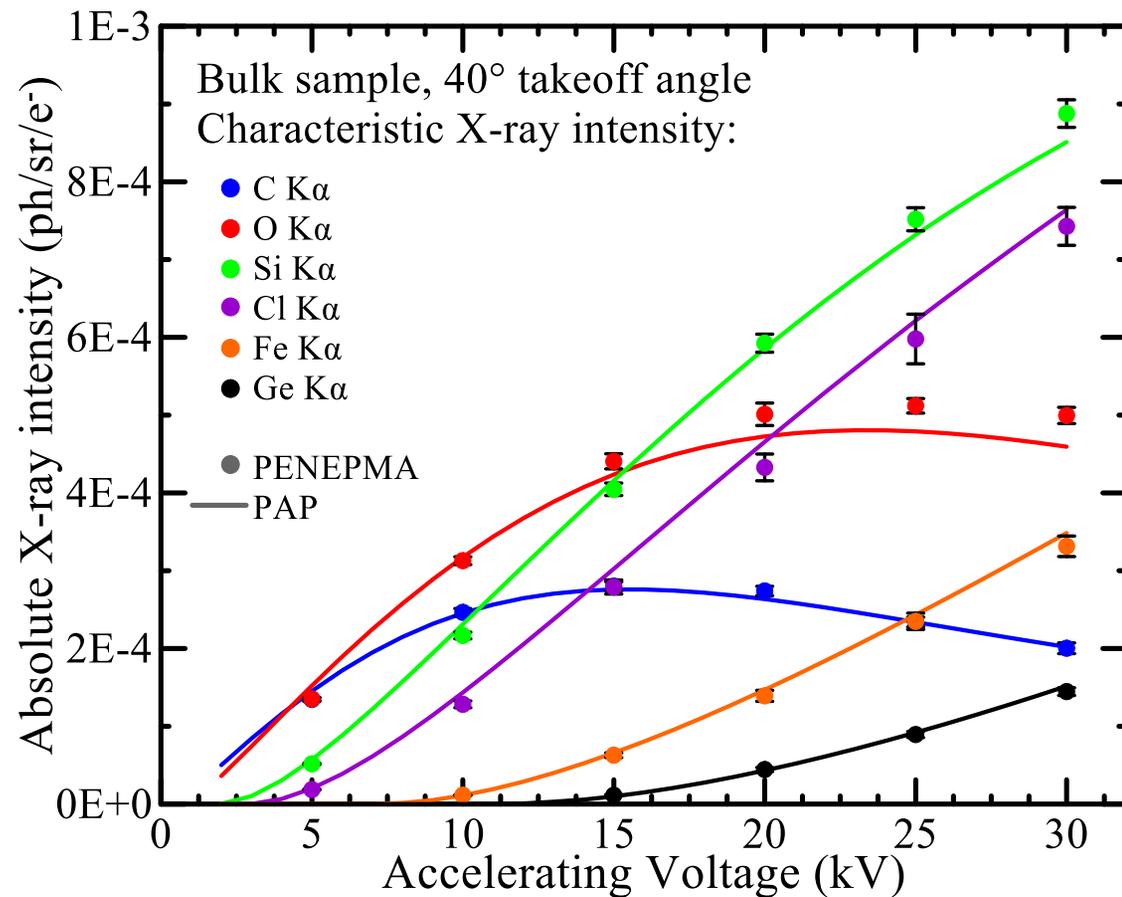


Secondary fluorescence (SF) can account up to ~15-20% of total intensity (especially for films).

(this is not considered in the CASINO program)

Absolute Characteristic X-ray Intensity

- Absolute X-ray intensity (ph/electron/sr) using recent atomic parameter databases
- Comparison with Monte Carlo simulations using PENEPMA
- Pure bulk sample



Secondary fluorescence by characteristic X-rays

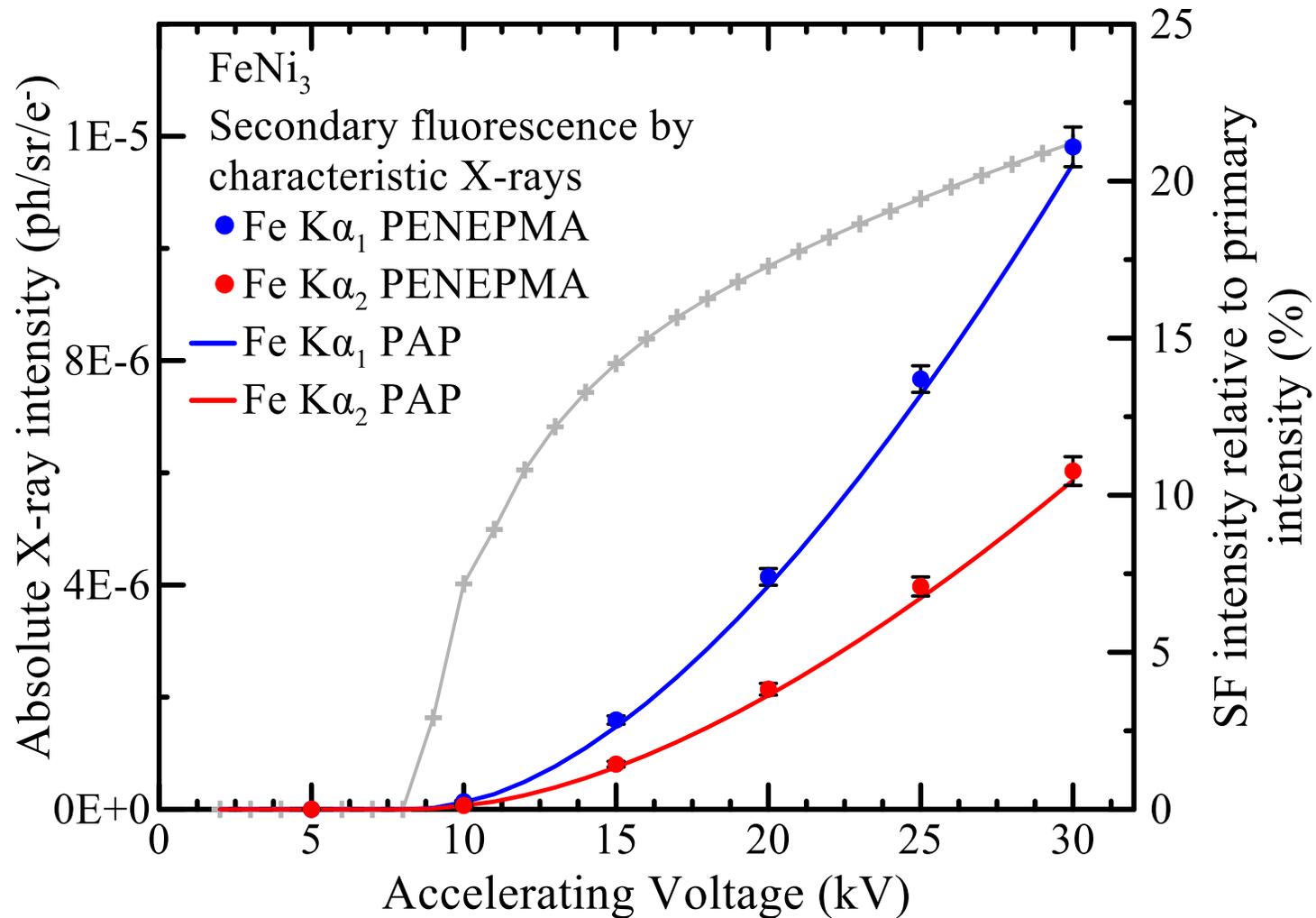
- Calculation scheme
 - Find all the characteristic X-rays with $E > E_{\text{ionization}}$ (even the low intensity X-rays)
 - Calculate $\phi(\rho z)$ distribution for all characteristic X-rays
 - Calculate SF generated by each $\phi(\rho z)$ distributions (numerical integration over mass depth)
 - Sum all the contributions to calculate final SF by characteristic X-rays



GMRFilm overestimates SF compared to Monte Carlo simulations (PENEPMAs)

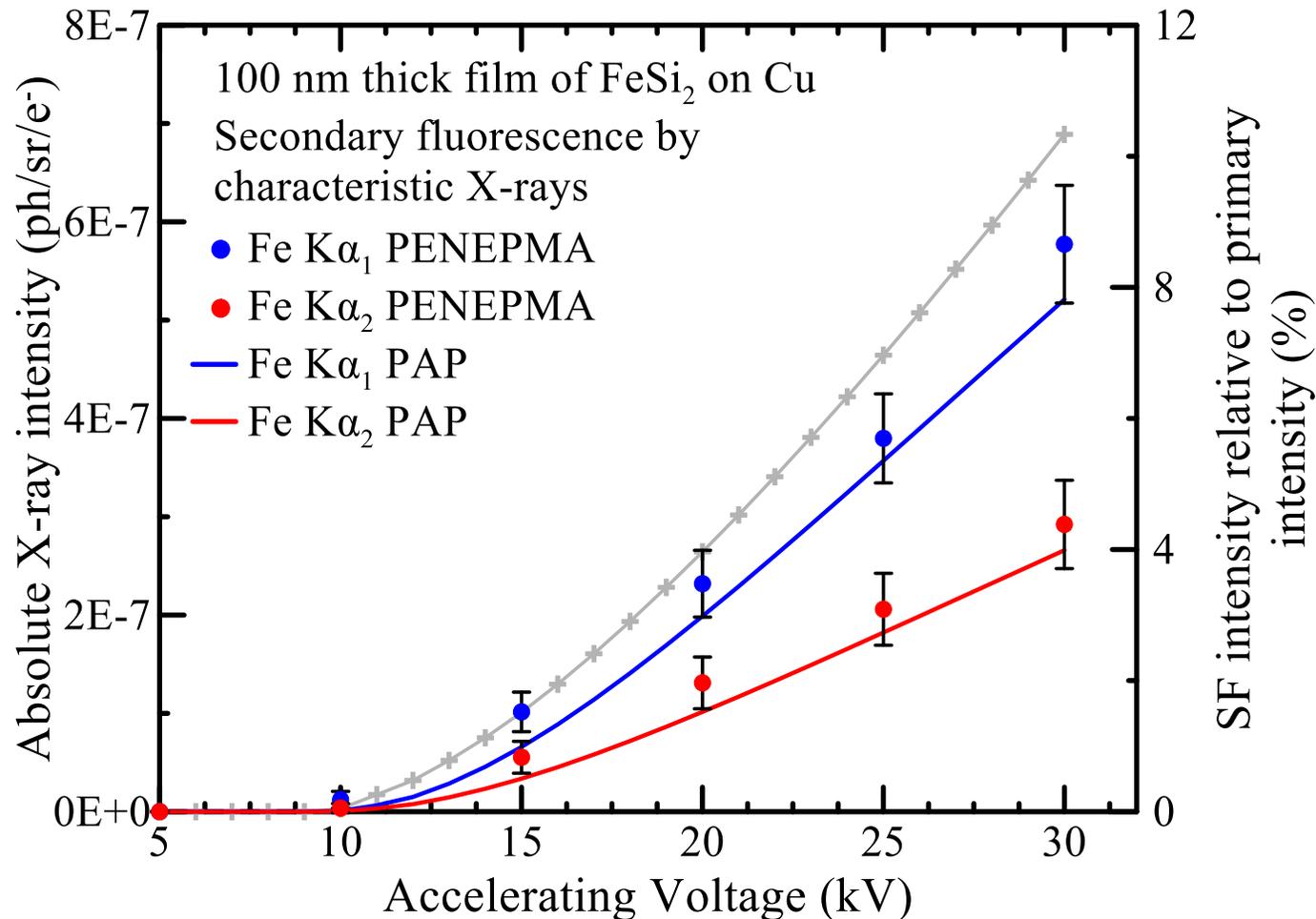
Secondary fluorescence by characteristic X-rays

- FeNi₃ bulk sample
Fluorescence of Fe K α by Ni (comparison with PENEPMA)



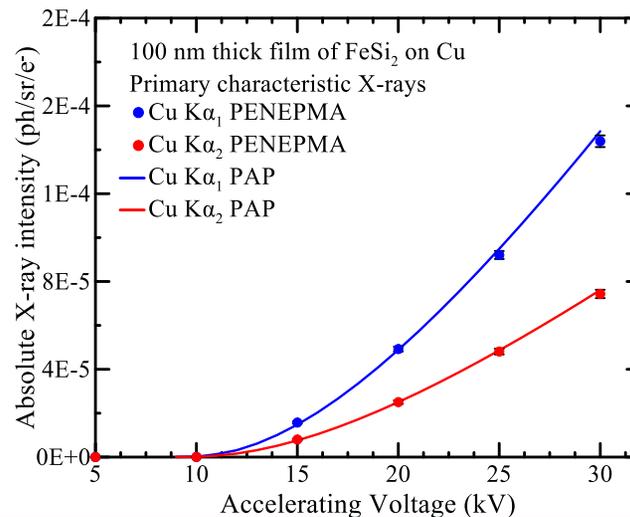
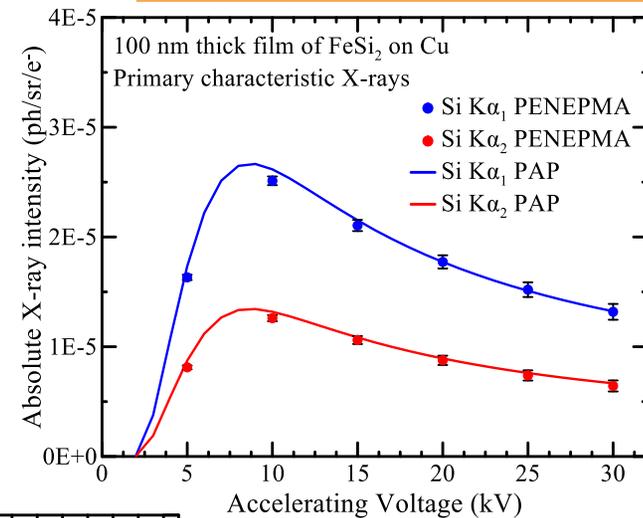
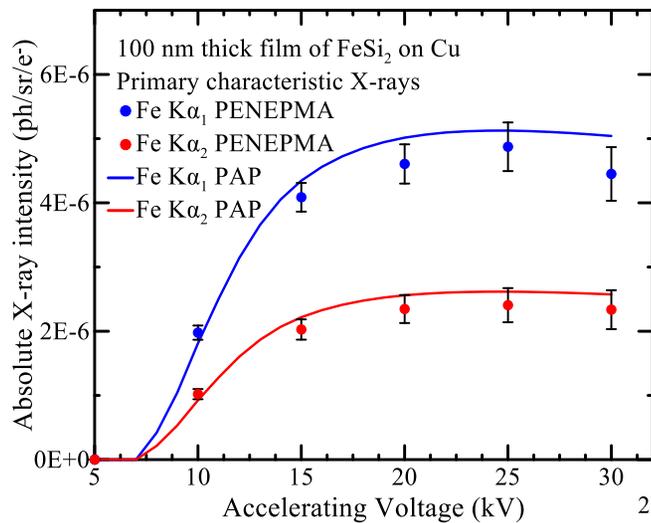
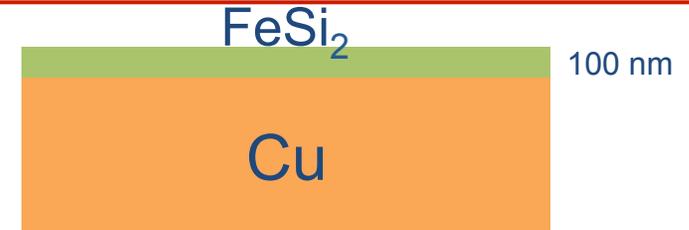
Secondary fluorescence by characteristic X-rays

- 100 nm thick FeSi_2 film on bulk Cu
Fluorescence of Fe $K\alpha$ by Cu
(comparison with PENEPMAs)



Characteristic X-rays

- 100 nm thick FeSi_2 film on bulk Cu
Characteristic X-rays



Secondary fluorescence by bremsstrahlung

- Calculation scheme



No published $\phi(\rho z, E)$ curve for the bremsstrahlung!

→ the energy range is discretized → E_i (from E_c to E_0)

→ the $\phi(\rho z, E_i)$ curve of a fictitious element is calculated and weighted by Kramers' law

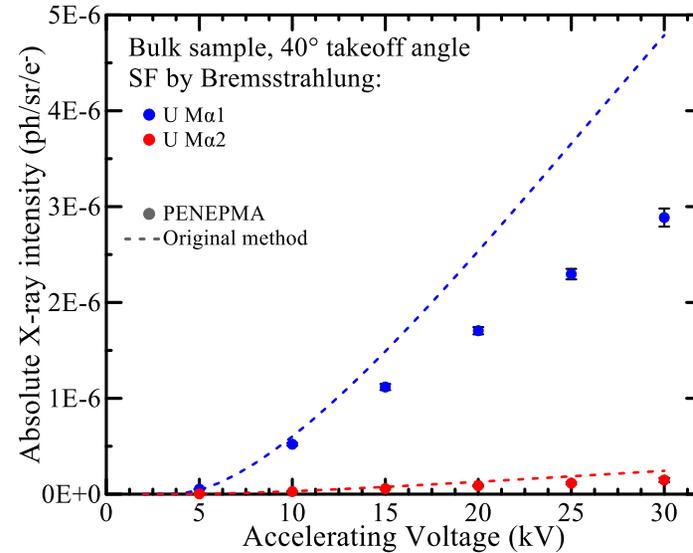
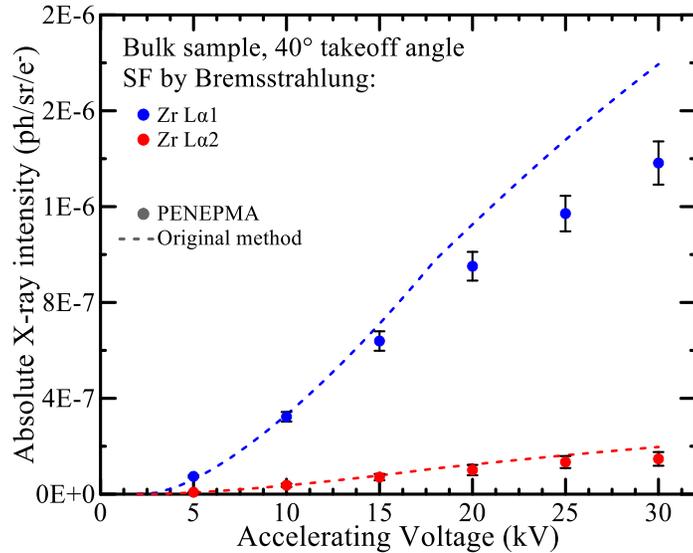
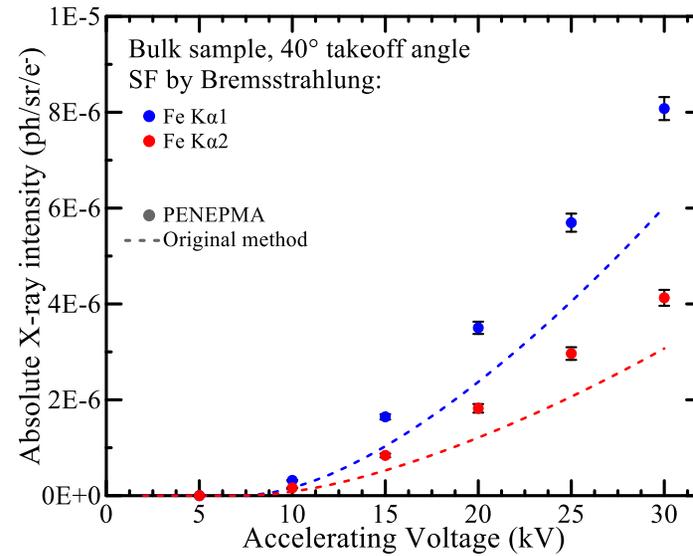
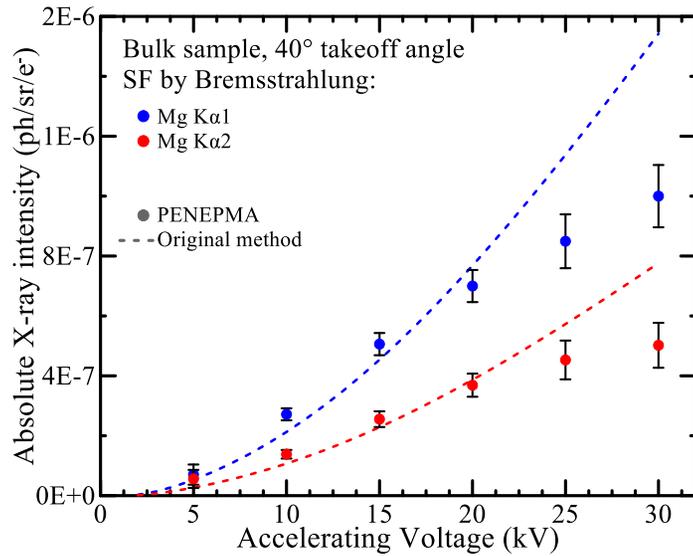
→ SF is calculated for bremsstrahlung of energy E_i

repeat with next energy E_i

→ All the SF contributions are integrated from E_c to E_0

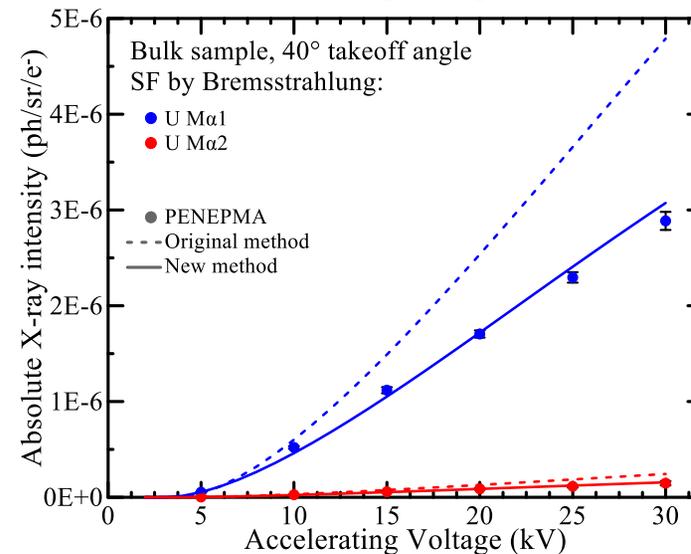
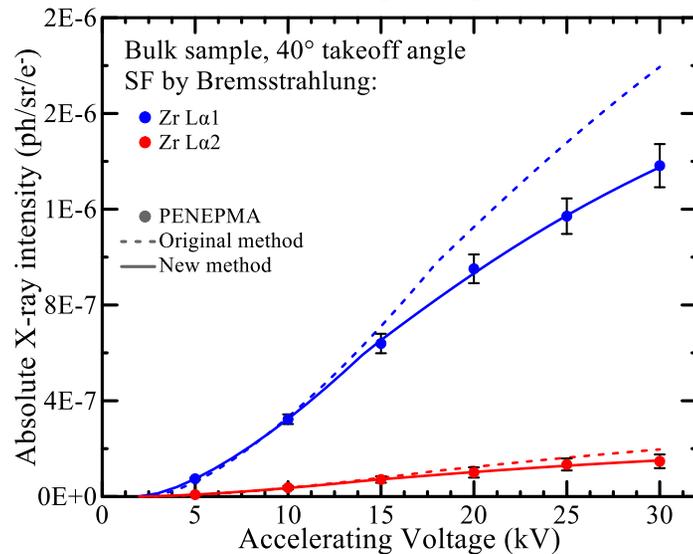
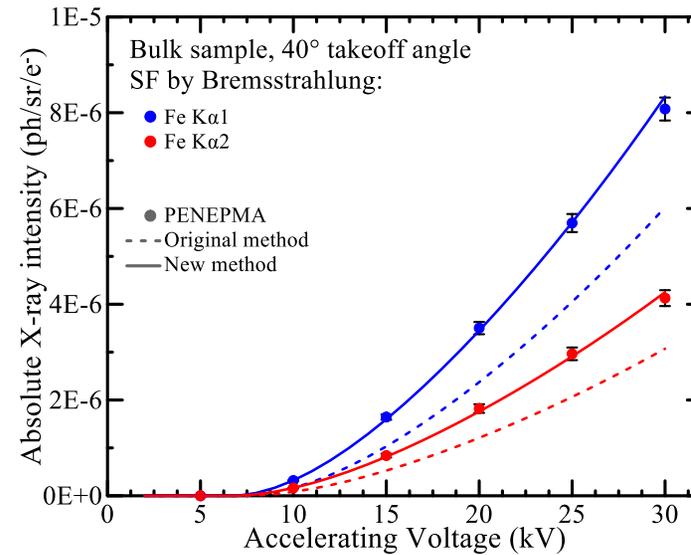
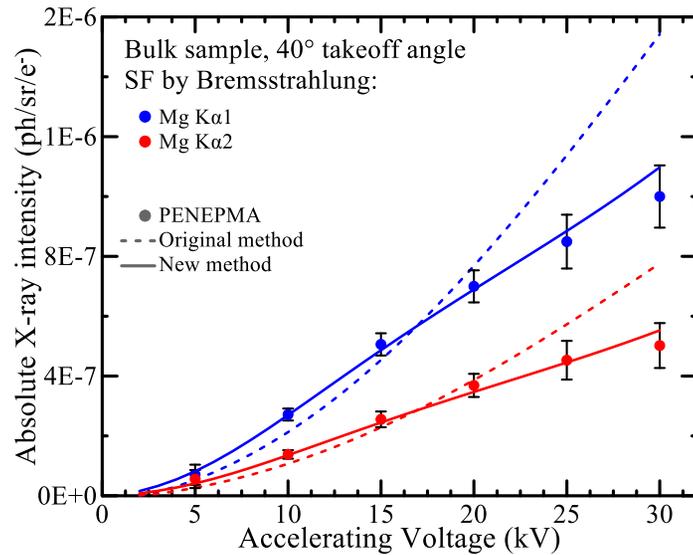
Secondary fluorescence by bremsstrahlung

- Procedure used in GMRFilm
→ usually overestimates SF compared to PENEPMA



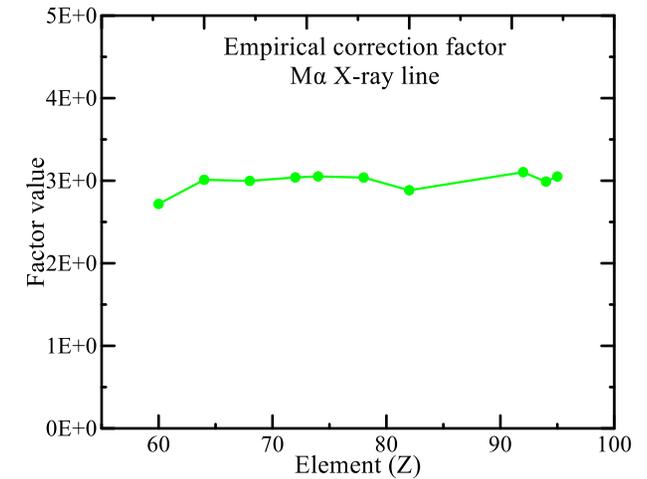
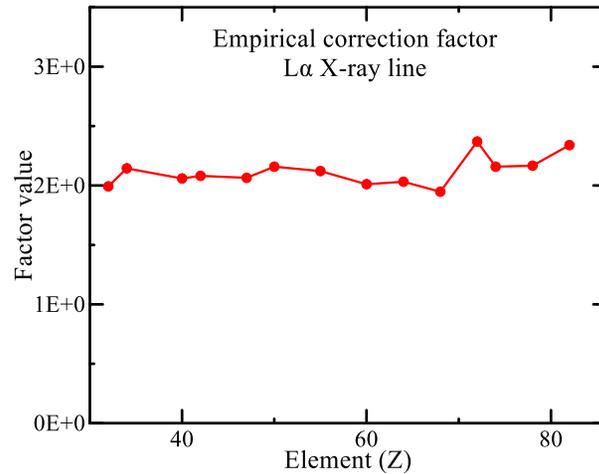
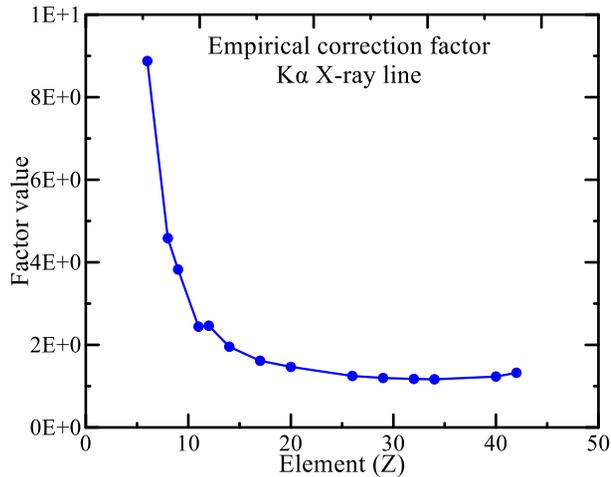
Secondary fluorescence by bremsstrahlung

- Using two correction factors: almost perfect matching with PENEPMA results

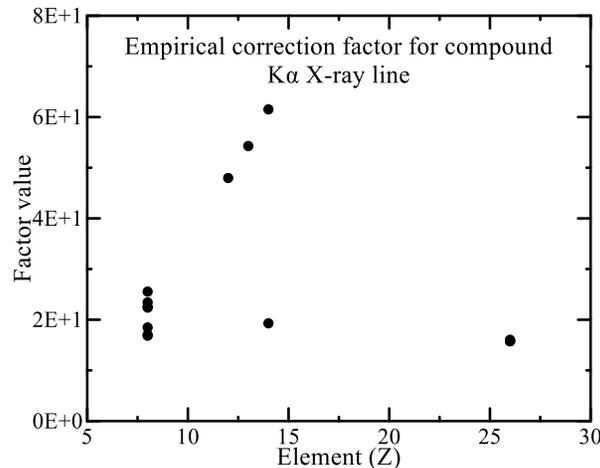


Secondary fluorescence by bremsstrahlung

- Correction factors are easy to predict for pure elements



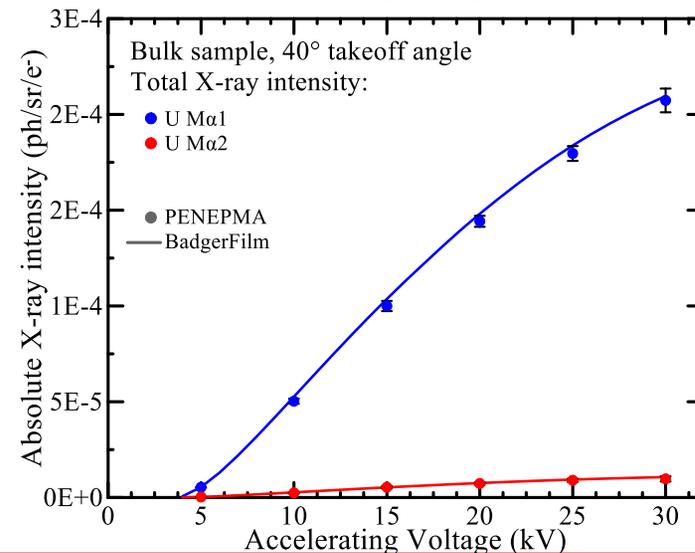
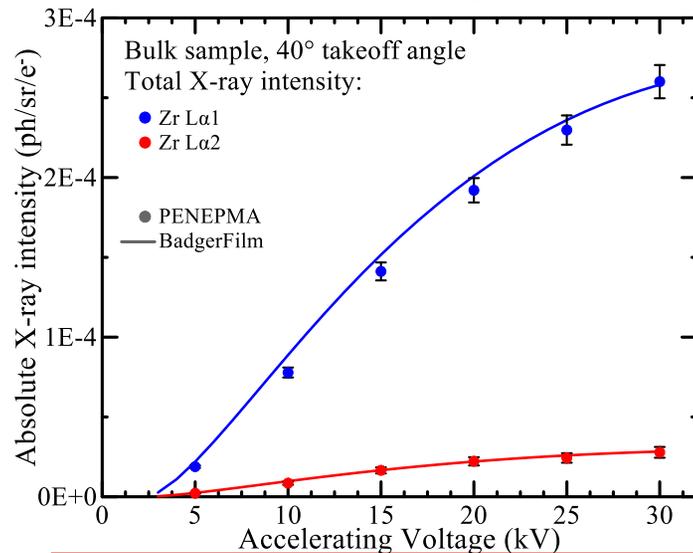
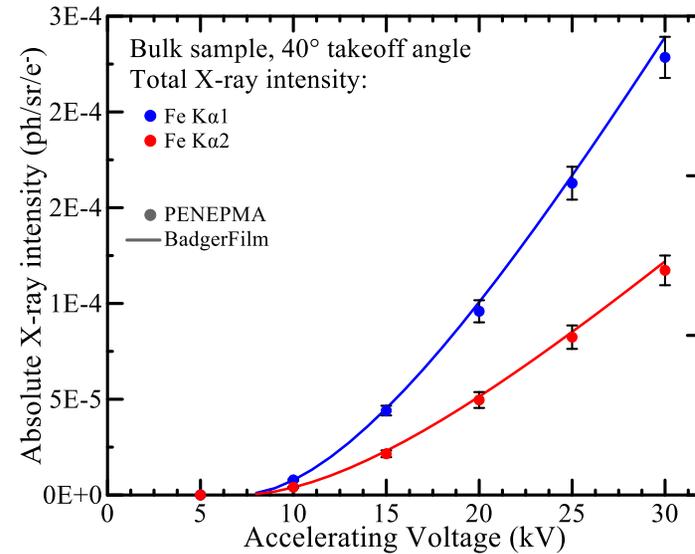
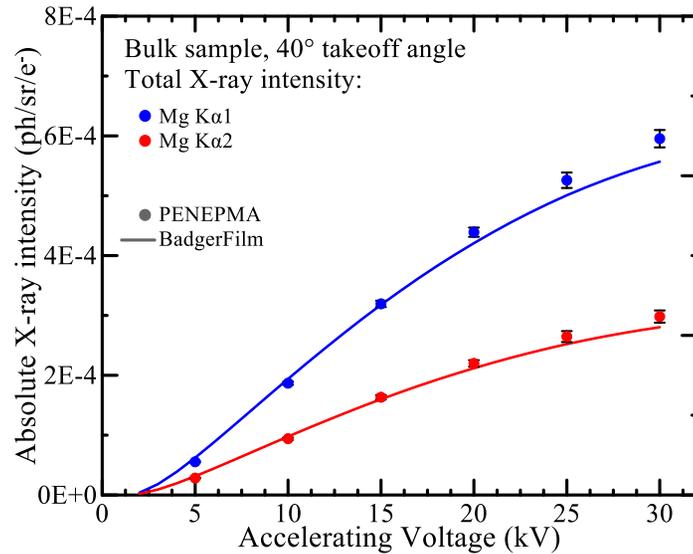
- However, correction factors are hard to predict for compounds



- Other method: use MC simulations to generate bremsstrahlung $\phi(\rho z, E)$ curves (Yuan et al. 2019)

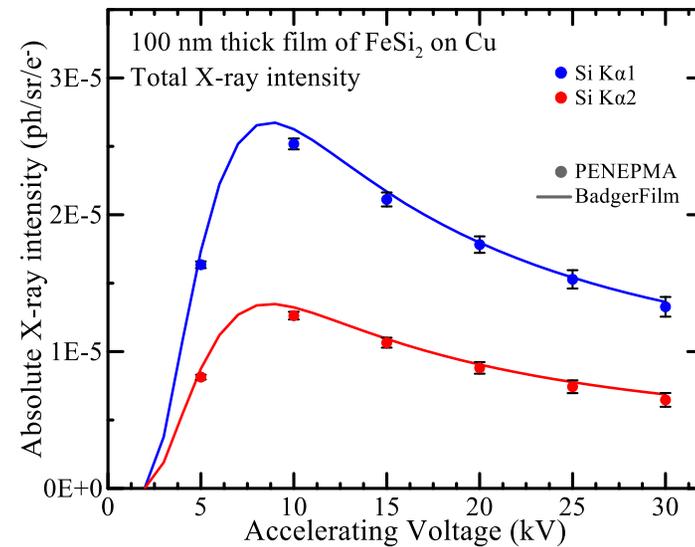
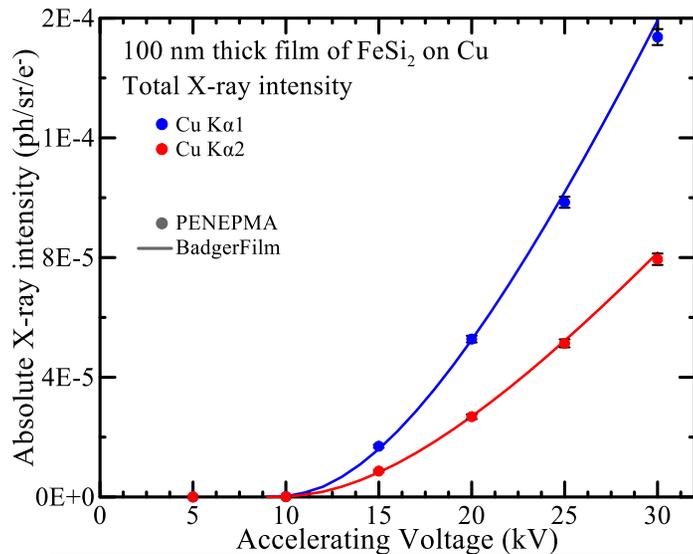
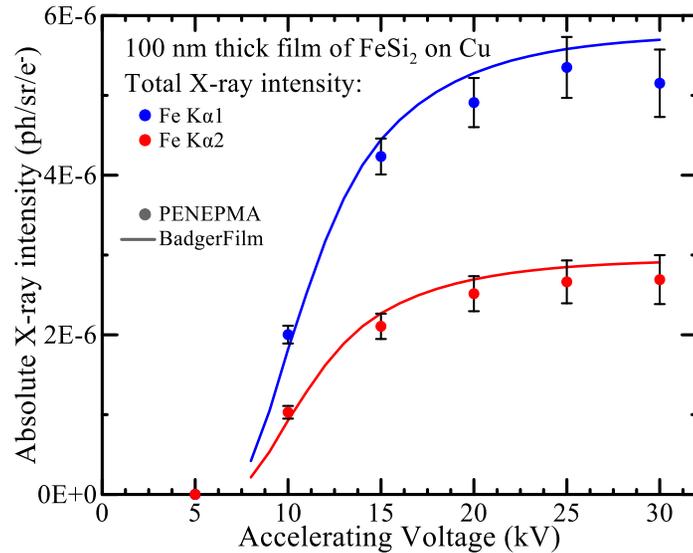
Absolute Total X-ray Intensity

- Absolute X-ray intensity (ph/electron/sr) using recent atomic data
 - Compound bulk sample



Absolute Total X-ray Intensity

- Absolute X-ray intensity (ph/electron/sr) using recent atomic data
 - Film on substrate



BadgerFilm Features

Fix thickness or composition

Custom standards

Load & Save

Export data

Converge even if far from solution

The screenshot displays the BadgerFilm software interface. On the left, there are settings for fluorescence, take-off angle (35 degrees), and the Pouchou, Pichoir (PAP) Scanning model. The 'Layers definition' section shows a single layer 'Substrate' with a thickness of 'Inf'. A table lists the layers with columns for Element (El), Line, concentration (conc), k-ratio, measured k-ratio, excitation energy (E), and Standard. The table shows Si and O layers with their respective parameters. A 'Load & Save' button is visible. The 'Export data' button is also present. The 'Converge even if far from solution' text points to the convergence parameters: NPEGGED = 1, NITER = 8, NFEV = 36, and a list of parameters P[0] through P[4]. The 'Custom standards' text points to the 'Standard' column in the table. The 'Fix thickness or composition' text points to the 'Thickness' field. On the right, there is a periodic table and a graph of k-ratio vs Energy (keV) for Al Ka, Si Ka, and O Ka lines.

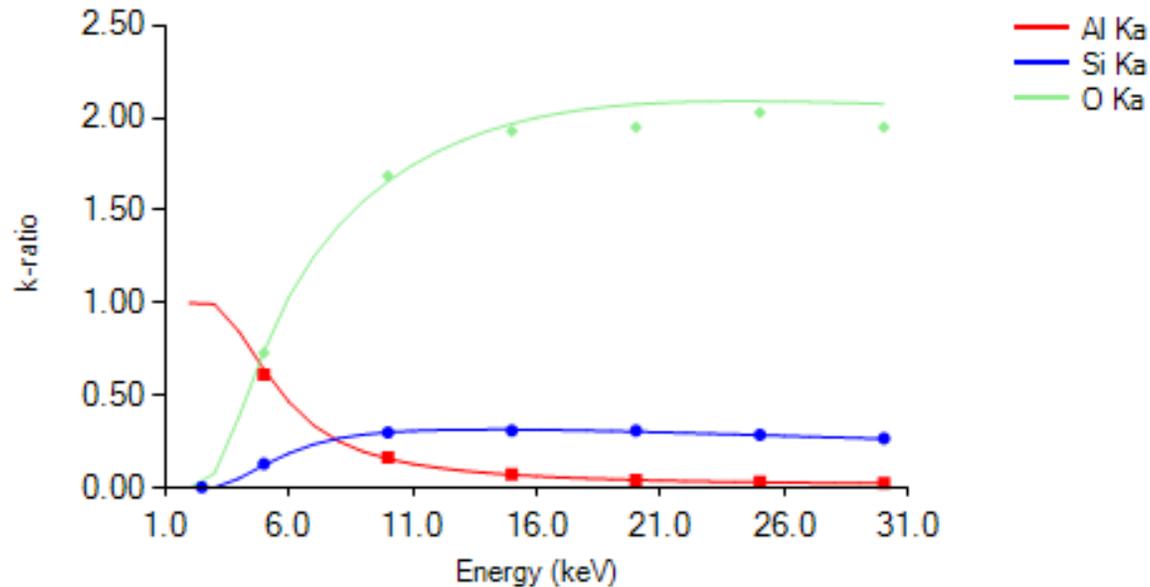
El	Line	conc (wt)	k-ratio	k-ratio meas.	E (kV)	Standard
Si	Ka	0.467400014...	0.30398816...	0.31	20	
Si	Ka	0.467400014...	0.28539445...	0.287	25	
Si	Ka	0.467400014...	0.26523222...	0.268	30	
O	Ka	0.532599985...	0.73699442...	0.73	5	Y3Fe5O12.txt
O	Ka	0.532599985...	1.65693981...	1.687	10	Y3Fe5O12.txt
O	Ka	0.532599985...	1.96908752...	1.93	15	Y3Fe5O12.txt
O	Ka	0.532599985...	2.07390891...	1.95	20	Y3Fe5O12.txt
O	Ka	0.532599985...	2.09021475...	2.03	25	Y3Fe5O12.txt

- Advanced options:
 - change atomic parameters (MACs, ...)
 - restrict the domain of variation of the variables (concentrations, thicknesses)

Thin film analysis – Example 1

- Al film on SiO₂ (data from Pouchou 2002)
- X-ray intensities: Al K α , Si K α and O K α
k-ratio measured at 5, 10, 15, 20, 25 and 30 kV
Standards used: Pure Al, Pure Si and Y₃Fe₅O₁₂

- BadgerFilm

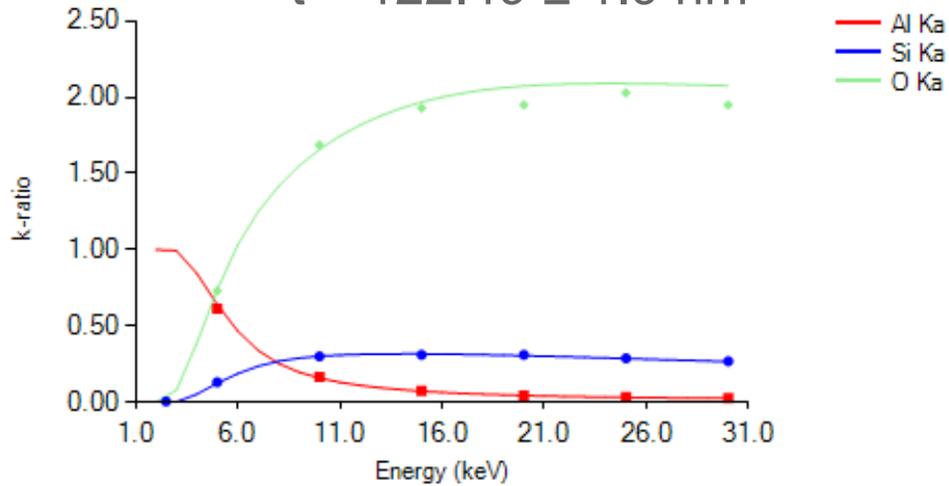


- $t = 122.49 \pm 1.9$ nm

Thin film analysis – Example 1

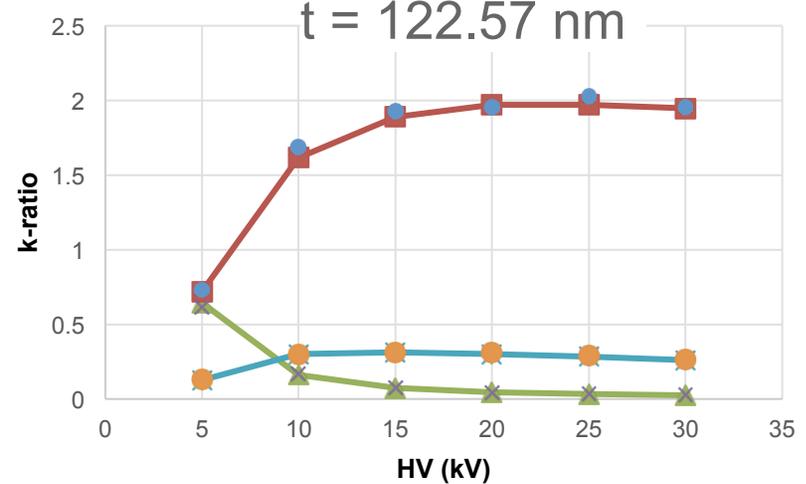
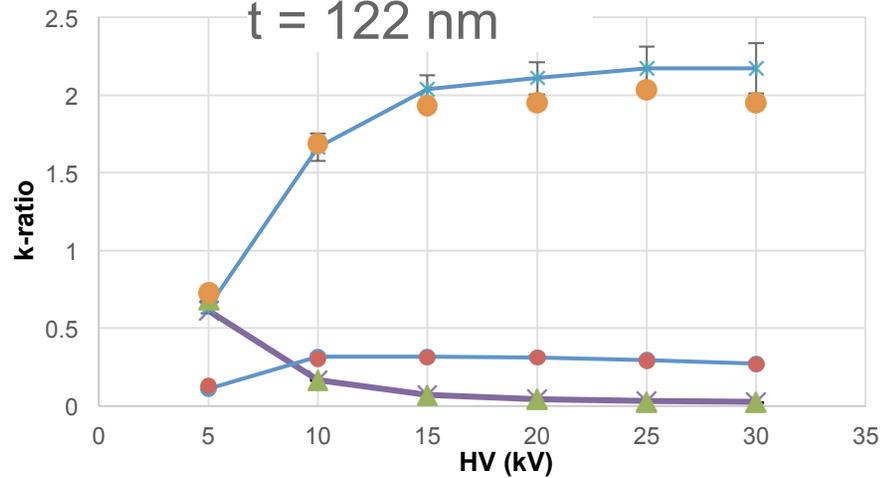
- BadgerFilm
t = 122.49 ± 1.9 nm

- STRATAGem
t = 122.34 nm



- PENEPMMA
t = 122 nm

- GMRFILM
t = 122.57 nm



Thin film analysis – Example 2

- Multilayer Ni-Cr on Fe-Gd-Pt on Si substrate (data from Pouchou 1993)
- X-ray intensities: Ni K α , Cr K α , Fe K α , Gd L α , Pt M α
k-ratio measured at 20, 25 and 30 kV
Standards used: Pure Elements for all

C:\Users\Aurélien\Desktop\Thin film prog test\Pouchou 1993.txt

Secondary fluorescence
 Characteristic fluorescence
 Bremsstrahlung fluorescence

Take-off angle (in degrees)

Phi(ρz) model
 Bastin's Scanning (1986)
 Bastin's Scanning (1990)
 Pouchou, Pichoir (PAP) Scanning (1990)
 Packwood's MAS (1986)

Units
 Thicknesses defined in:
 Angstrom $\mu\text{g}/\text{cm}^2$

Layers definition
 Number of layers + substrate:
 Layer 1
 Layer 2
 Substrate
 Thickness: Angstrom
 Fix thickness of the selected layer?
 Selected layer defined by:
 weight fraction atomic formula

Elt	Line	conc (wt)	k-ratio	k-ratio meas.	E (kV)	Standard
Fe	K α	0.499535351...	0.02531833...	0.0258	20	
Fe	K α	0.499535351...	0.01487999...	0.0147	25	
Fe	K α	0.499535351...	0.00988897...	0.0098	30	
Gd	L α	0.292110204...	0.01225288...	0.0123	20	
Gd	L α	0.292110204...	0.00756003...	0.0076	25	
Gd	L α	0.292110204...	0.00526366...	0.0052	30	
Pt	M α	0.206758648...	0.00811221...	0.0083	20	
Pt	M α	0.206758648...	0.00592102...	0.0058	25	

Layer density (g/cm^3)

*** TestLinFit status = {0} CHI-SQUARE = 2.93546680398359 (14 DOF)
 NPAR = 9
 NFREE = 7
 NPEGGED = 1
 NITER = 8
 NFEV = 79

P[0] = 688.417233134283 +/- 34.5435598265627 (INITIAL 100)
 P[1] = 241.801570746341 +/- 12.3972710304743 (INITIAL 100)
 P[2] = 1000000000 +/- 0 (INITIAL 1000000000)
 P[3] = 0.142993525857 +/- 0.00862961649453574 (INITIAL 0.5)
 P[4] = 0.853450601865417 +/- 0.0431048638886661 (INITIAL 0.5)
 P[5] = 0.499535345859573 +/- 0.0265292196081283 (INITIAL 0.33)
 P[6] = 0.292110206954519 +/- 0.0163839311051556 (INITIAL 0.33)
 P[7] = 0.206758649062583 +/- 0.0118983162341946 (INITIAL 0.33)

X axis Y axis
 Min 18 0
 Max 30 0.10

Thin film analysis – Example 2

- Multilayer Ni-Cr on Fe-Gd-Pt on Si substrate (data from Pouchou 1993)
- X-ray intensities: Ni $K\alpha$, Cr $K\alpha$, Fe $K\alpha$, Gd $L\alpha$, Pt $M\alpha$
k-ratio measured at 20, 25 and 30 kV
Standards used: Pure Elements for all

Method	Layer 1			Layer 2			
	Ni wt%	Cr wt%	T (Å)	Fe wt%	Gd wt%	Pt wt%	T (Å)
RBS measurements	14.4	85.6	683	51.4	28.6	20.0	246
Pouchou (1993)Strata	14.7	85.4	671	52.0	28.7	19.3	242
GMRF PAP w CF 30 kV	14.3	85.7	688	51.1	29.3	19.6	242
BadgerFilm	14.3	85.3	688	50.0	29.2	20.7	242

- Convergence even if initial values far from solutions
(Ni 50 wt%, Cr 50 wt%, Fe 33 wt%, Gd 33 wt% and Pt 33 wt%.
Thicknesses: Layer #1 = 100 Å, Layer #2 = 100 Å)

Conclusions

- Free Thin film analysis program (+ code available)
- Easy to use GUI
- Calculated absolute X-ray intensities similar to Monte Carlo simulations
- Good performances (film thickness and composition)
- Further developments:
 - More testing against other experimental data
 - Import STRATAGem file format
 - Uncertainties on experimental k-ratios

Support for this research came from the
National Science Foundation:

EAR-1337156 (JHF)

EAR-1554269 (JHF)

EAR-1849386 (JHF)



Thank you for your attention

Secondary fluorescence by characteristic X-rays

- Comparison with PENEPMA

