

XRS-FP Basic Setup & Analysis

Note: This document describes the basic setup and configuration of XRS-FP and implementation of a standardless analysis.



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DOCUMENT CHANGE LOG

Date	Person	Pages	Description
10-Mar-14	Sarah Cross	All	Created document
25-Mar-14	Sarah Cross	Most	Updated document
7-Apr-14	Sarah Cross	Many	Updated document
15-May-14	Brian Cross	15	Changed path to find files after installation of XRS-FP. Document v7.



1 QUICK GUIDE: XRS-FP SETUP & ANALYSIS FLOWCHART

A flowchart illustrating the steps involved in the basic setup and configuration of XRS-FP for standardless analysis is shown below in Figure 1:

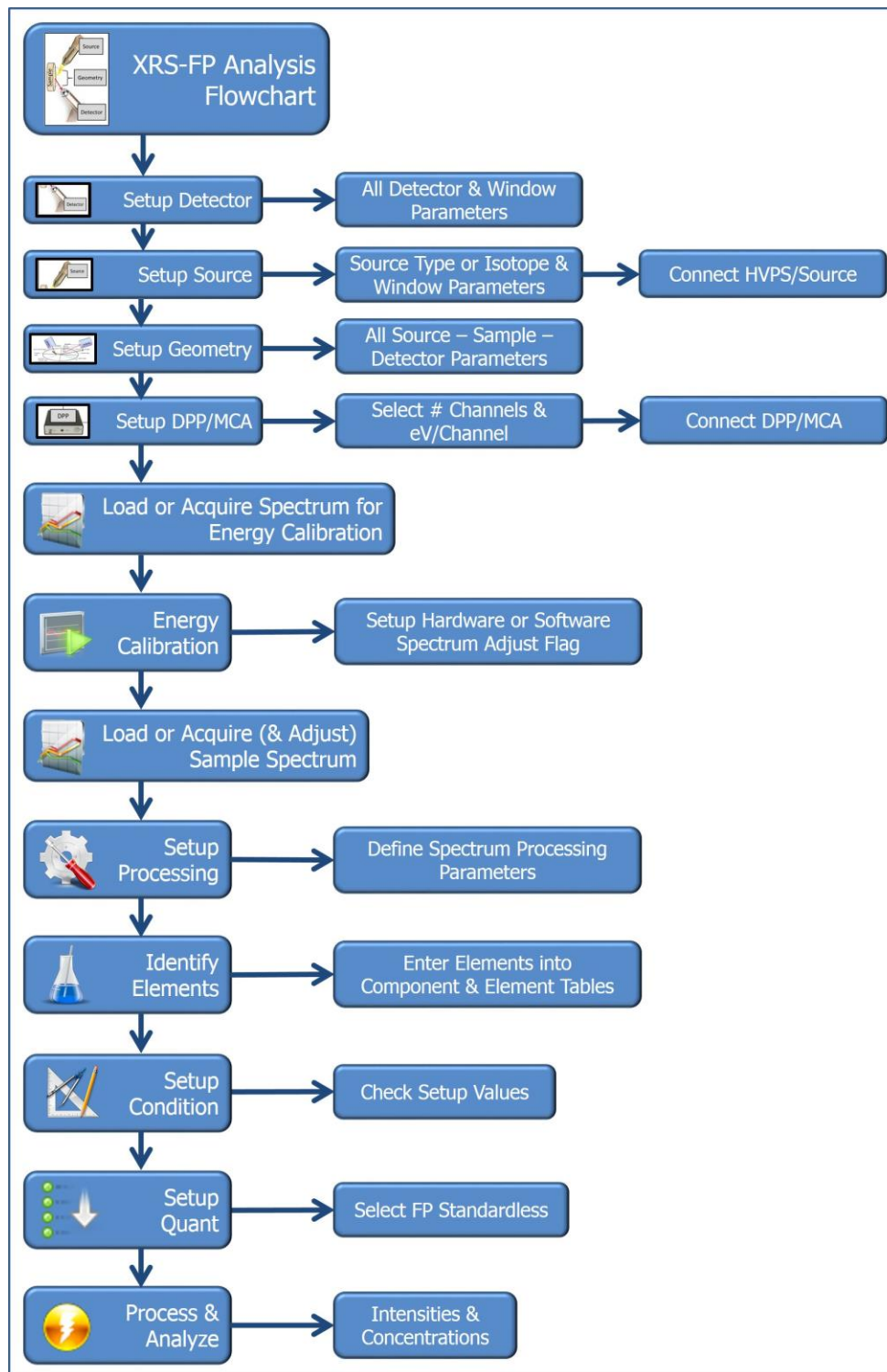


Figure 1. XRS-FP Flowchart. This flowchart describes the steps needed for basic setup and configuration of XRS-FP.

2 XRS-FP SETUP & STANDARDLESS ANALYSIS TUTORIAL

The following tutorial describes the basic setup of a **general** XRF system for analysis, the configuration of XRS-FP, energy calibration using Amptek hardware (although briefly, as this is discussed in detail in the “XRS-FP How to Calibrate with Amptek HW” document) and standardless analysis of stainless steel 316 (SS 316). This tutorial along with associated spectra (*.mca) and application (*.tfr) files guides an XRS-FP software user through the basic setup of their XRF system and subsequent standardless analysis of SS 316. This may be achieved in one of two ways:

- a) Using a live XRF setup for hardware (HW) control and data acquisition (note: that this is a generic guide and the particulars of a given XRF system will vary from instrument to instrument).
- b) Using the provided spectra (*.mca) and application (*.tfr) files **without** HW to emulate the setup and analysis.

Note: It is not necessary to connect the XRS-FP program to any hardware unless you wish to acquire spectra directly with XRS-FP. For **BOTH** methods listed above, the provided spectra (*.mca) and application (*.tfr) files will be used. If using method (a) various input parameters may need to be changed depending on the type of HW, geometry, etc., used for a specific XRF system.

1. If using a live XRF system ensure that the hardware (HW) components are setup in the desired geometry and connected appropriately (power cables, signal cables, etc.). Please see appropriate guides provided by the HW manufacturer(s) for correct setup and **safety** measures.

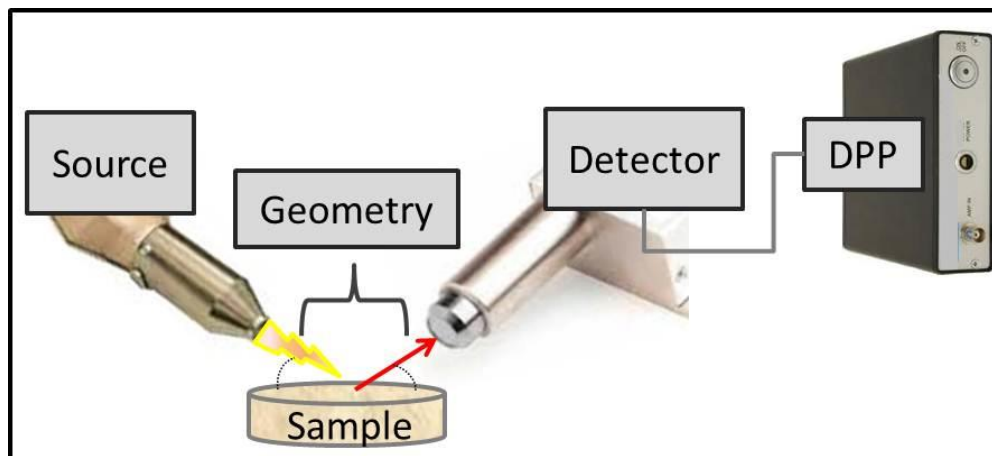


Figure 2. XRF Generic Setup. Above is a simple schematic of an XRF setup, including the source, detector and DPP. Note that for live acquisition both the source (x-ray tube) and DPP need to be connected to a computer for data acquisition and hardware (HW) control, and for running the XRS-FP analysis software; however, if working offline on previously acquired data or if using the files provided with this tutorial without HW there is obviously no need for the HW to be connected.

2. Launch XRS-FP – 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, the splash screen will load and then the Auto-Mode FP Analysis window and a separate Spectra-X window will be displayed. 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** -> **About** menu option.
3. From the Auto-Mode FP Analysis window, click **Expert Mode** (Fig. 3 below). This will show the contents of the “Master.tfr” file (see section 4.1 of the “XRS-FP Software Guide” for additional information on loading the software). Ensure the “Update Spectra” option is checked (on) (Fig. 3).

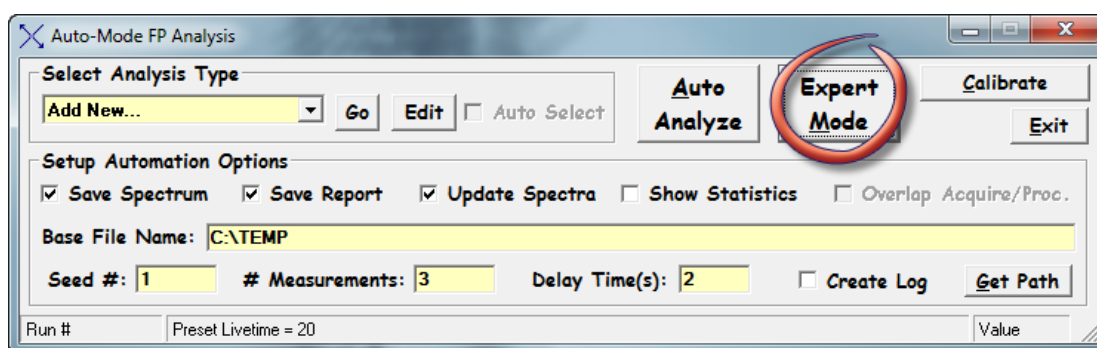


Figure 3. Auto-Mode FP Analysis Panel. Select the “Expert Mode” button. Ensure the “Update Spectra” option is checked (on).

4. From the XRS-FP Expert Panel: Select **File** -> **Open** -> “C:\CrossRoads Scientific\XRS-FP Basic Setup SS316 Tutorial Files\SS316 - Initial.tfr” (or equivalent location). See Fig. 4 below.

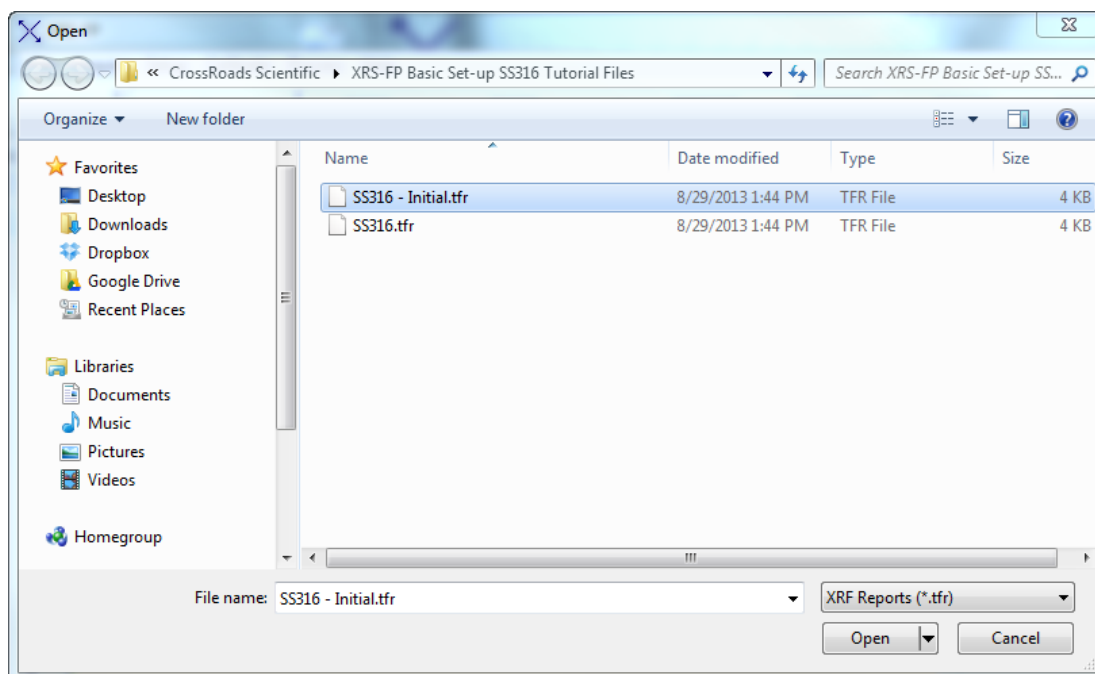


Figure 4. File Open Menu. Open the stainless steel SS316 TFR file, e.g. “SS316.tfr”.

This TFR (“Thin Film Report”) file, or configuration file, acts as a template for this tutorial. A TFR 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 Component Table, Elements Table and Thickness information have no results at this point, the Measurement & Processing information (spectrometer configuration) is already pre-defined and loaded for this application. See Figure 5 below.

Figure 5. XRS- FP Expert Panel. The “SS316 - Initial.tfr” 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 “Thickness Information” table the “Type” is set to “Bulk” and it is “Normalized” to 100%.

Note: If you are connected to HW, various input parameters may need to be changed in the TFR file depending on the type of HW, geometry, etc. used for a specific XRF system. The following steps will outline which parameters may need to be changed. Regardless of the method used for this tutorial (i.e. with or without HW), the steps outlined below will guide you through the process of setting up and configuring XRS-FP for use with an XRF system.

- a. **Specimen Component Table:** This is where the sample components are added to the TFR (also see section 5.2, “XRF Elemental FP Calibration or Standardization,” of the XRS-FP Software Guide). Components can be elements or compounds. For this tutorial, **enter Cr** as the first component. Having entered a component in the table, use the down arrow

key of your computer keyboard to enter additional components. Now enter **Mn** as the second component, **Fe** as the third component, **Ni** as the fourth component, **Mo** as the fifth component and **Si** as the sixth component. Notice that the “Type” is automatically set to “Calc” so the SW will calculate the concentration of each component; however, notice that the “Type” for **Si** is set to “Fixed” and the Concentration is set to 1.0000. The reason for this is there are several minor elements such as Si, S, P and C which cannot be analyzed. To account for this, we use 1% Si as a rough estimate. In the Specimen Component Table **enter “Fixed”** as the component “Type” for Si and set the “Conc” to **1.000**. See entered components below in Figure 6.

Specimen Component Table:

#	Component	Type	Conc.	Error	Units	Mole%	Error
1	Cr	Calc	0.0000	0.0000	wt. %	0.0000	0.0000
2	Mn	Calc	0.0000	0.0000	wt. %	0.0000	0.0000
3	Fe	Calc	0.0000	0.0000	wt. %	0.0000	0.0000
4	Ni	Calc	0.0000	0.0000	wt. %	0.0000	0.0000
5	Mo	Calc	0.0000	0.0000	wt. %	0.0000	0.0000
6	Si	Fixed	1.0000	0.0000	wt. %	0.0000	0.0000

Element Table:

#	Element	Line	Code	Intensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value	Conc	Threshold	Intensity	Ratio	ROI (keV)	Chi2	Quant	Calibration	
1	Si	Ka	1	0.00	0.00	0.00	1.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00
2	Cr	Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00
3	Mn	Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00
4	Fe	Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00
5	Ni	Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00
6	Mo	Ka	1	0.00	0.00	0.00	0.000	0.000	0.0000	0.000	0.000	0.000		Gaussian	None	0.000	0.000	0.00	FP	0.00

Measurement & Processing Conditions:

Code	X-Ray Source				Detector			Chamber	Time (secs)		Monitor	
	Target	Filter	mg/cm2	kV	uA	Type	Filter	mg/cm2	Atmos	Preset	Actual	Intensity
1	Ag	Al	539.780	45.0	10.0	Si drift	None	0.000	Air	50.0	27.546	0.0

Status: Updated Element Table Concentrations... 0 Off On 2048 20 0.59 No 1
Comment: FP Software for Bulk XRF Analysis

Figure 6. XRS- FP Expert Panel. The components, Cr, Mn, Fe, Ni, Mo and Si, are now filled in for this application. Notice that the elements are automatically entered as the components are entered and that the highest energy analyte line is also automatically selected as the components are entered (e.g. the Cr K α line was selected when Cr was entered).

Note: to create a “clean sheet” for future analysis (select **File** -> **New** from the XRS-FP Expert Panel. 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.

- b. **Element Table:** 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. For example, the Cr K α line is selected when Cr was entered for this application (see Fig. 6 above).

Note: In general, the appropriate line for analysis (Ka, Kb, La, Lb, Lg or Ma), **MUST** be selected. Although this line is filled in by the software, it is important to check that it is the best one for the application at hand.

- c. **Thickness Table:** Accurate XRF analysis requires definition of the thickness of the sample material. In the case of this tutorial, the stainless steel is infinitely thick, which means that it has greater thickness than the escape depth of the highest energy line. This is defined as “Type” “Bulk” in the “Thickness Table” and is the default type setting. The default thickness for bulk analysis is zero (0). The “Normalize” field of the thickness table refers to component concentrations. For standardless analysis the results **MUST** be normalized (see Fig. 6 above). Normalizing to 100% is not required for all bulk analyses, but is often employed.
5. From the XRS-FP Expert Panel: Select **Setup** -> **Detector**. This is where all the detector properties are set. If using HW with this tutorial, change the parameters so that they correspond to the XRF system in use. Otherwise, make sure all parameters are identical to those shown below in Figure 7. Select “OK” to exit the dialog and save the parameters. Note that the most important parameters involved in the detector setup are the detector material, thickness, resolution and window type.

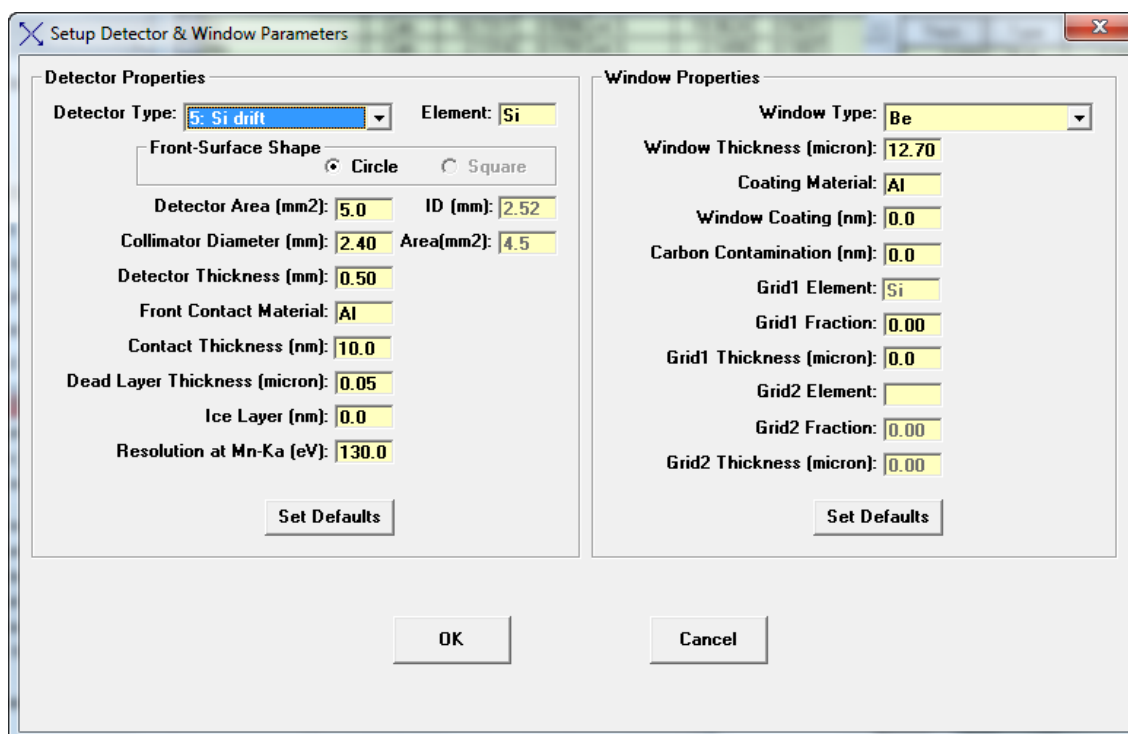


Figure 7. Setup Detector & Window Parameters Dialog. Check that the “Detector Type,” “Window Type,” and all corresponding parameters are as shown here, unless HW is being used with this tutorial.

6. Now, from the XRS-FP Expert Panel: Select **Setup** -> **Tube/Source**. This is where all the source properties are set. If using HW with this tutorial, change the parameters so that they correspond to

the particular source of the XRF system in use. Otherwise, make sure all parameters are identical to those shown below in Figure 8. Note that the most important parameters involved in the source setup are the tube type, model, tube anode material (element) and the window type. Select “OK” to exit the dialog and save the parameters.

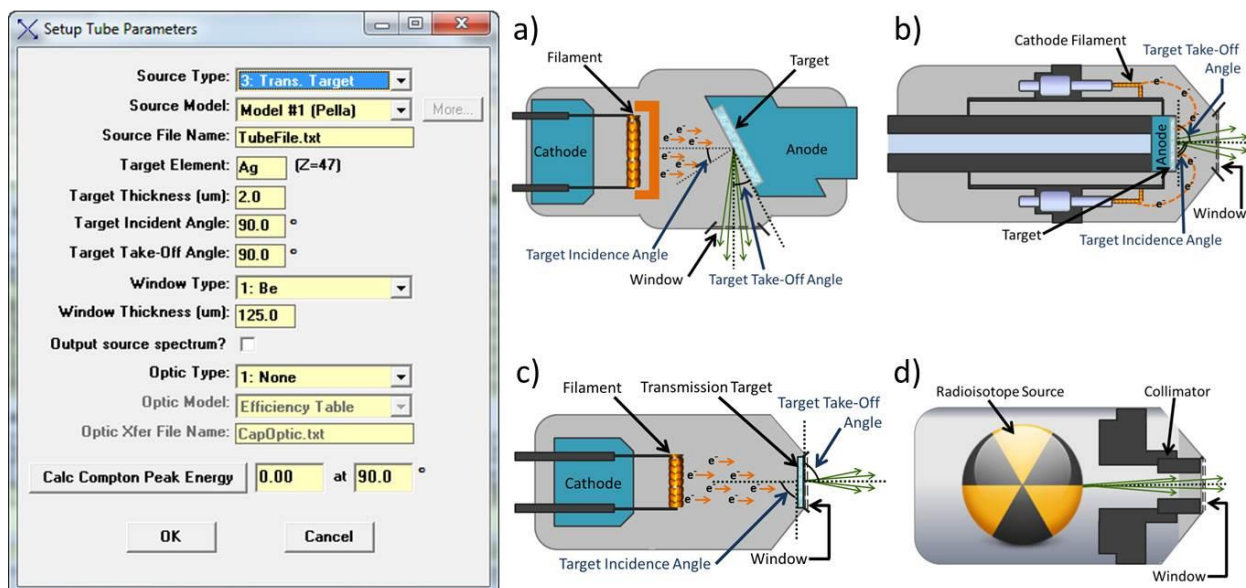


Figure 8. Setup Tube Parameters Dialog. Check that the “Source Type,” “Target Element,” “Window Type” and all corresponding parameters are as shown above, unless HW is being used with this tutorial. The four different source types are illustrated here, a) side window tube, b) end window tube, c) transmission target tube and d) radioisotope.

Figure 8 displays schematic diagrams of the four source types - side window tube, end window tube, transmission target tube and radioisotope source - that can be selected from the XRS-FP **Setup** -> **Tube/Source** dialog. The data acquired for this tutorial used a transmission target tube. The source angle parameters and all other associated geometry of the XRF system are very important and will be discussed further in step 7 in more detail.

7. Again from the XRS-FP Expert Panel: Select **Setup** -> **Geometry**. This is where all the angle and distance parameters are set. If using HW with this tutorial, change the parameters so that they correspond to the particular geometry of the XRF system in use. Otherwise, make sure all parameters are identical to those shown below in Figure 9. Note that the most important parameters involved in the geometry setup are the incidence angle, take-off angle, the tube-to-sample distance and the sample-to-detector distance. Select “OK” to exit the dialog and save the parameters.

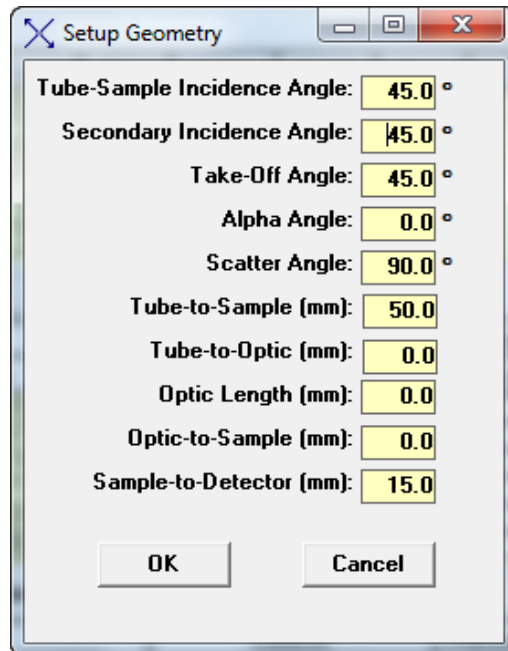


Figure 9. Setup Geometry Dialog. Check that the angle and distance parameters are as shown here, unless HW is being used with this tutorial. See Figures 10 and 11 below for explanation of the various angle and distance parameters.

Figures 10 and 11 below show schematic diagrams of the various angle and distance parameters involved in the geometry setup of an XRF system.

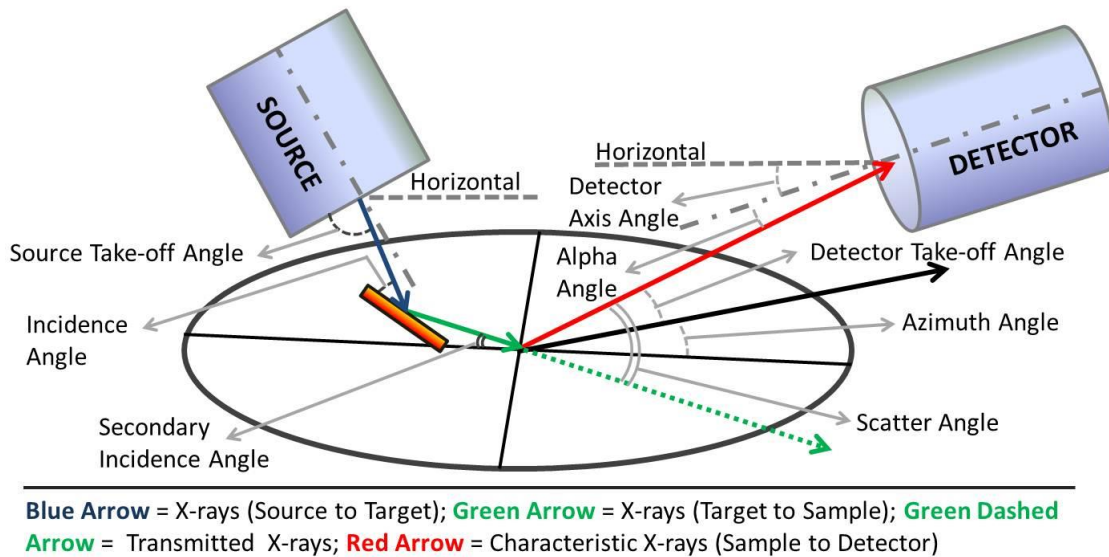


Figure 10. Geometry - Angles Schematic. All angle parameters listed for the geometry setup are described here.



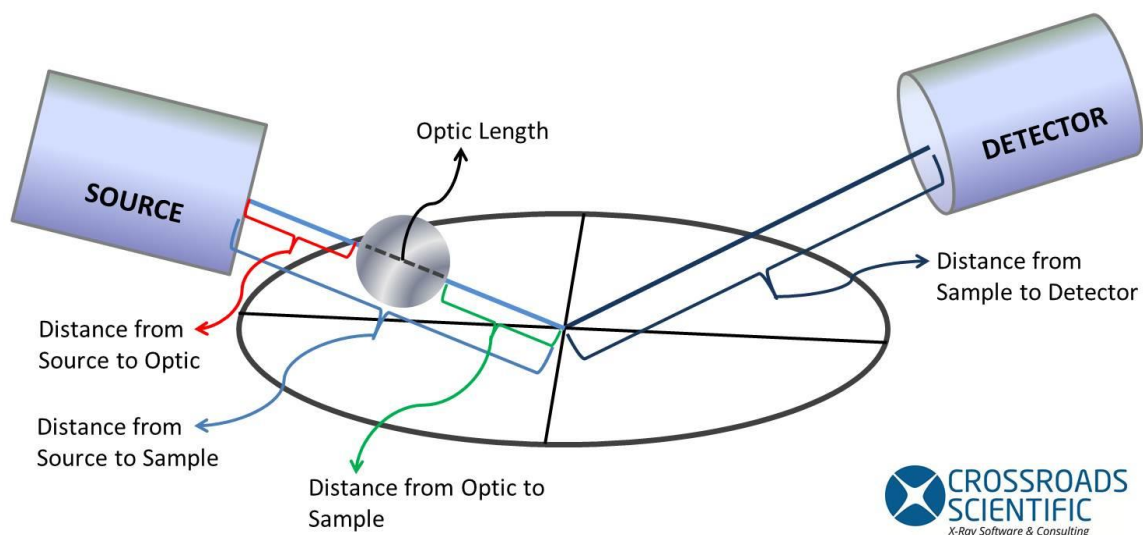


Figure 11. Geometry - Distances Schematic. All distance parameters listed for the geometry setup are described here.

8. From the XRS-FP Expert Panel: Select **Setup** -> **MCA/DPP**. If working offline (without HW) just enter the number of channels, with the eV per channel or range (keV). **If working with HW please see the following document for stepwise details on performing an energy calibration in XRS-FP (with Amptek HW): "XRS-FP How to Calibrate with Amptek HW.doc"**. Note that the two most important parameters involved in the DPP/MCA setup are the number of channels and range. Figure 12 shows the Amptek DPP/MCA Acquisition Setup parameters.

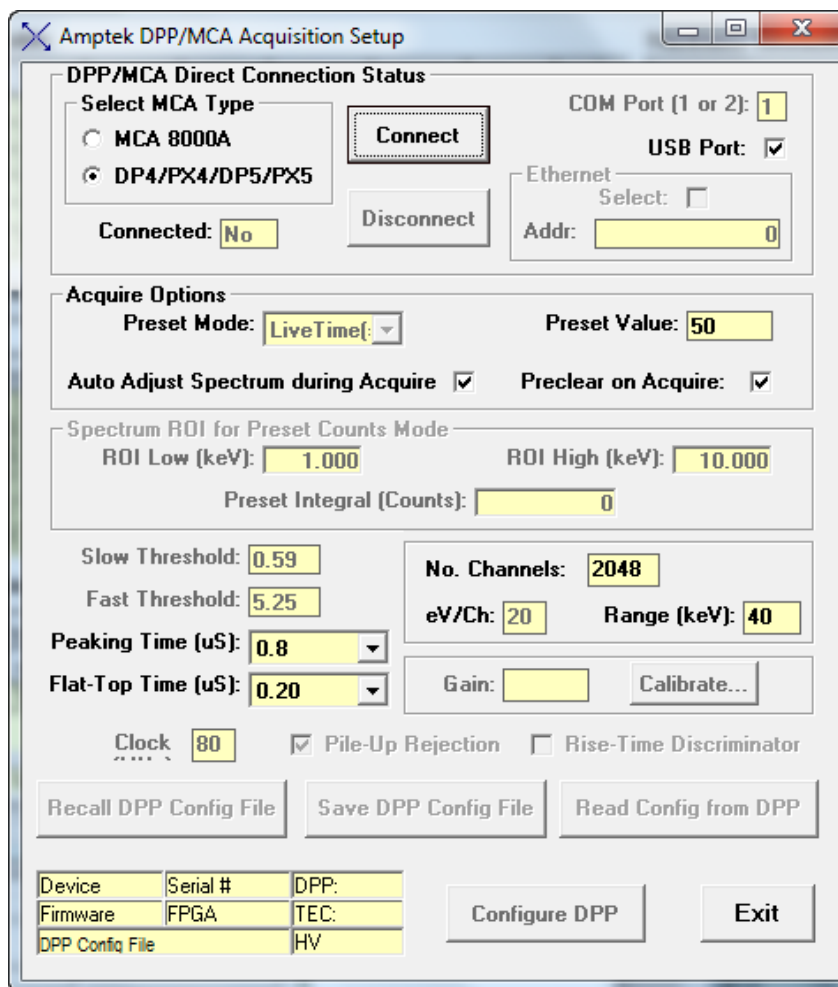


Figure 12. Setup MCA/DPP Dialog. Amptek DPP/MCA Acquisition Setup showing the No. Channels, eV/Ch and Range.

- Now select: **Setup -> Processing** from the XRS-FP Expert Panel. This will display the “Setup Processing Parameters” Dialog shown below in Figure 13 (see section 14.3, “Process Spectrum,” of the XRS-FP Software Guide for more detail). Note that spectra supplied for this tutorial have been energy adjusted (see section 12.11, “Setup Spectrum Adjust” of the XRS-FP Software Guide). To avoid doing a double adjust in this case, verify that the “Auto Adjust Spectrum Gain & Offset on Load” is **unchecked** in the “Setup Processing Parameters” dialog. See Figure 13 below. Note: if you are using your own spectra, you may need to change the Mn-Ka FWHM to a higher value.

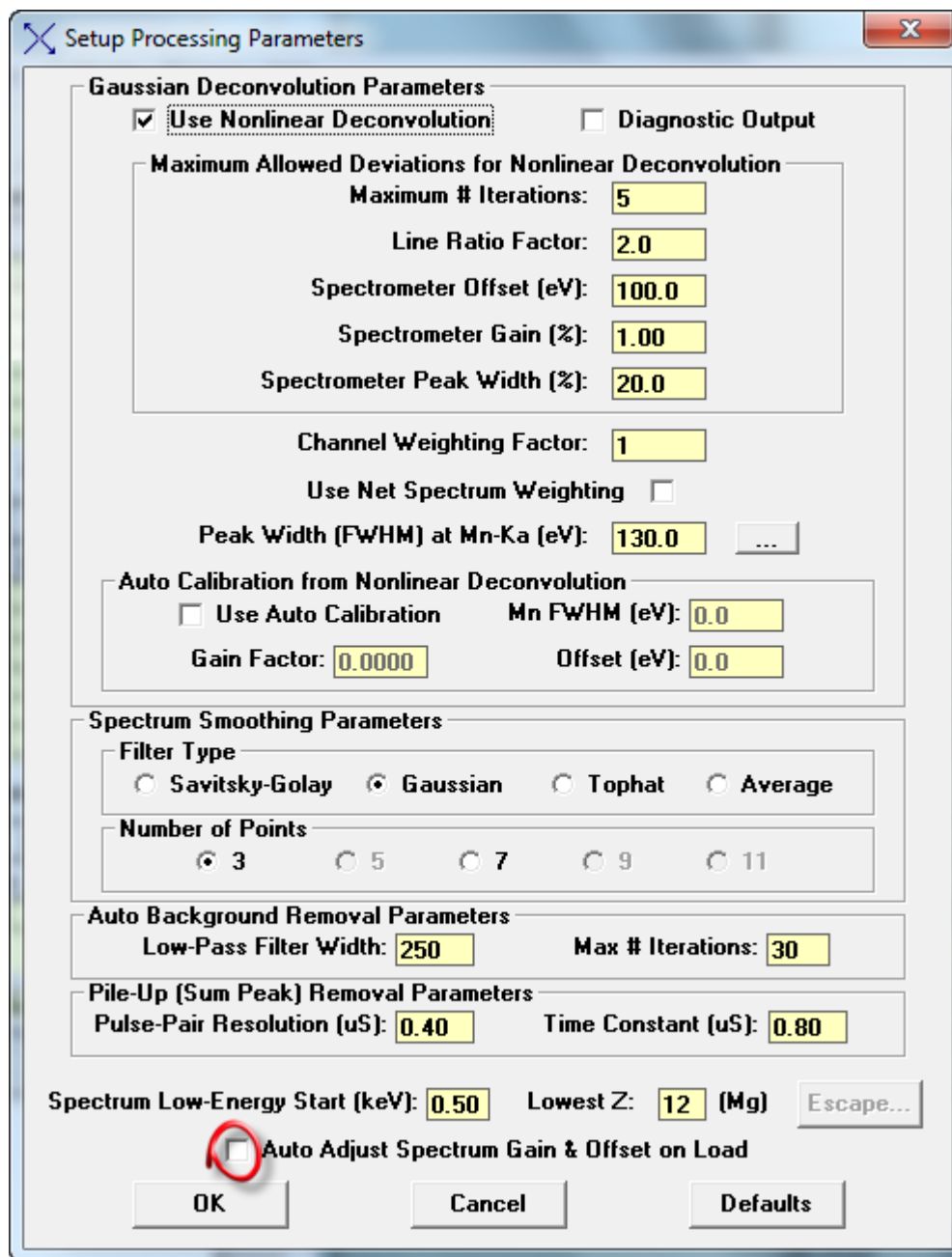


Figure 13. Setup Processing Parameters Dialog. Observe that the “Auto Adjust Spectrum Gain & Offset on Load” button is unchecked if using the files supplied with the SS316 tutorial, as the spectra have already been energy adjusted.

- Then select: **Setup -> Quant** from the XRS-FP Expert Panel. Check that the radio button for the “Quant Analysis Method” is set to “Fundamental Parameters” (FP) and the “FP Calibration Mode” is set to “Standardless” (see Fig. 14 below).

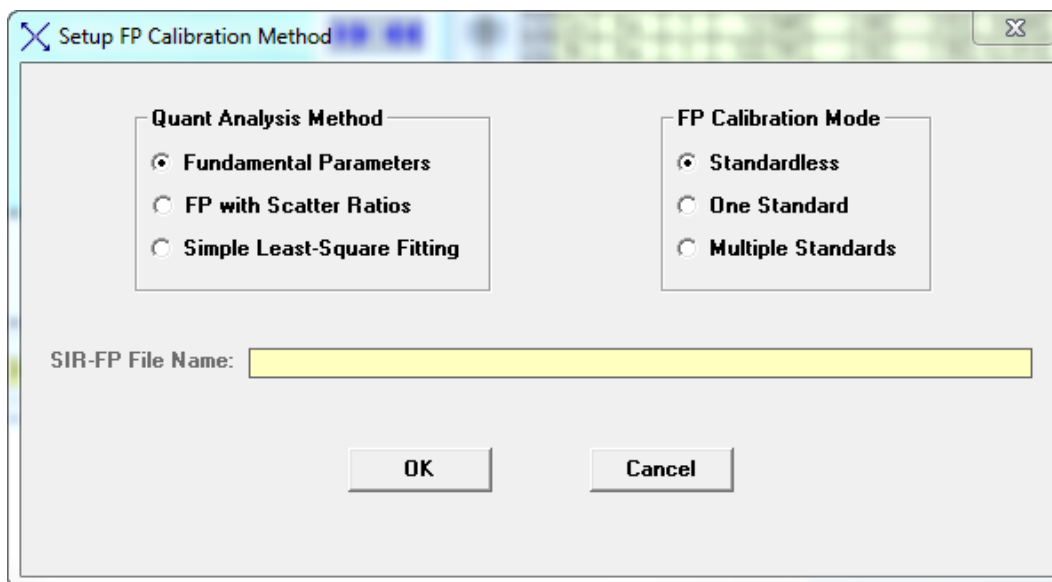


Figure 14. Setup Quant Dialog. Select the “Fundamental Parameters” method and the “Standardless” mode.

11. At this point our application, stainless steel 316, has been defined, XRS-FP has been configured for the setup of the XRF system used for acquisition (either the live XRF system in use or for the system previously used to collect the tutorial files) and it is calibrated (energy calibration). If using the supplied tutorial files **without** hardware proceed to step 12 below. If **using hardware** to do a live acquisition, ensure that the DPP is connected and *now* turn the source x-rays on (HV ON). Details for a specific hardware setup are beyond the scope of this tutorial; however, **please ensure that all safety measures are followed according to the hardware manufacturer guidelines!** Once the system is running and stable, acquire a spectrum of the stainless steel 316 standard. Select **File - > Save As** from the XRS-FP Expert Panel and save the spectrum as, for example, “SS316.mca” (or equivalent).
12. The next step is to extract intensities from the stainless steel 316 spectrum (*.mca file). Select **File -> Open -> “C:\CrossRoads Scientific\XRS-FP\Basic Setup Tutorial\SS316.mca”** (or equivalent location). See Figures 15 and 16 below. Note that the spectra provided for this tutorial are already adjusted and in calibration.

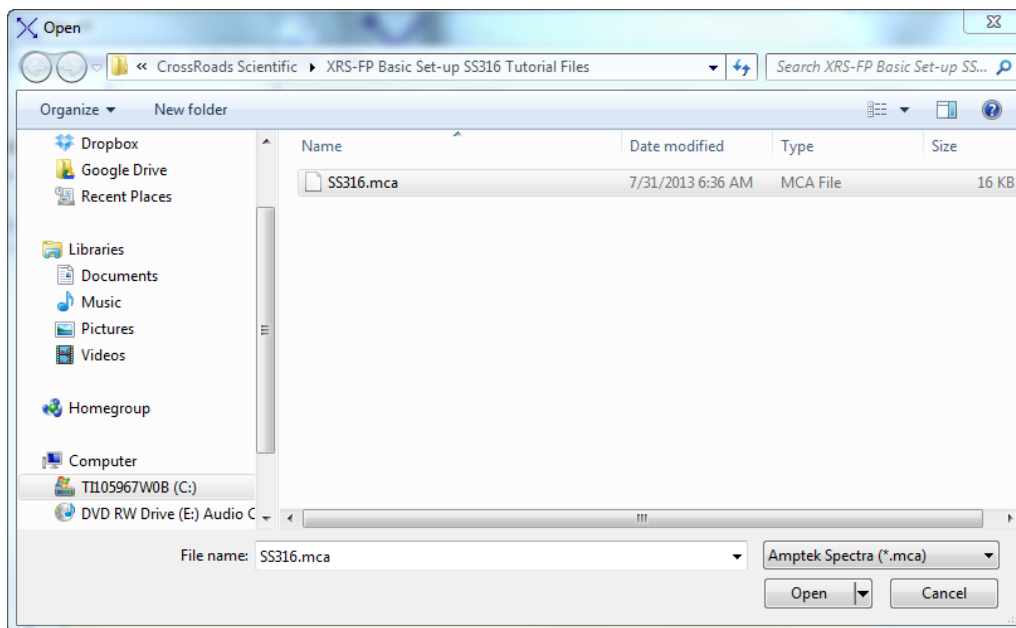


Figure15. File Open Menu. Open the stainless steel spectrum, *.mca file (e.g. SS316.mca).

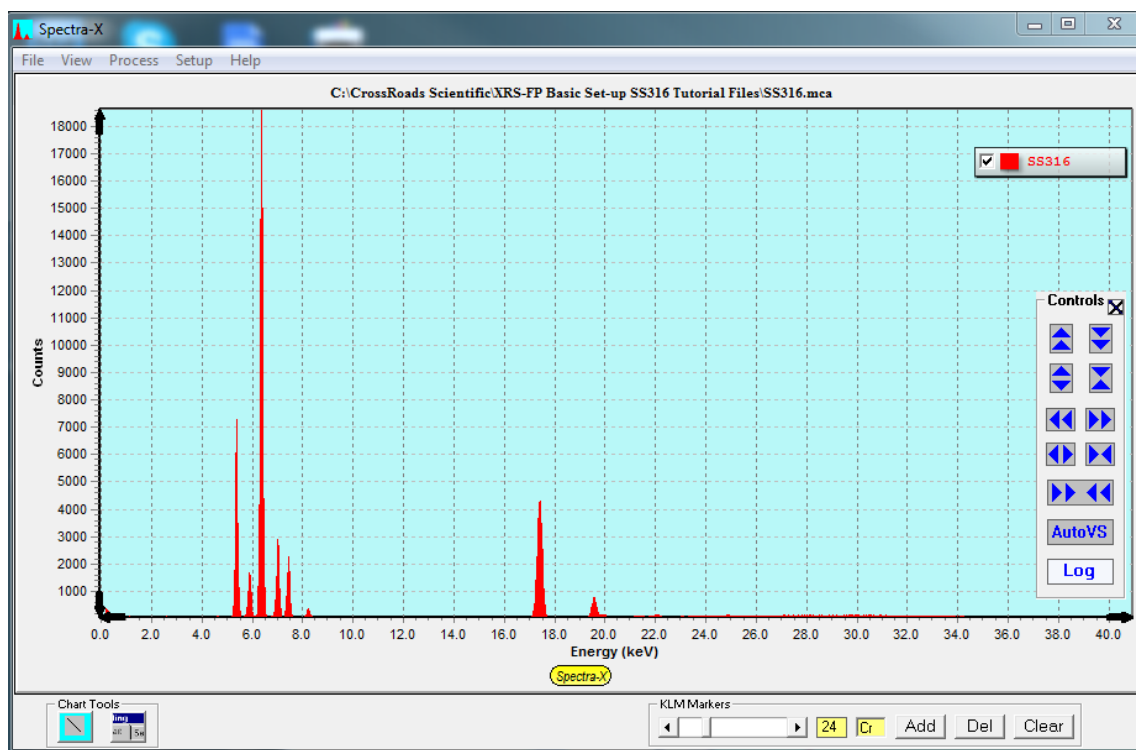


Figure16. Spectra-X Window. Loaded stainless steel mca file (SS316.mca).

13. To extract intensities from the stainless steel 316 spectrum, select **Process -> Spectrum -> All**, from the XRS-FP Expert Panel. Notice that there are now intensities displayed for each element in the “Element Table” (see Fig. 17 below).

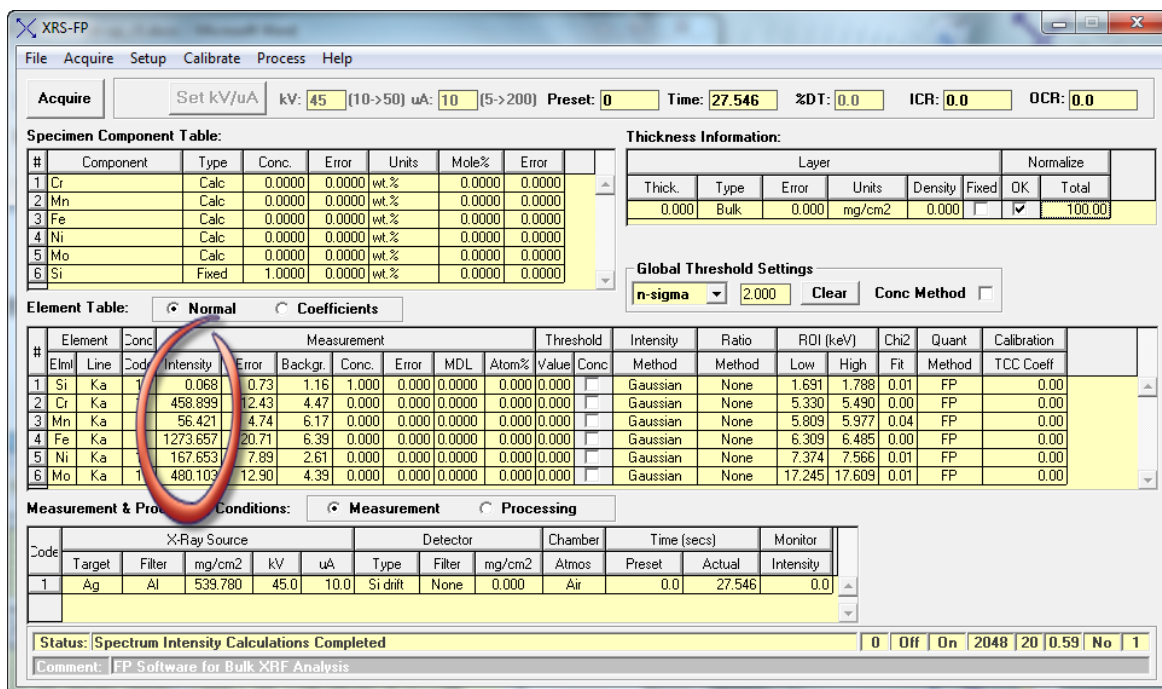


Figure 17. XRS- FP Expert Panel. Note that intensities are now displayed for each element in the “Element Table.”

- Then select: **Process -> Analyze** from the XRS-FP Expert Panel. Notice that there are now concentrations displayed for each component in the “Component Table” (see Fig. 18 below).

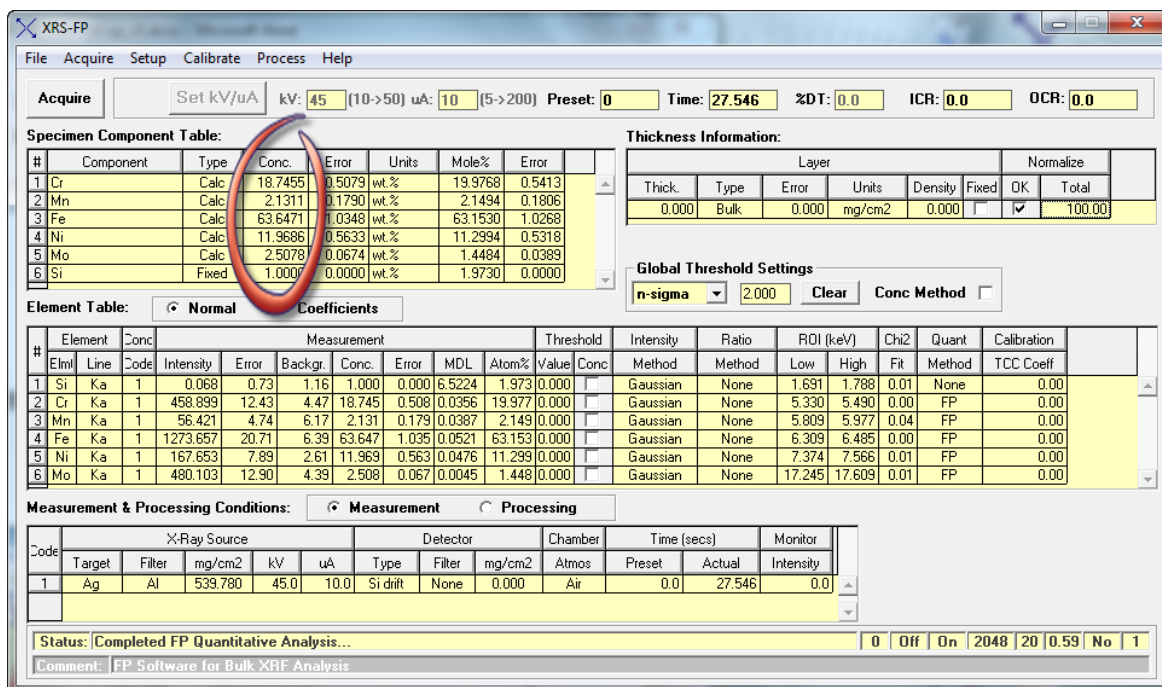


Figure 18. XRS- FP Expert Panel. Observe that the concentration for each component is now displayed in the “Specimen Component Table.”



15. Now save the TFR file by selecting **File** -> **Save As** from the XRS-FP Expert Panel. This can be saved as “**C:\CrossRoads Scientific\XRS-FP Basic Setup SS316 Tutorial Files\SS316-StandardlessAnalysis.mca**” or as an alternate filename of choice. The analysis results should be similar to those shown below in Figure 19.

```

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

Sample Table -----
Layer  Component  Type  Conc.  Error  Units  Mole%  Error
1      Cr        Calc  18.745  0.508  wt.%   19.977  0.541
1      Mn        Calc  2.131  0.179  wt.%   2.149  0.181
1      Fe        Calc  63.647  1.035  wt.%   63.153  1.027
1      Ni        Calc  11.969  0.563  wt.%   11.299  0.532
1      Mo        Calc  2.508  0.067  wt.%   1.448  0.039
1      Si        Fixed  1.000  0.000  wt.%   1.973  0.000

Element Table -----
Elmt  Line  Cond  Ratio  Intensity  Error  Intensity  Conc.  Conc  Calibration
      Code Code Method  (c/s)     (c/s)     Method      Method Method Coefficient
Si    Ka   1  None  0.068     0.7328  Gaussian  1.000  None  0.000
Cr    Ka   1  None  458.899   12.4342  Gaussian  18.745  FP    0.000
Mn    Ka   1  None  56.421    4.7401  Gaussian  2.131  FP    0.000
Fe    Ka   1  None  1273.657  20.7086  Gaussian  63.647  FP    0.000
Ni    Ka   1  None  167.653   7.8904  Gaussian  11.969  FP    0.000
Mo    Ka   1  None  480.104   12.8983  Gaussian  2.508  FP    0.000

Analysis Conditions -----
# Targ  Filter  Thick.  kV  uA  ---Detector---  Thick.  Atmos  Preset  Actual
      mg/cm2  Type  Filter  mg/cm2  Air  Time(s)  Time(s)
1 Ag    Al      539.78  45.0  10.0  Si drift None  0.0  Air    0.0    27.5

Processing Conditions -----
# No.  Escape  Sum  Back  C/R  Blank  ----Blank----
  Smths Peaks  Peaks  Type  Ratio  Rem.  ----File-----
1  2    Yes    Yes  Auto  No   No

```

Figure 19. SS316 Analysis Results. Concentrations for the five calculated components are shown here.

16. For comparison, Figure 20 below shows average compositions for SS316.



Stainless Steels Chromium-Nickel-Molybdenum

Types 316 (S31600), 316L (S31603), 317 (S31700), 317L (S31703)

316/316L Stainless Steel Chemical Composition

Represented by ASTM A240 and ASME SA-240

Element	Percent by Weight	
	Maximum Unless Range is Specified	
	316	316L
Carbon	0.08	0.030
Manganese	2.00	2.00
Silicon	0.75	0.75
Chromium	16.00	16.00
	18.00	18.00
Nickel	10.00	10.00
	14.00	14.00
Molybdenum	2.00	2.00
	3.00	3.00
Phosphorus	0.045	0.045
Sulfur	0.030	0.030
Nitrogen	0.10	0.10
Iron	Bal.	Bal.

Figure 20. SS316 Average Composition. Average composition for SS316 is shown here.



3 APPENDIX

XRS-FP is analysis software for use with X-Ray Fluorescence (XRF) Spectrometry, a widely used analytical technique. XRF analysis is based on the fact that incident x-rays excite atoms in a sample through ionization (the loss of an electron), which then emit characteristic radiation (x-rays of a particular energy) when they relax (an inner shell is filled by an electron from an outer-level shell), see Figure 21 below (for more detail see the XRS-FP Software Guide v51X, section 2 “About X-ray

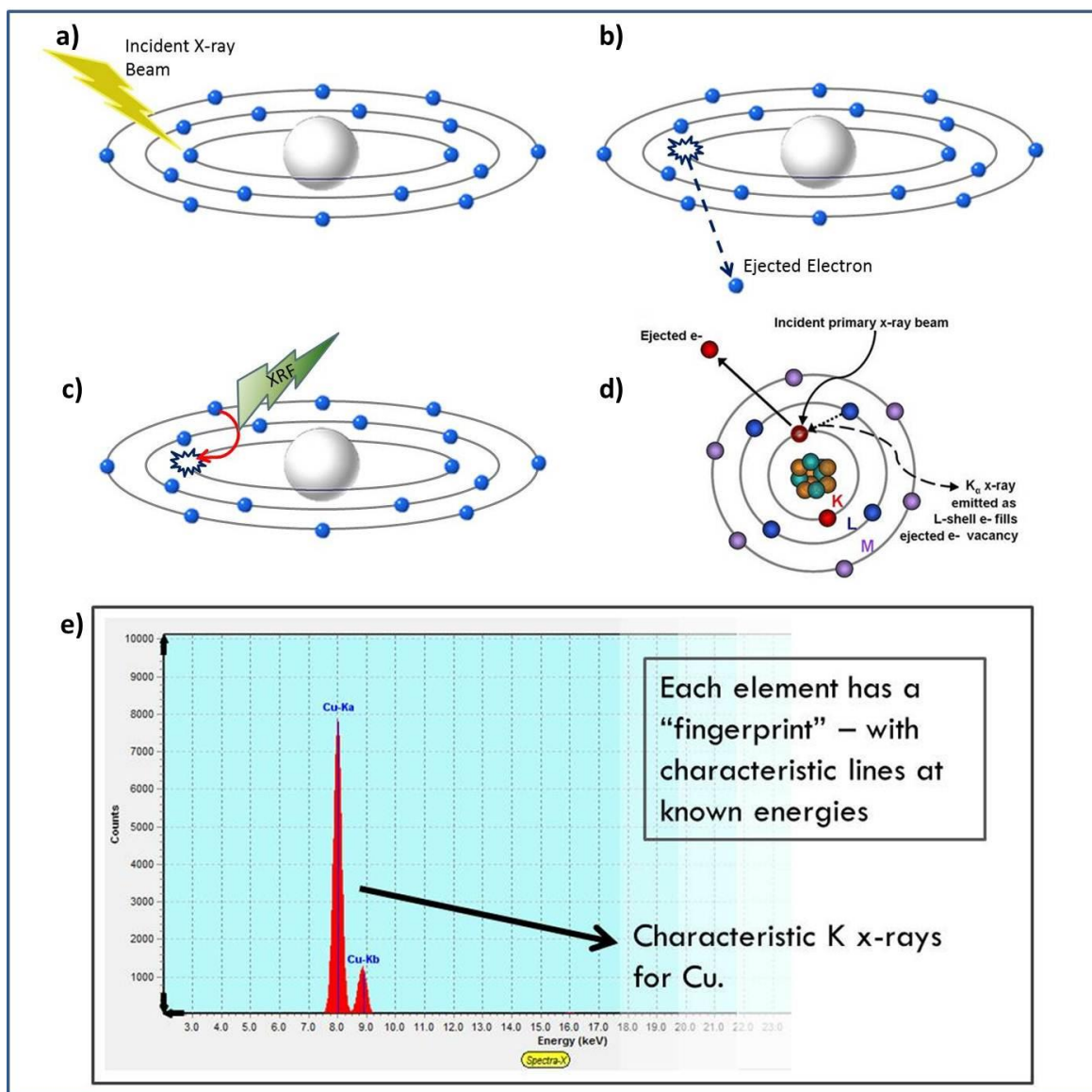


Figure 21. XRF Basics. a) Interaction of an x-ray photon with an atom (of sufficient energy), b) ionization of the atom by ejection of a core shell electron, c) vacancy filled by higher shell electron resulting in emission of an x-ray (photon). d) Schematic illustrating steps (a) through (c) including the emission of a characteristic K_{α} x-ray. e) Chemical elements emit characteristic radiations unique to each element when subjected to appropriate excitation.

Fluorescence”). A detector and signal processing electronics measure each emitted x-ray energy and stores them in “bins” as a histogram, or “spectrum.” The X-ray analysis software, XRS-FP, processes these “raw” spectra to obtain elemental peak areas that when divided by the acquisition time are known as intensities (counts per second, c/s). These values can then be used to determine the elemental concentration and/or sample thickness, using the so-called Fundamental Parameters (FP) method. XRF is capable of analyzing most elements in the periodic table non-destructively, and is therefore one of the most versatile analytical techniques currently available (Willis, Turner, & Pritchard, 2011).

The XRS-FP software consists of a main program that provides the user interface, and various hardware input and output functions, together with at least two libraries (DLL's) that provide the spectrum processing and FP calculations. It runs on standard PC's, and operating systems (Windows 8, 7, Vista, XP, 98, etc.), with 512 MB RAM of memory.

Complete XRF analysis is possible, with or without standards, using an internal database of fundamental parameters (FP) such as absorption coefficients, fluorescence yields, transition probabilities, etc., and complete modeling of detectors and sources. Spectrum processing libraries are available for removing spectrum artifacts (escape and sum peaks), background and for various least-squares peak-fitting models using synthetic Gaussian or experimental reference profiles.

The typical XRF “system” (Fig. 22 below) includes an x-ray source (either an x-ray tube or radioisotope) and detector/electronics, together with a sample within a chamber, which can be evacuated or operated in air. In addition, filters may be used with either the x-ray source and/or the

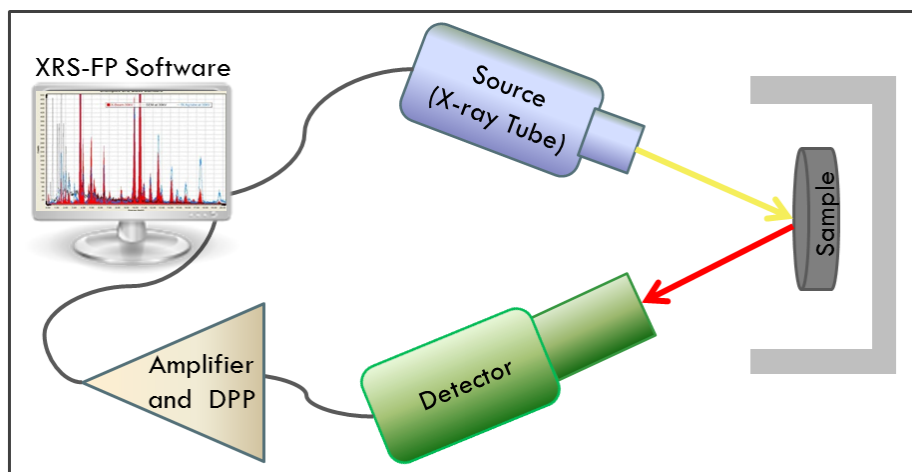


Figure 22. XRF “system”. Key components of an XRF instrument are shown above. This includes the source (x-ray tube or radioisotope), the sample and sample holder, the detector, an amplifier and signal processor and a computer for data acquisition, system control and for sample analysis using XRS-FP software.

detector. It is extremely important to know the geometry of your system and details about the components before setting up the XRS-FP software and doing any calibration or analysis work.

As briefly described above, the purpose of XRF analysis with FP is to convert elemental peak intensities (see previous section) to elemental concentrations and/or film thicknesses. This is achieved typically through a calibration step, where the XRF response function (related to parameters that are independent of the sample matrix) for each element is measured using a known standard of some kind. In some circumstances the analysis may be purely based upon theoretical equations, and the fundamental-parameter database, without any need for a calibration step. This is possible for simple bulk materials or single-layer films where the thickness is fixed, assuming the results can be normalized to 100%.

There are typically two steps in XRF analysis, whether or not the FP method is used. The first step is to calibrate each element from one or several standards (called the FP “Calibration” step). The second step is to produce the sample analysis of a given material, using the previously stored calibration coefficients, and the FP-based algorithms given a definition of the sample (i.e., elements, layers, and the distribution of the elements in the layers).

