

XRS-FP2 Software User Manual



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

www.CrossRoadsScientific.com
info@CrossRoadsScientific.com

Document Change Log

DATE	VERSION	PERSON	PAGES	DESCRIPTION
21-Dec-2015	1.0.0	C. Janko	All	Created document
13-Dec-2015	1.1.0	S. Cross	All	Updated document
9-Feb-2016	1.2.0	S. Cross	All	Updated document
21-Nov-2016	2.0.0	S. Cross	All	Updated document
14-Dec-2016	2.1.0	S. Cross	All	Updated document
21-Dec-2016	2.2.0	C. Janko	All	Formatting

Preface

This manual (©2015-2016) and the XRS-FP2 software (©2015-2016) it describes and any other related materials are copyrighted material owned by CrossRoads Scientific, LLC, with the exception of commercial third party software described below. All Rights Reserved.

CrossRoads Scientific's software is being distributed together with certain third party software that includes:

- (a) Adobe Reader
- (b) Steema Teechart
- (c) Farpoint Spread
- (d) Vendor Provided Software for Digital Pulse Processor and X-Ray Tube Control



This document contains proprietary information that belongs exclusively to CrossRoads Scientific, LLC, and should not be distributed without prior written consent from CrossRoads Scientific, LLC.

CrossRoads Scientific, LLC and its principals, officers, representatives, subsidiaries, employees, agents, heirs, and assigns assume no responsibility or liability, either express or implied, for injury, death, or losses to consumers, users or service personnel resulting from improper handling of the X-Ray Equipment used in conjunction with CrossRoads Scientific, LLC products by unauthorized, untrained or otherwise unqualified personnel.

CrossRoads Scientific, LLC expressly denies any responsibility or liability for abuse, neglect, misuse or tampering with system components by persons not authorized, trained or otherwise associated with CrossRoads Scientific, LLC.

This manual applies to all versions of XRS-FP2.

Safety Precautions and Warnings

The XRS-FP2 software has the ability to control x-ray generating devices. Safe operation requires careful attention to the serious hazards associated with the use of x-ray generating devices and ways to avoid or minimize the hazards, and familiarity with emergency procedures. Untrained or careless operation can damage the devices, its components or other property; cause poor performance; or lead to serious bodily injury.

Anyone who operates, services, maintains, or is otherwise associated with the XRS-FP2 software and the x-ray generating devices must read, understand, and be thoroughly familiar with the information in this manual, and take precautions to protect themselves, their associates, and the equipment.

Conventions

The conventions described below are used in this manual. Please familiarize yourself with these conventions before using the XRS-FP2 software or reading this manual.

Language

The XRS-FP2 software uses US English for the display of text.

Numeric Display Format

The XRS-FP2 software uses the following notation convention to display numerals:

- (a) The period character (.) is used as a decimal separator.
- (b) The comma character (,) is used as a thousands separator.

Take note of this notation convention when interpreting or entering numeric data. Incorrect interpretation or entry of numeric data could result in incorrect instrument setup and/or analysis of data.

Computer Terminology

This manual uses standard Microsoft Windows personal computer (PC) terminology. CrossRoads Scientific assumes you know how to use a standard Microsoft Windows personal computer to navigate through GUI and files on your PC. See the documentation that came with the PC. The following conventions are used in this manual.

Item	Description
Click	Press the left mouse button.
Right-click	Press the right mouse button.
Double-click	Press the left mouse two times in rapid succession. If you need to use the right mouse button, the instructions specify double right-click
CTRL-click	Hold down the CTRL key and press the right mouse button.
SHIFT-click	Hold down the SHIFT key and press the right mouse button.
Scroll	Rotate the scroll wheel on the mouse. A backward scroll rotates the scroll wheel with the finger moving away from the hand. A forward scroll rotates the scroll wheel with the finger moving toward the hand.
Hold	Press the mouse button and hold it down while you perform another function.
Drag	Position the cursor over an area of interest, click, hold the button down, and move the mouse to select an area, create a window, or relocate a selected item.
Right-click-drag	Press the right mouse button and hold it down while you move the mouse.
Select	Place the cursor over a name or button and click once, or place the cursor at the beginning of the name, click, hold, and drag across the name until it is highlighted (changes colors). In the case of a list, use the mouse to click the item in the list.
Open	Double-click the name of a window to open it.

Terms

The following abbreviations will be used to describe terms throughout this guide:

Term/Abbreviation	Description
XRF	X-Ray Fluorescence
EDS	Energy-Dispersive Spectrometry
FP	Fundamental Parameters (i.e. use of known database of x-ray interactions and equations)
MTFFP	Multilayer Thin-Film FP analysis
GUI	Graphical User Interface
System	X-ray source (either an x-ray tube or radioisotope), detector/electronics, sample chamber (vacuum or operated) and sample

Table of Contents

DOCUMENT CHANGE LOG.....	1
PREFACE	2
SAFETY PRECAUTIONS AND WARNINGS.....	2
CONVENTIONS.....	3
TABLE OF CONTENTS.....	5
1 INTRODUCTION.....	10
1.1 What is XRS-FP2?	10
1.2 X-Ray Spectroscopy Concept of Operations	10
1.3 XRS-FP2 Overview.....	11
2 GETTING STARTED WITH XRS-FP2	14
3 SOFTWARE LAYOUT	22
3.1 Workflows	22
4 SOFTWARE OVERVIEW.....	26
4.1 Software Architecture	26
4.1.1 GUI Layer.....	27
4.1.2 Non-GUI Layer.....	28
4.1.3 Hardware Layer.....	29
4.2 HASP Security Plug.....	30
4.3 Supported X-Ray Devices.....	30
4.4 Data Files	30
4.4.1 Analysis File	30
4.4.2 Spectrum File	31
4.4.3 Legacy Analysis File.....	31
4.5 Software Installation.....	31

4.6 Software Removal.....	35
4.7 Key Elements of the XRS-FP2 GUI	36
4.7.1 GUI Launch – Splash Startup Window	36
4.7.2 GUI Termination – Splash Shutdown Window.....	38
4.7.3 Main Window.....	39
4.7.4 Spectrum Window	41
4.7.5 Contextual Workflow Window.....	45
4.7.6 Organization of Analysis Parameters into Spreadsheet Windows.....	45
5 SETUP HARDWARE.....	48
5.1 DPP-MCA.....	48
5.1.1 Config	48
5.1.2 Peak Shape.....	49
5.1.3 MCA.....	50
5.2 X-Ray Source.....	53
5.3 Calibrate Energy.....	58
5.3.1 XRF Spectrometer Calibration and Monitoring.....	59
6 CONFIGURE.....	62
6.1 Detector	62
6.1.1 Detector - Manage	62
6.1.2 Edit	63
6.1.2.1 Detector Types – Si-Pin, Si(Li), and Ge	63
6.1.2.2 Detector Type – CdTe.....	65
6.1.2.3 Detector Type – PC.....	66
6.1.2.4 Detector Window Types.....	66
6.2 Geometry.....	67
6.2.1 Manage	68
6.2.2 Edit	69
6.2.2.1 XRF Analysis Mode - Angles.....	69
6.2.2.2 XRF Analysis Mode - Distances.....	70
6.2.2.3 EPXA Analysis Mode - Angles	71
6.2.2.4 EPXA Analysis Mode - Distances	72
6.3 Source	72
6.3.1 Manage	73
6.3.2 Edit	74
6.3.2.1 Source Parameters	74
6.3.2.2 Source Window Type – Alloy.....	76
6.3.2.3 Source Window Type – Multilayer	77
6.3.2.4 Source Type - Radioisotope.....	78

6.3.2.5	Optic Parameters	80
6.4	Detector Filters	81
6.4.1	Manage	82
6.4.2	Edit	83
6.5	Source Filters	84
6.5.1	Manage	85
6.5.2	Edit	86
7	FILE MANAGER.....	88
7.1	GUI Elements of File Manager	88
7.1.1	Spectrum Preview	88
7.1.2	Spectrum Overview.....	88
7.1.3	Analysis Preview.....	89
7.1.4	File Explorer	89
7.2	Import	90
7.3	Export.....	93
7.4	Load.....	93
7.5	Save.....	94
8	ADMIN.....	96
8.1	Customize Report.....	96
8.2	Analysis Mode	96
9	EASY & EXPERT MODES.....	97
9.1	Easy Mode	97
9.2	Expert Mode	97
10	HELP	98
10.1	About	98
10.2	User Manual	99
10.3	Basic Setup	99
10.4	Energy Calibration.....	100

10.5	Bulk Analysis.....	100
10.6	Standards Calibration.....	101
10.7	Thin Film.....	101
10.8	EPXA Analysis	102
11	XRF ANALYSIS WITH XRS-FP2.....	103
11.1	XRF Single-Layer Bulk	103
11.2	XRF Thin-Films	105
11.3	Supported Hardware.....	107
12	APPLICATION WORKFLOW	107
12.1	Definition.....	108
12.1.1	Layer Table (Thickness Information).....	108
12.1.2	Component Table	109
12.2	Methods	109
12.2.1	Element Table.....	110
12.2.2	Condition Code Table	111
12.2.3	R-hand Panel.....	114
13	ANALYZE WORKFLOW	117
13.1	Acquisition.....	117
13.1.1	Acquire Options.....	118
13.2	Element ID	118
13.2.1	Element ID Lists	119
13.2.2	Identified Elements (R-hand Panel)	120
13.3	Regions of Interest	120
13.4	Quantify	120
13.4.1	Spectrum Processing	121
13.4.2	Quantification.....	122
13.4.3	Quantify Options	122
13.4.4	Analysis Definition - Immediate Mode	123
14	STANDARDS WORKFLOW	124
14.1	Overview of Calibration Methods and Operations	124

14.2 Single Standard	124
14.2.1 Create	125
14.2.2 Import	125
14.2.3 Acquisition	126
14.2.4 Spectrum Processing and Calibrate	127
14.2.5 Save Standard and Finish	127
14.3 Multiple Standards.....	127
14.3.1 Options	128
14.3.1.1 MLSQ.....	129
14.3.2 Calibration	129
14.3.2.1 Validate	132
14.3.2.2 Plots.....	132
15 SPECTRUM PROCESSING.....	134
15.1.1 What is Spectrum Processing?	134
15.1.1.1 Smoothing	135
15.1.1.2 Escape Peak Removal	135
15.1.1.3 Sum Peak Removal	135
15.1.1.4 Background Removal.....	136
15.1.1.5 Blank Removal.....	136
15.1.1.6 Intensity Extraction	136
APPENDIX A: ABOUT X-RAY FLUORESCENCE (XRF)	138
Introduction to XRF	138
The Physics of XRF: Interactions of X rays and Matter	139
References	140
APPENDIX B: KEY XRF & FP REFERENCES	141

1 Introduction

1.1 What is XRS-FP2?

XRS-FP2 is a software package designed for the analysis of all types of materials using x-ray spectroscopy. This software package allows for complete XRF analysis using fundamental parameters (FP) for either bulk materials, single-layer thin-film materials, or multilayer analysis for thickness and composition. 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. In addition, XRS-FP2 has an alternative mode of operation, EPXA, that allows for complete spectrum processing and ZAF calculations for spectra taken on an SEM fitted with an EDS detector for either bulk or single-layer thin-film materials.

*Note that the multilayer thin-film (MTFFP) and electron beam (EPXA) options do not come standard with the XRS-FP2 software package, but are available options for purchase.

Typically, there are three main steps for XRF analysis using the XRS-FP2 software:

- Calibration with standards
- Quantitative analysis of unknowns
- Routine maintenance checks on the XRF system

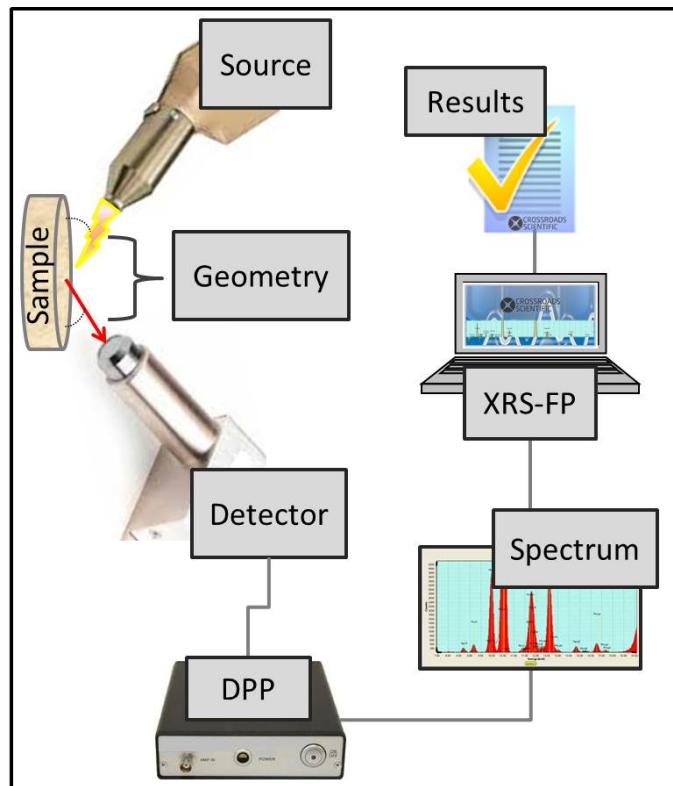
*Note: There is also the possibility of doing analysis without standards if the detector, geometry and tube information is adequately described, and you are only analyzing a bulk sample or a single-layer sample with a fixed film thickness. In addition, a simple least-squares calibration and quantitation can be achieved without using the full FP method.

An XRF “system” is meant to include an x-ray source (either an x-ray tube or radioisotope) and detector/electronics, together with a sample within some kind of chamber, which can be evacuated or operated in air. In addition, filters may be used with either the x-ray source and/or the detector. It is extremely important to know the geometry of your system before setting up the XRS-FP2 software and doing any calibration work.

1.2 X-Ray Spectroscopy Concept of Operations

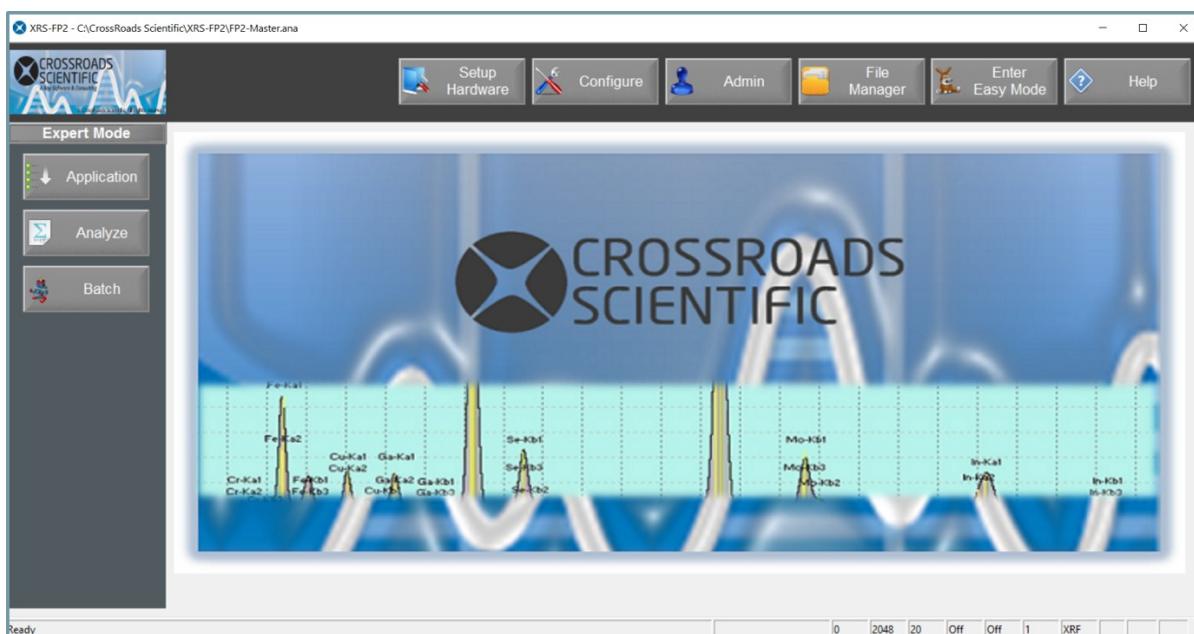
Although it is not necessary to connect the XRS-FP2 program to any hardware, unless you wish to acquire spectra directly with XRS-FP2, this is the main mode of operation for XRF analysis. If using a live XRF system ensure that the hardware (HW) components are setup in the desired geometry and connected appropriately (power cables, signal cables, etc.). Please see appropriate guides proved by the HW manufacturer(s) for correct setup and **safety** measures.

Below 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-FP2 analysis software; however, if working offline with previously acquired data there is obviously no need for the HW to be connected.

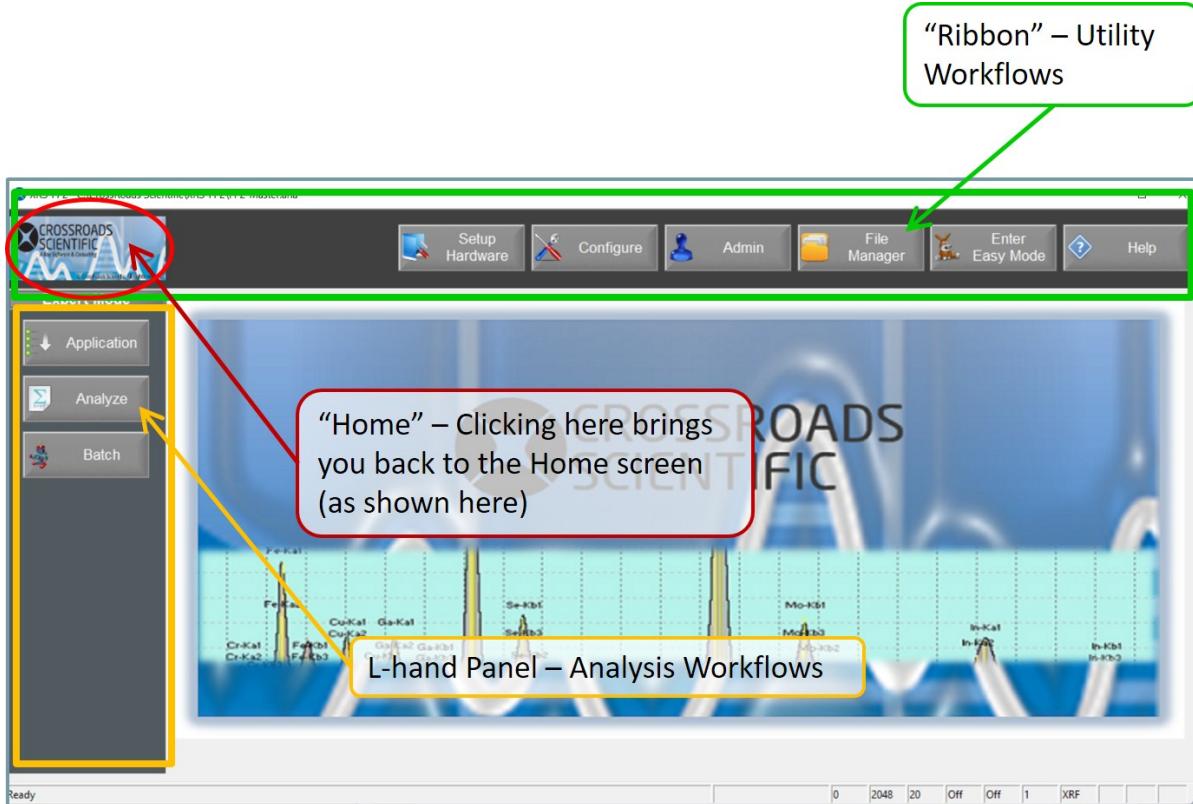


1.3 XRS-FP2 Overview

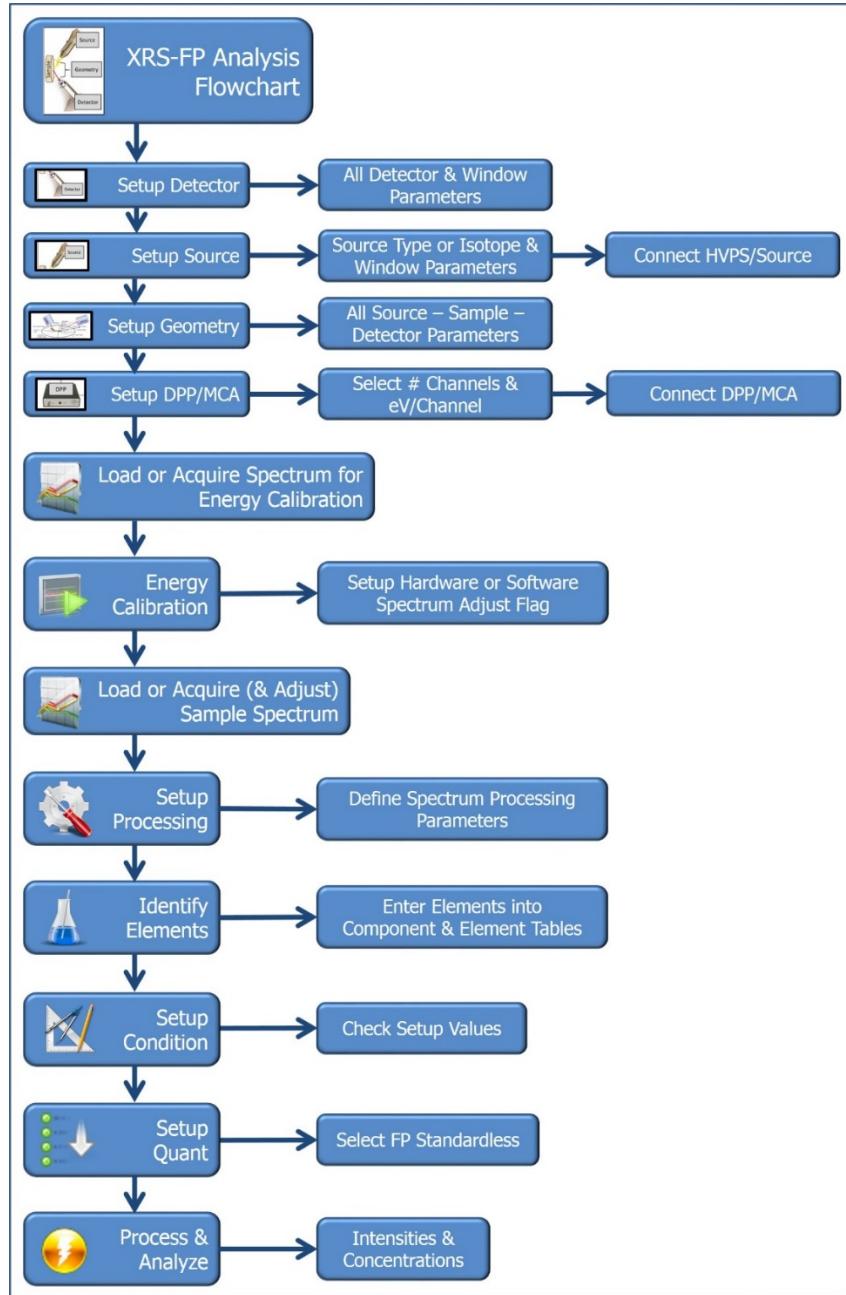
Once XRS-FP2 has been launched (either from the Windows Start-Apps Menu, from the Start-Programs Menu or from a desktop shortcut) a splash screen will load and then XRS-FP2 will be displayed. See the figure below. The splash screen will briefly show the values and options for the HASP security plug, and the software libraries that have been loaded. This can also be displayed by selecting the **Help** button (located in the top ribbon).



XRS-FP2 uses workflows to guide the user through the setup of the XRF system in use, data acquisition and analysis (see figure below). A more detailed description of the various workflows can be found in sections 1.4 and 1.6 of this manual. The top ribbon contains utility workflows that guide the user through hardware setup and configuration. The L-hand panel contains workflows that guide the user through the application definition and data acquisition and analysis.



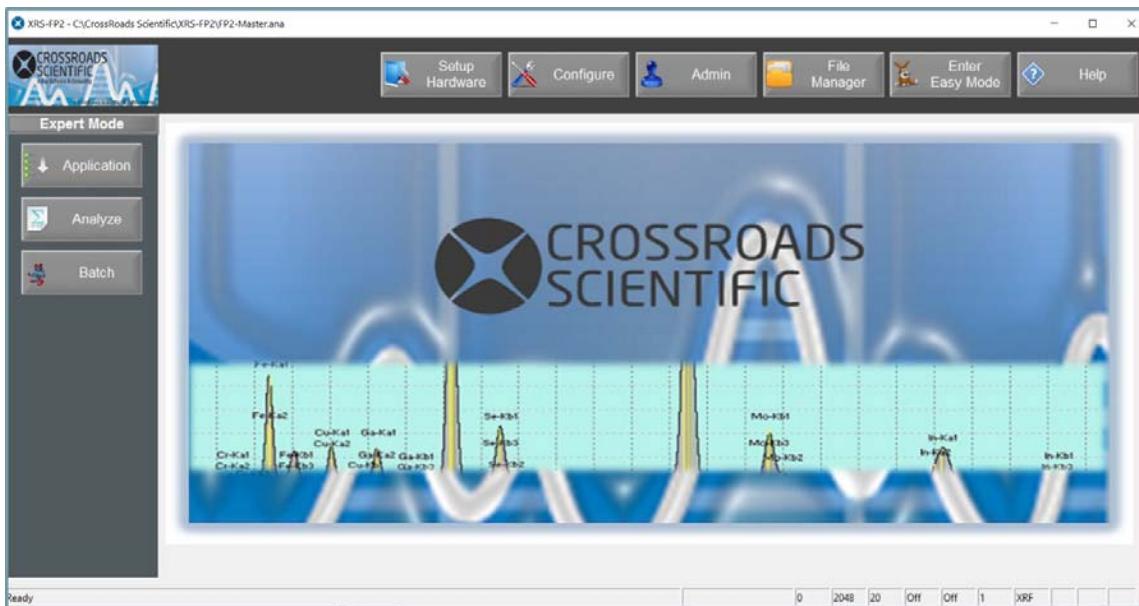
For accurate XRF analysis, it is important that the detector, source, geometry and DPP/MCA parameters be accurately defined in the software. The flowchart below illustrates the steps involved in the basic setup and configuration of XRS-FP2 for standardless analysis:



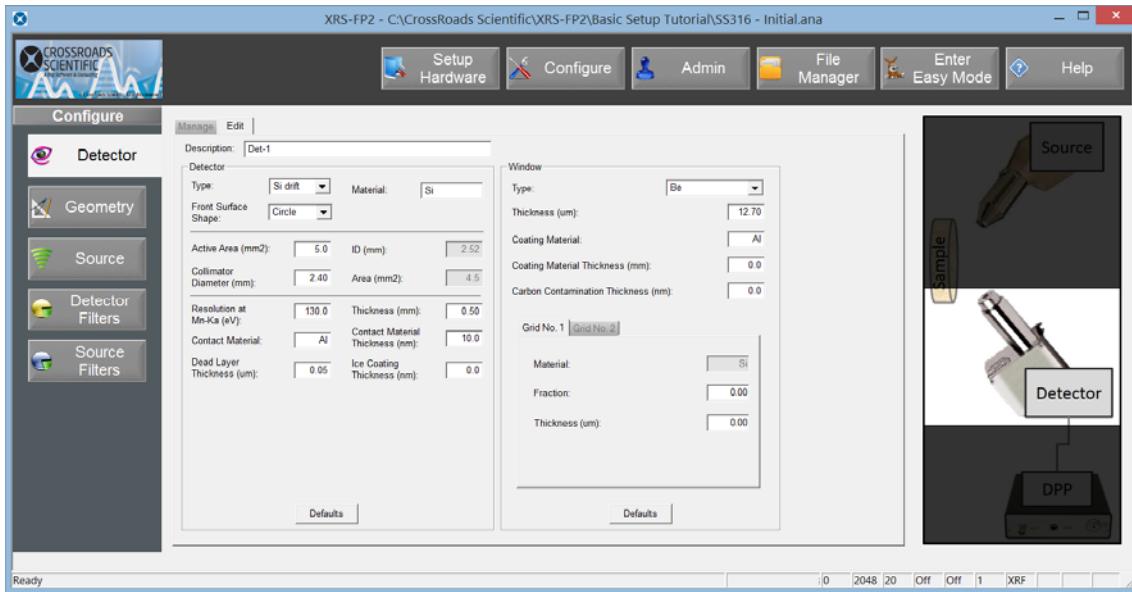
2 Getting Started with XRS-FP2

The following steps describe how to get started using XRS-FP2, including basic setup, configuration and analysis. These steps guide the user through a basic *standardless analysis*. *Note: for a more detailed tutorial describing configuration, setup and analysis using XRS-FP2, please see the “XRS-FP2_BasicSetup” tutorial in the Help section of XRS-FP2.

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 below).

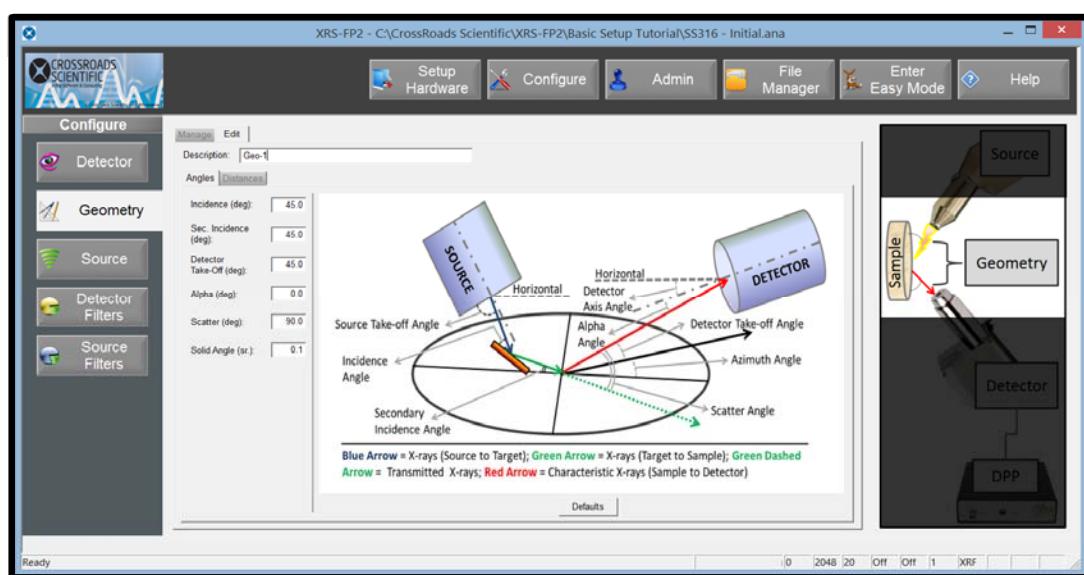


2. From the top ribbon of XRS-FP2 select the **Configure** button. This is where all the detector, geometry, source and filter properties are set. With the **Detector** button selected go to the “Edit” tab. Enter the parameters so that they correspond to the XRF system in use.

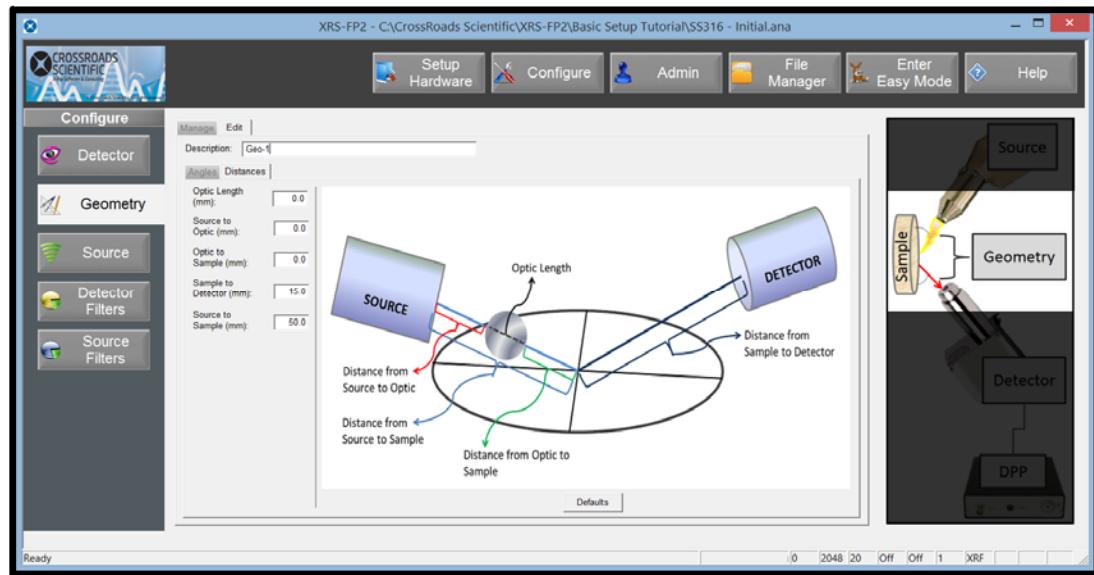


3. Still in the configure workflow, select the **Geometry** button and go to the “Edit” tab. This is where all the angle (Fig. A below) and distance (Fig. B below) parameters are set. Change the parameters so that they correspond to the particular geometry of the XRF system in use.

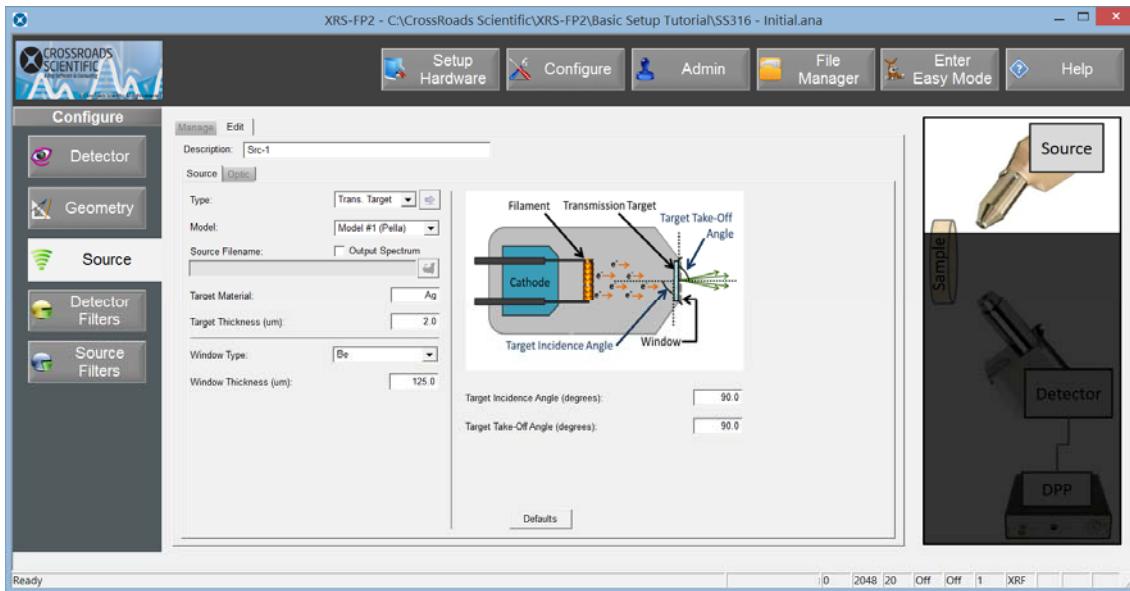
A.



B.

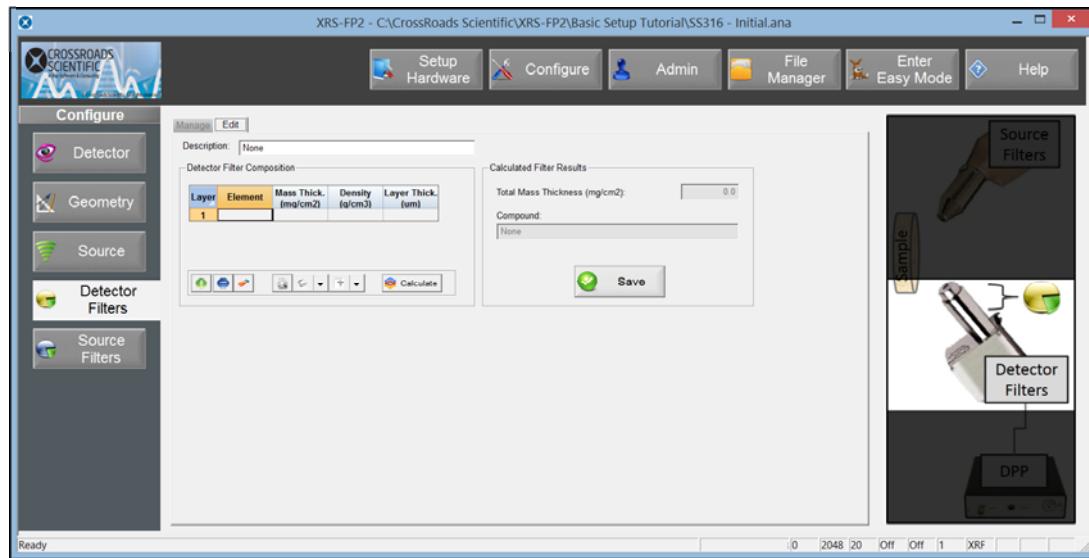


- Now select the **Source** button and go to the “Edit” tab. This is where all the source properties are set. If using HW with this tutorial, change the parameters so that they correspond to the particular source of the XRF system in use.

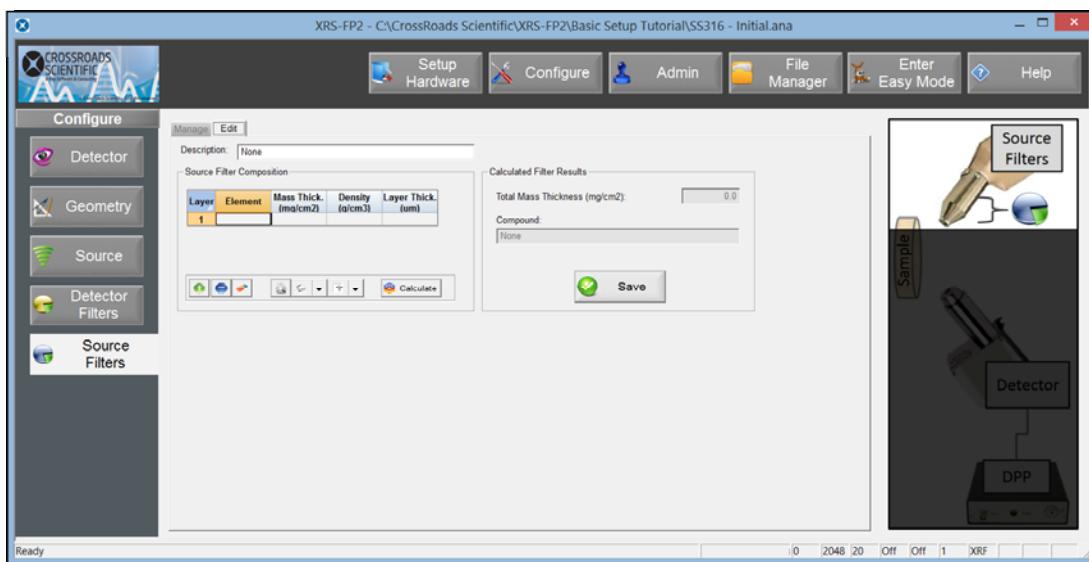


- If using detector filters or source filters with the XRF setup, select the **Detector Filters** button (Fig. A below) and/or **Source Filters** button (Fig. B below), go to the “Edit” tab and enter the detector/source filter composition information.

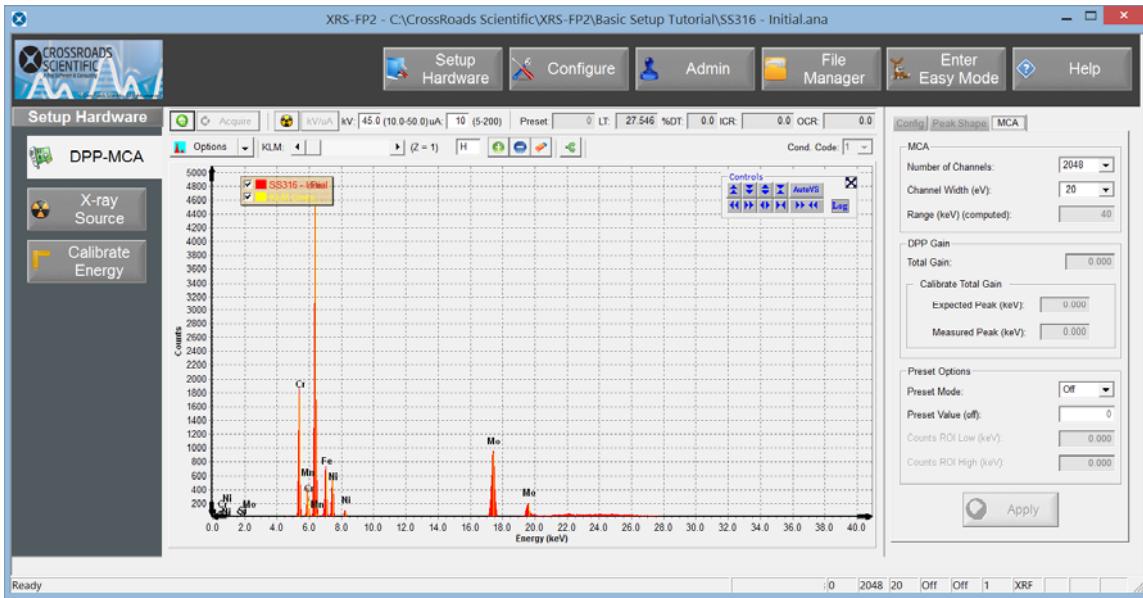
A.



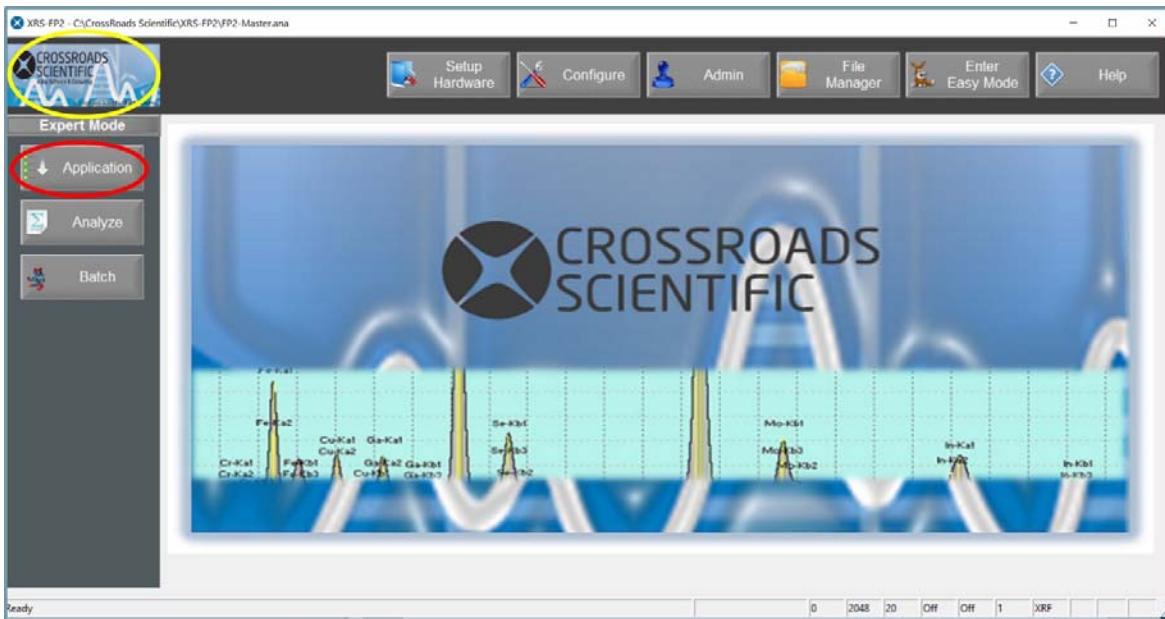
B.



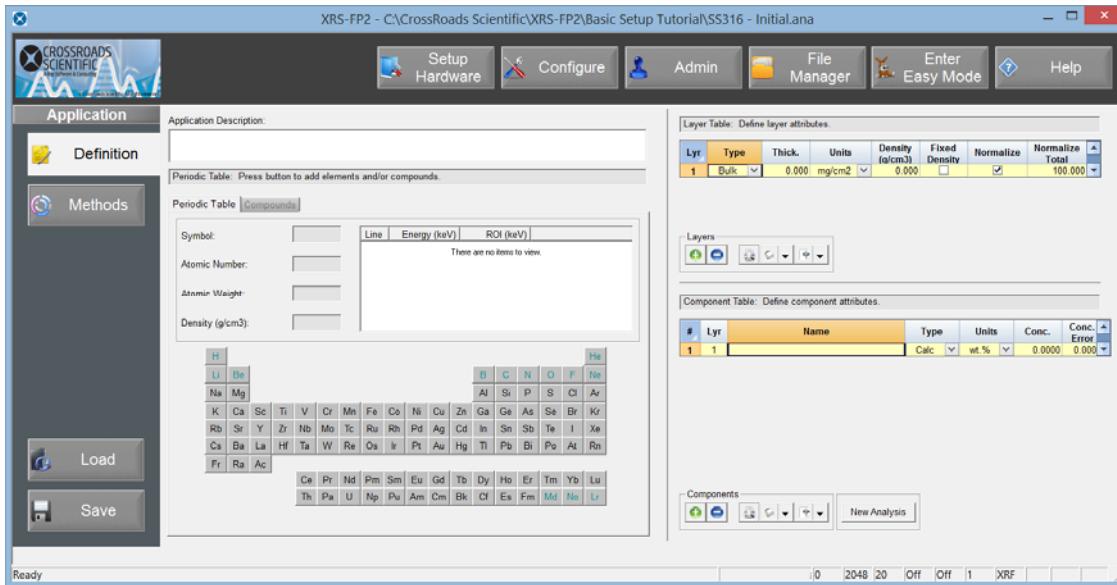
6. From the XRS-FP2 ribbon select the **Setup Hardware** button and go to the **DPP-MCA** button. If working offline (without HW) go to the MCA tab on the right-hand panel and check or enter the number of channels, with the eV per channel or range (keV). *If working with HW please see the energy calibration tutorial ("XRS-FP2 How to Calibrate with Amptek HW") in the Help section of XRS-FP2 for stepwise details on performing an energy calibration in XRS-FP with Amptek HW.* Note that the two most important parameters involved in the DPP/MCA setup are the number of channels and range.



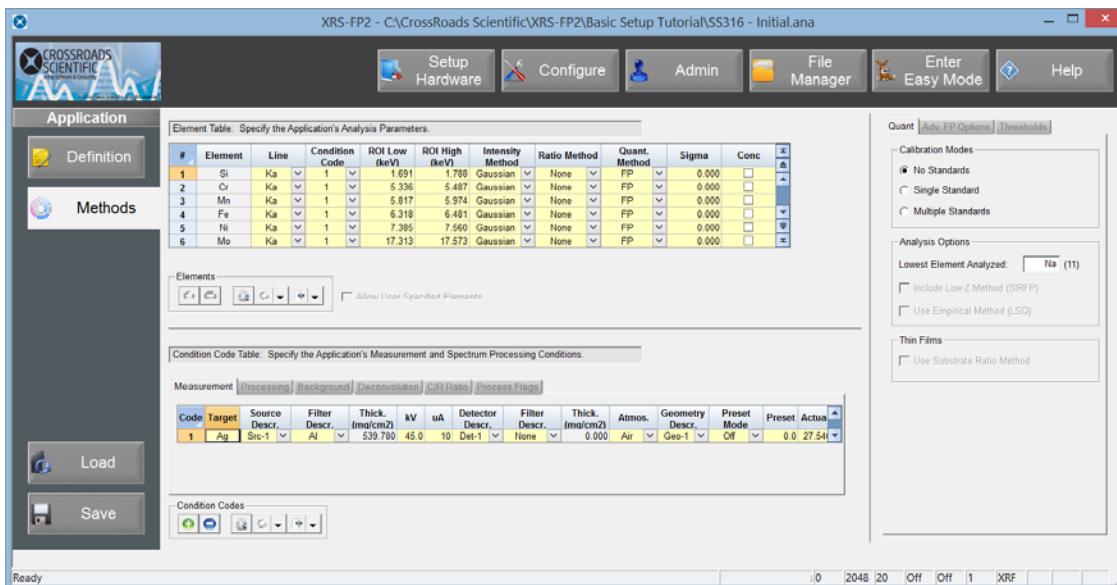
7. Now that the system has been configured and hardware setup, we move to the ***application workflow***, where the application and methods are defined. First click on the **Home** button (yellow circle below), then select the **Application** button (red circle below).



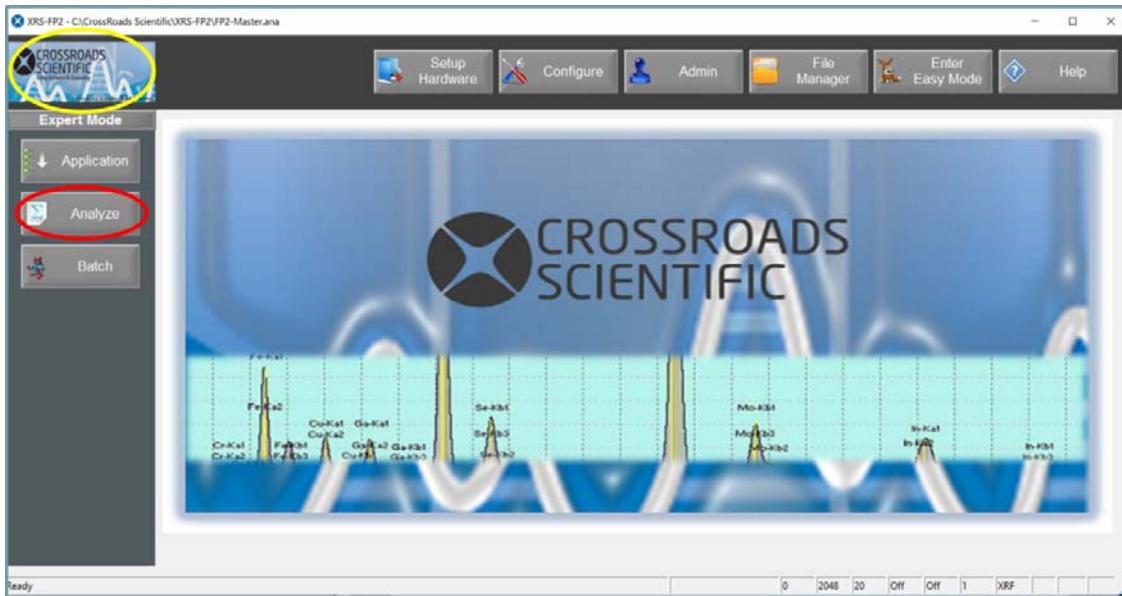
8. Select the **Definition Button** in the ***application workflow***. This is where the sample elements and compounds can be entered either by clicking on the periodic table or by entering them in the Component Table (in the right-hand panel).



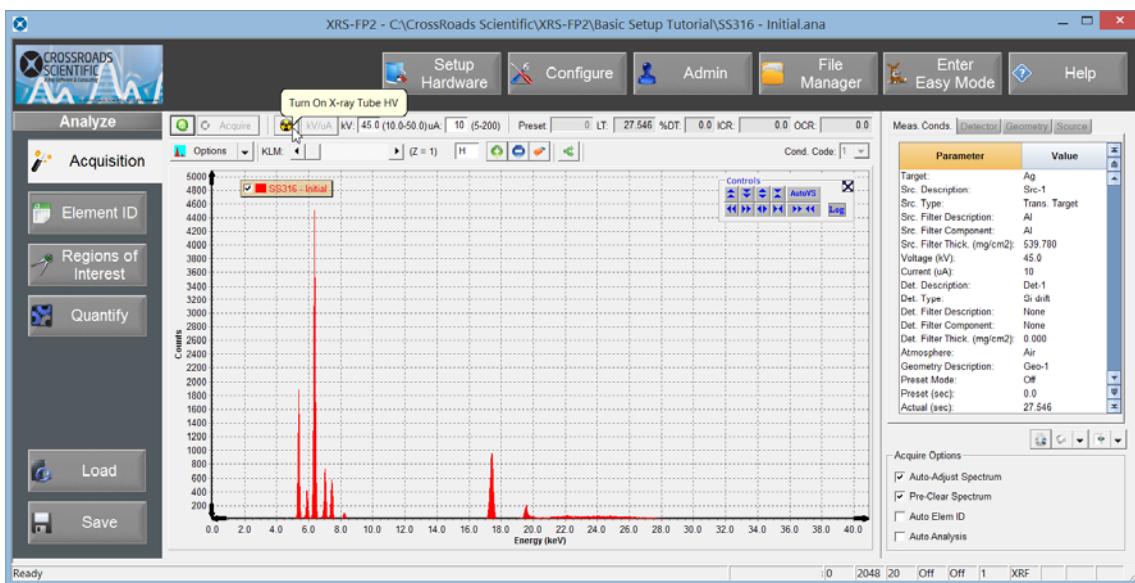
9. Then select the **Methods Button** in the *application workflow*. This is where application analysis parameters, quant method (calibration mode) and measurement and processing conditions can be defined. *Note that this brief guide to getting started with XRS-FP2 describes the steps necessary to perform a basic *standardless analysis* (i.e. Calibration Mode = No Standards).



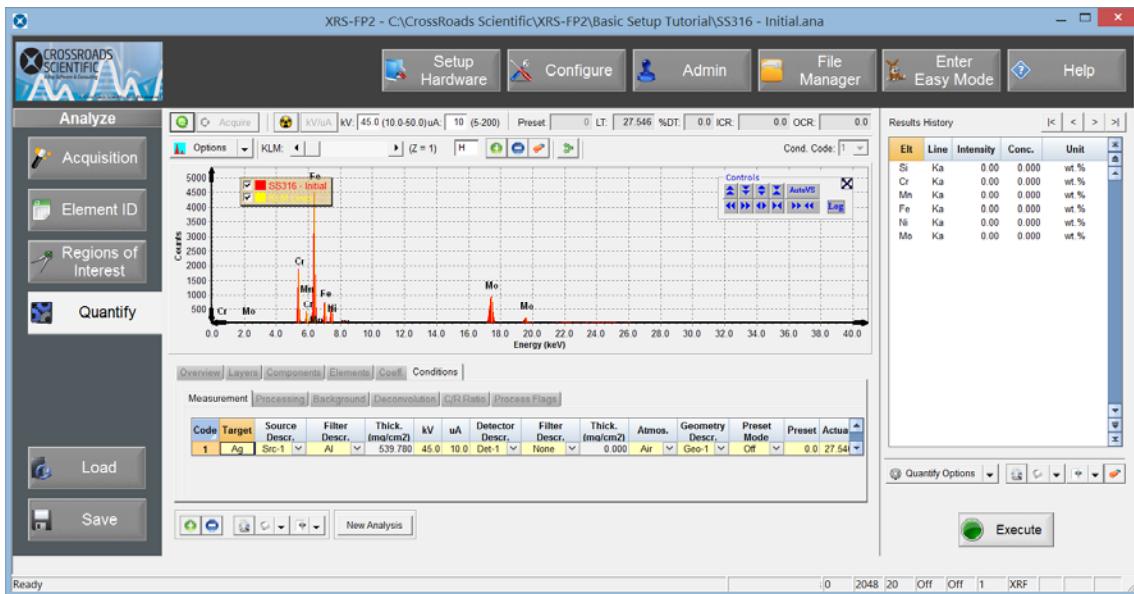
10. Now that the application has been defined, we move to the *Analyze workflow*. Go to the Home button (yellow circle below) and then select the **Analyze button** (red circle below). See figure below).



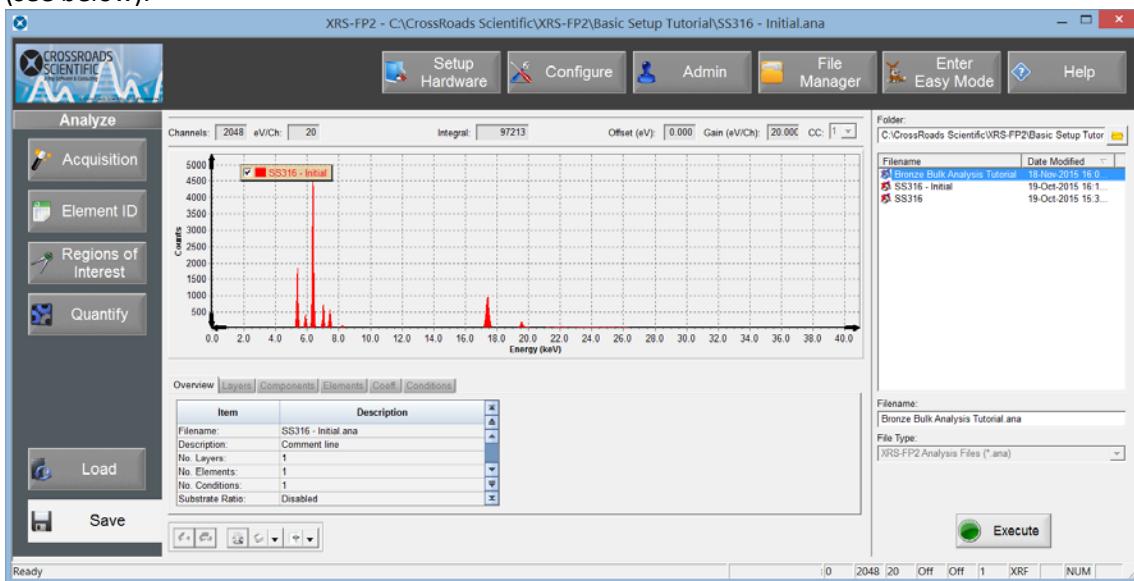
11. Select the **Acquisition** button (Fig. below). To do a live acquisition, ensure that the DPP is connected and now turn the source x-rays on (Spectrum Ribbon -> HV on; see figure below). Details for a specific hardware setup are beyond the scope of this tutorial; however, **please ensure that all safety measures are followed per the hardware manufacturer guidelines!** Once the system is running and stable, acquire a spectrum.



12. Then select the **Quantify** button and click on the **Execute** button (Fig. below) to extract intensities and concentrations from the sample spectrum. Note that the Execute button does a complete “process all” and quantification of the spectrum. You may also select the Quantify Options dropdown button to individually process and quantify the spectrum in a stepwise fashion.



13. The complete ANA file can be saved by selecting the **Save** button followed by the **Execute** button (see below).

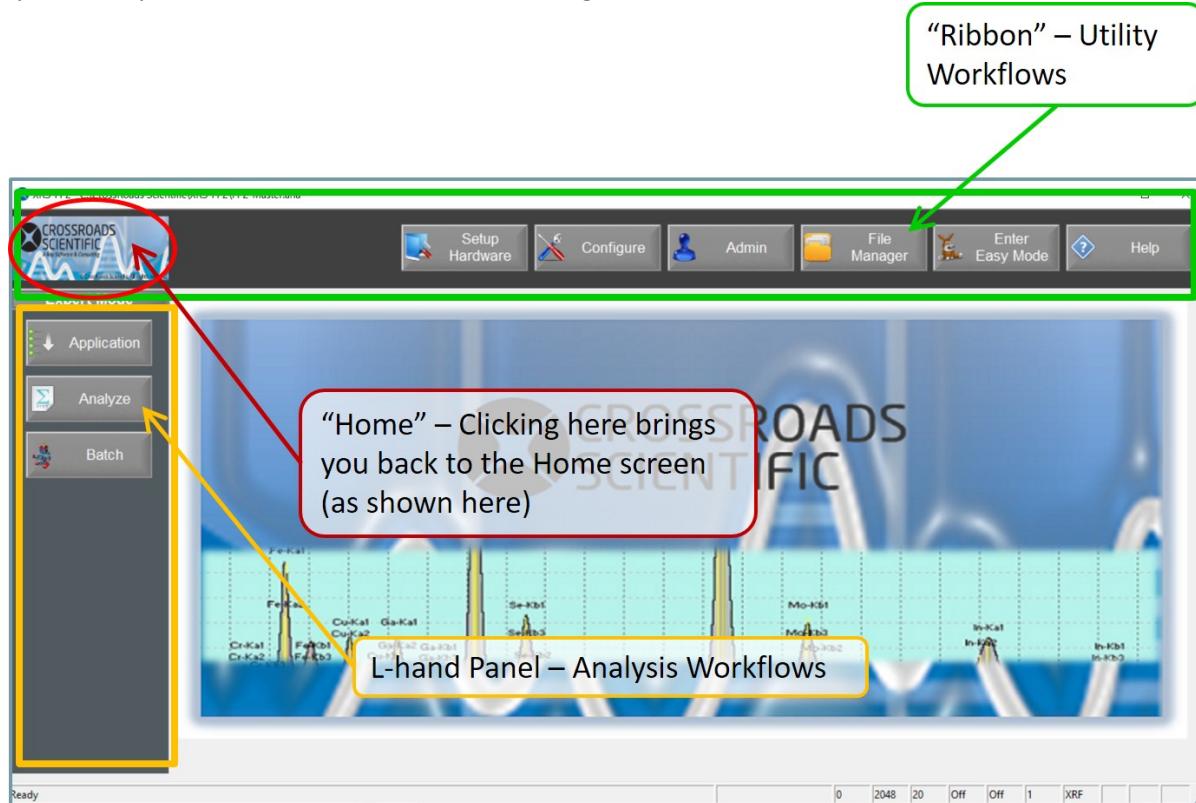


This completes the “getting started” guide for the setup, configuration and analysis of a sample using XRS-FP2.

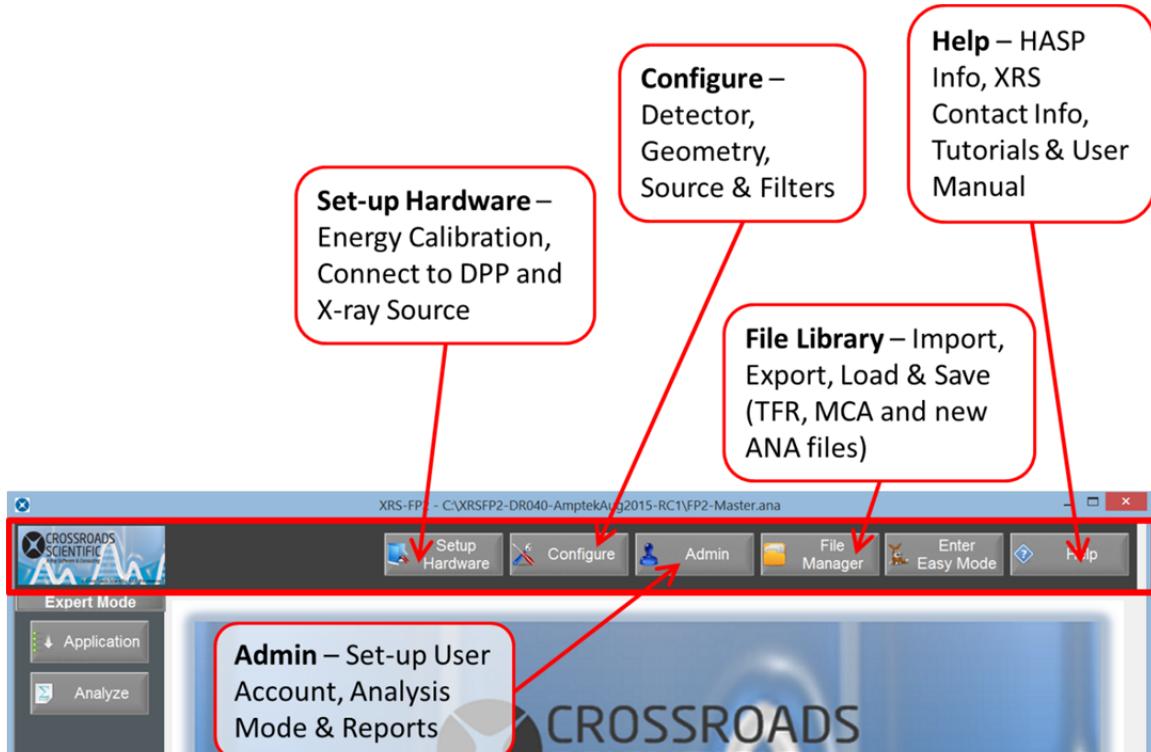
3 Software Layout

3.1 Workflows

XRS-FP2 was designed using workflows, which are meant to guide the user through complete hardware setup and analysis. As mentioned above, there are two main sets of workflows used in this software. The first are the utility workflows located in the top ribbon of the XRS-FP2 GUI and the second are the analysis workflows located in the L-hand panel of the XRS-FP2 GUI. The software is designed to guide the user from left to right and top to bottom. Although it is not mandatory to navigate the GUI in this way, these workflows are designed to lead the user through the various steps necessary for accurate XRF analysis. The utility and analysis workflows are illustrated in the figure below:

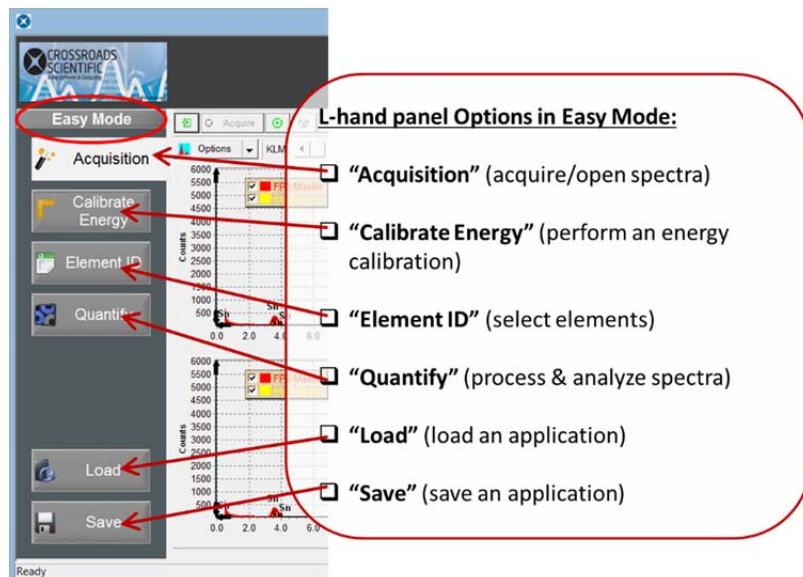


The ribbon contains all the utility workflows, such as Setup Hardware, Configure, Admin, File Manager and Help (see figure below).

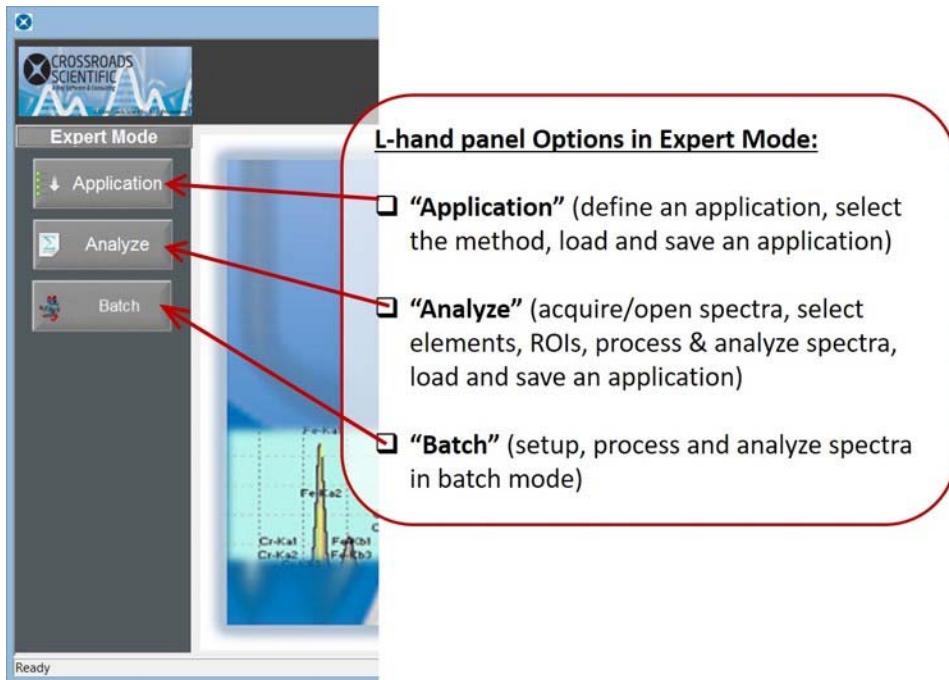


The L-hand panel contains the analysis workflows which vary depending on the user mode. XRS-FP2 was designed for two main modes of operation: Easy Mode and Expert Mode. Easy mode restricts the function and options available to the user. This mode is designed for routine analysis, where the system has already been setup, defined and calibrated by a more expert user. Expert mode allows the user to access all functionality and options available in the software. Please see Section 9 of this manual for more information on the Easy and Expert modes.

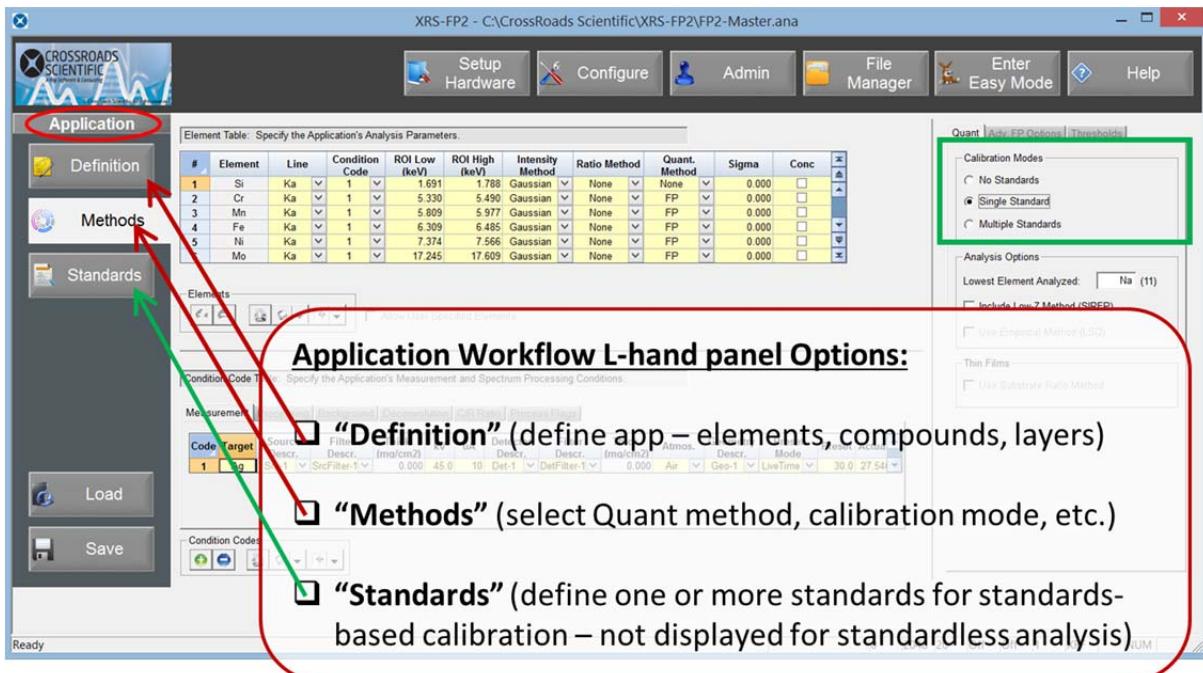
In Easy Mode, the utility workflows in the ribbon are hidden (except for Help) and the analysis workflow is limited to routine steps used in a typical application. See the figure below.



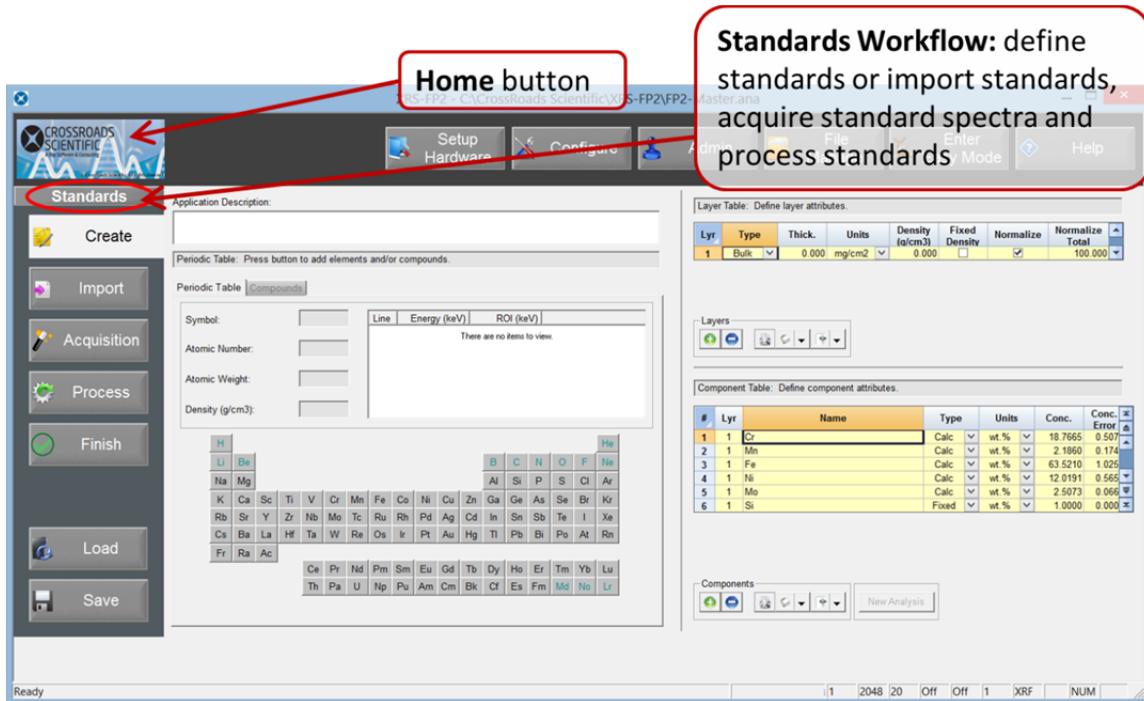
In Expert mode, all GUI/software options are available in both the ribbon and the L-hand panel. The L-hand panel is divided into two main analysis workflows, Application and Analyze (see figure below).



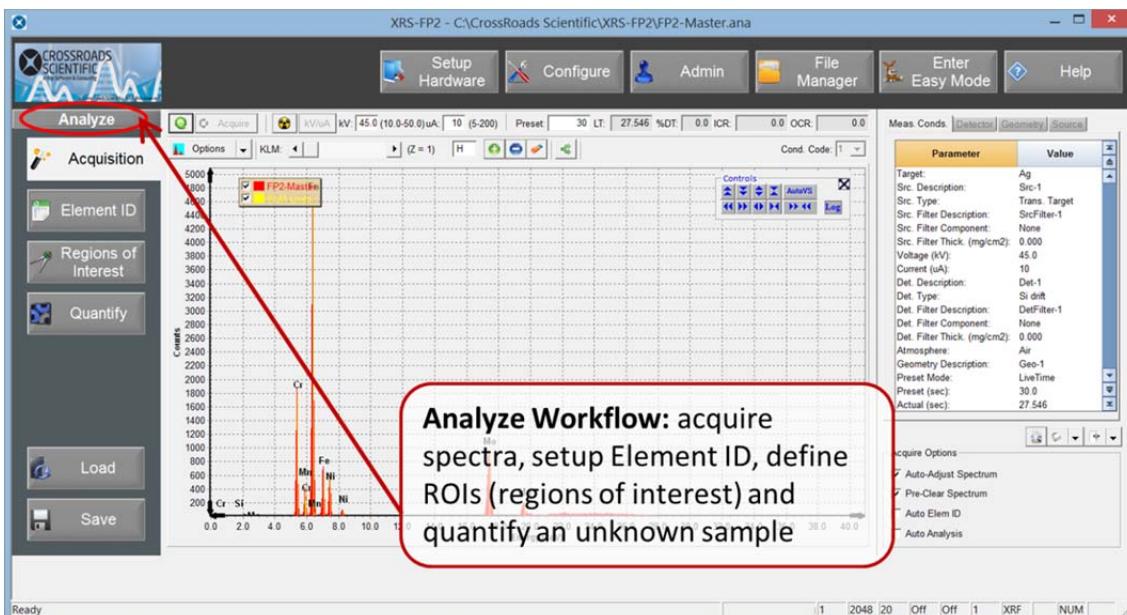
The Application workflow is where the XRF app is defined (elements, compounds, layers, etc.), the methods are selected (Quant method, Calibration Mode, etc.) and the standards are defined (when single or multiple standards are selected in the Calibration Mode). The figure below shows the various steps in the Application workflow.



In the Standards workflow, the standard is either created (elements and/or compounds and known concentrations entered) and corresponding spectrum acquired, or a previously stored standard can be imported. The standard is then processed, yielding theoretical calibration coefficients (TCC) for each element in the standard. The Finish button saves the generated TCC values and takes the user back to the Create button, at which point the process may then be repeated for all remaining standards. The Standards workflow is shown in the figure below.

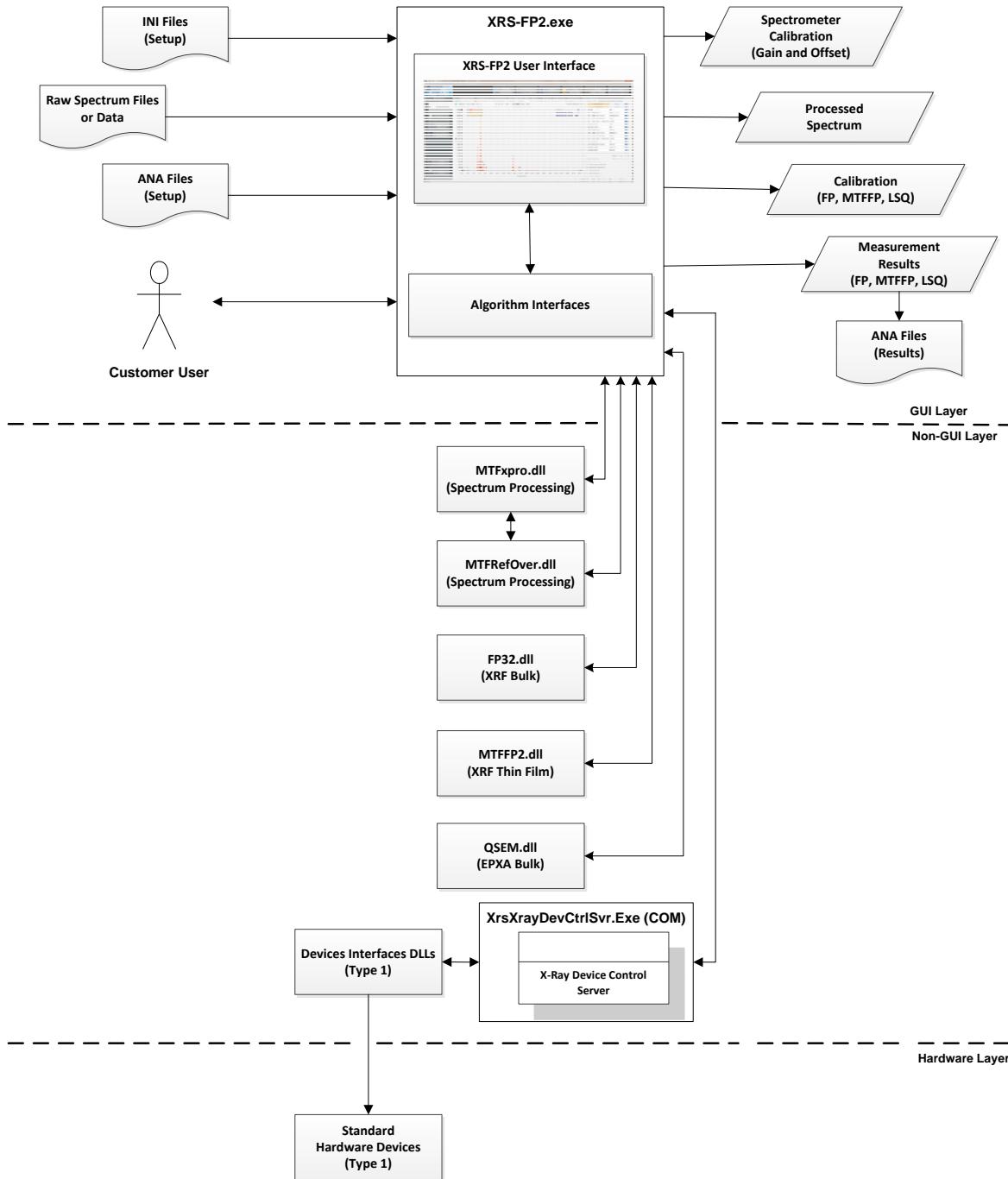


The Analyze workflow guides the user through the acquisition of spectra, element ID, region of interest setup and quantification for an “unknown” sample. See the figure below, showing the Analyze workflow.



4 Software Overview

4.1 Software Architecture



The above drawing represents a simplified software architecture for XRS-FP2 that shows the key components of the hardware and software system, together with the connection points.

The XRS-FP2 software is comprised of several Microsoft Windows program executables (EXE files), dynamic linked libraries (DLL), Active-X components (OCX), and a server that uses the Component Object Model (COM) technology. All of the main software components are connected to the XRS-FP2 program, which serve as the primary user-interface for the hardware control of x-ray devices (e.g. DPP, X-ray tube), acquisition of x-ray spectrum, processing of an x-ray spectrum, creation of elemental intensities, and then the conversion of these intensities to chemical composition.

4.1.1 GUI Layer

Details of the key software user-interface (GUI) layer components are listed in the table below.

Component	Description
INI File (Setup)	This file contains global program setup parameter and hardware dependent parameters that are used during the initialization and operation of the XRS-FP2 program.
Raw Spectrum Data or Files	A histogram representation of spectral data as acquired from the user's Digital Pulse Processor (DPP) hardware.
ANA Files (Setup)	ANA files are setup by the user to define a complete XRF application. There are several parameter groups that define the layer, component, element, conditions, calibration, and instrument parameters. In addition, the ANA file also contains the spectrum data.
XRS-FP2	<p>The main user interface that the customer interacts with for XRF (Bulk, Thin Film) or EPXA analysis. The user interface is composed of several EXEs, DLLs, and OCXs. The user interface is responsible for the analysis parameter setup, spectrum acquisition, spectrum processing, standards calibration and measurement. The user interface also includes a spectrum display, represented as a histogram of spectral peaks, plotted as counts (intensity) versus channels (energy).</p> <p>This software has been developed in C++ using Visual Studio 2008 SP1 and Visual Basic V6.0 SP6.</p> <p>In addition, the user interface integrates third party commercial software that includes Farpoint Spread, Steema</p>

	Teechart, and Adobe Reader.
Spectrometer Calibration (Gain and Offset adjustment)	A special calibration method to convert spectra from raw DPP (or MCA) format, which may not be calibrated, into a format compatible for processing with XRS-FP2. This spectrometer (DPP or MCA) calibration step provides the accurate gain and offset values to allow this conversion automatically.
Processed Spectrum	This represents the final result in the data reduction of a raw spectrum to obtain elemental intensities. Typical processing steps include data smoothing, removal of spectral artifact peaks, and peak overlap correction (or “deconvolution”).
Calibration (FP, MTFFP, or LSQ)	Standards based calibration methods which generate calibration coefficients. These coefficients are subsequently used in the computation of chemical compositions.
Measurement Results (FP, MTFFP, or LSQ)	Computed data that is the conversion of elemental intensities into chemical compositions with or without a calibration step.
ANA Files (Results)	The resulting ANA file, after a measurement, now contains both the elemental intensities and the chemical composition.

4.1.2 Non-GUI Layer

Details of the key software non-GUI layer components are listed in the table below.

Component	Description
MTFpro.dll	A non-GUI algorithm library that is responsible for spectrum energy calibration and spectrum processing. This software has been developed in C/C++ using Visual Studio V6.0 SP6.
MTFRefOver.dll	A non-GUI algorithm library that is responsible for Reference deconvolution. This software has been developed in C/C++ using Visual Studio V6.0 SP6.
FP32.dll (XRF Bulk)	XRF Bulk Applications - A non-GUI algorithm library that is responsible for converting elemental intensities into the measured composition (and layer thickness). The algorithms in this library also perform standards calibration. This software has been developed in C/C++ using Visual Studio

	V6.0 SP6.
MTFFP2.dll (XRF Thin Film)	XRF Thin Film Applications – A non-GUI algorithm library that is responsible for converting elemental intensities into the measured composition (and layer thickness). The algorithms in this library also perform standards calibration. This software has been developed in C/C++ using Visual Studio V6.0 SP6.
QSEM.dll (EPXA Bulk)	EPXA Bulk Applications - A non-GUI algorithm library that is responsible for converting elemental intensities into the measured composition (and layer thickness). The algorithms in this library also perform standards calibration. This software has been developed in C/C++ using Visual Studio V6.0 SP6.
XrsXrayDevCtrlSvr.Exe	A non-GUI MS COM server (with supporting DLLs), is responsible for x-ray device control of the customer's DPP and/or X-ray tube. This software has been developed in C++ using Visual Studio 2008 SP1. For more details on this COM interface, please contact CrossRoads Scientific.
Device Interface DLLs (Type 1)	Several non-GUI libraries which serve as the individual x-ray device interfaces. These DLLs are fabricated by CrossRoads Scientific. The software has been developed in C++ using Visual Studio 2008 SP1.

4.1.3 Hardware Layer

Details of the key hardware layer components are listed in the table below.

Component	Description
Standard Hardware Devices (Type 1)	Digital Pulse Processors and X-ray Tubes that are controlled via the XrsXrayDevCtrlSvr COM server and its associated device interface DLLs. Typically, the hardware devices have an associated vendor fabricated DLL for control of the device.

4.2 HASP Security Plug

Also, supplied with the software is a HASP security plug manufactured by SafeNet (formerly Aladdin Systems), which requires that drivers be installed. For support and driver downloads lease see:
www.safenet-inc.com/technical-support/

You can also download the latest HASP H4 and HL drivers from the SafeNet website:
www3.safenet-inc.com/support/hasp/hasp4/enduser.aspx#latestDD

Please note that **both** drivers must be installed.

The HASP security plug driver is normally done with the CrossRoads installation program, which installs the correct driver for the operating system, and should be part of the total software setup prior to using XRS-FP2. A later section of this manual describes how to install the HASP plug into either the parallel port or a USB port. Each plug has a unique code and serial number with options programmed by CrossRoads Scientific. If you have any problems with the HASP security plug, take note of the serial number (e.g. XRS1234) and contact CrossRoads Scientific for further details.

4.3 Supported X-Ray Devices

The XRS-FP2 software includes device interfaces for the following x-ray hardware:

- (a) Amptek DPP - DP5/PX5 with Firmware V6.X – USB Interface
- (b) Amptek X-Ray Tube – MiniX – USB Interface

The CrossRoads installation software will install and configure the software with the necessary files, to meet the customer's hardware; however, it is a prerequisite that the customer ensures that the hardware device driver (for the devices described above) is installed prior to the usage of the CrossRoads software, using the recommendation of the hardware supplier. Device drivers can be found on the following website links:

- (a) Amptek Devices - <http://www.amptek.com/software.html>

The above website link(s) also have installation directions which can be downloaded.

4.4 Data Files

The XRS-FP2 software uses several types of data files that contain information about acquisition, processing and analysis of spectra.

4.4.1 Analysis File

The XRS-FP2 software uses analysis (*.ana format) file which describes the definition of the system (configuration), the definition of the sample for analysis, the calibration coefficients and either the results from a calibration or the results from an analysis. This same file also stores a complete description of the spectrum data. In the case of multiple conditions, several spectra are stored in the ANA file – one spectrum per condition. The file structure is simple ASCII, with a CSV format.

Once a system energy calibration has been performed, the user can retrieve one of these files to define the complete system and analysis setup. Acquisition of a spectrum typically occurs, under known conditions. With a newly acquired spectrum, spectral processing is performed, which will generate spectral intensities. From the spectral intensities, quantitation is performed, whereby spectral intensities are converted to elemental concentrations.

Since the ANA file also contains a description of the spectrum data, the XRS-FP2 software has a feature to export the spectrum data into a stand-alone spectrum file.

4.4.2 Spectrum File

The XRS-FP2 software has capability to load and save stand-alone spectrum files. The supported spectrum files are as follows:

(a) Amptek Devices – Spectrum File (*.mca format) which is the format used by the Amptek ADMCA software for DP4/PX4 devices, and the Amptek DppMCA software for DP5/PX5 devices. The XRS-FP2 software is fully compatible in terms of reading/writing the spectrum data, so that either program can load/save the spectrum file.

4.4.3 Legacy Analysis File

The XRS-FP2 software has capability to read (import) the legacy analysis files, that were created with the older CrossRoads software. The supported files are as follows:

(a) XRS-FP, XRS-MTFFP – XRF based Analysis File (*.tfr format) which describes the definition of the system (configuration), the definition of the sample for analysis, the calibration coefficients and either the results from a calibration or the results from an analysis. In addition to the TFR file, the XRS-FP2 software will also read parameters from the XRS-FP.ini file.

(b) XRS-EPXA – EPXA Analysis File (*.edx format) which describes the definition of the system (configuration), the definition of the sample for analysis, the calibration coefficients and either the results from a calibration or the results from an analysis. In addition to the EDX file, the XRS-FP2 software will also read parameters from the QSEM.ini file.

The XRS-FP2 software does not support saving of legacy TFR or EDX files.

4.5 Software Installation

The XRS-FP2 software has a dedicated installation program, with is based on the third party Advanced Installer product. The wizard-style GUI allows the customer to install the software on the PC. The customer should note the following items regarding the installation program:

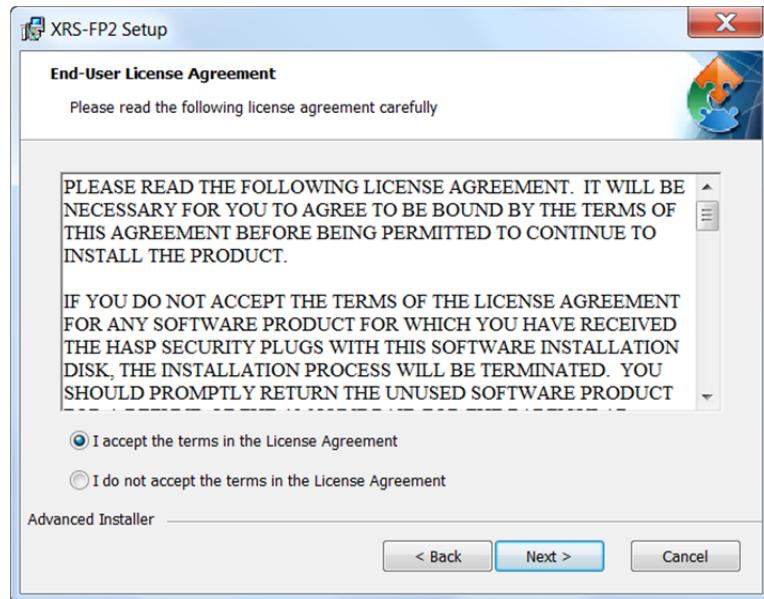
- (a) The installation program does not require that the HASP security plug to be installed.
- (b) The installation program does not require an Internet connection.
- (c) The installation program will install on Windows XP, Windows 7, Windows 8/8.1 and Windows 10.
- (d) The installation program will verify that the PC has at least 2 GB of RAM.

- (e) The installation program will verify that at least Microsoft .NET V3.5 is installed on the PC. If this software is not installed, and the PC has an Internet connection, then the software will download this component.
- (f) The installation program will verify that Microsoft Visual Studio 2008 Redistributables are installed on the PC. If this software is not installed, and the PC has an Internet connection, then the software will download this component.

Once the setup program (XRS-FP2_Setup.exe) is invoked, the user will see the following dialog window:



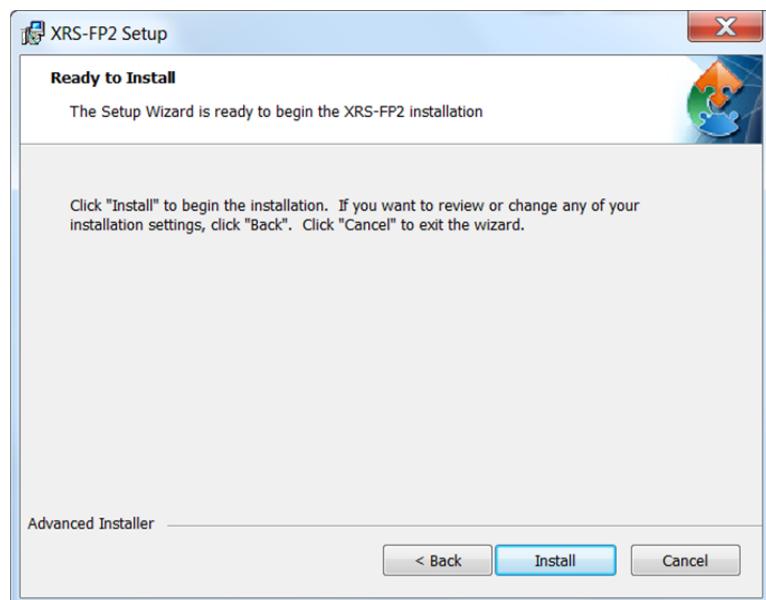
Press the Next button to display the End-User License Agreement dialog window:



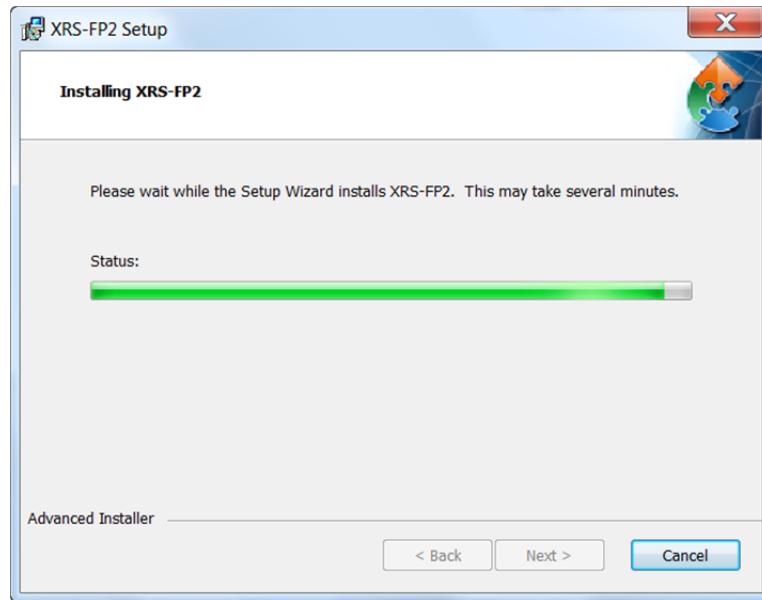
After accepting the license agreement terms, press the Next button to display the Installation Folder dialog window:



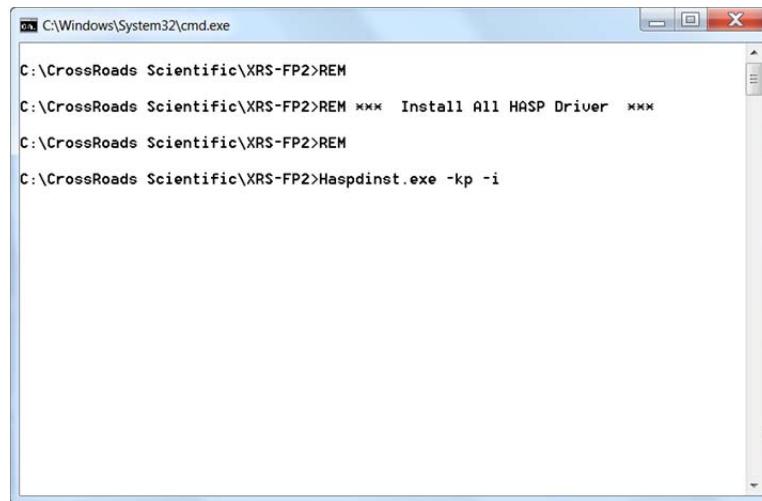
It is recommended that the customer install the software in the default folder shown, but the customer can select an alternative installation folder. After the selection of the installation folder, press the Next button to display the Ready to Install dialog window:



Press the Install button to begin the software installation. At this point, the XRS-FP2 software will be installed on the customer's PC, as noted by the following dialog window:

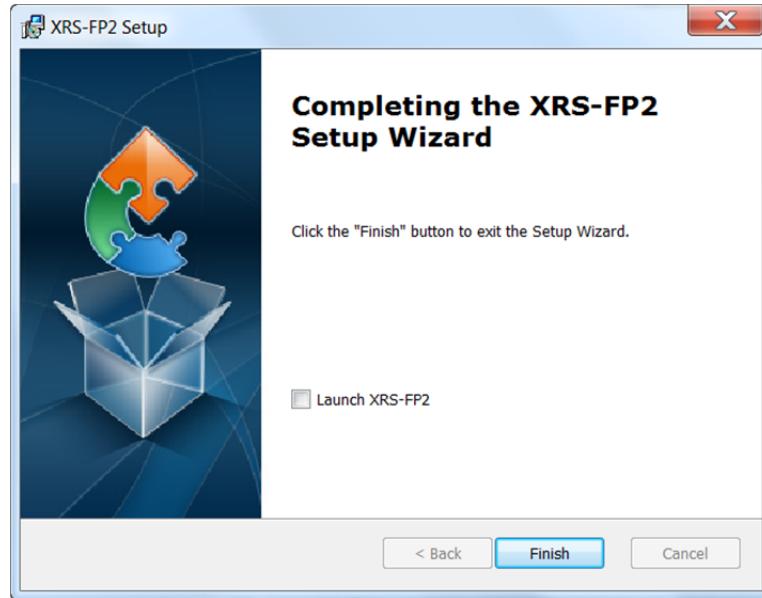


In addition, the software will install the HASP security plug drivers, as shown in the following dialog window.



Once the HASP security plug drivers are installed, the customer should acknowledge any dialog window messages that may appear at this stage of the installation.

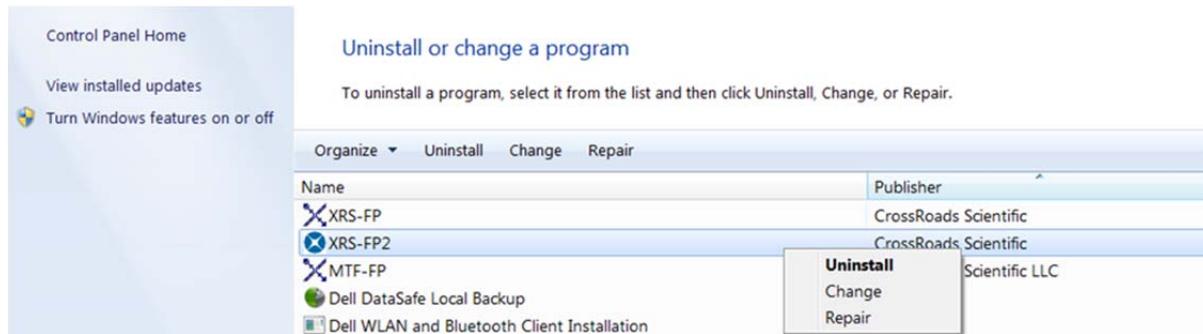
Eventually, the software will complete the installation of the XRS-FP2 software, as noted by the following dialog window:



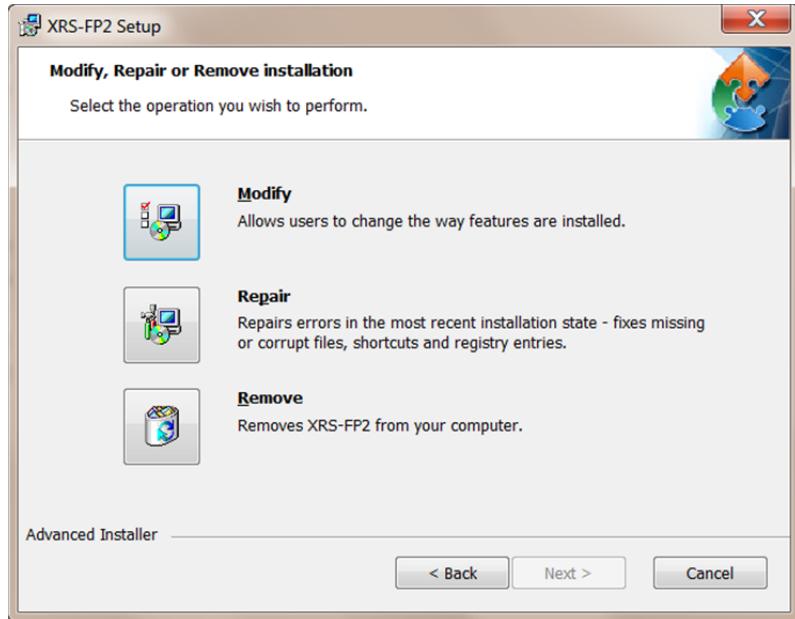
At this point the user should press the Finish button.

4.6 Software Removal

The XRS-FP2 software can be removed from the customer PC from the **Control Panel\All Control Panel Items\Programs and Features**, as shown below:



Alternatively, the user can invoke the setup program (XRS-FP2_Setup.exe) to see the following dialog window:



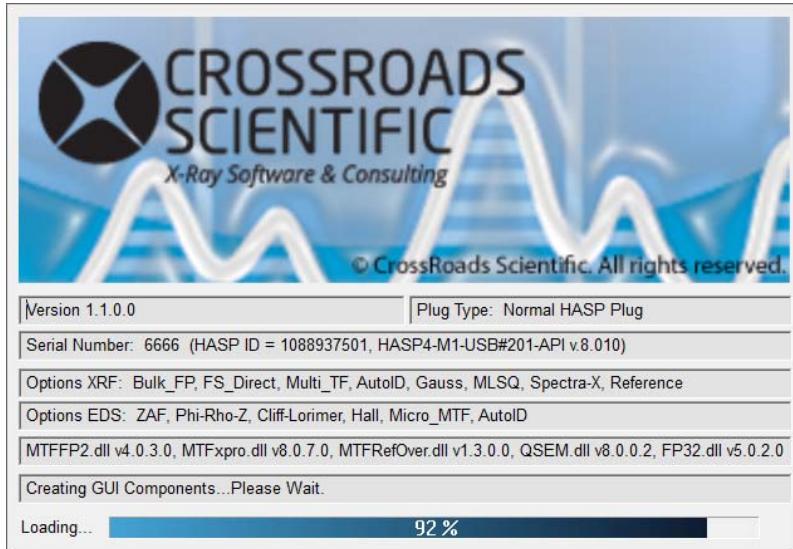
Please note that the removal of the XRS-FP2 software will also remove the HASP security plug drivers.

4.7 Key Elements of the XRS-FP2 GUI

The XRS-FP2 GUI is based on a “modern” user interface, as opposed to the traditional MS Windows GUIs of the past. The GUI has “touch” capabilities, if the software is launched on a touch enabled MS Windows PC/Tablet, running Windows 8/8.1 (or greater).

4.7.1 GUI Launch – Splash Startup Window

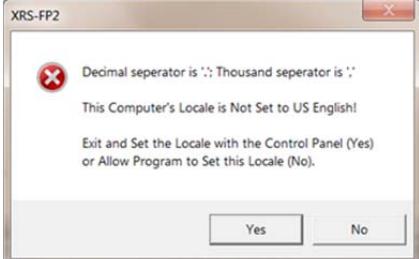
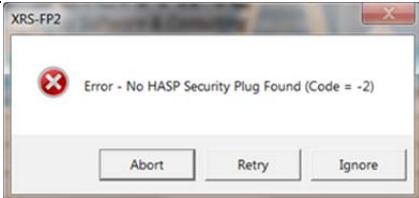
When XRS-FP2 is launched via the desktop icon (or the XRS-FP2 program group), the first GUI window the customer will see is the splash startup window as shown by the example below.



If the HASP security key is installed, then the window will show various status information about the HASP security key – serial number, type of key (normal, demo), hardware ID, the licensed options, and the versions of the algorithms DLLs. In addition, a progress indicator is shown, which provides feedback to the customer during the startup sequence.

During the startup sequence, it is possible to see potential severe error messages (i.e. XRS-FP2 cannot continue the startup sequence) or warning messages (i.e. XRS-FP2 can continue the startup sequence). These use cases are described below.

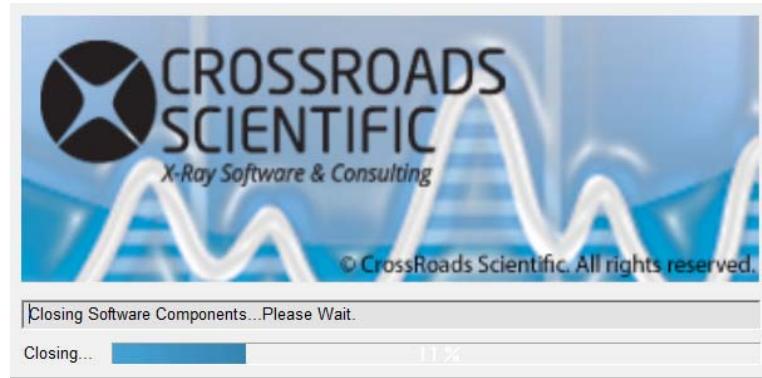
Dialog Message	Type	Description/Resolution
	Severe	Contact Crossroads Scientific to obtain an updated HASP Security plug.
	Severe	Install the HASP security plug drivers by running the XRS-FP2 installation.
	Warning	Press the Yes button to change the Locale, so that XRS-FP2 can continue the startup sequence. If the No button is selected, XRS-FP2 cannot continue the startup sequence.

	Warning	Press the Yes button to change the Decimal and/or Thousand separator(s), so that XRS-FP2 can continue the startup sequence. If the No button is selected, XRS-FP2 cannot continue the startup sequence.
	Warning	Install the HASP security plug into the PC's USB port.
<TODO>	Warning	During the startup sequence, XRS-FP2 verifies the minimum versions for several of its software components. XRS-FP2 will continue the startup sequence; however, analysis results may be incorrect. Contact Crossroads Scientific to obtain the latest software components.
<TODO>	Warning	One or more applications that use the x-ray devices may be executing, while XRS-FP2 is executing its startup sequence. The XRS-FP2 software will continue; however, connection to the x-ray devices will fail, since only one application can have control of the x-ray devices. If the customer wants to use XRS-FP2 to acquire spectrum, then the other applications should be closed.

<TODO>	Severe	One or more COM components are not registered. Re-install the XRS-FP2 software.
--------	--------	---

4.7.2 GUI Termination – Splash Shutdown Window

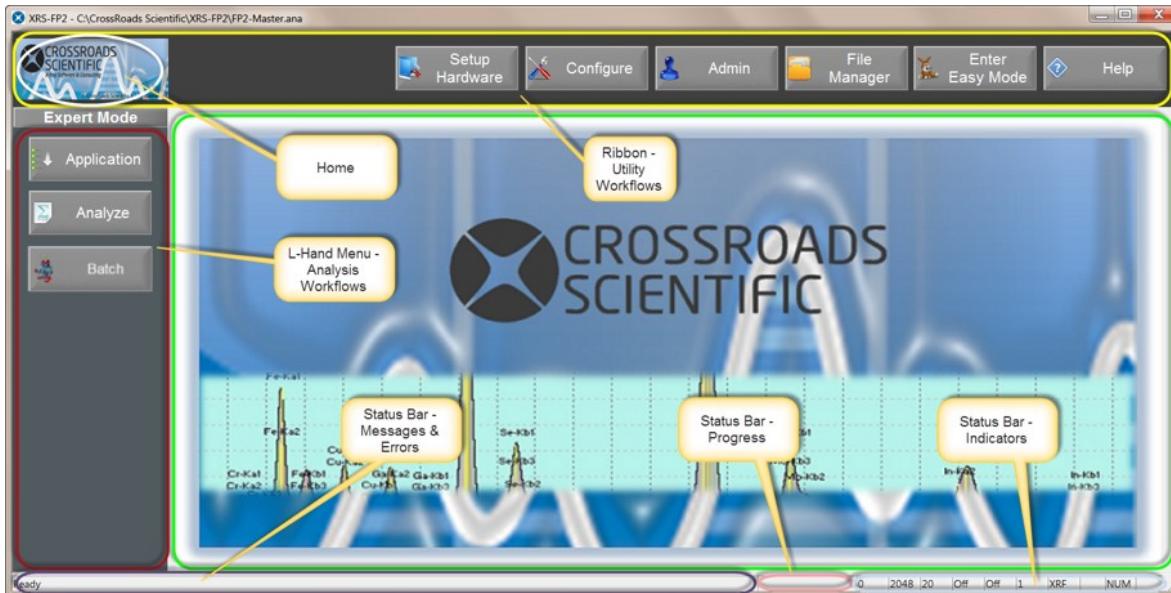
When the XRS-FP2 software is terminated (i.e. customer exits the software), the customer will see a splash shutdown window as shown by the example below.



This dialog window will be briefly displayed and shows that XRS-FP2 is shutting down.

4.7.3 Main Window

The XRS-FP2's GUI represents a “modern” UI - a UI paradigm shift from the more traditional Windows GUIs that show the familiar top-level menu of File, Edit, etc.



The XRS-FP2 main window’s key GUI components are described below:

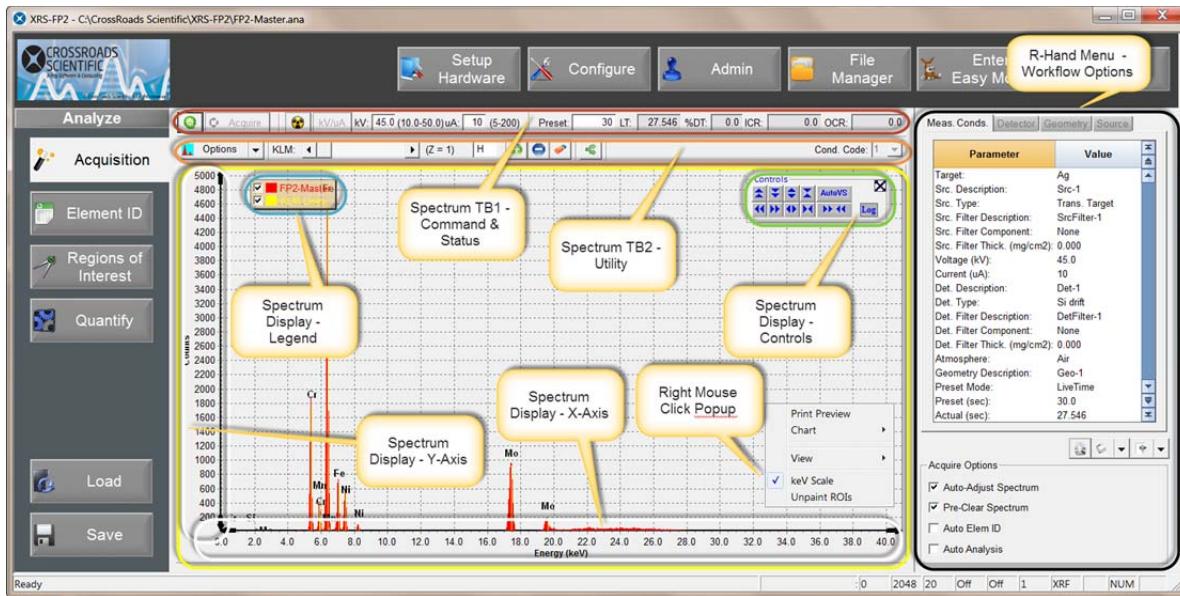
GUI Element	Description
Home	This area of the GUI is a hotspot, and the user will notice that the mouse pointer changes from a pointer to a hand icon, as the mouse is moved on/off the hotspot. Drag and click the mouse on this area of the GUI to return to the main window of the GUI.
Ribbon	This area of the GUI shows one-time setup workflows (e.g. x-

	ray hardware, energy calibration, instrument parameters), or common utility workflows (e.g. loading an application, saving an application). Each of these buttons will be described in detail later in this manual.
L-Hand Menu	This area of the GUI shows application definition and analysis workflows such as defining the application, standards setup and calibration, element ID, acquiring data, spectrum processing, and quantification.
Status Bar – Messages & Errors	In general, XRS-FP2 has very few “pop-up” message boxes. Most of the error messages and general status messages are displayed in this area of the GUI. In the event of an error, the customer will also hear a “Beep” sound.
Status Bar - Progress	This area of the GUI shows a progress bar, which is updated during acquisition of data, spectrum processing, standards calibration, and quantification.
Status Bar - Indicators	<p>This area of the GUI shows several status indicators. The 10 panes are defined as follows:</p> <ul style="list-style-type: none"> • Pane 1 – Standards Calibration Model (0: Standardless, 1: Single Standard, > 1 MLSQ or LSQ Models) • Pane 2 – Number of MCA Channels (1024, 2048, 4096) • Pane 3 – eV/Channel (5, 10, 20, 40, 80, 160) • Pane 4 – DPP Connection State (Off, On) • Pane 5 – X-Ray Tube Connection State (Off, On) • Pane 6 – Current (Active) Condition Code (1 – 8) • Pane 7 – Analysis Mode (XRF, EPXA) • Pane 8 – Keyboard CAP Key State • Pane 9 – Keyboard NUM Key State • Pane 10 – Keyboard SCROLL Key State

Lastly, the area of the GUI below the Ribbon and to the right of the L-Hand menu – this is the main “body” of the GUI. The body of the GUI will display different windows, depending on the workflow context.

4.7.4 Spectrum Window

For several of the workflows, the customer can navigate the XRS-FP2 software to see a Spectrum Window as shown below:



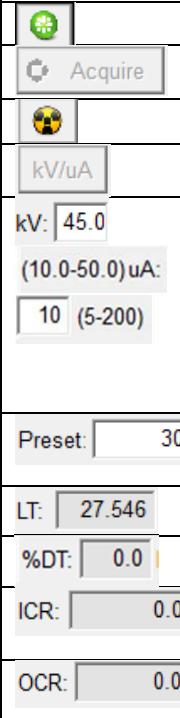
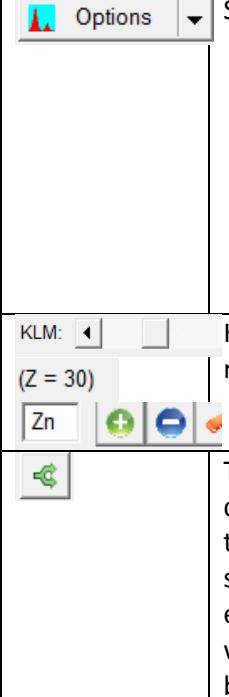
The spectrum display is a GUI window that displays the spectral data. This data is represented as a histogram, with a discrete number of channels (i.e. 2048). For each given bin (channel), the x-ray counts are accumulated and placed in the corresponding channel.

The spectrum display shows the main spectrum of interested, displayed in Group 0, which is shown in a solid color (i.e. BARS). Up to 6 compare spectra, shown as a line (i.e. DOTS) can be overlaid on the BARS spectrum. In addition, the spectrum display can also show other information such as the KLM markers, which are overlaid on the BARS spectrum.

You can also draw a “rubber band” around an area of the spectrum you wish to expand by clicking in the chart area and dragging the cursor to the right and to the bottom. To zoom out of the zoomed spectrum area, simply reverse this rubber banding by dragging the cursor upwards and to the left, and then the complete spectrum will be re-displayed.

The Spectrum Window’s GUI components/navigation are described below:

GUI Element	Description
Spectrum Display - Legend	Indicates the main spectrum of interest (solid BARS, group 0), 1 to 6 additional compare spectra (DOTS), KLM Markers, and the last processed spectrum. The customer can select which spectra are displayed via the checkbox that precedes the spectrum's

	label.																
Spectrum TB1 – Command & Status	<p>This toolbar represents common command operations and status for acquiring a spectrum. The toolbar items (left to right) are as follows:</p>  <table border="1"> <tr> <td>DPP Connect/Disconnect</td> </tr> <tr> <td>Acquire Start/Stop</td> </tr> <tr> <td>X-Ray Tube Connect and HV ON</td> </tr> <tr> <td>Set X-Ray Tube Voltage and Current</td> </tr> <tr> <td>kV: 45.0 (10.0-50.0) uA: 10 (5-200)</td> <td>Enter the X-Ray Tube Voltage and Current, and then press the kV/uA button to set the new values. With the HV ON, the monitored voltage and current values are displayed. With the HV OFF, the voltage and current min and max range values are displayed.</td> </tr> <tr> <td>Preset: 30</td> <td>Enter the preset value - time based (sec) or counts</td> </tr> <tr> <td>LT: 27.546</td> <td>Status - Live Time</td> </tr> <tr> <td>%DT: 0.0</td> <td>Status - Percent Dead-Time</td> </tr> <tr> <td>ICR: 0.0</td> <td>Status – Input Count Rate (cps) of the Slow Channel</td> </tr> <tr> <td>OCR: 0.0</td> <td>Status – Output Count Rate (cps) of the Fast Channel</td> </tr> </table>	DPP Connect/Disconnect	Acquire Start/Stop	X-Ray Tube Connect and HV ON	Set X-Ray Tube Voltage and Current	kV: 45.0 (10.0-50.0) uA: 10 (5-200)	Enter the X-Ray Tube Voltage and Current, and then press the kV/uA button to set the new values. With the HV ON, the monitored voltage and current values are displayed. With the HV OFF, the voltage and current min and max range values are displayed.	Preset: 30	Enter the preset value - time based (sec) or counts	LT: 27.546	Status - Live Time	%DT: 0.0	Status - Percent Dead-Time	ICR: 0.0	Status – Input Count Rate (cps) of the Slow Channel	OCR: 0.0	Status – Output Count Rate (cps) of the Fast Channel
DPP Connect/Disconnect																	
Acquire Start/Stop																	
X-Ray Tube Connect and HV ON																	
Set X-Ray Tube Voltage and Current																	
kV: 45.0 (10.0-50.0) uA: 10 (5-200)	Enter the X-Ray Tube Voltage and Current, and then press the kV/uA button to set the new values. With the HV ON, the monitored voltage and current values are displayed. With the HV OFF, the voltage and current min and max range values are displayed.																
Preset: 30	Enter the preset value - time based (sec) or counts																
LT: 27.546	Status - Live Time																
%DT: 0.0	Status - Percent Dead-Time																
ICR: 0.0	Status – Input Count Rate (cps) of the Slow Channel																
OCR: 0.0	Status – Output Count Rate (cps) of the Fast Channel																
Spectrum TB2 – Utility	<p>This toolbar represents common utility operations when reviewing the spectrum. The toolbar items (left to right) are as follows:</p>  <table border="1"> <tr> <td>Spectrum utility operations that include:</td> </tr> <tr> <td>(a) Clear (b) Open (Group 0) (c) Save As (Group 0) (d) Compare – Groups 1 to 6 (e) Close – Groups 1 to 6 (and Group 0) (f) Compress (g) Expand (h) Efficiency Correction</td> </tr> <tr> <td>KLM: [] (Z = 30) Zn [+] [-] []</td> <td>KLM Markers Controls, with the ability to add, remove, or clear all KLM markers.</td> </tr> <tr> <td>[]</td> <td>Toggle between full spectrum or split spectrum display. In the case of split spectrum display, the user can pan, zoom, and manipulate each spectrum window. For example, the low energy peaks may be shown in the top split window, whereas the high energy peaks may be shown in the bottom split window.</td> </tr> </table>	Spectrum utility operations that include:	(a) Clear (b) Open (Group 0) (c) Save As (Group 0) (d) Compare – Groups 1 to 6 (e) Close – Groups 1 to 6 (and Group 0) (f) Compress (g) Expand (h) Efficiency Correction	KLM: [] (Z = 30) Zn [+] [-] []	KLM Markers Controls, with the ability to add, remove, or clear all KLM markers.	[]	Toggle between full spectrum or split spectrum display. In the case of split spectrum display, the user can pan, zoom, and manipulate each spectrum window. For example, the low energy peaks may be shown in the top split window, whereas the high energy peaks may be shown in the bottom split window.										
Spectrum utility operations that include:																	
(a) Clear (b) Open (Group 0) (c) Save As (Group 0) (d) Compare – Groups 1 to 6 (e) Close – Groups 1 to 6 (and Group 0) (f) Compress (g) Expand (h) Efficiency Correction																	
KLM: [] (Z = 30) Zn [+] [-] []	KLM Markers Controls, with the ability to add, remove, or clear all KLM markers.																
[]	Toggle between full spectrum or split spectrum display. In the case of split spectrum display, the user can pan, zoom, and manipulate each spectrum window. For example, the low energy peaks may be shown in the top split window, whereas the high energy peaks may be shown in the bottom split window.																

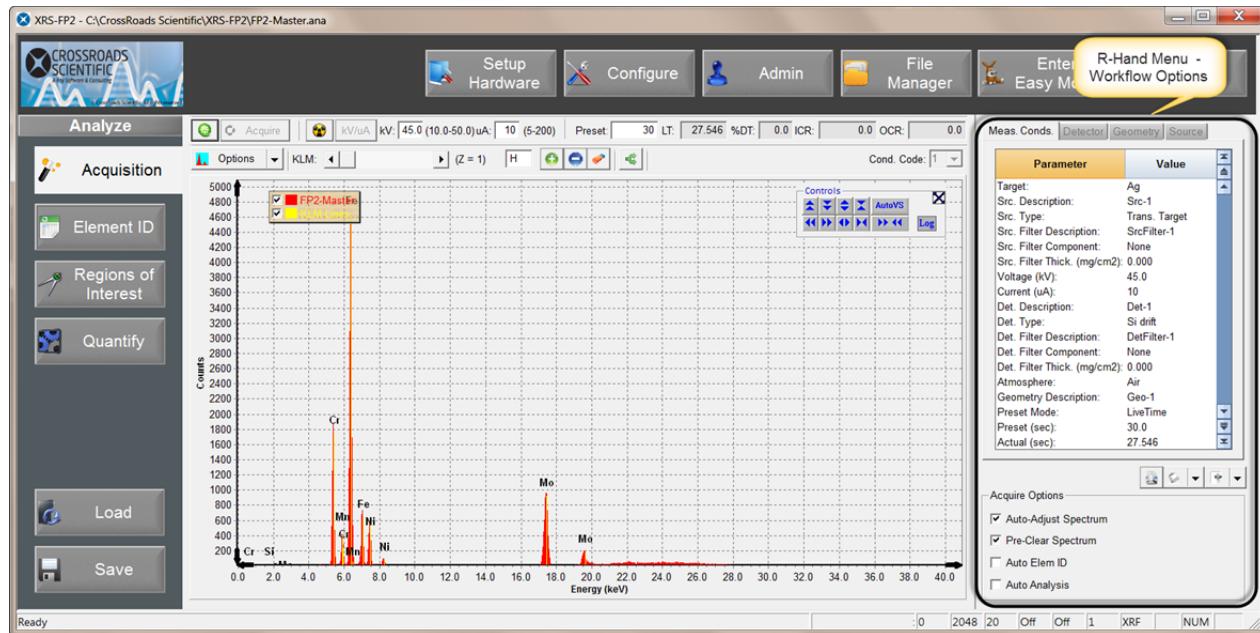
	Cond. Code: <input type="button" value="1"/> <input type="button" value="▼"/>																								
Spectrum Display - Controls	<p>The Spectrum Display Controls (manipulation of the displayed spectrum's data) are summarized below:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr><td></td><td>Vertical Expand Top</td></tr> <tr><td></td><td>Vertical Contract Top</td></tr> <tr><td></td><td>Vertical Expand Both</td></tr> <tr><td></td><td>Vertical Contract Both</td></tr> <tr><td></td><td>Y-axis Auto Full Scale (Screen/Spectrum)</td></tr> <tr><td></td><td>Left Expand</td></tr> <tr><td></td><td>Right Expand</td></tr> <tr><td></td><td>Horizontal Expand</td></tr> <tr><td></td><td>Horizontal Contract</td></tr> <tr><td></td><td>X-axis Full Scale</td></tr> <tr><td></td><td>Toggle Log / Linear Y-axis display</td></tr> <tr><td></td><td>Close the Controls Panel. Note - Use the Right Mouse Click Popup menu to display the Controls Panel.</td></tr> </table>		Vertical Expand Top		Vertical Contract Top		Vertical Expand Both		Vertical Contract Both		Y-axis Auto Full Scale (Screen/Spectrum)		Left Expand		Right Expand		Horizontal Expand		Horizontal Contract		X-axis Full Scale		Toggle Log / Linear Y-axis display		Close the Controls Panel. Note - Use the Right Mouse Click Popup menu to display the Controls Panel.
	Vertical Expand Top																								
	Vertical Contract Top																								
	Vertical Expand Both																								
	Vertical Contract Both																								
	Y-axis Auto Full Scale (Screen/Spectrum)																								
	Left Expand																								
	Right Expand																								
	Horizontal Expand																								
	Horizontal Contract																								
	X-axis Full Scale																								
	Toggle Log / Linear Y-axis display																								
	Close the Controls Panel. Note - Use the Right Mouse Click Popup menu to display the Controls Panel.																								
Spectrum Display – Y - Axis	<p>Y-axis controls are summarized below:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr><td></td><td>Click the mouse to pan the spectrum up.</td></tr> <tr><td></td><td>Click the mouse to pan the spectrum down.</td></tr> <tr><td>Axis Hotspot + Click-drag</td><td>Move the mouse to the Y-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse up or down, observing the panning of the spectrum in the Y-axis.</td></tr> </table>		Click the mouse to pan the spectrum up.		Click the mouse to pan the spectrum down.	Axis Hotspot + Click-drag	Move the mouse to the Y-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse up or down, observing the panning of the spectrum in the Y-axis.																		
	Click the mouse to pan the spectrum up.																								
	Click the mouse to pan the spectrum down.																								
Axis Hotspot + Click-drag	Move the mouse to the Y-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse up or down, observing the panning of the spectrum in the Y-axis.																								
Spectrum Display – X - Axis	<p>X-axis controls are summarized below:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr><td></td><td>Click the mouse to pan the spectrum left.</td></tr> <tr><td></td><td>Click the mouse to pan the spectrum right.</td></tr> <tr><td>Axis Hotspot + Click-drag</td><td>Move the mouse to the X-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse left or right, observing the panning of the spectrum in the X-axis.</td></tr> </table>		Click the mouse to pan the spectrum left.		Click the mouse to pan the spectrum right.	Axis Hotspot + Click-drag	Move the mouse to the X-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse left or right, observing the panning of the spectrum in the X-axis.																		
	Click the mouse to pan the spectrum left.																								
	Click the mouse to pan the spectrum right.																								
Axis Hotspot + Click-drag	Move the mouse to the X-axis, which enables the hotspot (i.e. mouse pointer shows a hand icon). With a Click-drag operation, move the mouse left or right, observing the panning of the spectrum in the X-axis.																								
Right Mouse Click Popup	<p>Right-Click on the spectrum display to show the popup menu. This menu has the following items:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr><td>Print Preview</td><td>This submenu will display a dialog window that contains a graphical snapshot of the spectrum display. Within the dialog menu, the user can customize how the spectrum will be printed.</td></tr> <tr><td>Chart ➤</td><td>This submenu consists of options to save, load or edit the spectrum display, namely: ➤ Save Template – Save display to *.tee file</td></tr> </table>	Print Preview	This submenu will display a dialog window that contains a graphical snapshot of the spectrum display. Within the dialog menu, the user can customize how the spectrum will be printed.	Chart ➤	This submenu consists of options to save, load or edit the spectrum display, namely: ➤ Save Template – Save display to *.tee file																				
Print Preview	This submenu will display a dialog window that contains a graphical snapshot of the spectrum display. Within the dialog menu, the user can customize how the spectrum will be printed.																								
Chart ➤	This submenu consists of options to save, load or edit the spectrum display, namely: ➤ Save Template – Save display to *.tee file																								



	<ul style="list-style-type: none">➤ Export – Export display to BMP, JPG, etc.➤ Import – Load a *.tee file➤ Edit – Edit the display (several options)➤ Reset – Reset the display to the Crossroads factory default settings
View ➤	<p>This submenu consists of several toggle items to enable/display the following items:</p> <ul style="list-style-type: none">➤ Cursor (On, Off)➤ Legend (On, Off)➤ Lines – Line Draw Mode (On, Off)➤ Peak ID (On, Off)➤ Controls (On, Off)➤ All KLM (30 or 6 lines shown for KLM markers)➤ Line Labels – Symbols Format - Element Symbol Only (e.g. Fe) or Element + Line (e.g. Fe-Ka)
keV Scale	Toggle between keV or channels scaling (x-axis)
Unpaint ROIs	N/A – Future Feature



4.7.5 Contextual Workflow Window



Another area of the XRS-FP2 GUI is the R-Hand menu window. This GUI window can be comprised of one or more dialog windows, where the contents of the GUI is defined by XRS-FP2's workflow context. For example, the x-ray hardware setup workflow would have its own R-Hand menu, which would be different than energy calibration's workflow R-Hand menu, and so on.

4.7.6 Organization of Analysis Parameters into Spreadsheet Windows

In various XRS-FP2 GUI windows, collections of parameters are organized in a spreadsheet style format, via the usage of the third-party software component, namely the Farpoint Spread ("Spread Control") GUI control. Examples of this spreadsheet GUI control are as follows:

- (a) Layer Table
- (b) Component Table
- (c) Element Table
- (d) Calibration Coefficients Table
- (e) Conditions Table
- (f) Standards Table

More details of the above spreadsheet GUI tables will be explained later in this manual.

A visual example of this GUI control is shown below (for the Element Table).

#	Element	Line	Condition Code	ROI Low (keV)	ROI High (keV)	Intensity Method	Ratio Method	Quant. Method	Sigma	Conc	▲
1	Si	Ka	▼	1	1.691	1.788	Gaussian	▼	None	▼	0.000
2	Cr	Ka	▼	1	5.330	5.490	Gaussian	▼	None	▼	0.000
3	Mn	Ka	▼	1	5.809	5.977	Gaussian	▼	None	▼	0.000
4	Fe	Ka	▼	1	6.309	6.485	Gaussian	▼	None	▼	0.000
5	Ni	Ka	▼	1	7.374	7.566	Gaussian	▼	None	▼	0.000
6	Mo	Ka	▼	1	17.245	17.609	Gaussian	▼	None	▼	0.000

The customer should note the following conventions:

- (a) Cells that are shown in a gray color – these are “read-only”, where the value cannot be changed by the customer.
- (b) Cells that are shown in a yellow color – the value can be changed (“edited”) by the customer.
- (c) Cell styles types consist of either an edit box, combo box, or checkbox.
- (d) When the user positions the mouse over a column headers (i.e. row 0), a tool tip is briefly shown.
- (e) In the case of a combo box cell type, if the user executes a Click action on the column header (which selects the entire column) and changes the combo box value in the first row, then all rows values are updated with row one’s value.
- (f) Columns can be resized if needed, by executing a Click action on the boundary of the column header row.

Keyboard navigation within the spreadsheet cells is described below.

Key	Action
up arrow	Moves active cell up one row
down arrow	Moves active cell down one row
right arrow	Moves active cell right one column
left arrow	Moves active cell left one
Shift+arrow key	Extends selection in direction of arrow key
Page Up	Moves active cell one page up
Page Down	Moves active cell one page down
Ctrl+Page Up	Moves active cell one page left
Ctrl+Page Down	Moves active cell one page right
Home	Moves active cell to first cell in row
End	Moves active cell to last cell in row that contains data
Ctrl+Home	Moves active cell to first row, first column
Ctrl+End	Moves active cell to last row and column that contain data
Tab	Moves active cell to next cell to the right (or at end of row moves to beginning of next row)
Shift+Tab	Moves active cell to next cell to the left (or at beginning of row moves up to end of row above)
Shift+space	Selects current row
Ctrl+space	Selects current column
Shift+Ctrl+space	Selects entire sheet

Ctrl+X or Shift+Del	Cuts current selection or active cell's data to Clipboard
Ctrl+V or Shift+Ins	Pastes Clipboard contents into active cell
Ctrl+C or Ctrl+Ins	Copies current selection or active cell's data to Clipboard
Enter	Accepts the "edited" value of the cell, upon positive data verification
Esc	If sheet is in edit mode, previous cell value replaces new value and edit mode is turned off
F2	If edit mode is on, cell value is cleared
F3	If edit mode is on in a date or time cell, current date or time is placed in cell
F4	If edit mode is on in a date cell, sheet displays a pop-up calendar to let you choose a date

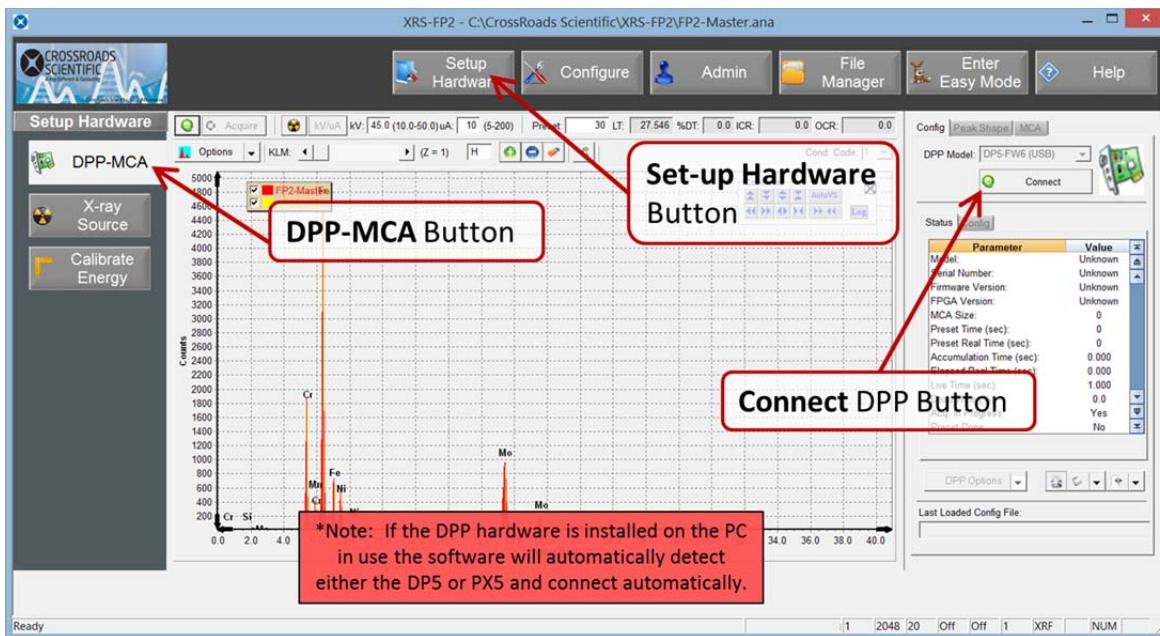
5 Setup Hardware

This section of the user manual describes how to setup the Amptek hardware (DPP/detector and x-ray source) in XRS-FP2. In addition, the basic steps necessary to perform a hardware energy calibration are also described in this section below.

*For a more in depth discussion on energy calibration please see the following tutorial, “XRS-FP2 How to Calibrate with Amptek HW”, located in the Help section of XRS-FP2.

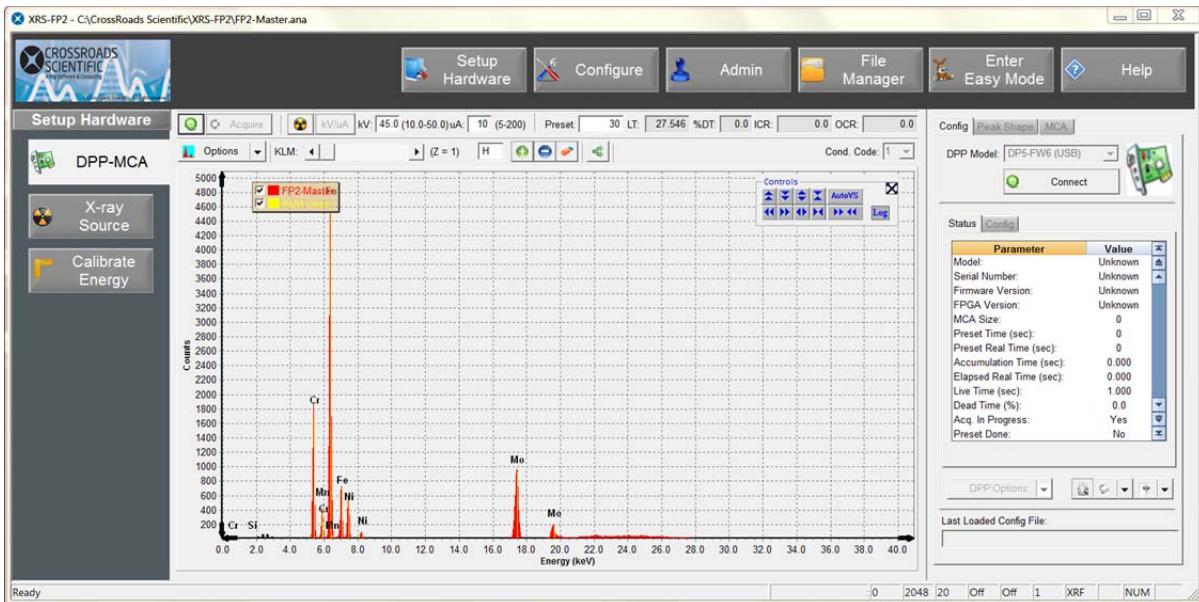
5.1 DPP-MCA

This area of the XRS-FP2 GUI allows the user to connect to the DPP, view the DPP status and config parameters, load a DPP config file and adjust necessary DPP parameters. The customer will see three tabs in the R-hand panel – Config, Peak Shape and MCA.



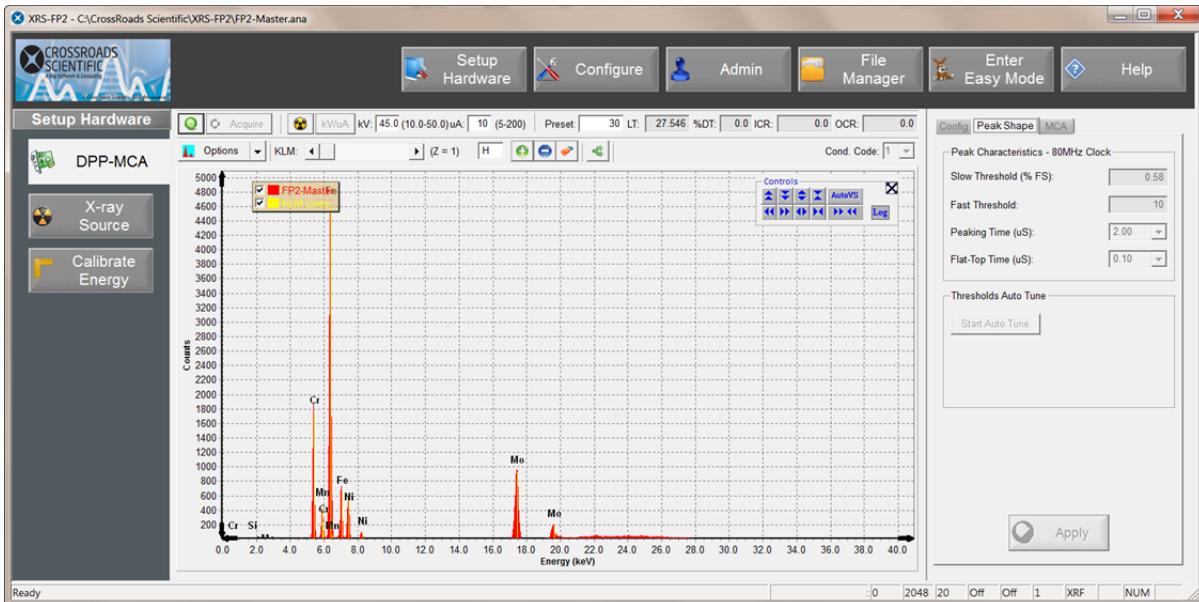
5.1.1 Config

The “Config” tab in the R-hand panel contains the **Connect** button to connect to the DPP hardware. The DPP Model is selected in the dropdown list box. When connected to the DPP, the status and configuration parameters/values are displayed in the R-hand panel. To select the various DPP options select the dropdown list box, “DPP Options”, located at the bottom of the R-hand panel. Note that the last loaded DPP configuration file is displayed for reference.



5.1.2 Peak Shape

The “Peak Shape” tab in the R-hand panel contains information regarding the peak characteristics, such as the fast and slow thresholds, the peaking time and the flat-top time. In addition, the user can auto tune the DPP thresholds using the **Start Auto Tune** button (located in the R-hand panel).

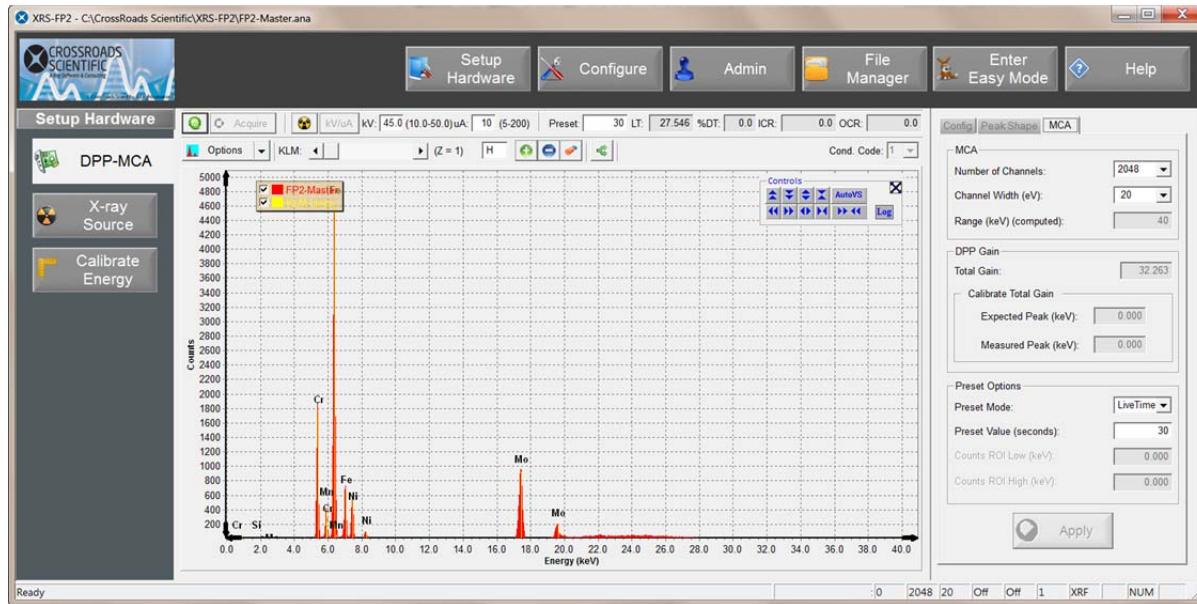


It is possible to control the Fast and Slow Thresholds in XRS-FP2; however, in newer DPP models this is better done by the Amptek software (e.g., DppMCA). It is also possible to select the Peaking Time (PT), with

a matching Flat-Top Time. These are selected from dropdown lists. Any change to the PT will result in a new default Flat-Top being selected, but this can be changed.

5.1.3 MCA

The “MCA” tab in the R-hand panel contains information about the number of channels, channel width and range. In addition, it contains details regarding the DPP gain and preset mode options.



Multichannel Analyzers (MCAs) are an essential component of x-ray spectroscopy instruments. A MCA analyzes a stream of voltage pulses and sorts them into a histogram, or “spectrum” of number of events, versus pulse-height, which may often relate to energy. The resultant spectrum can then be displayed and analyzed.

This GUI panel allows the customer to completely define the Spectrum display setup, gain, and preset options. Some of the options are disabled (e.g. DPP Gain), until the customer has established a connection with the DPP hardware.

The parameters that the customer can adjust in the R-Hand GUI “MCA” tab are defined below.

MCA Group

Parameter Name	Units	Range	Description
Number of Channels	N/A	1024, 2048, 4096	<p>Number of channels in the MCA. If the value is changed by the user, then the following occurs:</p> <p>If DPP is connected:</p> <ul style="list-style-type: none"> (a) The Range is recomputed automatically. <p>If DPP is disconnected:</p>

			<ul style="list-style-type: none"> (a) The Range is recomputed automatically. (b) Update Spectrum Display – eV/Channel and Number of Channels. (c) Update to XRS-FP2's Status Bar – eV/Channel and Number of Channels. (d) Clear BARS Spectrum Group, Remove KLM Markers, Clear ROIs, Clear Compare DOTS Groups.
Channel Width	eV	5, 10, 20, 40, 80, or 160	<p>The “width” of each channel in the MCA. Also known as “eV/Channel”. If the value is changed by the user, then the following occurs:</p> <p>If DPP is connected:</p> <ul style="list-style-type: none"> (a) The Range is recomputed automatically. <p>If DPP is disconnected:</p> <ul style="list-style-type: none"> (a) The Range is recomputed automatically. (b) Update Spectrum Display – eV/Channel and Number of Channels (c) Update to XRS-FP2's Status Bar – eV/Channel and Number of Channels. (d) Clear BARS Spectrum Group, Remove KLM Markers, Clear ROIs, Clear Compare DOTS Groups (e) Update Energy Calibration GUI - Gain
Range	keV	5, 10, 20, 40, 80, or 160	Computed value as the product of the Channel Width and the Number of Channels. This is typically the total energy range of the x-ray photons captured in the x-ray detector.

DPP Gain Group

Parameter Name	Units	Range	Description
Total Gain	N/A	0.0 to 500.0 (subj. to DPP)	DPP current gain value. When the value is modified, and sent to the DPP, the DPP searches for the nearest available ‘coarse gain’ for the analog front end. Next, it will then calculate the digital ‘fine gain’ to achieve the desired gain, while also normalizing for gain differences caused by peaking time variations.
Expected Peak	keV	Lowest energy of spectrum to upper range of spectrum	Expected (theoretical) peak for gain calibration.
Measured Peak	keV	Lowest energy of spectrum to upper range of spectrum	Actual measured peak for gain calibration.

Preset Options Group

The Livetime is always longer than the real (time-of-day clock) time, because of the so-called deadtime in the amplifier/pulse processor. Deadtime occurs when the electronics are processing an x-ray event and cannot accept a second event during that processing. During this “dead” period the livetime clock is stopped, and then restarted when the pulse processing has been completed.

If the spectral acquisitions have low count rate, then it is recommended that at least 100 seconds of livetime be used to allow for reasonable counting statistics.

Parameter Name	Units	Range	Description
Preset Mode	N/A	N/A	Determines how the acquisition will terminate. Possible selections include the following: (a) Livetime – Time during which counts are actually acquired (elapsed time) minus the time of day clock time. (b) Realtime – Time during which counts are actually acquired based on time of day clock. (c) Counts – The acquisition terminates when the spectral ROI reaches the preset value (d) Off – Setting this value to zero means that the acquisition runs continuously and must be terminated by pressing the Stop button on the Acquisition toolbar.
Preset Value	sec, counts, or off	0 to 2,147,483,647	Preset value
Counts ROI Low	keV	Lowest energy of spectrum to upper range of spectrum	Counts value at the Spectrum’s low ROI. Based on the number of channels in the spectrum and the calibration parameters (gain, offset), this value is computed to a specific channel.
Counts ROI High	keV	Greater than Lowest energy of spectrum to upper range of spectrum	Counts value at the Spectrum’s high ROI. Based on the number of channels in the spectrum and the calibration parameters (gain, offset), this value is computed to a specific channel. This value should be greater than the low ROI value.

Apply Button

When any parameter on the MCA GUI tab is modified, the customer should press the Apply button to send the updated values to the DPP.

- (a) A new total gain is computed, based on the gain calibration parameters. Spectral peaks are displayed, with the centroid “close” to the target theoretical energy of the expected peak. Bear in mind that a two-peak energy calibration (offset and gain adjustment) is still required for final peak alignment.

- (b) The spectral range is recomputed based on the number of channels and channel width.
- (c) If the resultant spectral range is different, then an automatic gain correction is applied.
- (f) Update Spectrum Display – eV/Channel and Number of Channels
- (g) Update to XRS-FP2's Status Bar – eV/Channel and Number of Channels.
- (h) Clear BARS Spectrum Group, Remove KLM Markers, Clear ROIs, Clear Compare DOTS Groups
- (i) Update Energy Calibration GUI – Gain
- (j) If a gain correction was applied, then the user is prompted to re-tune the fast/slow thresholds.

5.2 X-Ray Source

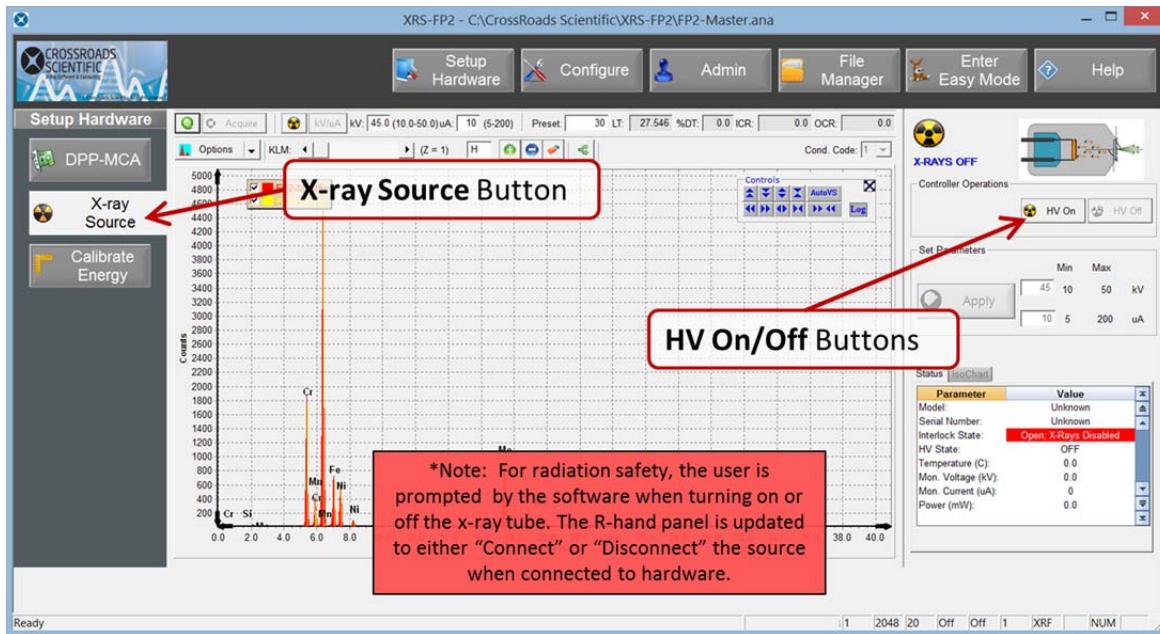
The XRS-FP2 GUI provides the capability to directly control the Amptek Mini-X x-ray tube (both the 40 kV and 50 kV models). This integrated control of the x-ray tube allows the user to energize the x-ray tube and set the voltage and current based on the condition codes defined in the analysis.

	<p>CAUTION!</p> <p>This device produces X-RAYS when energized. Please observe all safety precautions when using this device.</p> <p>Only qualified and authorized personnel shall operate this device.</p>	
---	---	---



NOTE: The Amptek Mini-X software drivers should be installed PRIOR to using XRS-FP2. Please see the Amptek website (www.amptek.com) to obtain the software drivers and installation instructions.

An example of the X-ray Source GUI panel is shown below, assuming that the x-ray device is “installed” per the INI file setup:



In order to control the x-ray tube, the XRS-FP2 software needs to know about the device. This is accomplished by the modification of two INI files as shown below. Both of these INI files are located in the same folder as XRS-FP2.exe.



NOTE: The XRS-FP2 software should be closed PRIOR to the modification of any INI files.

XRS-FP2.ini

```
[XrayDevices]
; X-Ray Tube Installed (1) or Not-Installed (0)
IsXrayTubeHWInstalled=1
```

XrsAmptekDeviceSetup.ini

```
[AmptekMiniX]
; X-Ray Tube Installed (1) or Not-Installed (0)
IsInstalled=1
; Minimum allowed value for the high voltage (kV). Default=10.
MinKV=10.0
; Maximum allowed value for the high voltage (kV). Default=50.
MaxKV=50.0
; Initial Default High Voltage (kV). Must be within voltage min/max range.
DefaultKV=45.0
; Minimum allowed value for the tube current (uA). Default=5.
MinCurrent=5.0
; Maximum allowed value for the tube current (uA). Default=200.
MaxCurrent=200.0
; Initial Default Current (uA). Must be within current min/max range.
DefaultCurrent=100.0
; Maximum allowed value for the tube power (watts). Default=4.
```

MaxPower=4.0

i **NOTE:** Please consult the Amptek Mini-X product specifications or user manual for maximum voltage and current values of the x-ray tube.

i **NOTE:** Remember to save the modified INI files PRIOR to starting the XRS-FP2 software.

Control of the x-ray tube is accomplished in two methods within the XRS-FP2 GUI, namely the dedicated X-ray Source GUI panel, or the Spectrum View's GUI toolbar, which is recapped below:

Action	Description
	X-Ray Tube Connect and HV ON
	Set X-Ray Tube Voltage and Current. This action is valid when the HV is ON.
kV: <input type="text" value="45.0"/> (10.0-50.0) uA: <input type="text" value="10"/> (5-200)	Enter the X-Ray Tube Voltage and Current, and then press the kV/uA button to set the new values. With the HV ON, the monitored voltage and current values are displayed. With the HV OFF, the voltage and current min and max range values are displayed.

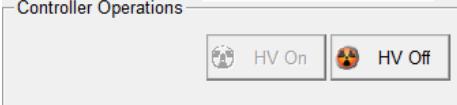
Either GUI is equivalent in the control, setting of parameters, and feedback of the x-ray tube.

Controlling High Voltage

i **NOTE:** X-rays will not be generated if the Mini-X's hardware interlock is not closed.

Action	Description
<p>Press the HV On button to establish device communications with the x-ray tube and turn ON high voltage. The user will be prompted as follows:</p> <p>Upon positive acknowledgement of the prompt, x-rays will be turned ON and the HV On button becomes disabled, while the HV Off button becomes enabled. The Spectrum View's GUI Toolbar will exhibit an equivalent display.</p>	<p>Controller Operations</p> <p>HV On HV Off</p> <p>Press the HV On button to establish device communications with the x-ray tube and turn ON high voltage. The user will be prompted as follows:</p> <p>XRS-FP2</p> <p>Turn X-RAY High Voltage ON?</p> <p>Yes No</p> <p>Upon positive acknowledgement of the prompt, x-rays will be turned ON and the HV On button becomes disabled, while the HV Off button becomes enabled. The Spectrum View's GUI Toolbar will exhibit an equivalent display.</p>



	<p>Turn OFF the high voltage. The user will be prompted as follows:</p>  <p>Upon positive acknowledgement of the prompt, x-rays will be turned OFF and the HV Off button becomes disabled, while the HV On button becomes enabled. The Spectrum View's GUI Toolbar will exhibit an equivalent display.</p>
---	--

X-Ray Status Indicator

This section of the GUI shows the x-ray status, as described below:

Action	Description
 X-RAYS OFF	Static icon that informs the user that x-rays are OFF. A text message is also shown in the GUI, indicating the x-ray high voltage status. The same icon is shown in the Spectrum View's Toolbar2.
 X-RAYS ON	Alternating (flashing) icon that informs the user that x-rays are ON. A text message is also shown in the GUI, indicating the x-ray high voltage status. The same alternating (flashing) icon is shown in the Spectrum View's Toolbar2.

High Voltage/Current Ready and Monitoring

This section of the GUI shows high voltage and current ready status, as described below:

Action	Description								
<p>kV: 45.0 (10.0-50.0) uA: 10 (5-200)</p> <p>Toolbar</p> <p>Min Max</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>45</td> <td>10</td> <td>50</td> <td>kV</td> </tr> <tr> <td>10</td> <td>5</td> <td>200</td> <td>uA</td> </tr> </table> <p>Set Parameters</p>	45	10	50	kV	10	5	200	uA	<p>Red Colored Background - Indicates that the voltage and current exceed the maximum power of the x-ray tube.</p> <p>If the HV is set OFF, the acceptable voltage and current ranges are show to the right of each value. If the HV is set ON, then the monitored voltage and current values are shown instead of the acceptable ranges.</p>
45	10	50	kV						
10	5	200	uA						
<p>kV: 45.0 (10.0-50.0) uA: 10 (5-200)</p> <p>Toolbar</p>	<p>Yellow Colored Background - Indicates that the voltage and current are ramping to the desired set points.</p> <p>If the HV is set OFF, the acceptable voltage and current ranges are show to the right of each value. If the HV is set ON, then the monitored voltage and current values are shown instead of the acceptable ranges.</p>								

<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; padding: 5px;">Min</th> <th style="text-align: center; padding: 5px;">Max</th> <th></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 5px;">45</td> <td style="text-align: center; padding: 5px;">10 50</td> <td style="text-align: center; padding: 5px;">kV</td> </tr> <tr> <td style="text-align: center; padding: 5px;">10</td> <td style="text-align: center; padding: 5px;">5 200</td> <td style="text-align: center; padding: 5px;">uA</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">Set Parameters</td> </tr> </tbody> </table> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;">kV:</td> <td style="width: 30%; text-align: center;">45.0 (10.0-40.0)</td> <td style="width: 30%;">uA:</td> <td style="width: 30%; text-align: center;">10 (5-200)</td> </tr> </table> <p style="text-align: center;">Toolbar</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; padding: 5px;">Min</th> <th style="text-align: center; padding: 5px;">Max</th> <th></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 5px;">45</td> <td style="text-align: center; padding: 5px;">10 50</td> <td style="text-align: center; padding: 5px;">kV</td> </tr> <tr> <td style="text-align: center; padding: 5px;">10</td> <td style="text-align: center; padding: 5px;">5 200</td> <td style="text-align: center; padding: 5px;">uA</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">Set Parameters</td> </tr> </tbody> </table>	Min	Max		45	10 50	kV	10	5 200	uA	Set Parameters			kV:	45.0 (10.0-40.0)	uA:	10 (5-200)	Min	Max		45	10 50	kV	10	5 200	uA	Set Parameters			<p>White Colored Background – If the HV is ON, indicates that the voltage and current have reached their desired set points. If the HV is OFF, then the modification of either the voltage or current values is updated in the active condition code.</p> <p>If the HV is set OFF, the acceptable voltage and current ranges are show to the right of each value. If the HV is set ON, then the monitored voltage and current values are shown instead of the acceptable ranges.</p>
Min	Max																												
45	10 50	kV																											
10	5 200	uA																											
Set Parameters																													
kV:	45.0 (10.0-40.0)	uA:	10 (5-200)																										
Min	Max																												
45	10 50	kV																											
10	5 200	uA																											
Set Parameters																													



NOTE: If the monitored current value is zero, this may indicate a that the x-ray tube's filament is burnt out.

Set Parameters

The section of the GUI below allows the user to change the voltage and current of the x-ray tube. This GUI is equivalent to the changing the voltage and current values in the Spectrum View's Toolbar2.

Set Parameters										
<input style="width: 100%; height: 100%;" type="button" value="Apply"/>	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; padding: 5px;">Min</th> <th style="text-align: center; padding: 5px;">Max</th> <th></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 5px;">45</td> <td style="text-align: center; padding: 5px;">10 50</td> <td style="text-align: center; padding: 5px;">kV</td> </tr> <tr> <td style="text-align: center; padding: 5px;">10</td> <td style="text-align: center; padding: 5px;">5 200</td> <td style="text-align: center; padding: 5px;">uA</td> </tr> </tbody> </table>	Min	Max		45	10 50	kV	10	5 200	uA
Min	Max									
45	10 50	kV								
10	5 200	uA								

Setting of the x-ray tube's voltage and/or the current can only be done when the HV is set to the ON state. Once the desired values are entered and within the range, then press the Apply button. From a hardware perspective, the actual x-ray tube's voltage and/or current are set governed by the following rules:

- (a) Lower kV --> Higher kV: The voltage is set first, and then the current.
- (b) Higher kV --> Lower kV: The current is set first, and then the voltage.

General Status

The x-ray tube's real-time status information is shown in the example Status tab GUI window below, including the last time the status information was updated.

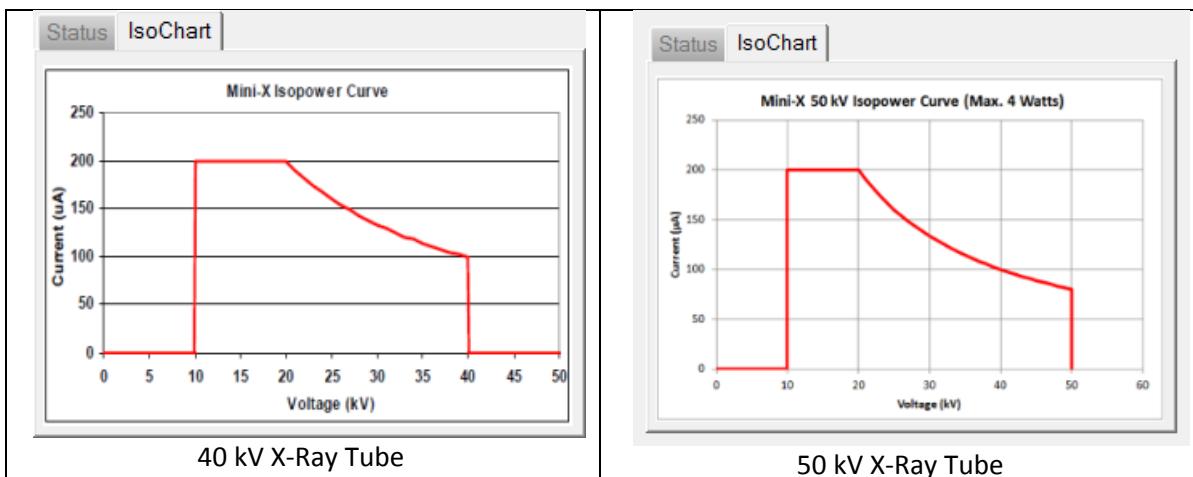


Parameter	Value
Model:	Mini-X (50 kV)
Serial Number:	01119702
Interlock State:	Closed; X-Rays Enabled
HV State:	ON
Temperature (C):	21.5
Mon. Voltage (kV):	34.8
Mon. Current (uA):	10
Power (mW):	350.0

Last Update: 20-Jan-2016 11:16:56

IsoChart

The x-ray tube has a maximum wattage rating as well as the kV and microamps which can be seen visually in the Mini-X IsoChart GUI window as shown below. The IsoChart curve is a plot of current vs. voltage.



The user should use precautions to not exceed the maximum ratings, although the XRS-FP2 software will guard against this possibility. For further information about the x-ray tube specifications (and ratings), please consult the Amptek Mini-X User Manual.

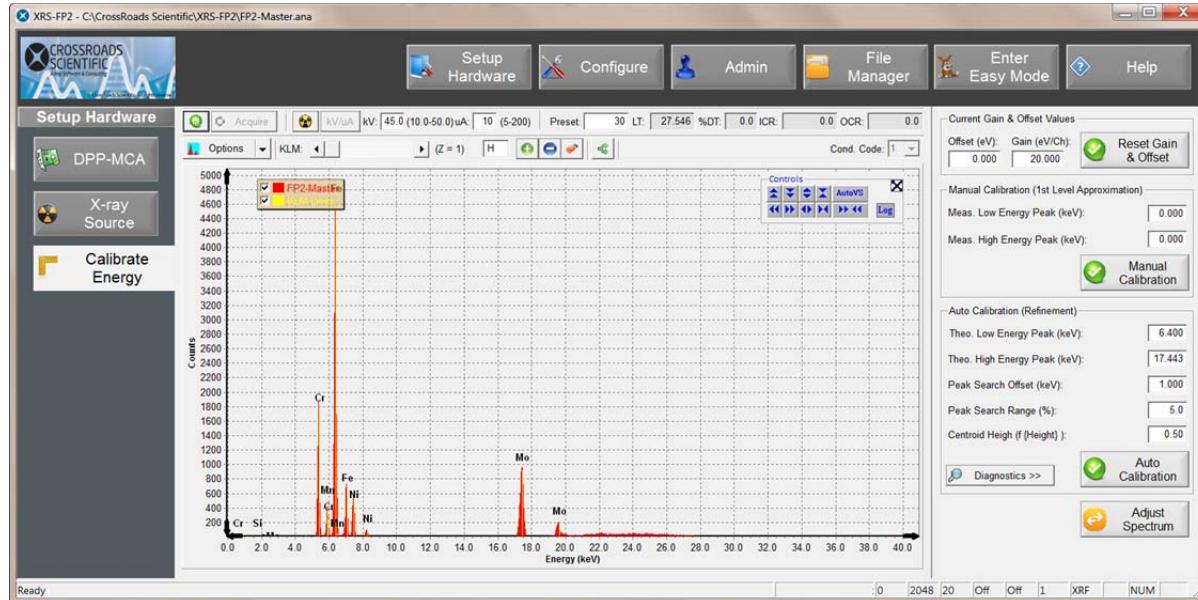
5.3 Calibrate Energy

The XRF system should be calibrated before it can be used for routine quantitative analysis. There are two main parts to this calibration.

1. The first is the spectrometer calibration (described below), which ensures that the x-ray peaks are found in the correct locations with respect to some known energy scale. This step may be ignored if you know that the spectrum will always be calibrated, using one of the standard scales (10, 20, 40 eV/channel, etc.).
2. The second is the FP calibration of the individual elemental sensitivities, also known as calibration coefficients. However, this step may be ignored if purely standardless analysis is used. Note: FP

calibration requires accurate knowledge of the tube spectrum, excitation conditions and analytical geometry parameters, as well as the detector/window characteristics.

Prior to these steps, of course, the analyst should choose the optimum experimental conditions, and this involves detailed knowledge of the XRF analytical technique. This particular discussion is beyond the scope of this software guide.



5.3.1 XRF Spectrometer Calibration and Monitoring

The spectrometer calibration refers primarily to the adjustment of the electronics (Analog Amplifier, ADC and MCA, or DPP) so that all peaks across a spectrum are all located at their appropriate energies. Unless this is the case, the spectrum processing cannot correctly convert the x-ray peaks to elemental intensities, and therefore incorrect values will be generated, resulting in incorrect assay analyses. If it is not possible to calibrate the hardware to give exact energy scales of 10, 20, 40, etc., then a secondary adjustment can be made in the software to each spectrum, assuming that the actual gain and offset are both accurately known. Often a special sample (with 2 well-separated and well-defined peaks) will be used to calibrate these factors. The same gain setting should be used for both the standards and the unknown sample assay analyses.

If you are using Amptek electronics, please refer to the appropriate manual from Amptek for installation of the hardware and driver software required for the USB connection. The initial setup parameters should be selected using the vendor's software, which should then be used to save these parameters in a configuration file. In all Amptek DPPs prior to the DP5/PX5 using FW6 the files are saved as the *.CFG file type. For the Amptek DP5 and PX5 with FW6 the file types are *.TXT. The default file names are DP5.TXT, PX5.TXT and DPP50.TXT respectively. This configuration file should be saved in the same folder as the XRS-FP2 software, as it will be accessed by the latter for setup and control of the specific DPP module. You should use the vendor's setup software for the appropriate detector type (Si pin diodes and drift detectors are very

different). You can also setup the configuration with the XRS-FP2 software itself, but you need to be very familiar with the settings in your specific DPP type.

If you want to allow for software calibration and “adjustment” within the XRS-FP software itself, to bring the scale to some integer value (e.g., 20 eV/channel) there is a special routine to perform this calibration. This routine (Calibrate Energy) is described in more detail in a later section, and uses a well-defined two-peak spectrum to be used to calculate the exact gain and offset parameters. Using these values, subsequent spectra can then be “adjusted” to bring them into the required scale. Note that this method is only meant to make relatively minor changes to the spectrum, of the order of a maximum of 20% change in the gain and offset values. More recent DPP hardware allows you to setup the configuration with more control than the older models, so it is possible to get very close to required settings for XRS-FP2, which assumes a zero offset energy, and 5, 10, 20, 40, 80 or 160 eV/channel.

To perform the XRS-FP2 **software** gain and offset spectrometer calibration, use the following steps:

- (a) Load XRS-FP2 and click the **Setup Hardware** button.
- (b) Place a suitable spectrometer calibration standard in the analysis position. This sample should contain two well-separated and identifiable peaks, which have known peak centroid energies. The two peaks should have comparable peak heights, and be the highest two peaks in the spectrum.
- (c) Click the **X-ray Source** button and turn on the x-rays (unless using a RI). Set the conditions to yield a dead time similar to that expected for the routine analysis. The dead time should normally be kept at about 50% or lower to avoid peak shifts and resolution changes.
- (d) Acquire a spectrum or Load one into the XRS-FP2 program. About 100 seconds should be sufficient, but aim to get at least 250,000 counts in the spectrum, of which at least 100,000 counts should be in the peaks of interest. Ensure that the background is not too high as this can affect the quality of the centroid peak find algorithm. If necessary, perform an automatic background removal.
- (e) Then select the **Calibrate Energy** button.
- (f) Now click the **Reset Gain & Offset** button from the R-hand panel. This ensures that any previous XRS-FP software calibration is reset (cleared) to the target values of a zero Offset energy (eV) and Gain (channel width in eV).
- (g) Next do a “Manual Calibration”. Use the cursor to find the centroid for each peak in the collected spectrum. Enter these values as the “Meas. Low Energy Peak” and “Meas. High Energy Peak” values in the “Manual Calibration (1st Level Approximation)” section. Now click on the **Manual Calibration** button. After this you should see changes in Offset and the Gain values.

Note: If the gain is more than 20% different from the nominal value (e.g., 10 eV/Ch), or the Offset is more than 1000 eV, then it is possible that something is wrong, unless the electronics cannot be adjusted further (e.g. the DP5 processor). If so, first check the (unadjusted)

spectrum and manually check the peak centroid energies with the spectrum cursor. If these are good, then this may indicate a necessity to recalibrate the electronics (if possible). Also, be sure that the software found the correct peaks and not a neighboring peak – this is likely to happen if the gain and offset are a long way off.

- (h) Now go to the “Auto Calibration (Refinement)” section in the R-hand panel. Before starting the automatic calibration, check the values for the Peak search offset and range. These two parameters control the search range for a “peak.” Obviously if the true peak is too far away from the expected location for the search range to find, then an incorrect value will be used and the calibrations values will be of no use.
- (i) Enter the centroid ($K\alpha$) values of the Low and High energy peaks used for calibration in the “Auto Calibration (Refinement)” section of the calibrate energy workflow. Now click on the **Calibrate Spectrum** button to perform the automatic calibration step.

Note: we are always referring to centroids and not the actual individual line energies. The centroids are the weighted average of the dependent line energies. The auto calibration typically results in a non-zero Offset value; however, the Gain value should not be too different from the target eV/channel

- (j) If the values look reasonable then click on the **Adjust Spectrum** button (bottom, R-hand panel). This will adjust the displayed spectrum based on the calibrated peak-energy locations. The Adjust function redistributes the channel counts into a spectrum with a zero offset and the required integer gain (eV/channel). At this point look at the spectrum to compare the “Adjusted” (calibrated) and “Original” spectra. The peaks should be in calibration with the normal gain (e.g., 10 eV/Ch) and zero
- (k) After successfully calibrating the spectrum go to the **DPP-MCA** button in the Setup Hardware workflow and select the “Auto-Adjust Spectrum” check box in under the MCA tab. This will then enable any future spectra to be automatically adjusted with the appropriate gain and offset values obtained from the energy calibration.

It is also important, before starting the next step, that the correct detector resolution value be entered into the software, as this parameter is key to performing good quality spectral peak.

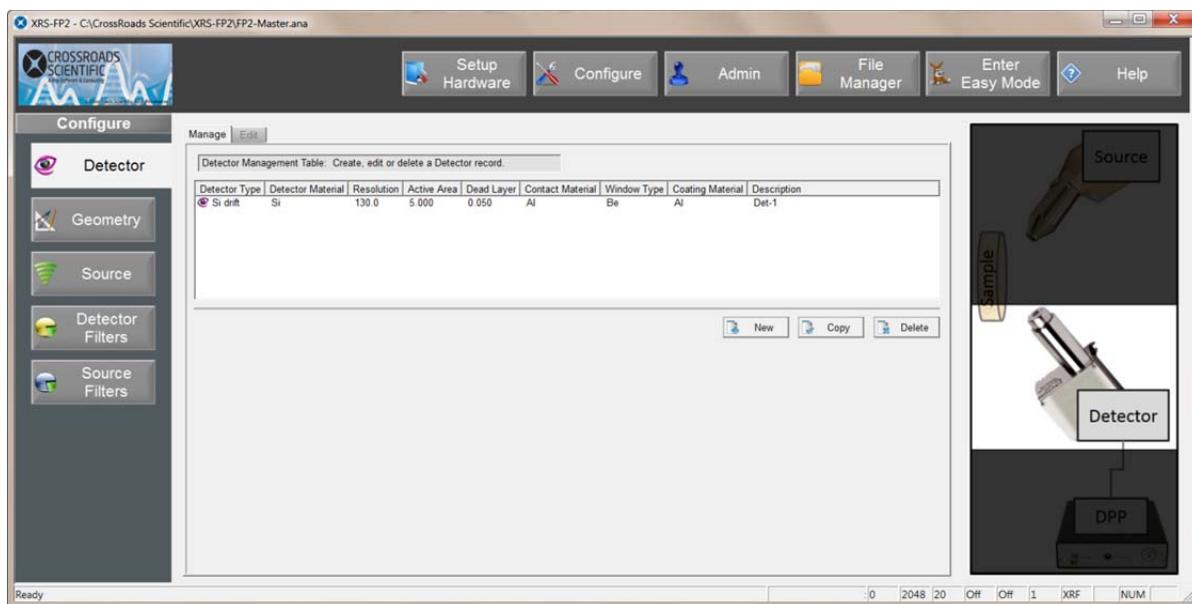
6 Configure

This section of the user manual describes system instrument parameters setups for the detector, geometry, x-ray source (XRF Analysis Mode), detector filters (XRF Analysis Mode), and source filters (XRF Analysis Mode).

6.1 Detector

This is the area of the XRS-FP2 GUI where the detector and detector window parameters are specified. The customer will see two tabs – Manage and Edit.

6.1.1 Detector - Manage



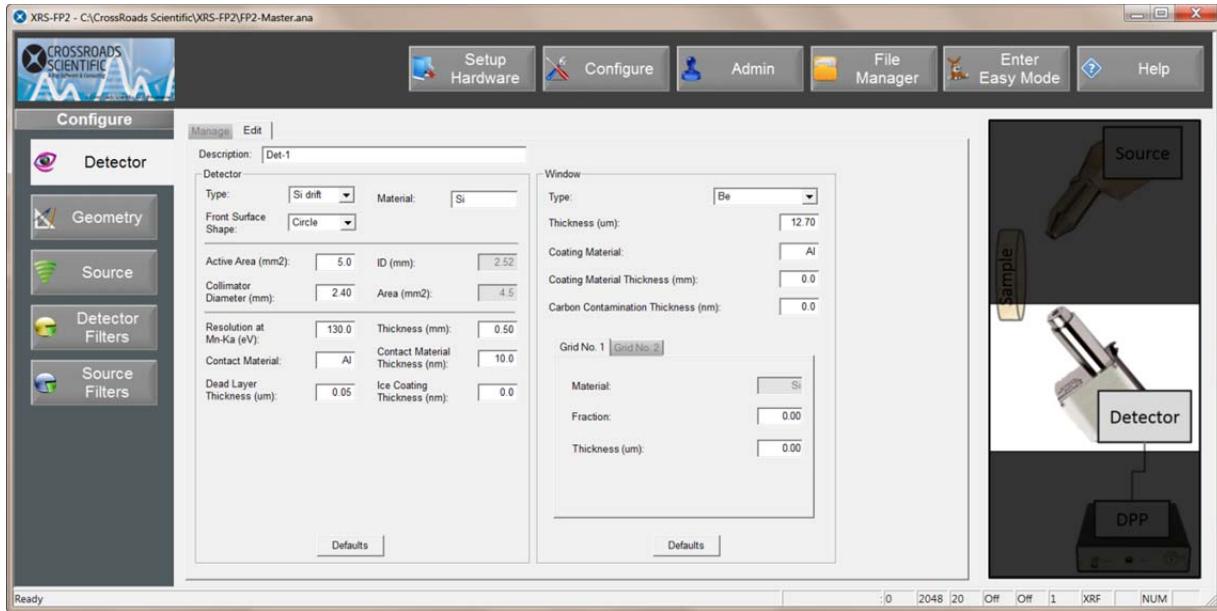
The XRS-FP2 software has the ability to store up to 8 possible detector parameter setups (also known as “records”) in the ANA file. The Manage GUI allows the customer to visualize the available detector records, with the possible following GUI actions:

Action	Description
Selection	Select an item in the list
Double-click	After making a selection from the list, invoke a Double-click action, which will bring the Edit tab to the foreground and display the selected record's parameters.
New	After making a selection from the list, pressing the New button will prompt the user to create a new record, whose values are set to zero. The Manage GUI will be updated to show the newly added record.
Copy	After making a selection from the list, pressing the Copy button will

	prompt the user to create a copy the selected record's parameters. The Manage GUI will be updated to show the newly copied record.
Delete	After making a selection from the list, pressing the Delete button will prompt the user to delete the selected record's parameters. The Manage GUI will be updated to show the remaining records.

6.1.2 Edit

6.1.2.1 Detector Types – Si-Pin, Si(Li), and Ge



This GUI panel allows the customer to completely define the type of detector being used for analysis. This is only important when standardless analysis is performed. If standards are used, then the detector efficiencies are implicitly calibrated with standards; however, the values must not be changed between calibration and analysis, without performing a recalibration.

Many of the options in this GUI panel may not be relevant to your detector, and if this is the case, simply set the parameter value to zero.



NOTE: For low-energy analysis it is important to setup the detector window correctly. This information will come from your detector supplier.

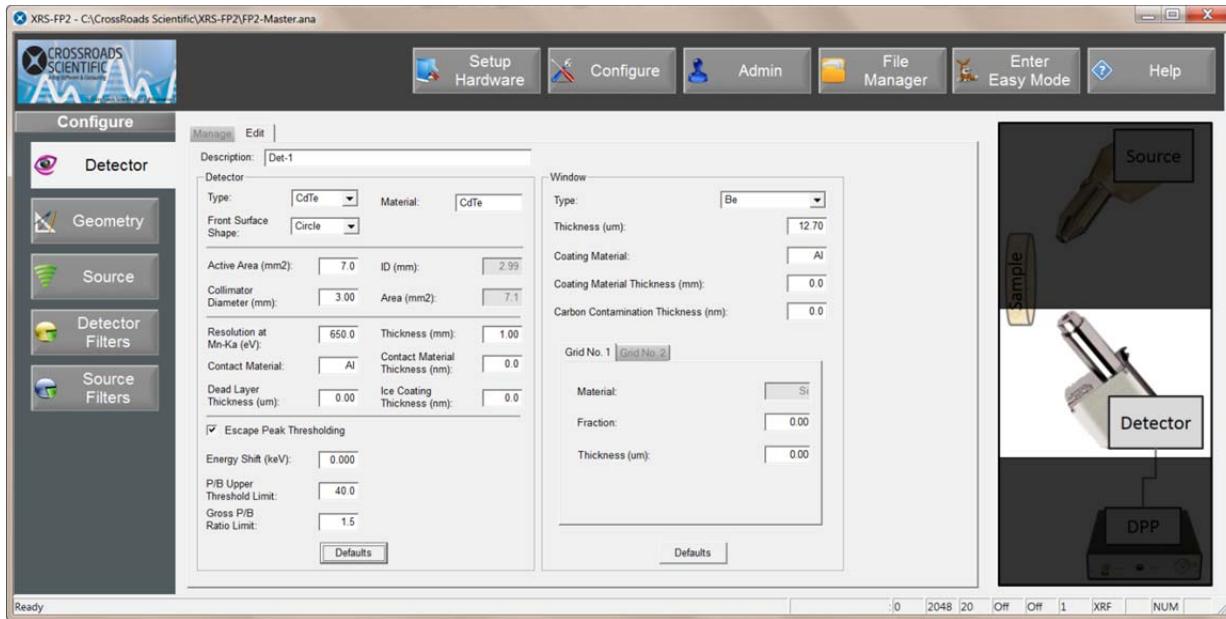
Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a "nick-name" for the detector.
Detector Type	N/A	N/A	Dropdown GUI control that allows the customer to

			specify the detector type.
Material	N/A	N/A	Atomic Symbol of Detector Element. If the detector type is PC, then "PC" will be displayed. If the detector type is CdTe, then "CdTe" will be displayed.
Front Surface Shape	N/A	N/A	Either Circle or Square
Active Area	mm ²	0.0 to 999999.0	Total (Active) Area of Detector
ID	mm	0.0 to 999999.0	Computed Value – Inner Diameter of Detector
Collimator Diameter	mm	0.0 to 999999.0	Diameter of Used Area of Detector
Area	mm ²	0.0 to 999999.0	Computed Value - Used Area of Detector
Resolution	eV	0.0 to 999999.0	Full-Width at Half-Maximum (FWHM) of Mn-Ka Peak
Thickness	mm	0.0 to 999999.0	Estimated Thickness (depth) of Detector Material
Contact Material	N/A	N/A	Atomic Symbol of Contact Material
Contact Material Thickness	nm	0.0 to 999999.0	Estimated Thickness (depth) of Contact Material
Dead Layer Thickness	um	0.0 to 999999.0	Estimated Thickness (depth) of any Dead (Inactive) Front Region of the Detector
Ice Coating Thickness	nm	0.0 to 999999.0	Estimated Thickness (depth) of Ice Coating

Pressing the Defaults button will update the GUI with factory default values for the selected detector type.



6.1.2.2 Detector Type – CdTe

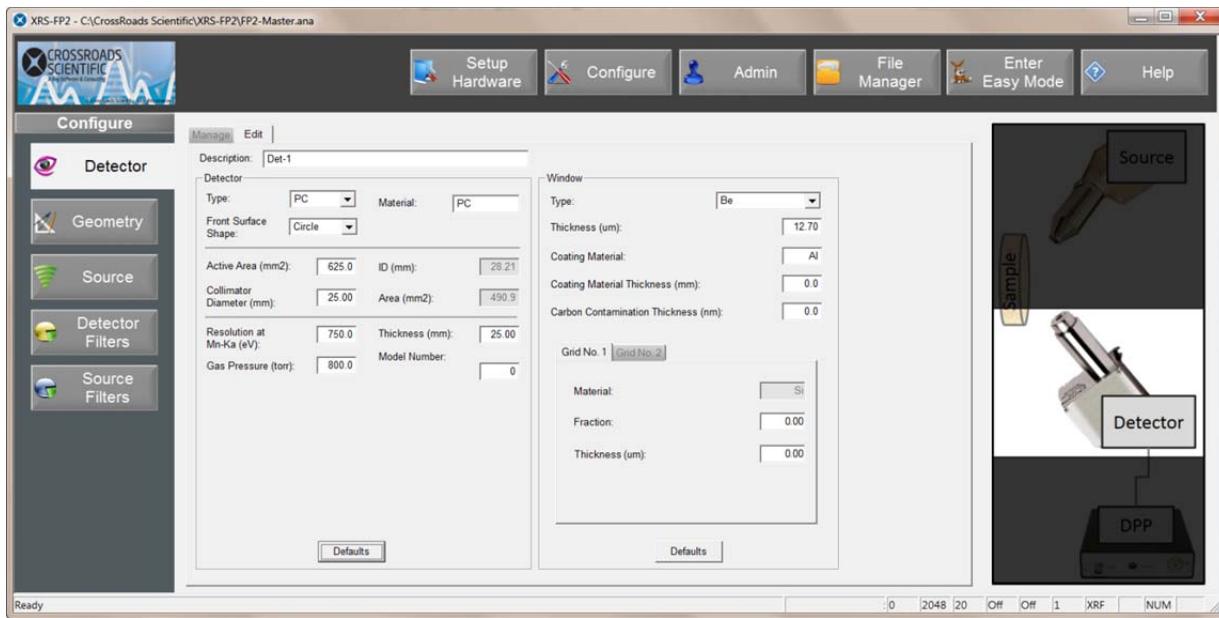


If the detector is of the CdTe type, then there are additional parameters (beyond those described with the Si-Pin, Si(Li) and Ge detector types) that the customer can adjust to fine tune the escape peak correction for the Cd and Te K escape events, as shown below.

Parameter Name	Units	Range	Description
Escape Peak Thresholding	N/A	N/A	The check box selects whether the escape peak correction is to be constrained at some level or not.
Energy Shift	keV	-999999.0 to 999999.0	The escape peak centroids do not always occur at exactly the correct energy locations, and so there is a constant energy shift parameter (positive or negative) that can adjust this expected position. The reasons for this are not known, but may be detector dependent or an approximation in the escape peak removal algorithm.
P/B Upper Threshold Limit	N/A	0.0 to 999999.0	Upper limit for the Peak/Background ratio of the net spectrum in any given channel.
Gross P/B Ratio Limit	N/A	0.0 to 999999.0	Upper limit for the Peak/Background ratio of the original (gross) spectrum in any given channel.

To further clarify the two P/B ratio constraints - if the height of the escape peak channel divided by the height of the estimated background value is greater than this limit ratio, then the amount subtracted will be limited to no more than this ration. This is to avoid over subtraction of the escape peaks, which has been observed on some occasions. There is also an upper limit in energy above which this ratio constraint is no longer applied. Currently this is fixed in the software to 40 keV and this parameter has no effect.

6.1.2.3 Detector Type – PC



If the detector is of the PC type, then there are additional parameters (beyond those described with the Si-Pin, Si(Li) and Ge detector types) that the customer can adjust, as shown below.

Parameter Name	Units	Range	Description
Gas Pressure	torr	0 to 10000	Gas Pressure for PC Detector
Model Number	N/A	0 to 100	Model Number of PC Detector

6.1.2.4 Detector Window Types

Again, this information will come from your detector supplier. In some cases, the parameter may not be relevant to your detector window, and if this is the case, simply set the parameter value to zero.

Based on the selection of the Detector Window Type, some parameters (e.g. Grid 1, Grid 2) may be set to a “read-only” value and cannot be changed by the customer.

The list of Detector Window parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Type	N/A	N/A	Dropdown GUI control that allows the customer to specify the window type.

Thickness	um		Estimated Thickness (depth) of Detector Front Window
Coating Material	N/A	N/A	Atomic Symbol of Window Coating Material
Coating Material Thickness	mm	0.0 to 999999.0	Estimated Thickness (depth) of Window Coating Material
Carbon Contamination Thickness	nm	0.0 to 999999.0	Estimated Thickness (depth) of Carbon Contamination Layer
Grid 1 - Material	N/A	N/A	Atomic Symbol (or Compound) for Grid 1
Grid 1 - Fraction	N/A	0.0 to 1.0	Fraction of Window Area for Grid 1
Grid 1 - Thickness	um	0.0 to 999999.0	Contact Electrode Thickness for Grid 1
Grid 2 - Material	N/A	N/A	Atomic Symbol (or Compound) for Grid 2
Grid 2 - Fraction	N/A	0.0 to 1.0	Fraction of Window Area for Grid 2
Grid 2 - Thickness	um	0.0 to 999999.0	Contact Electrode Thickness for Grid 2

Pressing the Defaults button will update the GUI with factory default values for the selected window type.

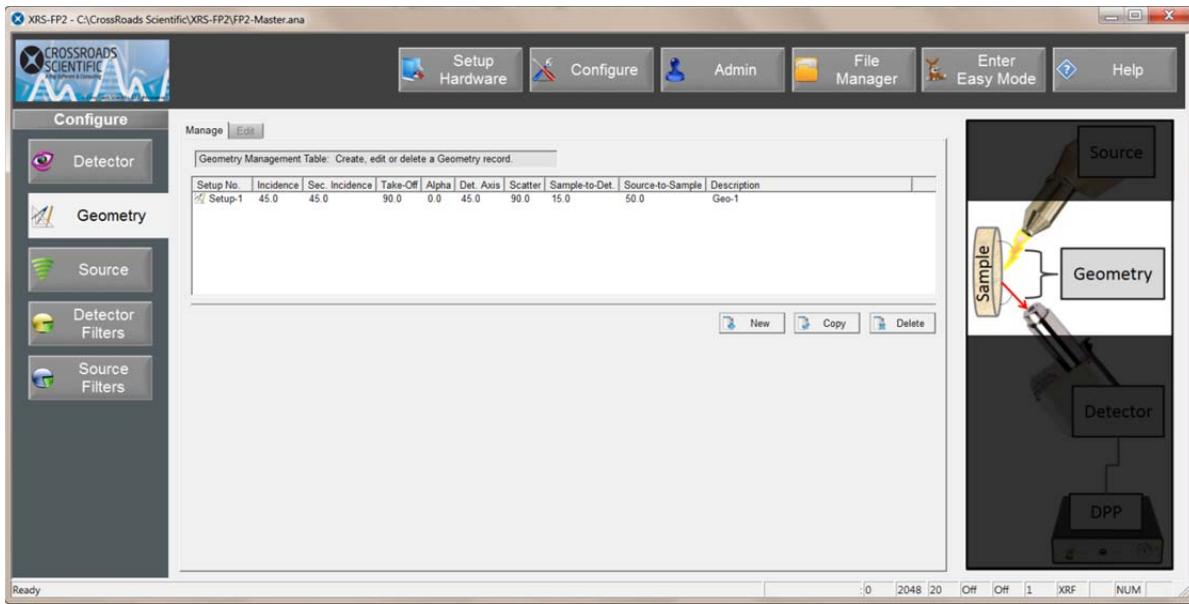
6.2 Geometry

This is the area of the XRS-FP2 GUI where the geometry parameters (angles and distances) are specified. The customer will see two tabs – Manage and Edit. It is important to correctly define the geometry of the system in use, for correct quantitation (e.g. FP) calculations to be performed. The most important of the geometry parameters are the Incident and Take-Off Angles for both XRF and EPXA analysis.

In the case of XRF analysis:

- (a) The optic parameters can probably be ignored for most XRF Bulk and EPXA systems.
- (b) The Tube-to-Sample and Sample-to-Detector distances are important when the analyses are NOT performed in vacuum, as these distances affect the absorption of the source and fluorescent x rays (i.e., from the sample) in air.
- (c) The Secondary Incident Angle is for Secondary-Target systems. For these systems, ensure that the target in the Condition Table matches the secondary target, not the tube target!
- (d) The scatter angle refers to the angle change between the incident x rays to the sample, and those to the detector, assuming a single line path in each case. Although this value can be derived from the other geometry values, it may deviate from the theoretical value because of over simplifications in the XRF geometry. It determines the shift in energy of the Compton scatter peaks with respect to the Rayleigh scatter peaks.

6.2.1 Manage

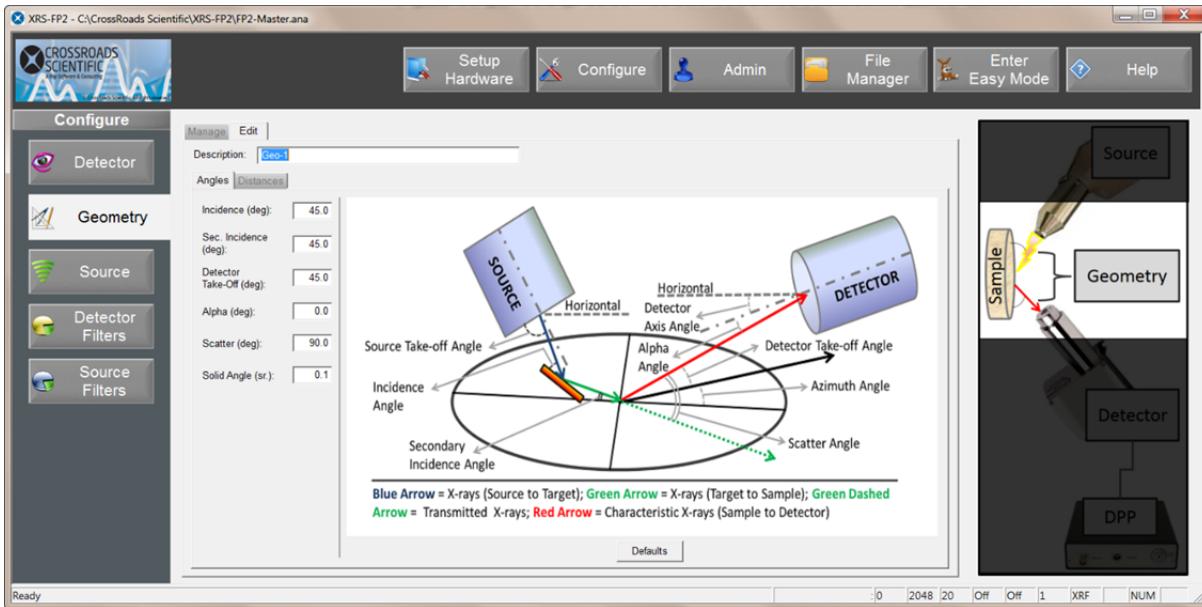


The XRS-FP2 software has the ability to store up to 8 possible geometry parameter setups (also known as “records”) in the ANA file. The Manage GUI allows the customer to visualize the available geometry records, with the possible following GUI actions:

Action	Description
Selection	Select an item in the list
Double-click	After making a selection from the list, invoke a Double-click action, which will bring the Edit tab to the foreground and display the selected record’s parameters.
New	After making a selection from the list, pressing the New button will prompt the user to create a new record, whose values are set to zero. The Manage GUI will be updated to show the newly added record.
Copy	After making a selection from the list, pressing the Copy button will prompt the user to create a copy the selected record’s parameters. The Manage GUI will be updated to show the newly copied record.
Delete	After making a selection from the list, pressing the Delete button will prompt the user to delete the selected record’s parameters. The Manage GUI will be updated to show the remaining records.

6.2.2 Edit

6.2.2.1 XRF Analysis Mode - Angles

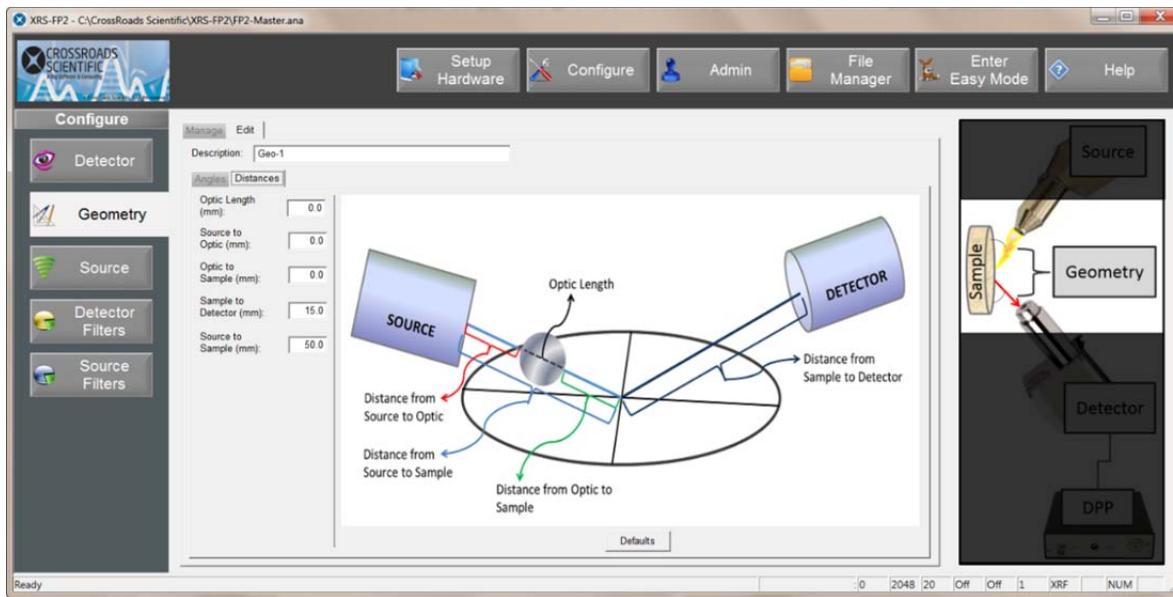


The list of Geometry parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a "nick-name" for the geometry.
Incidence	degrees	0.000001 to +180	Angle between x-rays from x-ray source and the (horizontal) sample plane
Sec. Incidence	degrees	0 to +90	Angle for a secondary target x-ray source to sample (if any)
Detector Take-Off	degrees	0.000001 to +180	Angle of emitted beam to sample
Alpha	degrees	-90 to +90	Angle between x-rays to the detector and a line perpendicular to the detector
Scatter	degrees	0 to +180	Angle between x-rays in and scattered out to the detector
Solid Angle	steradians	0.0 to 999999.0	Angle subtended by detector active area

Pressing the Defaults button will update the GUI with factory default values.

6.2.2.2 XRF Analysis Mode - Distances

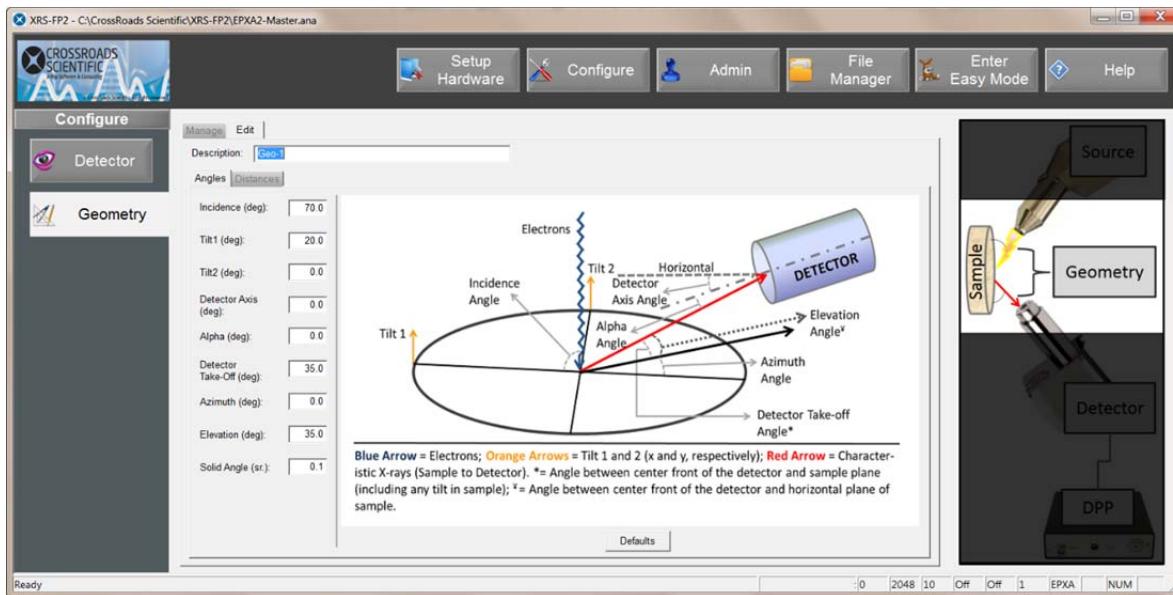


The list of Geometry parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a “nick-name” for the geometry.
Optic Length	mm	0.0 to 999999.0	Length of x-ray source optic (if any)
Source to Optic	mm	0.0 to 999999.0	Distance from x-ray source to optic (if any)
Optic to Sample	mm	0.0 to 999999.0	Distance between x-ray source optic (if any) and sample
Sample to Detector	mm	0.0 to 999999.0	Distance between sample and detector front surface
Source to Sample	mm	0.0 to 999999.0	Distance from x-ray source to sample

Pressing the Defaults button will update the GUI with factory default values.

6.2.2.3 EPXA Analysis Mode - Angles

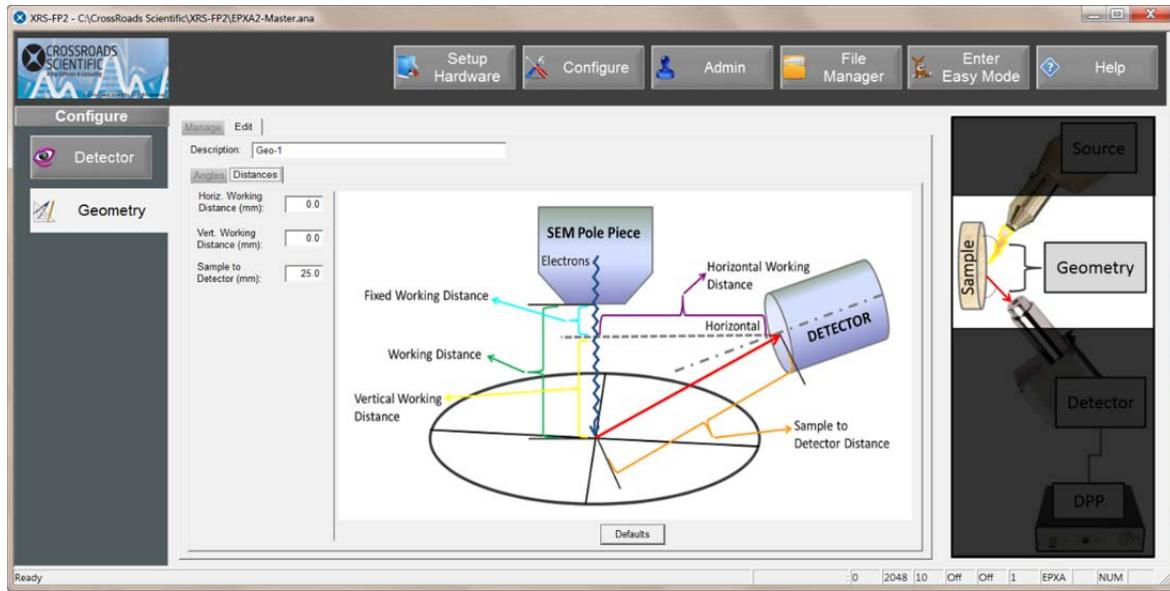


The list of Geometry parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a "nick-name" for the geometry.
Incidence	degrees	0.000001 to +180	Angle between x-rays from x-ray source and the (horizontal) sample plane
Tilt 1	degrees	-90 to +90	Tilt 1 Angle
Tilt 2	degrees	-90 to +90	Tilt 2 Angle
Detector Axis	degrees	0 to +90	Angle orthogonal to detector plane, above horizontal plane
Alpha	degrees	-90 to +90	Angle between x-rays to the detector and a line perpendicular to the detector
Detector Take-Off	degrees	0.000001 to +180	Angle of emitted beam to sample
Azimuth	degrees	-90 to +90	Rotation angle of detector from major tilt axis
Elevation	degrees	-90 to +90	Angle between exiting x-ray path and horizontal plane
Solid Angle	steradians	0.0 to 999999.0	Angle subtended by detector active area

Pressing the Defaults button will update the GUI with factory default values.

6.2.2.4 EPXA Analysis Mode - Distances



The list of Geometry parameters that the customer can adjust are noted below.

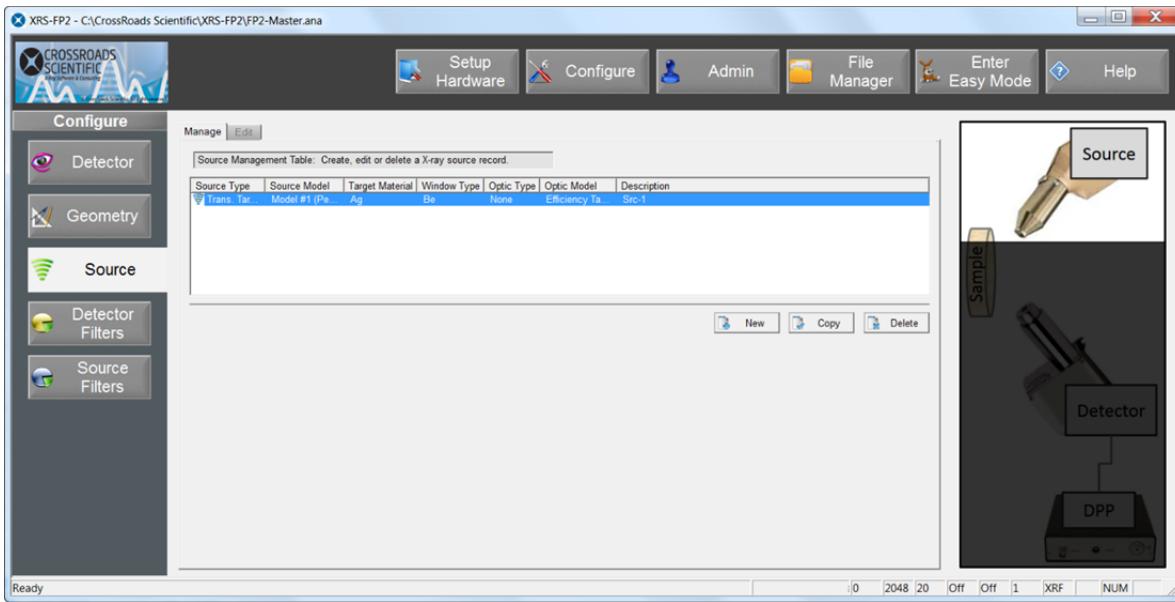
Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a “nick-name” for the geometry.
Horiz. Working Distance	mm	0.0 to 999999.0	Horizontal distance between detector crystal and electron beam path
Vert. Working Distance	mm	0.0 to 999999.0	Vertical distance between detector crystal and horizontal sample plane
Sample to Detector	mm	0.0 to 999999.0	Distance from x-ray source to sample

Pressing the Defaults button will update the GUI with factory default values.

6.3 Source

This is the area of the XRS-FP2 GUI where the x-ray source parameters are specified for XRF analysis mode only. The customer will see two tabs – Manage and Edit.

6.3.1 Manage

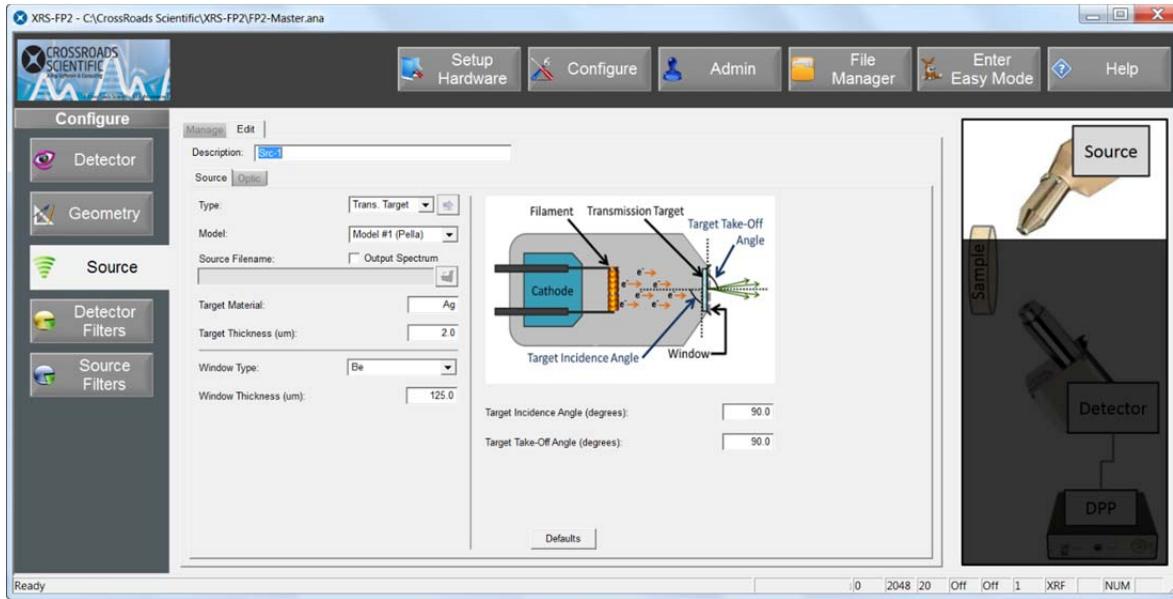


The XRS-FP2 software has the ability to store up to 8 possible x-ray source parameter setups (also known as “records”) in the ANA file. The Manage GUI allows the customer to visualize the available x-ray source records, with the possible following GUI actions:

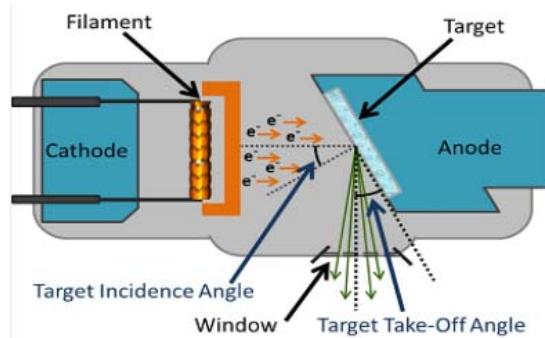
Action	Description
Selection	Select an item in the list
Double-click	After making a selection from the list, invoke a Double-click action, which will bring the Edit tab to the foreground and display the selected record’s parameters.
New	After making a selection from the list, pressing the New button will prompt the user to create a new record, whose values are set to zero. The Manage GUI will be updated to show the newly added record.
Copy	After making a selection from the list, pressing the Copy button will prompt the user to create a copy the selected record’s parameters. The Manage GUI will be updated to show the newly copied record.
Delete	After making a selection from the list, pressing the Delete button will prompt the user to delete the selected record’s parameters. The Manage GUI will be updated to show the remaining records.

6.3.2 Edit

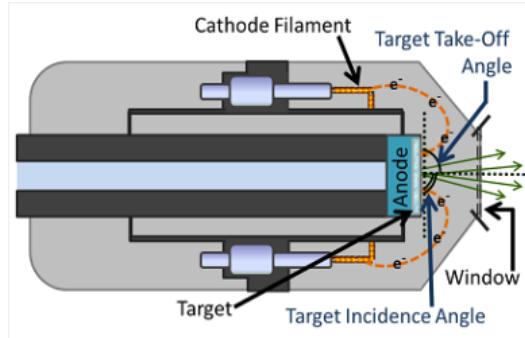
6.3.2.1 Source Parameters



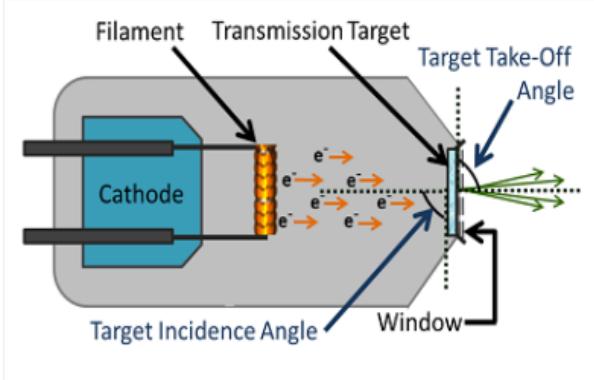
The XRS-FP2 software allows for 4 possible x-ray source types as shown by the diagrams below.



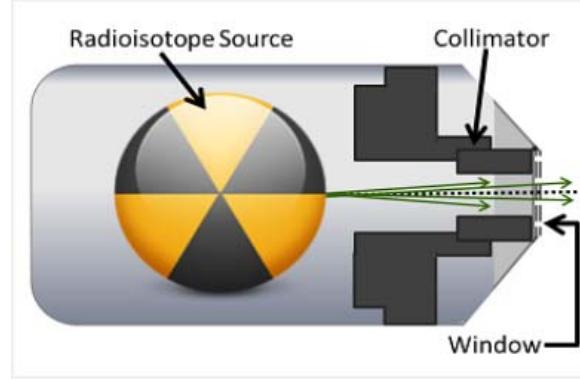
(a) Side Window



(b) End Window



(c) Transmission Target



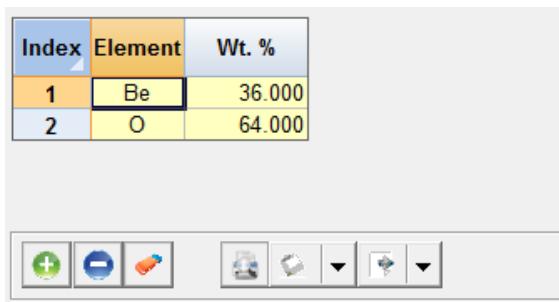
(d) Radioisotope

The list of Source parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a “nick-name” for the geometry.
Type	N/A	N/A	Possible selections include a) Side Window, b) End Window, c) Transmission Target, and d) Radioisotope
Model	N/A	N/A	Possible selections include either user defined Spectrum Model, or pre-defined models – specifically Pella or Ebel.
Source Filename	N/A	N/A	Spectrum Model - This can be a spectrum that has been collected from the output of a tube, and corrected for any detector efficiency factors. This file is in ASCII text format, where the first column is the wavelength (Angstroms), and the second is in the relative intensity at that wavelength. No attempt is made to generate the absolute tube flux at any wavelength, because of uncertainties about the system geometry. The calibration step takes care of this normalization, except for standardless analysis where the sample composition is normalized to 100%.
Output Spectrum	N/A	N/A	Get the x-ray source spectrum as seen by the sample
Target Material	N/A	N/A	Atomic Symbol for Target Material.
Target Thickness	um	0.0 to 999999.0	Estimated Thickness (depth) of Target Material
Window Type	N/A	N/A	Possible selections include a) Be, b) Alloy, c) Windowless, and d) Multilayer. Alloy and Multilayer window types involve a more detailed setup, which is described later in this user manual.
Window Thickness	um	0.0 to 999999.0	Estimated Thickness (depth) of Window
Target Incident Angle	degrees	0 to +90	Incident Angle with respect to target surface. Relative intensities assume a normal (90-degree) Take-Off Angle. This parameter is not displayed if the source type is a radioisotope.
Target Take-Off Angle	degrees	0 to +90	Take-Off Angle with respect to the target surface. This parameter is not displayed if the source type is a radioisotope.

Pressing the Defaults button will update the GUI with factory default values.

6.3.2.2 Source Window Type – Alloy



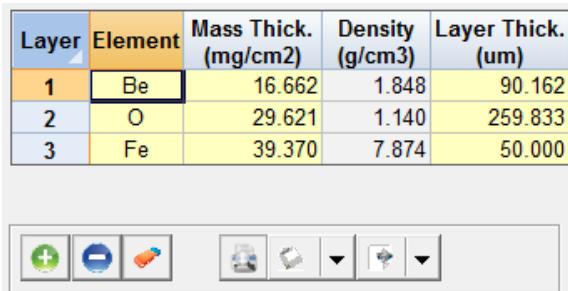
This option allows the customer to specify the x-ray source window composition in terms of the alloy's elemental composition (i.e. wt%). Up to 25 elements can be defined for the alloy's composition, with the elements being specified in any order. The alloy's total composition should not exceed 100%. This information is saved in the ANA file, and will get reset when the ANA file is loaded (along with other application parameters).

GUI navigation of Alloy source window setup is described below.

Action	Description
	Add a row to the end of the spreadsheet
	Delete the selected row of the spreadsheet
	Clear all rows in the spreadsheet, leaving row one initialized (i.e. empty cells)
	Displays a Print Preview dialog window, which displays a graphical format of the spreadsheet's data
	This button menu allows the spreadsheet's data to be copied to the clipboard in either a) graphical format, or b) text format
	This button menu allows the spreadsheet's data to be saved to a user specified data file. Supported formats include a) Comma Separated Value (*.csv), b) HTML (*.html), c) XML (*.xml), d) Excel 97-2003 Workbook (*.xls), and e) Excel 2007 Workbook (*.xlsx).
Down arrow	Add a row to the end
INSERT	Add a row to the end
DELETE	Delete the selected row

6.3.2.3 Source Window Type – Multilayer

Layer	Element	Mass Thick. (mg/cm ²)	Density (g/cm ³)	Layer Thick. (μm)
1	Be	16.662	1.848	90.162
2	O	29.621	1.140	259.833
3	Fe	39.370	7.874	50.000



This option for defining the x-ray source window treats any compounds as separate elemental layers, along with any special filters that may be mounted in front of the x-ray tube. In the example above, there is a BeO window, with an Fe filter. Note that the elements are expressed in mass thickness, or layer thickness with a standard value of density. The user can enter the values in either of the thickness columns, and the corresponding values are calculated automatically. Up to 25 elemental layers can be defined. This information is saved in the ANA file, and will get reset when the ANA file is loaded (along with other application parameters).

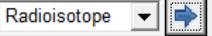
It makes no difference in which order the layers are specified, there will be the same amount of absorption as a function of energy. The intent of this option is to allow for special setups where there could be several filters in front of the conventional x-ray source window. These are assumed to be fixed in place. In cases where a filter is optionally used, this should be selected in the condition code table, where this only allows one elemental filter.

GUI navigation of Multilayer source window setup is described below.

Action	Description
	Add a row to the end of the spreadsheet
	Delete the selected row of the spreadsheet
	Clear all rows in the spreadsheet, leaving row one initialized (i.e. empty cells)
	Displays a Print Preview dialog window, which displays a graphical format of the spreadsheet's data
	This button menu allows the spreadsheet's data to be copied to the clipboard in either a) graphical format, or b) text format
	This button menu allows the spreadsheet's data to be saved to a user specified data file. Supported formats include a) Comma Separated Value (*.csv), b) HTML (*.html), c) XML (*.xml), d) Excel 97-2003 Workbook (*.xls), and e) Excel 2007 Workbook (*.xlsx).
Down arrow	Add a row to the end
INSERT	Add a row to the end
DELETE	Delete the selected row

6.3.2.4 Source Type - Radioisotope

The XRS-FP2 GUI supports a radioisotope as the source type. If this is the case, then GUI setup will be displayed, by the following convention:

Action	Description
Type:  	Flyout GUI button – Left Arrow - Hide the radioisotope setup GUI
Type:  	Flyout GUI button – Right Arrow - Show the radioisotope setup GUI

When the radioisotope source option is selected, the spectrum file method must be used to define the isotope source spectrum. Several files, corresponding to the common radioisotope sources are included with the XRS-FP2 software that include:

- (a) Am241.txt (Am241.ris)
- (b) Cd109.txt (Cd109.ris)
- (c) Co57.txt (Co57.ris)
- (d) Fe55.txt (Fe55.ris)

Note that for each *.txt file, there is a corresponding *.ris file. The *.txt file is used for quantitation, to provide the incident excitation “spectrum” in the same way as can be used for a tube spectrum. The *.ris file is used for deconvolution during spectrum processing. Thus, the file contents of each file type are different.

Selection of the *.txt file (for the Spectrum Model) is a prerequisite action that is done first, to ensure that the corresponding *.ris is loaded, as noted by the Co57 example below.



The relative intensities assume no window, and so this should be included in the setup if a window is used with the source.

The radioisotope setup GUI is shown below, again, using the Co57 example:

Gamma Lines Table:

#	Energy (keV)	Wavelength (Angs)	Relative Intensity	Decon. Inc.
*1	122.060	0.102	93.700	<input checked="" type="checkbox"/>
2	14.410	0.860	832.000	<input checked="" type="checkbox"/>
3	136.470	0.091	100.000	<input type="checkbox"/>

X-Ray Line Series Table:

#	Element	Line Series	Relative Intensity	Decon. Inc.
1	Fe	K	28.140	<input checked="" type="checkbox"/>

Radioisotope Source Filename:

This GUI contains information about the specific gamma and x-ray lines in the radioisotope source, and allows the user to select which ones to include for deconvolution and subsequent Compton peak processing.

The first row line is the one chosen by default to be the incident line to be used for the Rayleigh and Compton peak extraction. The appropriate x-ray lines for the selected radioisotope source are also shown, which can be included or not for spectral deconvolution, but they cannot be selected for the Compton peak extraction.

In some cases the file may not exist for the isotope of interest, in which the user will have to create the table by entering the appropriate Gamma and x-ray line energies and their relative intensities, and save it as a *.ris

file with the same name (and same path) as the *.txt source file. Example file structure of both the *.txt and *.ris file are provided below.

File Contents – Co57.txt

```
0.09085, 100.0
0.10157, 832.0
0.8604, 93.7
1.7561, 3.79
1.9381, 28.14
```

File Contents – Co57.ris

Overview =====

"Version: ",2.000

"Comment: ","File designed for use in deconvoluting XRF spectra excited by an RI Source"

```

Gamma Lines =====
"NumLines: ",3
""Energy(keV)","WaveLength(Angs)","RellIntens","IncDecon"""
122.06,0.102,93.7,"Yes"
14.41,0.86,832,"Yes"
136.47,0.091,100,"No"

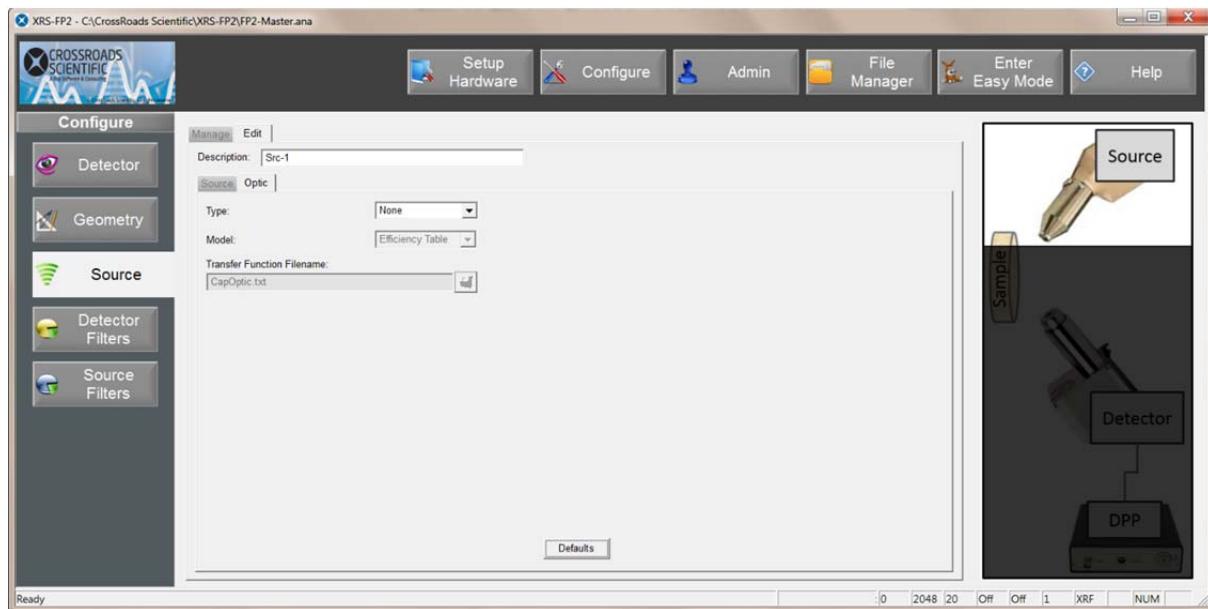
```

```

X-ray Line Series =====
"NumSeries: ",1
""Element","LineSeries","RellIntens","IncDecon"""
"Fe","K",28.14,"Yes"

```

6.3.2.5 Optic Parameters



In case the user has a capillary, or other optic between the source and the sample, there is an option for selecting the optic. Together with optic, a transfer function must also be provided. This is in the form of a lookup table, or file, and the file has a similar format to the source-model files (i.e., text format, with the first column again in Angstroms). The main difference is in the usage of the second column. This column refers to the efficiency of transfer between the input and the output of the optic, for the given wavelength.

This efficiency is “convolved” with the source spectrum (i.e., the two factors are effectively multiplied at the common wavelength), to provide the spectrum from the output of the optic.

Selecting the mirror option for the optic will result in the specified kV from the tube being used as a monochromatic source. This is for monochromatic sources that could be from either mirrors or curved crystals.

Note that other factors are also applied to the tube spectrum, such as (a) a filter and (b) any air absorption path. These factors are all, effectively, multiplicative, so that it does not matter in which order they are applied. Similarly, if the filter is before, or after, the optic it makes no difference. If there are multiple air paths then the appropriate distances should be entered into the Configure Geometry GUI.

The list of Optic parameters that the customer can adjust are noted below.

Parameter Name	Units	Range	Description
Description	N/A	N/A	Text string allowing the customer to specify a “nick-name” for the overall x-ray source (source and optic) setup.
Type	N/A	N/A	Possible selections include a) None, b) Capillary, and c) Mirror
Model	N/A	N/A	Possible selections include a) Efficiency Table, b) Fitted #1, and c) Fitted #2
Transfer Function Filename	N/A	N/A	Filename whose contents describe the transfer function

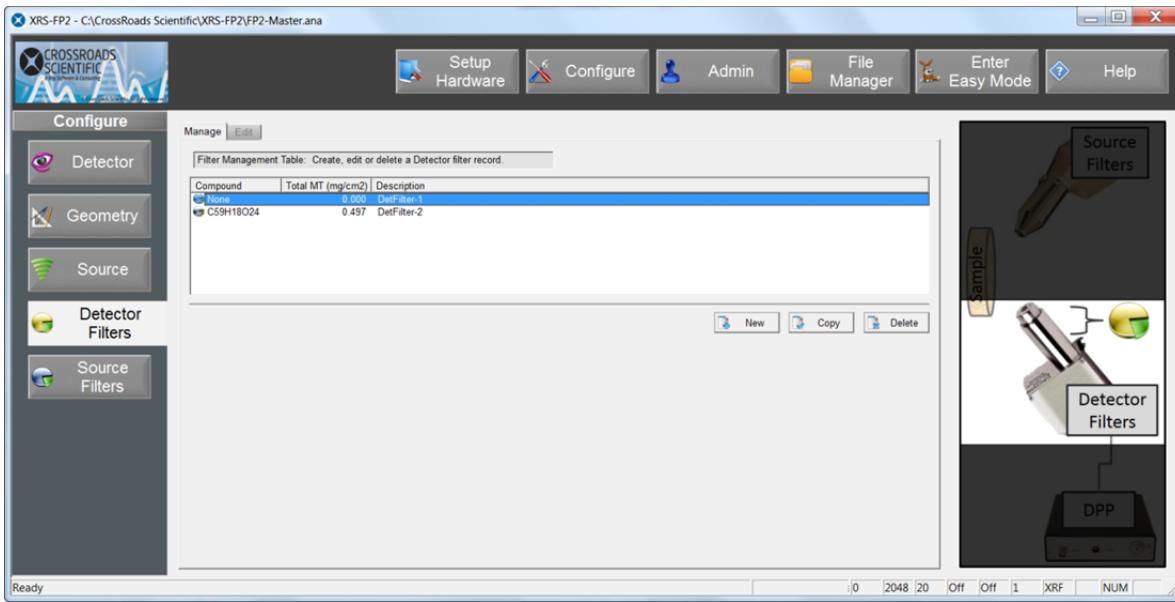
Pressing the Defaults button will update the GUI with factory default values.

6.4 Detector Filters

This is the area of the XRS-FP2 GUI where Detector filters are specified for XRF analysis mode. The intent of this option is to allow for special setups where there could be several filters in front of the conventional x-ray detector. These are assumed to be fixed in place. In cases where a filter is optionally used, this should be selected in the condition code table.

For each specified filter, the definition of the filter's composition is saved in the ANA file and are reset when the ANA file is loaded (along with other application parameters). The customer will see two tabs – Manage and Edit.

6.4.1 Manage

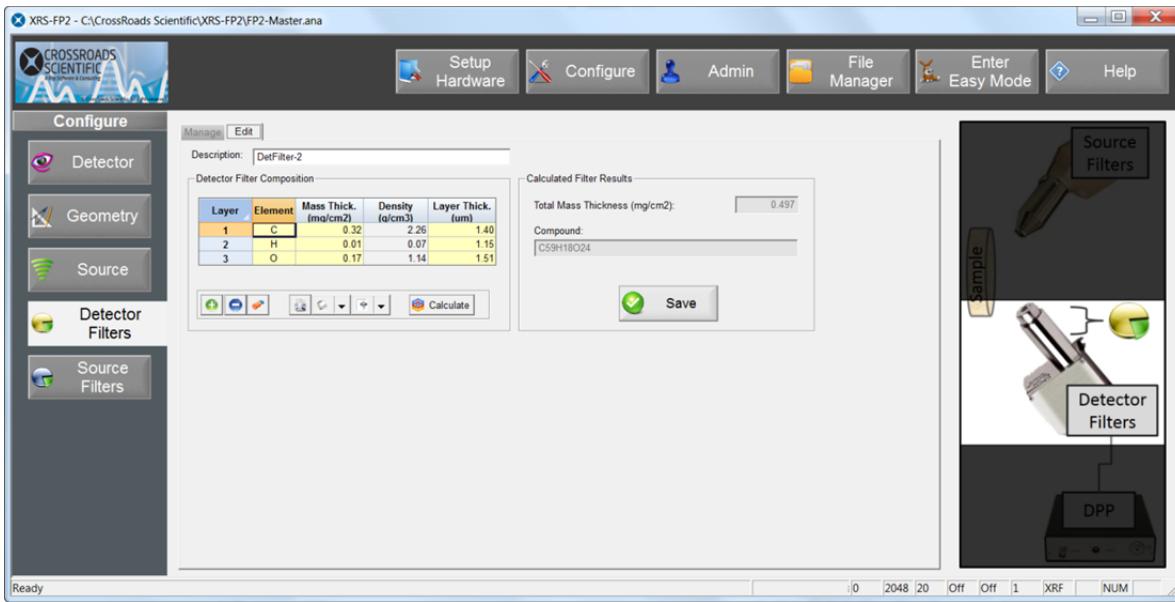


The XRS-FP2 software has the ability to store up to 8 possible detector filter setups (also known as “records”) in the ANA file. Each filter itself can have up to 4 elements. The Manage GUI allows the customer to visualize the available detector filter records, with the possible following GUI actions:

Action	Description
Selection	Select an item in the list
Double-click	After making a selection from the list, invoke a Double-click action, which will bring the Edit tab to the foreground and display the selected record’s parameters.
New	After making a selection from the list, pressing the New button will prompt the user to create a new record, whose values are set to zero. The Manage GUI will be updated to show the newly added record.
Copy	After making a selection from the list, pressing the Copy button will prompt the user to create a copy the selected record’s parameters. The Manage GUI will be updated to show the newly copied record.
Delete	After making a selection from the list, pressing the Delete button will prompt the user to delete the selected record’s parameters. The Manage GUI will be updated to show the remaining records.

The “None” Filter record (i.e. No filter) is always present and cannot be altered or deleted.

6.4.2 Edit



The constraints of a filter definition are noted below:

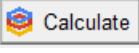
- (a) Up to 4 layers, with each layer containing a unique elemental symbol
- (b) Maximum of 20 characters, in total, which contain one or more elements and the associated number of atoms/element for the computed compound

The elements are expressed in mass thickness, or layer thickness with a standard value of density. The user can enter the values in either of the thickness columns, and the corresponding values are calculated automatically.

It makes no difference in which order the layers are specified, there will be the same amount of absorption as a function of energy.

GUI navigation of Multilayer detector filter setup is described below.

Action	Description
	Add a row to the end of the spreadsheet
	Delete the selected row of the spreadsheet
	Clear all rows in the spreadsheet, leaving row one initialized (i.e. empty cells)
	Displays a Print Preview dialog window, which displays a graphical format of the spreadsheet's data
	This button menu allows the spreadsheet's data to be copied to the clipboard in either a) graphical format, or b) text format

	This button menu allows the spreadsheet's data to be saved to a user specified data file. Supported formats include a) Comma Separated Value (*.csv), b) HTML (*.html), c) XML (*.xml), c) Excel 97-2003 Workbook (*.xls), and d) Excel 2007 Workbook (*.xlsx).
	Based on the number of elements and thickness values, this function will a) compute a resulting compound name and b) total mass thickness
Down arrow	Add a row to the end
INSERT	Add a row to the end
DELETE	Delete the selected row

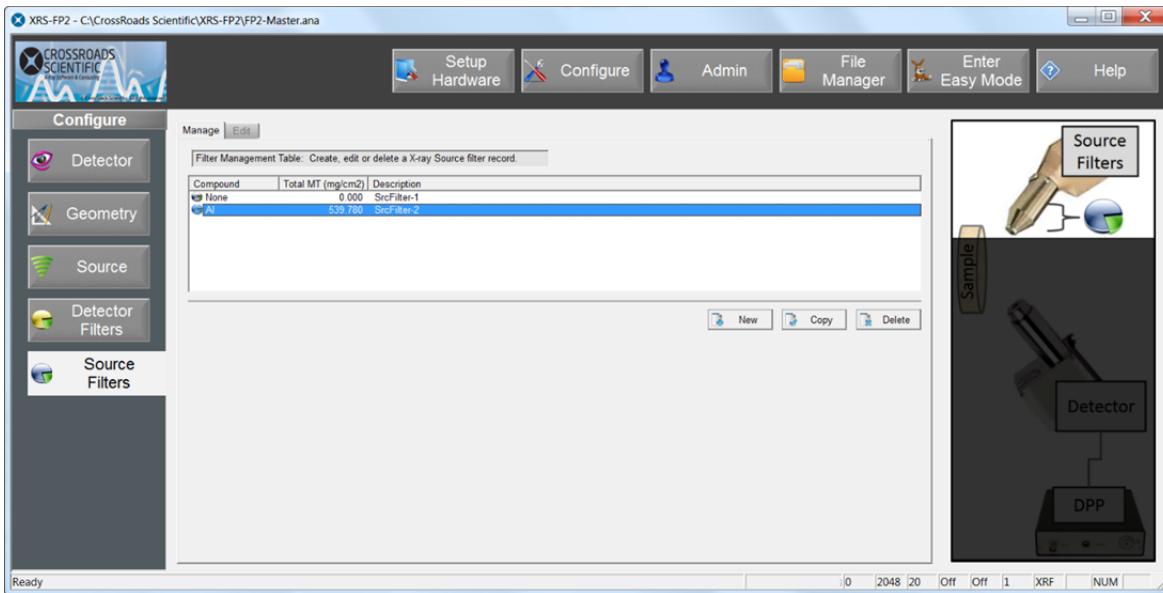
Once the filter is defined, with the resultant compound name and total mass thickness, press the Save button to save the filter data to the ANA file.

6.5 Source Filters

This is the area of the XRS-FP2 GUI where Source filters are specified for XRF analysis mode. The intent of this option is to allow for special setups where there could be several filters in front of the conventional x-ray source. These are assumed to be fixed in place. In cases where a filter is optionally used, this should be selected in the condition code table.

For each specified filter, the definition of the filter's composition is saved in the ANA file and are reset when the ANA file is loaded (along with other application parameters). The customer will see two tabs – Manage and Edit.

6.5.1 Manage

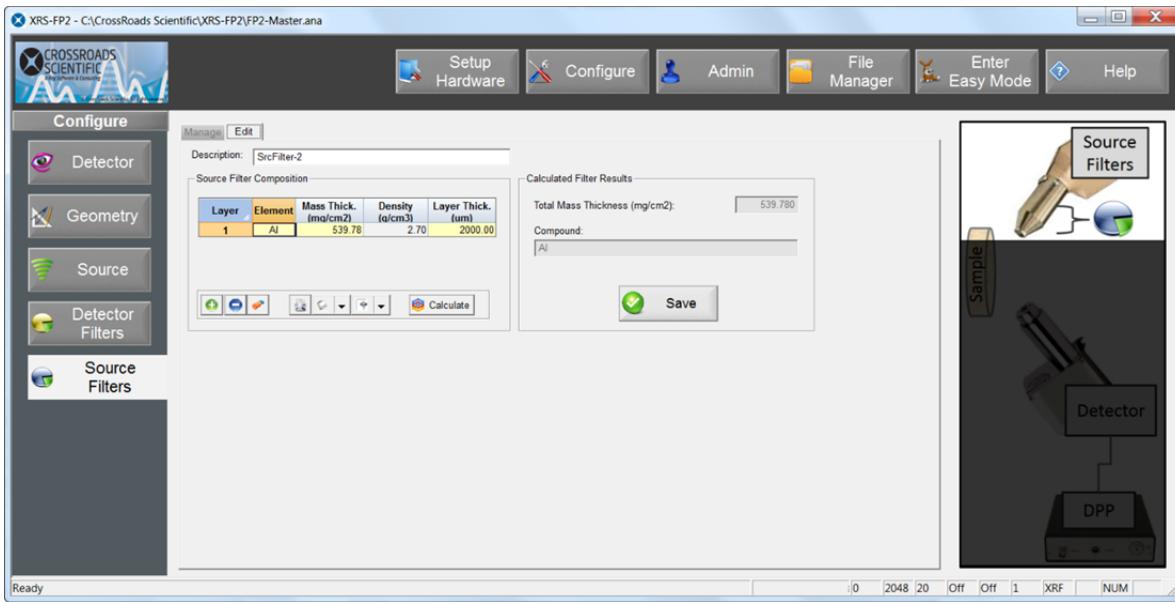


The XRS-FP2 software has the ability to store up to 8 possible source filter setups (also known as “records”) in the ANA file. Each filter itself can have up to 4 elements. The Manage GUI allows the customer to visualize the available source filter records, with the possible following GUI actions:

Action	Description
Selection	Select an item in the list
Double-click	After making a selection from the list, invoke a Double-click action, which will bring the Edit tab to the foreground and display the selected record's parameters.
New	After making a selection from the list, pressing the New button will prompt the user to create a new record, whose values are set to zero. The Manage GUI will be updated to show the newly added record.
Copy	After making a selection from the list, pressing the Copy button will prompt the user to create a copy the selected record's parameters. The Manage GUI will be updated to show the newly copied record.
Delete	After making a selection from the list, pressing the Delete button will prompt the user to delete the selected record's parameters. The Manage GUI will be updated to show the remaining records.

The “None” Filter record (i.e. No filter) is always present and cannot be altered or deleted.

6.5.2 Edit



The constraints of a filter definition are noted below:

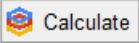
- (a) Up to 4 layers, with each layer containing a unique elemental symbol
- (b) Maximum of 20 characters, in total, which contain one or more elements and the associated number of atoms/element for the computed compound

The elements are expressed in mass thickness, or layer thickness with a standard value of density. The user can enter the values in either of the thickness columns, and the corresponding values are calculated automatically.

It makes no difference in which order the layers are specified, there will be the same amount of absorption as a function of energy.

GUI navigation of Multilayer source filter setup is described below.

Action	Description
	Add a row to the end of the spreadsheet
	Delete the selected row of the spreadsheet
	Clear all rows in the spreadsheet, leaving row one initialized (i.e. empty cells)
	Displays a Print Preview dialog window, which displays a graphical format of the spreadsheet's data
	This button menu allows the spreadsheet's data to be copied to the clipboard in either a) graphical format, or b) text format

	This button menu allows the spreadsheet's data to be saved to a user specified data file. Supported formats include a) Comma Separated Value (*.csv), b) HTML (*.html), c) XML (*.xml), c) Excel 97-2003 Workbook (*.xls), and d) Excel 2007 Workbook (*.xlsx).
	Based on the number of elements and thickness values, this function will a) compute a resulting compound name and b) total mass thickness
Down arrow	Add a row to the end
INSERT	Add a row to the end
DELETE	Delete the selected row

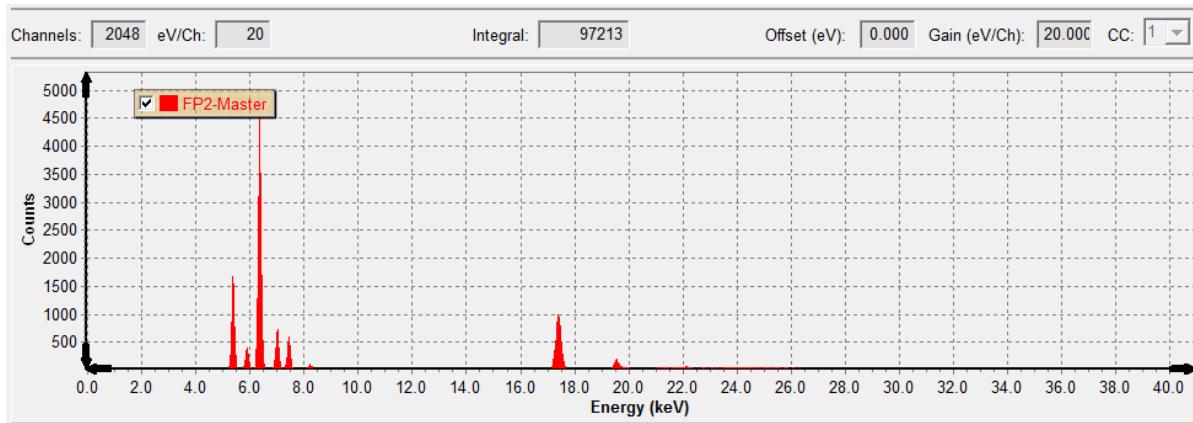
Once the filter is defined, with the resultant compound name and total mass thickness, press the Save button to save the filter data to the ANA file.

7 File Manager

This section of the user manual represents file management utilities within the XRS-FP2 software. Some of these utility workflows are common, and included in other XRS-FP2 workflows.

7.1 GUI Elements of File Manager

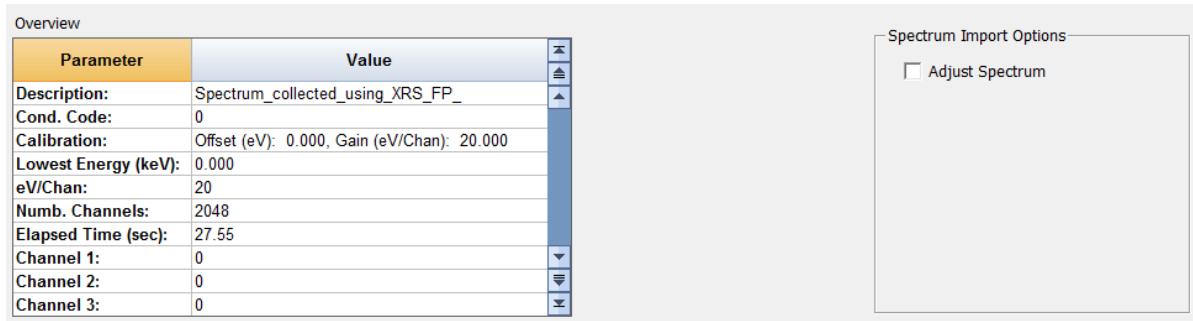
7.1.1 Spectrum Preview



The Spectrum Preview is enabled when the File Type selection in the File Explorer displays a spectrum file type (*.mca). As the customer navigates the File Explorer by selecting a file shown in the filename list, the Spectrum Preview's GUI window is updated with the spectral information. The customer can manipulate the spectral display area (e.g. scroll, pan, zoom, rubber band, etc.) as described earlier in this manual.

If multiple conditions are used, then the “CC” dropdown GUI will be enabled, allowing the customer to change the condition code, thus viewing the condition code’s associated spectrum.

7.1.2 Spectrum Overview



The Spectrum Overview displays the raw data stored in the spectrum file. The values displayed cannot be modified. The user can scroll through the spreadsheet table to examine parameters. In some cases, the right portion of the GUI window may show some optional actions (e.g. Adjust Spectrum), based on the workflow context.

7.1.3 Analysis Preview

The screenshot shows a software interface titled "Analysis Preview". At the top, there is a menu bar with tabs: Overview, Layers, Components, Elements, Coeff., and Conditions. Below the menu is a toolbar with several icons. The main area contains a spreadsheet table with the following data:

#	Lyr	Name	Type	Conc.	Conc. Error	Units	Mole %	Mole % Error
1	1	Cr	Calc	18.7317	0.5096	wt. %	19.9624	0.5431
2	1	Mn	Calc	2.1314	0.1791	wt. %	2.1498	0.1807
3	1	Fe	Calc	63.6547	1.0350	wt. %	63.1617	1.0270
4	1	Ni	Calc	11.9733	0.5634	wt. %	11.3041	0.5319
5	1	Mo	Calc	2.5090	0.0674	wt. %	1.4491	0.0389
6	1	Si	Fixed	1.0000	0.0000	wt. %	1.9730	0.0000

The Analysis Preview is enabled when the File Type selection in the File Explorer displays either an XRF analysis file (*.tfr) or EPXA analysis file (*.edx). As the customer navigates the File Explorer by selecting a file shown in the filename list, the Analysis Preview's GUI window is updated with the analysis definition. The customer can navigate the multi-tab window to see a breakdown of the analysis definition (e.g. layer, components, elements, etc.) along with the analysis conditions. The analysis definition toolbar, located below the multi-tab window, provides the additional features:

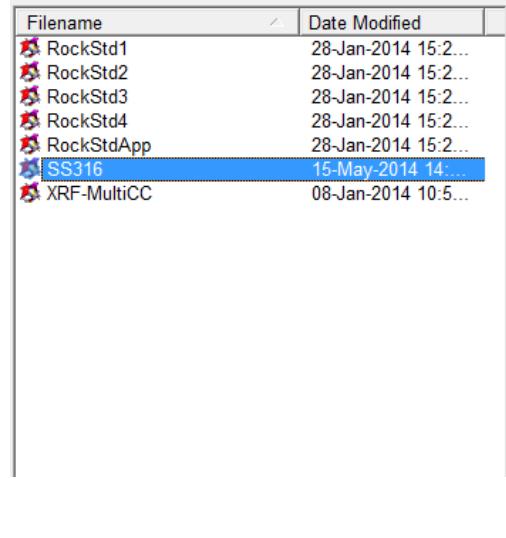
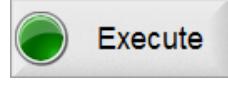
Action	Description
	Disabled - Add a row to the end of the spreadsheet. Not applicable for this workflow context.
	Disabled - Delete a row to the end of the spreadsheet. Not applicable for this workflow context.
	Displays a Print Preview dialog window, which displays a graphical format of the spreadsheet's data
	This button menu allows the spreadsheet's data to be copied to the clipboard in either a) graphical format, or b) text format
	This button menu allows the spreadsheet's data to be saved to a user specified data file. Supported formats include a) Comma Separated Value (*.csv), b) HTML (*.html), c) XML (*.xml), c) Excel 97-2003 Workbook (*.xls), and d) Excel 2007 Workbook (*.xlsx).

All data in the Analysis Preview GUI is considered “read-only” and cannot be modified.

7.1.4 File Explorer

The File Explorer GUI window is broken down into several components, noted below:

Action	Description
Folder: <input type="text" value="C:\CrossRoads Scientific\XRS-FP2\"/> 	Displays the working folder (path). The folder can be changed by the user by either entering a fully specified folder or press the File button, which will a pop-up dialog for the selection of the new working folder. Changing the working folder will automatically trigger an update of the list of files.

	<p>Displays the list of files for the current file type along with the file's last modified date. The user can click on either column header to change the sort order of the files, as depicted by a graphical "triangle". The sort options are:</p> <ul style="list-style-type: none"> (a) Filename Ascending (b) Filename Descending (c) Date Ascending (d) Date Descending <p>In the event that the filename or date is too long, the user can also click on the column divider to resize the column.</p> <p>Changing the file type will automatically trigger an update of the list of files.</p>
<input type="text" value="SS316.tfr"/>	<p>Displays the filename, typically updated when navigating the list of files. The user can optionally enter a fully specified filename (device, path, filename, extension). Please note that depending on the workflow context, this GUI control may not be enabled.</p>
<input type="text" value="XRF-FP/MTFFF Analysis Files (*.tfr)"/>	<p>Selection for the file type. Based on the selection, the File Manager's GUI elements will be updated, along with the list of files.</p>
<input type="text" value="C:\CrossRoads Scientific\XRS-FP\XRS-FP.ini"/>	<p>Defines the location of the INI files used for the legacy software. Default file folder (path) of the INI file are:</p> <ul style="list-style-type: none"> (a) XRS-FP - C:\CrossRoads Scientific\XRS-FP (b) XRS-MTFFF - C:\CrossRoads Scientific\MTF-FP (c) EPXA - C:\CrossRoads Scientific\EDS_Quant
 Execute	<p>This button performs the workflow "action". For example, if the workflow is Load, then the Execute button will load the selected ANA file into XRS-FP2's program memory.</p>

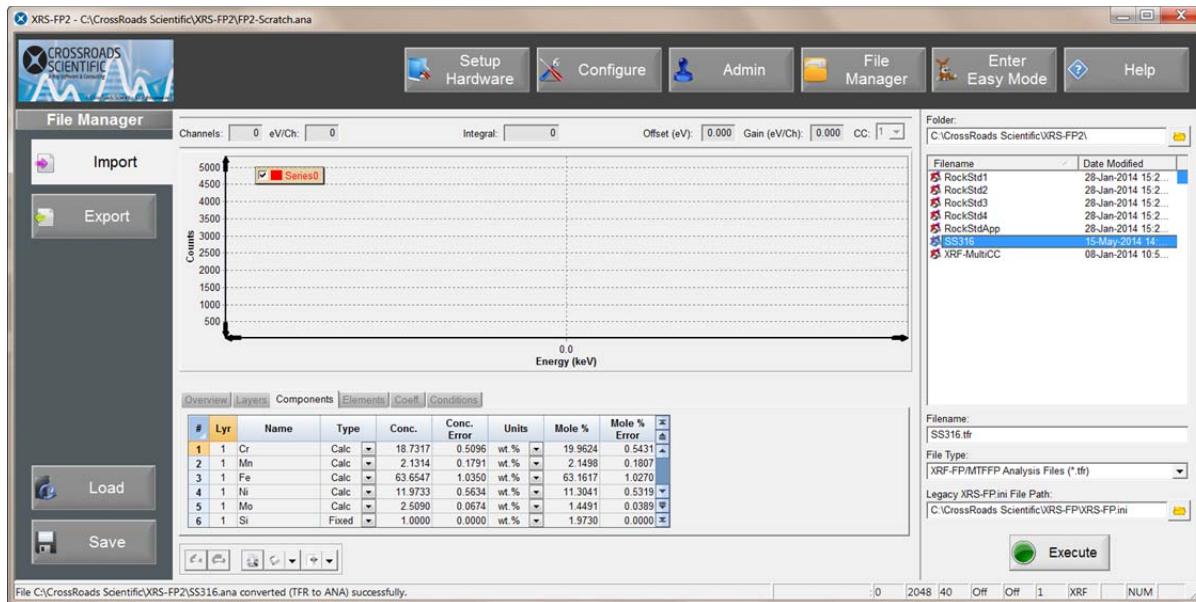
7.2 Import

This section of the manual is applicable to those customers who have the Crossroads Scientific older software products. If you do not have the older software products, then feel free to skip this section of the manual.

The Import feature within XRS-FP2 provides the following capabilities:

- (a) Import legacy XRS-FP (XRS-MTFFF) XRF analysis files, including the analysis parameters stored in XRS-FP.ini.
- (b) Import legacy XRS-EPXA analysis files, including the analysis parameters stored in QSEM.ini
- (c) Import stand-alone spectrum files (*.mca).

An example of the Import GUI is shown below:



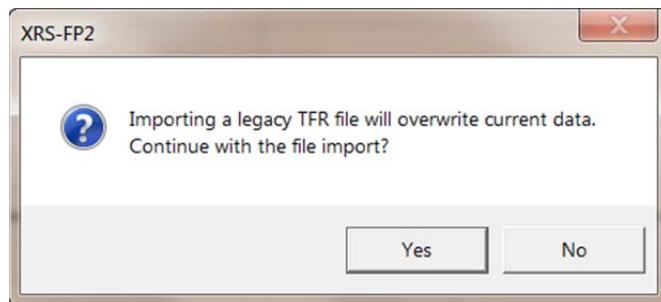
As noted earlier in the manual, the XRS-FP2 software essentially merges together the analysis definition and a spectrum into a single, resultant analysis file (*.ANA). The Import feature can accommodate single condition or multi-condition analysis.

When performing an Import of the legacy data, the sequence order is very important. If order of the sequence is not followed correctly, the resultant analysis file (*.ANA) may not be correct.

Single Condition

To perform a Single Condition Import, please follow these steps:

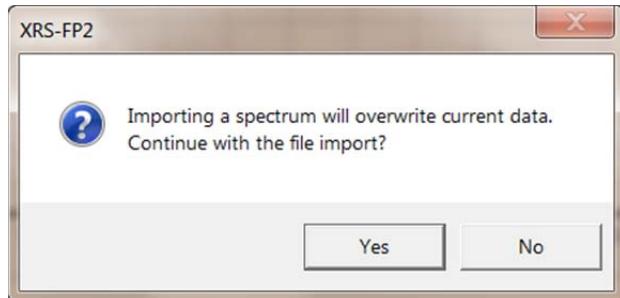
1. Select the folder (path) of the INI file for the legacy Crossroads software products.
2. Select the working folder (path) of the legacy analysis files
3. Ensure that the File Type is set to Analysis Files – XRF Analysis (*.tfr). In the case of EPXA analysis mode, then EPXA Analysis (*.edx).
4. From the list of files, select the desired file to import.
5. Press the Execute button. At this point, the following GUI prompt will appear:



Selecting the Yes button will convert the legacy analysis file (and the associated INI parameters) into XRS-FP2's program memory. Pressing the No button will abort the Import sequence.

6. Optionally, if there is an existing spectrum that corresponds to the analysis, then perform the following additional steps:
 - a. If required, select the working folder for the location of the spectrum files.

- b. Ensure that the File Type is set to Spectrum Files. At this point, the File Manager's Spectrum Preview and Spectrum Details Panel GUIs will be shown.
- c. From the list of files, select the desired file to import. As the user is navigating the list of spectrum files, the Spectrum Preview and Spectrum Details Panel GUIs will be reflected the contents of the file.
- d. Optionally, if the spectrum requires adjustment, select the checkbox on the Spectrum Overview GUI panel.
- e. Press the Execute button. At this point, the following GUI prompt will appear:



Selecting the Yes button will import the spectral information, merging it into XRF-FP2's program memory. Pressing the No button will abort the Import sequence; however, the previously imported legacy analysis data will still be in XRS-FP2's program memory.

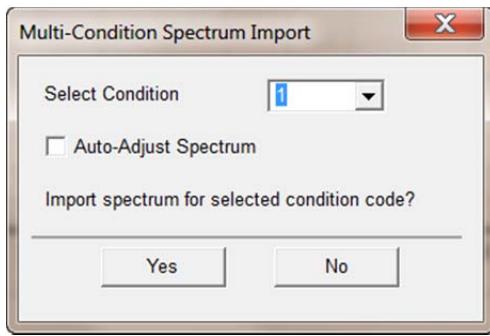
7. At this point, all legacy data has been imported into XRS-FP2's program memory. Now, the customer should save the data to file, via the Save button, described later in this manual.

Multiple Condition

In general, the Multiple Condition Import is almost the same as the Single Condition Import. The only difference is that the customer will add the associated spectrum for each condition code.

To perform a Multiple Condition Import, please follow these steps:

1. Follow the same steps 1-5, as described for the Single Condition Import.
2. Optionally, if spectra are to be added, then follow step 6a-6c; however, when you press the Execute button, you will see the following GUI prompt:



In the above dialog window, select the condition code that is to be associated with the spectrum to import. Optionally, if a Spectrum adjustment is to be performed on the imported spectrum's file data, then set the checkbox.

Now, pressing the Yes button will import the spectral information, merging it into XRF-FP2's program memory. Pressing the No button will abort the Import sequence; however, the previously imported legacy analysis data (and possible spectra) will still be in XRS-FP2's program memory.

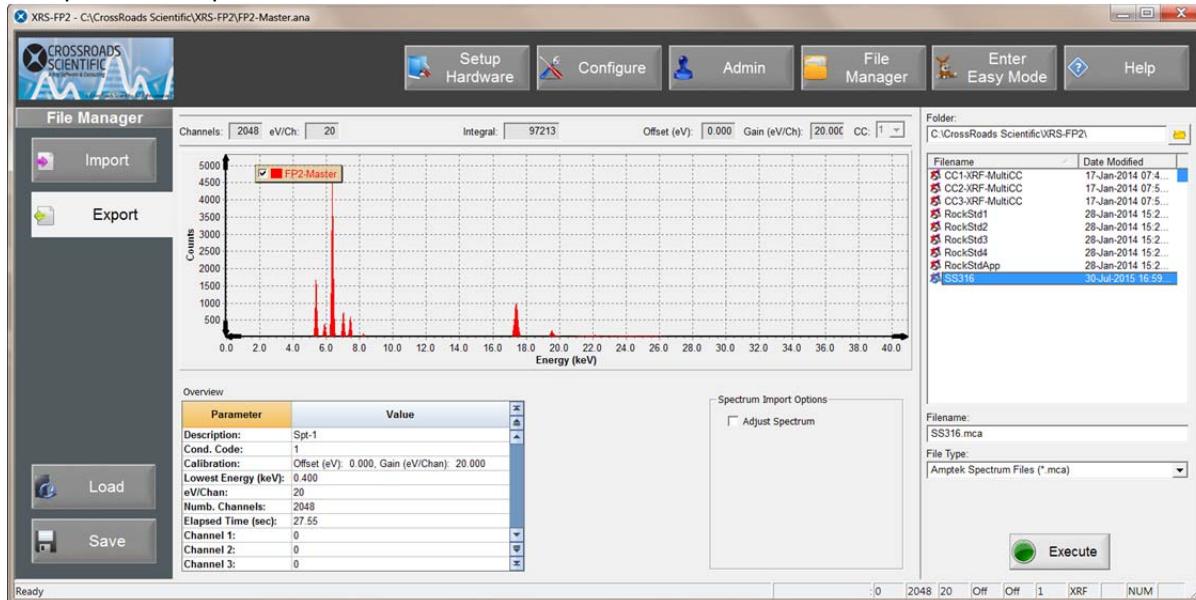
3. Repeat the above step 2, for all condition codes for the association of all spectrum files.
4. At this point, all legacy data has been imported into XRS-FP2's program memory. Now, the customer should save the data to file, via the Save button, described later in this manual.

Lastly, the Import workflow is a common feature that is combined with other XRS-FP2 workflows (e.g. Standards).

7.3 Export

The Export feature within XRS-FP2 provides a means to extract the spectral information from the analysis file (*.ana), and save it to an external, stand-alone spectrum file format.

An example of the Export GUI is shown below:



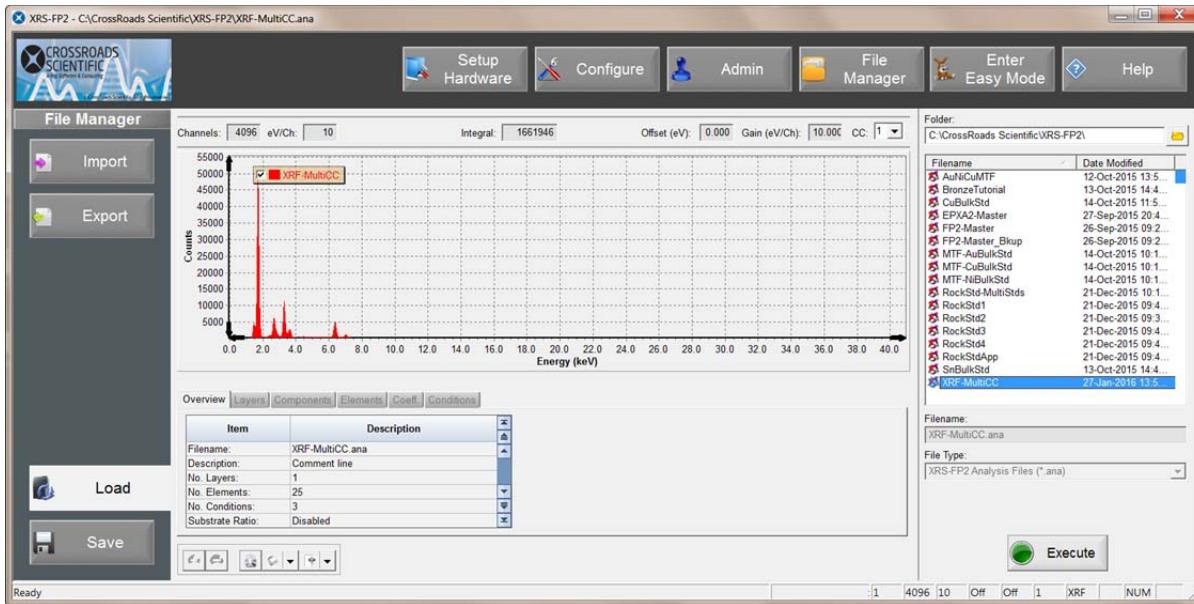
The Export GUI will display, within the Spectrum Preview and Overview, the spectral information contained within XRS-FP2's program memory. To Export the spectrum, enter the filename within the File Explorer's Filename edit GUI control and press the Execute button.

In the case of Multiple Conditions, where there is typically a spectrum associated with each condition code, the user should first select which condition code's spectrum is to be exported via the "CC" dropdown GUI control. Once the desired spectrum is shown in the Spectrum Preview and Overview GUI, then enter the filename and press the Execute button.

7.4 Load

The Load feature within XRS-FP2 provides a means to load a pre-existing analysis file (*.ana) into XRS-FP2's program memory.

An example of the Load GUI is shown below:



As noted earlier in the manual, as the user navigates the list of files in the File Explorer, the Spectrum Preview and Analysis Preview GUIs are updated. In the selected analysis file contained multiple condition codes, then the “CC” dropdown GUI control would be enabled, thus displaying spectrum associated with the condition code. It is possible that the Spectrum Preview GUI might not display a spectrum, as is the case, if the spectrum was not acquired (or cleared), not imported, or there is no sample definition (i.e. new analysis).

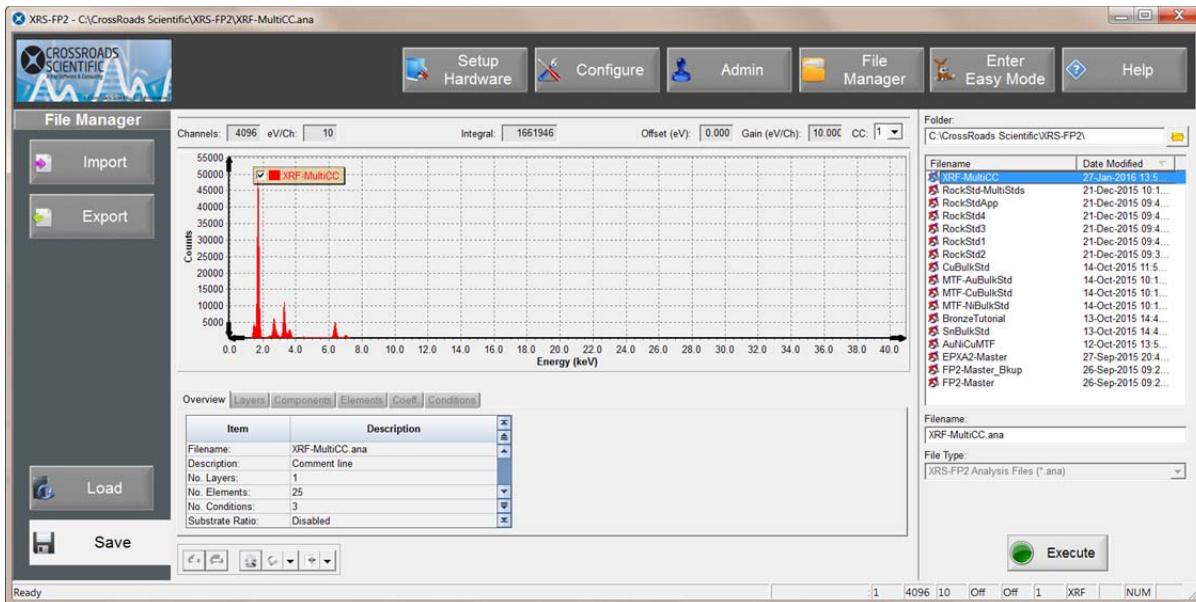
To perform a Load within XRS-FP2, select from the list of files, the desired analysis to load. Next, press the Execute button to load the file based analysis data (and spectrum, if it exists) into XRS-FP2’s program memory.

Lastly, the Load workflow is a common feature that is combined with several other XRS-FP2 workflows (e.g. Analyze).

7.5 Save

The Save feature within XRS-FP2 provides a means to save the contents of XRS-FP2’s program memory to disc based file.

An example of the Save GUI is shown below:



The Save feature shows the existing spectral data in the Spectrum Preview GUI and the analysis definition and conditions in the Analysis Preview GUI. In the case of multiple condition codes, the user can navigate each condition's code spectrum via the "CC" dropdown GUI control.

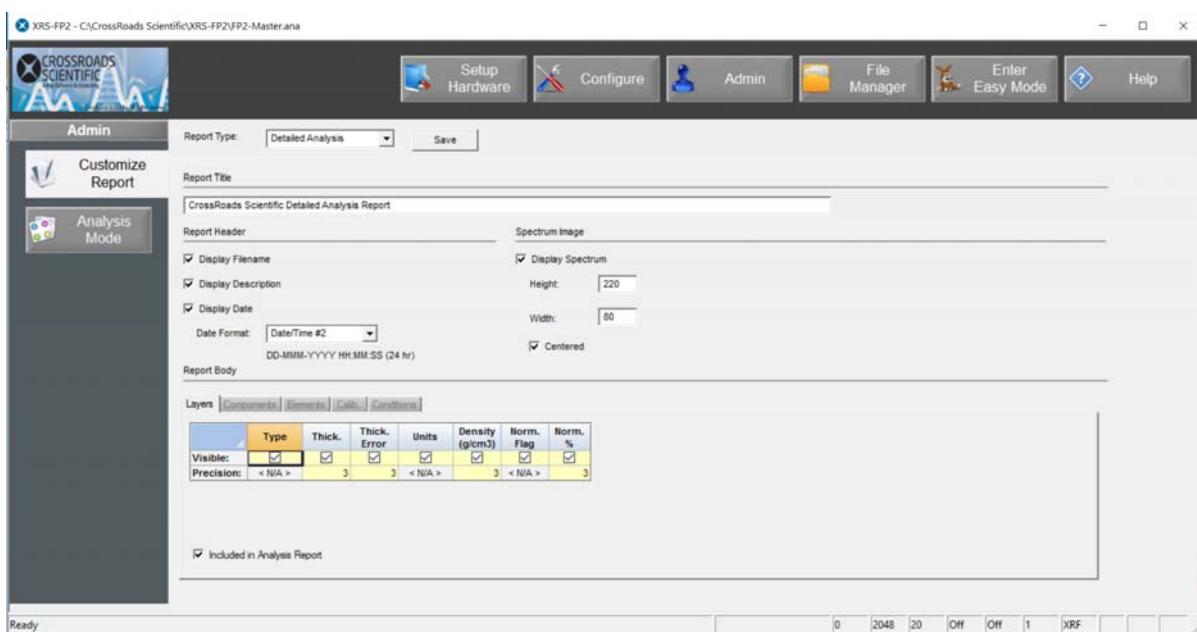
To perform a Save within XRS-FP2, select from the list of files to overwrite an existing file, or enter a new filename within the Filename edit GUI control. The file extension is not required. Once you have entered the filename, press the Execute button to save XRS-FP2's program memory to the named file. Once the file has been saved, the list of files, within the File Explorer will be updated, sorted by descending date (i.e. most recent file at the top of the list).

8 Admin

This section of the user manual describes the Admin capabilities within the XRS-FP2 software, including report setup and analysis mode options.

8.1 Customize Report

The Customize Report feature allows the user to select the Report Type, which includes Concise Analysis, Detailed Analysis, Element ID, Spectrum Regions, DPP-MCA Parameters and Instrument Parameters. The Report Title can be entered and the user can select which Report Header and Spectrum Image options and parameters to display. In addition, the user can customize the Report Body, including which parameters to display for the Layers, Components, Elements, Calibration and Conditions information. These options can be included in the Analysis Report if desired. See the figure below.



8.2 Analysis Mode

The Analysis Mode feature allows the user to view the current analysis mode being used in XRS-FP2, as well as the HASP security information associated with the user's HASP key. If the user has purchased both XRF (Bulk and/or Multi-Layer) as well as EPXA options, then the user can switch between analysis modes in this area of the software. For example, if the user is working in XRF mode but desires to switch to EPXA mode (assuming both XRF and EPXA options have been purchased), the user simply selects the radio button for EPXA followed by the Apply button. The software will ask if you want to change analysis mode at this point. If the user selects "Yes" the XRS-FP2 software will close and then automatically restart in EPXA mode. This is a new feature associated with XRS-FP2. Unlike the previous versions of CrossRoads Scientific's software, where each analysis mode had a different software package, XRS-FP2 integrates all software packages into one platform. Now the user has the ability to readily switch between one mode and another depending on the purchased software options associated with the customer's HASP key.

9 Easy & Expert Modes

XRS-FP2 allows the user to operate in two different modes: Easy Mode and Expert Mode. In Expert Mode, the user has access to all areas of the software, including application setup, analysis, batch mode, admin, file manager and hardware setup and configuration. Note that some software options vary depending on the purchased HASP key options (i.e. MLSQ, etc.). In Easy Mode, the user has less options and it is assumed that both the hardware setup and application have already been defined in Expert Mode.

9.1 Easy Mode

Easy Mode is designed to be used with hardware that has been previously setup and calibrated by an expert user. In addition, the application (components, elements, layers, processing conditions, etc.) can be setup in advance (in Expert Mode), saved as an *.ANA file and then used for routine analysis. Easy Mode allows a less experienced user to run routine analyses using a previously setup and defined system. In this mode, the user has the option to Acquire spectra, perform an Energy Calibration, run Element ID, Quantify samples, Load and Save files and access the Help documentation.

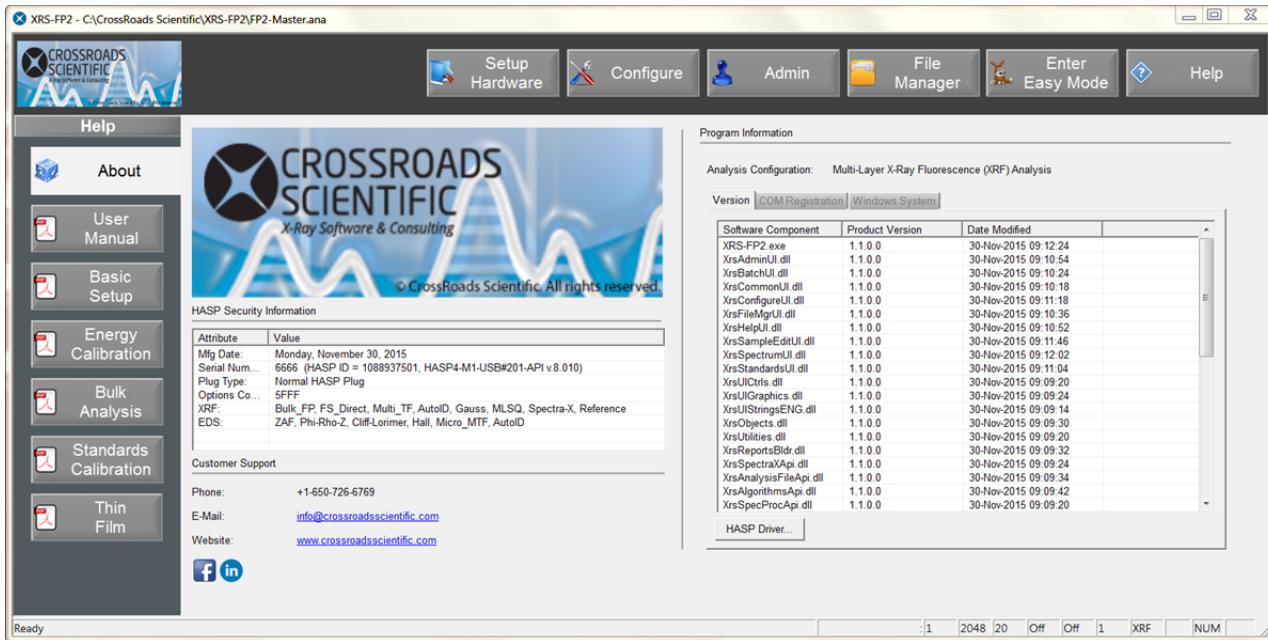
9.2 Expert Mode

Expert Mode allows the user to access all areas of the software, including application setup, analysis, batch mode, admin, file manager and hardware setup and configuration. Note that some software options vary depending on the purchased HASP key options (i.e. MLSQ, etc.). This mode is designed to be used by the more “expert user” and allows access to all capabilities and functions of the software, including hardware setup and configuration.

10 Help

This section of the user manual describes the built-in program information and the display of various PDF files via an Adobe Reader “plug-in”. For more details on how to use Adobe Reader, please visit the Adobe website (www.adobe.com).

10.1 About



The above screenshot shows the following information:

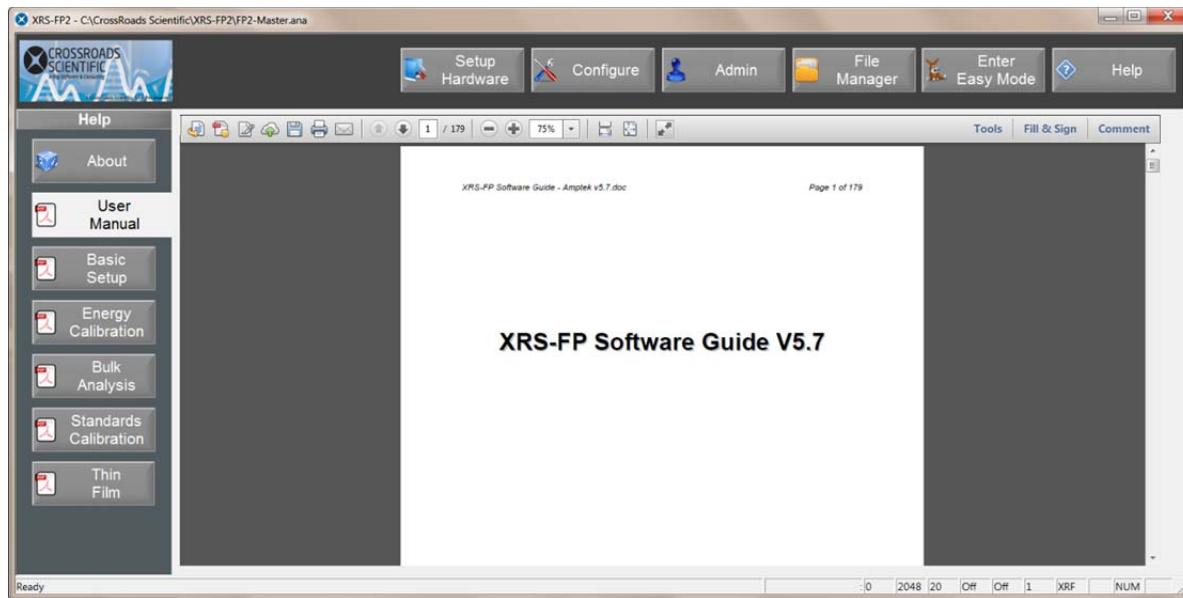
- HASP Security Plug status and licensed features.
- Customer Support information.
- Analysis Configuration – either:
 - Single Layer X-Ray Fluorescence (XRF) Analysis
 - Multi-Layer XRF Fluorescence (XRF) Analysis
 - Electron Probe X-Ray Analysis (EPXA)
- Program Information “tabbed” GUI:
 - XRS-FP2 software components versions. In addition, if the customer presses the HASP Driver... button, the HASP drivers software version information will be displayed in a separate pop-up window.
 - XRS-FP2's COM components - version and registration path information.
 - Windows System information.

In addition, when XRS-FP2 is launched, it automatically creates files that also contain the same program information. These ASCII text files are located in the same folder as the XRS-FP2.exe program and are named as follows:

- XRS-FP2_Versions.txt
- XRS-FP2_OleRegistration.txt
- XRS-FP2_SystemInfo.txt

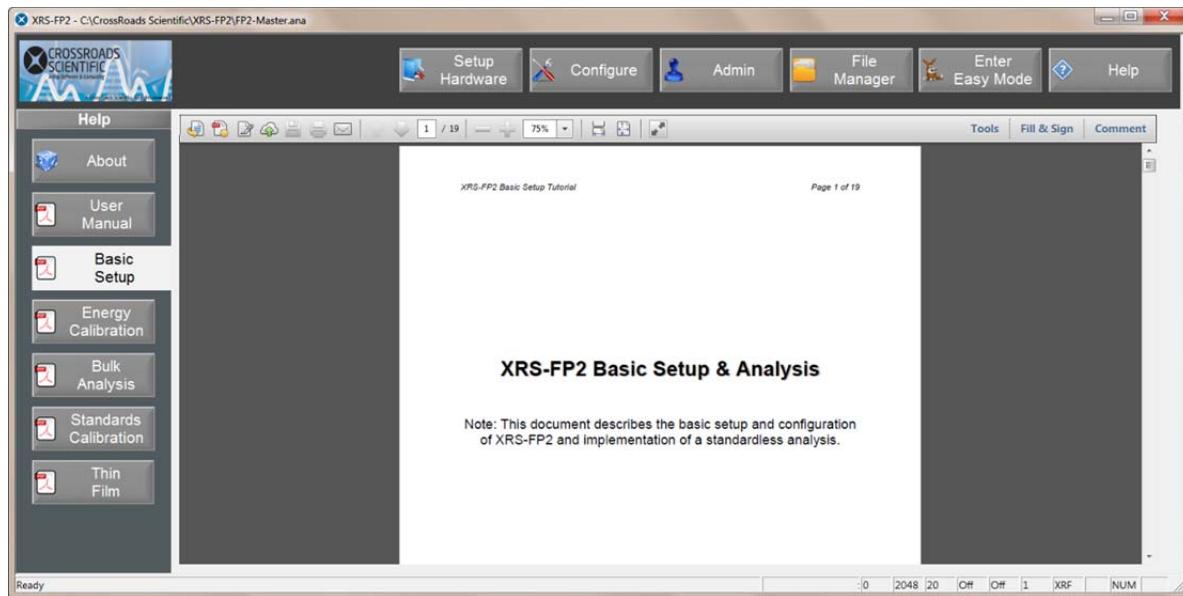
When requesting customer support with CrossRoads Scientific, it is recommended that these files be included with any support request.

10.2 User Manual



Selection of the User Manual button displays the “XRS-FP2 User Manual”.

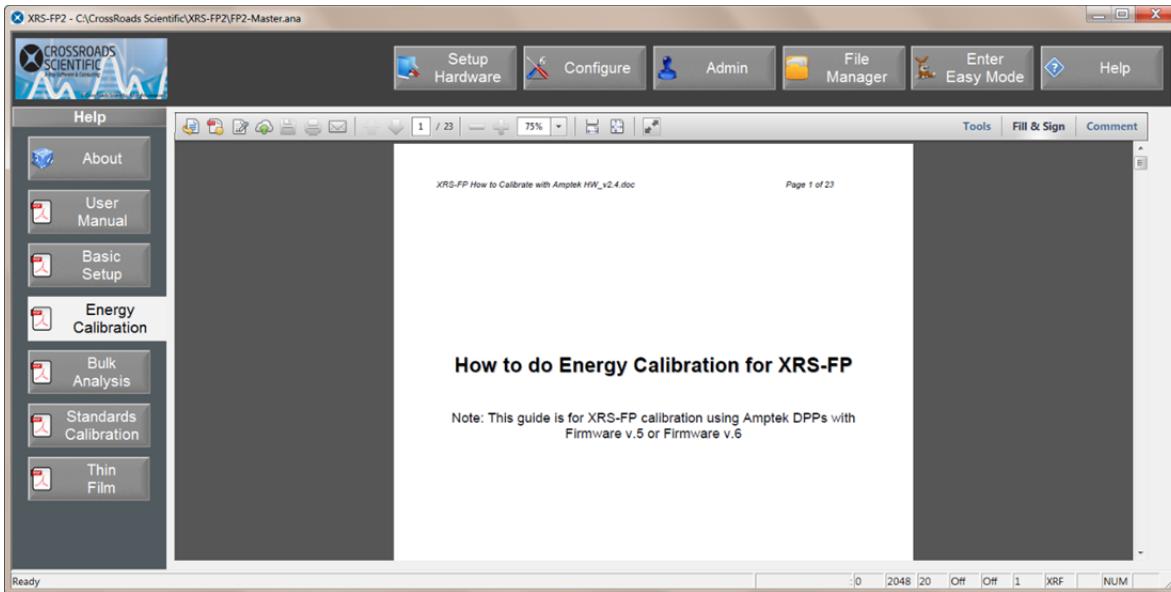
10.3 Basic Setup



Selection of the Basic Setup button displays the “XRS-FP2 Basic Setup & Analysis Tutorial”. This tutorial is the primer for XRS-FP2 and should be the initial document to review when first using XRS-FP2.

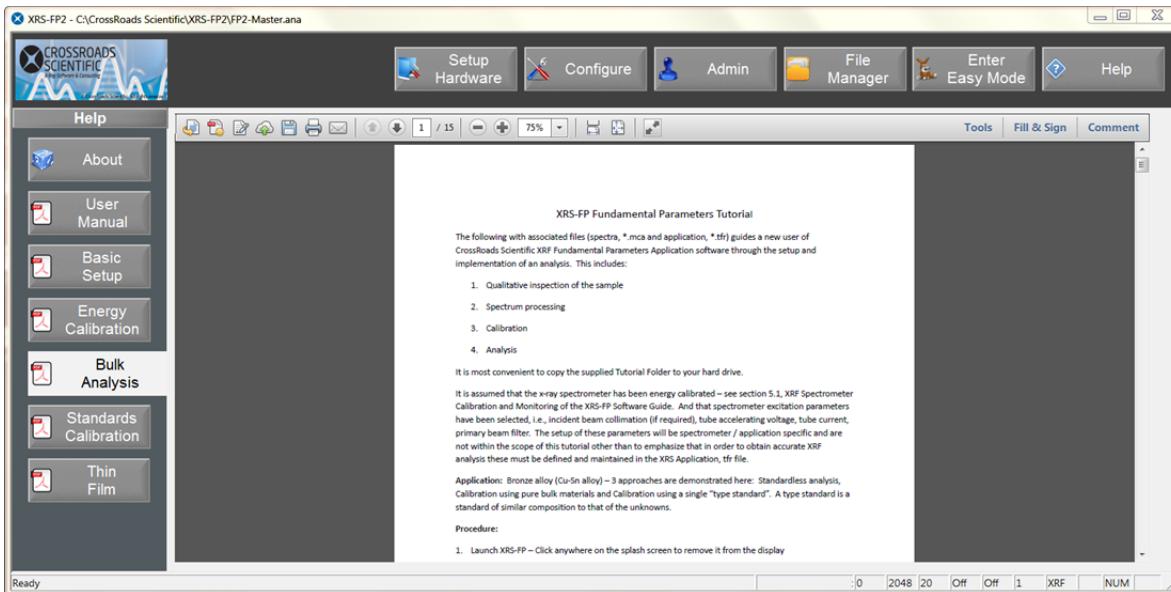


10.4 Energy Calibration



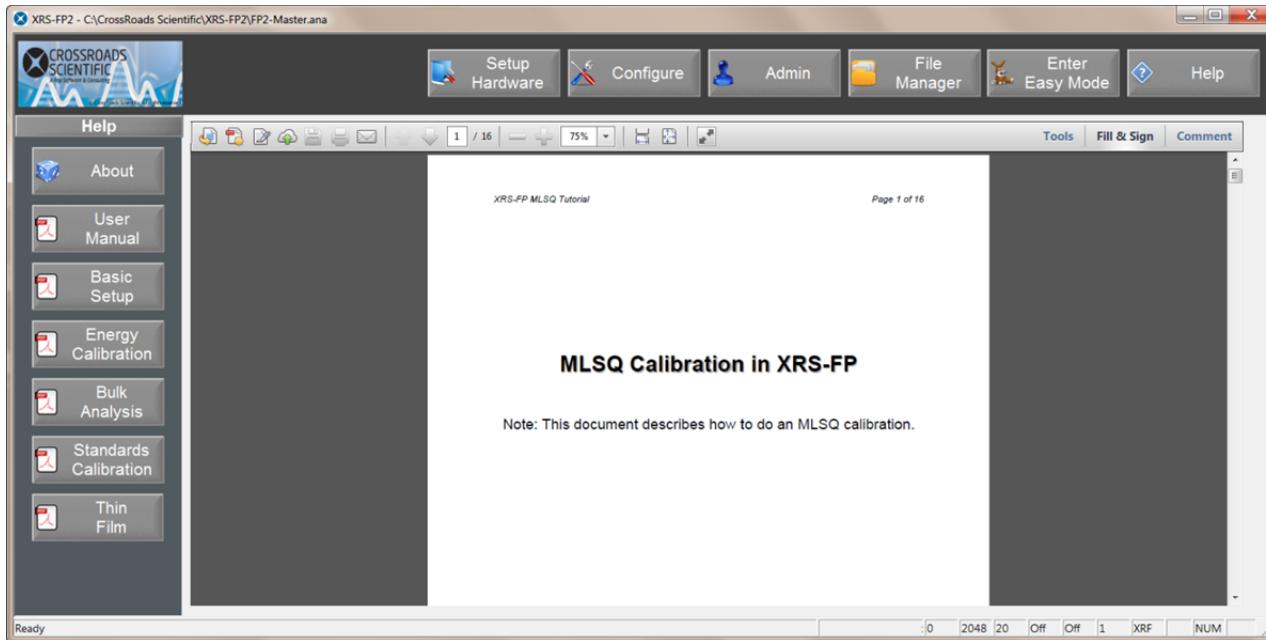
Selection of the Energy Calibration button displays the “How to do Energy Calibration for XRS-FP2”.

10.5 Bulk Analysis



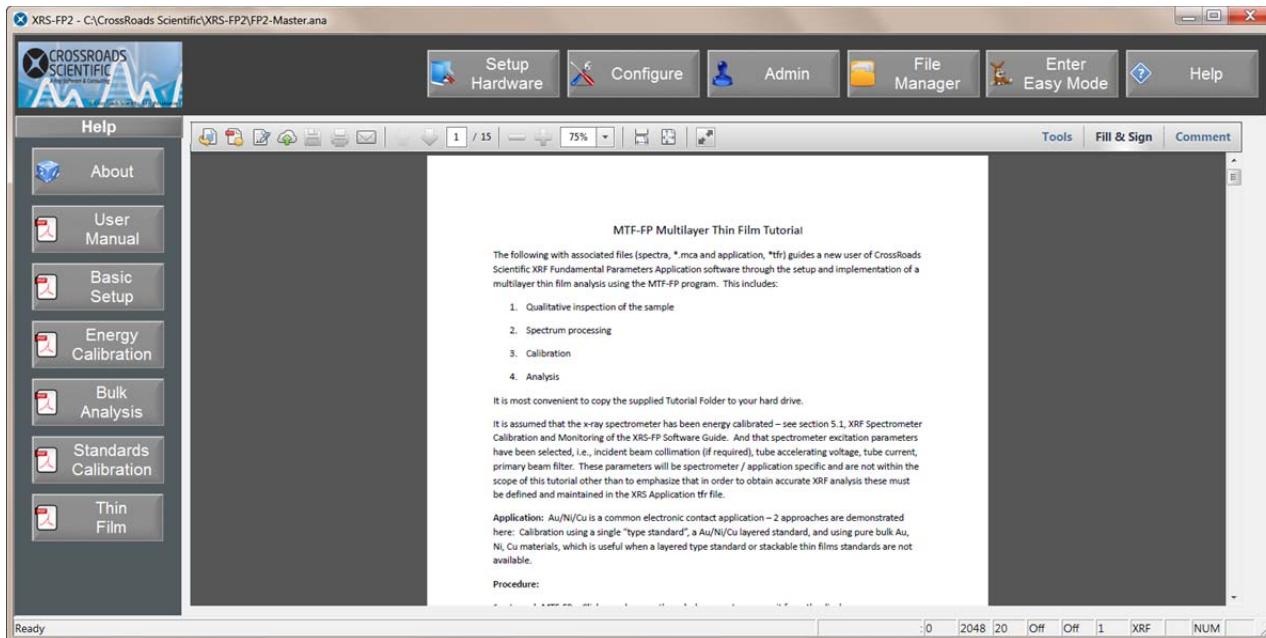
Selection of the Bulk Analysis button displays the “XRS-FP2 Bulk Analysis Tutorial”.

10.6 Standards Calibration



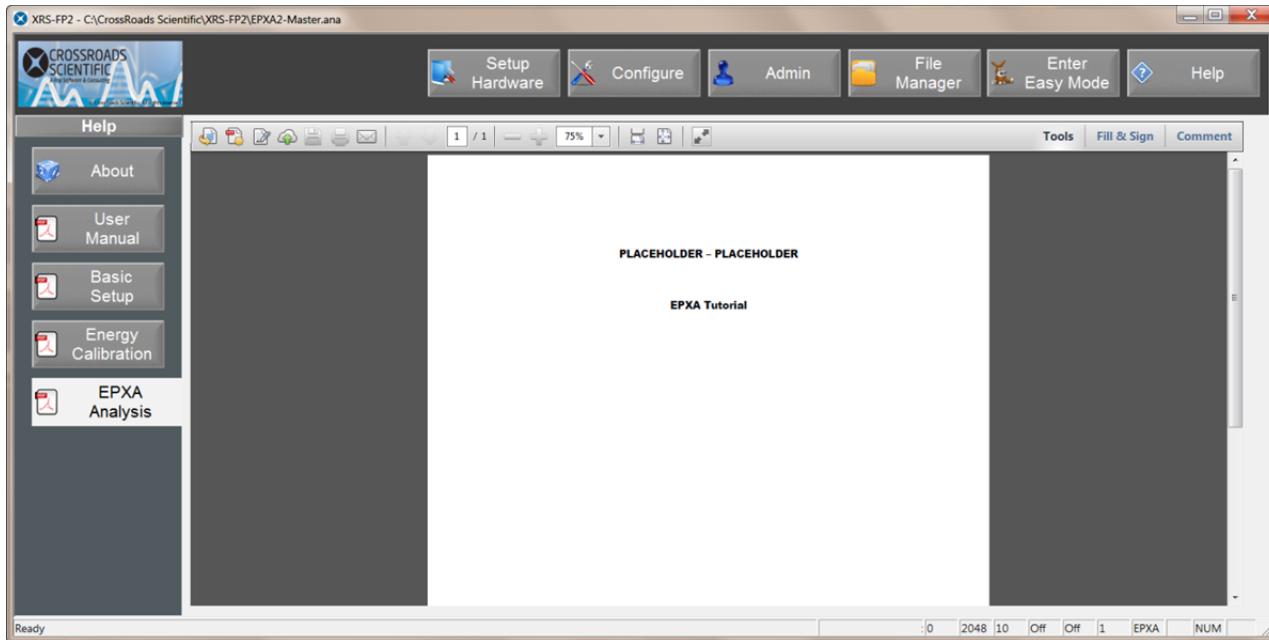
Selection of the Standards Calibration button displays the “XRS-FP2 Standards Calibration Tutorial”. This tutorial is further divided into sub-sections, which a) Multiple Least Squares (MLSQ) using FP (or MTFFP), b) Simple Least Squares, and c) Scatter Intensity Ratio (SIR) calibrations.

10.7 Thin Film



Selection of the Thin Film button displays the “XRS-FP2 Thin-Film Tutorial”.

10.8 EPXA Analysis



In XRS-FP2's EPXA analysis mode, the Selection of the EPXA Analysis button displays the "XRS-FP2 EPXA Tutorial".

11 XRF Analysis with XRS-FP2

11.1 XRF Single-Layer Bulk

Simply, the purpose of XRF analysis 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%.

The calculations take full account of all the absorption, fluorescence and scattering effects that occur when x rays interact with the sample, using the so-called FP equations. This is further described in the references at the end of this section. Analysis can be performed for all elements from H through Fm, using K, L or M lines in the energy range from 0.05 keV up to 120 keV.

Up to 8 excitation conditions can be used for a single sample analysis. Each excitation condition can vary almost any analysis setup, including the kV, acquire time, tube (or secondary) target, detector type, detector or tube filter, source focusing optic, atmosphere (air, vacuum, helium), and spectrum processing steps (e.g., deconvolution type, background removal, sum and escape peak removal).

When more than one excitation is used, at least one of the elements for each condition must be calibrated. Calibration factors may be generated using any type of standard (e.g., pure element or analytical “type” standard). A single “type” standard may be used, or the calibration may be done with a different standard for each element, or any combination of standards may be used. If not all the elements are calibrated, the missing calibration coefficients are derived from the existing ones by interpolation.

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

The standard XRS-FP2 software can be used for bulk or single-layer samples. In addition to this, there is a software option for multilayer analysis mode, which will support multilayer samples with up to 8 layers. Both the standard and multilayer software can calculate bulk composition and thickness analysis for up to 50 elements, calculated as either elements and/or compounds. The FP analysis software supports a single or multiple standard calibration scheme, or completely standardless analysis if the tube, detector, environmental and geometry parameters are known. After each calibration step, a set of calibration coefficients is generated, which should then be saved for later use in routine analysis.

Results can be normalized to any value, and MUST be normalized for standardless analysis or when the layer thicknesses are calculated. Elements (or compounds) can be calculated, fixed, or determined by difference. Elements can also be determined by stoichiometry from the compound formulae. Composition results can be calculated in units of Wt% or ppm, and for thin films, units such as ug/cm² and mg/cm² are used for

mass thickness. The latter can be converted to thickness (microns, microinches, nm, etc.) if the density is known. The density may be input or optionally calculated theoretically.

All the appropriate FP calculations are made both during calibration and for quantitation. Tube spectra, required for the direct fluorescence calculations, can be supplied by the user, or calculated from built-in models (Ebel, Pella et al.). These tube spectra can be convolved with experimental transfer functions to derive the expected tube spectrum passing through an optic such as a polycapillary bundle. The software can model different x-ray tube types (“reflection” or transmission), using either of the two analytical models, or by the use of a supplied source spectrum, for complete polychromatic source modeling. Different tube windows and filters may also be included. The tube window can be of any composition (e.g., BeO or glass), and may consist of several layers or coatings. Any tube anode element may be specified, as well as the tube (electron) incidence and take-off angles. The kV may range from 3 to 60 kV. Provision is provided for including a transmission efficiency file for use with, for example, polycapillary optics placed between the source and the sample.

Radioisotopes can be used, using a source file describing the relative line ratios. For secondary target excitation, monochromatic excitation is assumed.

The presence of air paths will also be calculated from the input geometry parameters, for both the source and detector paths. Single-element filters can also be inserted between the tube and the sample, and/or between the sample and the detector, and the software can accommodate both. The complete system geometry must be specified, including the sample incidence and take-off angles, the source-to-optic and/or source-to-sample distances, and the sample-to-detector distance.

Many detectors and windows can be fully modeled. This is necessary for standardless analysis, which is only possible when a single excitation condition is used. The detector parameters (window, thickness, etc.) are used to calculate the various absorption and efficiency effects when x rays pass through the window and get absorbed in the detector material. Although this is only strictly necessary when doing standardless analysis, the calculations are always done this way for consistency, and this also makes it easier to compare calibration coefficients between elements. If the theory and the FP database were perfect, all the calibration coefficients would have the same value. In practice, differences should be relatively small, especially in comparison with coefficients that did not fully compensate for the detector efficiencies. Usually when calibrating elements that all use the same line series (e.g., K), the coefficient variation is small (< 30%), but is often larger when calibrating from mixed lines (e.g., K and L) because it is difficult to make absolute calculations that include the line series information (e.g., fluorescence yields).

It is not necessary to collect pure-element spectra for FP analysis, as no direct ratioing is necessary for the elemental intensities in this software. The calculations are done this way to make it easier to do standardless analysis. Of course, it is possible to use pure-element standards if desired, and the complete FP calibration may be done this way, without any “type” standards being used at all. This is useful if the analyst does not have type standards readily available.

Both direct and secondary fluorescence effects are considered in the FP calculations. For thin-film analysis, secondary fluorescence both internal to the layer (intralayer) and external to each layer (interlayer) are considered, for all possible layers in the sample. This is the most complex calculation of all the FP interelement effects, and takes the longest time. Included in the FP database are all the required parameters to calculate or recall absorption coefficients, fluorescence yields, jump factors, Coster-Kronig transitions, line energies, line ratios, etc.

11.2 XRF Thin-Films

Thin-film thicknesses can be calculated either by fluorescence of the element(s) in the layer (the default mode), or by absorption. The latter is typically done by measuring fluorescence signals from a substrate (although it could be a thin film) under the layer in question. No attention is then paid to calculating the thickness by fluorescence by that layer, although the fluorescence signal may be used to calculate the layer composition. In the case where the layer thickness values are calculated by BOTH absorption AND fluorescence, this is termed as the “substrate ratioing” method. Because this is (usually) an over-determined system, the two sets of calculations can be “compared” or “ratioed” such that the effective tube flux is now allowed to float so that the calculations by the two methods come to an agreement for the thickness values.

When using calibration coefficients they must be non-zero. However, if some of the coefficients are missing (i.e., set to zero), then they will automatically be calculated from the existing coefficients for the other elements that are to be analyzed the way. When calculate calibration coefficients like this, “on-the-fly,” there are certain criteria that must be met. These include:

- (a) The target (tube) for the coefficient must match that for the analyte, and
- (b) The excitation kV for the coefficient must match that of the analyte, and
- (c) The elemental weight fraction for the coefficient must match that of the analyte, and
- (d) The coefficient, to be used for the calculation of missing coefficients, must be non-zero.

After assembling one or more of these coefficients from other analytes, a calculation is made for the missing coefficient. This calculation weights the nearest neighbors (i.e., closest atomic number, Z) to get an average value to be used for the missing coefficient.

When no calibration coefficients are defined, i.e., they are all zero, then this is treated as Standardless analysis, and the rules for the latter’s usage must be fulfilled. That is, there can be only one analysis condition, and the film thickness must be known (Fixed) or infinite. Again, for standardless analysis, no components can be derived by Difference, and the results must always be Normalized.

When using calibration coefficients, both film thicknesses and layer compositions can simultaneously be determined, provided that the complete layer composition is known, or calculated, so that the total concentration for each layer adds up to the Normalization Total (usually 100%, but can be any value \leq 100%). The previous sentence is true provided that any given element only occurs once in the multilayer sample definition. There are certain cases where an element can occur twice, and still be analyzed, and that will be discussed below.

Also, note that the sample must be defined in terms of the layer structure (up to 8 layers, including an infinite base or substrate), and the components in each layer. These components can be compounds or just elements. Any number of components can be Fixed in composition, and any number of layer thicknesses can be Fixed. If a component is defined as a compound (e.g., TiN), then any elements that are NOT analyzed (i.e., their atomic number is below the lowest element analyzed, or they are defined as being out in some other way) will be determined by stoichiometry (i.e., by the compound formula). For example, in the case of TiN, where the Ti is analyzed, the N concentration will be determined from the 1:1 atomic correspondence between Ti and N. It is always necessary in FP analysis to know the complete sample composition because all elements will have an effect on the matrix corrections.

Now let’s consider a different case where a compound has 2 (or more) elements that are BOTH analyzed. An example might be CoSi₃, where both Co and Si are analyzed. In this case, the composition of the

component CoSi₃ can be determined from both analytes and so the problem is overdetermined. The analysis then employs a least-squares method to get an “average” analysis based on both elements, where the weighting is related to the intensity of each element.

In the case where there is an element in more than one layer, there are several situations that are possible to solve. Without some additional information, the common-element problem has one too many unknowns. To solve this situation, the caller can Fix one of the element compositions (in one of the layers), or Fix the layer thickness (or both). For example, in the sample Cr/Mn-Cr, the top Cr layer can have a Fixed thickness, and so it is possible to arrive at a solution for the composition and thickness of the under layer.

A special case of this is when the substrate is infinite (i.e., a known thickness). For example, Cr-Fe/Fe can be solved when the underlying layer (Fe) is a bulk (i.e., infinitely thick with respect to incoming and exiting x rays).

There is one alternative method of analysis that can give an additional degree of freedom. It is possible to analyze elements either by fluorescence, or by absorption. Almost always each element is calculated by its fluorescence signal. However, it is possible to determine one layer thickness by Absorption, provided there is a signal penetrating that layer from an underlying layer, which would usually be a substrate. It is best if the substrate composition is known and “Fixed”, but it is possible to calculate both the layer thickness and the substrate composition. This is similar to the case above for Substrate Ratioing, but the application is different.

Because it is not possible to calculate the film thicknesses and composition by a direct calculation, it is necessary to use an iterative technique. This technique uses the “forward” calculation of the elemental intensities from a “known” sample definition. Of course, when one wants to analyze an unknown, this definition (thicknesses and composition) is not known. Therefore, the MTFFP software uses an iteration technique to arrive at the best solution. Starting with relatively crude estimates of thicknesses and composition, the software starts to calculate the intensities on the basis of the first estimate, and then compare the generated intensities with the measured ones. From this comparison a better estimate is made of the sample composition, and the process repeats until the thickness and composition changes are within certain criteria. As one can imagine, because both the thickness and composition are changing simultaneously during this iteration process, the calculations are quite complex and the convergence may be quite slow for complex samples. For simple (e.g., bulk) samples, the convergence often occurs in 3-4 iterations, whereas for complex multilayer samples the convergence may require many tens of iterations.

One of the more complex situations is where there is a common element. Because this introduces an additional complexity, the convergence can be slower than a comparable sample without the common-element problem.

In the present version of the software, the maximum number of iterations is set to be 50 for the multilayer sample case. If this value is exceeded an error return is generated (see below). However, it is still possible than the returned values of thickness and composition are good, but there is an uncertainty since the final convergence was not reached.

The criteria for convergence are as follows:

- (a) For compositions > 1%, the relative composition change must be < 0.02%,
- (b) For compositions ≤ 1%, and > 0.0001%, the relative composition change must be < 2%,
- (c) For compositions ≤ 0.0001%, the convergence criterion is not applied,

- (d) For mass thicknesses < 0.02 or > 50 mg/cm², then the relative thickness change must be < 1%,
- (e) For mass thicknesses < 0.2 or > 5 mg/cm², then the relative thickness change must be < 0.2%,
- (f) For mass thicknesses ≥ 0.2 and ≤ 5 mg/cm², then the relative thickness change must be < 0.05%.

If the calibration mode uses one of the methods where the calibration coefficients are a function of thickness and/or composition (i.e., iCalMode > 2), then the coefficients are recalculated during each iteration.

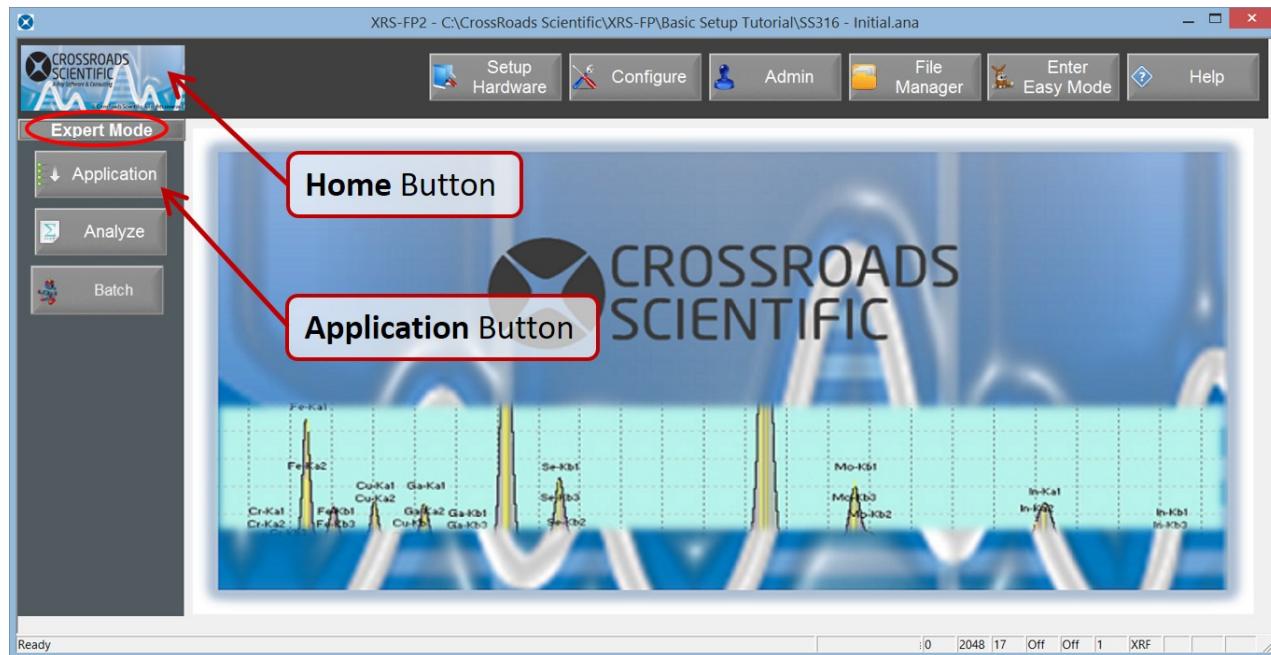
At the end of the calculations, the composition errors are estimated from the intensity errors and the calibration coefficient errors, by adding the relative errors in quadrature. Then the elemental composition errors are propagated to the components, to calculate the relative errors on a component basis. No effort is made to generate error estimates for the thickness calculations.

11.3 Supported Hardware

TODO – Insert Here – Line 1

12 Application Workflow

The **application workflow** is where the application and methods are defined. From the **Home** screen (Expert Mode) select the **Application** button (see figure below).



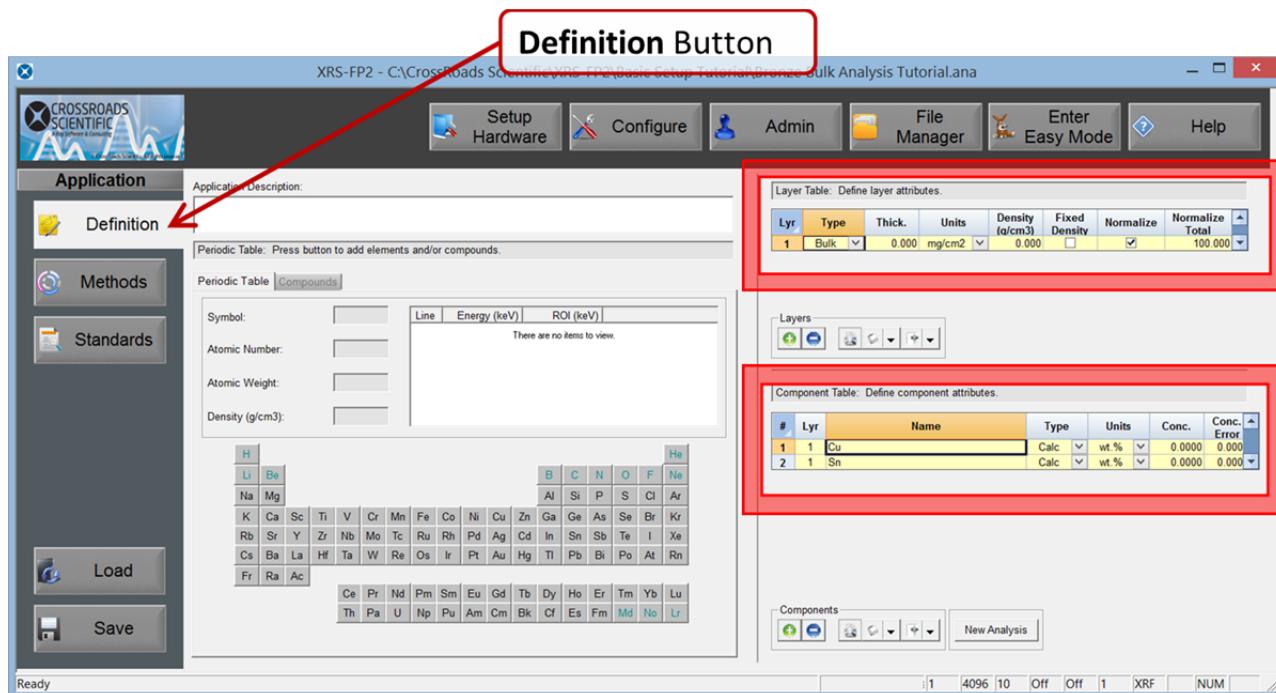
12.1 Definition

The definition page consists of two tables in the R-hand panel for application data entry (see figure below).

The two tables are:

- Layer Table - definition of the (mass) thickness of the sample, if known, and layer attributes
- Component Table - definition of the Components in a specimen

The L-hand side of the definition page allows the user to enter an “Application Description” (if desired). The user may select elements from the periodic table (Periodic Table tab) or compounds from the Compounds tab. Once selected these elements/compounds are automatically entered by the software into the Component Table. To delete a wrongly entered element/compound, simply select it in the “Name” column followed by the backspace key, or by highlighting an entire row in the Component Table followed by the backspace key, or by using the “Remove row” button under the Component Table. To add a row (element or compound) the user can use the “Add row” button under the Component Table or the down arrow key.



12.1.1 Layer Table (Thickness Information)

If the sample is infinitely thick then leave the thickness as zero, and set the “Type” to “Bulk.” If the thickness or mass thickness is known, then enter the value (with the appropriate units) and set the “Type” to “Fixed”. Set the “Type” to “Calc” if the thickness is to be calculated for sample analysis. Appropriate units should also be selected. Also see the multilayer thin-film sections of this user manual for more detail.

If the density is known (i.e., when a linear thickness is entered), then enter a value; if it is set to zero, the software will automatically calculate a theoretical value based upon the sample composition. Note that the density can be set to Fixed or Calculated. In general, it is important to specify a normalization factor (default is 100%). Normalization **MUST** be checked if the layer thickness is to be calculated or the analysis is done without calibration (i.e. standardless).

For the multilayer thin-film (MTFFP) option of this software, this table has some extra functionality to define multilayer samples. The maximum number of layers in a sample is 8.

12.1.2 Component Table

The Component Table defines the compounds (and elements) that will be analyzed using FP. Under the “Name” heading components can be entered one row at a time or as described in the section above. Typically, the component will simply be an element symbol (e.g., Fe), but as mentioned above, it could be compounds such as oxides (e.g., Fe₂O₃) or more complex ones such as FeSO₄.

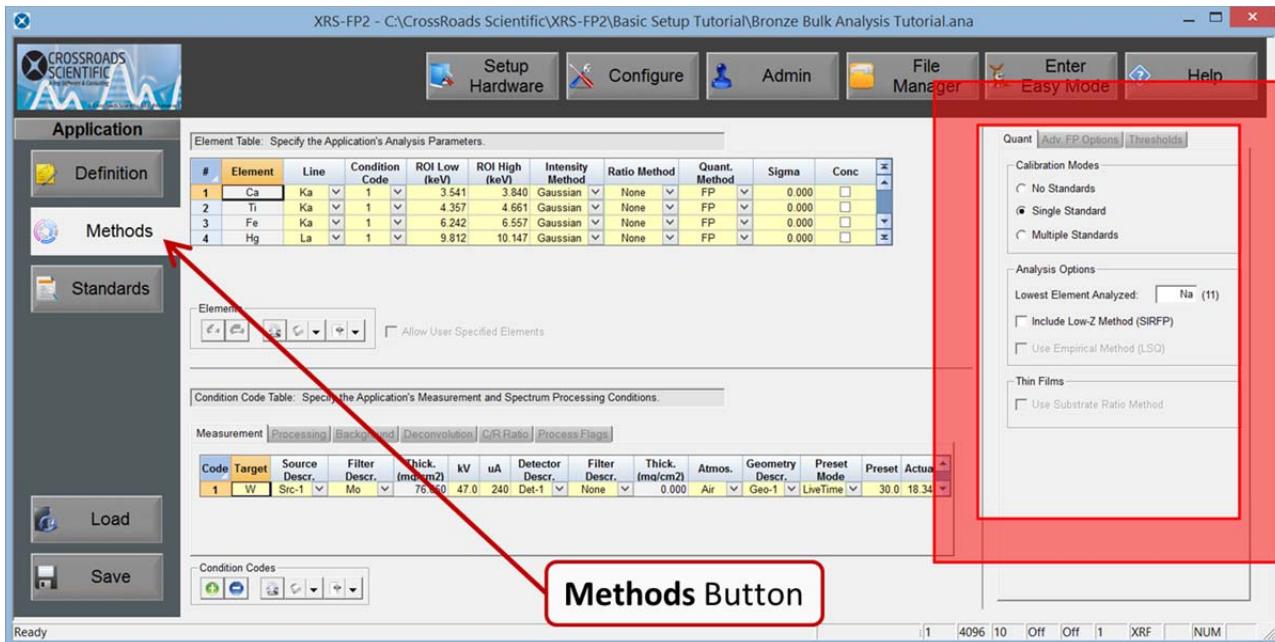
Some components must be entered with a space between single-character elements in order to avoid ambiguity. An example of this is “CaC O₃.” In this case, if a space had not been used between “C” and “O”, it would have been assumed to be “Co” (cobalt). Care should be taken in entering components, to avoid such ambiguous entries. Note that illegal entries will be reset to a blank state.

In the case where oxygen is *not* analyzed, which is usually the case since the x-ray energy is too low to be detected, the Fe₂O₃ will be calculated on the basis of the Fe concentration, but the oxide information will be used to make the correct matrix corrections during the FP calculations. However, if S *can* be analyzed, as well as Fe, then the FeSO₄ can be calculated on the basis of either Fe or S, or *both*. The latter case gives us the possibility to analyze mixed compounds. Continuing the example from above, if *both* Fe₂O₃ and FeSO₄ are entered as separate components then the FeSO₄ can be determined from the S concentration, and the remaining Fe (and O) ascribed to the Fe₂O₃ component. The software handles this internally and automatically during the FP calculations.

As the compounds are entered, the element table will automatically be filled in. For each component, you must define the calculation (“Type”) method. By default, each component will be calculated (“Calc”), but they can also be specified as “Fixed” (e.g., if not analyzable, such as H₂O), by Difference (“Diff”), or by “SIRFP” (Scatter Intensity Ratio method for low-Z elements). The units can be wt% or ppm, and also as ug/cm² or mg/cm². The latter can be used for FP calculations only. The concentrations will be converted (e.g., from Wt% to ppm) if the units are changed.

12.2 Methods

The methods page consists of two tables, the Element Table and the Condition Code Table, in the main panel (see figure below).



12.2.1 Element Table

The Element Table is filled in automatically during either entry to the Component Table or after FP calibration. However, you MUST select the appropriate line for analysis (Ka, Kb, La, Lb, Lg or Ma), the condition code (see above), the quantitative analysis (“Quant”) method (e.g., FP or MTFFP or LSQ) and the intensity extraction method (Integrate, Gauss or Reference). 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. This line is automatically filled in by the software, but the user should check to see if it is the best line for the particular application and setup parameters.

Note that the columns for Intensity and Quant methods can be selected (click on the header cell when the down arrow is shown), in which case any change to one element/row will be copied to all the others.

The maximum number of elements that can be analyzed is currently 50 for both single and multilayer samples.

The user can ratio the intensities to the Compton scatter peak intensity (see later in the Process-Compton section), the Rayleigh scatter peak, the local background, the tube current, or use the Compton and Rayleigh scatter peaks to make estimates of unanalyzed low atomic number elements in the sample.

Also, when you select an element row (click on the # button at the far left), the low and high ROI values are used to paint an ROI in the currently loaded spectrum, *if* the Intensity Method is set to Integrate. For more information on painting ROI's, see the Regions of Interest section in this manual (Analyze workflow -> **Regions of Interest** button). Unselecting the element row will automatically clear the ROI.

You can also choose thresholds for each element. There are 2 types of thresholds that can be defined, either sigma based or a fixed value for each element. Individual thresholds based on the sigma (estimated error) for each element can be set individually.

Highlighting the Sigma column will copy the entered value to all the elements, and then each element can be individually changed to whatever value is determined by the user.

In addition, the sigma value can be based upon the Intensity or the Concentration – the Intensity is the default unless the Concentration check box is checked (Conc column). The default is Intensity thresholding. Any intensity (or concentration) below the threshold will be set to zero.

You can also define Upper and Lower limits for each concentration in the Element Table. This is different from the thresholding described above, and cannot be used with the thresholding. I.e., there are 3 different options for the post-processing of concentrations or intensities. See section 12.2.3 below for more information.

12.2.2 Condition Code Table

The Condition Code Table displays the application setup and spectrum processing parameters. These are parameters either previously entered in the Configure and Setup Hardware workflows or read in upon loading an ANA file. In addition, these parameters can be entered and/or edited in the immediate mode, i.e. directly in the Condition Code Table itself.

It is important to ensure that the target anode matches the one entered in the Configure -> Source workflow. A previously defined source (Configure -> Source) and filter (Configure -> Source Filters) if there is one, can be selected from the “Source Descr.” and “Filter Descr.” columns, respectively. The filter thickness can also be entered (“Thick.”). Similarly, the tube KV for analysis can be entered for this condition, along with the tube current. Note that hovering over an item in the table will bring up the details (i.e. hovering over the selected “Source Descr.” item will display the source type, source model, target material, window type, etc.)

In the case of using a radioactive isotope (RI) as a source, just make sure that the KV matches the highest energy available from the source that can excite lines in the spectrum. The RI source spectrum will be used for the computations, but the KV value is used to match to the edges of the selected element lines in the Element Table. You can still specify a filter with the RI source, and it will be applied to the source spectrum.

Also specify whether the chamber is in vacuo or in air (“Atmos”). A previously defined detector (Configure -> Detector) and filter (Configure -> Detector Filters) if there is one, can be selected from the “Detector Descr.” and “Filter Descr.” columns, respectively. The filter thickness can also be entered (“Thick.”).

In addition, a previously defined geometry (Configure -> Geometry) can be selected from the “Geometry Descr.” Columns. The Preset Mode, Preset time and Actual time can also be modified here.

Note that there can be up to 4 different conditions defined for any analysis. Different elements can be analyzed under different conditions (e.g., at different KV settings, or with a filter in one case but not another). Under the element table ensure that the correct condition code is selected. You can select an individual condition as the current one with Setup-Condition or by clicking and highlighting the appropriate row in the Condition Table. During an automated analysis, the different conditions are selected automatically including the x-ray tube control if that is available.

To display the processing features in the XRS-FP2 software select the Processing tab in the Condition Code Table. You can select the lowest energy to be using spectrum processing, the number of smooths, the



smoothing filter type and the number of points per smooth. The user can select from a variety of different smoothing operators when using the Smooth step. The default is a 3-point Gaussian smooth (1:2:1 weighting), and others are more sophisticated, but if the same effective number of smoothing steps is performed the results are usually very comparable. The effective number is dependent upon the model. For example, a 5-point Gaussian smooth is equivalent to two 3-point smooths.

In addition, you can select whether to include sum peak and escape peak corrections. There are two Sum-Peak parameters that may be changed. The first is the pulse-pair resolution time (default = 1 microsecond), which describes how close in time that 2 pulses can be detected as individual events, as opposed to a pile-up or sum event. Keep in mind that the pulse detection is a random process (in time), and so events may occur almost at the same time, or at greater separation times, even for the same average count rate. The second parameter is only relevant for x-ray events below about 1 keV. Since the pile-up detector, which uses a fast time constant, may not detect low-energy x-ray events the main channel will be subject to many more pile-up events in the low-energy region. The main amplifier time constant then determines the pulse-pair resolution at these lower energies.

You can modify the background processing parameters by selecting the Background tab in the Condition Code Table. Here the background method, filename (for use with a stored background), ROIs, filter width and iterations can be set. You can select between None, Auto (default) or File for the background method. File uses a spectrum file as the background component, normalizing the 2 spectra by the ratio of the livetimes. The exact details of the automatic background removal method are proprietary, but the method is based on general signal-processing techniques that seek to distinguish fast-changing regions of the spectrum (i.e., peaks) from slowly changing regions (i.e., background). This is relatively simple for large peaks on small and flat backgrounds, but often the situation is not that straightforward.

For example, there are sometimes regions of the background that have relatively high curvature, and there are often small noisy peaks superimposed on high backgrounds. The background shape arises from several effects, but primarily from the scattered bremsstrahlung x-ray continuum from an x-ray tube, which, in turn, depends upon the tube KV, and the mean atomic number of the sample.

Superimposed upon this continuum are the absorption edges of elements in the sample. Also, at low energies, one may see edge effects from the detector and window components. These absorption edges are not visible as discrete “steps” in the spectrum, because they are convoluted with the detector response function, which results in the smearing of these steps.

The basis of the automatic background estimator, therefore, is to “filter” the spectrum in such a way as to remove the sharper peaks and leave a smooth background, which is subsequently subtracting from the original spectrum. The automatic background setup parameter “Low-Pass Filter Width” controls the width that distinguishes the peaks – a larger width parameter would be more suitable for wider peaks. The typical range for this parameter is between 1 and 2 times the FWHM for the Mn-K α peak.

The “Number of Iterations” controls the number of repeated operations – too low a number may result in an over estimate of the background, and vice versa.

In addition, you can choose to select “Blank Remove” to do a blank background removal. The blank filename and ROIs can be entered here. You can select a blank spectrum for removing some artifact in the measured spectrum, again normalized by the lifetime ratio. Note that it is not recommended that blank removal be used unless it is the only remaining option. It is recommended that all system impurities, environmental contamination, etc. be addressed before resorting to blank subtraction.

The Deconvolution tab contains the parameters used to setup the various Gaussian deconvolution options used to extract net peak intensities from an XRF spectrum with overlapped peaks. There are two options for the Gaussian method, which are the linear or nonlinear deconvolution. These parameters can be described as follows:

a) Nonlinear Deconvolution:

When this check box is Unchecked, then the program will employ the Linear method, where the peak positions and widths are fixed, and the line series for each element are fitted using stored line ratios. When checked, the Nonlinear method is used, and the other parameters become effective. The Nonlinear method allows for the peak positions, line ratios and peak widths to change.

b) Line Ratio Factor

This refers to the amount that daughter lines (line ratios) are allowed to change from their original database values; for example, the Ka2 line is usually about 50% of the Ka1 parent line; in the linear fit the ratio of Ka2/Ka1 will be fixed (in this example) at 0.5; for the nonlinear fit, assuming the default factor of 2.0, this ratio will be allowed to vary from $0.5/2.0 = 0.25$ up to $0.5*2.0 = 1.0$ (i.e., same height as parent Ka1).

c) Spectrometer Offset (eV)

This is the maximum allowable zero shift (eV) when calculating the value of a peak position at any channel in the spectrum (also see (5)).

d) Spectrometer Gain (%)

This is the maximum percentage shift in the value of the calculated gain at a given peak position energy (channel); both (4) and (5) are used to calculate the maximum allowable shift for an x-ray line being fitted; each peak position is constrained to move no more than the values of the gain and zero (offset) shifts at that peak energy (whichever is the larger); after this constraint, the values each peak position are fit to a linear least-squares equation including gain and zero offset parameters; these values then replace the values from the nonlinear fitting.

e) Spectrometer Peak Width (%)

This is the maximum allowable percentage change of the fitted peak width at the energy for each fitted line; for example, if the specified FWHM is 200 eV at Mn-Ka, and the width deviation is 35%, the estimated width would be allowed to vary from 130 to 270 eV at this energy; again, these values are fitted subsequently by a linear least-squares fit to smooth out any variations in the estimated values for each line.

f) Maximum # Iterations

For the Nonlinear method, this limits the maximum number of iterations before the program exits with the last calculated values; there is also one linear fit done before, and another after, the nonlinear fitting, using the final estimated values from the nonlinear fitting.

g) Channel Weighting Factor

This factor controls the weighting of each channel used in the least-squares fitting. If a value of zero is entered, then no weighting is used. If a value of 1 is entered, then each channel is weighted by the standard deviation of that channel.

An option in is the use of Net Spectrum weighting. Normally the original spectrum is used for weighting each channel, but the Net option uses the processed spectrum ready for deconvolution. This is beneficial some times when there are small peaks on a relatively large background.

h) Spectrum Type

This is the type of spectrum used for weighting – original/gross or net.

i) Spectrum Chi2

This is the final spectrum Chi2.

j) Diagnostics Output

When checked, this causes output of some internal diagnostics for the Gaussian deconvolution to a text file. It also causes scratch files to be written after routine processing for Escape, Sum, and Background removal, as well as the Gauss-fit spectrum if that method is used.

k) Gain Factor

This is the nonlinear deconvolution intermediate computed value for gain.

l) Offset (eV)

This is the nonlinear deconvolution intermediate computed value for offset.

m) Peak Width (FWHM)

This parameter is the value of the peak Full-Width at Half Maximum (FWHM) at the energy (5.9 keV) of the Mn-K α peak. The parameter is used to calculate the width of each peak at a given energy. It is critical that this value be set accurately, particularly in the case of linear deconvolution. Visually check the displayed fit against the original spectrum to judge the goodness of fit. For the nonlinear method this parameter defines the starting point for the peak widths at each energy (see above).

The Compton and Rayleigh (C/R) Ratio parameters are displayed under the C/R Ratio tab in the Condition Code Table. The C/R processing options are only displayed when the C/R Ratio check box is selected. The Compton and Rayleigh ROI values can be left at zero, in which case default values will be assigned prior to the Compton and Rayleigh peak integration.

12.2.3 R-hand Panel

Calibration Modes:

The Quant tab in the R-hand panel allows for the user to select the type of calibration mode to be used with an analysis. The user may select “No Standards” (standardless), “Single Standard” (one standard) or “Multiple Standards”. The selection of these different calibration modes causes the GUI to change automatically to either remove or include workflows for one or more standards. Single standard analysis adds a third button to the application workflow. Multiple standards based analysis adds yet a fourth button to allow for the theoretical calibration coefficients (TCCs) to be merged. These workflows are discussed later in this manual in the Standards Workflow section. Note that there are several tutorials available for

calibrating and using the FP, MLSQ and SIR-FP methods. These contain example files and step-by-step instructions to performing calibrations.

As mentioned above, there are three different options in the right panel for calibration modes. If the model is set to Standardless, then no standard calibration is required. However, the software must be setup accurately and the results must be normalized to some value (default is 100%). In addition, the sample must be infinitely thick, or its mass thickness known (Fixed).

The other two options required at least one standard. If the single-standard option is chosen then only one calibration is performed and the system is ready for analysis using that standard calibration, and its calibration coefficients.

If multiple standards are selected, then the user calibrates each standard in turn in sequence. There are two ways to do this, either with live spectra or with saved spectrum files. With the multi-standard approach, ALL standards are employed, along with several models for how to allow for variations of the calibration coefficients with different concentrations and mass thicknesses of each element. This method will be described in more detail in the Standards section. For this method you should collect spectra of each standard and process each one according to the standards workflow (described later in more detail). Once all single standards are processed go to the calibration workflow (also described later in more detail) to perform the merged calibration using coefficients obtained from all the single standards.

The user can also select the lowest atomic number (Z) that can be analyzed by any quantitation method (the default is Na). All elements with lower atomic numbers must be determined by difference, by stoichiometry, or be fixed in concentration. In addition, the SIR-FP method can also be selected (“Include Low-Z Method”) in the Quant tab and used to estimate the low atomic number fraction in a sample analysis. Note: for more information on the SIR-FP method see the SIR-FP tutorial included in the Help section of the software. Another option on the Setup-FP panel is for using the SIR-FP method, which means a Scattered-Intensity Ratio variation of FP analysis. This method can only be used on bulk samples. The SIR-FP method uses information from the Rayleigh and Compton scatter peaks to provide additional information about elements (typically with low atomic numbers) that cannot be analyzed, because their x-ray lines are not detectable.

Note that this method should not be used in conjunction with the Peak-to-Compton method as these two would then be in conflict. This method is described further in the Process-Analyze and Calibration-SIRFP sections.

Adv. FP Options:

As noted in the heading of this tab, these parameters are for advanced users and applications only. If in doubt use the default settings.

The “Maximum Number of Iterations” parameter sets the limit on the maximum number of iterations during each FP quantitation. If convergence has not been reached then an error (“Results Not Converged”) will be returned by the FP library function. The “Concentration Convergence Criterion” parameter controls when the software determines that concentration convergence has been achieved – i.e., the results for each element is not changing by more than each criterion from one iteration to the next. Similarly, the “Thickness Convergence Criterion” parameter controls when the software determines that thickness convergence has been achieved – i.e., the results for each layer thickness is not changing by more than each criterion from one iteration to the next.

The “X-ray Source Histogram Width” parameter determines the width, in wavelength units (nm), of the source histogram calculated for the x-ray source spectrum. A smaller value will give a more accurate model, but be slower for the overall FP calculations. The default value is 0.002 nm (i.e., 0.02 Angstroms).

The “Preclear Concentrations before Quantitation” option determines whether the elemental and component concentrations sent to the FP library, prior to the quantitation step, are set to zero or not. The effect of this is that pre-clearing of these concentrations causes the library function to estimate the initial concentrations from the intensities for this analysis. This was the previous method of analysis, with no options.

If the element concentrations are not cleared then these values are used as the initial estimates of concentrations for the current analysis, using whatever intensities have been calculated from the spectrum processing steps. In the case where the samples do not change much from analysis to analysis, the use of the prior concentrations would result in a significant advantage in terms of speed as the total number of iterations would almost certainly be reduced compared with the opposite setup. If in doubt, then check the PreClear option to be on.

You can optionally save the “Diagnostic File Output”. If checked this will result in the FPiters.txt file being created during the FP quantitation. This file shows the intermediate and final results after each FP analysis iteration.

Thresholds:

There are 2 types of thresholds that can be defined, either sigma (estimated error) based or a fixed value for each element. Typing a value in the “Sigma N-Value” box will copy this value to all the elements, and then each element can be individually changed to whatever value is determined by the user. The sigma value can be based upon the Intensity or the Concentration – the Intensity is the default unless the Concentration check box is checked.

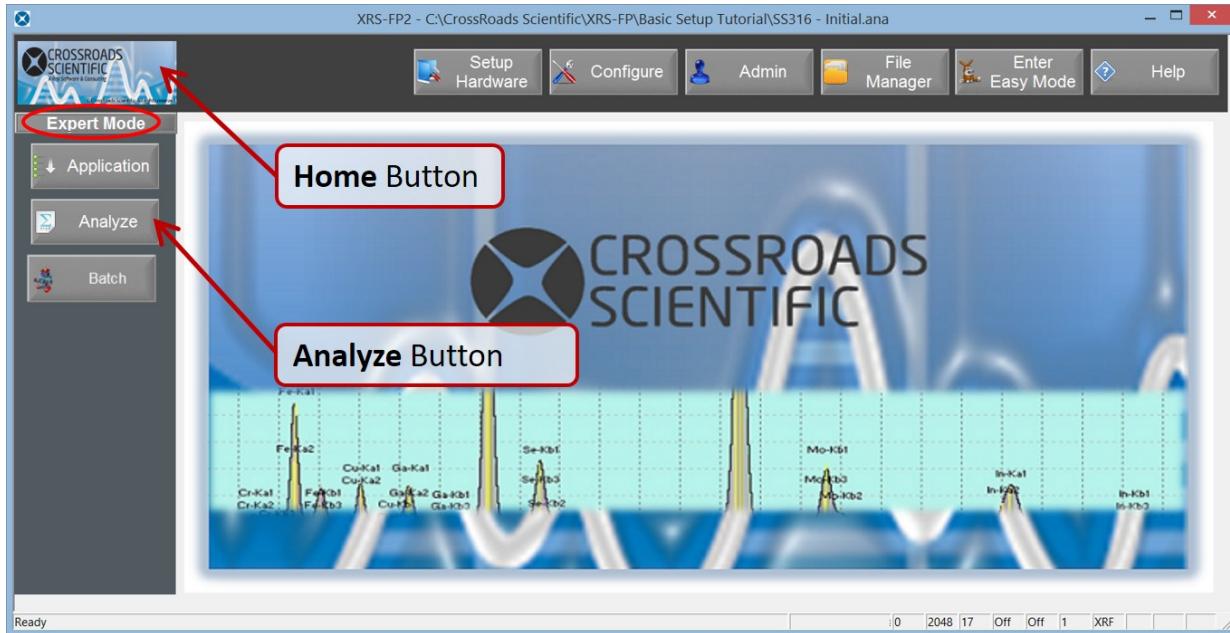
You can also define Upper and Lower limits for each concentration in the Element Table. This is different from the thresholding described above, and cannot be used with the thresholding. I.e., there are 3 different options for the post-processing of concentrations or intensities.

Alternatively, the thresholds can be based upon a Fixed value for each element, again either for Intensities or for Concentrations. The use of Upper and Lower limits causes concentration results that are within the limits to be displayed in green, and ones outside the limits to be displayed in red. There is a special option in the software that allows the control of a digital output module, whereby one of two switches are turn on depending upon the values of the concentrations and their limits. If any one of the concentrations is out of limits (red) then the output logic switch is set for the out-of-limits condition. If all the concentrations are within their individual limits, then a second output logic switch is turned on and the first one turned off. Please consult with CrossRoads Scientific, LLC if you would like details or customization of this digital logic output.

Finally, the thresholds can also be based upon an Offset value for each element. This offset can either be for Intensities or for Concentrations.

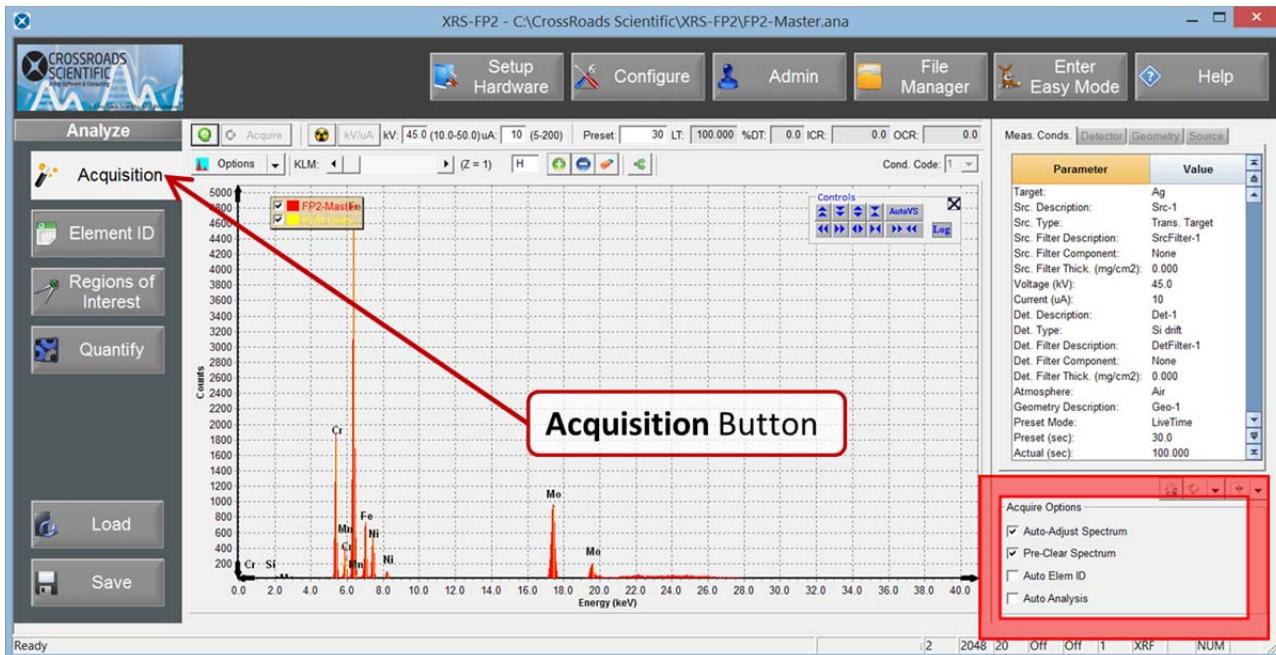
13 Analyze Workflow

The **analyze workflow** is where sample analysis is done. From the **Home** screen (Expert Mode) select the **Analyze** button (see figure below).



13.1 Acquisition

The acquisition page consists of the main spectrum window and acquisition toolbar (top of spectrum view). The R-hand panel has four tabs - Meas. Conds, Detector, Geometry and Source - which describe the parameters and values for each area (see figure below). For more information on the GUI and navigation controls see the Spectrum Window section of this user manual.

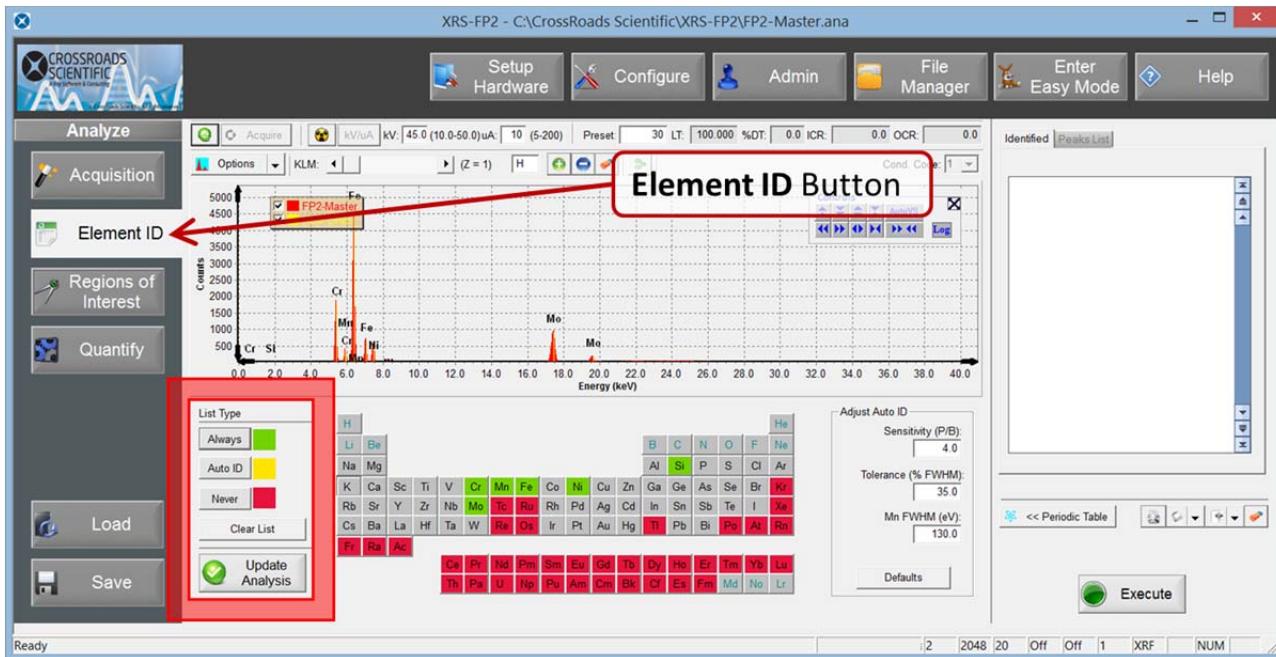


13.1.1 Acquire Options

The bottom section of the R-hand panel contains the “Acquire Options” (see figure above). The first is the “Auto-Adjust Spectrum” (on-Acquire) checkbox. This works *during* the acquisition, so the spectrum should always appear in the calibrated position. The second option is the “Pre-Clear Spectrum” option, which will clear the spectral data before the start of a new acquisition. The third option, “Auto Elem ID”, performs an element ID during acquire and the fourth option, “Auto Analysis”, executes spectrum processing and quantification during acquire.

13.2 Element ID

This page sets up the parameters for doing an Automatic Element ID (peak identification). The spectrum view at the top of the page displays the acquired or loaded spectrum of interest. Once the element ID is performed (**Execute** button) the spectral peaks are automatically identified and elemental x-ray lines are assigned.



13.2.1 Element ID Lists

There are three types of element lists: Always (always present, green), Auto ID (automatically identified, yellow) and Never (never present, red). Before executing the **Element ID** button, all elements shown in grey in the periodic table will be included in the possible Auto-ID. Typically there are many elements that can be identified that are known not to be present. Likewise, there are some that can be assumed to always be there. There are two options to assist with this knowledge – the **Always** and **Never** present lists. After selecting the button for the specific list, clicking on the element buttons will add those elements to the specified list.

To the right of the period table is the “Adjust Auto ID” section. This section contains several factors that will control the Auto-ID processing. The “Sensitivity” factor affects the levels at which peaks above background are recognized. The higher this value, the more likely peaks will be detected, including false peaks. If the value is too low then true peaks may not be recognized. The “Tolerance” factor affects how much latitude is allowed in assigning a line energy to a peak maximum. The larger the value, the wider the window for including possible line matches. Again, this may result in too many lines being identified. On the other hand, too small a value will not accommodate peak shifts and peak overlaps that can cause peaks to be at unexpected locations. This factor is expressed as a percentage of the width of the peak, at each energy, as the peak changes with energy. The default detector Mn-K α FWHM is shown, although the parameter can also be entered elsewhere.

13.2.2 Identified Elements (R-hand Panel)

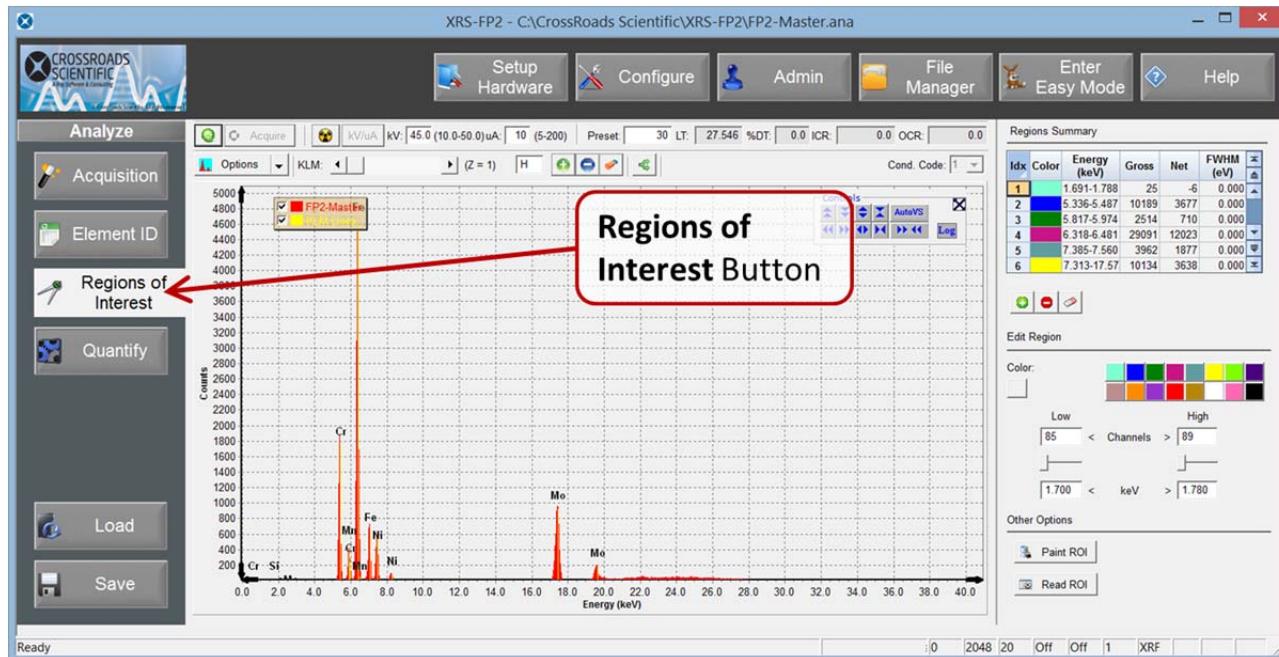
After clicking the **Element ID** button a list of peaks (Peaks List) and x-ray line (Identified tab) assignments are displayed in the R-hand panel.

13.3 Regions of Interest

This area allows you to define and paint regions of interest (ROIs) on the current spectrum in the spectrum window. The default list of ROIs is taken from the contents of the currently loaded ANA file. The ROI values are calculated, by default, to be 1.2x the calculated FWHM at the line energy of the analyte.

For example, if the Mn FWHM is 130 eV, and the Mn-Ka1 and Mn-Ka2 lines are at 5.898 and 5.887 keV respectively. The default half-width is $0.6 \times 130 = 78$ eV, and so the default Mn-Ka ROI starts at $5.887 - 0.078 = 5.809$ keV, and finishes at $5.898 + 0.078 = 5.976$ (rounded up for the more exact values internally to 5.977).

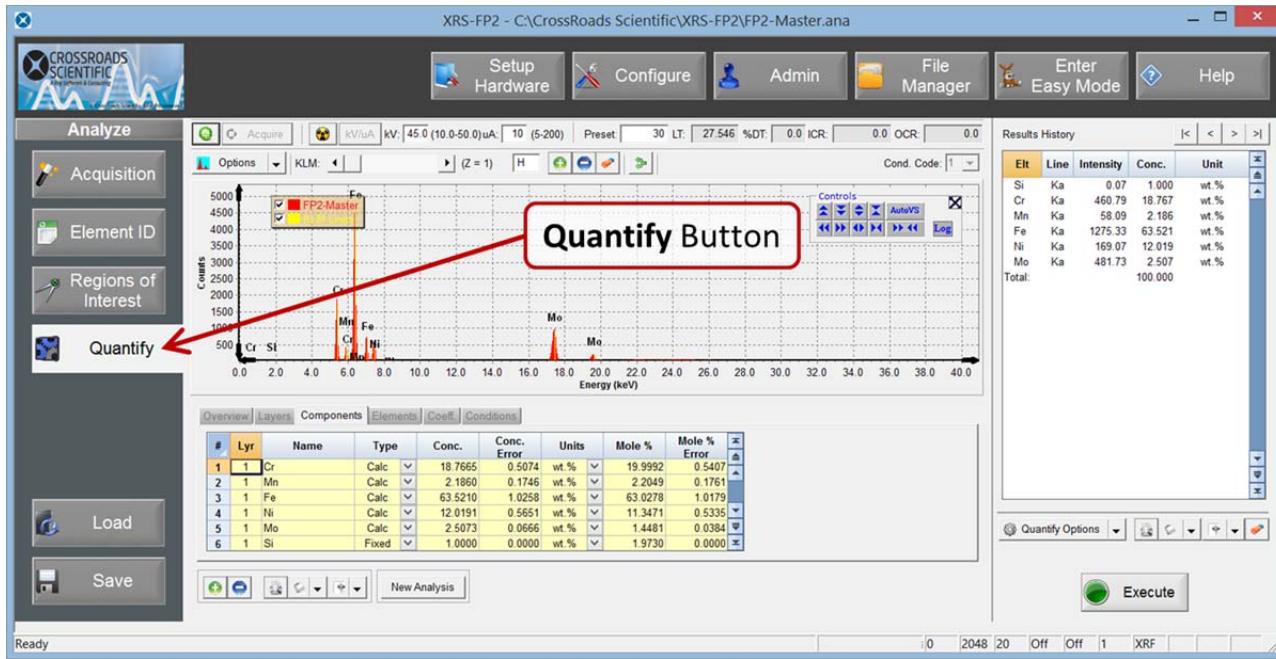
You can then click on the Paint ROI button to send the ROIs to Spectrum view and these ROIs will be displayed on the spectrum. Clicking the Read ROI button loads the values into both the Regions Summary Table and also the Element Table.



13.4 Quantify

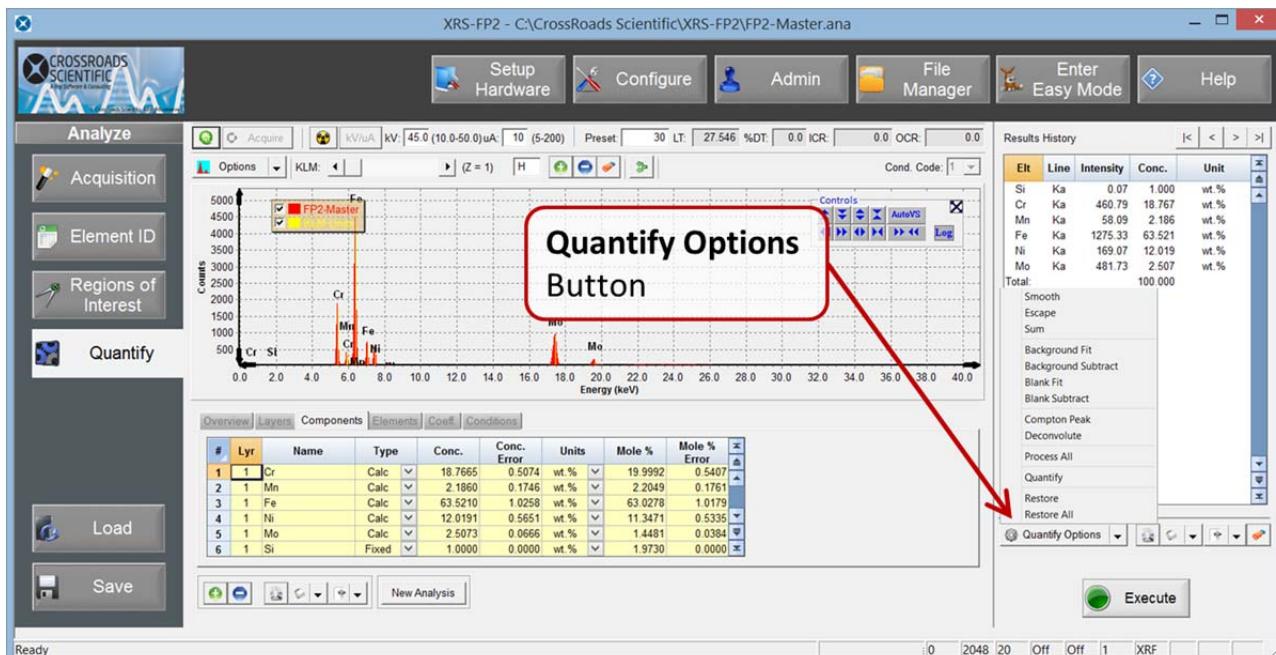
The **Quantify** button in the analyze workflow is where the results are obtained for an analysis. This page contains a slit screen view showing both the sample spectrum as well as a table containing the analysis

overview, layers, components, elements, coefficients and conditions. Note that the parameters in this table can be changed on the fly in the immediate mode.



13.4.1 Spectrum Processing

Selecting the Execute button in the Quantify view performs a “process all” (all the spectrum processing steps selected in the Condition Code Table for the current condition) and “quantify” (analyze) all in one step. However, the user has the option to single step through the spectrum processing options by individually selecting the processing options from the “Quantify Options” drop-down list box. See figure below.



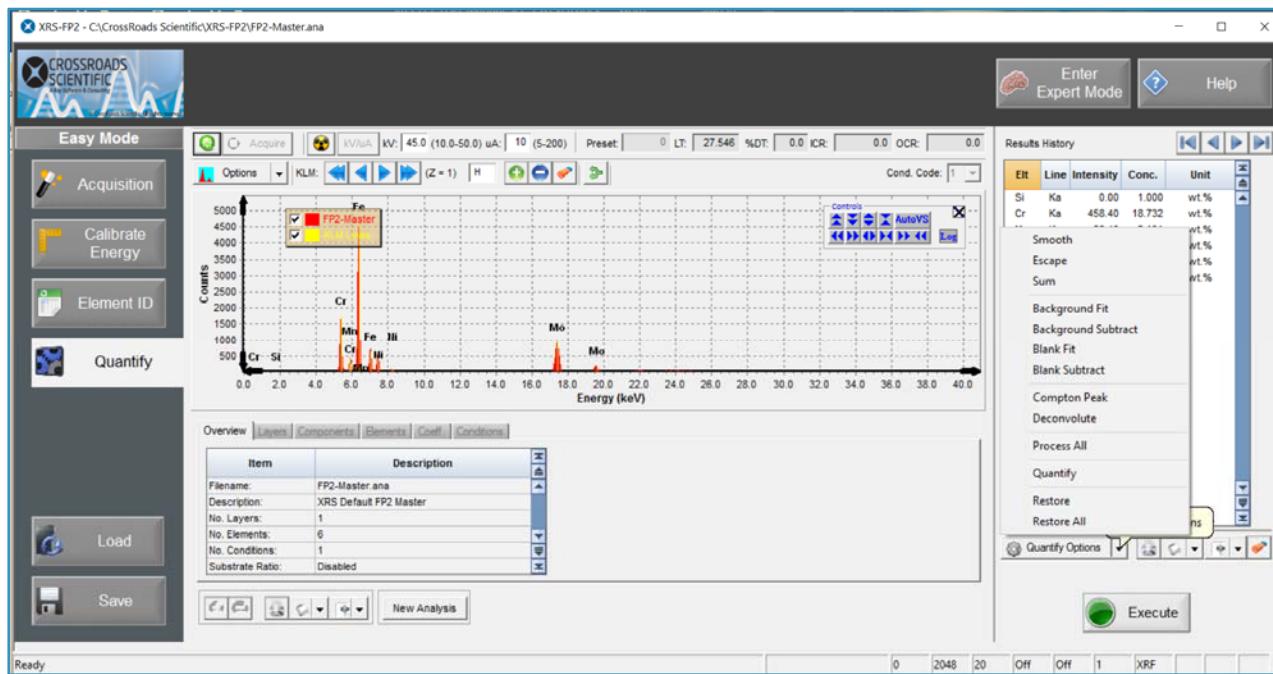
13.4.2 Quantification

This is the main command for quantitative analysis using either FP or LSQ (empirical fitting). Using all the previous setup information and the intensities supplied by the Process Spectrum command(s) (see above), the **Execute** button converts the elemental intensities into compositions using the FP library and other information described above.

After this command is finished (it can take up to a minute or more for complex FP calculations), the elemental and component compositions will be updated in the table and the ANA file can be saved and/or printed. The FP method itself is relatively straightforward at this point, producing results using the calibration coefficients, or possibly standardless for samples with a known thickness. In addition to the table being updated the R-hand panel of the GUI will display the “Results History” in a strip chart fashion, including element, line, intensity, concentration and units.

13.4.3 Quantify Options

As mentioned above, the **Quantify Options** button allows the user to individually select the spectrum processing options in a stepwise fashion. These options include: Smooth, Escape, Sum, Background Fit, Background Subtract, Compton Peak and Deconvolute (see figure below). The user can also select the Process All option to perform all selected options in one step, or the Quantify option to calculate assay concentrations. The Restore option restores the spectrum by one step (to the state prior to the last spectrum processing option selected), and the Restore All option restores the spectrum to its initial state. See Section 15 for more detail regarding the individual spectrum processing options.



13.4.4 Analysis Definition - Immediate Mode

The user can modify the application information on the fly in “immediate mode”. Under the spectrum display in the Quantify panel there is a table containing all the application information, including the Overview, Layers, Components, Elements, Coeff. and Conditions (see figure above). These parameters can be changed (unless they are “greyed out”). For example, the user can add or remove components to their application, add or remove layers, or alter the measurement and processing conditions.

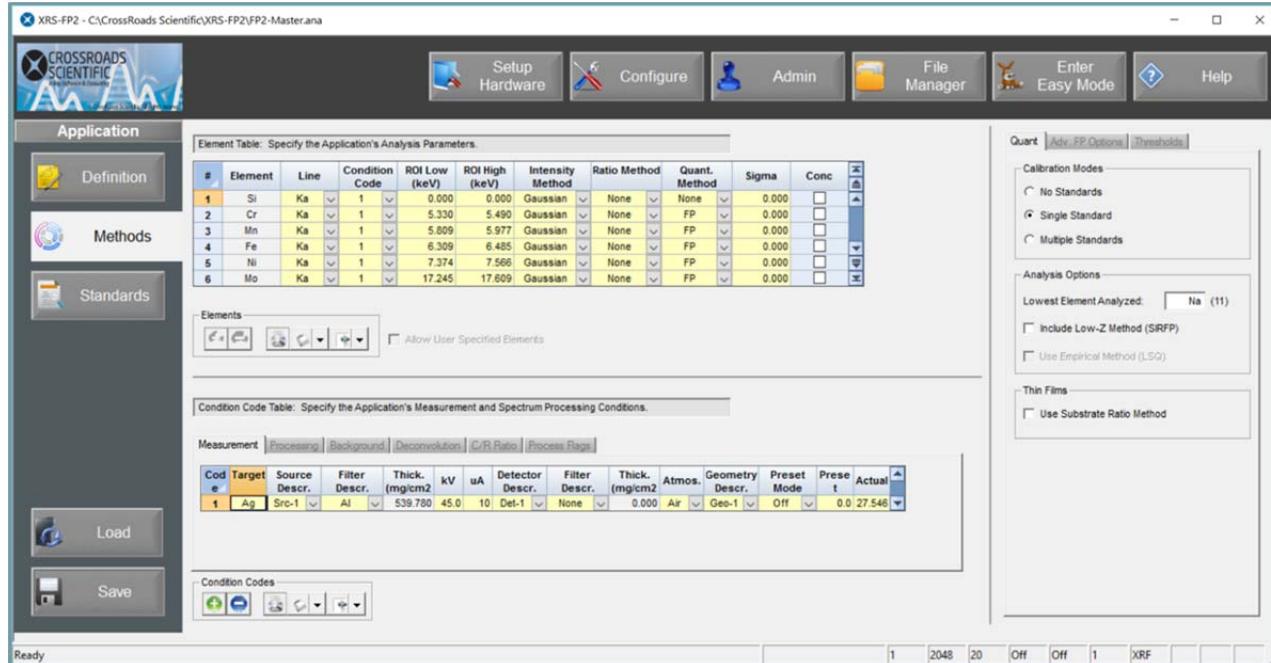
14 Standards Workflow

14.1 Overview of Calibration Methods and Operations

In addition to standardless analysis, there is the option to create a single or multiple standard FP calibration. Using a known standard reference material or materials (with certified component concentrations), the user calculates the response factors (sensitivities) for all the elements of interest to be used in that application. This standardization process generates calibrate coefficients, which are later used by the main FP program for analysis of an “unknown” material. To create a calibration for the XRF system, the user must collect spectra for each of the elements of interest, analyze them and then generate the appropriate FP calibration coefficients or TCC (theoretical calibration coefficients) values. The easiest way to do the calibration would be with one multi-element standard. However, it is also possible to use individual bulk or thin-film pure-element standards, or any combination of single and multi-element standards.

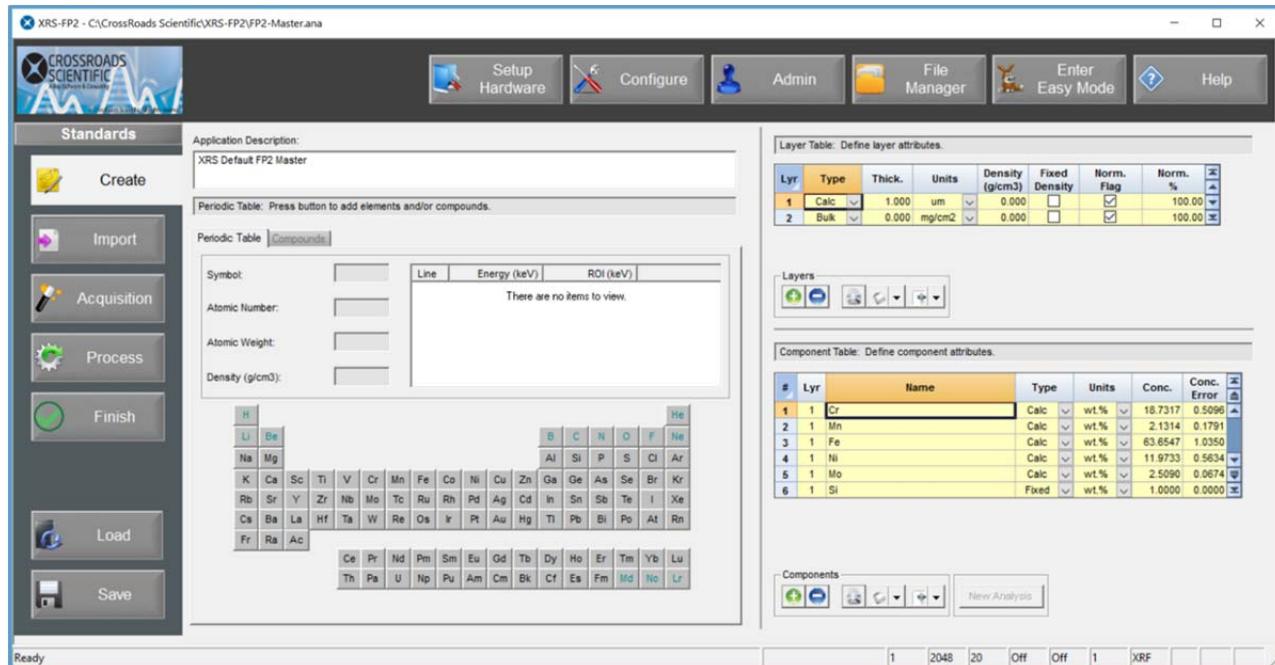
14.2 Single Standard

For a single standard FP calibration select the **Methods** button in the Application workflow. Then select the Calibration Mode radio button for “Single Standard” in the R-hand panel under the “Quant” tab. This will bring up a new button in the Application workflow called **Standards**. See figure below.



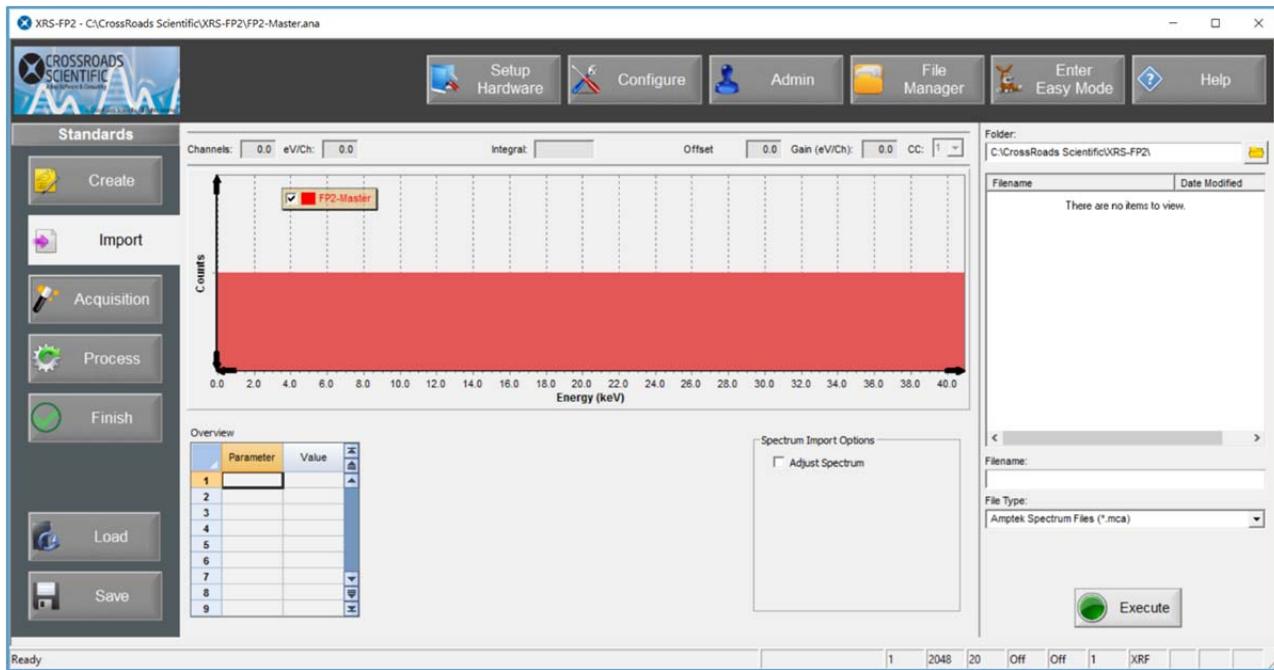
14.2.1 Create

With the **Create** button selected the standard component values (concentrations) can be entered. Note that the component values are entered in the “Conc” column of the standard Component Table (or they can be selected using the period table), along with the units and calculation method. See figure below.



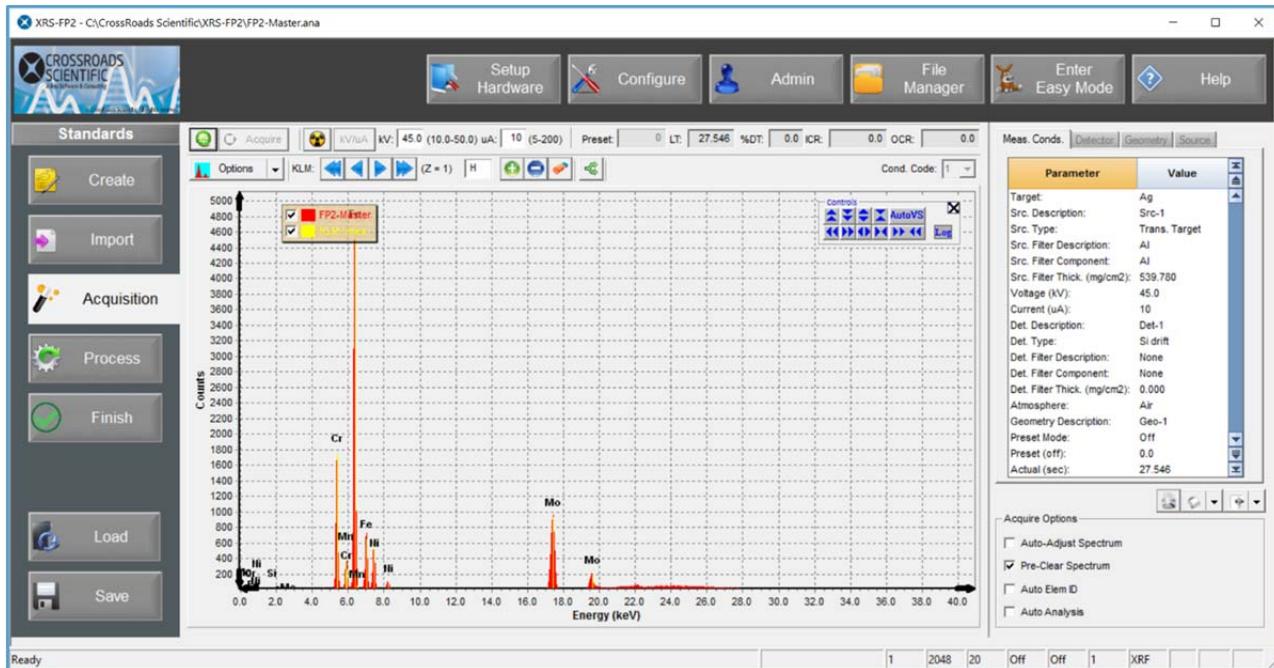
14.2.2 Import

At this point you have the option to either import or acquire a spectrum for the standard. To import a spectrum, select the **Import** button and then go to the R-hand panel and select a spectrum file to open (i.e. *.MCA file). See figure below.



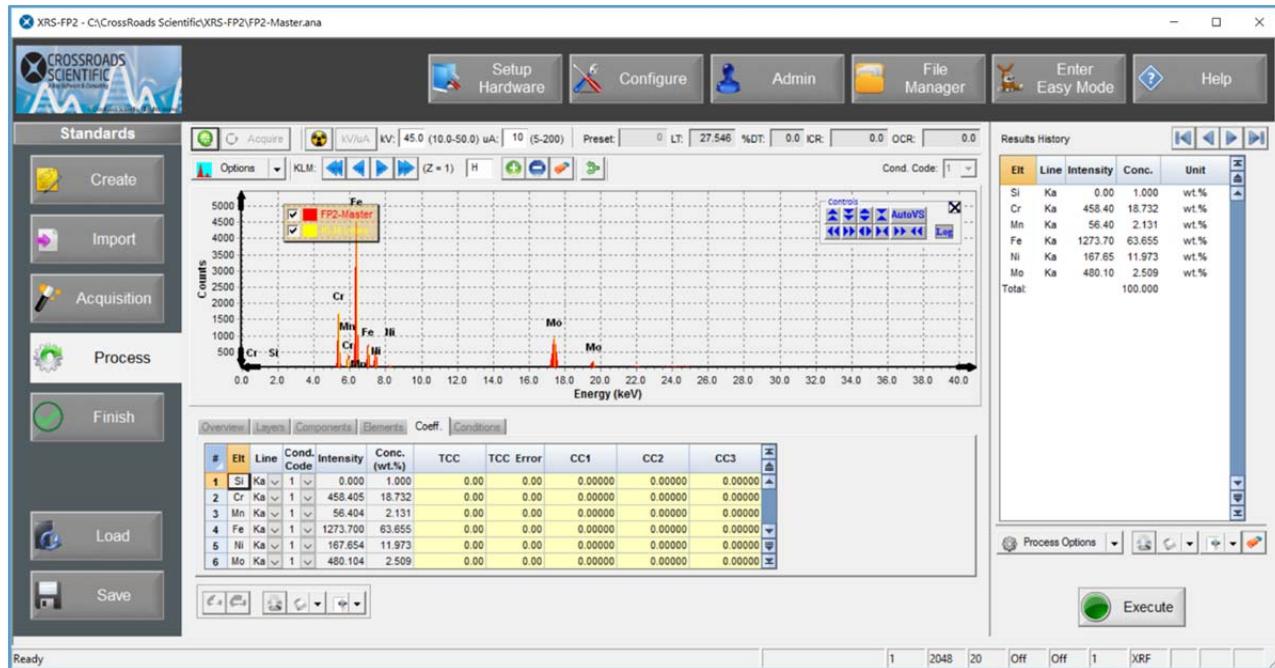
14.2.3 Acquisition

To acquire a spectrum for the standard, select the **Acquisition** button. See figure below.



14.2.4 Spectrum Processing and Calibrate

To process the spectrum and generate FP Theoretical Calibration Coefficients (TCCs) in one step, select the **Process** button and click on the **Execute** button in the R-hand panel. Note that the TCC values will be displayed under the “Coeff.” tab. See Figure below.



14.2.5 Save Standard and Finish

Then save the standard ANA file by selecting the **Save** button. This can be saved as any filename of choice. When finished, select the **Finish** button.

14.3 Multiple Standards

In XRS-FP2 there is a software option where multiple standards can be used for the FP calibration of each element. This secondary least-squares calibration of the FP coefficients (MLSQ) can be done with various models, in order to allow for any variations in the theoretical FP calibration coming from either errors in the physical models or the FP database itself. There is incomplete and inaccurate knowledge of some of the inter-element effects, especially in the low-energy range, or where the standards may not be completely homogeneous.

The MLSQ method will be described below in more detail as well as in the Standards Calibration tutorial in the Help section of XRS-FP2. This method can be used with either multi-element type standards or pure-element standards. In fact, there are few limits on the types of standards that can be used, and they can be mixed together in any way. For example, a standard list might include single elements that are in the bulk

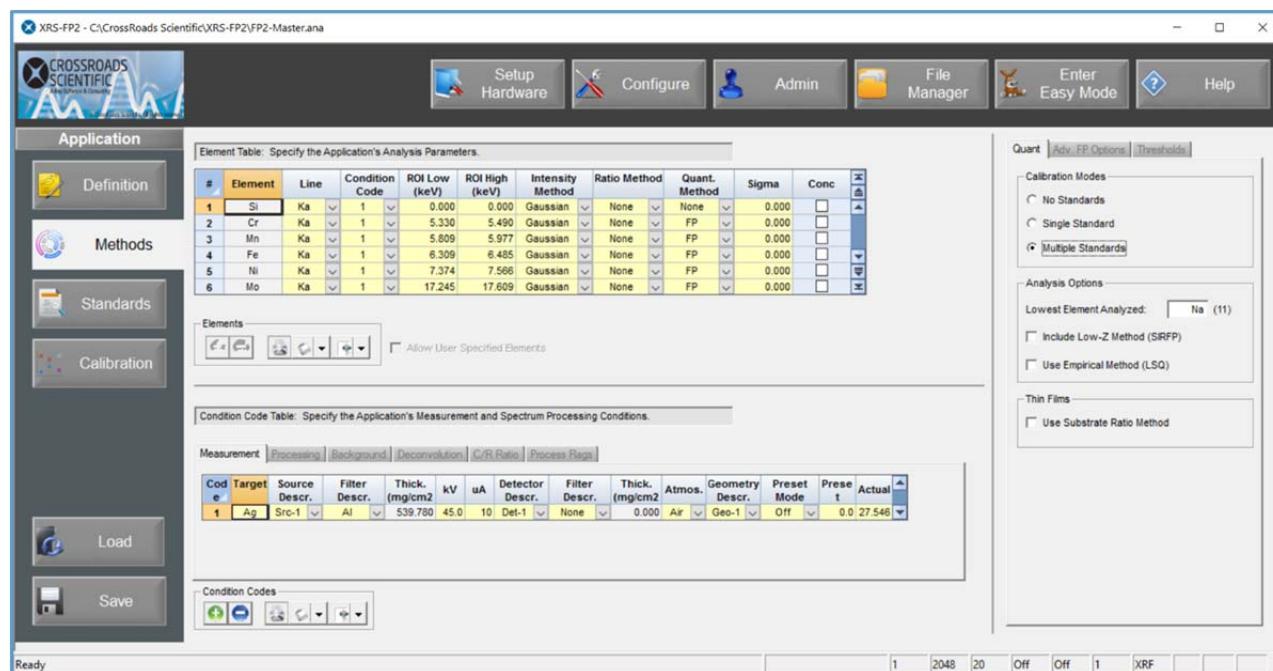
(infinitely thick) state, or as thin films, and they can also be multi-element standards with all or some of the total range of elements to be calibrated.

Note that MLSQ method is not the same as LSQ method, which uses a simple empirical calibration curve of intensities vs. concentrations, using a least-squares fitting technique without FP.

In a multi-standard calibration, **ALL** entered **standards are employed**, along with several models for how to allow for variations of the calibration coefficients with different concentrations and mass thicknesses of each element. This method will be described in more detail below. But typically for this method, you will first calibrate each standard in turn. You can perform these single standard calibrations either with live spectra or with saved spectrum files. Using these calibrations, information from each of these single-standard calibrations is then merged into the defined MLSQ multi-standard model for a final secondary calibration that is the basis of the MLSQ method. The single-standard FP Theoretical Calibration Coefficients (TCCs) from several standards are “blended” together, choosing from several different models to perform a secondary calibration for each element. A least-squares fitting procedure allows the matrix of TCC values for the different standards to be expressed in terms of 1 to 3 different secondary coefficients for each element, which allow the generation of “variable” TCC values over the range of the calibration matrix.

14.3.1 Options

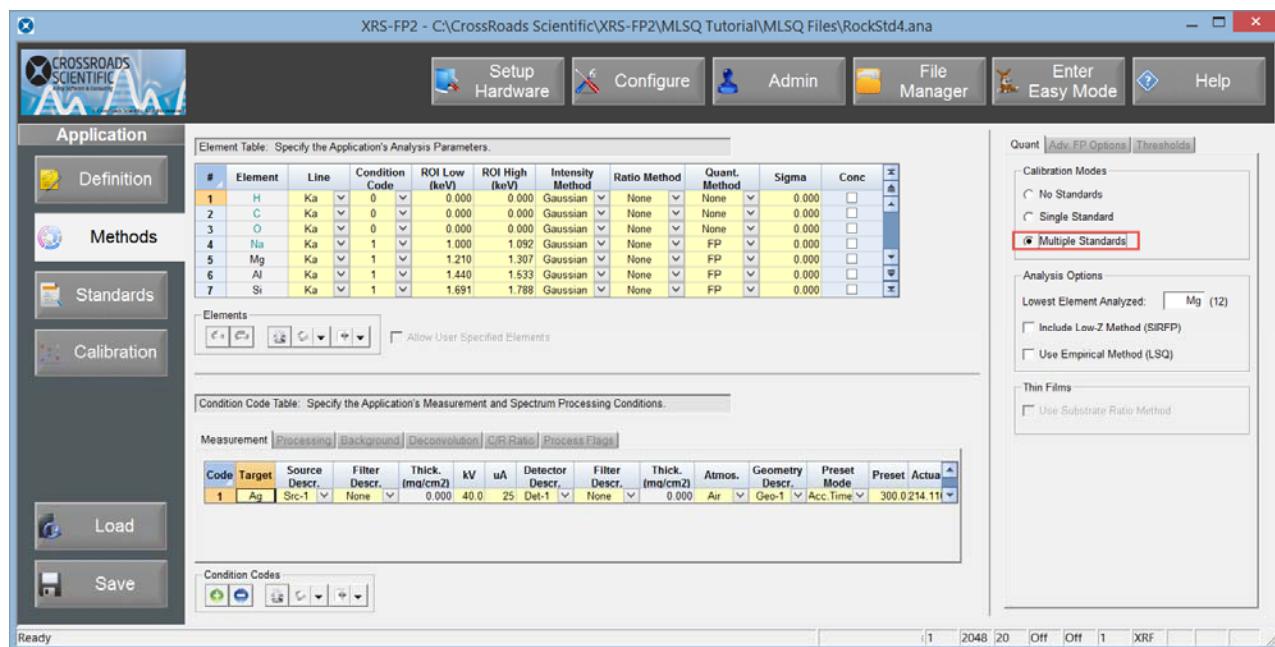
For a multiple standards (MLSQ) FP calibration select the **Methods** button in the Application workflow. Then select the Calibration Mode radio button for “Multiple Standards” in the R-hand panel under the “Quant” tab. This will bring up two new buttons in the Application workflow: **Standards** and **Calibration**. See figure below.



Note that there several “Analysis Options” available in the R-hand panel. For example, to create a scatter intensity ratio (SIR) calibration the checkbox for “Include Low-Z Method (SIRFP)” must be selected. For more information regarding the SIR-FP method procedure, please see the “Standards Calibration” document in the Help section of XRS-FP2. In addition, there is the option to “Use Empirical Method (LSQ)”. The LSQ method uses a simple empirical calibration curve of intensities vs. concentrations, which uses a least-squares fitting technique without FP.

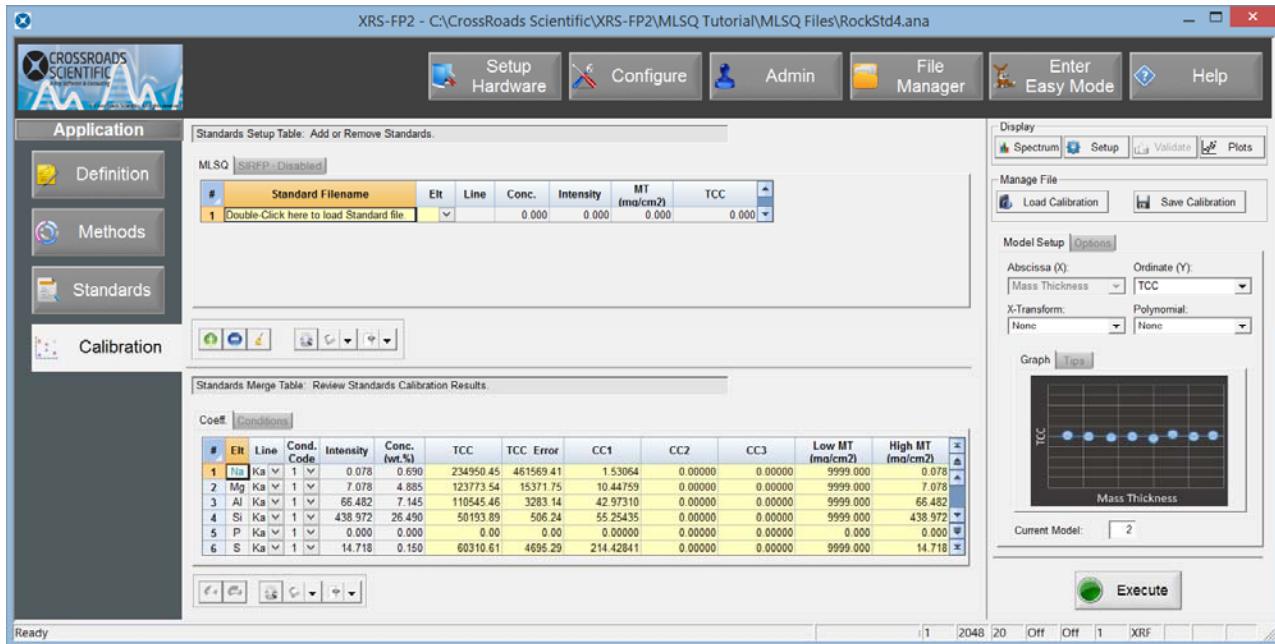
14.3.1.1 MLSQ

To create a multi-standard calibration (MLSQ), follow the steps outlined above for a single FP standard. After saving the first single standard, repeat the workflow for each additional standard to be combined in the multipoint calibration. Once all single standards are complete select the **Finish** button. This will bring up the **Methods** button in the Application workflow (shown below). Change the application quant method (calibration mode), in the R-hand panel under the “Quant” tab, to “**Multiple Standards**”. See figure below.

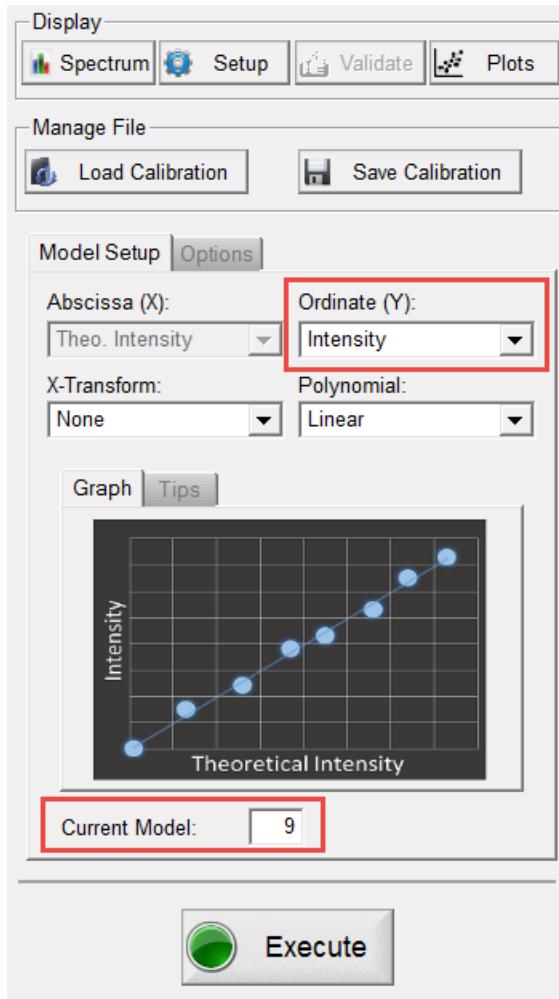


14.3.2 Calibration

To perform the TCC merge for the MLSQ calibration, go to the Calibration workflow by selecting the **Calibration** button in the Application workflow. See figure below.



Double click in the MLSQ “Standard Filename” column to load the ANA filename to be used for the MLSQ calibration. To add additional ANA files (standards) simply use the down-arrow key or select the plus button to add a row. After all the individual standards have been added to the MLSQ table, go to the “Model Setup” tab in the R-hand panel (see figure below). Select the type of model to be used by clicking on the “Ordinate (Y)” drop-down menu button. The least-squares fitting column “Polynomial” can either be “Linear” or “Quadratic”, which has an additional quadratic term. The model number (“Current Model”) is displayed on the “Graph” tab and depends on the options selected.



There are currently 10 options available in FP analysis, which correspond to the CalMode value:

1. This is the simple single-standard FP calibration, which is not considered in this workflow.
2. This is for the simple averaging model, where the TCC (Theoretical Calibration Coefficient) from each standard, for the same element, is averaged over the range of the standards.
3. This is where the TCC values on the Y-axis are fitted against the logarithm of the mass thickness, i.e., Log(MT), on the X-axis. This is also known as the Linear-Log model.
4. This is the same as model 3, except that the TCC is fitted against the reciprocal of the mass thickness of the standard (1/MT) on the X-axis. This is known as the Linear-Reciprocal method.
5. This method is not currently available.
6. This is the same as model 3, except that a quadratic fitting equation is used.
7. This is the same as model 4, except that a quadratic fitting equation is used.
8. This is a quadratic least fit of the TCC against a partial mass thickness (concentration weighted).
9. This is a linear fit of the measured intensity of the element on the Y-axis against a theoretically calculated intensity based upon the TCC value on the X-axis. The fits are forced through a (0, 0) origin, which avoids several instabilities observed with non-zero intercepts.
10. This is the same as model 9, except that the fitting equation is a quadratic. As in model #9, the fit is forced through a (0, 0) origin.

Note: if the model is set to zero, then the FP analysis will be done in a standardless mode. Many of these models are specifically designed for use with a series of thin-film standards, where the mass thickness is commonly used.

The more versatile models, such as models 9 and 10, can be used with both multilayer thin-film standards and single-layer standards, including bulk samples. The linear model is particularly suitable for removing some constant bias from a series of measurements, such as when a residual background signal might be involved.

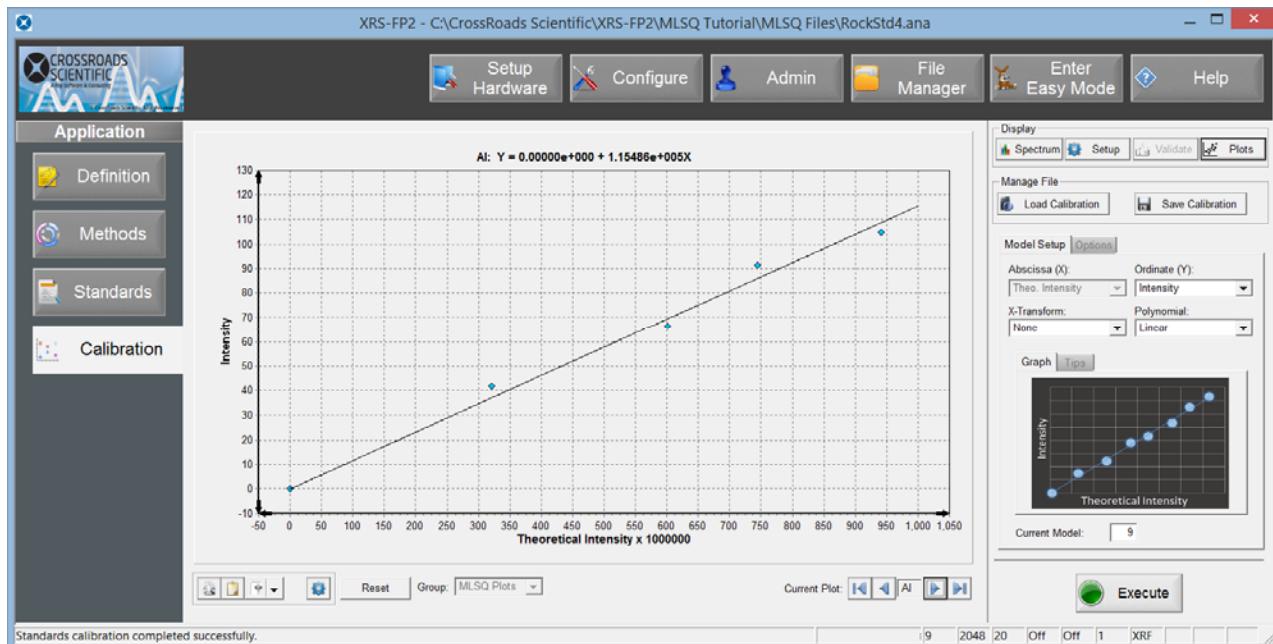
The **Execute** button not only calibrates each ANA file, but also processes the corresponding spectrum. The average value of the TCC is used as the starting point for the analysis, and refinements of this are calculated during the FP quantitation. The latest values of intensities, mass thicknesses and concentrations (depending on the chosen model) are used to update the TCC value at the end of each iteration.

14.3.2.1 Validate

The **Validate** button allows the user to run back the standards as an unknown and compare the input values from those calculated by the software. This is a useful tool for visualizing the quality of the MLSQ calibration created.

14.3.2.2 Plots

After the calibration, the fit can be inspected by clicking on the **Plot** button which will display the least squares plot for each element (see figure below). The “Previous” and “Next” buttons are used to display plots for each of the elements. Scroll through all the plots and observe the quality of the fit for each element. After scrolling through all plots, the panel will close or you can use the **Exit** button at any time.

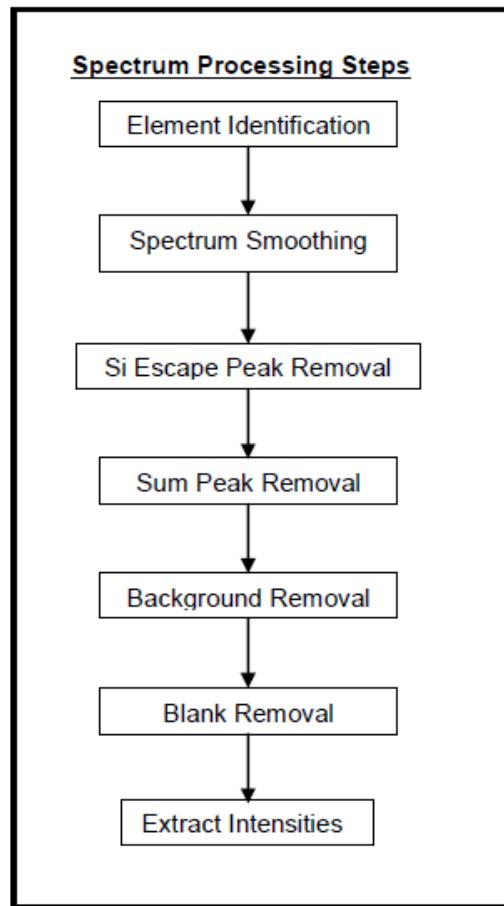


15 Spectrum Processing

15.1.1 What is Spectrum Processing?

An XRF spectrum consists of peaks, corresponding to the various elements in the sample, superimposed on a background, which arise from x-ray scatter and detector effects. It is the job of “spectrum processing” to effectively remove the signal (i.e., net peak intensity) from the noise (i.e., the background and artifact peaks). There is an additional complication caused by peak overlap, which usually means that we cannot simply integrate regions around a peak and arrive at an accurate intensity, for a given element (and x-ray line). There are empirical analysis methods, which implicitly “calibrate out” these overlaps and other spectrum artifacts, in arriving at the composition and thickness of a sample, but FP and other data reduction methods require the correct net intensities as input for calibration and quantitation.

It is best to remove these spectral “interferences” prior to the conversion to a quantitative analysis, since this generally removes several levels of uncertainty from the analysis. There are several steps in the typical processing of x-ray spectra. Some of these steps are optional, such as spectrum smoothing and sum-peak removal, but others are mandatory, such as background removal and intensity extraction. The diagram below summarizes the typical processing steps.



The first step, element identification, is not really a spectrum-processing step, but is required prior to extracting intensities. It is implicit in this description that, with every element, there is a specified x-ray line that will be used for the final analysis. This x-ray line is the one that must be “extracted” in the final step. However, in order to extract the intensities for the specified x-ray line, it will often be necessary to extract many x-ray lines for each element, to provide overlap correction, etc. This is described in more detail in the section below on Gaussian deconvolution.

15.1.1.1 *Smoothing*

Smoothing of the spectrum is recommended as a first step in spectral processing. This is particularly recommended for spectra that have poor statistics (e.g., short counting times). This operation performs a Gaussian (1:2:1) smooth of each channel in the spectrum, for the specified number of times. Repetitive 1:2:1 smoothing is effectively the same as applied wider filters. A value of 2 is normally recommended for the number of smooths. For noisy spectra, larger values can be specified. For spectra with good statistics this step can be left out.

15.1.1.2 *Escape Peak Removal*

Escape peaks arise when internal fluorescence occurs, inside the detector material itself, and the detector does not absorb these fluorescent x rays. This function is only currently valid for Si and Xenon (PC) detectors, and predicts the fraction of parent characteristic x rays that get lost as Si-K (or Xe-L) escape photons. Thus for Si detectors, the escape peaks are centered about 1.75 keV below each parent peak. This corresponds to the energy of a Si-K x ray, with a small correction for incomplete-charge collection effects within the detector.

It is recommended that, for Si detectors, the escape peaks always be removed. The software removes the escape peaks from the spectrum, and adds the equivalent “original” x-ray event at the parent peak’s energy.

15.1.1.3 *Sum Peak Removal*

Sum, or pileup, peaks arise because two incoming x rays arrive at the pulse processor (amplifier) within a time frame that is less than the fast discriminator can detect the peak from the first event. This results in peaks that have energies with the sum of the two incoming x-ray events. For example, two incoming Fe-K α photons (each with an energy of 6.4 keV), which pileup, would produce a count at 12.8 keV.

The critical parameter, which determines the level of the pulse pileup, is the Pulse Pair Resolution time. This is the time, in seconds, during which it is impossible to separate two incoming events. It corresponds to the peaking time for the fast discriminator, unless the events occur at low energies that are below the discriminator noise floor. This parameter must be accurately set for reasonable performance of this function, and is sometimes difficult to calculate for complex digital pulse processors (DPP’s).

This step is only recommended for spectra where a high deadtime is present. It is a relatively time-consuming process (a few seconds) and is not normally required if the deadtime is maintained below about 25%. This correction is not as accurate as the escape peak removal, and may leave some residual sum peaks in the spectrum. It should be tested for the specific detector and application conditions to verify the effectiveness, using the spectrum display program.

15.1.1.4 *Background Removal*

Background removal is typically the next spectrum-processing step. The only method used, in the current software, is the Automatic background method. The automatic method determines the background by gradually “snipping” the peaks from the spectrum until only the “true” background remains. This residual is then subtracted from the spectrum to leave the net spectrum.

Although the exact details of the automatic background removal are proprietary, the method is based on general signal-processing techniques that seek to distinguish fast-changing regions of the spectrum (i.e., peaks) from slowly changing regions (i.e., background). This is relatively simple for large peaks on small and flat backgrounds, but often the situation is not that simple. For example, in the spectrum taken directly from the x-ray tube, there are regions of the background that have relatively high curvature, and there are often small noisy peaks superimposed on high backgrounds. The background curvature arises from several effects, including the deceleration effects of electrons in bulk solids, which produce the characteristic bremsstrahlung x-ray continuum, whose shape depends on the anode atomic number and the incident electron-beam energy (high voltage, in kV).

This tube spectrum is scattered off the sample (and may be filtered), which changes the shape of the background, and reduces its overall intensity, compared with the sample fluorescence peaks. Nevertheless, the background is typically a substantial fraction of the total spectrum, and the regions surrounding each peak, and so it must be removed prior to extracting the net intensities.

The basis of the automatic background is to “filter” the spectrum in such a way as to remove the sharper peaks, leaves the smooth background, which is subsequently subtracting from the original spectrum. The number of iterations, and the filter width, control the automatic background operation process and must be set accurately for this method to work correctly. This is particularly true for the filter width parameter, because it is very dependent on the detector resolution. The number-of-iterations parameter controls the number of repeated operations – too low a number may result in an over estimate of the background.

15.1.1.5 *Blank Removal*

Blank removal is required when there are artifact peaks in the spectrum that cannot easily be predicted from theory. For example these might be an Argon peak from air, or Cu and Fe contamination peaks from an x-ray tube or detector collimator. This is done by collecting a spectrum without any of the analyte peaks present, and then subtracting this spectrum from that of the sample to be analyzed.

15.1.1.6 *Intensity Extraction*

After the preliminary spectrum processing is complete, the net peak intensities must be calculated. There are two methods currently available within the XRS-FP2 software, simple peak integration and least-squares peak fitting using synthetic Gaussian peak profiles for each fitted line.

The **Integrate** method, or simple peak integration, simply totals the counts for each channel in the defined Region Of Interest (ROI) of the analyzed line for each element. There is no correction for peak overlap. The chief advantage for simple peak integration is that the repeatability is generally better, which can be useful in the case of simple spectra with little or no peak overlap. Using simple peak-overlap correction, the repeatability will be slightly worse because there are more parameters involved. Generally, least-squares

methods are more accurate than integration and overlap-correction methods, but suffer from worse repeatability because of the increasingly complex corrections.

The **Gaussian Deconvolution** method corrects for peak overlaps by synthesizing peaks for all the expected lines in the region of the analyte peaks, so that a complete peak fitting occurs for both the analyte and the overlapping lines. This is the preferred method for general spectrum processing, since it uses nonlinear fitting to give greater flexibility to the peak deconvolution by allowing the peak ratios, widths and positions to change in order to better fit the acquired spectrum.

Gaussian peak profiles have the advantage of not requiring stored references, and can be “adjusted” in position, width and shape (line ratios), which helps when there are changes in the spectra from matrix effects, or changes in the x-ray spectrometer performance (gain, offset and detector resolution). To account for these shifts, some type of “nonlinear” fitting is necessary because the least-squares fitting cannot be performed directly unless all these shift and shape parameters are fixed. These methods are capable of greater accuracy in the peak fitting, but can suffer from a worsening in precision, again because of the increase in the number of degrees of freedom and the fact that local “false” minima can give rise to false solutions.

The deconvolution method is selected via the user interface in XRS-FP and each element can have a different method, if necessary.

For more technical details on the Spectrum Processing algorithms, please contact Crossroads Scientific to obtain the Algorithms Technical Software Reference.

Appendix A: About X-Ray Fluorescence (XRF)

In general terms XRF is induced after the atomic impact of energetic photons, protons or electrons. This impact, with sufficient energy, can ionize an atom by the ejection of a core-shell (such as K, L or M) electron, as illustrated by the Bohr atom model schematic shown in Figure 1¹. The generated vacancy is filled from a higher-shell electron (e.g., M, L or N) - a process that results in the emission of an x-ray photon whose energy is equal to the difference in binding energies of the two shells involved in the transition. The emitted photon has an energy that is characteristic for each element as the binding energy is proportional to the squared nuclear charge¹.

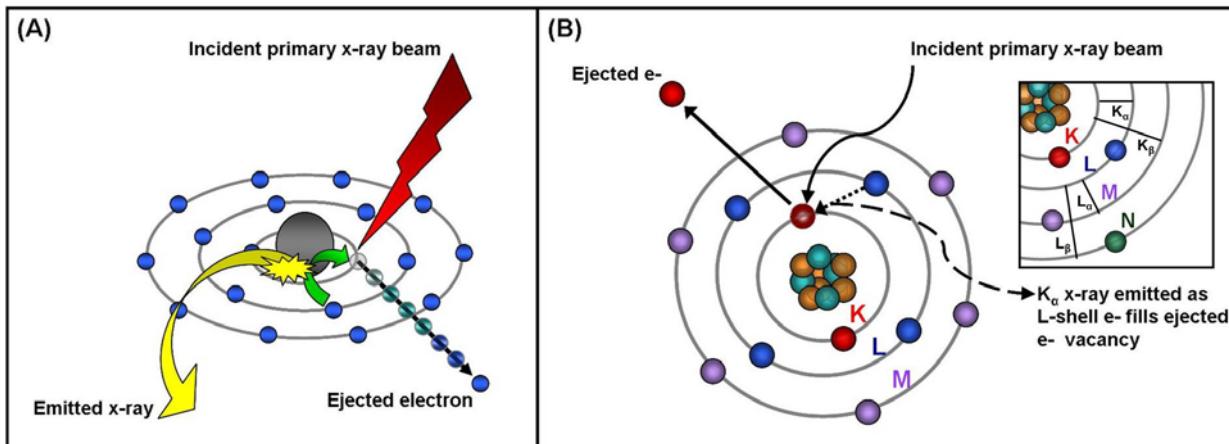


Figure 1. (A) Schematic representation of the basic process of X-Ray Fluorescence (XRF) where X-ray excitation leads to ejection of a core-shell electron from the atom. The generated vacancy is filled through a higher-shell electron resulting in the emission of a photon whose energy is equal to the difference in the binding energies of the two shells involved in the transition. **(B)** Bohr atom model illustrating the electronic transitions in a calcium atom.

With recent advances in x-ray optics, hard x rays can be focused to small spots from sub-micron to hundreds of microns in size, using a Fresnel zone plate, refractive lenses, diffractive crystals, layered-synthetic multilayers or Kirkpatrick-Baez mirror system¹. Raster scanning the specimen with an XY stage, with the acquisition of an x-ray spectrum at each point, yields quantitative topographical x-ray maps for a wide range of elements, including most biologically-relevant transition metals¹.

Introduction to XRF

X-ray Fluorescence (XRF) is usually associated with the emission of characteristic “secondary” (fluorescent) x rays from a material excited using high-energy x or gamma rays. This technique allows the determination of elemental composition as described later in more detail. The two main types of XRF methodologies are energy dispersive (EDXRF), using a solid-state cooled detector (usually silicon), and wavelength dispersive (WDXRF), which use a scanning crystal spectrometer as the dispersive element. Although detectable elements vary according to the instrument configuration and set-up, EDXRF typically detects elements from at least sodium (Na) to uranium (U), while WDXRF can extend down to beryllium (Be). Elemental concentrations can be measured from 100% down to ppm and even sub-ppm (ppb) levels. Detection limits depend on the specific element, the sample matrix and the design of the XRF instrument itself.

XRF is an analytical technique widely used for fast, non-destructive elemental or chemical analysis in the fields of material science, polymer science, environmental science, geochemistry, electronics, forensic science, archaeology and recently for biological and medical applications. Recent advances in x-ray technology have led to the development of XRF analysis capable of high spatial resolution, thus providing high sensitivity characterization in an image format for each element.

The Physics of XRF: Interactions of X rays and Matter

X rays are characterized by having energies lying within the ultraviolet and gamma radiation range in the electromagnetic spectrum (Fig. 2a). Wavelengths are typically in the range of 0.01 to 10 nm, with equivalent energies of about 125 to 0.125 keV. Work by Wilhelm Röntgen in the late nineteenth and early twentieth century established the penetrating nature of x rays, which permitted its use initially in medical imaging (radiography), and for this work he was later awarded the Nobel Prize.

However, the interaction of x rays with matter is more complex than just the absorption effects used in radiography. If absorption occurs there is a loss of a core electron which leads to subsequent characteristic fluorescence (as described later in more detail). Although the main x-ray interaction is absorption, scattering, reflection and diffraction can also occur. X-ray scattering occurs with or without a loss in energy, known as Compton and Rayleigh scattering respectively (Fig. 2b). In materials with a finite thickness some of the x rays may also be transmitted. All these different effects have their own well-known probabilities, which depend on the x-ray energy and incident angle, as well as the sample composition, thickness and density.

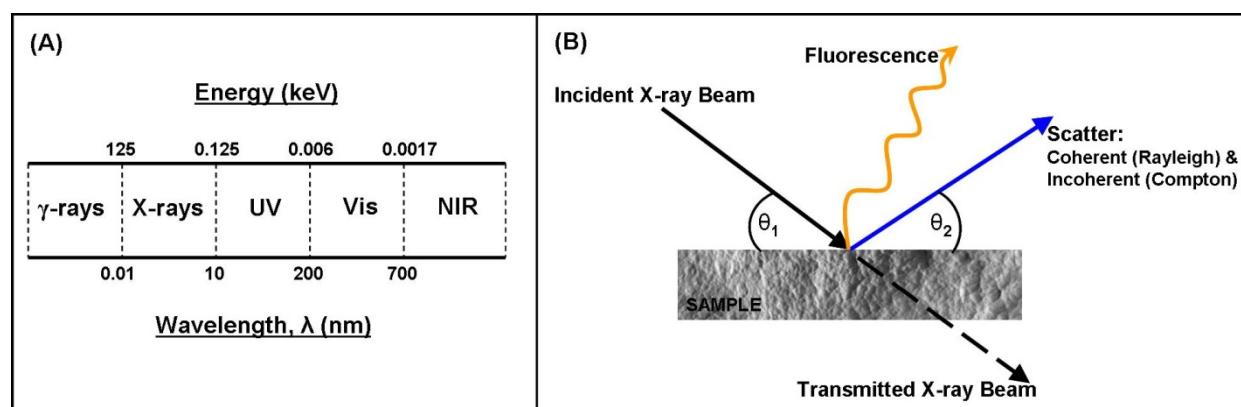


Figure 2. (A) The electromagnetic spectrum. X rays are characterized by having energies lying within the ultraviolet and gamma radiation range (of about 125 to 0.125 keV) and wave-lengths typically in the range of 0.01 to 10 nm. (B) Schematic of the interaction of x rays with a sample; θ_1 and θ_2 represent the incident and take-off angles, respectively.

In more detail, the exposure of atoms to energetic x rays (the primary radiation source) may induce ionization of the component atoms, when the energy is greater than that of its ionization potential (the so-called absorption edge). Ionization consists of the ejection of one or more core electrons from the atom. An incoming x ray can be energetic enough to remove tightly bound electrons from an inner orbital (K, L or M) of an atom within the atom producing a “hole” in the orbital and rendering the electronic configuration of the atom highly unstable.

To restore equilibrium, an electron from an outer orbital (L, M or N) “falls” into the lower orbital to fill this hole. This process results in a loss of energy, and the excess energy is usually emitted in the form of a fluorescent x ray, the energy of which is equal to the energy difference of the two orbitals involved. Sometimes the emitted x-ray photon can be re-absorbed before leaving the atom and this results in the loss of a so-called Auger electron. For x-ray emission below about 1 keV the Auger process dominates.

As noted above, energy difference between the expelled and replacement electrons produces a photon with an energy that is characteristic of the element in question. Therefore, the energy of the emitted fluorescent x ray can be used to identify and quantitatively measure the amount of any element in the sample, when these events are accumulated over time.

For each element a number of possible fluorescent transitions are possible as most atoms comprise a number of electron orbitals (i.e. K, L and M shells, etc.), thus holes may be formed in various shells. The main transitions are shown in figure 1b, although there is a fine structure from the sub-shell orbitals not shown here. The number of XRF lines available for any element depends on the number of possible transitions, and their individual probabilities. When the x-ray events are summed into a spectrum taken over time, the various line ratios can be seen for each element, and the respective ratios of the lines for all the elements. Together these lines and their ratios form a characteristic fingerprint for a specific element.

References

1. Fahrni, C. Biological applications of X-ray fluorescence microscopy: exploring the subcellular topography and speciation of transition metals. *Current Opinion in Chemical Biology* **11**, 121-127 (2007).

Appendix B: Key XRF & FP References

- (a) "Principles and Practice of X-ray Spectrometric Analysis," 2nd Edition, by E.P. Bertin, Plenum Press, New York, NY (1975).
- (b) "Principles of Quantitative X-Ray Fluorescence Analysis," by R. Tertian and F. Claisse, Heyden & Son Ltd., London, UK (1982).
- (c) "Handbook of X-Ray Spectrometry: Methods and Techniques," eds. R.E. van Grieken and A.A. Markowicz, Marcel Dekker, Inc., New York (1993).
- (d) "An Analytical Algorithm for Calculation of Spectral Distributions of X-Ray Tubes for Quantitative X-Ray Fluorescence Analysis," P.A. Pella, L. Feng and J.A. Small, X-Ray Spectrometry 14 (3), 125-135 (1985).
- (e) "Addition of M- and L-Series Lines to NIST Algorithm for Calculation of X-Ray Tube Output Spectral Distributions," P.A. Pella, L. Feng and J.A. Small, X-Ray Spectrometry 20, 109-110 (1991).
- (f) "Quantification of Continuous and Characteristic Tube Spectra for Fundamental Parameter Analysis," H. Ebel, M.F. Ebel, J. Wernisch, Ch. Poehn and H. Wiederschwinger, X-Ray Spectrometry 18, 89-100 (1989).
- (g) "An Algorithm for the Description of White and Characteristic Tube Spectra ($11 \leq Z \leq 83$, $10\text{keV} \leq E_0 \leq 50\text{keV}$)," H. Ebel, H. Wiederschwinger and J. Wernisch, Advances in X-Ray Analysis, 35, 721-726 (1992).
- (h) "Spectra of X-Ray Tubes with Transmission Anodes for Fundamental Parameter Analysis," H. Ebel, M.F. Ebel, Ch. Poehn and B. Schoßmann, Advances in X-Ray Analysis, 35, 721-726 (1992).
- (i) "Comparison of Various Descriptions of X-Ray Tube Spectra," B. Schoßmann, H. Wiederschwinger, H. Ebel and J. Wernisch, Advances in X-Ray Analysis, 39, 127-135 (1992).
- (j) "Relative Intensities of K, L and M Shell X-ray Lines," T.P. Schreiber & A.M. Wims, X-Ray Spectrometry 11(2), 42 (1982).
- (k) "Calculation of X-ray Fluorescence Cross Sections for K and L Shells," M.O. Krause, E.Ricci, C.J. Sparks and C.W. Nestor, Adv. X-ray Analysis, 21, 119 (1978).
- (l) X-Ray Data Booklet, Center for X-ray Optics, ed. D. Vaughan, LBL, University of California, Berkeley, CA 94720 (1986).
- (m) "Revised Tables of Mass Attenuation Coefficients," Corporation Scientifique Claisse Inc., 7, 1301 (1977).
- (n) "Atomic Radiative and Radiationless Yields for K and L shells," M.O. Krause, J. Phys. Chem. Reference Data 8 (2), 307-327 (1979).
- (o) "The Electron Microprobe," eds. T.D. McKinley, K.F.J. Heinrich and D.B. Wittry, Wiley, New York (1966).
- (p) "Compilation of X-Ray Cross Sections," UCRL-50174 Sec II, Rev. 1, Lawrence Radiation Lab., University of California, Livermore, CA (1969).

- (q) "X-ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at E = 50-30,000 eV, Z = 1-92," B.L. Henke, E.M. Gullikson and J.C. Davis, *Atomic Data and Nuclear Tables*, 54, 181-342 (1993).
- (r) "Reevaluation of X-Ray Atomic Energy Levels," J.A. Bearden and A.F. Burr, *Rev. Mod. Phys.*, 39 (1), 125-142 (1967).
- (s) "Fluorescence Yields, ω_k ($12 \leq Z \leq 42$) and ω_l ($38 \leq Z \leq 79$), from a Comparison of Literature and Experiments (SEM)," W. Hanke, J. Wernisch and C. Pohn, *X-Ray Spectrometry* 14 (1), 43 (1985).
- (t) "Least-Squares Fits of Fundamental Parameters for Quantitative X-Ray Analysis as a Function of Z ($11 \leq Z \leq 83$) and E ($1 \leq E \leq 50$ keV)," C. Poehn, J. Wernisch and W. Hanke, *X-Ray Spectrometry* 14 (3), 120 (1985).
- (u) "Calculation of X-Ray Fluorescence Intensities from Bulk and Multilayer Samples," D.K.G. de Boer, *X-Ray Spectrometry* 19, 145-154 (1990).
- (v) "Theoretical Formulas for Film Thickness Measurement by Means of Fluorescence X-Rays," T. Shiraiwa and N. Fujino, *Adv. X-Ray Analysis*, 12, 446 (1969).
- (w) "X-Ray Fluorescence Analysis of Multiple-Layer Films," M. Mantler, *Analytica Chimica Acta*, 188, 25-35 (1986).
- (x) "General Approach for Quantitative Energy Dispersive X-ray Fluorescence Analysis Based on Fundamental Parameters," F. He and P.J. Van Espen, *Anal. Chem.*, 63, 2237-2244 (1991).
- (y) "Quantitative X-Ray Fluorescence Analysis of Single- and Multi-Layer Thin Films," *Thin Solid Films* 157, 283 (1988).
- (z) "Fundamental-Parameter Method for Quantitative Elemental Analysis with Monochromatic X-Ray Sources," presented at 25th Annual Denver X-ray Conference, Denver, Colorado (1976).