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 **<u>bulk</u>** homogeneous materials (not 10-100 nm thin layers).

➔ What are the issues for thin films?

➔ How to perform thin film analysis?

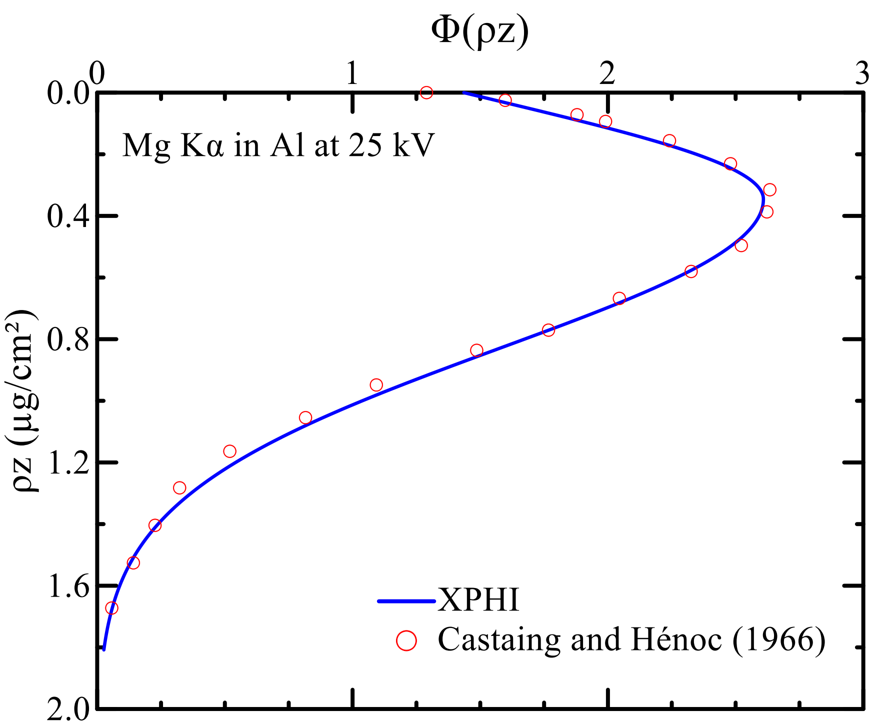
➔ How precise/accurate are such analyses?

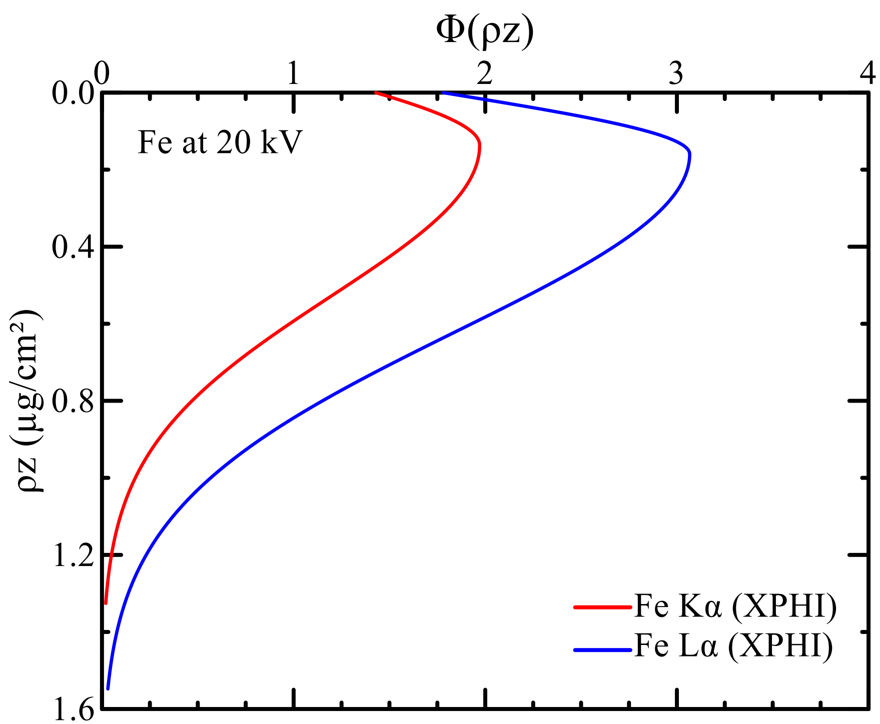
Phi-rho-z for bulk materials

- 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

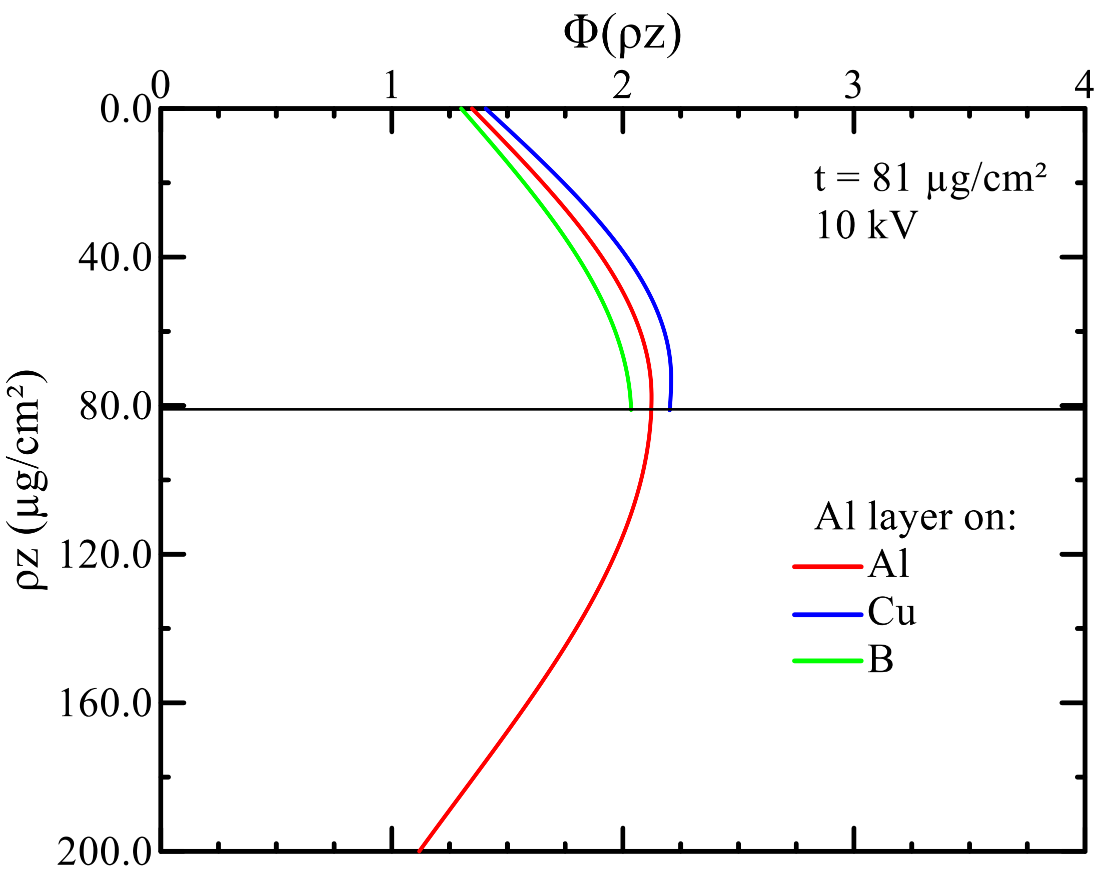




Phi-rho-z for thin film

- 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

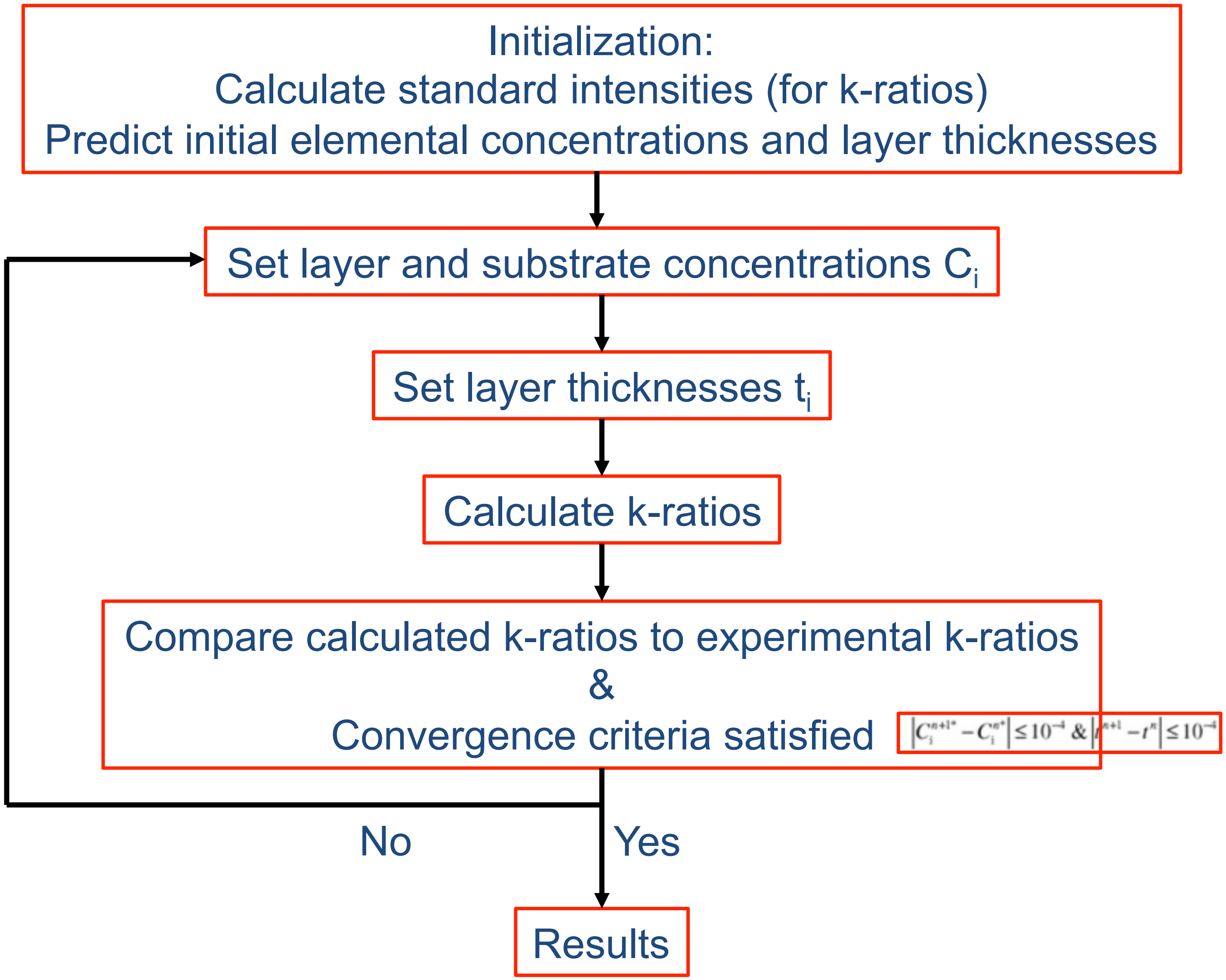
- Integration of the $\phi(\rho z)$ to calculate total emitted X-ray intensity for a given layer

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

- ➔ 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

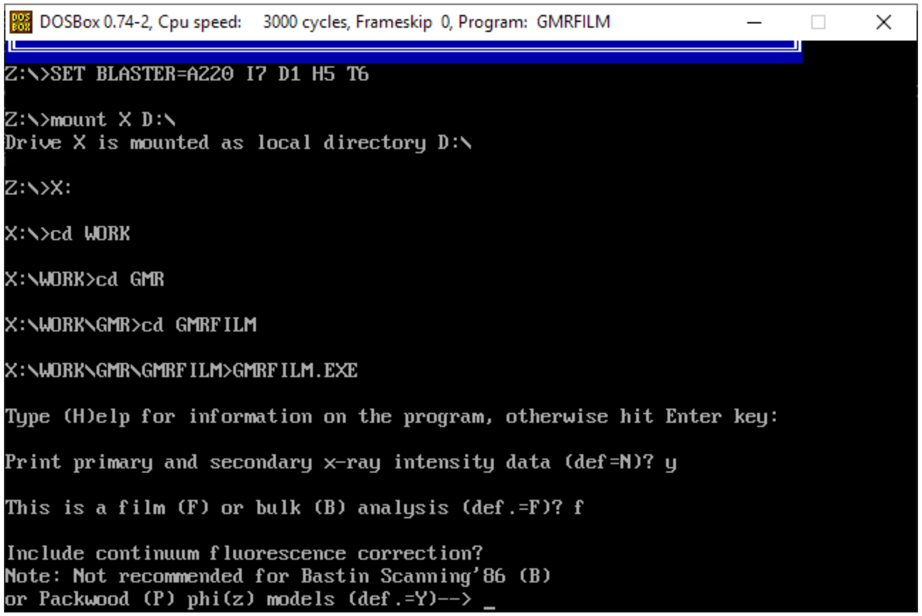
- → Iteration until convergence



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



BadgerFilm

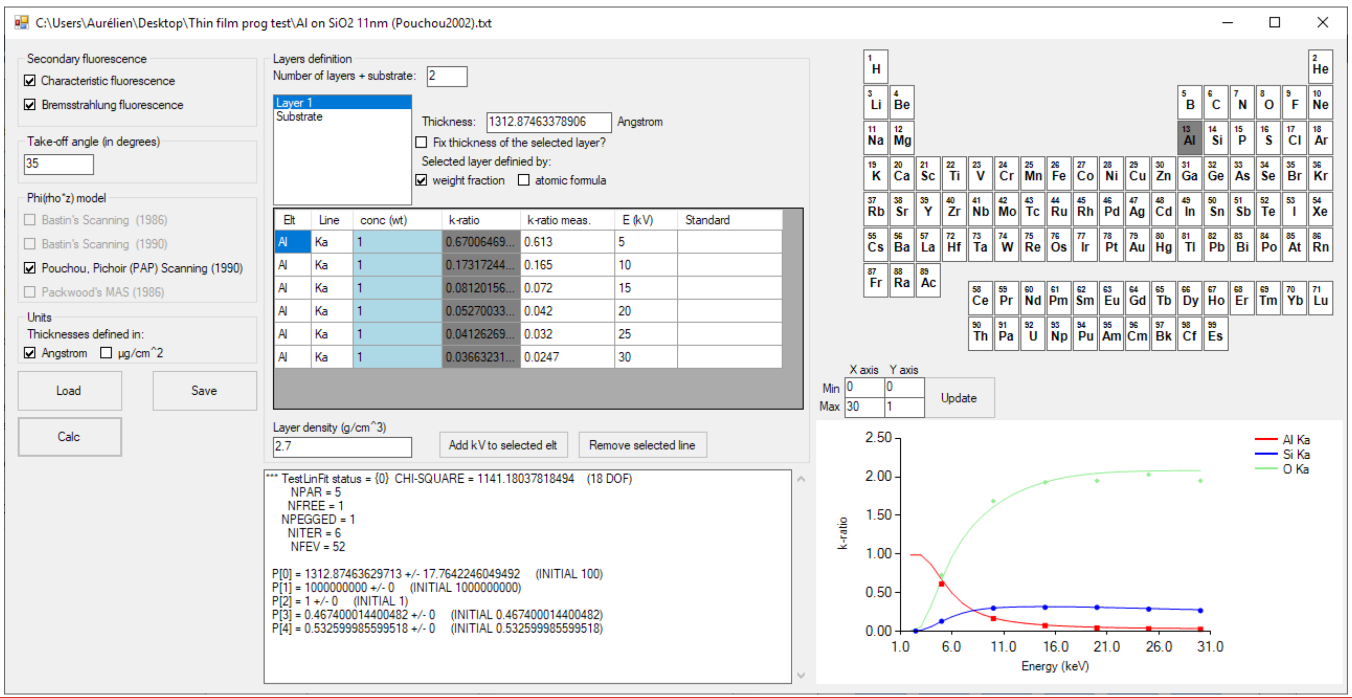
- Development of a thin film analysis program
  ➔ User-friendly graphical interface

  ➔ 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:

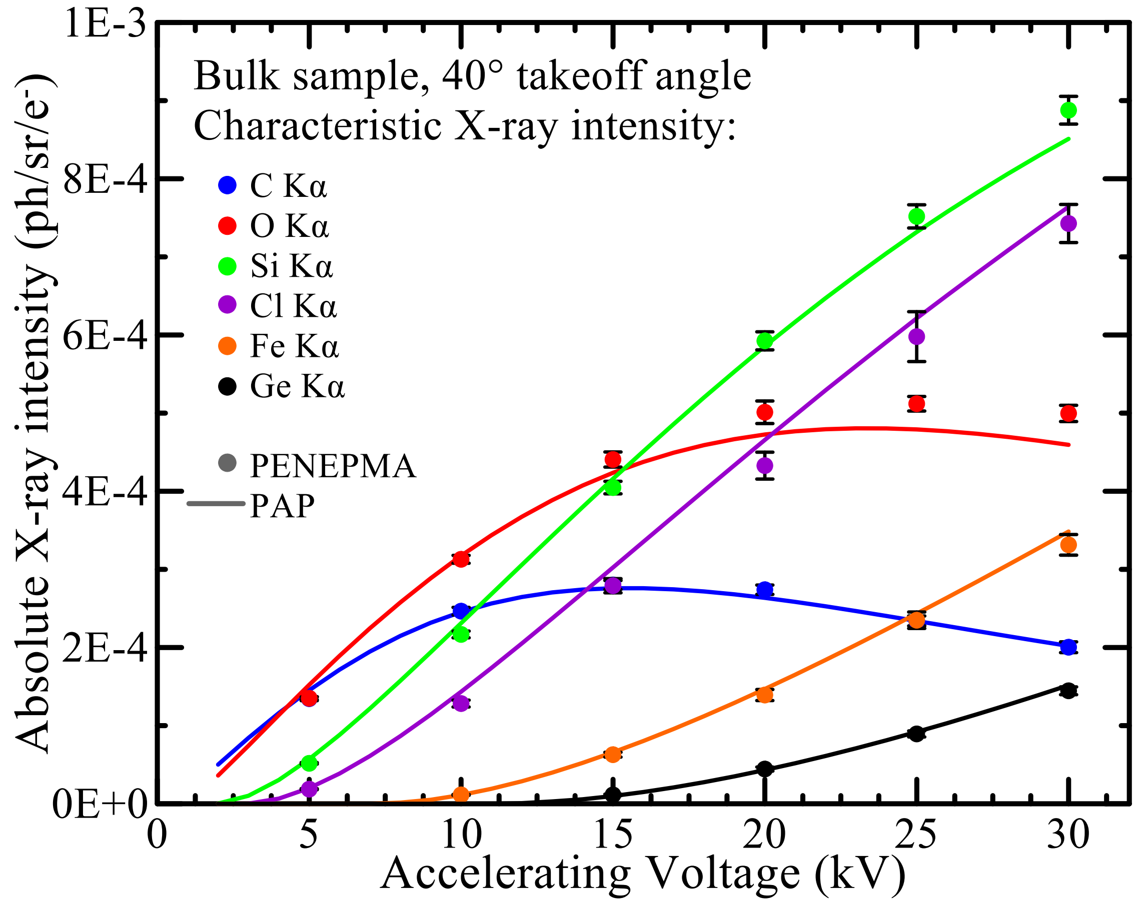
2) X-ray intensity generated by Characteristic X-rays

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 $E>E_{ionization}$ (even the low intensity X-rays)

  ➔ Calculate $\phi(\rho z)$ distribution for all characteristic X-rays

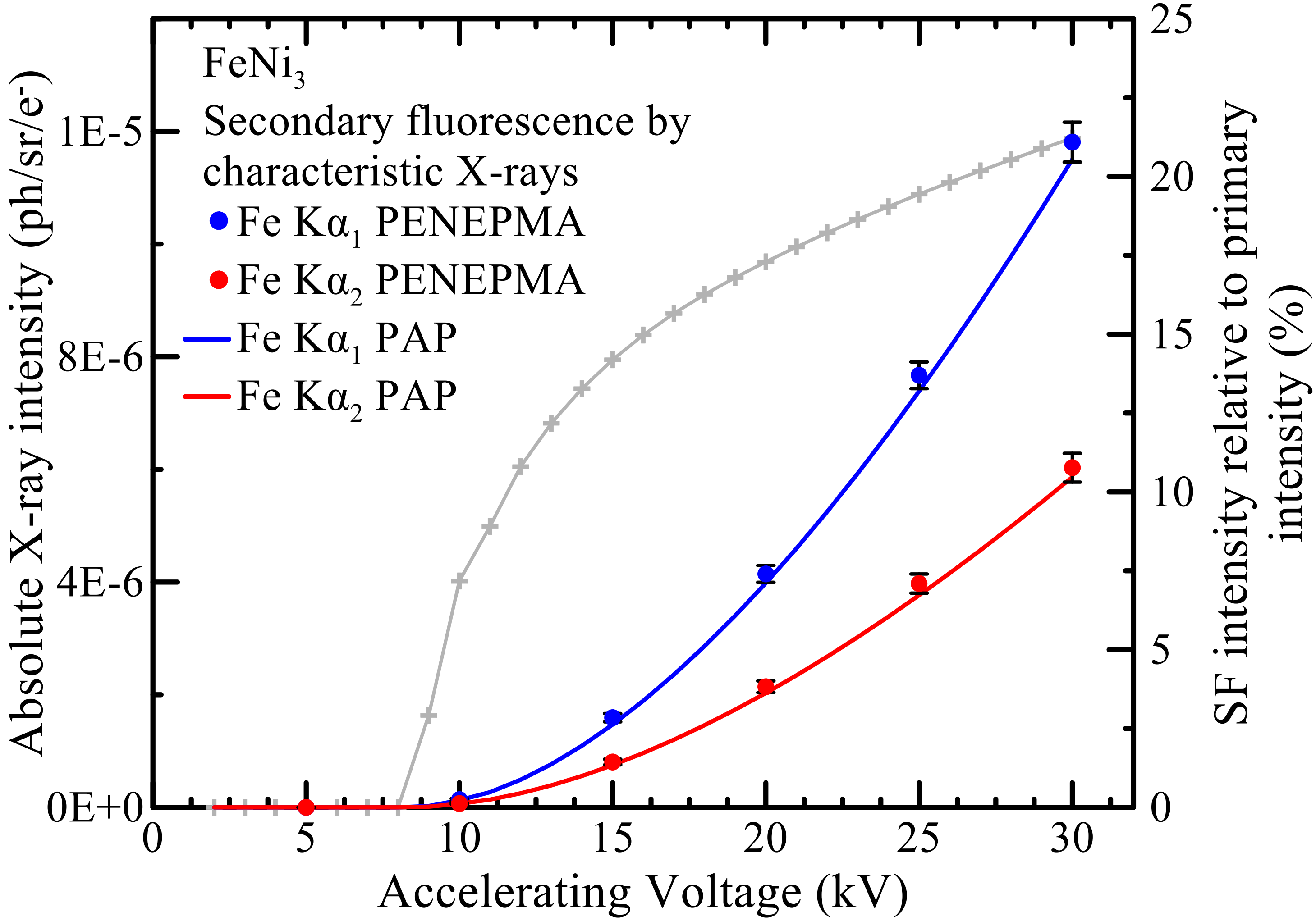
  ➔ Calculate SF generated by each $\phi(\rho z)$ distributions (numerical integration over mass depth)

  ➔ Sum all the contributions to calculate final SF by characteristic X-rays

⚠ GMRFilm overestimates SF compared to Monte Carlo simulations (PENEPMA)

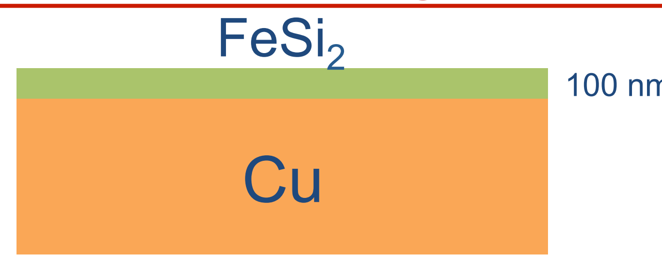
Secondary fluorescence by characteristic X-rays

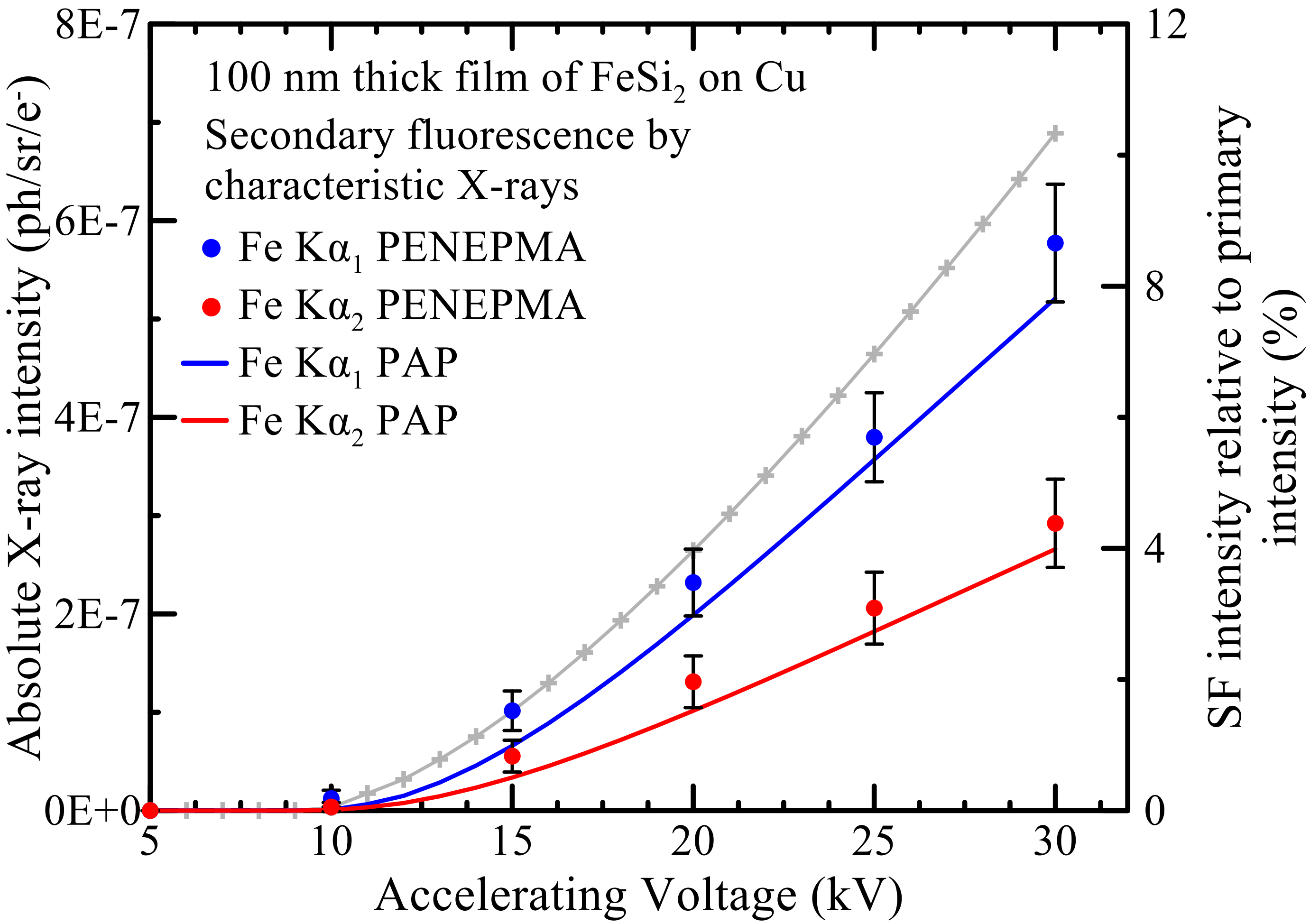
- $FeNi_3$ bulk sample
  Fluorescence of Fe Kα by Ni (comparison with PENEPMA)



Secondary fluorescence by characteristic X-rays

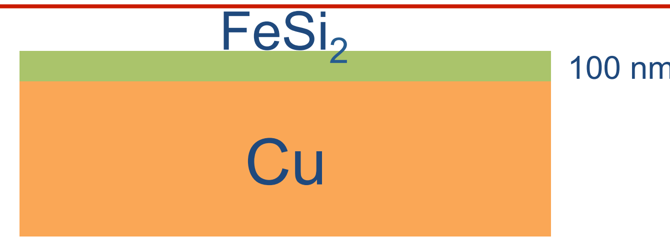
- 100 nm thick $FeSi_2$ film on bulk Cu
  Fluorescence of Fe Kα by Cu
  (comparison with PENEPMA)

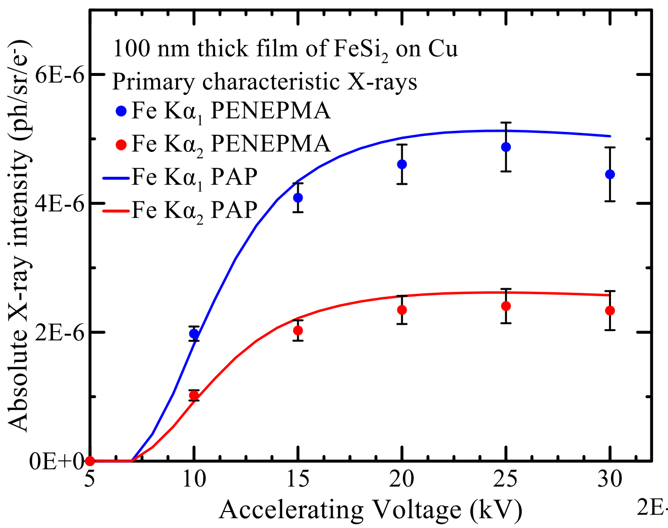


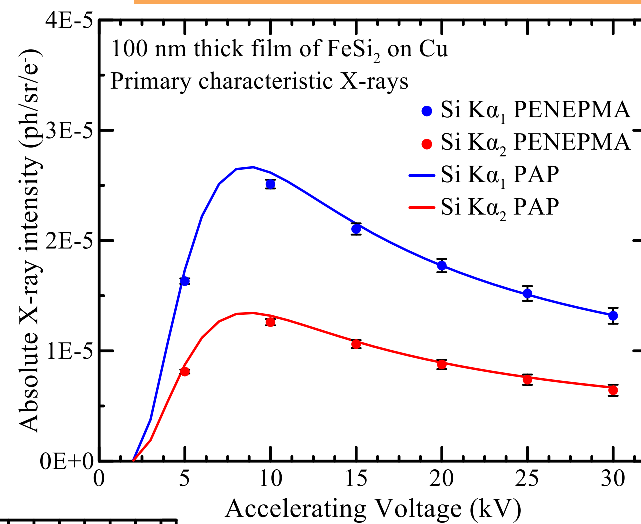


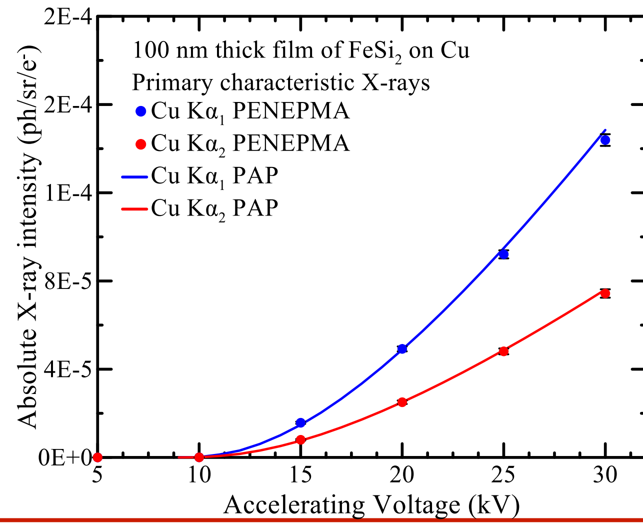
Characteristic X-rays

- 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 → Ei (from Ec to E0)

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

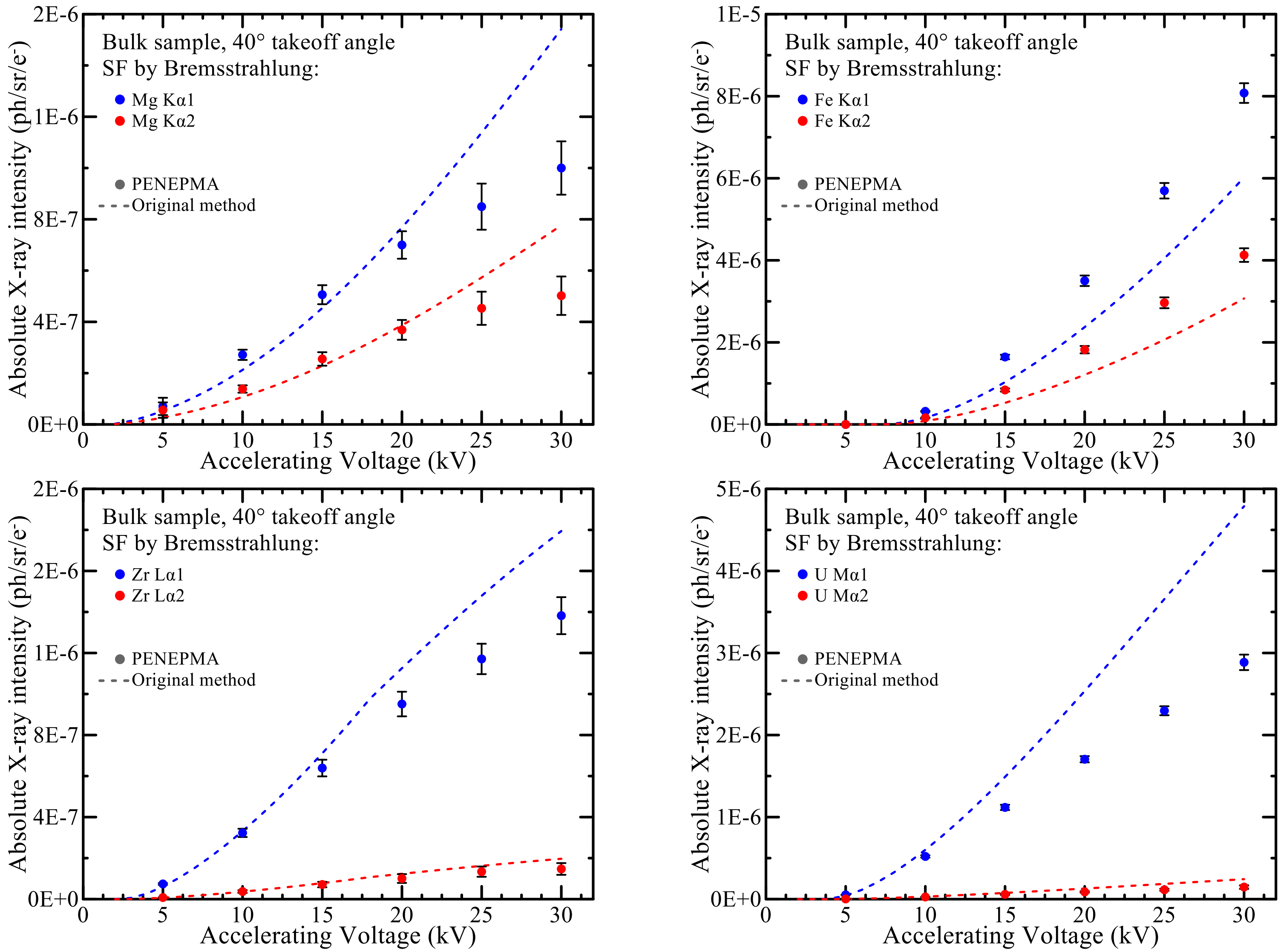
➔ SF is calculated for bremsstrahlung of energy Ei

repeat with next energy Ei

➔ All the SF contributions are integrated from Ec to E0

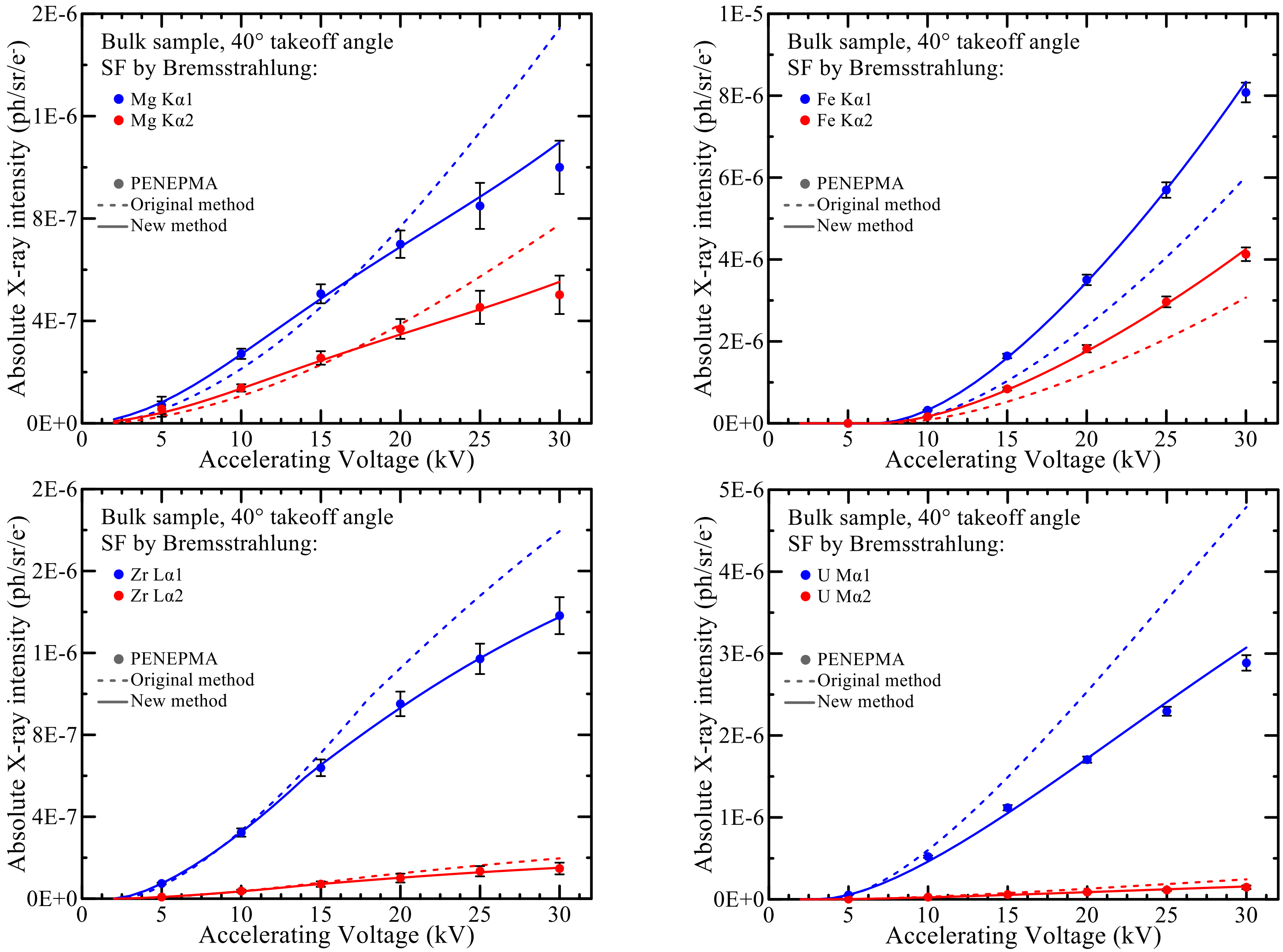
Secondary fluorescence by bremsstrahlung

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



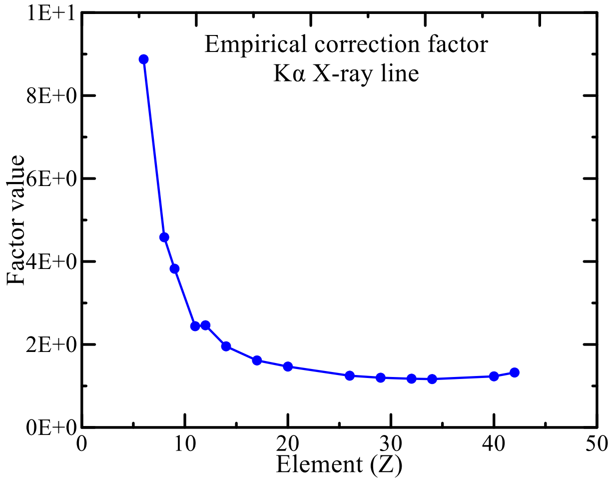
Secondary fluorescence by bremsstrahlung

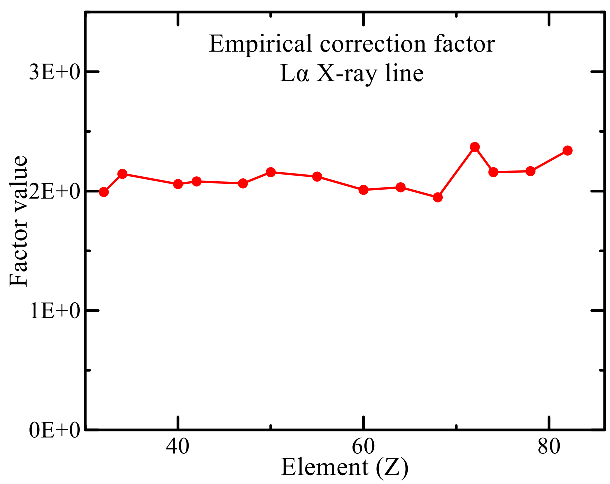
- Using two correction factors: almost perfect matching with PENEPMA results

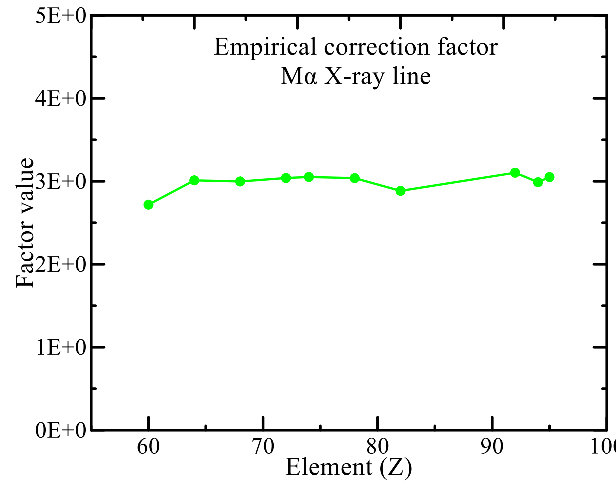


Secondary fluorescence by bremsstrahlung

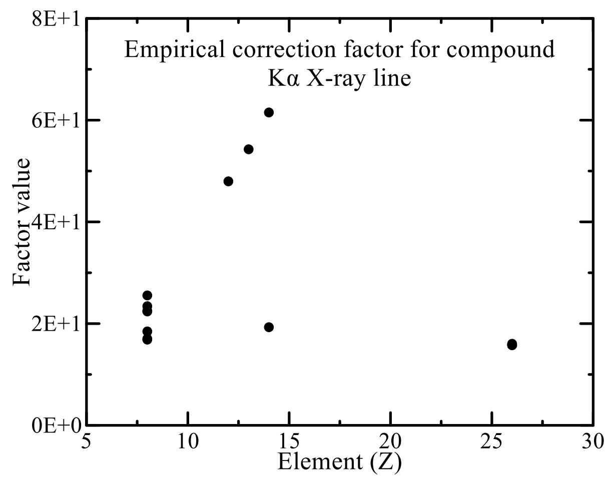
- Correction factors are easy to predict for pure elements







- However, correction factors are hard to predict for compounds

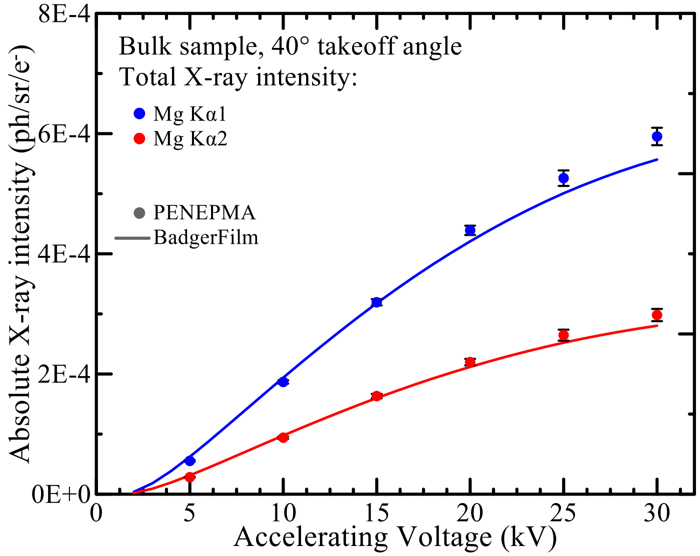


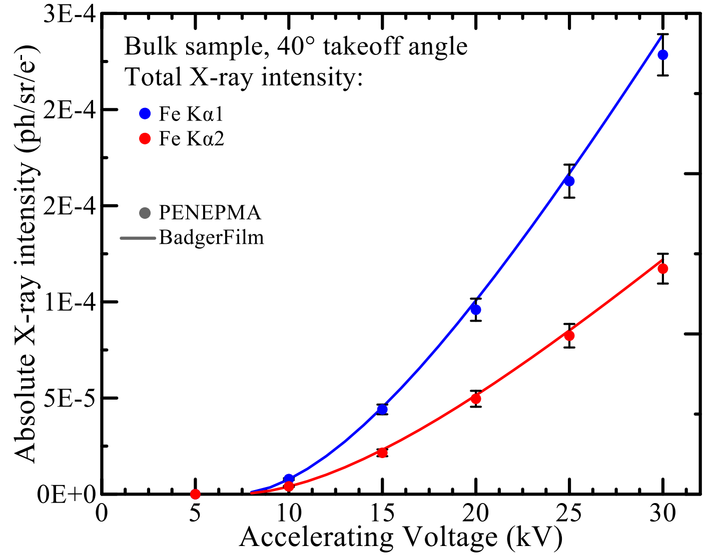
- Other method: use MC simulations to generate bremsstrahlung $\phi(\rho z, E)$ curves (Yuan et al. 2019)

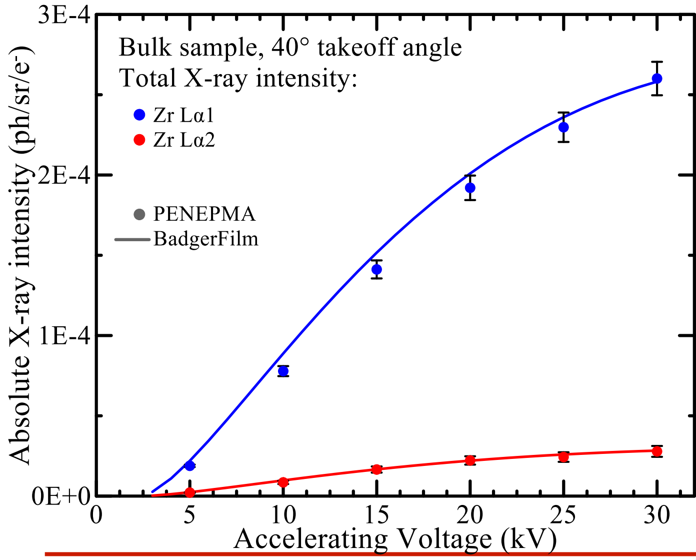
Y. Yuan et al., Microscopy and Microanalysis (2019), 25, 92–104

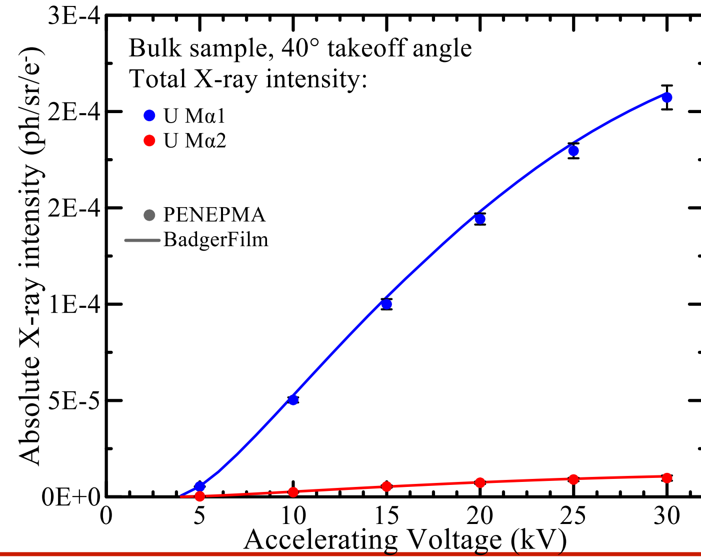
Absolute Total X-ray Intensity

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



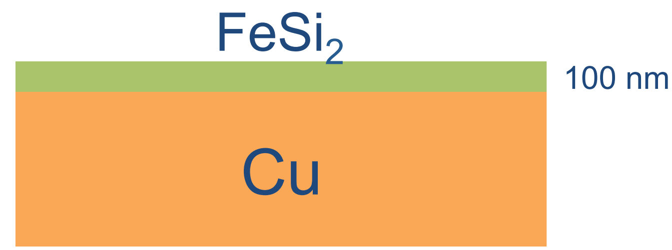


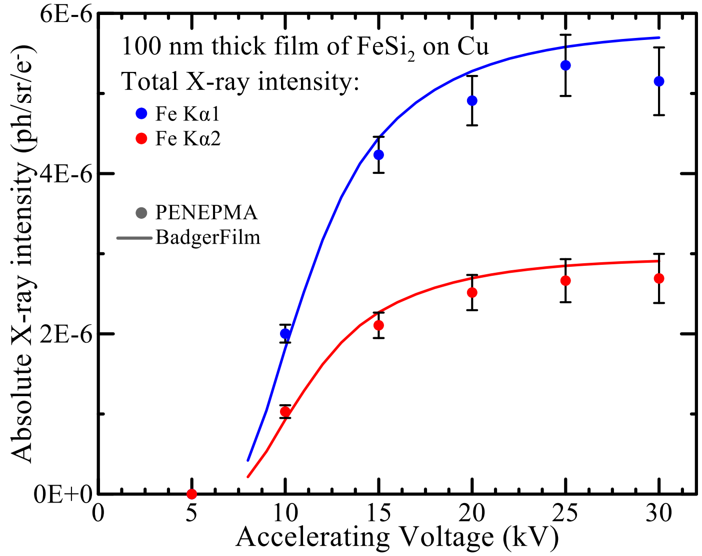


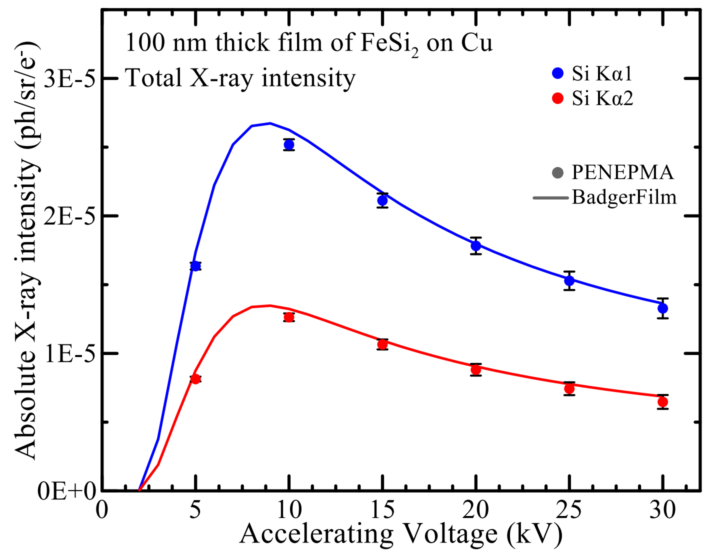


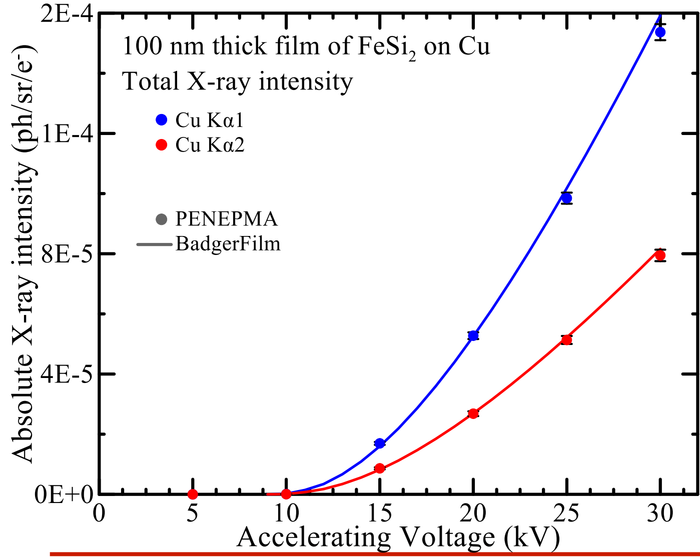
Absolute Total X-ray Intensity

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

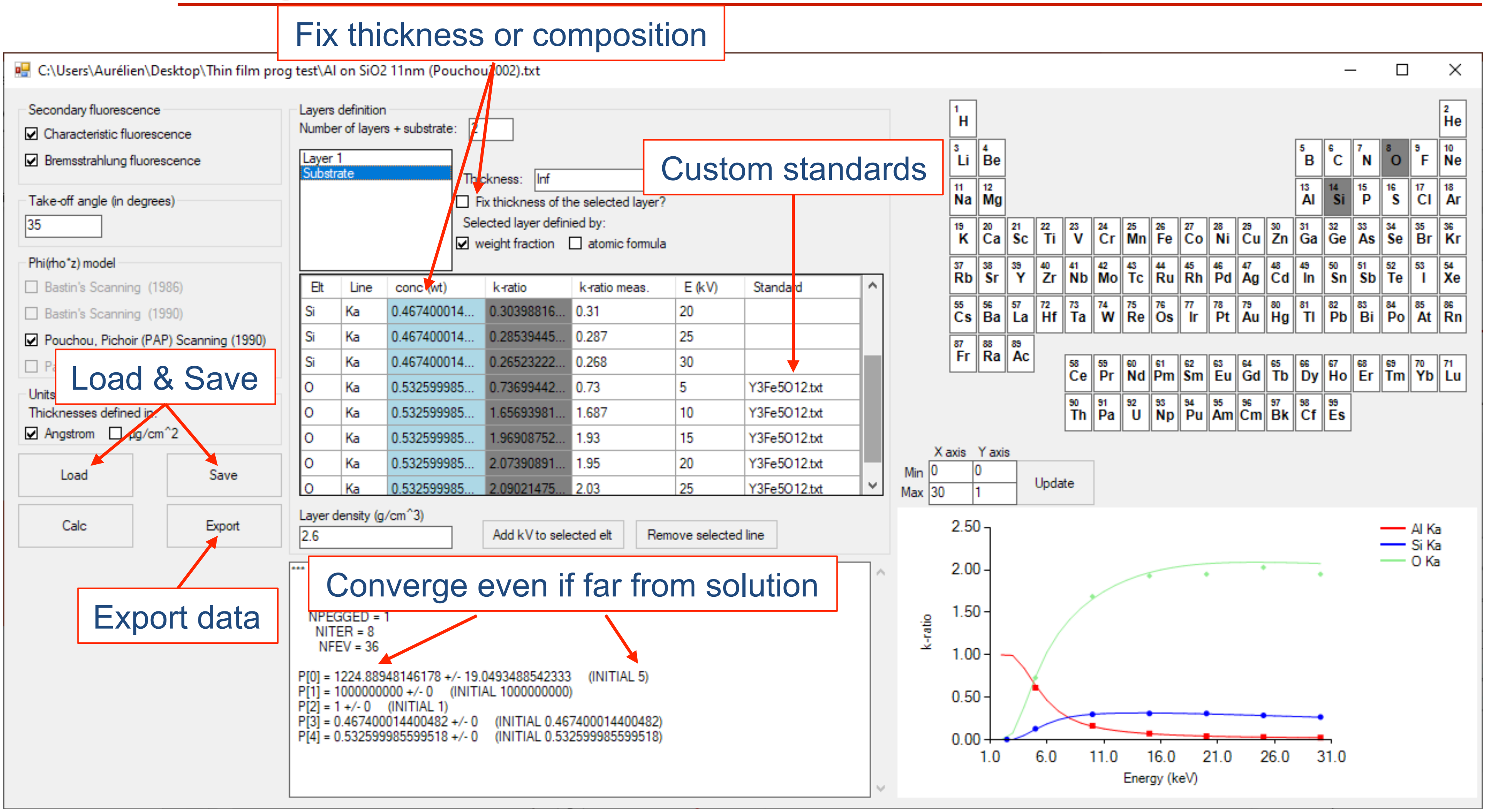








BadgerFilm Features



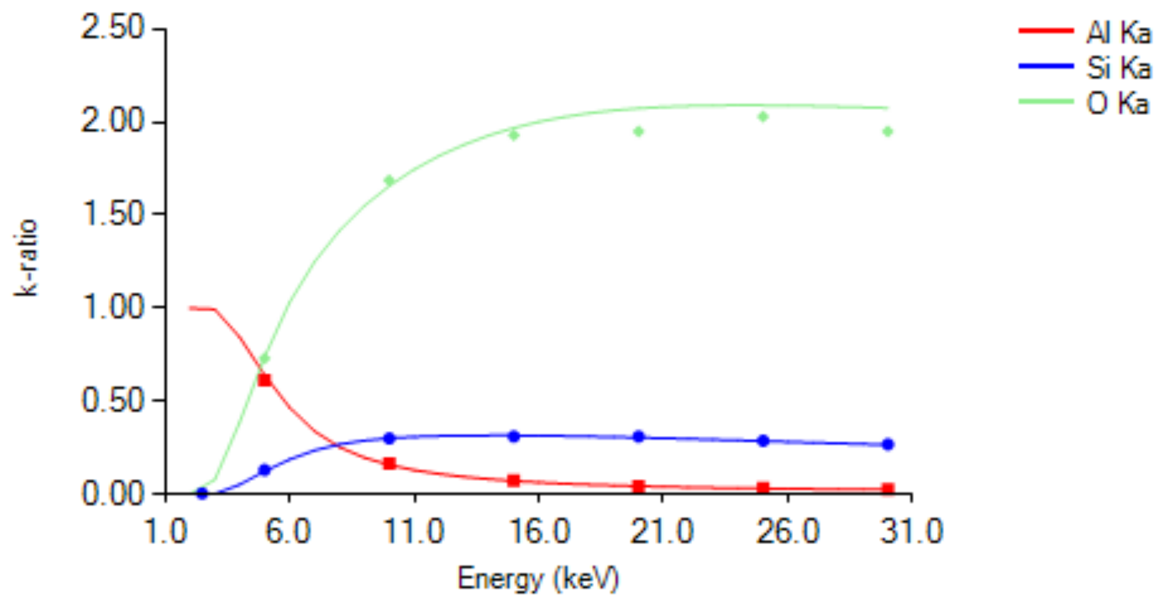
Elt	Line	conc (wt)	k-ratio	k-ratio meas.	E (kV)	Standard
Si	Ka	0.467400014...	0.30398816...	0.31	20	
Si	Ka	0.467400014...	0.28539445...	0.287	25	
Si	Ka	0.467400014...	0.26523222...	0.268	30	
O	Ka	0.532599985...	0.73699442...	0.73	5	Y3Fe5O12.txt
O	Ka	0.532599985...	1.65693981...	1.687	10	Y3Fe5O12.txt
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 SiO_2 (data from Pouchou 2002)
- X-ray intensities: Al Kα, Si Kα and O Kα
  k-ratio measured at 5, 10, 15, 20, 25 and 30 kV
  Standards used: Pure Al, Pure Si and $Y_3Fe_5O_{12}$

- BadgerFilm

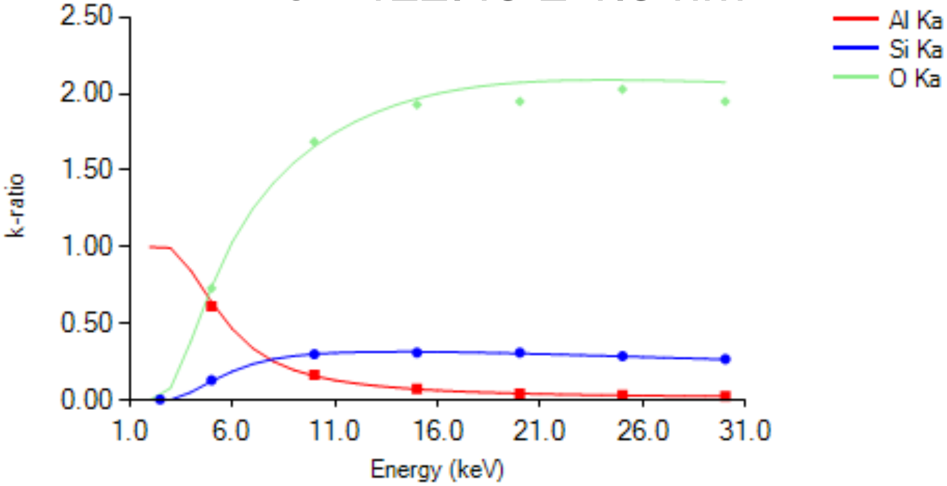


- t = 122.49 ± 1.9 nm

J.L. Pouchou, Mikrochimica Acta, 138 (2002) 133-152

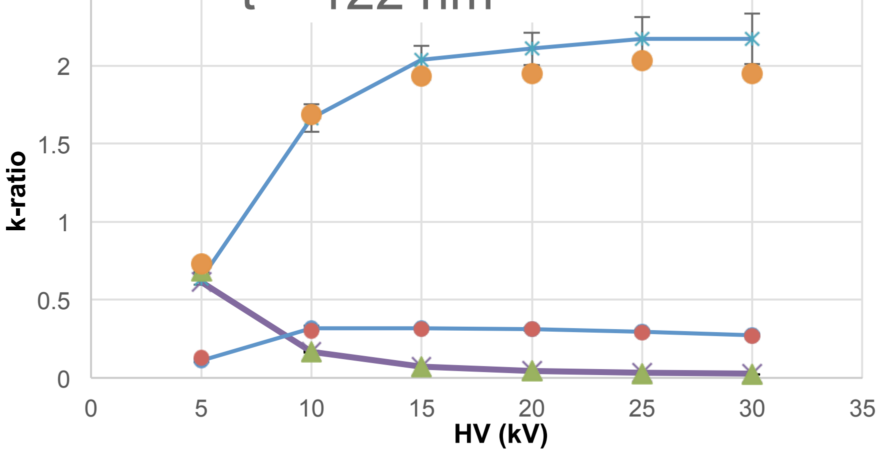
Thin film analysis – Example 1

- BadgerFilm
  t = 122.49 ± 1.9 nm

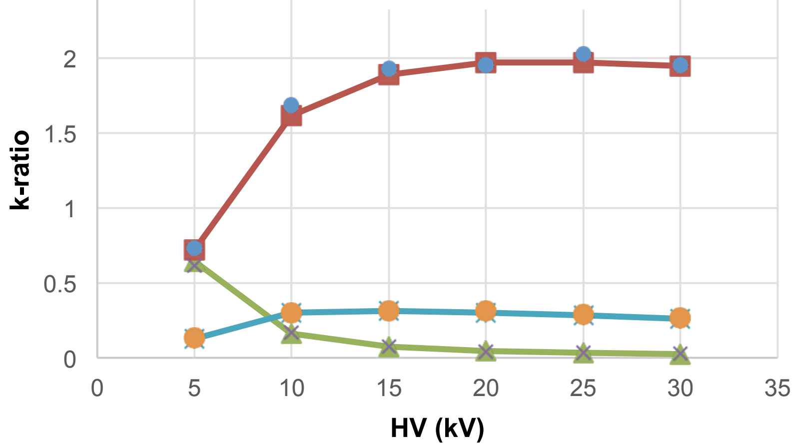


- STRATAGem
  t = 122.34 nm

- PENEPMA
  t = 122 nm

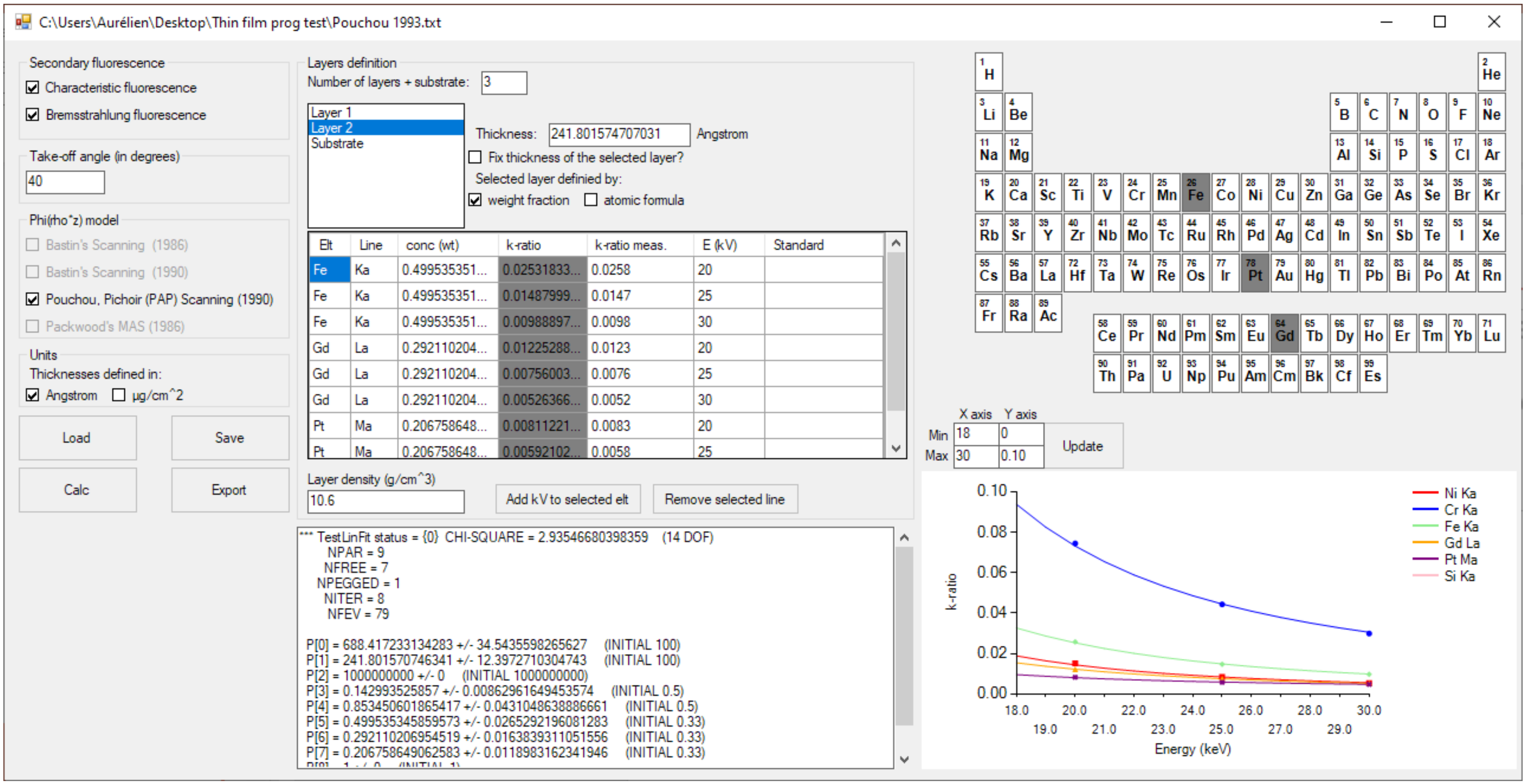


- GMRFILM
  t = 122.57 nm



Thin film analysis – Example 2

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



Thin film analysis – Example 2

- Multilayer Ni-Cr on Fe-Gd-Pt on Si substrate (data from Pouchou 1993)
- X-ray intensities: Ni Kα, Cr Kα, Fe Kα, Gd Lα, Pt Mα
  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)

J.L. Pouchou, Analytica Chimica Acta, 283 (1993) 81-97

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

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Thank you for your attention

Secondary fluorescence by characteristic X-rays

- Comparison with PENEPMA