

# Multilayer Thin-Film Analysis

Note: This document describes how to do multilayer thin-film analysis in XRS-FP2



**CrossRoads Scientific**

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

[info@CrossRoadsScientific.com](mailto:info@CrossRoadsScientific.com)

[www.CrossRoadsScientific.com](http://www.CrossRoadsScientific.com)



# TABLE OF CONTENTS

Table of Contents .....	2
Document Change Log .....	3
1   MLSQ Overview.....	4
2   Quick Guide: MLSQ Calibration .....	Error! Bookmark not defined.
3   MLSQ Tutorial .....	5



## DOCUMENT CHANGE LOG

Date	Person	Pages	Description
23-Feb-16	Sarah Cross	All	Created document for MTF Guide
10-May-16	Sarah Cross	Most	Updated document
26-May-16	Sarah Cross	Most	Updated document
19-Dec-16	Sarah Cross	Most	Updated document



# 1 MULTILAYER THIN-FILM OVERVIEW

The multilayer thin-film (MTF) software option in XRS-FP2 can analyze up to 8 layers for thickness and composition. This option (available for purchase) is integrated directly into the standard XRS-FP2 software package. The overall functionality of the software is as described in the user manual and other documentation; however, the added MTF option will support multilayer samples.

The layer attributes of a multilayer thin-film sample are defined in the Layer Table of the Application workflow. If the sample is infinitely thick, as in the standard operating mode of XRS-FP2, then the thickness is set to zero in the Layer Table and the Type is set to “Bulk”. If the thickness or mass thickness is known, a value is entered (with appropriate units) and the Type is set to “Fixed”. The Type is set to “Calculate” if the thickness is to be calculated for sample analysis and appropriate units should be set. If the density is known (i.e., when a linear thickness is entered), a value is entered. Note that if it is set to zero, the software will automatically calculate a theoretical value based upon the sample composition. The density option can be set to Fixed (or Calculated), which is more obvious than remembering to set the value to zero for calculating. The Layer Table also contains a normalization factor (default to 100%). Normalization **MUST** be checked if the layer thickness is to be calculated or if the analysis is done without calibration (i.e. standardless). Layers, or rows, can be added to define multilayer samples. The down arrow or the plus and minus buttons can be used to add/remove layers. An example of the layer attributes for a multilayer sample is shown below. Note that in this example there are 4 different layers (red box in figure below), with one component (element or compound) per layer, although there is no restriction to only one component per layer. Also note that the layer number for each component is shown in both the Layer Table as well as in the Component Table below. The maximum number of layers in a sample is 8.

The screenshot displays the XRS-FP2 software interface. The top menu bar includes Setup Hardware, Configure, Admin, File Manager, Enter Easy Mode, and Help. The left sidebar shows Application, Definition, and Methods. The main window is titled 'XRS-FP2 - C:\CrossRoads Scientific\XRS-FP2\FP2-Master.ana'.

**Layer Table: Define layer attributes.**

Lyr	Type	Thick.	Units	Density (g/cm3)	Fixed Density	Normalize	Normalize Total
1	Calc	16.481	ug/cm2	1.690	<input type="checkbox"/>	<input checked="" type="checkbox"/>	100.000
2	Calc	18.088	ug/cm2	2.795	<input type="checkbox"/>	<input checked="" type="checkbox"/>	100.000
3	Calc	15.127	ug/cm2	11.350	<input type="checkbox"/>	<input checked="" type="checkbox"/>	100.000
4	Calc	17.038	ug/cm2	10.500	<input type="checkbox"/>	<input checked="" type="checkbox"/>	100.000

**Component Table: Define component attributes.**

#	Lyr	Name	Type	Units	Conc.	Conc. Error
1	1	SiO	Calc	wt. %	100.0000	0.000
2	2	MoO3	Calc	wt. %	100.0000	0.000
3	3	Pb	Calc	wt. %	100.0000	0.000
4	4	Ag	Calc	wt. %	100.0000	0.000



## 2 MULTILAYER THIN-FILM TUTORIAL

The following tutorial along with associated files (\*.ana) guides the user through the setup and implementation of a multilayer thin film analysis using XRS-FP2. This includes: a) qualitative inspection of the sample, b) spectrum processing, c) calibration and d) analysis.

It is assumed that the x-ray spectrometer has been energy calibrated – see the Energy Calibration guide in the Help section of XRS-FP2. It is also assumed that the spectrometer excitation parameters have been selected, i.e., incident beam collimation (if required), tube accelerating voltage, tube current, primary beam filter. These parameters will be spectrometer/application specific and are not within the scope of this tutorial other than to emphasize that to obtain accurate XRF analysis these must be defined and maintained in the XRS Application ANA file.

**Application:** Au/Ni/Cu, a common electronic contact application.

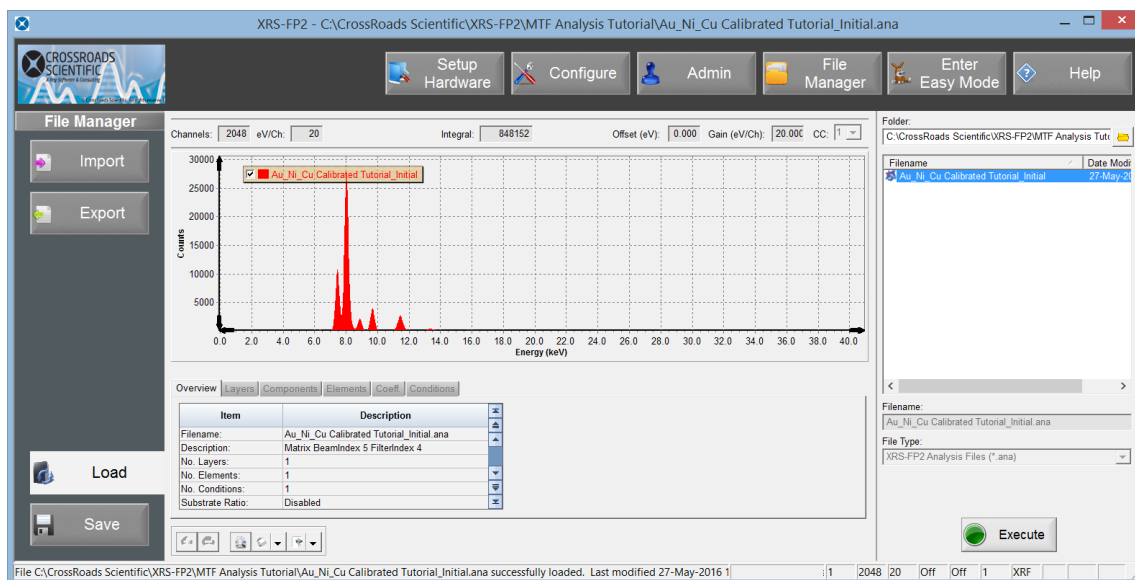
Two approaches are demonstrated here:

- 1) Calibration using a single “type standard” - such as a Au/Ni/Cu layered standard
- 2) Calibration using pure bulk Au, Ni, Cu materials - which is useful when a layered type standards or stackable thin-film standards are not available

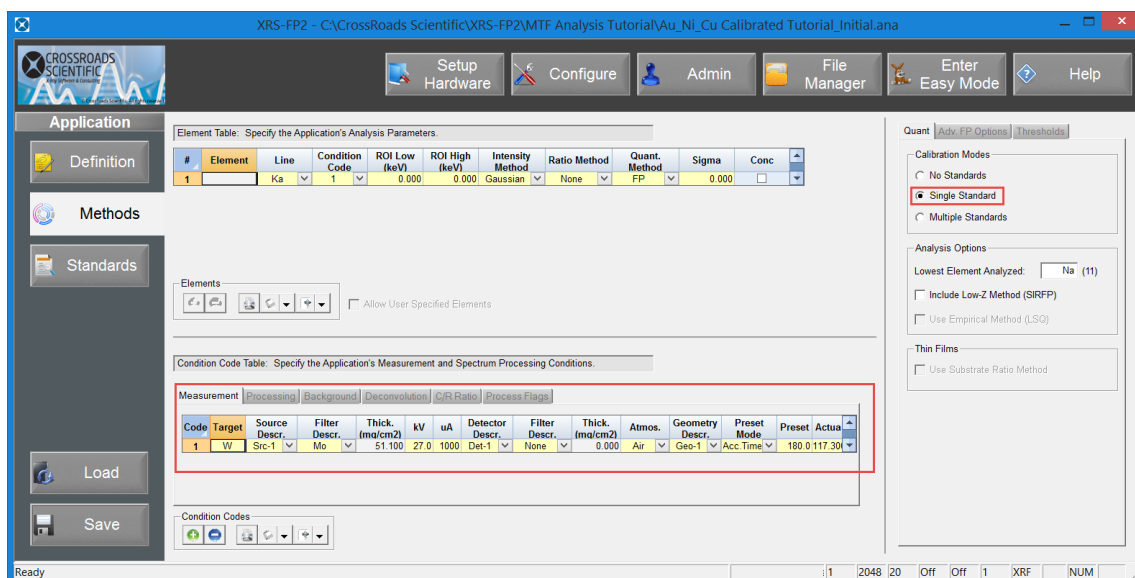
### 2.1 Single Type Standard Procedure:

1. Launch XRS-FP2.
2. Select the **File Manager** button.
3. Then select the **Load** button.
4. In the R-hand panel select the “**Au\_Ni\_Cu Calibrated Tutorial\_Initial.ana**” file. Then click the **Execute** button to load this file. See Figure 1 below.





5. Select the **Home** button then select the **Application** button, which takes us to the Application workflow.
6. Now select the **Methods** button. Since we are using a single type standard for the first approach to this application, select the radio button for "Single Standard" under the Calibration Modes section of the "Quant" tab (R-hand panel). See Figure 2 below.



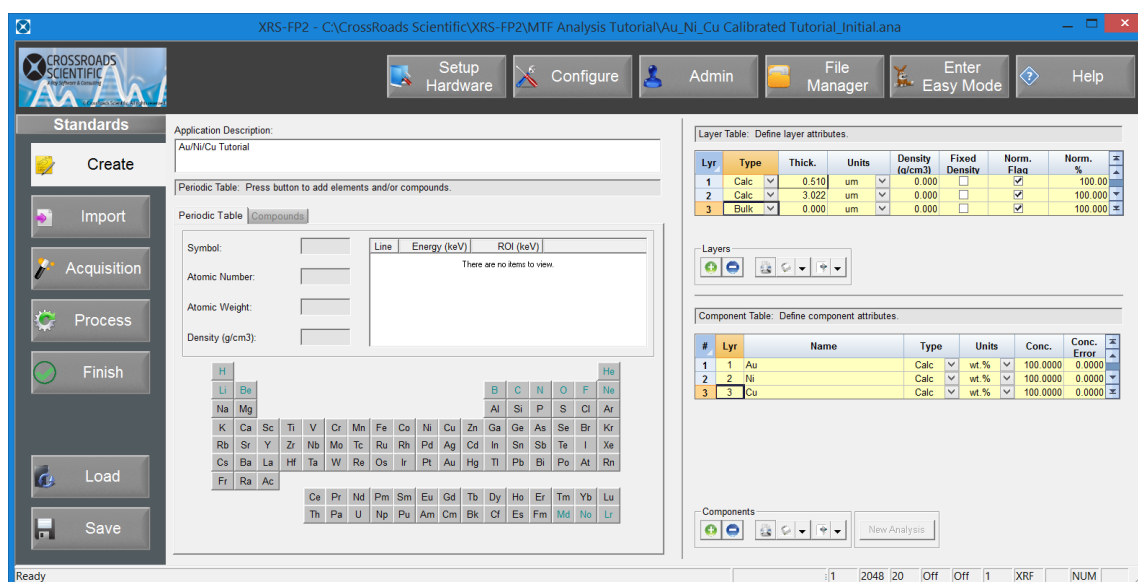
7. Note the spectrometer configuration in the Condition Code Table (Fig. 2 above). Although it is beyond the scope of this tutorial to go into detail on specific spectrometer configuration setup, we

will briefly review the excitation conditions used for the application presented here. Referring to the Condition Code Table shown above (Fig. 2), note that the spectrometer is configured with a tungsten (W) target tube. A primary filter is used to remove the W L emissions from acquired spectra that would otherwise interfere with application analyte emissions. An accelerating potential is selected that is sufficient to fluoresce the desired x-ray emissions of the analytes. In this case, Au emissions – LII critical potential is 13.733keV, so a 27keV tube potential was selected (1.5 – 2X the critical potential). This is also sufficient energy to fluoresce the Ni and Cu analytes. A 1000 $\mu$ A tube current was selected to provide count rates that would provide efficient analysis. This can be judged by the %DT (dead time) – which should be less than 50%.

8. Now select the **Standards** button in the application workflow. This is where we will define the single type standard used with the first approach to this application.
9. With the **Create** button selected, go to the Layer Table. This is where calibration standard thickness for each component layer is entered for calibration. The convention used for thin film analysis in XRS-FP2 is to number the layers from the top (Lyr 1) down. Layers are added either using the down arrow key or the **Add** button at the bottom of the table. In this application we have Au on Ni on Cu (substrate), so add 2 layers to the Layer Table, making a total of 3 layers.
  - a. Set the thickness (“Thick.”) of the first layer (Lyr 1) to 0.51 and the units to  $\mu$ m (this is the Au layer). Then set the thickness of the second layer to 3.022  $\mu$ m (for the Ni Layer). These are the layer thickness of our “Type” Standard – see Figure 3 below.
  - b. The third layer in this application is the Cu substrate, which is infinitely thick to the Cu emission (i.e. the intensity does not change as a function of the layer thickness). This is designated by selecting “Bulk” from the “Type” dropdown box. The default thickness value for Bulk is zero (i.e. no thickness is measured and units are irrelevant). It is important to define this layer for this application, because the Cu K $\beta$  fluoresced from the substrate has an enhancement effect on the Ni K emissions above it – Cu K $\beta$  has an energy of 8.907 keV, which is just above the critical potential of Ni K emissions of 8.331 keV. Note that the default “Type” (type of analysis) is “Calc” (calculate), so since we will be calculating/measuring the thickness of the first 2 layers (Au and Ni) these will remain unchanged.
  - c. The “Norm” (Normalize) field of the thickness table refers to component concentration. In thin film work layer concentration needs to be normalized to 100%. For this application, as noted previously, the layers are 100% pure metal, but it is good practice to **set the analyzed layer compositions to 100% by entering 100 in the “Norm. %” field and checking the “Norm. Flag” box**. See Figure 3 below.



10. Now go to the Component Table where we will add the application components. Components can be elements or compounds. In this application we are working with pure, elemental metals. In row #1 of the Components Table enter Au (note that you can also add elements and compounds by selecting them from the Periodic Table). To add another component use the down arrow key or the **Add** button at the bottom of the table. Now enter Ni and repeat this process to add the final component, Cu. Since this is a layered system, the component layer/position must be defined. The Component Table uses the same convention as the Layer Table – top down ordering where layer 1 is the top layer. In this case Au is Lyr 1, Ni is Lyr 2, and Cu is Lyr 3. Enter these values in the corresponding “Lyr” Column. Note that the Component Table order is unimportant, but the Lyr number as described is critical. Since these are pure metals, the standard and analyzed component concentrations will always be 100% (both Wt. and Mole). See Figure 3 below.

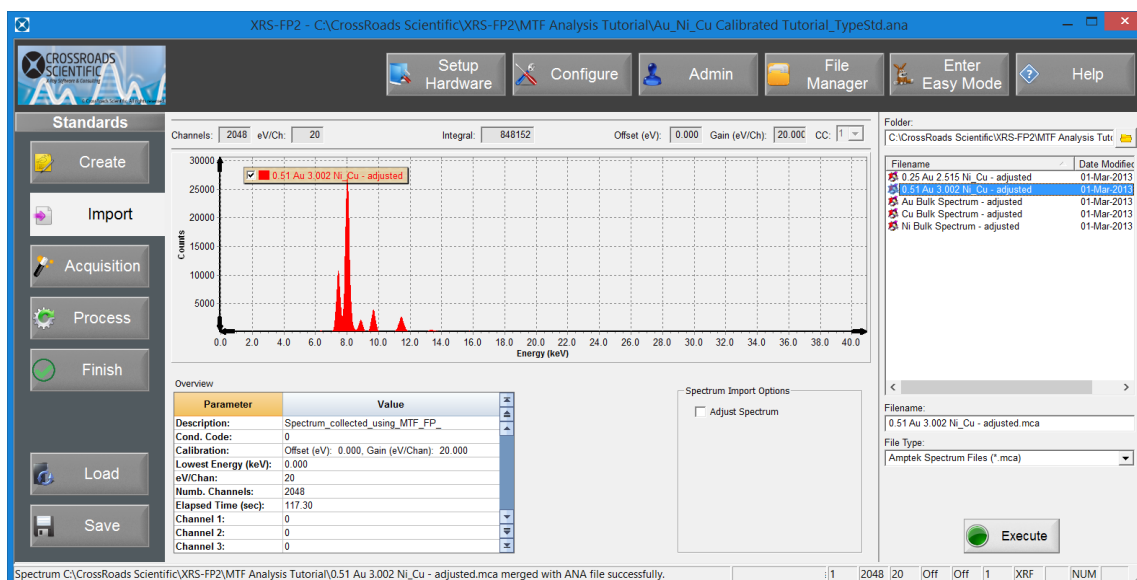


**Figure 3. Standards Workflow – Multilayer Type Standard Definition.** Add three layers for this type standard – set the thicknesses for the 1<sup>st</sup> and 2<sup>nd</sup> layer and set the 3<sup>rd</sup> layer (substrate) to Bulk and Normalize to 100%. Then add the components for this application – Lyr 1, Au; Lyr2, Ni; Lyr 3 Cu. Ensure the layer number is correct and set the concentrations to 100%.

11. At this point we can either import or acquire a spectrum. For this tutorial select the **Import** button and then choose the “0.510 Au 3.022 Ni\_Cu – adjusted.mca” file. Then select the **Execute** button to load this spectrum. Note that spectra supplied for this tutorial have already been energy adjusted (calibrated). See Figure 4 below.

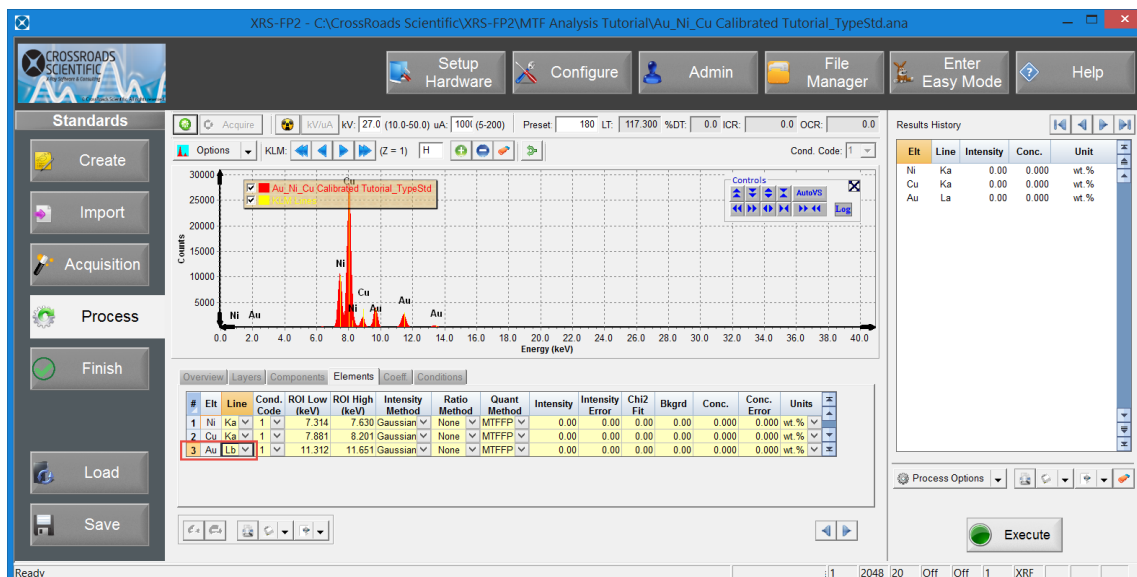






**Figure 4. Standards Workflow – Spectrum Import.** Open the “0.510 Au 3.002 Ni\_Cu – adjusted.mca” file for the single type standard.

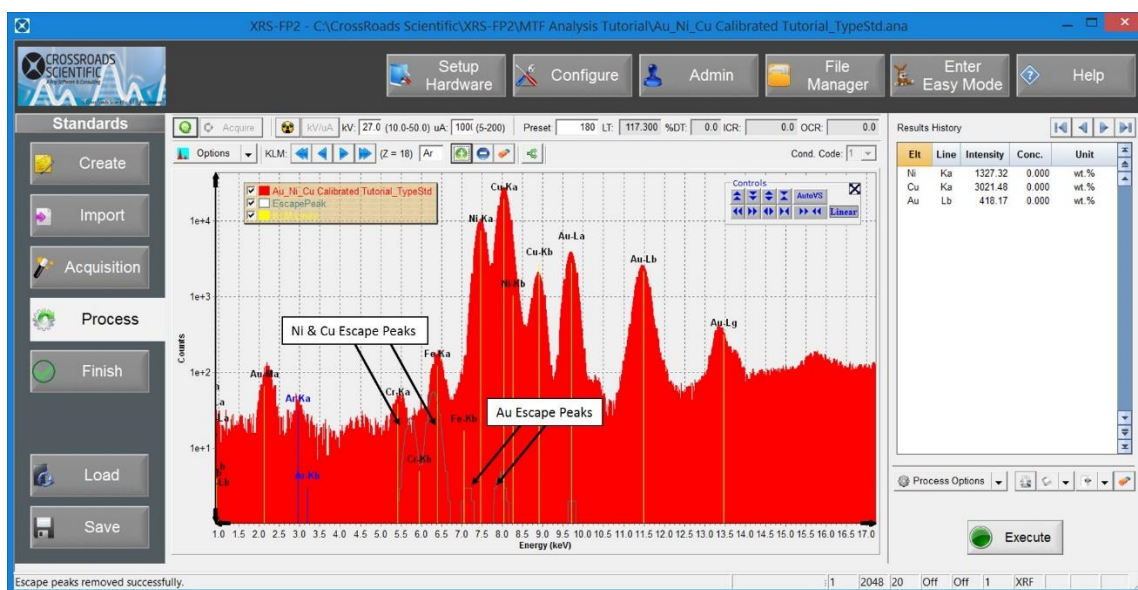
12. Then select the **Process** button in the Standards Workflow. Go to the “Elements” tab in the table below the spectrum view and change the Au “Line” to L $\beta$  (Fig. 5 below).



**Figure 5. Standards Workflow – Process.** Change the Au “Line” to L $\beta$  in the “Elements” tab below the spectrum view.

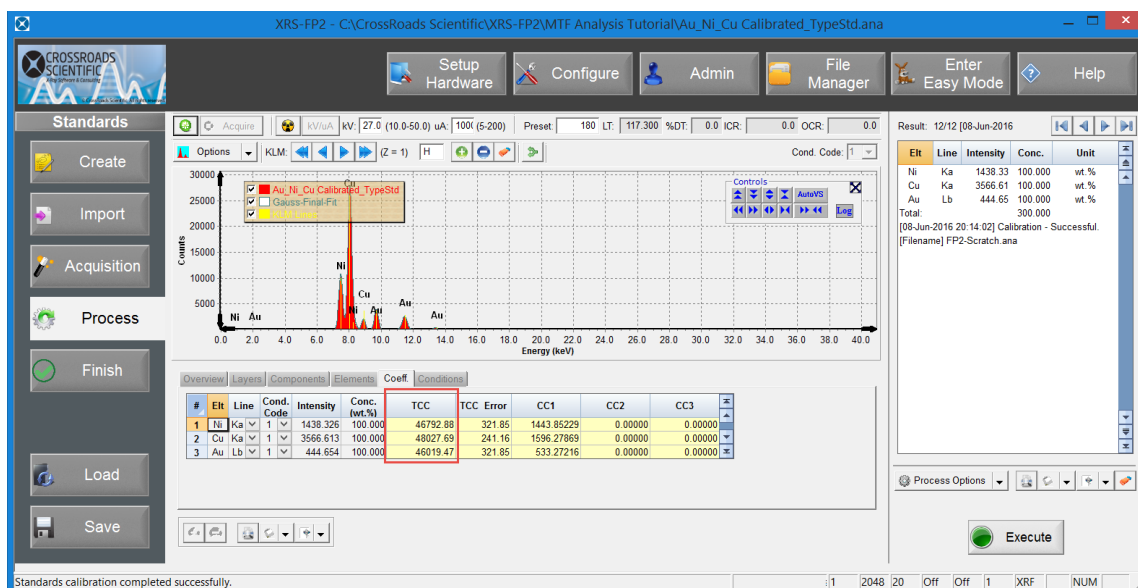
Note that it is always a good idea to qualitatively inspect the spectrum prior processing. The spectrum, “0.510 Au 3.002 Ni\_Cu – Adjusted.mca”, displayed below (Fig. 6) is presented in Log mode, which can be very useful for qualitative inspection. Although this is a spectrum acquired from an XRF calibration standard, we find a small Fe peak (happens to be a system peak, i.e. from the spectrometer) and a trace of Cr (perhaps a contaminant from the standard). These peaks are very small and will not interfere with the application setup and calibration. With Au being the top layer

there is some sensitivity for Au M emissions. The Spectrometer has an air path, so we see an Ar peak detected. Our analyte peaks and associated escape peaks are noted. We can also see that there is a peak overlap – the Ni K $\beta$  with the Cu K $\alpha$ . In this case, the K $\beta$  - K $\alpha$  overlap does not have a direct effect on calibration and quantification because we know the Cu is infinitely thick and have defined it as such, and the Cu K $\alpha$  energy is below the both Ni and Au critical potentials so there is no enhancement from the Cu K $\alpha$  on the Ni and Au layers. However, the Cu K $\beta$ , as noted earlier, is above the Ni K absorption edge, and there is some tailing of the Cu K $\alpha$  into the Ni K $\alpha$  region that will need to be taken into account. So, we have chosen to use non-linear Gaussian fitting for this exercise to obtain accurate Ni K $\alpha$  intensities. To select the extraction method, click on the “Processing” tab under the “Condition” tab and set the “Smooth Filter” to “Gaussian” (note that Gaussian is the default Method). To implement the non-linear Gaussian fitting option, go to the “Deconvolution” tab and check the box for “Non-Linear” deconvolution.



**Figure 6. Spectrum Inspection.** Visual inspection of the “0.510 Au 3.022 Ni\_Cu – Adjusted.mca” spectrum shows some artifact peaks (Fe and Cr), an Ar peak due to the air path, peak overlap, etc. These elements illustrate the importance of peak inspection for accurate analysis.

- Still in the Process view, select the **Execute** button in the R-hand panel (Fig. 6 above), which simultaneously processes the standard spectrum, extracts net intensities and generates theoretical calibration coefficients (TCC values) for each analyte line. See Figure 7 below. Note that as components are defined, the Element Table is filled in defaulting to what would nominally be the most intense analyte line available. For example, Au L $\alpha$ , Ni K $\alpha$ , and Cu K $\alpha$ . Also note that elements are listed in order of increasing atomic number in the Elements Table.



**Figure 7. Standards Workflow - Process.** Selecting the Execute button in the R-hand panel performs spectrum processing, intensity extraction and generates theoretical calibration coefficients (TCC values) in one step. Note that the “Process Options” dropdown button allows the user to walk stepwise through the individual steps should this be preferred.

If you click on the “Conditions” tab in the table below the spectrum view, you’ll see that we have chosen to apply one smooth function, remove escape peaks (as noted above, there are small Au escape peaks convoluted with the Ni and Cu regions) and apply the Auto Background removal. See Figure 8 below. The background low pass filter width parameter is set in the “Background” tab. Selecting the Execute button above applied these three functions and extracted intensities from this spectrum (Smooth-Escape Peak Removal-Background Removal-Deconvolution), using Non-linear Gaussian fitting. As mentioned above each function could also be applied manually (via the “Process Options” dropdown menu). Manual selection is very useful when selecting functions and associated parameters. Net peak intensities are extracted, integrated and displayed in the Intensity field of the “Element” tab. Intensities are expressed as count rates – counts/second.

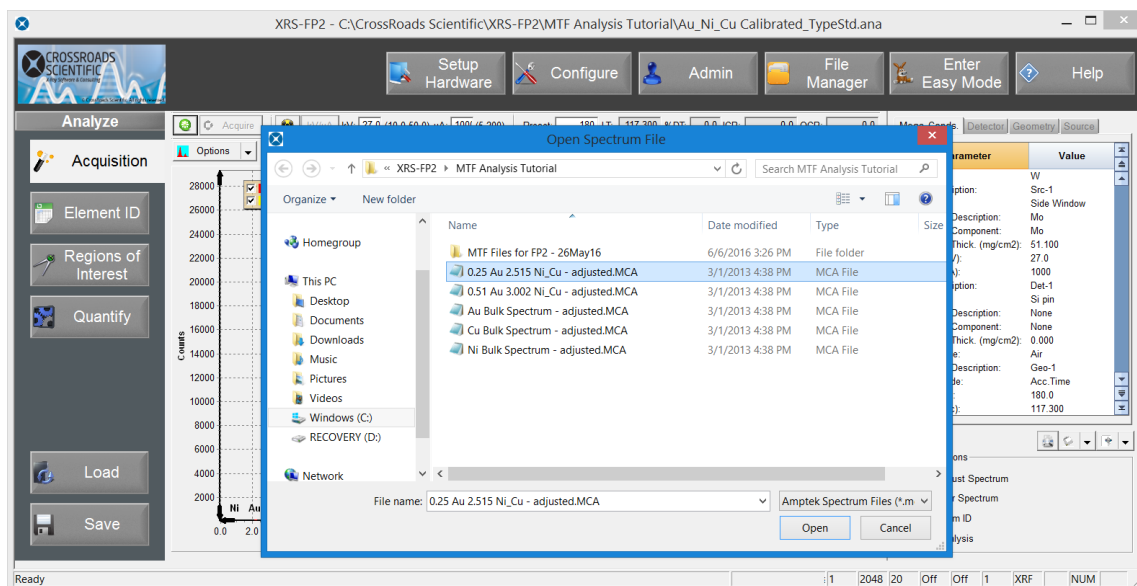
Conditions												
Measurement Processing Background Deconvolution C/R Ratio Process Flags												
Code	Lowest Eng. (keV)	Numb. Smooths	Smooth Filter	Smooth Points	Sum Peak	Inc. Bkard	Add PileUp	Esc Peak	Dpp Descr.	Pulse Pair Res. (uS)	Time Const. (uS)	
1	0.500	1	Gaussian	3	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Dpp-1	0.30	2.00	

**Figure 8. Standards Workflow – Conditions Tab.** Note the conditions used for spectrum processing and background removal.

- Now select the **Save** button and save the defined multilayer type standard (i.e. “Au\_Ni\_Cu Calibrated\_TypeStd.ana”).



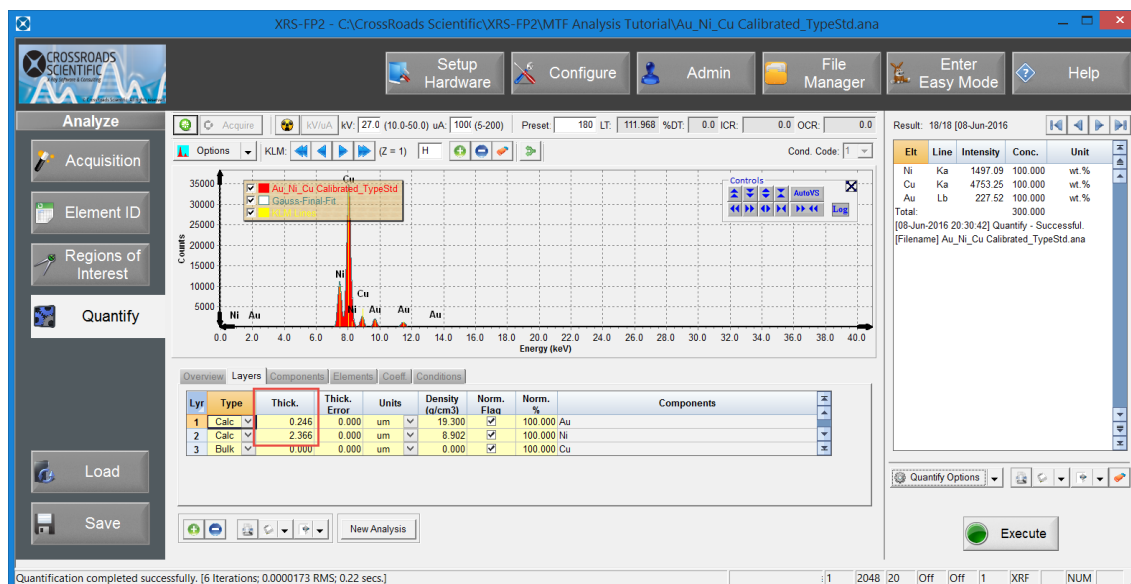
15. At this point we are ready to use the single standard TCC values generated above to analyze an unknown.
16. Go to the **Home** button, then select the **Analyze** button which brings us to the Analyze workflow.
17. With the **Acquisition** button selected go to the “Options” dropdown button (above the spectrum view) and select “open...” This will bring up the “Open Spectrum File” dialog (see Fig. 9 below). Open the unknown spectrum - “0.25 Au 2.513 Ni\_Cu – adjusted.mca”.



**Figure 9. Analyze Workflow – Acquisition Tab.** Open the unknown spectrum (i.e. “0.25 Au 2.513 Ni\_Cu – adjusted.mca”) to be analyzed.

18. Now click the **Quantify** button. Go to the “Layers” tab in the table below the spectrum view. Then click the Execute button in the R-hand panel. This will perform the spectrum processing (intensity extraction) and calculate the layer thicknesses in one step. The TCC calibration coefficients and FP algorithms are applied to the intensities extracted from the sample spectrum and calculated Au and Ni thicknesses are reported in the “Thick.” column of the “Layers” tab, shown below in Figure 10 (certified values for this material are 0.25  $\mu\text{m}$  Au and 2.515  $\mu\text{m}$  Ni).





**Figure 10. Analyze Workflow – Quantify Tab.** The TCC calibration coefficients and FP algorithms are applied to the intensities extracted from the sample spectrum and calculated Au and Ni thicknesses are reported in the “Thick.” column of the “Layers” tab (certified values for this material are 0.25  $\mu\text{m}$  Au and 2.515  $\mu\text{m}$  Ni).

19. Finally, click the **Save** button and save the results of the analysis.

## 2.2 Multipoint Bulk Calibration Procedure:

If thin-film type standard(s) are not available, which can be a common situation in thin-film work, then a good option is calibrating with bulk (infinitely thick) pure metals, alloys or compounds. In the following exercise we will utilize the Au/Ni/Cu application developed above and re-calibrate it using TCCs derived from bulk Au, bulk Ni and bulk Cu materials.

Note: In this case, because Cu is the substrate and is infinitely thick, therefore, dominating the fluorescence from the sample, we will be able to use the same excitation conditions that were used for the type standard calibration and be optimized in terms of count throughput for the application. This may not always be the case. For instance, if the application was for the measurement of thin films on Si, then Si would be dominant elemental mass of the sample stack and optimizing excitation based on the sample would result in impractical and perhaps even erroneous dead times when acquiring spectra from bulk coating materials. In such a case the excitation parameters would have to be established from the bulk metal materials and will not be optimized for the count throughput of the thin-film sample.



1. From the Analyze workflow or from the file manager select the **Load** button and load the “Au\_Ni\_Cu Calibrated\_TypeStd.ana” file created above. This will be used as a template.
2. Then select the **Home** button followed by the **Application** button. Then click on the **Methods** button. In the R-hand panel select the radio button for “Multiple Standards” under the Calibration Modes section of the “Quant” tab. See Figure 11 below.

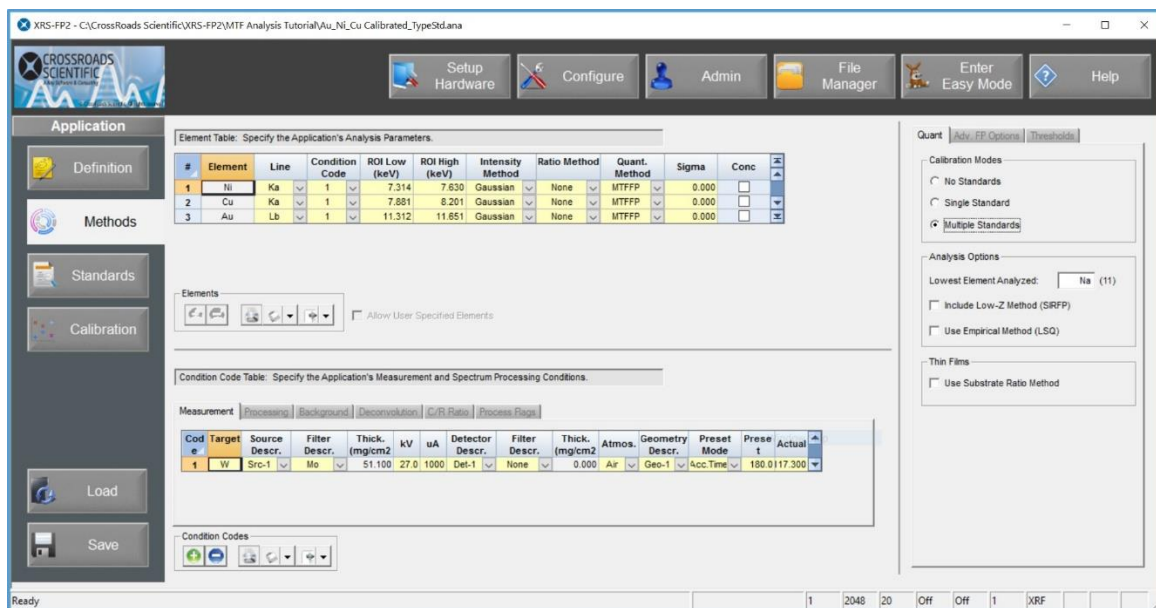


Figure 11. Application Workflow – Methods. Select the radio button for multiple standards.

3. Next select the **Standards** button. In the **Create** view, remove two of the rows in both the Layer Table and the Component Table. Enter Au in the Component Table and set the concentration to 100%. Then set the “Type” to Bulk in the Layer Table. See Figure 12 below.

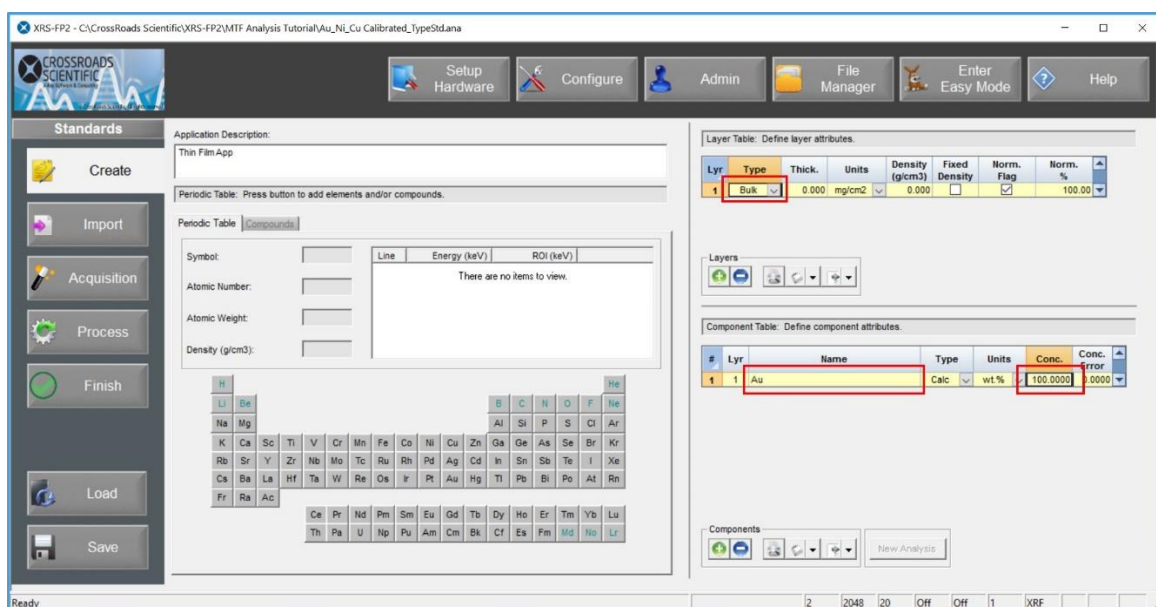


Figure 12. Standards Workflow – Create. Define the first pure element, bulk standard (i.e. bulk Au).



4. Now select the **Import** button. From the R-hand panel click on the “Au Bulk Spectrum – adjusted.mca” file and select the **Execute** button to load the spectrum file for this bulk standard (see Fig. 13 below).

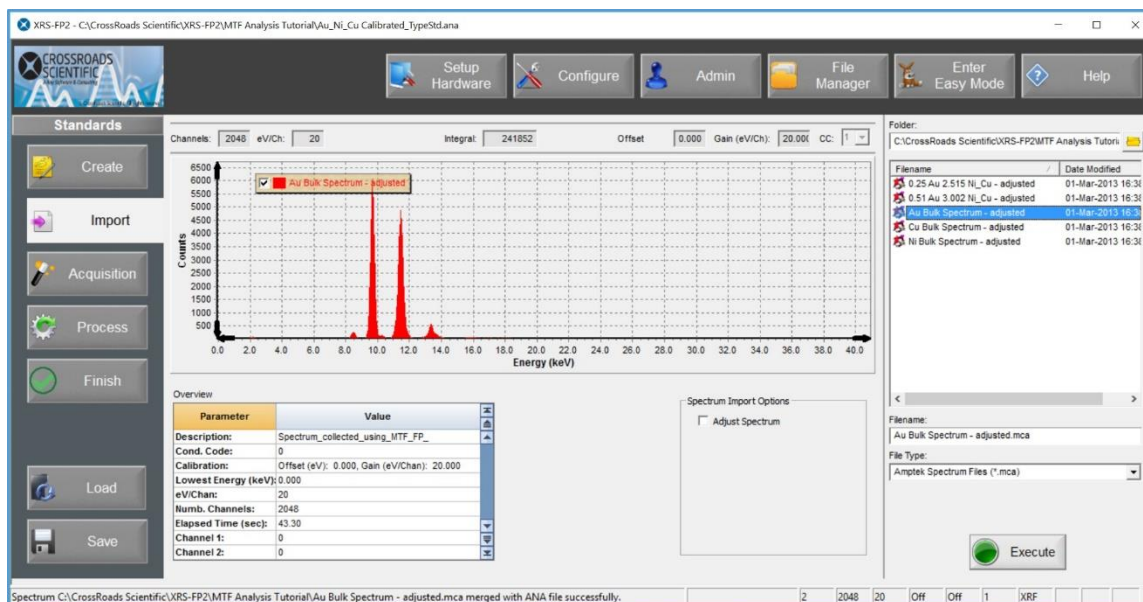


Figure 13. Standards Workflow – Import. Import the “Au Bulk Spectrum- adjusted.mca” file.

5. Then select the **Process** button. As with the type standard calibration, we will use the Au L $\beta$  line. Change the “Line” field of the Elements tab to display L $\beta$  (Fig. 12 below). In the R-hand panel select the **Execute** button to process the spectrum and obtain a TCC value for Au. See Figure 14 below.

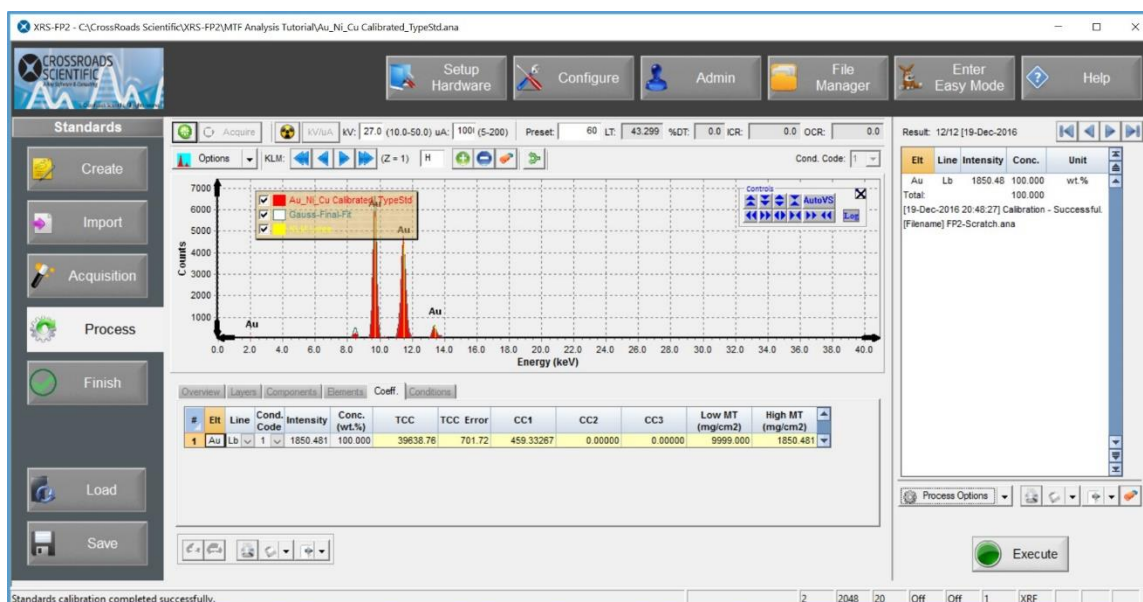


Figure 14. Standards Workflow – Process. Change the Au “Line” to L $\beta$ , then process the bulk Au spectrum and obtain a TCC value.

6. Then select the **Save** button and save the bulk Au single standard calibration.
7. Select **Yes** when prompted to add the single standard to the MLSQ setup.
8. Repeat steps (3-7) above for the following two bulk standards: Cu and Ni. Be sure to save the calibration after obtaining a TCC value for Cu and Ni.
9. Having obtained single standard calibrations (with TCC values) for Au, Ni and Cu, select the **Load** button. Recall the “Au\_Ni\_Cu Calibrated\_TtypeStd.ana” by selecting the **Execute** button in the R-hand panel.
10. Select the **Finish** button, which will bring you to the Methods view. In the R-hand panel select the radio button for “Multiple Standards” under the Calibration Modes section of the “Quant” tab.
11. Then select the **Calibration** button.
12. Enter the three single standard calibration files in the MLSQ table under the “Standard Filename” column. Double click in the “Standard Filename” column and add the three standards created above using the down arrow key or plus button to add additional rows as needed. See Figure 15 below.

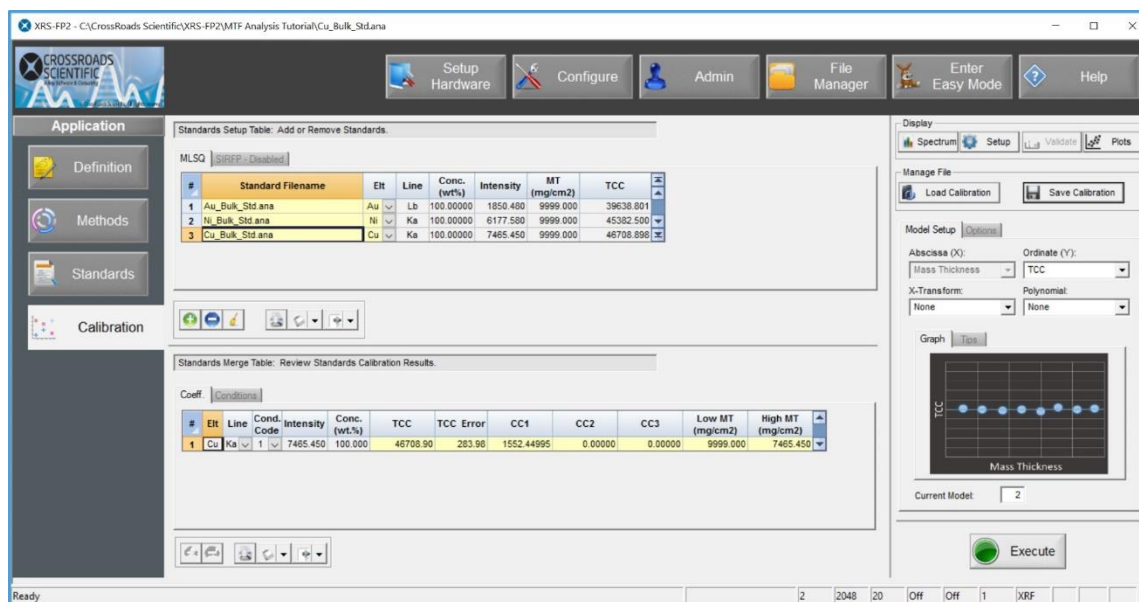


Figure 15. Application Workflow – Calibration. Add the three bulk standard files to the MLSQ calibration table.

13. Check the Model Setup in the R-hand panel. The “Ordinate (Y)” should be set to “TCC” and the “Current Model” should be model 2. See Figure 15 above.





14. Then select the **Execute** button in the R-hand panel to merge the TCC values for the three single, bulk standards into a single MLSQ calibration file.
15. We now have a new calibration for the Au/Ni/Cu system based on pure bulk materials. To save the MLSQ calibration, select the **Save Calibration** button the R-hand panel and save both the \*.ANA and \*.CAL files (i.e. "Au\_Ni\_Cu\_BulkMultiStds.cal" and "Au\_Ni\_Cu\_BulkMultiStds.ana").
16. We can now use the TCC values from the "Au\_Ni\_Cu\_BulkMultiStds.ana" file generated above to analyze an unknown.
17. Select the **Home** button, followed by the **Analyze** button. Then select the **Load** button and load the MLSQ calibration file saved above ("Au\_Ni\_Cu\_BulkMultiStds.ana"). Next select the **Acquisition** button and go to the "Options" dropdown button (above the spectrum view) and select "open..." This will bring up the "Open Spectrum File" dialog. Open the unknown spectrum - "0.25 Au 2.513 Ni\_Cu – adjusted.mca".
18. Now click the **Quantify** button. Go to the "Layers" tab in the table below the spectrum view. Then click the **Execute** button in the R-hand panel. This will perform the spectrum processing (intensity extraction) and calculate the layer thicknesses in one step. The TCC calibration coefficients and FP algorithms are applied to the intensities extracted from the sample spectrum and calculated Au and Ni thicknesses are reported in the "Thick." column of the "Layers" tab (certified values for this material are 0.25  $\mu\text{m}$  Au and 2.515  $\mu\text{m}$  Ni).
19. Finally, click the **Save** button and save the results of the analysis.

