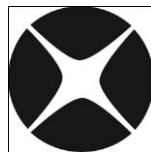


MLSQ Calibration in XRS-FP

Note: This document describes how to do an MLSQ calibration.



CrossRoads Scientific

785 Main St. Suite E, Half Moon Bay, CA 94019

info@CrossRoadsScientific.com

www.CrossRoadsScientific.com



TABLE OF CONTENTS

Table of Contents	2
Document Change Log	3
1 MLSQ Overview.....	4
2 Quick Guide: MLSQ Calibration	5
3 MLSQ Tutorial	6



DOCUMENT CHANGE LOG

Date	Person	Pages	Description
02-Oct-13	Sarah Cross	All	Created document for MLSQ Guide
13-Oct-13	Sarah Cross	Most	Updated document



1 MLSQ OVERVIEW

In XRS-FP there is a software option where multiple standards can truly be used with each element, and least-squares fitting can be done with various models, in order to allow for any variations from the theory of FP calibration. This method will be described below in more detail and can be used to calibrate using either type or pure-element standards. Note that this is not the same as using a simple least-squares fitting technique without FP.

If multiple standards are selected in the “Setup FP Calibration Method,” then the user sequentially calibrates each standard in turn. There are two ways to do this, either with live spectra or with saved spectrum files. In XRS-FP there are two options for doing a multiple-standard calibration. The differences in these two methods will be briefly described.

In the original multiple-standard model, you could provide any number of standards, **BUT only the last one for each element would be used**. Typically this method was for use with a single standard (usually a pure element) for each element to be calibrated. Since there are no standards with the same element there is not a conflict for which coefficient to use. In the case where several standards have the same element, then only the last one in the sequence would be used. However, this may not be the intended choice when several multi-element standards are used together.

The original multi-standard approach is described in some detail in the section 5.2 of the “XRS-FP Software Guide” on a generalized calibration scheme. After setting the multiple-standard model in this Setup-FP panel, proceed to calibrate each standard in turn (with only the elements in the standard), and then run a typical unknown sample, making sure to define all elements of interest in this sample, which must correspond to all the elements that have been calibrated with the standards. At this point, as soon as the actual sample analysis is performed, the standards information is merged together resulting in a single set of calibration coefficients for the analysis.

You can now optionally save this analysis report, complete with the merged calibration coefficients, as a “secondary” standard. In other words, future analyses can then be done with a “single” standard, where the report file (*.tfr) for this calibration is loaded (with its calibration coefficients), and the system is then immediately ready for subsequent analysis of unknown samples with this calibration.

In the newer multi-standard approach, **ALL standards are employed**, along with several models for how to allow for variations of the calibration coefficients with different concentrations and mass thicknesses of each element. This method will be described in more detail below. For this method you should collect spectra of each standard and process each one, creating and saving a TFR file, as if it was a single-standard FP calibration. See the following sections in this document for more detail.



2 QUICK GUIDE: MLSQ CALIBRATION

As described above, there are two basic ways of using multiple standards for FP calibration. The original method typically used just one standard per element and so the calibration coefficient, for any given element, only came from one standard file. In this more complex version described here, **calibration coefficients from ALL standards can be used together**, choosing from several different models to allow various least-squares fits.

The following procedure briefly explains the steps required to do a multiple-standard (MLSQ) calibration, where calibration coefficients from all standards are used together:

- a. Enter information for the first standard into the XRS-FP Expert Panel and load the MCA spectrum file. Select: **Process -> Spectrum -> All** from the XRS-FP Expert Panel.
- b. From the XRS-FP Expert Panel: go to **Setup -> Quant**. Select the radio buttons for “Fundamental Parameters” with “**One Standard**” in the “Setup FP Calibration Method” dialog and then click OK.
- c. Now select: **Calibrate -> FP** from the XRS-FP Expert Panel. This generates calibration TCC coefficients. Save the TFR file by selecting **File -> Save As** from the XRS-FP Expert Panel.
- d. Repeat steps (a-c) for **ALL** the individual MLSQ standards
- e. Having obtained TFR files for all the MLSQ standards select, **Setup -> Quant**. Then select the radio buttons for “**Fundamental Parameters**” with “**Multiple Standards**”. Click “OK” to exit.
- f. Now Select: **Calibrate -> MLSQ** from the XRS-FP Expert Panel. Double click in the “TFR Standard Filename” cell to load the TFR filenames to be used for the MLSQ calibration.
- g. Click the “**Choose Model**” button in the “TFR Files for Multi-Standard XRF Calibration” dialog. Select the type of model to be used by clicking on the “Ordinate (Y)” drop-down menu button in the “Define Model for MLSQ Fitting” dialog. And select the “Intensity” model in the “Ordinate (Y)” column for this method. See section 13.4 of the “XRS-FP Software Guide” for more detail. Then click the “Exit” button.
- h. Click the “**Calibrate**” button in the “TFR Files for Multi-Standard XRF Calibration” dialog. Note: The “Calibrate” button is used if each standard has ALREADY been calibrated individually, as if each one were a single standard (as described here).



- i. Now click the **“Plot”** button to display the least squares plot for each element. Then click **“Exit.”**
- j. Now click the **“Save Calibration”** button to save the complete MLSQ calibration file. This will save 2 files for the MLSQ calibration (an *.lsq file and a *.tfr file).

3 MLSQ TUTORIAL

The following tutorial along with associated spectra (*.mca) and application (*.tfr) files guides an XRS-FP software user through an MLSQ FP calibration.

1. Launch XRS-FP – Click anywhere on the splash screen to remove it from the display.
2. 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 1 below.

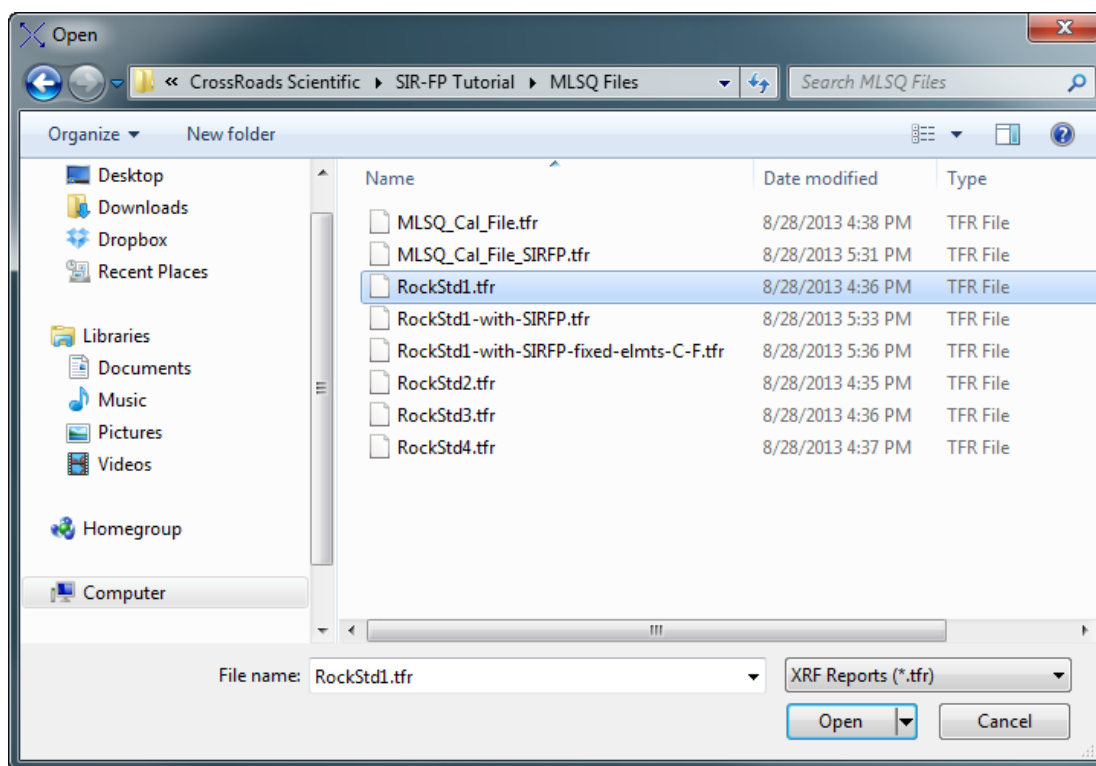


Figure 1. File Open Menu. Open the first MLSQ TFR file, e.g. “RockStd1.tfr”.

3. 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 2 will be displayed. Note that the spectra for this tutorial are already adjusted and in calibration

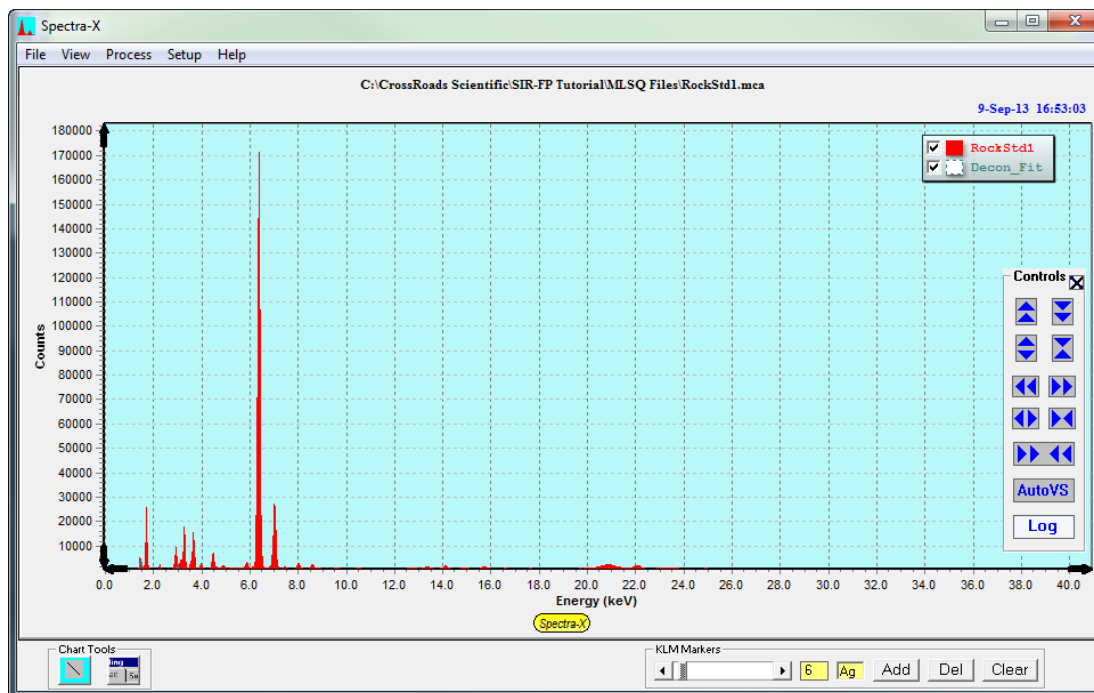


Figure 2. MLSQ Standard Spectrum. Spectrum for the first MLSQ standard, "RockStd1.mca".

4. Select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel.
5. Then from the XRS-FP Expert Panel: Select **Setup** -> **Quant**. This will bring up the "Setup FP Calibration Method" dialog shown below in Figure 3. 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.

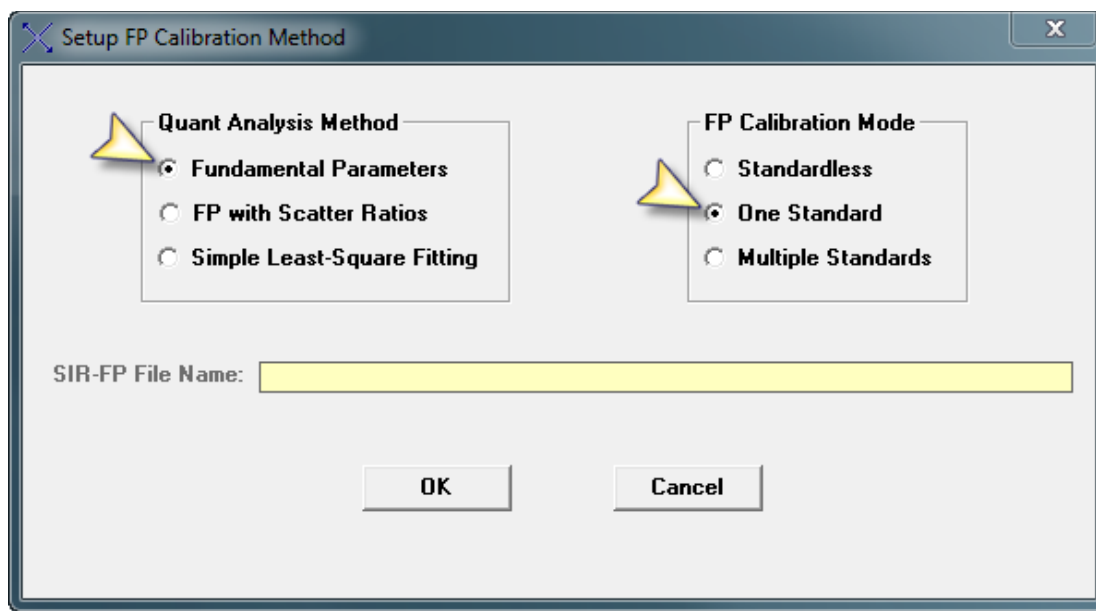


Figure 3. Setup FP Calibration Method. Select “Fundamental Parameters” for the “Quant Analysis Method” and “One Standard” for the “FP Calibration Mode”.

6. 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”.
7. 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.
8. **REPEAT steps 2-7** 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”).
9. 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 4. Now select the radio buttons for “Fundamental Parameters” with “**Multiple Standards**”. Click “OK” to exit the dialog.

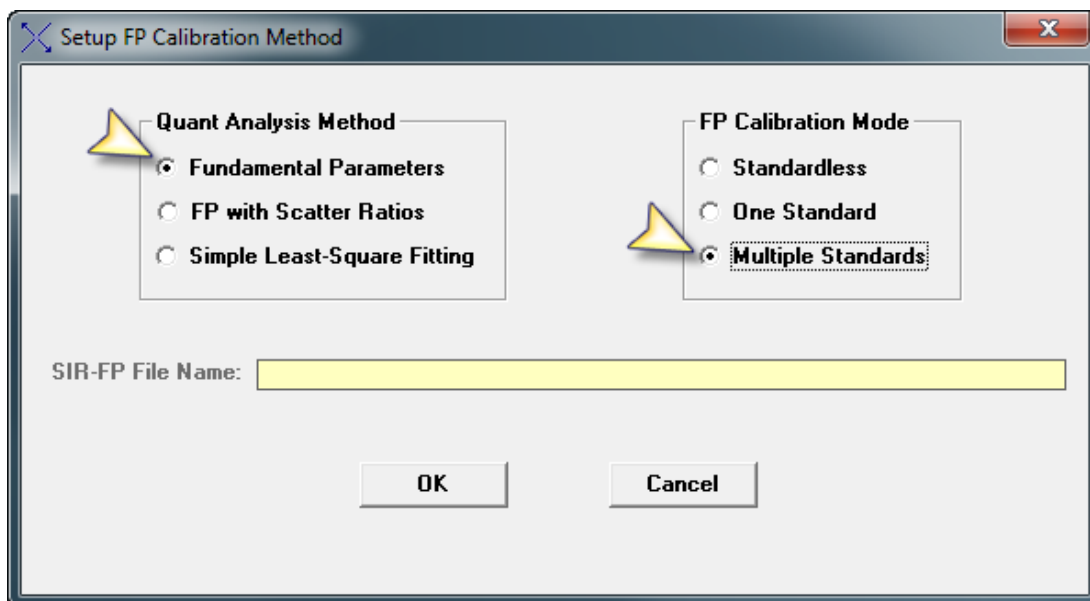


Figure 4. Setup FP Calibration Method. Select “Fundamental Parameters” for the “Quant Analysis Method” and “Multiple Standards” for the “FP Calibration Mode”.

10. 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 5.

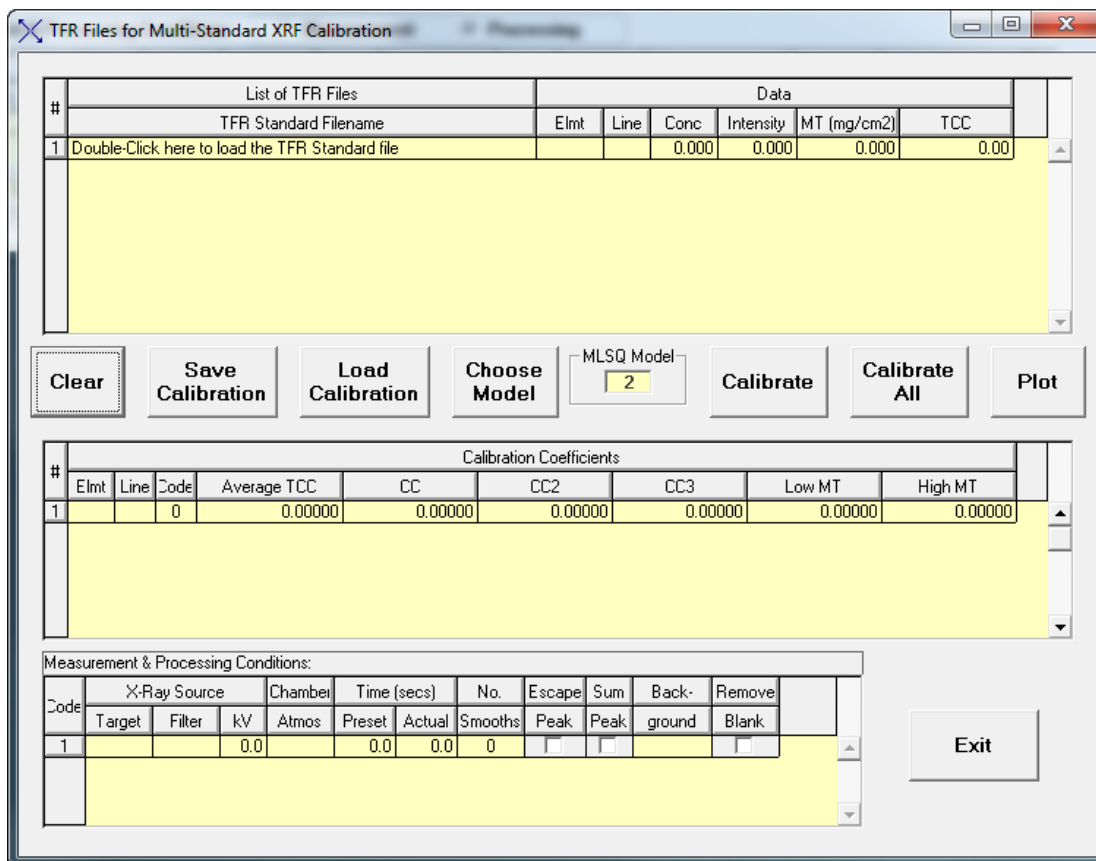


Figure 5. TFR Files for Multi-Standard XRF Calibration. Dialog displayed from the “Calibrate -> MLSQ” menu item.



11. 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 8 below.
12. Now click the “Choose Model” button in the “TFR Files for Multi-Standard XRF Calibration” dialog (Fig 8). This will bring up another dialog called, “Define Model for MLSQ Fitting” (see Fig. 6 below). Select the type of model to be used by clicking on the “Ordinate (Y)” drop-down menu button (Fig. 6). Select the “Intensity” model in the “Ordinate (Y)” column for this method (Fig. 7).

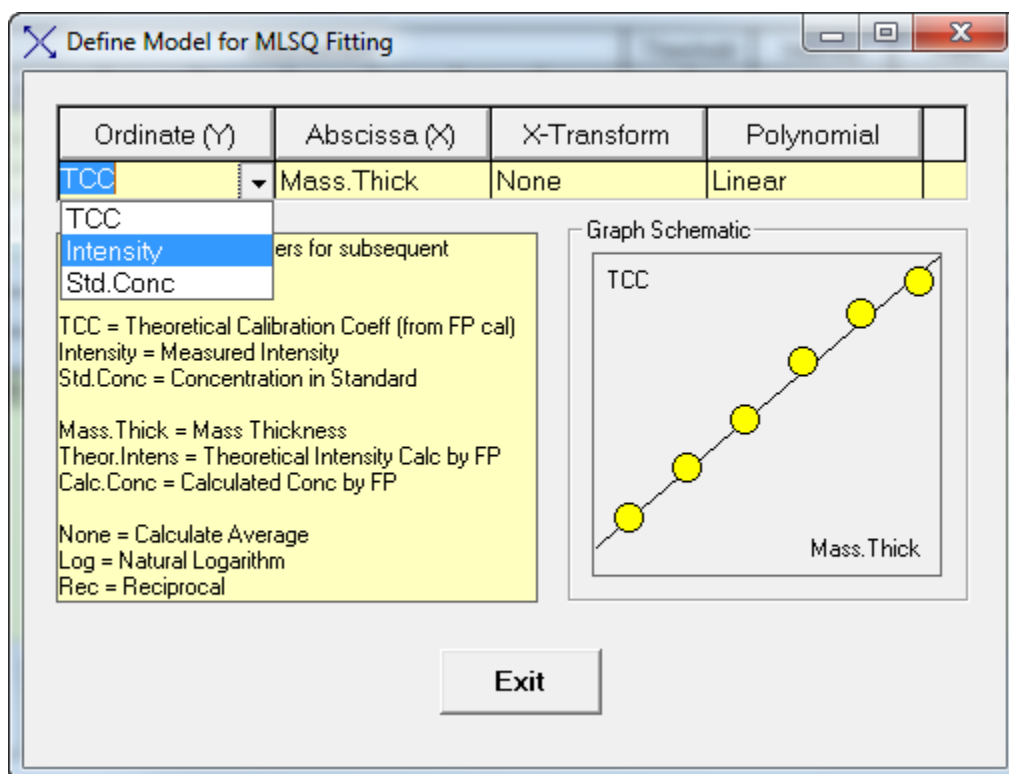


Figure 6. Define Model for MLSQ Fitting Dialog. Under the “Ordinate (Y)” column select the drop-down menu button to select the type of model to be used with this method.

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

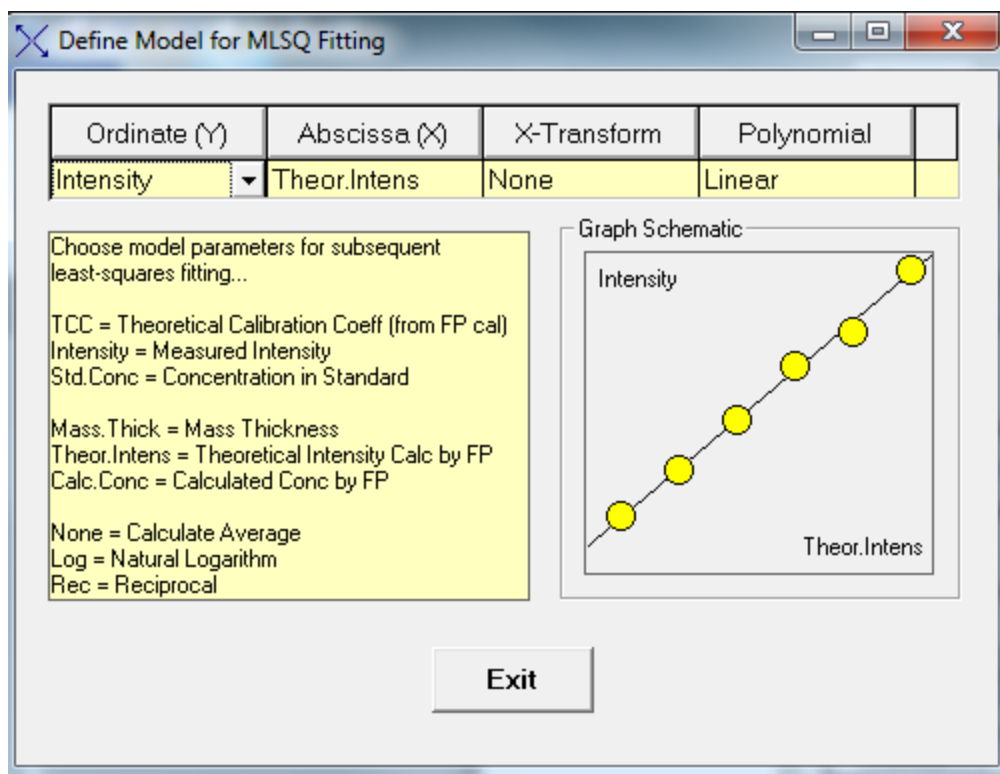


Figure 7. Define Model for MLSQ Fitting Dialog. Under the “Ordinate (Y)” column select the drop-down menu button to select the “Intensity” model.

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

13. In the “TFR Files for Multi-Standard XRF Calibration” dialog click on the **“Calibrate”** button. See figure 8 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.

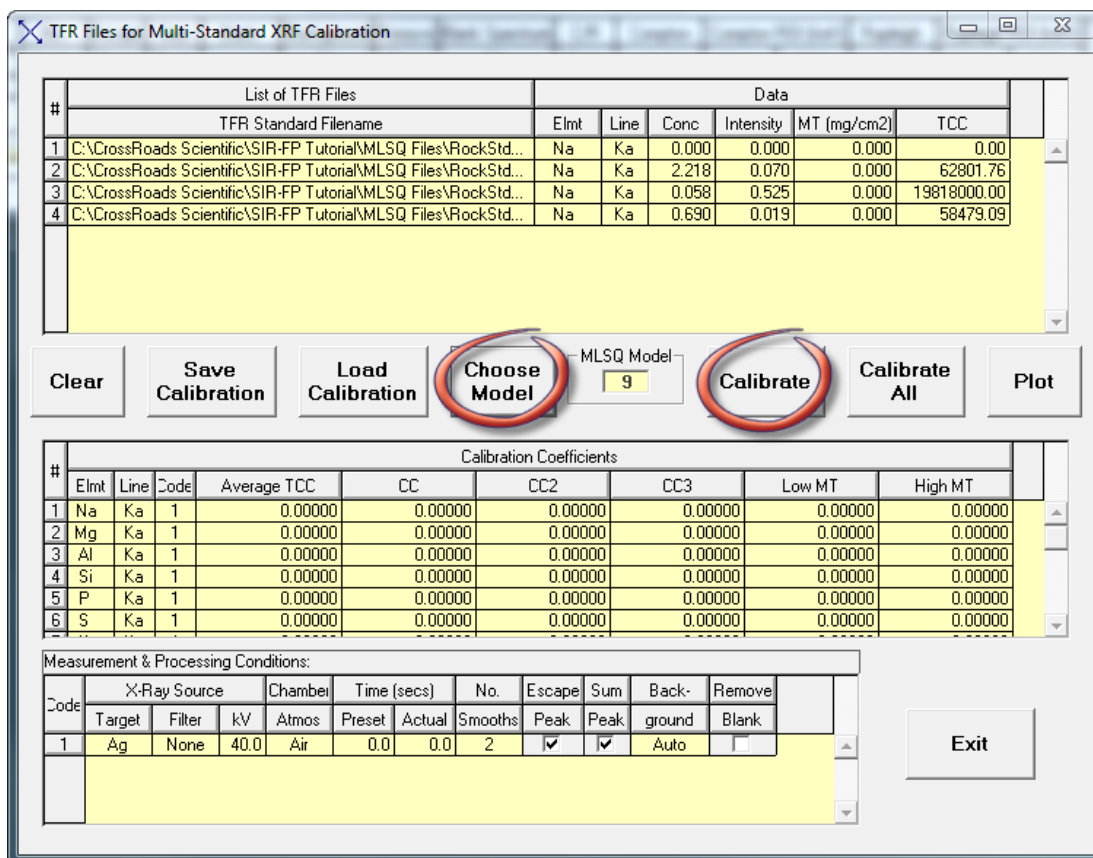


Figure 8. TFR Files for Multi-Standard XRF Calibration Dialog. All four MLSQ standards saved from step 8 above (i.e. “RockStd1.tfr”, “RockStd2.tfr”, “RockStd3.tfr” and “RockStd4.tfr”) have been loaded. The “Choose Model” button brings up the dialog called “Define Model for MLSQ Fitting”, where the type of model is selected. Select the “Calibrate” button to perform the full MLSQ calibration.

14. The “Plot” button displays the least squares plot for each element (see Figs. 9-10). The “Previous” 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.



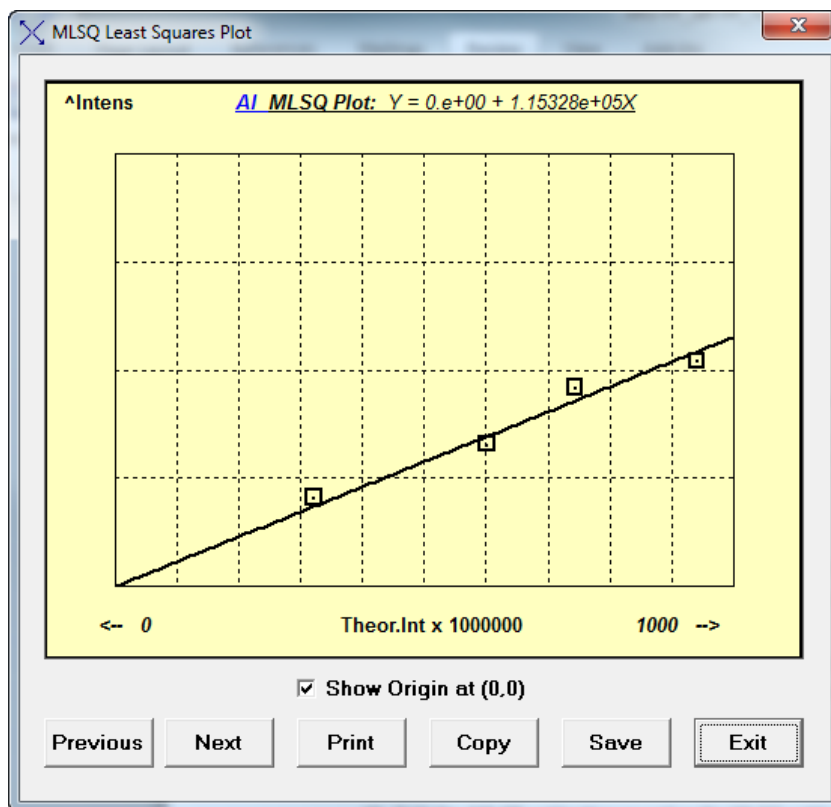


Figure 9. MLSQ Least Squares Plot for Al. Least squares plot for Al.

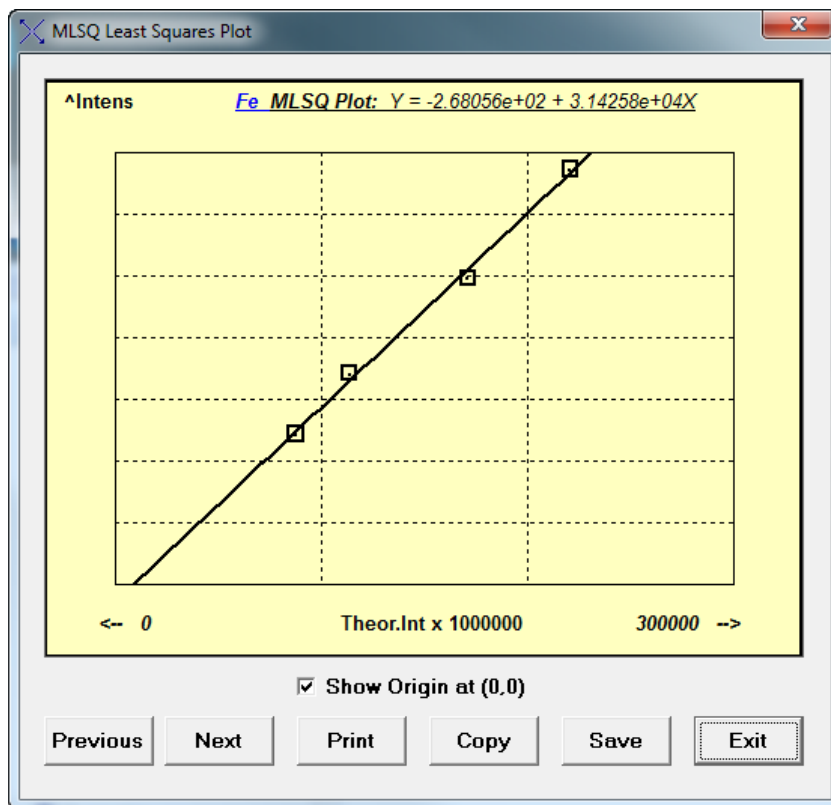


Figure 10. MLSQ Least Squares Plot for Fe. Least squares plot for Fe.



15. Now click the **“Save Calibration”** button (see Fig. 11 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.

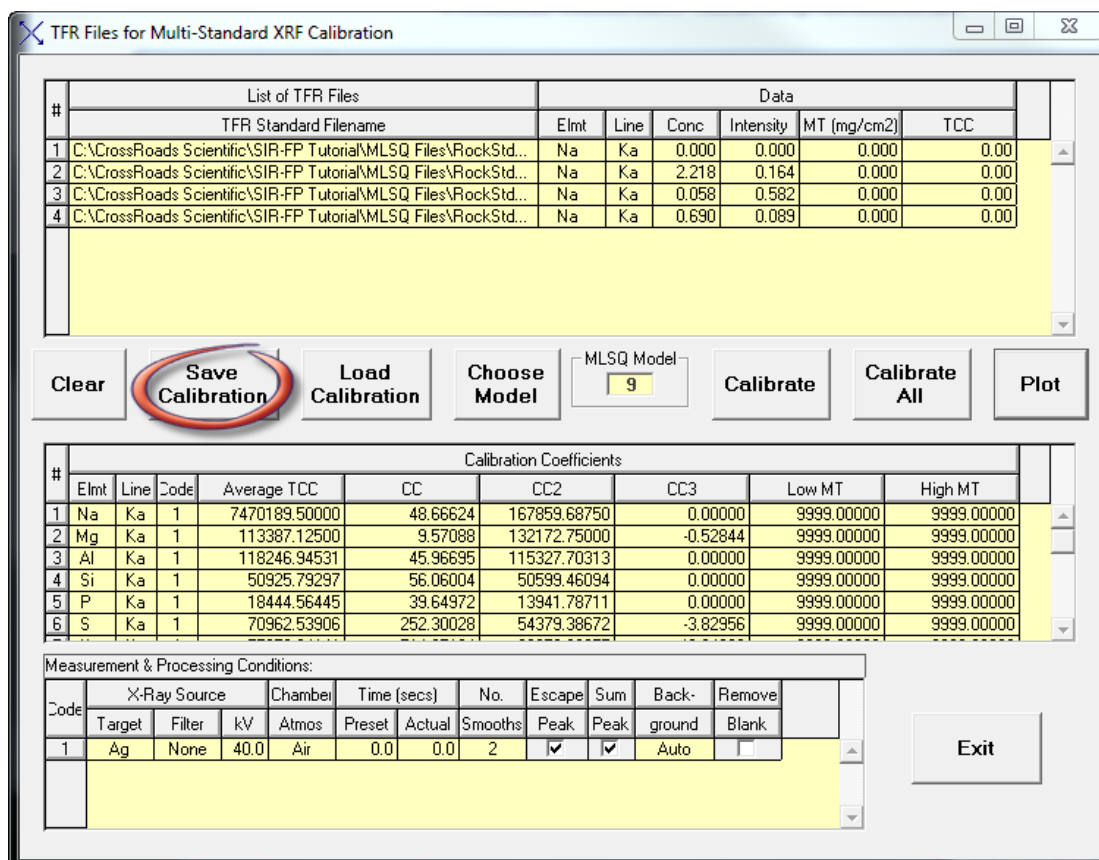


Figure 11. TFR Files for Multi-Standard XRF Calibration Dialog. Save the full MLSQ calibration (an *.lsq file and a *.tfr file) using the “Save Calibration” button.

16. We now have a complete MLSQ calibration. At this point, this method can be used for analysis of an unknown sample. The user would open the TFR saved from the MLSQ calibration (step 15 above) from the XRS-FP Expert Panel. For example, select **File** -> **Open** -> **“MLSQ_Cal_File.tfr”**. Define a sample for analysis by setting up the “Component Table” for an “unknown” in the XRS-FP Expert Panel. Then collect or open an “unknown” spectrum for analysis. Then select: **Process** -> **Spectrum** -> **All** from the XRS-FP Expert Panel. And finally select: **Process** -> **Analyze** from the XRS-FP Expert Panel. This will perform the full analysis of the “unknown” using the MLSQ method, thus yielding concentrations for the elements analyzed in the unknown sample.