# *Soft X-ray EPMA: choosing the right MACs*

***Xavier Llovet***
CCiTUB, University of Barcelona, Spain

***Philippe Pöml***
European Commission, JRC, Karlsruhe, Germany

***Aurélien Moy and John Fournelle***
Department of Geoscience, University of Wisconsin, Madison

## Use of soft X-rays for microanalysis

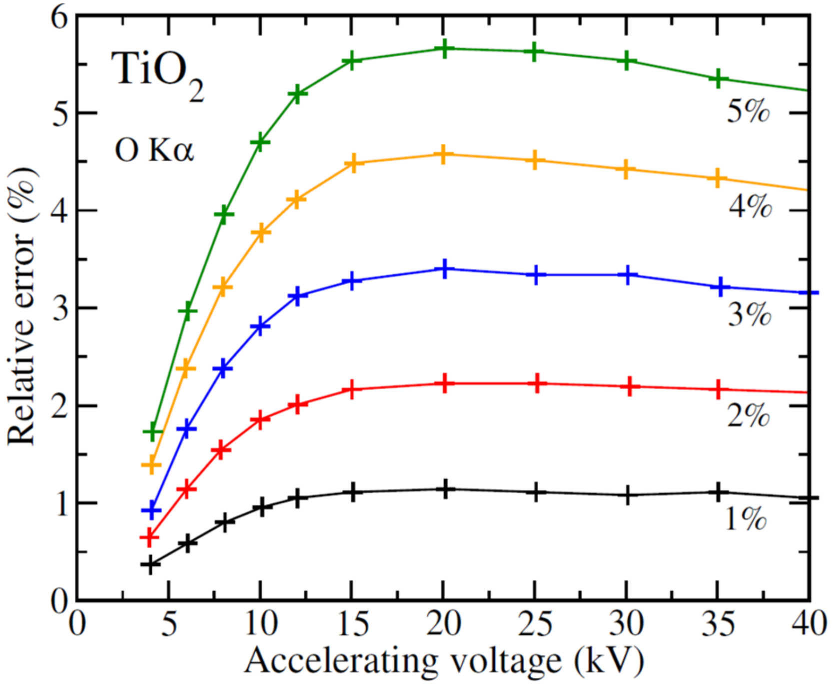
- Renewed interest due to advances in measurements of soft X-rays (synthetic multilayers, windowless EDS, SXES) and incorporation of FE guns in electron beam instruments
- K-lines of light elements (Li, Be, B, C, N, O, F). Play a critical role in many materials
- L-lines transition metals (Sc to Cu) and M-lines REEs: required for high-resolution EPMA (low voltage) of natural and technological materials

Difficulties

- Soft X-rays produced in electron transitions involving ***valence electrons***, thus they are affected by ***chemical bonding***
- Potential large errors in evaluated concentrations because matrix corrections do not include corrections for chemical bonding
- X-ray absorption: dominant correction

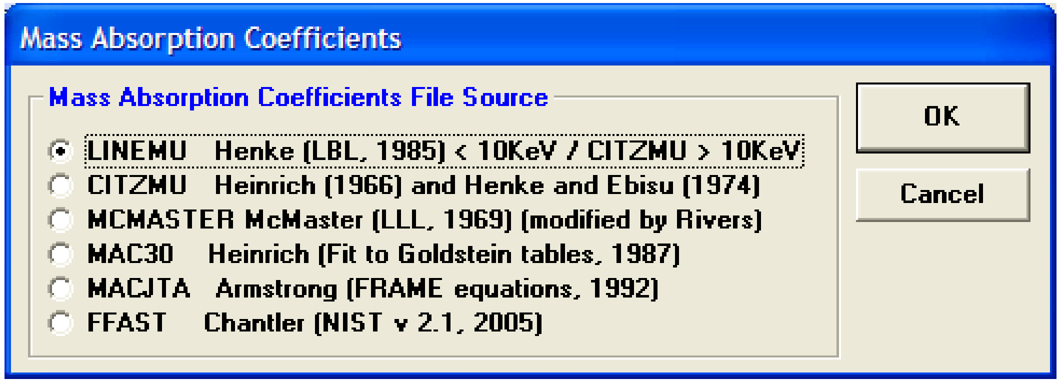
# ● Key parameter: the mass attenuation coefficient ($\mu/\rho$)

- ● None of existing matrix corrections programs can provide accurate EPMA concentrations for soft X-rays without reliable MACs
- ● Concentrations sensitive to MAC choice for soft X-rays: a variation of 1% in the MAC leads to a variation of 1% in the evaluated concentration



Sensitivity of O concentration to MAC uncertainty for O Kα X-rays emitted from TiO2
MAC = 20,000 $cm^2/g$

# Sources of MACs for soft X-rays



Mass Absorption Coefficients File Source

● LINEMU Henke (LBL, 1985) < 10KeV / CITZMU > 10KeV
○ CITZMU Heinrich (1966) and Henke and Ebisu (1974)
○ MCMASTER McMaster (LLL, 1969) (modified by Rivers)
○ MAC30 Heinrich (Fit to Goldstein tables, 1987)
○ MACJTA Armstrong (FRAME equations, 1992)
○ FFAST Chantler (NIST v 2.1, 2005)

MAC choices in Probe for EPMA

- Semi-empirical databases: fits to experimental data + theoretical calculations to extrapolate across Z to fill the empty gaps
  - Henke et al. (1982), Henke et al. (1993), etc..
- Analytical formulas: fits to experimental data
  - Heinrich (1966), Heinrich (1986), Farthing-Walker (1990), etc..
- Theoretical (atomic) calculations:
  - NIST-FFAST Chantler (2005), Sabattucci & Salvat (2016), etc..

Accuracy of MAC datasets for soft X-rays poorly documented: unclear if newer tabulations shold replace older ones!

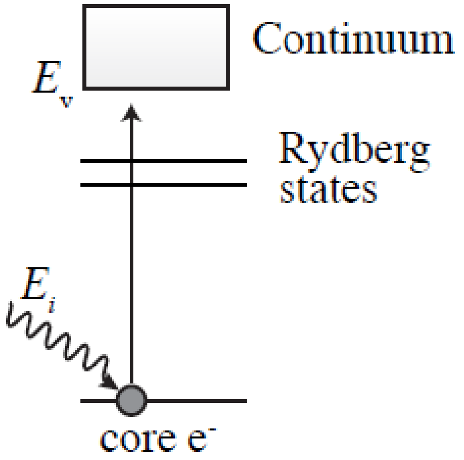
- **Theoretical MAC calculations**

For soft X-rays: $\boxed{\frac{\mu}{\rho} \sim \frac{N_\mathrm{A}}{A_\mathrm{M}}\sigma_\mathrm{ph}}$ Photoelectric cross section

Photoelectric effect: a photon is absorbed by the target atom and an atomic electron is excited to an empty orbital, bound or free

$$d\sigma^{\mathrm{ion},1}_{b;n_a\kappa_a m_a}(W,\boldsymbol{\zeta}) = \frac{(2\pi)^2 e^2}{W}\frac{k_b\left(\epsilon_b + \mathrm{m_e}c^2\right)}{c\hbar}\left|M^{\mathrm{ion}}_{b;n_a\kappa_a m_a}(W,\boldsymbol{\zeta})\right|^2 d\hat{\mathbf{k}}_b,$$

$$M^{\mathrm{ion}}_{b;n_a\kappa_a m_a}(W,\boldsymbol{\zeta}) = \boldsymbol{\zeta}\cdot\left\langle\psi^{(-)}_{\mathbf{k}_b m_{Sb}}\middle|\tilde{\boldsymbol{\alpha}}\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})\middle|\psi_{n_a\kappa_a m_a}\right\rangle$$



Sabbattucci & Salvat, Rad. Phys. Chem (2016) **121** 122

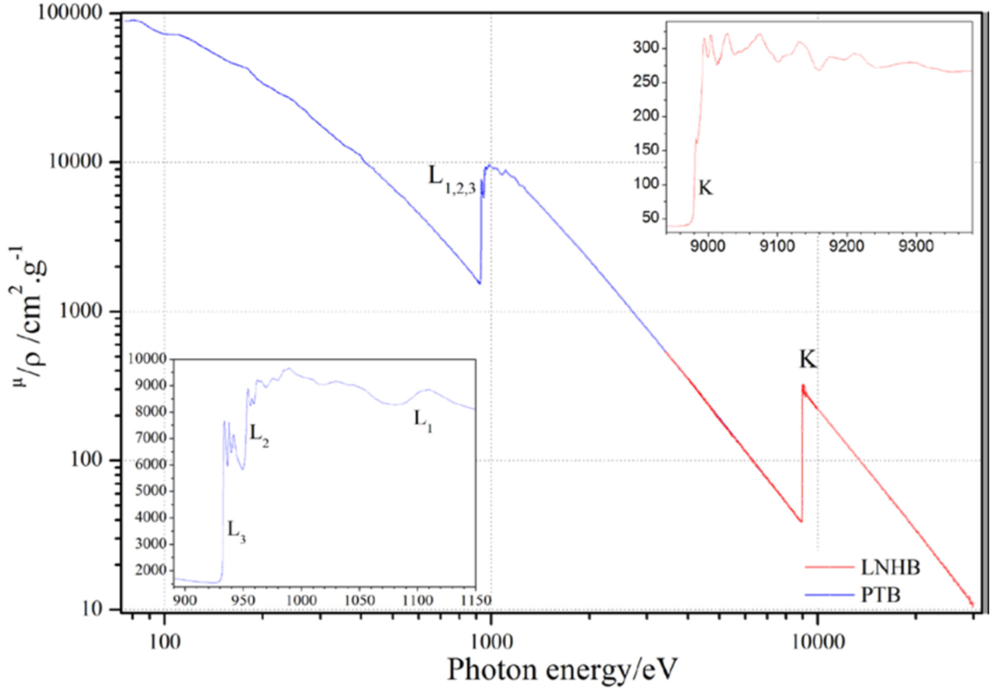
Additivity rule for compounds: $\boxed{\left(\frac{\mu}{\rho}\right) = \sum_i c_i \left(\frac{\mu}{\rho}\right)_i}$

# ● Photoabsorption measurements

Experimentally determined by measuring the X-ray intensity *I* emitted through a layer of an absorbing element of mass thickness $\rho t$:

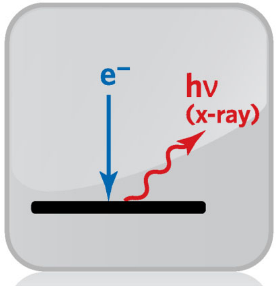
$$\boxed{\left(\frac{\mu}{\rho}\right) = -\frac{1}{\rho t}\ln\frac{I}{I_0}}$$

- Saloman, Hubbell & Scofield (1988) compilation of experimental data published prior to 1998
- Ménesguen et al (2016, 2018a, 2018b): high-resolution photoabsorption measurements performed by an international initiative



Ménesguen et al. (2016) Metrologia **53** 7

# Measuring the MAC with the EPMA

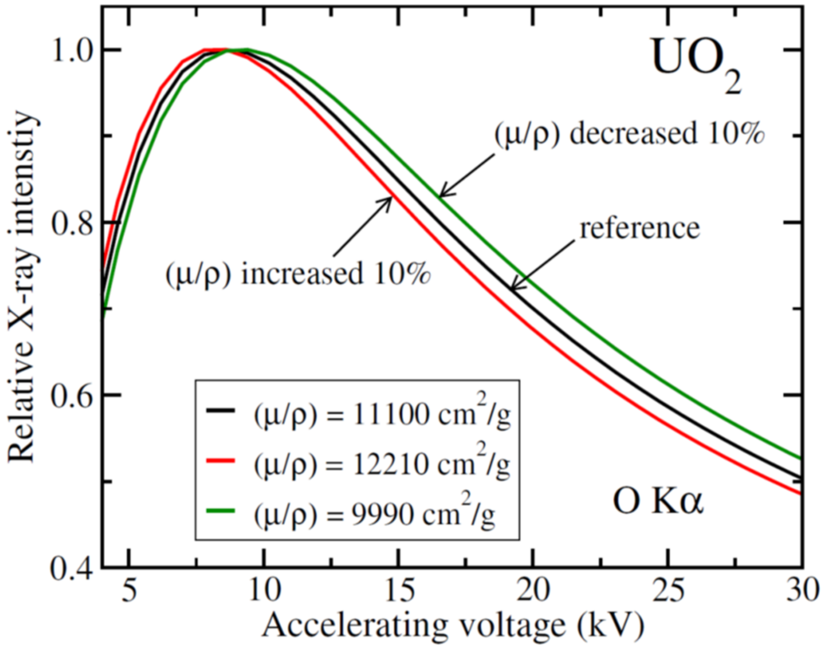


Assumption: MAC is the unknown in the quantification equation

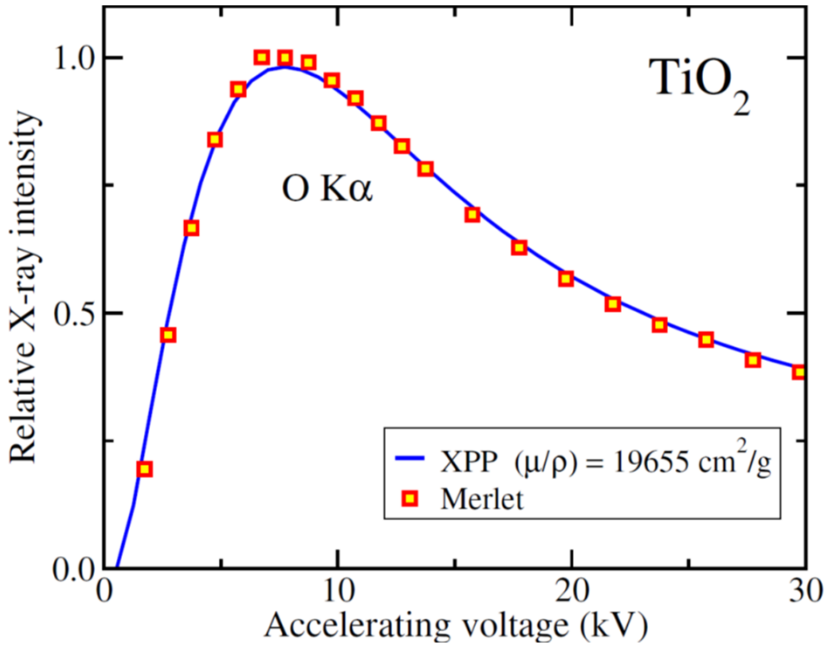
$$I_i(E_0) \sim c_i \int_0^\infty \Phi_i(\rho z; E_0) \exp\left[-\frac{(\mu_i/\rho)\,\rho z}{\sin\chi}\right] \mathrm{d}\rho z$$

Software currently available: BadgerFilm and XMAC.

Technique developed by Pouchou (1998) and others

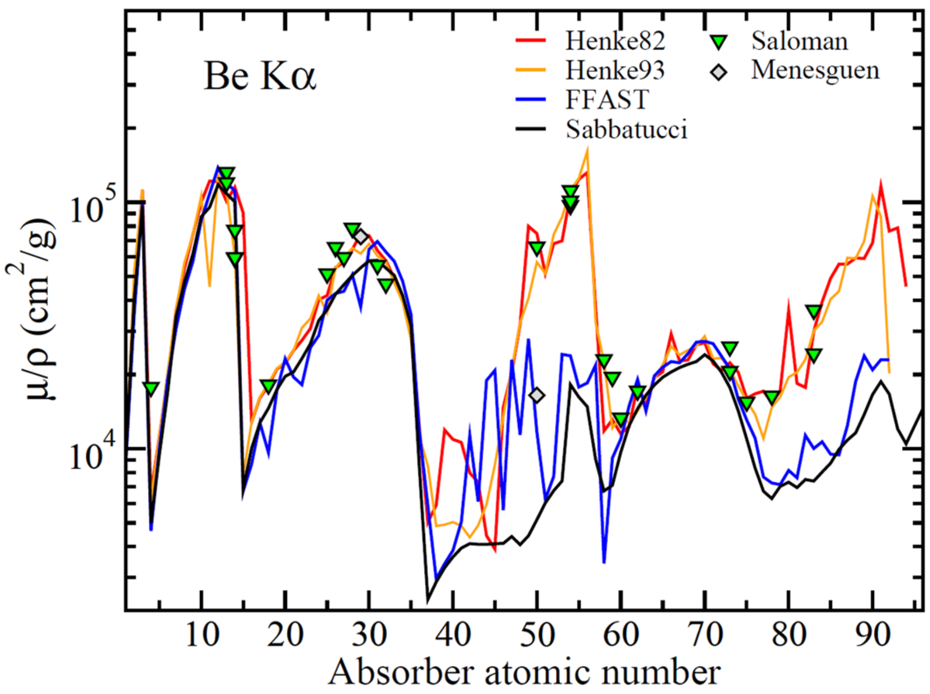


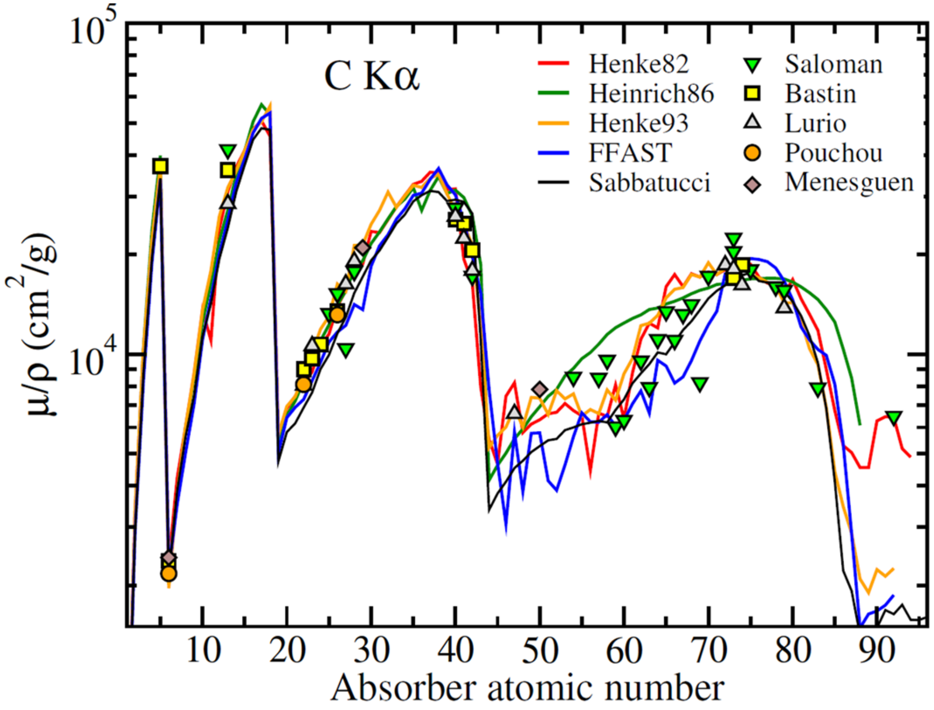
Sensitivity of the MAC to the X-ray intensity



Experimental data: Kyser (1972), Bastin & Heijligers (1988, 1989, 1990, 1997), Pouchou & Pichoir (1988), Pöml & Llovet (2020), etc..

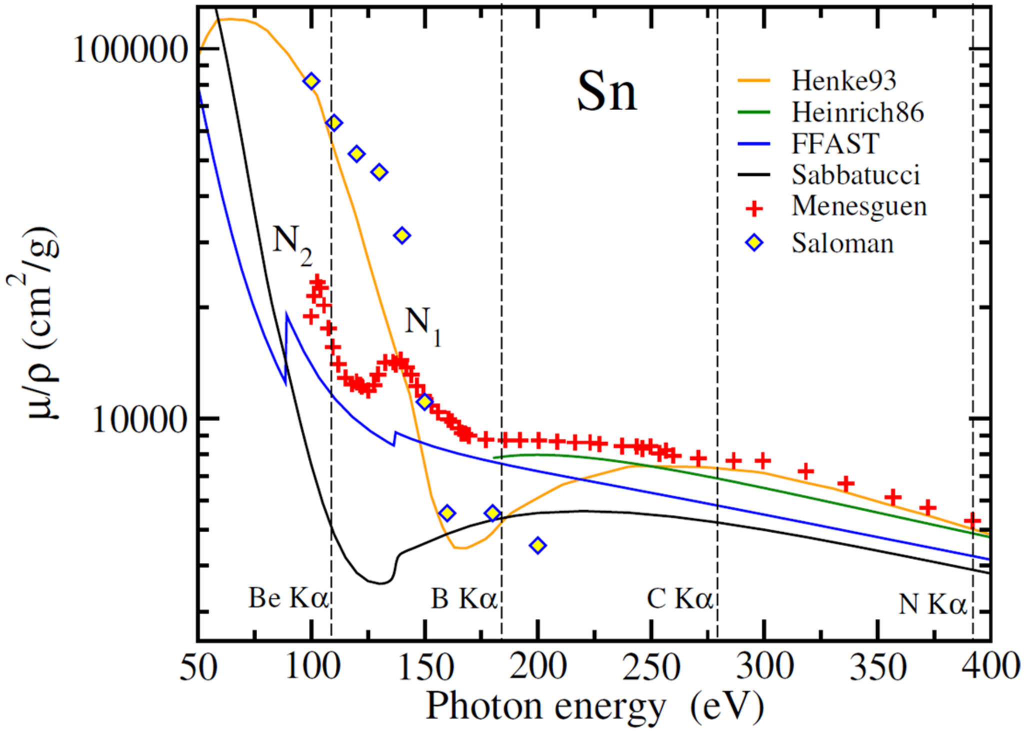
## Comparison with experimental data: Be and C emitters

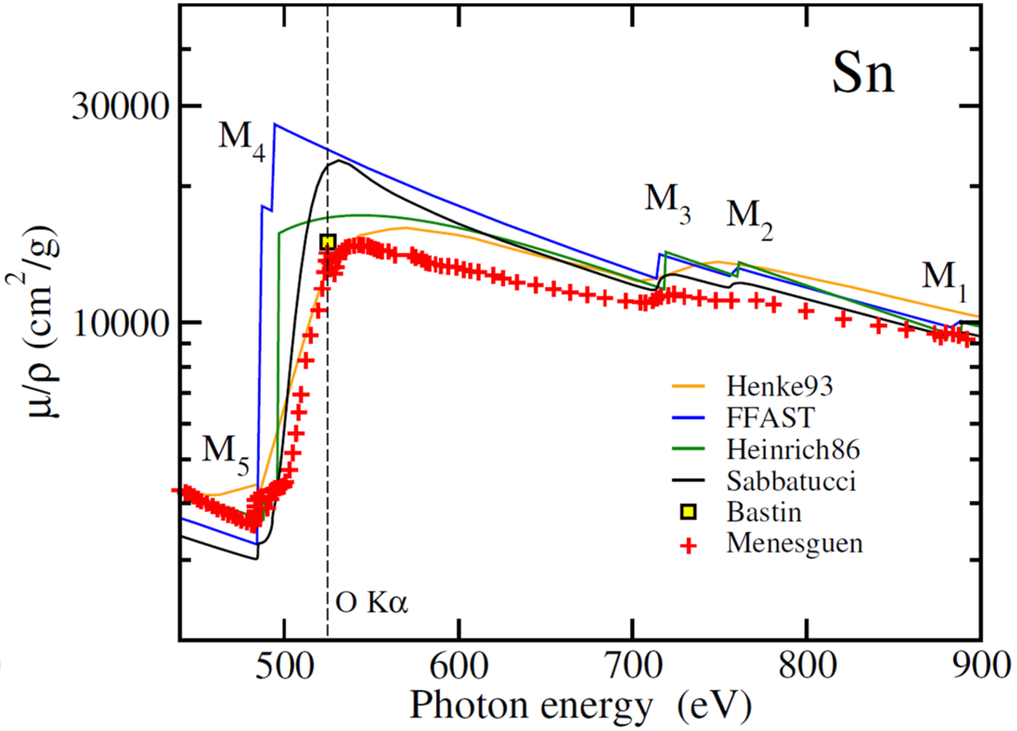




- Significant discrepancies between the diferent tabulations
- Large spread of the experimental data (high-Z absorbers)

## ● Comparison with experimental data: Sn absorber





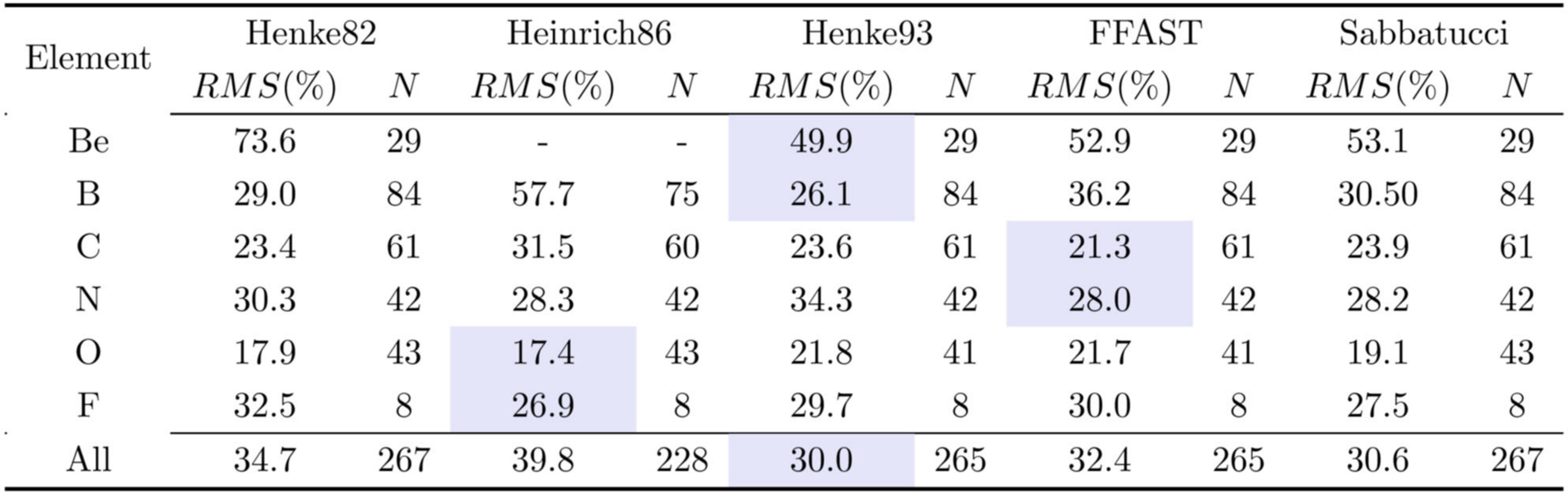
- EPMA measurements in good agreement with high-resolution photoabsorption data
- Discrepancies larger close to absorption edges and at lower X-ray energies

## Light elements: quantitative evaluation

Root mean square percentage deviation

$$\mathrm{RMS} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\Delta_i)^2}$$

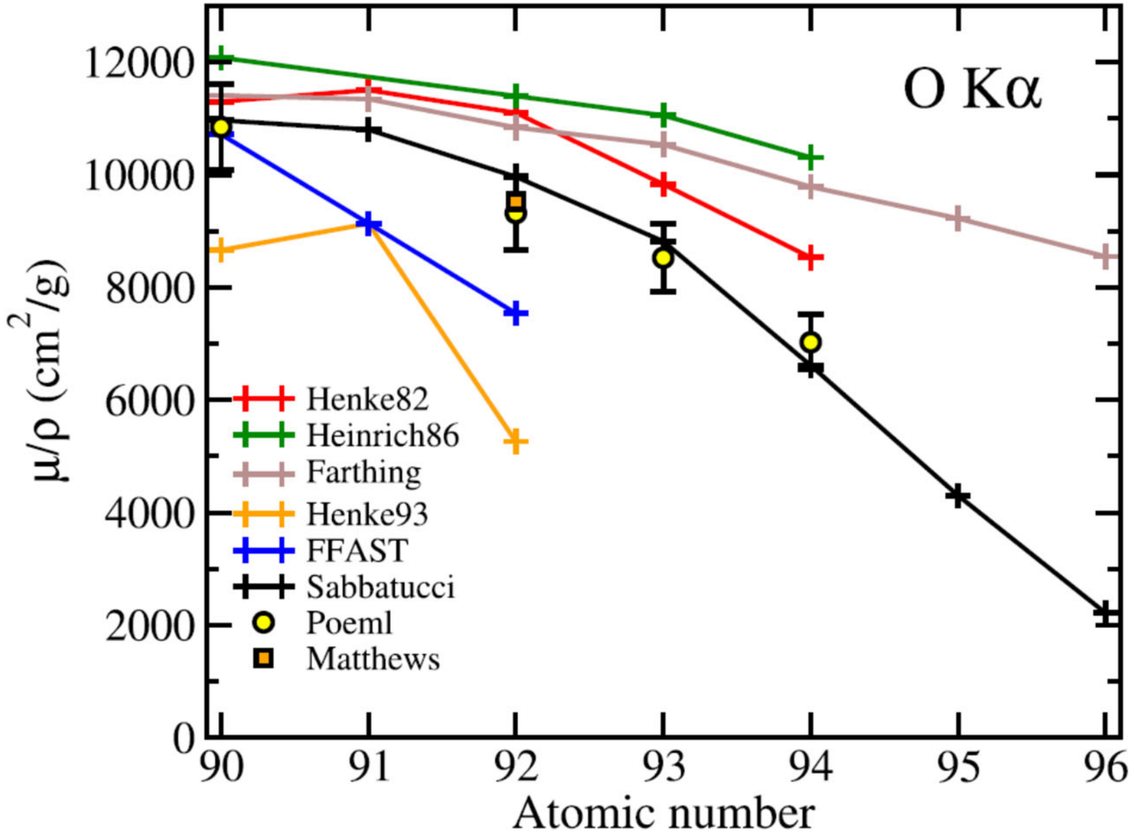
$$\Delta_i = \frac{(\mu/\rho)_{\mathrm{tab}} - (\mu/\rho)_{\mathrm{exp}}}{(\mu/\rho)_{\mathrm{exp}}} \times 100$$



| Element | Henke82 | | Heinrich86 | | Henke93 | | FFAST | | Sabbatucci | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *RMS*(%) | *N* | *RMS*(%) | *N* | *RMS*(%) | *N* | *RMS*(%) | *N* | *RMS*(%) | *N* |
| Be | 73.6 | 29 | - | - | 49.9 | 29 | 52.9 | 29 | 53.1 | 29 |
| B | 29.0 | 84 | 57.7 | 75 | 26.1 | 84 | 36.2 | 84 | 30.50 | 84 |
| C | 23.4 | 61 | 31.5 | 60 | 23.6 | 61 | 21.3 | 61 | 23.9 | 61 |
| N | 30.3 | 42 | 28.3 | 42 | 34.3 | 42 | 28.0 | 42 | 28.2 | 42 |
| O | 17.9 | 43 | 17.4 | 43 | 21.8 | 41 | 21.7 | 41 | 19.1 | 43 |
| F | 32.5 | 8 | 26.9 | 8 | 29.7 | 8 | 30.0 | 8 | 27.5 | 8 |
| All | 34.7 | 267 | 39.8 | 228 | 30.0 | 265 | 32.4 | 265 | 30.6 | 267 |

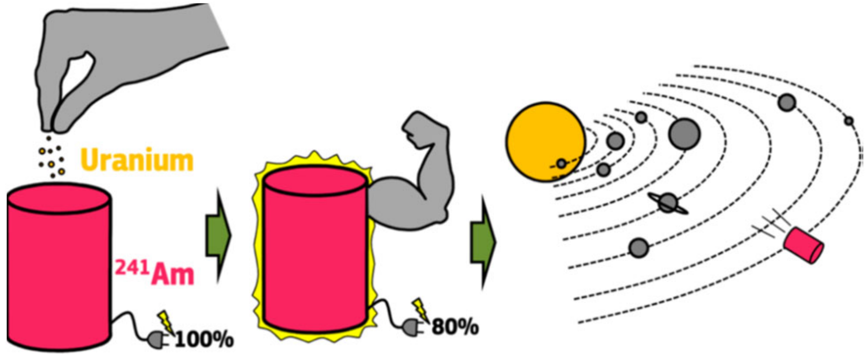
- Henke93 provides the lowest RMS, followed closely by Sabbatucci-Salvat
- More experimental data needed to draw definite conclusions, for high-Z absorbers

## ● Actinide absorbers



Recent EPMA based measurements for O Ka X-rays in good agreement with Sabbatucci-Salvat's MACs

# ● EPMA analysis of U-doped Am oxide



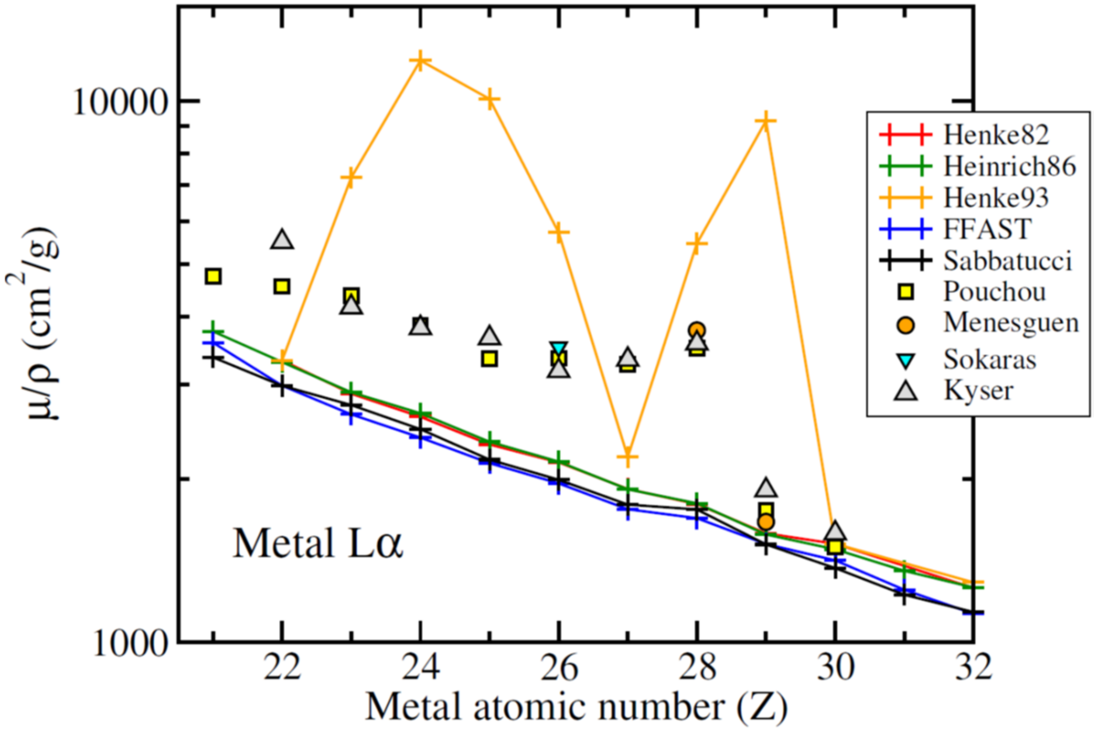
U-doped Am oxide developed as a radioisotope heater for space missions into deep space, where energy from the sun is not available

Vigier et al. Inorg. Chem. 2018, 57, 4317−4327

| **MAC source** | **U (wt.%)** | **Np (wt.%)** | **Pu (wt.%)** | **Am (wt.%)** | **O (wt.%)** | **Total** |
|---|---|---|---|---|---|---|
| Farthing-Walker | 11.2 | 5.01 | 1.57 | 72.2 | 17.1 | 107.2 |
| Sabbatucci-Salvat | 11.0 | 5.02 | 1.55 | 71.2 | 10.3 | 99.1 |

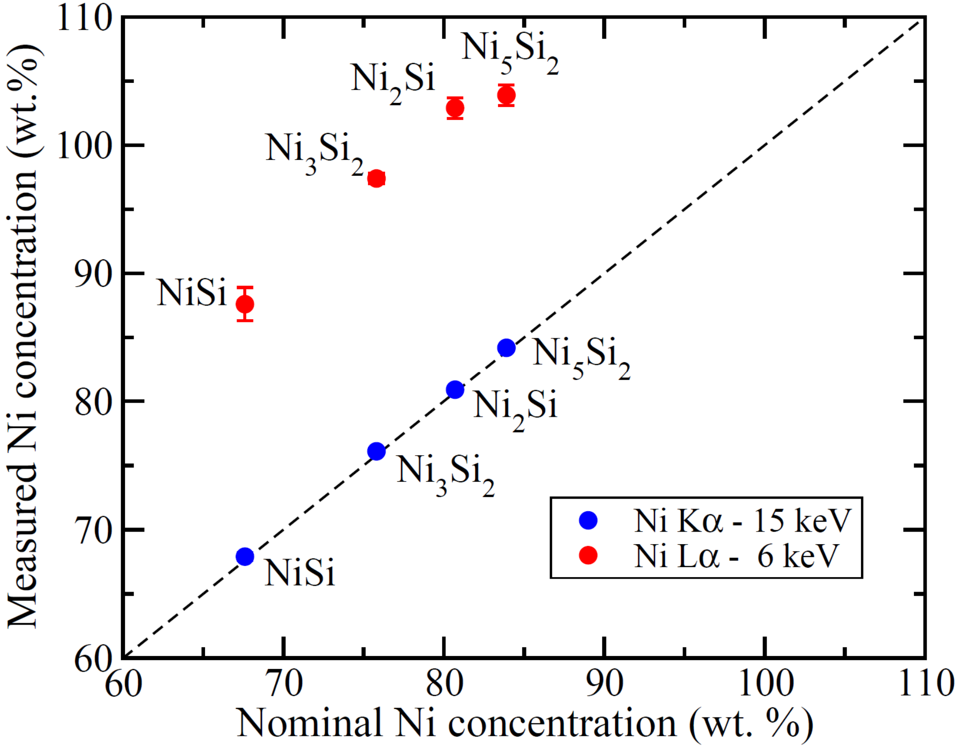
The use of the Sabbatucci-Salvat MACs provided a total closer to 100%

- **Comparison with experimental data: transition metals**



- Tabulations consistently underestimate experimental data by 30-40%
- Henke93 much higher than other tabulations (except for Ti, Co and Zn)

- **EPMA analysis of Ni silicides using Lα lines**

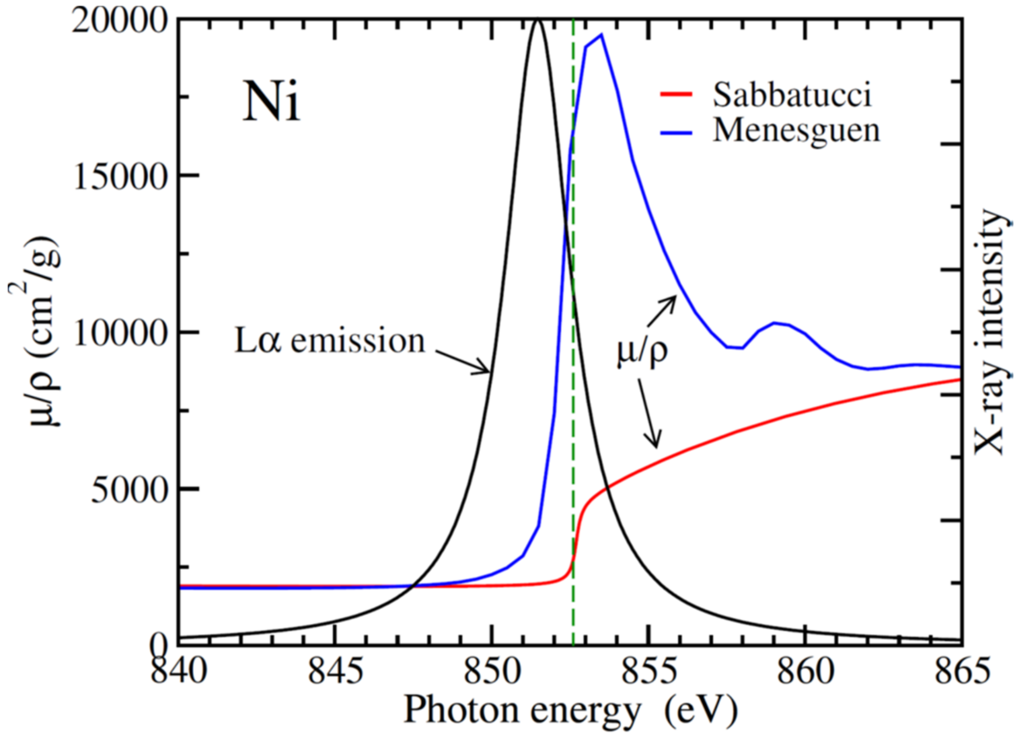


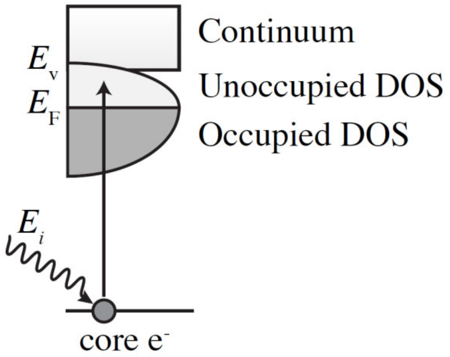
**Ni Lα:** deviation between measured and nominal concentrations of **20-30%**

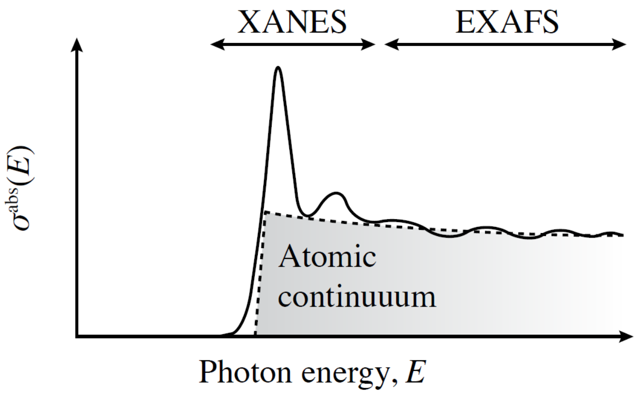
Llovet et al. (2016) Micros. Microanal. **22** 1233-1243

# Absorption peaks at the edges

Ni: [Ar] $3d^9\ 4p^1$

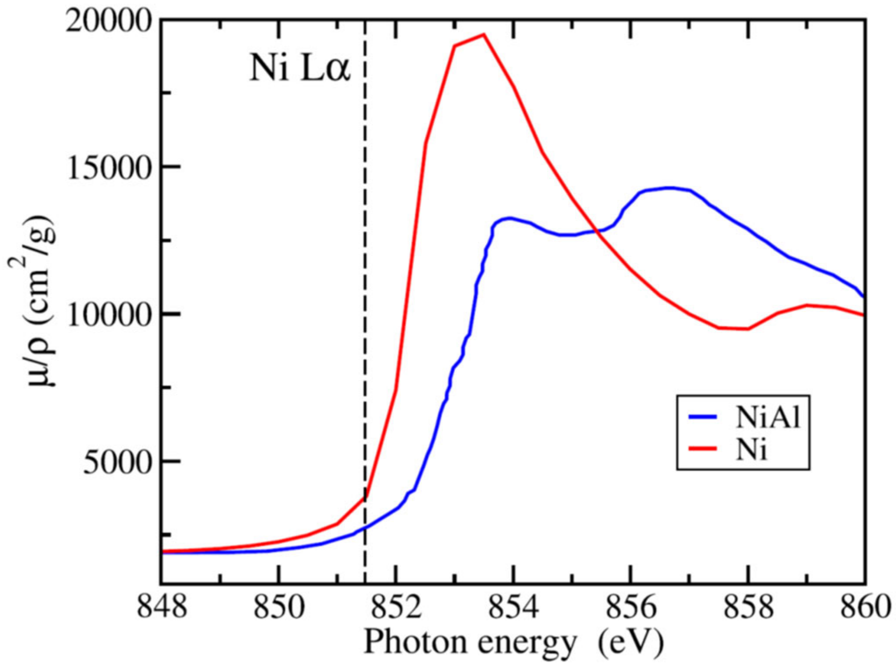


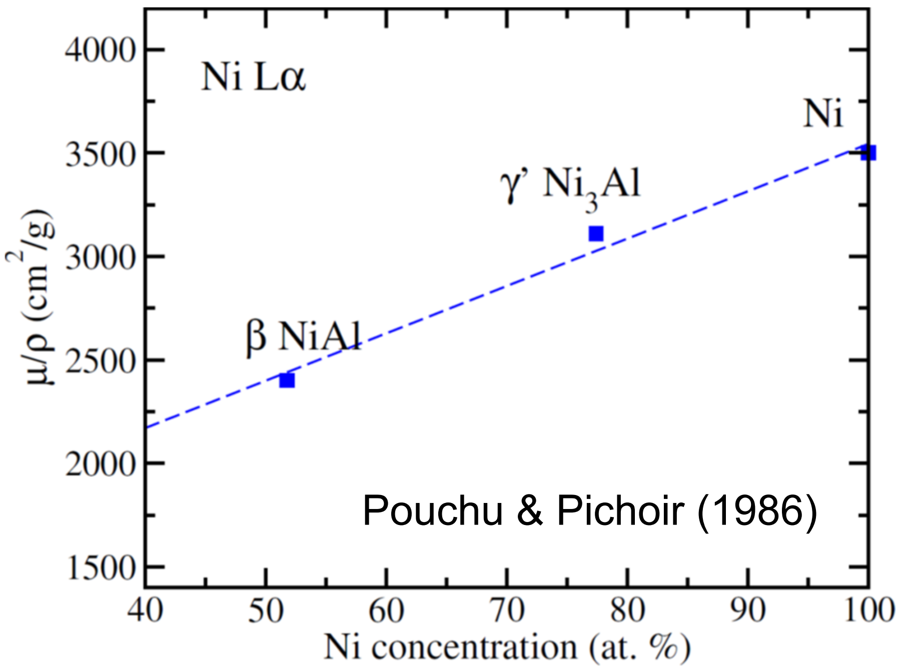




- Absorption peak: excitation of the unocuppied states of the 3*d* band, sensitive to the chemical state of the element
- Self-absorption: MAC increases rapidly across the X-ray line width (2.58 eV)

# MAC sensitivity to chemical bonding: NiAl

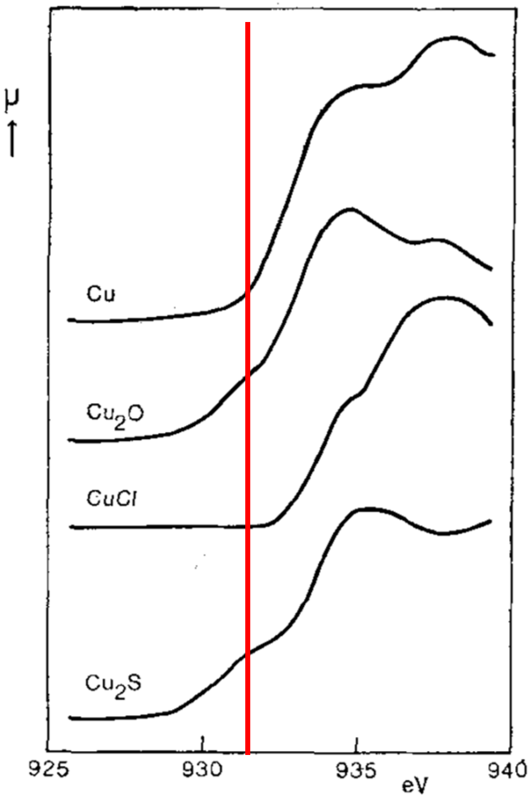




Pouchu & Pichoir (1986)

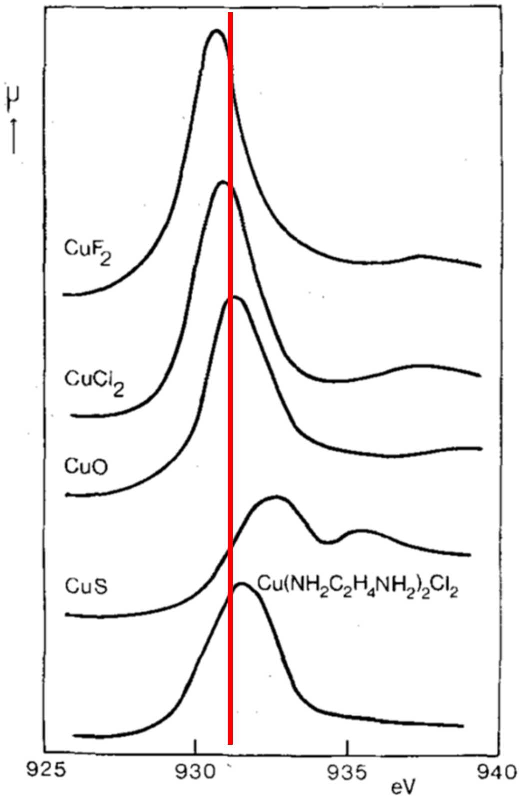
- Sensitivity to chemical bonding for NiAl: the filling of the 3d states by electrons from Al reduces the intensity of the absorption peak
- Breakdown of the additivity rule used to calculate MACs for compounds
- MAC measurements with the EPMA is a practical solution

## MAC sensitivity to chemical bonding: Cu compounds



$Cu^0$: [Ar] $4s^1$ $3d^{10}$

$Cu^{1+}$: [Ar] $3d^{10}$

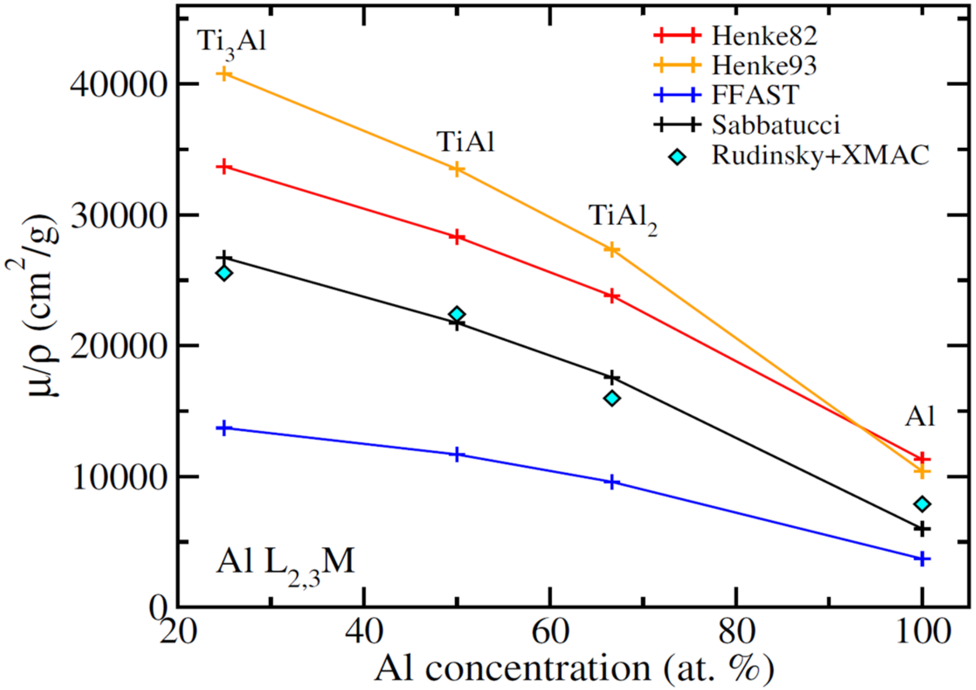


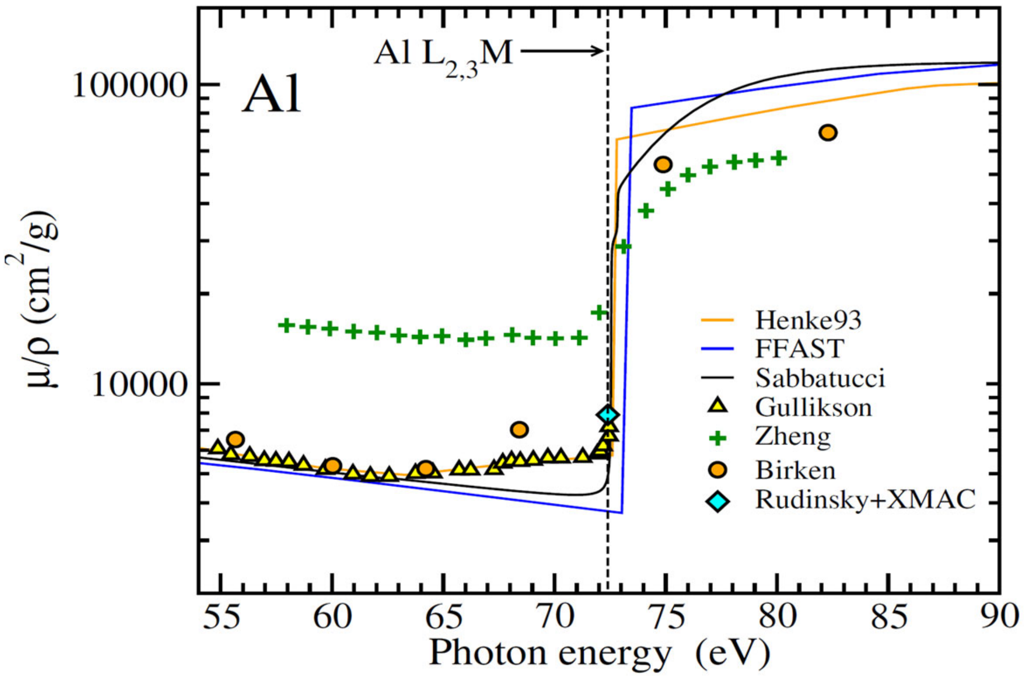
$Cu^{2+}$: [Ar] $3d^9$

Kosler (1975)

$Cu^{2+}$ compounds affected by self-absorption due to the presence of absorption peaks

# Ultra soft X-rays: Al L2,3M X-rays (72.4 eV)





- MACs measured by Rudinsky et al (2020) using EPMA-SXES reprocessed with XMAC and Badgerfilm
- Good agreement with the MACs from Sabbatucci-Salvat for pure Al and several TiAl compounds

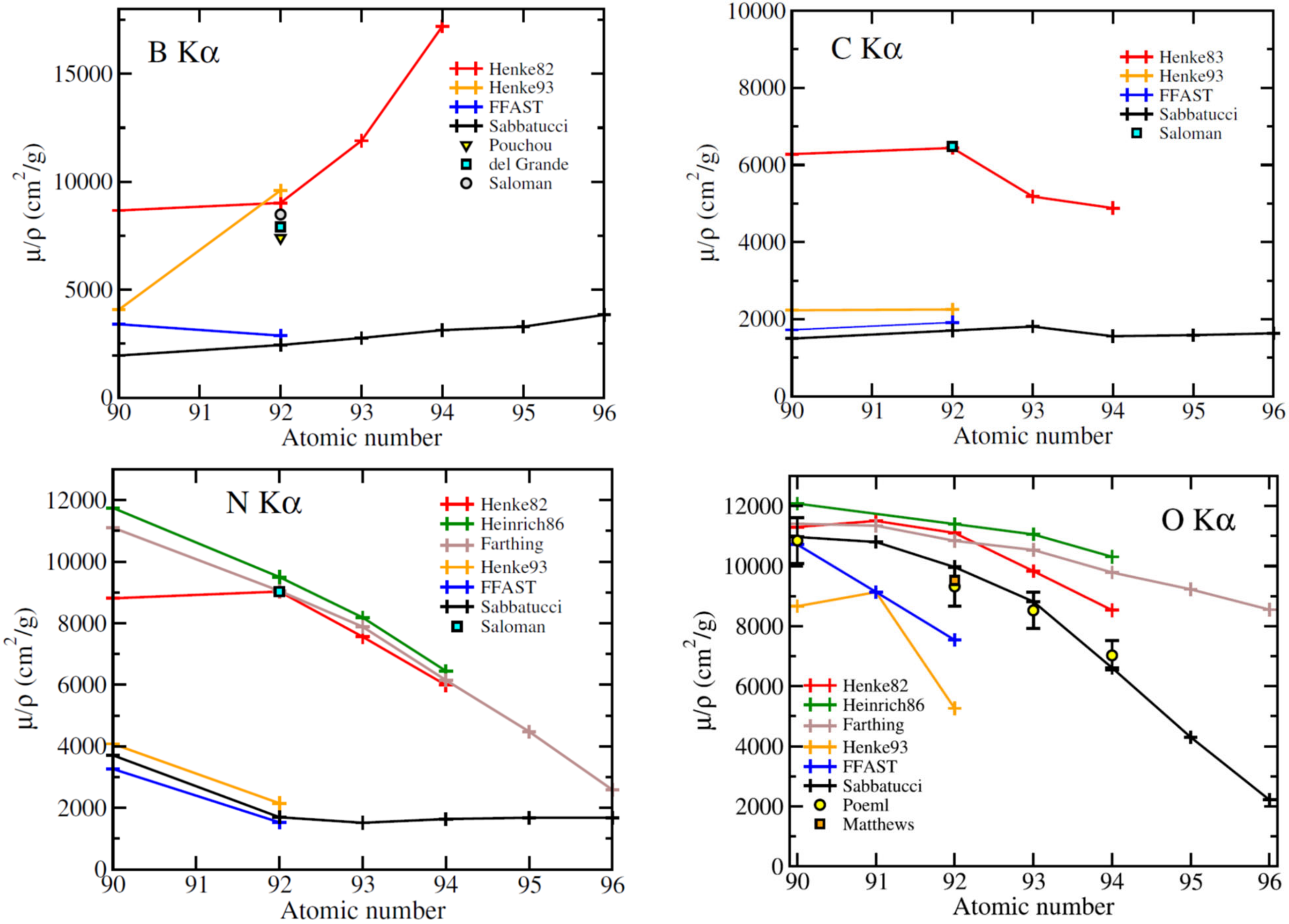
# ● Conclusions

- An assessment of the accuracy levels in MAC tabulations for soft X-rays has been presented by comparing tabulated MACs with experimental data available in the literature.

- The **1993 Henke** tabulation provides the lowest RMS value for light elements, but the theoretical MACs of **Sabattucci-Salvat** perform better if L-lines of transition metals and ultra-soft X-rays are considered

- EPMA allows determining the MAC when tabulated data is controversial or inexistent, especially near or between absorption edges.

Pöml P & Llovet X (2020) Micros. Microanal. **26** 194
Llovet X,  Moy A & Fournelle JH (2022) Micros. Microanal. **28** 123
Llovet X, Pöml P, Moy A & Fournelle JH (2023) Micros. Microanal. **29** 540


B Kα
Henke82
Henke93
FFAST
Sabbatucci
Pouchou
del Grande
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μ/ρ (cm$^2$/g)
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Atomic number
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Henke93
FFAST
Sabbatucci
Saloman
μ/ρ (cm$^2$/g)
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FFAST
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