BADGERFILM: A “NEW” THIN FILM ANALYSIS PROGRAM (WITH OTHER USEFUL APPLICATIONS) FOR EPMA

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EPMA of thin film

- Electron Probe Microanalysis (EPMA)
  ➔ effective and nondestructive technique to determine thickness and composition of layered specimens.

Conventional EPMA 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?

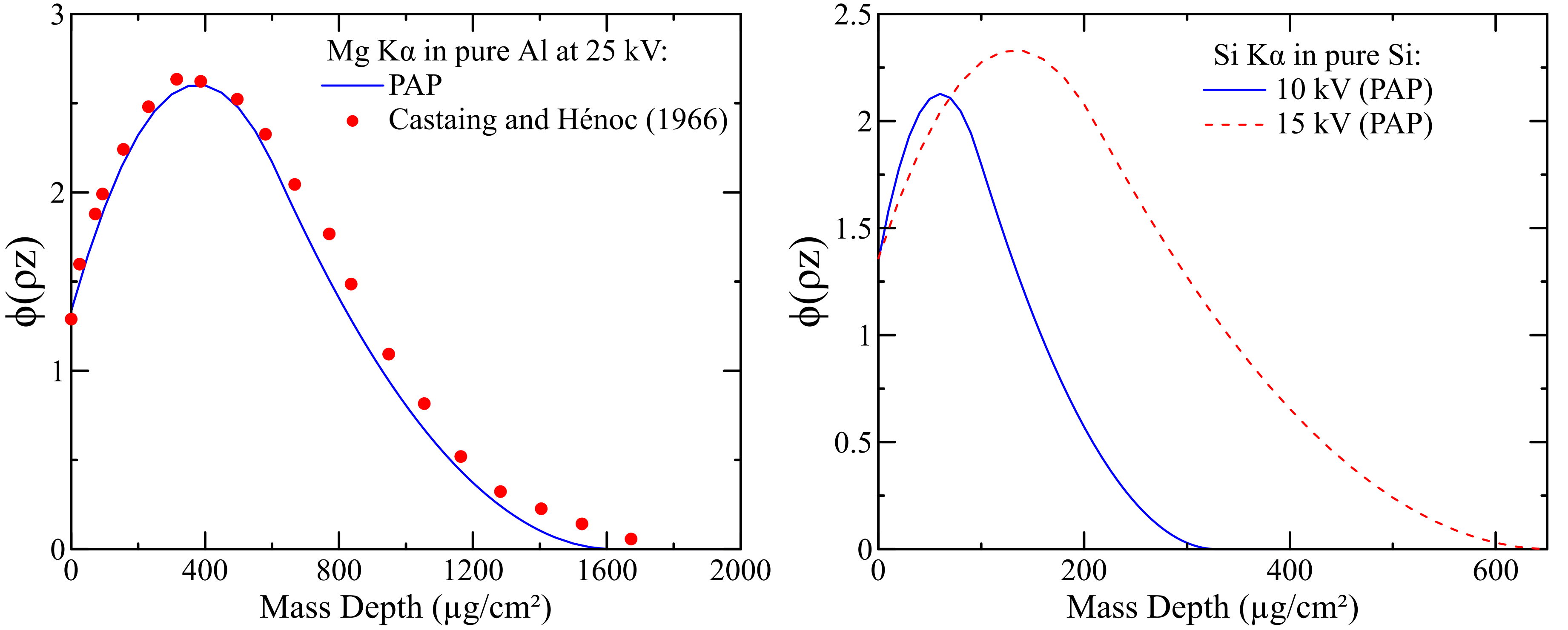
➔ How precise/accurate are such analyses?

Phi-rho-z distribution in bulk materials

- Transformation of k-ratios into elemental composition
  ➔ matrix-correction procedures
    ➔ assume homogeneous composition

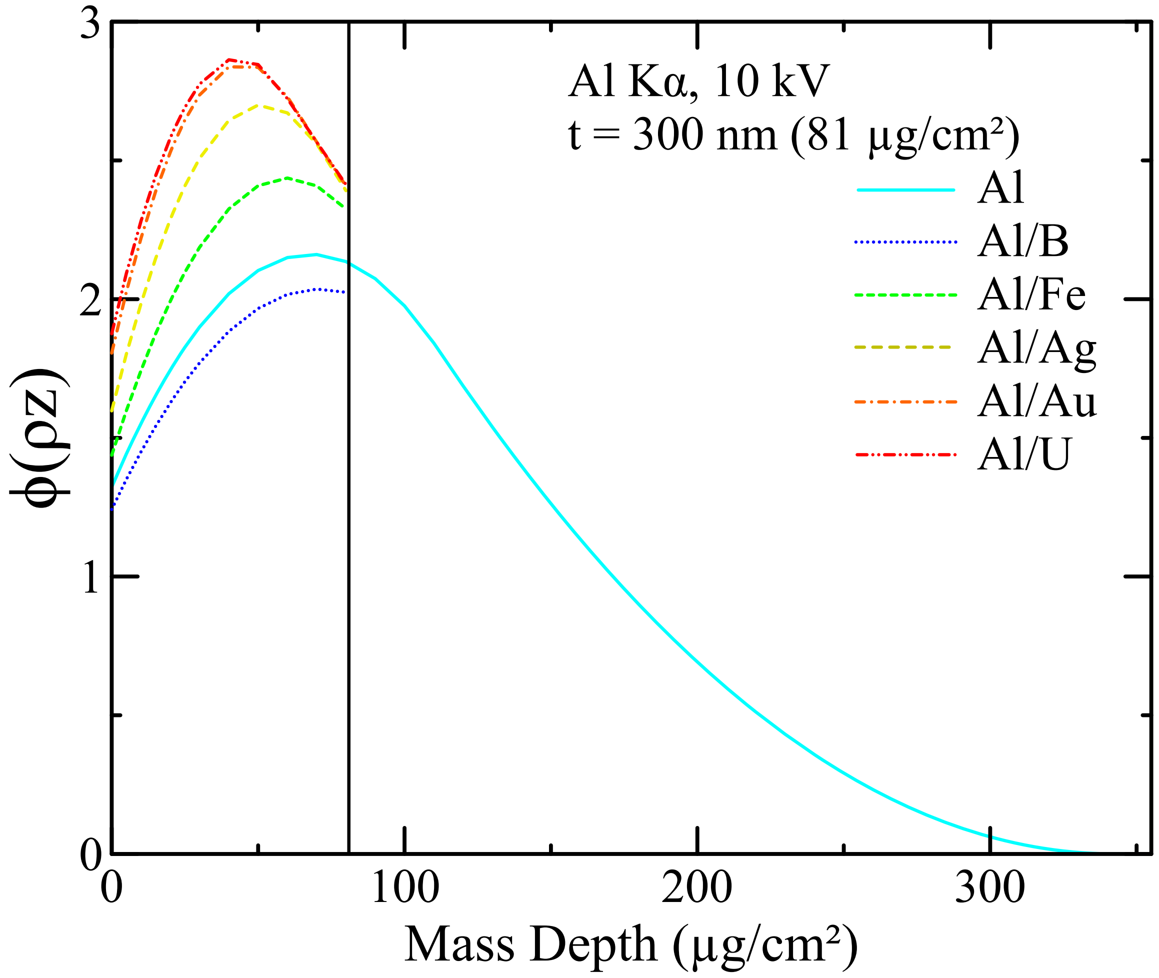
- Phi-rho-z procedure (PAP, XPP, XPHI, ...)
  ➔ realistic description of the ionization depth distribution

  ➔ different for each sample, element, characteristic X-ray and kV.



Phi-rho-z distribution in thin films

- Phi-rho-z distributions can be used for thin films
  ➔ but modification of the original theory required



Characterization of thin films

- Calculation of a theoretical k-ratio:

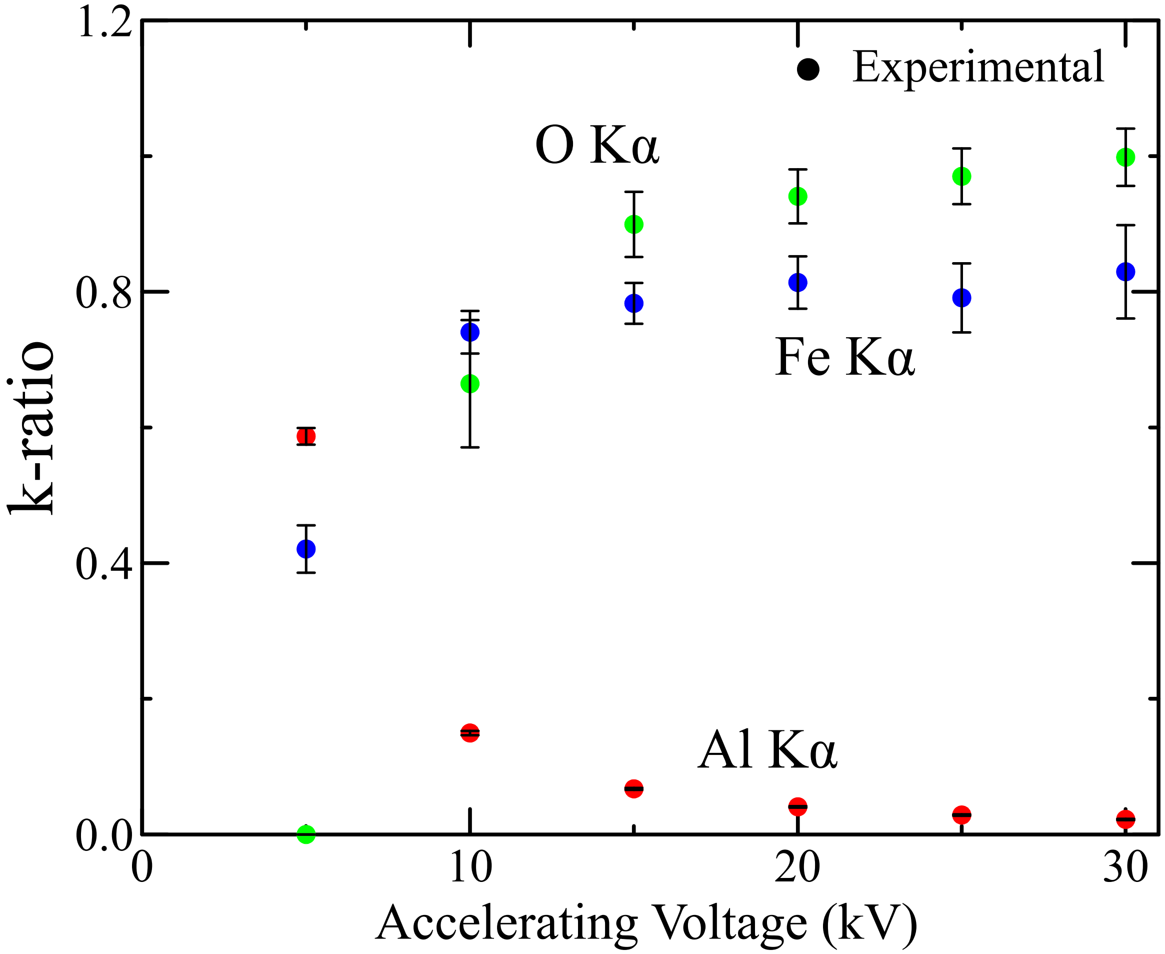
$$k_i = \frac{A\ C_i \int_{\rho z_1}^{\rho z_2} \Phi_i(\rho z, C)\ e^{-\frac{\mu}{\rho}(E,C)\ \frac{\rho z}{\sin\theta}}\ d\rho z}{B\ C_i^{std} \int_0^{\infty} \Phi_i^{std}(\rho z, C^{std})\ e^{-\left(\frac{\mu}{\rho}(E,C^{std})\right)_{std} \frac{\rho z}{\sin\theta}}\ d\rho z}$$

- C_i: concentration of element *i*.
- $\Phi_i(\rho z)$: ionization depth distribution for element I and associated X-ray line.
- $\frac{\mu}{\rho}$: mass absorption coefficient (dependent of the X-ray energy and sample composition).
- $\rho z_1, \rho z_2$: mass depth of the layer.
- θ: takeoff angle of the spectrometer.

➔ The calculations are repeated in an iterative process in which the thicknesses and compositions are adjusted until the calculated k-ratios match the experimental k-ratios.

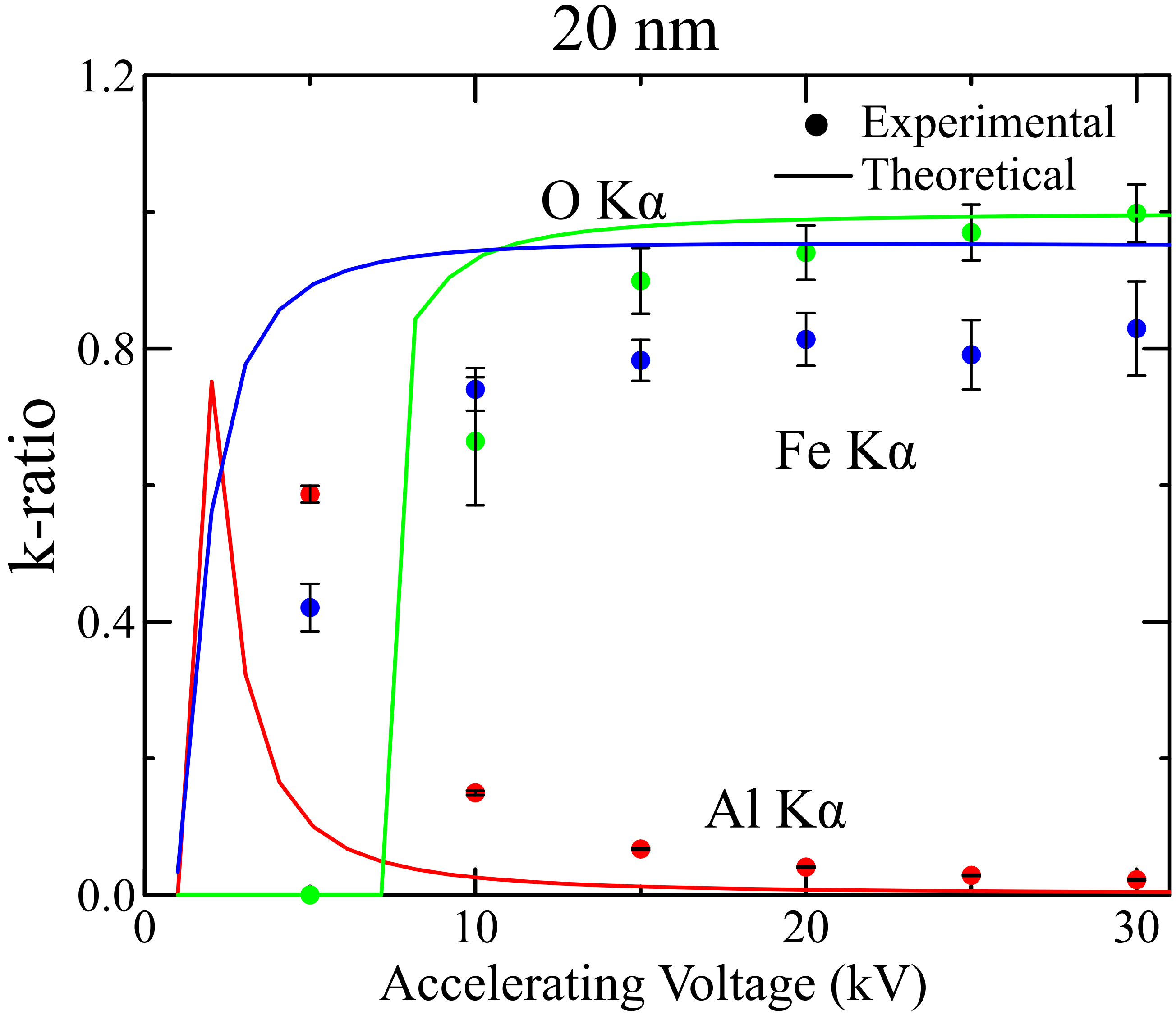
Thin film characterization procedure

- Experimental k-ratios are measured for each elements
- Measurements repeated at different kVs.



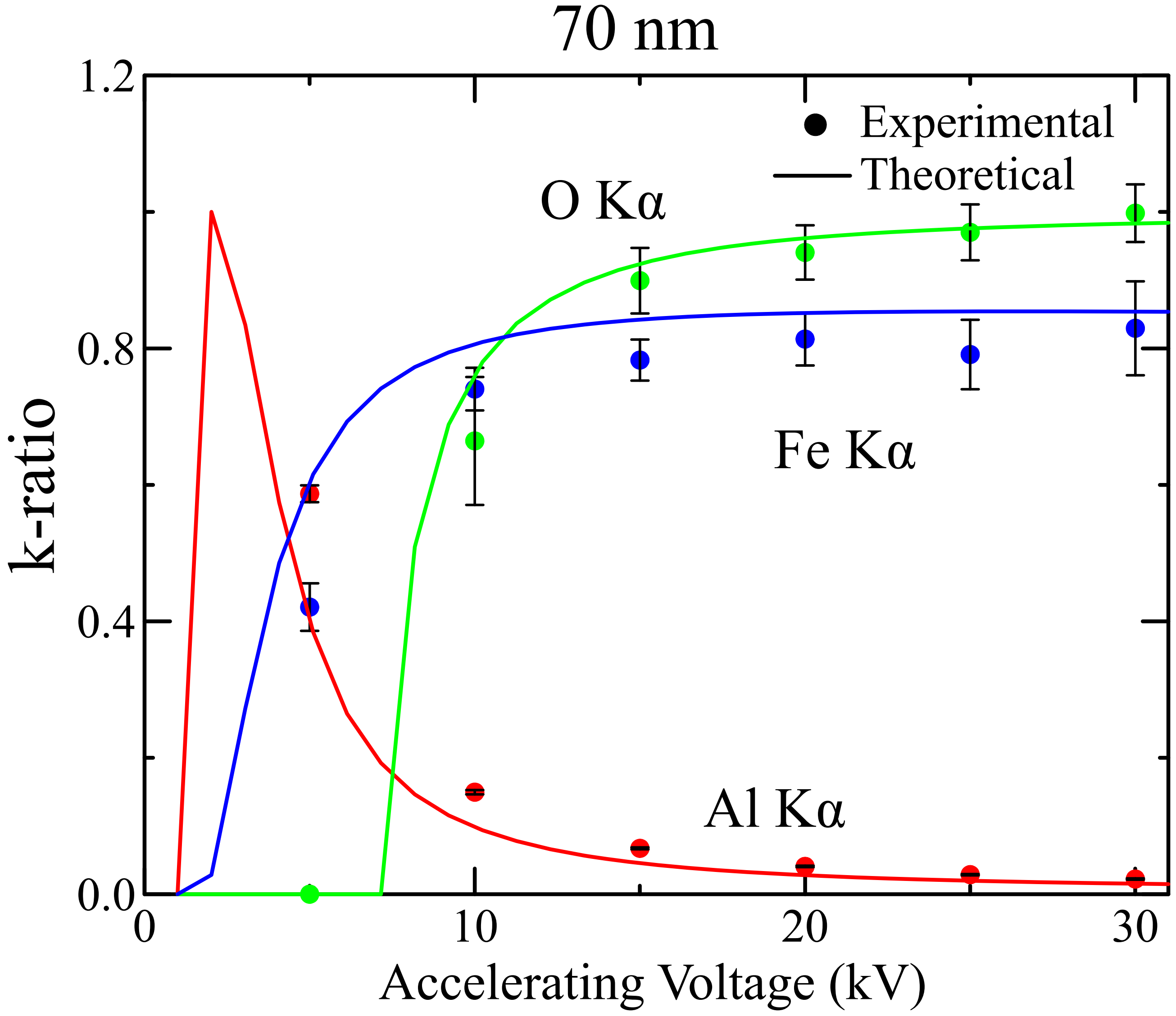
Thin film characterization procedure

- ➔ Iteration until convergence. E.g., Al on Fe_2O_3



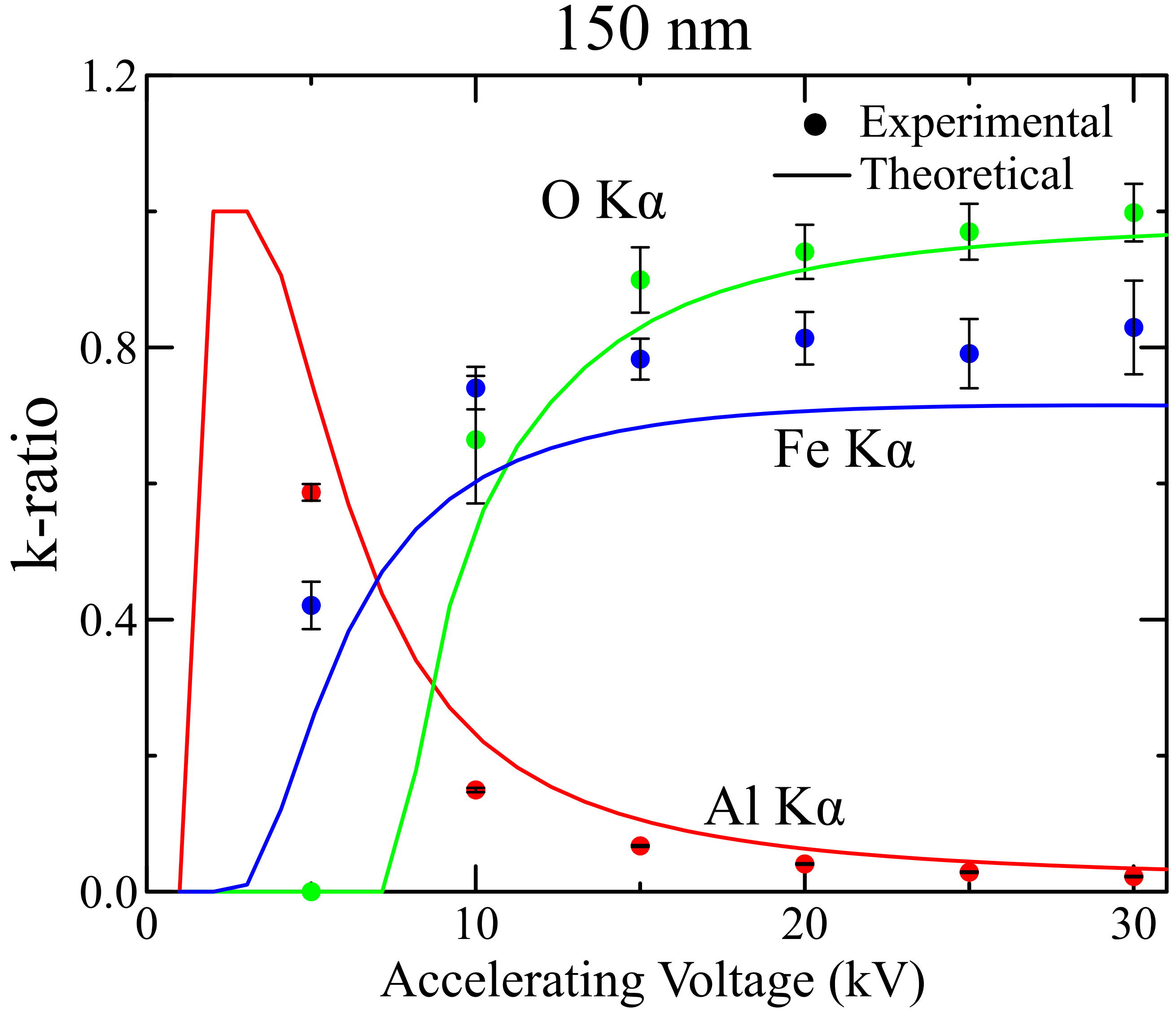
Thin film characterization procedure

- ➔ Iteration until convergence. E.g., Al on Fe_2O_3



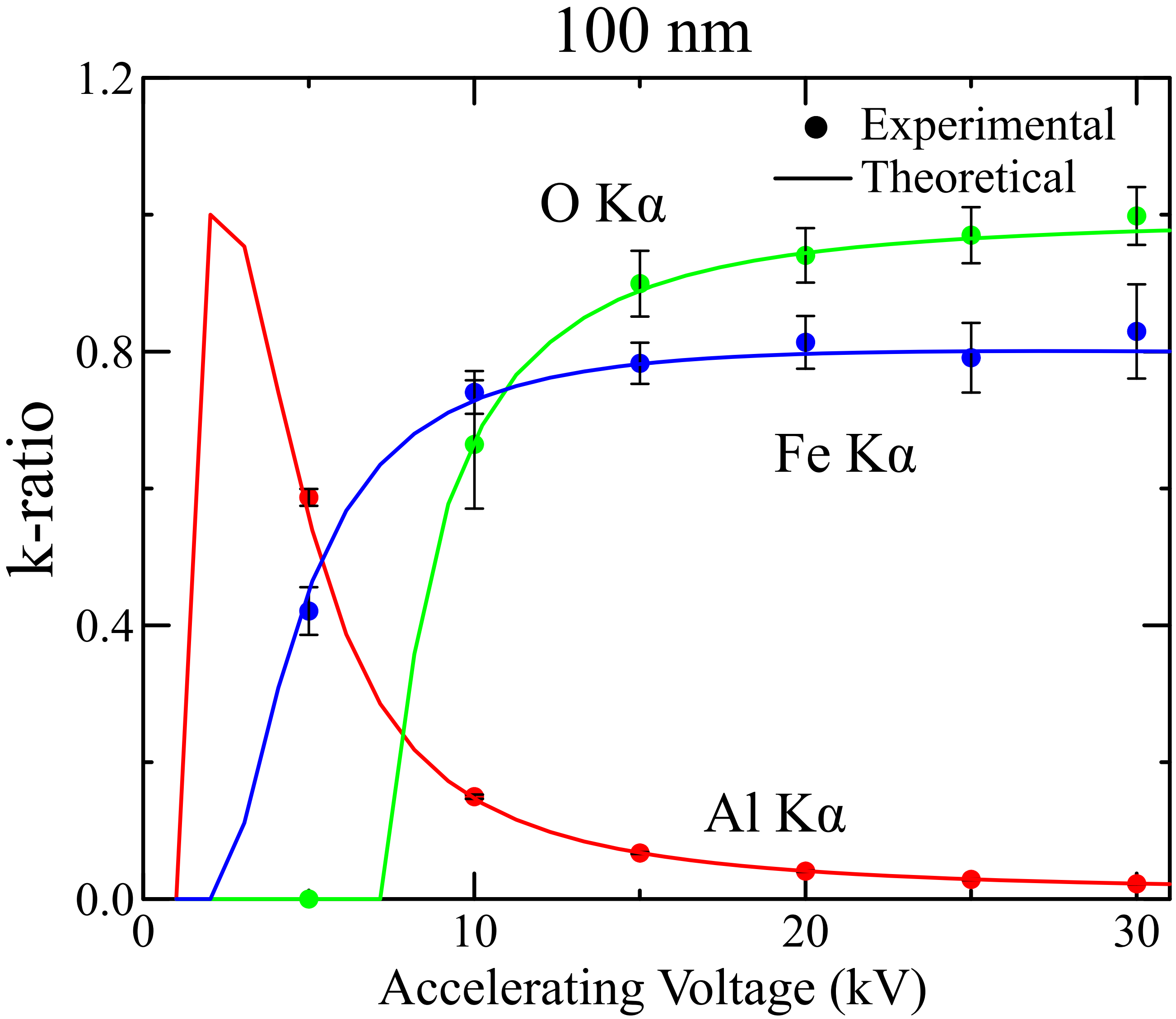
Thin film characterization procedure

- ➔ Iteration until convergence. E.g., Al on Fe_2O_3



Thin film characterization procedure

- ➔ Iteration until convergence. E.g., Al on Fe_2O_3



Thin film analysis programs

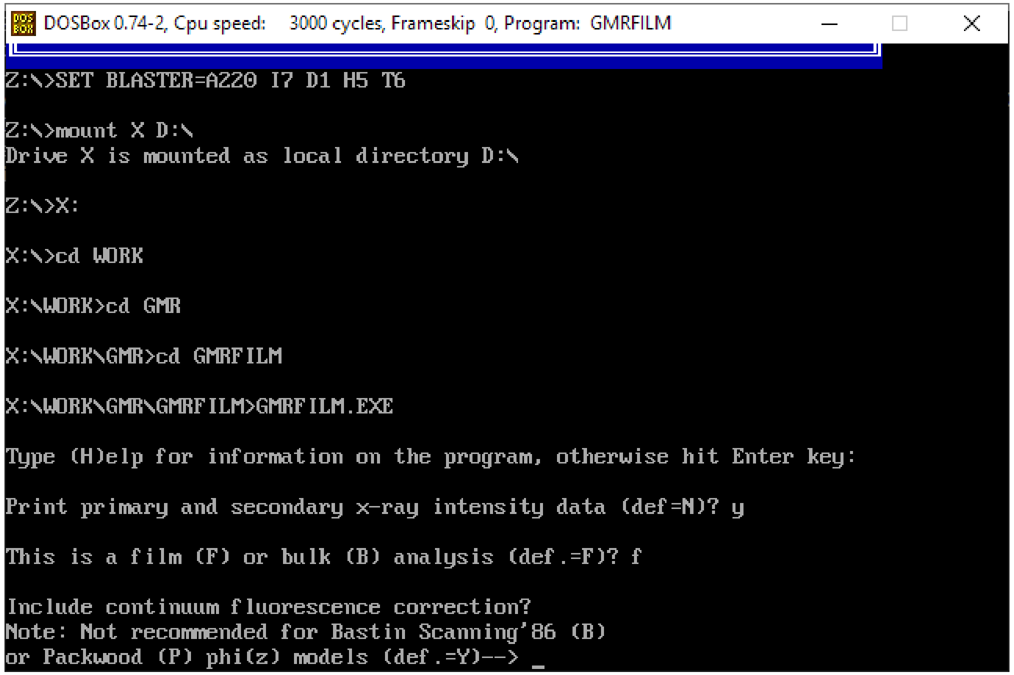
➔ Commercial solutions:

- STRATAGem (SAMx)
- XFILM (Merlet)?
- LayerProbe (Oxford Instruments)
- Layer Quant and STATAGem-SX (CAMECA)

➔ Free solution:

- GMRFilm (Waldo, GMR)
  ➔ - DOS style
  - command prompt
  - no multi-voltage

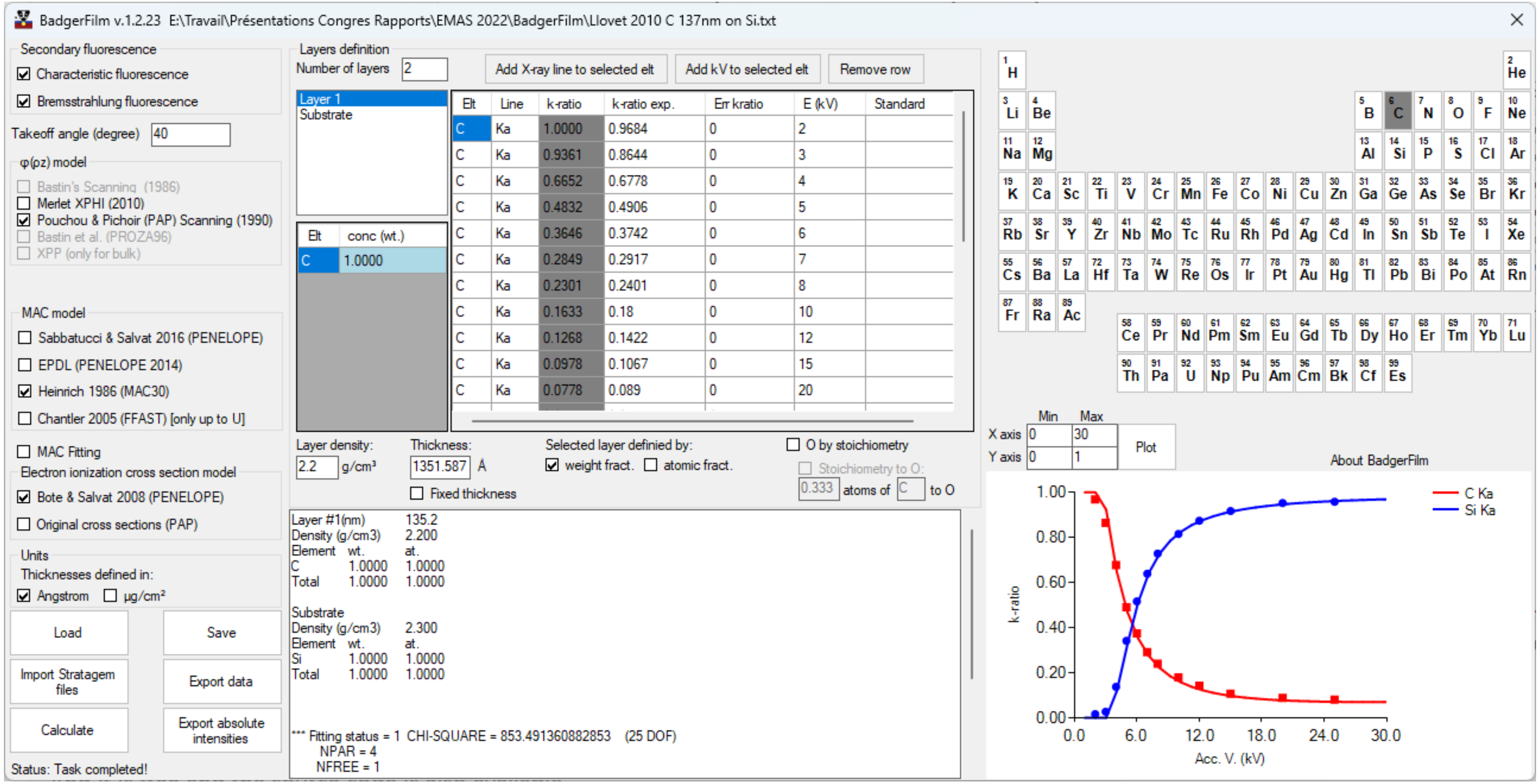
<u>Limited for large set of data</u>



```
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
  - ➔ Free and open-source
  - ➔ User-friendly graphical interface
  - ➔ Robust non-linear fitting algorithm
  - ➔ Elements up to Einsteinium (Z=99)
  - ➔ Implements several phi-rho-z algorithms and MAC databases



BadgerFilm v.1.2.23 E:\Travail\Présentations Congres Rapports\EMAS 2022\BadgerFilm\Llovet 2010 C 137nm on Si.txt

Secondary fluorescence
☑ Characteristic fluorescence
☑ Bremsstrahlung fluorescence

Takeoff angle (degree) 40

φ(ρz) model
☐ Bastin's Scanning (1986)
☐ Merlet XPHI (2010)
☑ Pouchou & Pichoir (PAP) Scanning (1990)
☐ Bastin et al. (PROZA96)
☐ XPP (only for bulk)

MAC model
☐ Sabbatucci & Salvat 2016 (PENELOPE)
☐ EPDL (PENELOPE 2014)
☑ Heinrich 1986 (MAC30)
☐ Chantler 2005 (FFAST) [only up to U]

☐ MAC Fitting

Electron ionization cross section model
☑ Bote & Salvat 2008 (PENELOPE)
☐ Original cross sections (PAP)

Units
Thicknesses defined in:
☑ Angstrom ☐ µg/cm²

Status: Task completed!

Layers definition
Number of layers 2

Layer 1
Substrate

Elt	conc (wt.)
C	1.0000

Elt	Line	k-ratio	k-ratio exp.	Err kratio	E (kV)	Standard
C	Ka	1.0000	0.9684	0	2	
C	Ka	0.9361	0.8644	0	3	
C	Ka	0.6652	0.6778	0	4	
C	Ka	0.4832	0.4906	0	5	
C	Ka	0.3646	0.3742	0	6	
C	Ka	0.2849	0.2917	0	7	
C	Ka	0.2301	0.2401	0	8	
C	Ka	0.1633	0.18	0	10	
C	Ka	0.1268	0.1422	0	12	
C	Ka	0.0978	0.1067	0	15	
C	Ka	0.0778	0.089	0	20	

Layer density: 2.2 g/cm³
Thickness: 1351.587 Å
☐ Fixed thickness
Selected layer defined by:
☑ weight fract. ☐ atomic fract.
☐ O by stoichiometry
☐ Stoichiometry to O:
0.333 atoms of C to O

```
Layer #1(nm)      135.2
Density (g/cm3)   2.200
Element  wt.      at.
C        1.0000   1.0000
Total    1.0000   1.0000

Substrate
Density (g/cm3)   2.300
Element  wt.      at.
Si       1.0000   1.0000
Total    1.0000   1.0000


*** Fitting status = 1  CHI-SQUARE = 853.491360882853   (25 DOF)
     NPAR = 4
    NFREE = 1
```

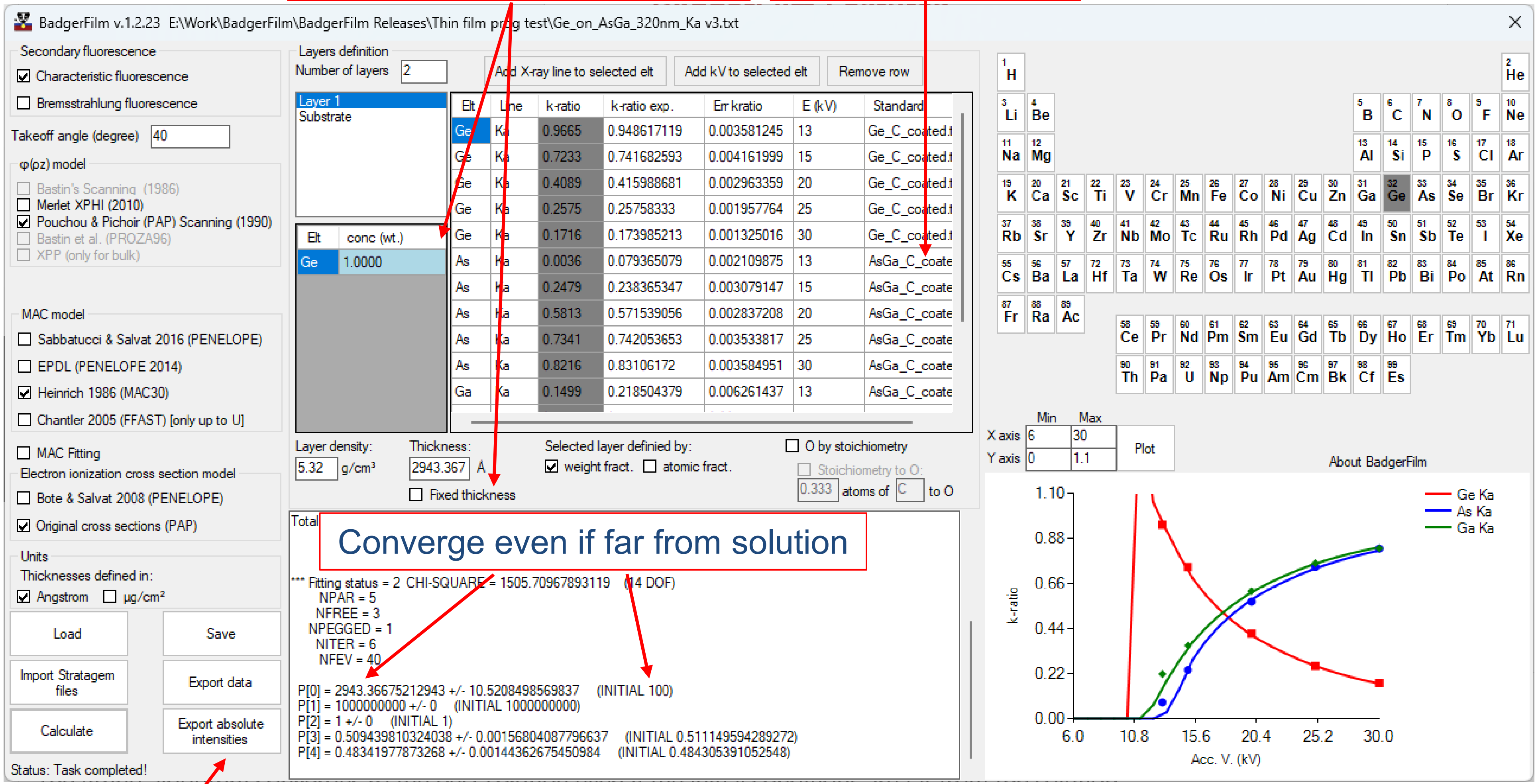
X axis Min 0 Max 30
Y axis Min 0 Max 1

A. Moy and J.H. Fournelle, Microscopy and Microanalysis, 27(2), 266-283.
A. Moy and J.H. Fournelle, Microscopy and Microanalysis, 27(2), 284-296.

BadgerFilm Features

Fix thickness or composition

Custom standards



BadgerFilm v.1.2.23 E:\Work\BadgerFilm\BadgerFilm Releases\Thin film prog test\Ge_on_AsGa_320nm_Ka v3.txt

Secondary fluorescence
☑ Characteristic fluorescence
☐ Bremsstrahlung fluorescence

Takeoff angle (degree) 40

φ(ρz) model
☐ Bastin's Scanning (1986)
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☐ XPP (only for bulk)

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☐ Bote & Salvat 2008 (PENELOPE)
☑ Original cross sections (PAP)

Units
Thicknesses defined in:
☑ Angstrom ☐ µg/cm²

Status: Task completed!

Layers definition
Number of layers 2
Layer 1
Substrate

Elt	conc (wt.)
Ge	1.0000

Elt	Line	k-ratio	k-ratio exp.	Err kratio	E (kV)	Standard
Ge	Ka	0.9665	0.948617119	0.003581245	13	Ge_C_coated.t
Ge	Ka	0.7233	0.741682593	0.004161999	15	Ge_C_coated.t
Ge	Ka	0.4089	0.415988681	0.002963359	20	Ge_C_coated.t
Ge	Ka	0.2575	0.25758333	0.001957764	25	Ge_C_coated.t
Ge	Ka	0.1716	0.173985213	0.001325016	30	Ge_C_coated.t
As	Ka	0.0036	0.079365079	0.002109875	13	AsGa_C_coate
As	Ka	0.2479	0.238365347	0.003079147	15	AsGa_C_coate
As	Ka	0.5813	0.571539056	0.002837208	20	AsGa_C_coate
As	Ka	0.7341	0.742053653	0.003533817	25	AsGa_C_coate
As	Ka	0.8216	0.83106172	0.003584951	30	AsGa_C_coate
Ga	Ka	0.1499	0.218504379	0.006261437	13	AsGa_C_coate

Layer density: 5.32 g/cm³
Thickness: 2943.367 Å
☐ Fixed thickness
Selected layer definied by:
☑ weight fract. ☐ atomic fract.
☐ O by stoichiometry
☐ Stoichiometry to O:
0.333 atoms of C to O

X axis Min 6 Max 30
Y axis Min 0 Max 1.1

Total

Converge even if far from solution

```
*** Fitting status = 2  CHI-SQUARE = 1505.70967893119    (14 DOF)
      NPAR = 5
     NFREE = 3
   NPEGGED = 1
     NITER = 6
      NFEV = 40

 P[0] = 2943.36675212943 +/- 10.5208498569837     (INITIAL 100)
 P[1] = 1000000000 +/- 0     (INITIAL 1000000000)
 P[2] = 1 +/- 0     (INITIAL 1)
 P[3] = 0.509439810324038 +/- 0.00156804087796637     (INITIAL 0.511149594289272)
 P[4] = 0.48341977873268 +/- 0.00144362675450984     (INITIAL 0.484305391052548)
```

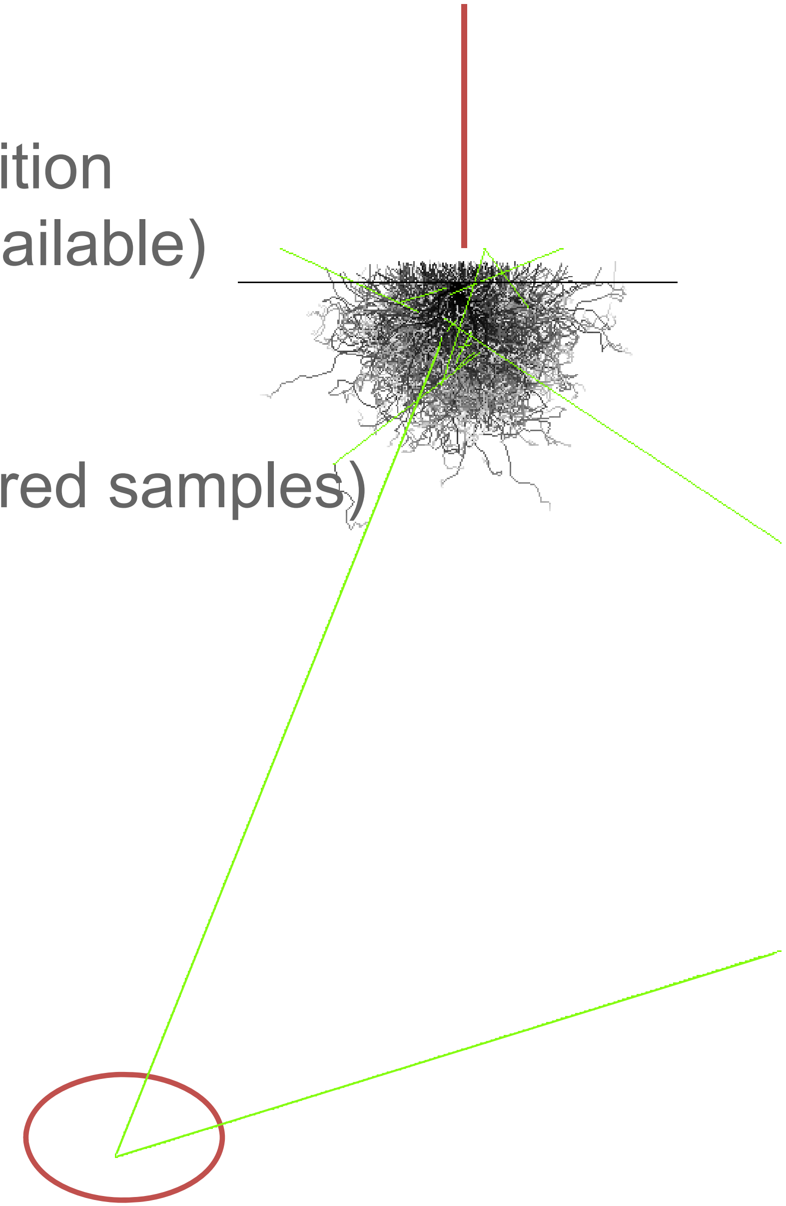
Export data

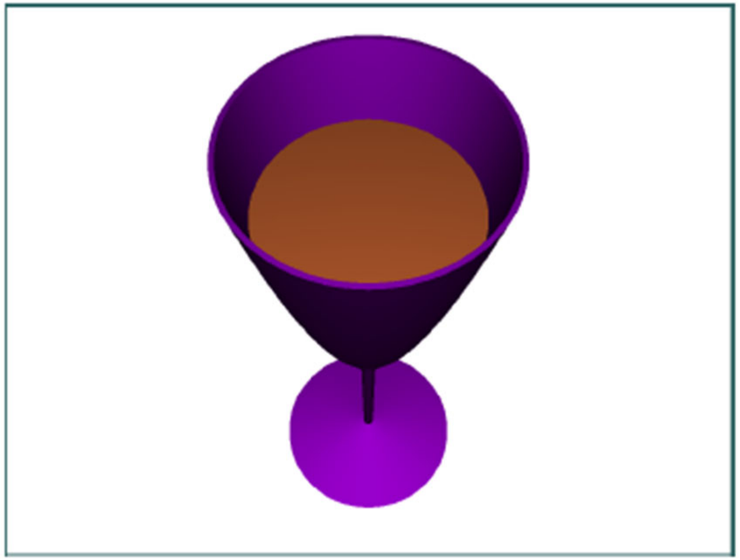
- Advanced options:
  → change atomic parameters (MACs, ...)
  → restrict the domain of variation of the variables (concentrations, thicknesses)

Performance of the implemented models

Validation with:

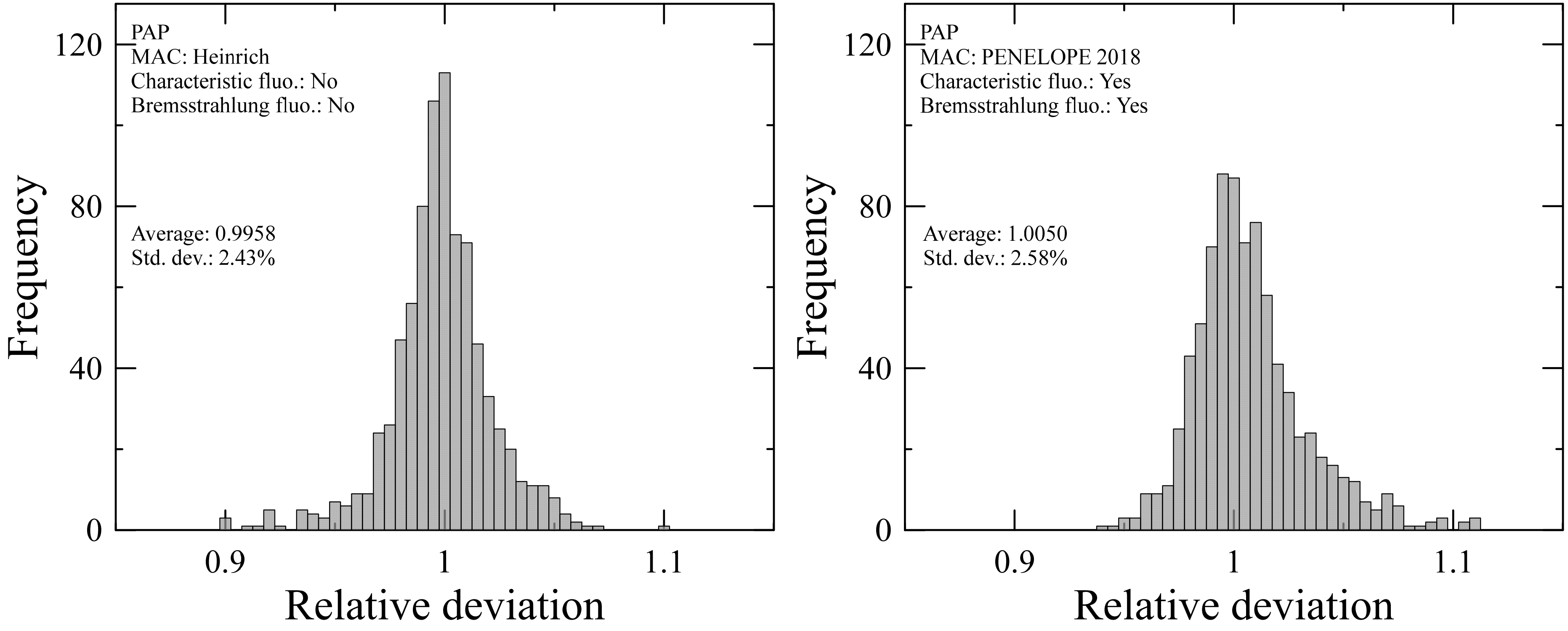
- Experimental k-ratios
  ➔ bulk standards of known composition
  ➔ multilayer standards (very few available)
- Monte Carlo simulations
  ➔ PENEPMA/PENELOPE
  - handles complex geometries (layered samples)
  - Includes secondary fluorescence





Performance of the implemented models

- Experimental data
  ➔ Test on the 826 entries of binary compounds data of Pouchou and Pichoir (1991).



- Centered around 1.0, sharp distribution.
- Secondary fluorescence slightly broadens the distribution.

POUCHOU, J.-L. & PICHOIR, F. (1991). Quantitative analysis of homogeneous or stratified microvolumes applying the model 'PAP'. In Electron Probe Quantitation, Heinrich, K. F. J. & Newbury, D. E. (Eds.), pp. 31–75.

Performance of the implemented models

- Comparison with Monte Carlo simulations
- 3 “types” of X-ray intensities can be distinguished

1) Characteristic X-ray intensity generated by primary electrons from the beam.

Secondary fluorescence:

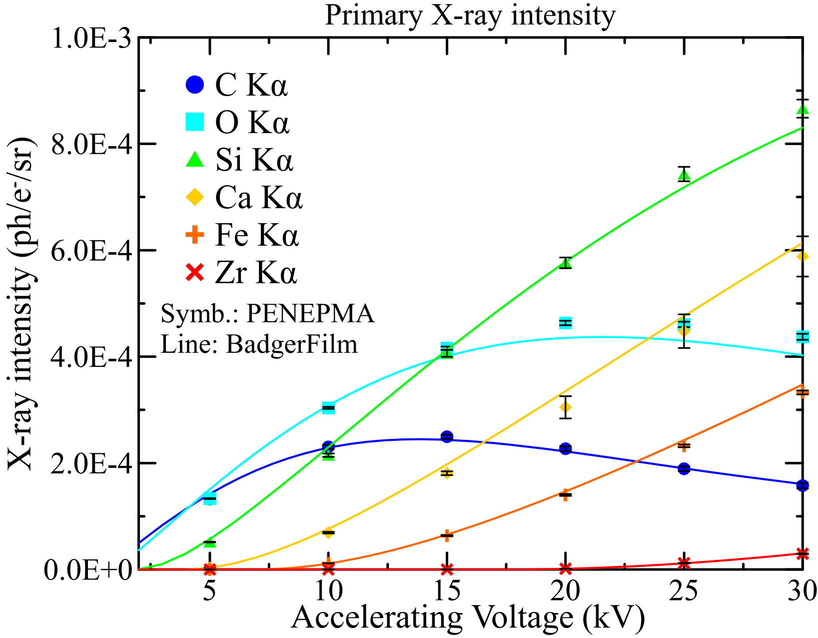
2) X-ray intensity generated by other characteristic X-rays.

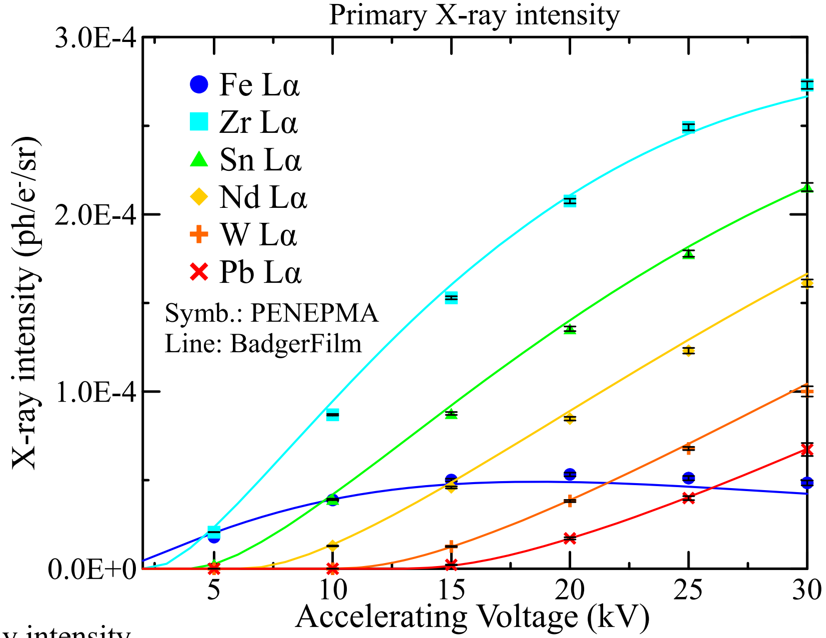
3) X-ray intensity generated by bremsstrahlung.

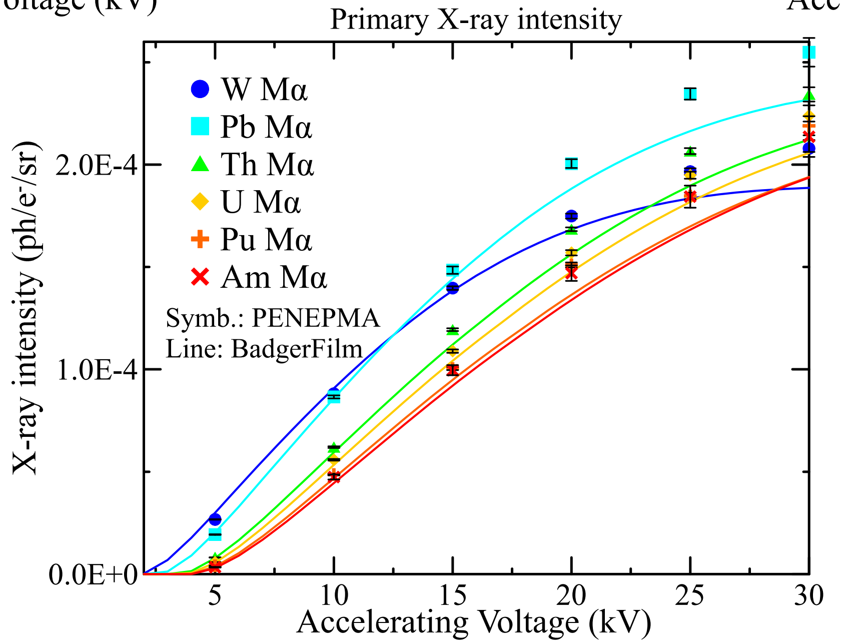
⚠ Secondary fluorescence (SF) can account up to ~15-20% of total intensity (especially for films).
(Note: SF is not always considered in MC programs)

Absolute Primary Characteristic X-ray Intensity

- Absolute X-ray intensity (ph/electron/sr) compared to PENEPMA simulations

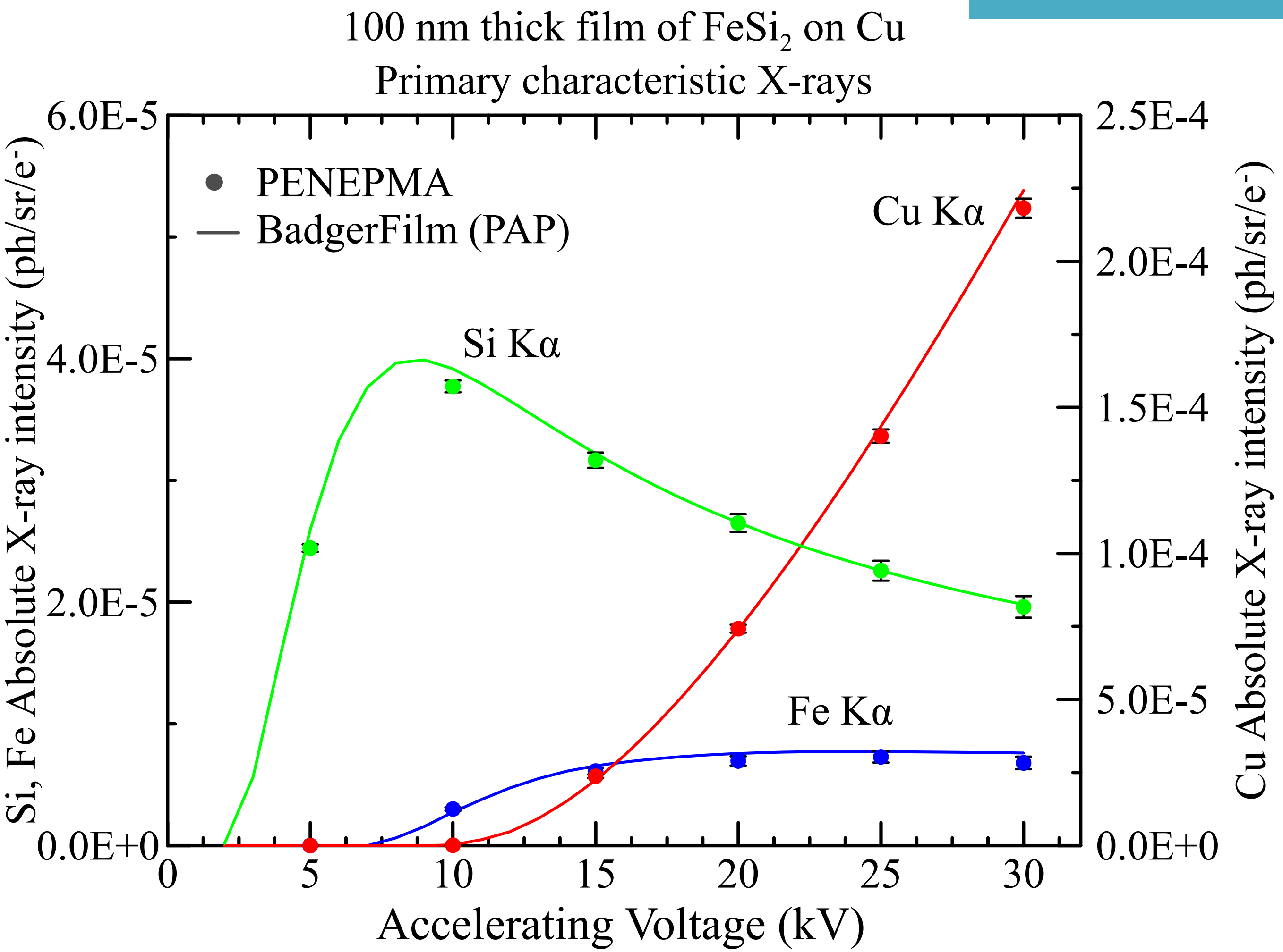






Primary Characteristic X-rays

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



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

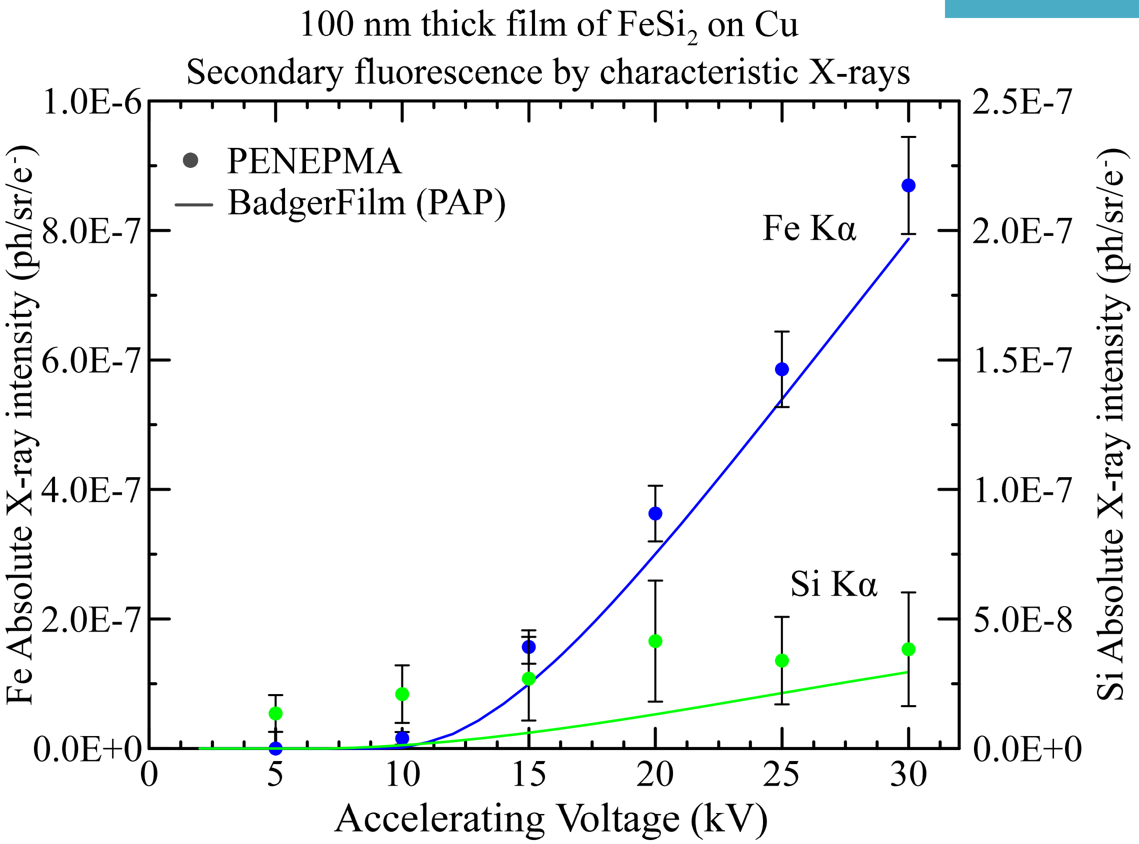
  ➔ Calculate SF generated by each $\phi(\rho z)$ distributions (numerical integration over mass depth)

  ➔ 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

- 100 nm thick $FeSi_2$ film on bulk Cu
  Fluorescence of Fe Kα by Cu



- Characteristic SF for Fe Kα → ~5% of total Fe Kα X-ray intensity
- Characteristic SF for Si Kα → ~0.1% of total Si Kα X-ray intensity

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

$$I_{Brem} = K\ I\ Z\ \frac{E_0 - E}{E}$$

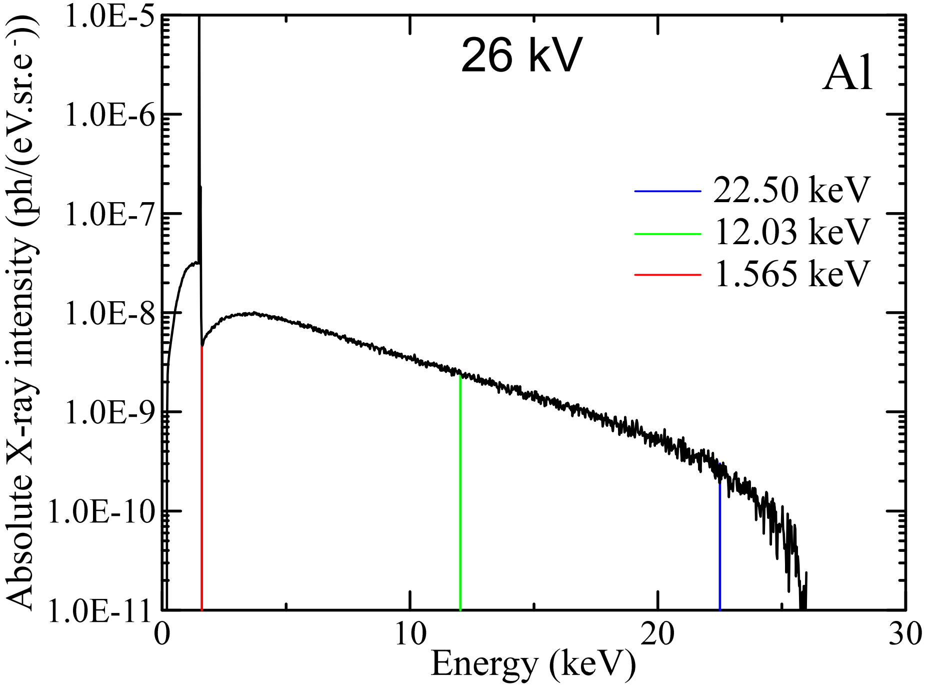
➔ SF is calculated for bremsstrahlung of energy Ei

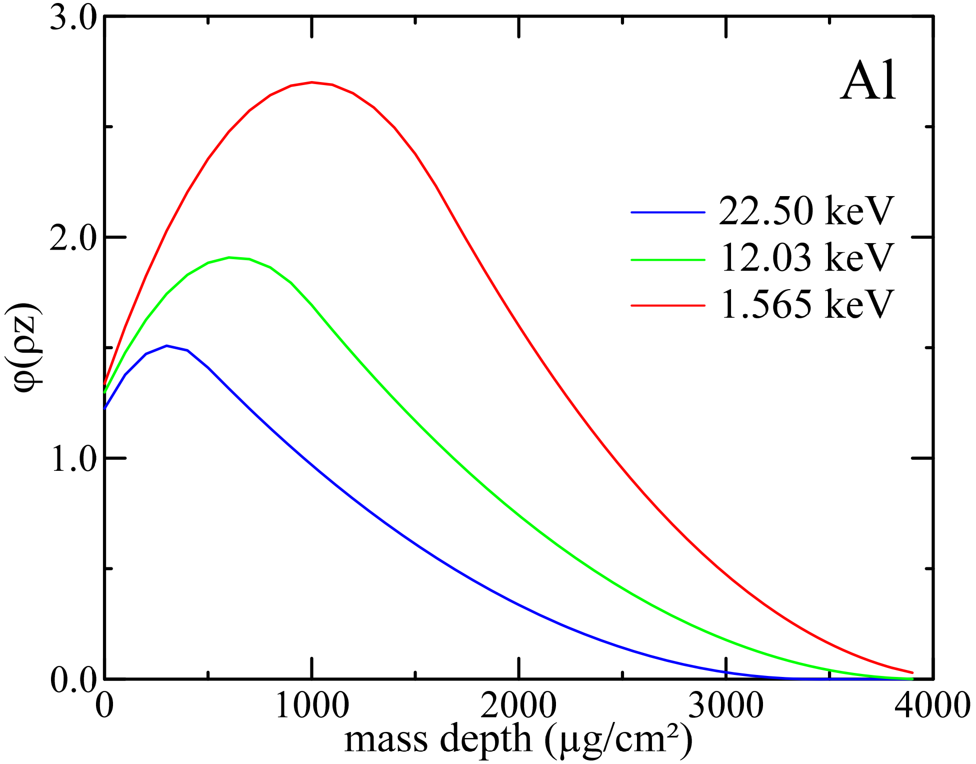
repeat with next energy Ei

➔ All the SF contributions are summed from Ec to E0

Secondary fluorescence by bremsstrahlung

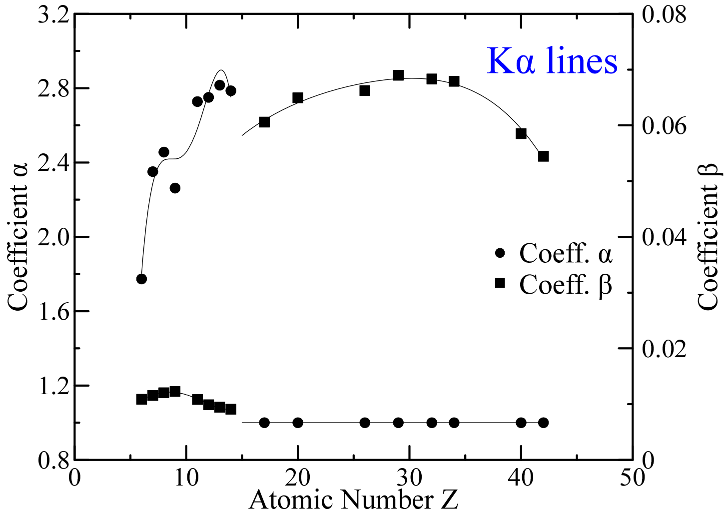
- E.g., $\phi(\rho z, E)$ distributions at different X-ray energies corresponding to a fictitious element in a matrix of Al.

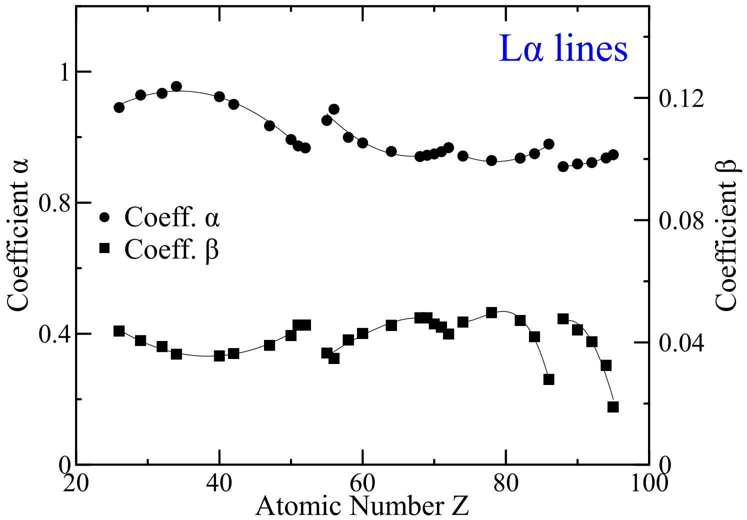


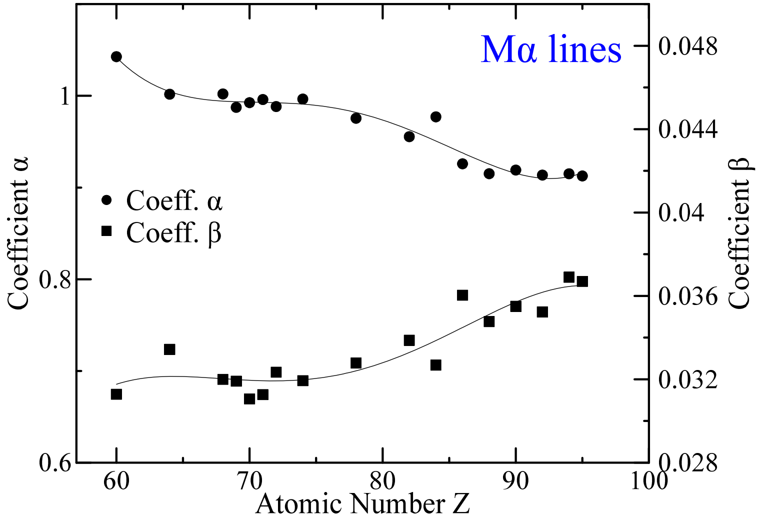


Secondary fluorescence by bremsstrahlung

- Correction factors for the secondary fluorescence by the bremsstrahlung





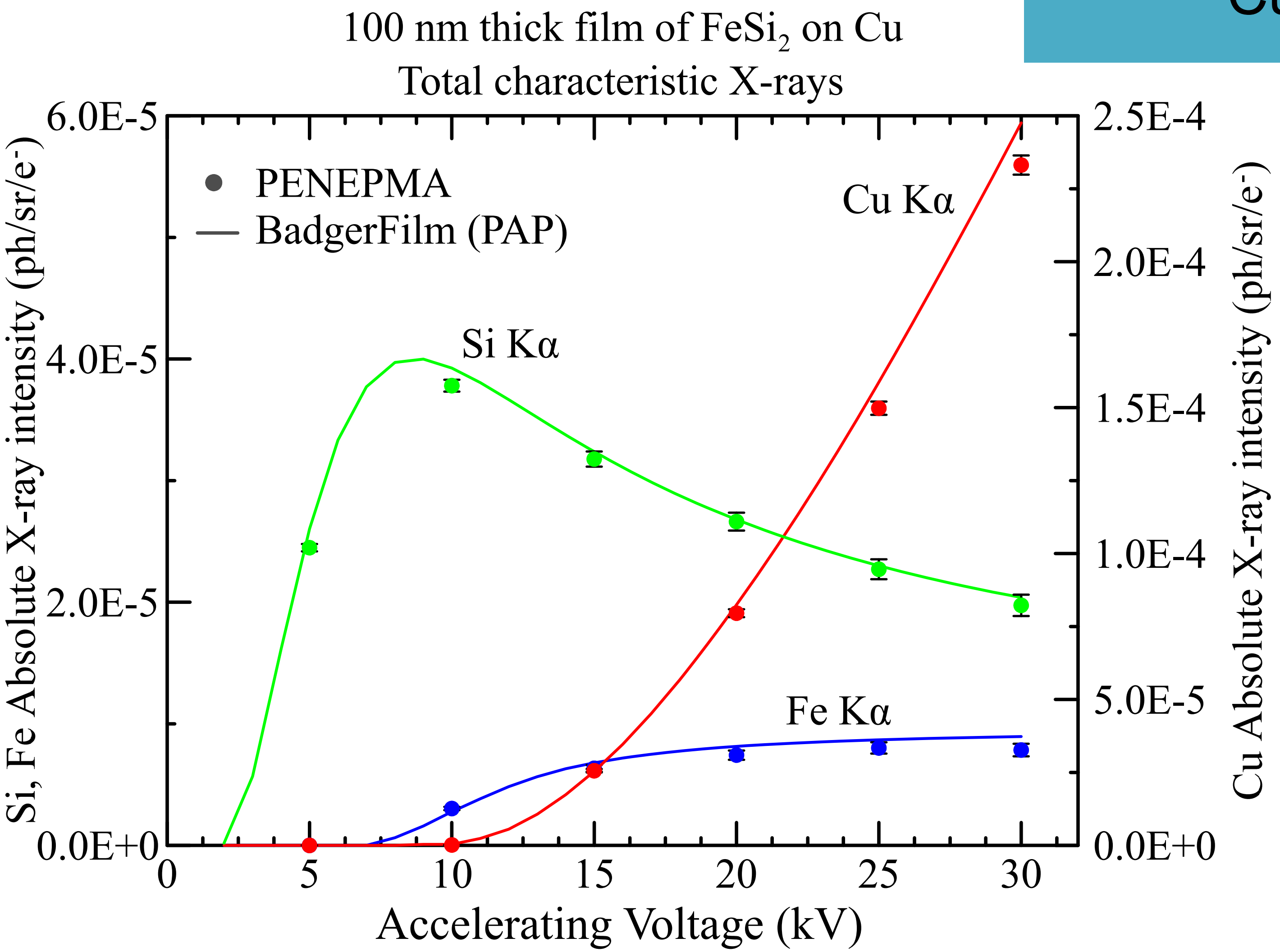


- Other method: use MC simulations to generate bremsstrahlung $\phi(\rho z, E)$ distributions (Yuan et al. 2019).

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

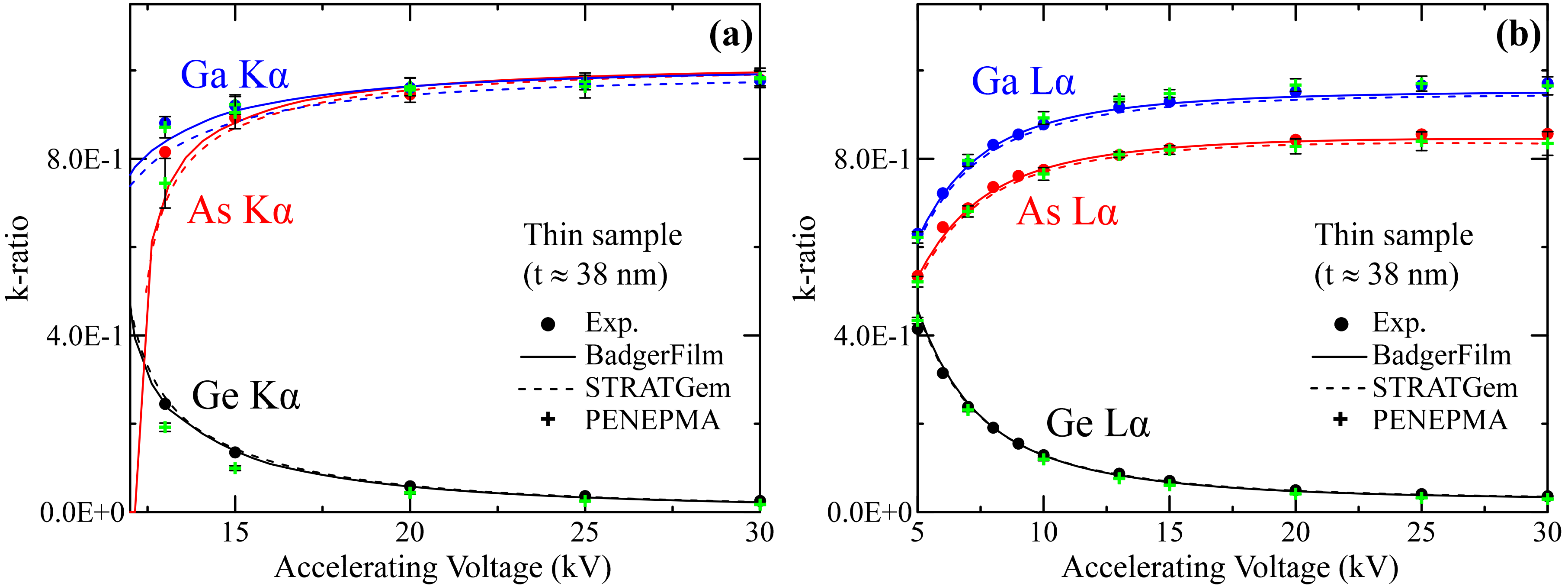
Absolute Total X-ray Intensity

- Absolute X-ray intensity (ph/electron/sr)



Thin film analysis – Practical example

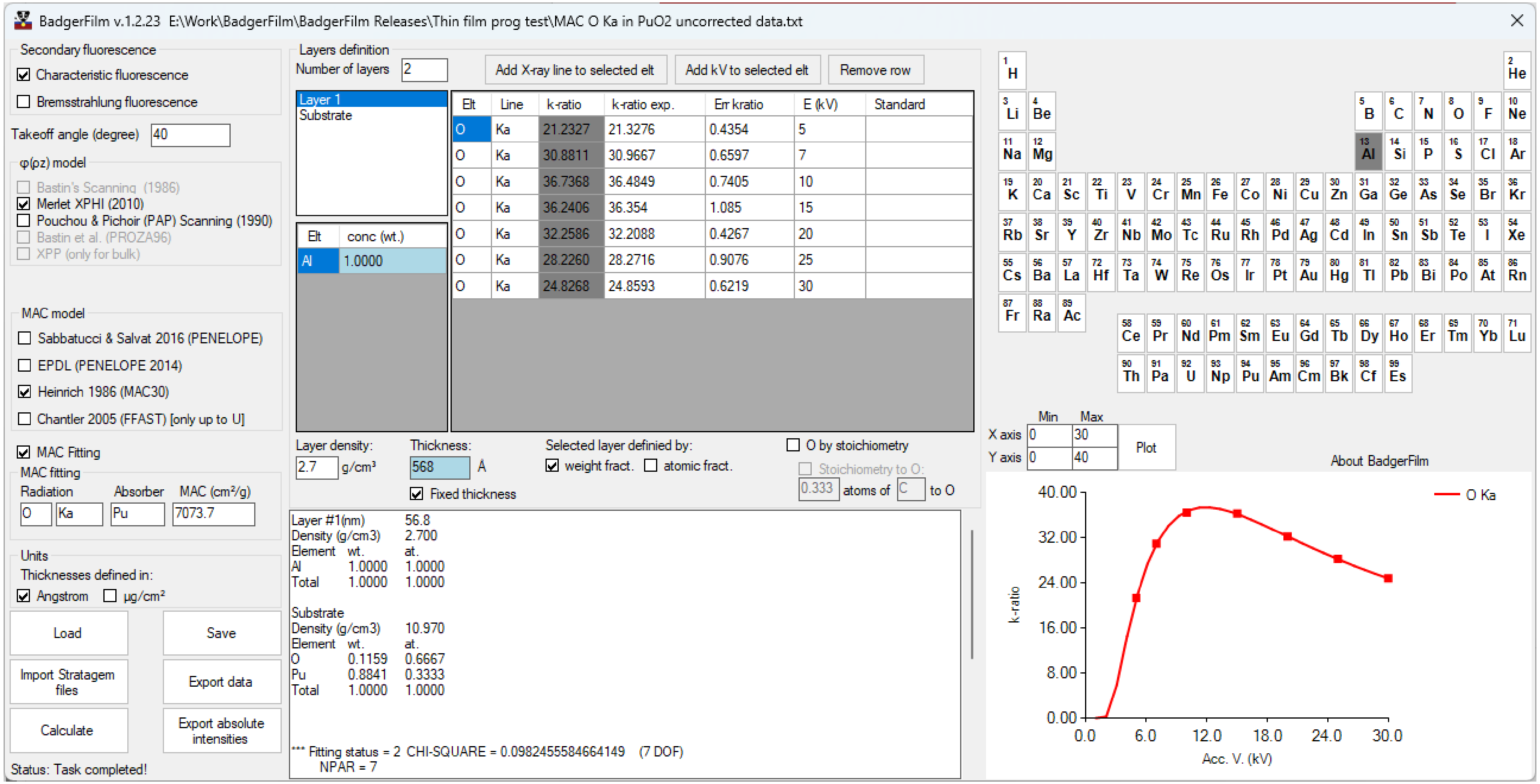
- Ge film on AsGa: ~38 nm +/- 2 nm.
- X-ray intensities: Kα and Lα lines



	Film thickness (nm)	
X-ray reflectometry	38.0 +/- 2.0	
	Kα X-ray lines	Lα X-ray lines
BadgerFilm	43.1 +/- 0.1	41.7 +/- 0.5
STRATAGem	43.9	41.2
PENEPMA	42.0	42.0

Something Different – MAC determination

- BadgerFilm can be used to determine MACs from EPMA measurements.
- Example: O Kα MAC by actinides (data from Pöml and Llovet, 2020).



BadgerFilm v.1.2.23 E:\Work\BadgerFilm\BadgerFilm Releases\Thin film prog test\MAC O Ka in PuO2 uncorrected data.txt

Secondary fluorescence
☑ Characteristic fluorescence
☐ Bremsstrahlung fluorescence

Takeoff angle (degree): 40

φ(ρz) model
☐ Bastin's Scanning (1986)
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☑ MAC Fitting

MAC fitting

Radiation		Absorber	MAC (cm²/g)
O	Ka	Pu	7073.7

Units
Thicknesses defined in:
☑ Angstrom ☐ µg/cm²

Status: Task completed!

Layers definition
Number of layers: 2

Layer 1
Substrate

Elt	conc (wt.)
Al	1.0000

Elt	Line	k-ratio	k-ratio exp.	Err kratio	E (kV)	Standard
O	Ka	21.2327	21.3276	0.4354	5	
O	Ka	30.8811	30.9667	0.6597	7	
O	Ka	36.7368	36.4849	0.7405	10	
O	Ka	36.2406	36.354	1.085	15	
O	Ka	32.2586	32.2088	0.4267	20	
O	Ka	28.2260	28.2716	0.9076	25	
O	Ka	24.8268	24.8593	0.6219	30	

Layer density: 2.7 g/cm³
Thickness: 568 Å
☑ Fixed thickness

Selected layer defined by:
☑ weight fract. ☐ atomic fract.

☐ O by stoichiometry
☐ Stoichiometry to O:
0.333 atoms of C to O

```
Layer #1(nm)        56.8
Density (g/cm3)     2.700
Element   wt.       at.
Al        1.0000    1.0000
Total     1.0000    1.0000

Substrate
Density (g/cm3)     10.970
Element   wt.       at.
O         0.1159    0.6667
Pu        0.8841    0.3333
Total     1.0000    1.0000


*** Fitting status = 2  CHI-SQUARE = 0.0982455584664149    (7 DOF)
     NPAR = 7
```

	Min	Max
X axis	0	30
Y axis	0	40

P. Pöml and X. Llovet, Microscopy and Microanalysis (2020), 26, 194–203

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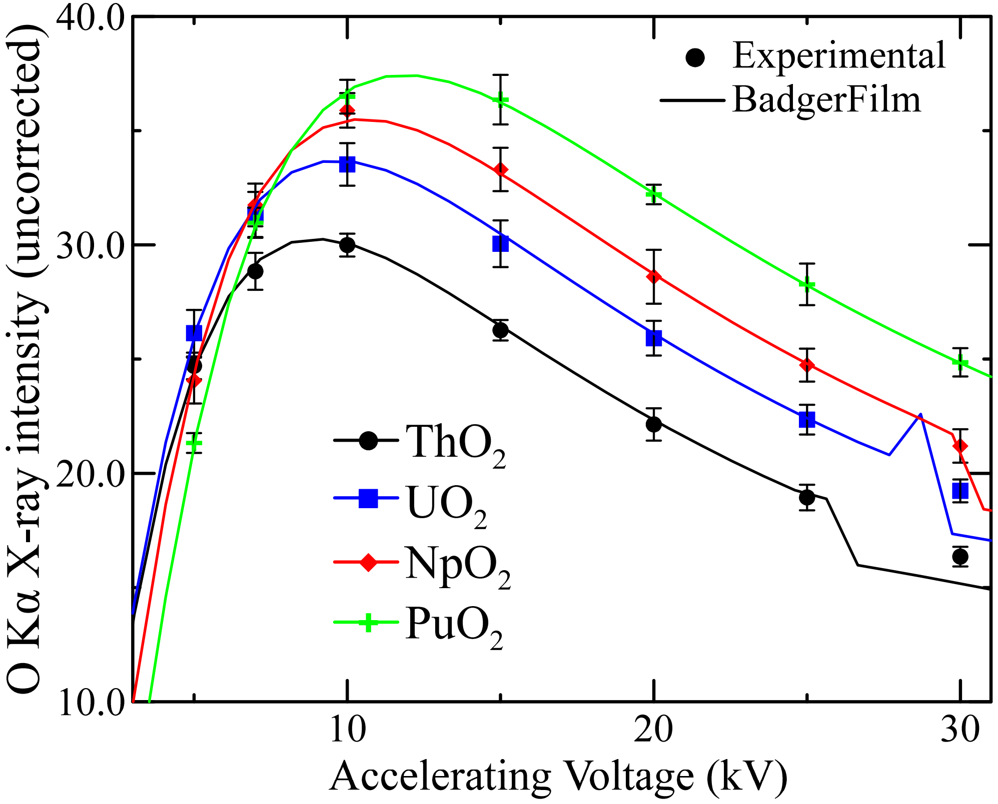
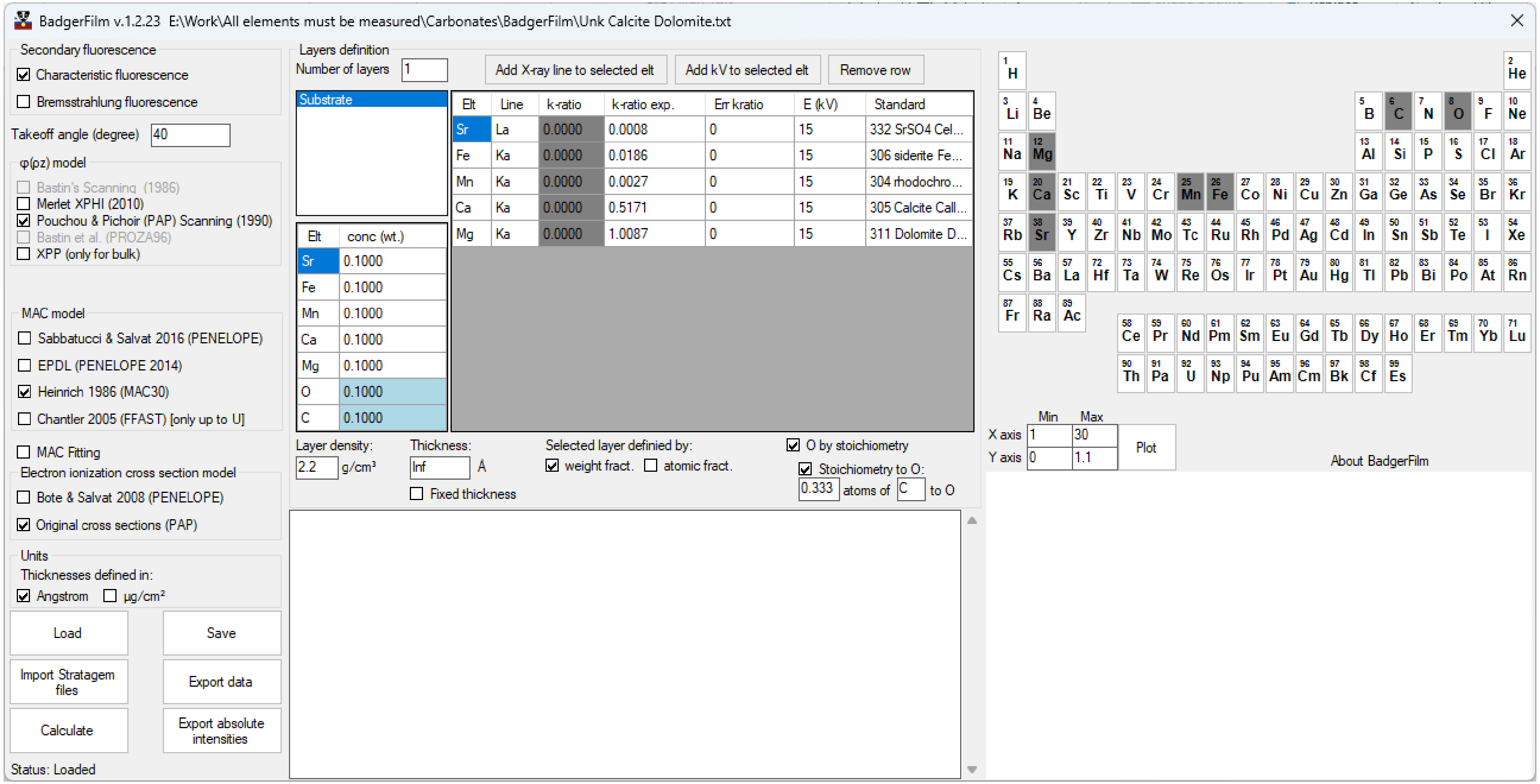


MACs for O K*α* in Actinide Absorbers (in cm^2/g)		
	Pöml & Llovet, 2020	BadgerFilm
Th	10846	10821
U	9318	9321
Np	8524	8556
Pu	7025	7074

P. Pöml and X. Llovet, Microscopy and Microanalysis (2020), 26, 194–203

Something Different – Bulk quantification

- BadgerFilm can be used for traditional quantifications.
- BadgerFilm naturally considers any coating on top of the sample.
- BadgerFilm can calculate O and another element by stoichiometry.



BadgerFilm v.1.2.23 E:\Work\All elements must be measured\Carbonates\BadgerFilm\Unk Calcite Dolomite.txt

Secondary fluorescence
☑ Characteristic fluorescence
☐ Bremsstrahlung fluorescence

Takeoff angle (degree) 40

φ(ρz) model
☐ Bastin's Scanning (1986)
☐ Merlet XPHI (2010)
☑ Pouchou & Pichoir (PAP) Scanning (1990)
☐ Bastin et al. (PROZA96)
☐ XPP (only for bulk)

MAC model
☐ Sabbatucci & Salvat 2016 (PENELOPE)
☐ EPDL (PENELOPE 2014)
☑ Heinrich 1986 (MAC30)
☐ Chantler 2005 (FFAST) [only up to U]

☐ MAC Fitting

Electron ionization cross section model
☐ Bote & Salvat 2008 (PENELOPE)
☑ Original cross sections (PAP)

Units
Thicknesses defined in:
☑ Angstrom ☐ µg/cm²

Status: Loaded

Layers definition
Number of layers 1

Substrate

Elt	conc (wt.)
Sr	0.1000
Fe	0.1000
Mn	0.1000
Ca	0.1000
Mg	0.1000
O	0.1000
C	0.1000

Elt	Line	k-ratio	k-ratio exp.	Err kratio	E (kV)	Standard
Sr	La	0.0000	0.0008	0	15	332 SrSO4 Cel...
Fe	Ka	0.0000	0.0186	0	15	306 siderite Fe...
Mn	Ka	0.0000	0.0027	0	15	304 rhodochro...
Ca	Ka	0.0000	0.5171	0	15	305 Calcite Call...
Mg	Ka	0.0000	1.0087	0	15	311 Dolomite D...

Layer density: 2.2 g/cm³
Thickness: Inf Å
☐ Fixed thickness

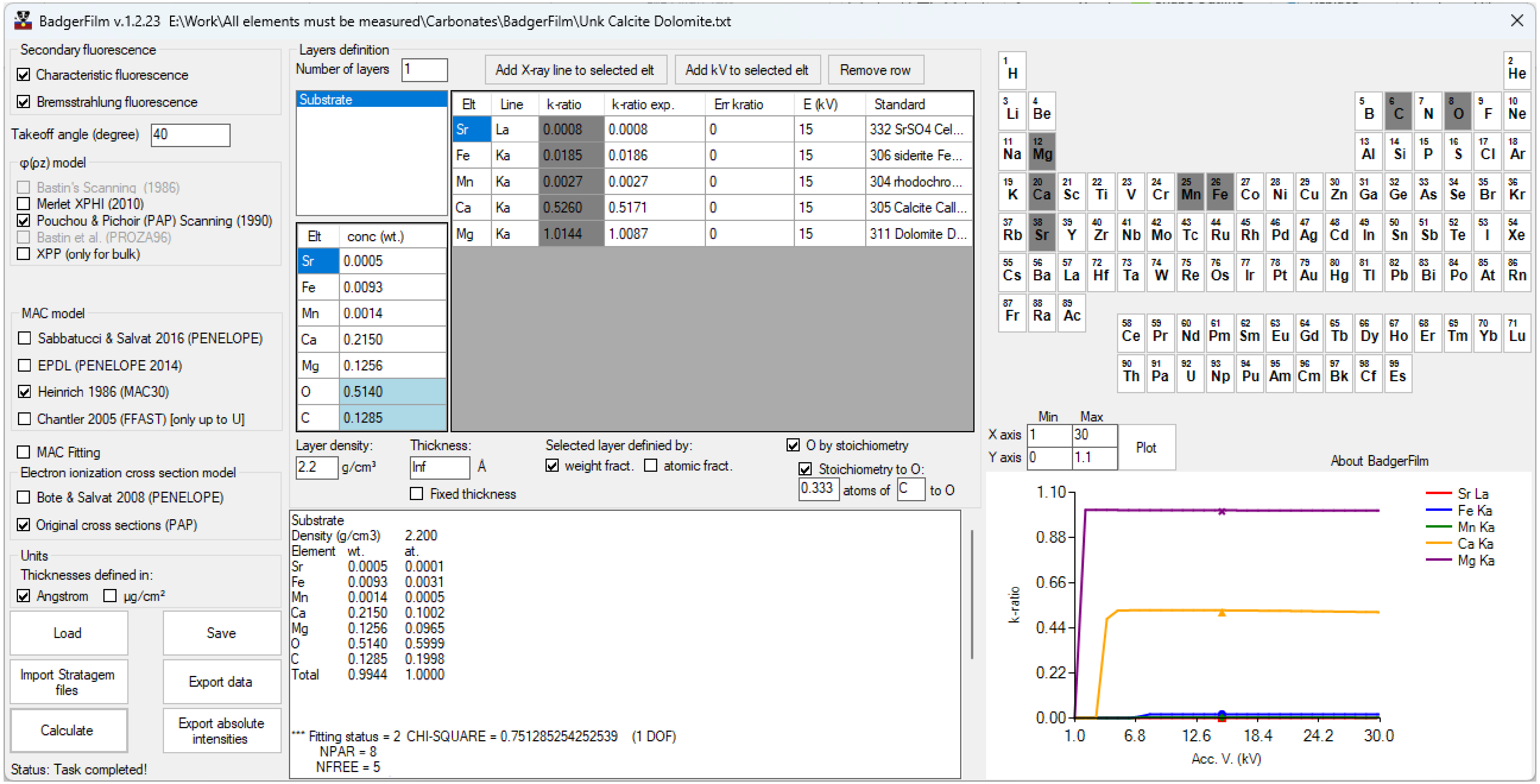
Selected layer defined by:
☑ weight fract. ☐ atomic fract.

☑ O by stoichiometry
☑ Stoichiometry to O:
0.333 atoms of C to O

	Min	Max
X axis	1	30
Y axis	0	1.1

Something Different – Bulk quantification

- BadgerFilm can be used for traditional quantifications.
- BadgerFilm naturally considers any coating on top of the sample.
- BadgerFilm can calculate O and another element by stoichiometry.



BadgerFilm v.1.2.23 E:\Work\All elements must be measured\Carbonates\BadgerFilm\Unk Calcite Dolomite.txt

Secondary fluorescence
☑ Characteristic fluorescence
☑ Bremsstrahlung fluorescence

Takeoff angle (degree): 40

φ(ρz) model
☐ Bastin's Scanning (1986)
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☑ Heinrich 1986 (MAC30)
☐ Chantler 2005 (FFAST) [only up to U]

☐ MAC Fitting

Electron ionization cross section model
☐ Bote & Salvat 2008 (PENELOPE)
☑ Original cross sections (PAP)

Units
Thicknesses defined in:
☑ Angstrom ☐ µg/cm²

Status: Task completed!

Layers definition
Number of layers: 1
Substrate

Elt	conc (wt.)
Sr	0.0005
Fe	0.0093
Mn	0.0014
Ca	0.2150
Mg	0.1256
O	0.5140
C	0.1285

Elt	Line	k-ratio	k-ratio exp.	Err kratio	E (kV)	Standard
Sr	La	0.0008	0.0008	0	15	332 SrSO4 Cel...
Fe	Ka	0.0185	0.0186	0	15	306 siderite Fe...
Mn	Ka	0.0027	0.0027	0	15	304 rhodochro...
Ca	Ka	0.5260	0.5171	0	15	305 Calcite Call...
Mg	Ka	1.0144	1.0087	0	15	311 Dolomite D...

Layer density: 2.2 g/cm³
Thickness: Inf Å
☐ Fixed thickness
Selected layer definied by:
☑ weight fract. ☐ atomic fract.
☑ O by stoichiometry
☑ Stoichiometry to O:
0.333 atoms of C to O

X axis: Min 1, Max 30
Y axis: Min 0, Max 1.1

```
Substrate
Density (g/cm3)     2.200
Element   wt.       at.
Sr        0.0005    0.0001
Fe        0.0093    0.0031
Mn        0.0014    0.0005
Ca        0.2150    0.1002
Mg        0.1256    0.0965
O         0.5140    0.5999
C         0.1285    0.1998
Total     0.9944    1.0000


*** Fitting status = 2  CHI-SQUARE = 0.751285254252539    (1 DOF)
      NPAR = 8
     NFREE = 5
```

- Results: $Sr_{0.001}Fe_{0.031}Mn_{0.005}Ca_{1.002}Mg_{0.965}(CO_3)_2$

Conclusions

- Free Thin film analysis program
- Easy to use GUI
- Source code available
- Calculated absolute X-ray intensities in agreement with Monte Carlo simulations
- Good performances for film thickness and composition in agreement with other programs and methods.
- Better extraction of the substrate composition for known coating, e.g., protective coats for low kV EPMA; Au-coated SIMS mounts.
- Can be used for MACs determination.
- Further developments:
  - More testing against other experimental data
  - Implementation of other $\phi(\rho z)$ models.

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Thank you for your attention

Contact: amoy6@wisc.edu
BadgerFilm: https://github.com/Aurelien354/BadgerFilm

Phi-rho-z distribution in thin films

- Total emitted X-ray intensity ➔ Integration of the $\phi(\rho z)$ distribution and absorption coefficient:

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

- C_i: concentration of element *i*.
- $\Phi_i(\rho z)$: ionization depth distribution for element I and associated X-ray line.
- $\frac{\mu}{\rho}$: mass absorption coefficient (dependent of the X-ray energy and sample composition).
- $\rho z_1, \rho z_2$: mass depth of the layer.
- θ: takeoff angle of the spectrometer.

Characterization of thin films

- Calculation of a theoretical k-ratio:

$$k_i = \frac{C_i \int_{\rho z_1}^{\rho z_2} \Phi_i(\rho z)\, e^{-\frac{\mu}{\rho}\frac{\rho z}{\sin\theta}}\, d\rho z}{C_i^{std} \int_0^{\infty} \Phi_i^{std}(\rho z)\, e^{-\left(\frac{\mu}{\rho}\right)_{std}\frac{\rho z}{\sin\theta}}\, d\rho z}$$

Repeat the k-ratio calculations for:

- ➔ all the elements
- ➔ all the layers and for the substrate
- ➔ different kVs

➔ All the calculations are repeated in an iterative process in which the thicknesses and compositions are adjusted until the theoretical k-ratios match the experimental k-ratios.