

XRS-FP2 Fundamental Parameters Tutorial

Note: This tutorial guides a new XRS-FP2 user through the setup and analysis of a bronze alloy using a standardless, single standard and multiple standard approach.



CrossRoads Scientific

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

info@CrossRoadsScientific.com

www.CrossRoadsScientific.com



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DOCUMENT CHANGE LOG

Date	Person	Pages	Description
13-Jun-15	Sarah Cross	All	Created document
11-Jul-15	Sarah Cross	Some	Updated document
18-Nov-15	Sarah Cross	Some	Updated document
26-Apr-16	Sarah Cross	Some	Updated document
23-May-16	Sarah Cross	Some	Updated document
16-Dec-16	Sarah Cross	Some	Updated document



1 XRS-FP2 FUNDAMENTAL PARAMETERS OVERVIEW

The following document along with associated files (*.ana) guides a new user of CrossRoads Scientific's XRF Fundamental Parameters Application Software (XRS-FP2) through the setup and implementation of an analysis. This includes:

1. Qualitative inspection of the sample
2. Spectrum processing
3. Calibration
4. 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 or in the XRS-FP2 Software User Manual). And that spectrometer excitation parameters have been selected, i.e., incident beam collimation (if required), tube accelerating voltage, tube current, primary beam filter. The setup of these parameters will be spectrometer / application specific and are not within the scope of this tutorial other than to emphasize that in order to obtain accurate XRF analysis these must be defined and maintained in the XRS Application, ANA file.

Application: Bronze alloy (Cu-Sn alloy) – 3 approaches are demonstrated here: Standardless analysis, calibration using pure bulk materials and calibration using a single “type standard”. A type standard is a standard of similar composition to that of the unknowns.



2 BRONZE ALLOY – STANDARDLESS ANALYSIS

The following steps describe the standardless analysis of a bronze alloy (Cu-Sn alloy):

1. **Launch XRS-FP2** – either run the software from the Windows Start-Programs menu, or double-click on a shortcut (if one has been created on the desktop). First, a splash screen will load and then XRS-FP2 will be displayed. See figure 1 below. The splash screen will briefly show the values and options for the HASP security plug, and the software libraries that have been loaded. This can also be displayed by selecting the **Help** button (located in the top ribbon).

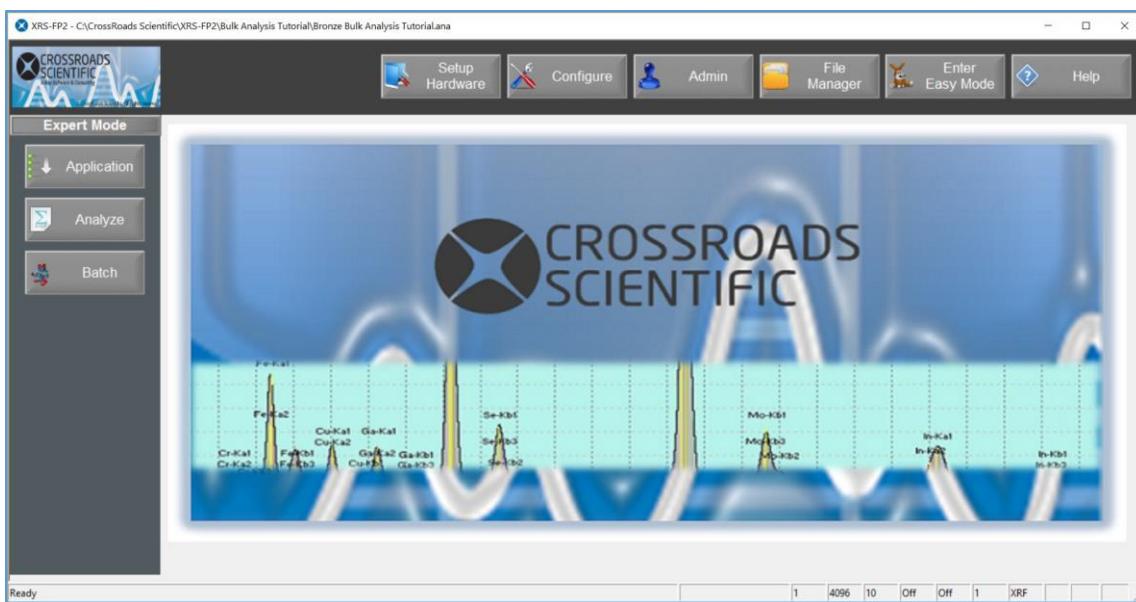


Figure 1. XRS-FP2. XRS-FP2 home page.

2. Select the **File Manager** button from the top ribbon, then select the **Load** button and locate the “Bronze Bulk Analysis Tutorial.ana” file in the “C:\CrossRoads Scientific\XRS-FP2\Bulk Analysis Tutorial” directory (or equivalent location). Select the “Bronze Bulk Analysis Tutorial.ana” file in the right-hand panel of XRS-FP2 and either double click or use the **Execute** button to load the file. See figure 2 below.

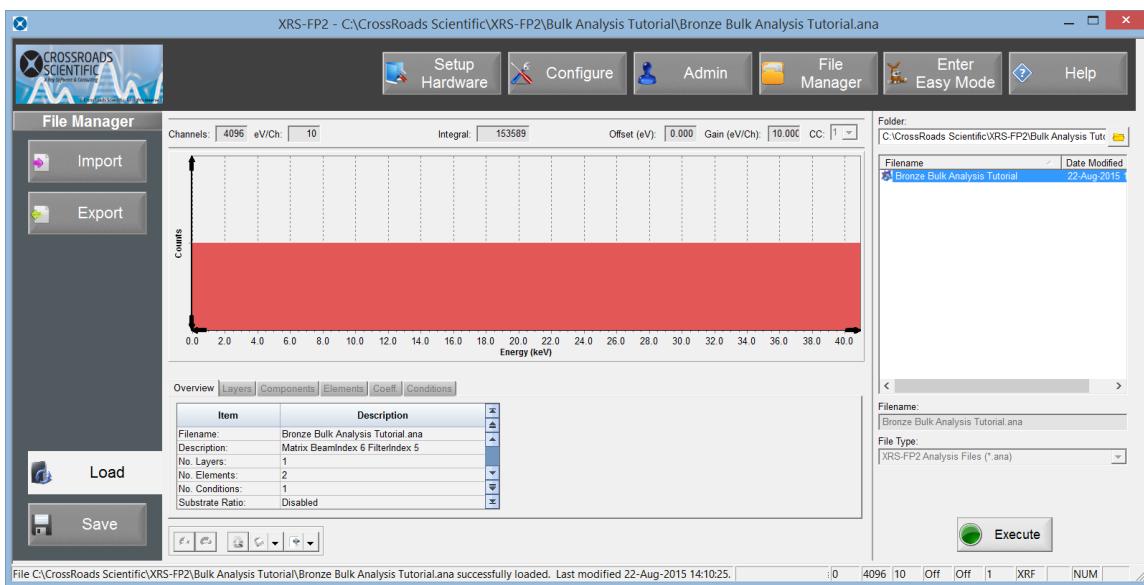


Figure 2. File Manager. Open the Bronze Bulk Analysis Initial ANA file, e.g. “Bronze Bulk Analysis Tutorial.ana”.

This ANA (“analysis”) file, acts as a template for this tutorial. An ANA file contains the elements and calibration coefficients (if employed) that are required for routine XRF analysis, along with a description of the various analysis and system setup. Although the components tab, elements tab and layer tab have no results at this point, the conditions tab (spectrometer configuration) is already pre-defined and loaded for this application. See Figure 3 below.

Measurement														
Code	Target	Source ID	Filter	Thick. (mg/cm ²)	kV	uA	Detector ID	Filter	Thick. (mg/cm ²)	Atmos.	Geometry ID	Preset Mode	Preset	Actual
1	W	Src-1	Mo	76.650	47.0	240.0	Det-1	None	0.000	Air	Geo-1	Time	30.0	18.3

Figure 3. XRS-FP2 Conditions Tab. The “Bronze Bulk Analysis Tutorial.ana” file acts as a template for this application. Note that this file contains the proper measurement & processing information for this application (i.e. spectrometer configuration information). Also note that in the layers tab, the “Type” is set to “Bulk” and it is “Normalized” to 100%.

It is not within the scope of this tutorial to go into the details of setting up specific spectrometer configurations. However, we will briefly review the excitation conditions used for the example presented here. Referring to the Measurement tab of the XRS-FP2 Conditions view on your display (shown above, Figure 3), 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, Cu from the Bronze. An accelerating potential is selected that is sufficient to fluoresce the desired x-ray emissions of the analytes. In this case, dictated by the Sn emissions – K critical potential is 29.190 keV, so, 47 kV tube potential was selected (~1.5 -2 X) the critical potential, if possible. This is also sufficient energy to



fluoresce the Cu analyte line. A 240 μA tube current was selected to provide count rates that would provide efficient analysis. This can be judged by %DT (dead time) – typically 45% \pm 10%.

- Now click on the **Home** button (Fig. 4, yellow circle), then select the **Application** button (Fig. 4, red circle).

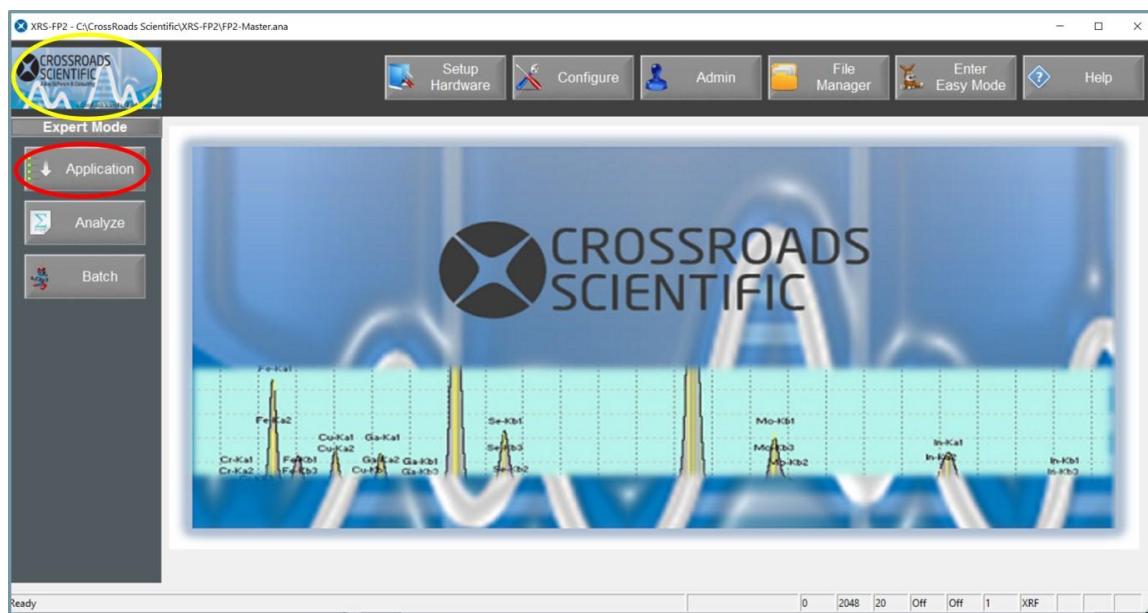


Figure 4. XRS-FP2 Application Setup. From the XRS-FP2 home screen select the application button to setup the application.

- Select the **Definition** button.
- To create a “clean sheet” for analysis click the **New Analysis** button below the component table. This will clear all of the application information, i.e., Component Table, Elements Table and Thickness information; however, the Measurement information (spectrometer configuration) will be retained.
- The definition workflow is where the sample elements and compounds can be entered either by clicking on the periodic table or by entering them in the Component Table (in the right-hand panel). In this tutorial, we are working with alloying metals, elemental metals. Select or enter **Cu** as the first component. Having entered a component in the table, use the down arrow key of your computer keyboard or the “plus” and “minus” buttons to enter additional components. Now enter **Sn** for the second component. See Figure 5 below. Notice that the “Type” is automatically set to “Calc” so the SW will calculate the concentration of each component.

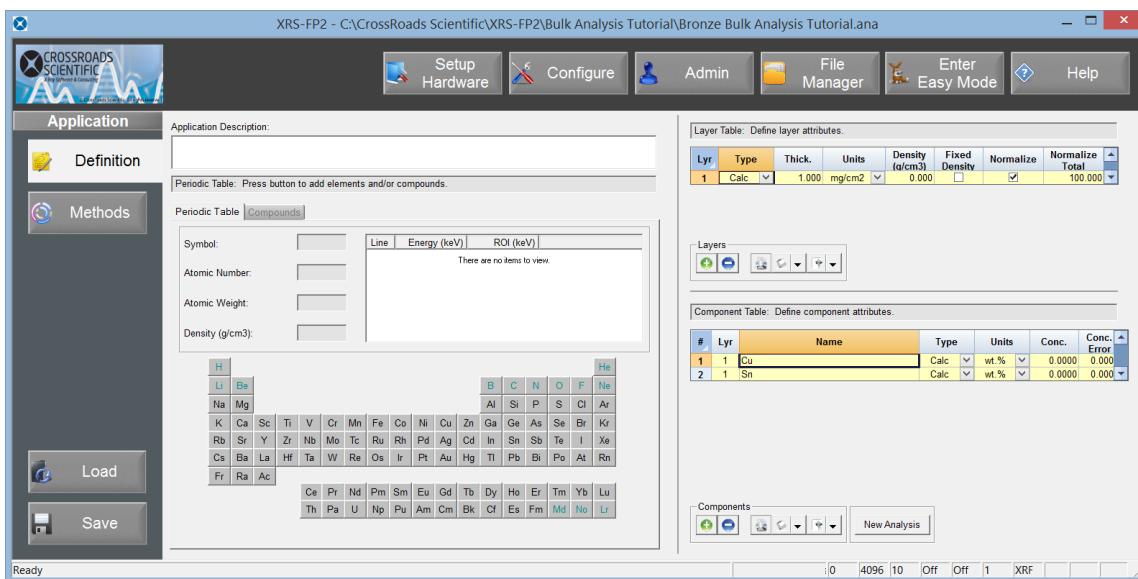


Figure 5. XRS-FP2 Application Workflow - Definition. The application definition is input here.

In addition to defining the sample components, the layer attributes of a sample are also defined here. Accurate XRF analysis requires definition of the thickness of the sample material. In the case of this tutorial, the bronze is infinitely thick, which means that it has greater thickness than the escape depth of the highest energy line, the Sn K α . This is defined as “Type” “Bulk” in the “Layer Table”, which is the default type setting. The default thickness for bulk analysis is zero (0). XRS-FP2 facilitates the analysis of less than infinitely thick samples by calculating the thickness; the **Type** field is set using the pull down to and selecting **Calculate**. Note that thickness of less than infinitely thick samples can also be **Fixed** (thickness and units must then be defined in the fields provided), or calculated by absorption (Absn) from the absorption of an emission from material below the layer being analyzed. Density and Unit fields only apply to less than infinitely thick samples. The “Normalize” field of the thickness table refers to component concentrations. For standardless analysis the results **MUST** be normalized (see Fig. 5 above). Normalizing to 100% is not required for all bulk analysis, but is often employed.

7. Select the **Methods** button. As components are defined (see above), the “Element Table” is filled in and the line is set to the highest energy line that gets excited by the source kV. Note that the line must have an associated edge energy that is below the specified kV in the Condition Table, otherwise the intensity will be reported as zero. In this case, the Cu K α and Sn K α . These are appropriate selections for this application (see Fig. 6 below).

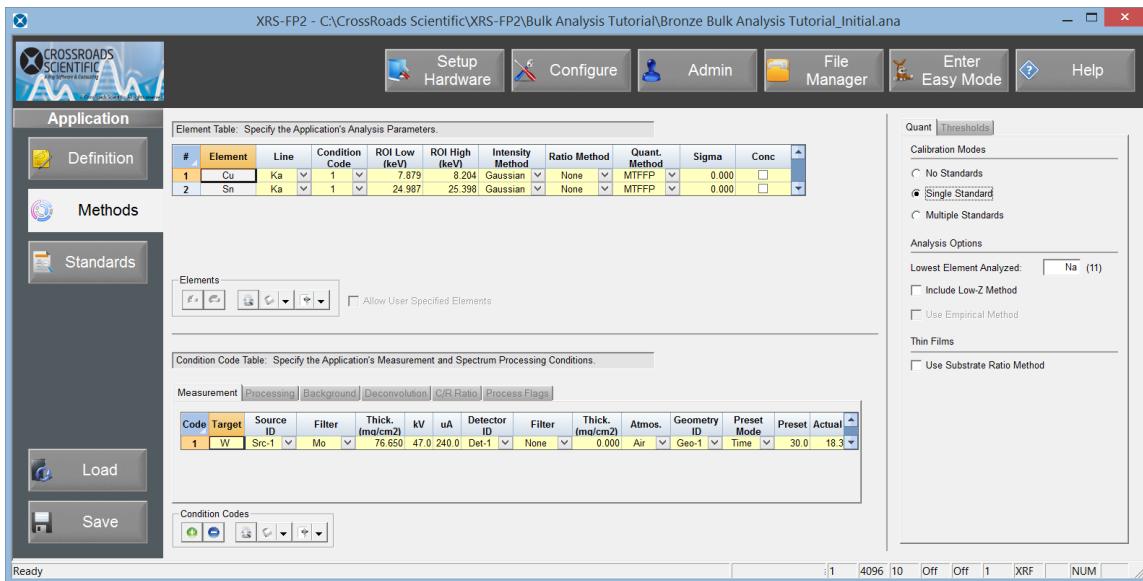


Figure 6. XRS-FP2 Application Workflow - Methods. The application methods are input here.

- Set the application quant method (calibration mode). In the R-hand panel under the “Quant” tab select the radio button for “**No Standards**” (i.e. standardless). Figure 7 below.

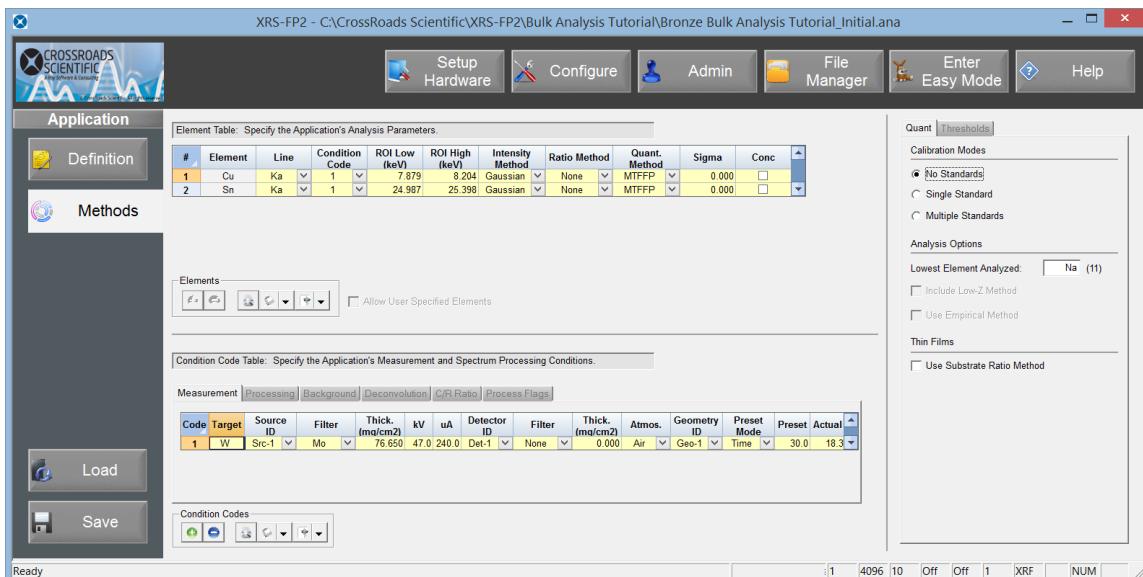


Figure 7. XRS-FP2 Application Workflow – Calibration Mode. The quant method is set to standardless (i.e. no standards).

- Now click on the **Home** button and then select the **Analyze** button (Fig. 8, red circle).



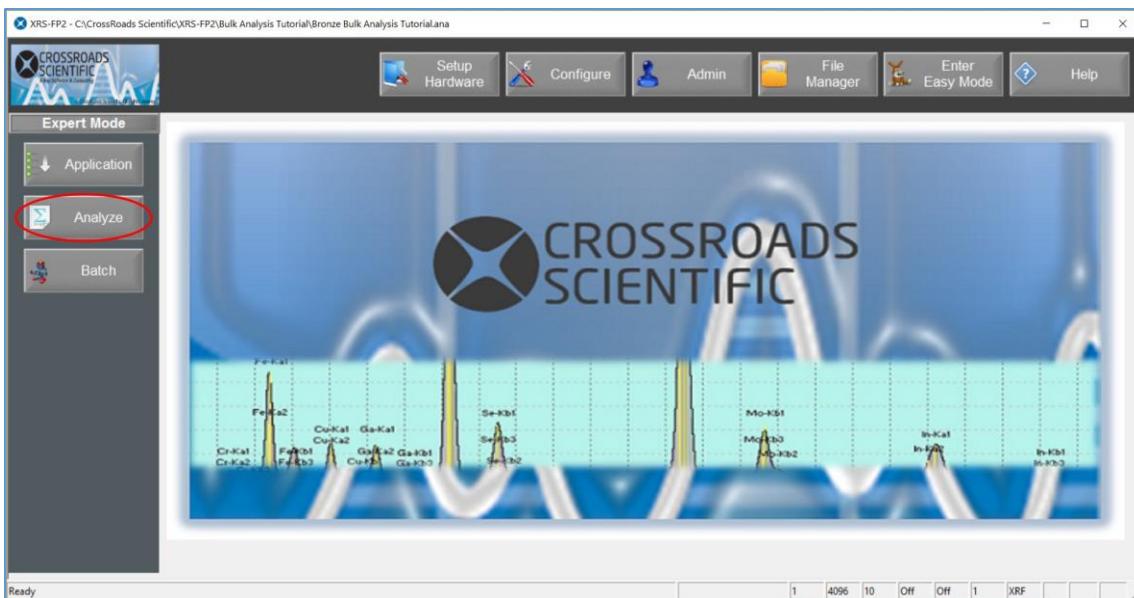


Figure 8. XRS-FP2 Analyze Workflow. From the XRS-FP2 home screen select the analyze button.

10. Then select the **Quantify** button from the L-hand panel. Notice that the bronze spectrum (adjusted) associated with this particular application is loaded in this view (Fig. 9 below). Clicking on the “Log” button in the “Controls” panel in the spectrum view can be very useful for quantitative inspection. Here we see the Cu and Sn analyte peaks are identified, as well as trace Pb (not uncommon to bronzes) and a small Zr system peak (coming from the spectrometer, not the sample). The Pb and Zr are very small peaks and will not interfere with the application calibration setup or analysis.

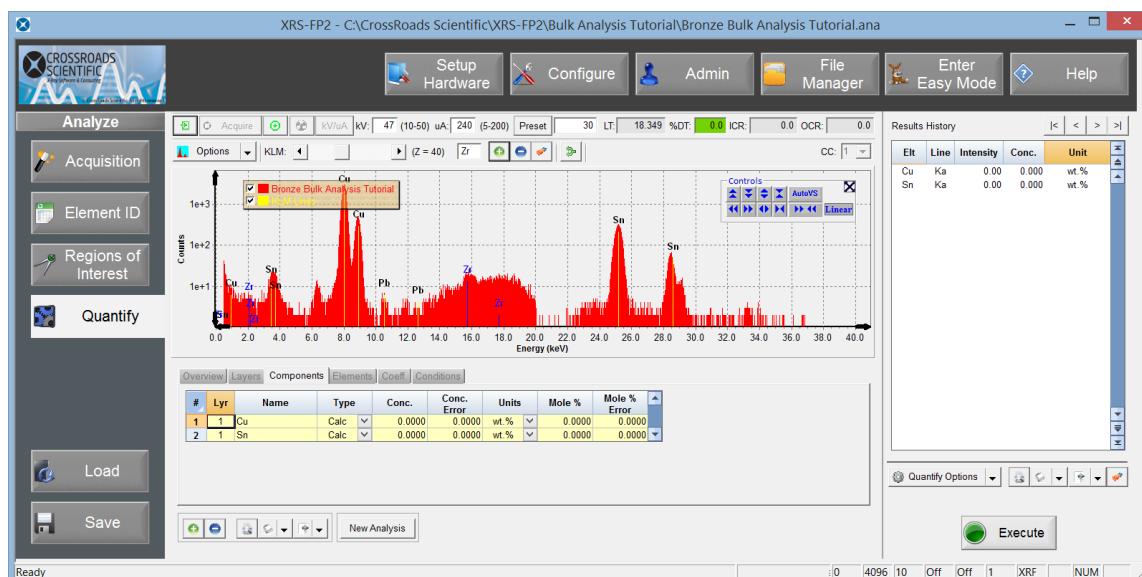


Figure 9. XRS-FP2 Analyze Workflow - Quantify. Visual inspection of the bronze spectrum associated with this application.



11. Click on the “Conditions” tab in the Quantify view, then click on the “Processing” tab to view the spectrum processing conditions. See Figure 10 below. We have chosen to apply one smooth function, remove escape peaks, and apply the Auto Background removal (“Background” tab).

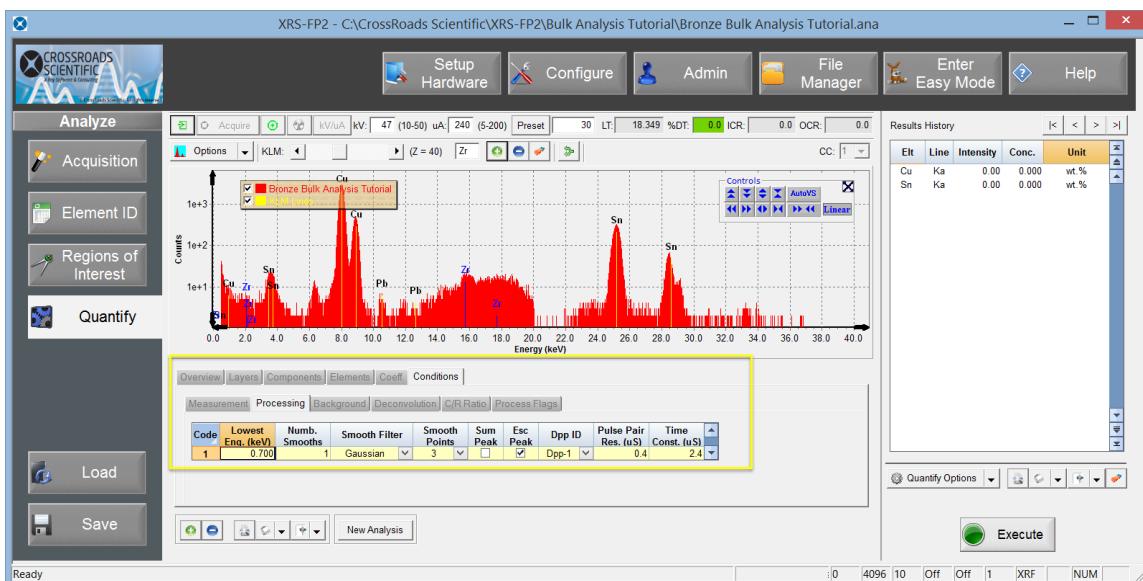


Figure 10. XRS-FP2 Analyze Workflow - Quantify. Spectrum processing conditions associated with this application.

12. Now select the **Execute** button in the R-hand panel in the Quantify workflow (Fig. 10 above) to extract intensities and concentrations for the elements in the bronze spectrum. Note that the Execute button does a complete “process all” (smooth, escape peak removal, background removal, deconvolution) and quantification of the spectrum. You may also select the Quantify Options button to individually process and quantify the spectrum in a stepwise fashion.

Note that there are several peak intensity extraction options. By clicking on the Intensity Method fields (“Elements” tab) for the analyte lines in the table these are displayed – Intensity, Gaussian, Integrate and Reference. The tutorial uses the Gaussian fit of which there are 2, linear and nonlinear. Nonlinear is used here and is set as a processing condition parameter (“Deconvolution” tab under the “Conditions” tab in the table). Each Processing Function can also be applied manually (individually). Manual selection is very useful when selecting functions and associated parameters. Net peak intensities are extracted, integrated and displayed in the Intensity field under the “Elements” tab. Intensities are expressed as count rates – counts/second.

Notice that there are now results - intensities and concentrations (wt%) – from the standardless analysis displayed for each element in the results listed in the right-hand panel (see Fig. 11 below). These results are also listed in the table below the spectrum display under the



“Components” and “Elements” tabs. Note that standardless results are always normalized to 100% and the total sample matrix must be defined.

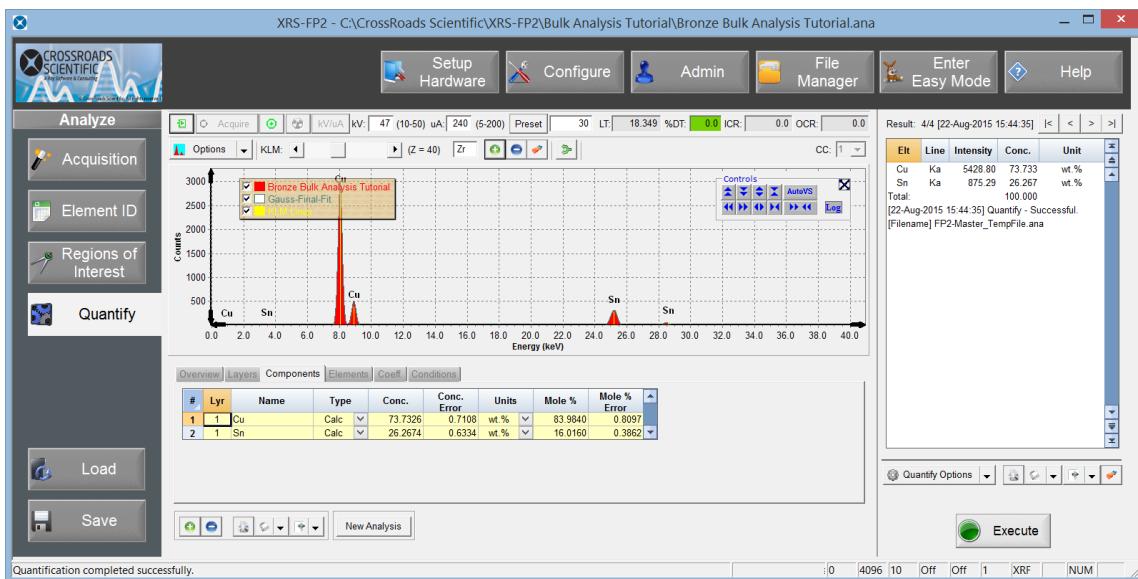


Figure 11. XRS-FP2 Quantify Panel. Note that intensities and concentrations are now displayed for each element.

*This completes the **standardless analysis** portion of this bronze tutorial.

Note that most instrumental analysis requires calibration to a standard material. However, XRF is somewhat unique, since x-ray physics are very well defined there are analysis circumstances where analysis can be performed without standards – truly standardless analysis. Standardless analysis requires X-ray fundamental parameters algorithms be employed (XRS-FP2 is a fundamental parameters analysis program) and that all the components in the sample material be defined either by the XRF analysis or input by the user and that the sample material be infinitely thick. The tutorial application meets these criteria.



3 BRONZE ALLOY – SINGLE STANDARD CALIBRATION

Standardless Analysis is convenient and provides a good semi-quantitative analysis. However, in addition to this method, we can calibrate using a “type” standard. This method provides a quantitative approach using a standard material having composition similar to the “unknown” materials that will be analyzed to establish Calibration Coefficients (TCC). This is often the preferable standardization method, particularly if the standard is derived from the same process as the unknowns in a routine analysis regime. For the tutorial we will use the bronze spectrum that we have been employing as the Type Standard spectrum. The following steps describe calibration using a single type standard for the analysis of a bronze alloy (Cu-Sn alloy):

1. Click on the **Home** button (Fig. 12, yellow circle), then select the **Application** button (Fig. 12, red circle).

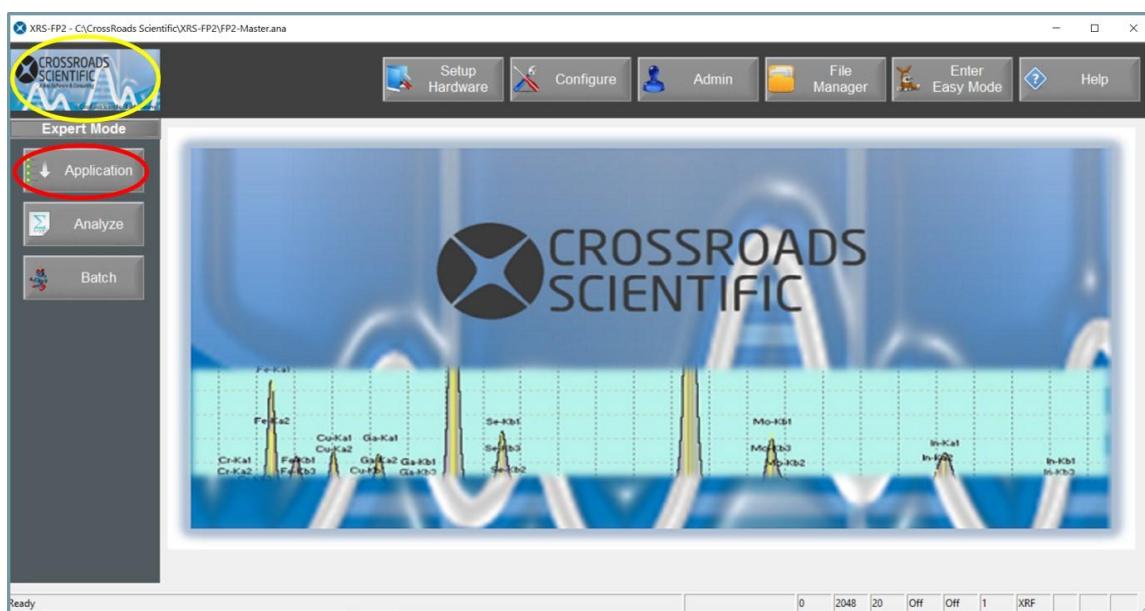


Figure 12. XRS-FP2 Application Setup. From the XRS-FP2 home screen select the application button to setup the application.

2. Select the **Definition** button.
3. To create a “clean sheet” for analysis click the **New Analysis** button below the component table. This will clear all of the application information, i.e., Component Table, Elements Table and Thickness information; however, the Measurement information (spectrometer configuration) will be retained.

4. Again, select or enter **Cu** as the first component. Then use the down arrow key of your computer keyboard or the “plus” and “minus” buttons to enter **Sn** for the second component.
5. Select the **Methods** button.
6. Set the application quant method (calibration mode), in the R-hand panel under the “Quant” tab, to **“Single Standard”** (Fig. 13 below).

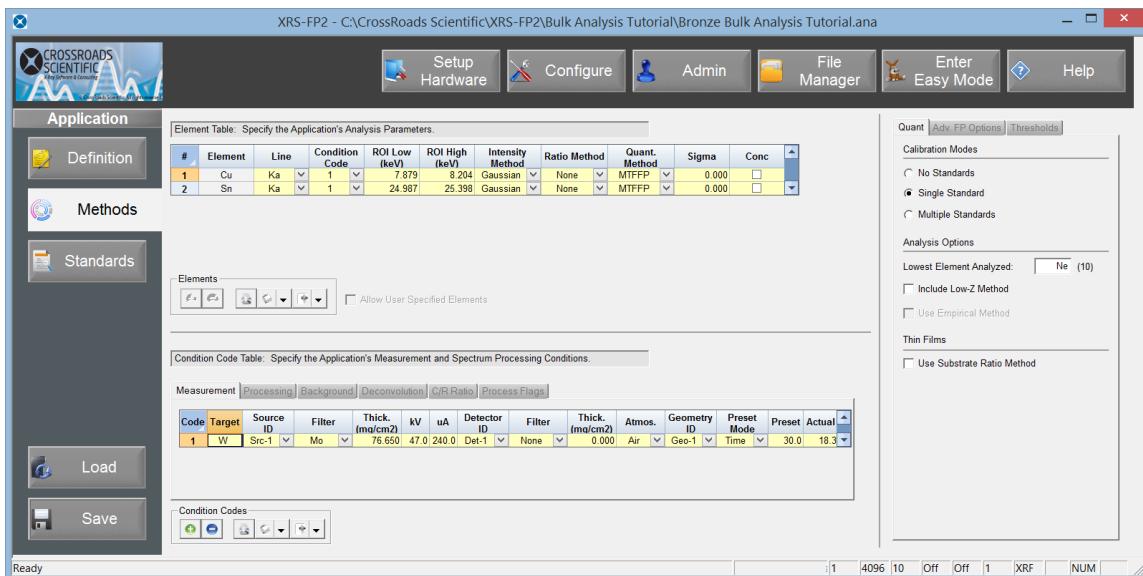


Figure 13. XRS-FP2 Application Workflow – Single Standard Calibration Mode. The quant method is set to single standard.

7. Now select the **Standards** button from the L-hand panel in the Application workflow.
8. Select the **Create** button. Now enter the standard values (concentrations) for the Cu and Sn elements – 78 wt% Cu and 22 wt% Sn. Enter these values in the “Conc” column of the standard Component Table.
9. Then click on the **Import** button and select the “Bronze Spectrum Adjusted.mca” file to import for our type standard spectrum. Click the **Execute** button in the R-hand panel to import the file. See Figure 14 below. Note that you have the option of importing standard spectra or acquiring spectra from standards for calibration. For the later select the **Acquisition** button in the Standards workflow.

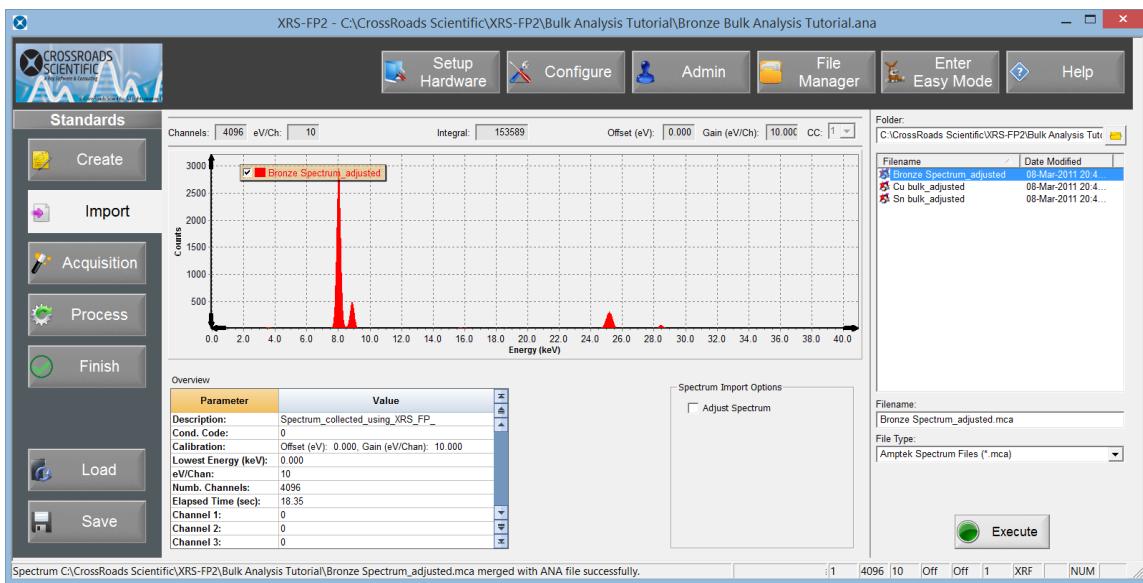


Figure 14. XRS-FP2 Standards Workflow – Import. Import the spectrum for the type standard.

- Now select the **Process** button. Then select the **Execute** button in the R-hand panel to process the type standard spectrum and generate calibration coefficients (TCC). Calibration coefficients, sensitivity factors, will now be listed for each element (Cu & Sn in this case) under the “Coeff.” Tab. See Figure 15 below.

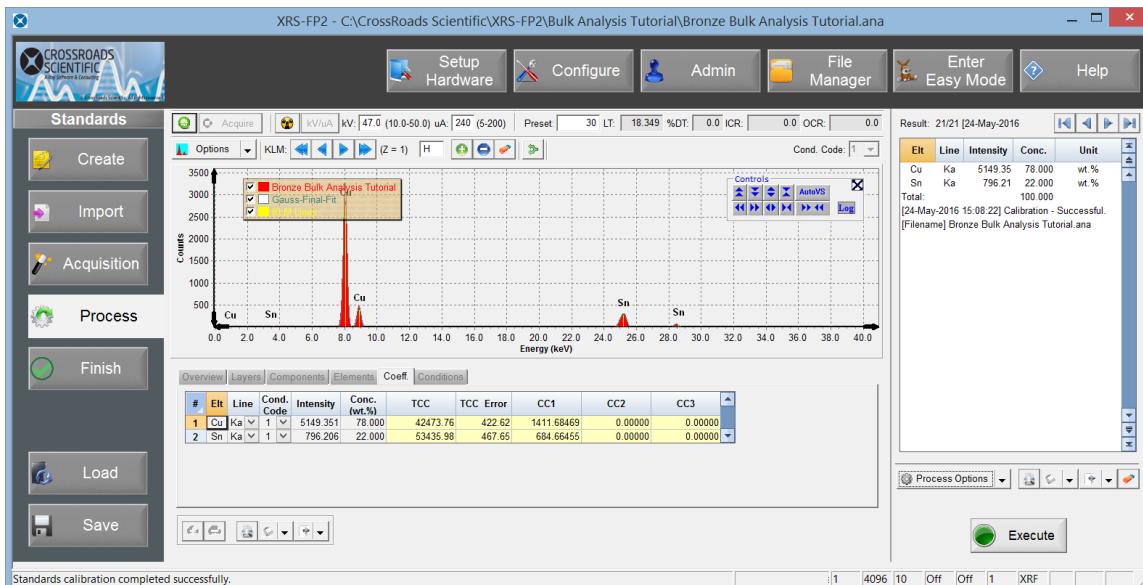


Figure 15. XRS-FP2 Standards Workflow – Process. Process the spectrum for the type standard and generate TCCs.

- Then select the **Save** button. Save the Type Standard Calibration to a new name such as “Bronze Bulk Analysis Type Std.anal”. This completes the single, type standard calibration portion of this process.
- Now, click on the **Home** button and then select the **Analyze** button (Fig. 16, red circle).



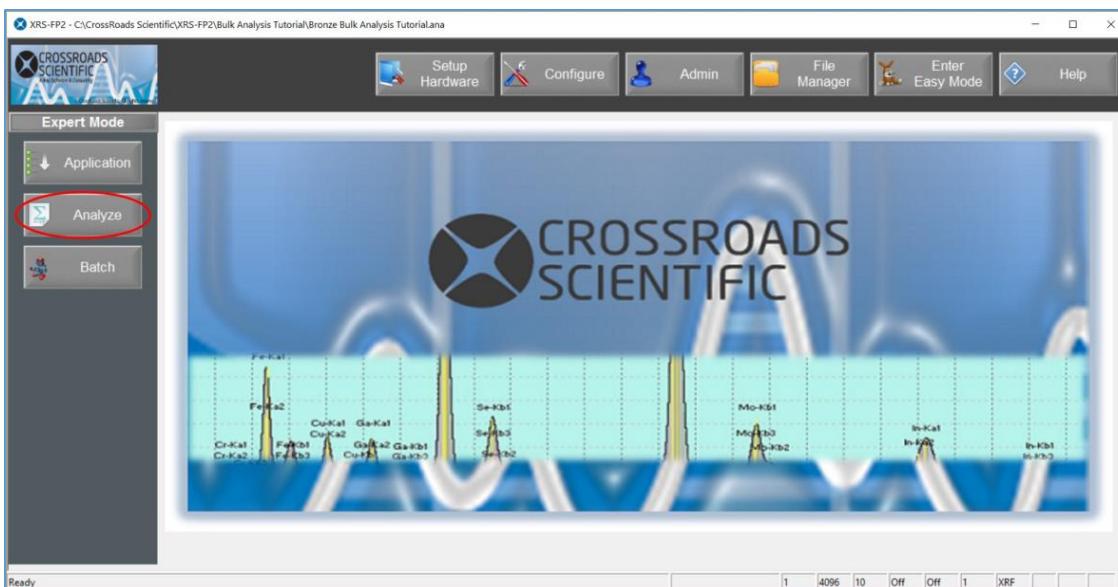


Figure 16. XRS-FP2 Analyze Workflow. From the XRS-FP2 home screen select the analyze button.

13. Select the **Quantify** button from the L-hand panel. Then navigate to the “Components” tab and set the Cu & Sn values in the “Conc.” column to zero (0). Notice that the TCCs from the single standard calibration are stored in the “Coeffs.” tab.
14. We are now ready to quantitatively analyze the bronze spectrum (“Bronze Spectrum_adjusted”) as an “unknown” using our single, type standard calibration. Select the **Execute** button in the R-hand panel to perform a process all and analyze the “unknown” spectrum. Having done this we get values for Cu & Sn nearly identical to those put in as the standard concentration values, see Figure 17 below.

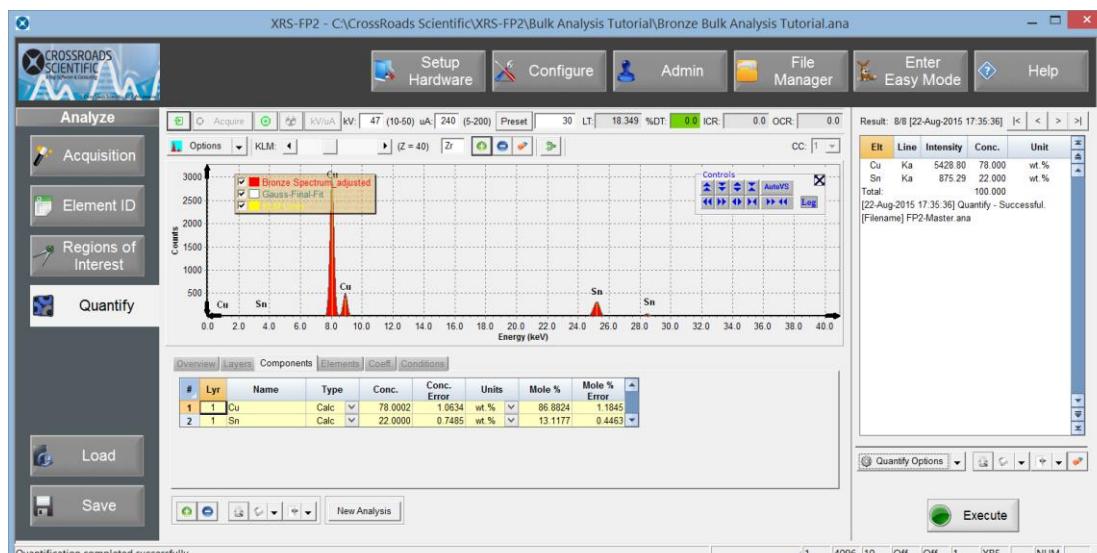


Figure 17. XRS-FP2 Analyze Workflow - Quantify. Results for the Cu & Sn after running the standard spectra back as an “unknown” against the single, type standard calibration.

*This completes the **single, type standard analysis** portion of this bronze tutorial.



4 BRONZE ALLOY – MULTIPLE STANDARD CALIBRATION

Another quantitative approach is using multiple pure elemental bulk materials or compounds to establish Calibration Coefficients. The tutorial application provides a good example for this approach as pure bulk Sn and pure bulk Cu are easily obtained. The following steps describe a calibration using multiple pure bulk standards for the analysis of a bronze alloy (Cu-Sn alloy):

1. Click on the **Home** button (Fig. 18, yellow circle), then select the **Application** button (Fig. 18, red circle).

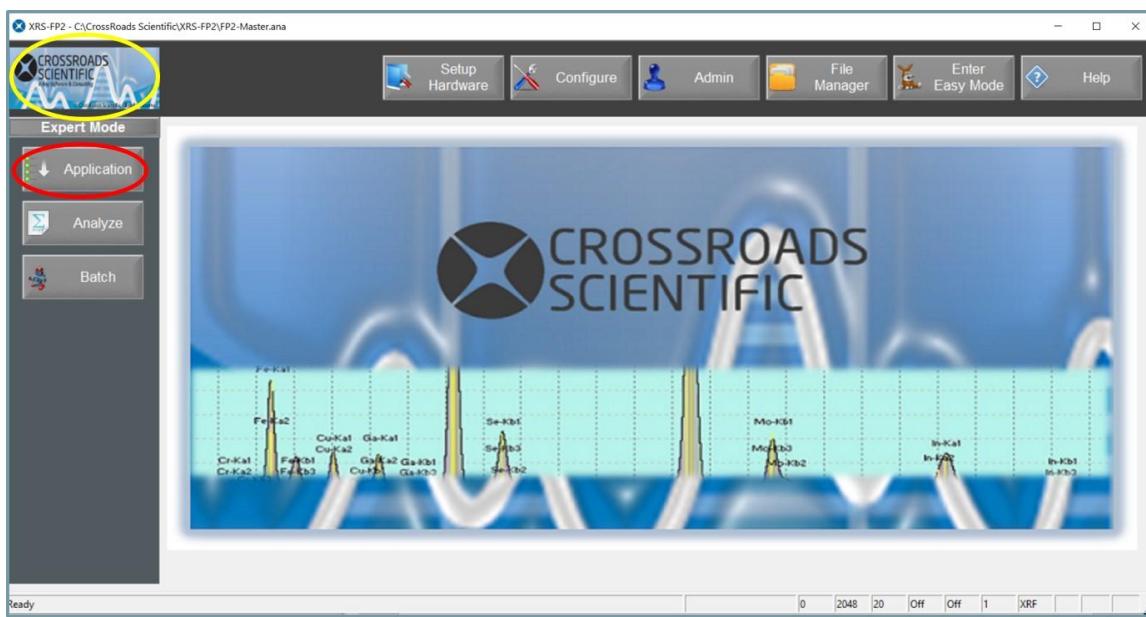


Figure 18. XRS-FP2 Application Setup. From the XRS-FP2 home screen select the application button to setup the application.

2. Select the **Definition** button.
3. To create a “clean sheet” for analysis click the **New Analysis** button below the component table. Remember, this will clear all of the application information, i.e., Component Table, Elements Table and Thickness information; however, the Measurement information (spectrometer configuration) will be retained.
4. Select or enter **Cu** as the first standard – pure bulk Cu.
5. Select the **Methods** button.
6. Set the application quant method (calibration mode), in the R-hand panel under the “Quant” tab, to “Single Standard” (Fig. 19 below).



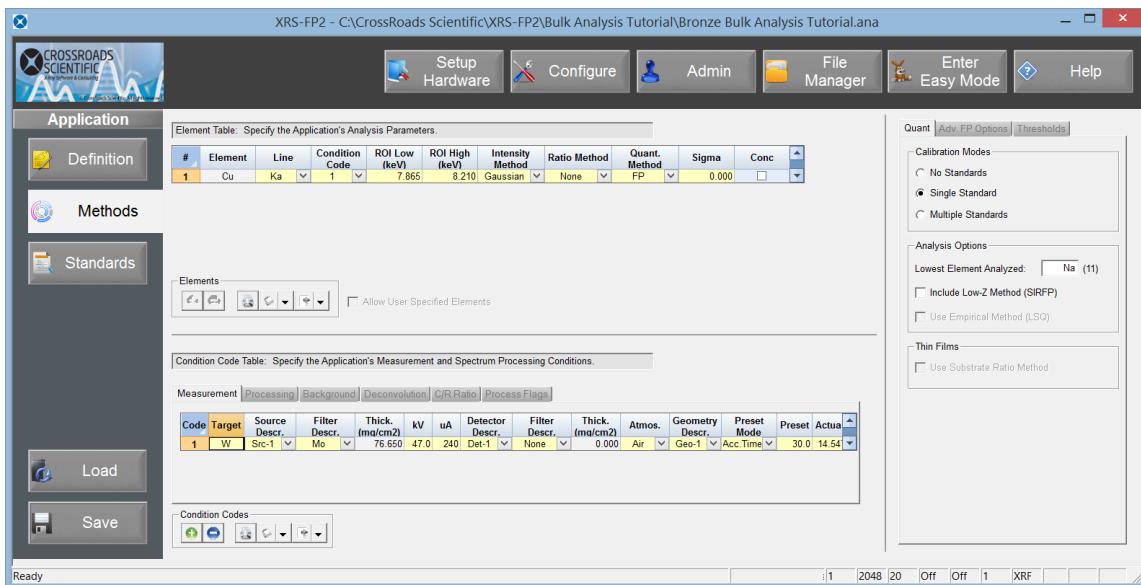


Figure 19. XRS-FP2 Application Workflow – Single Standard Calibration Mode. The quant method is set to single standard.

- Now select the **Standards** button from the L-hand panel in the Application workflow.
- Select the **Create** button. Now enter the standard value (concentration) for the pure bulk Cu standard – 100 wt% Cu. Enter this value in the “Conc” column of the standard Component Table. See Figure 20 below.

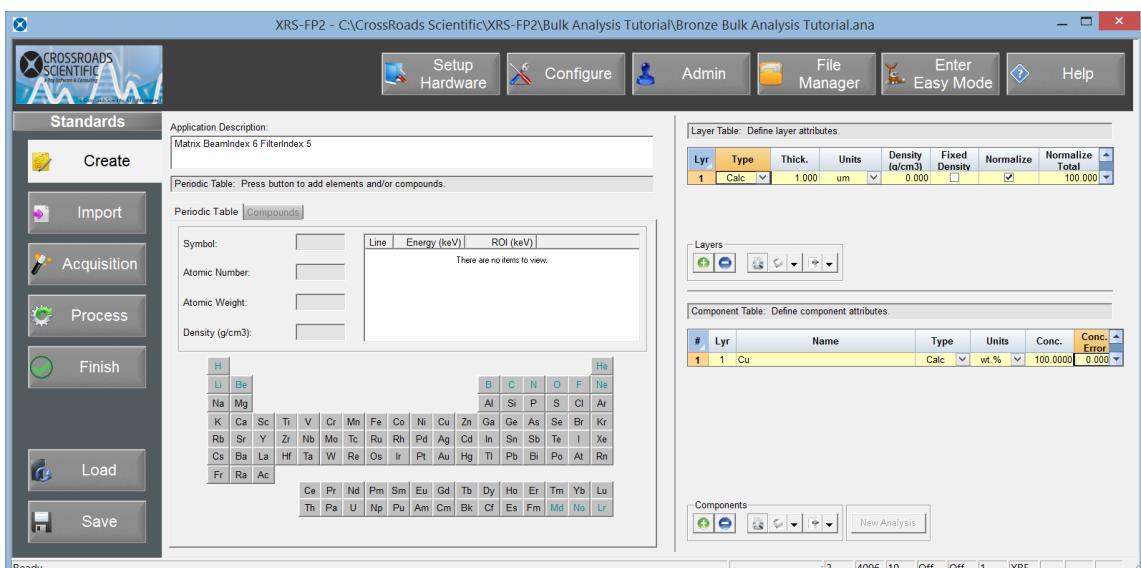


Figure 20. XRS-FP2 Standards Workflow – Create. Enter Cu for the pure bulk Cu standard and set the concentration to 100 (wt%).

9. Click on the **Import** button and select the “Cu Bulk_adjusted.mca” file to import for our pure bulk Cu standard spectrum. Click the **Execute** button in the R-hand panel to import the file. See Figure 21 below. Note that you have the option of importing standard spectra or acquiring spectra from standards for calibration. For the later, select the **Acquisition** button in the Standards workflow.

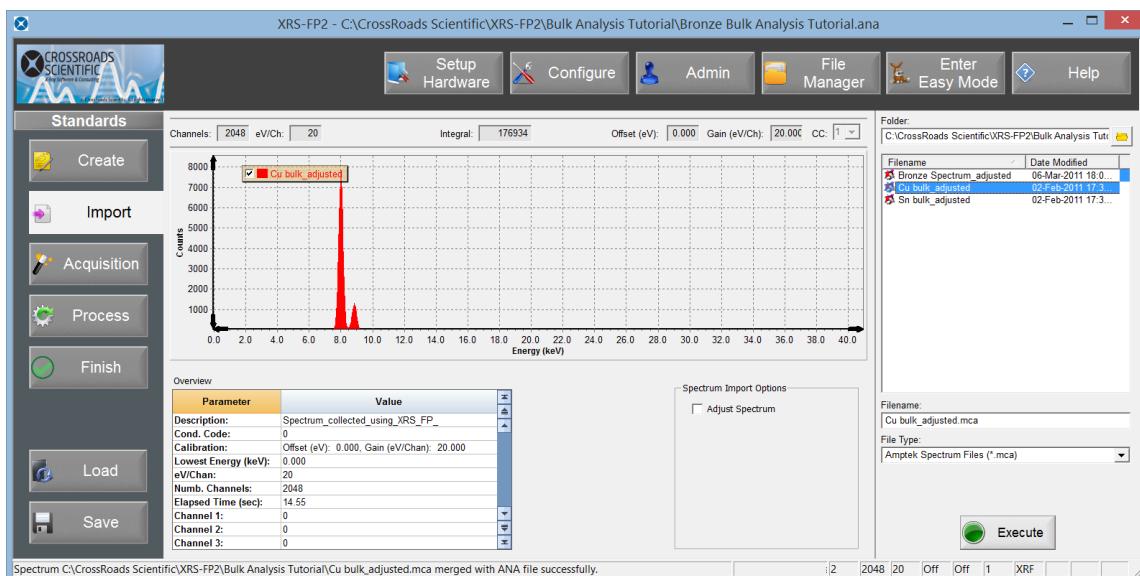


Figure 21. XRS-FP2 Standards Workflow – Import. Import the spectrum for the pure bulk Cu standard.

10. Now select the **Process** button. Then select the Execute button in the R-hand panel to process the pure bulk Cu standard spectrum and generate a calibration coefficient (TCC). The Cu calibration coefficient, sensitivity factor, will now be listed under the “Coeff.” Tab (Fig. 22).

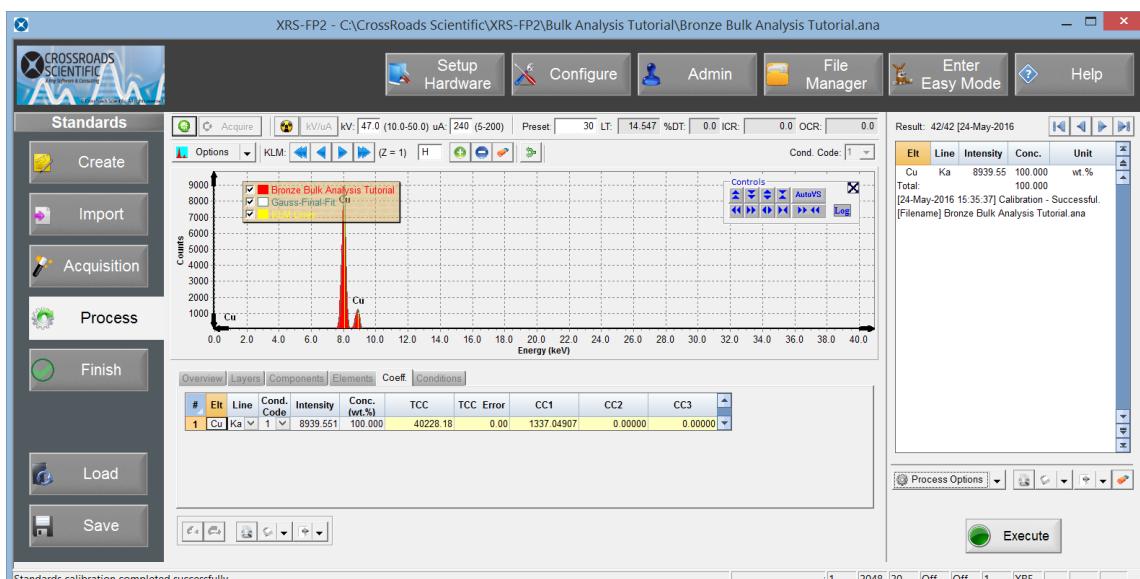


Figure 22. XRS-FP2 Standards Workflow – Process. Process the spectrum for the bulk Cu standard to generate the TCC.



11. Then select the **Save** button. Save the pure bulk Cu Calibration to a new name such as “Bronze Bulk Analysis Bulk Cu Std.ana”. See Figure 23 below.

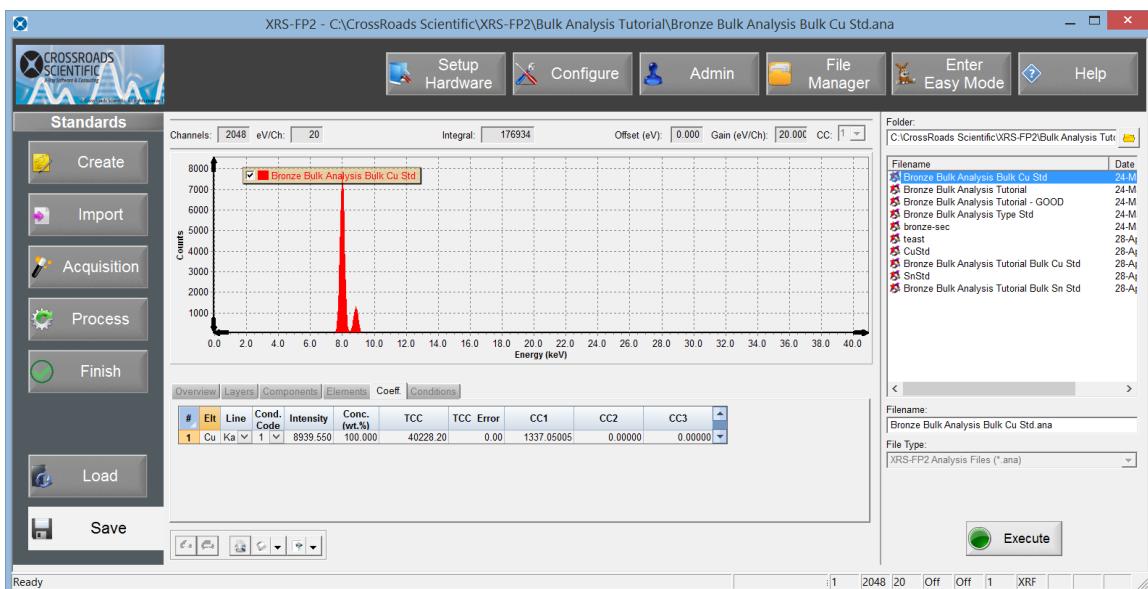


Figure 23. XRS-FP2 Standards Workflow – Save. Save the bulk Cu standard.

12. Now select the **Create** button again. Enter the standard value (concentration) for the pure bulk Sn standard – 100 wt% Sn. Enter this value in the “Conc” column of the standard Component Table.
13. Click on the **Import** button and select the “Sn Bulk_adjusted.mca” file to import for our pure bulk Sn standard spectrum. Click the **Execute** button in the R-hand panel to import the file. See Figure 24 below. Note that you have the option of importing standard spectra or acquiring spectra from standards for calibration. For the later, select the **Acquisition** button in the Standards workflow.

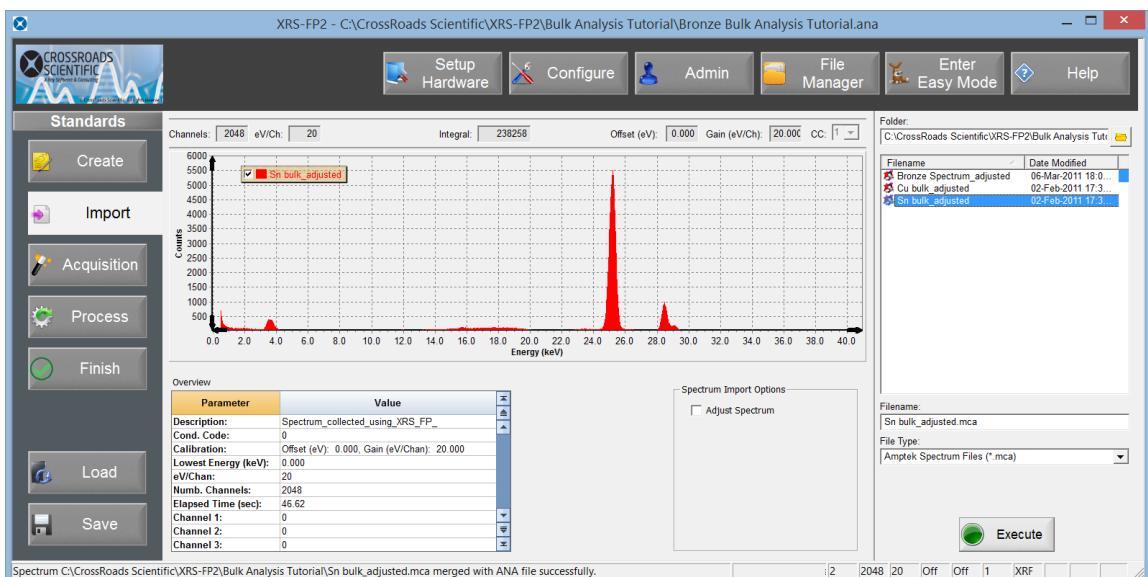


Figure 24. XRS-FP2 Standards Workflow – Import. Import the spectrum for the pure bulk Sn standard.

- Now select the **Process** button. Then select the Execute button in the R-hand panel to process the pure bulk Sn standard spectrum and generate calibration coefficients (TCC). The Sn calibration coefficient, sensitivity factor, will now be listed under the “Coeff.” Tab (Fig. 25).

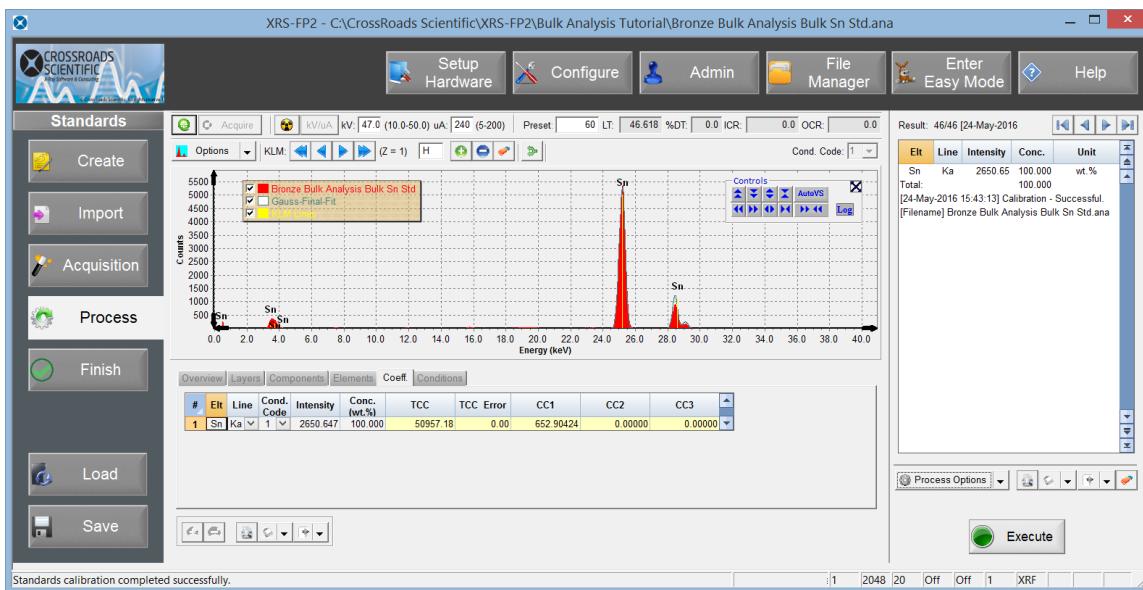


Figure 25. XRS-FP2 Standards Workflow – Process. Process the spectrum for the bulk Sn standard to generate the TCC.

- Then select the **Save** button. Save the pure bulk Sn Calibration to a new name such as “Bronze Bulk Analysis Bulk Sn Std.ana”.
- Now select the **Home** button. Then click on the **Definition** button. Enter **Cu** and **Sn** as the two components in this application. Double check that the Layer Table is normalized to 100%.
- Then click on the **Methods** button in the Application workflow. Now change the application quant method (calibration mode), in the R-hand panel under the “Quant” tab, to “**Multiple Standards**” (Fig. 26 below).

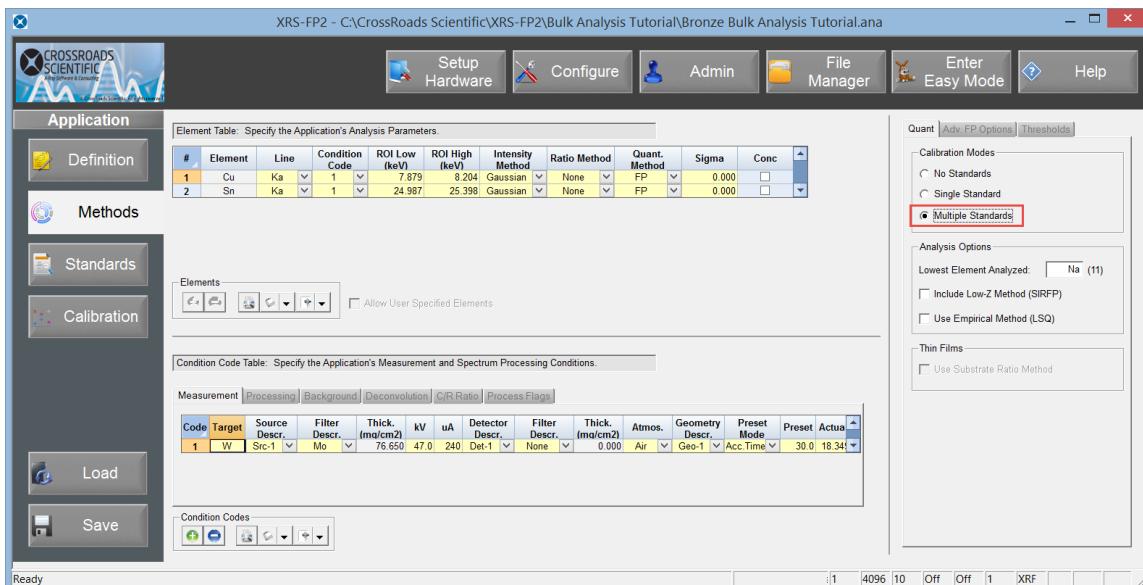


Figure 26. XRS-FP2 Application Workflow – Multiple Standards Calibration Mode. The quant method is set to multiple standards.

- Then go to the Calibration workflow by selecting the **Calibration** button (Fig. 27 below). Double click in the MLSQ “Standard Filename” column to add the two bulk standards created above (Cu & Sn) to the MLSQ Standards Setup Table.

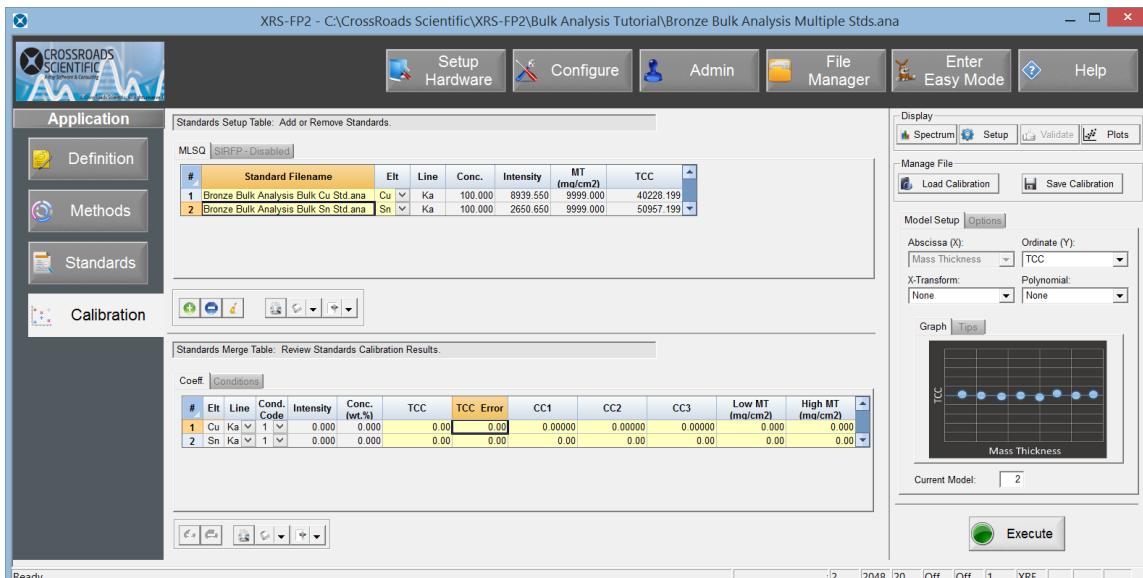


Figure 27. XRS-FP2 Application Workflow – Multiple Standards Calibration Mode. The single standards created above are added to the multiple standards (MLSQ) Standards Setup Table.

- In order to create a multipoint calibration, complete with merged calibration coefficients (i.e. the TCC values from the individual standard files created above), the MLSQ model needs to be set. There are several models to choose from, which allow for variations of the calibration coefficients



with different concentrations and mass thicknesses of each element. Select the type of model to be used by clicking on the “Ordinate (Y)” drop-down menu button in the “Model Setup” tab in the R-hand panel and select the “Intensity” model (Model #9) in the “Ordinate (Y)” column for this application (Fig. 28 below). Then click on the **Execute** button in the R-hand panel of the Calibration workflow. Note that the TCC values for Cu and Sn are now displayed in the Standards Merge Table. See Figure 28 below.

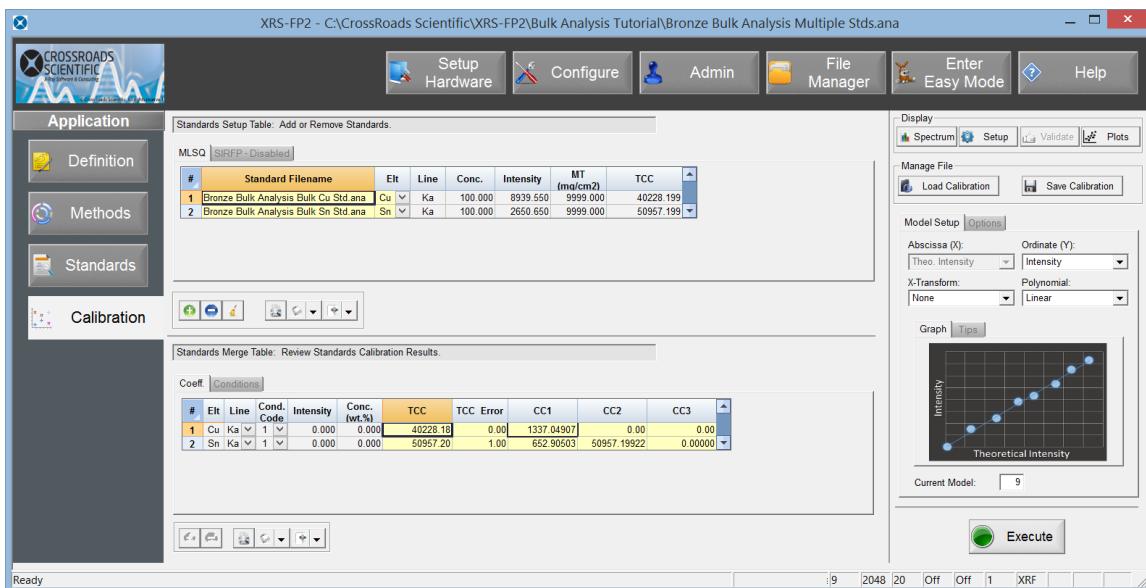


Figure 28. XRS-FP2 Calibration Workflow. Merge the TCC values for the bulk Cu & Sn standards to generate the Standards Merge Table for each element.

20. Click on the **Save Calibration** button in the R-hand panel to save the calibration for future use. Select “Yes” to save both a calibration file (*.cal) and an analysis file (*.ana) file (i.e. “Bulk Analysis Tutorial MultiStds.cal” and “Bronze Bulk Analysis Multiple Stds.ana”).
21. Select the **File Manager** button, then click the **Import** button and import the “Bronze Spectrum_adjusted.mca” spectrum file. This will be used as the “unknown” file again.
22. Now, click on the **Home** button and then select the **Analyze** button (Fig. 29, red circle).



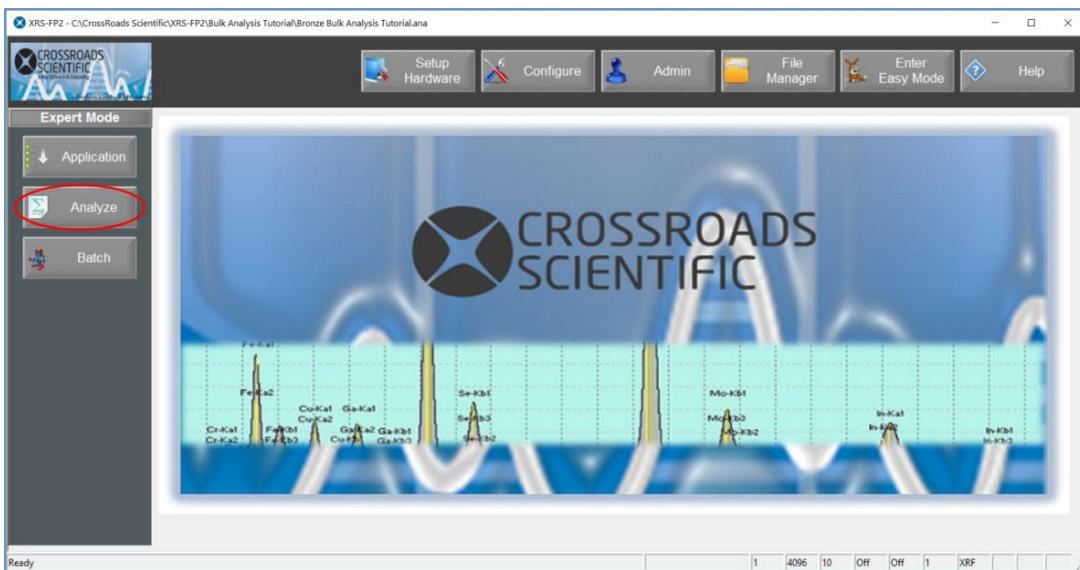


Figure 29. XRS-FP2 Analyze Workflow. From the XRS-FP2 home screen select the analyze button.

23. Click the **Quantify** button from the L-hand panel. Then navigate to the “Components” tab and set the Cu & Sn values in the “Conc.” column to zero (0). Notice that the TCCs from the single standard calibration are stored in the “Coeffs.” tab.
24. We are now ready to quantitatively analyze an “unknown”. Click the **Options** dropdown button above the spectrum view and open the “Bronze Spectrum_adjusted.mca” spectrum file (this will be used as the “unknown” file again). Select the **Execute** button in the R-hand panel to perform a process all and analyze the “unknown” spectrum. Having done this we get results for Cu & Sn concentration values, see Figure 30 below.

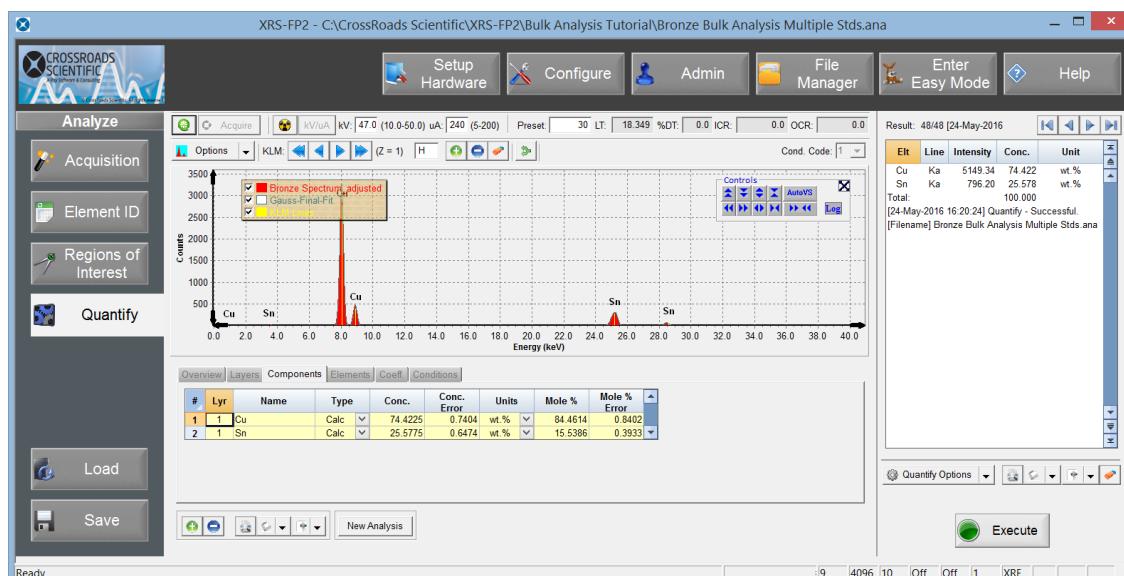


Figure 30. XRS-FP2 Analyze Workflow - Quantify. Results for the Cu & Sn after running the “Bronze Spectra_adjusted.mca” file back as an “unknown” against the multiple standard calibration.

*This completes the ***multiple standard analysis*** portion of this bronze tutorial.

