XRS-FP Fundamental Parameters Tutorial

The following with associated files (spectra, *.mca and application, *.tfr) guides a new user of CrossRoads Scientific XRF Fundamental Parameters Application software 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 most convenient to copy the supplied Tutorial Folder to your hard drive.

It is assumed that the x-ray spectrometer has been energy calibrated – see section 5.1, XRF Spectrometer Calibration and Monitoring of the XRS-FP Software Guide. 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, tfr 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.

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

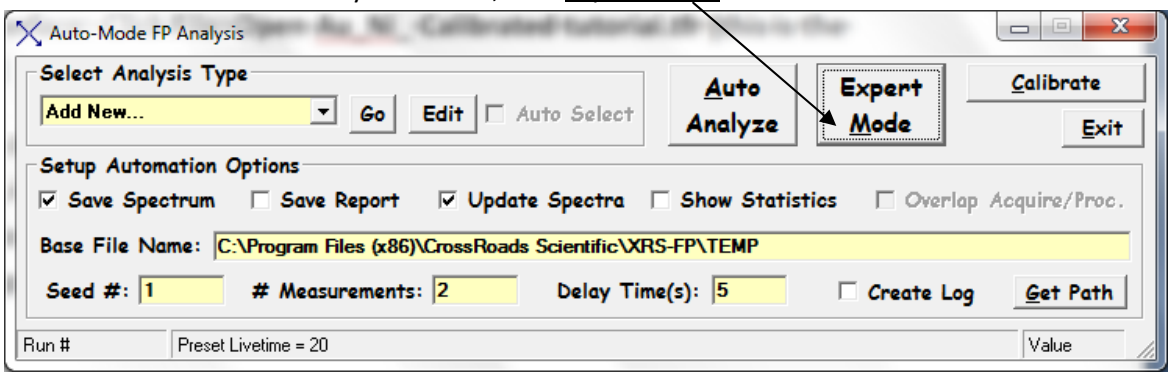

Figure 1

This will recall the Master.tfr file (see section 4.1, Loading the Software of the XRS-FP Software Guide).

3. From the XRS-FP Analyzer interface: Click **File>Open** (file type XRF report, *.tfr) **Bronze Bulk Analysis Tutorial.tfr** (this is the completed tfr / application)

   3.1. To start afresh, from the XRS-FP Analyzer interface click: **File>New** - this will clear all of the application information, i.e., Component Table, Elements Table and Thickness information. The Measurement information (spectrometer configuration) is retained. There is now a "clean sheet" for set up of an application.

   As noted above, 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 Conditions of the New XRS-FP Analyzer view on your display and presented below, Figure 2. 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% ±10%.

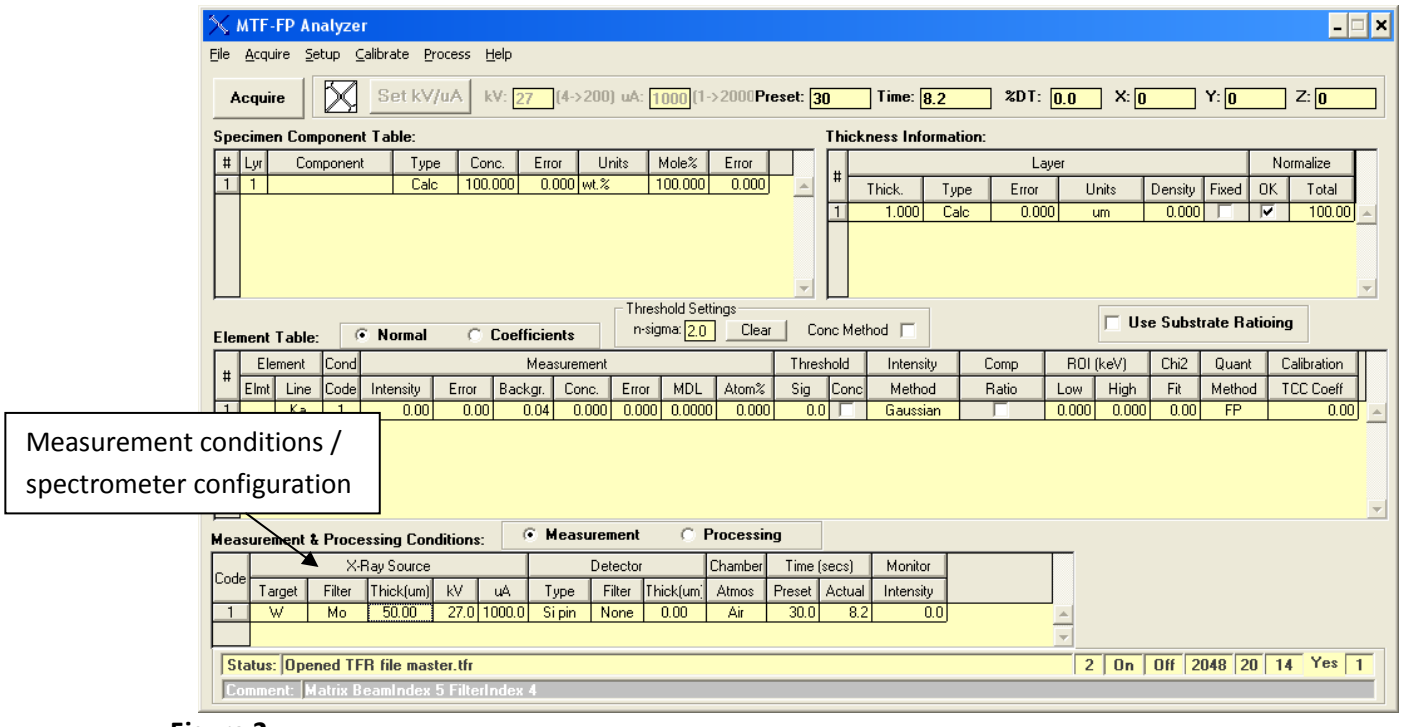

Figure 2

4. Specimen / Application Components: Add the application components (see section 5.2, XRF Elemental FP Calibration or Standardization of the XRS FP Software Guide). Components can be

elements or compounds. In this application we are working with alloying metals, elemental metals. In line 1 of the Components table enter Cu. To add another component, use the down arrow of your computer keyboard. Enter Sn and on line 2, # 2 component.

Sample Components

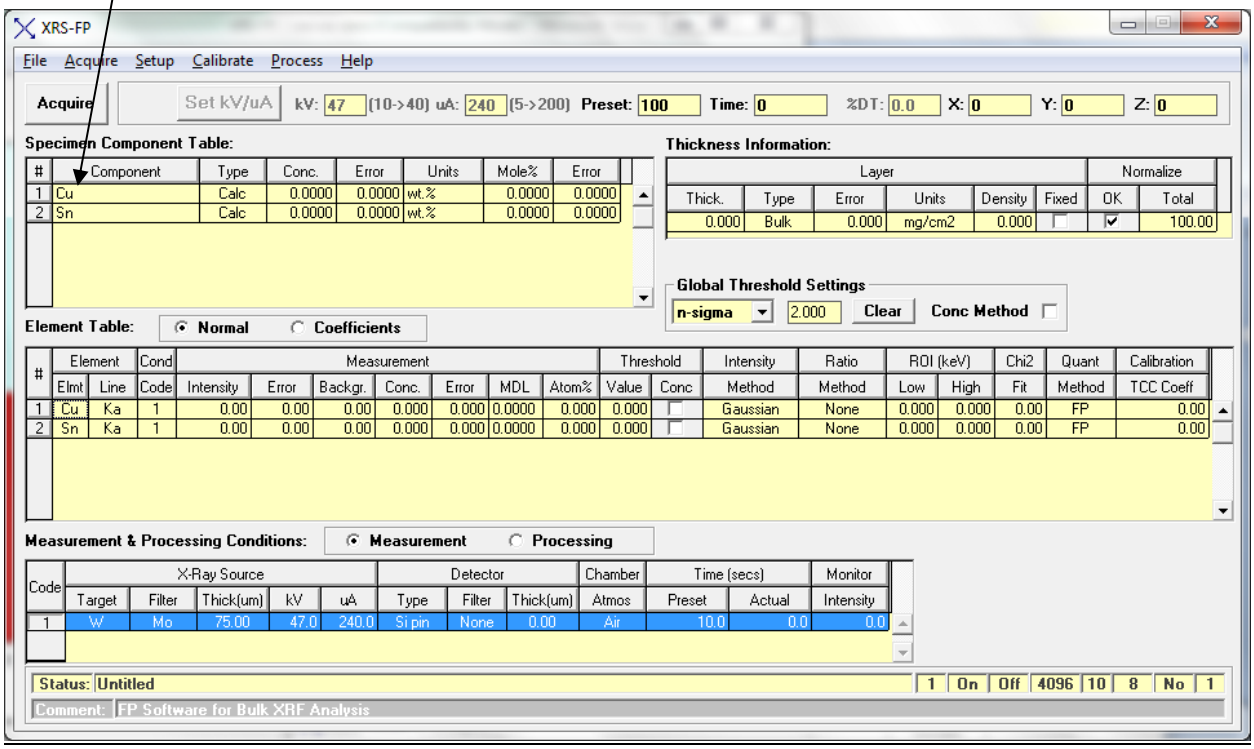

Figure 3

5. Element Table: As components are defined, the Element Table is filled in defaulting to what would nominally be the most intense analyte line available. In this case, the Cu Kα and Sn Kα. These are appropriate selections for this application.

6. Thickness Table: 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 Kα. This is defined as bulk and is the default **Type** setting in the Thickness Table. The default thickness for bulk analysis is zero (0). XRS-FP 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**. 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.

   6.1. The Normalize field of the thickness table refers to component concentration. In thin film work layer concentration needs to be normalized to 100%. Normalizing to 100% is not required for bulk analysis, but is often employed. If not already done, this is a very good point to save the tfr that you are creating by clicking **File>Save As** – (file type, XRF report, *.tfr) Enter the File Name

Bronze Bulk Analysis.tfr. At this point the application is defined. The next steps are to extract analyte intensities from the standard spectrum acquired under the excitation conditions defined in the Measurement and Processing Conditions Table and derive Calibration coefficients (sensitivities for each analyte emission).

7. Spectrum Processing / Extracting Net Intensities (see Section 14.3, Process Spectrum of the XRS Software Guide): Spectra supplied for this tutorial have been energy adjusted (see section 12.11, Setup Spectrum Adjust of the XRS Software Guide). To avoid doing a double adjust, **from the XRS-FP Interface – Setup>Process> and make certain that the Auto Adjust Spectrum Gain & Offset on Load is unchecked, Figure 4, following.**

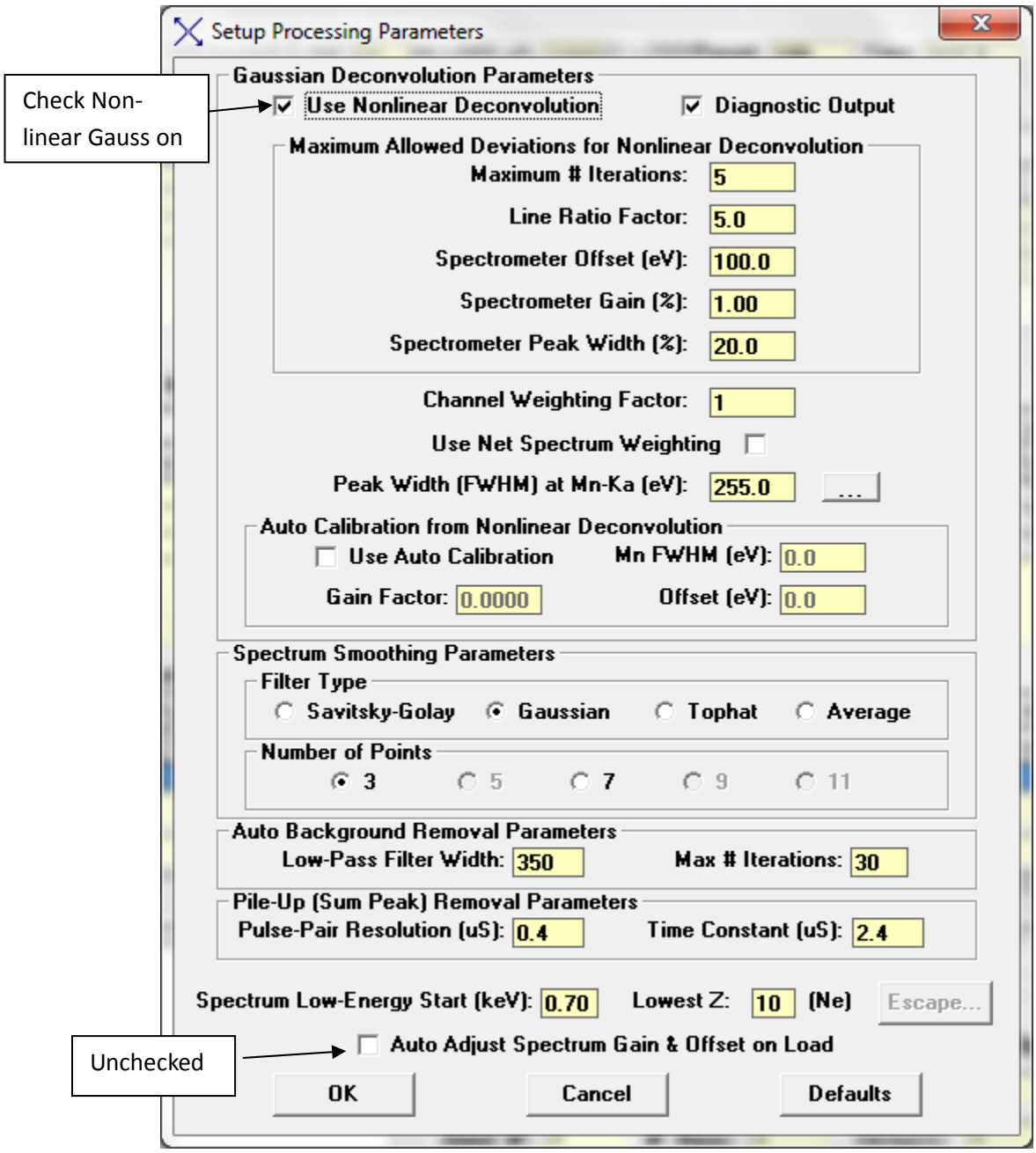

Figure 4

7.1. Recall the Bronze spectrum: From the XRS-FP Analyzer interface - **File>Open** (the Tutorial File type is Amptek Spectrum (*.mca), **Bronze Spectrum_Adjusted.mca** – Figure 5.

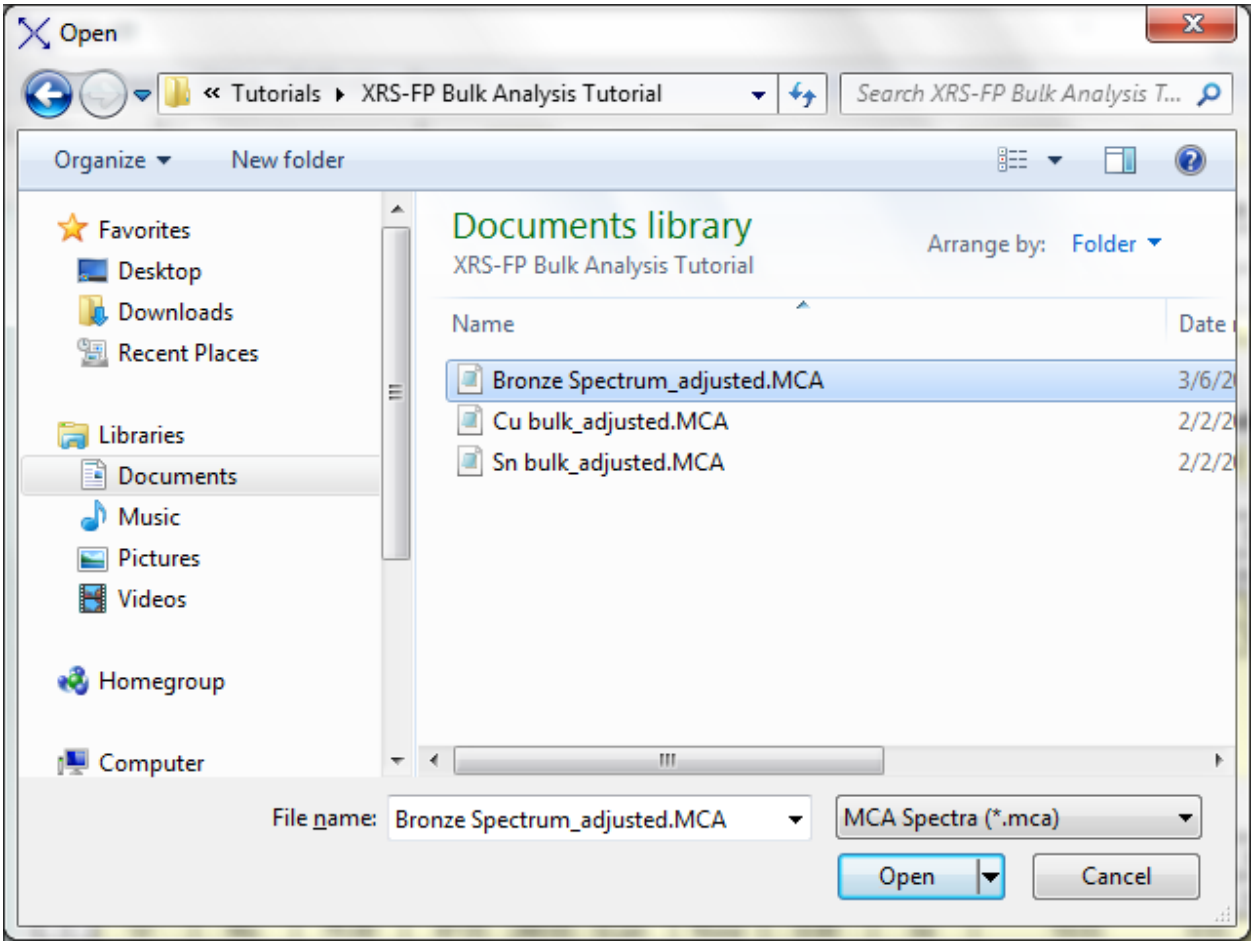

Figure 5

It is always a good idea to qualitatively inspect the spectrum prior processing. The spectrum, Bronze Spectrum_Adjusted that has been recalled below (Figure 6) is presented in Log mode, which can be very useful for qualitative inspection. Cu and Sn analyte peaks are identified, as well as, the processed escape peaks (black dotted line spectrum), trace of 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.

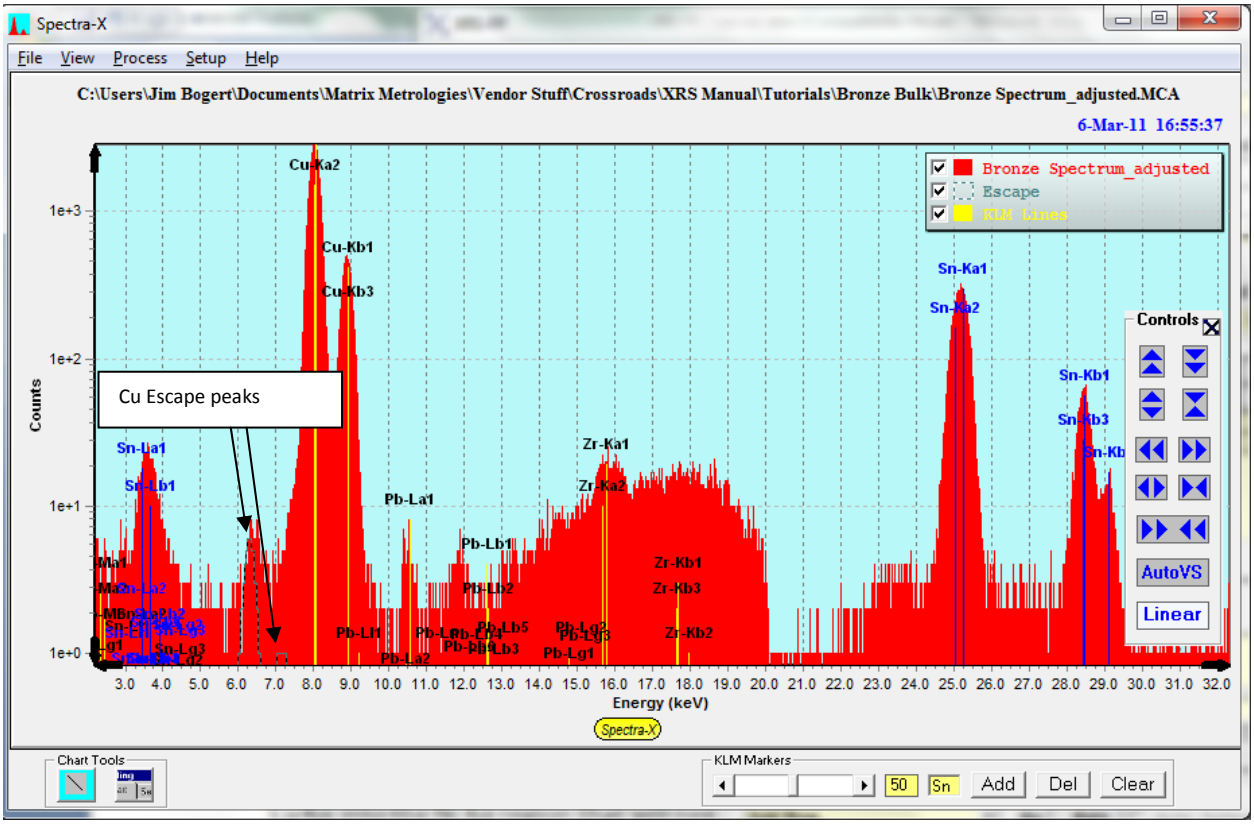

Figure 6

7.2. Spectrum Smooth, Escape Peak Removal Background Removal and Deconvolute: **Click the Processing Radio Button above the Measurement & Processing Conditions Table** to obtain the view of the XRS-FP Analyzer interface below – **Figure 7**, re section 3.1 and 3.2, Spectrum Processing of the XRS-FP Software Guide. We have chosen to apply one smooth function, remove escape peaks, and apply the Auto Background removal. Background low pass filter width parameter is set in **Setup>Processing** – see Figure 4 above. To apply these three functions and extract intensities from the XRS-FP Analyzer Interface **Click: Process>Spectrum>All** (Smooth-Escape Peak Removal-Background Removal-Deconvolution). There are several peak intensity extraction options. By clicking on the Intensity Method fields for the analyte lines of the Element Table these are displayed – Intensity, Gaussian and Reference. The tutorial uses the Gaussian fit of which there a 2, linear and nonlinear. Nonlinear is used here and is set as a processing parameter **Setup>Processing** (see Figure 4 above). 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 of the Element Table of the XRS-FP Analyzer Interface. Intensities are expressed as count rates – counts/second - see Figure 8 below. Note that the intensities that you obtain may be slightly different from those displayed in Figure 8.

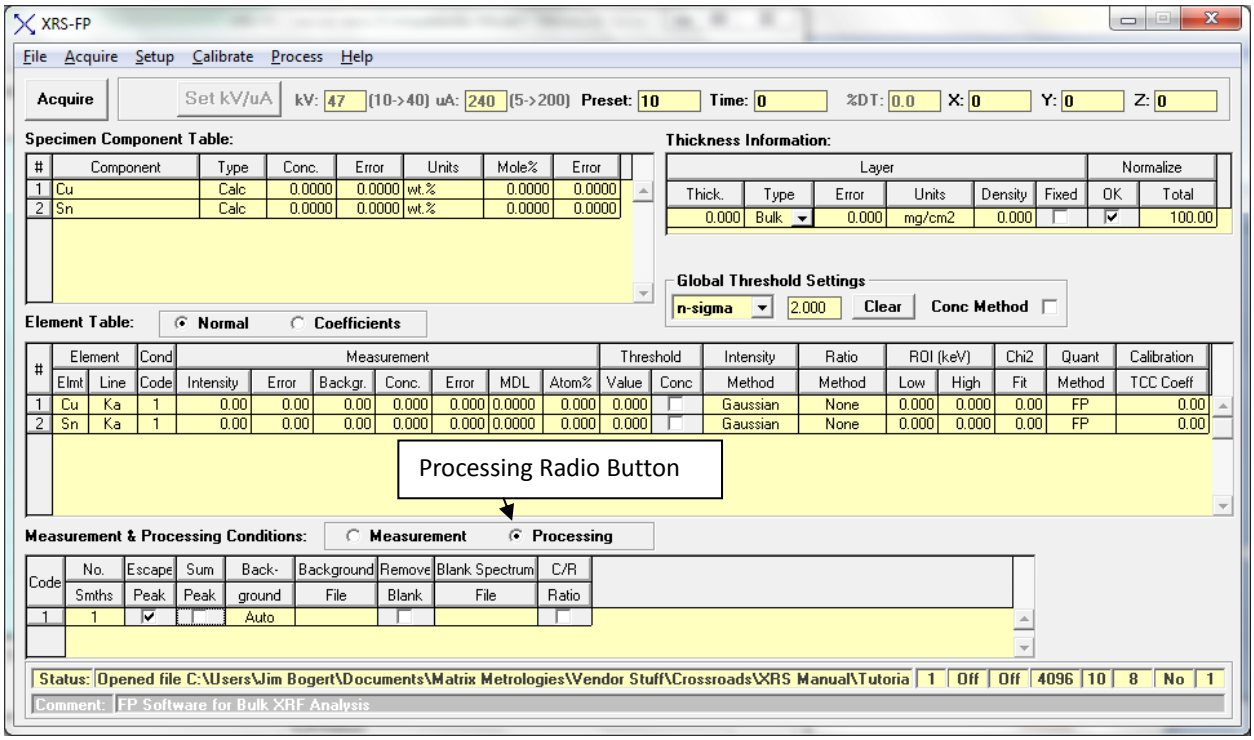

Figure 7

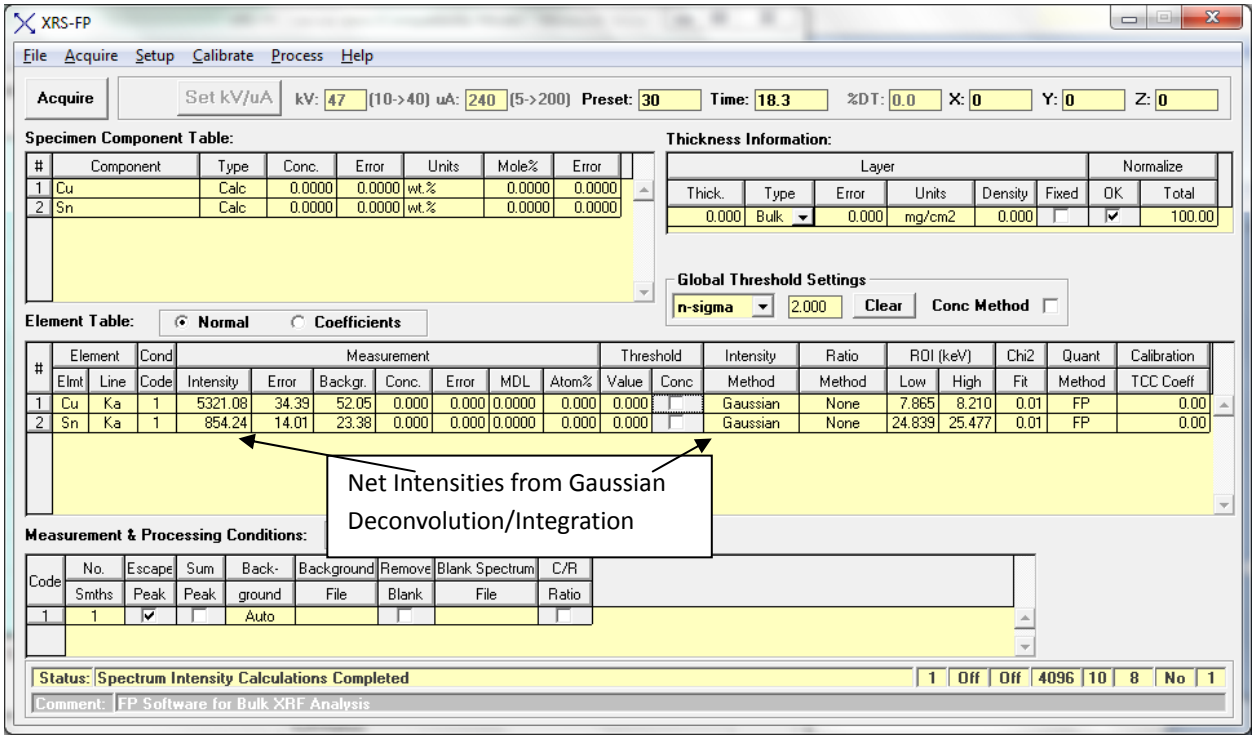

Figure 8

8. Calibrate – unique case: Most instrumental analysis requires calibration to a standard material. XRF is somewhat unique. Because 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-FP is a fundamental parameters analysis program, 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.

8.1. So, having defined the elements in the bronze and extracted the net intensities a Standardless analysis can be made. **Click Process>Analyze** and results of the standardless analysis of the bronze are displayed – Wt% (Conc. in the Component Table) and Mole% (see Figure 9). Note that standardless results are always normalized to 100% - the total sample matrix must be defined.

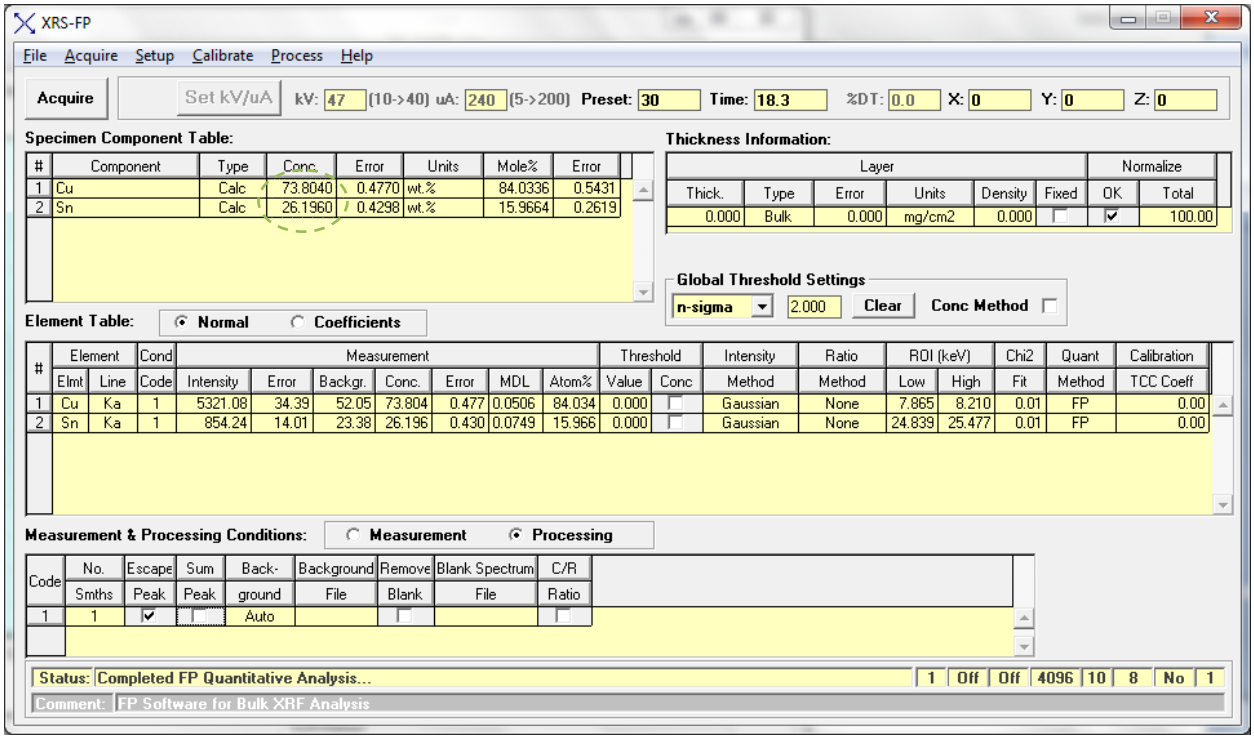

Figure 9 Standardless Analysis

9. Calibration with Pure Elemental or Compound Standards: Standardless Analysis is convenient and provides a good semi-quantitative analysis. Another quantitative approach is using pure elemental bulk materials or compounds to establish Calibration Coefficients. The tutorial application provides a good example for this approach – pure bulk Sn and pure bulk Cu are easily obtained. To implement this approach create a new tfr from the Bronze Bulk Analysis.tfr.

9.1. **File>Open** (file type tfr) **Bronze Bulk Analysis** that was created in step 6.1 above. Then perform a **File>New** command and enter Cu in the component table (Cu Kα) is the default. A pure bulk Cu spectrum was acquired under the same excitation conditions that were defined for the Bronze application. Recall this file from the tutorial disk/folder – **Open>File** (file type MCA spectra, *.mca) **Cu Bulk_adjusted.** Process this spectrum as described previously – **Process>Spectrum>All**

9.1.1. Now Setup Quantification to determine the Calibration Coefficient (TCC) for Cu Kα for these excitation conditions – input the Concentration of the Cu in the Component Table to 100% and click **Setup>Quant- Fundamental Parameters Calibration Method** and click on the Multiple Standard radio button (we will be using 2 pure metals standards) and **OK** - Figure 10

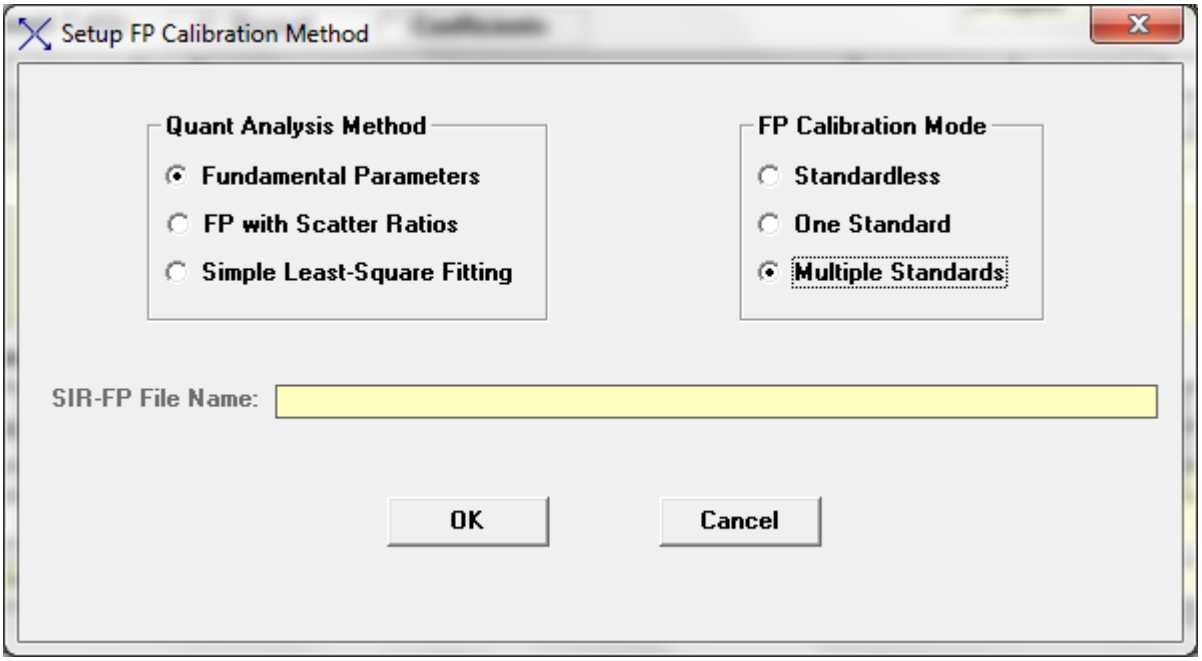

Figure 10

9.2. Generate the Cu Calibration Coefficient – **Calibrate>FP** a TCC calibration coefficient for Cu is generated – Figure 11

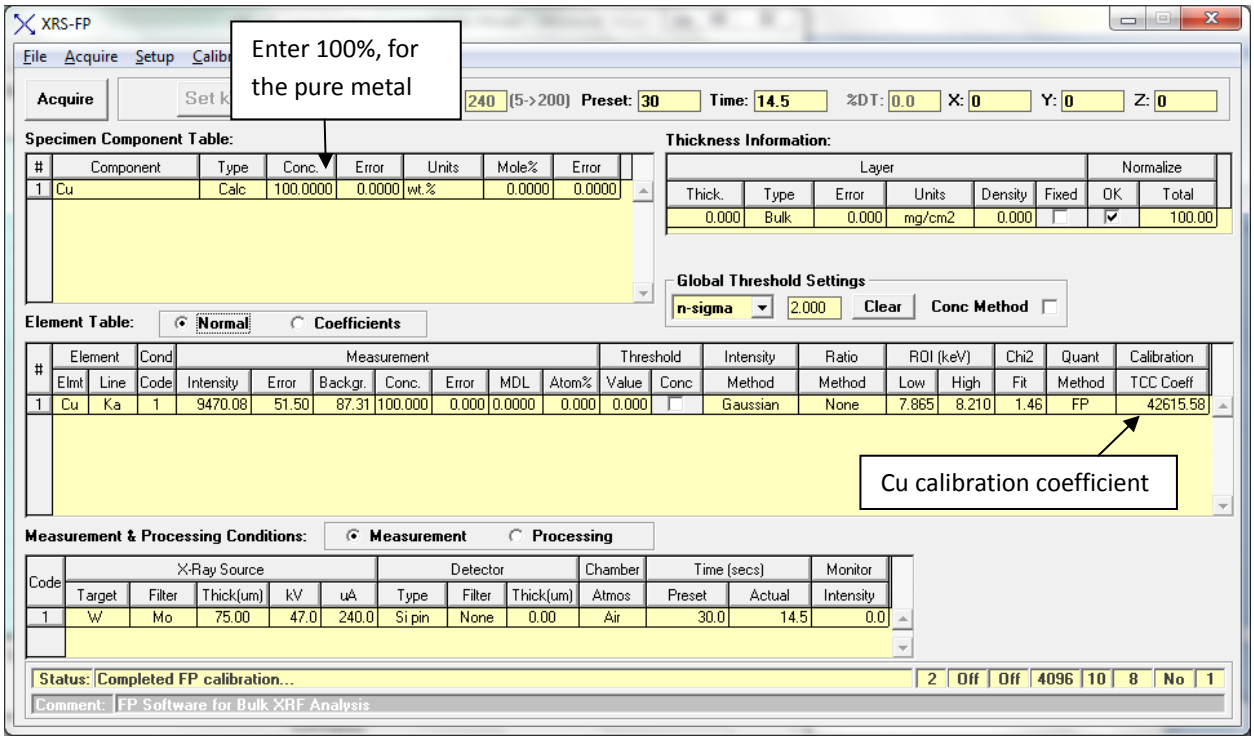

Figure 11

9.3. To generate the Sn Kα TCC, edit the tfr replacing Cu in the Component Table with Sn and recall the previously collected pure bulk Sn spectrum – **File>Open** (file type MCA spectrum) **Sn bulk_adjusted** and process the spectrum to extract the net Sn Kα Intensity - **Process>Spectrum>All**

9.4. Generate the Sn Calibration Coefficient – **Calibrate>FP** a TCC calibration coefficient for Sn is generated – Figure 12

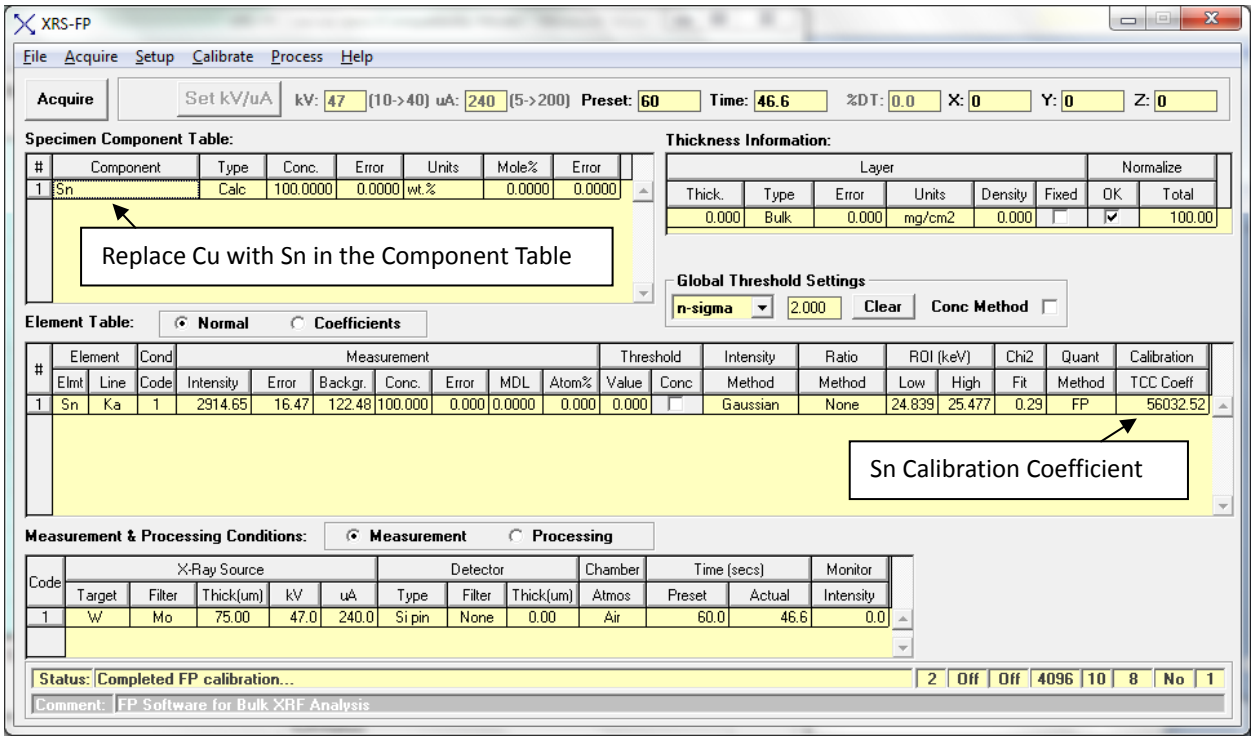

Figure 12

9.5. These TCC coefficients are easily transferred to the Bronze application by opening the Bronze application –**File>Open** (file type XRF reports, *.tfr) **Bronze Bulk Analysis**
Enter Cu and Sn intensities in the Intensity fields of the Element Table – any intensities will do for this process – see the example below, Figure 13. Now click **Process>Analyze** the TCCs calculated from the bulk Cu and bulk Sn spectra (residing in memory) are written to the TCC field of the Bronze Analysis application. The composition reflects the analysis based on the intensities that were manually entered. We now have a Bronze application calibrated to pure bulk Cu and pure bulk Sn. Save this tfr - **File>Save As** (XRF reports, *.tfr) **Bronze Analysis Pure Element Cal**.

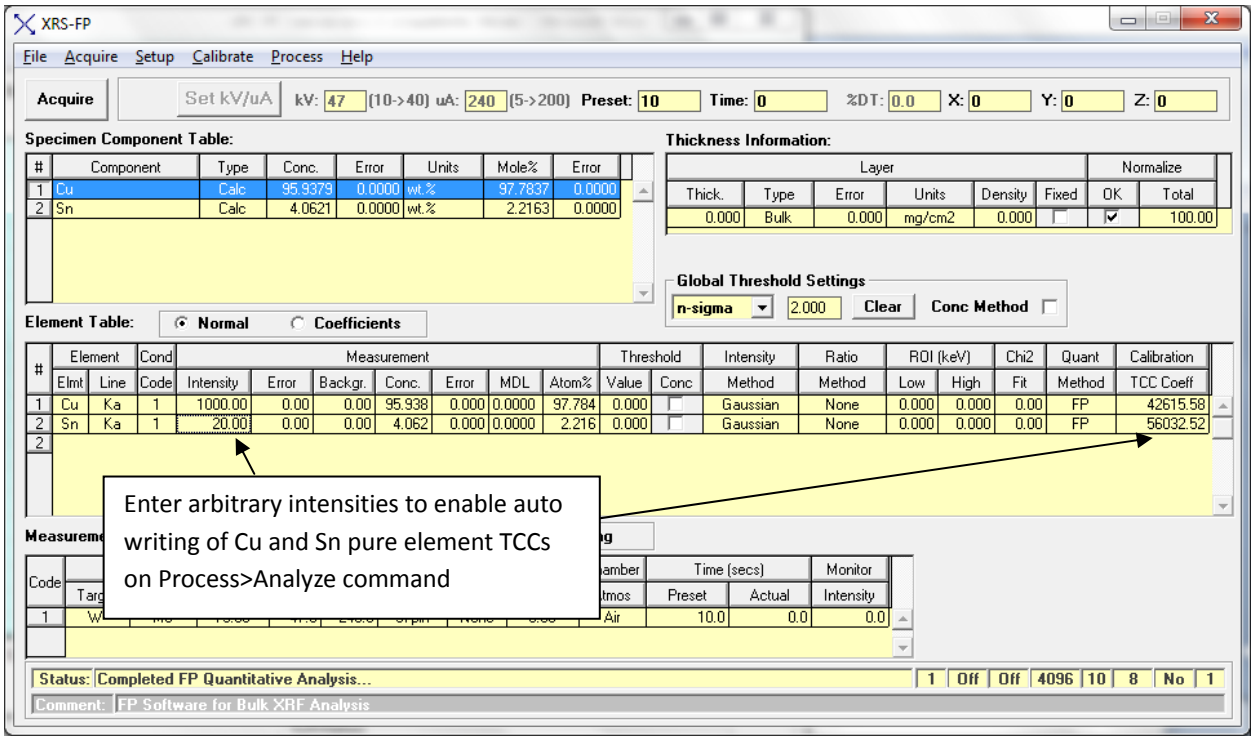

Figure 13

9.5.1.Let's use this new pure elemental metal calibrated tfr to analyze the bronze spectrum.

1. Recall the bronze spectrum – **File>Open** (file type MCA spectra, *.mca) **Bronze Spectrum_adjusted**

2. Process the spectrum to extract net intensities – **Process>Spectrum>All**

3. Quantify – **Process>Analyze** – Figure 14 below. Compare these results to the standardless results – Figure 9. Cu values are within 6% relative and Sn values are within 16% relative.

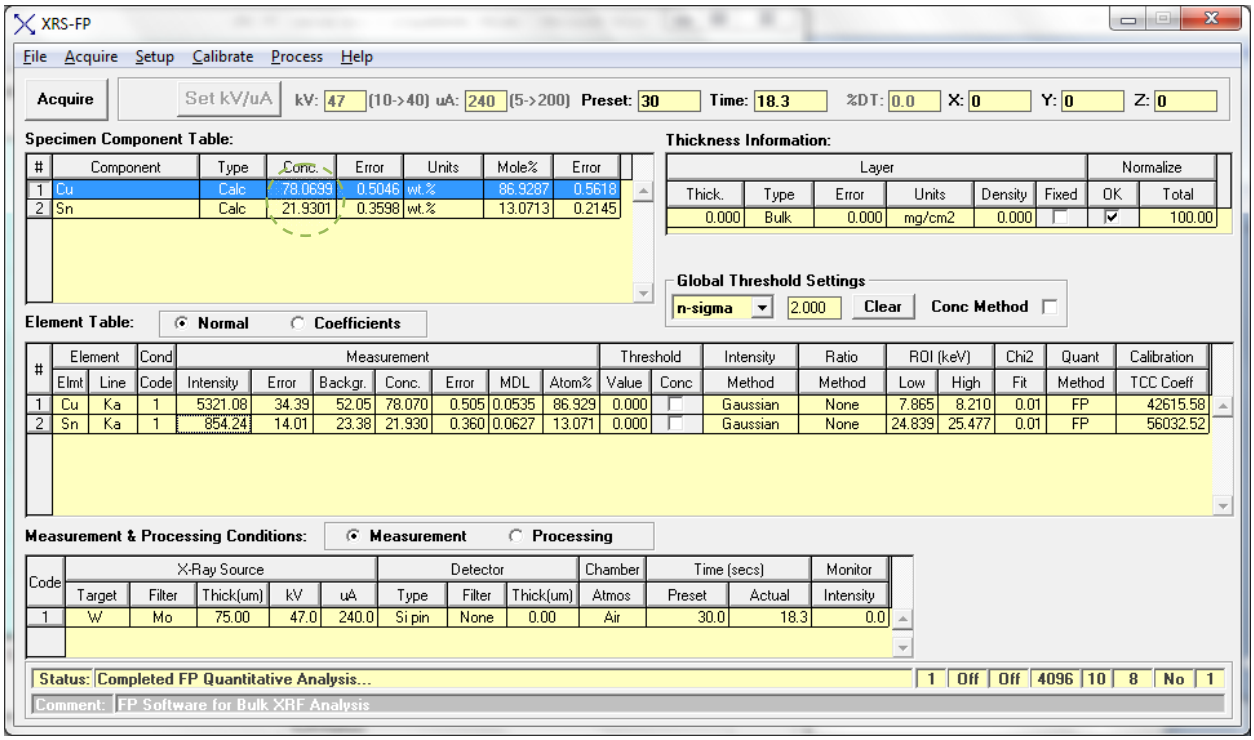

Figure 14

10. Calibration with "Type" Standard: A Type Standard is a standard material having composition similar to the materials that will be analyzed with the system calibration. 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 and the composition determined from the pure element calibration - rounded values.

    10.1. From the XRS-FP Analyzer interface, recall the newly created, calibrated tfr, Bronze Bulk Analysis Pure Element Cal: **File>Open** (type file XRF report) **Bronze Bulk Analysis Pure Element Cal**

    10.2. The intensities in this tfr file are those from the Bronze Spectrum_adjusted.mca, so, it is not necessary to reprocess the spectrum, but we will round the composition to 78 wt% Cu and 22 wt% Sn. Enter **these values in the Conc.** column of the Component Table. So, we have the net intensities and composition of the Type Standard defined.

    10.3. To Calibrate, determine Calibration Coefficients from the Bronze Type Standard – click **Setup>Quant** click on the Single Standard radio button and **OK**

    10.4. Generate Calibration Coefficients – click **Calibrate>FP** you will note a small change in the TCC values due to the rounding of the standard composition – Figure 15 below. At this point you would want to save the Type Standard Calibration to a new name – **File>Save As** (file type, XRF report, *.tfr) **Bronze Bulk Analysis Type Std**

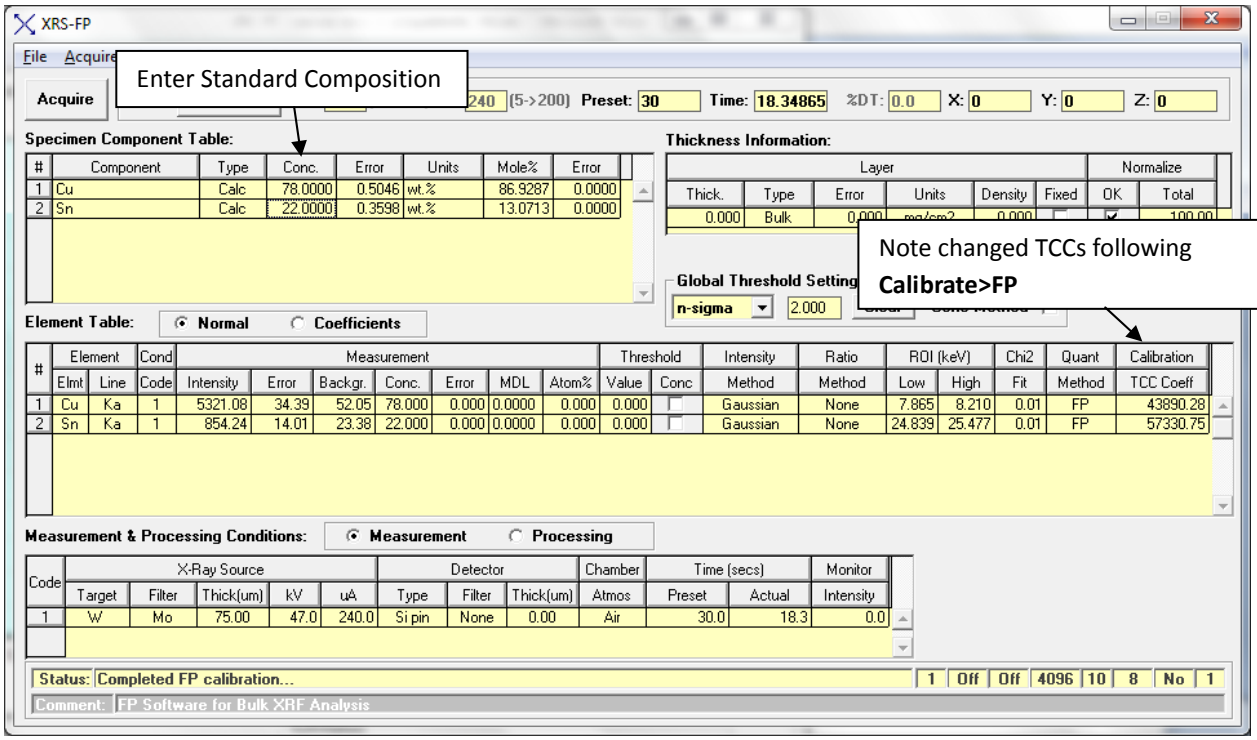
XRS-FP
File Acquire
Enter Standard Composition
Acquire
Preset: 30
Time: 18.34865
%DT: 0.0
X: 0
Y: 0
Z: 0
Specimen Component Table:
Thickness Information:
Note changed TCCs following
Calibrate>FP
Global Threshold Setting
n-sigma
2.000
Element Table:
Normal
Coefficients
Measurement & Processing Conditions:
Measurement
Processing
Status: Completed FP calibration...
Comment: FP Software for Bulk XRF Analysis

Figure 15