SIR-FP Tutorial

Note: This tutorial describes the use of the Scattered-Intensity Ratio method (SIR-FP).

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DOCUMENT CHANGE LOG

Date	Person	Pages	Description
20-Jun-13	Sarah Cross	All	Created document for SIR-FP Tutorial
01-Jul-13	Sarah Cross	Most	Updated document
23-Jul-13	Sarah Cross	Most	Updated document
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10-Sep -13	Sarah Cross / Brian Cross	Most	Updated document

1 SIR-FP OVERVIEW

What is SIR-FP (Scattered-Intensity Ratio with FP)? The SIR-FP method uses information from the Rayleigh and Compton scatter peaks to provide additional information about elements in a sample (typically elements with low atomic numbers) that cannot be analyzed using the FP method, because their x-ray lines are not detectable. The SIR-FP method can estimate the low atomic number fraction in sample analysis. Knowledge of these low Z elements is important as it permits one to better correct and account for FP matrix effects, thereby improving the accuracy of the elements that are detectable.

The SIR-FP option allows the user to select a series of TFR files that have been created from deliberately low-Z (atomic number) standards. Calibration of these standard files calculates a least-squares fit of the C/R (Compton-to-Rayleigh) ratios as a function of the mean Z of the material. Using this calibration one can then go on to do an FP calibration using single or multiple standards.

The complete SIR-FP method calibration requires both the SIR calibration as well as an FP calibration. The FP calibration can either be single or multi-standard (MLSQ). SIR **cannot** be used with standardless FP.

Note: The SIR-FP method should not be used in conjunction with the Peak-to-Compton method otherwise these two methods would be in direct conflict.

2 SIR-FP APPLICATION

The following procedure along with associated spectra (*.mca) and application (*.tfr) files guides an XRS-FP software user through the SIR-FP calibration and subsequent analysis. This includes:

1. SIR calibration using low-Z standards
2. Integrating the SIR calibration with a single standard FP calibration
3. Integrating the SIR calibration with a MLSQ FP calibration

4. Analysis of an unknown using the complete SIR-FP method

The same SIR-FP method is also available for the multilayer FP software, XRS-MTFFP.

Please note that spectra collected for the SIR and the FP calibrations must be obtained under the same conditions. The same is true for the analysis of unknowns using the SIR-FP calibrations.

This tutorial was created using the analysis of rocks as an example. Secondary standards with varying atomic number (from low Z, such as carbon, to medium Z, such as Ti) will form the basis of the SIR calibration. This calibration will construct a least-squares fit of C/R ratios vs. Z for all the standards. It is recommended that at least 6 standards are used for this method. Following the SIR calibration, an FP calibration will be described for all measured elements. Combining the SIR and FP calibrations will then allow analysis of "unknown" samples.

*It is recommended that you keep two full copies of the "SIR-FP Tutorial" folder on your computer. One will serve as the "working" folder and the other will be the "backup" folder, as some files will be overwritten during the tutorial.

3 PROCEDURE

1. Launch XRS-FP – Click anywhere on the splash screen to remove it from the display.

2. From the Auto-Mode FP Analysis window, click Expert Mode (Fig. 1 below). This will show the contents of the "Master.tfr" file (see section 4.1 of the "XRS-FP Software Guide" for additional information on loading the software).

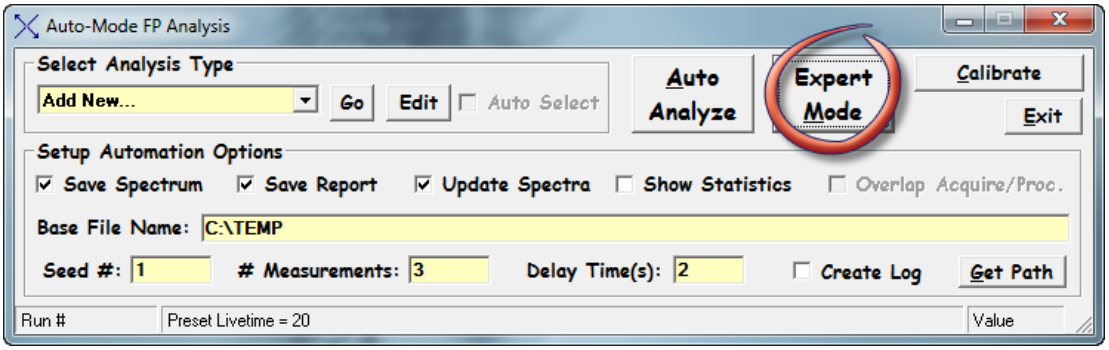


Figure 1. Auto-Mode FP Analysis Panel. Select the "Expert Mode" button.

SIR Calibration:

3. From the XRS-FP Expert Panel: Select **File** -> **Open** -> **"C:\CrossRoads Scientific\SIR-FP Tutorial\SIR Files\Initial.tfr**" (or equivalent file location). See Figure 2 below.

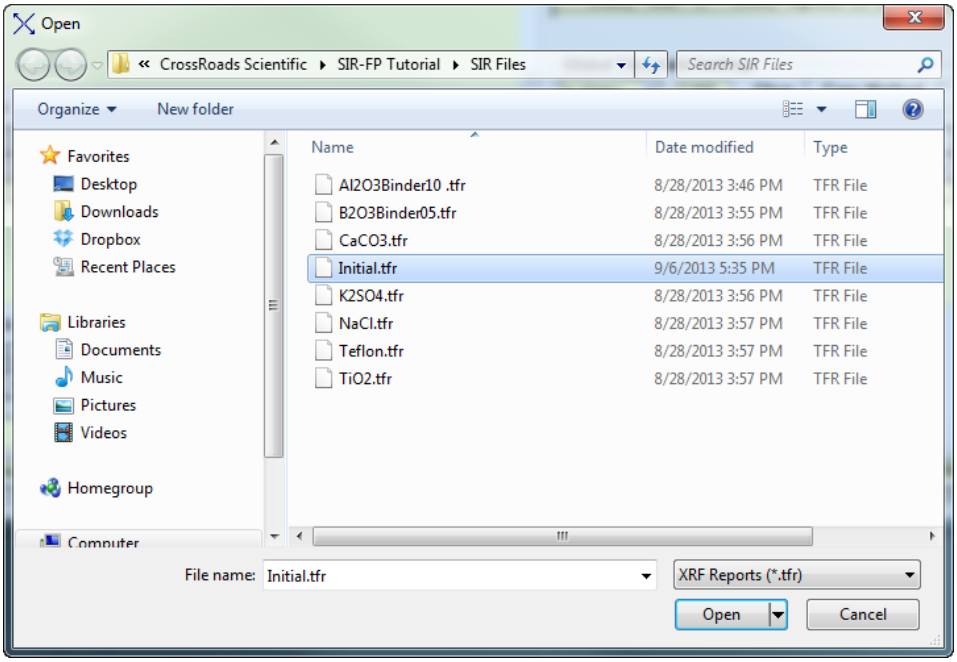


Figure 2. File Open Menu. Open the "Initial.tfr" file under the "SIR Files" folder. This file acts as a template for this application.

This TFR file acts as a template for this application. Although the Component Table, Elements Table and Thickness information have no data at this point, the Measurement & Processing information (spectrometer configuration) is already pre-defined and loaded for this application. Note: if there is data in the "Measurement & Processing Conditions" Table in the Compton and

Rayleigh columns under the "Processing" radio button, **un-check and then re-check the "C/R Ratio" box**. This will clear the Compton and Rayleigh data in this table and create a "clean sheet" to begin the application (see Fig. 3).

Note that since the Compton and Rayleigh regions of interest (ROIs) are zero, the Gaussian deconvolution for the spectrum processing will automatically assign the regions for the first sample analyzed. For more information on setting and using ROIs see the section "Process Spectrum – Compton Peak" in the "XRS-FP Software Guide."

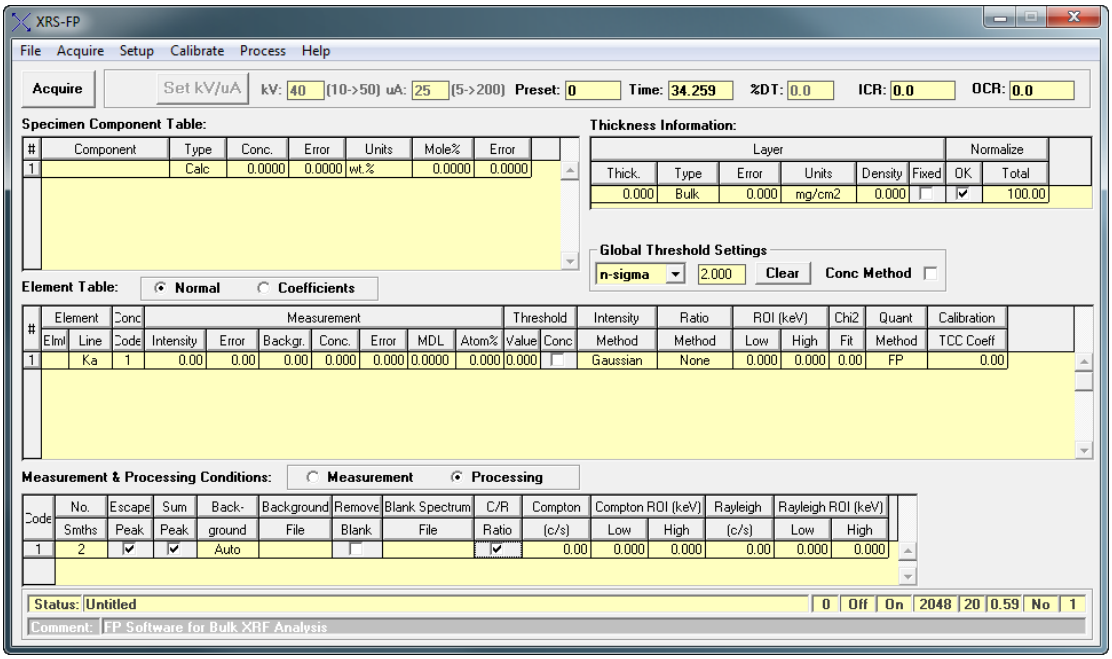


Figure 3. XRS- FP Expert Panel. The "Initial.tfr" file acts as a template for this application. Note that this file inputs the proper Measurement & Processing information for this application (i.e. spectrometer configuration information).

4. From the XRS-FP Expert Panel: Select **Setup** -> **Processing** and make sure all parameters are identical to those shown below in Figure 4. Select "OK" to exit the dialog and save the parameters.

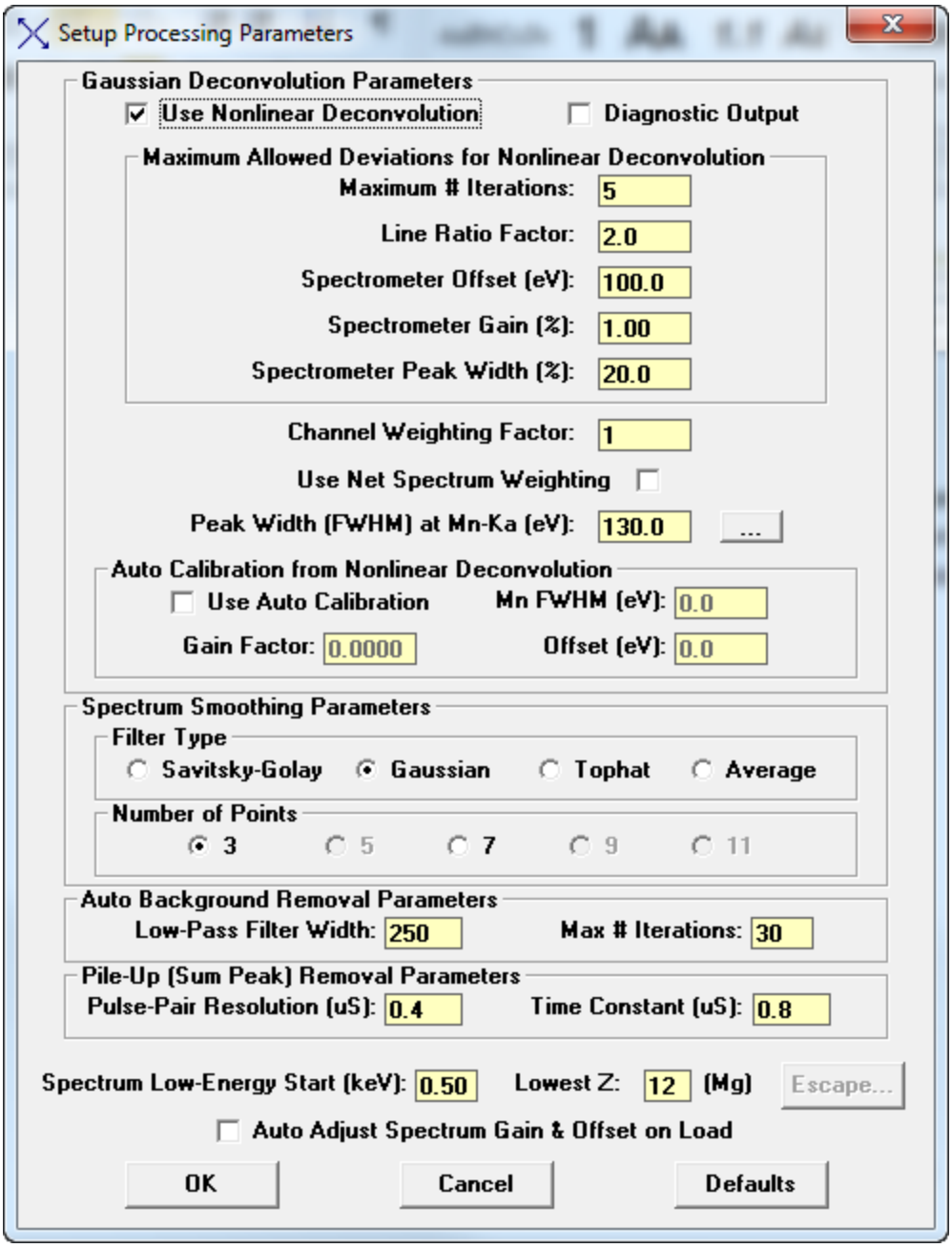


Figure 4. Setup Processing Parameters Dialog. Check that all parameters are as shown here.

5. Now from the XRS-FP Expert Panel: Select **File** -> **Open** -> **"…SIR-FP Tutorial\SIR Files\Al2O3Binder10.mca**" (this is the MCA spectrum file for our 1st low-Z standard). See Figure 5 below. Note that the spectra for this tutorial are already adjusted and in calibration.

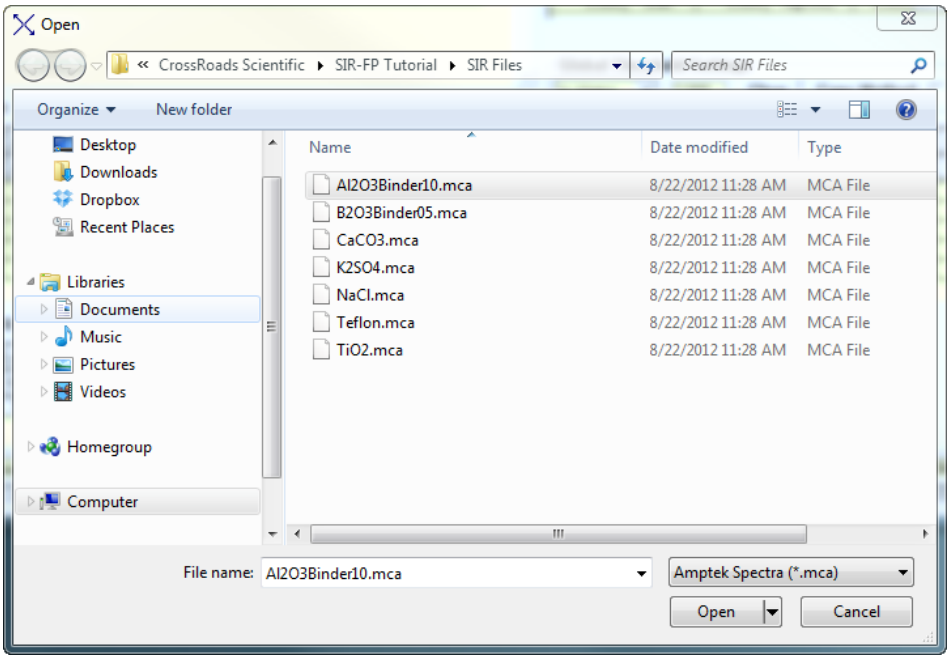


Figure 5. File Open Menu. Open the first low-Z standard *.mca file (e.g. Al2O3Binder10.mca) under the "SIR Files" folder.

6. Enter the component information in the "Specimen Component Table" (see Fig. 6). For this first low-Z standard ("Al2O3Binder10") enter the following components: "H74C37ON" then click "enter" (which will fill the individual elements in the "Element Table"), then "Al2O3" and "enter". Set the "Concentration" to 10 and 90 wt.% respectively.

Note that the Layer "Type" is set to "Bulk" in the "Thickness Information" table (which is mandatory for use with an SIR-FP calibration) and it is "Normalized" to a "Total" of 100% (see Fig. 6 below).

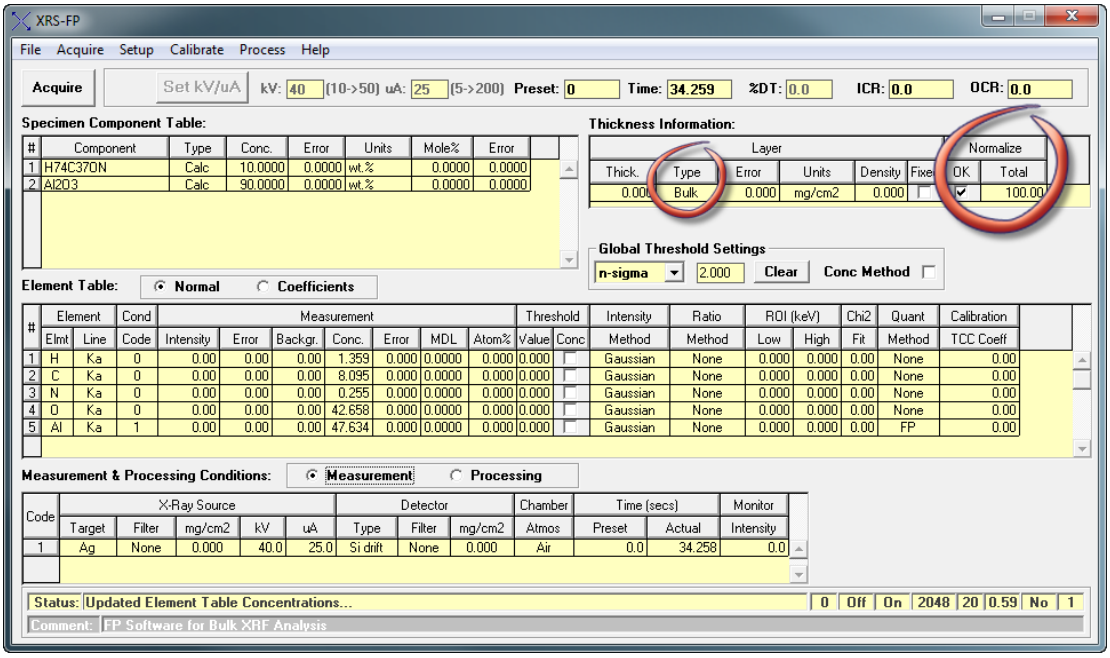


Figure 6. XRS- FP Expert Panel. Note the component information of the low-Z standard is entered in the "Specimen Component Table" and the thickness is set to "Bulk" and "Normalized" to 100% in the "Thickness Information" table.

Also note that the **"C/R Ratio" checkbox is selected** under the "Processing" conditions set in the "Measurement & Processing Conditions" Table (see Fig. 7). This must be selected for use with the SIR-FP calibration.

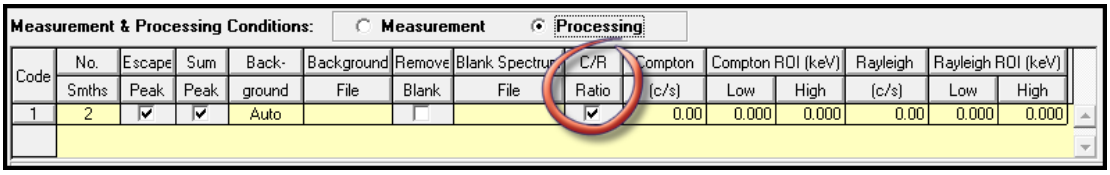
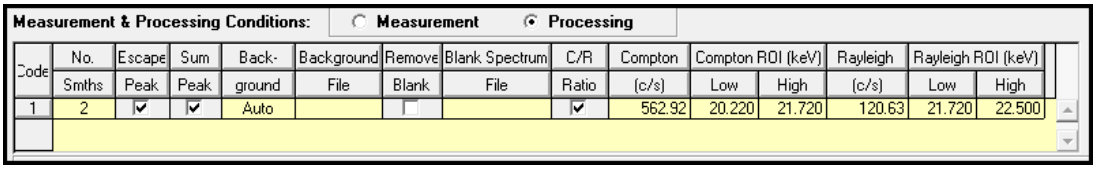


Figure 7. Measurement & Processing Conditions Table. Note that the "C/R Ratio" box is selected under the "Processing" conditions.

> Note: All processing conditions must be the **SAME** for all MCA files used in the SIR-FP calibration.

7. From the XRS-FP Expert Panel: Select **Process** -> **Spectrum** -> **All.** Notice that there is now data for the Compton (c/s), Compton ROI (keV), Rayleigh (c/s) and Rayleigh ROI (keV) columns in the "Processing Conditions" table (see Fig. 8). Note that the Compton (c/s) and Rayleigh (c/s) values may vary due to the background removal during processing.



Measurement & Processing Conditions: ○ Measurement ◉ Processing

Code	No. Smths	Escape Peak	Sum Peak	Back-ground	Background File	Remove Blank	Blank Spectrum File	C/R Ratio	Compton (c/s)	Compton ROI (keV) Low	Compton ROI (keV) High	Rayleigh (c/s)	Rayleigh ROI (keV) Low	Rayleigh ROI (keV) High
1	2	☑	☑	Auto		☐		☑	562.92	20.220	21.720	120.63	21.720	22.500

Figure 8. Measurement & Processing Conditions Table. Data is shown under the Compton and Rayleigh columns after spectrum processing.

8. Now save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as "Al2O3Binder10.tfr" or as an alternate filename of choice.

9. **REPEAT steps 5 - 8** above for **ALL** the low-Z standards within the SIR folder. Remember to enter the components that correspond to the loaded MCA file for each standard. Also, check that the layer information is normalized to 100% and the C/R Ratio in the Processing Conditions table is checked. Do not clear the C/R information between standards, because we want to use the same Compton and Rayleigh ROIs. After processing the spectrum, remember to save the TFR file before moving on to the next standard! The following figures (Fig. 9-14) show screen shots of the XRS-FP Expert Panel for each of the remaining 6 SIR low-Z standards (data shown is after completion of step 8 above for each standard):

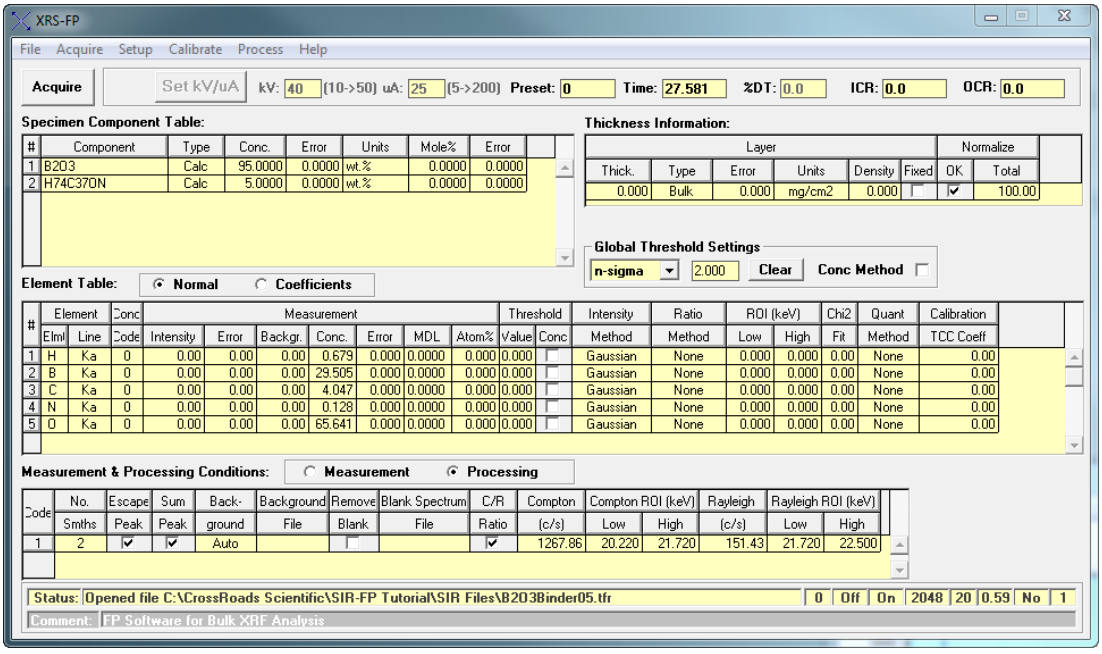


Figure 9. XRS- FP Expert Panel. Data after processing B2O3Binder05.mca.

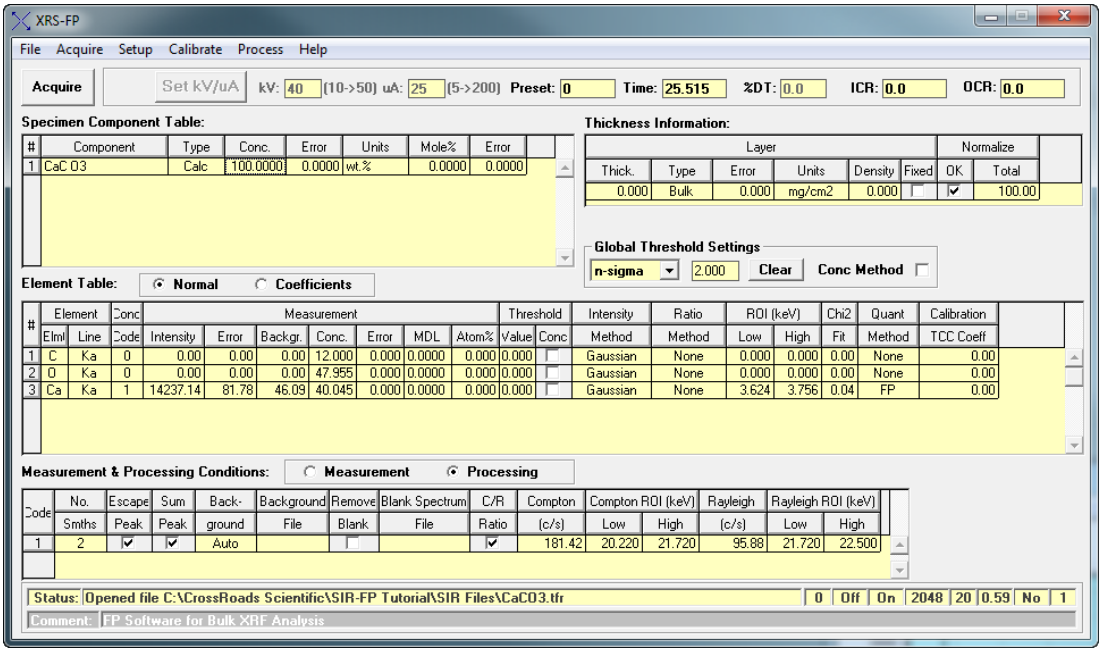


Figure 10. XRS- FP Expert Panel. Data after processing CaCO3.mca. Note that in order for XRS-FP to process the carbon and oxygen elements in this low-Z standard, the compound MUST be entered as "CaC O3" in the "Component Table", i.e. with a space between the C and the O. Also be sure to enter "O" for oxygen, as the number "0" will not be recognized as the element oxygen!

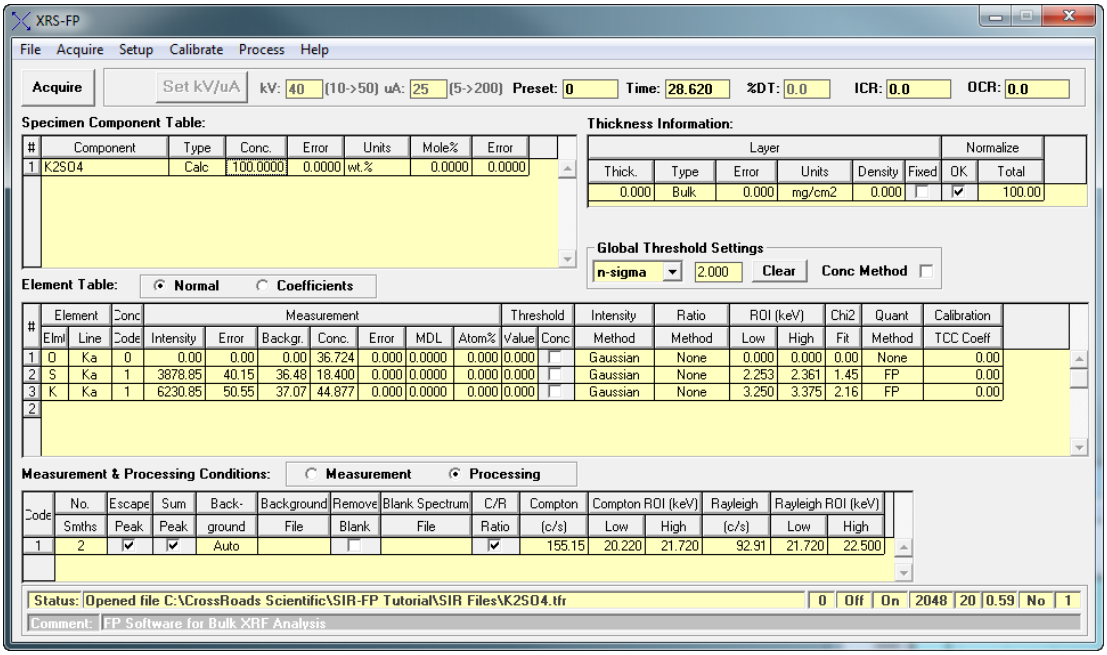


Figure 11. XRS- FP Expert Panel. Data after processing K2SO4.mca.

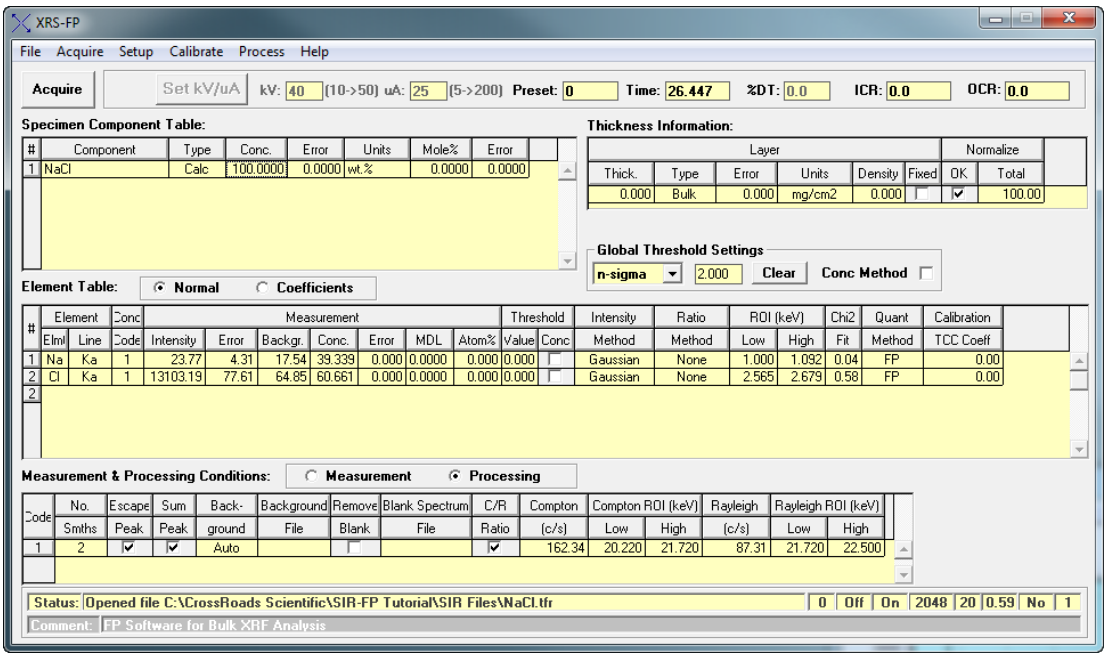


Figure 12. XRS- FP Expert Panel. Data after processing NaCl.mca.

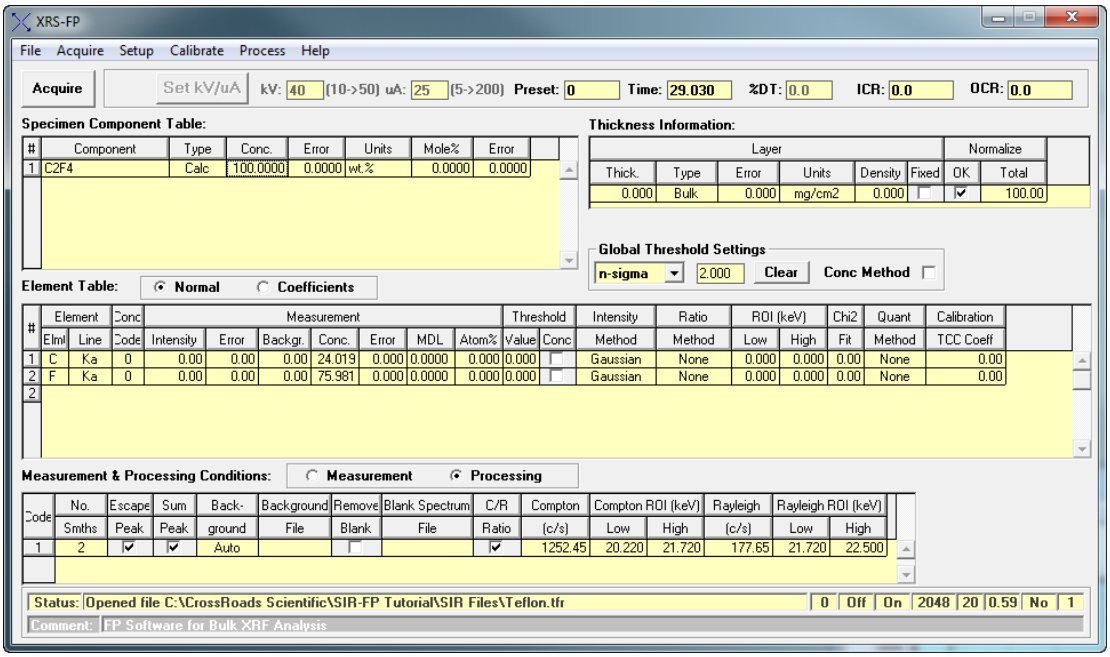


Figure 13. XRS- FP Expert Panel. Data after processing Teflon.mca.

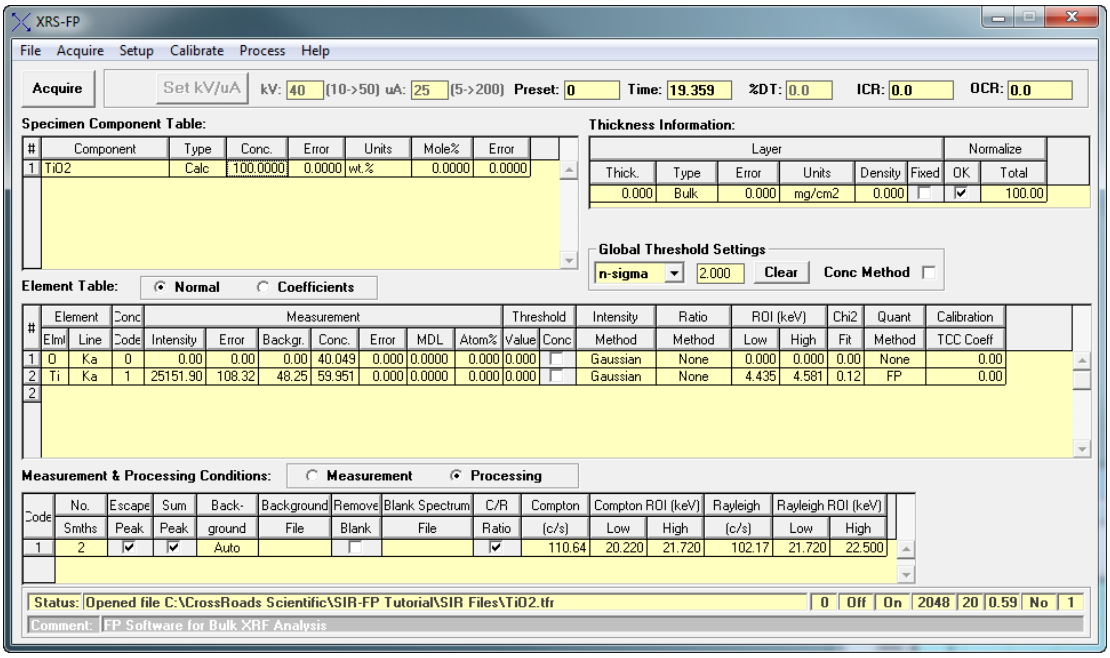


Figure 14. XRS- FP Expert Panel. Data after processing TiO2.mca.

10. Now go to the XRS-FP Expert Panel: Select **Calibrate** -> **SIR-FP.** This will display the "SIRFP Files for Calibration of C/R Ratios vs. Mean-Z" dialog. Double click in the "TFR Filename" cell to select the TFR filenames to be used for calibration (i.e. the *tfr files created above for all the low-Z standards). See Figure 15 below. To add additional TFR files (standards) simply use the down-arrow key to add a row. After each TFR file is loaded the Mean Z and C/R Ratio for that standard is displayed in appropriate columns (Fig 15). Note: a previously created SIR calibration file can also be loaded instead of loading each TFR file in turn.

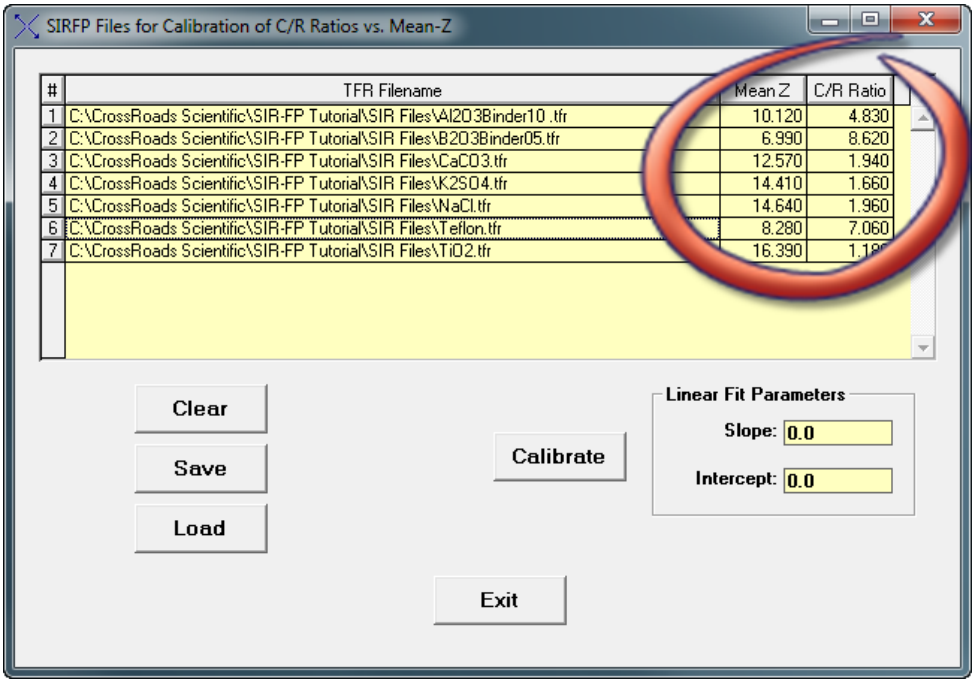


Figure 15. SIRFP Files for Calibration of C/R Ratios vs. Mean-Z Dialog. TFR files created from the low-Z standards are entered. The associated Mean Z and C/R Ratio are displayed for each file.

11. Once <u>all</u> the TFR files have been loaded (see above), click on the **"<u>Calibrate</u>"** button to do the least-squares fit of the two variables (C/R Ratio vs. Mean Z). Note: each of the variables is actually converted to a log function so that the scope can cover a wider range in detail. It was found that log-log plots produced better linear fits that the straight linear fitting.

At this point there should be a plot that looks like the following (see Fig. 16).

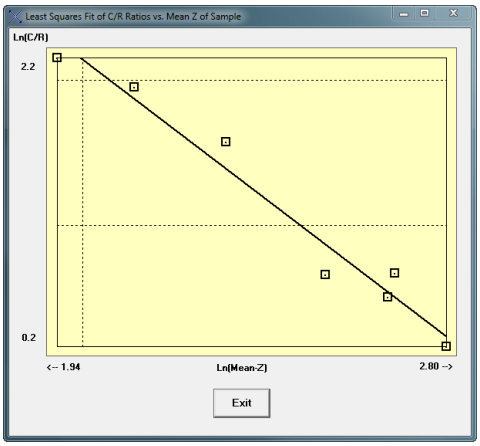


Figure 16. Least Squares Fit of C/R Ratios vs. Mean-Z of Sample. The resulting calibration curve is displayed Ln(C/R) vs. Ln(Mean-Z).

12. Click on the "Exit" button in the least-squares plot above (Fig. 16) and then click on the "**Save**" button (Fig. 17 below) to save the full SIR-FP calibration as an *.sir file (i.e. "Tutorial.sir"). Then click on the "Exit" button.

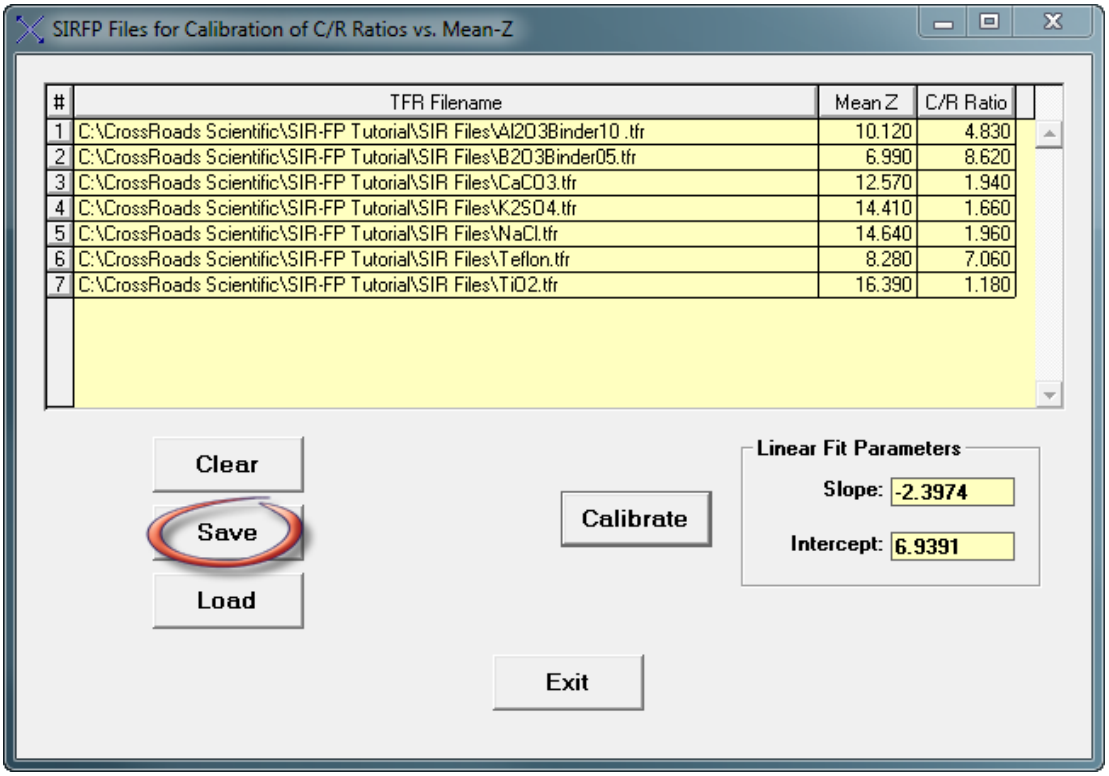


Figure 17. Saving the SIR-FP Calibration file. The SIR-FP calibration is saved as an *.sir file using the "Save" button.

Note: For practical applications, if the tube or any parameter is changed, then the entire calibration must be done again using the actual standards and live acquisition.

Single Standard FP Calibration:

13. Having completed the calibration of the low-Z standards and obtained an SIR calibration file (*.sir), we will now make a single standard FP calibration as the next step. Select **File** -> **Open** -> **"C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\RockStd1.tfr**" (or equivalent file location).

14. Now open the corresponding spectrum file from the XRS-FP Expert Panel: Select **File** -> **Open** -> **"…SIR-FP Tutorial\FP Files\RockStd1.mca**"

15. Select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel.

16. Then from the XRS-FP Expert Panel: Select **Setup** -> **Quant.** This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 18. Select the radio buttons for "Fundamental Parameters" with "**One Standard**". Then click OK.

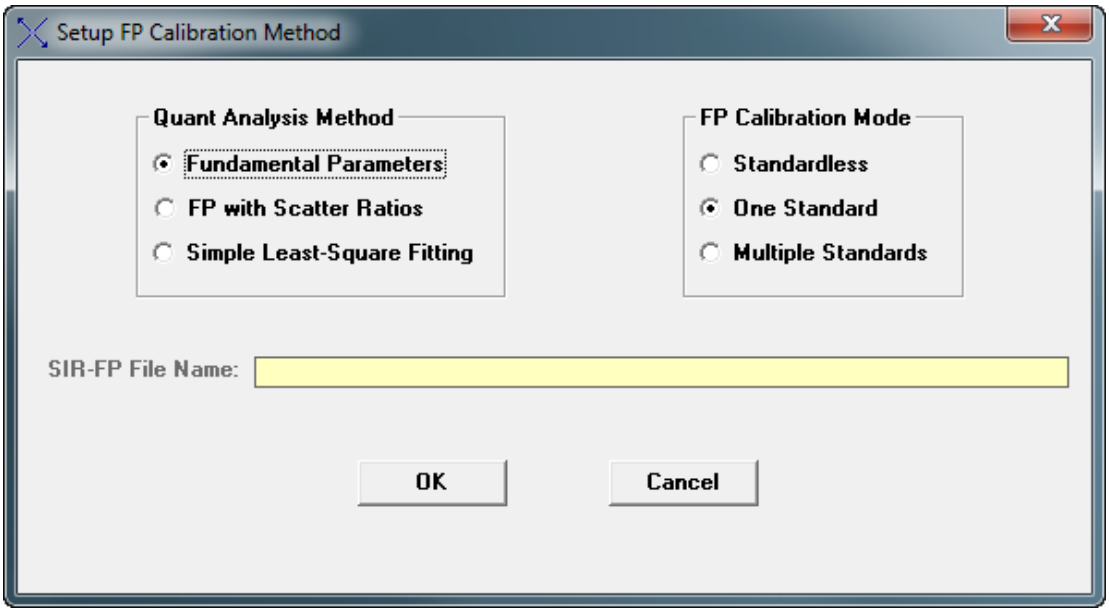


Figure 18. Setup FP Calibration Dialog. For the single standard FP calibration select the radio buttons for "Fundamental Parameters" with "One Standard." Then select "OK" to exit.

17. Now select: **Calibrate** -> **FP** from the XRS-FP Expert Panel. This generates TCC's which are populated under the "Calibration TCC Coefficients" column in the "Element Table" (see Fig. 19 below).

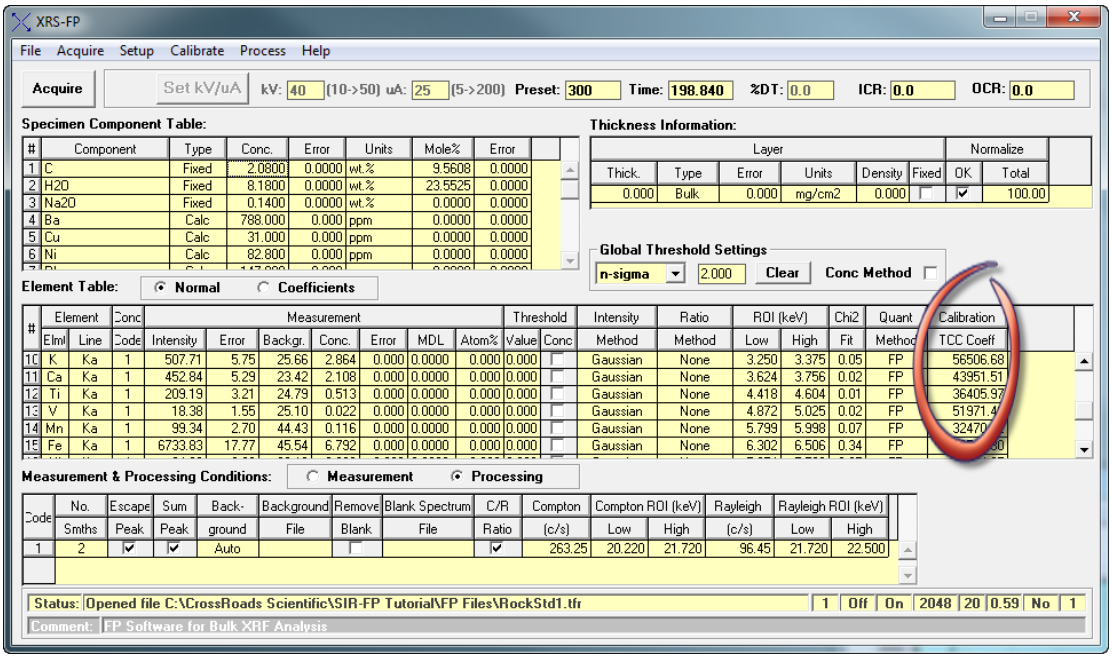


Figure 19. XRS- FP Expert Panel. Calibration coefficients (TCCs) are generated after selecting "Calibrate -> FP."

18. Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be re-saved as "RockStd1.tfr" or as an alternate filename of choice.

19. Having obtained the TFR file above, select **Setup** -> **Quant.** This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 20. Now we want to combine the single standard FP calibration with the previously obtained SIR calibration. To do this, select the radio buttons for "**FP with Scatter Ratios**" with "**One Standard.**" In the "SIR-FP File Name" text box double click to add the SIR file saved from the SIR calibration in step 12 above (e.g. Tutorial.sir). Then click "OK".

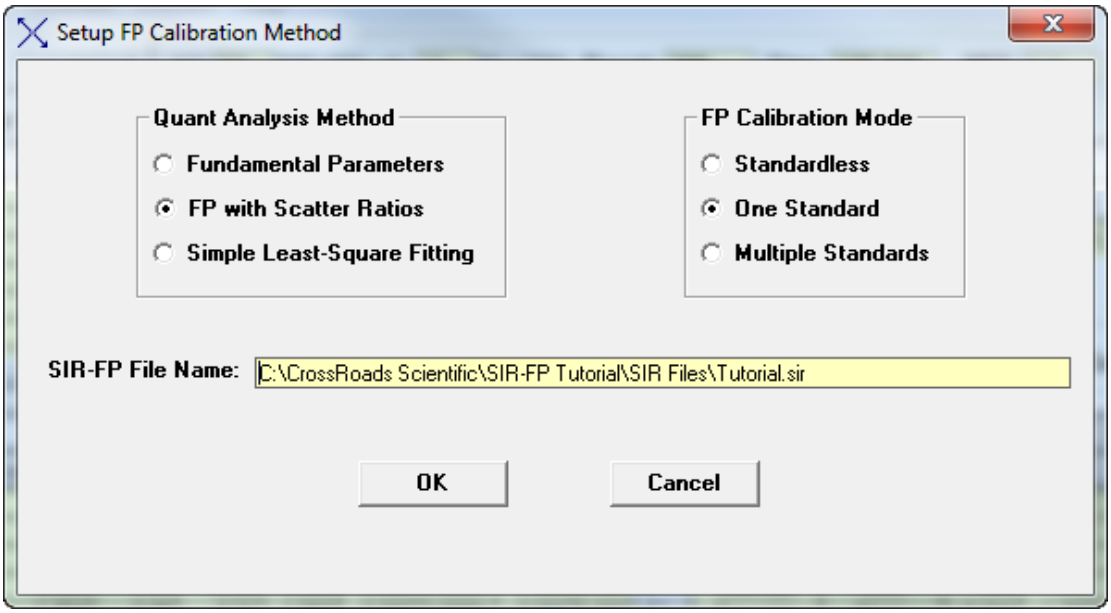


Figure 20. Setup FP Calibration Dialog. To combine the single standard FP calibration with the previously obtained SIR calibration, select the radio buttons for "**FP with Scatter Ratios**" with "One Standard." Then select "OK" to exit.

20. This will bring up the dialog shown in Figure 21. Select **"Yes"** to "Reset All Elements to the SIRFP method?"

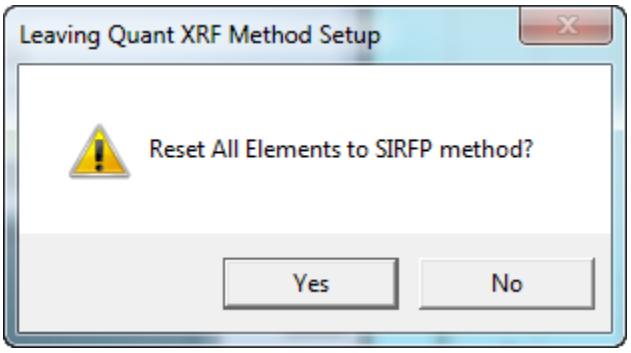


Figure 21. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to the SIRFP method.

21. Now save the full FP and SIR calibration TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be re-saved as "FP_Cal_File_SIRFP.tfr" or as an alternate filename of choice. This TFR file contains a link to the SIR file created previously (i.e., Tutorial.sir).

22. At this point we are ready to define a sample for analysis. From the XRS-FP Expert Panel set-up the "Component Table" for an "unknown". Clear the 3 "fixed" element lines at top (i.e. C, H2O and Na2O). Add 2 lines at the bottom of the "Component Table". These are "fictional elements" at this point. The Component name is left blank (see Fig. 22 below). Set the "Type" for these two lines as "SIR-FP" (all other "Components" are set to "Calc"). Check that the "Thickness Information"

Table is “Normalized” (check box selected) to 100%. Note that oxygen is determined by stoichiometry.

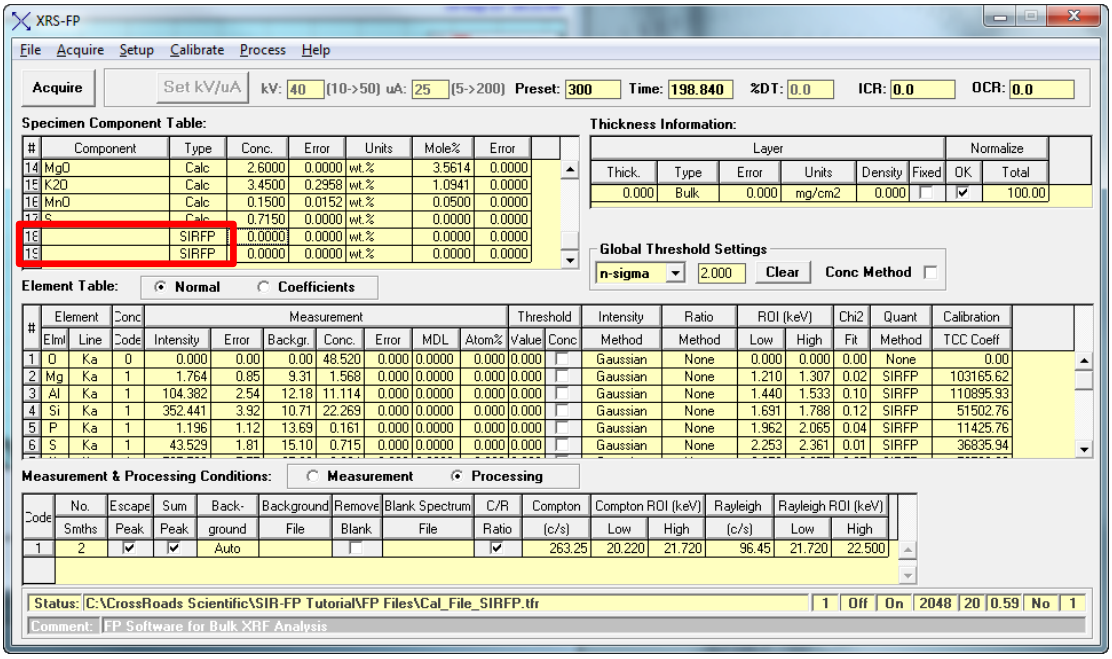


Figure 22. XRS- FP Expert Panel. Add two blank rows at the bottom of the “component Table” to be used for the SIR-FP elements in the analysis of the “unknown” sample.

23. From the XRS-FP Expert Panel open an “unknown” spectrum. For the purpose of this tutorial select **File** -> **Open** -> **“…SIR-FP Tutorial\FP Files\UnknownRock.mca.**”

24. Now select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel.

25. Then select: **Process** -> **Analyze.**

26. Now save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as **“C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\UnknownRock_FP-SIR_AutoZ.tfr”** or as an alternate filename of choice. See figure 23 below to compare the data

obtained from the analysis of the “unknown” sample.

Layer Table

#	Thick	Type	Error	Units	Density	Norm.	Total
1	0.00	Bulk	0.00	mg/cm2	0.00	On	100.00

Sample Table

Layer	Component	Type	Concn.	Error	Units	Mole%	Error
1	Ba	Calc	795.11	116.858	ppm	0.030	0.004
1	Cu	Calc	189.61	4.765	ppm	0.016	0.000
1	Ni	Calc	83.469	10.919	ppm	0.007	0.001
1	Rb	Calc	148.32	8.630	ppm	0.009	0.001
1	Sr	Calc	179.60	9.133	ppm	0.011	0.001
1	V	Calc	221.74	26.440	ppm	0.023	0.003
1	Zr	Calc	135.21	8.487	ppm	0.008	0.000
1	P2O5	Calc	0.373	0.492	wt.%	0.138	0.182
1	SiO2	Calc	48.033	0.755	wt.%	42.057	0.661
1	TiO2	Calc	0.862	0.019	wt.%	0.568	0.012
1	Al2O3	Calc	21.174	0.728	wt.%	10.925	0.375
1	Fe2O3	Calc	9.787	0.037	wt.%	3.224	0.012
1	CaO	Calc	2.974	0.049	wt.%	2.790	0.046
1	MgO	Calc	2.622	1.789	wt.%	3.422	2.335
1	K2O	Calc	3.478	0.056	wt.%	1.942	0.031
1	MnO	Calc	0.151	0.006	wt.%	0.112	0.004
1	S	Calc	0.721	0.042	wt.%	1.183	0.070
1	N	SIRFP	3.851	0.000	wt.%	14.466	0.000
1	O	SIRFP	5.799	0.000	wt.%	19.069	0.000

Element Table

Elmt	Line Code	Cond Code	Ratio Method	Intensity (c/s)	Error (c/s)	Intensity Method	Conc.	Conc Method	Calibration Coefficient
O	Ka	0	None	0.000	0.0000	Gaussian	41.558	None	0.000
Mg	Ka	1	None	1.764	0.8510	Gaussian	1.581	SIRFP	103165.600
Al	Ka	1	None	104.382	2.5362	Gaussian	11.207	SIRFP	110895.900
Si	Ka	1	None	352.441	3.9165	Gaussian	22.453	SIRFP	51502.760
P	Ka	1	None	1.196	1.1151	Gaussian	0.163	SIRFP	11425.760
S	Ka	1	None	43.529	1.8118	Gaussian	0.721	SIRFP	36835.940
K	Ka	1	None	507.708	5.7542	Gaussian	2.887	SIRFP	56506.680
Ca	Ka	1	None	452.836	5.2860	Gaussian	2.125	SIRFP	43951.510
Ti	Ka	1	None	209.188	3.2137	Gaussian	0.517	SIRFP	36405.970
V	Ka	1	None	18.382	1.5499	Gaussian	0.022	SIRFP	51971.480
Mn	Ka	1	None	99.339	2.7048	Gaussian	0.117	SIRFP	32470.720
Fe	Ka	1	None	6733.831	17.7701	Gaussian	6.845	SIRFP	30515.300
Ni	Ka	1	None	24.885	2.3018	Gaussian	0.008	SIRFP	83404.870
Cu	Ka	1	None	93.348	2.3460	Gaussian	0.019	SIRFP	0.000
Rb	Ka	1	None	51.767	2.1297	Gaussian	0.015	SIRFP	45275.890
Sr	Ka	1	None	62.071	2.2318	Gaussian	0.018	SIRFP	47553.230
Zr	Ka	1	None	45.356	2.0131	Gaussian	0.014	SIRFP	49012.100
Ba	Ka	1	None	17.754	1.8450	Gaussian	0.080	SIRFP	3552374.000

Figure 23. Data from Unknown Sample (FP/SIR/AutoZ) . Data obtained from analysis of the unknown sample, “UnknownRock.mca,” using the single standard FP calibration, the SIR calibration and “Auto Z,” where the software estimates the two low-Z matrix elements.

27. Here is an example using the same single standard FP calibration as described above; however, rather than allowing the software to estimate the 2 low-Z elements they are entered by the user (i.e. fixed). This method is designed to be used if you know something about the unknown sample. For the tutorial we will use H and N as our “preferred elements” in “Component Table”. Enter these elements into the last two rows of the “Component Table.” Set the concentration (“Conc.”) to zero and select “Type -> SIR-FP” (Fig. 24). Also check that the thickness information is still normalized to a total of 100% (Fig. 24).

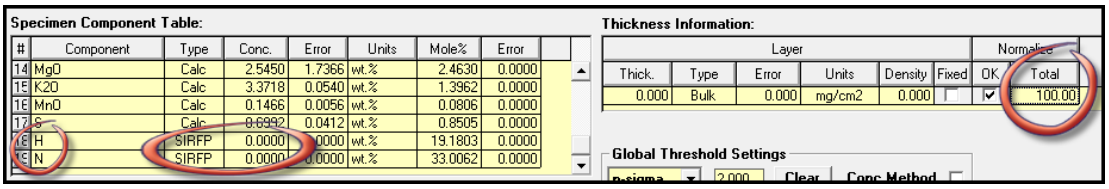


Figure 24. XRS- FP Expert Panel. Enter H and N as the two "fixed" elements in the "component Table."

28. Now select **Process** -> **Analyze** (again). This time to get the concentration for the two "fixed" elements, H and N.

29. Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as **"C:\CrossRoads Scientific\SIR-FP Tutorial\FP Files\UnknownRock_FP-SIR_FixedZ.tfr"** or as an alternate filename of choice. See figure 25 below to compare the data obtained from the analysis of the "unknown" sample.

Layer Table

#	Thick	Type	Error	Units	Density	Norm.	Total
1	0.00	Bulk	0.00	mg/cm2	0.00	On	100.00

Sample Table

Layer	Component	Type	Concn.	Error	Units	Mole%	Error
1	Ba	Calc	770.60	113.255	ppm	0.022	0.003
1	Cu	Calc	183.80	4.619	ppm	0.011	0.000
1	Ni	Calc	80.914	10.585	ppm	0.005	0.001
1	Rb	Calc	143.77	8.365	ppm	0.007	0.000
1	Sr	Calc	174.08	8.852	ppm	0.008	0.000
1	V	Calc	214.97	25.633	ppm	0.016	0.002
1	Zr	Calc	131.05	8.226	ppm	0.006	0.000
1	P2O5	Calc	0.362	0.477	wt.%	0.099	0.131
1	SiO2	Calc	46.617	0.733	wt.%	30.264	0.476
1	TiO2	Calc	0.835	0.018	wt.%	0.408	0.009
1	Al2O3	Calc	20.535	0.706	wt.%	7.856	0.270
1	Fe2O3	Calc	9.487	0.035	wt.%	2.317	0.009
1	CaO	Calc	2.883	0.048	wt.%	2.005	0.033
1	MgO	Calc	2.545	1.737	wt.%	2.463	1.681
1	K2O	Calc	3.372	0.054	wt.%	1.396	0.022
1	MnO	Calc	0.147	0.006	wt.%	0.081	0.003
1	S	Calc	0.699	0.041	wt.%	0.851	0.050
1	H	SIRFP	0.496	0.000	wt.%	19.177	0.000
1	N	SIRFP	11.853	0.000	wt.%	33.008	0.000

Element Table

Elmt	Line Code	Cond Code	Ratio Method	Intensity (c/s)	Error (c/s)	Intensity Method	Conc.	Conc Method	Calibration Coefficient
C	Ka	0	None	0.000	0.0000	Gaussian	0.000	None	0.000
N	Ka	0	None	0.000	0.0000	Gaussian	11.853	None	0.000
O	Ka	0	None	0.000	0.0000	Gaussian	40.321	None	0.000
Mg	Ka	1	None	1.764	0.8510	Gaussian	1.535	SIRFP	103165.600
Al	Ka	1	None	104.382	2.5362	Gaussian	10.868	SIRFP	110895.900
Si	Ka	1	None	352.441	3.9165	Gaussian	21.791	SIRFP	51502.760
P	Ka	1	None	1.196	1.1151	Gaussian	0.158	SIRFP	11425.760
S	Ka	1	None	43.529	1.8118	Gaussian	0.699	SIRFP	36835.940
K	Ka	1	None	507.708	5.7542	Gaussian	2.799	SIRFP	56506.680
Ca	Ka	1	None	452.836	5.2860	Gaussian	2.060	SIRFP	43951.510
Ti	Ka	1	None	209.188	3.2137	Gaussian	0.501	SIRFP	36405.970
V	Ka	1	None	18.382	1.5499	Gaussian	0.021	SIRFP	51971.480
Mn	Ka	1	None	99.339	2.7048	Gaussian	0.114	SIRFP	32470.720
Fe	Ka	1	None	6733.831	17.7701	Gaussian	6.636	SIRFP	30515.300
Ni	Ka	1	None	24.885	2.3018	Gaussian	0.008	SIRFP	83404.870
Cu	Ka	1	None	93.348	2.3460	Gaussian	0.018	SIRFP	0.000
Rb	Ka	1	None	51.767	2.1297	Gaussian	0.014	SIRFP	45275.890
Sr	Ka	1	None	62.071	2.2318	Gaussian	0.017	SIRFP	47553.230
Zr	Ka	1	None	45.356	2.0131	Gaussian	0.013	SIRFP	49012.100
Ba	Ka	1	None	17.754	1.8450	Gaussian	0.077	SIRFP	3552374.000

Figure 25. Data from Unknown Sample (FP/SIR/FixedZ) . Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the single standard FP calibration, the SIR calibration and "Fixed Z," where the user enters the two preferred ("fixed") low-Z matrix elements.

MLSQ Calibration:

30. Having completed the analysis of an "unknown" sample using a single standard FP calibration combined with the SIR calibration, we will now go on to use the MLSQ method to obtain an FP calibration from all non-low-Z elements. First, from the XRS-FP Expert Panel: Select **File** ->

Open -> **"C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\RockStd1.tfr**" (or equivalent file location). See Figure 26 below.

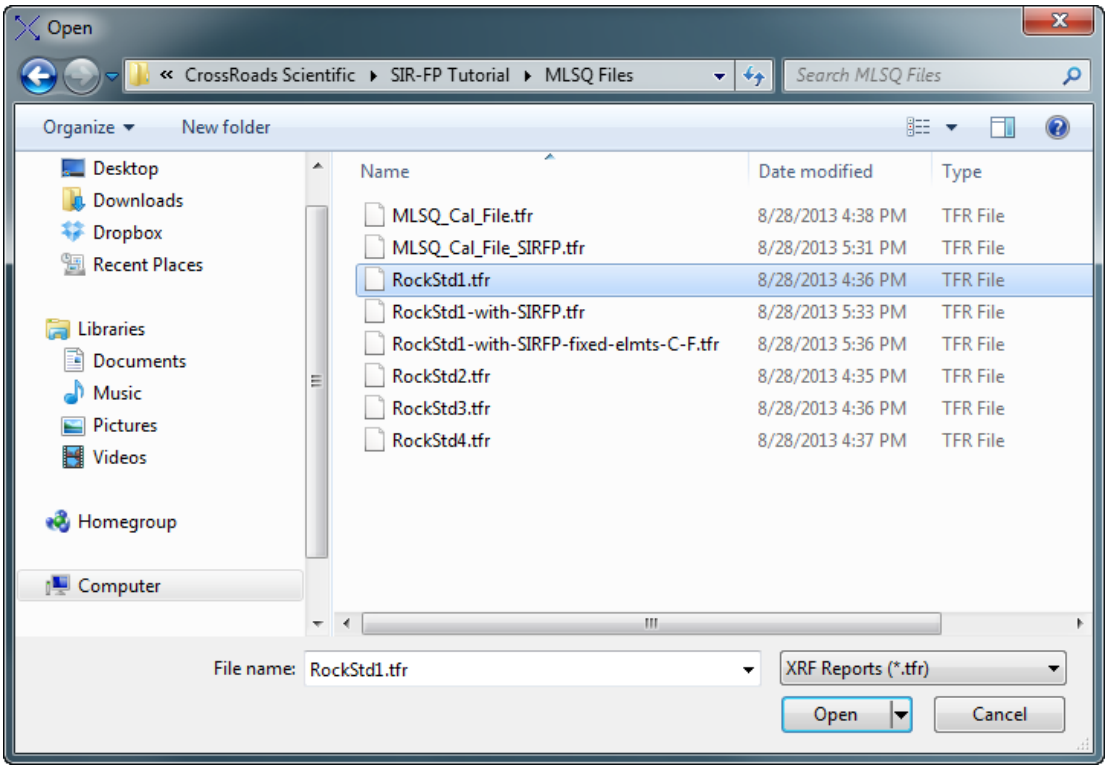


Figure 26. File Open Menu. Open the first MLSQ TFR file, e.g. "RockStd1.tfr".

31. Now from the XRS-FP Expert Panel: Select **File** -> **Open** -> **"…SIR-FP Tutorial\MLSQ Files\RockStd1.mca**" (this is the MCA spectrum file for our 1st MLSQ standard). A spectrum similar to that below in Figure 27 will be displayed. Note that the spectra for this tutorial are already adjusted and in calibration

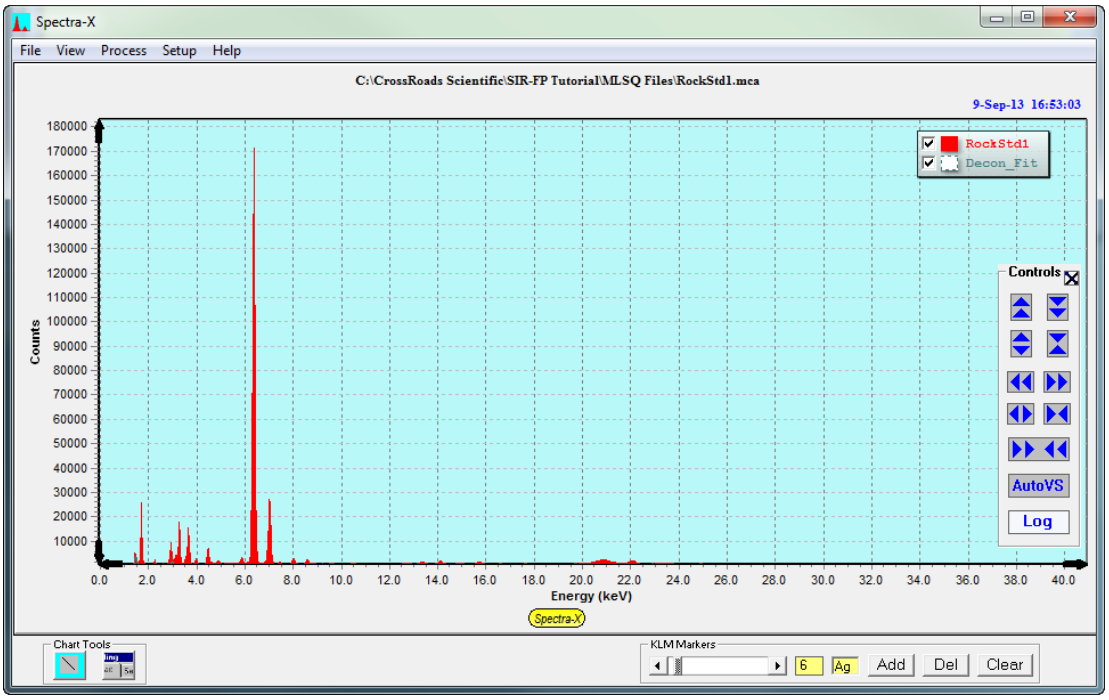


Figure 27. MLSQ Standard Spectrum. Spectrum for the first MLSQ standard, "RockStd1.mca".

32. Select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel.

33. Then from the XRS-FP Expert Panel: Select **Setup** -> **Quant.** This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 28. Select the radial buttons for "Fundamental Parameters" with "**One Standard**". Then click OK. Note it is important to select single standard as the "FP Calibration Mode" as each standard used for the MLSQ calibration will first be processed as a single standard and only later will these files be merged.

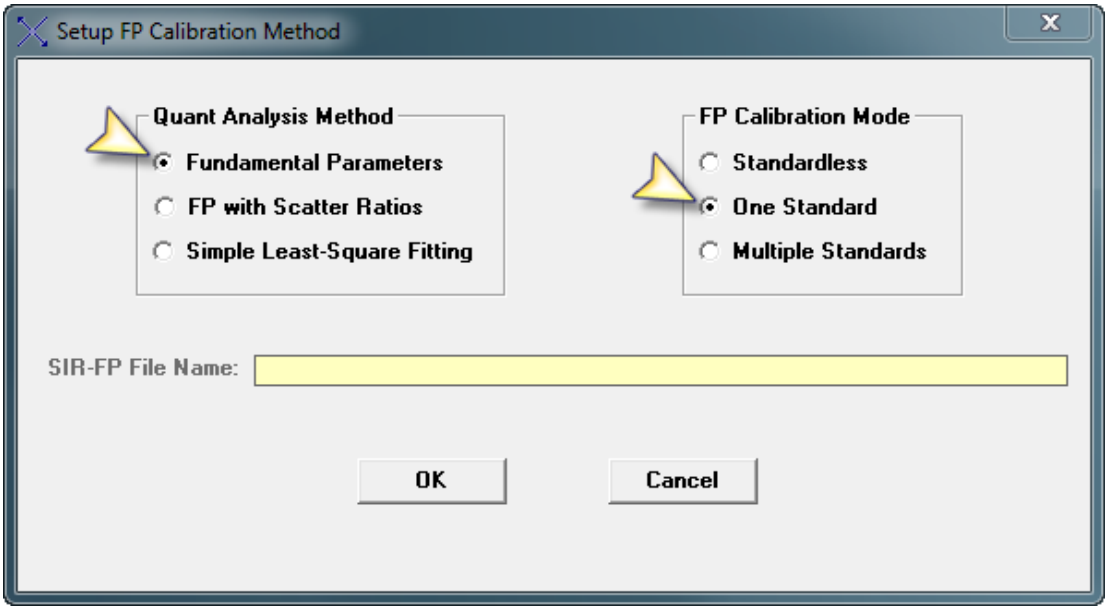


Figure 28. Setup FP Calibration Method. Select "Fundamental Parameters" for the "Quant Analysis Method" and "**One Standard**" for the "FP Calibration Mode".

34. Now select: **Calibrate** -> **FP** from the XRS-FP Expert Panel. This generates TCC's which are populated under the "Calibration TCC Coefficients" column in the "Element Table".

35. Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be re-saved as "RockStd1.tfr" or as an alternate filename of choice.

36. **REPEAT steps 30-35** above for **ALL** the individual MLSQ standards within the "MLSQ Files" folder. Remember to select "Fundamental Parameters" with "One Standard" under the "Setup -> Quant" Dialog for each of the four MLSQ standards (i.e. "RockStd1", "RockStd2", "RockStd3", "RockStd4").

37. Having obtained the 4 TFR files above for the 4 MLSQ standards, select **Setup** -> **Quant.** This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 29. Now select the radio buttons for "Fundamental Parameters" with "**Multiple Standards**". Click "OK" to exit the dialog.

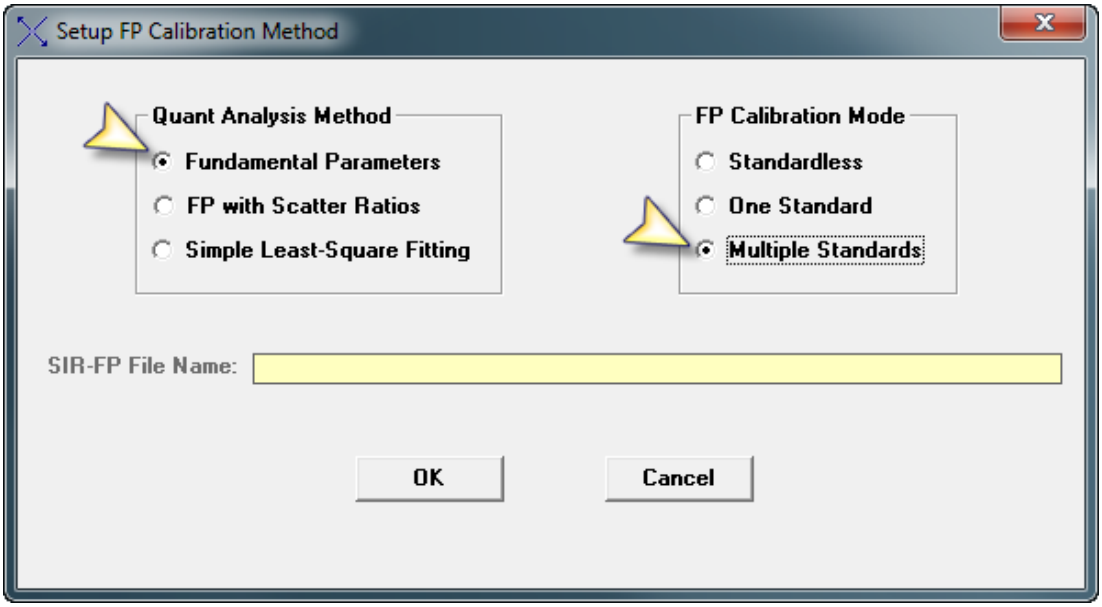


Figure 29. Setup FP Calibration Method. Select "Fundamental Parameters" for the "Quant Analysis Method" and "**Multiple Standards**" for the "FP Calibration Mode".

38. If you have just finished an SIR-FP analysis from the previous step above it will prompt the following dialog (see Fig. 30 below). Select "Yes".

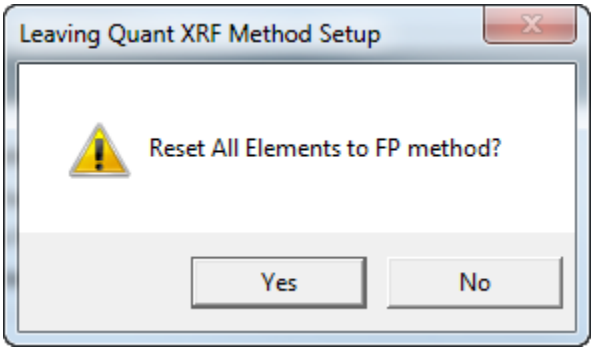


Figure 30. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to the FP method.

39. Now Select: **Calibrate** -> **MLSQ** from the XRS-FP Expert Panel. This will bring up the dialog, "TFR Files for Multi-Standard XRF Calibration", shown below in Figure 31.

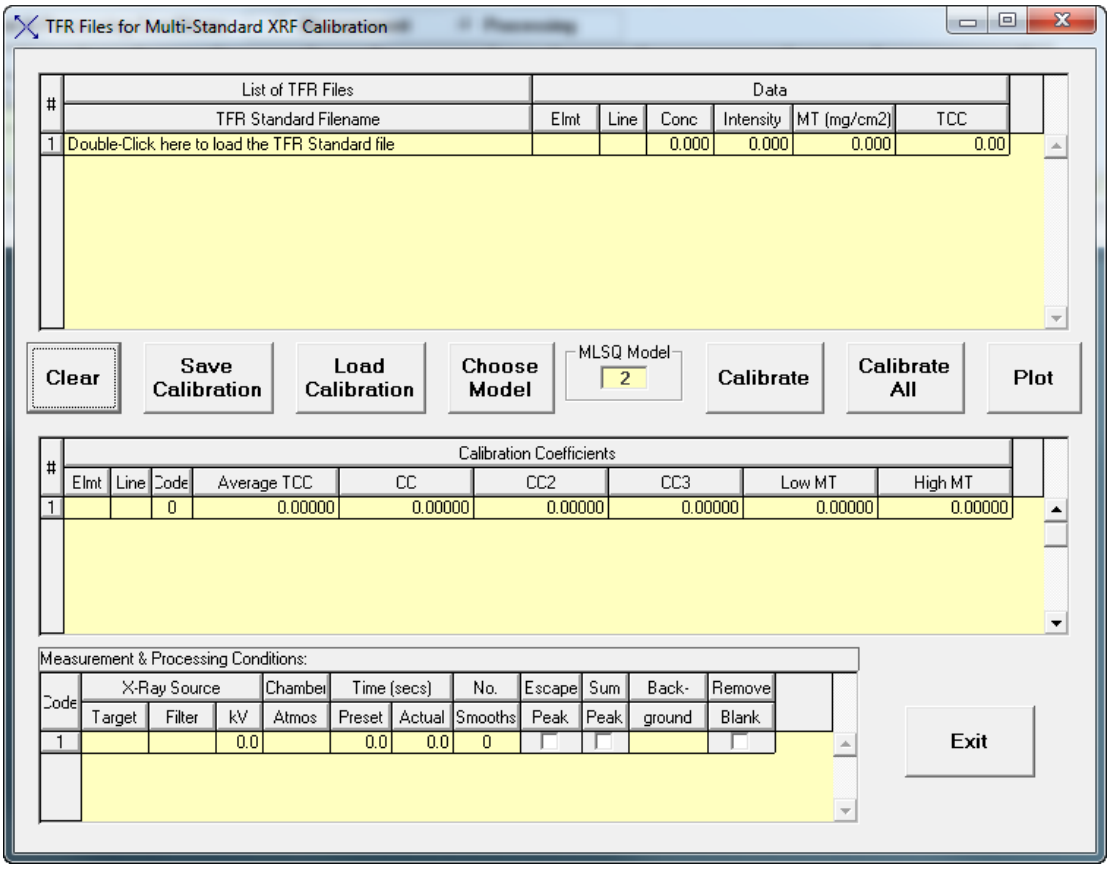


Figure 31. TFR Files for Multi-Standard XRF Calibration. Dialog displayed from the "Calibrate -> MLSQ" menu item.

40. Double click in the "TFR Standard Filename" cell to load the TFR filenames to be used for the MLSQ calibration (eg. "RockStd1.tfr"). To add additional TFR files (standards) simply use the down-arrow key to add a row. Then load "RockStd2.tfr" and subsequently use the same method for the other two standards, "RockStd3.tfr" and "RockStd4.tfr". See Figure 34 below.

41. Now click the "Choose Model" button in the "TFR Files for Multi-Standard XRF Calibration" dialog (Fig 34). This will bring up another dialog called, "Define Model for MLSQ Fitting" (see Fig. 32 below). Select the type of model to be used by clicking on the "Ordinate (Y)" drop-down menu button (Fig. 32). Select the "Intensity" model (model #9) in the "Ordinate (Y)" column for this method (Fig. 33).

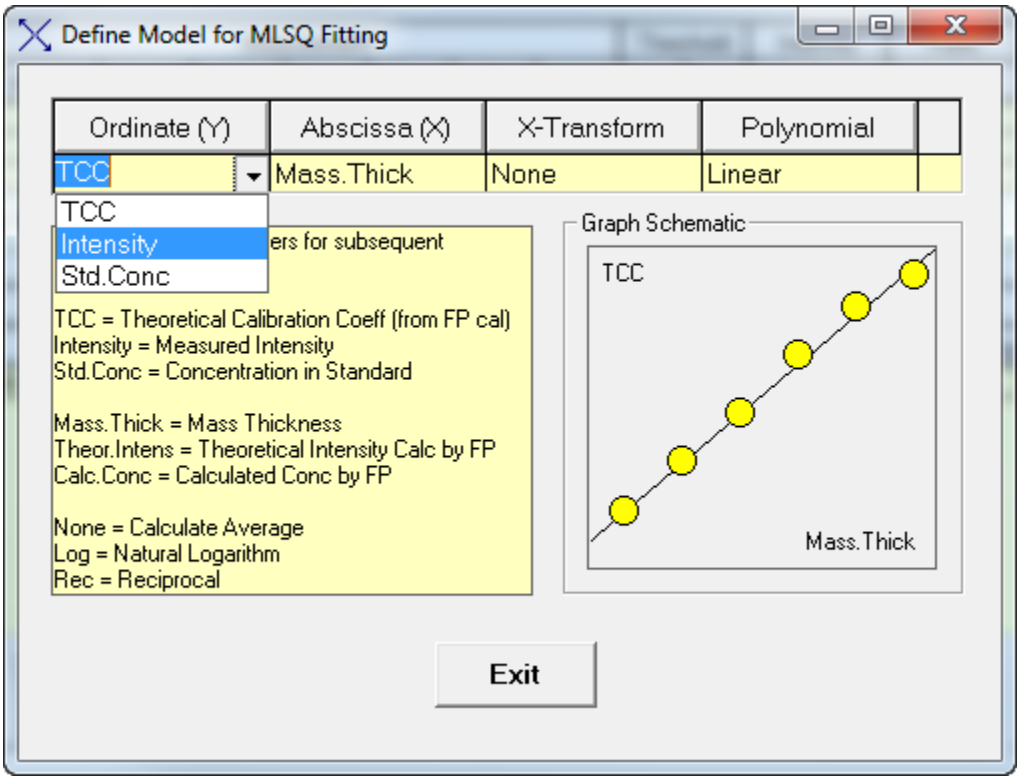


Figure 32. Define Model for MLSQ Fitting Dialog. Under the "Ordinate (Y)" column select the drop-down menu button to select the type of model to be used with this method.

The fitting "Polynomial" can either be "Linear" (Slope & intercept) or quadratic, which has an additional quadratic term. Use "Linear" for this tutorial.

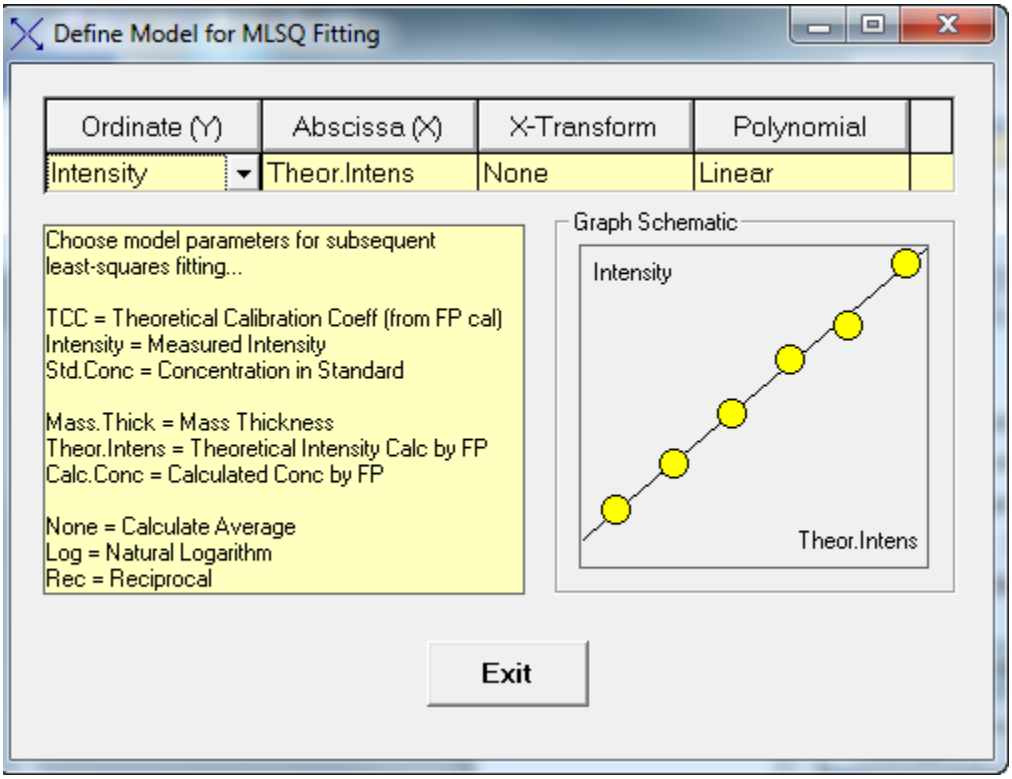


Figure 33. Define Model for MLSQ Fitting Dialog. Under the "Ordinate (Y)" column select the drop-down menu button to select the "Intensity" model (model #9). Note this is the ideal model for use with this method.

Then click the "Exit" button to go back to the main "Calibrate -> MLSQ" dialog.

42. In the "TFR Files for Multi-Standard XRF Calibration" dialog click on the **"Calibrate"** button. See figure 34 below. Note: The "Calibrate" button is used if each standard has ALREADY been calibrated individually, as if each one were a single standard (as done in this tutorial).

Recommended Method for MLSQ Calibration:

A. Calibrate each standard for the MLSQ calibration as if it were a single standard (individually). Then load these TFR files into the MLSQ calibration (as done in this tutorial). Now select the "Calibrate" button.

B. Alternatively, the "Calibrate All" button can be used which does the spectrum processing and single standard calibration for each standard listed in the "List of TFR Files". We recommend the user follow the method described in (A) above, as it allows for a better understanding of the process and is more controllable.

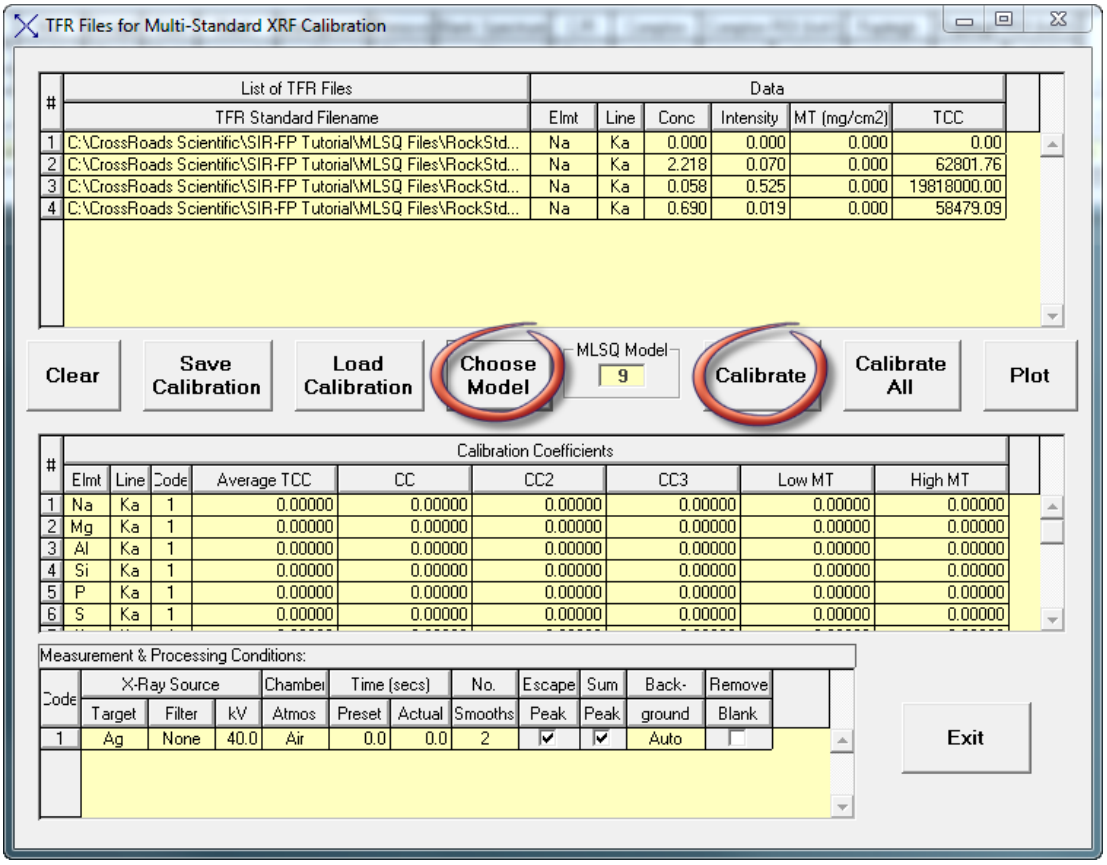


Figure 34. TFR Files for Multi-Standard XRF Calibration Dialog. All four MLSQ standards saved from step 36 above (i.e. "RockStd1.tfr", "RockStd2.tfr", "RockStd3.tfr" and "RockStd4.tfr") have been loaded. The "Choose Model" button brings up the dialog called "Define Model for MLSQ Fitting", where the type of model is selected. Ideally this is the "Intensity" model (model #9). Select the "Calibrate" button to perform the full MLSQ calibration.

43. The "Plot" button displays the least squares plot for each element (see Figs. 35-36). The "Pervious" and "Next" buttons display plots for all the elements. Click the "Next" button to scroll through all the plots and observe the quality of the fit for each element. Having scrolled through all elements the dialog will automatically close, or you can use the "Exit" button.

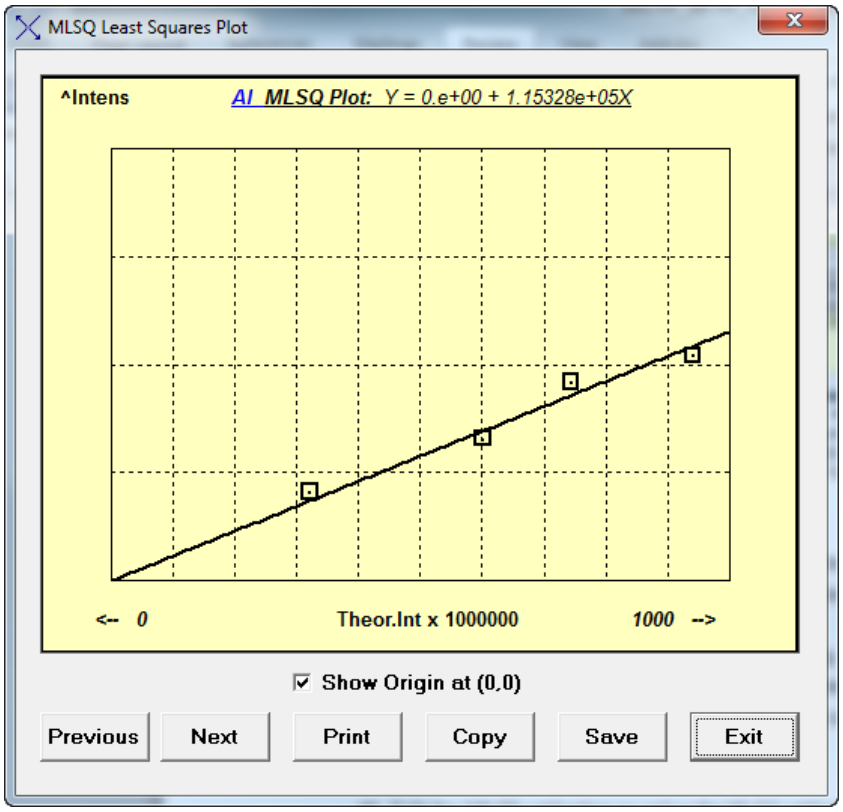


Figure 35. MLSQ Least Squares Plot for Al. Least squares plot for Al.

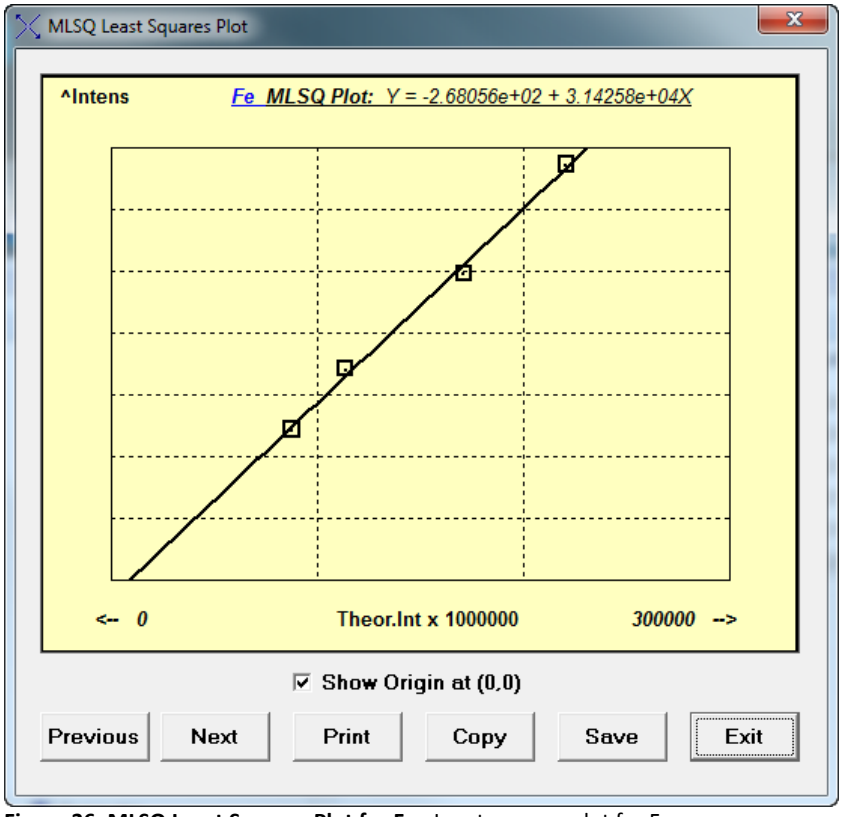


Figure 36. MLSQ Least Squares Plot for Fe. Least squares plot for Fe.

44. Now click the **"Save Calibration"** button (see Fig. 37 below) to save the full MLSQ calibration file. This will save 2 files for the MLSQ calibration (an *.lsq file and a *.tfr file). For example, the two files saved in this tutorial are the default names: "MLSQ_Cal_File.lsq" and "MLSQ_Cal_File.tfr." Save these files in this location: C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files.

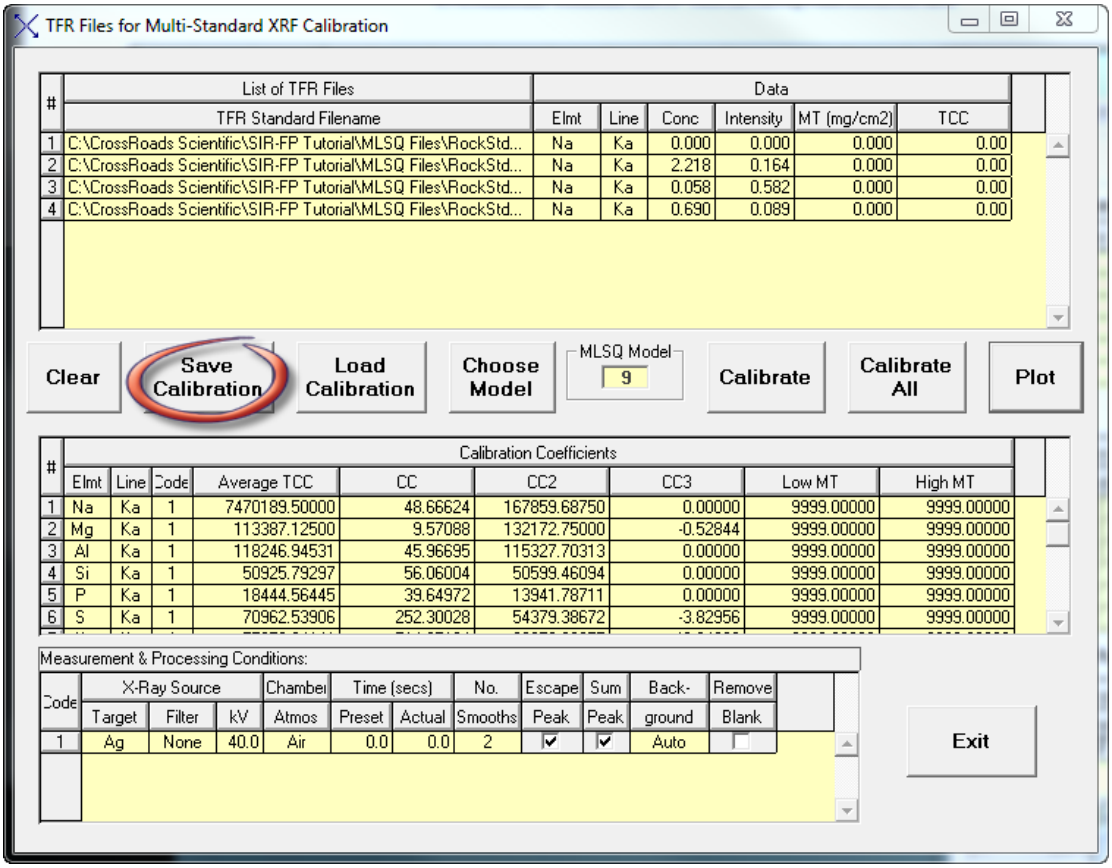


Figure 37. TFR Files for Multi-Standard XRF Calibration Dialog. Save the full MLSQ calibration (an *.lsq file and a *.tfr file) using the "Save Calibration" button.

45. We now have a complete MLSQ calibration in addition to our SIR calibration. At this point the two methods can be combined and used for analysis of an unknown sample. From the XRS-FP Expert Panel open the TFR saved from the MLSQ calibration (step 44 above). For example, select **File** -> **Open** -> **"MLSQ_Cal_File.tfr".**

46. Now from the XRS-FP Expert Panel: Select **Setup** -> **Quant.** This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 38. Select the radio buttons for **"FP with Scatter Ratios"** with **"Multiple Standards"**. In the "SIR-FP File Name" text box double click to

add the TFR file saved from the SIR calibration in step 12 above (e.g. Tutorial.sir). Then click "OK".

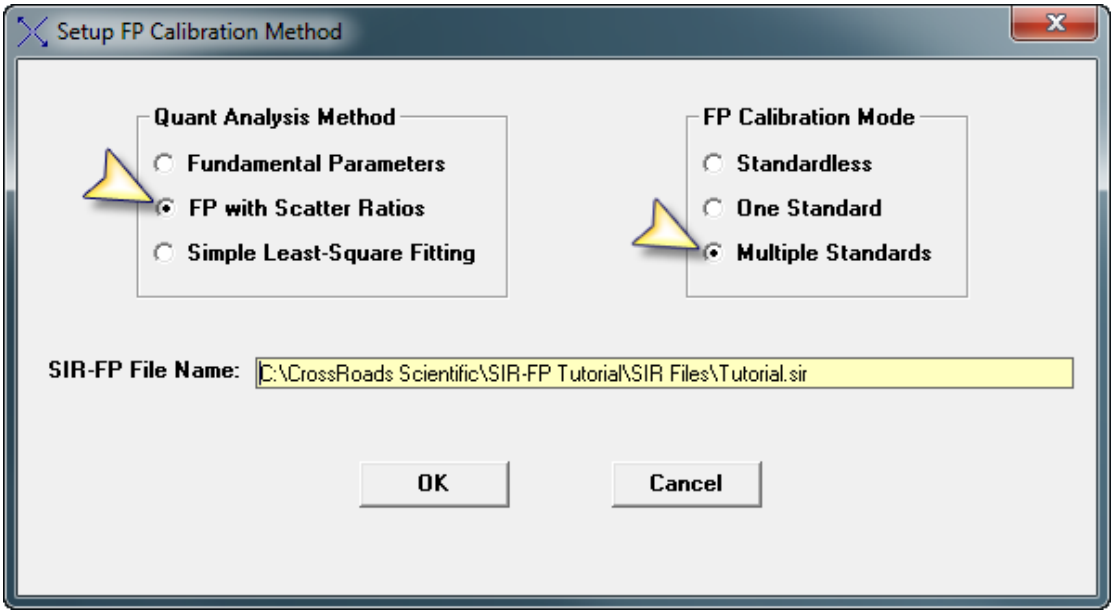


Figure 38. Setup FP Calibration Method Dialog. Select "**FP with Scatter Ratios**" for the "Quant Analysis Method" and "**Multiple Standards**" for the "FP Calibration Mode". Load the SIR-FP File name saved from the SIR calibration (e.g. Tutorial.sir).

47. This will bring up the dialog shown in Figure 39. Select **"Yes"** to "Reset All Elements to SIRFP method?"

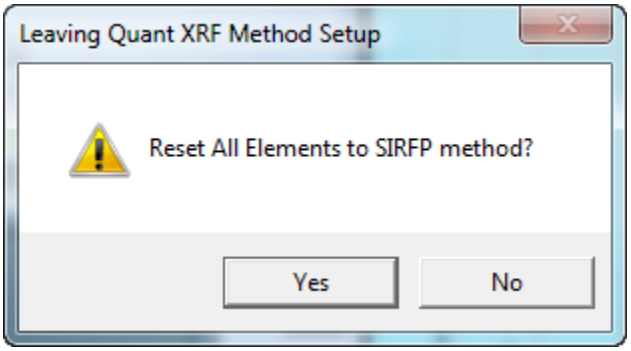


Figure 39. Leaving Quant XRF Method Setup Dialog. Select "Yes" to "Reset All Elements to SIRFP method?"

48. At this point we are ready to define a sample for analysis. From the XRS-FP Expert Panel set-up the "Component Table" for an "unknown". Clear the 3 "fixed" element lines at top. Add 2 lines at the bottom of the "Component Table". These are "fictional elements" at this point. The Component name is left blank. Set the "Type" for these two lines as "SIR-FP" (all other

"Components" are set to "Calc"). Check that the "Thickness Information" Table is "Normalized" (check box selected) to 100%. See Figure 40 below.

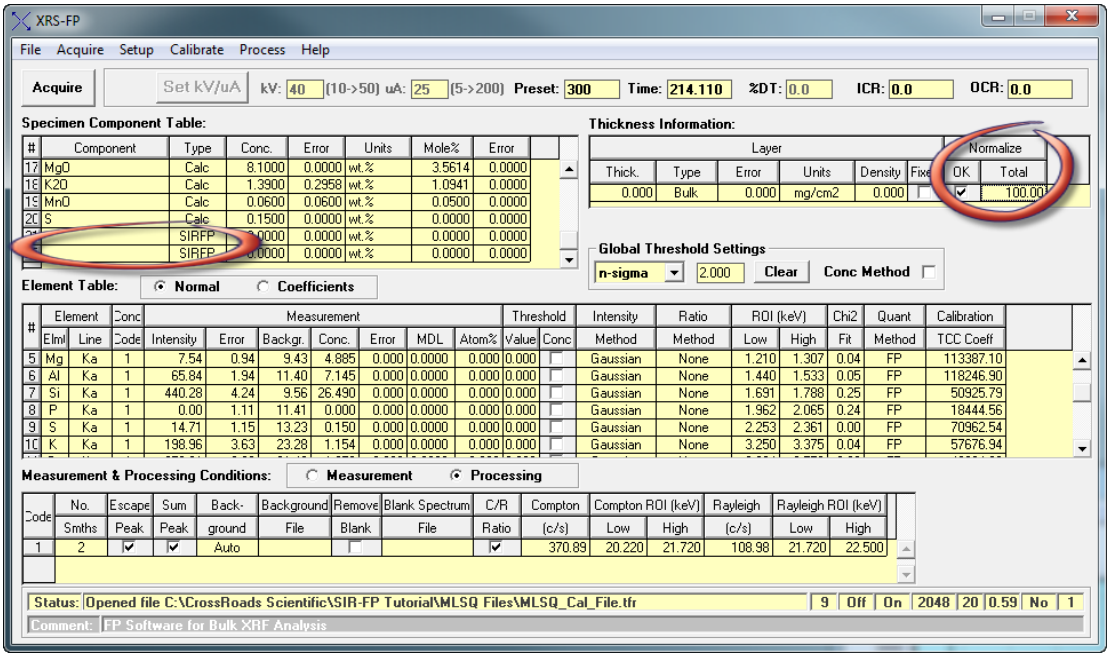


Figure 40. XRS- FP Expert Panel – Define a Sample for Analysis. Delete the first 3 "fixed" elements in the "Component Table" and add 2 lines at the bottom of the "Component Table" for analysis of the "unknown". Leave the "Component" field blank and set their "Type" to "SIRFP" (all other "Components" are set to "Calc"). Check that the "Thickness Information" Table is "Normalized" to 100%.

Note: For analysis using the SIR-FP method two elements must be designated as type "SIR-FP" in the "Component Table". There are two ways to do this:

A. Either specify the 2 elements in the "Component Table". For example, if the low-Z unanalyzed material might be a hydrocarbon then H and F could be defined.

B. Or leave the 2 components blank in the "Component Table" (as described above). If the components are left blank the software will find two elements that estimate what the low-Z unanalyzed material is.

49. Now save the full MLSQ and SIR calibration TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be re-saved as "**"C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\MLSQ_Cal_File_SIRFP.tfr**" or as an alternate filename of choice

50. Now from the XRS-FP Expert Panel open an "unknown" spectrum for analysis. For the purpose of this tutorial select **File** -> **Open** -> **"…SIR-FP Tutorial\MLSQ Files\UnknownRock.mca.**"

51. Select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel.

52. Finally select: **Process** -> **Analyze** from the XRS-FP Expert Panel. This will perform the full analysis of the "unknown" using the combined SIR-FP and MLSQ methods, thus yielding elements with concentrations that estimate the 2 "blank elements" for low-Z unanalyzed material, as well as concentrations for the other elements analyzed in the unknown sample. See figure 41 below to compare the data obtained from the analysis of the "unknown" sample

Layer Table ----------

#	Thick	Type	Error	Units	Density	Norm.	Total
1	0.00	Bulk	0.00	mg/cm2	0.00	On	100.00

Sample Table ----------

Layer	Component	Type	Concn.	Error	Units	Mole%	Error
1	Ba	Calc	1087.89	155.503	ppm	0.047	0.007
1	Cu	Calc	253.43	24.305	ppm	0.024	0.002
1	Ni	Calc	111.49	12.097	ppm	0.011	0.001
1	Rb	Calc	149.23	11.582	ppm	0.010	0.001
1	Sr	Calc	182.34	15.133	ppm	0.012	0.001
1	V	Calc	270.80	40.101	ppm	0.031	0.005
1	Zr	Calc	130.84	7.362	ppm	0.008	0.000
1	P2O5	Calc	0.307	0.287	wt.%	0.128	0.119
1	SiO2	Calc	48.848	0.717	wt.%	48.111	0.706
1	TiO2	Calc	0.933	0.022	wt.%	0.691	0.016
1	Al2O3	Calc	20.522	0.761	wt.%	11.911	0.442
1	Fe2O3	Calc	9.823	0.044	wt.%	3.640	0.016
1	CaO	Calc	2.722	0.051	wt.%	2.872	0.053
1	MgO	Calc	2.681	1.364	wt.%	3.936	2.003
1	K2O	Calc	3.318	0.068	wt.%	2.084	0.042
1	MnO	Calc	0.141	0.007	wt.%	0.117	0.006
1	S	Calc	0.534	0.055	wt.%	0.985	0.102
1	N	SIRFP	1.821	0.000	wt.%	7.694	0.000
1	O	SIRFP	3.540	0.000	wt.%	13.093	0.000

Element Table ----------

Elmt	Line Code	Cond Code	Ratio Method	Intensity (c/s)	Error (c/s)	Intensity Method	Conc.	Conc Method	Calibration Coefficient
O	Ka	0	None	0.000	0.0000	Gaussian	46.202	None	0.000
Mg	Ka	1	None	1.764	0.8510	Gaussian	1.617	SIRFP	113387.100
Al	Ka	1	None	104.382	2.5362	Gaussian	10.861	SIRFP	118246.900
Si	Ka	1	None	352.441	3.9165	Gaussian	22.834	SIRFP	50925.790
P	Ka	1	None	1.196	1.1151	Gaussian	0.134	SIRFP	18444.560
S	Ka	1	None	43.529	1.8118	Gaussian	0.534	SIRFP	70962.540
K	Ka	1	None	507.708	5.7542	Gaussian	2.754	SIRFP	57676.940
Ca	Ka	1	None	452.836	5.2860	Gaussian	1.945	SIRFP	49934.990
Ti	Ka	1	None	209.188	3.2137	Gaussian	0.559	SIRFP	33556.480
V	Ka	1	None	18.382	1.5499	Gaussian	0.027	SIRFP	47622.900
Mn	Ka	1	None	99.339	2.7048	Gaussian	0.109	SIRFP	39846.670
Fe	Ka	1	None	6733.831	17.7701	Gaussian	6.871	SIRFP	29381.590
Ni	Ka	1	None	24.885	2.3018	Gaussian	0.011	SIRFP	68170.730
Cu	Ka	1	None	93.348	2.3460	Gaussian	0.025	SIRFP	231839.300
Rb	Ka	1	None	51.767	2.1297	Gaussian	0.015	SIRFP	44298.390
Sr	Ka	1	None	62.071	2.2318	Gaussian	0.018	SIRFP	47402.430
Zr	Ka	1	None	45.356	2.0131	Gaussian	0.013	SIRFP	50522.960
Ba	Ka	1	None	17.754	1.8450	Gaussian	0.109	SIRFP	2504930.000

Figure 41. Data from Unknown Sample (MLSQ/SIR/AutoZ) . Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the MLSQ calibration, the SIR calibration and "Auto Z," where the software estimates the two low-Z matrix elements.

53. Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as **"C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\UnknownRock_MLSQ-SIR_AutoZ.tfr"** or as an alternate filename of choice.

54. Here is an example using the same MLSQ calibration as described above; however, rather than allowing the software to estimate the 2 low-Z elements they are entered by the user (i.e. fixed). This method is designed to be used if you know something about the unknown sample. For the tutorial we will use H and O as our "preferred elements" in "Component Table". Enter these elements into the last two rows of the "Component Table." Set the concentration ("Conc.") to zero and select "Type -> SIR-FP" (Fig. 42). Also check that the thickness information is normalized to a total of 100% (Fig. 42).

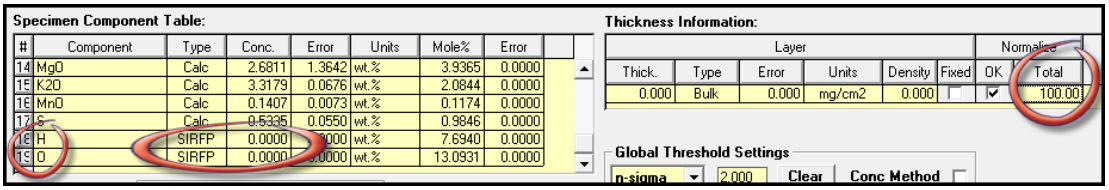


Figure 42. XRS- FP Expert Panel. Enter H and O as the two "fixed" elements in the "component Table."

55. Now select **Process** -> **Analyze** (again). This time to get the concentration for the two "fixed" elements, H and O.

56. Save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as **C:\CrossRoads Scientific\SIR-FP Tutorial\MLSQ Files\UnknownRock_MLSQ-SIR_FixedZ.tfr"** or as an alternate filename of choice. See figure 43 below to compare the data obtained from the analysis of the "unknown" sample.

Layer Table

#	Thick	Type	Error	Units	Density	Norm.	Total
1	0.00	Bulk	0.00	mg/cm2	0.00	On	100.00

Sample Table

Layer	Component	Type	Concn.	Error	Units	Mole%	Error
1	Ba	Calc	1090.20	155.833	ppm	0.023	0.003
1	Cu	Calc	253.95	24.355	ppm	0.012	0.001
1	Ni	Calc	111.72	12.123	ppm	0.006	0.001
1	Rb	Calc	149.54	11.606	ppm	0.005	0.000
1	Sr	Calc	182.73	15.165	ppm	0.006	0.001
1	V	Calc	271.34	40.182	ppm	0.016	0.002
1	Zr	Calc	131.12	7.377	ppm	0.004	0.000
1	P2O5	Calc	0.308	0.287	wt.%	0.064	0.059
1	SiO2	Calc	48.937	0.718	wt.%	23.917	0.351
1	TiO2	Calc	0.935	0.022	wt.%	0.344	0.008
1	Al2O3	Calc	20.563	0.762	wt.%	5.922	0.220
1	Fe2O3	Calc	9.843	0.044	wt.%	1.810	0.008
1	CaO	Calc	2.727	0.051	wt.%	1.428	0.027
1	MgO	Calc	2.686	1.367	wt.%	1.957	0.996
1	K2O	Calc	3.325	0.068	wt.%	1.036	0.021
1	MnO	Calc	0.141	0.007	wt.%	0.058	0.003
1	S	Calc	0.535	0.055	wt.%	0.489	0.050
1	H	SIRFP	0.371	0.000	wt.%	10.805	0.000
1	O	SIRFP	51.099	0.000	wt.%	93.786	0.000

Element Table

Elmt	Line Code	Cond Code	Ratio Method	Intensity (c/s)	Error (c/s)	Intensity Method	Conc.	Conc Method	Calibration Coefficient
H	Ka	0	None	0.000	0.0000	Gaussian	0.370	None	0.000
O	Ka	0	None	0.000	0.0000	Gaussian	92.790	None	0.000
Mg	Ka	1	None	1.764	0.8510	Gaussian	1.620	SIRFP	113387.100
Al	Ka	1	None	104.382	2.5362	Gaussian	10.883	SIRFP	118246.900
Si	Ka	1	None	352.441	3.9165	Gaussian	22.875	SIRFP	50925.790
P	Ka	1	None	1.196	1.1151	Gaussian	0.134	SIRFP	18444.560
S	Ka	1	None	43.529	1.8118	Gaussian	0.535	SIRFP	70962.540
K	Ka	1	None	507.708	5.7542	Gaussian	2.760	SIRFP	57676.940
Ca	Ka	1	None	452.836	5.2860	Gaussian	1.949	SIRFP	49934.990
Ti	Ka	1	None	209.188	3.2137	Gaussian	0.560	SIRFP	33556.480
V	Ka	1	None	18.382	1.5499	Gaussian	0.027	SIRFP	47622.900
Mn	Ka	1	None	99.339	2.7048	Gaussian	0.109	SIRFP	39846.670
Fe	Ka	1	None	6733.831	17.7701	Gaussian	6.885	SIRFP	29381.590
Ni	Ka	1	None	24.885	2.3018	Gaussian	0.011	SIRFP	68170.730
Cu	Ka	1	None	93.348	2.3460	Gaussian	0.025	SIRFP	231839.300
Rb	Ka	1	None	51.767	2.1297	Gaussian	0.015	SIRFP	44298.390
Sr	Ka	1	None	62.071	2.2318	Gaussian	0.018	SIRFP	47402.430
Zr	Ka	1	None	45.356	2.0131	Gaussian	0.013	SIRFP	50522.960
Ba	Ka	1	None	17.754	1.8450	Gaussian	0.109	SIRFP	2504930.000

Figure 43. Data from Unknown Sample (MLSQ/SIR/FixedZ) . Data obtained from analysis of the unknown sample, "UnknownRock.mca," using the MLSQ calibration, the SIR calibration and "Fixed Z," where the user enters the two preferred ("fixed") low-Z matrix elements.