XRF-XFS-XAS- Auto v.1.0 (beta) Manual

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ALS XFM Beamline 10.3.2

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XRF-XFS-XAS- Auto

This automated data analysis software consists of three parts for

1. μX-ray fluorescence mapping (in blue)
2. μX-ray fluorescence spectroscopy (in green)
3. μX-ray absorption spectroscopy (in pink)

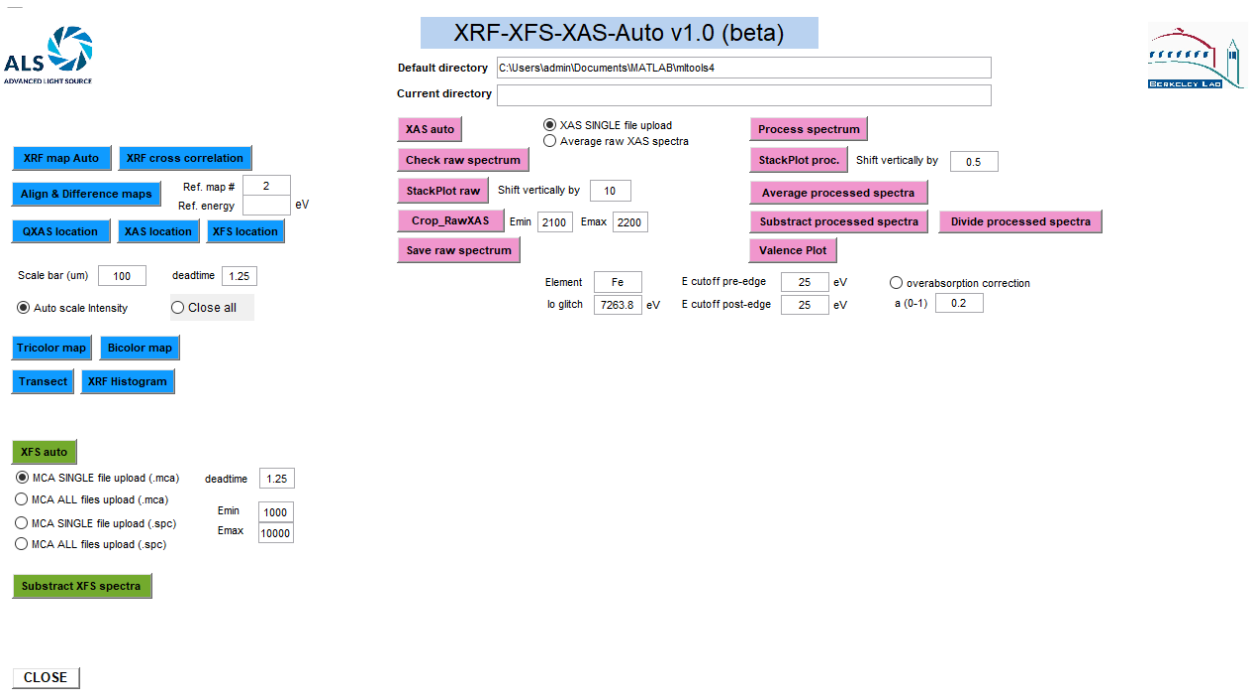

Fig.1

The analysis features for each part are described below.

1. Micro- X-ray Fluorescence mapping (μXRF)

1.1 Elemental XRF maps

Before displaying your maps, you need to apply a deadtime correction to your raw maps, for this, enter a deadtime correction value next to “deadtime”: This correction will be automatically applied to all elemental channels, except the “Total” one (**Fig.2**).

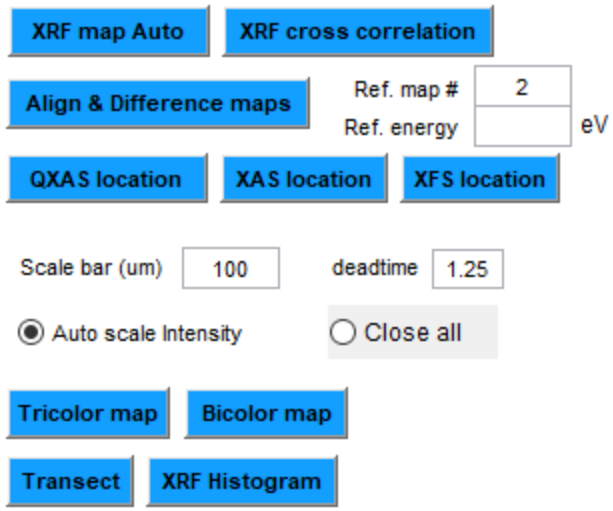

Fig. 2

To open elemental maps click on “XRF maps auto” (**Fig. 2**). Select the raw .xrf map file that you want to open (**Fig. 3**). You can open up to 2 map files maximum. Maps are read, deadtime corrected and normalized by the dwell time and Io (incident beam intensity).

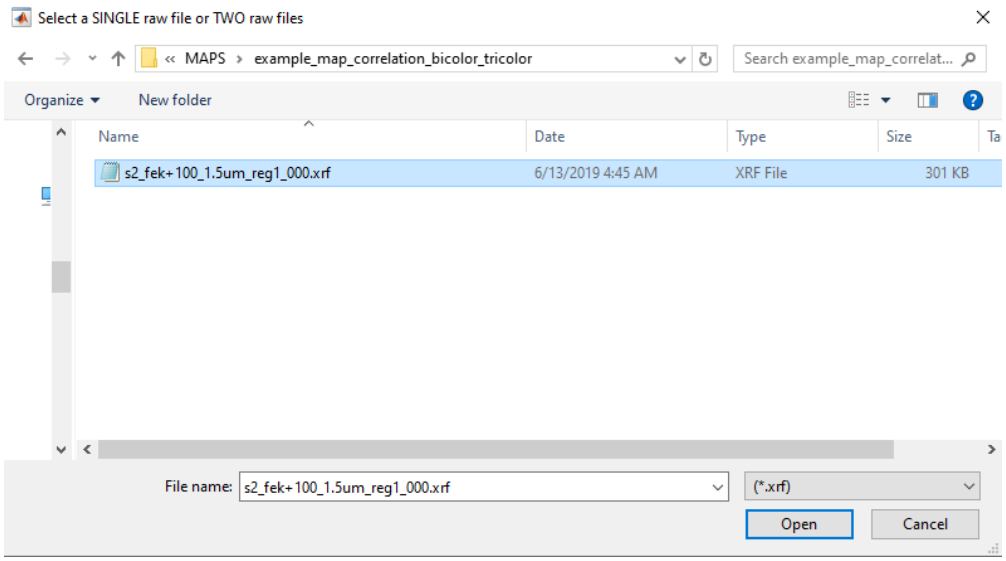

Fig. 3

The following window will then pop asking which elemental map you want to display (**Fig. 4**), in this case Fe, Ca and K.

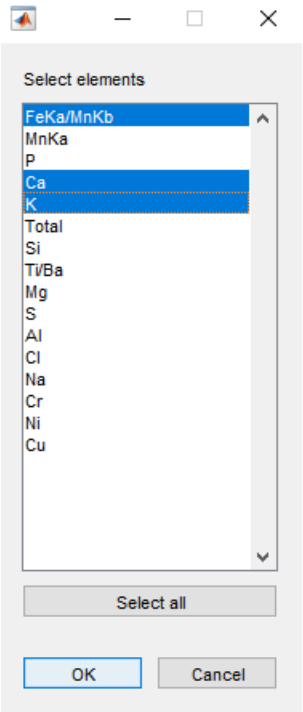

Fig.4

Elemental maps are then displayed (**Fig.5**) and automatically saved as .bmp files within the same folder.

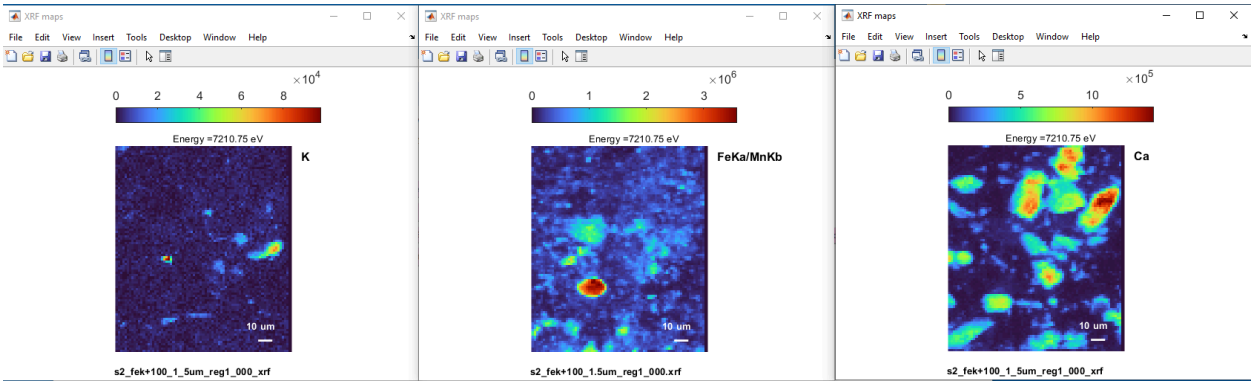

Fig. 5

In case you need to change the scale bar, just type another value next to “scale bar” (**Fig.2**) and click on “XRF map auto” again, the current maps will close automatically, the ones with the updated scale bar will then be displayed and the previous .bmp maps will be overwritten. Once you’re done, click on the “close all” button (**Fig.2**) to close all maps.

1.3 Tricolor and bicolor maps

Tricolor and bicolor maps use the RGB convention: Red=1st element, Green=2nd element and Blue=3rd element.

1.3.1 Tricolor map

First click on the “XRF map auto” button (**Fig.2)** and follow the steps in section 1.1. You must have only three elemental maps opened, in this case Fe, Ca and K, so close all maps that you don’t need. Press the “tricolor map” button, a composite map of these three elemental maps will be displayed (**Fig. 6)**, with iron in red, calcium in green and potassium in blue. The tricolor map is saved automatically as a bmp file within the same folder.

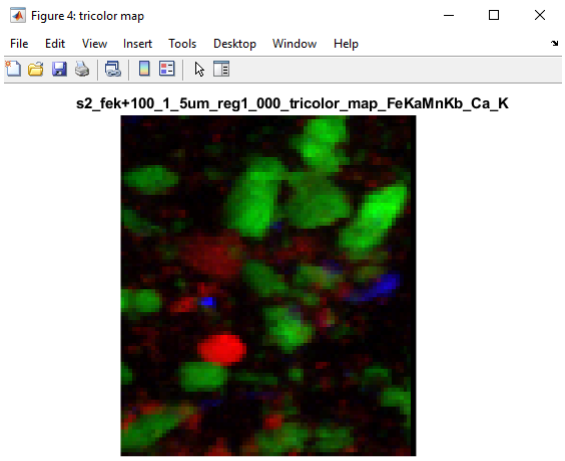

Fig. 6

1.3.2 Bicolor map

First click on “XRF map auto” (**Fig.2)** and follow steps in section 1.1. You must have only two elemental maps opened, in this case Fe and Ca, so close all maps not needed. Press the “bicolor map” button, a composite map of these two elemental maps will be displayed (**Fig.7)**, with iron in red and calcium in green. The bicolor map is saved automatically as a bmp file within the same folder.

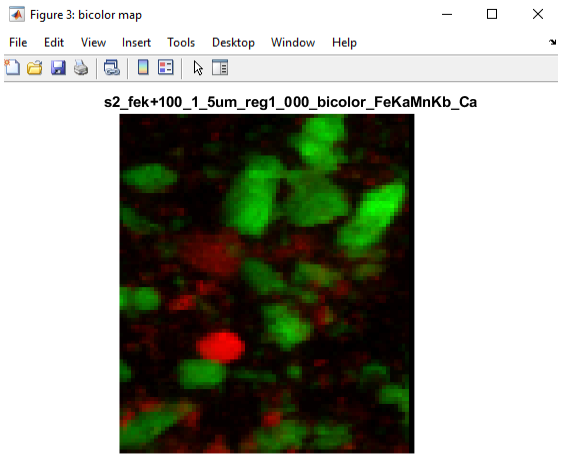

Fig. 7

1.4 XRF cross-correlation

- In the case where you want to look at the correlation of two elements from the same map, click on “XRF map auto” (**Fig.2**), pick a single map file, select elements, in this example Fe and Ca. Then press on the “XRF cross-correlation” button. A message window will pop-up (**Fig. 8**), then press “No”.

- In the case where you want to check the correlation between two elements coming from two different maps (recorded at different energies), click on “XRF map auto” (**Fig.2**), select the two maps and then select elements. Press on the “XRF cross-correlation” button. A message window will pop-up (**Fig. 8**), then press “Yes”.

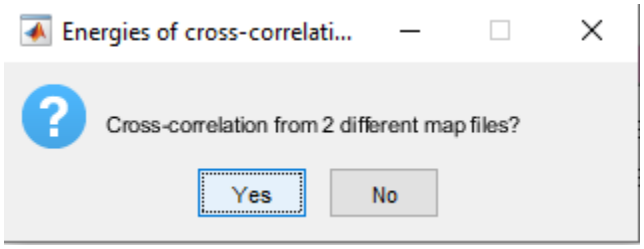

Fig. 8

Then select the first element (**Fig. 9**), press “OK” and select the 2nd element, and press “OK”.

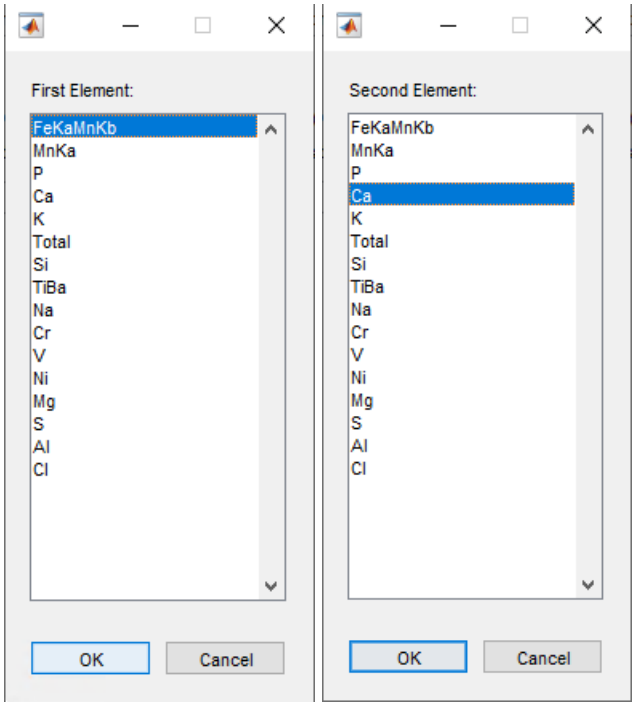

Fig. 9

The correlation plot between these 2 elements is displayed (**Fig. 10**). The plot is saved automatically as CorrelationPlot_element1_element2 within the same folder. To check correlation between other elements, press on the “XRF cross-correlation” button again and repeat the steps above. You can generate as many correlation plots as you want. Press “Close all” when you’re done.

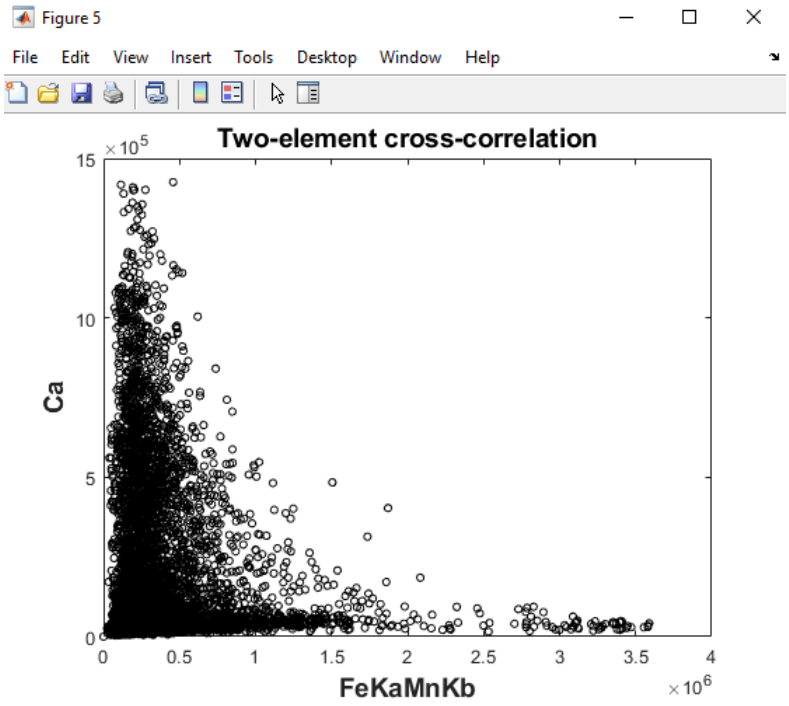

Fig. 10

1.5 Histogram

Click on “XRFmap auto” first to select your raw map, then pick your elements. You can display the histogram on one elemental map by pressing the “XRF Histogram” button, see example **Fig.11**. You’ll need to have one map displayed only.

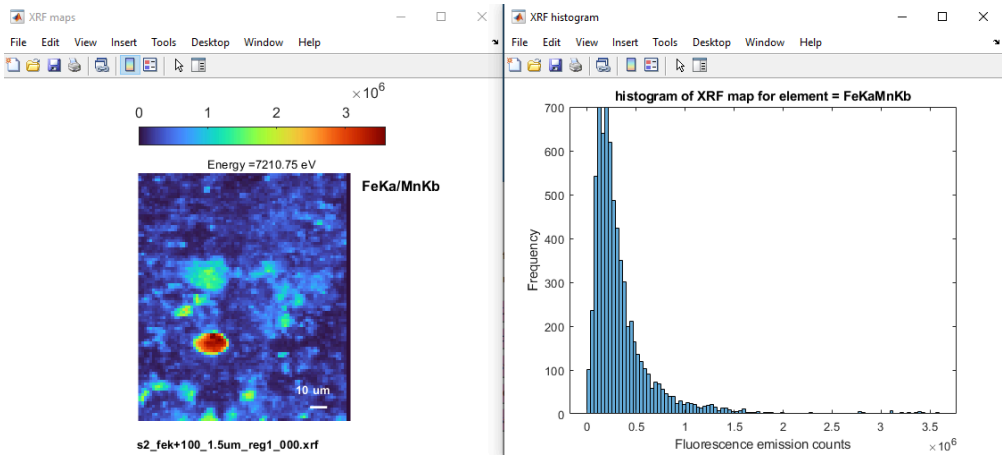

Fig.11

1.6 Align and Difference maps

To obtain “difference” maps, you must first align all maps to a reference map in the set, typically one recorded below the edge. For this, in the reference map number box (**Fig.12**), type the number of the reference map, with scan 000 corresponding to map# 1. Click on the “Align and Difference maps” button.

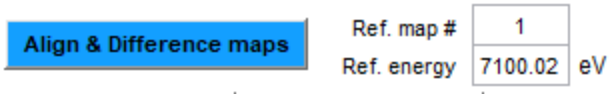

Fig. 12

Select any map in the folder that contains all the maps you want to align (**Fig. 13**) then click “open”

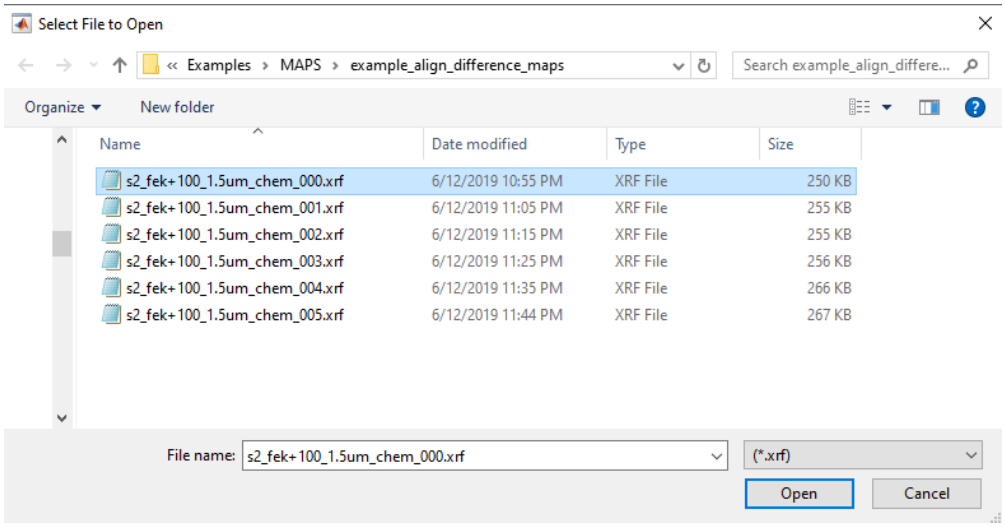

Fig. 13

In the “Pick elemental map for the offset” window (**Fig.14)**, choose an elemental map, K in this example, where you have small features, for instance a particle, that you can use to align the maps. Once the K map is displayed, zoom on a small and bright feature, then press “ ok” to continue. The location of the feature is used to properly register the maps at different energies. If you encounter the message “too low contrast for accurate alignment”, try another feature on the same map where the contrast is higher or try another element for the offset map. Then, pick the element for the “difference” map, Fe in this example, and click “OK”. Note that all maps are automatically deadtime-corrected.

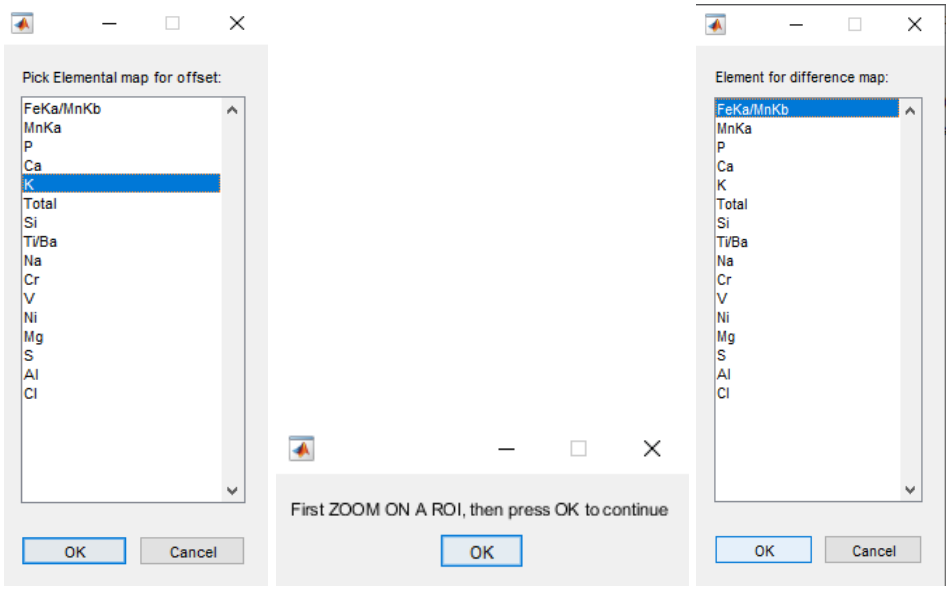

Fig. 14

Difference maps are then displayed (**Fig. 15**) and automatically saved within the same folder.

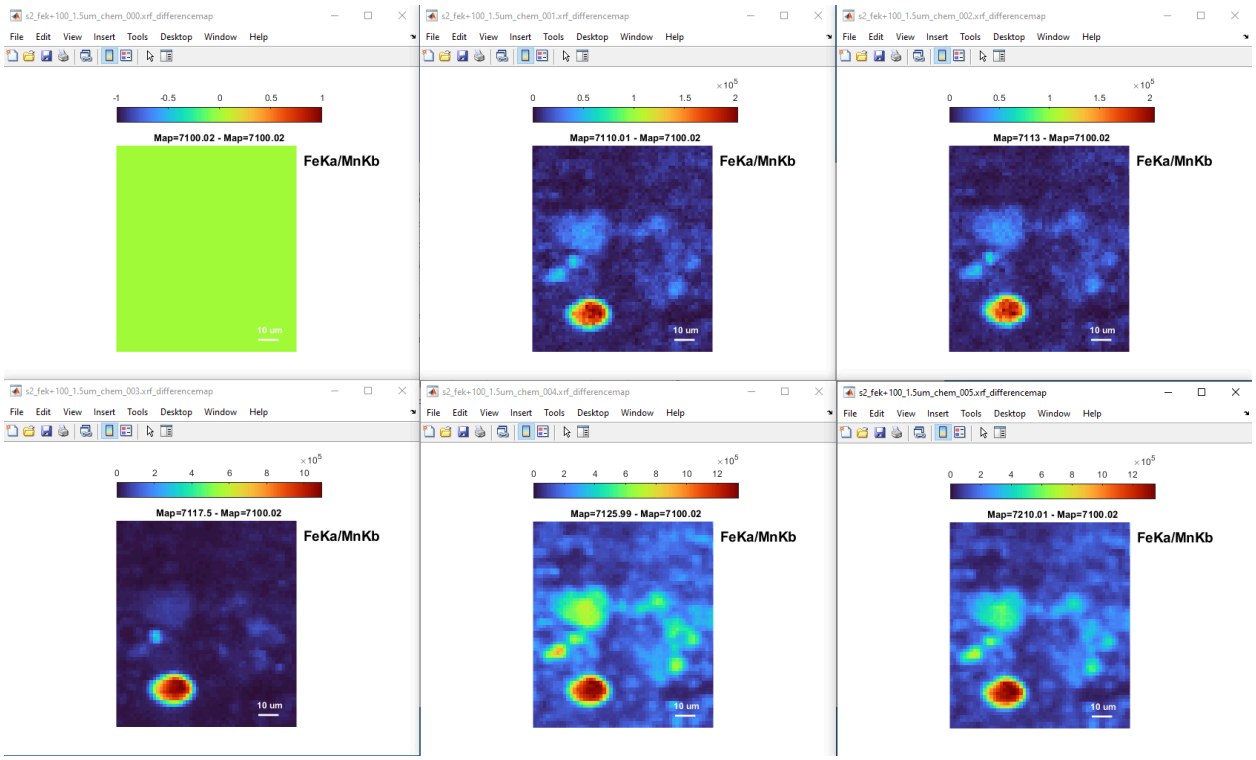

Fig. 15

1.7 Transect

To check the profile along a transect in the region of your sample, click on “XRF maps auto” to display elemental maps, close the maps that you don’t need, then click on the “transect” button (**Fig.2**). A message window will pop-up (**Fig. 16**), press “OK” to activate the cursor on the map

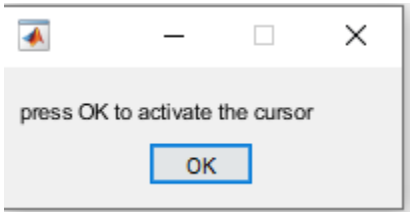

Fig. 16

Then click on a starting point and an ending point of the transect on the map. Be sure to choose points that are inside the map area only (**Fig. 17**).

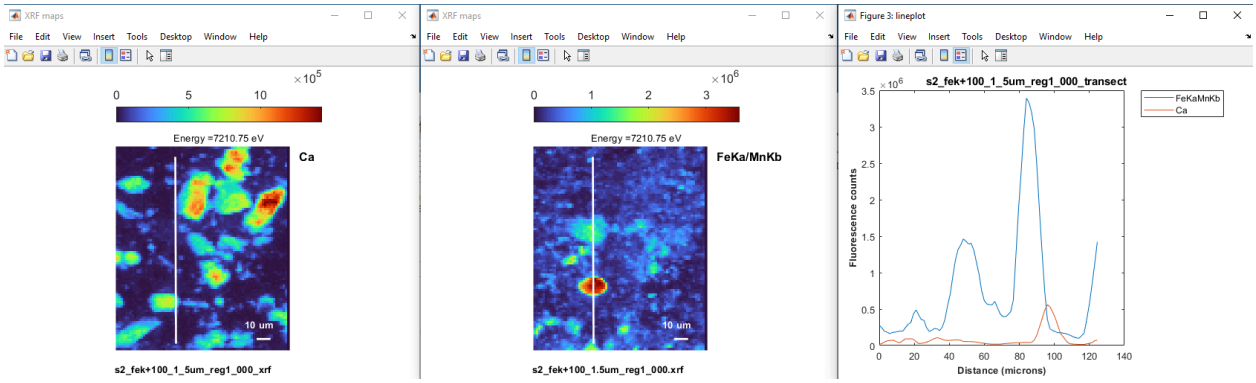

Fig. 17

The transect plot and annotated maps with transect location are automatically saved as “filename_transect#.bmp” in a folder named “filename_transect#”.
To do another transect, just press the “transect” button again, and repeat steps above. Transects are obtained from all elemental maps displayed. If there’s an elemental transect that you don’t want, just close the corresponding map and repeat. Once you’re done, press the “close all” button.

1.8 QXAS location

To display the locations where you collected QXAS spectra (.qx files), click on “XRF map auto” to display your maps, then press on the “QXAS location” button **(Fig. 2**). Select a QXAS file (.qx), the QXAS location will be shown on the maps as a white-empty circle, labeled with the scan# above it (**Fig. 18**). These maps are automatically saved as .bmp in a folder named “filename_XAS”.

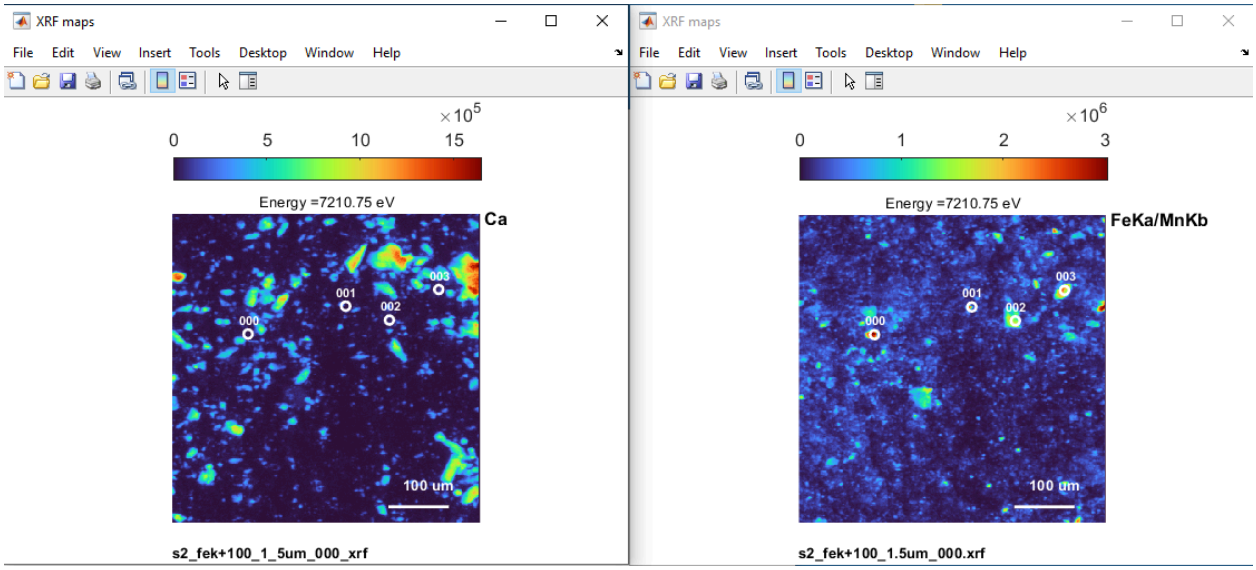

Fig. 18

1.9 XAS location

To display the locations where you collected XAS spectra (.dat files), click on “XRF map auto” to display your maps, then press on the “XAS location” button **(Fig. 2**). Select a XAS file (.dat), the XAS location will be shown on the maps as a white-empty circle, labeled with the scan# above it.

These maps are automatically saved as .bmp in a folder named “filename_XAS”.

1.10 XFS location

To display the locations where you collected XFS spectra, click on “XRF map auto” to display your maps, then press on the “XFS location” button (**Fig.2**). Select an XFS file (.mca), the XFS location will be shown on the maps as a white-empty circle, labeled with the scan# above it (**Fig. 19**). These maps are automatically saved as .bmp in a folder named “filename_XFS”.

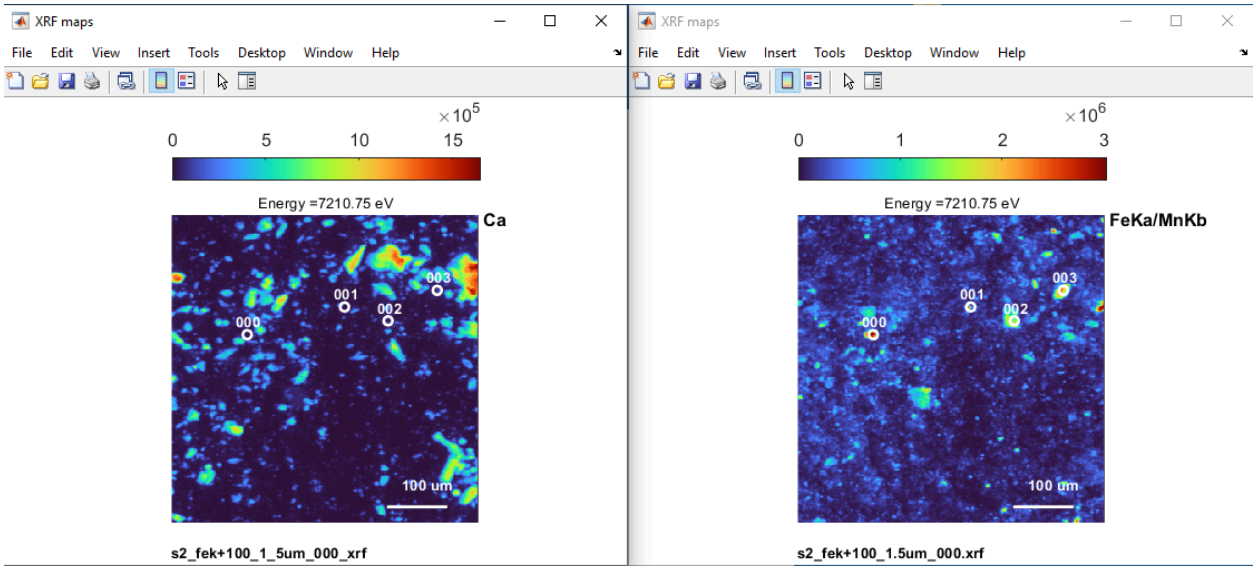

Fig. 19

2. Micro- X-ray fluorescence (μXFS) processing

You have the option of either processing raw XFS spectra (.mca files), or just displaying old processed XFS spectra (.spc), see **Fig.20**. The first option is preferred, as automatic energy calibration is performed in this case. In both cases XFS spectra are deatime-corrected, acquisition time and Io normalized.

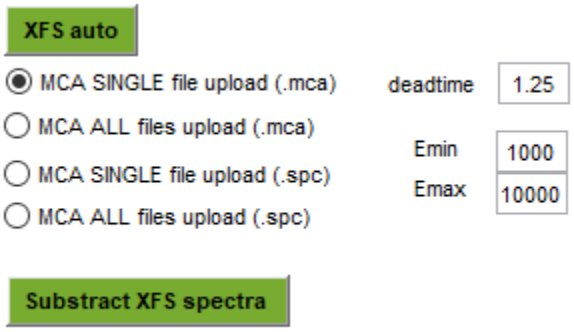

Fig. 20

Fluorescence emission lines corresponding to K-L3 and L3-M5 transitions are labeled on all plots. Ka emissions lines are labeled, but not the Kb to avoid too many labels displayed. The elastic/compton peak is not labeled.

2.1 Single raw file (.mca)

To process raw files (.mca), enter the deadtime correction value, in the “deadtime” window (**Fig. 20**), then choose the “MCA single file upload (.mca)”. The energy is calibrated using two

emission lines ArKa and FeKa in this example, with Ecalib(Ar) = 2957.7 eV, Ecalib(Fe) = 6403.84 eV. **Fig. 21** illustrates the energy calibration.

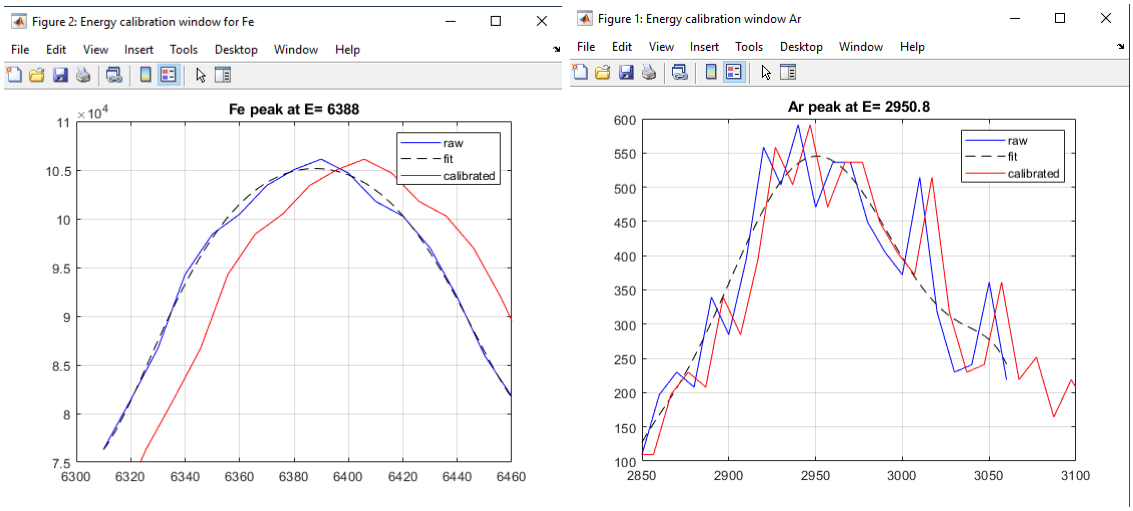

Fig. 21

The spectrum is then displayed in base 10 logarithmic scale (**Fig. 22)**, with peaks labeled (Ka and La lines only).
This plot is saved as .bmp and data are saved as excel files within the same folder.

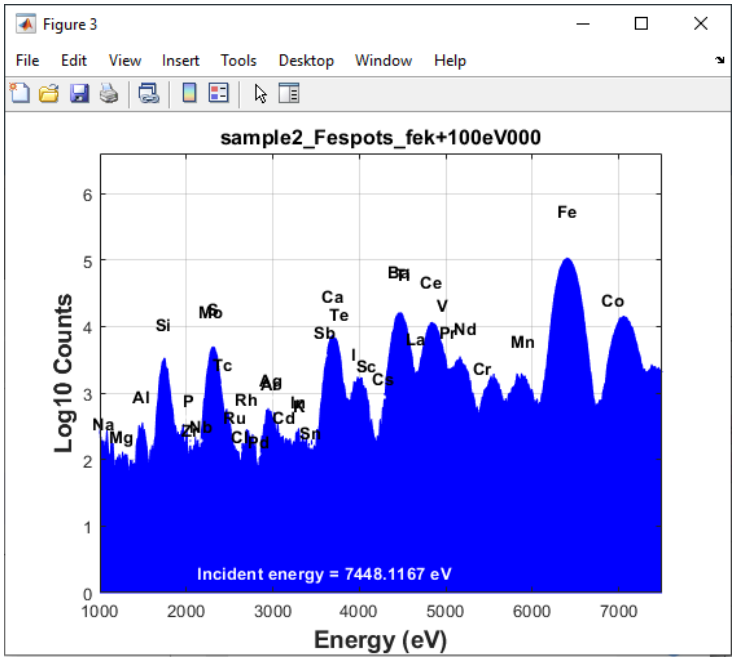

Fig. 22

2.2 Single processed file (.spc)

Choose the “MCA single file upload (.spc)” option (**Fig. 20**), select a .spc file and the XFS spectrum will be displayed in log10 scale with fluorescence emission lines labeled (Ka and La lines), see **Fig. 23.**
This plot is automatically saved as .bmp and data saved as excel files within the same folder.

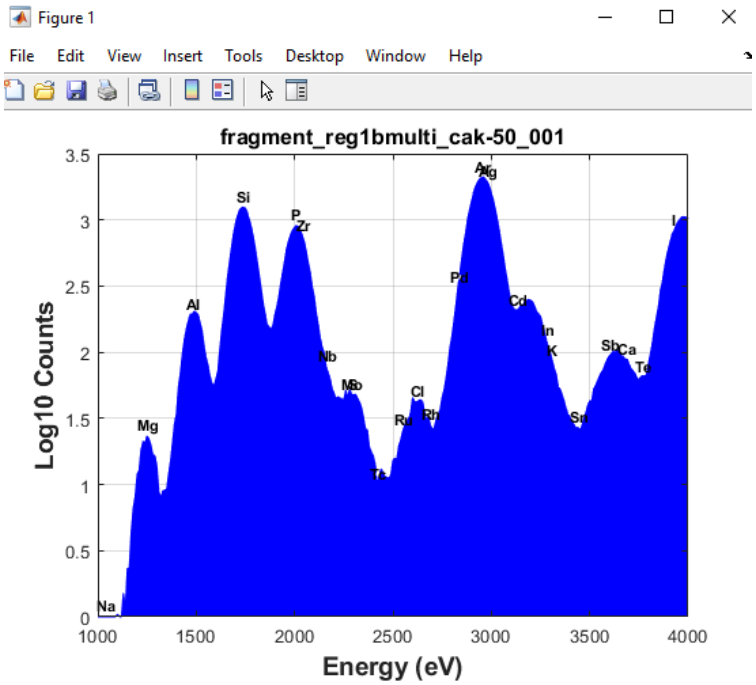

Fig. 23

2.3 Multiple raw (.mca) and processed (.spc) files

If you want to analyze multiple raw spectra (.mca files), click on the “MCA all files upload” button (**Fig.20**) then choose any .mca file in the folder where all your files are. Same for the .spc files, except choose the “SPC all files upload”.
All files contained in the folder will be plotted, the plots saved automatically as .bmp files and data saved as excel files within the same folder.

2.4 Substract XFS processed spectra

In the case where you want to subtract two processed XFS spectra, click on the “Substract XFS spectra” button (**Fig.20**), then pick the first processed XFS spectrum (.xls), spectrum#1, and then pick a second one, spectrum#2. The difference spectrum#1 minus spectrum#2 will be displayed. This feature is useful for instance when you want to background-subtract your data, provided that you have recorded a background spectrum.

3. Micro- X-ray absorption spectroscopy (μXAS)

This software is intended for the analysis of μ-XANES and extended μ-XANES spectra only. You can open both .qx files (Q-XAS) and .dat files (XAS). Note that incomplete (Q-)XAS spectra cannot be processed.

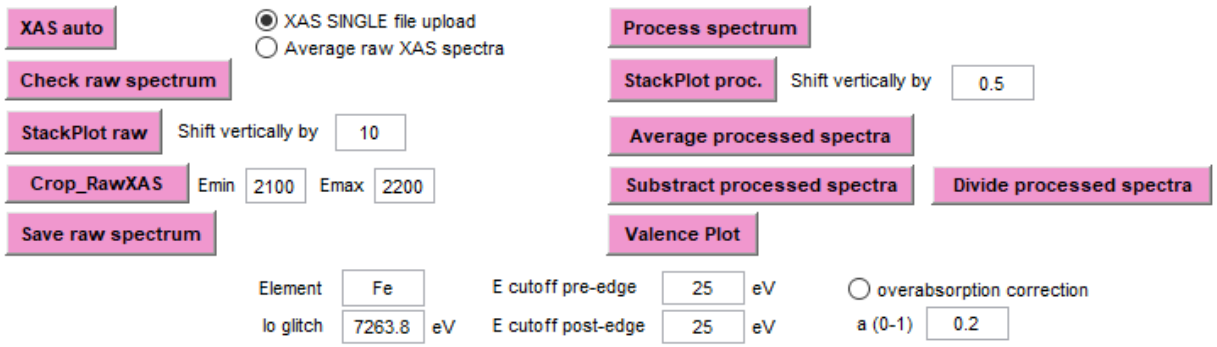

Fig. 24

3.1 Displaying and inspecting raw spectra

3.1.1 Displaying raw spectra

To open a raw spectrum, first click on “XAS SINGLE file upload”, put the element, then press on “XAS auto” (**Fig. 24**). The raw spectrum will be displayed on the “Raw” panel. In this example (**Fig.25**), the absorption spectrum of an iron foil, recorded in transmission mode (one active scaler, #14). Scaler #0 corresponds to the incident beam intensity, Io.

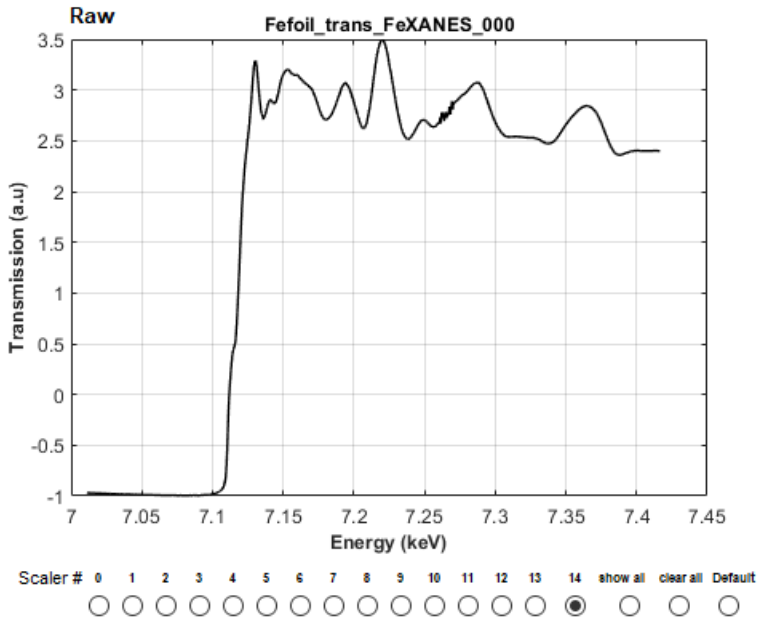

Fig. 25

You can select all scalers, unselect them or clear them all by clicking the corresponding buttons. If your data were collected in fluorescence mode with the multi-element SDD detector, several scalers will be active and you can check each channel individually to see if you have any outliers. You can save the raw spectrum by pressing “Save raw spectrum”.

3.1.2 Check QXAS raw spectra

A useful option for checking a QXAS raw spectrum is to look at the shape of the spectrum at the beginning and end of its acquisition. Press “XAS auto” to upload a raw spectrum, then press “Check raw spectrum”**.** The average over the first 3 lines and over the last 3 lines of the quick-XAS spectrum containing 20 lines total, will be overlaid, as illustrated in this example, **Fig. 26.** This feature is useful to check for radiation beam-induced damage or for sample drifting for instance.

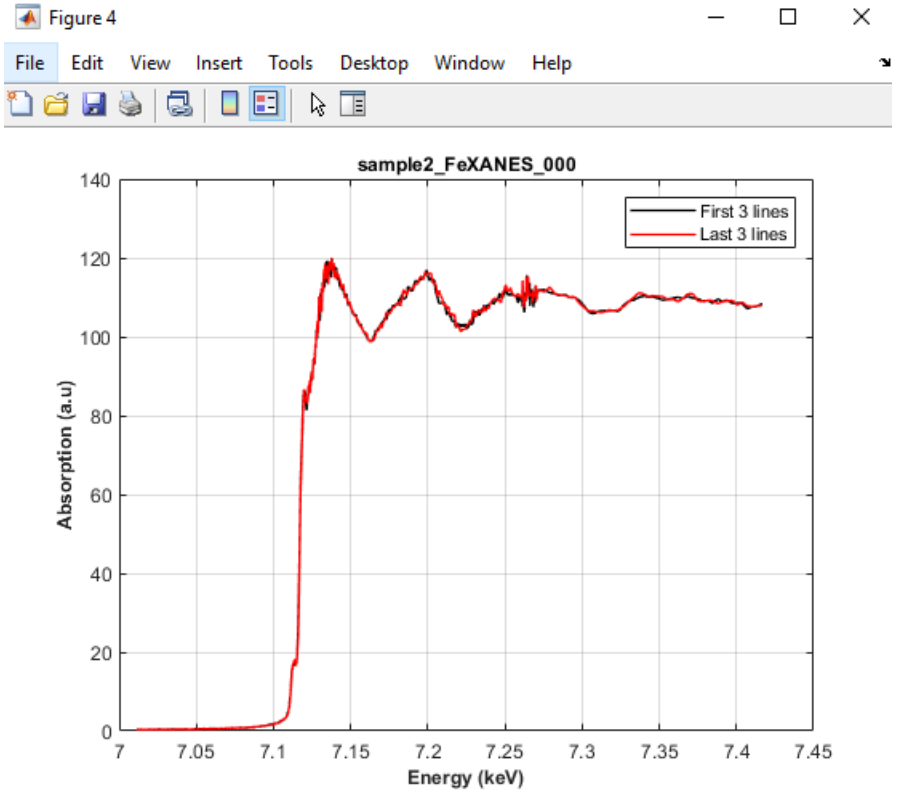

Fig. 26

3.1.3 Stack Plot raw spectra

This feature is used to quickly screen which raw spectra collected on your sample you want to further process. Press the ”StackPlot raw” button, and select all spectra that you want to display (**Fig. 27)**. You can change the vertical shift value for easier viewing.
This plot is automatically saved within the same folder as Stack_Plot_raw_#.

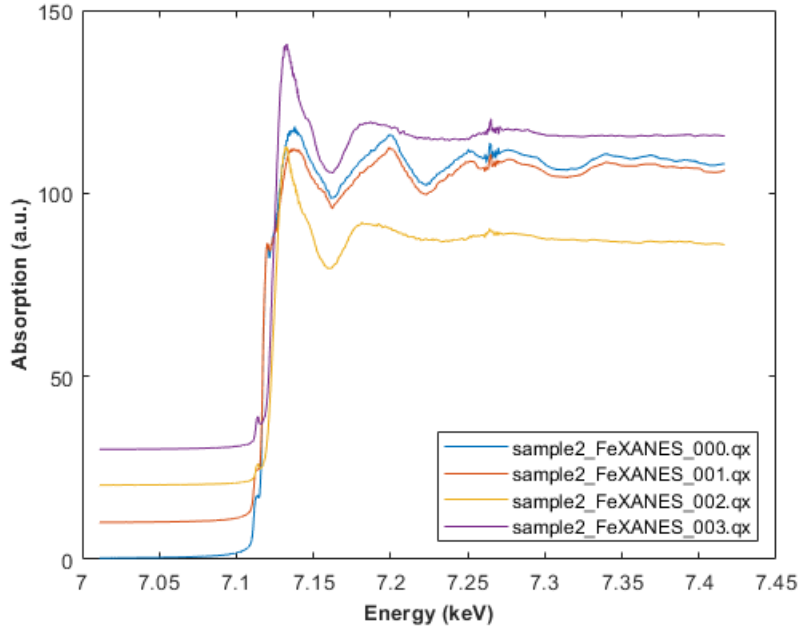

Fig. 27

3.1.4 Average of raw spectra

To average several raw spectra, recorded consecutively at the same location on the sample, select “Average raw spectra”, then press “XAS auto” (**Fig. 24)**. Select all spectra you want to average then click “open”. The average will be displayed on the “Raw” panel.
This feature is useful to get a quick preview of the average spectrum while you’re still collecting data, and allows you to make sure that you have collected enough scans at this location.

3.1.5 Crop raw spectra

You can crop raw spectra by entering “Emin” and “Emax” values and then press the “Crop_RawXAS” button (**Fig. 28**). The cropped spectrum will then be displayed.

Fig.28

3.2 XAS spectrum processing

To process a raw spectrum, make sure to click back on “Default” on the scalers in the Raw panel. Once you click on “process spectrum”, the spectrum is automatically deadtime-corrected.

3.2.1 Energy calibration

Type the value of the Io glitch in the “Io glitch” window and put the element (**Fig. 24**). Then press “process spectrum”, the spectrum will be automatically calibrated

3.2.2 Pre-edge background subtraction, post-edge normalization

Click on the “process spectrum” button, then three options for the pre-edge fit will pop (**Fig. 29**).

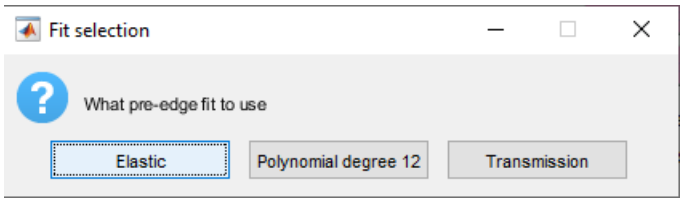

Fig. 29

“Elastic”: the default option for spectra recorded in fluorescence mode. Following the equation: Y= a + b/(Eo-E) + c/(E-EF)^2, Eo= absorption energy, Ef= fluorescence emission energy.

Polynomial degree 12: for spectra recorded in fluorescence mode
Following the equation: $Y= a_0 + a_1 E + a_2 E^2 + a_3 E^3 + ...a_{12} E^{12}$

Transmission: for spectra recorded in transmission mode.
Following the equation: $Y= a E^{-2.7} + b$; E=energy (eV)

In the case of the “Elastic” and “Transmission” options, the program will automatically compute the E pre-edge cutoff that minimizes NSS2, with NSS2=$\sum(\mu exp - \mu fit)2/\sum(\mu exp)2$

Zoom in to inspect the pre-edge, and if not satisfied, you can play with the E cut off pre-edge value as illustrated in **Fig.30**, E cut off pre-edge= 35 and E cut off post-edge= 15 in this case.

For the post-edge, a polynomial order 2 is used, following the equation:
$Y= a_0 + a_1 E + a_2 E^2$
Make sure to check that this fit goes well in the middle of the “EXAFS” oscillations, as illustrated in **Fig.31**. If not, change the E cut off post-edge value.

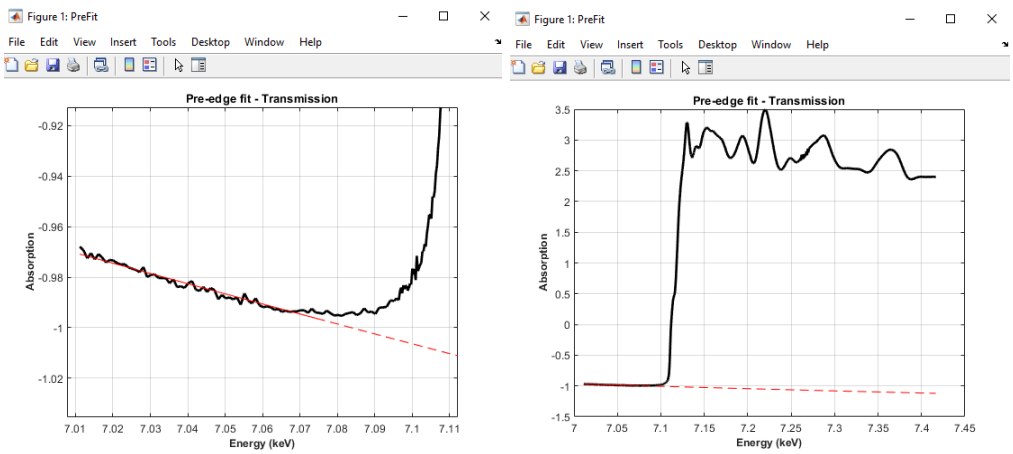

Fig.30

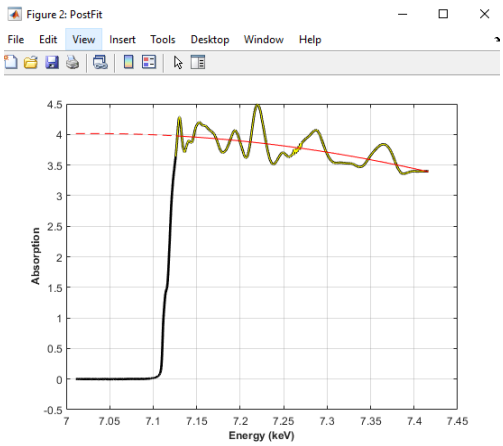

Fig.31

The processed spectrum, pre-edge background subtracted and post-edge normalized will then be displayed on the “Processed” panel (**Fig. 32**).

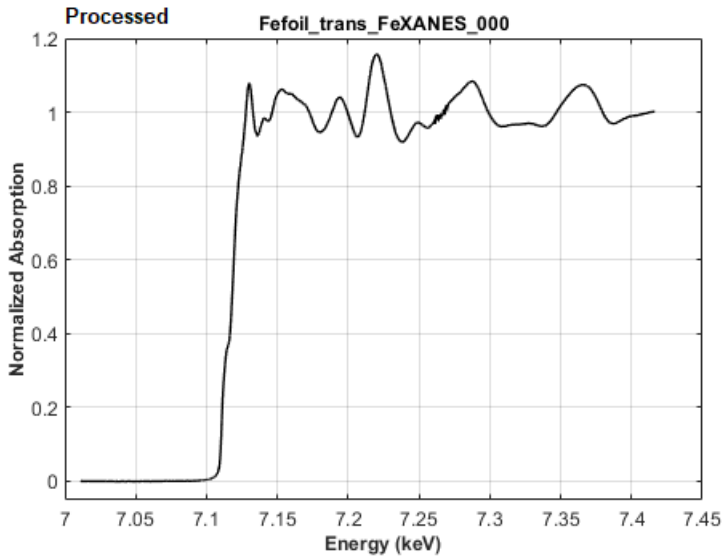

Fig. 32

At this stage, a “Select standard folder” dialog window will appear. If you click “cancel”, no fit will be performed and you will then have the option of saving the processed spectrum. Select “Yes” on the following window **(Fig. 33)** to save the spectrum otherwise press ‘“No”.

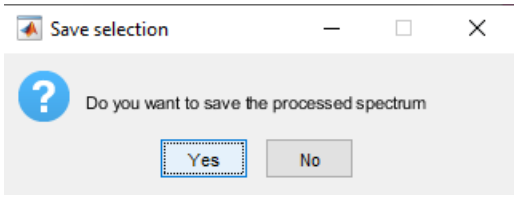

Fig. 33

If a “Standard” folder is selected the program will then automatically proceed with least-square linear combination (LSQ) fitting of the processed experimental spectrum. You will be asked to select the folder containing the set of standards as illustrated in **Fig. 34**.

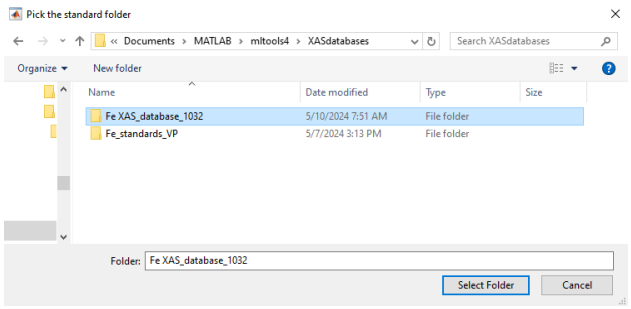

Fig. 34

Then, you’ll be asked how many standards you want to use for the LSQ fitting. You can use a combination of up to 4 standards (**Fig. 35**).

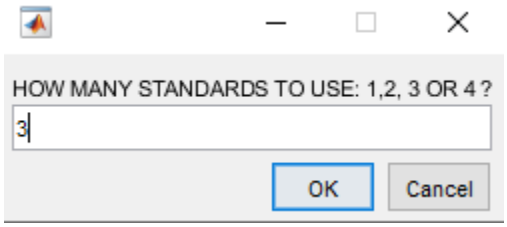

Fig. 35

If you’re not sure how many standards to use, start with 1, then 2, 3 and 4. Look at the sum-sq values, if they differ by less than 10%, then the extra component added is very likely not required. After selecting the number of standards used to fit, press “ok”. The top 5 best LSQ combination fits will be displayed as illustrated in **Fig. 36**, with an iron foil recorded in transmission mode using one standard.

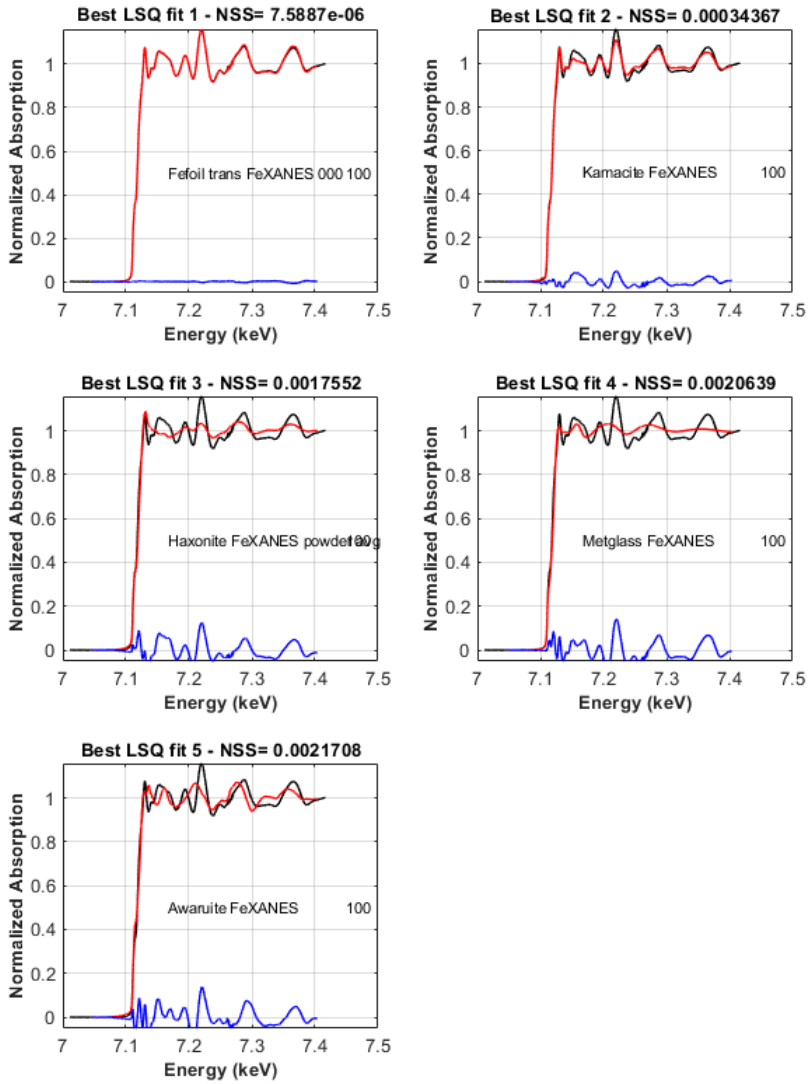

Fig. 36

The best mathematical fit is #1 where the NSS1 and NSS2 values are minimum, with

NSS2=$\sum(\mu exp - \mu fit)2/\sum(\mu exp)2$

NSS1=$\sum(\mu exp - \mu fit)2$

where μ= normalized absorption.

Note that when using up to 3 components it takes less than 10 sec for the fits to be displayed while when using 4, it takes about 20 minutes! Once the fits are displayed, always inspect the spectral fine features and look at the NSS values and how they differ and choose your fit. A dialog window will ask you to choose between the top 5 best fits (**Fig. 37**). In this example, we chose Fit#1 which is not only the best mathematical combination but also what makes sense.

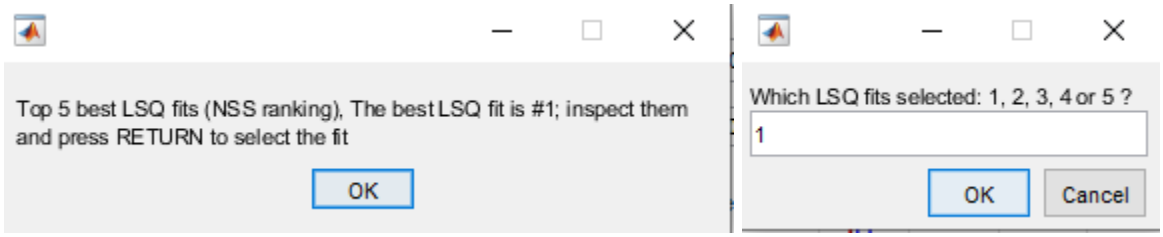

Fig. 37

A table showing the major components, their percentage and NSS values will be displayed and saved automatically as an excel and a pdf file (**Fig. 38**) as well as the fits and residuals (**Fig. 39**)

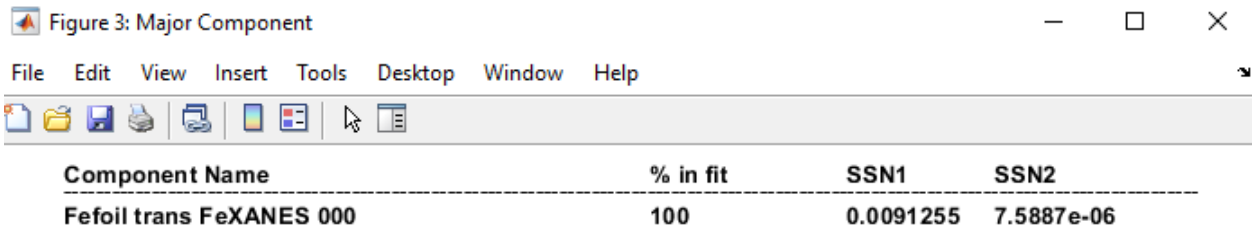

Fig. 38

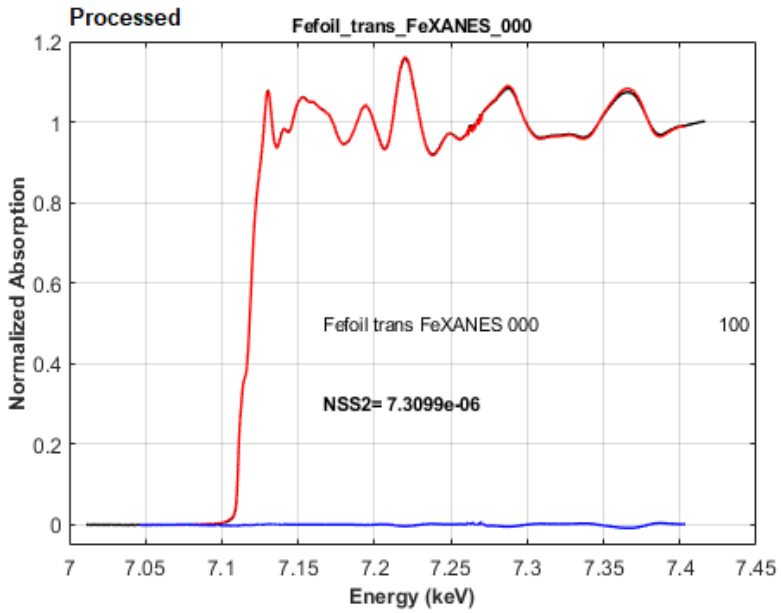

Fig. 39

The processed experimental spectrum (in black), the fit (in red) and residual (in blue) will be displayed on the “Processed” panel. Several files are automatically saved in the same folder named ”filename_XAS”:

- Plot in a bmp format

- excel files of the best fit and the processed spectrum
- txt files of the processed spectrum

3.2.3 Over-absorption correction

If the fit of the experimental spectrum recorded on a “hot” (i.e very high count) point is not satisfactory, apply an over-absorption correction factor, “a” , to the spectrum to correct for distortions (**Fig. 40**)

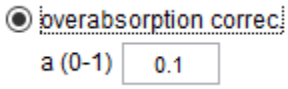

Fig. 40

This factor can vary between 0 and 1, however is typically <0.5. The over-absorption correction factor **a** is applied following the equation: Y = Y/(a+1-Y*a).
After the over-absorption value is entered, press “Process spectrum” and follow the steps described in the previous section.

3.3 Displaying processed spectra

3.3.1 Stack Plot processed spectra

This feature is used to quickly plot your processed spectra. Press the ”StackPlot proc.” button (**Fig. 24**), and select all processed spectra (.xls files) that you want to display. You can change the vertical shift value for easier viewing. This plot is automatically saved within the same folder.

3.3.2 Average processed spectra

To average several processed spectra, for instance recorded consecutively at the same location on the sample, press “Average processed spectra”, then select all spectra you want to average (.xls files), once done press “cancel”. The individual spectra and the average of these spectra will be displayed and saved as a bmp file. The average spectrum is also saved as an excel file within the same folder.

3.3.3 Substracting processed spectra

You can subtract two processed spectra by clicking “substract processed spectra”. Select the first xls file then the second, the difference of the two will be displayed and the graph saved as bmp file, the difference spectrum is also saved as an excel file within the same folder.

3.3.4 Dividing processed spectra

You can divide two processed spectra by clicking “divide processed spectra”. Select the first xls file then the 2nd, the division of the two will be displayed and the plot saved as a bmp file. The ratio of spectra is also saved as an excel file within the same folder.

3.4 Valence scatter Plot

The valence scatter plot is used to quickly classify XANES spectra according to metal(loid) valence state. It computes the normalized absorption values, Mu (E), at two specific energies, E1 and E2. A scatter plot (Mu1, Mu2) is obtained, with Mu1=Mu(E1) and Mu2=Mu(E2). In the case of Fe, E1=7117.5 eV and E2=7113 eV. Each datapoint on that plot corresponds to one spectrum. This method has been previously described elsewhere, it has been slightly revised and expanded to other metals and metalloids.
Press “Valence Plot”; the following window below will appear **(Fig. 41**).

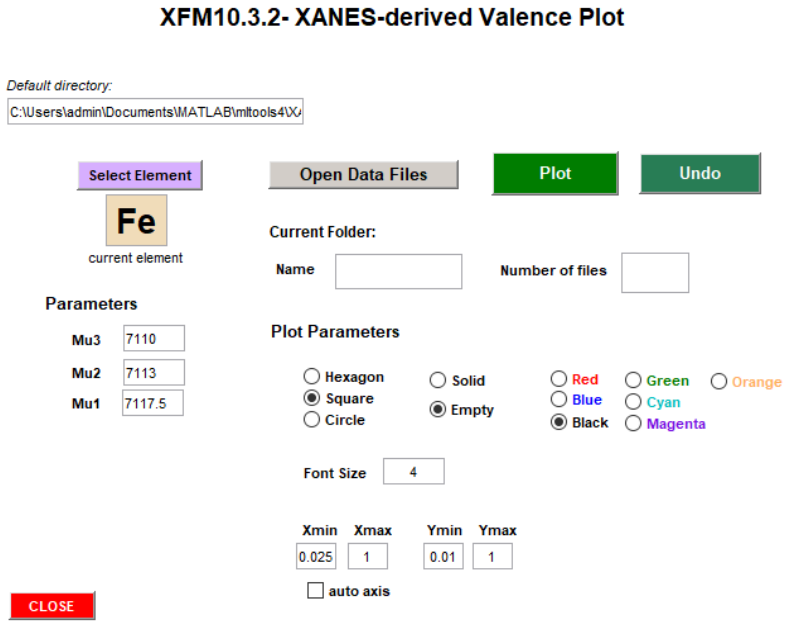

Fig. 41

Then press “select element” and pick one of the three available (**Fig. 42**), in this example here, Fe.

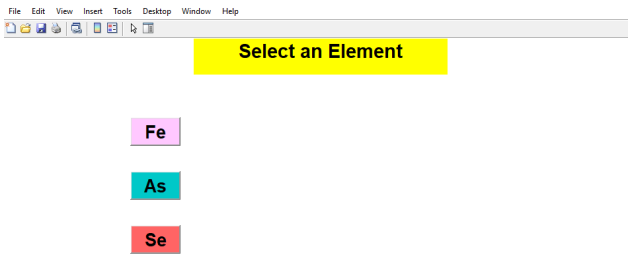

Fig. 42

Click on “open data files” and select the files for the standards in the folder Fe_standards_VP, then press “Plot”; do this for all Fe standards, except the “mixed valence” ones and you’ll obtain the scatter plot below, each datapoint corresponds to one spectrum (**Fig. 43**).

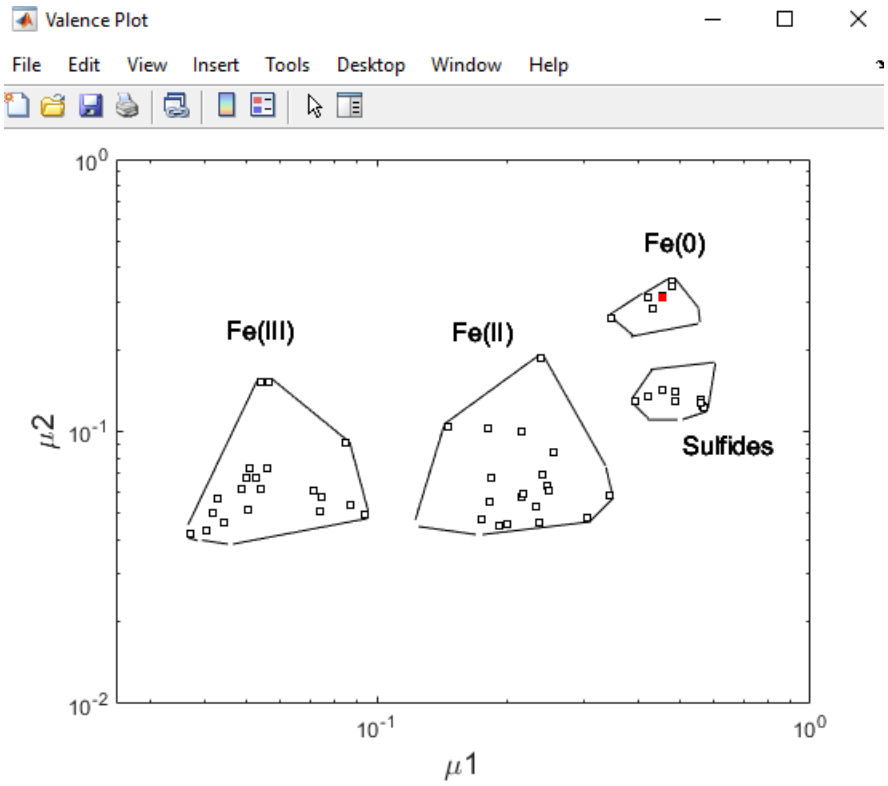

Fig. 43

Open the experimental XAS (xls file), select the desired plot options listed under plot parameters (circle, solid, red, font size 5 is recommended, **Fig. 41**), then press “Plot”. Note that the polygons are only indicative.
In the case where the experimental datapoint lands within the Fe (II) group, then it could be either a pure Fe(II) or a combination of Fe(III) with sulfides or metal. You’ll have to check your LSQ fitting results for this spectrum to assess as both are complementary.

==========END==========.