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High Precision X-Ray Measurements 2023
June 19–23, 2023 - Laboratori Nazionali di Frascati INFN

Investigating Metals’ Content and Oxidation States in Edible Liquids using XRF Analysis with VOXES X-ray Spectrometer

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MITIQO

In situ **M**onitoring of **T**oxicity, geographical **I**ndication, and **Q**uality of **O**live oil, wine, and other edible liquids

Outline

1. The VOXES X-ray Spectrometer

2. XES spectra with VOXES

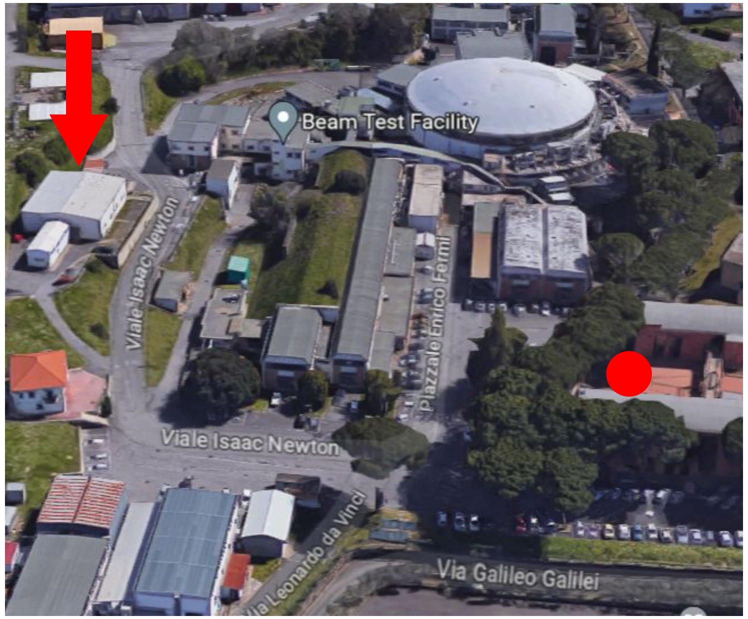
3. Applications: content and oxidation states of metal

High resolution von-Hamos X-Ray spectrometer using HAPG for Extended Sources in a broad energy range

VOXES is an high resolution and high efficiency X-ray spectrometer in the range of energies 2 - 20 keV using Highly Annealed Pyrolytic Graphite (HAPG) bent crystals able to work with ‘extended’ sources

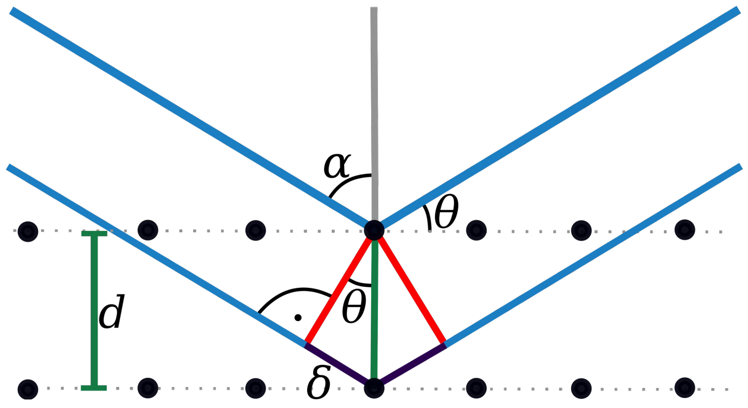
To be used in (for example):

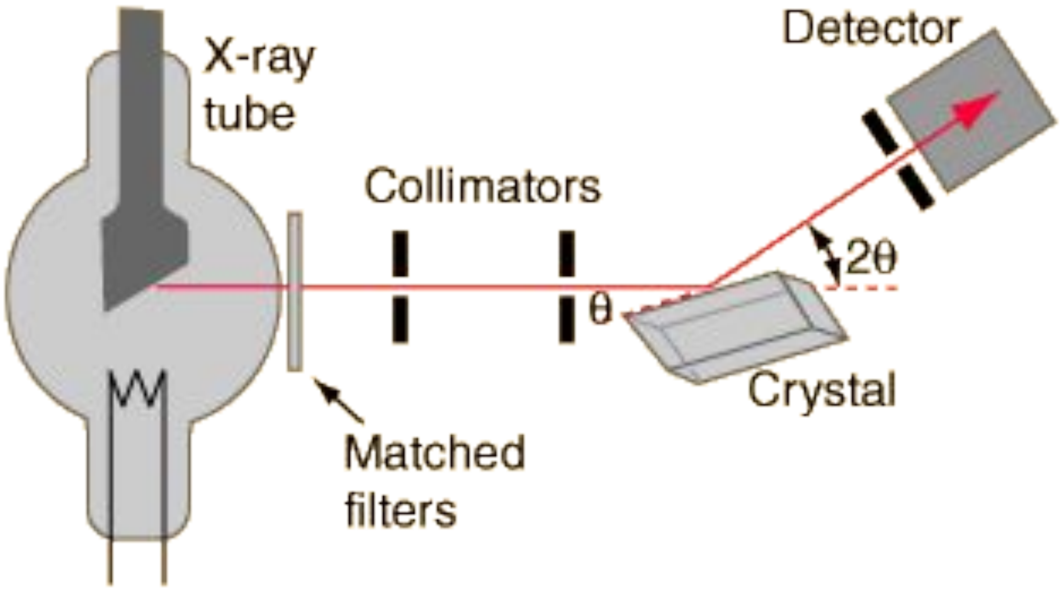
- Kaonic atoms experiments
  (kaon mass, isotopic shift, etc..)
- Elemental mapping
- XRF of trace metals
- Food control
- Medical applications
- Others.



X-Ray Emission Spectroscopy (XES) with crystals

$$n\lambda = 2d \sin \theta_B$$





FWHM ~ 1-10 eV can be achieved depending on the quality of the crystal and the dimensions of the detectors

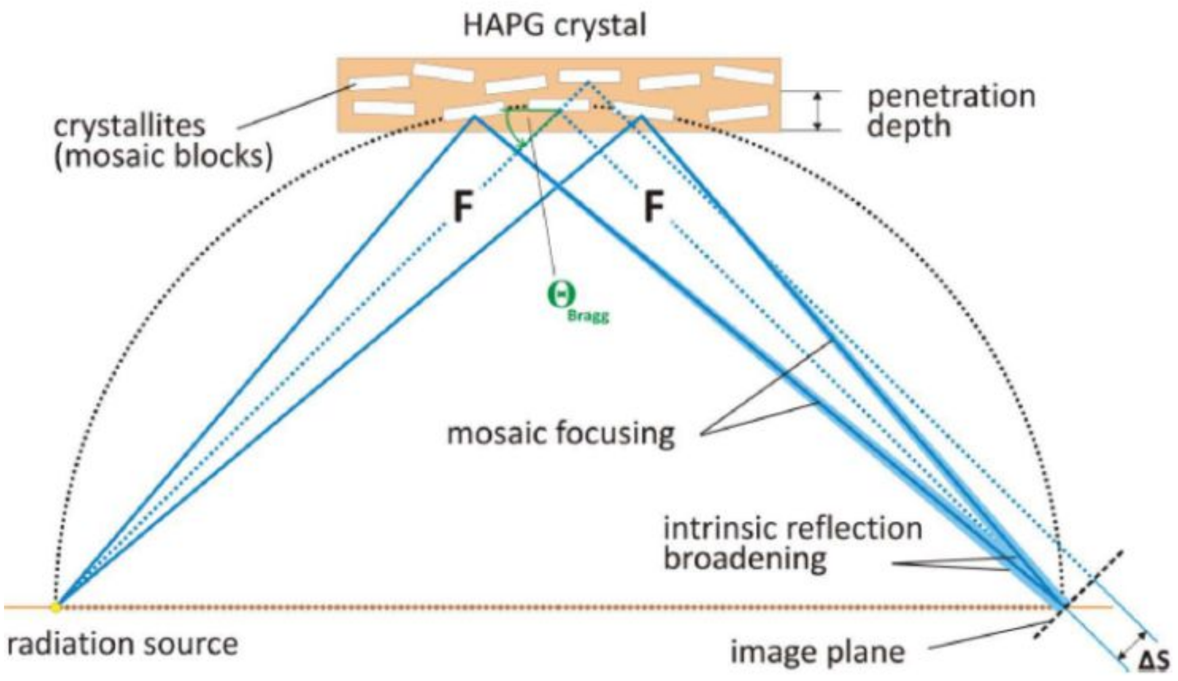
But….

- Small solid angles can be covered
- Typical efficiencies : $10^{-5} – 10^{-8}$
- Typical d (Si) ≈ 5.5 Å (good for E < 6 keV)
- Typical source size 10-100 mm

HAPG mosaic crystals improve the efficiency

Mosaic crystal consist in a large number of nearly perfect small crystallites.

Mosaicity makes it possible that even for a fixed incidence angle on the crystal surface, an energetic distribution of photons can be reflected



Pyrolitic Graphite mosaic crystals (d = 3.354 Å):

- Bending does not influence resolution and intensity
- Mosaic spread down to 0.05 degree
- Integral reflectivity ~ 10^2 higher than for other crystals
- Variable thickness (efficiency)
- Excellent thermal and radiation stability

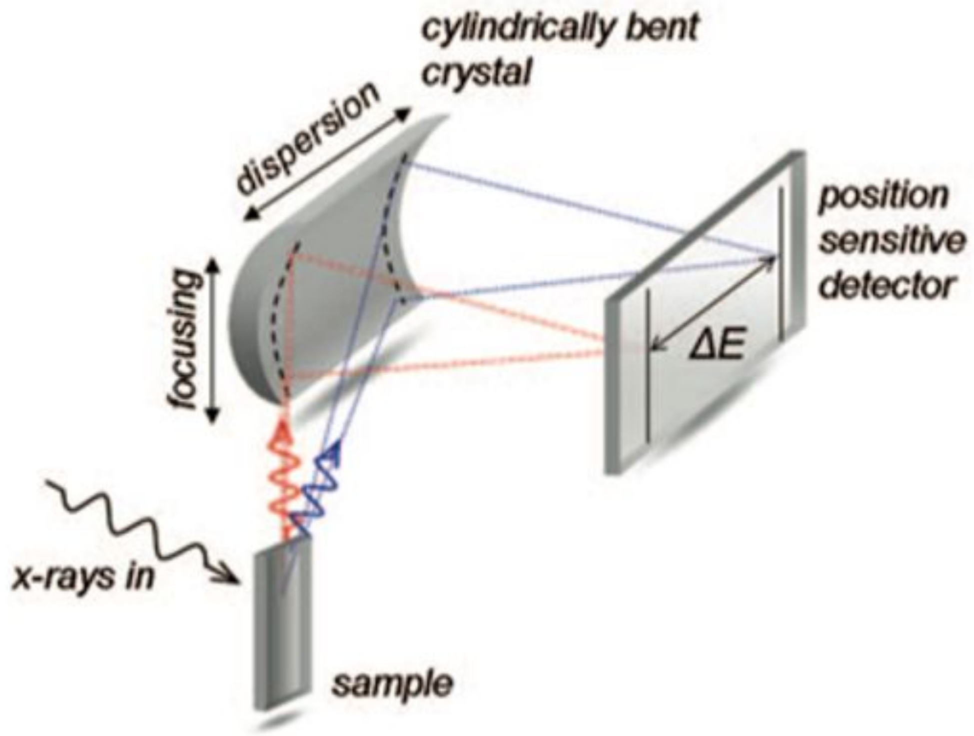
Increase of efficiency (focusing) ~ 50

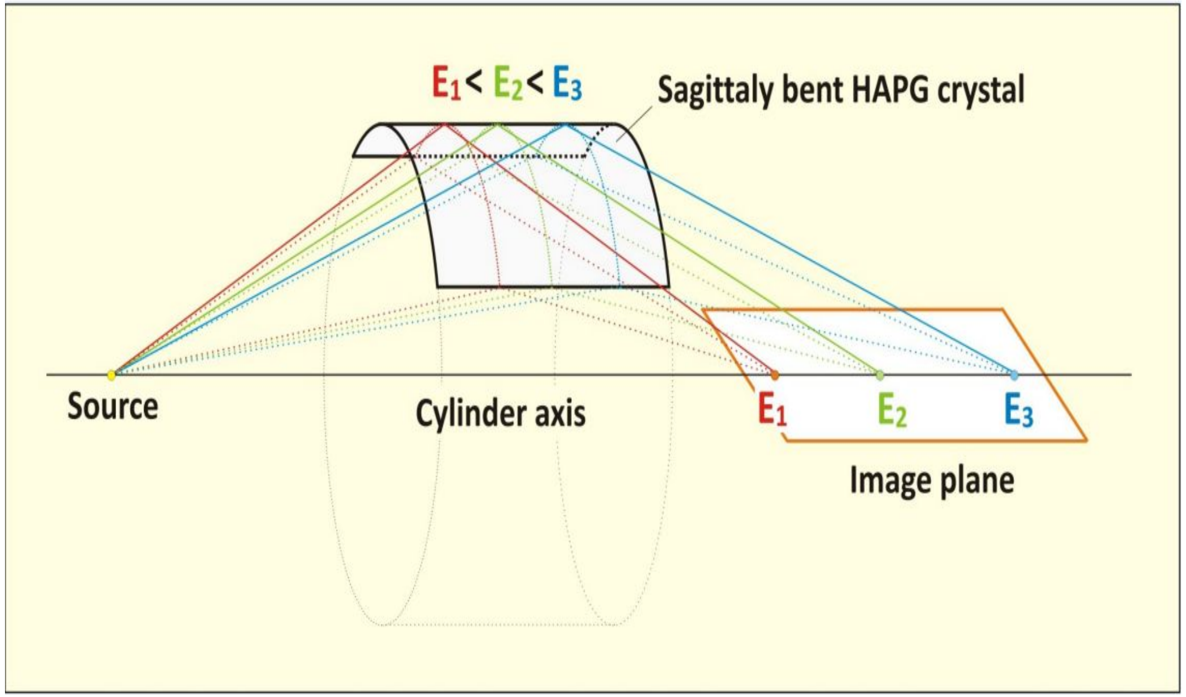
Loss in resolution

Improving the solid angle with Von Hamos configuration

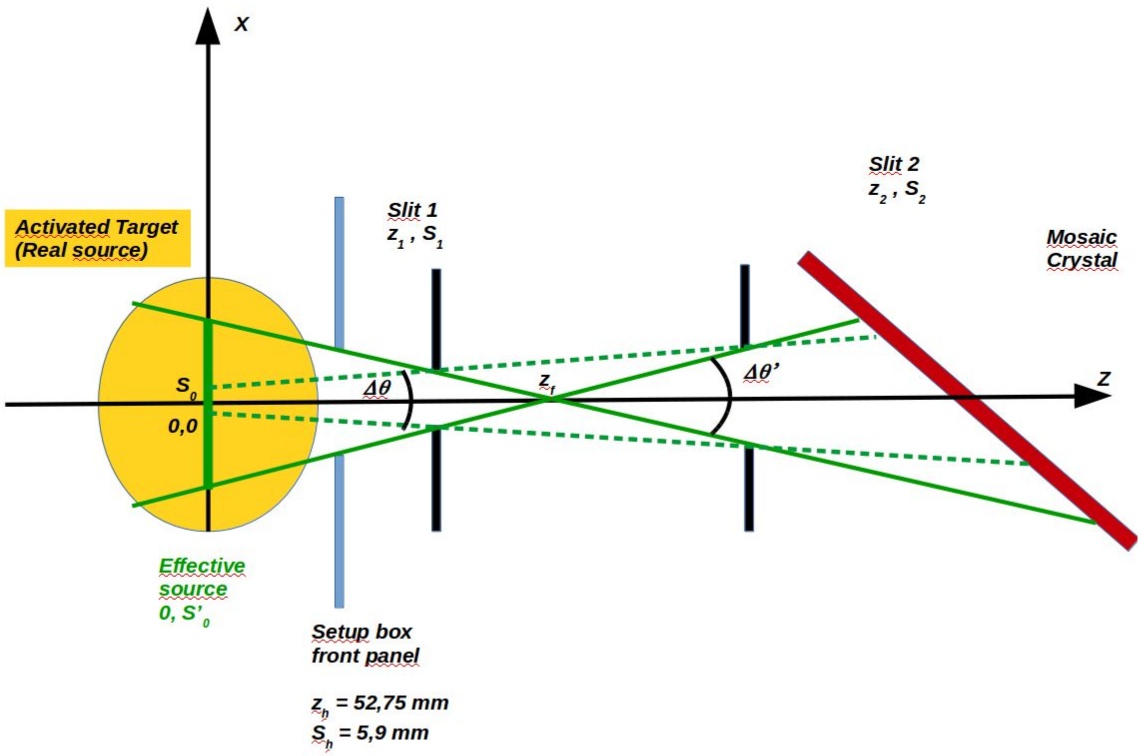
Von Hamos configuration can further improve the signal collection efficiency.

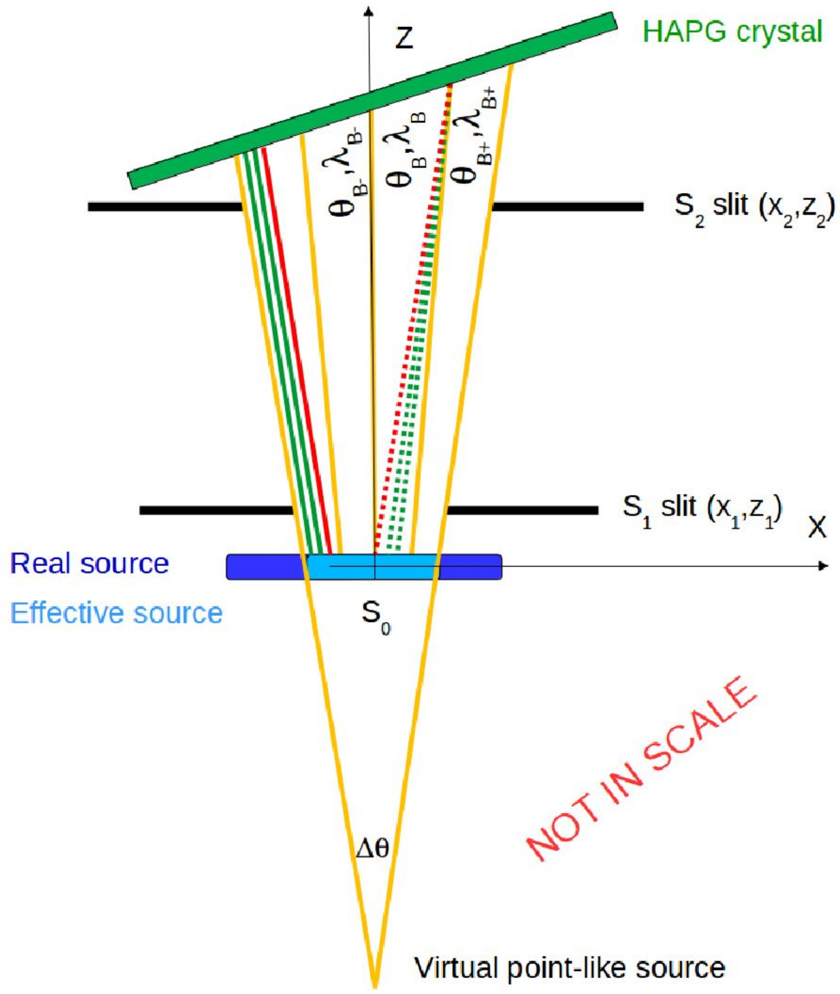
In this configuration, also the vertical dimension of the X-ray source can be exploited





VOXES: enlarging the source size with two slits

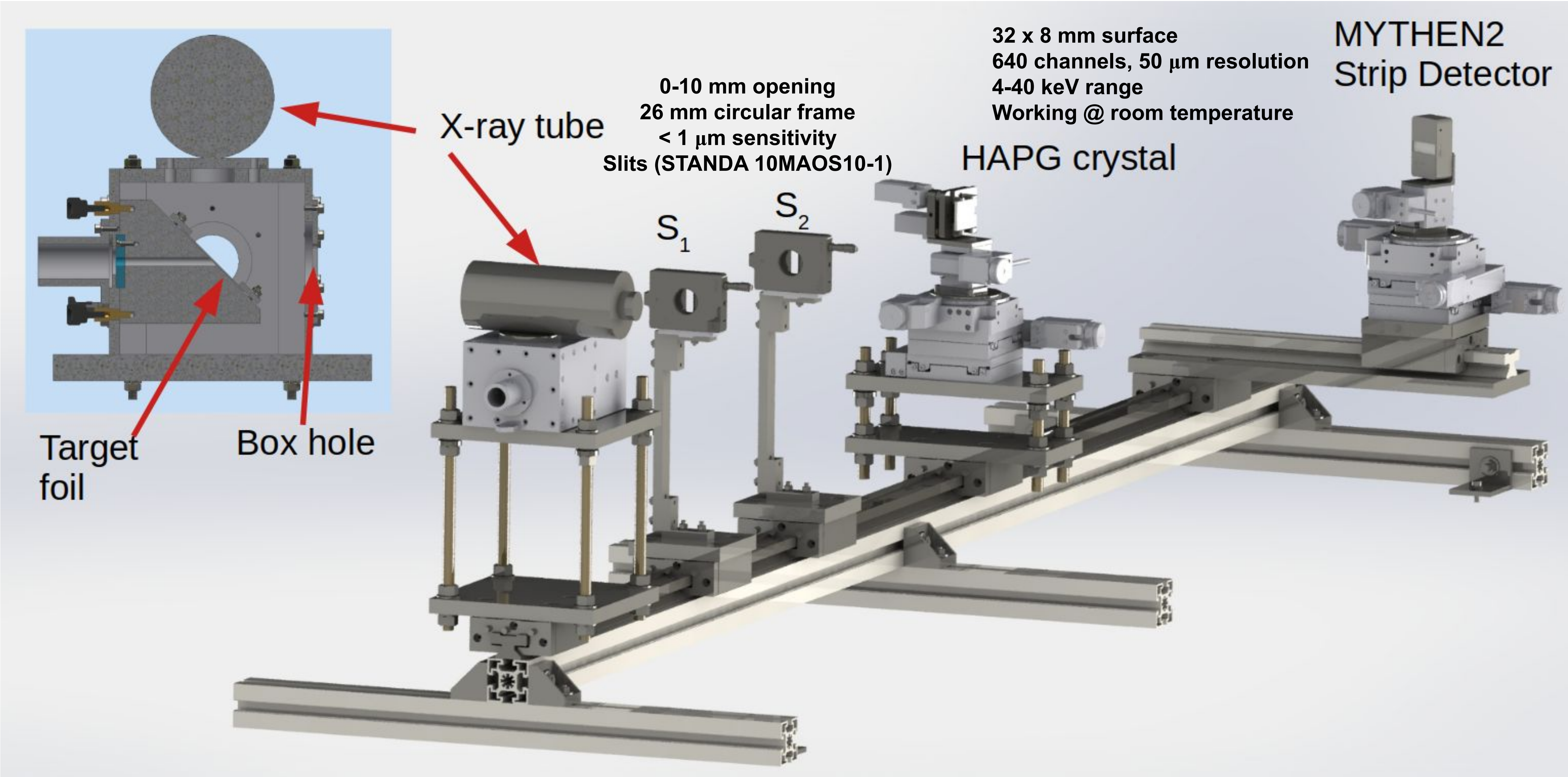




The shape of the "signal" beam can be optimized to increase the effective source size

On the other hand, this may lead to a worsening of the resolution

The VOXES setup



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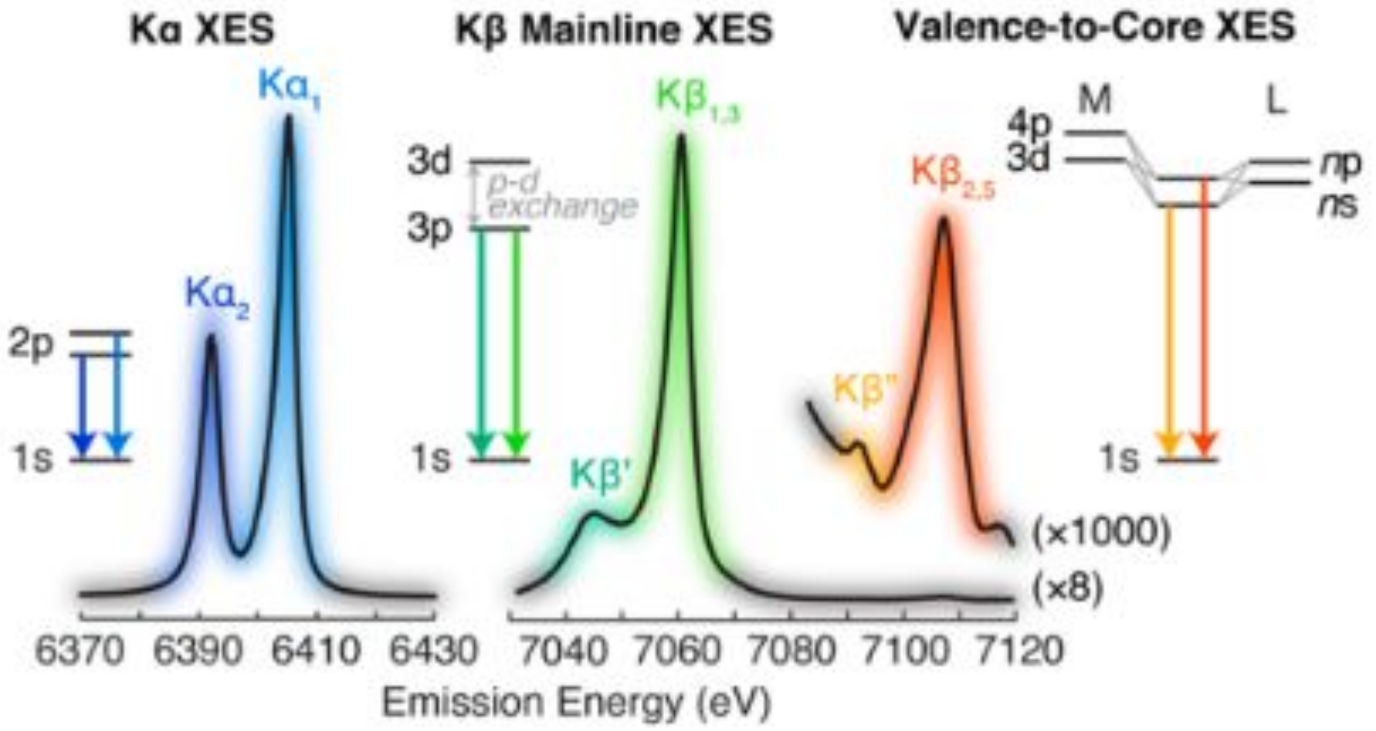
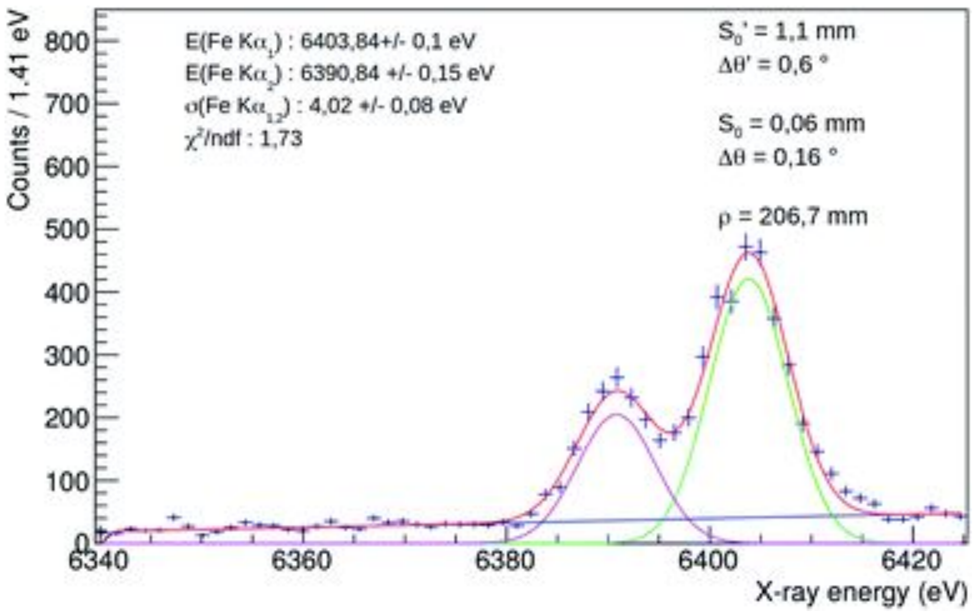
X-ray Emission Spectroscopy (XES) with VOXES

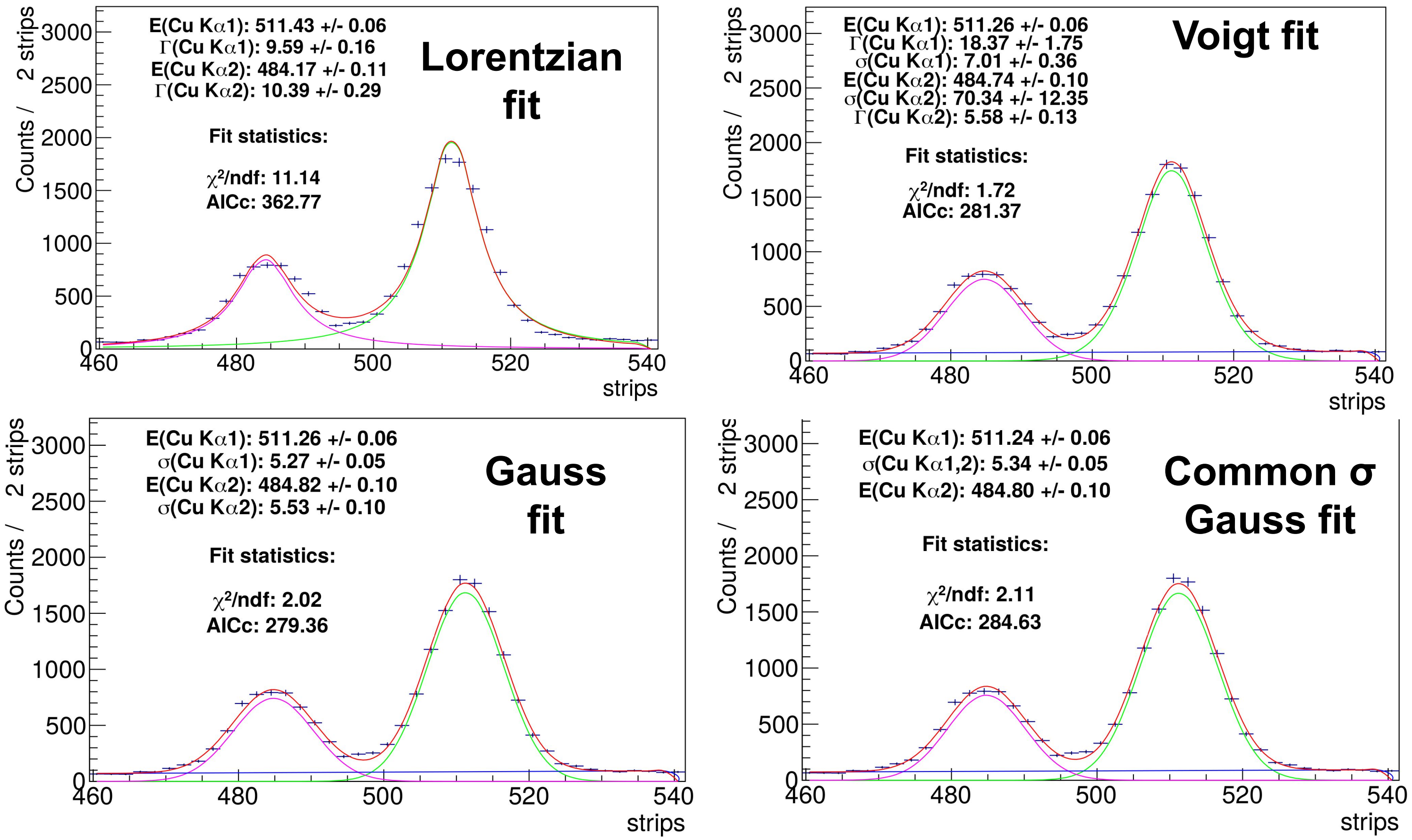




Nicole Lee, Taras Petrenko, Uwe Bergmann, Frank Neese, and Serena DeBeer, Journal of the American Chemical Society 2010 132 (28), 9715-9727 DOI: 10.1021/ja101281e

Which is the correct shape to be used for peak fitting?

Natural linewidths are Lorentzian but….



Is Voigt really better?

Akaike Information Criteria:

$$\mathrm{AIC} = 2p + N \cdot ln\left(\frac{R}{N}\right)$$

N = num of fitted points
p = num of fit parameters

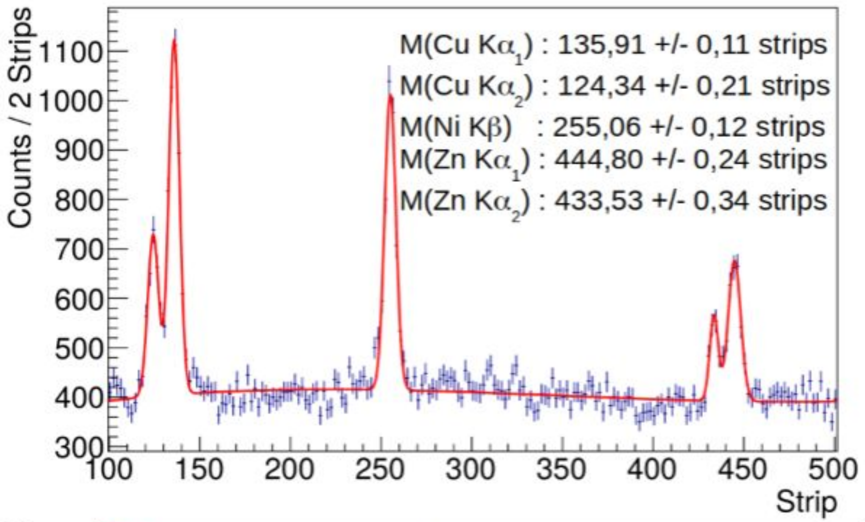
$$\mathrm{AICc} = \mathrm{AIC} + \frac{2 \cdot p \cdot (p+1)}{N-p-1}$$

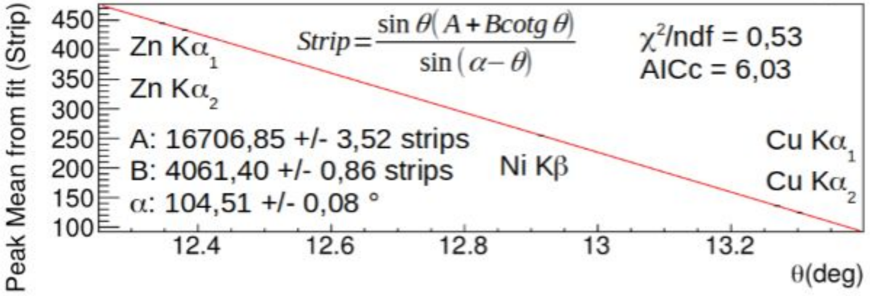
(for N/p < 40)

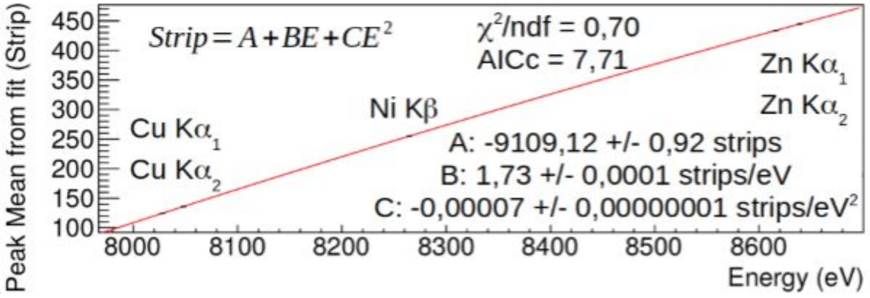
Not much information loss using gaussian shape

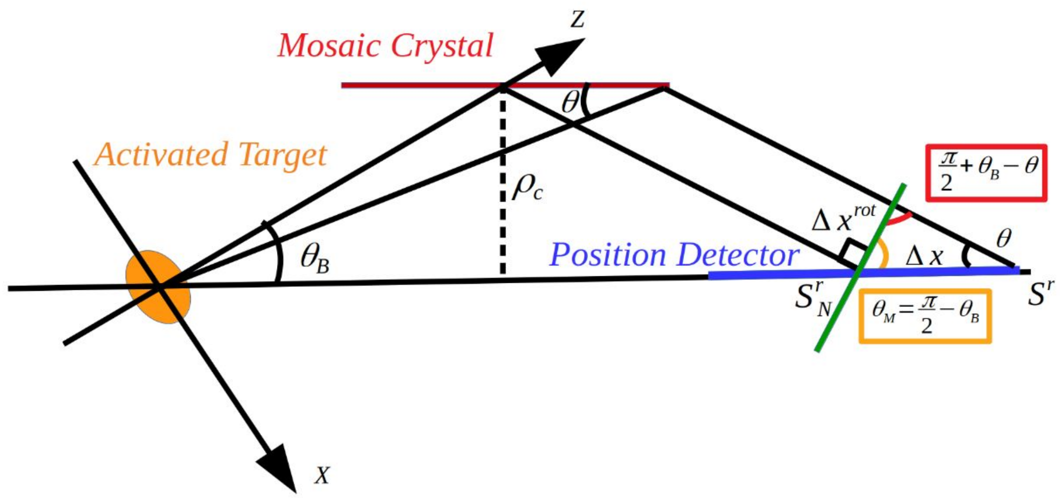
Energy calibration with Bragg spectroscopy

$S_0' = 540\,\mu m$ and $\Delta\theta' = 0{,}27°$









Standard VH calibration: $\Delta x = 2\rho_c \cdot (\cot\theta_B - \cot\theta)$

Semi VH calibration: $\Delta x^{rot} = \dfrac{2\rho_c \cdot (\cot\theta_B - \cot\theta)\cdot \sin\theta}{\sin(\frac{\pi}{2} - \theta_M - \theta)}$

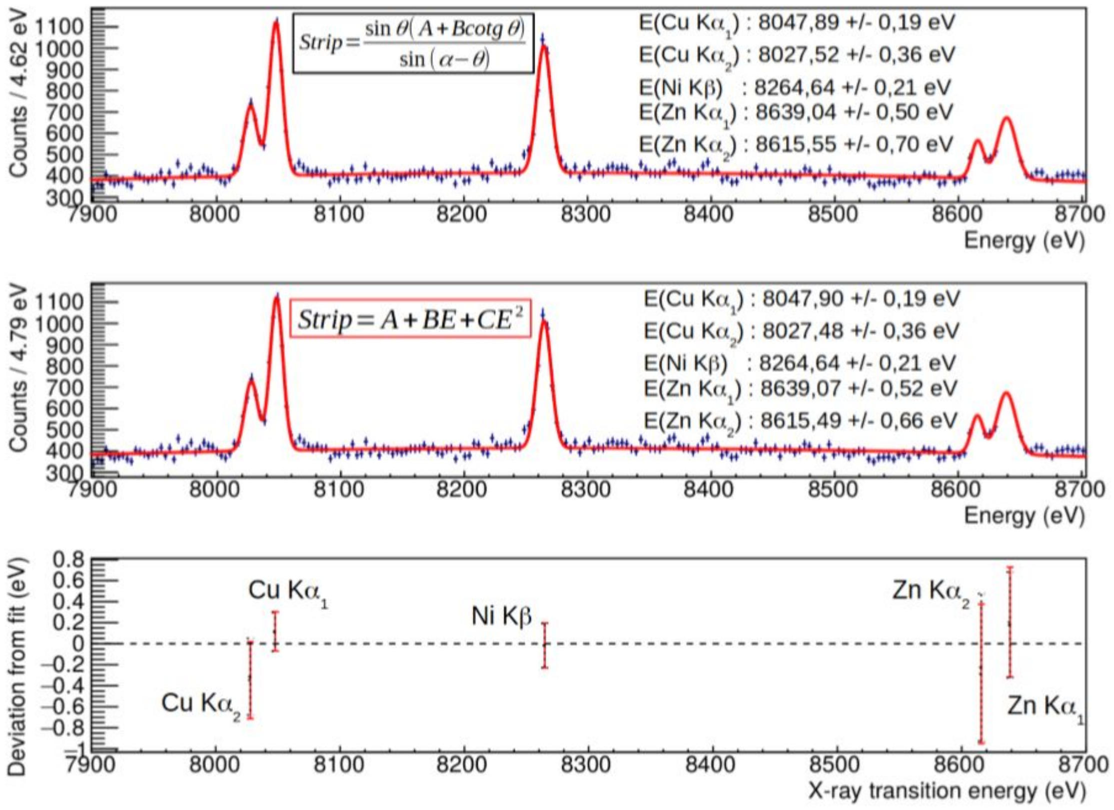
Parametric form: $\Delta x^{rot} = \dfrac{(A + B\cdot\cot\theta)\cdot\sin\theta}{\sin(\alpha - \theta)}$

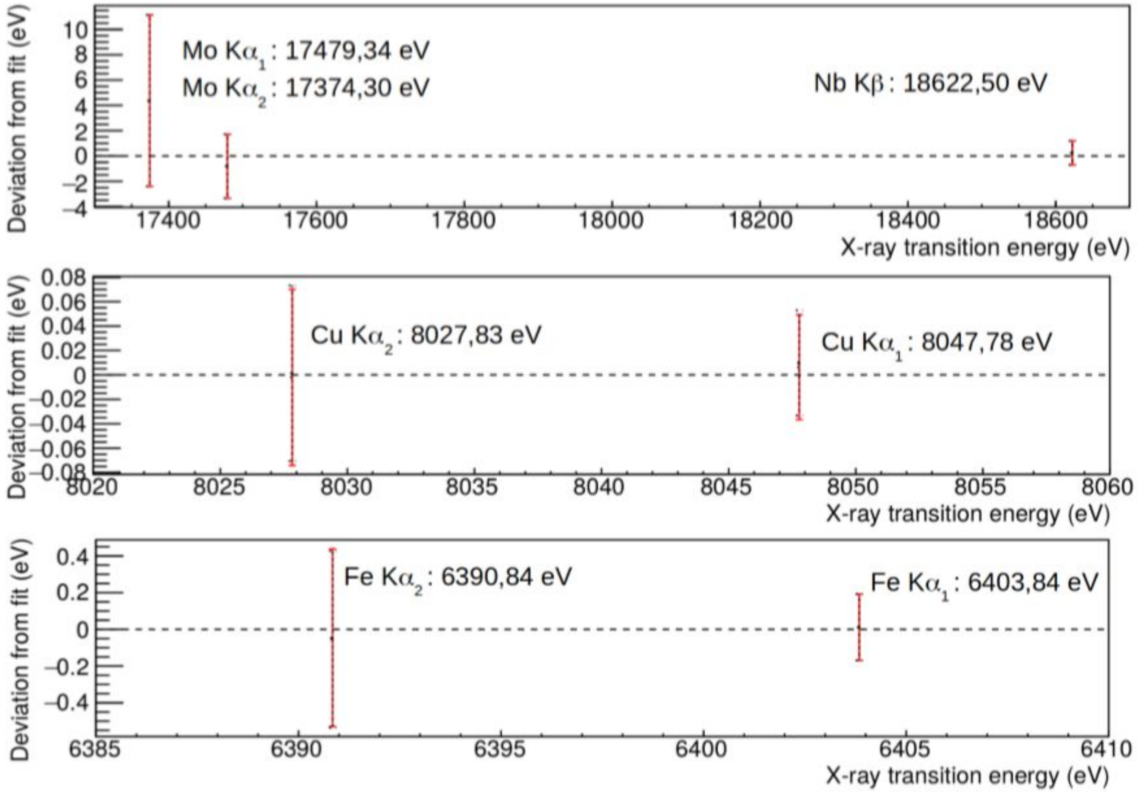
Given the small q values (sinq ≈ q), is it also possible to calibrate with a polynomial?

Information loss???

Energy calibration with Bragg spectroscopy

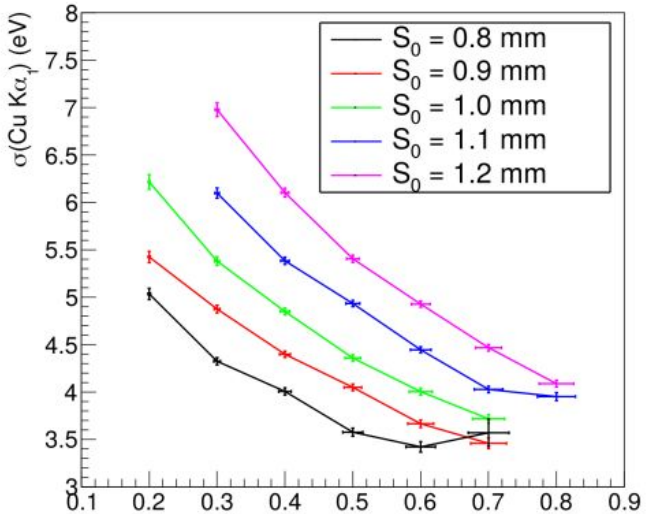
The (small) information loss is not influencing the peak positions

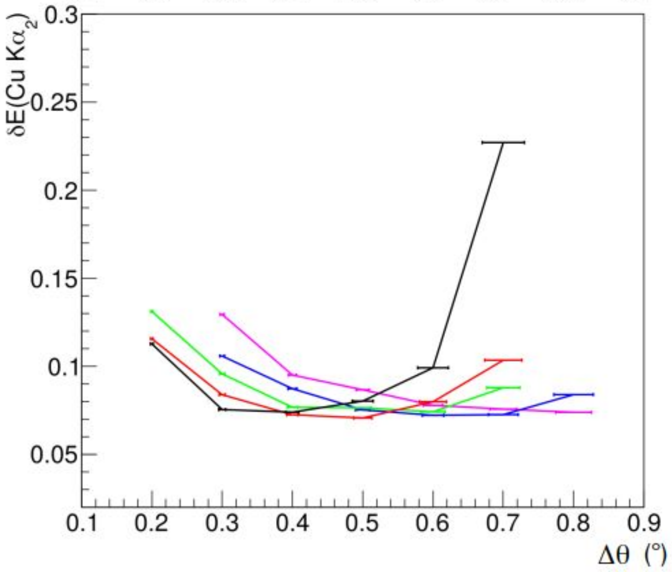




Also valid for higher and wider energy ranges (and higher θ, Δθ values)

Finding the best S_0' and Δθ' for XES spectra



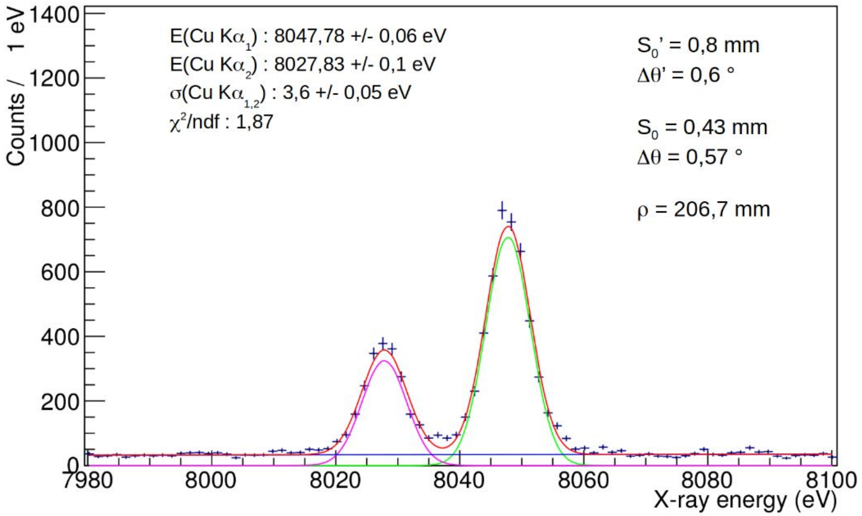


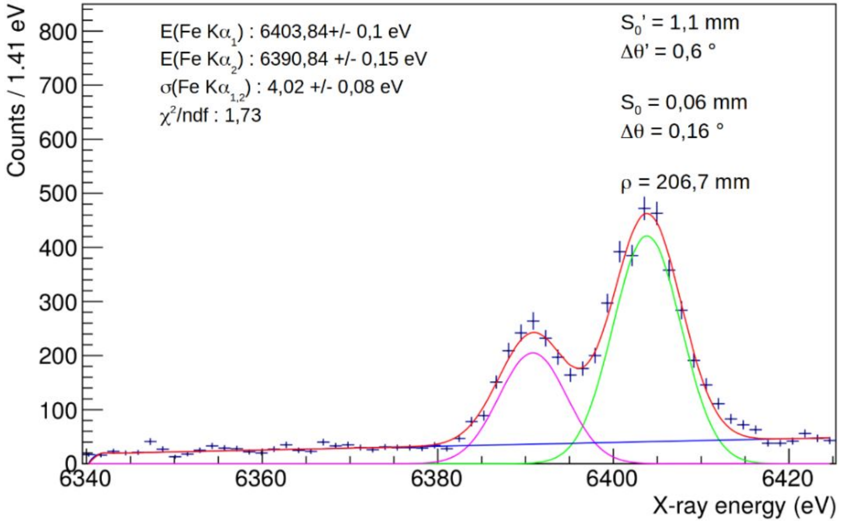
In the limit of a background free pure gaussian peak, the precision is related to the resolution via:

$$\delta E = \frac{\sigma E}{\sqrt{N}}$$

Given the energy and r_c it is alwasy possible to find the optimal configuration to obtain the best peak position precision

Valid for all energies (tested for 6-20 keV)





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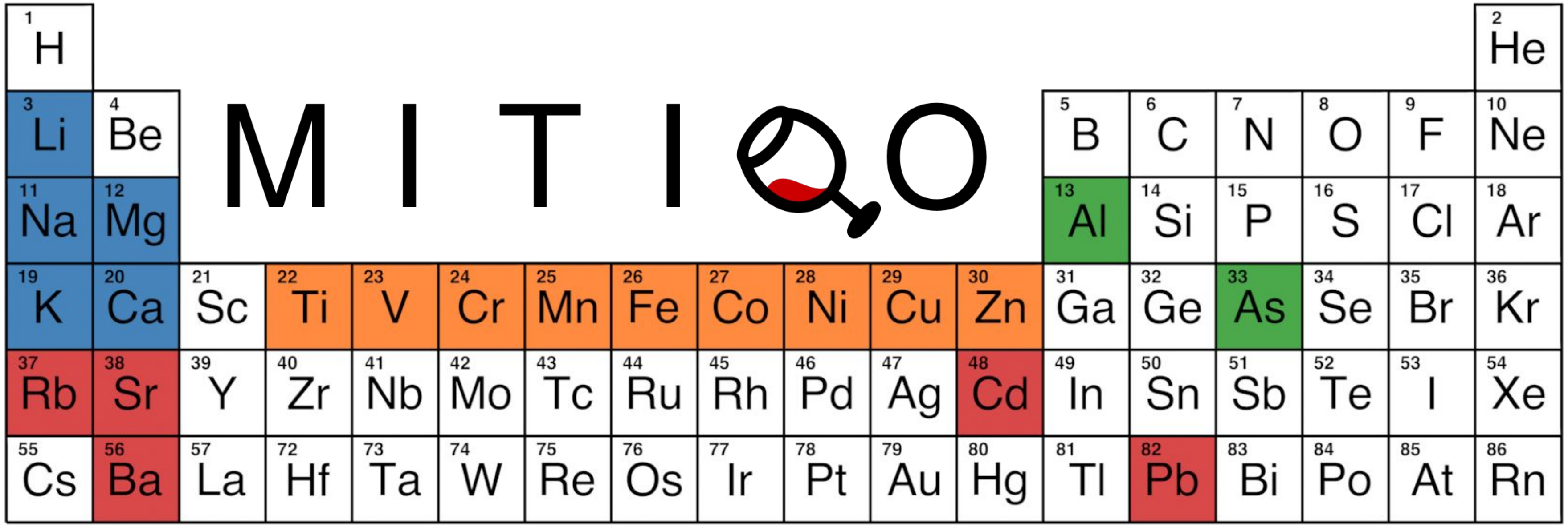
What metals are present in wine?

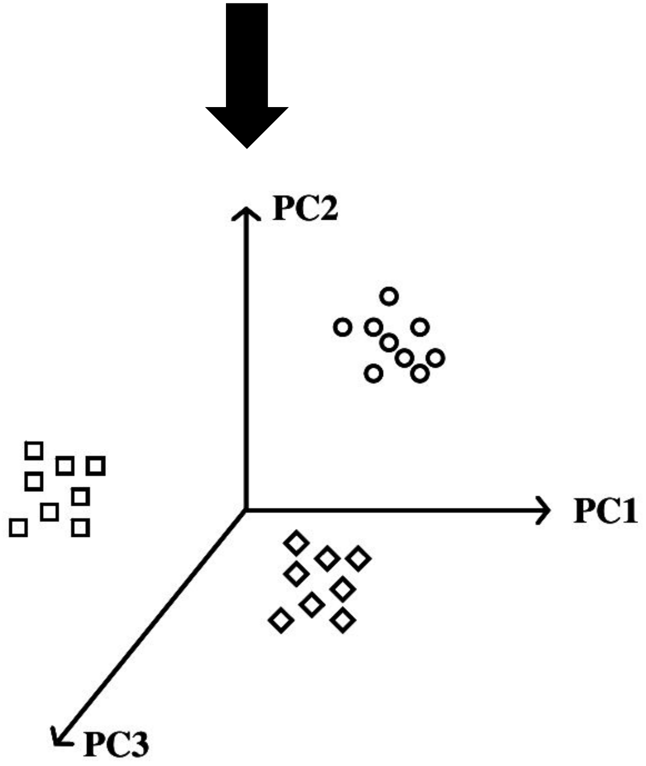


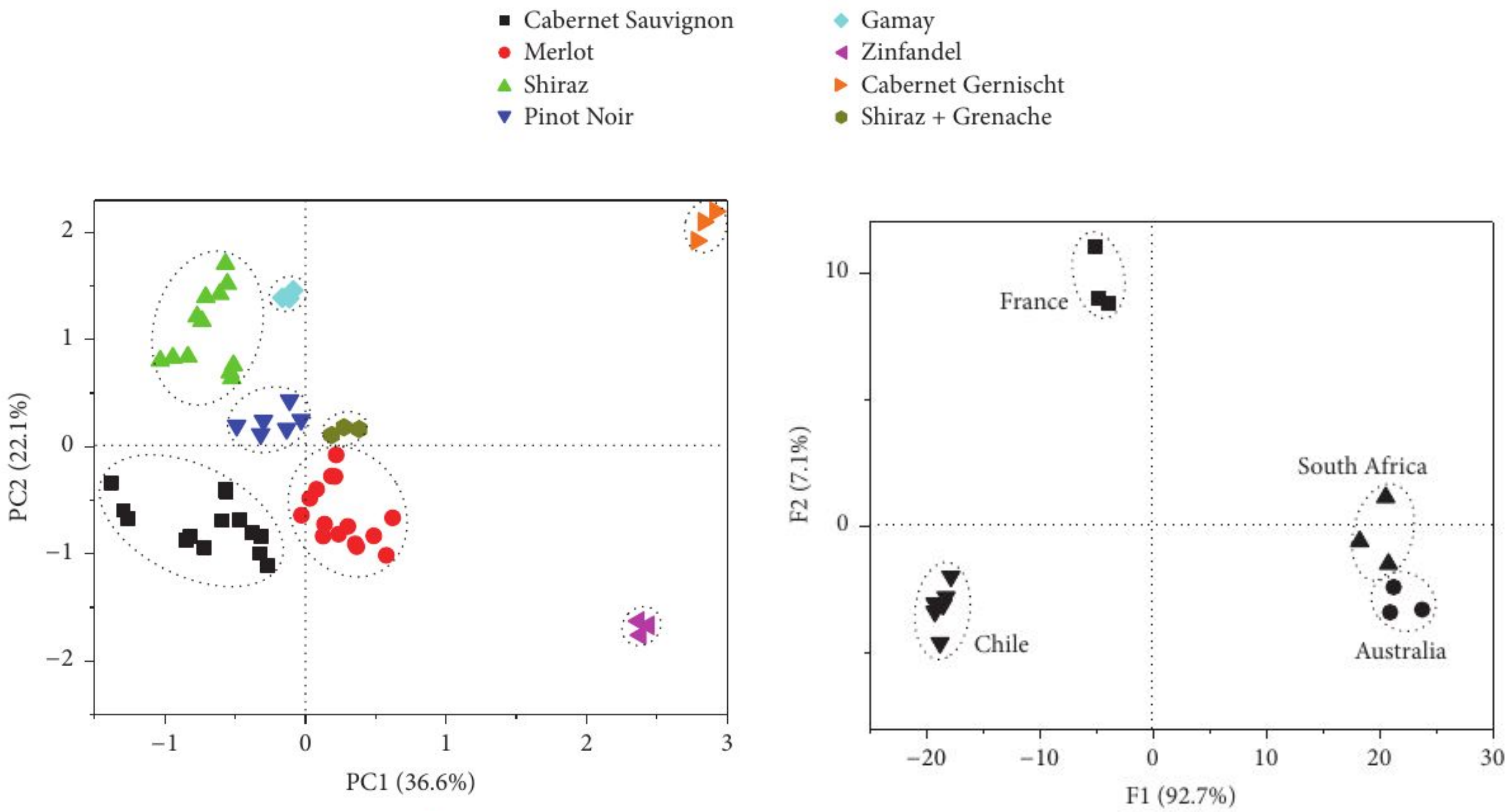
Trade organization or country	Concentration/mg l^{-1}																		Reference
	Ag	Al	As	B	Br	Cd	Cr	Cu	F	Fe (red)	Fe (rosé)	Fe (white)	Na	Ni	Sb	Sn	Pb	Zn	
OIV	–	–	0.2	80	1	0.01	–	1	–	–	–	–	–	–	–	–	0.15	5	[7]
Brazil	–	–	–	–	–	0.2	–	–	–	–	–	–	–	–	–	–	0.5	–	[29]
Croatia	0.1	10	0.2	80	1	0.01	0.1	1	1	20	15	10	20	0.1	0.2	10	0.2	5	[80]
Hungary	–	–	0.05	–	–	0.02	–	1	–	–	–	–	–	–	–	–	0.25	–	[27]
Australia	–	–	0.1	–	–	0.05	–	5	–	–	–	–	–	–	–	–	0.2	5	[53]
Germany	–	8	0.1	–	–	0.01	–	5	–	–	–	–	–	–	–	–	0.3	5	[53]
Italy	–	–	–	–	–	–	–	10	–	–	–	–	–	–	–	–	0.3	5	[53]

Tariba, B. Metals in Wine—Impact on Wine Quality and Health Outcomes. Biol Trace Elem Res 144, 143–156 (2011)

Metals as a fingerprint for geographical origin of wine

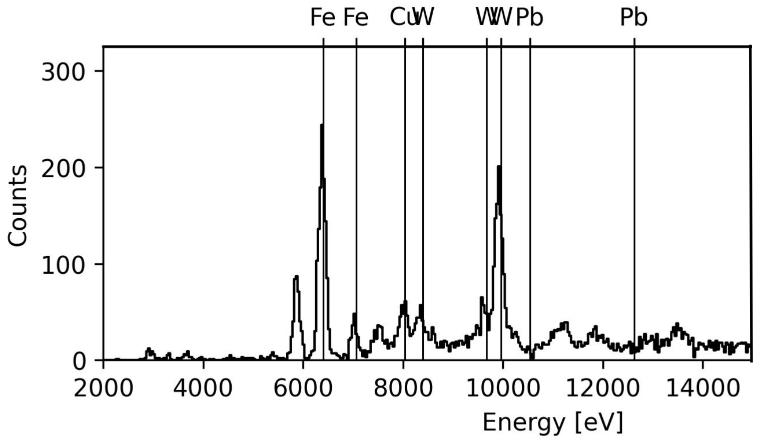
	1	2	3	...	N
Al	$C_{Al, 1}$	$C_{Al, 2}$	$C_{Al, 3}$		$C_{Al, N}$
Ba	$C_{Ba, 1}$	$C_{Ba, 2}$	$C_{Ba, 3}$		$C_{Ba, N}$
Ca	$C_{Ca, 1}$	$C_{Ca, 2}$	$C_{Ca, 3}$		$C_{Ca, N}$
...					
M	$C_{M, 1}$	$C_{M, 2}$	$C_{M, 3}$		$C_{M, N}$



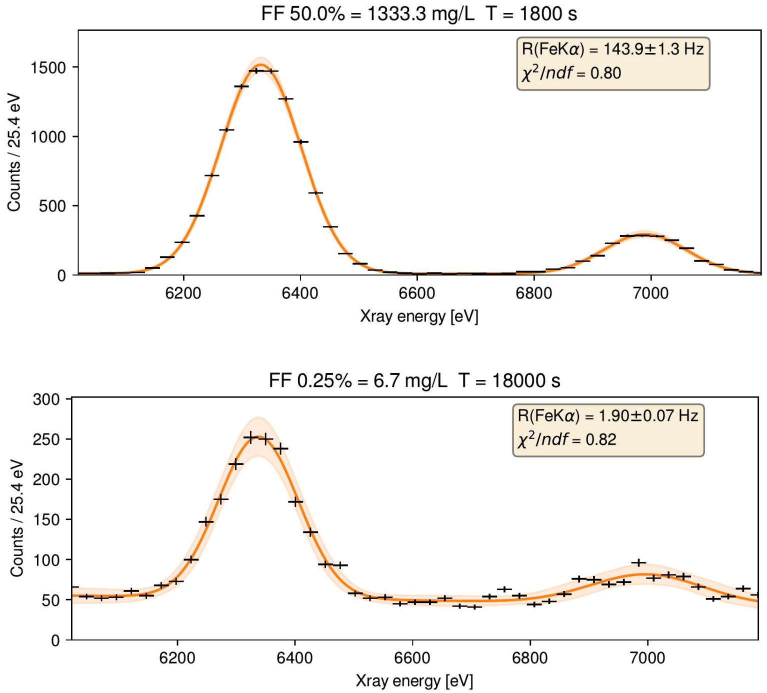


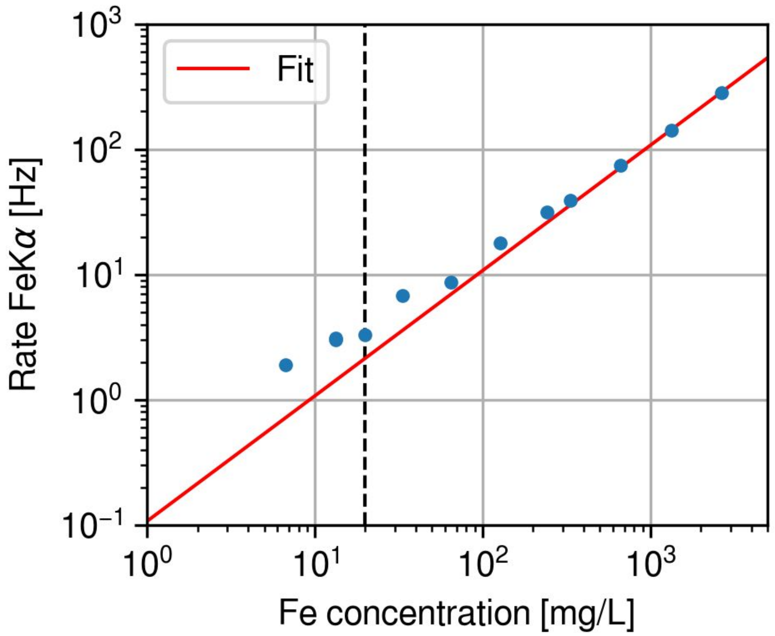
Huang, Xian-Yong & Jiang, Zi-Tao & Tan, Jin & Li,. 2017. 1-7. 10.1155/2017/2038073.

Metal content with the pindiode: dry and liquid samples

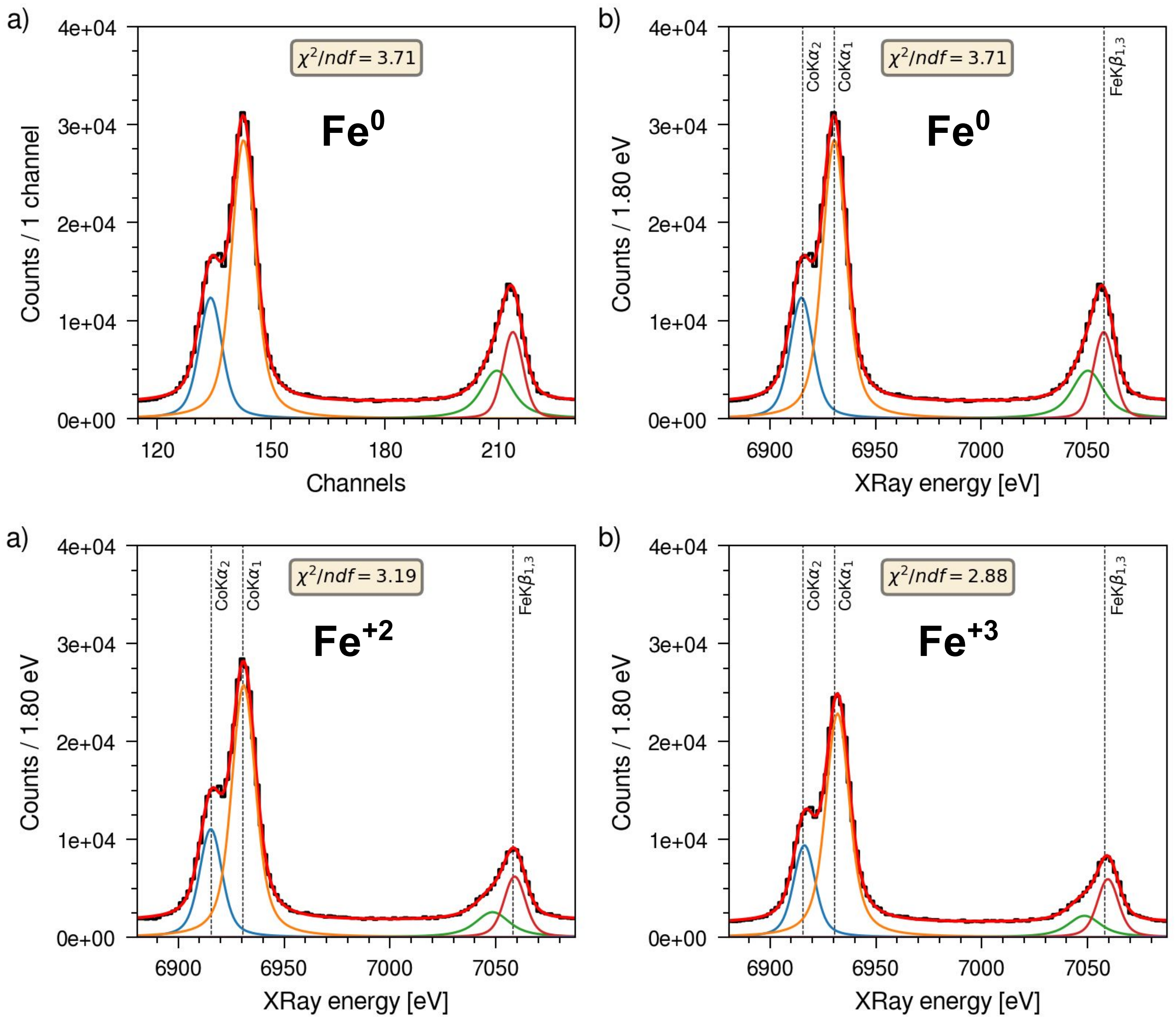


FerroFolin diluition
2666 mg/L of Fe

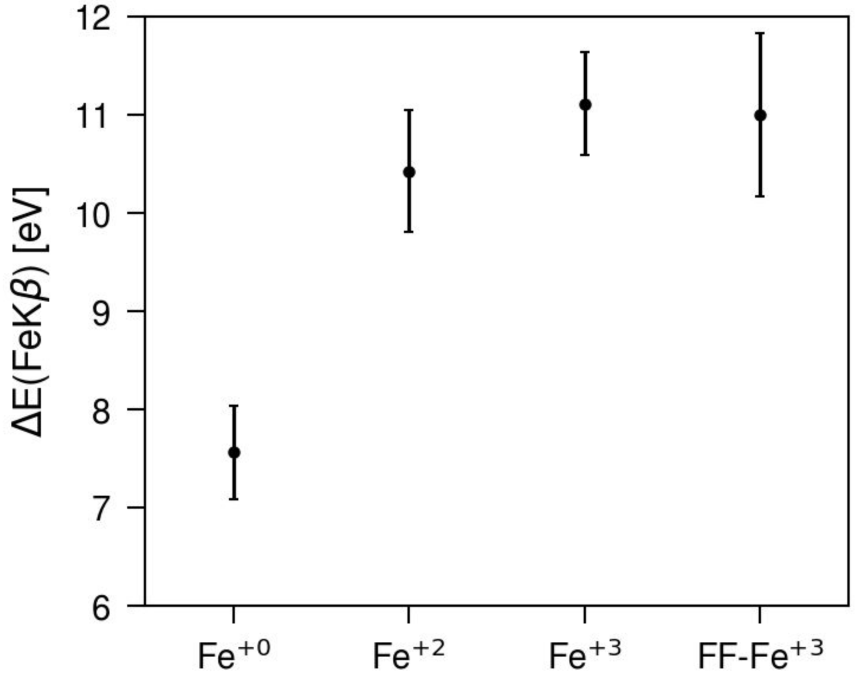




Detecting Iron oxidation state in solids and liquids



$$\Delta E = E(FeK\beta_{1,3}) - E(FeK\beta')$$



Conclusion

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Thanks for your attention!