

Lecture 4

Analytical standardization

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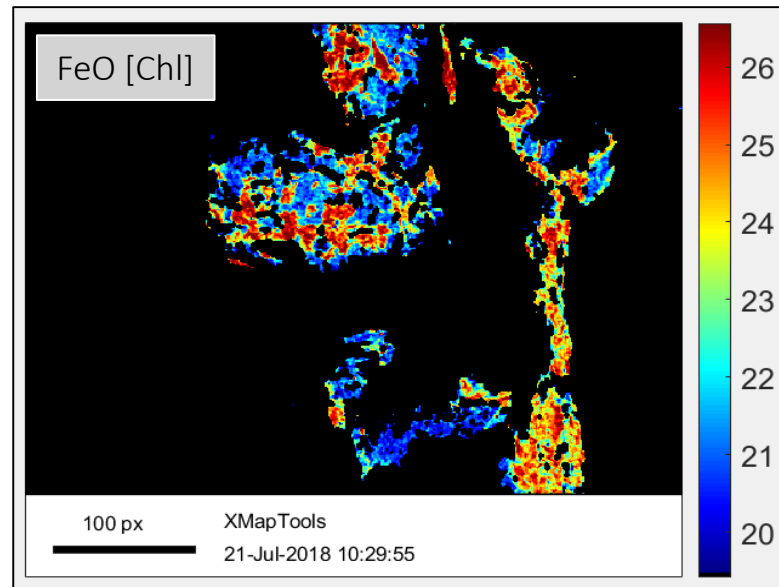
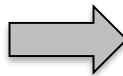
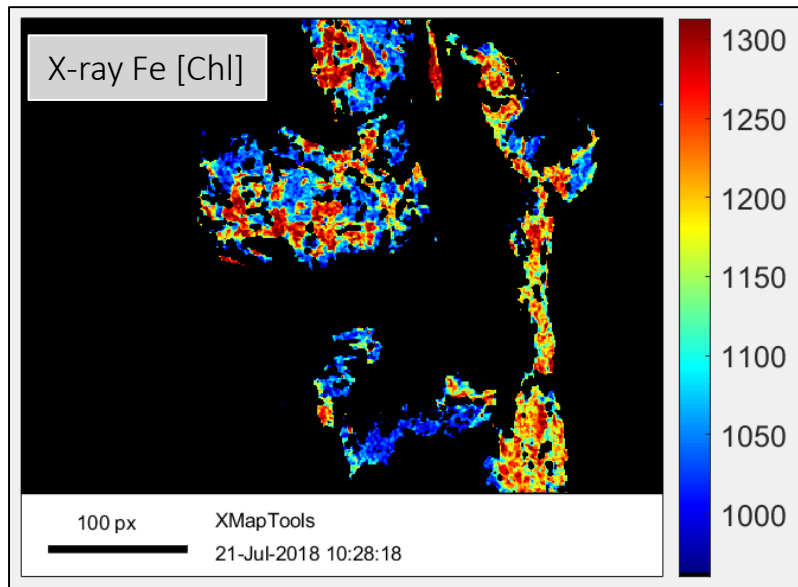
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² University of Bern -

- What is the analytical standardization?
- Why is it important?
- How does it work?
- Tools for the analytical standardization in XMAPTOOLS

ANALYTICAL STANDARDIZATION IN XMapTOOLS

Aim: transform one element X-ray map into a map of oxide weight-% concentration

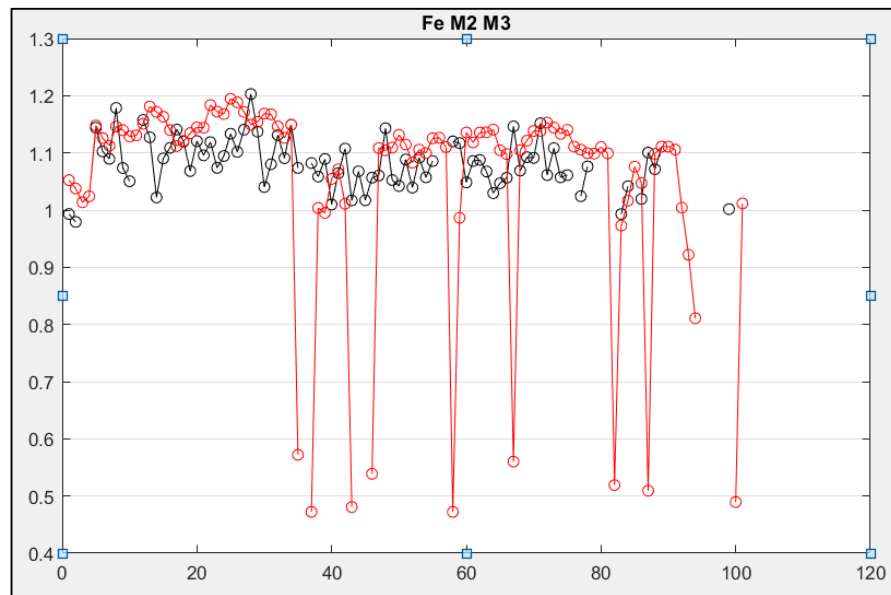
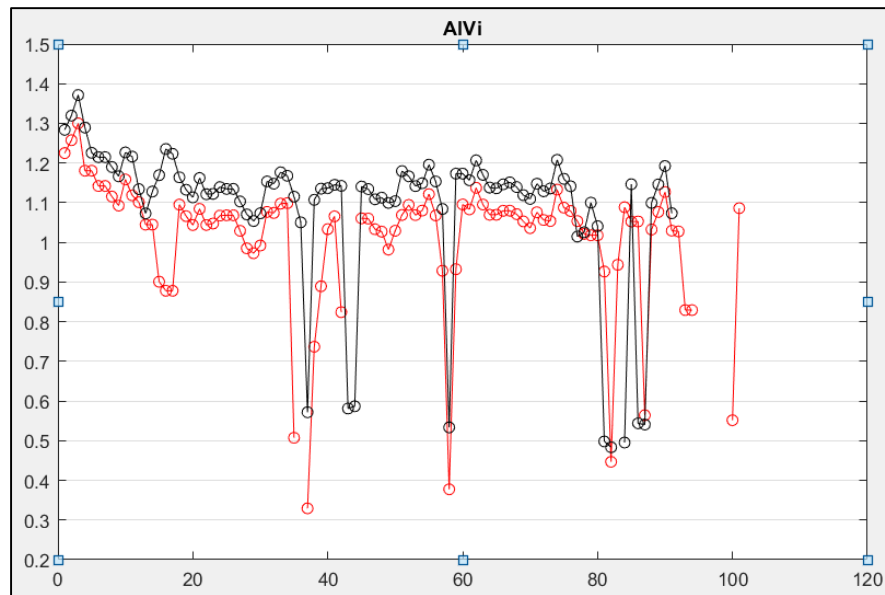


- Already quantified maps (e.g. provided by new CAMECA Microprobes based on ZAF correction)
- Quantification with internal standards (spot analyses, e.g. with XMAPTOOLS)

ANALYTICAL STANDARDIZATION IN XMapTOOLS

X-ray map calibrated with XMapTools (internal standards) - CHLORITE

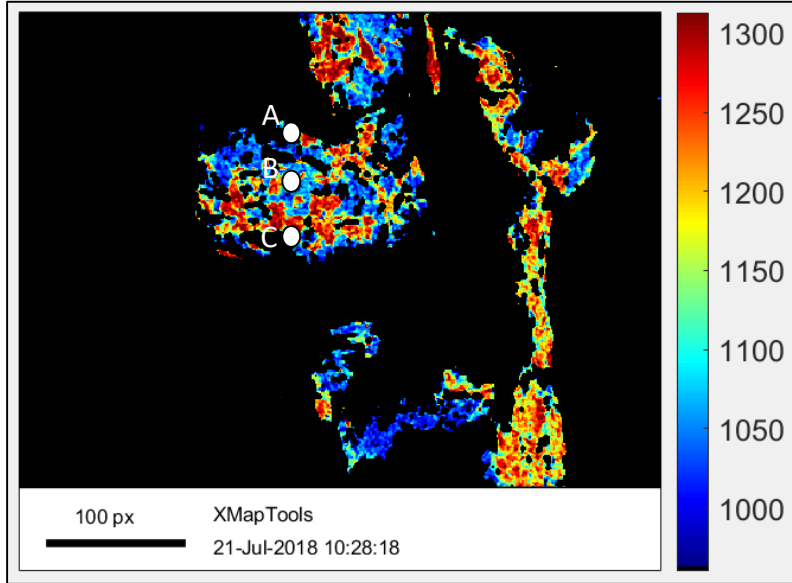
Quantified map with ZAF correction



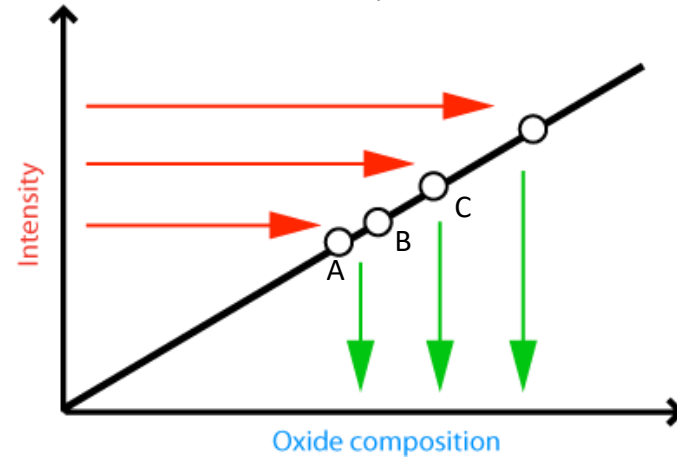
Quantification with internal standards can be applied in theory to all kind of maps (μ XRF, MEB) if the position of the spot analyses is exactly constrained.

ANALYTICAL STANDARDIZATION IN XMapTOOLS

Concept and Tools



X-Ray intensity of Si, Al, Fe... of A, B, C on the map
=
SiO₂, Al₂O₃, FeO wt%... of corresponding point
analysis A, B, C



$$\frac{C_i^{unk}}{C_i^{std}} \approx \frac{I_i^{unk}}{I_i^{std}}$$

Castaing's relation without any significant matrix difference between the standards and the unknown



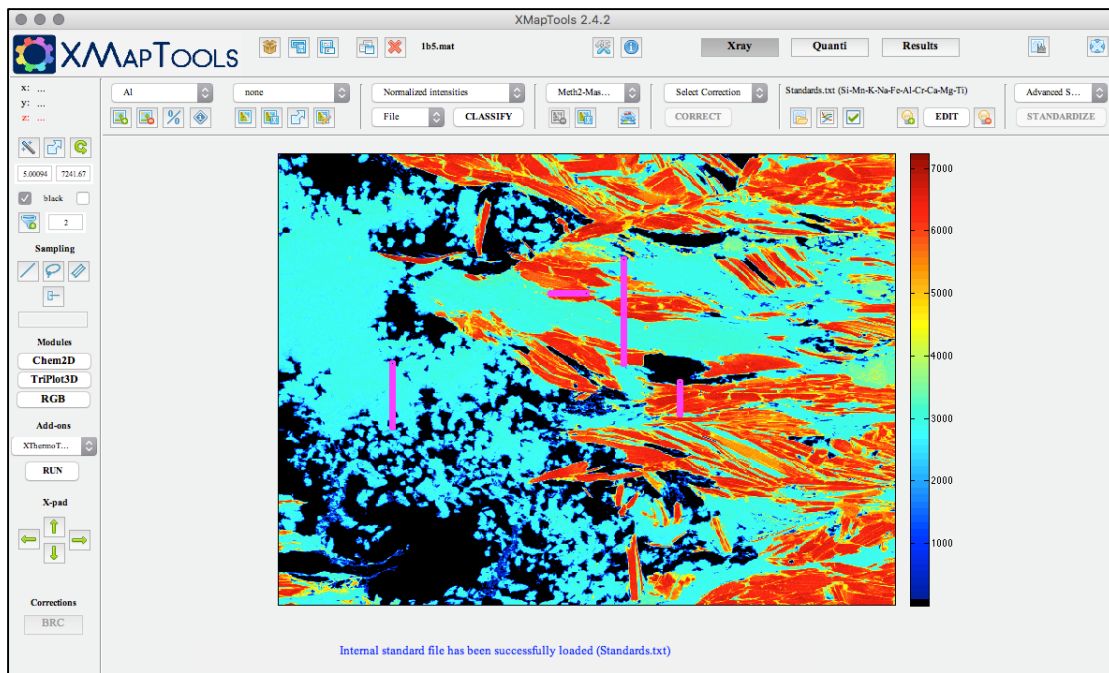
$$C_{unknown}^i = \frac{C_{standard}^i}{I_{standard}^i} I_{unknown}^i$$

(for net intensity corrected from background)

ANALYTICAL STANDARDIZATION IN XMapTOOLS

The important steps for a good standardization ...

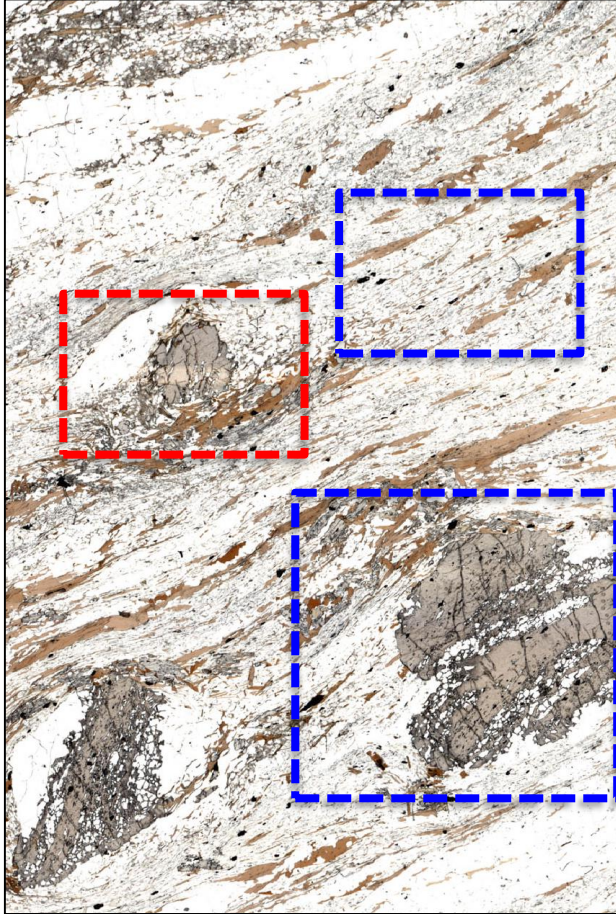
- ① Generate and import the file containing the internal standards
- ② Check the quality and position of the internal standards
- ③ Choose the standardization tool available in XMAPTOOLS
- ④ Check the quality of the map standardization



To make profiles of internal standards...

- 10-20 pts each phase of interest
- One horizontal and one vertical profile as position check
- Step size of the profile should be a multiple factor of the size of the map

ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE



Sample MA9330

Metapelite from the Central Alps (Switzerland)

Todd & Engi, (1997) JMG; Boston et al. (2017), Lithos

<i>Prograde</i>	garnet, muscovite, quartz, \pm plagioclase, \pm biotite
<i>Peak</i>	biotite, muscovite, quartz, kyanite, cordierite, plagioclase
<i>Retrograde</i>	biotite, chlorite

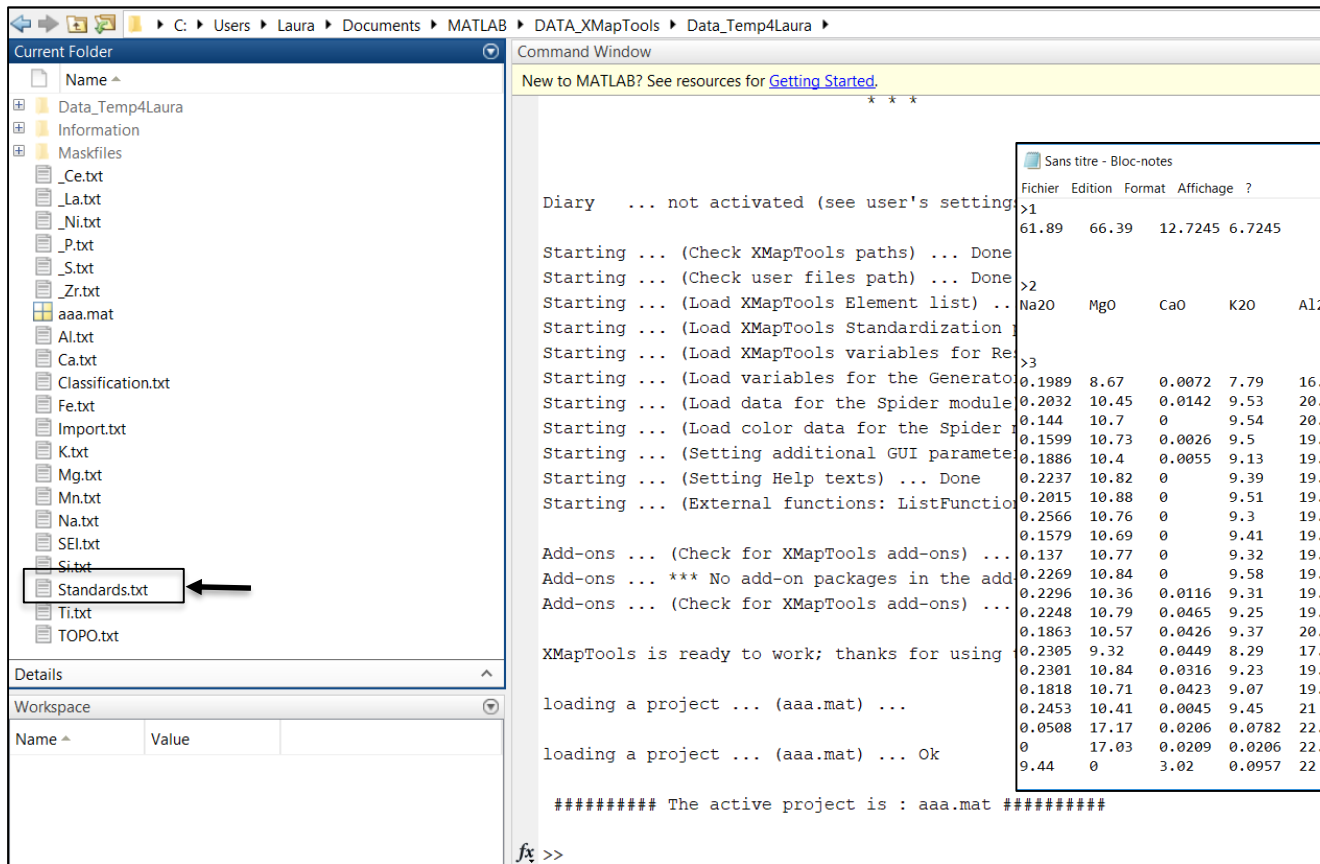
Map 1 – Mineral matrix –	1000 x 750 pixels, 6 μ m step size 100 ms dwell time – 42 h
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Map 2 – Retrogression –	1000 x 750 pixels, 6 μ m step size 100 ms dwell time – 42 h
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Map3 – Garnet porphyroblast –	1000 x 1000 pixels, 10 μ m step size 60 ms dwell time – 33 h
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ANALYTICAL STANDARDIZATION IN XMapTools: PRACTICAL EXERCISE

1. Generate and import the file containing the internal standards



The screenshot shows the MATLAB XMapTools interface. The 'Current Folder' pane on the left displays a directory structure with files like `_Ce.txt`, `_La.txt`, `_Ni.txt`, `_P.txt`, `_S.txt`, `_Zr.txt`, `aaa.mat`, `Al.txt`, `Ca.txt`, `Classification.txt`, `Fe.txt`, `Import.txt`, `K.txt`, `Mg.txt`, `Mn.txt`, `Na.txt`, `SEI.txt`, `Si.txt`, **`Standards.txt`** (highlighted with a black arrow), `Ti.txt`, and `TOPO.txt`. The 'Command Window' on the right shows the execution of the `aaa.mat` script, which includes commands for loading XMapTools paths, user files, element lists, and standardization. The output shows the successful loading of the `Standards.txt` file. The 'Workspace' pane at the bottom is empty.

```
Diary ... not activated (see user's settings)

Starting ... (Check XMapTools paths) ... Done
Starting ... (Check user files path) ... Done
Starting ... (Load XMapTools Element list) ... Done
Starting ... (Load XMapTools Standardization) ... Done
Starting ... (Load XMapTools variables for Regression) ... Done
Starting ... (Load variables for the Generator) ... Done
Starting ... (Load data for the Spider module) ... Done
Starting ... (Load color data for the Spider) ... Done
Starting ... (Setting additional GUI parameters) ... Done
Starting ... (Setting Help texts) ... Done
Starting ... (External functions: ListFunctions) ... Done

Add-ons ... (Check for XMapTools add-ons) ... Done
Add-ons ... *** No add-on packages in the add-on directory ... Done
Add-ons ... (Check for XMapTools add-ons) ... Done

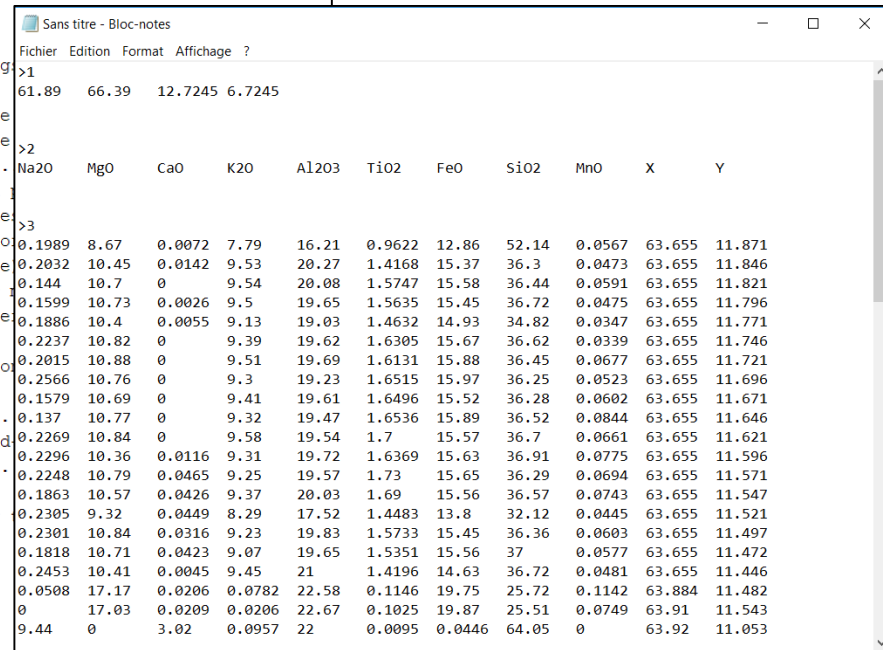
XMapTools is ready to work; thanks for using XMapTools

loading a project ... (aaa.mat) ...

loading a project ... (aaa.mat) ... Ok

##### The active project is : aaa.mat #####
```

File: *Standards.txt*



The screenshot shows a text editor window titled 'Sans titre - Bloc-notes'. The content of the file `Standards.txt` is displayed, showing a table of analytical data. The table has 12 columns: `Na2O`, `MgO`, `CaO`, `K2O`, `Al2O3`, `TiO2`, `FeO`, `SiO2`, `MnO`, `X`, and `Y`. The data is organized into three sections, each starting with a prompt like `>1`, `>2`, and `>3`.

	Na2O	MgO	CaO	K2O	Al2O3	TiO2	FeO	SiO2	MnO	X	Y
>1	61.89	66.39	12.7245	6.7245							
>2											
>3	0.1989	8.67	0.0072	7.79	16.21	0.9622	12.86	52.14	0.0567	63.655	11.871
	0.2032	10.45	0.0142	9.53	20.27	1.4168	15.37	36.3	0.0473	63.655	11.846
	0.144	10.7	0	9.54	20.08	1.5747	15.58	36.44	0.0591	63.655	11.821
	0.1599	10.73	0.0026	9.5	19.65	1.5635	15.45	36.72	0.0475	63.655	11.796
	0.1886	10.4	0.0055	9.13	19.03	1.4632	14.93	34.82	0.0347	63.655	11.771
	0.2237	10.82	0	9.39	19.62	1.6305	15.67	36.62	0.0339	63.655	11.746
	0.2015	10.88	0	9.51	19.69	1.6131	15.88	36.45	0.0677	63.655	11.721
	0.2566	10.76	0	9.3	19.23	1.6515	15.97	36.25	0.0523	63.655	11.696
	0.1579	10.69	0	9.41	19.61	1.6496	15.52	36.28	0.0602	63.655	11.671
	0.137	10.77	0	9.32	19.47	1.6536	15.89	36.52	0.0844	63.655	11.646
	0.2269	10.84	0	9.58	19.54	1.7	15.57	36.7	0.0661	63.655	11.621
	0.2296	10.36	0.0116	9.31	19.72	1.6369	15.63	36.91	0.0775	63.655	11.596
	0.2248	10.79	0.0465	9.25	19.57	1.73	15.65	36.29	0.0694	63.655	11.571
	0.1863	10.57	0.0426	9.37	20.03	1.69	15.56	36.57	0.0743	63.655	11.547
	0.2305	9.32	0.0449	8.29	17.52	1.4483	13.8	32.12	0.0445	63.655	11.521
	0.2301	10.84	0.0316	9.23	19.83	1.5733	15.45	36.36	0.0603	63.655	11.497
	0.1818	10.71	0.0423	9.07	19.65	1.5351	15.56	37	0.0577	63.655	11.472
	0.2453	10.41	0.0045	9.45	21	1.4196	14.63	36.72	0.0481	63.655	11.446
	0.0508	17.17	0.0206	0.0782	22.58	0.1146	19.75	25.72	0.1142	63.884	11.482
	0	17.03	0.0209	0.0206	22.67	0.1025	19.87	25.51	0.0749	63.91	11.543
	9.44	0	3.02	0.0957	22	0.0095	0.0446	64.05	0	63.92	11.053

ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

1. Generate and import the file containing the internal standards

X-ray map coordinates (Xmin, Xmax, Ymin, Ymax)

List of analyzed elements + X, Y

Quantitative compositional analyses for
each point + X, Y coordinates

>1										
61.89	66.39	12.7245	6.7245							
>2										
Na2O	MgO	CaO	K2O	Al2O3	TiO2	FeO	SiO2	MnO	X	Y
>3										
0.1989	8.67	0.0072	7.79	16.21	0.9622	12.86	52.14	0.0567	63.655	11.871
0.2032	10.45	0.0142	9.53	20.27	1.4168	15.37	36.3	0.0473	63.655	11.846
0.144	10.7	0	9.54	20.08	1.5747	15.58	36.44	0.0591	63.655	11.821
0.1599	10.73	0.0026	9.5	19.65	1.5635	15.45	36.72	0.0475	63.655	11.796
0.1886	10.4	0.0055	9.13	19.03	1.4632	14.93	34.82	0.0347	63.655	11.771
0.2237	10.82	0	9.39	19.62	1.6305	15.67	36.62	0.0339	63.655	11.746
0.2015	10.88	0	9.51	19.69	1.6131	15.88	36.45	0.0677	63.655	11.721
0.2566	10.76	0	9.3	19.23	1.6515	15.97	36.25	0.0523	63.655	11.696
0.1579	10.69	0	9.41	19.61	1.6496	15.52	36.28	0.0602	63.655	11.671
0.137	10.77	0	9.32	19.47	1.6536	15.89	36.52	0.0844	63.655	11.646
0.2269	10.84	0	9.58	19.54	1.7	15.57	36.7	0.0661	63.655	11.621
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0.2248	10.79	0.0465	9.25	19.57	1.73	15.65	36.29	0.0694	63.655	11.571
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0.1818	10.71	0.0423	9.07	19.65	1.5351	15.56	37	0.0577	63.655	11.472
0.2453	10.41	0.0045	9.45	21	1.4196	14.63	36.72	0.0481	63.655	11.446
0.0508	17.17	0.0206	0.0782	22.58	0.1146	19.75	25.72	0.1142	63.884	11.482
0	17.03	0.0209	0.0206	22.67	0.1025	19.87	25.51	0.0749	63.91	11.543
9.44	0	3.02	0.0957	22	0.0095	0.0446	64.05	0	63.92	11.053

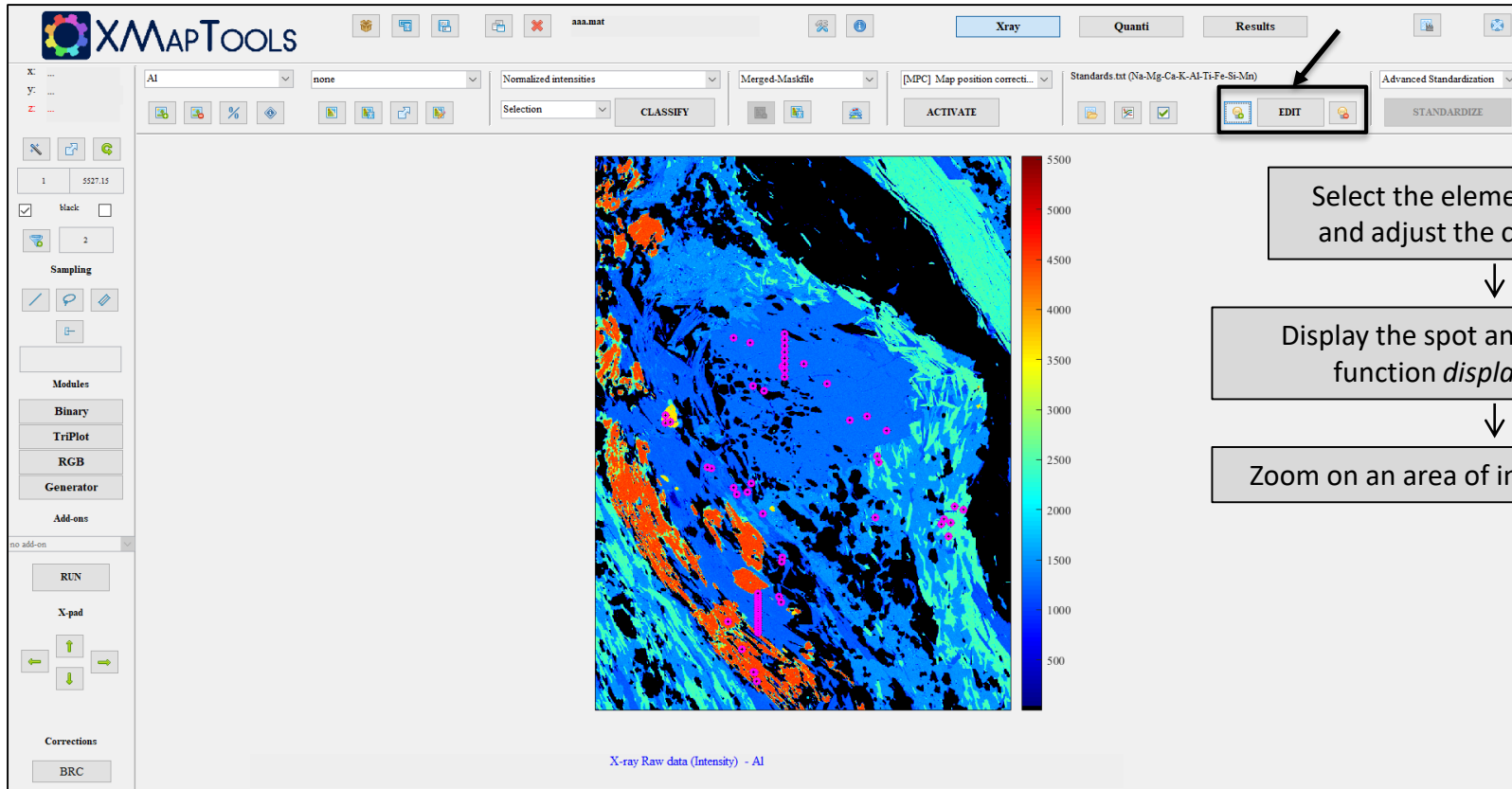
ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

Load the file *Standards.txt* using the function *import standard file*

The screenshot displays the XMapTools software interface. The top toolbar contains buttons for 'Xray', 'Quanti', and 'Results'. A red arrow points to the 'Standards.txt' button in the 'Xray' section, which is highlighted by a black box. The main window shows a color-coded map of a sample, with a vertical color scale on the right ranging from 500 to 5500. The map is labeled 'X-ray Raw data (Intensity) - Al'. The left sidebar contains various toolbars and modules, including 'Sampling', 'Modules', and 'Add-ons'. The 'Standards.txt' button is located in the top right corner of the main window, next to the 'EDIT' button.

ANALYTICAL STANDARDIZATION IN XMapTOOLS

2. Check the quality and position of the internal standards on the map



Select the element of interest
and adjust the color contrast



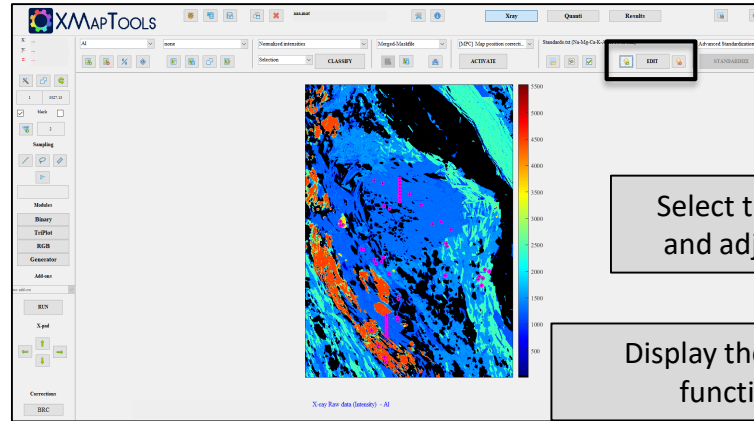
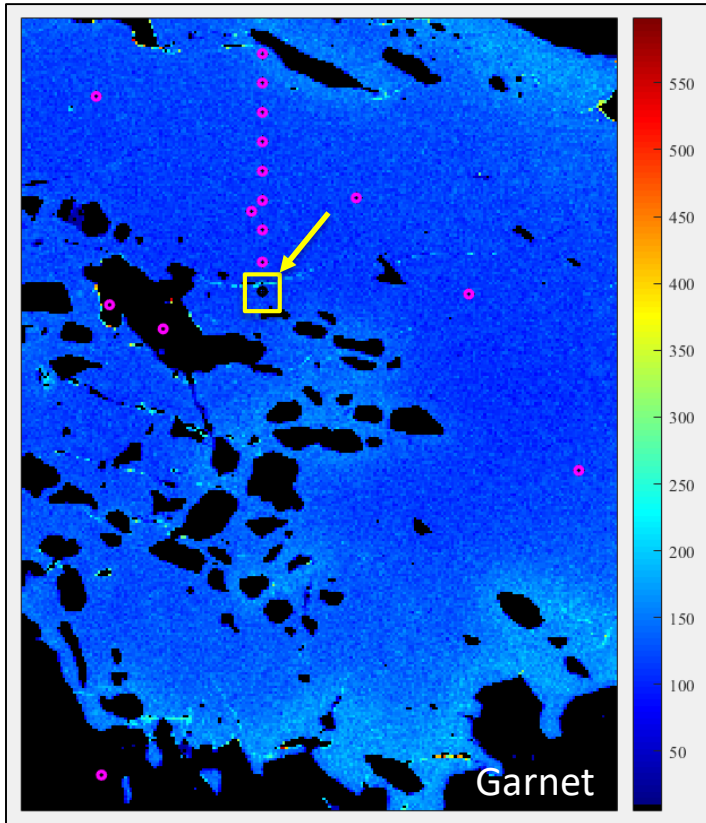
Display the spot analyses using the
function *display standards*



Zoom on an area of interest (suggested)

ANALYTICAL STANDARDIZATION IN XMapTOOLS

2. Check the quality and position of point analyses on the map



Select the element of interest and adjust the color contrast



Display the spot analyses using the function *display standards*



Zoom on an area of interest (suggested)



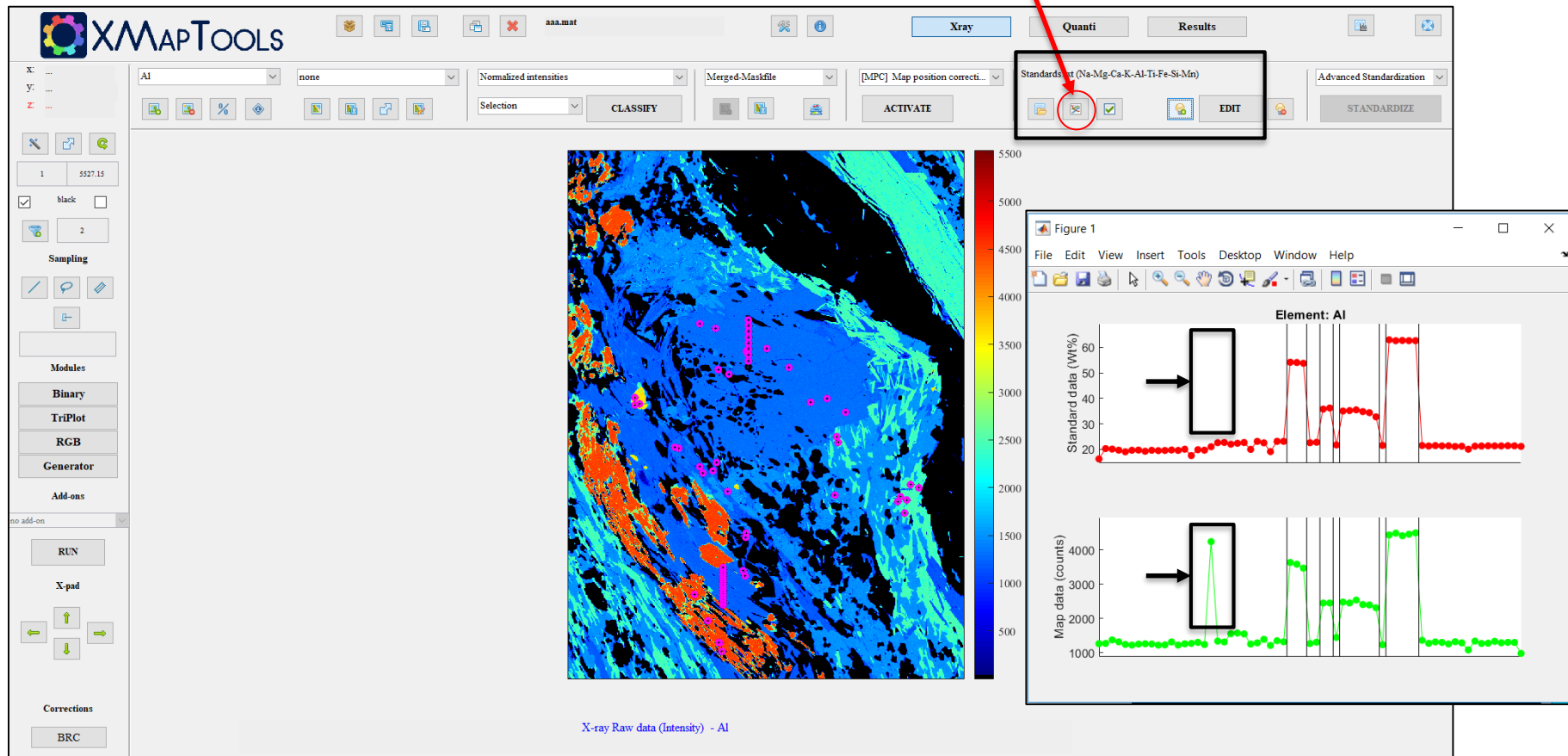
Press EDIT and select/unselect spot analyses



Right clicking to validate and save the changes made

ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

Check the quality of the position of the internal standards



ANALYTICAL STANDARDIZATION IN XMAPTOOLS

2. Check the quality and position of the internal standards on the map

Use the function *check quality of std/maps positions* (size 10*10 pixels²)

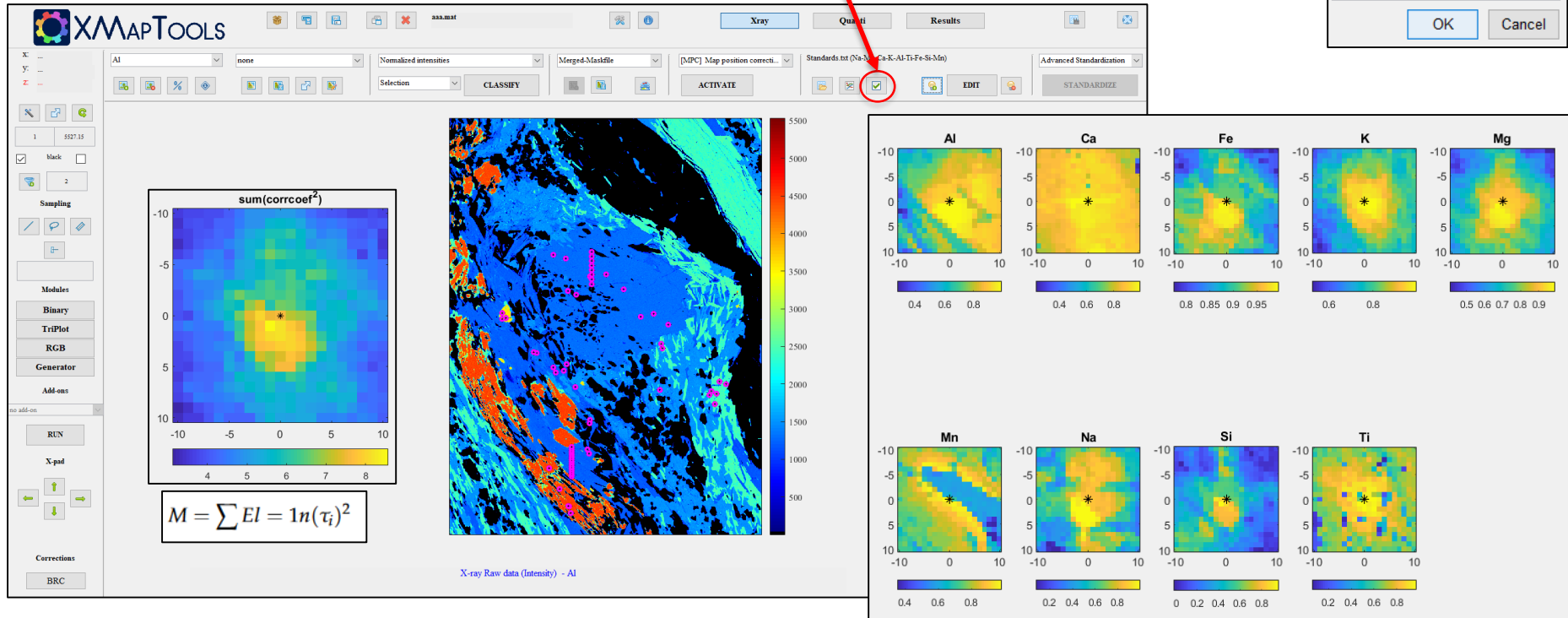
$$(X_j - \Delta X, Y_j - \Delta Y)$$
$$(X_j + \Delta X, Y_j + \Delta Y)$$

Dialog box for X-Shift and Y-Shift [(XY)ref system].

X-Shift [(XY)ref system]: 10

Y-Shift [(XY)ref system]: 10

Buttons: OK, Cancel



ANALYTICAL STANDARDIZATION IN XMapTools: PRACTICAL EXERCISE

XMapTools 2.5.1

XMAPTOOLS

aaa.mat

Xray Quant Results

Mg Garnet Normalized intensities Merged-Maskfile

Select Correction
[BRC] Border removing correction
[TRC] TOPO-related correction
[MPC] Map position correction tool
[SPC] Standard position correction tool
[IDC] Intensity drift correction
[BA1] Background correction (using maps)
[RM1] Clean pixels (area, all maps)

Standards.txt (Na-Mg-Ca-K-Al-Ti-Fe-Si-Mn)

Advanced Standardization

EDIT STANDARDIZE

CLASSIFY

Selection

6.00011 598.071

black

2

Sampling

Modules

Binary

TriPlot

RGB

Generator

Add-ons

no add-on

RUN

X-pad

Corrections

BRC

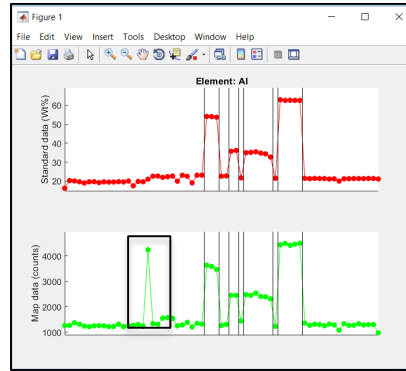
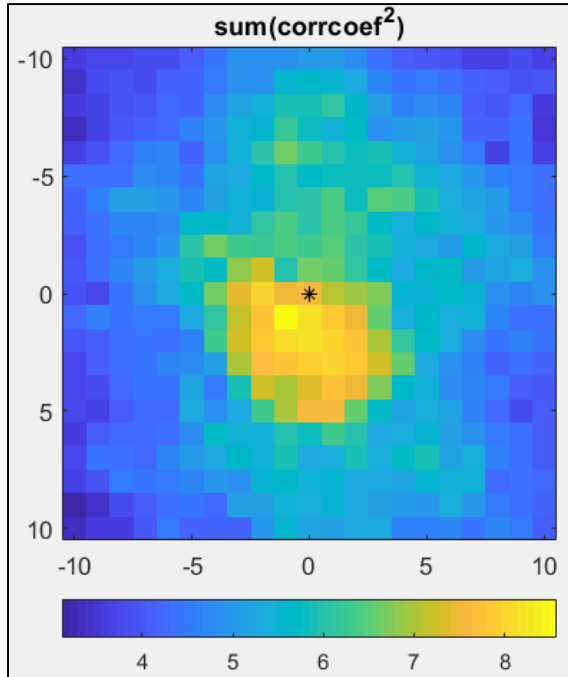
SPC correction mode off - the correction has been applied to standard positions

1

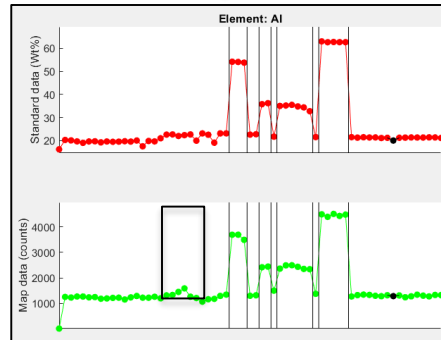
2

ANALYTICAL STANDARDIZATION IN XMapTOOLS

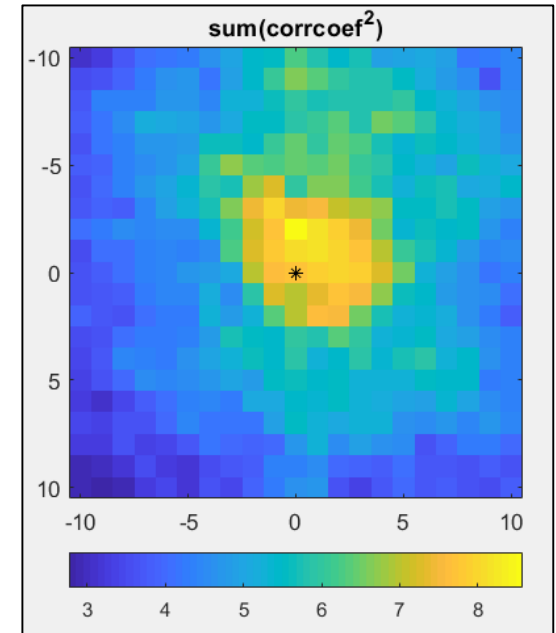
Function *check quality of std/maps positions* (size 10*10 pixels²)



Use the *Standard correction tool (SPC)*
(e.g. shift the x,y position of the standards)

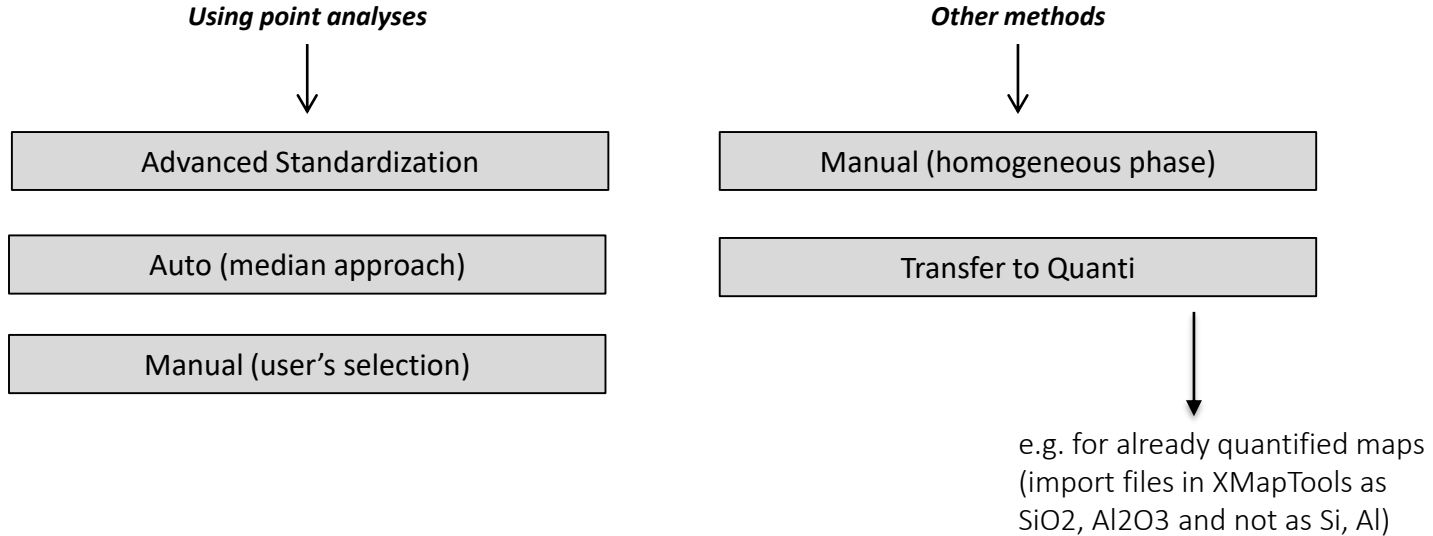


New function *check quality of std/maps positions* (size 10*10 pixels²)



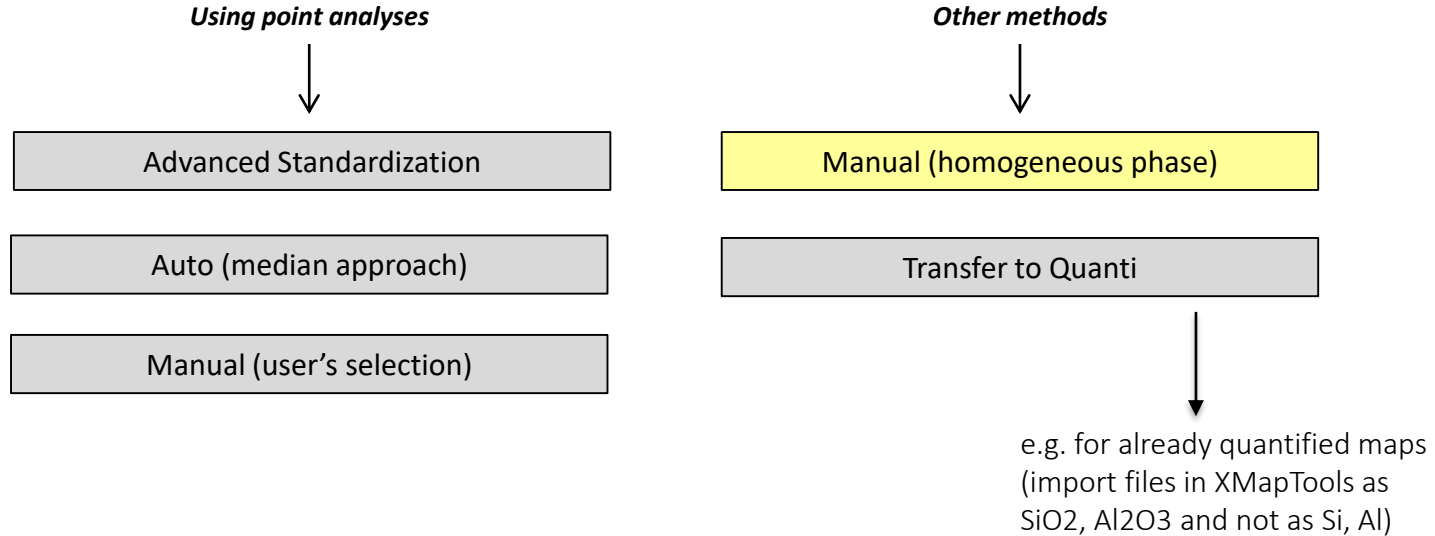
ANALYTICAL STANDARDIZATION IN XMapTOOLS

3. Choose the standardization tool in XMapTOOLS



ANALYTICAL STANDARDIZATION IN XMapTOOLS

3. Choose the standardization tool in XMapTOOLS



ANALYTICAL STANDARDIZATION IN XMAPTOOLS: PRACTICAL EXERCISE

Quartz: homogeneous phase → *Manual standardization*

The screenshot displays the XMAPTOOLS software interface. The main window shows a map of Quartz with a color scale ranging from 1000 to 7000. The map is labeled "X-ray Raw data (Intensity) - Si". The interface includes a top menu bar with "Xray", "Quanti", and "Results" tabs. A left sidebar contains various tool icons and a "Modules" section with buttons for "Binary", "TriPlot", "RGB", and "Generator". A right sidebar contains a list of chemical elements for standardization, with "SiO2" highlighted and its value set to 100. The "Advanced Standardization" dropdown menu is open, showing options: "Advanced Standardization", "Auto (median approach)", "Manual (user selection)", and "Transfer to quanti".

Chemical elements and their values for standardization:

Chemical Element	Value
Al2O3	0
CaO	0
FeO	0
K2O	0
MgO	0
MnO	0
Na2O	0
SiO2	100
TiO2	0

Buttons: OK, Cancel

ANALYTICAL STANDARDIZATION IN XMapTOOLS

3. Choose the standardization tools in XMAPTOOLS

Using point analyses



Advanced Standardization

Auto (median approach)

Manual (user's selection)



Uses the **medial postition C** (X_C , Y_C) of the calibration **points**. The calibration curve is defined as:

$$Y = \frac{Y_C}{X_C} X$$

Any calibration curve intersects the X- and Y-axis origin. **But..** this is not necessarily verified for low-concentrated elements (background)

Other methods



Manual (homogeneous phase)

Transfer to Quanti



e.g. for already quantified maps
(import files in XMapTools as
SiO₂, Al₂O₃ and not as Si, Al)

ANALYTICAL STANDARDIZATION IN XMapTOOLS

3. Choose the standardization tools in XMapTOOLS

Using point analyses



Advanced Standardization

Auto (median approach)

Manual (user's selection)

Takes into account a 'pseudo' background correction.
The calibration curve is defined by the **centrer of the cluster of standard points** (X_C , Y_C) and the **background point B** (0, Y_B).

$$Y = \frac{Y_C - Y_B}{X_C} X + Y_B$$

Other methods



Manual (homogeneous phase)

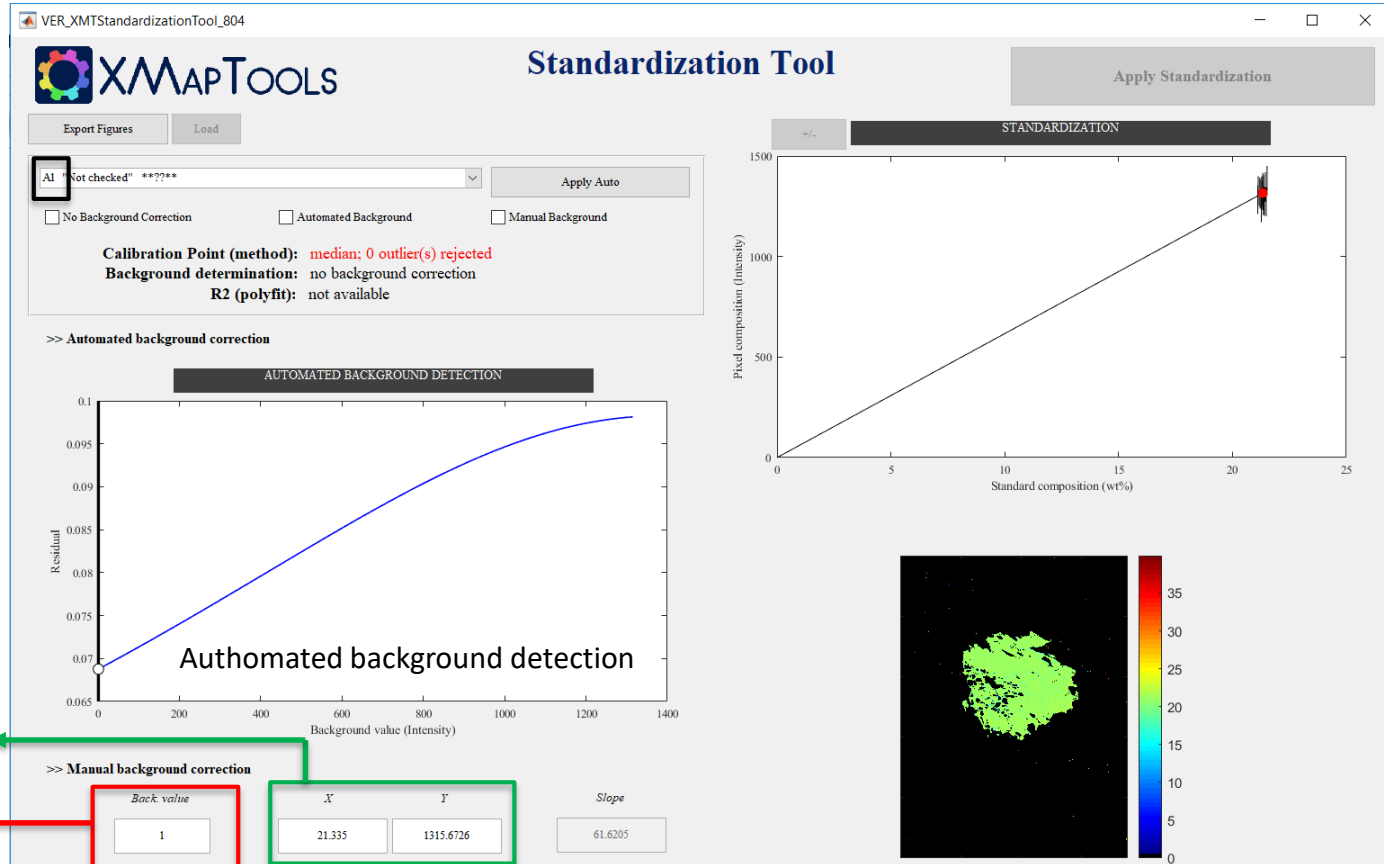
Transfer to Quanti

e.g. for already quantified maps
(import files in XMapTools as
SiO₂, Al₂O₃ and not as Si, Al)

ANALYTICAL STANDARDIZATION IN XMAPTOOLS

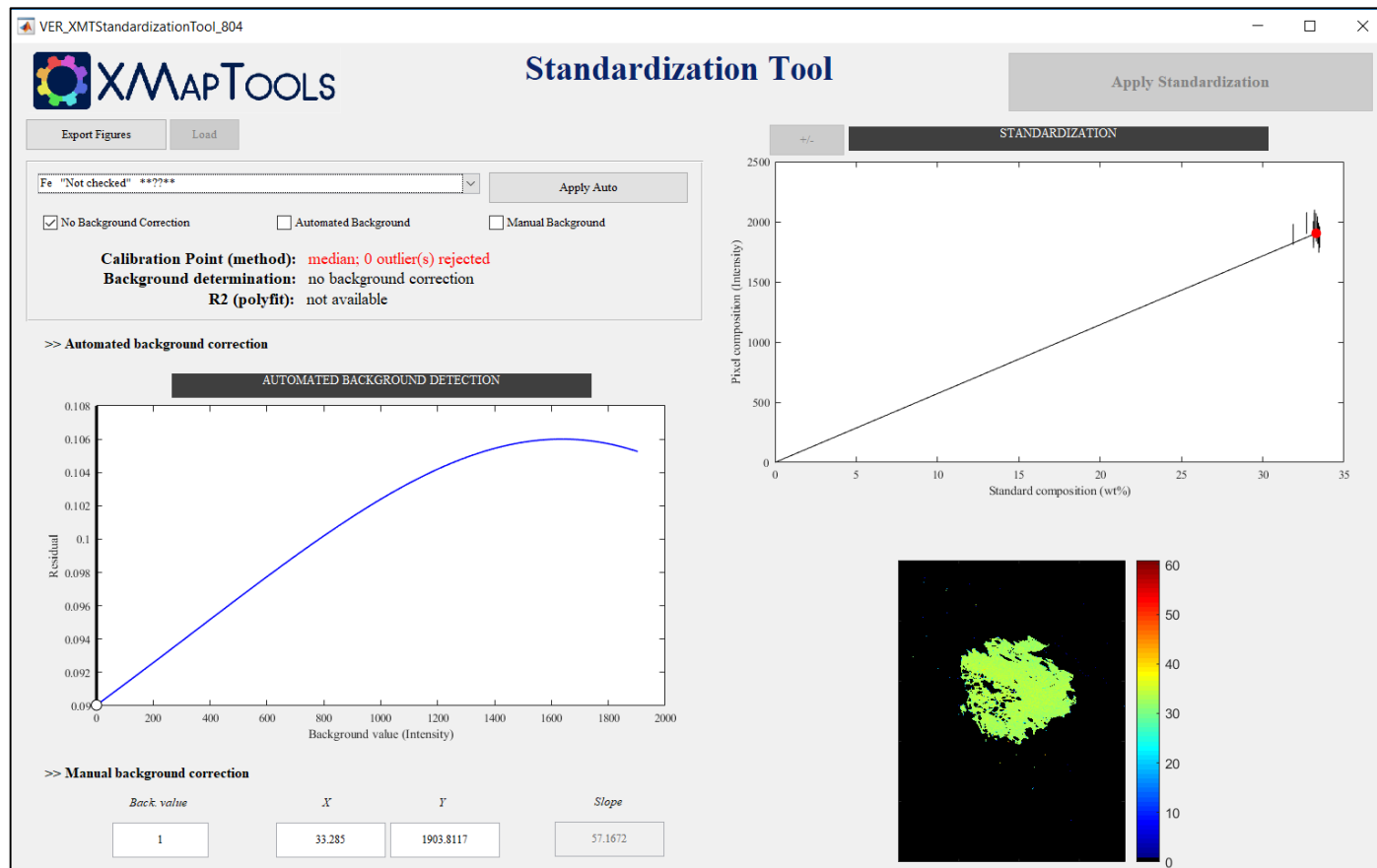
*Standardize the phase **garnet** (method advanced): **Al***

For high intensity/background ratios the correction is not applied



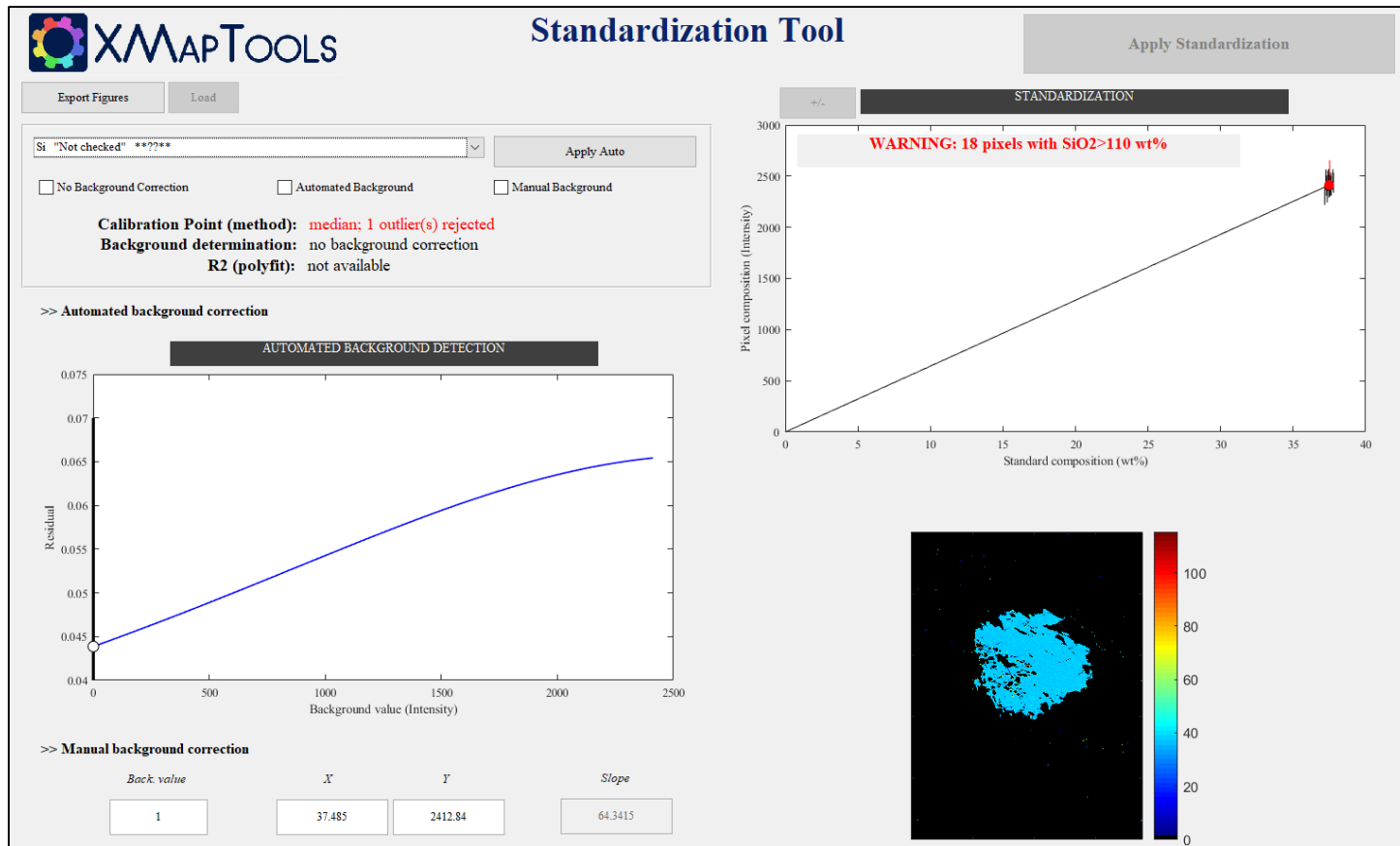
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): *Fe*



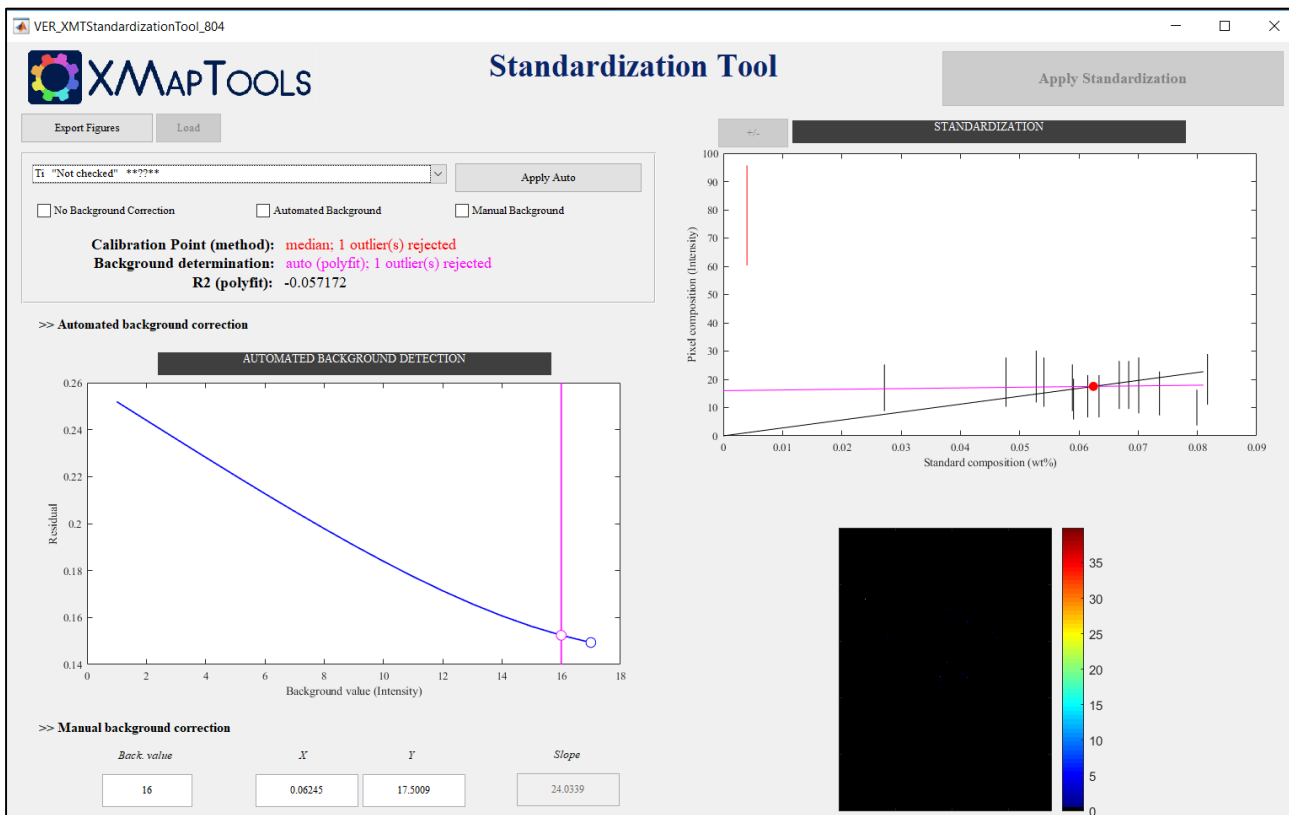
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): *Si*



ANALYTICAL STANDARDIZATION IN XMapTOOLS

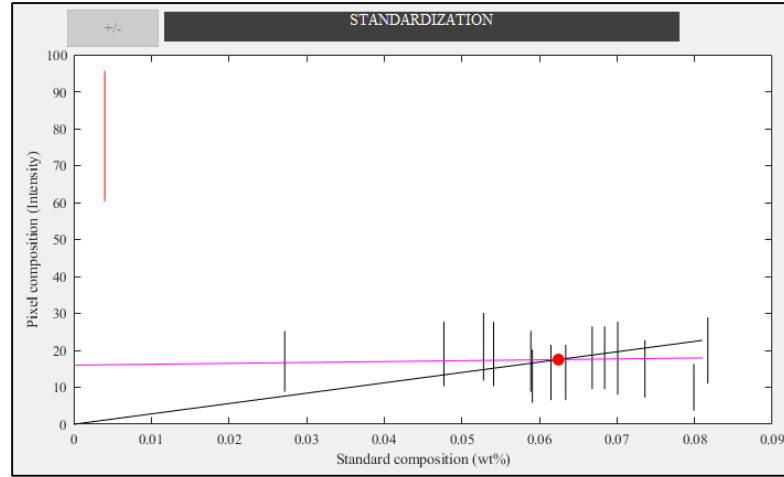
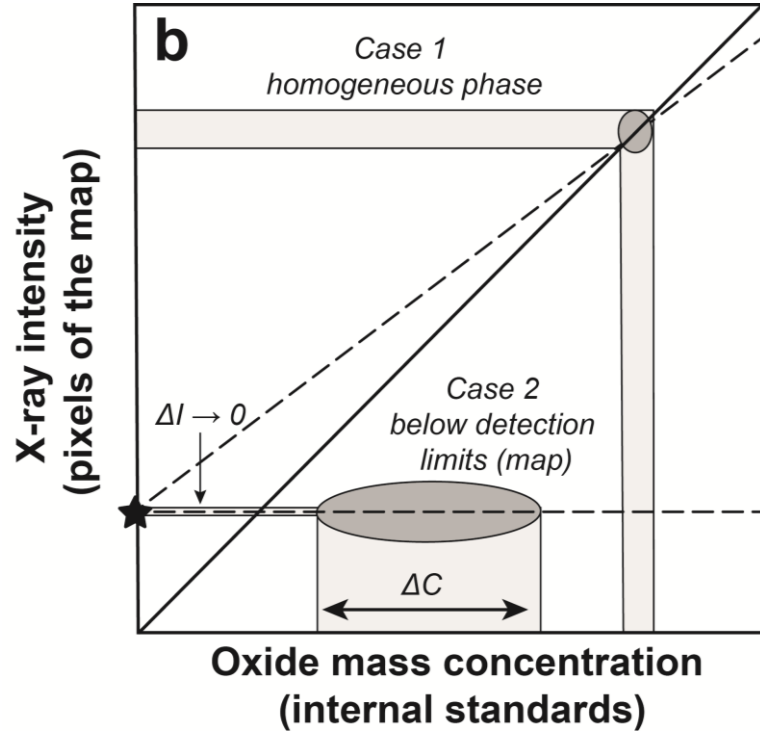
*Standardize the phase **garnet** (method advanced): **Ti***



- For low intensity/background ratios the correction has to be applied
- Correction can be applied only if the same spectrometer configuration has been used for internal standards and X-ray maps

ANALYTICAL STANDARDIZATION IN XMapTOOLS

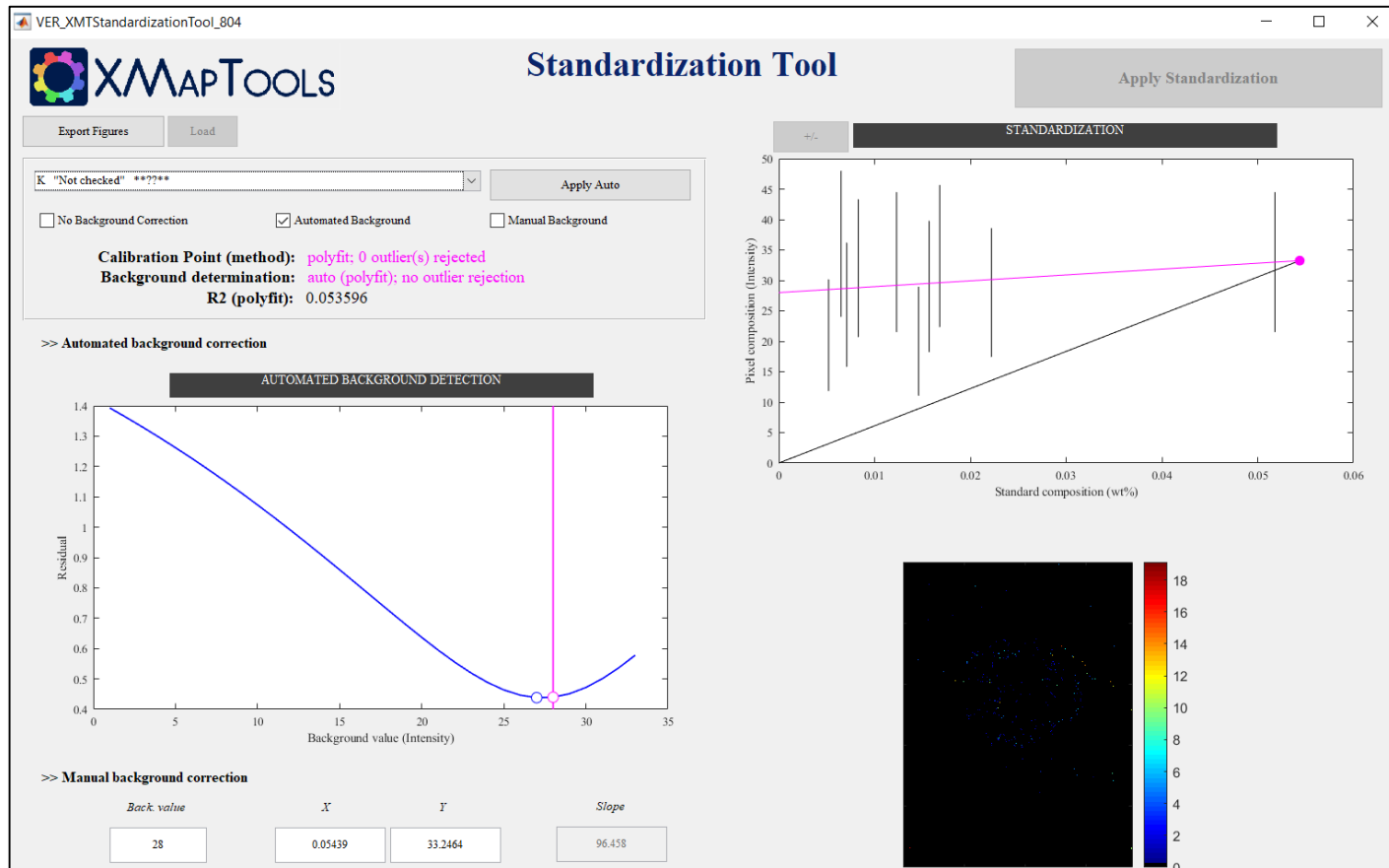
Standardize the phase **garnet** (method advanced): Ti



ΔC = captured compositional variability of the standards used to fit the slope of the calibration curve and to approximate the corresponding background

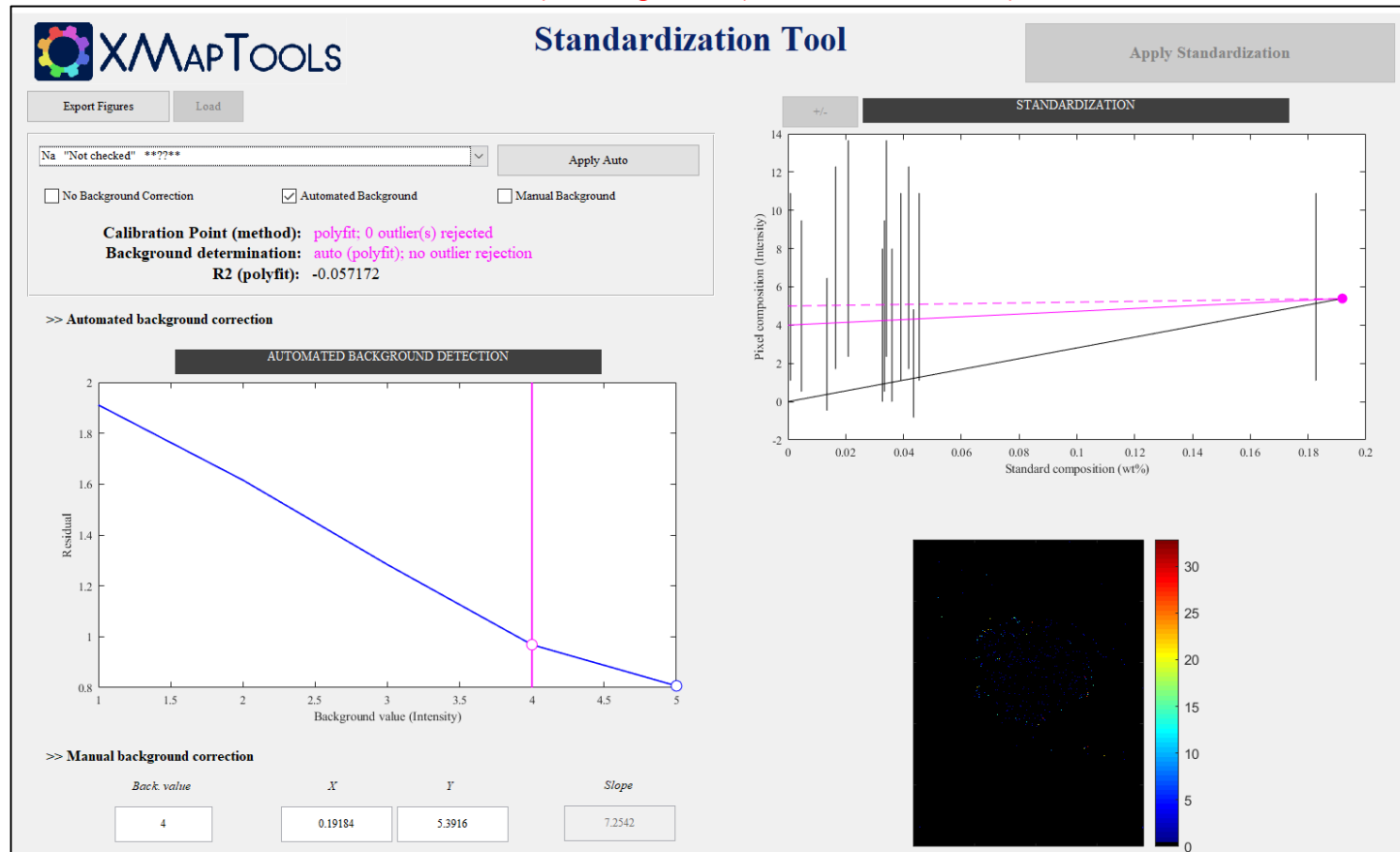
ANALYTICAL STANDARDIZATION IN XMapTOOLS

*Standardize the phase **garnet** (method advanced): K*



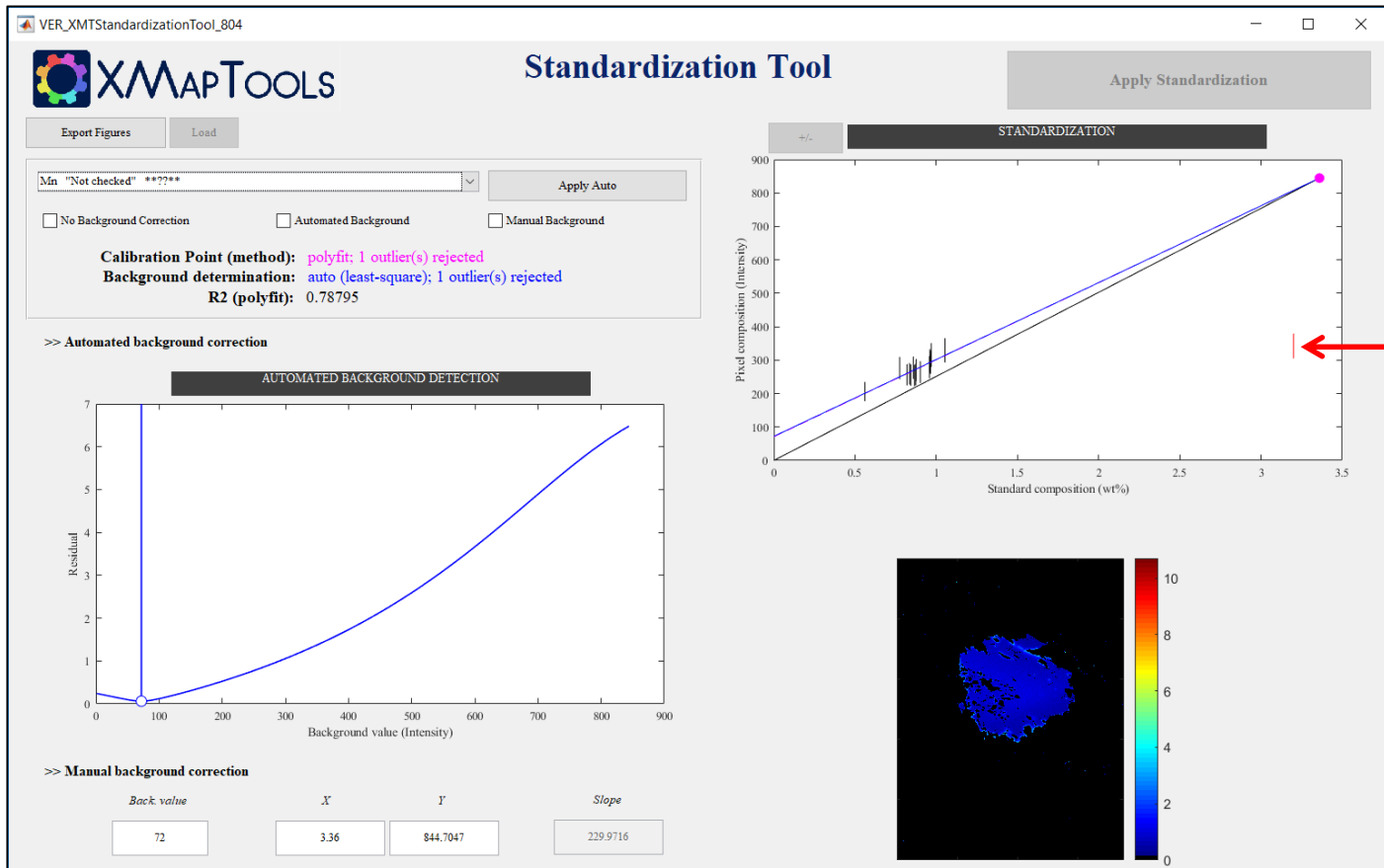
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): Na



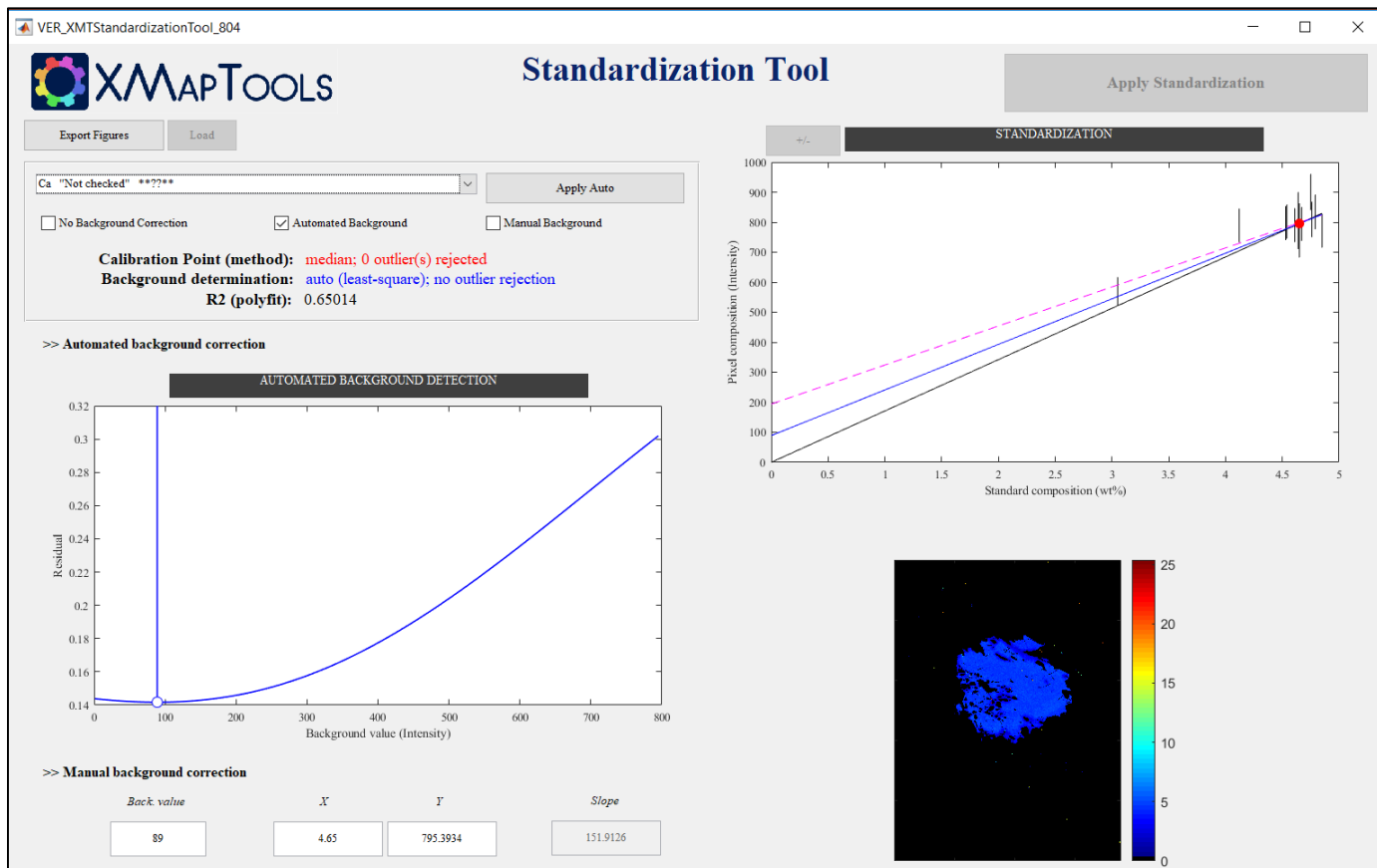
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): Mn



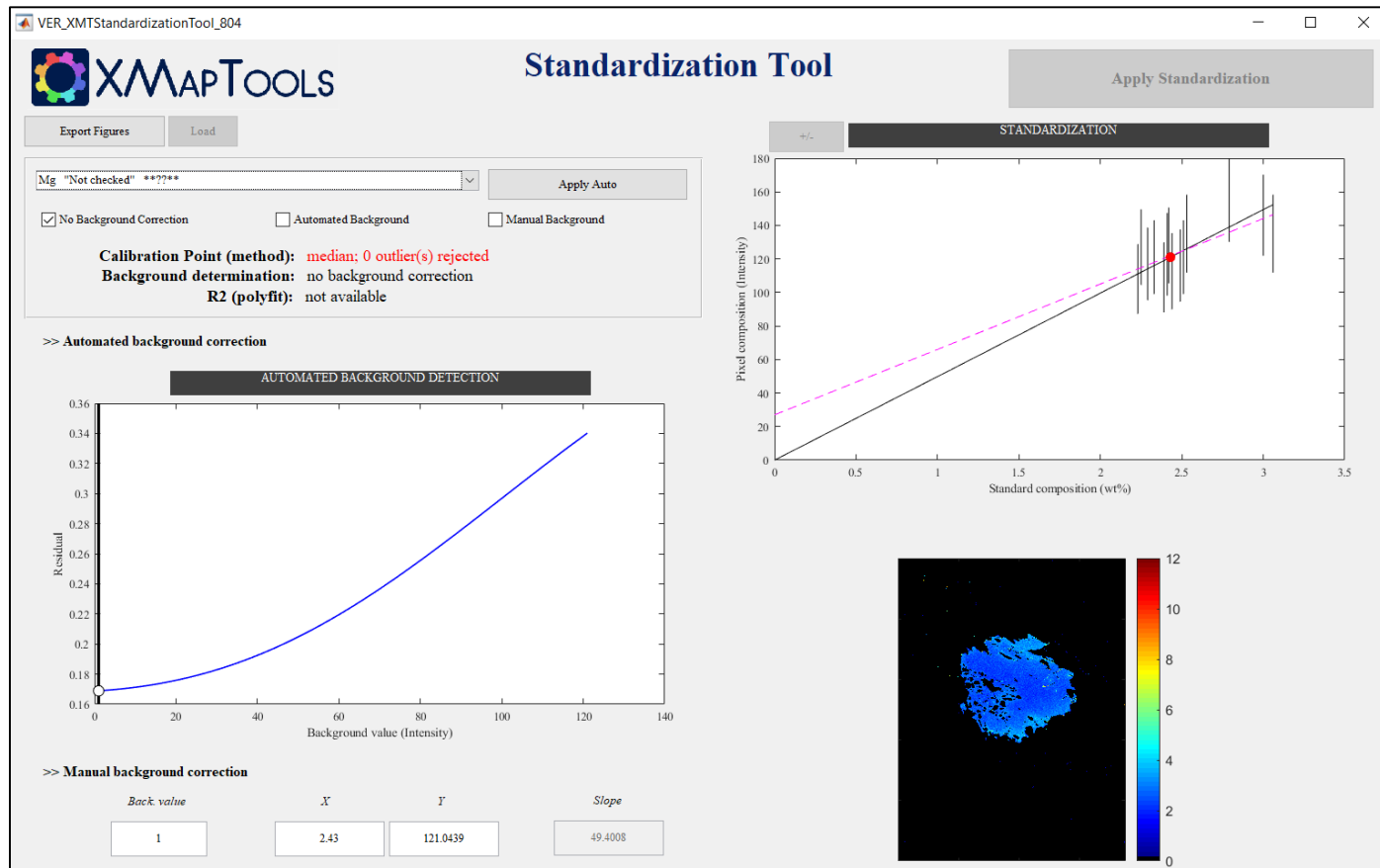
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): *Ca*



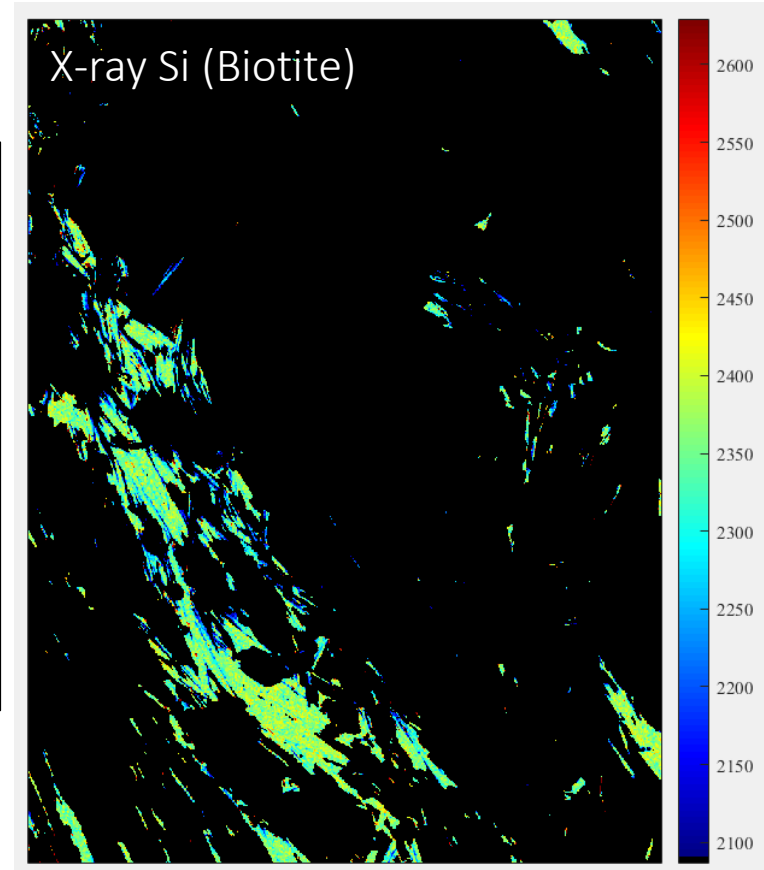
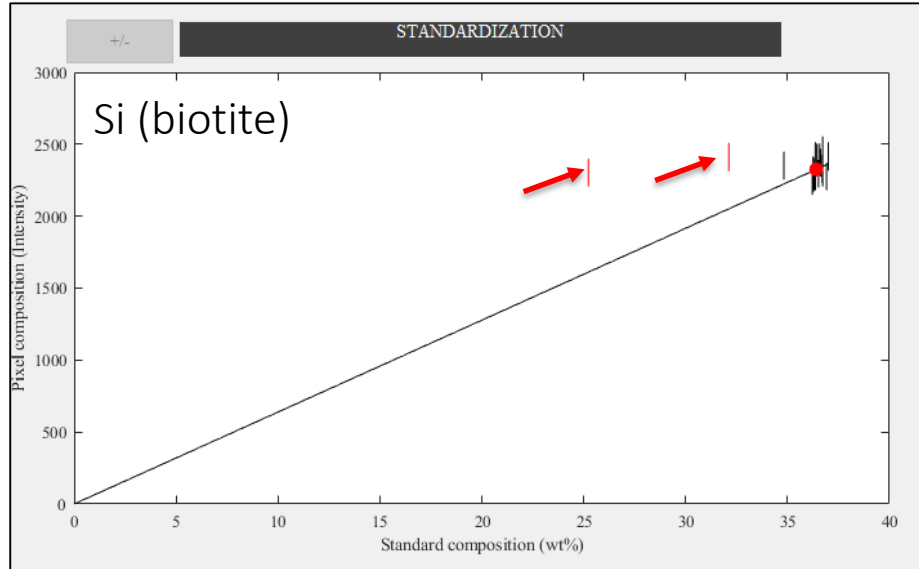
ANALYTICAL STANDARDIZATION IN XMapTOOLS

Standardize the phase *garnet* (method advanced): *Mg*



ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

Some outliers may come from the interference/pixels with close mineral phases (here chlorite and biotite)



ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

The screenshot displays the XMapTools software interface. The top menu bar includes 'Xray', 'Quanti', and 'Results'. The main workspace shows a map of Si intensity with a color scale from 2100 to 2550. A dropdown menu for 'Select Correction' is open, listing various correction tools. The 'BRC' (Border removing correction) option is highlighted. A callout box points to this option, explaining its function.

Select Correction

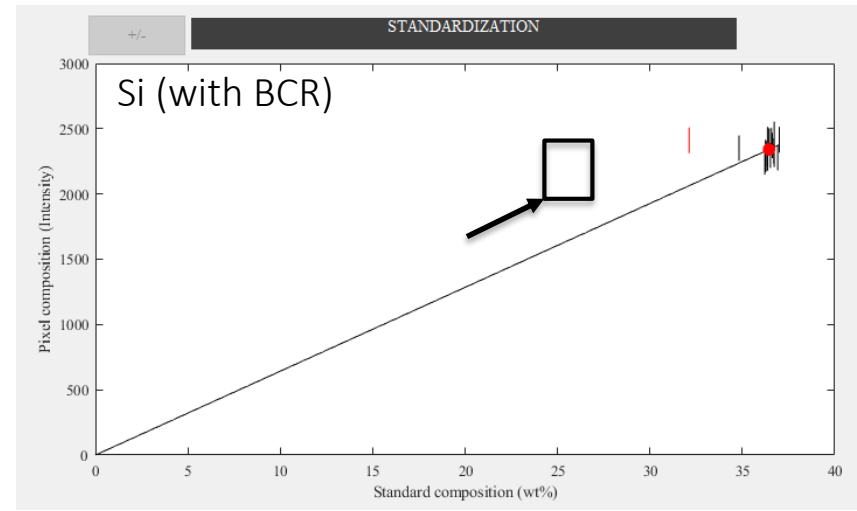
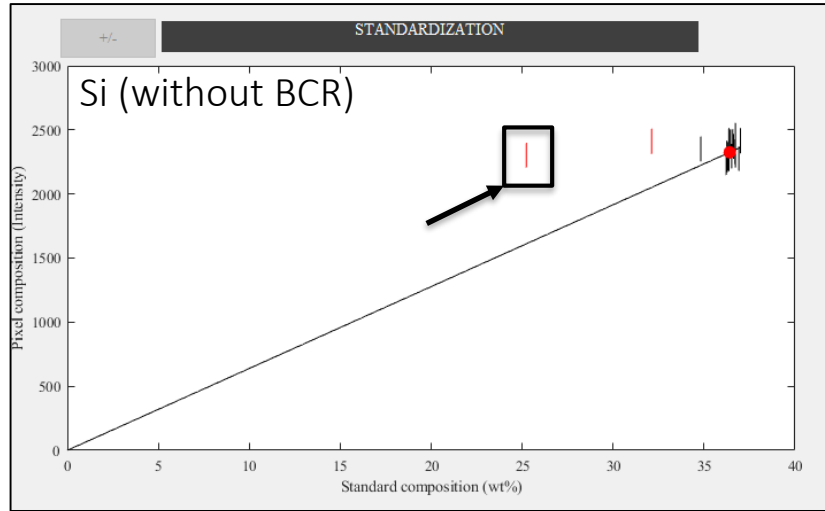
- [BRC] Border removing correction
- [TRC] TOPO-related correction
- [MPC] Map position correction tool
- [SPC] Standard position correction tool
- [IDC] Intensity drift correction
- [BA1] Background correction (using maps)
- [RM1] Clean pixels (area; all maps)

Check by applying the 'border' correction (BRC) that remove the boundray pixels of a selected phase

X-ray Raw data (Intensity) - Si

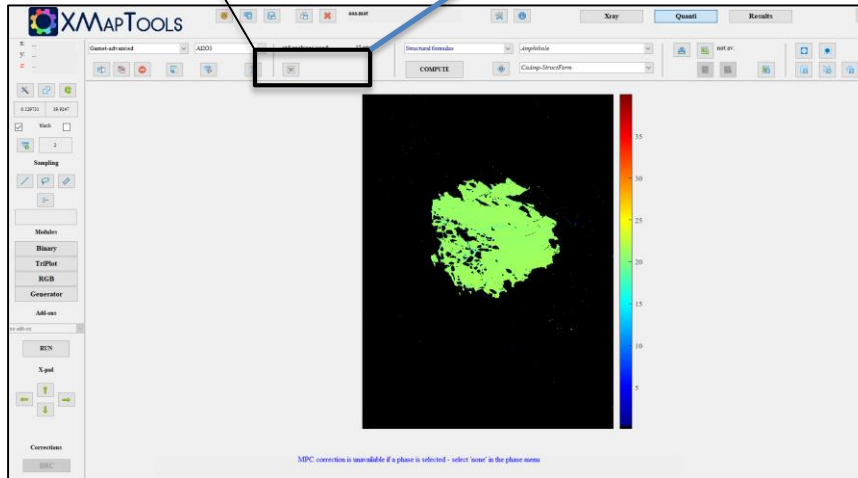
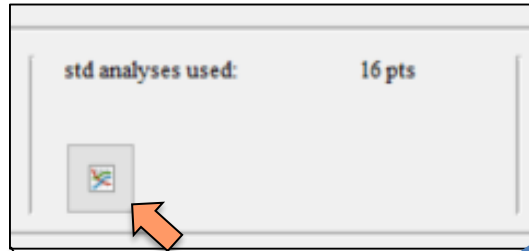
ANALYTICAL STANDARDIZATION IN XMapTOOLS: PRACTICAL EXERCISE

Advance standardization (Chlorite)

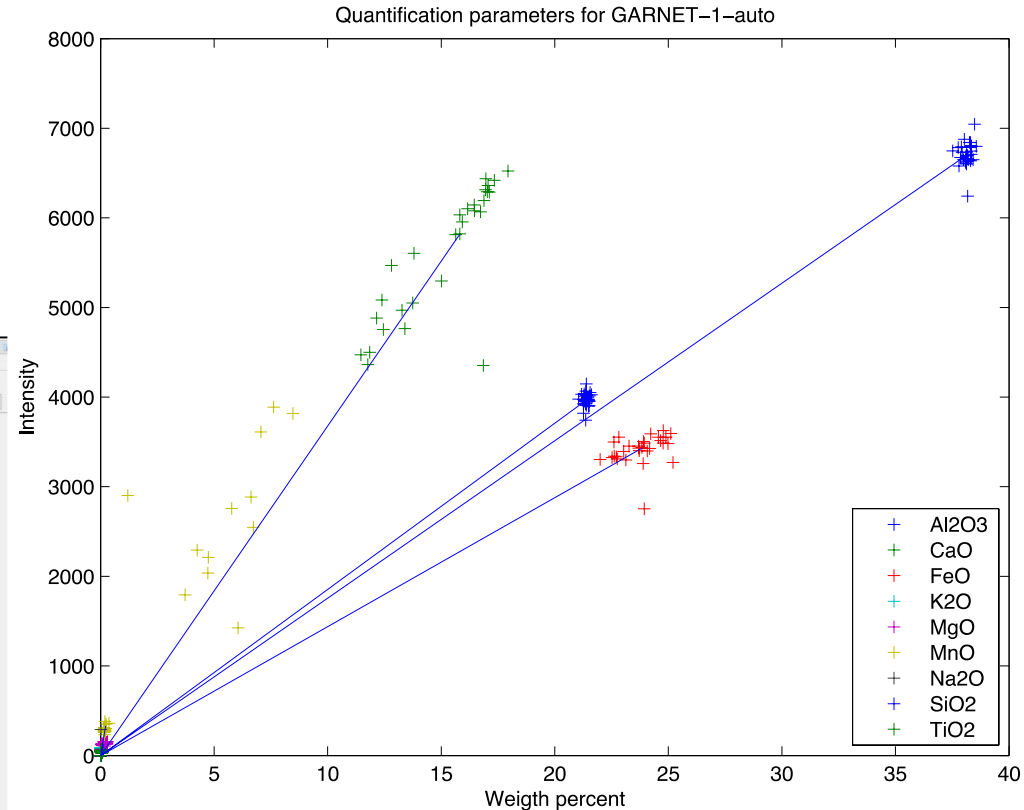


ANALYTICAL STANDARDIZATION IN XMapTOOLS

4. Check the quality of the map standardization (in 'Quanti')



Standardized maps vs spot analyses



QUESTIONS / DISCUSSION

