

XRF (PYMCA) TUTORIAL

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In this lecture:

- Theory: a quick overview of XRF process
- Things to keep in mind: typical spectral features (and artefacts!)
- PyMCA: useful information and how to extract it

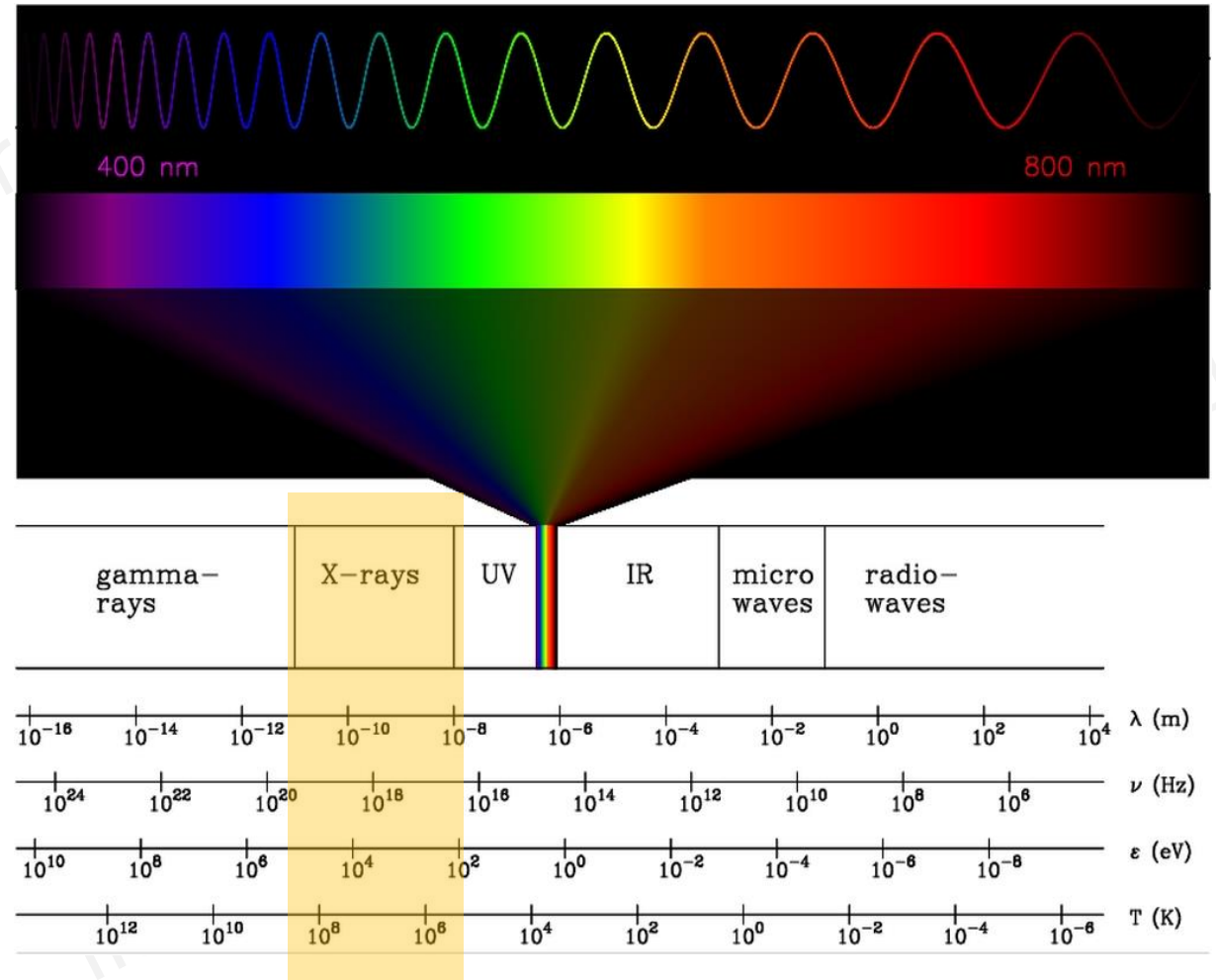
X-ray fluorescence

XRF

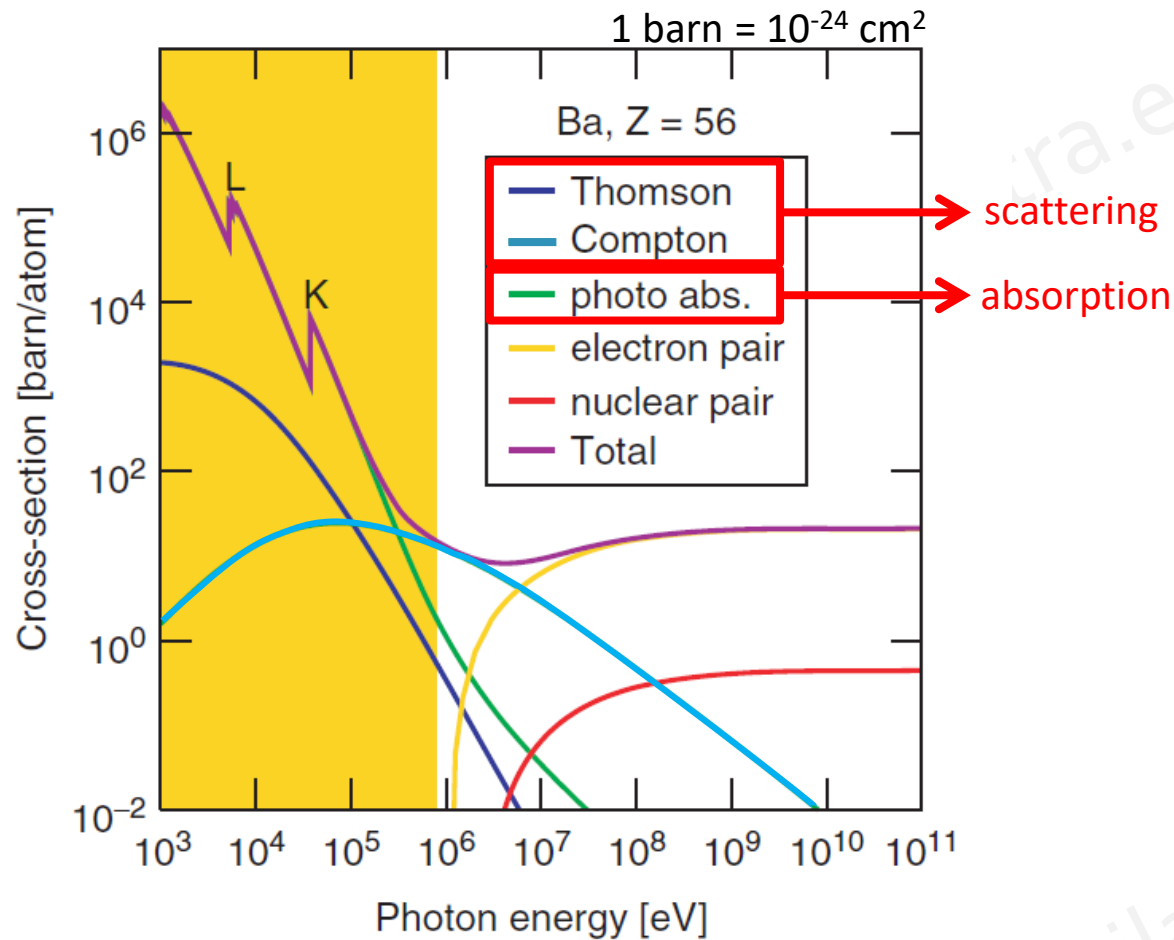
A process involving light and matter

Energy vs wavelength

$$E = h\nu = c/\lambda$$



X-rays and electrons



Light-matter interaction depends on λ

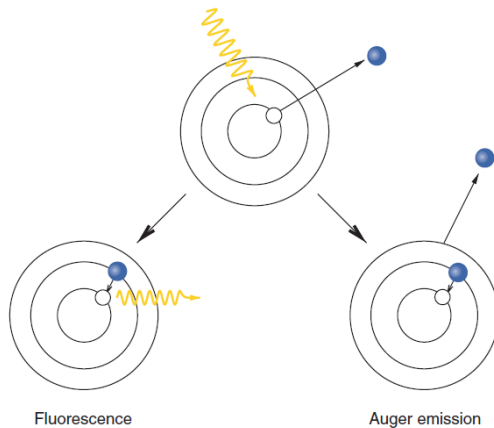
Due to their λ
x-rays interact
mainly
with electrons in matter

From 0.1 to 100 keV there are two main types of interaction

X-ray absorption

Fluorescence is a secondary effect of X-ray absorption

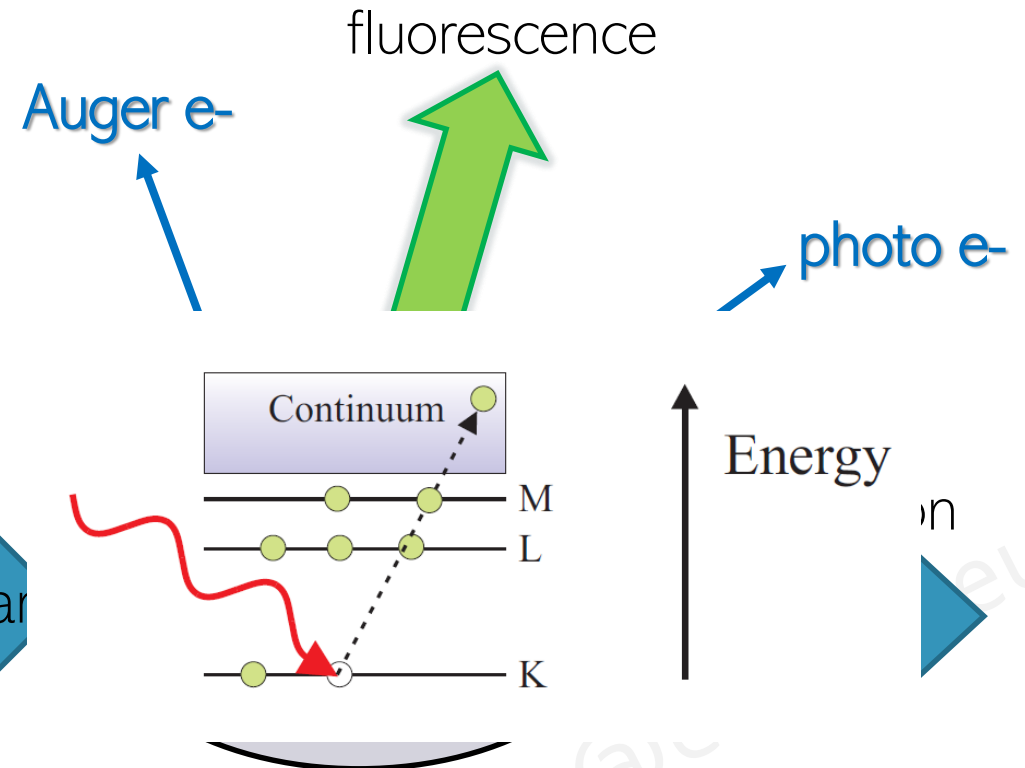
Upon photon absorption, an electron is expelled from the atom, leaving it ionized (excited state):



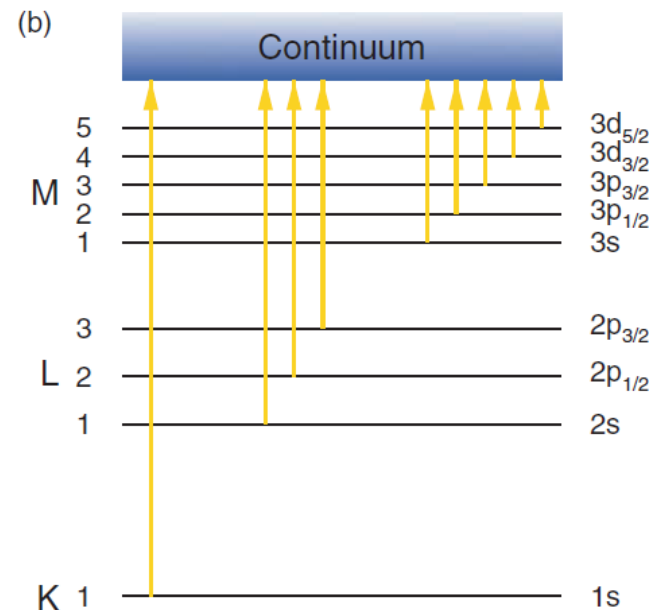
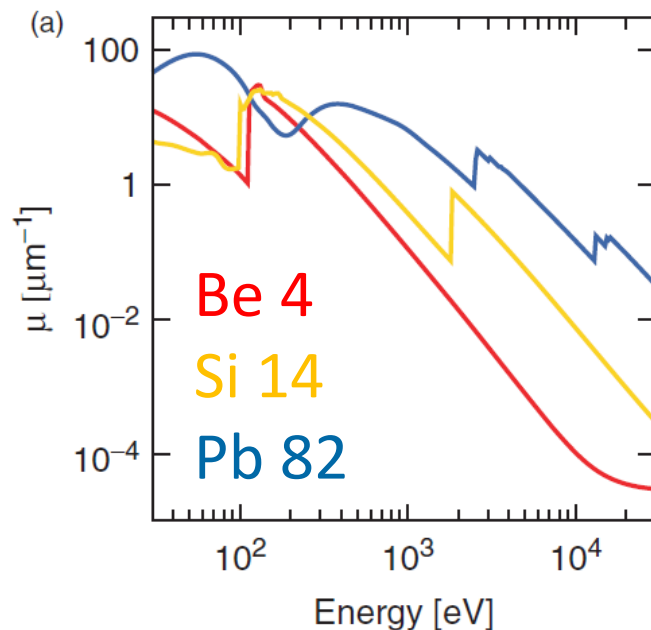
Secondary effects

Upon decay, the energy of the system is conserved through the emission of:

- a photon (fluorescence);
- or
- an electron (Auger)



The absorption coefficient



Absorption profiles are different for each element.

When we vary the photon energy, each sharp increase in absorption (absorption edge) corresponds to the extraction of a given electron.

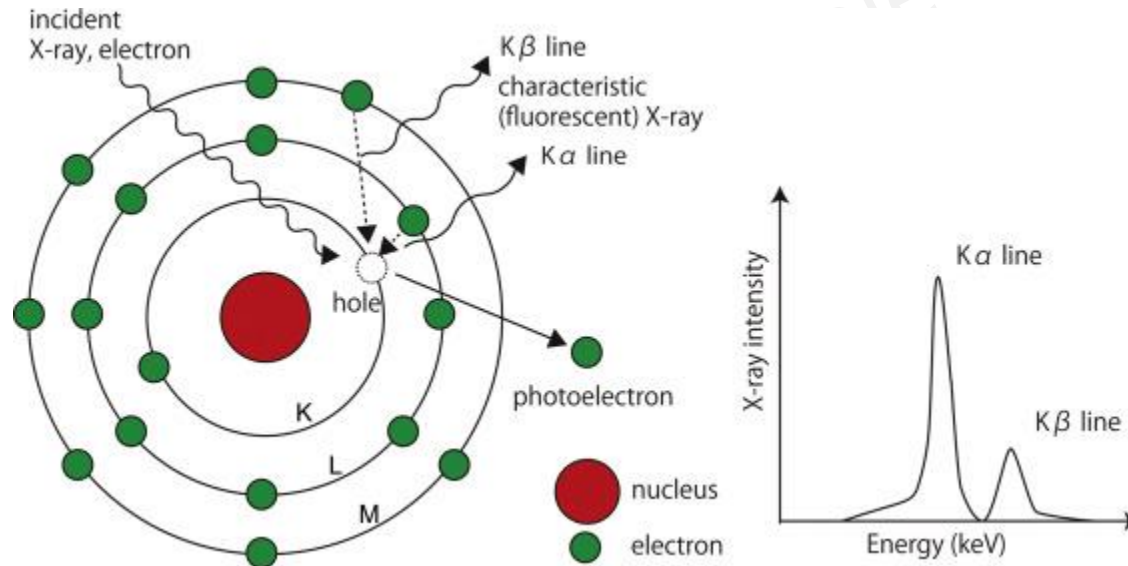
Each edge is identified using a letter and a number.

Absorption depends on photon energy.

No Absorption = no fluorescence!

Fluorescence emission

Fluorescence energy depends on the transition.



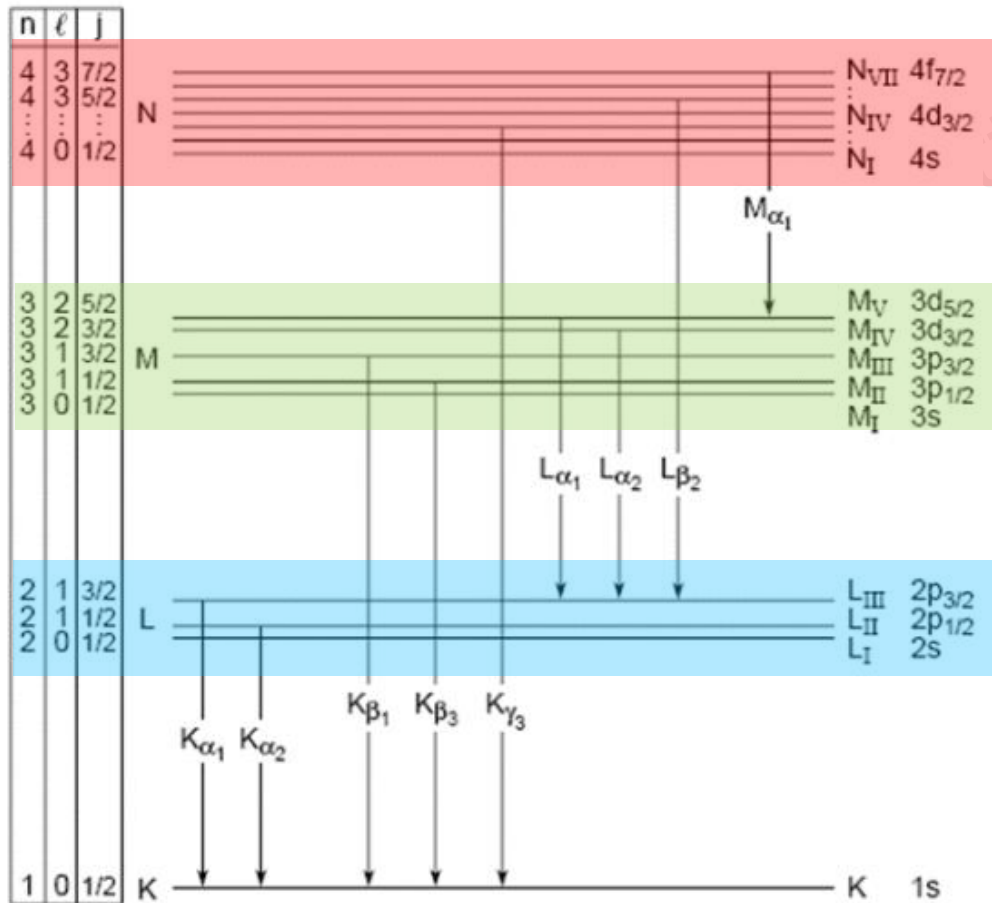
In the **ionized** state, the atom has a **core-hole** that can be filled by different **electrons**.

The energy of the fluorescence photon depends on the energy difference between the initial and final energy of the electron involved in the decay.

Quantum mechanics: electrons **have specific energies** for each element.

This strict dependence is the core of **element specificity** of absorption/fluorescence techniques.

Emission lines nomenclature



Latin letter + Greek letter + number
e.g.: **K α 1**

Core-hole level + shell of electron decaying + subshell

In PyMCA: Latin letter + latin letter + number
e.g.: **K L 3**

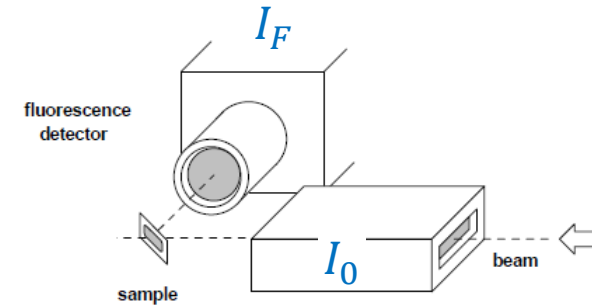
Core-hole level + shell of electron decaying + subshell

Measurement geometries

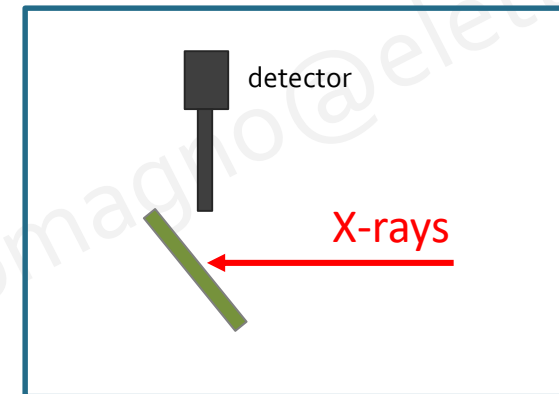
Fluorescence detection in standard geometry (45/45)

Trace-level detection limits in dilute systems; can assess concentrated thin-films or surface layers of thick, non-transparent samples.

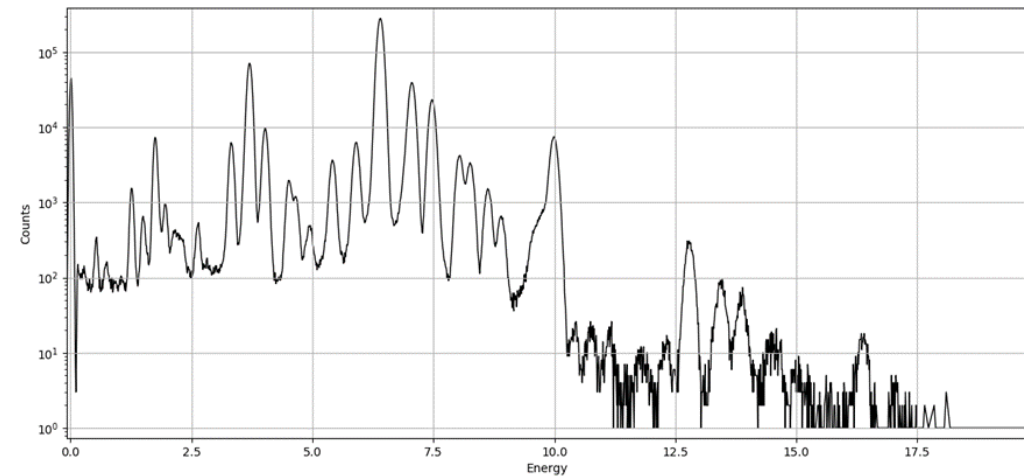
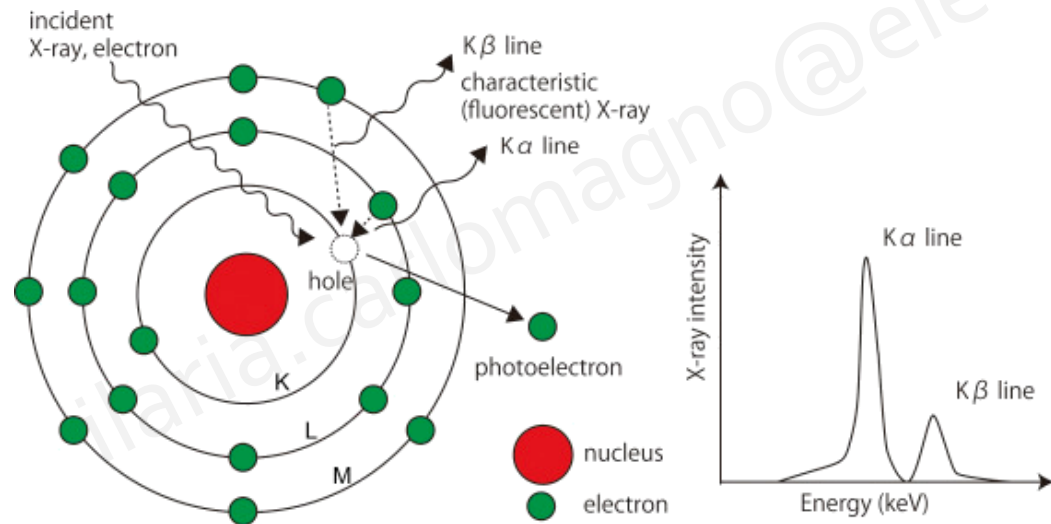
$$\mu(E)t = \alpha \propto \frac{I_F}{I_0}$$



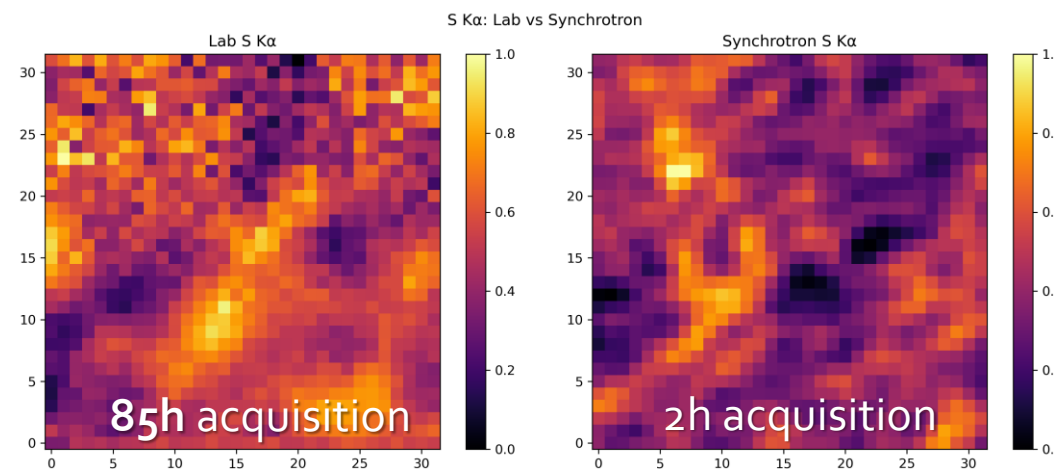
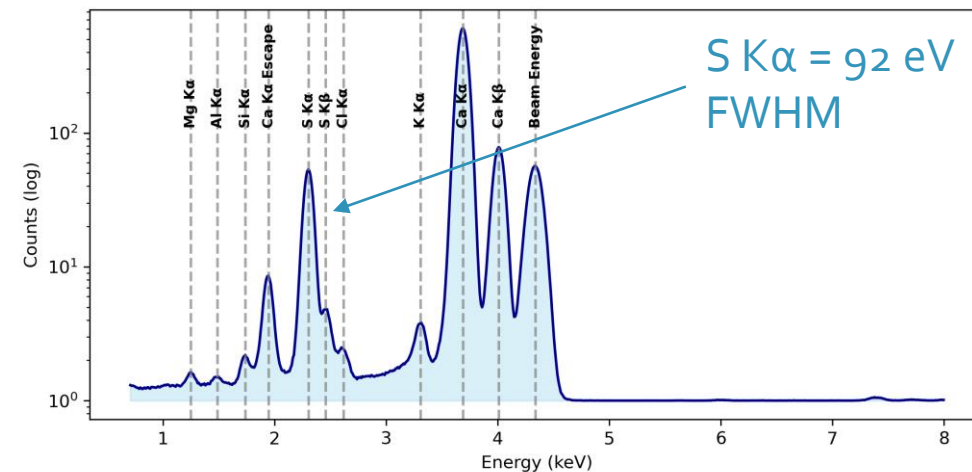
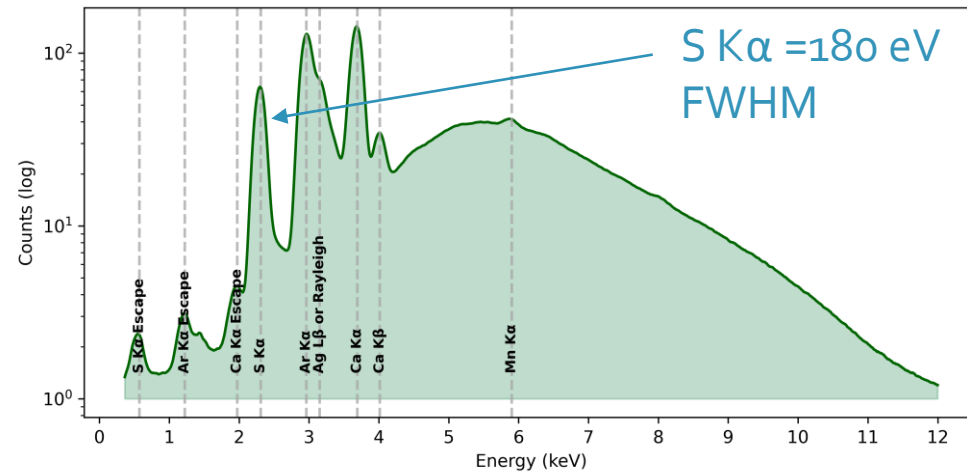
Top view



A typical (synchrotron) spectrum



Laboratory vs synchrotron: paper samples



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SCATTERING

Compton and Rayleigh scattering

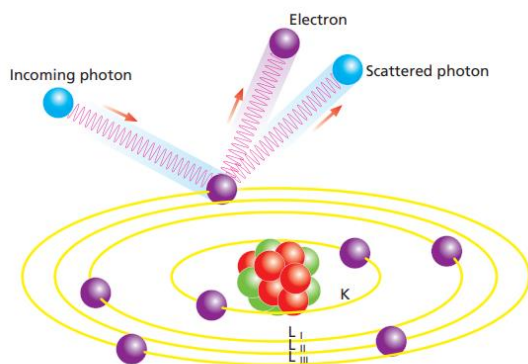


Figure 10. Compton scatter

Upon collision, **the photon loses a part of its energy** to the electron that was hit. The energy loss depends on the angle at which the electron was hit.

Light elements have loosely bound electrons, favoring Compton scattering.

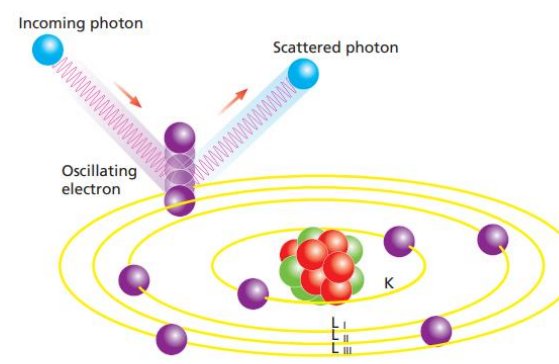


Figure 11. Rayleigh scatter

When photons collide with strongly bound electrons, the latter stay in their shell but start oscillating at the frequency of the incoming radiation.

Due to this oscillation, the **electrons emit radiation at the same frequency (energy) as the incoming radiation**. This gives the impression that the incoming radiation is reflected (scattered) by the atom.

NOISE

Detection limit

A commonly accepted definition:

“the **net** intensity of a peak being **3 times higher** than the **standard deviation** of the **background noise**.”

$$N_p > 3\sigma_b$$

The standard deviation of the background noise (σ_b) equals the square root of the counts

$$\sigma_b = \sqrt{N_b}$$

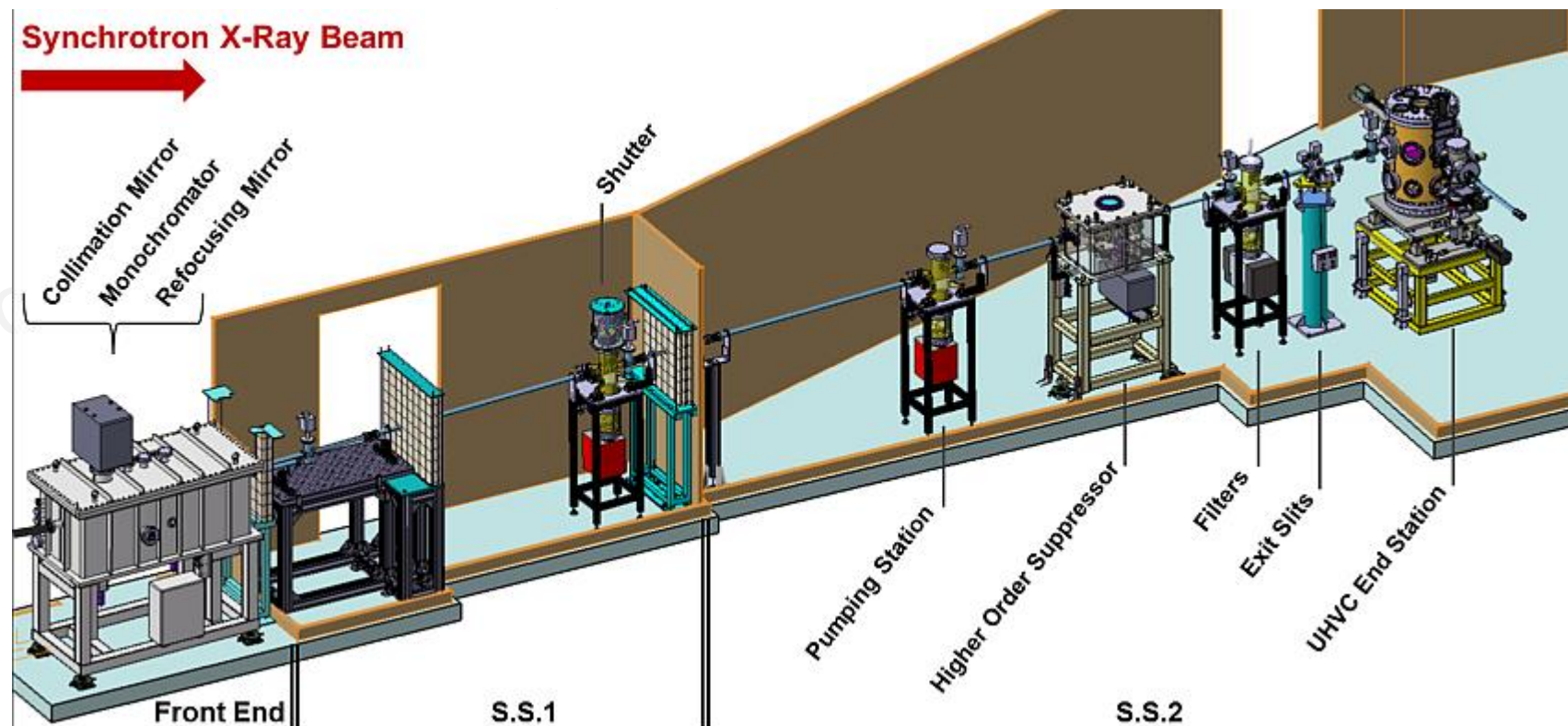
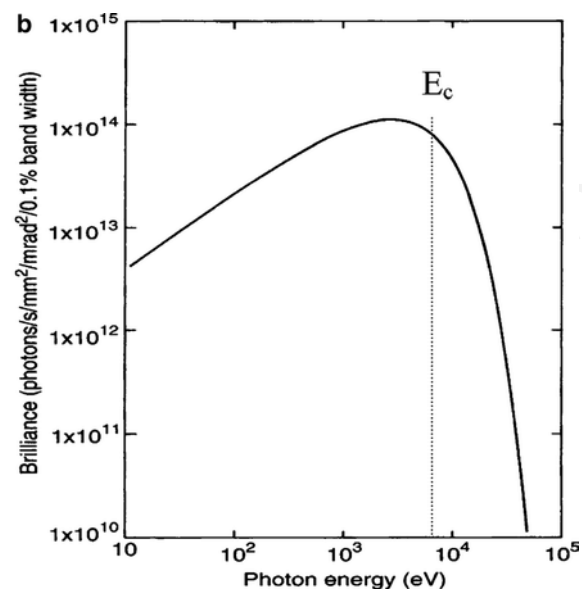
Elements are said to be detectable if:

$$\Rightarrow \frac{\overset{\text{counts on the peak}}{N_p}}{\underset{\text{counts on the background}}{\sqrt{N_b}}} \geq 3$$

XRF BEAMLINE

The XRF beamline

<https://www.elettra.eu/lightsources/elettra/elettra-beamlines/microfluorescence/beamline-description.html>



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XRF at the beamline

Optics, slits, sample manipulator define:

- Beam size down to $20 \times 20 \mu\text{m}^2$
(i.e. spatial resolution)
- X-ray energy (2 – 14 keV)
(i.e. maximize elemental sensitivity)
- Incidence/exit angle of X-rays
(i.e. modulating surface sensitivity)



Photo by Ilaria Carlomagno

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XRF at the beamline

Detectors

- Beam monitoring system – I_0
- Photodiodes
- Silicon Drift Detector (SDD)
 - sensitive to photon energy



Photo by Ilaria Carlomagno

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Inside the chamber

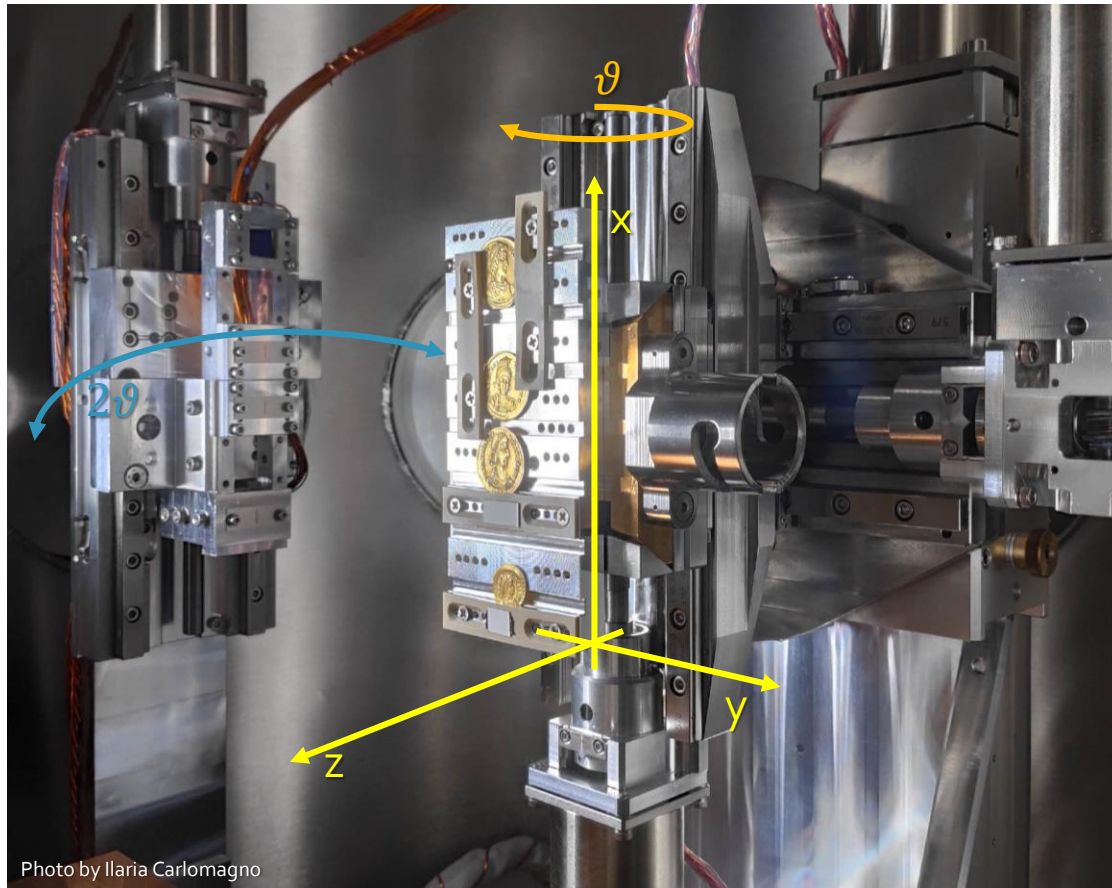
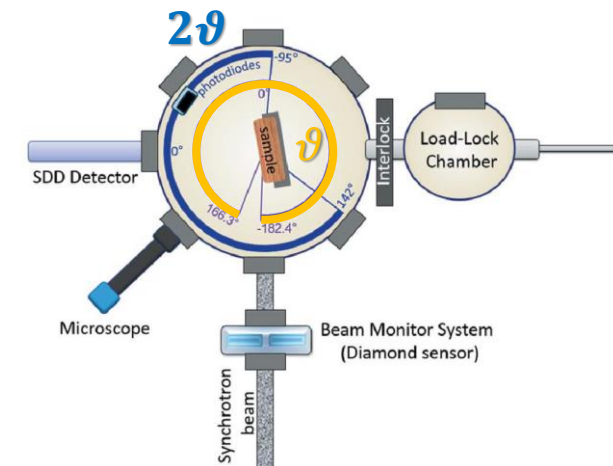


Photo by Ilaria Carlomagno

- High vacuum conditions to enhance the detection of low energy photons
- Motorized sample movements (x, y, z, θ) allow fine positioning of the sample to be achieved

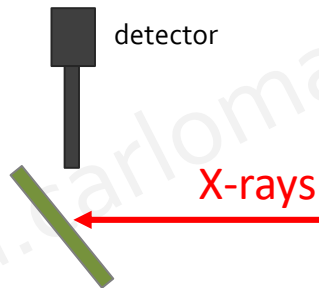


J. Synchrotron Rad. (2018). 25, 189–203

- Standard geometry is $45^\circ/45^\circ$
- Minimised scattering from the sample

Geometries

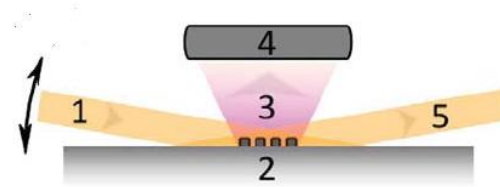
Standard 45/45 geometry



Detector is always perpendicular to the incoming beam!

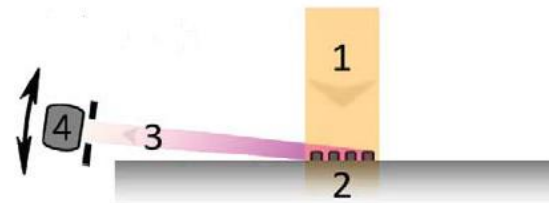
Grazing angle geometries

Grazing incidence



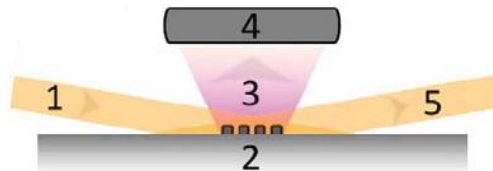
Surface sensitivity
(depth profiling)
SR is crucial for low concentrations!

Grazing exit



Surface mapping
Depth and lateral inhomogeneity

Total reflection



Trace element analysis
Surface contamination

XRF in a nutshell

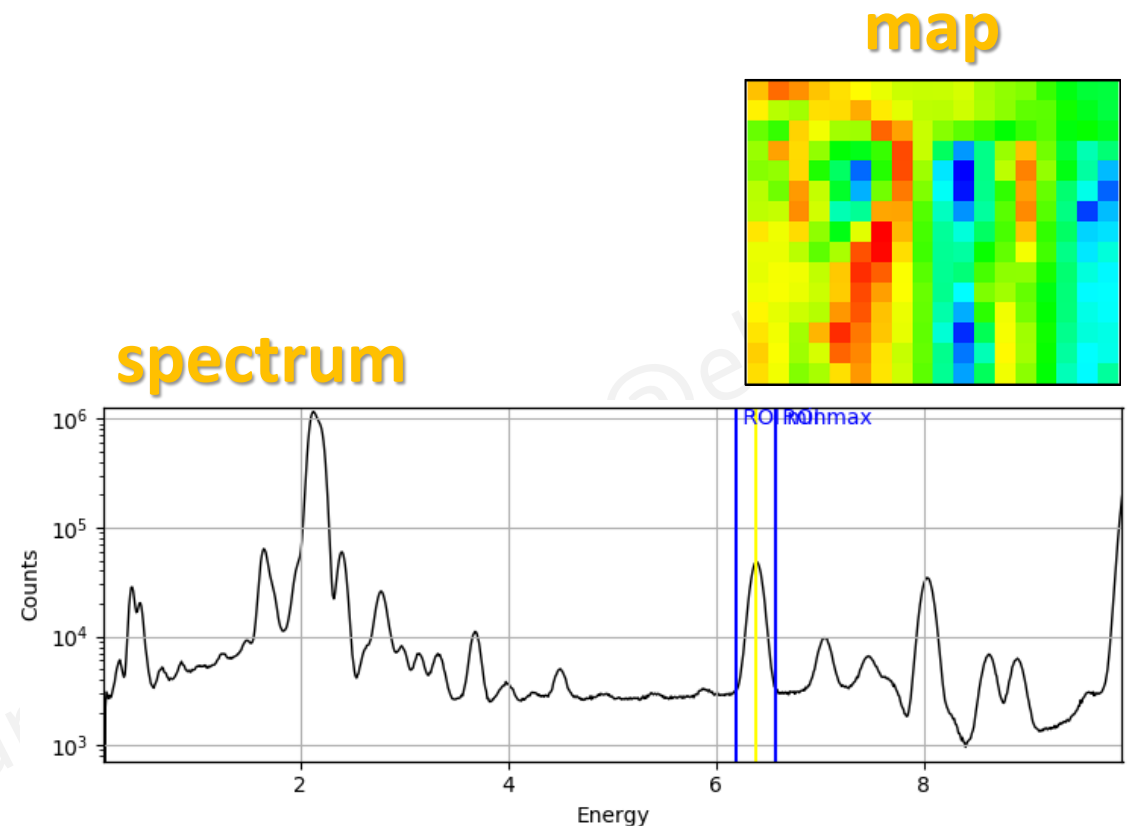
XRF technique

- Provides the distribution of the elements
- Element sensitive “mapping”
- Spatial resolution linked to the beam size

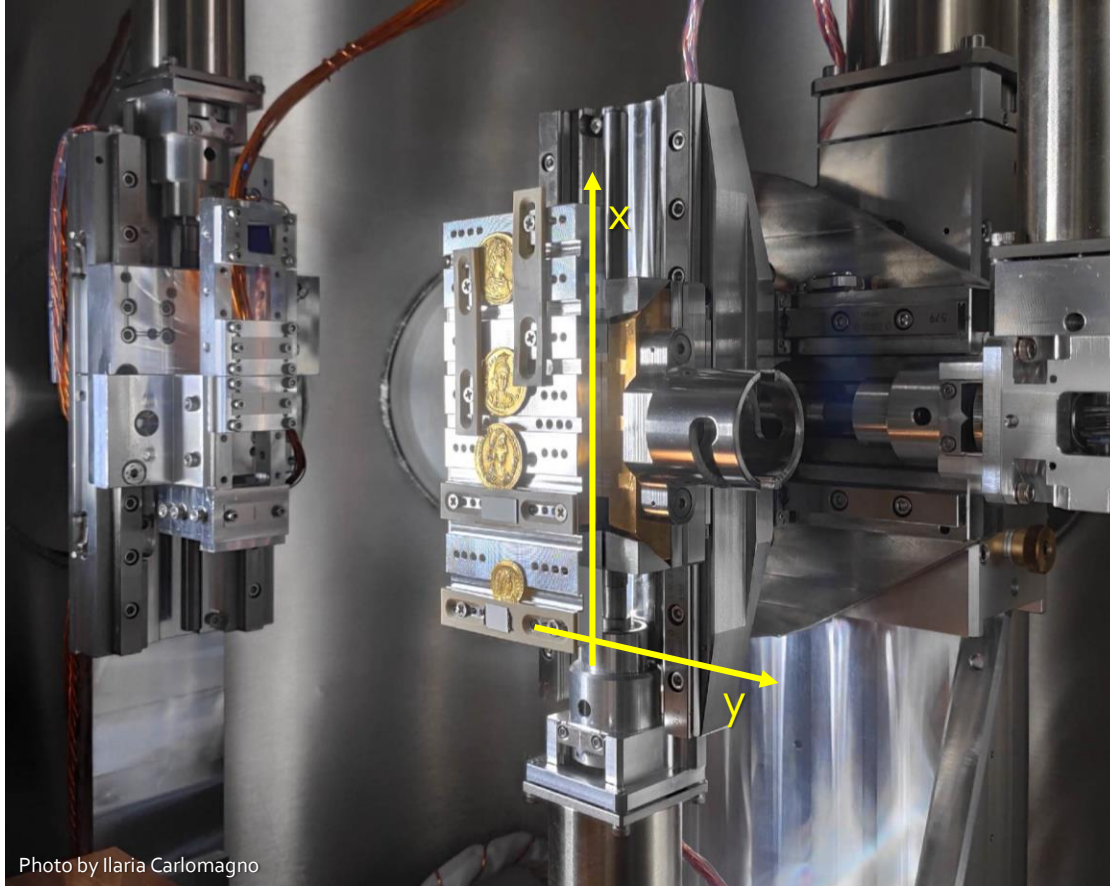
Data = spectra + maps

Answers the questions:

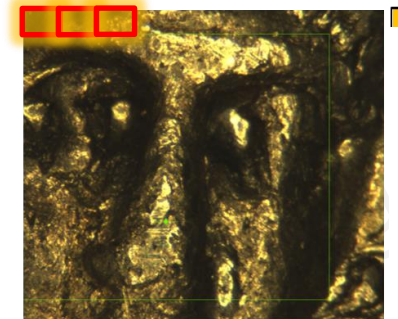
- What elements are on my sample?
- ...and where are they?
- How much of each element?



Inside the chamber

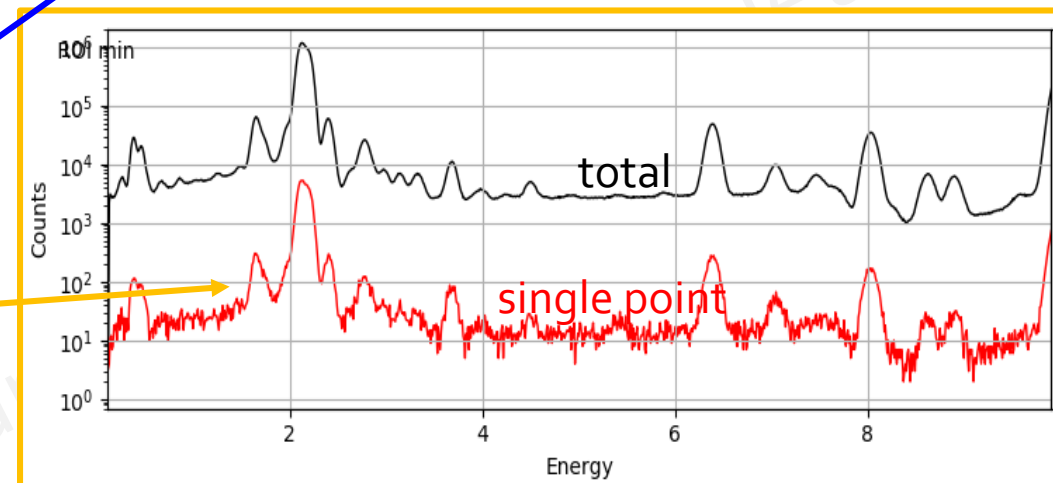
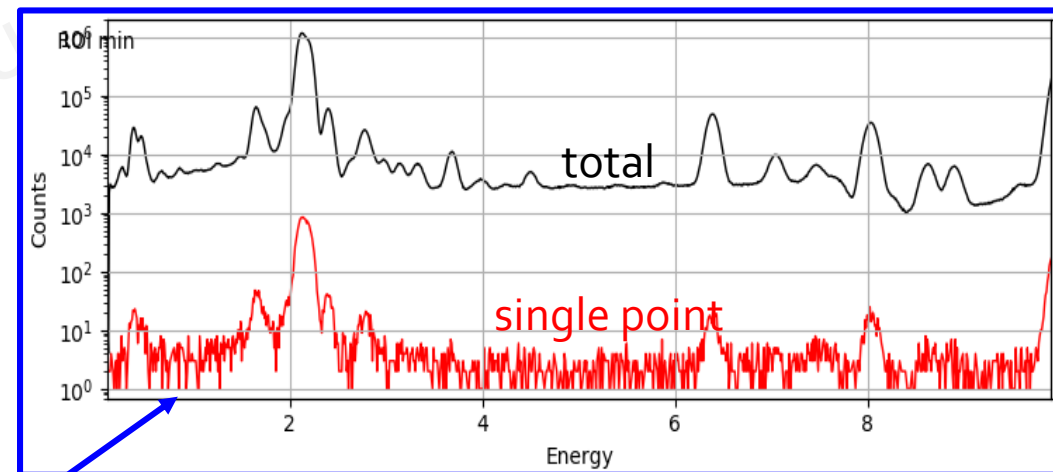
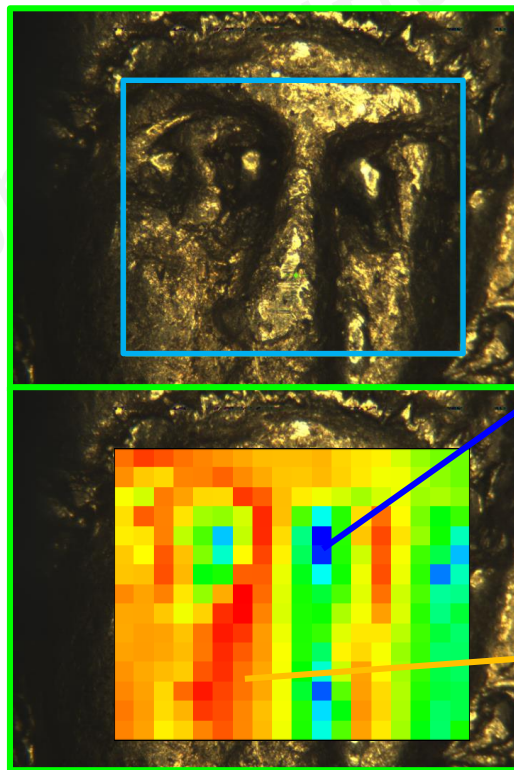


- Samples are scanned in front of the beam
- The beam hits a different area at every step
- The detectors collect the fluorescence emission from each point
- The data are represented in the same order as they were collected



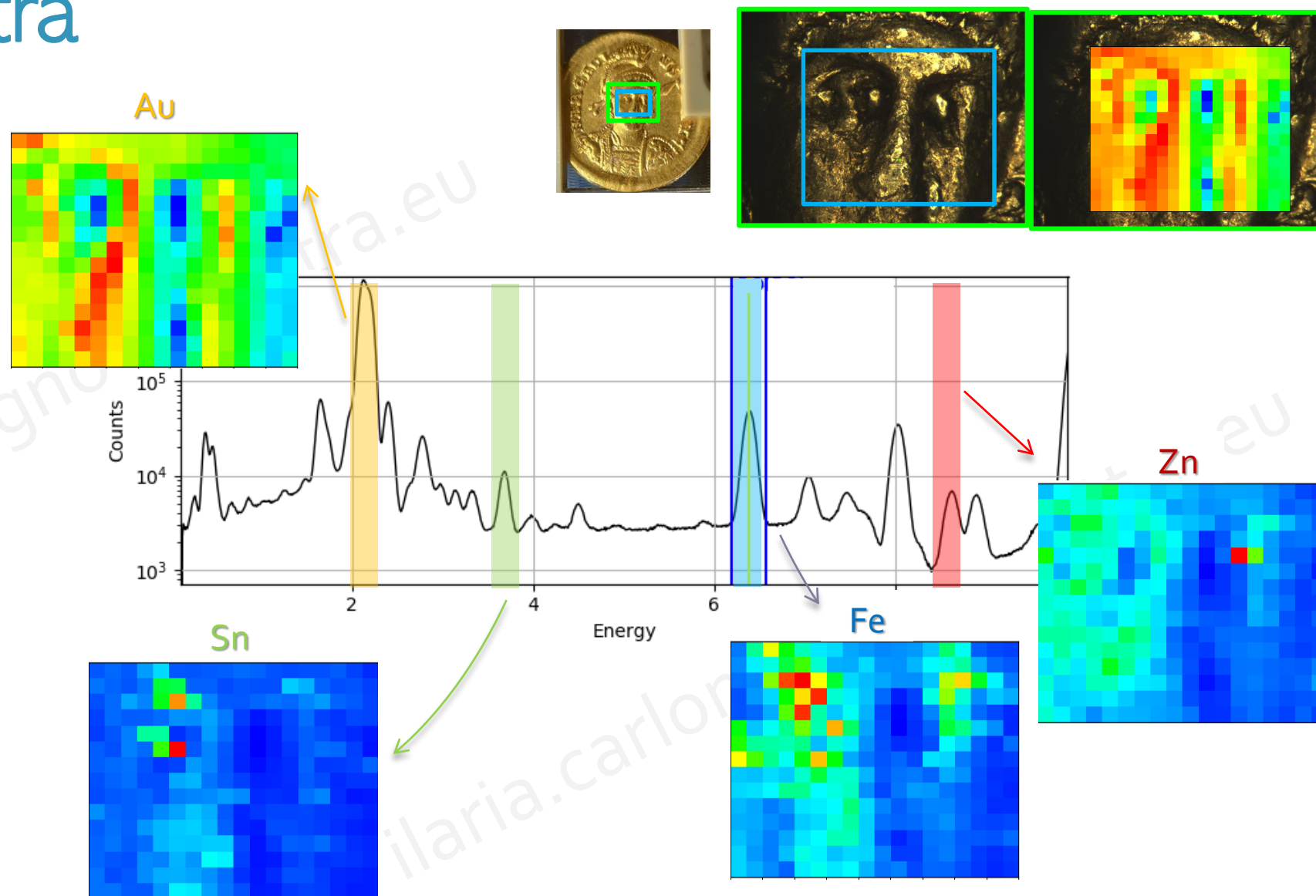
Single point spectra

We can deal with one spectrum at a time: we can choose whether to consider single points or sum up the contribution from similar areas (e.g. total spectrum).



Maps vs spectra

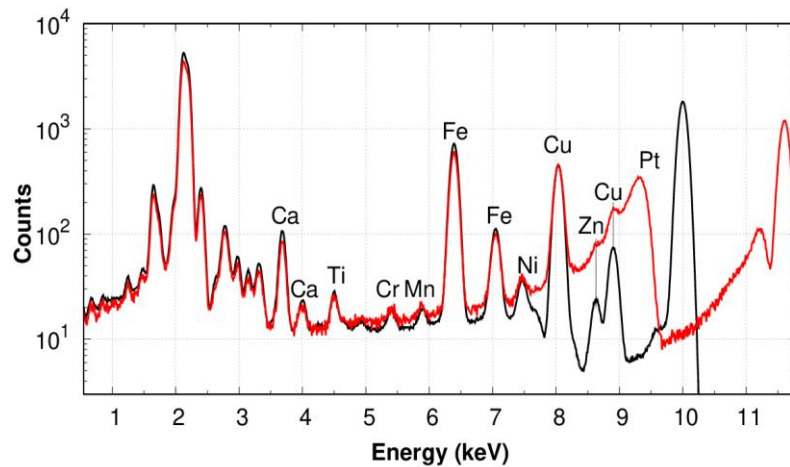
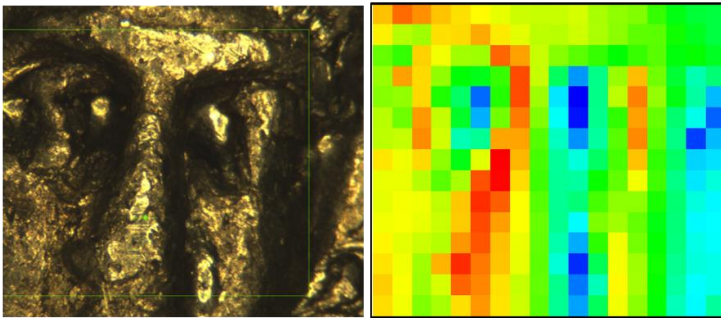
We can also work in the opposite direction and focus on a specific energy region of the spectrum...



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A practical example

Coin B



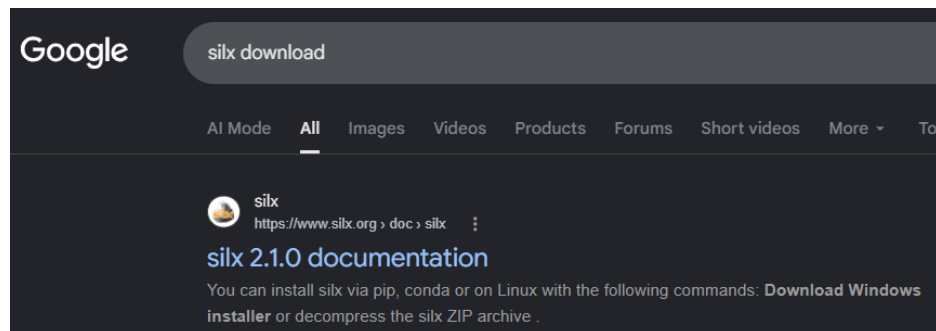
Relatively easy:

- stable X-ray source
- motion control (sample)
- Synchrotrons
- (Laboratory X-ray sources)
- Portable devices
- $45/45^\circ$ geometry
- $100 \times 100 \mu\text{m}^2$ resolution
- $h\nu = 10 \text{ keV}$ and **11.6 keV**

HANDS ON!

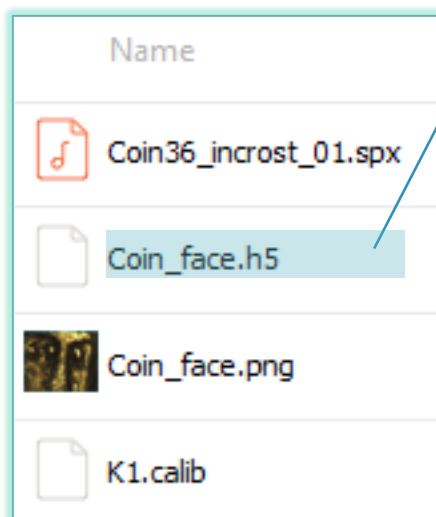
Exploring h5 files with SILX

1

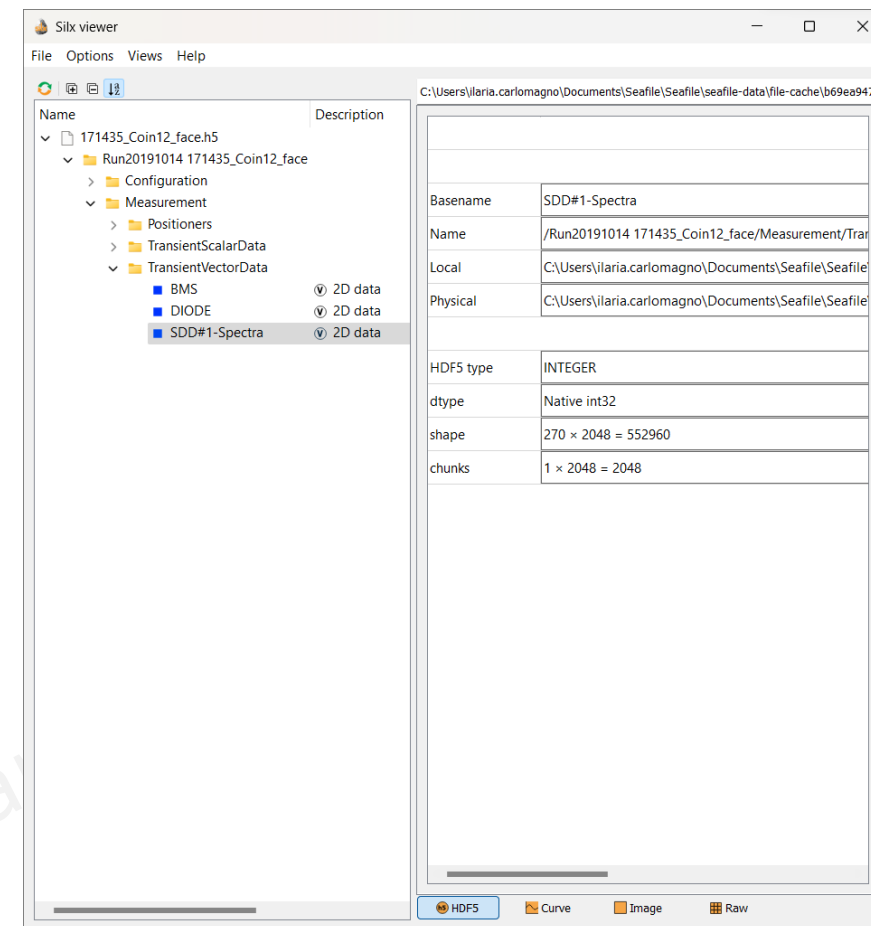


2

Data for exercises:
<https://drive.elettra.eu/d/b0b0c8eb775749138b10/>



3

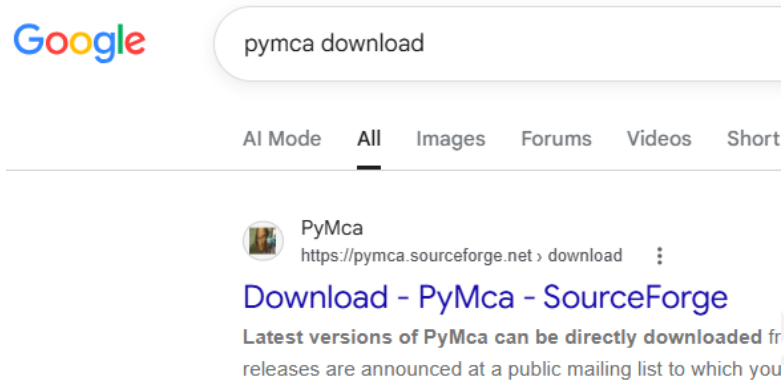


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PYMCA TUTORIAL

Install PyMCA in 2 steps:

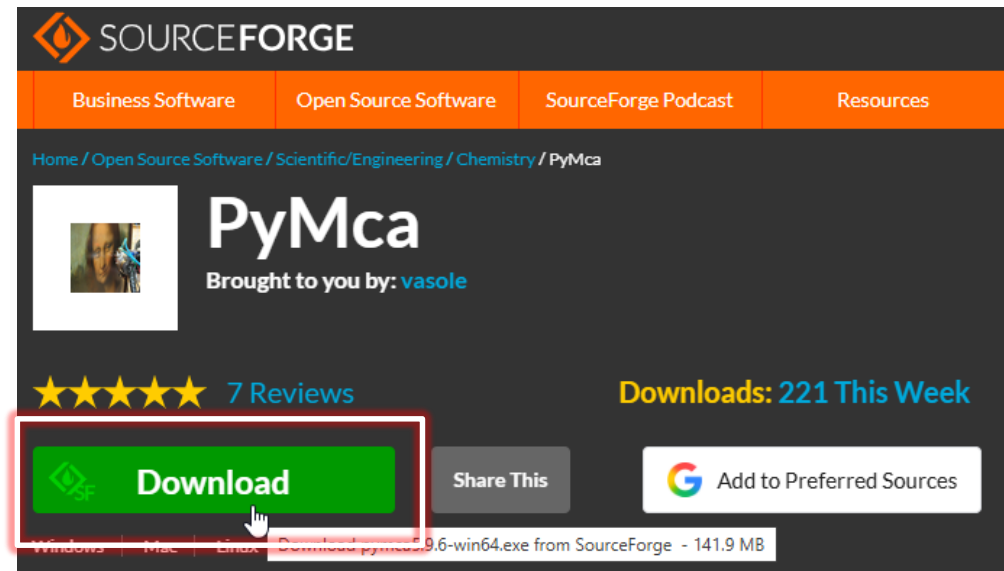
1



or

<https://sourceforge.net/projects/pymca/>

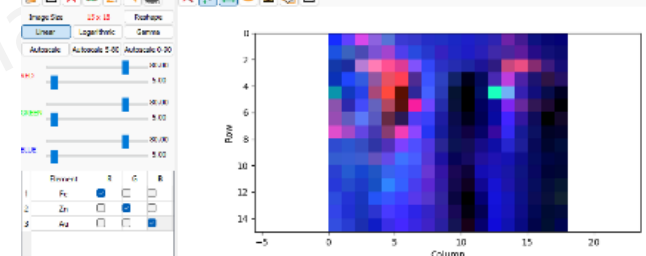
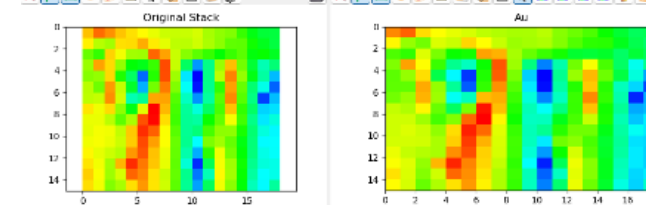
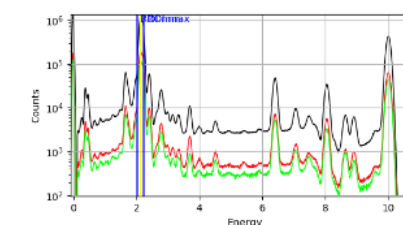
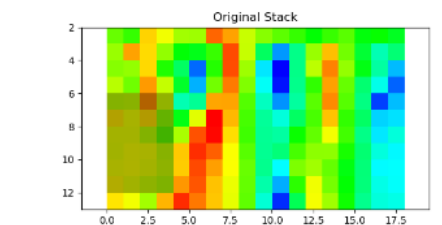
2



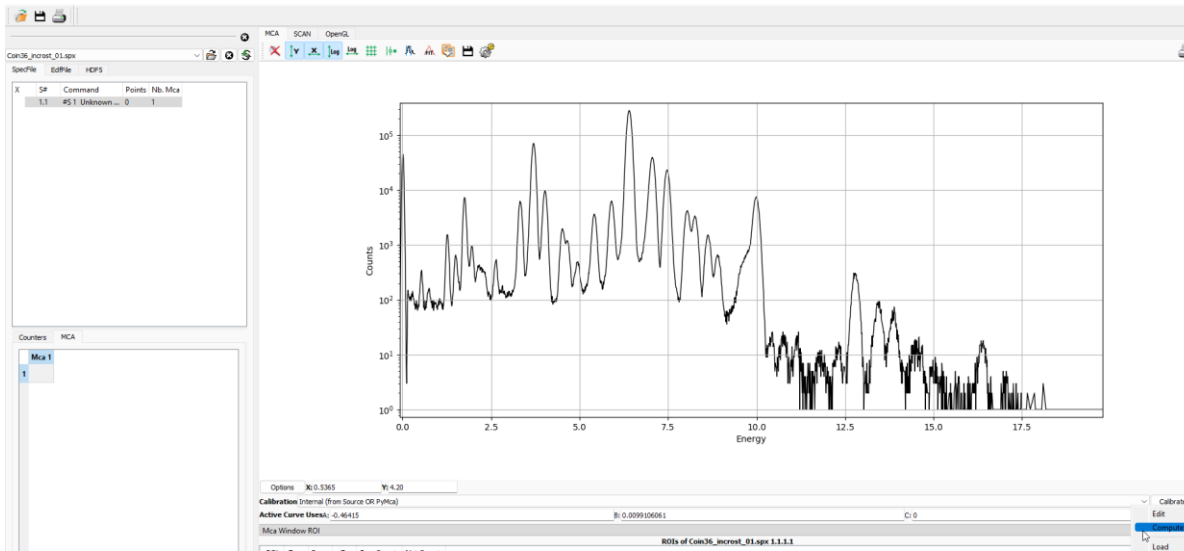
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What we will do:

- Import maps in the ROI imaging tools
(and be sure of the map size using HDF View)
- Calibrate the spectra
(creating and saving our own calibration file)
- Load the motor positions on the map
(check for upside down images)
- Normalize data using the I_0
- Extract spectra from selected regions
- Use ROIs
- Peak identifier
- RGB correlator
- Fast XRF fitting

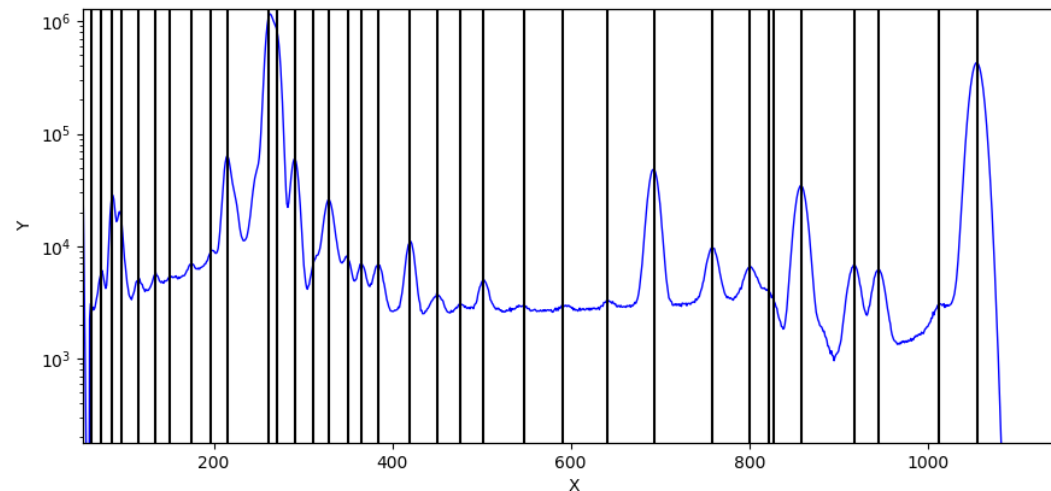


Importing single spectra



PyMCA (main window)

Calibrate the spectrum



Search Parameters

Sensitivity: 2.5

Fwhm (pts): 6 ☐ Auto

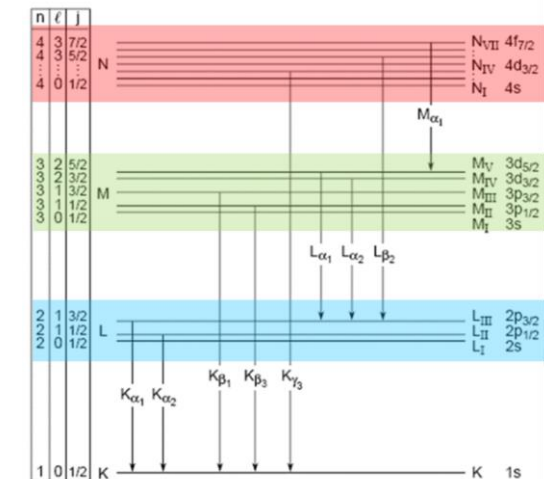
Yscaling: 1.000000 ☐ Auto

Peak	Channel	Element	Line	Energy	Use	Calc. Energy
------	---------	---------	------	--------	-----	--------------

Order: 1st A: 0 B: 1 C: 0.0 Add as: Stack SUM

You can use:

- the known (reference) peaks

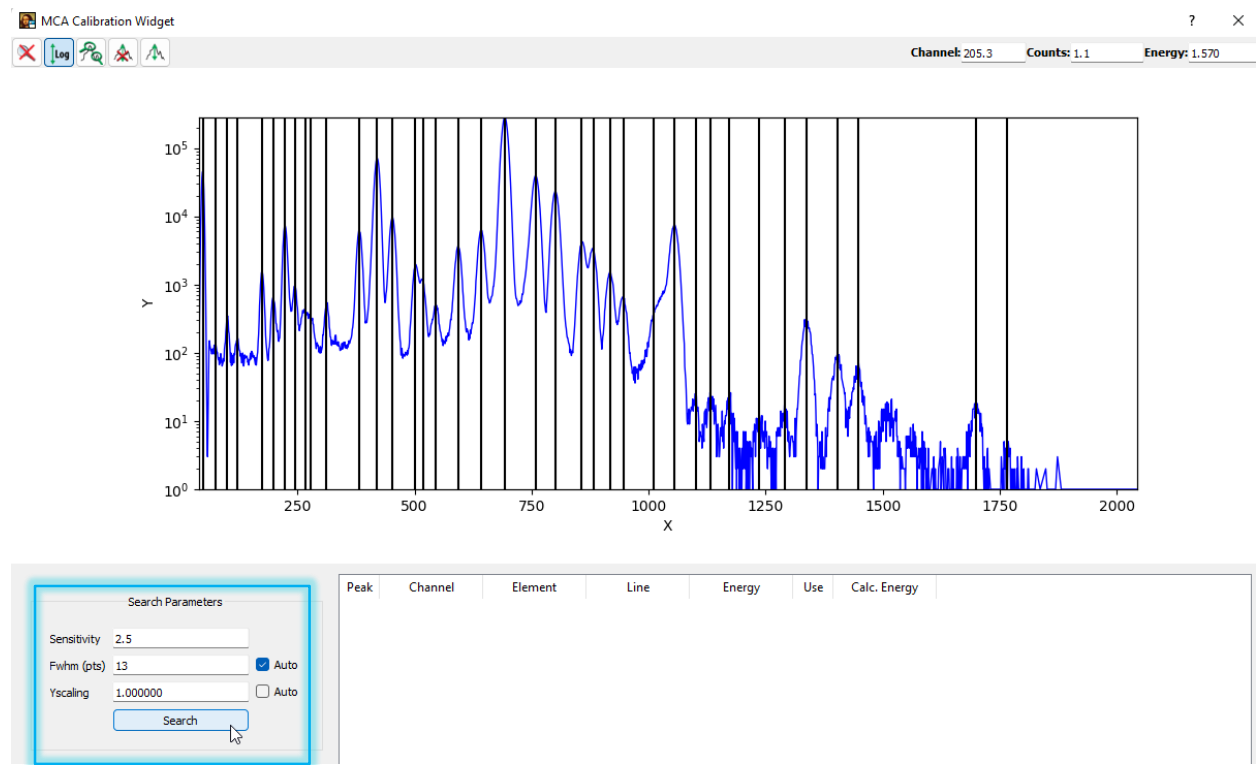


- the elastic scattering peak

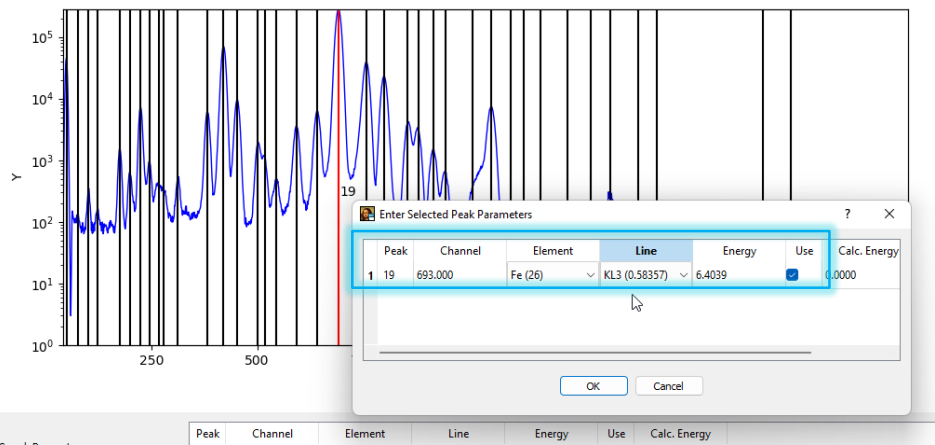
You can **save** your calibration file, so that you won't have to do this procedure every time you open a spectrum.

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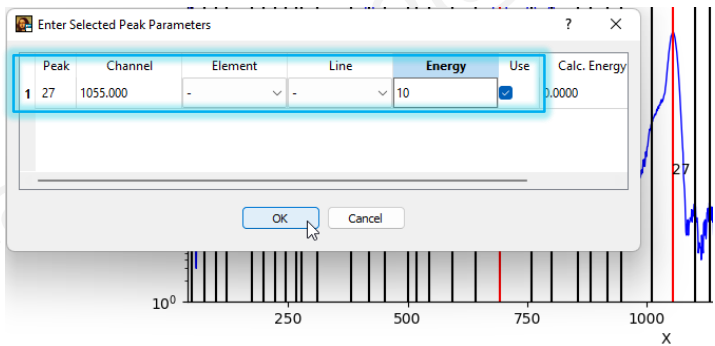
Calibration: auto-search



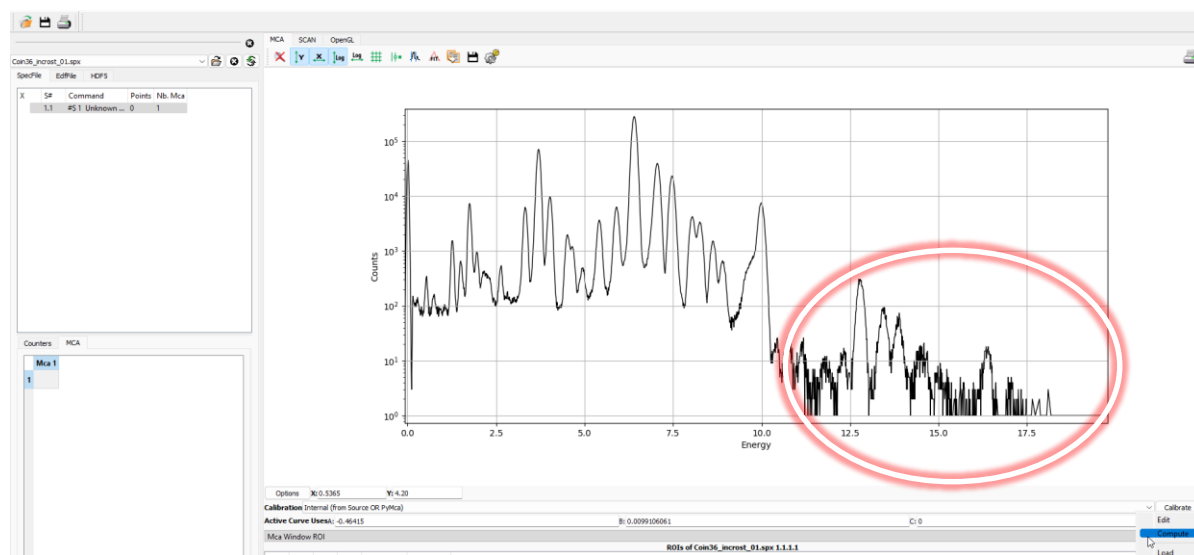
Fe K α line



elastic peak



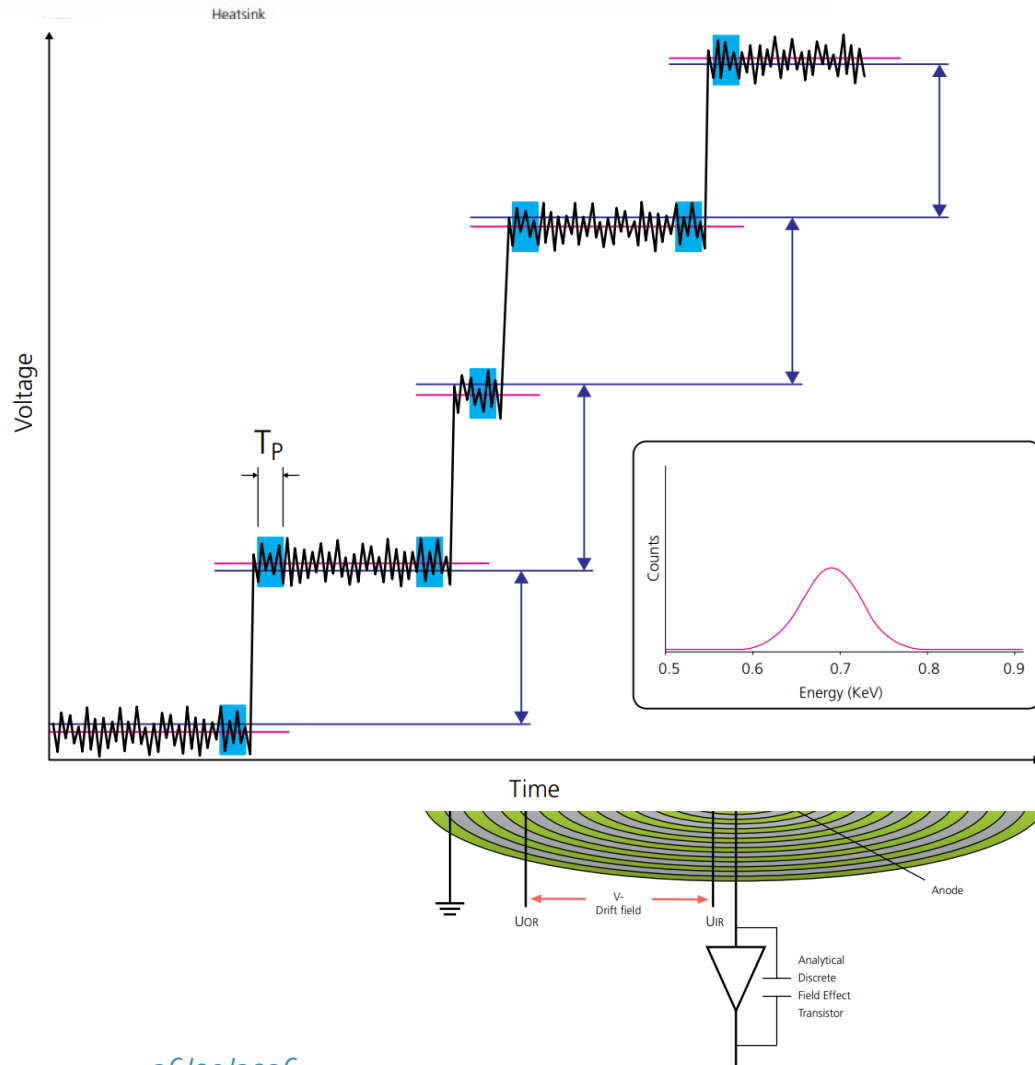
Can you recognize all the peaks?



PyMCA (main window)

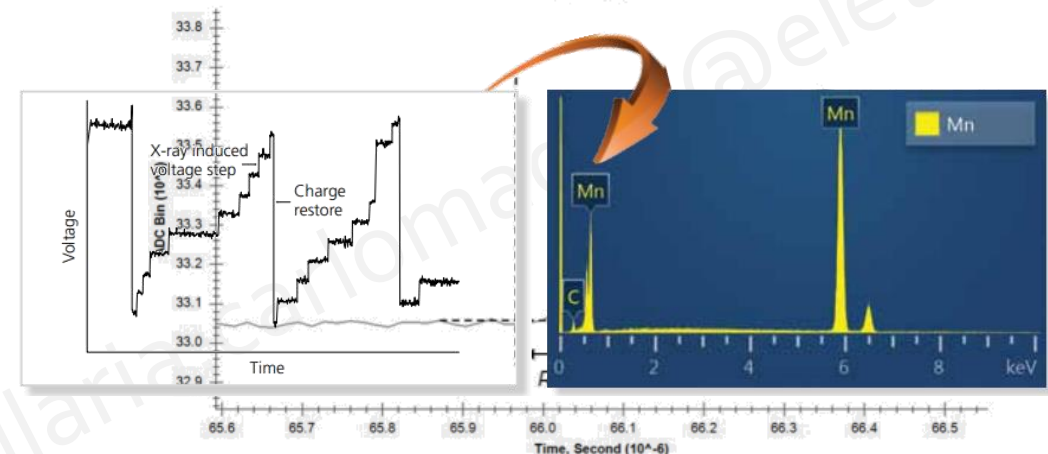
Where are the peaks above the elastic coming from?

Silicon Drift Detectors (SDD)



SDDs convert the photons into an electric signal.

- 1) Si crystal absorbs the X-ray: free **charges** are generated (number of charges $\propto$ photon energy)
- 2) the Field Effect Transistor preamplifier converts the charges into a **voltage** signal (pulse height $\propto$ number of charges collected)
- 3) the pulse processor measures the voltage and returns a voltage 'ramp' where each photon appears as a step



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<https://engineering.temple.edu/sites/engineering/files/Oxford%20EDS-%20Silicon%20Drift%20Detectors%20Explained.pdf>

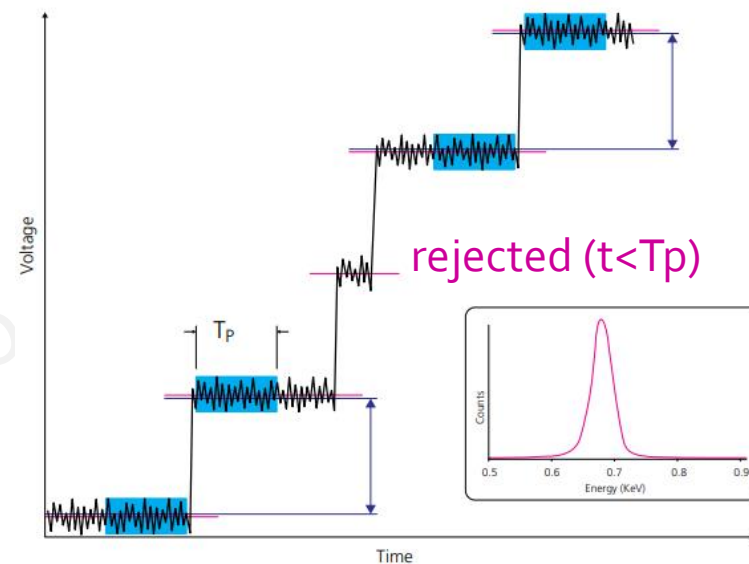
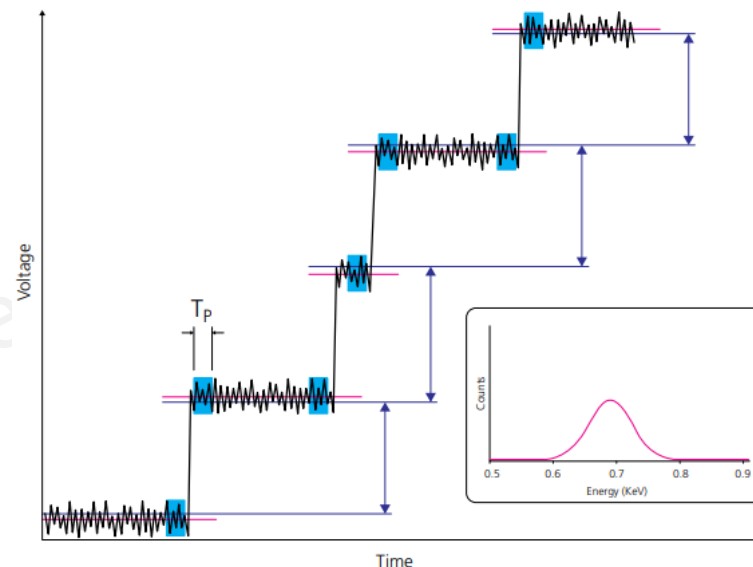
Pulse processor

Counts every step and adds each count to the relative channel (energy).

Pile-up artefacts: two events too close in time might be seen as a single photon of $E_1 + E_2$ energy!

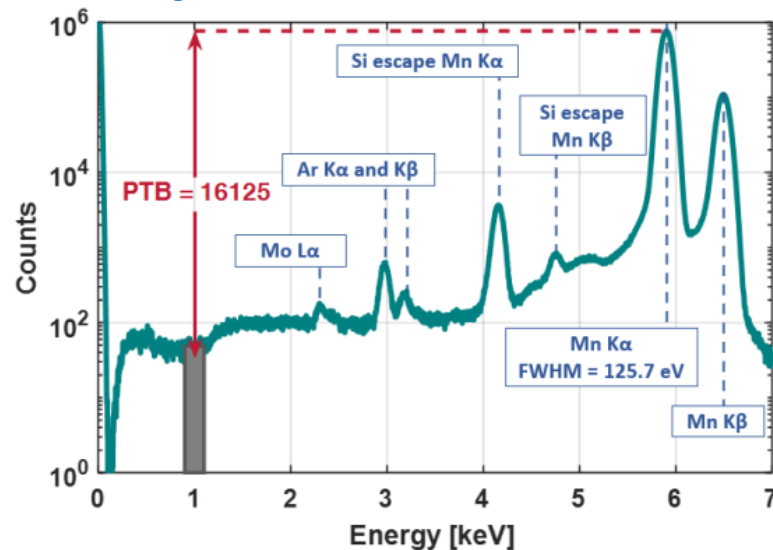
Longer processing time T_p → lower voltage noise
longer measuring time
fewer events measured

The **longest process time** used by a processor gives the **best resolution possible** while the shortest process time gives the maximum throughput into the spectrum.



Escape peaks

Image from: G. Utica *et al* 2021 *JINST* 16 P07057



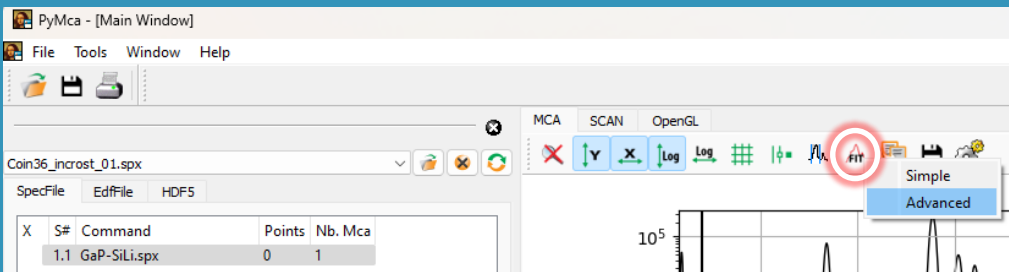
- When a high intensity peak is involved, escape peaks can originate within the detector crystal (in our case Si).
- **Fluorescence photons** passing through the Si volume can produce a **photoelectron from an inner shell of a crystal atom (Si)**.
- The excited atom can emit a fluorescence X-ray photon, mostly a K α photon. It is most of the times reabsorbed thus contributing to the charge pulse. However, that photon can also escape from the crystal. In that case, it carries off the definite energy of the Si K α .
- The charge pulse appear as corresponding to a photon energy $E_{\text{initial}} - E_{\text{Si K}\alpha}$ and therefore show up in the spectrum as separate spurious peaks.

Let's go back to our

PYMCA TUTORIAL

ADVANCED FIT

Quick configuration from PyMCA main window



"FIT" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Fit Function: Mca Hypermet
Continuum type: NO Continuum
Polynomial order: 1
Non-analytical (or estimation) background algorithm: Strip
SNIP Background Width: 24
Strip Background Width: 1
Strip Background Iterations: 6000
Strip Background Smoothing Width (Savitsky-Golay): 16
☐ Strip Background use Anchors 0 0 0 0
Statistical weighting of data: Poisson (1/Y)
Number of fit iterations: 10
Minimum chi² difference (%): 0.001
☐ Perform a fit using the selected strategy
☐ Perform a Linear Fit Fixing non-linear Parameters to Initial Values
☒ Limit fitting region to :
1 First channel : 105
Last channel : 1050
Include:
☒ Stripping ☒ Escape peaks ☒ Pile-up peaks ☒ Scattering peaks
☐ Short tail ☐ Long tail ☒ Step tail
Load From Fit Load Save Cancel OK

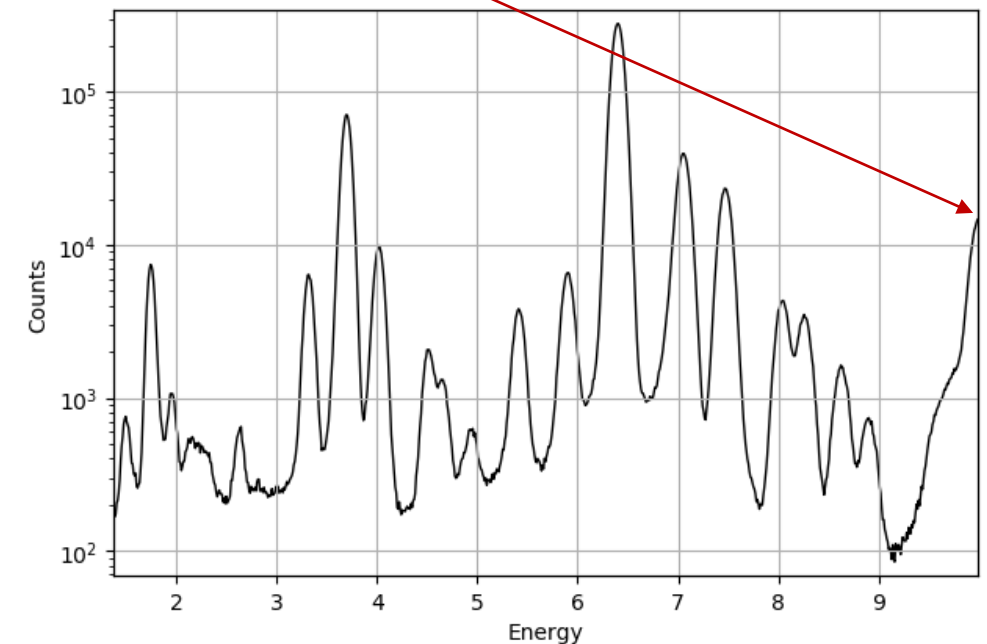
1. Set the fitting region so that peaks for $Z < 14$ and the elastic peak are excluded

First channel = 200;

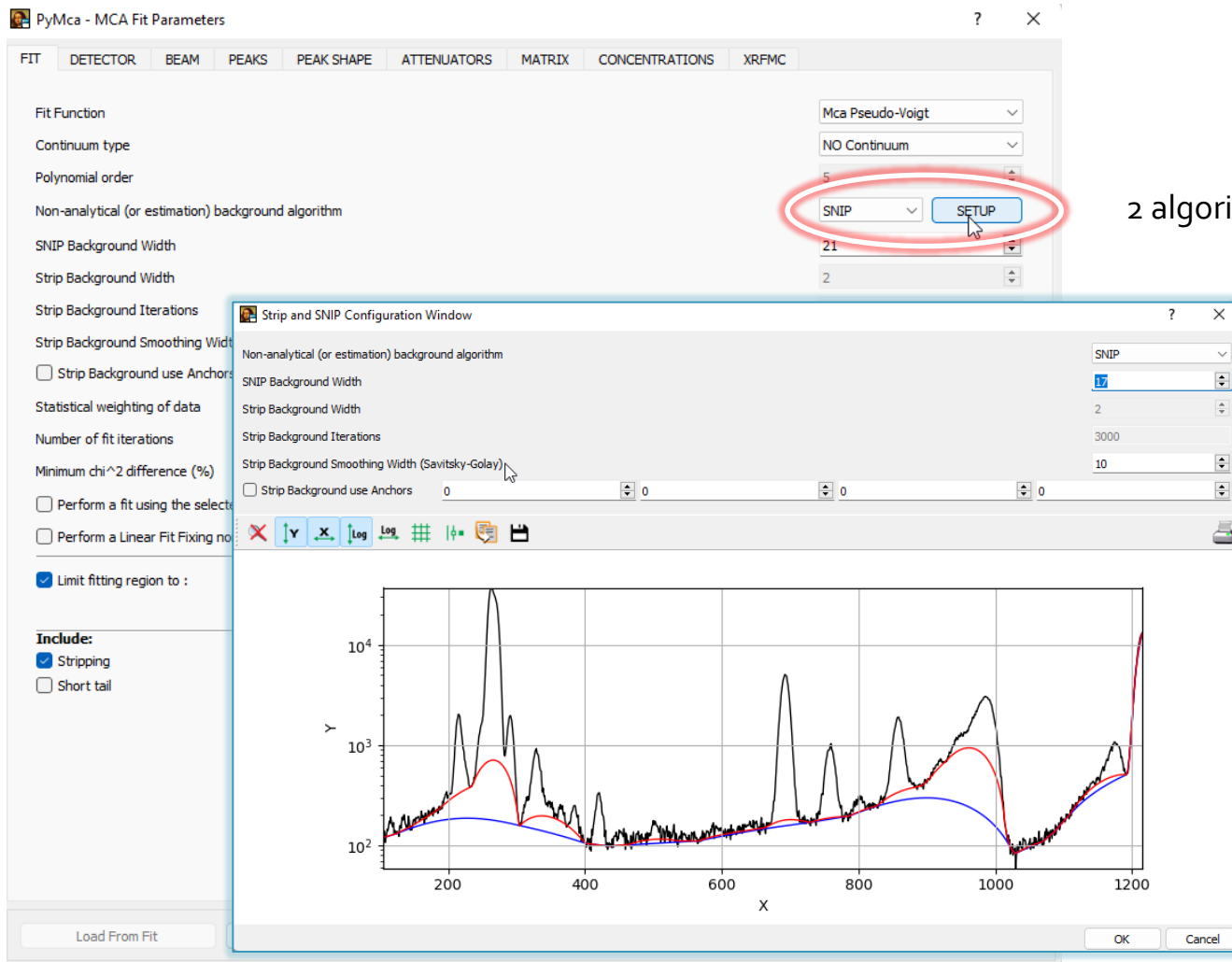
Last channel depends on the energy used.

PyMca implements a poor description of the scattering peaks.

Unless you absolutely need it, you will obtain better results by **limiting the high-energy side of the region to the tail of the scattering peak.**



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2 algorithms can be easily set through the SETUP button.

In the SETUP menu, one can set the **SNIP/strip** bkg width so that the **red curve** looks reasonable.

For **strip** algorithm, one can also choose the number of iterations*.

The **final** bkg will be calculated using a **Savitsky-golay filter (blue curve)** to correct for a bkg passing by the lower band of the statistical noise associated to the spectrum.

This algorithm considers N neighbours for each point and then fits a polynomial in this range, to even out the contributions from the noise.

Anchors can be set to fix some points where the bkg must pass.

* Aim for the **lowest number of iterations** that gives you acceptable results. (Avoid 20k iterations!). That default value is there just for historical reasons. A strip background width of around 70% of your peaks FWHM and 4000 iterations should be a good starting point.

For linear fits without strip background or no background at all, you should set the strip background to **ZERO iterations** because even if you decide not to use the strip background, it is internally used to evaluate the starting parameters of the analytical background models. If you are not going to use any background or you are performing a linear fit it is just wasted time.

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"DETECTOR" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Detector Composition: Si

Maximum Number of Escape energies: 4

	Fixed	Value	Delta
Spectrometer zero (keV)	☐	-0.487604342605	+/- 0.1
Spectrometer gain (keV/ch)	☐	0.00994189524047	+/- 0.0001
Detector noise (keV)	☐	0.055	+/- 0.01
Fano factor (Si ~ 0.12, Ge ~ 0.1)	☐	0.114	+/- 0.01
Pile-up Factor	☐	1e-08	+/- 1e-08

☐ Ignore calibration from input data

Load From Fit Load Save Cancel OK

Adjust the pile-up factor if you see weird pile up peaks (shown in pink) in the fit spectrum

"BEAM" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

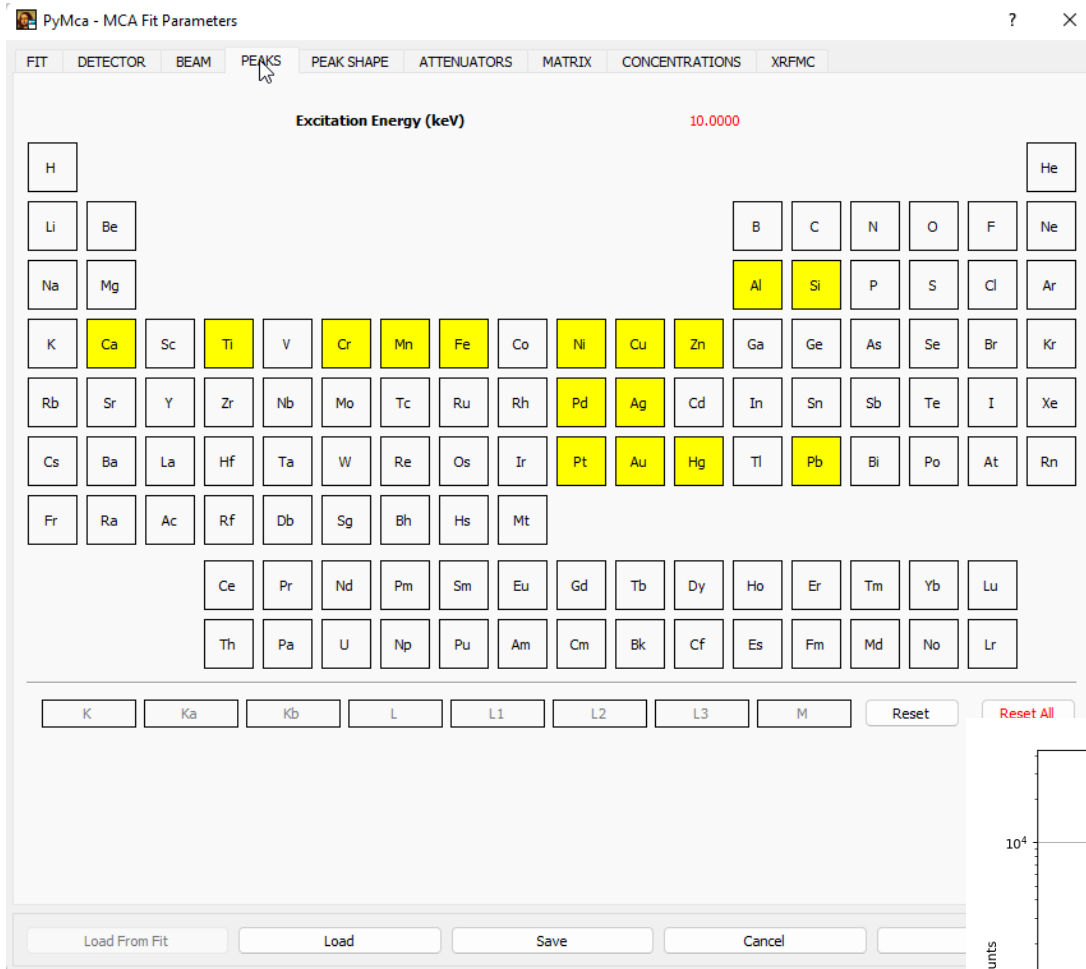
Open X-Ray Tube Setup

Use	Energy	Weight	Use	Energy	Weight	Use	Energy	Weight
☒ Energy 0	10.000000	1	☐ Energy 20		0	☐ Energy 40		0
☐ Energy 1		0	☐ Energy 21		0	☐ Energy 41		0
☐ Energy 2		0	☐ Energy 22		0	☐ Energy 42		0
☐ Energy 3		0	☐ Energy 23		0	☐ Energy 43		0
☐ Energy 4		0	☐ Energy 24		0	☐ Energy 44		0
☐ Energy 5		0	☐ Energy 25		0	☐ Energy 45		0
☐ Energy 6		0	☐ Energy 26		0	☐ Energy 46		0
☐ Energy 7		0	☐ Energy 27		0	☐ Energy 47		0
☐ Energy 8		0	☐ Energy 28		0	☐ Energy 48		0
☐ Energy 9		0	☐ Energy 29		0	☐ Energy 49		0
☐ Energy 10		0	☐ Energy 30		0	☐ Energy 50		0
☐ Energy 11		0	☐ Energy 31		0	☐ Energy 51		0
☐ Energy 12		0	☐ Energy 32		0	☐ Energy 52		0
☐ Energy 13		0	☐ Energy 33		0	☐ Energy 53		0
☐ Energy 14		0	☐ Energy 34		0	☐ Energy 54		0
☐ Energy 15		0	☐ Energy 35		0	☐ Energy 55		0
☐ Energy 16		0	☐ Energy 36		0	☐ Energy 56		0
☐ Energy 17		0	☐ Energy 37		0	☐ Energy 57		0
☐ Energy 18		0	☐ Energy 38		0	☐ Energy 58		0
☐ Energy 19		0	☐ Energy 39		0	☐ Energy 59		0

Insert the beam energy in keV.
For monochromatic sources, use a weight = 1

Load From Fit Load Save Cancel OK

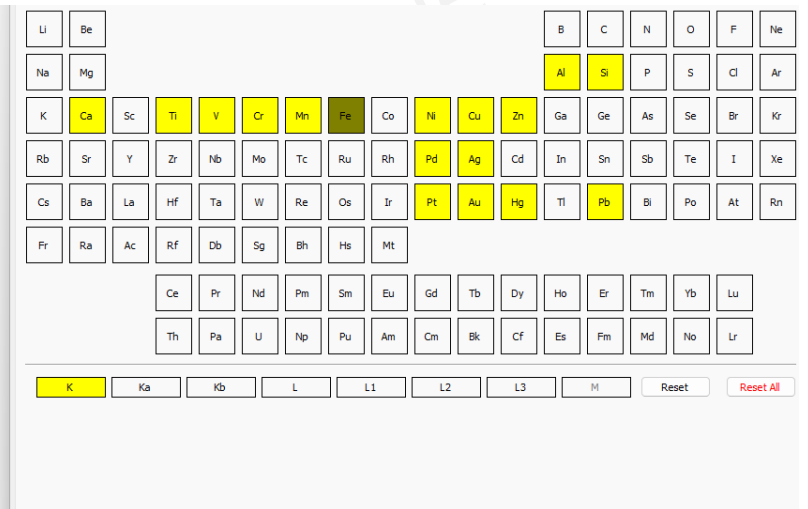
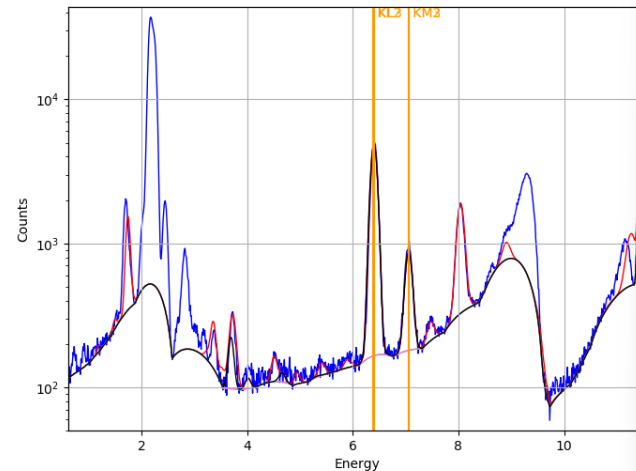
"PEAKS" tab



Select the elements justifying the peaks in your spectrum. When selecting an element, you can also choose the lines. Only available lines (for the exciting energy) can be selected.

Selecting **K** will fit K_alpha and K_beta with tabulated ratios. Selecting the **Ka** and **Kb** will fit them as independent contributions.

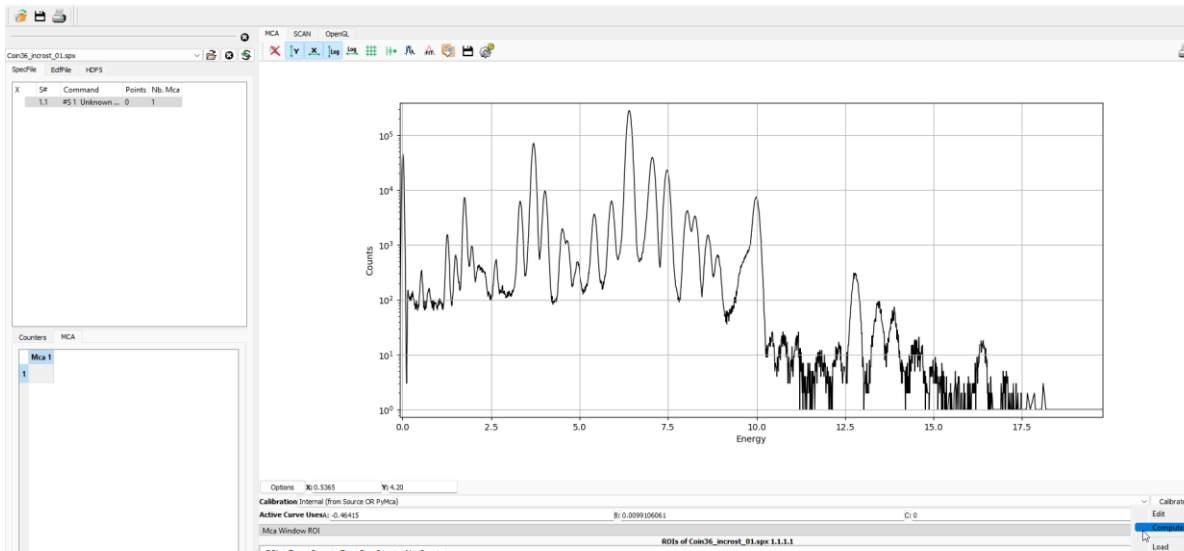
When selecting a line, the plot will show the energy position of that (or those) lines.



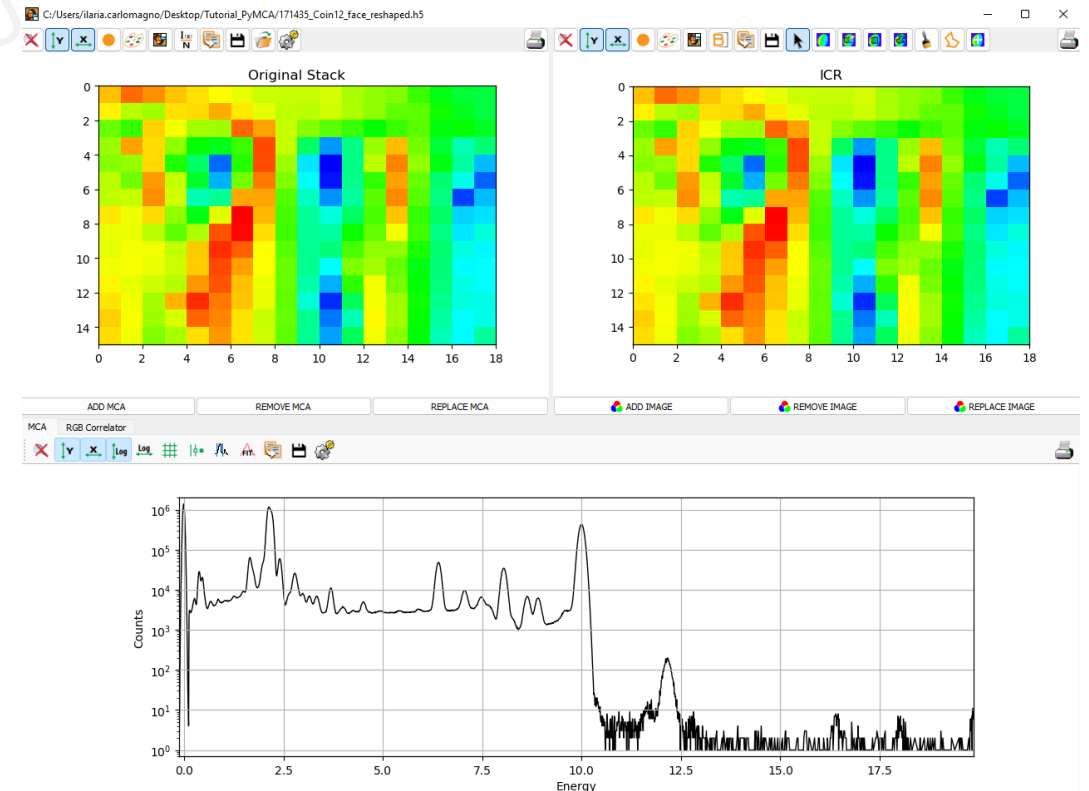
PYMCA TUTORIAL

ROI imaging tool

Importing single spectra vs maps

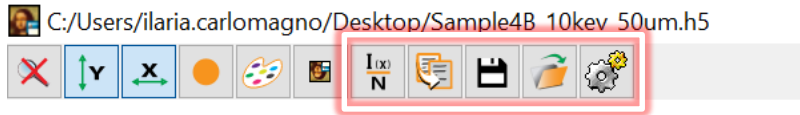


PyMCA (main window)
single spectra



ROI imaging tools
(2D)

Graphical options



- Zoom buttons
- Aspect ratio
- Colormap
- Flip image
- Normalize for pixels number
- Copy / save plot
- Open another window
- Tools

Graphical options

 C:/Users/ilaria.carlomagno/Desktop/Sample4B_10kev_50um.h5



- Zoom buttons
- Aspect ratio
- Colormap
- Flip image
- Normalize for pixels number
- Copy / save plot
- Open another window
- Tools



- (...)
- Background subtraction
switch from RAW intensity to NET
intensity

Graphical options

 C:/Users/ilaria.carlomagno/Desktop/Sample4B_10kev_50um.h5



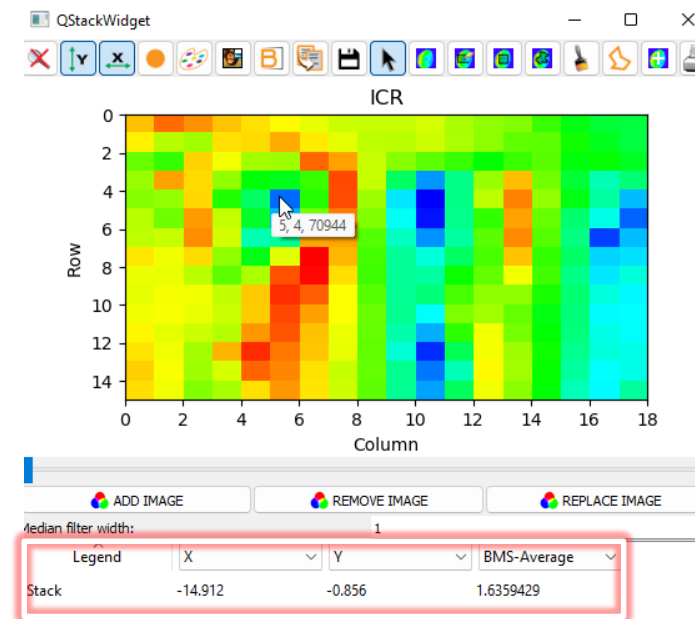
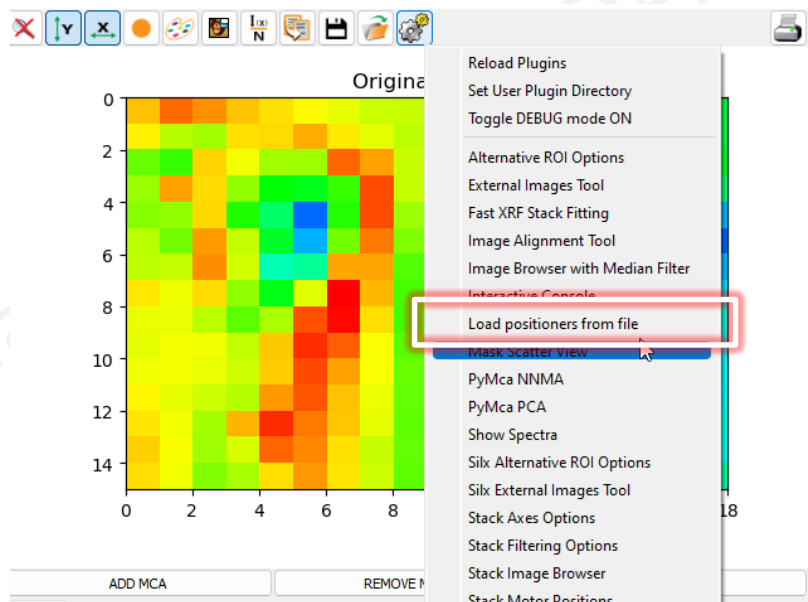
- Zoom buttons
- Aspect ratio
- Colormap
- Flip image
- Normalize for pixels number
- Copy / save plot
- Open another window
- Tools



- (...)
- Background subtraction
switch from RAW intensity to NET
intensity
- Selection tools
 - Pencil
 - Rectangular selection
 - Brush
 - Intensity selection

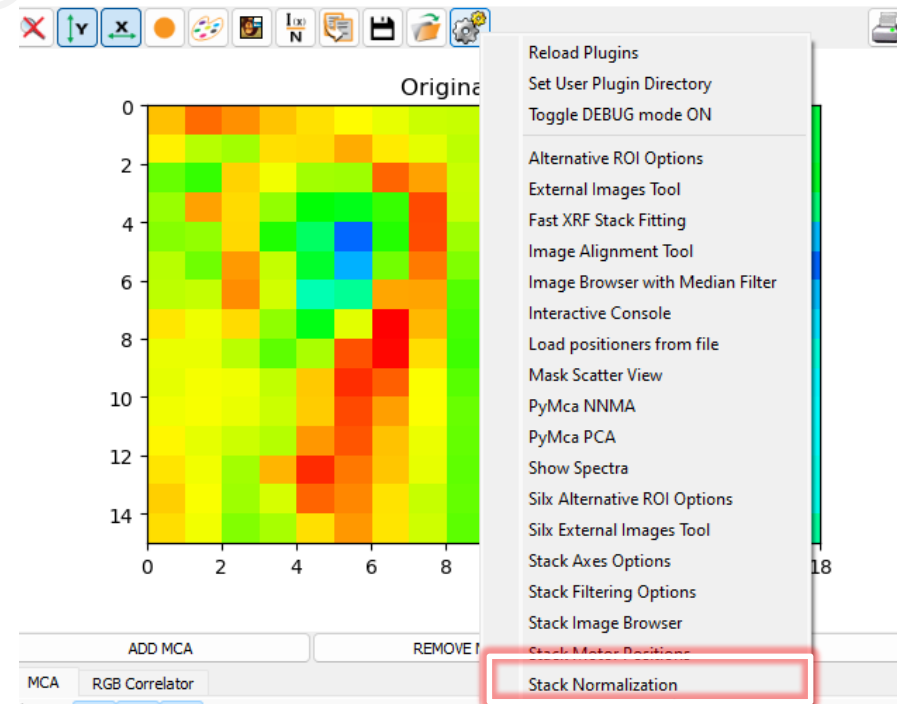
Inspect single pixel values

- Load positioners
- Stack motors positions

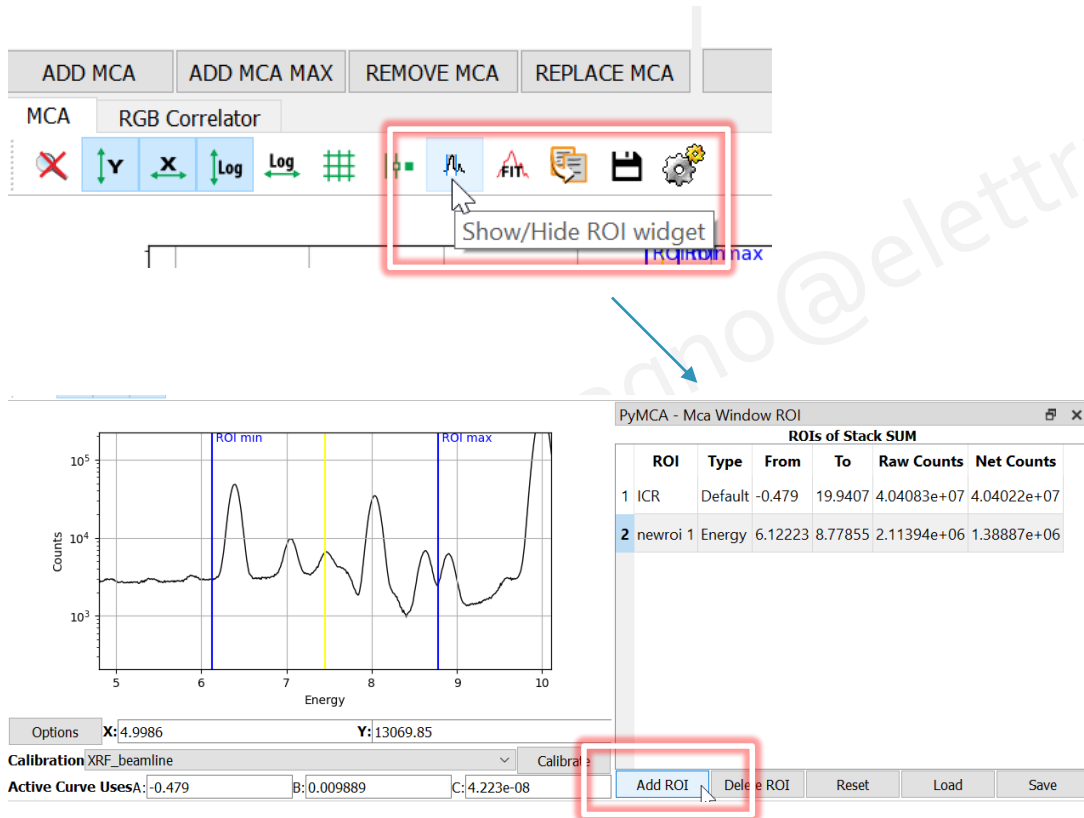


Single pixel normalization

- Image I/I_0 normalization

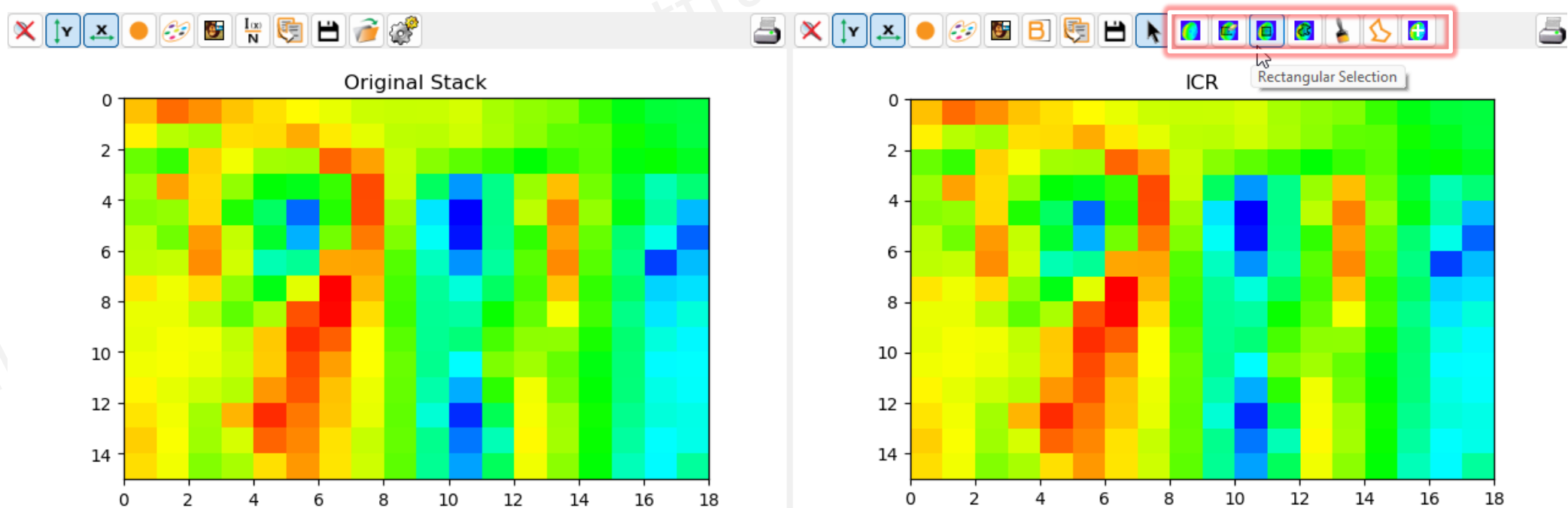


ROIs



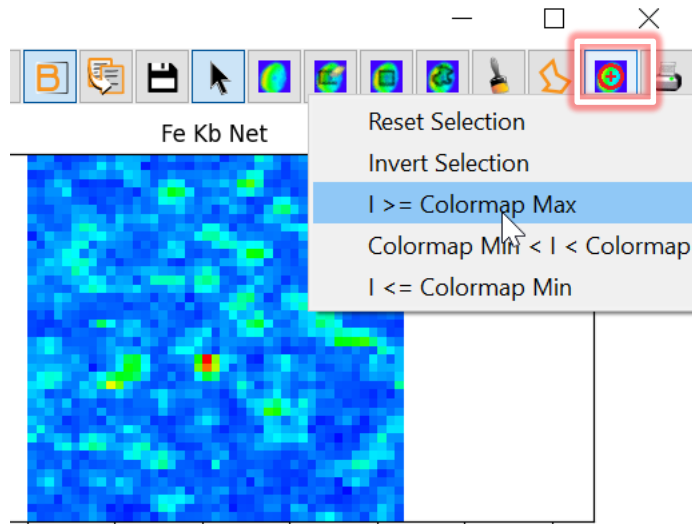
- One or more Regions Of Interest (ROI) can be used to see the distribution of the intensity related to a particular peak in the spectrum.
- Once defined, you can click on a ROI and see how the map in the top right changes.

Extract spectra from selected regions



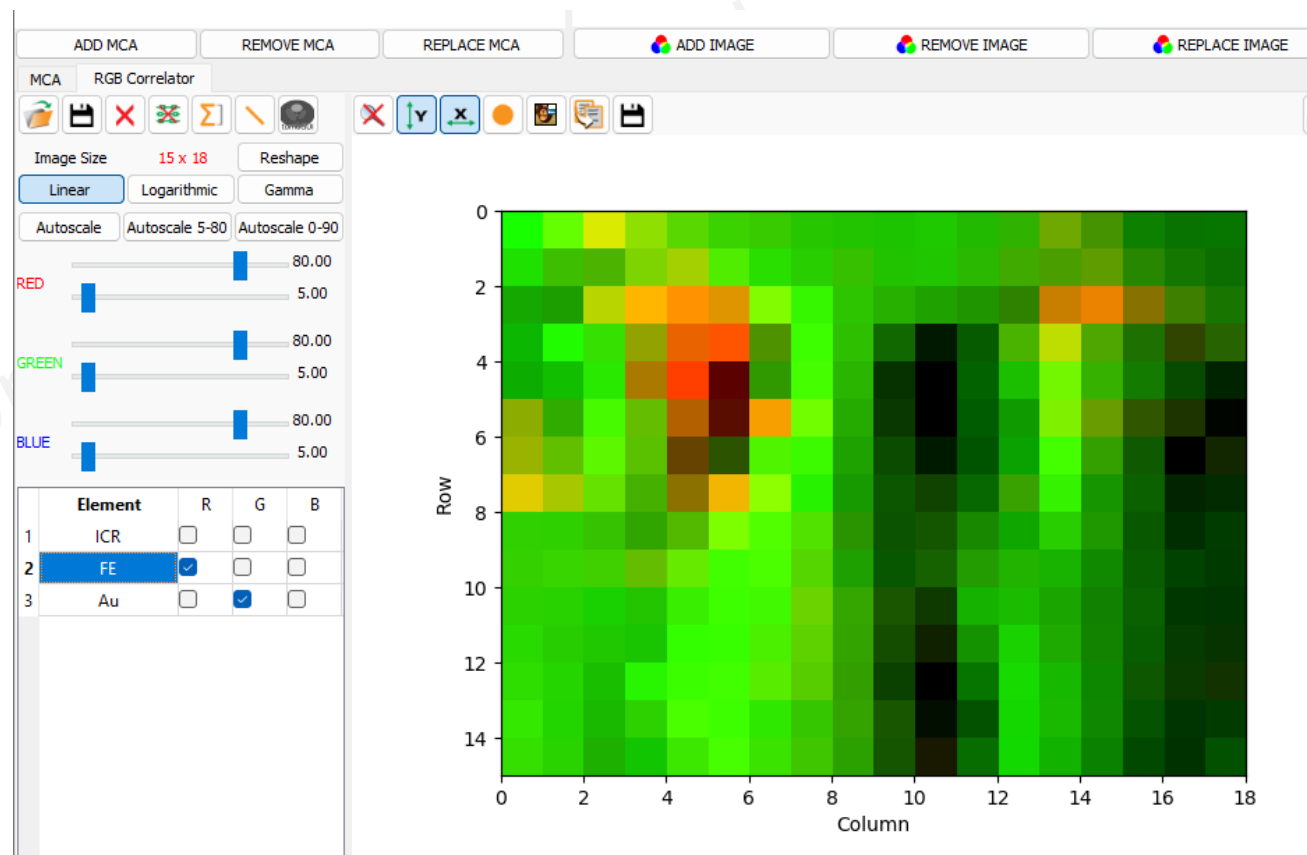
26/09/2026

Selected area: ADD MCA or IMAGE



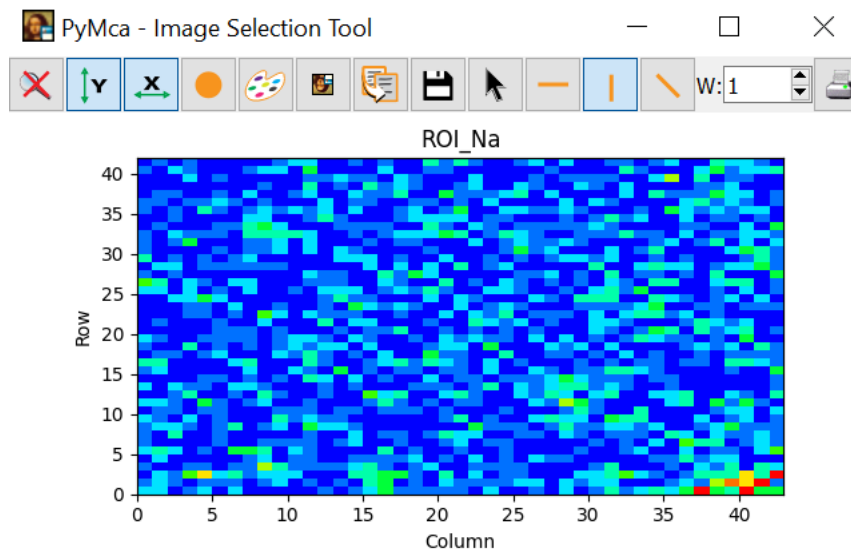
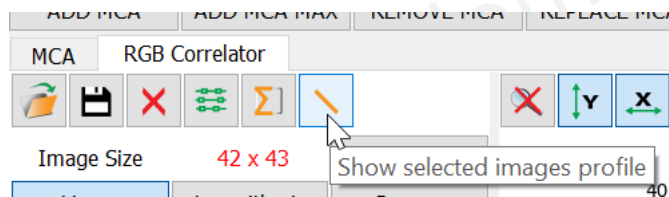
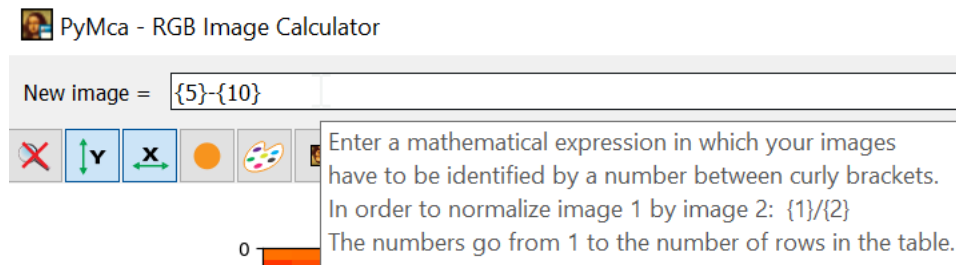
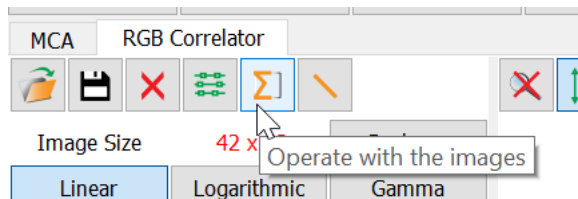
When the regions are hard to select manually, you can try with the intensity tool.

RGB correlator

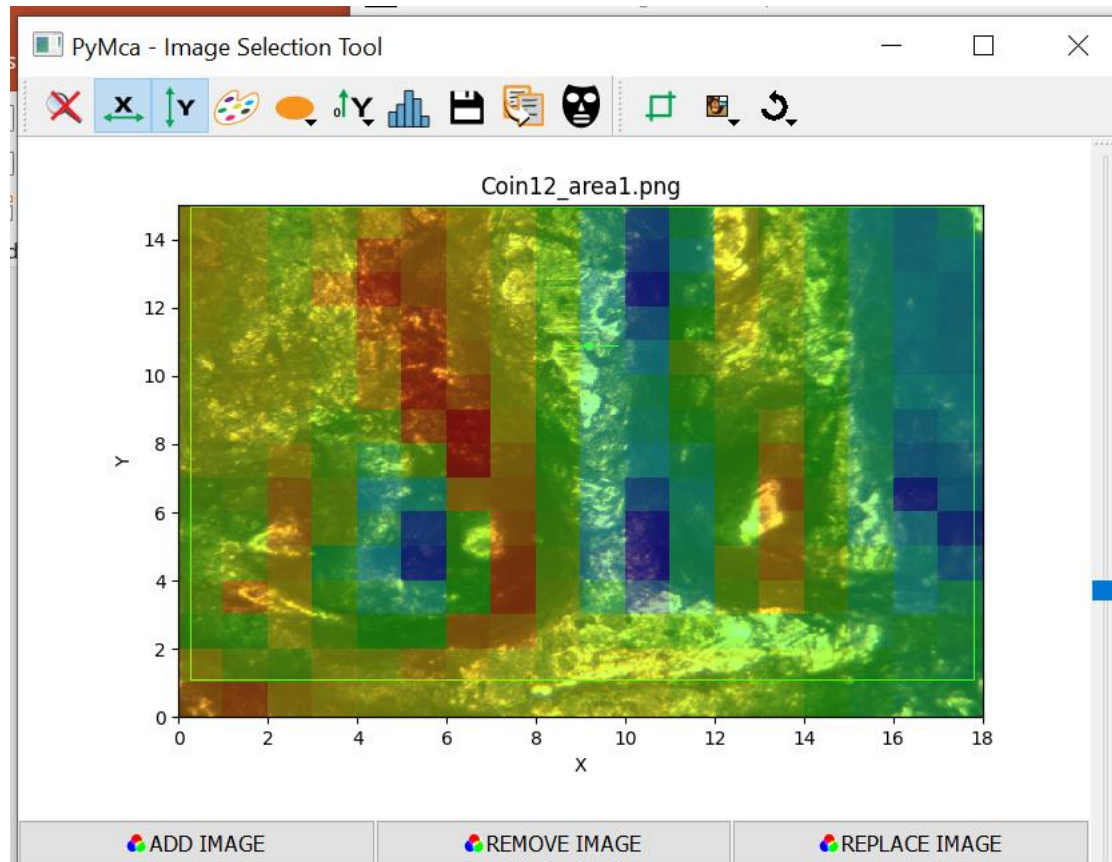


26/09/2026

RGB image calculator and profiles



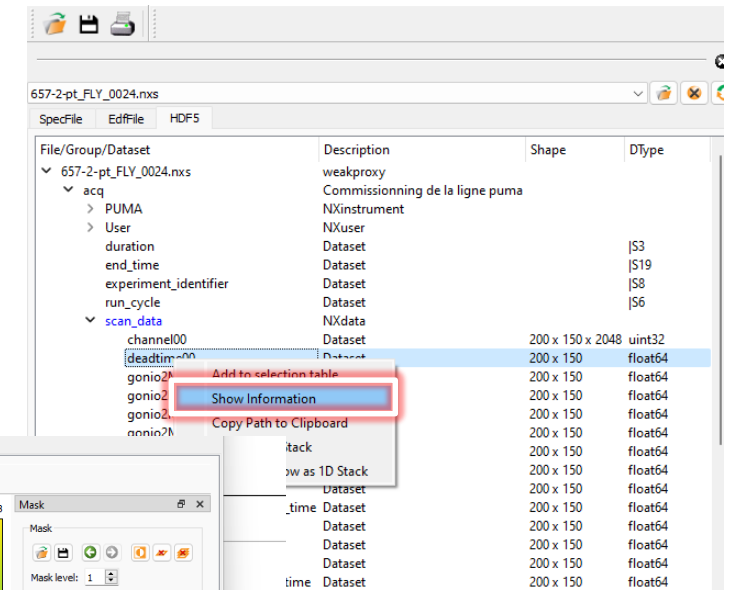
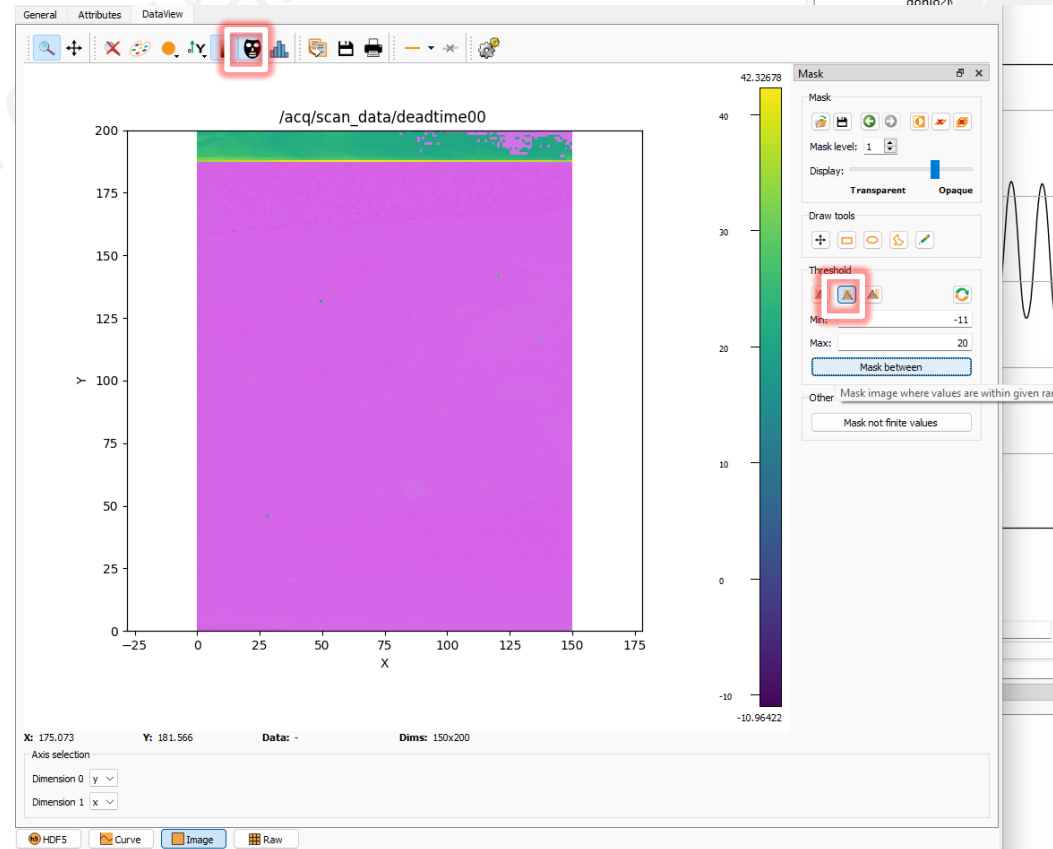
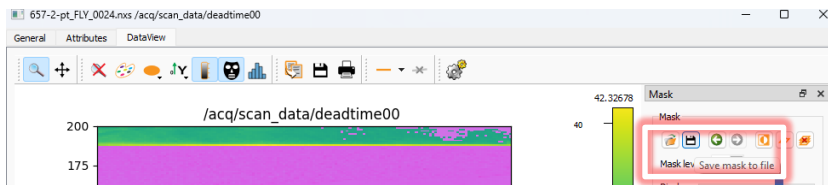
Silx external image & mask

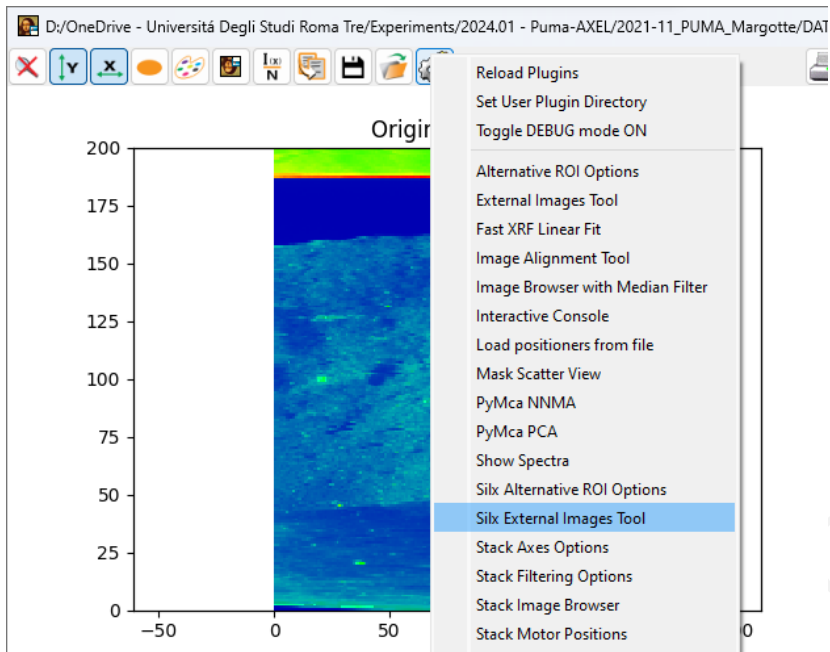


26/09/2026

Create a mask (e.g. deadtime)

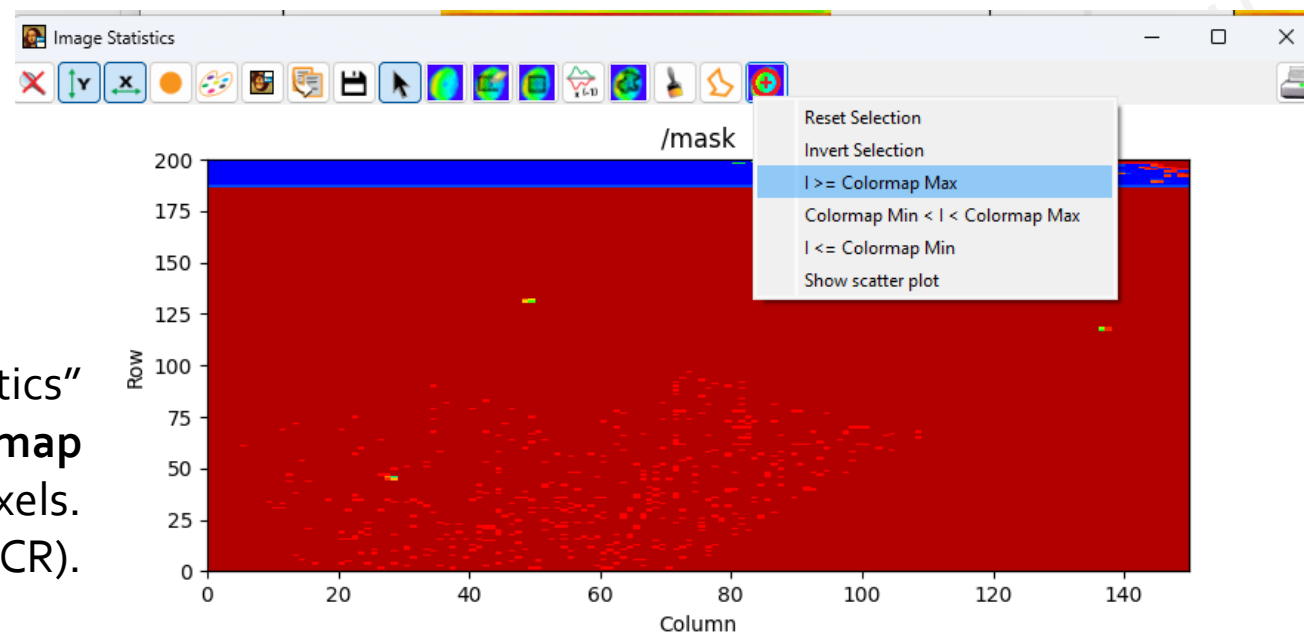
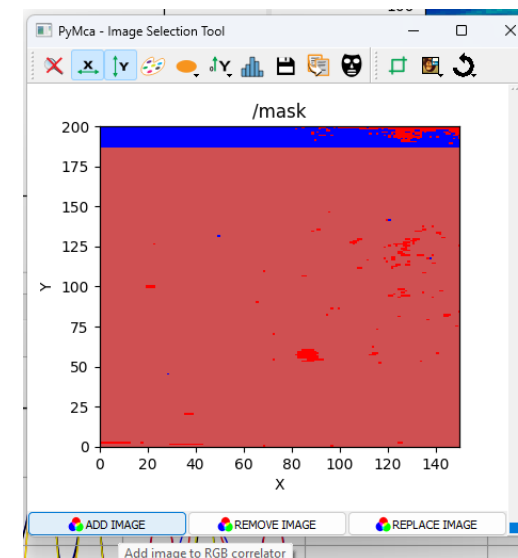
- Select “IMAGE” at the bottom of the window
- Click on the MASK icon
- Select “Mask between” and insert minimum and max allowed values for the deadtime
- Click “mask between” and check the selection (will pop up in pink)
- Save mask to file





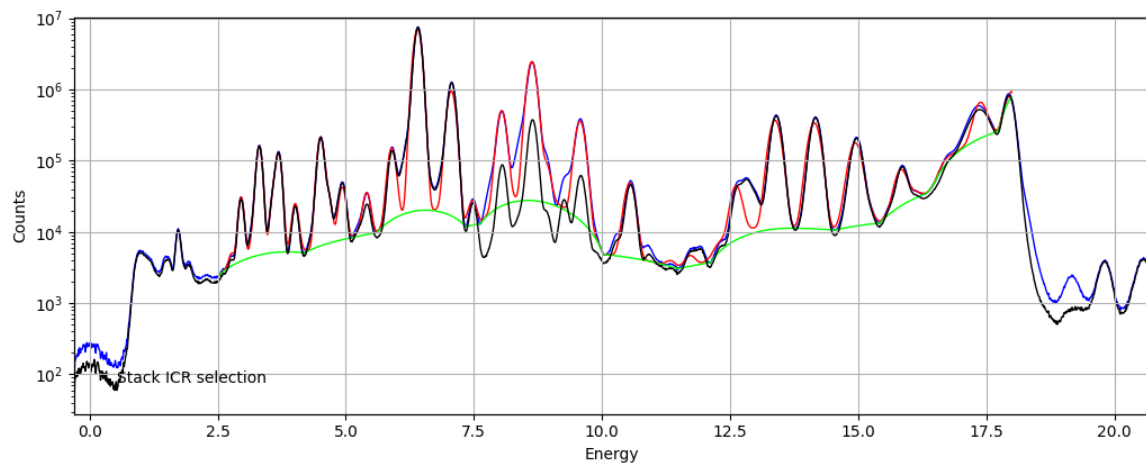
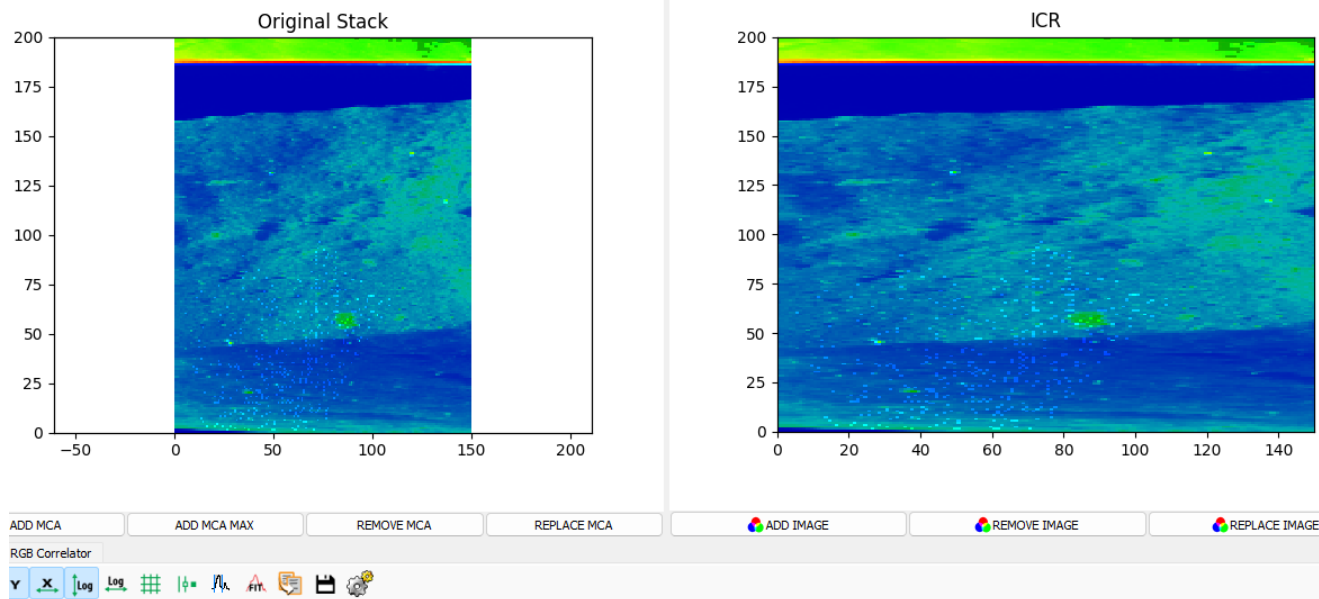
1. Silx External Images Tool
select **mask.h5**

2. ADD IMAGE (to the RGB correlator)



3. From "Image statistics"
Select only **I >= colormap**
This will select only positive pixels.
This selection will also be applied to main image (ICR).

26/09/2026



Adding the MCA of the new selection will make a new graph (the black one in this image) pop up. Now the peaks are distributed in a pretty different fashion!

QUANTITATIVE ANALYSIS

Quantification

- **Quantitative results**

major elements (conc. range 100% - 5%);
rel. uncertainty < 1%
minor elements (conc. range 5% - 0.1%);
rel. uncertainty 5%
trace elements (<0.1%); rel. uncert. >5 %



Requires homogeneous samples

- **Semi-quantitative results**

rel. uncertainties within 5-30%



Most of cases

- **Qualitative results**

presence/absence of elements



Most of cultural heritage cases

Expected intensity

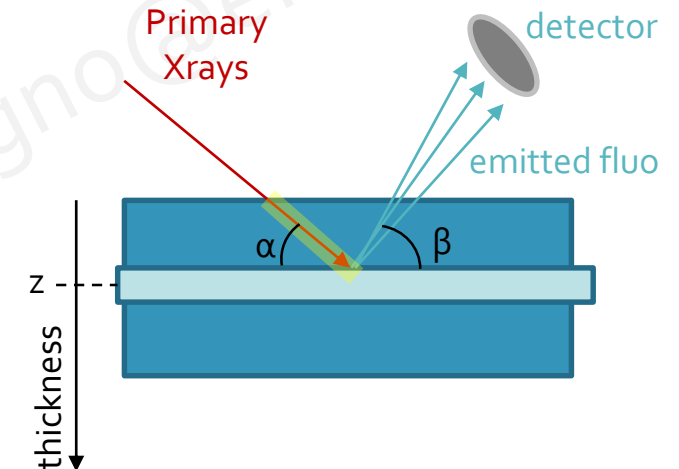
The **measured intensity** depends on the intensity of primary beam reaching a depth z .
(Lambert-Beer formula)

$$I(z) = I_0 e^{-\mu \rho z} = I_0 e^{-\underbrace{\mu_{tot}(E_0)}_{\text{mass attenuation coeff. at } E_0} \underbrace{\rho_{tot}}_{\text{mass density}} \underbrace{\frac{z}{\sin \alpha}}_{\text{path travelled}}}$$

$$\mu_{tot}(E_0) = \sum w_i \mu_i(E_0)$$

Let's assume our sample is 95% Al and 5% Fe:

$$\mu_{tot}(E_0) = \sum w_i \mu_i(E_0) = 0.95 \mu_{Al}(E_0) + 0.05 \mu_{Fe}(E_0)$$



A further element to consider is the number of Fe vacancies in the layer dz at depth z .
The emitted Fe fluo will depend on the intensity that reaches the layer, I_z , accounting for:

[10.1016/j.apradiso.2014.10.012](https://doi.org/10.1016/j.apradiso.2014.10.012)

$$I_{Fe}(E_0) = I_z \tau_{Fe}(E_0) \rho_{Fe} \frac{dz}{\sin \alpha}$$

density of Fe

fraction of photons being absorbed by Fe atoms (by any shell)

For $K\alpha$ emission only:

$$I_{Fe}(E_0) = I_z \tau_{K,Fe}(E_0) \rho_{Fe} \frac{dz}{\sin \alpha} \omega_k f_{K\alpha}$$

$$\tau_{K,Fe}(E_0) = \tau_{Fe}(E_0) \left(1 - \frac{1}{J_{Fe,k}} \right)$$

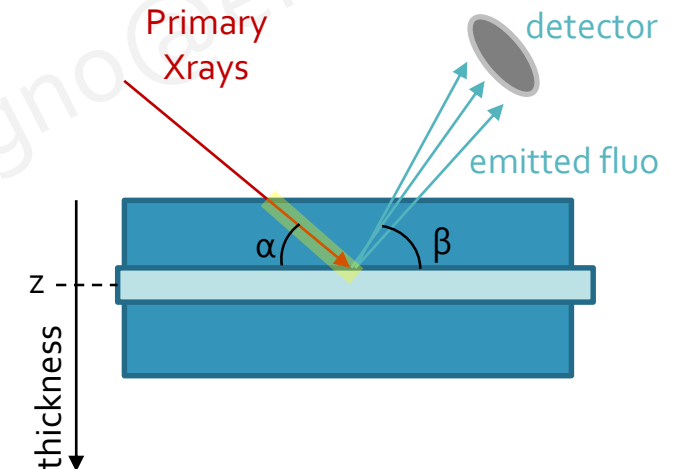
K-shell Fe fluo yield

$K\alpha$ to total K ($K\alpha + K\beta$) ratio

K-edge jump ratio

K shell absorption jump factor: probability that a K shell electron is ejected rather than any other shells. It is the fraction of the total absorption associated with a given shell rather than any other shell.

26/09/2026



$$dI_{Fe}(E_0) = I_z f_{K\alpha} \omega_k \left(1 - \frac{1}{J_k}\right) \tau_{Fe}(E_0) \rho_{Fe} \frac{dz}{\sin \alpha}$$

But we need to consider the fraction of photons reaching the detector...

The **path travelled** by fluo photons depends on β and have to consider the attenuation term at the fluo energy $E_{FeK\alpha}$:

$$\frac{\Omega}{4\pi}$$

Detector acceptance

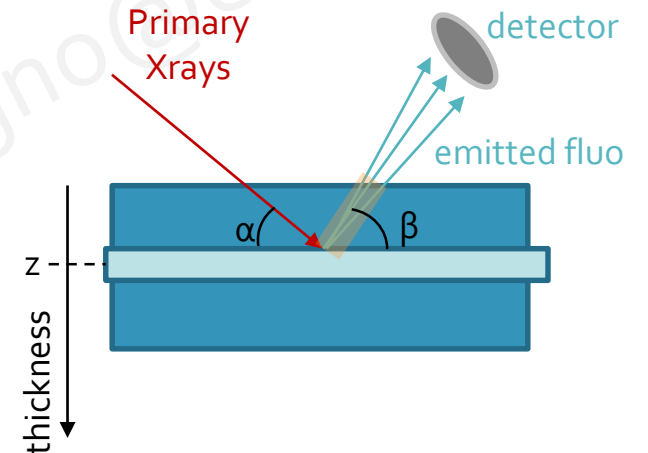
$$\varepsilon(E_{FeK\alpha})$$

Detector efficiency, including any attenuation from the sample to the sensor (det. windows)

$$e^{-\left(\mu_{tot}(E_{FeK\alpha}) \frac{z}{\sin \beta}\right)}$$

Absorption term for outgoing X-rays of energy $E_{FeK\alpha}$

$$dI_{FeK\alpha}(E_0) = dI_{Fe}(E_0) \frac{\Omega}{4\pi} \varepsilon(E_{FeK\alpha}) e^{-\left(\mu_{tot}(E_{FeK\alpha}) \frac{z}{\sin \beta}\right)}$$



$$dI_{FeK\alpha}(E_0) = dI_{Fe}(E_0) \frac{\Omega}{4\pi} \varepsilon(E_{FeK\alpha}) e^{-\left(\mu_{tot}(E_{FeK\alpha}) \frac{z}{\sin \beta}\right)}$$

$$dI_{Fe}(E_0) = I_z f_{K\alpha} \omega_k \left(1 - \frac{1}{J_k}\right) \tau_{Fe}(E_0) \rho_{Fe} \frac{dz}{\sin \alpha}$$

$$I_{Fe}(z) = I_0 e^{-\frac{\mu_{tot}(E_0) \rho_{tot} z}{\sin \alpha}}$$

And we finally have:

$$dI_{FeK\alpha} dz = I_0 G \varepsilon(E_{FeK\alpha}) K_{Fe} \rho_{Fe} \tau_{Fe}(E_0) e^{-(\chi_{tot} \rho_{tot}) z} dz$$

geometric term

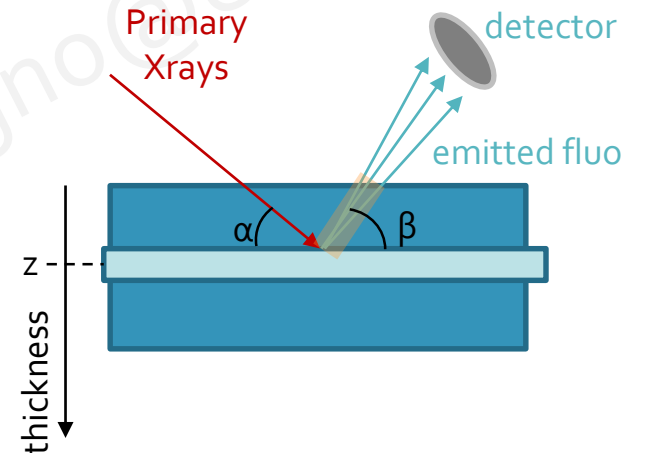
$$G = \frac{\Omega}{4\pi \sin \alpha}$$

"fundamental" constant

$$K_{Fe} = f_{K\alpha} \omega_k \left(1 - \frac{1}{J_k}\right)$$

absorption term

$$\frac{\mu_{tot}(E_{FeK\alpha})}{\sin \beta} + \frac{\mu_{tot}(E_0)}{\sin \alpha}$$



Integrating over the entire sample:

$$I_{FeK\alpha} = I_0 G \varepsilon(E_{FeK\alpha}) K_{Fe} Q_{Fe} \tau_{Fe}(E_0) \int_{z=0}^{z=t} e^{-(\chi_{tot} Q_{tot})z} dz$$

$$= I_0 G \varepsilon(E_{FeK\alpha}) K_{Fe} Q_{Fe} \tau_{Fe}(E_0) \frac{1 - e^{-(\chi_{tot} Q_{tot})t}}{\chi_{tot} Q_{tot}} =$$

$$\frac{Q_{Fe}}{Q_{tot}} = w_{Fe} \quad \text{weight fraction of Fe}$$

$$= I_0 G \varepsilon(E_{FeK\alpha}) K_{Fe} w_{Fe} \tau_{Fe}(E_0) \frac{1 - e^{-(\chi_{tot} Q_{tot})t}}{\chi_{tot}}$$

geometric term

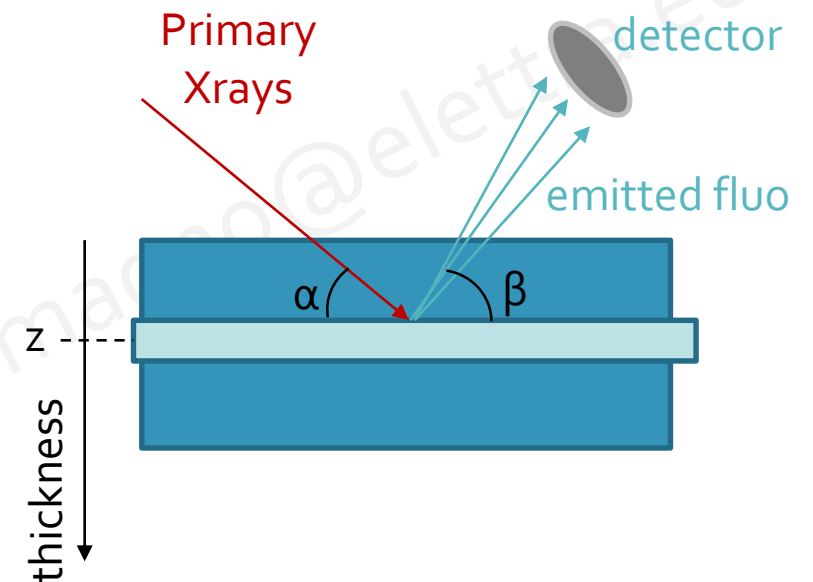
$$G = \frac{\Omega}{4\pi \sin \alpha}$$

"fundamental" constant

$$K_{Fe} = f_{K\alpha} \omega_k \left(1 - \frac{1}{J_k} \right)$$

absorption term

$$\chi_{tot}(E_0, E_{FeK\alpha}) = \frac{\mu_{tot}(E_{FeK\alpha})}{\sin \beta} + \frac{\mu_{tot}(E_0)}{\sin \alpha}$$



Thickness effect

$$I_{FeK\alpha} = I_0 G w_{Fe} \varepsilon(E_{FeK\alpha}) K_{Fe} \tau_{Fe}(E_0) \frac{1 - e^{-(\chi_{tot} \rho_{tot})z}}{\chi_{tot}}$$

We define the sensitivity for the specific element:

$$I_{FeK\alpha} = I_0 G w_{Fe} S_{Fe} \frac{1 - e^{-(\chi_{tot} \rho_{tot})z}}{\chi_{tot}}$$

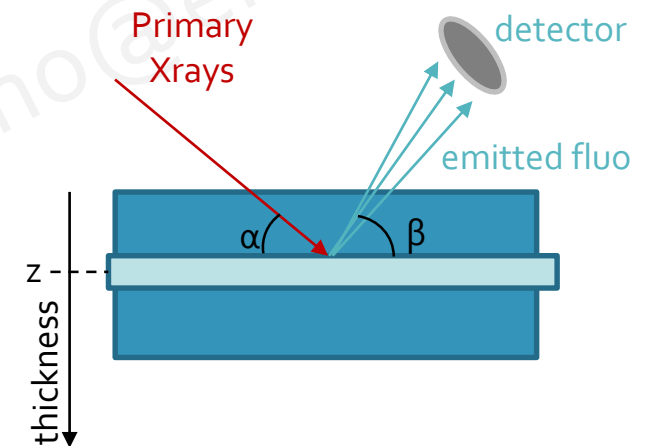
What happens for **infinitely thick samples**?

$$I_{FeK\alpha} = I_0 G w_{Fe} S_{Fe} \frac{1}{\chi_{tot}}$$

$\varepsilon(E_{FeK\alpha})$ Detector efficiency

$K_{Fe} = f_{K\alpha} \omega_k \left(1 - \frac{1}{J_k}\right)$ Fundamental constant

$\tau_{Fe}(E_0)$ fraction of photons being absorbed by Fe atoms (any shell)

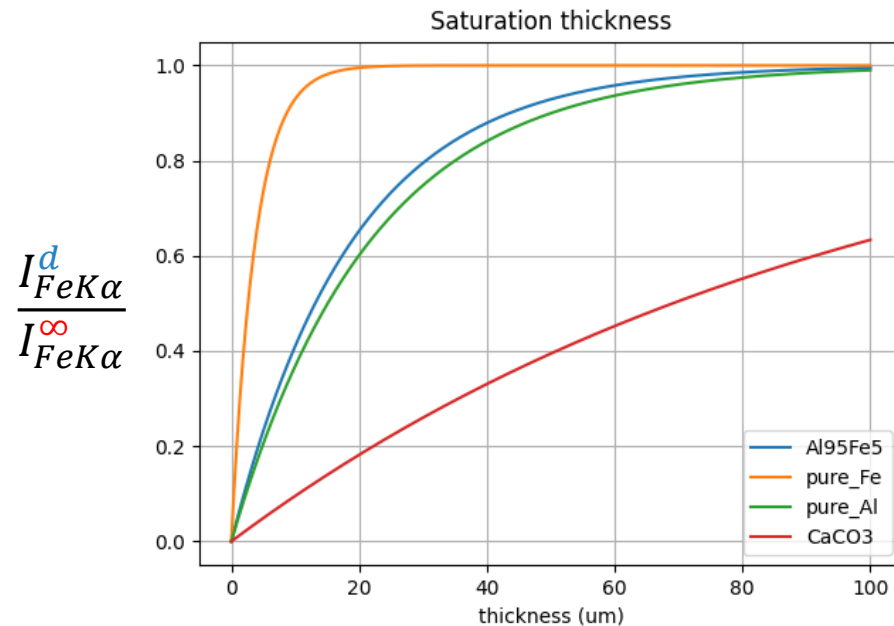


Expected intensity

$$I_{FeK\alpha}^d = I_0 G w_{Fe} S_{Fe} \frac{1 - e^{-(\chi_{tot} \rho_{tot})z}}{\chi_{tot}}$$

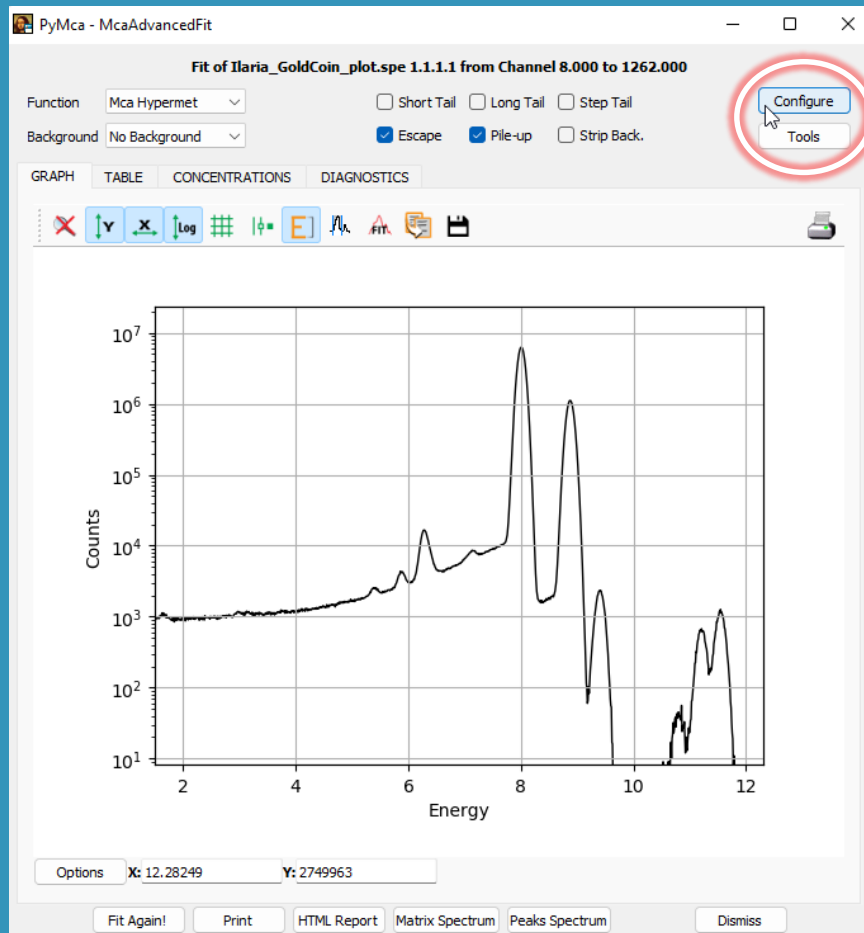
For infinitely **thick** samples:

$$I_{FeK\alpha}^{\infty} = I_0 G w_{Fe} S_{Fe} \frac{1}{\chi_{tot}}$$



When do we reach the approximation of infinitely thick sample?

Depends on the material!



ADVANCED FIT

Full configuration

"FIT" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Fit Function: Mca Hypermet
Continuum type: NO Continuum
Polynomial order: 1
Non-analytical (or estimation) background algorithm: Strip
SNIP Background Width: 24
Strip Background Width: 1
Strip Background Iterations: 6000
Strip Background Smoothing Width (Savitsky-Golay): 16
☐ Strip Background use Anchors 0 0 0 0
Statistical weighting of data: Poisson (1/Y)
Number of fit iterations: 10
Minimum chi² difference (%): 0.001
☐ Perform a fit using the selected strategy
☐ Perform a Linear Fit Fixing non-linear Parameters to Initial Values
☒ Limit fitting region to :
1 First channel : 105
Last channel : 1050
Include:
☒ Stripping ☒ Escape peaks ☒ Pile-up peaks ☒ Scattering peaks
☐ Short tail ☐ Long tail ☒ Step tail
Load From Fit Load Save Cancel OK

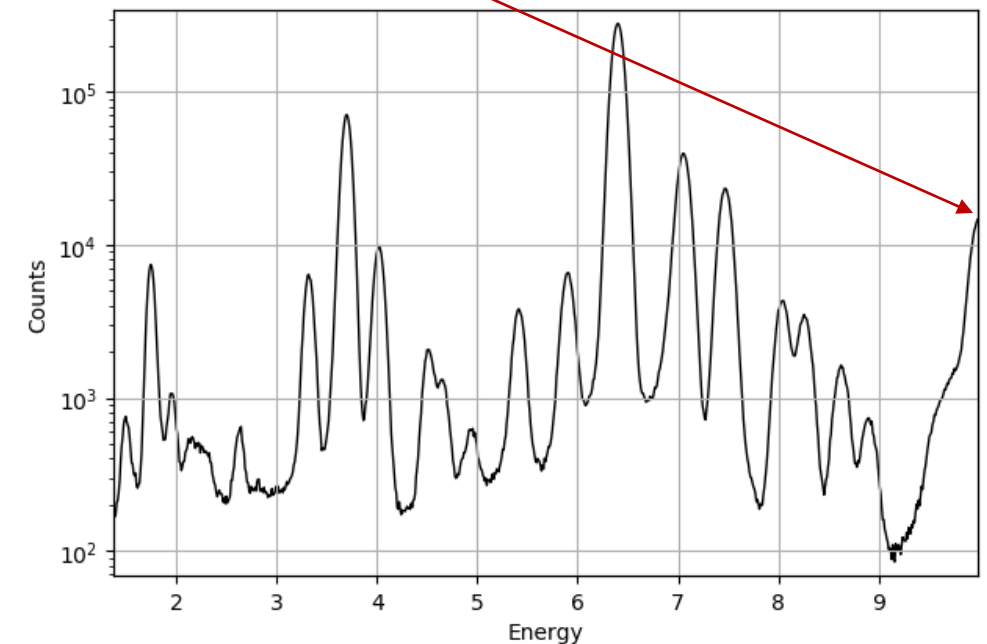
1. Set the fitting region so that peaks for $Z < 14$ and the elastic peak are excluded

First channel = 200;

Last channel depends on the energy used.

PyMca implements a poor description of the scattering peaks.

Unless you absolutely need it, you will obtain better results by **limiting the high-energy side of the region to the tail of the scattering peak.**



26/09/2026

"FIT" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Fit Function: **2** Mca Hypermet

Continuum type: **3** NO Continuum

Polynomial order: 1

Non-analytical (or estimation) background algorithm: Strip **SETUP**

SNIP Background Width: 24

Strip Background Width: 1

Strip Background Iterations: 6000

Strip Background Smoothing Width (Savitsky-Golay): 16

☐ Strip Background use Anchors 0 0 0 0

Statistical weighting of data: Poisson (1/Y)

Number of fit iterations: 10

Minimum chi² difference (%): 0.001

☐ Perform a fit using the selected strategy

☐ Perform a Linear Fit Fixing non-linear Parameters to Initial Values

☒ Limit fitting region to : First channel : 105 Last channel : 1050

Include:

☒ Stripping ☒ Escape peaks ☒ Pile-up peaks ☒ Scattering peaks

☐ Short tail ☐ Long tail ☒ Step tail

Load From Fit Load Save Cancel OK

2. Fit Function

Hypermet better for high energies (40-150 keV)
Pseudo-voigt better for lower ones.

3. The continuum is modelled in two ways:

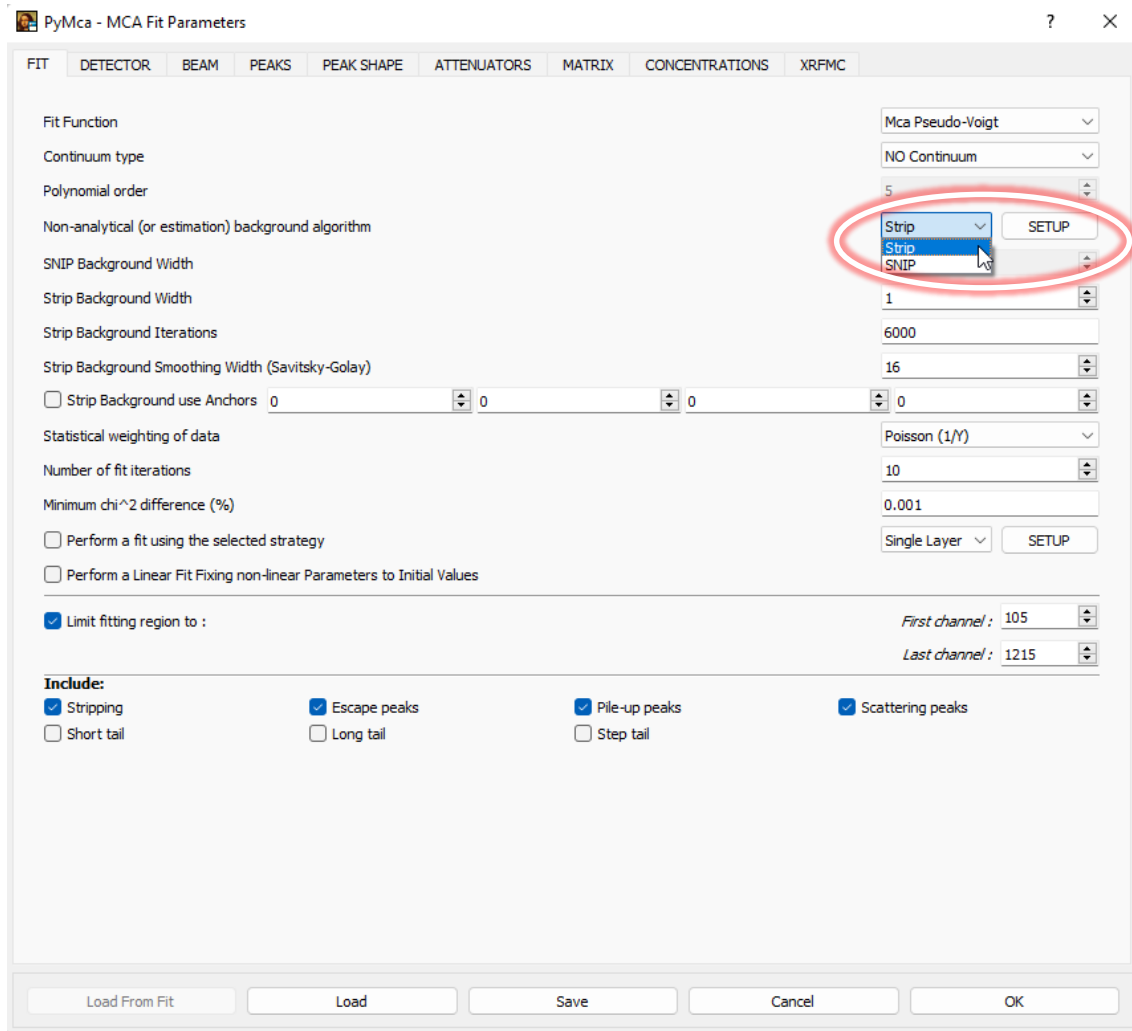
- (i) the estimated background is subtracted from the experimental data prior to the least-squares fitting of the fluorescence peaks;
- (ii) in the fitting mode the continuum is described by an analytical function which enters into the least-squares fitting algorithm.

Background can be estimated through an iterative procedure in which the content of each channel is compared against the average of the content of its neighbours at a distance of i channels. If the content is above the average, it is replaced by the average. In order to speed up the procedure, i can be taken as a fraction of the peaks full-width-half-maximum (FWHM) at the beginning of the iterative process, being one at the end of it.

An optional Savitsky–Golay smoothing at the beginning of the process is possible as recommended in [7].

The analytical functions currently supported to describe the background are polynomials of user selectable degree on $x = (E - E_{\text{mean}})$ or on $x = \exp(E - E_{\text{mean}})$ where E is the energy of the considered point of the spectrum and E_{mean} is the energy at the center of the fitting region.

"FIT" tab



Bkg algorithm

(i) **Strip**

if the intensity of the i -th channel, $y(i)$, is above the average value of the channels within a width w :

$$y(i) > \frac{y(i+w) + y(i-w)}{2}$$

then $y(i)$ is replaced by the average value.

After several iterations, the bkg is the value of the spectrum after the peaks have been stripped.

(ii) **SNIP**

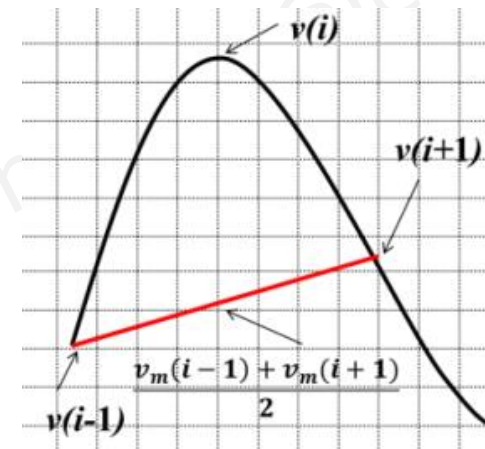
more **complex**, requires pre-processing ("the log square root (LLS) operator,") where $y(i)$ is transformed into $v(i)$:

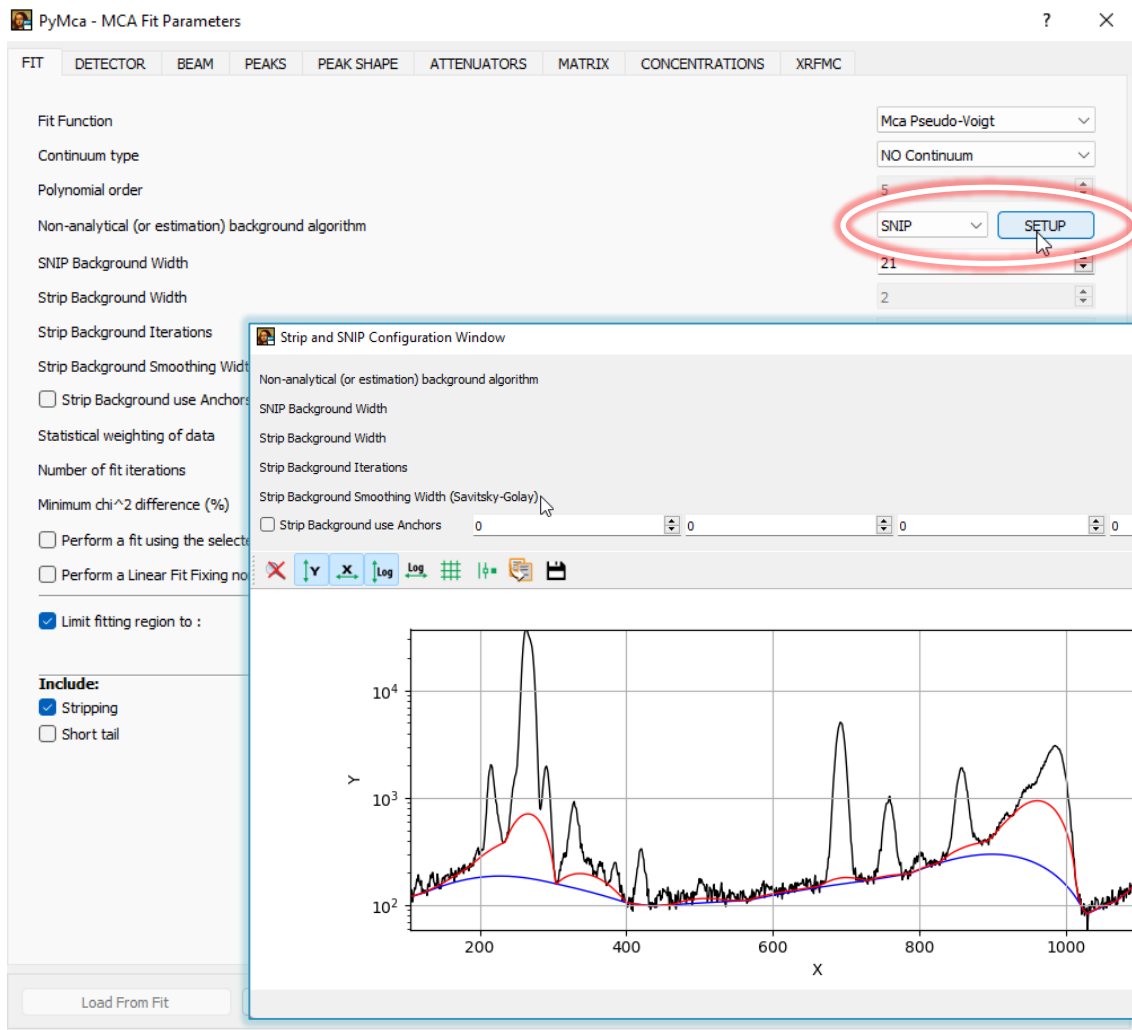
$$y(i) \rightarrow v(i) = \log(\log(\sqrt{y(i) + 1} + 1) + 1)$$

The log enhances the **sensitivity to weak peaks**.

Then, a stripping procedure is applied:

$$v(i) = \min\{v(i), \frac{v(1-M) + v(i+M)}{2}\}$$





Both algorithms are easily set through the SETUP button.

In the SETUP menu, one can set the SNIP/strip bkg width so that the red curve looks reasonable.

For strip algorithm, one can also choose the number of iterations.

The **final** bkg will be calculated using a Savitsky-golay filter (**blue** curve) to correct for a bkg passing by the lower band of the statistical noise associated to the spectrum.

This algorithm considers N neighbours for each point and then fits a polynomial in this range, to even out the contributions from the noise.

Anchors can be set to fix some points where the bkg must pass.

You should always aim to the **lowest number of iterations** that gives you acceptable results. (Avoid 20k iterations!). That default value is there just for historical reasons. A strip background width of around 70% of your peaks full-width at half maximum and a number of iterations around 4000 should be a good starting point. If you are using linear fits without strip background or no background at all, you should set the strip background number of iterations to zero because even if you decide not to use the strip background, it is internally used to evaluate the starting parameters of the analytical background models. If you are not going to use any background or you are performing a linear fit it is just wasted time.

26/09/2026

"DETECTOR" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Detector Composition: Si

Maximum Number of Escape energies: 4

	Fixed	Value	Delta
Spectrometer zero (keV)	☐	-0.487604342605	+/- 0.1
Spectrometer gain (keV/ch)	☐	0.00994189524047	+/- 0.0001
Detector noise (keV)	☐	0.055	+/- 0.01
Fano factor (Si ~ 0.12, Ge ~ 0.1)	☐	0.114	+/- 0.01
Pile-up Factor	☐	1e-08	+/- 1e-08

☐ Ignore calibration from input data

Load From Fit Load Save Cancel OK

Adjust the pile-up factor if you see weird pile up peaks (shown in pink) in the fit spectrum

"BEAM" tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Open X-Ray Tube Setup

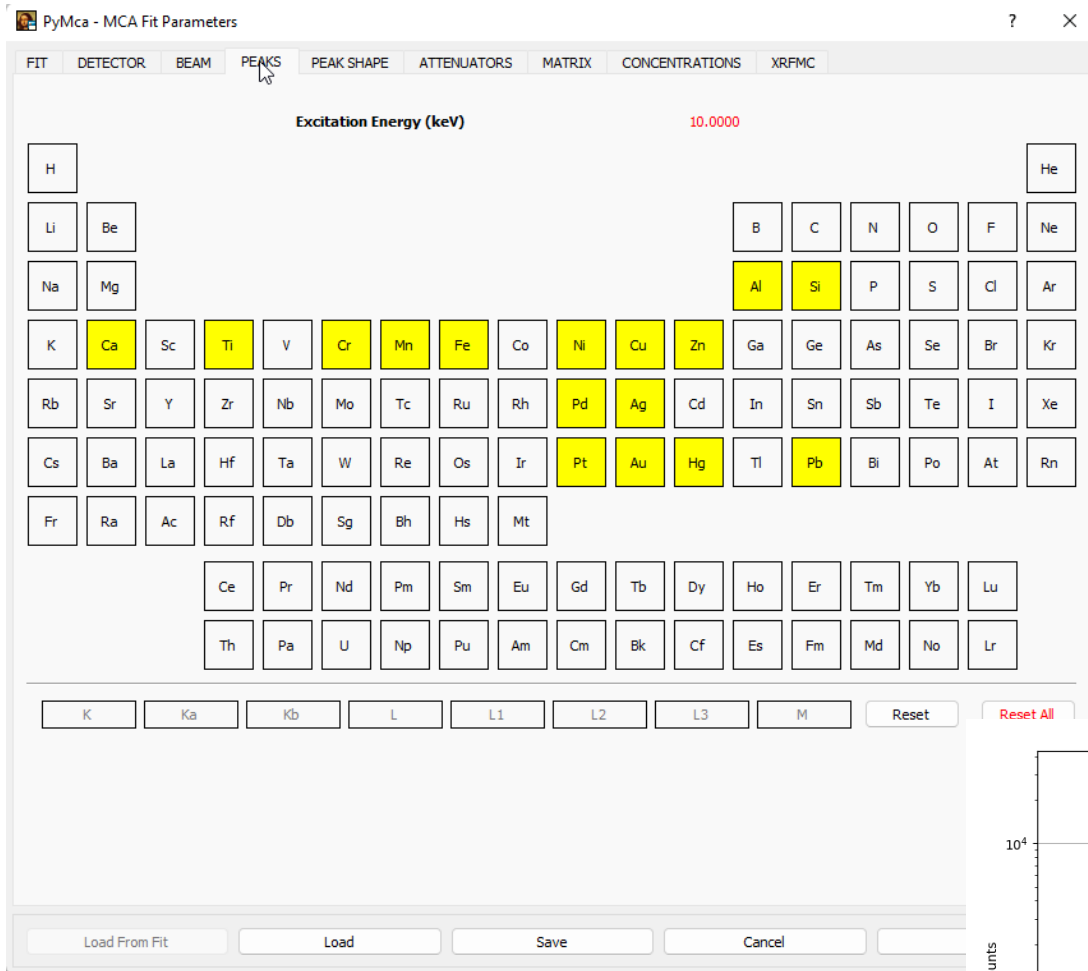
Use	Energy	Weight	Use	Energy	Weight	Use	Energy	Weight
☒ Energy 0	10.000000	1	☐ Energy 20		0	☐ Energy 40		0
☐ Energy 1		0	☐ Energy 21		0	☐ Energy 41		0
☐ Energy 2		0	☐ Energy 22		0	☐ Energy 42		0
☐ Energy 3		0	☐ Energy 23		0	☐ Energy 43		0
☐ Energy 4		0	☐ Energy 24		0	☐ Energy 44		0
☐ Energy 5		0	☐ Energy 25		0	☐ Energy 45		0
☐ Energy 6		0	☐ Energy 26		0	☐ Energy 46		0
☐ Energy 7		0	☐ Energy 27		0	☐ Energy 47		0
☐ Energy 8		0	☐ Energy 28		0	☐ Energy 48		0
☐ Energy 9		0	☐ Energy 29		0	☐ Energy 49		0
☐ Energy 10		0	☐ Energy 30		0	☐ Energy 50		0
☐ Energy 11		0	☐ Energy 31		0	☐ Energy 51		0
☐ Energy 12		0	☐ Energy 32		0	☐ Energy 52		0
☐ Energy 13		0	☐ Energy 33		0	☐ Energy 53		0
☐ Energy 14		0	☐ Energy 34		0	☐ Energy 54		0
☐ Energy 15		0	☐ Energy 35		0	☐ Energy 55		0
☐ Energy 16		0	☐ Energy 36		0	☐ Energy 56		0
☐ Energy 17		0	☐ Energy 37		0	☐ Energy 57		0
☐ Energy 18		0	☐ Energy 38		0	☐ Energy 58		0
☐ Energy 19		0	☐ Energy 39		0	☐ Energy 59		0

Load Table Save Table

Insert the beam energy in keV.
For monochromatic sources, use a weight = 1

Load From Fit Load Save Cancel OK

"PEAKS" tab

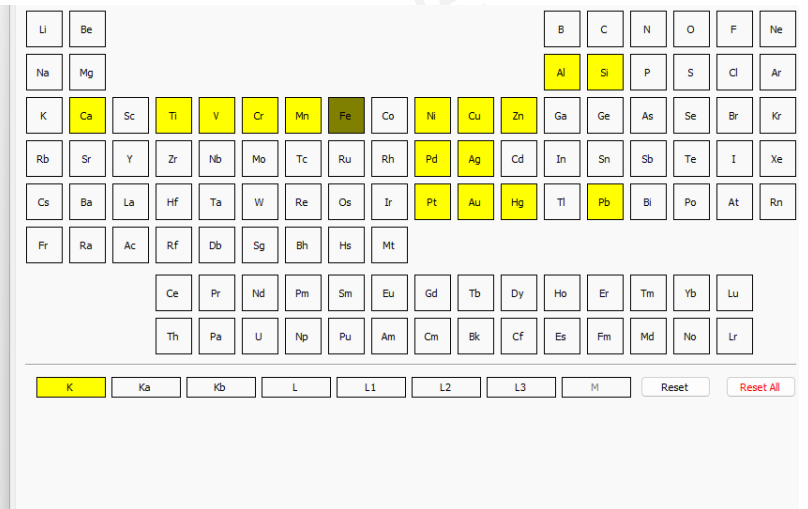
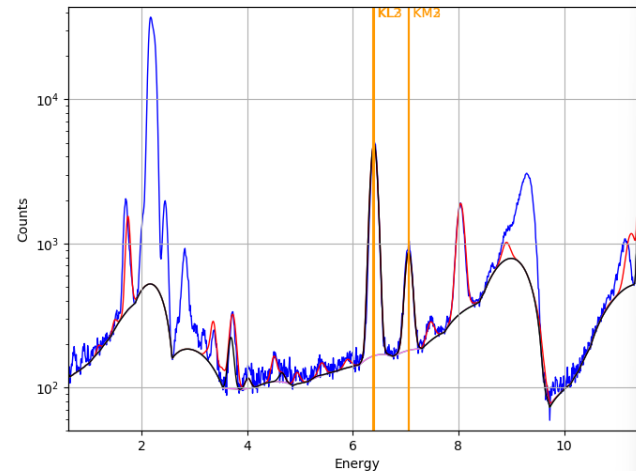


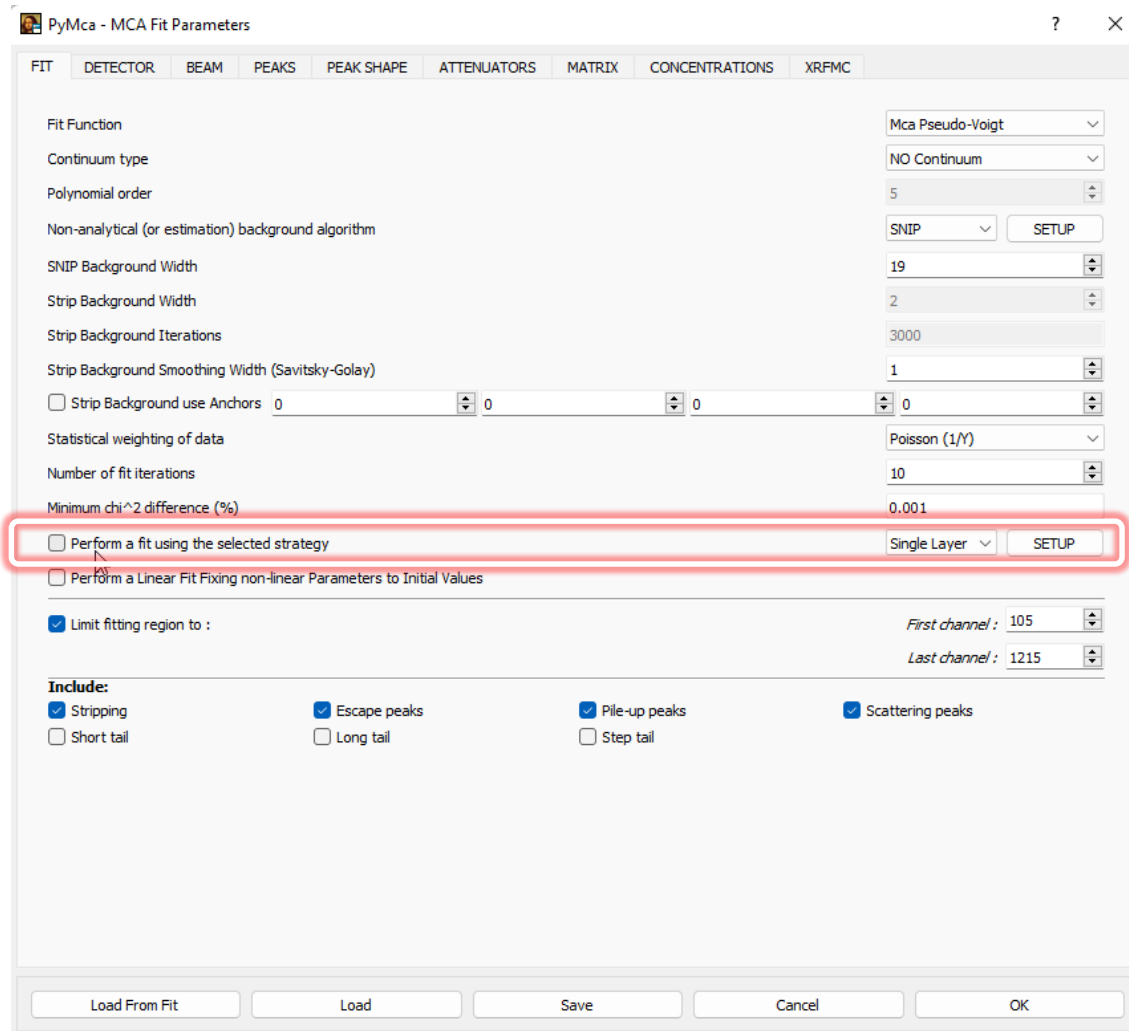
Select the elements justifying the peaks in your spectrum.

When selecting an element, you can also choose the lines. Only available lines (for the exciting energy) can be selected.

Selecting **K** will fit K_alpha and K_beta with tabulated ratios. Selecting the **Ka** and **Kb** will fit them as independent contributions.

When selecting a line, the plot will show the energy position of that (or those) lines.





There are two strategies for fitting:

(i) **Single layer**

(ii) **Multilayer**

The single layer strategy is selected and set up here.

The multilayer strategy can be set up in the ATTENUATORS and MATRIX tabs.

SINGLE LAYER strategy:

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Fit Function: Mca Pseudo-Voigt
Continuum type: NO Continuum
Polynomial order: 1
Non-analytical (or estimation) background algorithm: Strip
SNIP Background Width: 26
Strip Background Width: 1
Strip Background Iterations: 2500
Strip Background Smoothing Width (Savitsky-Golay): 8
☐ Strip Background use Anchors 979 0 0 0
Statistical weighting of data: Poisson (1/Y)
Number of fit iterations: 10
Minimum chi^2 difference (%): 0.001
☒ Perform a fit using the selected strategy
☐ Perform a Linear Fit Fixing non-linear Parameters to initial values
☒ Limit fitting region to : First channel : 105 Last channel : 1210
Include:
☒ Stripping ☒ Escape peaks ☒ Pile-up peaks ☒ Scattering peaks
☐ Short tail ☐ Long tail ☐ Step tail
Load From Fit Load Save Cancel OK

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Attenuator	Name	Material	Density (g/cm3)	Thickness (cm)	Funny Factor
☒ Filter 0	C	C		3.3e-05	1.0
☒ Filter 1	B	B		4.24e-06	1.0
☒ Filter 2	Si grid	Si		0.127	0.227
☒ Filter 3	Al	Al		7.02e-06	1.0
☒ Filter 4	O	O		9.66e-06	1.0
☒ Filter 5	N	N		3.89e-06	1.0
☐ Filter 6	Filter 6	C		2e-05	1.0
☐ Filter 7	Filter 7	O		0.006788	1.0
☒ BeamFilter0	BeamFilter0	Be		0.005	1.0
☒ BeamFilter1	BeamFilter1	C		0.01	1.0
☒ Detector	Detector	Si		0.045	1.0
☒ Matrix	Matrix	SingleLayerStrategyMaterial		1	1.0

Efficiency Term

26/09/2026

(You can't use this strategy for fast fitting!)

Multilayer strategy:

PyMca - MCA Fit Parameters

ATTENUATORS

Attenuator	Name	Material	Density (g/cm3)	Thickness (cm)	Funny Factor
☒ Filter 0	C	C	1.0	3.3e-05	1.0
☒ Filter 1	B	B	1.0	4.24e-06	1.0
☒ Filter 2	Si grid	Si	1.0	0.127	0.227
☒ Filter 3	Al	Al	1.0	7.02e-06	1.0
☒ Filter 4	O	O	1.0	9.66e-06	1.0
☒ Filter 5	N	N	1.0	3.89e-06	1.0
☐ Filter 6	Filter 6	C	1.58	2e-05	1.0
☐ Filter 7	Filter 7	O	0.001429		
☒ BeamFilter0	BeamFilter0	Be	1.848		
☒ BeamFilter1	BeamFilter1	C	1.58		
☒ Detector	Detector	Si1	2.33		
☒ Matrix	Matrix	MULTILAYER	1.0		

Plot T(filters) * (1 - T(detector)) Efficiency Term

1. Enable it from the ATTENUATORS tab, by selecting the MATRIX checkbox and choosing MULTILAYER from the dropdown list

PyMca - MCA Fit Parameters

MATERIAL EDITOR

Enter name of material to be defined: Coin

Number of Compounds: 7

Material	Mass Fraction
1 Au	94
2 Ag	0.1
3 Pt	0.1
4 Zn	0.01
5 Pd	1
6 Hg	0.01

Default Density (g/cm3): 19
Default Thickness (cm): 1

Material Name/Comment: Coin composition guess

Buttons: Load From Fit, Load, Save, Cancel, OK

2. Define the composition (or best guess) of each layer you intend to use. Simply type the name and add as many compounds as needed.

PyMca - MCA Fit Parameters

MATRIX

Incoming Angle (deg.): 45
Outgoing Angle (deg.): 45
Scattering Angle (deg.): 90

This matrix definition will only be considered if Matrix is selected and material is set to MULTILAYER in the ATTENUATORS tab.

Layer	Name	Material	Density (g/cm3)	Thickness (cm)
☒ Layer0	Layer0	Incr	3.0	0.03
☒ Layer1	Layer1	Coin	19.0	1.0
☐ Layer2	Layer2	-	0.0	0.0
☐ Layer3	Layer3	-	0.0	0.0
☐ Layer4	Layer4	-	0.0	0.0
☐ Layer5	Layer5	-	0.0	0.0
☐ Layer6	Layer6	-	0.0	0.0
☐ Layer7	Layer7	-	0.0	0.0
☐ Layer8	Layer8	-	0.0	0.0
☐ Layer9	Layer9	-	0.0	0.0

Buttons: Load From Fit, Load, Save, Cancel, OK

3. In the MATRIX tab, activate the layers you want to use and set a tentative value for density and thickness.

PyMca - MCA Fit Parameters

MATRIX

☒ From matrix composition

Flux (photons/s): 3e+08 x time(seconds): 1680
Active Area (cm2): 0.0398 distance (cm): 1

Matrix Reference Element: Auto

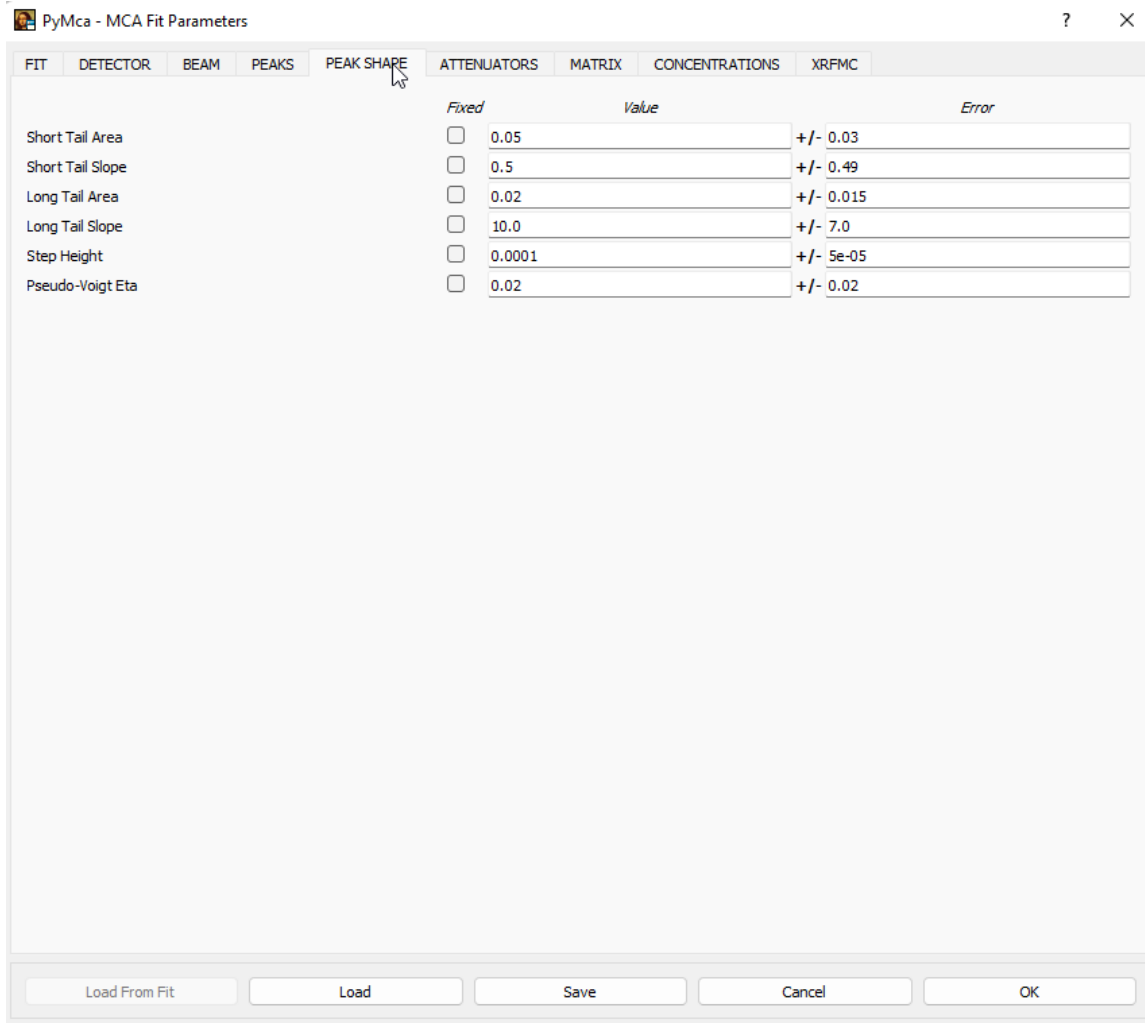
☒ Consider secondary excitation

Buttons: Load From Fit, Load, Save, Cancel, OK

4. Make sure that, in the CONCENTRATIONS tab, you check the relative checkbox.

26/09/2026

"PEAK SHAPE" tab



The image shows the "PyMca - MCA Fit Parameters" dialog box with the "PEAK SHAPE" tab selected. The dialog has several tabs: FIT, DETECTOR, BEAM, PEAKS, PEAK SHAPE, ATTENUATORS, MATRIX, CONCENTRATIONS, and XRFMC. The "PEAK SHAPE" tab contains a table of parameters with checkboxes for "Fixed", input fields for "Value", and input fields for "Error". The parameters listed are: Short Tail Area, Short Tail Slope, Long Tail Area, Long Tail Slope, Step Height, and Pseudo-Voigt Eta. The default values are: Short Tail Area (0.05), Short Tail Slope (0.5), Long Tail Area (0.02), Long Tail Slope (10.0), Step Height (0.0001), and Pseudo-Voigt Eta (0.02). The errors are: Short Tail Area (+/- 0.03), Short Tail Slope (+/- 0.49), Long Tail Area (+/- 0.015), Long Tail Slope (+/- 7.0), Step Height (+/- 5e-05), and Pseudo-Voigt Eta (+/- 0.02). At the bottom of the dialog are buttons for "Load From Fit", "Load", "Save", "Cancel", and "OK".

	Fixed	Value	Error
Short Tail Area	☐	0.05	+/- 0.03
Short Tail Slope	☐	0.5	+/- 0.49
Long Tail Area	☐	0.02	+/- 0.015
Long Tail Slope	☐	10.0	+/- 7.0
Step Height	☐	0.0001	+/- 5e-05
Pseudo-Voigt Eta	☐	0.02	+/- 0.02

Standard parameters. The default values are usually a good starting point.

Insert all the beam filters (BF) and filters (F) that the beam crosses before (BF) and after (F) interacting with the sample.
Don't forget the detector (Si thickness)!

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Attenuator	Name	Material	Density (g/cm3)	Thickness (cm)	Funny Factor	
☒	Filter 0	C	1.0	3.3e-05	1.0	
☒	Filter 1	B	1.0	4.24e-06	1.0	
☒	Filter 2	Si grid	Si	0.127	0.227	
☒	Filter 3	Al	1.0	7.02e-06	1.0	
☒	Filter 4	O	1.0	9.66e-06	1.0	
☒	Filter 5	N	1.0	3.89e-06	1.0	
☐	Filter 6	Filter 6	C	1.58	2e-05	1.0
☐	Filter 7	Filter 7	O	0.001429	0.006788	1.0
☒	BeamFilter0	BeamFilter0	Be	1.848	0.005	1.0
☒	BeamFilter1	BeamFilter1	C	1.58	0.01	1.0
☒	Detector	Detector	Si1	2.33	0.045	1.0
☒	Matrix	Matrix	ategyMaterial	1.0	1.0	1.0

SLEW window

450 µm of Si

Material Editor

Enter name of material to be defined: Air

Number of Compounds: 5

Material	Mass Fraction
1 C1	0.000124
2 N1	0.75527
3 O1	0.23178
4 Ar1	0.012827
5 Kr1	3.2e-06

Default Density (g/cm3): 0.0012048

Default Thickness (cm): 1

Material Transmission

Mass Att. Coefficients

Material Name/Comment: Dry Air (Near sea level) density=0.001204790 g/cm3

Load From Fit Load Save Cancel OK

Info on the geometry can be inserted in the MATRIX tab.

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

Incoming Angle (deg.): 45

Outgoing Angle (deg.): 45

☒ Scattering Angle (deg.): 90

This matrix definition will only be considered if Matrix is selected and material is set to MULTILAYER in the ATTENUATORS tab.

Layer	Name	Material	Density (g/cm3)	Thickness (cm)	
☒	Layer0	Layer0	Incr	1.0	1e-06
☒	Layer1	Layer1	Coin	1.0	1e-06
☐	Layer2	Layer2	-	0.0	0.0
☐	Layer3	Layer3	-	0.0	0.0
☐	Layer4	Layer4	-	0.0	0.0
☐	Layer5	Layer5	-	0.0	0.0
☐	Layer6	Layer6	-	0.0	0.0
☐	Layer7	Layer7	-	0.0	0.0
☐	Layer8	Layer8	-	0.0	0.0
☐	Layer9	Layer9	-	0.0	0.0

In case you use the multilayer strategy, here you also define the order of each layer and the thickness.

Load From Fit Load Save Cancel OK

“CONCENTRATION” tab

PyMca - MCA Fit Parameters

FIT DETECTOR BEAM PEAKS PEAK SHAPE ATTENUATORS MATRIX CONCENTRATIONS XRFMC

☒ From fundamental parameters

Flux (photons/s) x time(seconds) ☐ Use Automatic Factor

Active Area (cm2) distance (cm)

☐ From matrix composition

Matrix Reference Element:

☒ Consider attenuators in calculations

☒ Consider secondary excitation

☐ Consider tertiary excitation

☐ use Monte Carlo code to correct higher order excitations

☐ Elemental mM concentrations (assuming 1 l of solution is 1000 * matrix_density grams)

Load From Fit Load Save Cancel OK

26/09/2026

THE END

Additional resources:

First steps: <https://www.silx.org/doc/PyMca/latest/tutorials.html>

ROI imaging <https://www.youtube.com/watch?v=1wdt6VhK28Y>