

# XRS-FP Software Guide V6.4.4



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## DOCUMENT CHANGE LOG

Date	Person	Pages	Description
25-Jul-01	Brian Cross	All	Created document for Amptek Software, v.1.1.3
20-Dec-01	Brian Cross	All	Major upgrades from v.1.1.3 to v.1.2.3
29-Dec-01	Brian Cross	Most	Corrections and additions for v.1.2.4
13-Aug-04	Brian Cross	Many	v.2.1.4 updates for DP4, Blank, C/R, etc.
27-Jul-05	Brian Cross	Some	v.2.2.3 for Compton Peak usage, Automation
20-Dec-05	Brian Cross	Most	v.3.0.1 Major additions for MLSQ, SIR-FP & MTF-FP quantitative options, & PX4 digital pulse processor.
13-Mar-08	Brian Cross	Many	v.3.3.0 Major updates for analysis using simple least-squares calibrations, Reference deconvolution, concentration and intensity thresholding and many other small changes, plus support for CdTe detectors.
23-Apr-08	Brian Cross	39, 40	v.3.3.1 Add text to the explanation for the CdTe escape peak removal constraints.
19-Aug-08	Sarah Cross	Many	v.4.0.3 Added new sections for XRF introduction and background. General editing.
21-Aug-08	Brian Cross	Most	v.4.0.3 General edits and convert to using Spectra-X spectrum display instead of Amptek ADMCA. Added documentation for Batch processing and charting, Auto-ID, and Spectra-X.
1-Jan-09	Brian Cross	Some	v.4.2.3 Add Mini-X support, Background File option, Company Name input and misc. documentation.
1-May-09	Brian Cross	27	v.4.3.1 Added to section 5.1 re spectrometer gain and offset calibration.
31-May-09	Brian Cross	Some	v.4.3.2 Updated text for MLSQ methods. Support for DP5 digital pulse processor. Updated Spectra-X features (v.1.4.0.0).
Sep-09	Brian Cross	Most	v.4.5.0 Major updates to Spectra-X, etc. Spectra-X v.1.5.0.0 and above requires v.8 of the TeeChart component (replaces v.7) as shown in the Help-About for Spectra-X.

Date	Person	Pages	Description
Feb-10	Brian Cross	Several	v.4.6.0 XRS-FP now compatible with Windows 7 and Vista, including 64-bit versions. New HASP installer. Updated interface to Amptek DPP's (incl. DP5). Additional parameters available in Batch processing. Check at startup for presence of US Windows Locale. Improved form resizing. Updated reading of *.txt and *.csv spectrum files. Added Upper/Lower Limit feature for concentration checking in Element Table. Allow MLSQ to use bulk stds. for thin-film calibration. Increased # decimal places from 3 to 4 for Wt% in Sample Table.
Feb-12	C. Janko	Several	v.5.0 Refactor Software Architecture Section to support new DPP devices.
July-13	Sarah Cross	Several	v.5.1 Misc. changes
Oct-13	Brian Cross	Many	v.5.6 Updates to DPP acquire sections for new DPP devices.
16-May-14	Brian Cross	Most	v.5.7 Revised most of document
4/5-Jan-15	Brian Cross	Several	v.5.9.10 New features, bug fixes.
11-Jan-16	Brian Cross	Several	v.6.4.4 New features, bug fixes. Max # elements from 30 to 55. Max # components from 25 to 50. Max # standards from 30 to 50. Max # conditions from 4 to 8.

## GETTING STARTED

### 1.1 *Introduction*

This software guide describes the basic functions that the XRS-FP (or XRS-MTFFP) program is designed to perform. It is assumed that you are familiar with the basics of operating a Windows application and that you are familiar with the common terms and techniques of X-Ray Fluorescence (XRF) and Energy-Dispersive Spectrometry (EDS) analysis. The following abbreviations will be used to describe terms throughout this guide:

- **XRF**      X-Ray Fluorescence
- **EDS**      Energy-Dispersive Spectrometry
- **FP**      Fundamental Parameters (i.e., using a known database of x-ray interactions and equations for using them)
- **MTFFP**      Multilayer Thin-Film FP analysis

There are two software packages available from CrossRoads Scientific for XRF analysis. The first is the XRS-FP program that can analyze bulk and single-layer samples. The second software package, XRS-MTFFP, can analyze up to 8 layers for thickness and composition. Both programs will be described in this document, although you may not have both programs. The name XRS-FP will be used to describe either program unless there is a feature that is specific to XRS-MTFFP.

In addition to the brief description of XRF outlined below, the following books are recommended to gain familiarity with XRF and EDS analysis:

- “Principles and Practice of X-ray Spectrometric Analysis,” 2<sup>nd</sup> Edition, by E.P. Bertin, Plenum Press, New York, NY (1975).
- “Principles of Quantitative X-Ray Fluorescence Analysis,” by R. Tertian and F. Claisse, Heyden & Son Ltd., London, UK (1982).
- “Radiation Detection and Measurement,” 2<sup>nd</sup> Edition, by G.F. Knoll, John Wiley & Sons, New York, NY (1989).
- “Handbook of X-Ray Spectrometry: Methods and Techniques,” eds. R.E. van Grieken and A.A. Markowicz, Marcel Dekker, Inc., New York (1993).
- “Quantitative X-Ray Spectrometry,” 2<sup>nd</sup> Edition, by R. Jenkins, R.W. Gould and D. Gedcke, Marcel Dekker, Inc., New York (1995).
- “XRF in the Workplace,” by J. Willis, K. Turner and G. Pritchard, PANalytical Australia, Australia (2011).

Of course, there are many other excellent books and periodicals available on these topics, some of which may be more appropriate to your particular application.

There are three main steps for XRF analysis using the XRS-FP software:

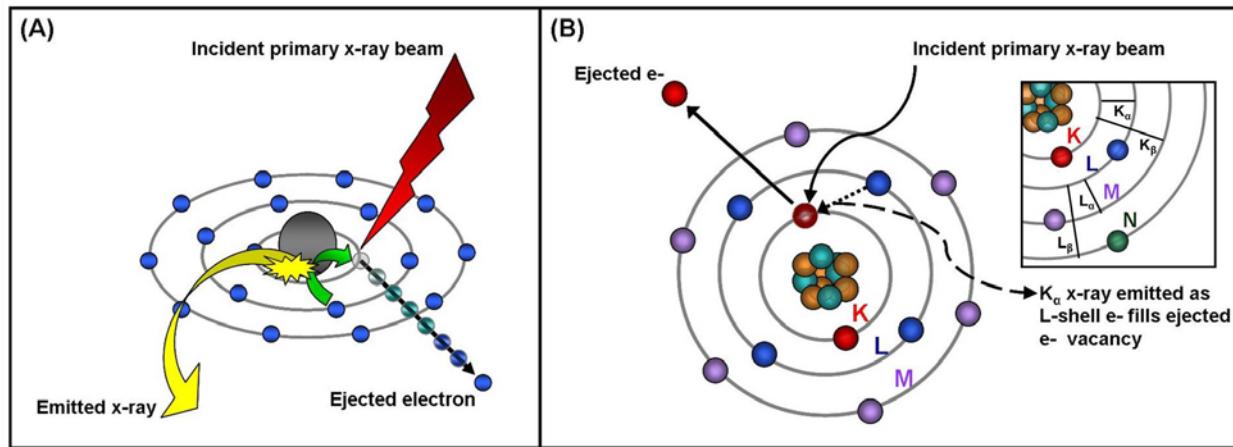
- First the system is usually calibrated using standards
- Subsequently, it can then be used for the quantitative analysis of unknowns
- And finally, routine maintenance checks may be performed on the XRF system

Note: There is also the possibility of doing analysis without standards, as long as 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, one can also use simple least-squares calibration and quantitation, without using the full FP method.

The “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-FP software and doing any calibration work.

## 2 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 1<sup>1</sup>. 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 charge<sup>1</sup>.



**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 system<sup>1</sup>. 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 metals<sup>1</sup>.

## 2.1 Introduction to XRF

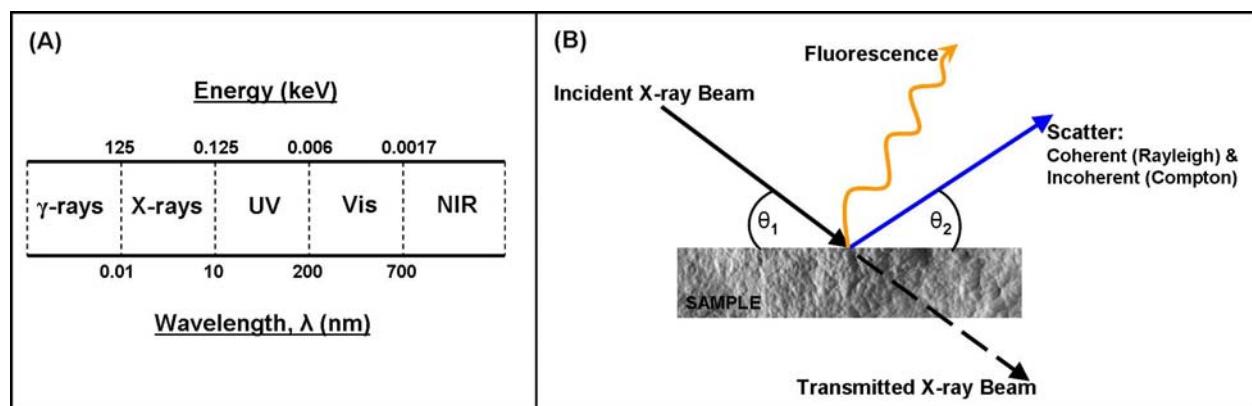
X-ray Fluorescence (XRF) is usually associated with the emission of characteristic “secondary” (fluorescent) x rays from a material excited using high-energy x or gamma rays. This technique allows the determination of elemental composition as described later in more detail. The two main types of XRF 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 lead to the development of XRF analysis capable of high spatial resolution, thus providing high sensitivity characterization in an image format for each element.

## 2.2 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;  $\theta_1$  and  $\theta_2$  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.

### 2.3 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).

## 3 THE PURPOSE OF XRS-FP SOFTWARE

### 3.1 *Introduction to Spectrum Processing*

In general, an XRF spectrum consists of peaks, corresponding to the various elements in the sample, superimposed on a background, which comes 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 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 methods require the correct net intensities as input for calibration and quantitation.

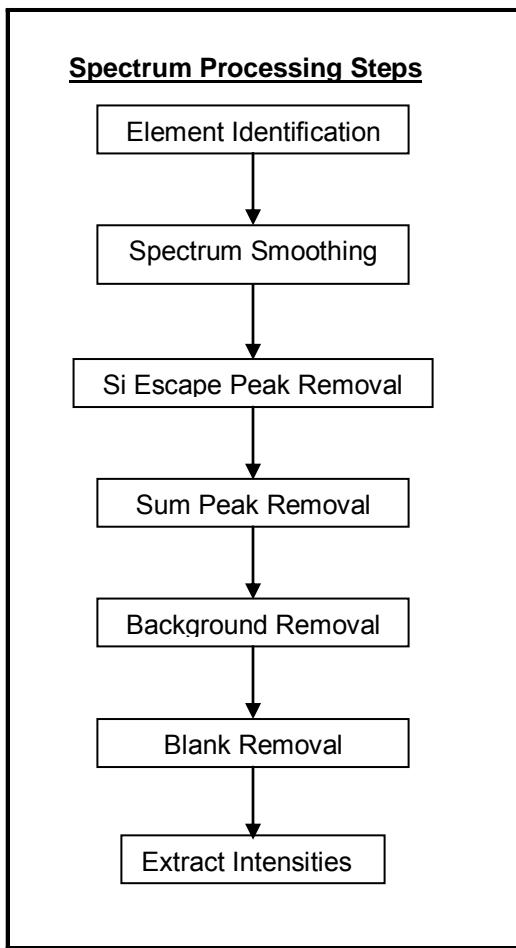


Figure Outline of Spectrum Processing Steps.

In general it is better to remove these spectral “interferences” prior to the conversion to a quantitative analysis, since this removes several levels of uncertainty from the analysis. There are several steps in

the typical processing of XRF spectra. Some of these are optional, such as spectrum smoothing and sum-peak removal, but others are mandatory, such as background removal and intensity extraction. In the figure above the typical processing steps are outlined.

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 line that will be used for the final analysis. This line is the one that must be “extracted” in the final step. However, in order to extract the intensities for the specified line, it will often be necessary to extract many lines for each element, to provide overlap correction, etc. This is described in more detail in the section below on Gaussian deconvolution.

## **3.2 The Spectrum-Processing Functions**

### **3.2.1 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 typically 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. Several of these broader filters (Savitsky-Golay, etc.) are available in the software, but most of them give very similar results to the repetitive 1:2:1 smoothing. Values of 1 or 2 are 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.

### **3.2.2 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 valid for Si, Cd-Te and Xenon (PC) detectors, and predicts the fraction of parent characteristic x rays that get lost as Si-K (or Cd-L, Te-L 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 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.

### **3.2.3 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 $\alpha$  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 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, via the spectrum display program.

### 3.2.4 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, leaving the smooth background which is subsequently subtracted 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, as it is highly 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.

### 3.2.5 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.

### 3.2.6 Intensity Extraction

After the preliminary spectrum processing is complete, the net peak intensities must be calculated. There are several methods currently available in the spectrum-processing libraries; simple peak integration, overlap correction, and least-squares peak fitting using either synthetic Gaussian peak profiles for each fitted line, or stored Reference profiles. The **Integrate** method 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 **Overlap** method applies pre-stored overlap factors to these simple integrals to correct for the overlap of one peak in the integration region of another. (Although this method is in the spectrum processing library, it is not currently supported by the software user interface.)

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. The **Reference Deconvolution** method corrects for peak overlaps, again using a least-squares method, but by using stored Reference profiles peaks instead of synthetic peaks. The **Reference** method is usually applied with linear least-squares fitting, but the **Gaussian** method often 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.

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

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 Reference-profile method (sometimes known as the “library-least-squares” method) has the advantage of matching the peak profiles more accurately than the purely Gaussian profiles, but has the disadvantage of less flexibility in adjusting for line-ratio changes (XRF matrix effects) or peak position and width changes.

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

### **3.2.7 Peak Integration**

For each element to be analyzed by this method, a Region Of Interest (ROI) must be defined (either manually, or automatically via the library). The contents of each channel that lies within this region (including the end channels) are added together to form the Peak Integral, which is then divided by the acquisition time (livetime) in seconds to produce the peak intensity in counts/second.

### **3.2.8 Peak Overlap Factor Method**

This method is similar to the Peak Integration method described above, except that Overlap Factors are applied to correct the overlap of one peak in the ROI of another. These Overlap Factors are calculated by acquiring a pure element spectrum for each element to be analyzed and then, for all the elements to be analyzed in the sample, integrals calculated for each ROI in that spectrum. This is repeated for each element. For  $n$  elements, we end up with  $n \times n$  integrals. These integrals are each divided into their parent integral, for each element, to yield a set of  $n \times n$  Overlap Factors which have values  $\leq 1$ .

These Overlap Factors are then applied when analyzing the unknown sample by reducing the set of simultaneous equations. This method is fast, but requires the collection of pure-element spectra for each element to be analyzed and this matrix of factors has to be re-calculated for each different sample, depending upon the elements to be analyzed. The advantage of the Gaussian Deconvolution (see below) method for peak-overlap correction is that no *a priori* steps are required when setting up the elements for analysis.

### **3.2.9 Gaussian Deconvolution**

Gaussian deconvolution fits individual Gaussians for every known line in the spectrum as a means of determining net peak intensities from the spectrum. The elements that have been defined in the spectrum (i.e., for quantitative analysis), each have a pre-selected major line for that element (i.e.,  $K\alpha$ ,  $K\beta$ ,  $L\alpha$ ,  $L\beta$ ,  $L\gamma$ , or  $M\alpha$ ) that will be used for the (FP) analysis. In reality, each of these major lines is composed of other individual lines (e.g., the  $K\alpha$  line is really composed of  $K\alpha_1$  and  $K\alpha_2$  lines), which are typically not resolved by most detectors. It is convenient to use these rolled-up lines, as they have better statistics when combined, and have almost the same energies, which does not cause a problem for subsequent FP calculations. The latter assume a single energy is used for each element analyzed.

However, for the Gaussian peak fitting, it is necessary to use all the individual lines, not only for the major line being analyzed, but for the neighboring lines that may overlap both with the parent line of interest, and **all** the other analyzed lines in the spectrum. The first part of the program searches the lines for each element (up to 30), and includes those on the list for fitting that either contribute to the analyzed lines, or to the overlap of those lines. This means that even for simple spectra, where only 3 elements are being analyzed, there could be 50 or more lines being fit in the least-squares calculations.

The spectrum *StartEV* and *kV* parameters will limit which lines are actually used. For example, if the spectrum was acquired at 20 kV and Sn is on the element list, only the L-series lines for Sn can be fit, because the K-series lines for Sn are above 20 kV. More specifically, it is the line-series edge (e.g., K or L-III) that must be below the excitation kV. Usually a margin (about 1 kV) is added to this; otherwise the excitation efficiency would be too low to be useful. Thus it is very important that the *kV* be entered correctly (this is also true for the subsequent FP calculations).

There are two kinds of Gaussian peak fits that are provided in the software. The first is the linear least-squares method. This method allows only the peak heights to be adjusted during the fitting process. Usually this kind of fit is adequate. It is, however, important that both the spectrum energy calibration is correct (certainly within one channel across the complete spectrum) and that the detector resolution value be set correctly.

The relative peak heights within a series (e.g.,  $K\alpha_1$ ,  $K\alpha_2$ ,  $K\beta_1$ ,  $K\beta_2$ , and  $K\beta_3$  for the K-series) are taken from tabulated values and are not allowed to vary during the linear fitting. This means that if there are large absorption or enhancement effects in the sample, which could affect the line ratios, then this type of fit may not perform as well as the nonlinear fit.

The second method uses a nonlinear least-squares fitting procedure. This method fits the peak heights, positions, and widths to the spectrum. This is a nonlinear fitting process, because these variables are not directly solvable by standard linear least-squares fitting. Standard nonlinear algorithms are employed (such as the Marquardt-Levenberg method), which allow the three parameters for each peak to be adjusted independently. However, in order to make this method work well for x-ray spectra, it is mandatory to include constraints in the fitting process. The appropriate constraints are: (1) the relative line ratios for each line series that is used in the fit, (2) the expected or allowable deviations of peak widths, and (3) the expected or allowable deviations of peak positions.

The relative line ratios are reasonably well known, but they can change depending upon the following factors: (a) the *kV* of the tube spectrum, (b) the sample thickness and take-off angle, and (c) the composition of the sample. In the latter case, there may be absorption edges of other elements, between the major lines, that will cause some lines (i.e., the ones just above the edge) to be preferentially absorbed. Therefore it is advantageous to allow these ratios to change, depending upon the sample spectrum. However, if we allow the ratios to be completely ignored, nonlinear fitting will often produce completely erroneous peak fitting, where the fitting error ( $\chi^2$ ) is small, but the solution is completely bogus (even negative peak heights may result).

To avoid these problems, the software only allows the line ratios to change by certain factors (with respect to the most dominant line). The default factor is 2.0, which means that the K $\beta$ :K $\alpha$  ratio could change up or down by a maximum of a factor of 2.0, from the default line ratio stored in the software. So, if the K $\beta$ :K $\alpha$  ratio started at 0.1, the maximum allowed would be 0.2, and minimum would be 0.05. This is known as constrained fitting.

Similar constraints are applied to the fitting of the peak widths and position (i.e., centroid) locations. X-ray peak resolutions are a well-known function of both the peak energy and the "system" resolution (typically defined for the Mn-K $\alpha$  peak). So, again, the fitted peak widths are constrained to conform to this equation, within certain limits. The default variation, for each peak, is 35%. For example, if the peak had an initial predicted resolution of 200 eV, the maximum allowable width, for this peak, would be 270 eV, and the minimum would be 130 eV. These parameters are defined with the Setup-Gauss functions.

Similarly for the peak positions, there is a well-characterized equation that relates peak position (energy) to the spectrometer zero (offset) and gain (eV/channel). Both these are allowed to vary independently, but the calculated values must be within both the limits defined in the Setup-Gauss definitions. The default allowable zero deviation is  $\pm 0.040$  keV, and default allowable fractional gain variation is  $\pm 0.002$ . The value of 0.040 keV means that any channel can have an offset of any value lying between  $0 \pm 0.040$  keV. The percentage gain variation value of 0.2% corresponds to a fractional change of 0.002, which means that, for example, a channel at 30 keV could change by up to 0.060 keV. The larger of these two allowable variations is the one that is enforced.

The nonlinear technique is slower than the linear method, especially when analyzing many elements, but it may be necessary for some analysis situations. For one or two elements, the nonlinear Gauss fitting typically will take just a second or two, whereas for more than 10 elements this time could stretch to a minute. The use of L or M lines, which contain many sub-lines, will slow considerably the speed of the nonlinear method.

### 3.2.10 Reference Deconvolution

The Reference Deconvolution method, also known as Library Least Squares fitting, is an alternative to Gaussian deconvolution and has advantages, disadvantages and similarities to the latter. This deconvolution method uses stored References instead of Gaussian profiles. It has the advantage of more exactly matching the peak shapes, especially when some detectors do not yield symmetrical Gaussian profiles (e.g., CdTe detectors). Any low or high energy tailing will automatically be recorded with the Reference, assuming that this tailing is not a function of count rate. Sometimes, other components of an x-ray spectrum can be included in the Reference, for example, background regions and escape peaks, by choosing the appropriate Region Of Interest (ROI).

The chief disadvantage of the Reference method is that there can be no allowance for peak shifts, width changes and line-ratio changes. This means that the spectrometer must remain stable from the

measurement of the standards (& References) to the unknown sample measurement. Because there are no analytical expressions for the peak profile, it is not possible to differentiate the model and yield slope vectors for the M-L method (see previous section).

The least-squares fitting algorithms used by Reference deconvolution are the same ones that are used for Gaussian deconvolution, except that Reference deconvolution can only use the linear least-squares method. References are stored experimental spectra, and so it is not possible to adjust their peak shapes and positions during the deconvolution process as it is when using synthetic Gaussian profiles.

### **3.3 *Introduction to XRF Analysis using FP***

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

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 4 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 & 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-FP software can be used for bulk or single-layer samples. The optional software package XRS-MTFFP will support multilayer samples, for up to 8 layers. Both packages can calculate

bulk composition and thickness analysis for up to 30 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/cm<sup>2</sup> and mg/cm<sup>2</sup> 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.

Some key references are noted in the table list below.

### 3.3.1 FP References

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- (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).
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- (l) X-Ray Data Booklet, Center for X-ray Optics, ed. D. Vaughan, LBL, University of California, Berkeley, CA 94720 (1986).
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- (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).
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- (s) "Fluorescence Yields,  $\omega_k$  ( $12 \leq Z \leq 42$ ) and  $\omega_l$  ( $38 \leq Z \leq 79$ ), from a Comparison of Literature and Experiments (SEM)," W. Hanke, J. Wernisch and C. Pohn, *X-Ray Spectrometry* 14 (1), 43 (1985).
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## 4 SOFTWARE OPERATION

### 4.1 Loading the Software

Either run the software from the Windows Start-Programs menu, or double-click on a shortcut (if one has been created on the Windows desktop). First, the splash screen will be loaded, then the main program and the separate Spectra-X window. The splash screen will show the values and options for the HASP security plug, and the software libraries that have been loaded.

After the main program is loaded, a master configuration file is then automatically loaded. This file is named "Master.tfr" and MUST reside in the same directory as the XRS-FP program. This file contains the elements and calibration coefficients required for routine XRF analysis, along with a base description of the various analysis and system setups.

A version of this file is supplied with the software, but it is almost certain that the user will need to change this for the application and system at hand. Note that a TFR file having any filename can be created and used for future applications. However, a copy of "Master.tfr" must remain in the XRS-FP directory as this configuration file is automatically used when the software loads. This file can be edited with Notepad but the user should be very careful in doing this as one small mistake can invalidate the complete file (having a copy of "Master.tfr" can be useful should you need to go back to the "default" configuration).

There is also another start-up file, XRS-FP.ini, which contains parameters that are less specific to the analytical setup, although some of them can affect the spectrum processing. There are other sections in this file that describe some options in the software such as a password setup and the calling of an external program. This file can be edited with Notepad but the user should again be very careful in doing this, although it is more robust than the TFR file editing. XRS-FP.ini is updated automatically by the software any time a change is made to one of its parameters. This is not true for the Master.tfr file, because there can be many TFR files used – one for each application – and so this file should be saved manually.

The list of elements should be known in advance (for routine analysis). This list may have *more* elements than those actually in a given sample (and these should be reported at low levels), but should *not* have less elements than the sample. It is critical that the sample is as completely defined as possible for accurate FP analysis. If unanalyzable elements or compounds (e.g., H, C, O or C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) are present, they should be specified as Fixed with a best guess (or knowledge) about their concentrations, or analyzed by stoichiometry if possible.

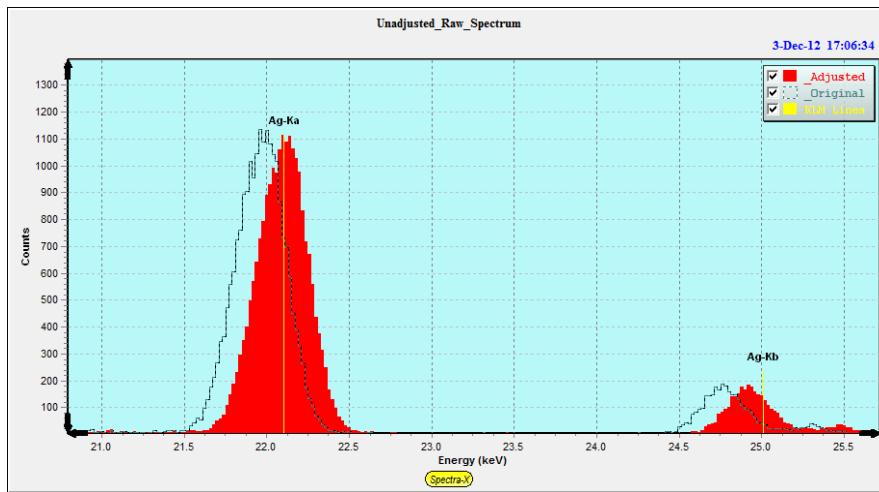
In addition to the element list, the file also contains the x-ray (K, L or M) line and FP calibration coefficient to be used for each element. If the coefficients are all zero (i.e., the elements are not calibrated), then the analysis will be done on a "standardless" basis.

See later for more information on setting up and using the TFR files.

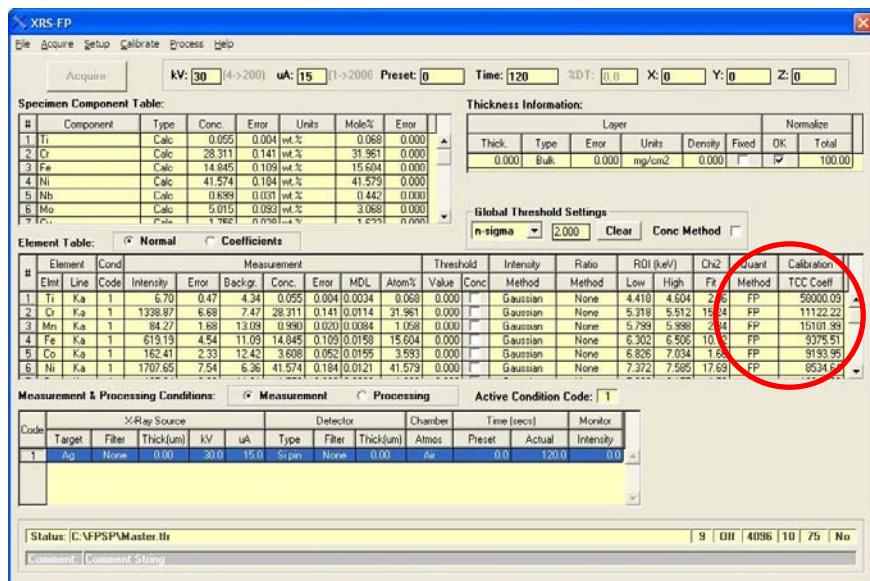
## 5 FP CALIBRATION & ANALYSIS

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**, 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 (see section 3.3.1 "FP References" for suggested reading).

## 5.1 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 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 operation (Calibrate-Spectrum) is described in more detail in a later section, and is designed to use a well-defined two-peak spectrum 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-FP, which assumes a zero offset energy, and 5, 10, 20, 40, 80 or 160 eV/channel.

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

- (a) Load the software and invoke the “Calibrate Spectrum Gain and Offset” panel using either the “Setup Spectrum Adjust” or “Calibrate Spectrum” menu commands (see later section).
- (b) At this point the existing or default values for Offset and Gain will be displayed in the top right-hand corner of the panel. When the software first loads, these values come from the XRS-FP.ini file, in the XRS-FP software directory. If this is the first time you are doing a calibration then click on the Reset Gain & Offset button to reset the values back to the target values (e.g., 20 eV/ch with a zero offset).
- (c) Ensure at this point to Uncheck the check boxes for the “Auto Adjust Spectrum Gain & Offset” options in the Setup-Processing and Setup-MCA panels.
- (d) 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.
- (e) Turn on the x rays, as necessary, and 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.
- (f) Acquire a spectrum or, if you do not have a live system load a spectrum file, into the XRS-FP program (see later for more information on this procedure). About 50 seconds should be sufficient, but aim to get at least 100,000 counts in the spectrum, of which at least 50,000 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.
- (g) Assuming the 5 peak-search parameters are set correctly (these are the 5 parameters shown under the “Setup Parameters for Auto Calibrate” in the Calibrate Spectrum Gain and Offset panel), press the button to Calibrate the Spectrum (“Calibrate Spectrum” button). At the end of this operation, the new values for gain and offset should be displayed.
- (h) Check the quality of the displayed gain and offset values. 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 DP4 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.
- (i) After getting bad values (see above) or the Adjust does not work well (see below), then reset the Offset and Gain values (use the “Reset Gain & Offset” button), and repeat the Calibrate

Spectrum step above, or use a Manual Calibration to assist the automatic calibration in finding the correct peaks. To perform a Manual Calibration, first ensure you have an unadjusted (raw) spectrum, then click the “Reset Gain & Offset” button to reset the values to their target ones (e.g., Offset of 0 eV, and a Gain of 20 eV/channel). Next, use the cursor in the Spectra-X window to identify the centroid channels for the two peaks of interest (these should be 2 well-separated and well-defined K $\alpha$  peaks), then enter their displayed energy values in the Low energy and High energy peak text boxes. Now click on the “Calculate Gain & Offset” button again to get approximate values for the Gain and Offset. Now click on the “Calibrate Spectrum” button and the automatic algorithm should refine these initial estimates of Gain and Offset.

- (j) If the values look reasonable then press the “Adjust Spectrum” button, and this will process the spectrum so that the peaks should be in calibration with the normal gain (e.g., 10 eV/Ch) and zero offset values. Check the spectrum display to verify this. Note that the “Apply Calibration” button does NOT adjust the spectrum, but just adjusts the horizontal scale – this is not useful for routine spectrum adjustment and processing, so you should only use this option with care. Use the “Adjust Spectrum” button instead.
- (k) After successfully calibrating this spectrum (i.e., the spectrometer), then press the “OK” button, which saves these parameters in the XRS-FP.ini file for later use in routine analysis.
- (l) After exiting this panel be sure to check one of two check boxes, in order to use the Adjust function as a routine automated method. In the first method you can check the “Auto Adjust Spectrum Gain & Offset on Load” option in the Setup-Processing panel. This will then enable any future spectrum files to be automatically adjusted when loaded with the appropriate gain and offset values. Alternatively, you can use the Auto Adjust Spectrum during Acquire button option in the Setup-MCA panel. If you have a live system, then this option will affect spectra as they are being acquired, and the spectra will be auto-adjusted so that the peaks are immediately shown in their correct locations.

It is also important, before starting the next step, that the correct detector resolution value be entered into the software (see the Setup-Processing dialog), as this parameter is key to performing good quality spectral peak fitting (see the later section on Process Spectrum – Deconvolute).

## **5.2 XRF Elemental FP Calibration or Standardization**

The next step is to calculate the response factors (sensitivities) for all the elements of interest, unless standardless analysis is going to be used. This standardization process generates calibration coefficients that are later used by the main FP program. For standardless analysis the user can skip this section.

For the XRF system we need to collect spectra for each of the elements of interest, analyze them and then generate the appropriate FP calibration coefficients. 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.

The description below assumes that ONLY one standard is effectively used for each element, even though multiple standards may be employed. In other words, the last calibration for any given element will be the one used. When using a single standard for each element, or a single multi-element standard for all elements, this is not an issue, but when mixing modes unpredictable results could be obtained if the last standard used had inaccurate values for use in the calibration.

In the v.3.0.0 or later software, there is a new option where multiple standards can truly be used with each element, and least-squares fitting can be done with various models, in order to allow for any variations from the theory of FP calibration. This will be described in the later section on Calibration. This can be used to calibrate using either type or pure-element standards. Note that this is not the same as using a simple least-squares fitting technique without FP.

The following description assumes everything is setup and optimized. You should check through the rest of this manual for tips on how to ensure that things are working OK (e.g., that spectrum resolution is as expected).

- (a) After having performed the spectrometer calibration (see above section), then make sure that all the parameters are set correctly in the Condition table, etc.
- (b) In the Setup FP Calibration dialog, select the appropriate radio button for "Single" or "Multiple" Standards and press OK. *This is very important.*
- (c) Enter a description of the standard in the Component Table, including compound formulae, concentrations, and the thickness of the standard (if it is a thin film).
- (d) If the standard is a thin film, set the Density to 0.0, so that a theoretical value is used (to convert between thickness and mass thickness), unless you know the exact density of the thin-film.
- (e) Ensure the Normalize option is checked, and the Total set to 100.0%.
- (f) If you are acquiring the spectra live then ensure the "Auto Adjust Spectrum Gain & Offset" option is checked, unless you are sure that the spectra are all well calibrated. Otherwise read a spectrum file one at a time, ensuring that each one is calibrated either before or after loading.
- (g) Now place the standard in the spectrometer, turn on the x rays, and set the conditions (i.e., tube kV, microamps, and vacuum) to exactly the same as those that will be used for later routine sample analysis. If you working without an x-ray source then just load a spectrum file.
- (h) After the tube and chamber environment (e.g., transition from air to vacuum) have stabilized, acquire a spectrum for this standard, with a minimum of 50,000 counts in the analyte peak(s). Typically the acquire times should be about 100 to 300 seconds for the standards.

- (i) If you have acquired a spectrum then save it, if desired (recommended), in one of the supported formats.
- (j) Check the spectrum is OK, with peaks in the expected positions, and that there are no unexpected contaminant peaks!
- (k) Either step through the appropriate spectrum processing steps using the various Process commands, or use the Process Spectrum All command. The latter performs all processing steps as defined in the Condition Table. The spectrum processing should yield net intensities, for the elements defined in the Element Table.
- (l) Select the Calibrate FP menu item, which will then calculate the calibration coefficient(s) and display them in the Element Table.
- (m) At this point, optionally (highly recommended) save the results as a \*.tfr file.
- (n) Then repeat steps (c) through (m) above, until all the elements have been calibrated, using the standards.
- (o) The next step is a useful “trick” to set things up correctly for future routine analysis of all these elements. Do not change any setup in the software until the remaining steps are complete.
- (p) Reconfigure the Component (and Element) Table to describe the unknown sample to be analyzed, checking to see that the Condition Table matches the conditions used in the previous standardization steps. These tables do not need the concentrations entered in the Component and Element Tables, but may need the thickness if it is known. Otherwise set the Thickness Type to Calculated or Bulk, as appropriate. Also, for XRS-MTFFP, ensure that the layer information is set correctly in the Layer and Component tables (i.e., the layers are defined, and each element has a specified layer).
- (q) Now acquire a spectrum for the unknown sample, or load one from a file.
- (r) Load and process the spectrum exactly as the standards were done above, yielding appropriate elemental intensities in the Element Table.
- (s) Now select the Process Analyze menu item and this will perform an FP analysis of this sample. The first part of this operation will be to merge all the calibration coefficients from the previous calibration step(s). At the end of this process, values for concentrations will be calculated and stored in the Component and Element Tables. Also, the calibration coefficients for all the elements will now be displayed in the rightmost column of the Element Table. These are what we need for future analysis.
- (t) You should now save this “Report” as a master \*.tfr file, for subsequent analysis. In other words, instead of repeating the calibration procedure described above, merely load this \*.tfr file and the calibration coefficients will be available for all the elements defined. Note that for

“Auto-Mode FP Analysis,” (see later) you should save this file with the name of “Master.tfr” in the same directory as the software.

Should the calibration process be interrupted, or need to be rerun for any reason, then the saved \*.tfr files can be opened one at a time and the calibration be redone offline, i.e., without the need for live acquisition. If the tube or any parameter is changed, then this calibration must be done again using the actual standards and live acquisition.

### **5.3 XRF FP Assay Analysis**

Once the system has been calibrated (see the two sections above), then assay analysis of samples can be performed exactly as outlined as the end of the previous section. Each time a sample analysis is saved (\*.tfr file) it becomes a secondary “standard” available for subsequent analysis.

## 6 MAINTENANCE

On a routine basis, the user should acquire a spectrum from a suitable sample to check the general system performance. Check both the total counts (assuming the conditions do not change) and the peak resolution, and enter the values in a log. Other parameters that should be logged include the software gain and offset parameters (if used)

Any significant change in either value would require a system recalibration.

A peak resolution change would require changing the FWHM value in the Setup-Processing dialog (see later for more details on this). Any significant change in the number of counts would usually be traced to source intensity or geometry variations, although there could be other causes. The operator can adjust the x-ray source so that the same number of counts are collected as the baseline value, taken at the time of the original setup.

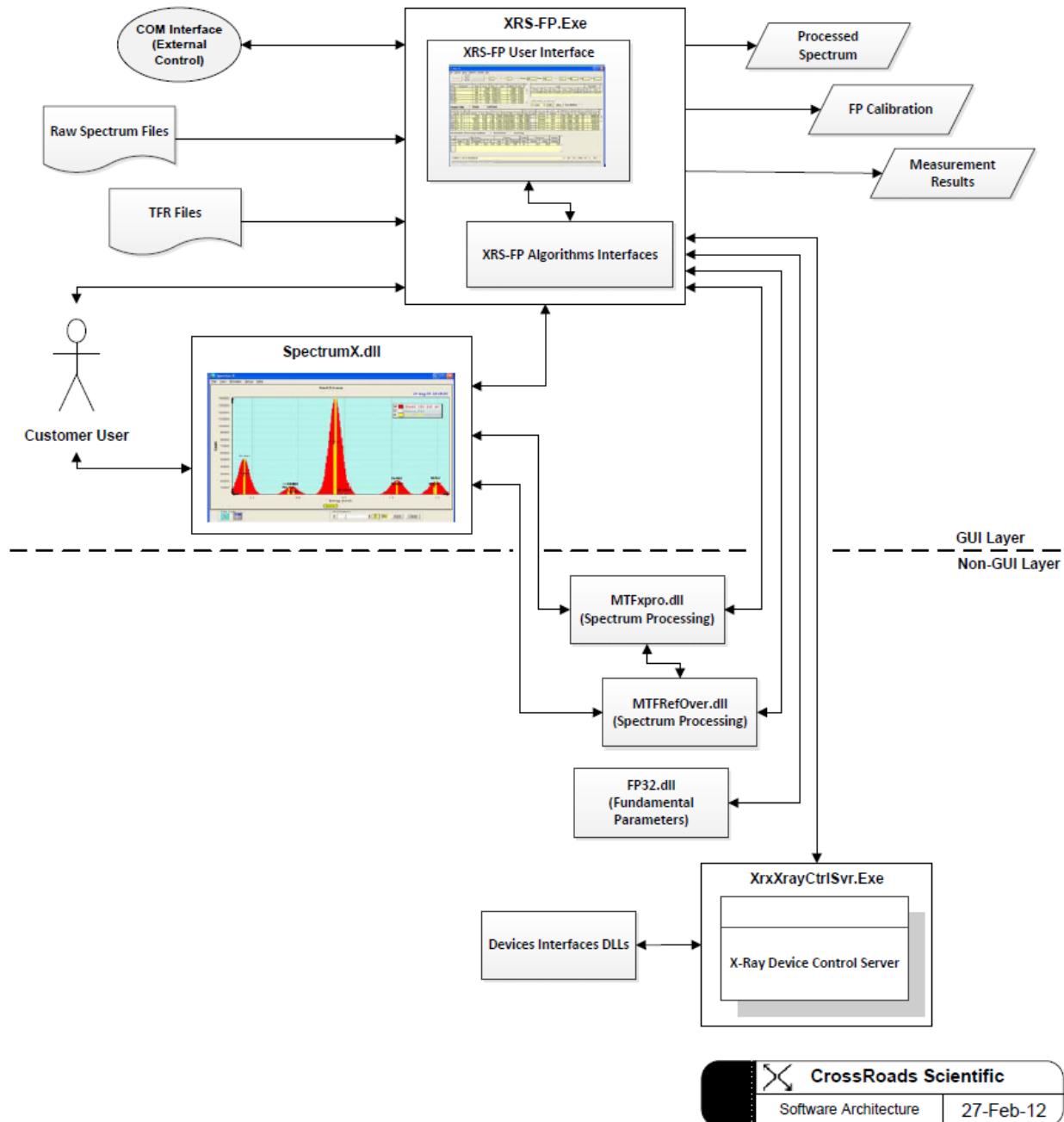
The "System Check" (a button on the simple panel for automated analysis) is used for routine monitoring of the MCA gain and offset. It is also available from the Main Panel, and is described later in this guide. As noted elsewhere, any time that the peak shifts get too large, the electronics should be readjusted.

If electronics are readjusted then reset the Offset and Gain parameters in the "Calibrate Spectrum Gain and Offset" panel. Clicking on the "Initialize Gain & Offset" button does this. Now acquire a new spectrum from the XRF spectrometer calibration standard, and invoke the "Calibrate Spectrum" command. Then Adjust the spectrum (see above) and press the OK button.

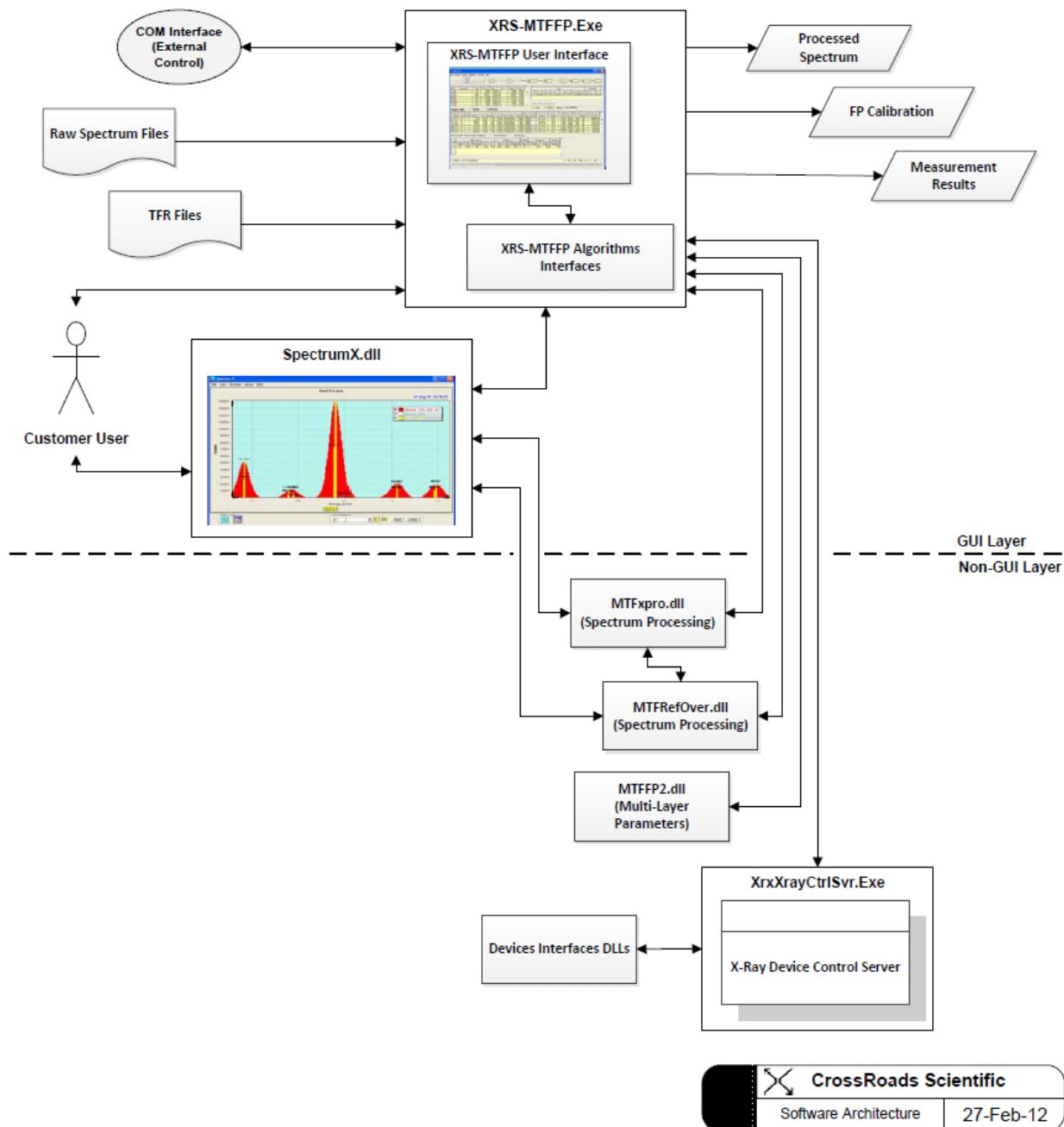
## 7 SOFTWARE OVERVIEW

### 7.1 Software Architecture

#### XRS-FP (Bulk Analysis)



### XRS-MTFFP (Multi-Layer Thin Film Analysis)



A simplified software architecture drawing is shown above, with the key components of the hardware and software system, together with the connection points

The above two drawings represent the XRS-FP and XRS-MTFFP V5.X software architecture, respectively. The electronics interfaces to the hardware devices (e.g. digital pulse processor) are not shown for the sake of brevity.

The XRS-FP (or XRS-MTFFP) is comprised of several MS Windows program executables (EXE), dynamic linked libraries (DLL) and Active-X components (OCX). All of the main software components are connected to the XRS-FP (XRS-MTFFP) program, which serve as the primary user-interface for the 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.

Details of the key software components are listed in the table below.

Component	Description
XRS-FP.exe (Bulk Analysis Version)  XRS-MTFFP.exe (Multi-Layer Thin Film Version)	<p>A Visual Basic (VB) user-interface (GUI) with internal algorithms interfaces, which is responsible for the XRF parameters setup, spectrum acquisition, spectrum processing, and FP calibration and measurement. Besides SpectraX, this is the key interface used by the customer for input and output. This same program has a “public” MS COM interface for external control by other MS Windows programs. This software has been developed using Visual Basic V6.0 with SP6.</p> <p>There are also the standard Microsoft Visual Basic support files and three third-party OCX components that are registered during the software installation:</p> <ul style="list-style-type: none"> <li>(a) PVDT80.OCX (v.8.0 or later), from Infragistics, used for the DataTable spreadsheets,</li> <li>(b) TeeChart7.ocx (or 8 or 2014 or later), from Steema Software, and</li> <li>(c) ACXPP.OCX, which is used for the Print Preview function.</li> </ul>
SpectraX.dll	<p>A Visual Basic (VB) user-interface (GUI) which is used for spectrum display and manipulation of the displayed spectrum data. The same program has a “private” MS Active-X interface, which serves the XRS-FP (XRS-MTFFP) client program(s). This software has been developed in BASIC using Visual Basic V6.0 with SP6.</p>
MTFxpro.dll	<p>A non-GUI algorithm’s library which is responsible for spectrum calibration and spectrum processing. This software has been developed in C/C++ using Visual Studio V6.0 with SP6.</p>

MTFRefOver.dll	A non-GUI algorithm's library which is responsible for reference and overlap spectrum deconvolution. This software has been developed in C/C++ using Visual Studio V6.0 with SP6.
FP32.dll (Bulk Analysis Version) MTFFP2.dll (Multi-Layer Thin Film Version)	A non-GUI algorithm's library which is responsible for conversion of elemental intensities into measured results. The algorithms in this library also perform standards calibration. This software has been developed in C/C++ using Visual Studio V6.0 with SP6.

## 7.2 Security Plug

Also supplied with the software is a HASP security plug manufactured originally by SafeNet Inc. (formerly Aladdin Knowledge Systems), which requires that a driver be installed. You can also download the latest driver from the SafeNet web site – be sure to use the HASP H4 driver (*the later HL or HASP/LDK drivers should be installed for more recent operating systems such as Windows 7 and 8*).

See the following web page <http://sentinelcustomer.safenet-inc.com/sentineldownloads/> for the most recent support and driver downloads, in particular the Sentinel HASP/LDK - Command Line Run-time Installer (current version 6.65, released 8-Dec-2014). This installation was previously done with the HINSTALL.EXE program. The most recent version of this command-line installer software is called haspdinst.exe. This program installs the correct driver for the operating system, and should be part of the total software installation procedure (also executed from the batch file Install HASP Driver.bat in the software directory).

See later for a description on 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 plug, take note of this serial number (e.g., XRS 1234).

### 7.3 Data Files

The CrossRoads XRF software uses two main types of files for the complete acquisition, processing and analysis of XRF spectra. The first type is the spectrum file, for which there are several formats supported.

The second file type (\*.tfr file) contains both the definition of the system (configuration), the definition of the samples for analysis, the calibration coefficients and either the standard composition or the results of an analysis. Once a system calibration has been performed, the user can retrieves one of these files to define the complete system setup.

Subsequent sample analyses require the acquisition of a spectrum, under known conditions, followed by spectral and FP analysis to generate a full sample report that can subsequently be printed, and saved as a file. Any third-party program can read these files, as they are in simple ASCII format, and an external program can also be called to do this automatically.

Lastly, there is a general XRS-FP.ini file that provides storage of other common parameters used by the XRS-FP (XRS-MTFFP) software.

## 7.4 Software Installation

The CrossRoads software has a dedicated installation program, based on the InstallShield product. The wizard-style GUI allows the user to install the CrossRoads software smoothly on any PC. The installation is an EXE file that can be executed as any Windows program. Note that on certain operating systems with increased security settings (e.g., Windows 8) you should run the InstallShield program by clicking on the file with the right mouse button and selecting the “Run as administrator” option to start the program, otherwise you may get an error that you have insufficient security privileges. You may also need to disable the User Account Control on your Windows PC. Finally, on some Windows 8.x systems you may have to modify the BIOS to complete the installation, but this is difficult for Win 8 machines. On Windows 8 you may need to modify the UEFI settings. This is described in the following article:

<http://www.makeuseof.com/tag/how-to-access-the-bios-on-a-windows-8-computer/>

On the BIOS System Configuration tab select the >Boot Options page and change “Secure Boot” from Enabled to Disabled. Then select Save Settings and Exit to re-boot the PC. During this process it may ask you to enter a 4-digit pass code (which is displayed on the screen) to confirm that this is a manual operation and not some virus doing the job! Once the setup program is invoked, the user will see the following example dialog window:

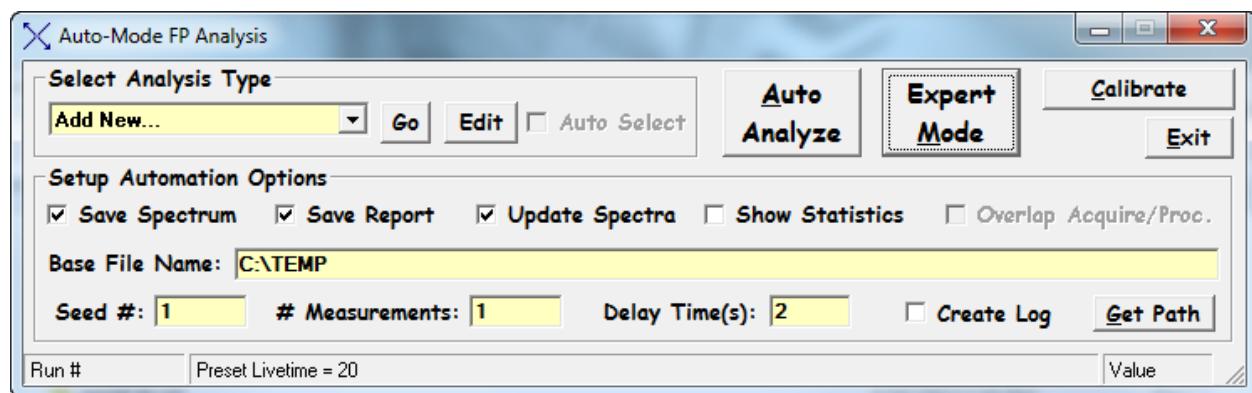


At this point, simply respond to the wizard-style buttons to install the software. If there was an older version of the CrossRoads software, then you will be prompted for its removal prior to the installation of the new software version. Use the Windows Uninstall option in Control Panel for this. During the software installation, you may notice a few moments where the installation seems to be “stopped”. This is the normal operation, where the software installs/updates the HASP device drivers. Click OK in any dialogs and then the installation will complete.

## 8 AUTO- MODE (ROUTINE) FP ANALYSIS

There are 3 buttons (plus Exit) on this initial (simplified) start-up screen, which is the first one seen after the start-up splash screen, when the software is finished loading. In the example, below, the Save Spectrum and Save Report File options have been checked, and the default path and file name has been entered, which will be used to save spectra (\*.mca) and report (\*.tfr) files. Note that any existing file(s) will be overwritten with the new file(s).

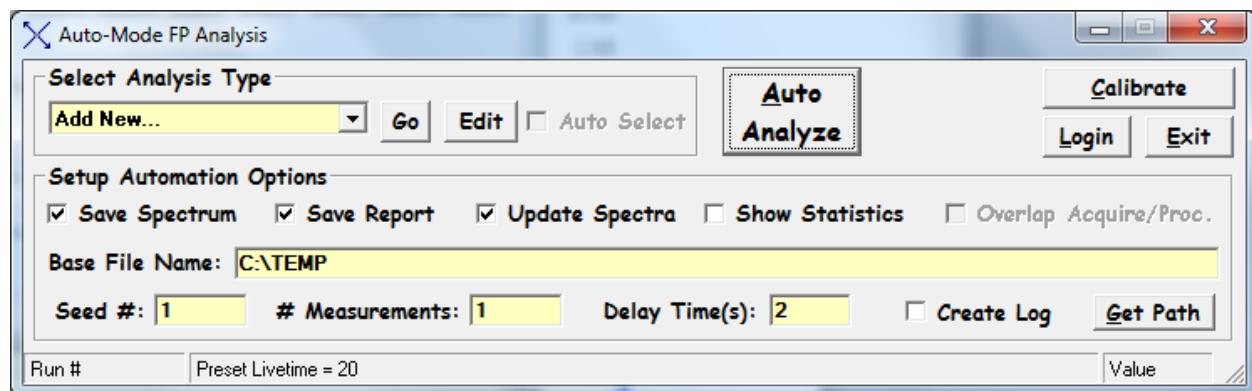
Normally the buttons are as shown below (i.e., Analyze, System-Check and Expert-Mode). This is the default start-up screen. By clicking the Expert-Mode button the user will be taken to the main FP analysis screen (i.e., Supervisor Mode), as described in the next section.



However, the software also allows the user to specify a password in the XRS-FP.ini file, so that this password must be entered before the Supervisor Mode can be entered. This must be entered in the section titled [Security] in the XRS-FP.ini file. By default, this line is setup with no password as follows:

Password=

When the software reads *no* key word present, then it bypasses the Login button and allows the user to enter immediately the Supervisor Mode (as described above).

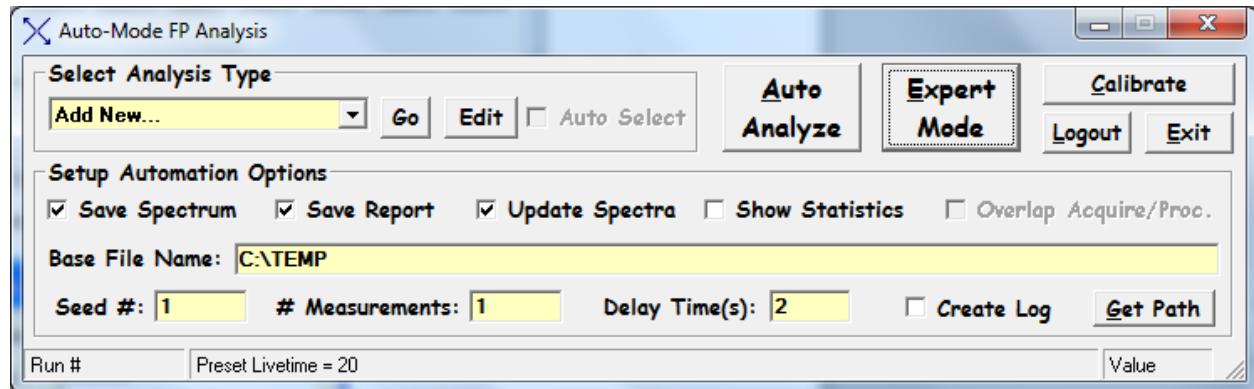


## 8.1 Login

Press the optional “Login” button to select the password dialog panel. There are two entries, one for “User Name” and the other for “Password.” The password is set to the word that is entered in the XRS-FP.ini file, in the [Security] following the keyword “Password=.” The case must match for each letter entered. At present, the “User Name” is not really used, although the software could easily be adapted to employ the “User Name” in some other way in the future.



If the password is correct (i.e., matches the word in the \*.ini file), then the following screen will be loaded:



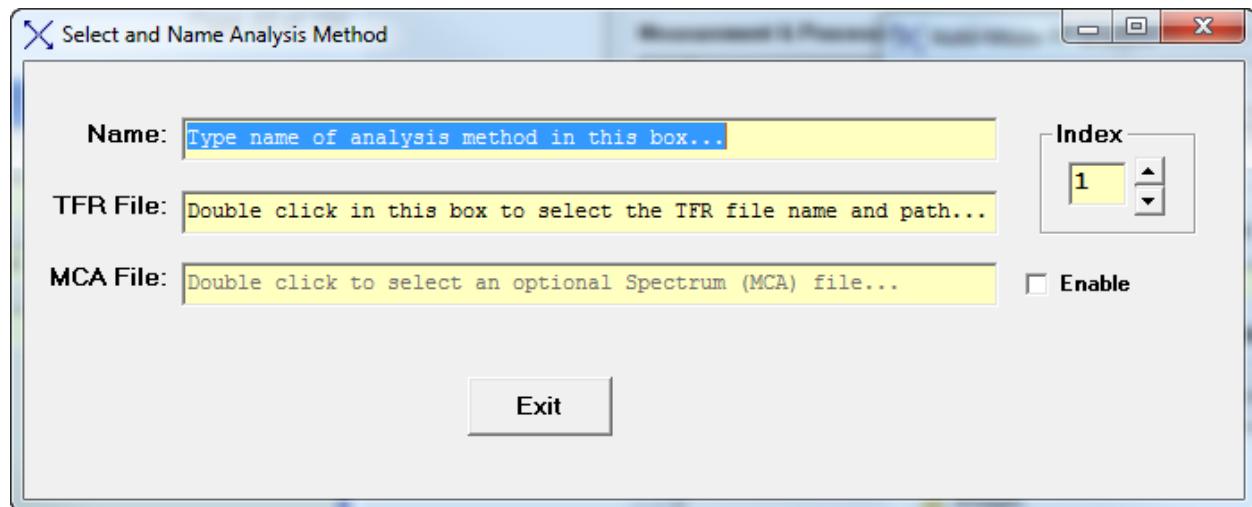
Again, clicking on the Supervisor Mode button allows the Main Screen to be displayed (see later in this document).

You should note the various options that may be selected at this point. In addition to the check boxes that allow you to save either the Spectrum (e.g., MCA) and/or the Report (TFR) files and/or a Graphical Statistical Summary, you can select the path and filename either by typing them in, or use the Get Path button that pops a dialog to allow you to browse existing folder paths:

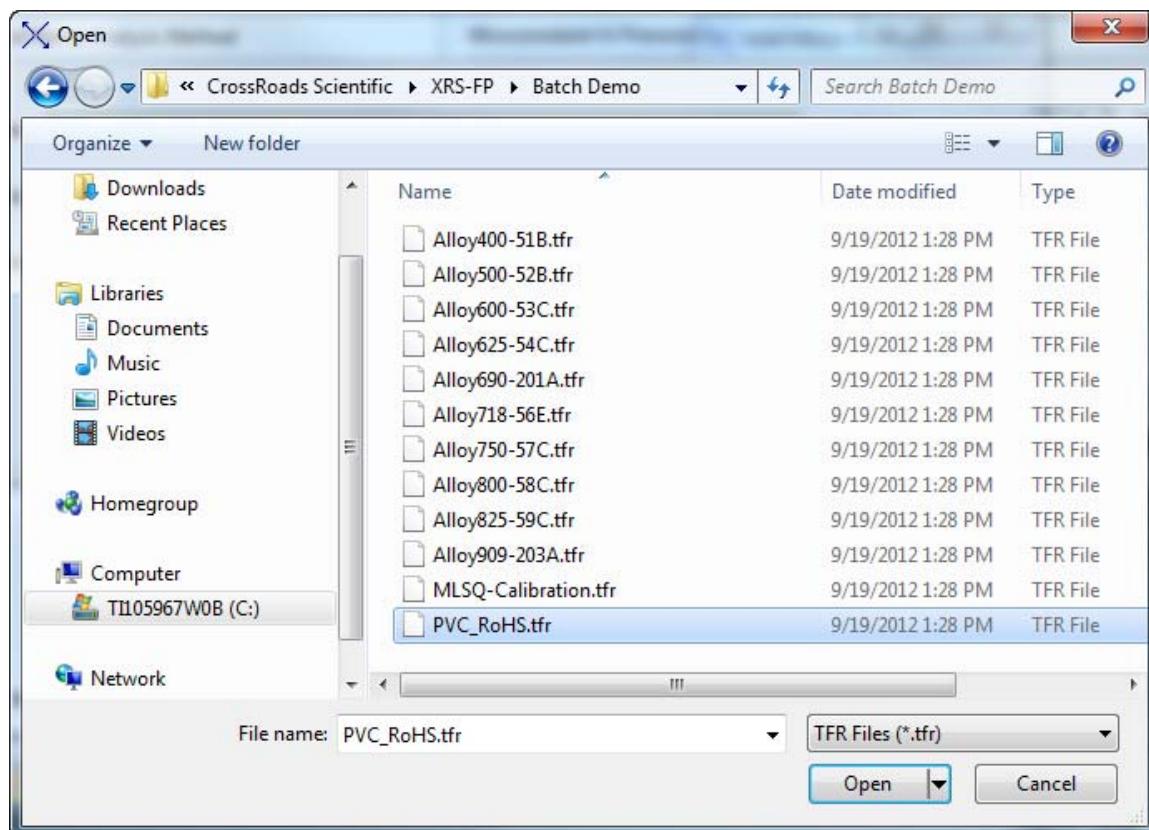
There are some other options that allow you to setup the software for acquiring and analyzing a sequence of spectra. You may specify the seed number (a starting number that will be appended to the file name), which will be incremented for each new spectrum acquired (e.g. Temp0001.mca, Temp0002.mca, etc.). If zero is input, then the program will loop indefinitely until the Cancel button is pressed. You may also specify the total number of measurements and a delay (clock) time between each one.

A noteworthy feature of the XRS-FP software is the ability to define different applications, each governed by a specific TFR file. Once these applications are defined then an individual application can be selected

from the Automation panel without having to use the Expert Screen at all. Initially the list will be blank, as shown in the examples above. Clicking on the Add New item in the list, will bring up a screen similar to the following one:

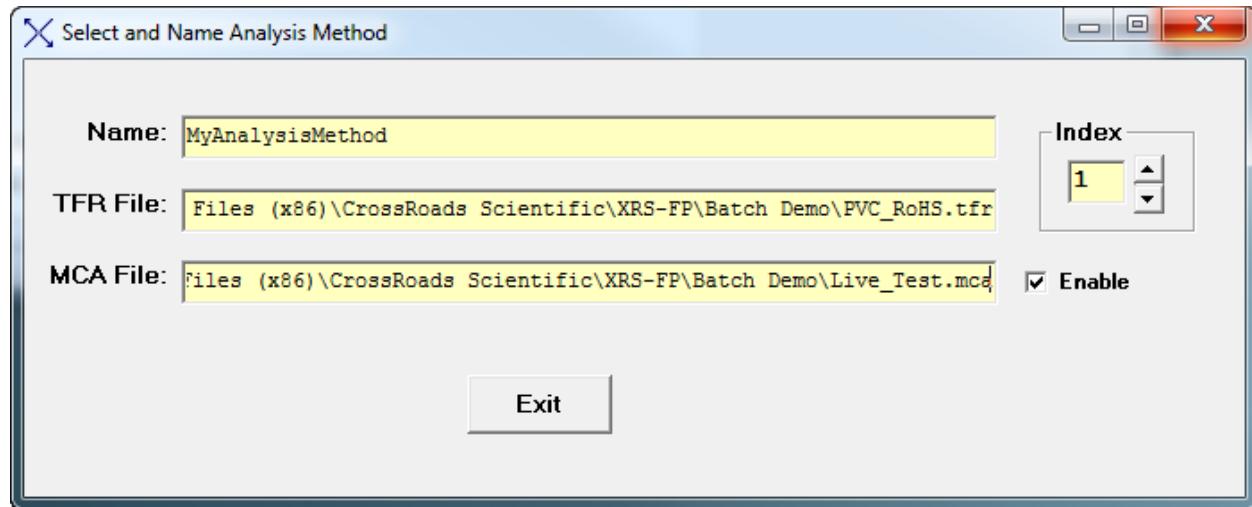


Just type in the application name in the “Name” text box, and double click on the TFR File text box to load a dialog similar to the following:



Once the TFR file has been selected, then you can also select a typical spectrum file that matches this application. Note that to do this you must first check the enable button for selecting spectra. This feature

will be used in the future to automatically match an unknown spectrum to a predefined application class. After these selections, the panel might look like this:



## 8.2 Auto Analyze

The Auto Analyze button performs routine analysis of one or more samples, using MCA electronics connected to the software, and assumes the application has previously been setup (and calibrated), with a fully configured Master.tfr file. Of course, the samples are assumed to be homogeneous across the analysis surface in both composition and thickness, but may or may not be infinitely thick with respect to the incident and emitted x-ray beams.

If the user knows the mass thickness (e.g., in units of mg/cm<sup>2</sup>) of the sample (e.g., from weighing the filter, of a known area), then this value should be entered. To convert from mass to mass thickness (i.e., mass per unit area), divide by the area of the sample. If the mass thickness is not known, the software will estimate it during the analysis, unless the file has been configured for bulk analysis. The sample must be larger than the “analyzed area” (i.e., the intersections of the “cones” from the x-ray source and detector) to use or calculate a mass thickness value. If it is smaller, then one *must* assume a bulk sample, and normalize the composition (e.g., to 100%).

After clicking on the Analyze button, the software will step through the following operations in order to perform the analysis:

- (1) Prompting the user to turn on the x-ray tube (if used), and to set the voltage and current to the values required by the Master.tfr configuration file.
- (2) Setting the spectrum acquisition time from the Condition Code.
- (3) Connecting to the MCA or DPP via the appropriate driver and/or server.
- (4) Starting the spectrum acquisition and waiting until it is complete.

- (5) Reading the spectrum from the MCA, or from the DPP, and then displaying it in Spectra-X.
- (6) If the check box associated with a user-defined file name is checked, then the spectrum is written to this file. Note that the full path and filename should be specified, but the extension should not be entered. If the path is not specified, then the files will be saved in the current working directory for \*.tfr files.
- (7) Next the spectrum in memory is processed, and the resulting intensities (in c/s) are saved in the TFR form in memory (see next section).
- (8) Next, the intensities are converted to composition, using the setup parameters defined by the Master.tfr file, and the FP program.
- (9) Now, if the check box is checked, the TFR data in memory is written out to a TFR file with the specified name, in the specified directory (path).
- (10) The program displays the main panel with the reported results, or continues in the automation loop if that was requested.

At the end of the processing a summary file is written in a CSV format that can be read into Excel for further analysis. If the check box for Show Graphics is selected then a simple statistical analysis is performed on the acquired results and parameters such as average, standard deviation, etc., are displayed in a chart. This feature is discussed more in the section describing Process-Batch.

### **8.3 Calibrate**

This button loads the same form as described under Setup -> Spectrum Adjust in the Main Panel section (see below).

### **8.4 Expert Mode**

This button loads the Main Panel (Supervisor Mode), providing full access to all the parameters for acquisition and the processing of spectra, as described in the next section.



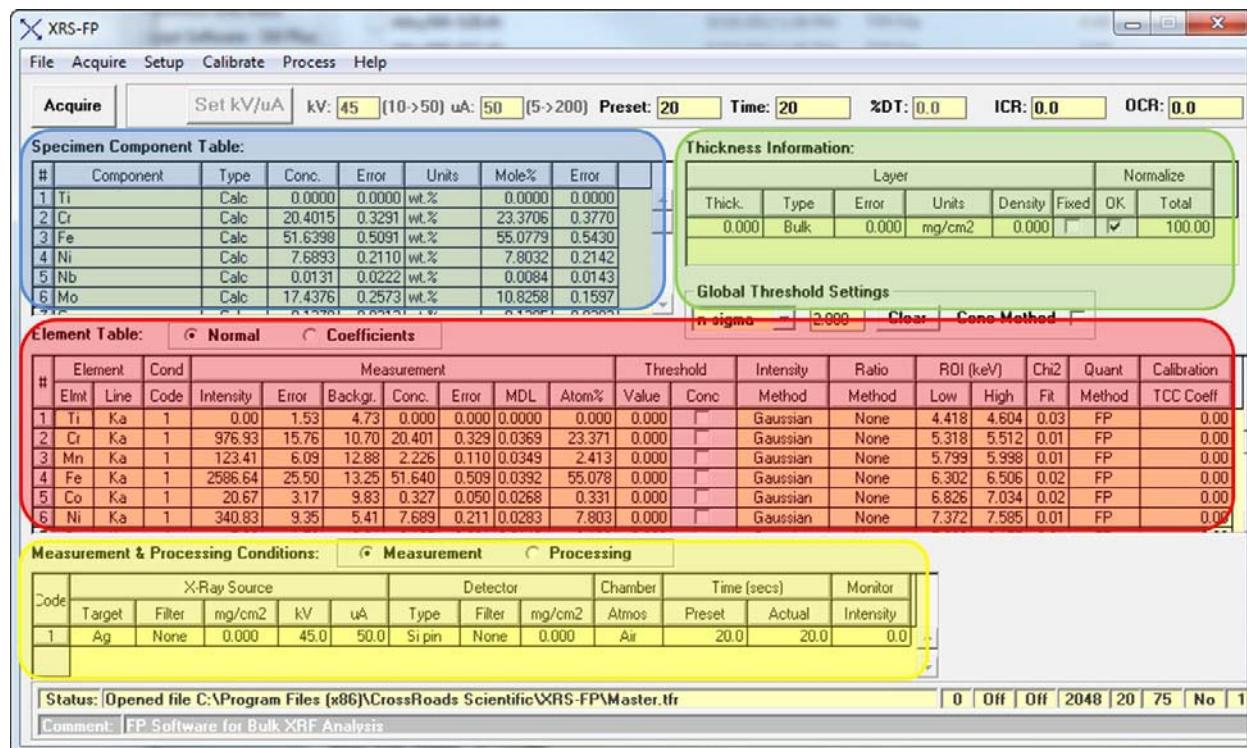
Whenever data is entered into a text box or cell, the action of leaving this cell actually causes the data to be read and checked. Highlighting can be done by double clicking, and sometimes this brings up a secondary menu if appropriate.

## 9 MAIN SCREEN (SUPERVISOR MODE)

The main Expert Panel screen of the XRS-FP software is resizable. The main user interface (GUI) consists of three main sections. The first is the menu bar along the top of the screen. Below this line is a status/entry bar for single-button spectrum Acquire (if enabled), the entry of tube kV and microamps, and the acquire times. Below this line is the main section, which consists of four spreadsheet tables for both data entry and display of results.

The four tables are for:

- (1) Definition of the Components in a specimen (blue region in figure below)
- (2) Definition of the (mass) Thickness of the sample, if known (green region in figure below)
- (3) Definition of the Elements in the components, and the x-ray line (Ka, Kb, La, Lb, Lg or Ma), and the methods to be used for intensity extraction and quantitation, with thresholding (red region in figure below)
- (4) Definition of the acquisition and spectrum processing conditions (yellow region in figure below)



At the bottom of the form is a general status line area. There is an area for general status messages regarding the spectrum acquisition, processing and XRF (FP) analysis. To the right of this box there are 6 smaller boxes. They contain: (1) the FP calibration mode, (2) the Auto-Adjust on Load status, (2) the Auto-Adjust on Acquire status, (4) the number of channels in the spectrum, (5) the eV/channel (10, 20,

40, etc.), (6) the ADC/DPP slow threshold, (7) the connection status of the MCA/DPP to the XRS-FP program, and (8) the active Condition Code. There is an extra line at the bottom of the screen that shows a general comment field. Below are some more details on each of these areas and their respective functions.



OR *Important Tips:*

To navigate in the spreadsheet tables you can click or double-click on any cell and edit it.

You can also highlight any row and delete it by pressing the Delete key on the keyboard.

You can use the up, down, right and left arrow keys to move around the spreadsheet.

You can insert a new row using the Insert key, and add a row at the bottom of any (Component or Condition) table by moving the down arrow key below the bottom row.

Columns can be resized if needed; use the left mouse button to select the boundary in the header row.

## 9.1 Specimen Component Table

This table defines the compounds (and elements) that will be analyzed using FP. Under the component heading enter each component, one row at a time. Just use the down arrow key to add extra rows at the bottom of any table, and the delete key to delete the highlighted row. Normally each component will simply be an element symbol (e.g., Fe), but they could be compounds such as oxides (e.g., Fe<sub>2</sub>O<sub>3</sub>) or more complex ones such as FeSO<sub>4</sub>.

Some components must be entered with a space between single-character elements in order to avoid ambiguity. An example of this is “CaC O<sub>3</sub>.” 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. Illegal entries will generate error messages.

In the case where oxygen is *not* analyzed, which is typically the case (because the x-ray energy is too low to be detected), the Fe<sub>2</sub>O<sub>3</sub> 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 FeSO<sub>4</sub> 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* Fe<sub>2</sub>O<sub>3</sub> and FeSO<sub>4</sub> are entered as separate components then the FeSO<sub>4</sub> can be determined from the S concentration, and the remaining Fe (and O) ascribed to the Fe<sub>2</sub>O<sub>3</sub> component. The software handles this internally, 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 method. By default, each component will be calculated, but they can be specified as Fixed (e.g., if not analyzable, such as H<sub>2</sub>O), or by Difference. The units can be wt% or ppm,

and also as ug/cm<sup>2</sup> or mg/cm<sup>2</sup>. 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.

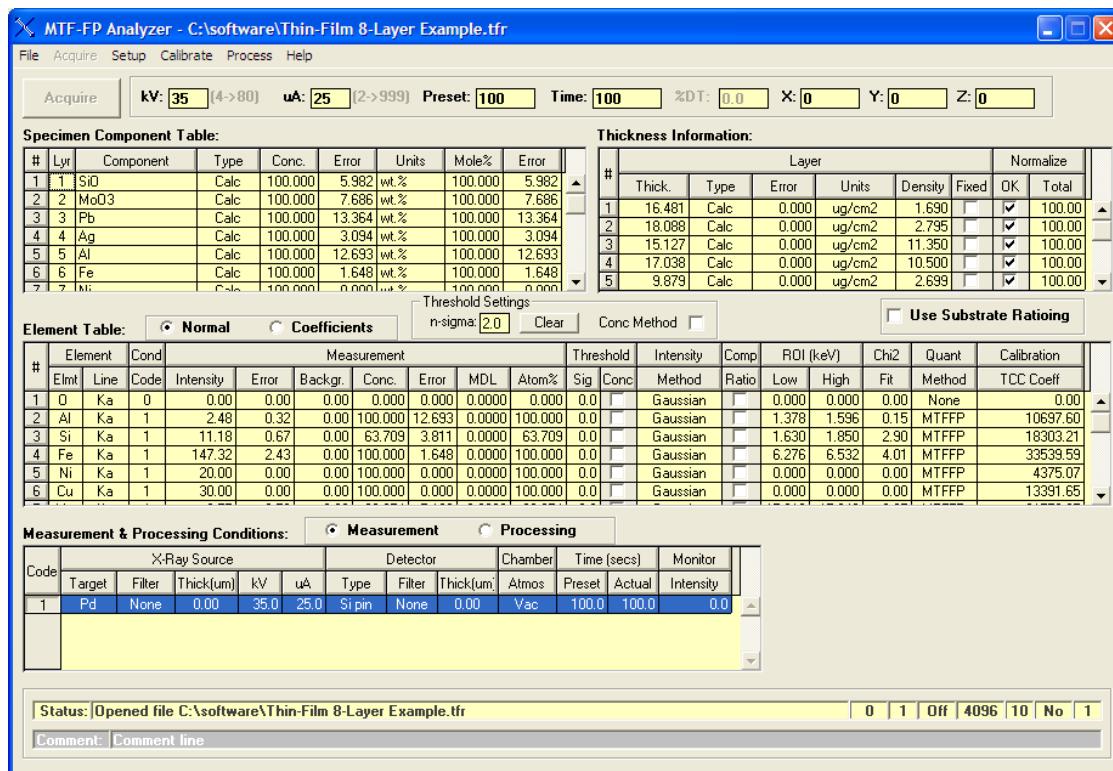
In v.4.5.0 of the XRS-FP software, there is a new feature that copies the concentrations of the components to their elemental equivalents in the Element Table, as *they are entered*. Of course, compound information is broken down into the individual elemental concentrations.

## 9.2 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 "Calculate" if the thickness is to be calculated for sample analysis. Appropriate units should also be selected. Also see section 2.1 in the Operation of Software section.

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. In newer versions of the software (v.3.3.0) you can select Fixed or Calculated for the density option, which is more obvious than remembering to set the value to zero for calculating. Also specify in this table a normalization factor (default to 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 XRS-MTFFP software, this table has some extra functionality to define multilayer samples. An example of the screen for a multilayer sample is shown below. Note that in this example there are 6 different layers, with one component (element or compound) per layer, although there is no restriction to only one component per layer. Note that this panel also shows the layer number in both tables. The maximum number of layers in a sample is 8, as shown in the example below.



### 9.3 Element Table

Most of this information is created 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 below), the quantitative analysis 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 filled in by the software, but check to see if it is the one you want to use.

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 30 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 Setup-ROI function in XRS-FP, or Paint-ROI in Spectra-X. Unselecting the element row will automatically clear the ROI.

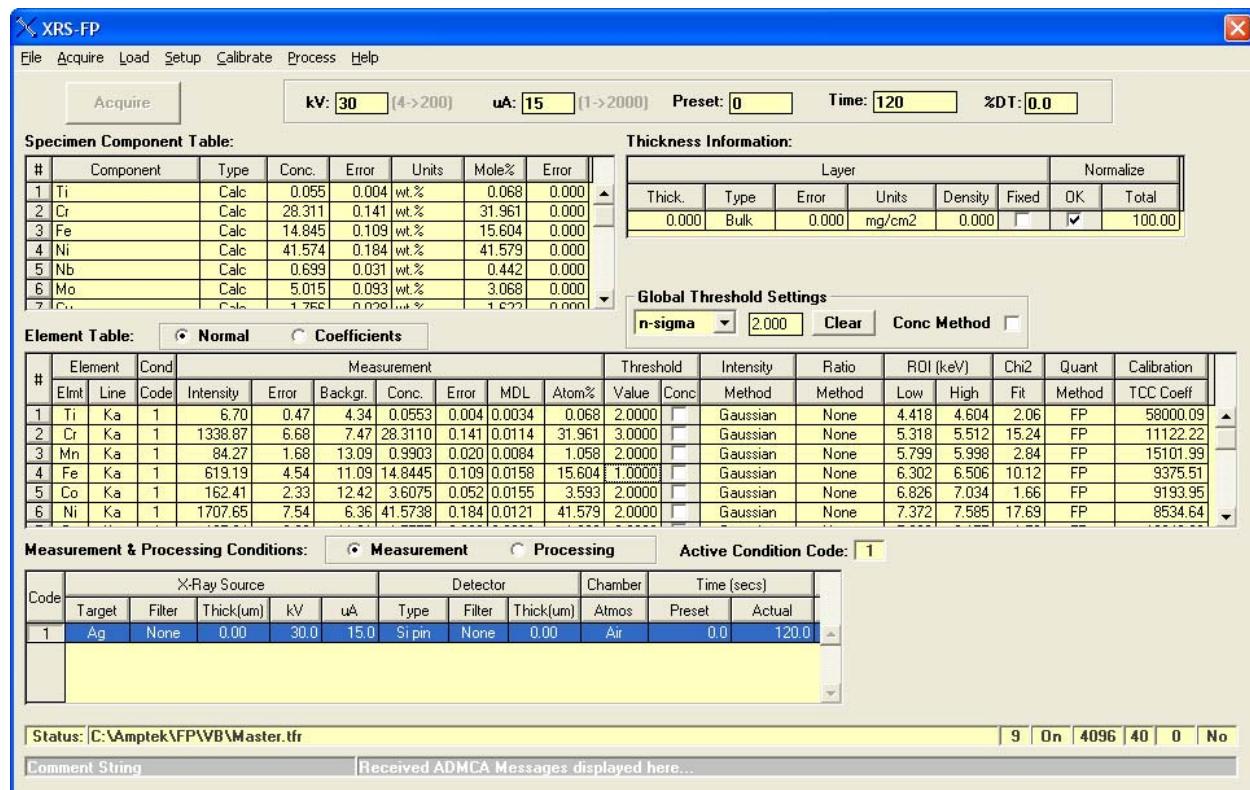
You can also choose thresholds for each element. There are 2 types of thresholds that can be defined, either sigma based or a fixed value for each element. The following example shows the selection of thresholds on the basis of the sigma (estimated error) for each element.

Typing a value in the Global Settings 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.

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. In the following example the default is left for Intensity thresholding. Any intensity (or concentration) below the threshold will be set to zero.

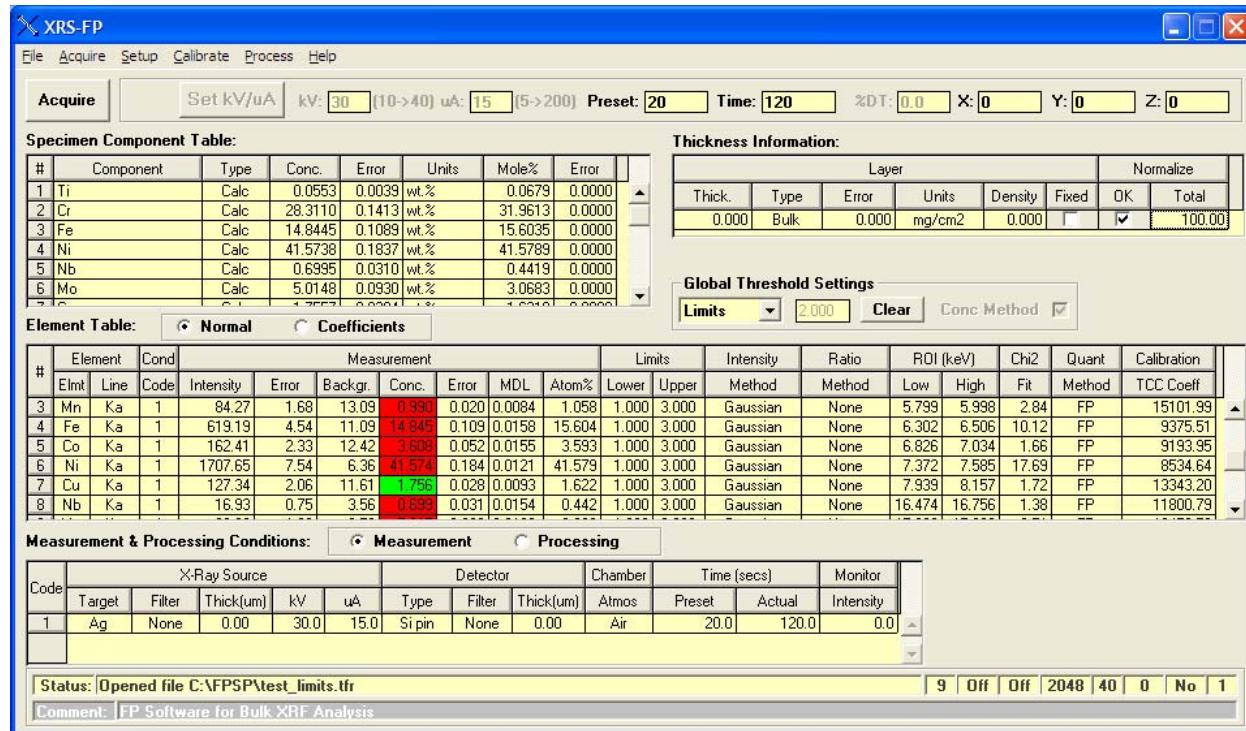
You can also define Upper and Lower limits for each concentration in the Element Table. This is different from the thresholding described above, and cannot be used with the thresholding. I.e., there are 3 different options for the post-processing of concentrations or intensities.

The figure below shows an example of thresholding using the Intensity method (the conc boxes are all unchecked).



Alternatively the thresholds can be based upon a Fixed value for each element, again either for Intensities or for Concentrations.

The figure below shows an example of the use of Upper and Lower limits.



In this simple example all the Lower Limits are set to 1.0% and the Upper Limits are set to 3.0%. Those concentration results that are within the limits are shown in green, and the ones out of limits are displayed in red. There is a new 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 if you would like details or customization of this digital logic output.

## 9.4 Measurement & Processing Conditions Table

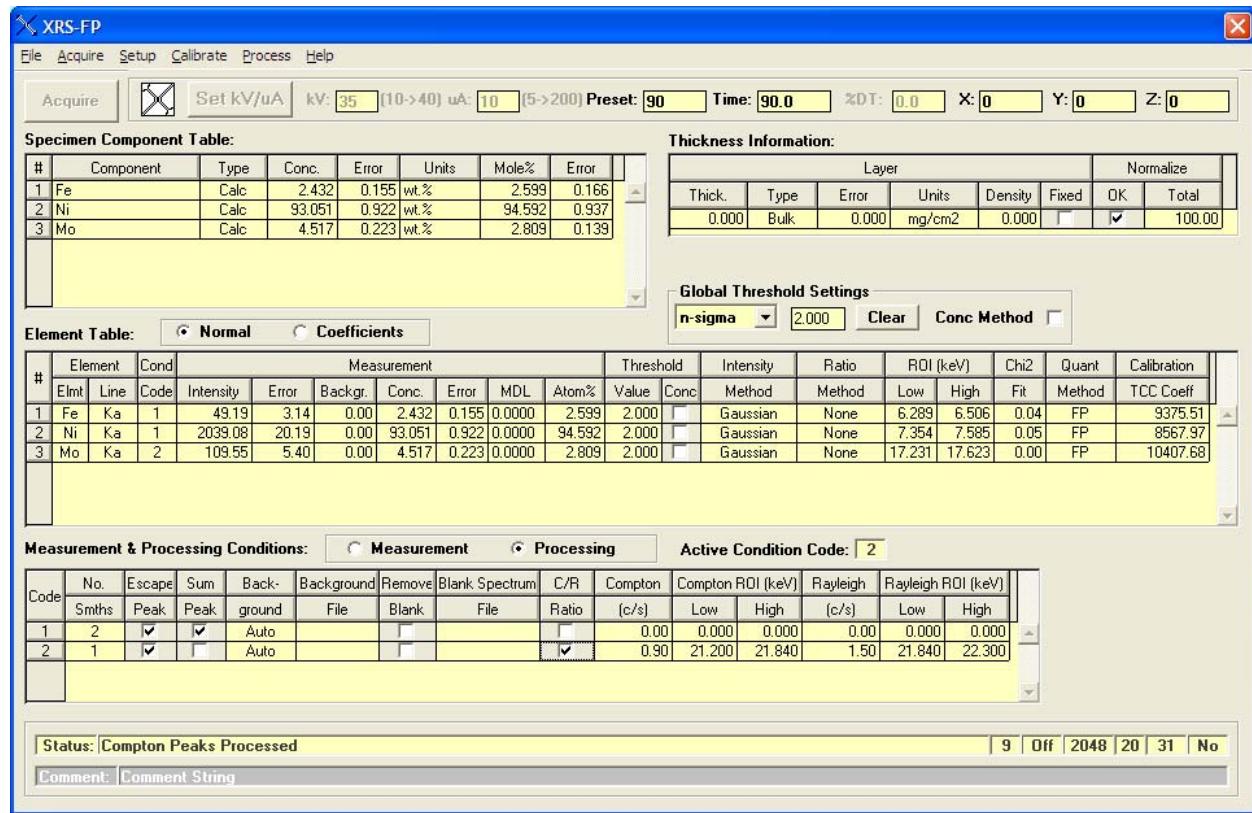
Ensure that the target anode matches the one entered in the Setup Tube dialog. Enter an element symbol for the tube filter, if there is one, and its thickness in microns. Enter the tube KV of the analysis, for this condition and the tube current.

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, and the type of detector (the default is the Si pin diode). The spectrum processing parameters should be also entered as they are used to control the spectrum processing.

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-FP software select the Processing radio button, which displays a second panel, such as the following example:



You can select the number of smooths, and whether to include escape peak and sum peak corrections. You can select the background method between Automatic (the default) or File, which uses a spectrum file as the background component, normalizing the 2 spectra by the ratio of the lifetimes. Similarly, you can select a blank spectrum for removing some artifact in the measured spectrum, again normalized by the lifetime ratio.

Some of the possible 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.

## 10 FILE MENU

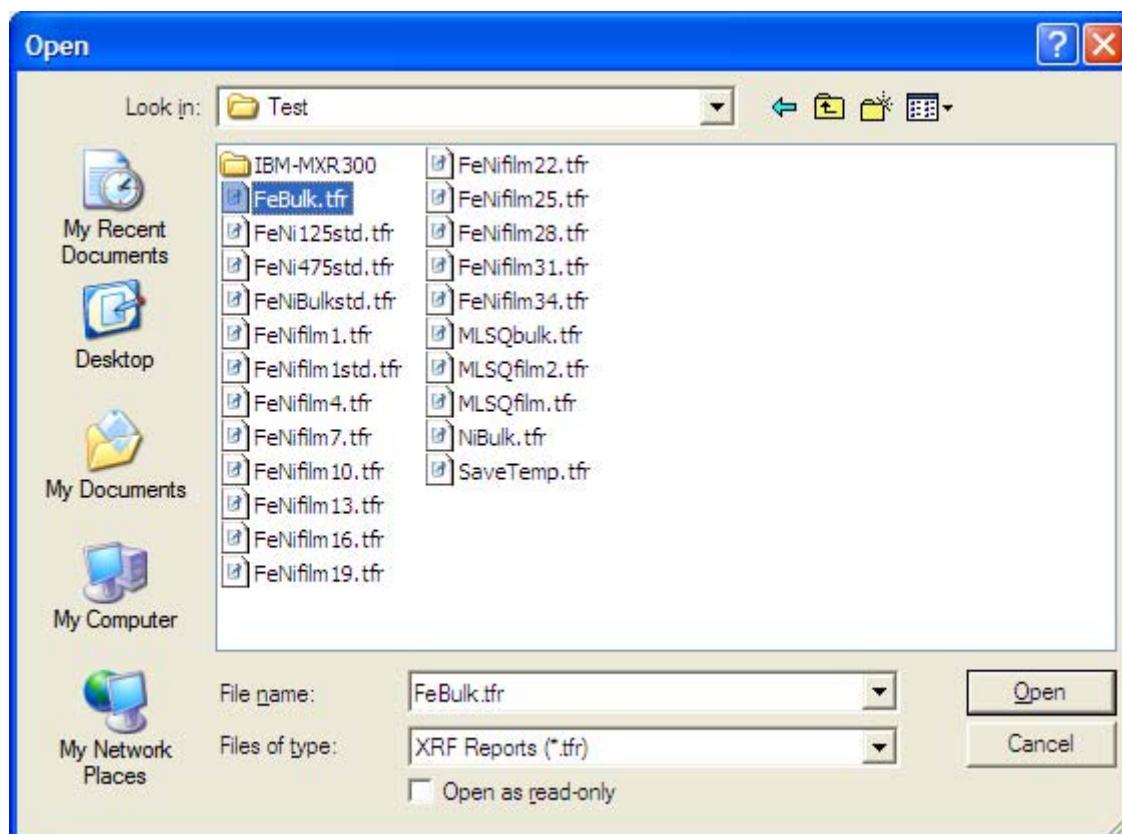
This contains typical File operations such as Opening a thin-film report (TFR), Saving files, and for Printing a copy of the reports.

### 10.1 File New

The File New function clears the existing TFR report, and sets the report name to "Untitled."

### 10.2 File Open

The File Open function brings up a dialog for loading files. The recognized file types include “\*.tfr” (thin-film reports), “\*.mca” (Amptek or XIA format spectra), “\*.mxs” (Moxtek format spectra) and “\*.sp0” (Iridium format spectra). In addition, the “\*.\*” option provides a list of all available files in the specified directory. Other file extensions are included for special applications and interfaces, including generic file types such as \*.txt and \*.csv text files.



The thin-film report files (\*.tfr) contain all the information about an analysis or calibration. After loading any file, a message is displayed that confirms the file name and the last date the file was modified. Opening any type of spectrum file loads the spectrum data into the main processing group and resets all the processing flags. If the Auto-Adjust on Load flag is set (see Setup-Processing), then the Gain and

Offset parameters loaded with XRS-FP (from the \*.ini file or a recent spectrum calibration) will be applied in making the adjustment to the spectral data.

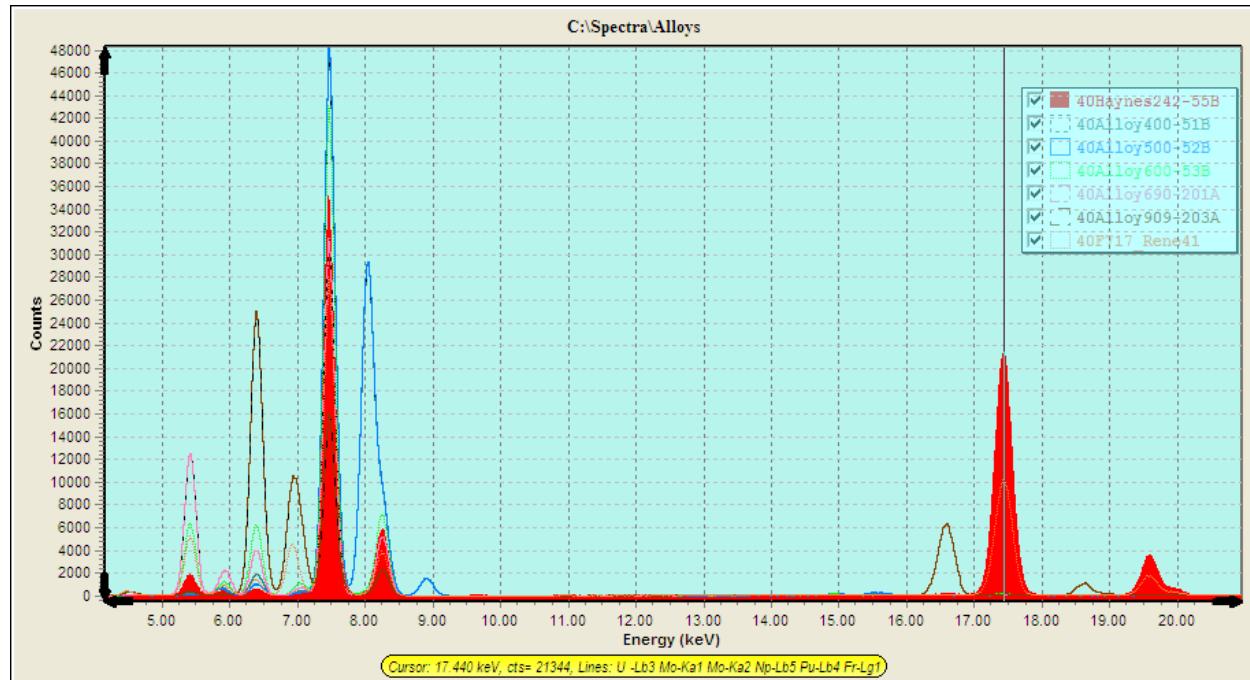
When reading some spectrum files, these may have internal calibration factors and, if so, these parameters are read and a primary spectrum Adjust (energy scale correction) is made to the spectral data to reflect these “internal” calibration parameters.

XRS-FP performs a spectrum Adjust so that the data will be in the form expected by the XRS-FP software. If the Adjust flag Setup-Processing is set on for “Adjust on File Load” then this operation will be done as the last step after the file loading.

Another feature of the software allows \*.ini files to be opened and loaded into the software. When this is done the software is restarted and all parameters are reset to those from the new \*.ini file.

### **10.3 File Compare**

This option allows you to load up to 6 additional spectra in Compare groups (1-6), in addition to the standard Main group. The spectra are sent to Spectra-X for display and comparison purposes. An example showing the comparison of 7 alloy spectra is shown below.

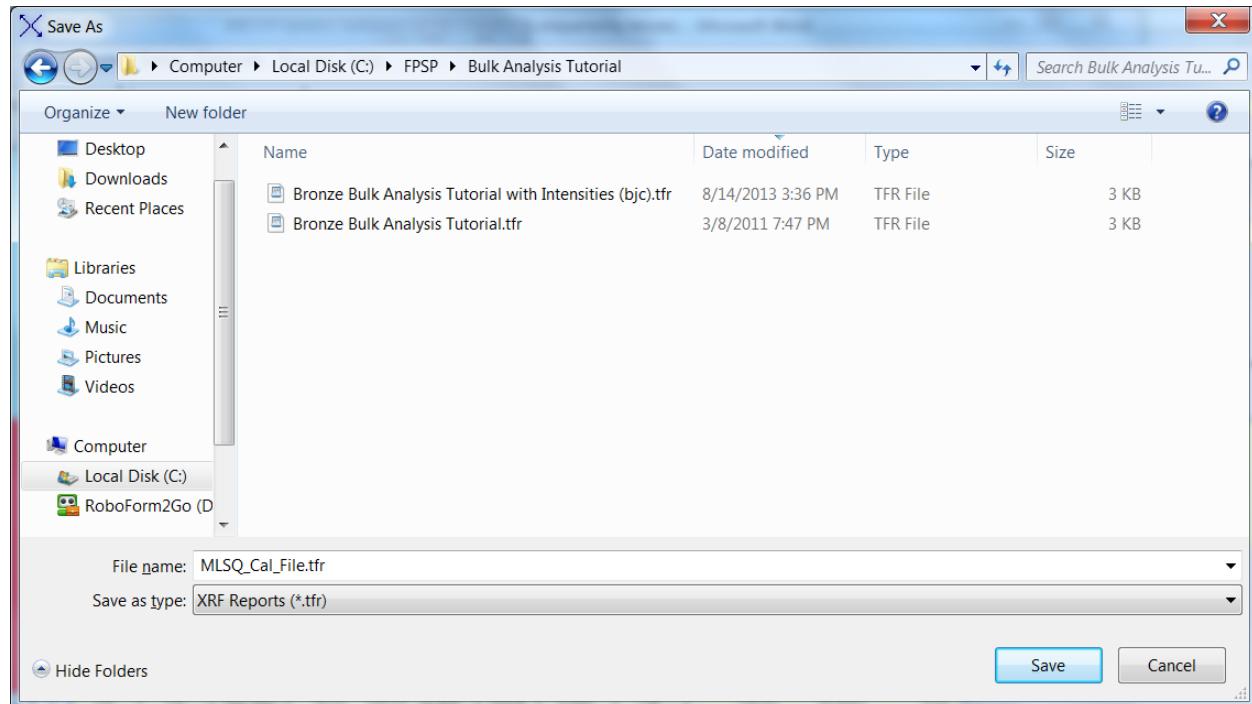


### **10.4 File Save**

The File Save function saves the current data in the TFR data tables into the TFR file that was last opened. If the current title is “Untitled” then the SaveAs dialog is invoked (see below). Make sure that the filename has the correct (\*.tfr) extension to avoid any confusion in recognizing a file type later.

## 10.5 File SaveAs

The File SaveAs function allows the user to save either the current TFR setup and results data (as a “\*.tfr” file), with any specified file name, or to save any spectrum currently in memory (as a “\*.mca”, “\*.mxs” or a “\*.sp0” file). Here is an example of the File-SaveAs dialog:



After the save, a message is displayed confirming the operation, with certain file properties shown.

*Important Tips:*

When saving a file be careful to select the *correct file extension* for the desired type (spectrum or TFR). If the wrong extension is appended to the file it will not be readable.

## 10.6 File Print

The File Print allows the printout of most of the TFR data shown on the screen, with the current title, date and time.

*Important Tips:*

When printing a file there may be a pause before the file starts printing.  
This is quite normal, especially if the printer is on a network.

An example TFR file printout, for an analysis with 3 condition codes is shown below.

## CrossRoads Scientific XRF Analysis Report

```

File: C:\FPSP\MLSQ_Cal_File.tfr                               11:09:17 AM 13-May-14
Comment line

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

Sample Table =====
Layer Component  Type  Concn.  Error  Units  Mole%  Error
1 Al2O3          Calc   17.340  0.000  wt.%  0.000  0.000
1 Ba              Calc   2400.00 0.000  ppm   0.000  0.000
1 CaO             Calc   0.680  0.000  wt.%  0.000  0.000
1 Ce              Calc   11.000 0.000  ppm   0.000  0.000
1 Cl              Calc   0.000  0.000  ppm   0.000  0.000
1 Co              Calc   0.000  0.000  ppm   0.000  0.000
1 Cr              Calc   12.000 0.000  ppm   0.000  0.000
1 Cu              Calc   19.000 0.000  ppm   0.000  0.000
1 Fe2O3           Calc   1.440  0.000  wt.%  0.000  0.000
1 K2O             Calc   15.350 0.000  wt.%  0.000  0.000
1 La              Calc   0.000  0.000  ppm   0.000  0.000
1 MgO             Calc   0.450  0.000  wt.%  0.000  0.000
1 MnO             Calc   0.000  0.000  wt.%  0.000  0.000
1 Nb              Calc   0.000  0.000  ppm   0.000  0.000
1 Ni              Calc   7.000  0.000  ppm   0.000  0.000
1 Pb              Calc   5.000  0.000  ppm   0.000  0.000
1 Rb              Calc   530.00 0.000  ppm   0.000  0.000
1 SiO2            Calc   63.630 0.000  wt.%  0.000  0.000
1 Sr              Calc   62.000 0.000  ppm   0.000  0.000
1 TiO2            Calc   0.040  0.000  wt.%  0.000  0.000
1 V               Calc   10.000 0.000  ppm   0.000  0.000
1 Y               Calc   0.000  0.000  ppm   0.000  0.000
1 Zn              Calc   10.000 0.000  ppm   0.000  0.000
1 Zr              Calc   33.000 0.000  ppm   0.000  0.000
1 Na2O            Fixed   0.760  0.000  wt.%  0.000  0.000

Element Table =====
Elmt Line Cond Ratio Intensity Error Intensity Conc. Conc Calibration
Code Code Method (c/s) (c/s) Method Method Method Coefficient
O  Ka  0 None  0.000  0.0000 Gaussian 45.674 None  0.000
Na Ka  0 None  0.000  0.0000 Gaussian 0.564 None  0.000
Mg Ka  1 None  37.558 26.4534 Gaussian 0.271 FP   863100.000
Al Ka  1 None  2738.462 68.8884 Gaussian 9.177 FP   784953.000
Si Ka  1 None  16360.250 73.9205 Gaussian 29.744 FP   808346.900
Cl Ka  1 None  432.563 36.8270 Gaussian 0.000 FP   7024767.000
K  Ka  1 None  17115.580 76.1544 Gaussian 12.743 FP   1193370.000
Ca Ka  1 None  742.506 40.3368 Gaussian 0.486 FP   1357073.000
Ti Ka  1 None  60.384 13.5183 Gaussian 0.024 FP   1315296.000
V   Ka  1 None  46.564 12.4994 Gaussian 0.001 FP   1310132.000
Cr Ka  2 None  0.000  3.1581 Gaussian 0.000 FP   5890424.000
Mn Ka  2 None  10.207 5.0165 Gaussian 0.000 FP   6467205.000
Fe Ka  2 None  2303.911 27.4525 Gaussian 1.007 FP   6741350.000
Co Ka  2 None  26.747 11.1028 Gaussian 0.000 FP   0.000
Ni Ka  2 None  14.568 7.0247 Gaussian 0.001 FP   4972292.000
Cu Ka  2 None  13.942 3.3121 Gaussian 0.002 FP   7429322.000
Zn Ka  2 None  9.758 3.1782 Gaussian 0.001 FP   7107924.000
Rb Ka  2 None  2809.083 30.0045 Gaussian 0.053 FP   8660137.000
Sr Ka  2 None  352.976 12.0870 Gaussian 0.006 FP   9131651.000
Y   Ka  2 None  0.000  13.9246 Gaussian 0.000 FP   9202722.000
Zr Ka  2 None  767.824 17.9546 Gaussian 0.003 FP   9392910.000
Nb Ka  2 None  16.075 12.5575 Gaussian 0.000 FP   8706768.000
Ba Ka  3 None  2209.917 29.6654 Gaussian 0.240 FP   22701820.000
La Ka  3 None  21.467 17.1912 Gaussian 0.000 FP   15482770.000
Ce Ka  3 None  35.590 17.9428 Gaussian 0.001 FP   23505340.000
Pb La  2 None  7.828 3.2351 Gaussian 0.001 FP   14980680.000

Analysis Conditions =====
# Targ Filter Thick. KV uA ---Detector--- Thick. Atmos Preset Actual
                mg/cm2      Type Filter mg/cm2        Time(s) Time(s)
1 Rh     None    0.00 10.0 20.0 Si drift None  0.0 He   20.0 30.0
2 Rh     Ag     131.25 40.0 100.0 Si drift None  0.0 He   100.0 30.0
3 Rh     Cu     582.40 50.0 300.0 Si drift None  0.0 He   100.0 30.0

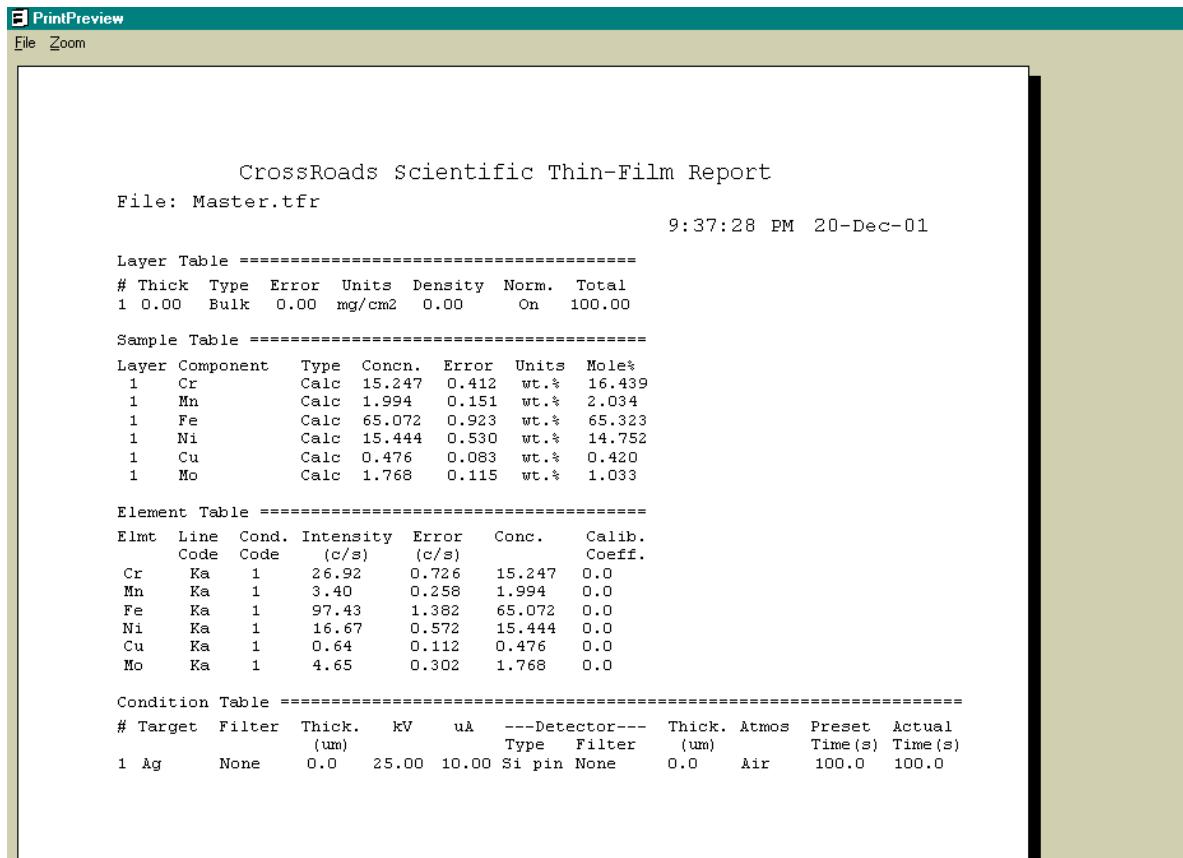
Processing Conditions =====
# No. Escape Sum Back C/R Blank ---Blank---
Smths Peaks Peaks Type Ratio Rem. ---File---
1 2 Yes Yes Auto Yes No
2 2 Yes Yes Auto Yes No
3 2 Yes Yes Auto No  No

Compton/Rayleigh Results =====
# Compton ---ROI(keV)--- Rayleigh ---ROI(keV)---
(c/s) Low   High  (c/s) Low   High
1 0.00  2.680 2.580  0.00  2.580 2.820
2 6566.67 18.790 19.830 2763.86 19.830 20.500
3 0.00  0.000 0.000  0.00  0.000 0.000

```

## 10.7 File Print Preview

This function allows the operator to view the TFR data in preview mode, before sending the data to a printer. A limited zoom capability is available. The data may be printed directly from the Preview panel, but at slightly poorer resolution than the standard Print operation.



```

PrintPreview
File Zoom

CrossRoads Scientific Thin-Film Report
File: Master.tfr
9:37:28 PM 20-Dec-01

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

Sample Table =====
Layer Component Type Concn. Error Units Mole%
1 Cr Calc 15.247 0.412 wt.% 16.439
1 Mn Calc 1.994 0.151 wt.% 2.034
1 Fe Calc 65.072 0.923 wt.% 65.323
1 Ni Calc 15.444 0.530 wt.% 14.752
1 Cu Calc 0.476 0.083 wt.% 0.420
1 Mo Calc 1.768 0.115 wt.% 1.033

Element Table =====
Elmt Line Cond. Intensity Error Conc. Calib.
Code Code (c/s) (c/s)
Cr Ka 1 26.92 0.726 15.247 0.0
Mn Ka 1 3.40 0.258 1.994 0.0
Fe Ka 1 97.43 1.382 65.072 0.0
Ni Ka 1 16.67 0.572 15.444 0.0
Cu Ka 1 0.64 0.112 0.476 0.0
Mo Ka 1 4.65 0.302 1.768 0.0

Condition Table =====
# Target Filter Thick. kV uA ---Detector--- Thick. Atmos Preset Actual
              (um)          Type Filter (um)           Time(s) Time(s)
1 Ag     None      0.0    25.00 10.00 Si pin None      0.0    Air    100.0 100.0

```

## 10.8 File External

This function checks for the existence of an external program, as specified in the [Security] section of the \*.ini file, following the keyword "Program=". If this program exists, then the current report file data (\*.tfr file) is transferred to the external specified program (e.g., Wordpad.exe, or Excel.exe). There is no restriction to the program being called – it could any windows program that is capable of accepting text data.

## **10.9 File Hook**

If available, this function reconnects XRS-FP to the internal messaging system. It is only for advanced diagnostic usage.

## **10.10 File Unhook**

If available, this function disconnects XRS-FP from the internal messaging system. It is only for advanced diagnostic usage.

## **10.11 File Hide**

This function hides the Main Panel and displays the Runtime Panel (startup panel).

## **10.12 File Hide-SpectraX**

This function hides the Spectra-X spectrum display panel. The panel can be shown again by clicking on the button in the Windows Task Bar.

## **10.13 File Exit**

The File Exit function performs an orderly exit from the program, and closes any connections to the hardware, and saves certain parameters to the XRS-FP.ini configuration file.

## 11 ACQUIRE MENU

The Acquire Menu (& button) is enabled only if a successful “internal” connection has been made either to a supported MCA or DPP product. The connection is made using the Setup-MCA/DPP panel Connect button.

### 11.1 Acquire Start/Stop

The Acquire Start menu item is the same as the Acquire button. Both start the acquisition of a spectrum using either the MCA or DPP hardware. Once the acquisition is started the Acquire Stop button is enabled, and the Acquire button caption is changed to “Stop.” Note it is recommended that during acquisition other functions are not performed except to Stop or Clear the acquisition.

The spectrum is updated periodically during acquisition, at the rate of about one update per second. The exact update rate will depend upon the number of channels in the spectrum.

### 11.2 Acquire Clear

This menu item clears both the spectral data and the elapsed acquire time. If the acquisition is in progress, then it will continue after the Clear operation, but with the data and time both reset. There is an option in the software to automatically clear the data and time whenever acquire is started. This option can be selected in the Setup-MCA/DPP panel. Whenever acquisition is started from the Runtime automation panel this pre-clear is always forced.

### 11.3 Acquire Time

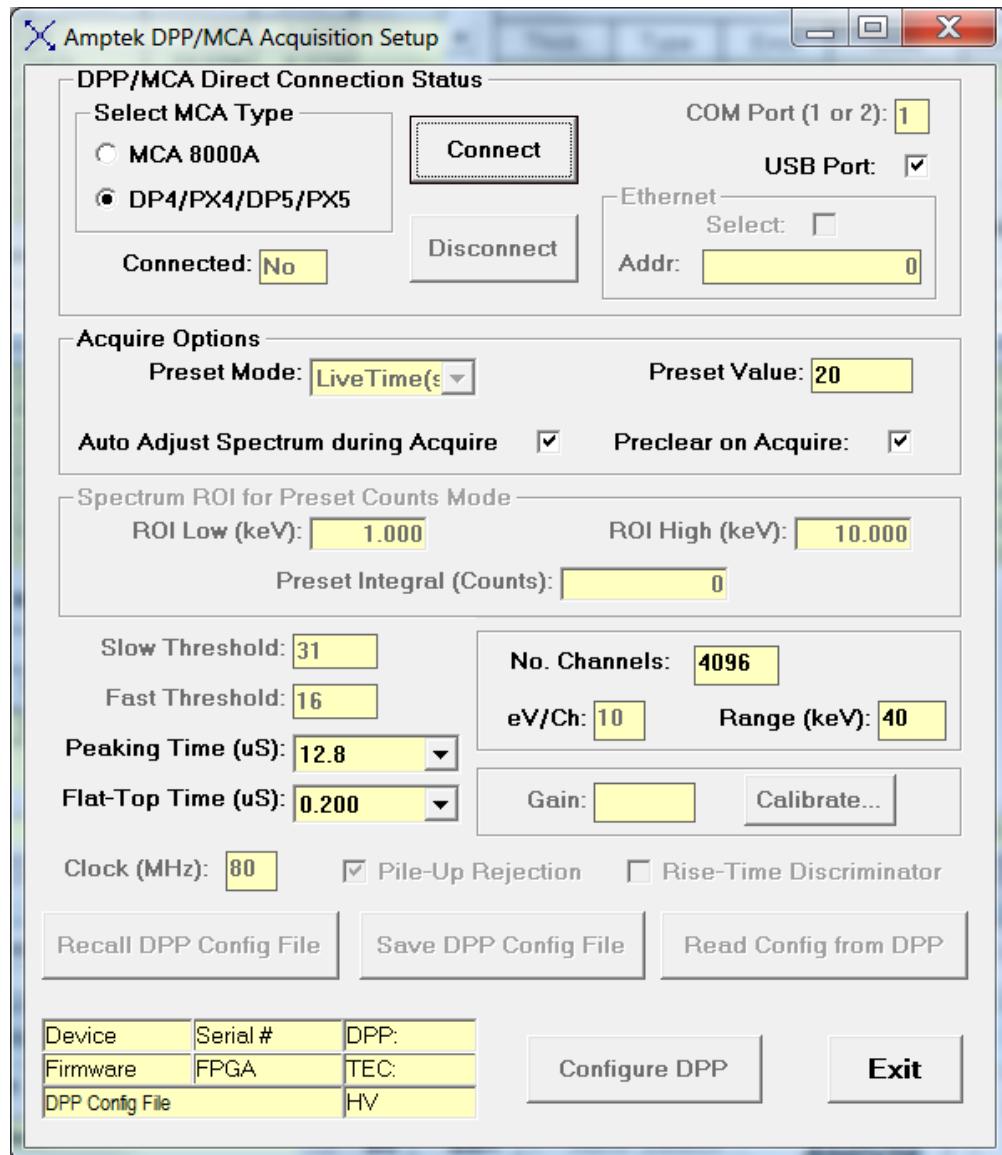
This menu item brings up a dialog box to allow entry of the spectrum acquisition time, in seconds. This preset is either live time or real time depending upon the supported device.

## 12 SETUP MENU

This menu contains several items that bring up their own dialogs. The complete XRF analysis system must be setup correctly, prior to performing any analysis.

### 12.1 Setup MCA/DPP

This command brings up the Setup screen to allow connection to a variety of Amptek detectors and their electronics.



This operation brings up a panel that allows the user to Select the type of hardware (MCA or DPP) being used, with either the Amptek MCA 8000A or one version of a DPP (DP4/PX4/DP5/PX5), and to Connect,

or Disconnect the hardware. The MCA 8000A uses a serial COM port, and all versions of the DPP currently use the USB port.

Some of the buttons or text boxes are only valid for the DPP hardware. The number of channels is valid for both the MCA 8000A and the DPP, but this setting works differently for each set of hardware, so consult the hardware documentation supplied by Amptek.

The eV/channel is only changeable in hardware for the MCA (8000A). For DPPs the Range is used to set both the “range” of the spectrum and the integer eV/channel. For example, if the number of channels is fixed at 2048, then changing the DPP Range from 40 to 20 keV, changes the eV/channel from a value of 20 to 10.

Note that this does not change the hardware for any of the DPP models – this is done by changing the Gain value in the Setup/DPP panel. The Range and eV/channel values must closely match the hardware gain values, any final adjustment being done in software to allow for gain and offset adjustment (see Calibrate/Spectrum).

All settings for the DPP should be set using the appropriate Configuration file. For the Amptek DPP models with Firmware version 5, these files have the extension “.cfg.” The default file for a DP4 DPP (or any DPP emulating a DP4) is the file DP4.cfg. Similarly for a PX4, or any DPP emulating a PX4, the file is PX4.CFG.

For Amptek DPP models with Firmware version 6, the interface and configuration files are completely different. The default files are either PX5.txt (for a PX5 device) or DP5.txt (for a DP5). It is very important that you know what version of the hardware and firmware you are using for your DPP.

These files MUST be located in the XRS-FP software directory and default copies of these files will be installed by the installation procedure for XRS-FP. However, it is very important that you setup the appropriate file for your device using the appropriate Amptek setup software. The XRS-FP software will load the appropriate DPP configuration file automatically when the Connect button is selected in Setup-DPP. However, if your configuration file is incorrectly setup, then results may be poor, or the device may not connect at all.

Please refer to the manual with your MCA hardware to learn how to adjust these parameters. For the 8000A MCA, you use the program PMCA.exe. Most important is to setup the ADC threshold values correctly. If the threshold value is too low then a large amount of noise will be seen in the spectrum. If it is too high then the lower energy part of the spectrum could be cutoff.

For the older MCA8000A devices, the gain is used to mean the number of channels, because this directly affects the gain factor of the ADC. (Note that the ADC gain is completely independent of the Amplifier gain, which is set with a multi-turn potentiometer.)

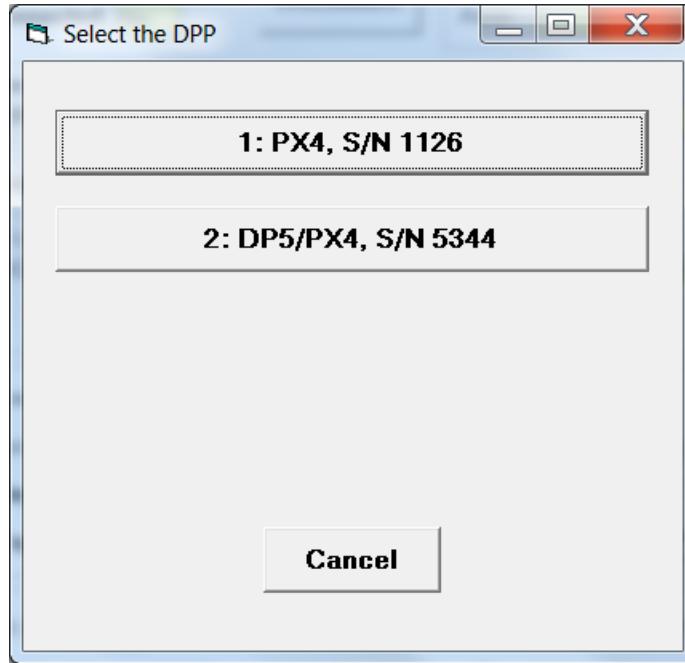
For a Firmware 5 DPP, or the DP4/PX4, use the Amptek program ADMCA.exe to do the initial setup and calibration of the DPP hardware, and then save the configuration in a configuration (\*.cfg) file with the

correct name that matches your device. After saving the \*.cfg file, copy it into the folder that contains XRS-FP (or equivalent software).

Note that to load these settings automatically when XRS-FP is first loaded, you should name the \*.cfg files for Firmware 5 as either DP4.CFG or PX4.CFG. This is very important!

Use the name DP4.CFG when you are using a DP4 digital pulse processor or a DP5 running in DP4 emulation mode. Use the name PX4.CFG when the DPP is a PX4 or a DP5 running in normal (PX4) mode.

After selecting the Connect button on the Setup-DPP panel, the default configuration file will normally be loaded (see below). In the case of the Amptek DP4/PX4 DPPs and/or the DP5 with Firmware v.5, you can connect more than one device to the PC (XRS-FP v.6.2.4 or higher), and then select the appropriate device from a menu such as the following example:



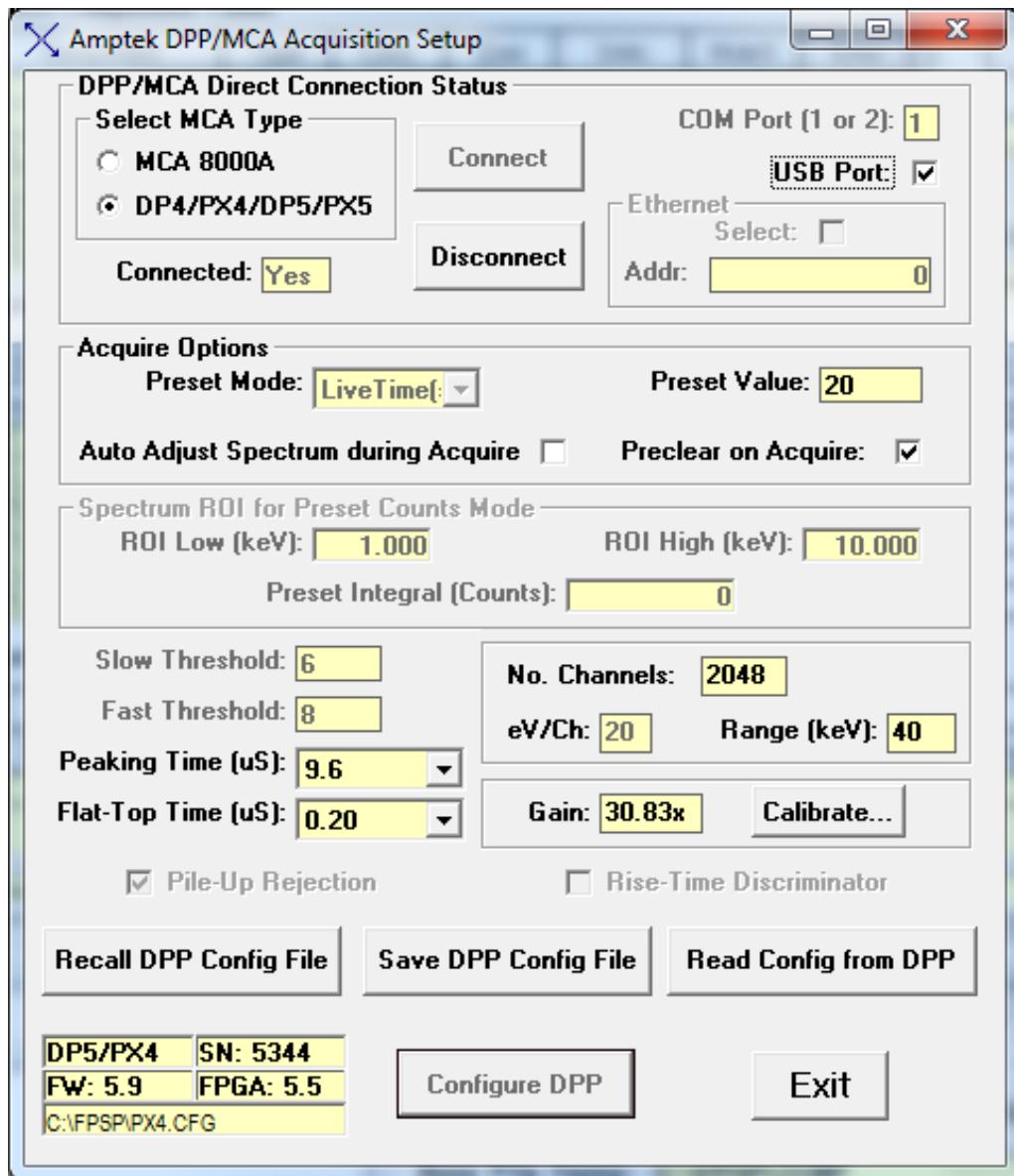
After selecting the appropriate device by clicking on the button, the Connect dialog will begin in the same way as if there was only one device connected to the PC. This option is NOT currently available for the latest Amptek electronics such as the DP5 with FW6 or the PX5. XRS-FP always selects the first DPP in the list for FW6, even though a list of devices may appear.

You can also load configuration files manually at any time, but for automatic loading follow the naming guidelines above. When the file is loaded manually you will get a confirmation panel confirmation the current DPP configuration, such as the following example:



This panel can also be shown by clicking on the “Read Config from DPP” button. The configuration file contains many more parameters than the ones shown on the Setup panel. After loading these default values, the parameters on the Setup screen can be adjusted for routine operation.

After clicking the OK button the Setup DPP/MCA panel will be filled in with several parameters extracted from the CFG file. It will look like the following figure.



Also displayed in this dialog is the Range. In the above example it is 40 keV (actually, it is 40.96, but the convention is to just display to the nearest factor of 10). It describes the upper end of the spectrum, i.e., the product of the eV/channel and the number of channels.

At present the Range is not used to control the DPP or MCA 8000A. The only parameter that controls the hardware is the number of channels. Just ensure that the eV/channel and Range correspond to the values actually associated with the spectrum definition in ADMCA. This is very important.

The XRS-FP software only allows the following values for number of channels: 1024, 2048, and 4096. The highest value is a limit imposed by the spectrum processing software. In addition, the eV/ch must be an integer value, such as 5, 10, 20, 40, 80 or 160. This value is used by the spectrum processing software.

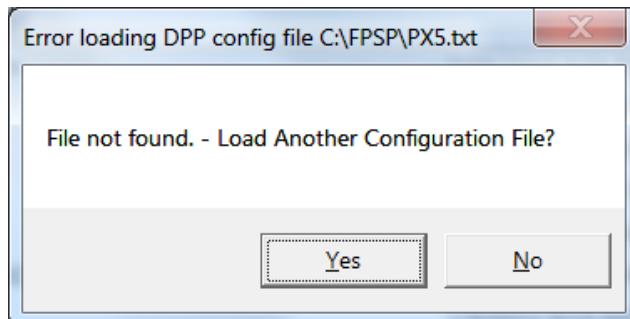
For Amptek DPP models that use Firmware 6 or above there is a different interface protocol and now the setup of the DPP (PX5 or DP5) must be done with the Amptek program DppMCA. This is very similar to ADMCA.exe, but there are several more parameters to be setup, plus the gain ranges are more extensive than the Firmware 5 devices.

Also, DppMCA contains an automatic setup for the Fast and Slow Threshold settings, which is very useful for the first setup of a DPP and detector. As described previously, the configuration files now have an extension of \*.txt, and are named either PX5.txt or DP5.txt. Again, after creation using DppMCA, the appropriate TXT configuration file must be copied to the XRS-FP software directory.

Note that for advanced users there is now an option to remove the configuration file from the XRS-FP software folder, and use ONLY the setup from the Amptek software, i.e., ADMCA or DppMCA.

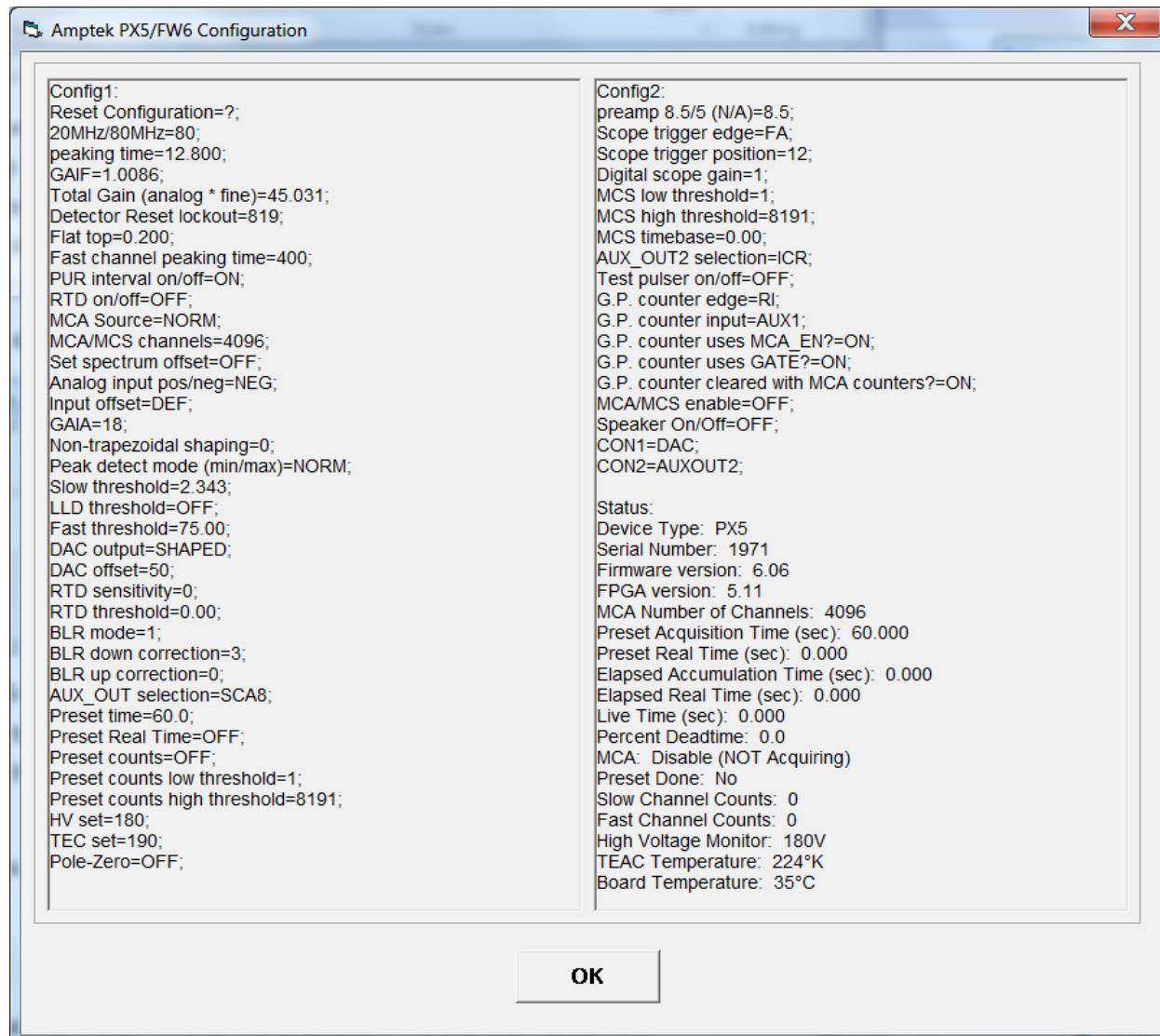
After setting up the DPP using one of these two programs, this current configuration can be “left” in the DPP after the program has been closed (note also that the Amptek setup software cannot be running at the same time as XRS-FP as the DPP can only be connected to one program at a time).

If there is no configuration file found, then a prompt will be made as follows:



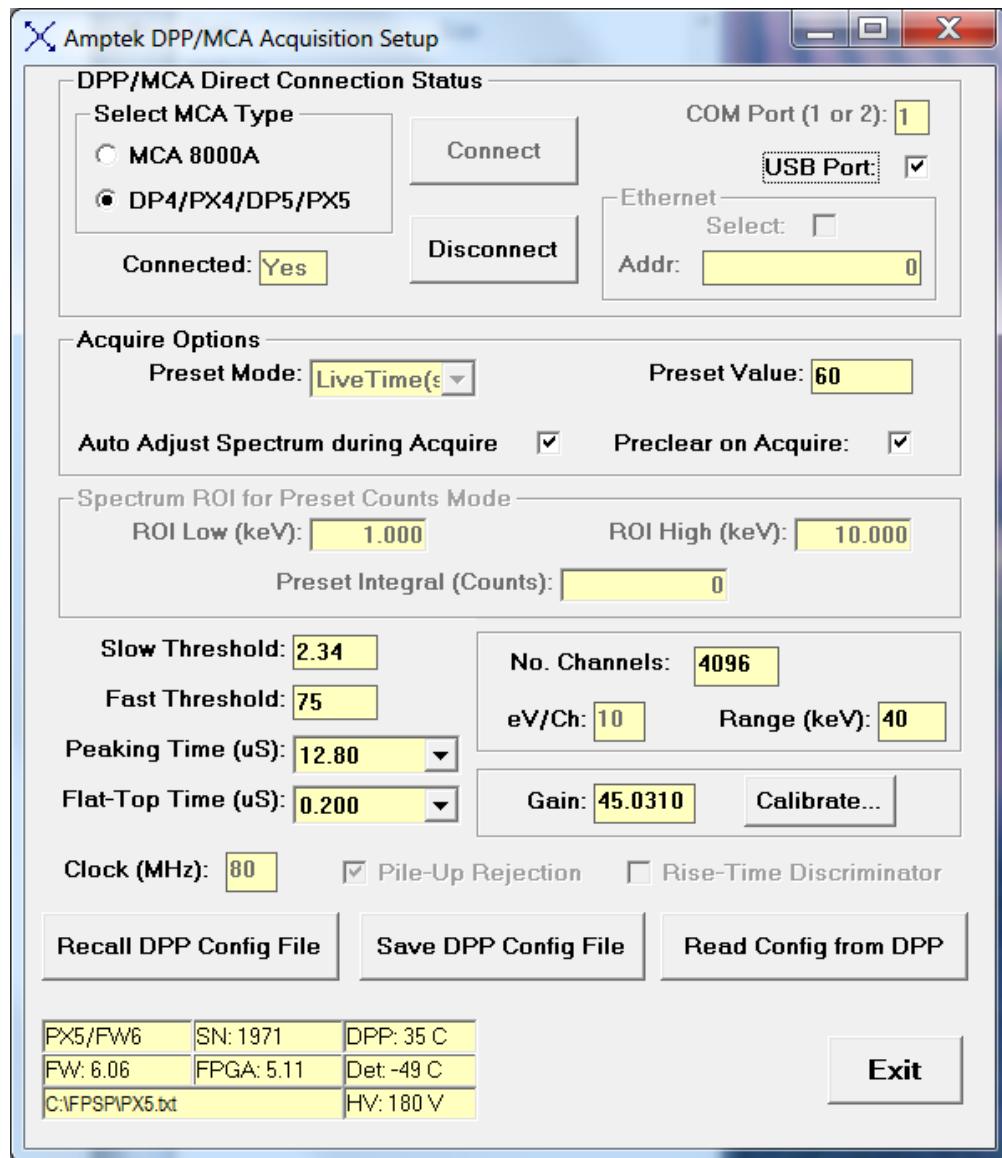
If you answer “No” to this prompt then XRS-FP will simply connect to the DPP without any reconfiguration of the hardware. This is useful if you want to be sure there are no changes taking place between the two steps. However, for routine operation it is recommended that the XRS-FP configuration file be loaded every time the software connects to the DPP.

After connecting to a Firmware 6 DPP, you will get a popup panel something like the following figure:



There are two Configuration sections and one Status section. The latter is the readout of the current status of the DPP. After clicking OK on this panel, you will get the final Setup-DPP panel, similar to the next figure. In addition, there is information shown after connection that displays the DPP and detector temperatures, and the High Voltage bias readout from the detector control.

After a connection is made to the DPP, if there is a current spectrum stored within the DPP firmware, then this spectrum is loaded into XRS-FP and displayed on the Spectra-X window (v.6.1.3 or later). During this process the number of channels may be updated to match the stored spectrum (v.6.2.3).



The Setup-MCA/DPP panel can be used to select and control several parameters such as the Preset Time for the acquisition. For the MCA 8000A this value is the Preset Livetime. 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.

In the early Amptek DPP's (such as the DP4, PX4 and the DP5 FW5), there is no true preset livetime function, and so this time is actually the clock or real time. This is the reverse of the 8000A, so that *now* the elapsed livetime will be less than the preset or elapsed real time. It is important to differentiate the two because this has a large effect on the way that spectrum processing must be done. In all cases, the net counts must be divided by the measured livetime, irrespective of the processor and the manner in

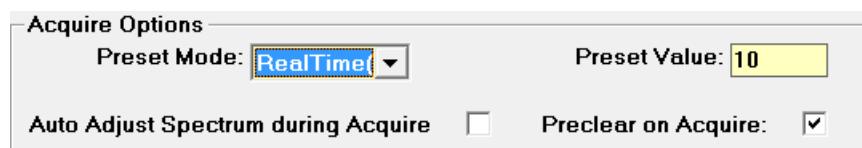
which the preset is defined. If the counts were divided by real time, a systematic error would be introduced because the count rate is not accounting for deadtime losses. For example, if the tube current were doubled, the input count rate should also be doubled (this is the rate into the pulse processor), but because of deadtime losses, the output (processed) count rate would *not* be doubled, especially at higher dead times (above, say, 30%).

So, if you had calibrated with a standard at, say, 5% dead time, and then made a measurement with the deadtime at 50%, the results would be inaccurate by potentially large amounts if we relied on real time instead of livetime. Of course, if you are doing standardless analysis, normalized to 100%, then this issue is not important, but it is very important when you use calibration standards.

In the newer Amptek DPPs (e.g., DP5 FW6, or PX5), the Preset Livetime function exists, but there is a subtlety to the actual definition. For more information please contact the excellent Amptek application note on the subject. There are actually 3 different counting times:

- a) The Time-Of-Day clock time, aka Real Time.
- b) The Elapsed or Accumulation Time. This is the time when the DPP is actively acquiring, and is shorter than (a). Also known as the Acquisition Time.
- c) The Livetime. This is the most important parameter as it reflects the time during which counts are actually acquired. Item (b) minus (a) is essentially the dead time.

In XRS-FP (again for FW6) the Preset Livetime is really the Preset Accumulation Time. This means that the true livetime is always less than the Preset value (this amount may be small and not observable). In v.6.3.1 of XRS-FP we added the option for Preset Real Time as an option to Livetime (again this is for DP5 FW6).



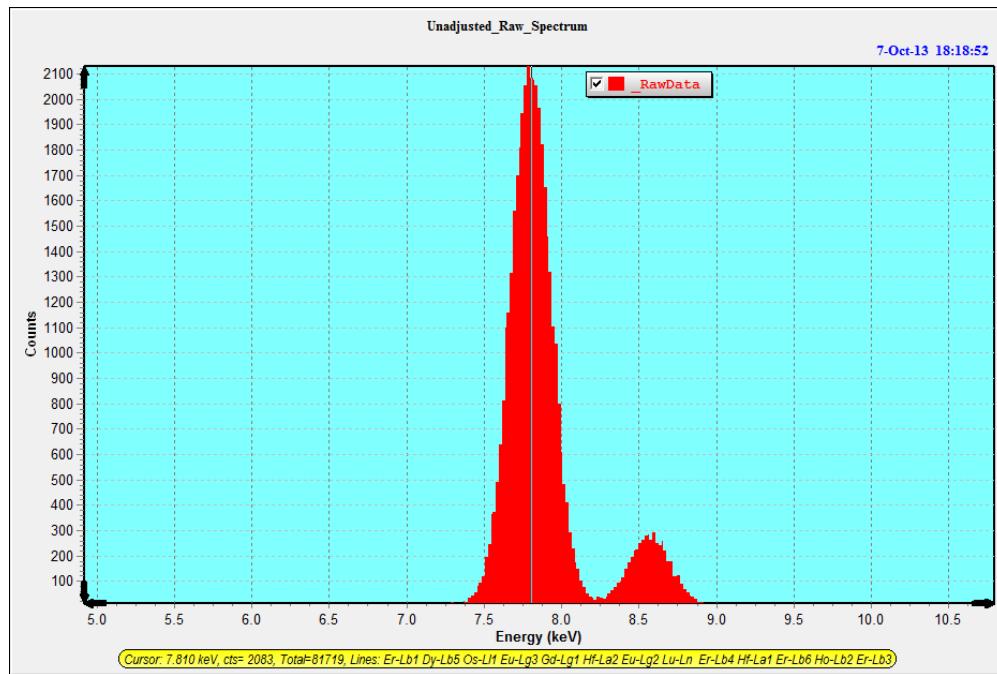
It is possible to control the Fast and Slow Thresholds, but in newer DPP models this is better done by the Amptek software (e.g., DppMCA). It is also possible to select the Peaking Time (PT), with a matching Flat-Top Time. These are selected from drop-down lists. Any change to the PT will result in a new default Flat-Top being selected, but this can be changed.

The expectation with the XRS-FP software is that the user will select first the overall range of the spectrum to be acquired. This normally would cover the total energy range of x-ray photons captured in the detector. Also, you want this to be versatile for different settings for analysis. For example, an initial setting of 4096 channels with a Range of 40 keV (actually 40.96 keV, but the convention is to truncate to the nearest integer), would produce an eV/channel of 10. This is a good “rule-of-thumb” for most XRF analyses.

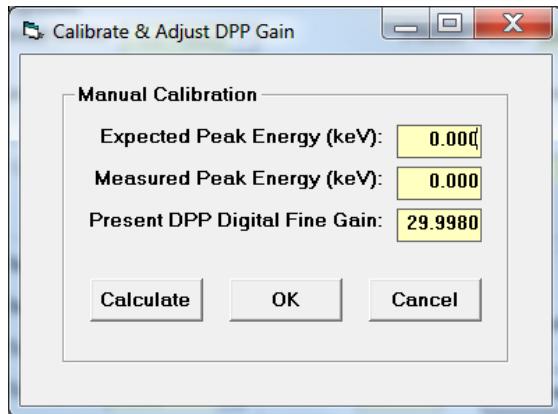
There is not much to be gained by using a smaller eV/channel, except in special circumstances. However, this range may not be enough to cover all the peaks of interest, in which case a range value of 80 keV would be an alternative. Since there is a maximum of 4096 channels available to XRS-FP, there will be small degradation in peak resolution by now going to 20 eV/channel. Also, the spectrum processing time is determined directly by the number of channels, so some users select 20 eV/channel and 2048 channels for a Range of 40 keV as an alternative.

The newer versions of the software have a new feature that allows the user to get the DPP approximately “in calibration,” which means showing the peaks in the correct locations expected by the software. Having selected the parameters in the previous paragraph, we can now do a coarse adjustment of the DPP itself by changing the value of the overall gain in hardware. This is accomplished by using the Calibrate button in this Setup-DPP panel. This is very different from the XRS-FP software gain and offset adjustment, which will be described later.

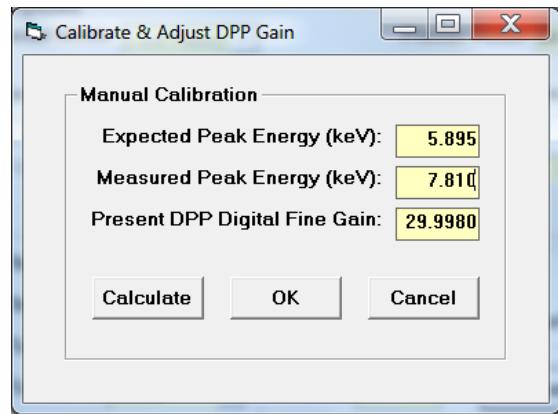
First, acquire a spectrum, without any software adjustment at all, such as the following spectrum of an Fe-55 source, with Mn-K peaks. The Mn-Ka peak centroid should be at 5.895 keV. Note that in the following spectrum it is some way off from this value.



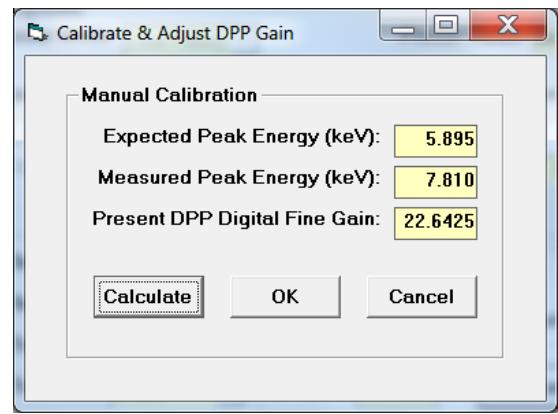
After clicking on the Calibrate button, a dialog pops up as follows:



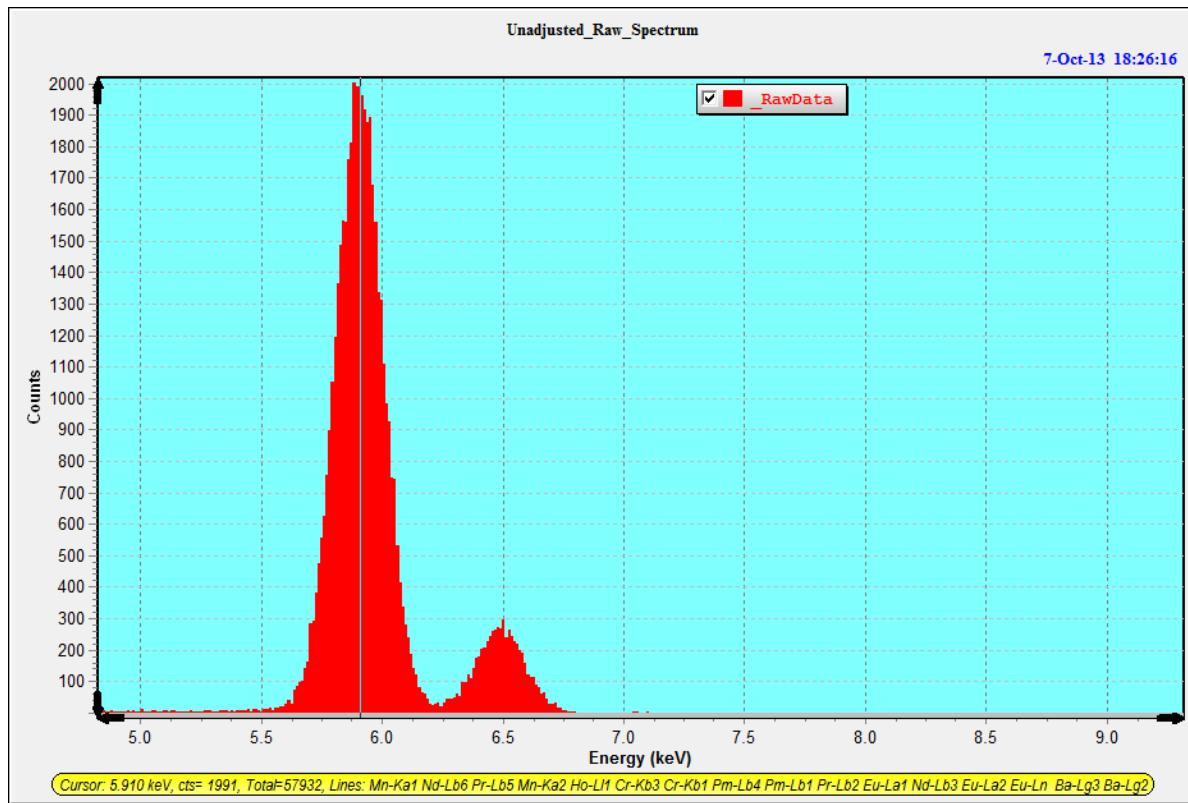
It shows the current DPP gain value, and two text boxes to enter the expected peak position and the measured peak position. After entering these values from the above spectrum, the dialog looks like this:



After clicking the Calculate button, the Gain value gets updated as follows:



Now, if we acquire a spectrum, the new spectrum will have the peaks in approximately the correct location, as follows:



The new estimated centroid value is now 5.910, close to the target value of 5.895 keV. Don't expect the alignment to be perfect because complete energy calibration requires two peaks because there is an offset adjustment as well as the gain.

After making this change to the Gain value is very important to now save the updated DPP configuration file using the "Save DPP Config File" button and updating the appropriate default file in the XRS-FP software directory.

In the Acquire section, there are 2 further options available. The first is the Pre-Clear option, which will clear the spectral data before the start of a new acquisition. The second option is the Auto-Adjust-Spectrum-on-Acquire checkbox. This is related to the Auto-Adjust option shown in the Setup-Processing panel, but works *during* the acquisition, so the spectrum should always appear in the calibrated position.

It is very important that you do not confuse the two parameters and, in particular, that you do not use them both together! The software has protection against this happening but it is still possible that this situation could arise if the XRS-FP.ini file is edited manually, for example.

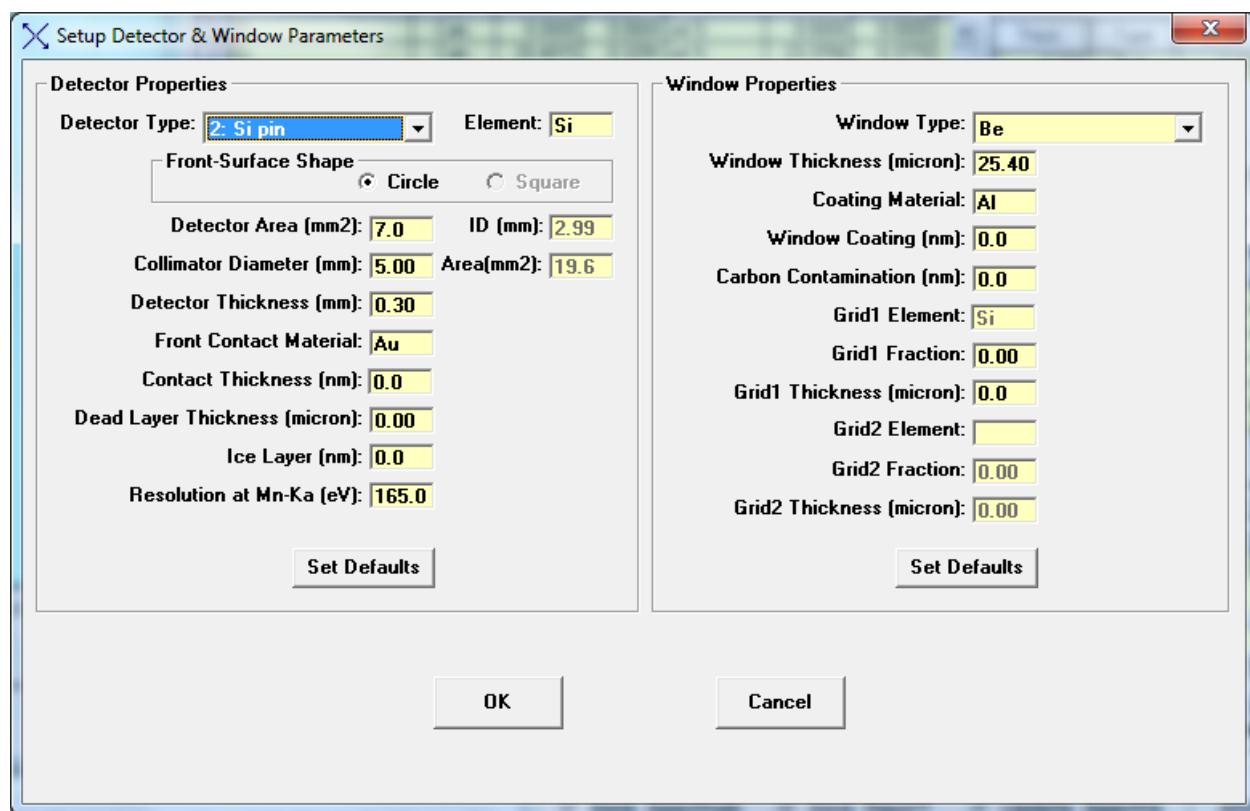
If spectra are acquired manually, they are usually saved unadjusted. This means that when the file is re-loaded, the spectrum *must* be adjusted, assuming they are out of calibration. This is usually the case for the DP4, but with the DP5 or PX4 it is possible to calibrate the hardware to produce calibrated spectra at 10, 20, eV/channel, etc.

When the Auto-Adjust parameter is set, spectra are adjusted when they are read from a disk file. During live acquisition though, the spectrum is not adjusted automatically. When using the automatic analysis

(the Auto-Mode panel), the spectra are first adjusted and *then* saved (adjusted) to disk, before further spectrum processing.

When the Auto-Adjust-Spectrum-on-Acquire option is checked, the spectra are already adjusted, so no further adjustment should be required on loading a spectrum from disk, etc.

## 12.2 Setup Detector



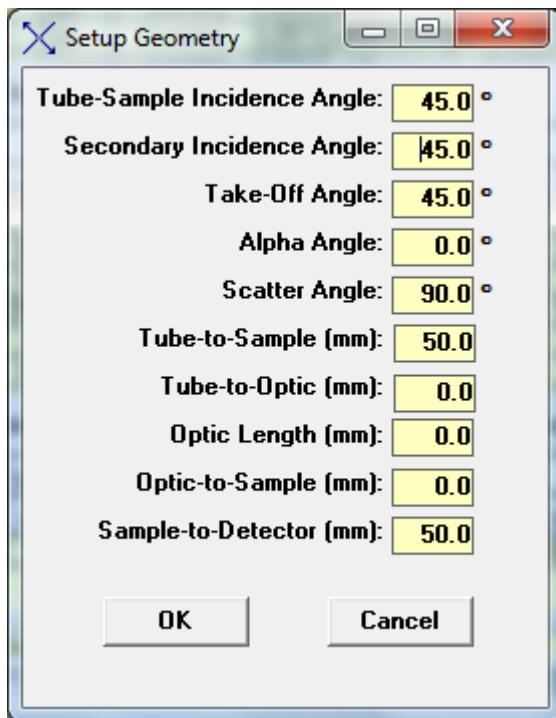
This dialog allows the user to completely define the type of detector being used. This is only important when standardless analysis is performed. If standards are used, then the detector efficiencies are implicitly calibrated with standards. However, the values must not be changed between calibration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

Many of the options in this dialog may not be relevant to your detector. In which case, simply leave them as zero. Note that the resolution value in this dialog is equivalent to the one used in Setup-Processing.

In v.3.3.0 software there is support for the Si drift and CdTe detectors that was not available before.

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

## 12.3 Setup Geometry

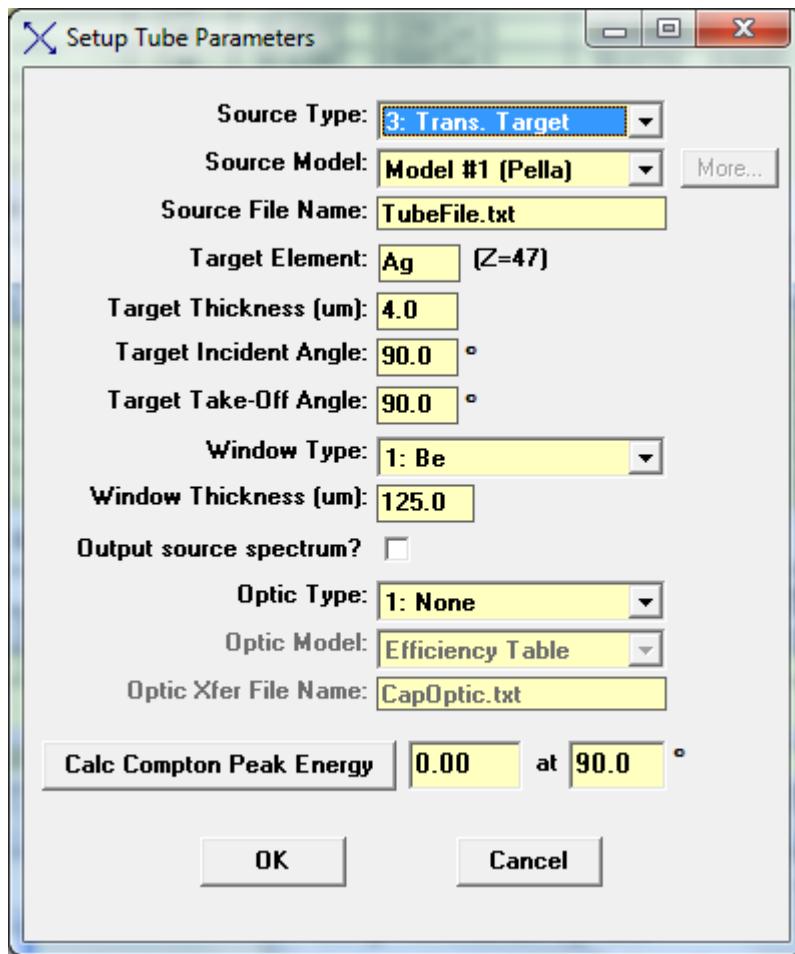


It is important to correctly define the geometry of the system in use, for correct FP calculations to be performed. The most important of these are the Incident and Take-Off Angles. The optic can probably be ignored for most XRF systems. The Tube-to-Sample and Sample-to-Detector distances are important when the analyses are NOT performed in vacuo, as these distances affect the absorption of the source and fluorescent x rays (i.e., from the sample) in air.

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!

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.

## 12.4 Setup Tube/Source



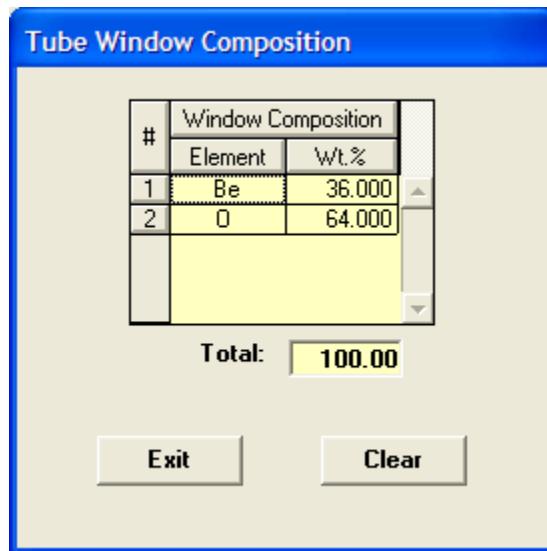
The source type (typically an x-ray tube) must be correctly defined for accurate analysis using FP. If the tube anode is changed, it is very important that the Tube Anode (target) Element be correctly defined, along with the Anode Take-Off Angle, which is the angle that x rays leave the tube target, with respect to the target plane. This is the case even there is no tube control.

For the parameter Source Model, the default option is the Fitted Model #1. This option selects the tube spectrum model of Pella et al (the usual model). The next option (Fitted Model #2) uses the analytical model of Ebel et al.

In addition to the built-in tube models, there is also an option to use 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%.

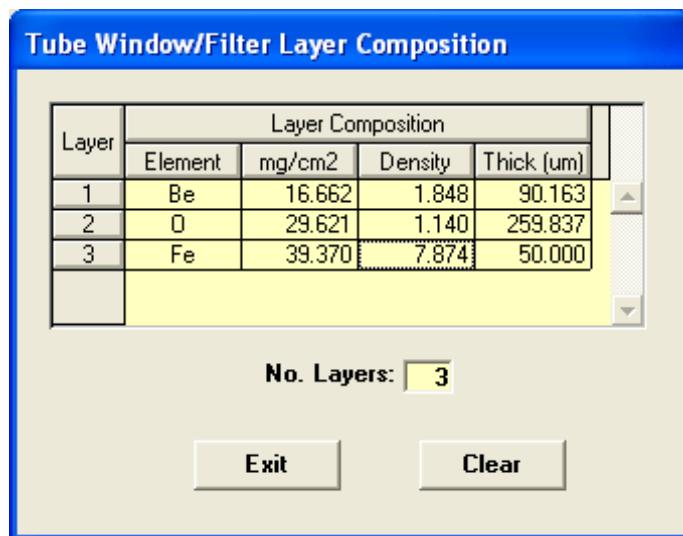
Several different types of tubes can be accommodated. There is also an option for using radioisotopes as an x-ray source (option 4 in the list of Source Types).

The tube take-off angle is very important, as the relative intensities assume a normal (90-degree) take-off. The target (electron) incident angle obviously has no affect for the isotope sources. The Window Type and Thickness are also important parameters for FP analysis. The window can be an alloy (as shown above), although the typical window would be beryllium. If the alloy window is selected, then the following dialog shows up, allowing the definition of the window alloy composition:



The alloy values get saved at the end of each TFR file, and will get reset when that file is loaded, along with other system parameters.

Another option is to choose "multilayer" tube windows, and this brings up a dialog panel such as:



This option treats any compounds as separate elemental layers, along with any special filters that may be mounted in front of the tube. In the example above, there is a BeO window, with an Fe filter. Note that

now the elements are expressed in mass thickness, or thickness with a standard value of density. You can enter the values in either of the thickness columns, and the corresponding values are calculated automatically. The information is saved in the TFR file in the same way as for the alloy windows.

Of course 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 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.

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.

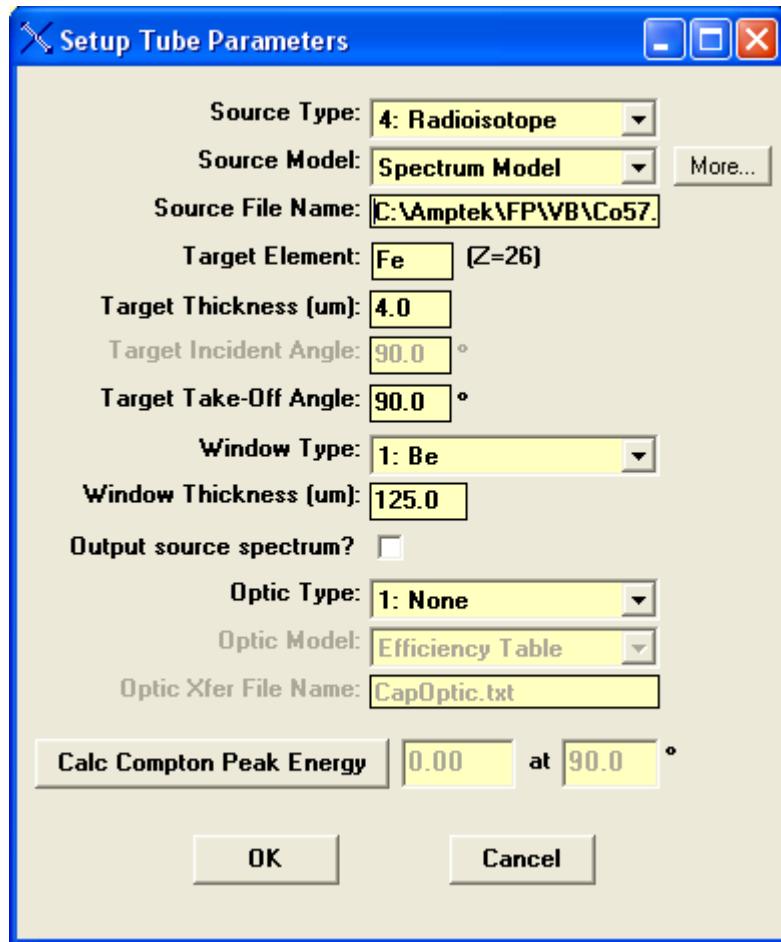
Selecting the mirror option for the optic will result in the specified kV from the tube being used as a monochromatic source. This is for monochromatic sources that could be from either mirrors or curved crystals. The multilayer optic option is not yet supported.

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 Setup-Geometry page.

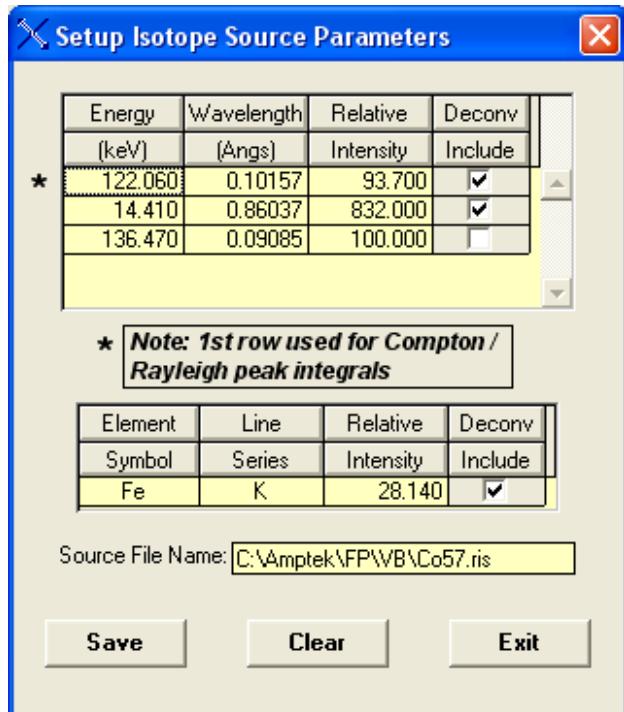
When the radioisotope (RI) source option is selected, the spectrum file method must be used to define the isotope source spectrum. Several files, corresponding to the common radioisotope sources, are included with the software (Am241.txt, Cd109.txt, Co57.txt, and Fe55.txt). The relative intensities assume no window, and so this should be included in the setup if a window is used with the source. Each \*.txt file gets processed upon loading into a special panel that is only accessible when a RI source is selected. The \*.txt files are used for the FP part of the analysis, to provide the incident excitation “spectrum” in the same way as can be used for a tube spectrum.

Note that this \*.txt file is quite different from an associated \*.ris file (see below), which is only used for the deconvolution part of the processing.

For example, the Co57.txt file has been selected in the panel below.



Now the “More...” button is enabled, so that clicking on this loads the following panel.



This contains information about the specific gamma and x-ray lines in the RI source, and allows the user to select which ones to include for deconvolution and subsequent Compton peak processing. The information comes from a \*.ris file with the same name as the \*.txt file previously selected for the RI source.

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. Note that the appropriate x-ray lines for the selected RI source are also shown, which can be included or not for spectral deconvolution, but they cannot be selected for the Compton peak extraction.

Note also that this file may not exist for the isotope of interest, in which you will have to create the table, enter 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.

There is also an option to output the calculated source spectrum, and this is saved in wavelength units vs. intensity. This spectrum can be read into Excel, or other programs, to see what source spectrum is being used. Keep in mind that this wavelength-based spectrum will look quite different to an energy-based spectrum because of the inverse relationship.

The source options described in this section do not directly control the x-ray source. The control options are setup directly in the XRS-FP.ini file, and apply when a suitable tube and high-voltage power supply is included in the software package. The only controllable x-ray source that is fully compatible with the software at this time is the Mini-X source, available from Amptek, as described in the next section.

It is possible to load an external program that can control an x-ray source, completely independently from the XRS-FP software. To do this, enter the name of a program in the [Tube] section, as shown in the following example:

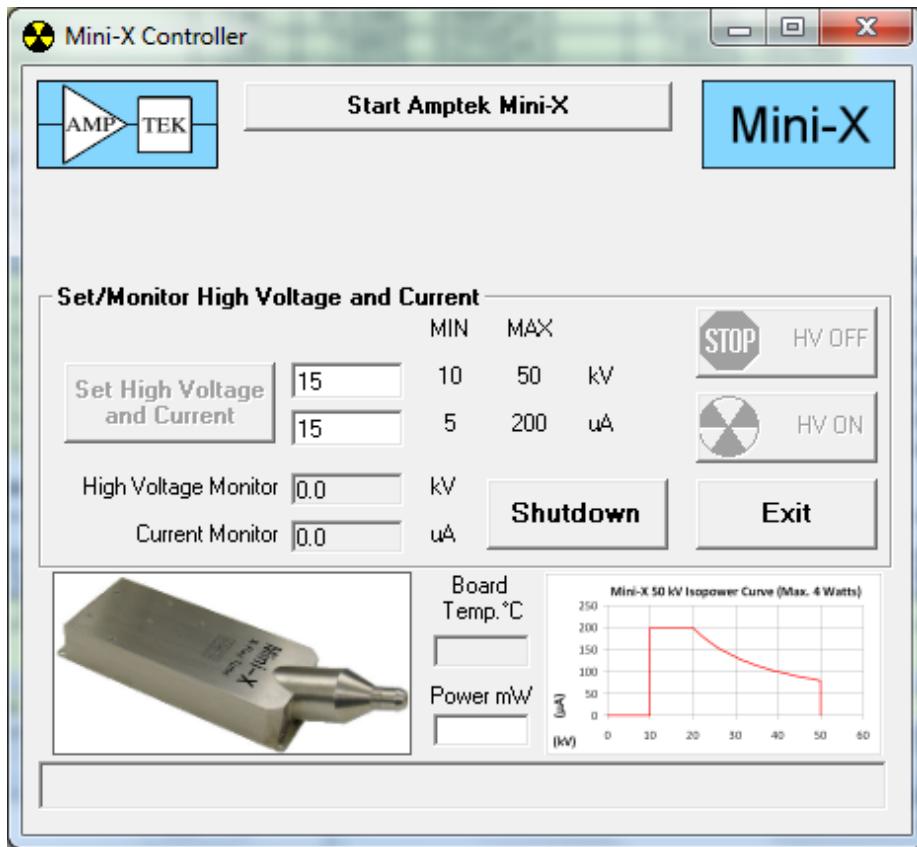
```
[Tube]
; Tube Type. 0= No Tube (Default), 1= Minix, -1= Use external program
TubeType=1

; Name of External Program to call for controlling Tube / HVPS (Default= none)
TubeProgram=C:\TubeControl\TubeControl
```

This setup will automatically load the TubeControl.exe program when the XRS-FP software loads. It is the responsibility of this external program to control the tube and there is no interaction with XRS-FP.

## 12.1 Setup Mini-X

This feature is for controlling the Mini-X x-ray tube from Amptek (v.4.2.3). The following panel was derived from the Amptek program for controlling the tube, but was modified to better integrate with XRS-FP. In this way the tube can be controlled from the settings directly in XRS-FP and full automation used as, for example, with the use of multiple conditions for a single sample analysis (see Setup-Condition).



In order to see this option in the Setup menu, ensure the tube has been selected in the XRS-FP.ini file, where all the setup parameters are saved. A typical setup for the tube section [Tube] is shown below:

```
[Tube]
; Tube Type. 0= No Tube (Default), 1= MiniX.
TubeType=1

; Minimum allowed value for the high voltage (kV). Default=10 (integer).
kVmin=10

; Maximum allowed value for the high voltage (kV). Default=50 (integer).
kVmax=50

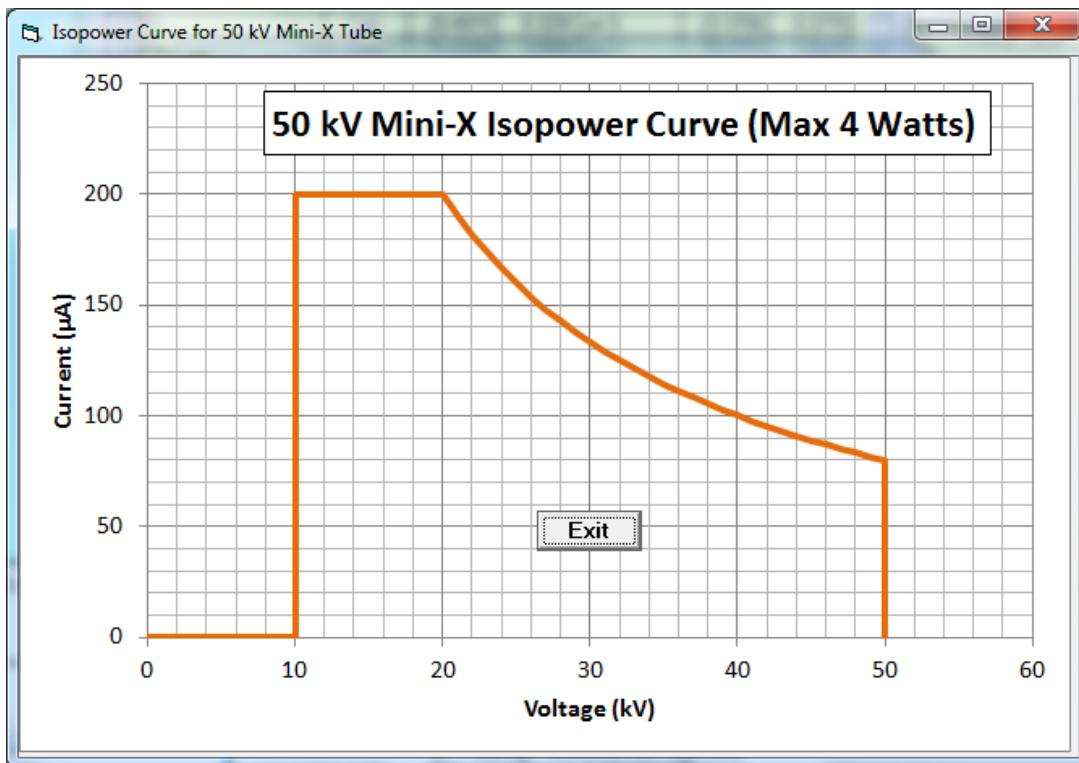
; Minimum allowed value for the tube current (microamps). Default=5 (integer).
uAmin=5

; Maximum allowed value for the tube current (microamps). Default=200 (integer).
uAmax=200

; Maximum allowed value for the tube power (Watts). Default=4 (integer).
Wattsmax=4
```

Unless the TubeType is set to 1, the menu item will not be visible. The other values should correspond with the ratings on your x-ray tube.

Note that this tube has a maximum wattage rating as well as the kV and microamps, and this can be seen visually in the Mini-X Isopower Curve of current vs. voltage. Double-click on this chart to display a larger version, as shown below:



The user should be careful not exceed the maximum ratings, although the software should guard against this possibility. For further information about the tube, consult the Amptek Mini-X User's Manual.

Before using the tube, assuming all the drivers are installed correctly, you should click on the "Start Amptek Mini-X" button. This initializes the software connection to the tube. After a short pause the "HV ON" button should be enabled. Now click the "HV ON" to enable the high voltage, at which point the kV and microamps are now selectable in either the Mini-X panel or the main XRS-FP panel.

Note that this is a 2-step operation – first the kV and microamp values are entered, and then the "Set kV/uA" button is clicked to actually control the tube power. At this time, the values read back from the tube should correspond approximately to the set point values. If not, then this may indicate that the tube is malfunctioning.

For example, if the current readout is zero, this may indicate that the tube filament has burnt out. If the tube cannot be enabled, check that the Interlock connection has been made correctly. If the interlock connection is broken a message will be displayed in the Mini-X panel.

The Mini-X panel can be closed (press "Exit") and then the controller will just run in the background. This is different from the Amptek standalone program, where this would cause a complete shutdown of the tube.

In XRS-FP a manual shutdown can be performed from the Mini-X panel. You can turn off the x-ray tube

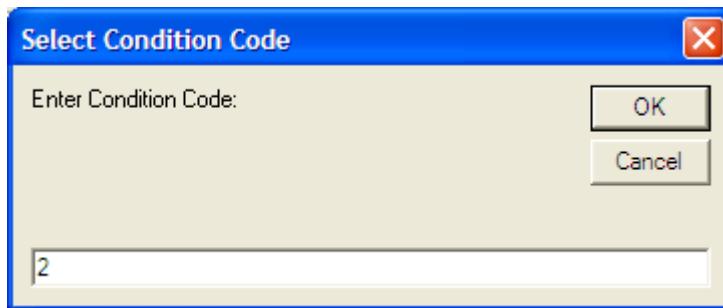
by clicking with the left mouse button on the flashing  picture on the XRS-FP main panel, or on the "HV OFF" button on the Mini-X button.

For automated analysis, using the Runtime panel, the software will automatically cycle through the conditions designated in the Element Table, automatically setting the appropriate tube values. The software will also prompt the user to turn ON the x-ray tube for the first control occurrence in the automation.

For any non-automated (i.e., manual) operation, such as selecting a certain condition, the tube settings in the text boxes on the status/entry bar will be set, but to actually control the tube you must click on the "Setup kV/uA" button.

## 12.2 Setup Condition

This command allows the user to select the active conditions code, with the following dialog:



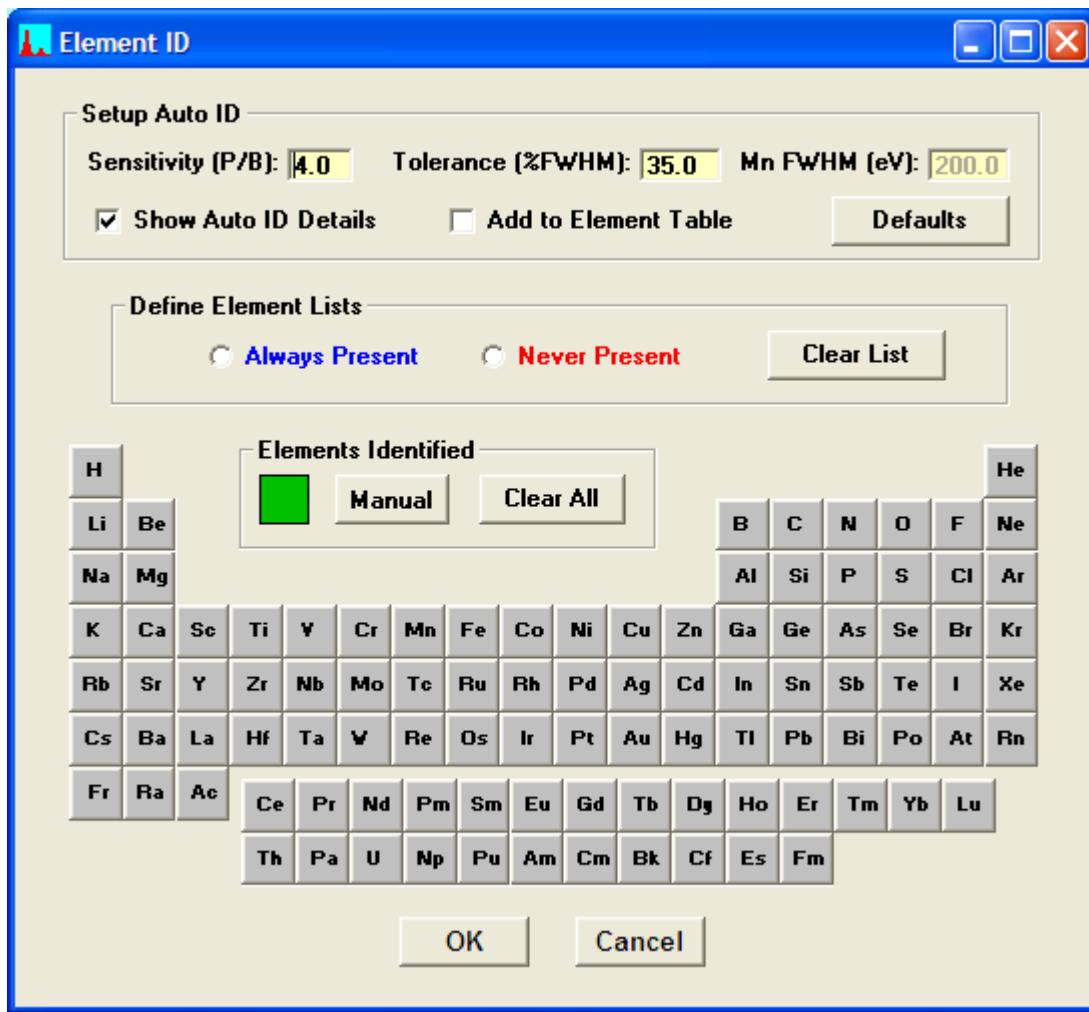
After selecting the condition code, then that condition is highlighted and the associated parameters used to define the measurement conditions, including the acquire time and the tube control, and the processing options. You can also just click on the Code column for the desired condition row to select it as the active condition code.

Measurement & Processing Conditions:											<input checked="" type="radio"/> Measurement	<input type="radio"/> Processing	Active Condition Code: <b>2</b>
Code	X-Ray Source					Detector			Chamber	Time (secs)		Monitor	Intensity
	Target	Filter	Thick(um)	kV	uA	Type	Filter	Thick(um)	Atmos	Preset	Actual		
1	Ag	None	0.00	20.0	15.0	Si pin	None	0.00	Air	20.0	20.0	0.0	
2	Ag	Al	50.00	35.0	10.0	Si pin	None	0.00	Air	15.0	15.0	0.0	

In conjunction with this table, the elements to be processed with the selected condition should also be defined. With manual acquisition and processing, you should load each spectrum, select the matching condition code, process the spectrum, and then proceed to the next one, if more than one condition is used for an analysis. After all the spectra have been processed, then use the Process-Analyze menu command to do the final FP analysis.

## 12.3 Setup AutoID

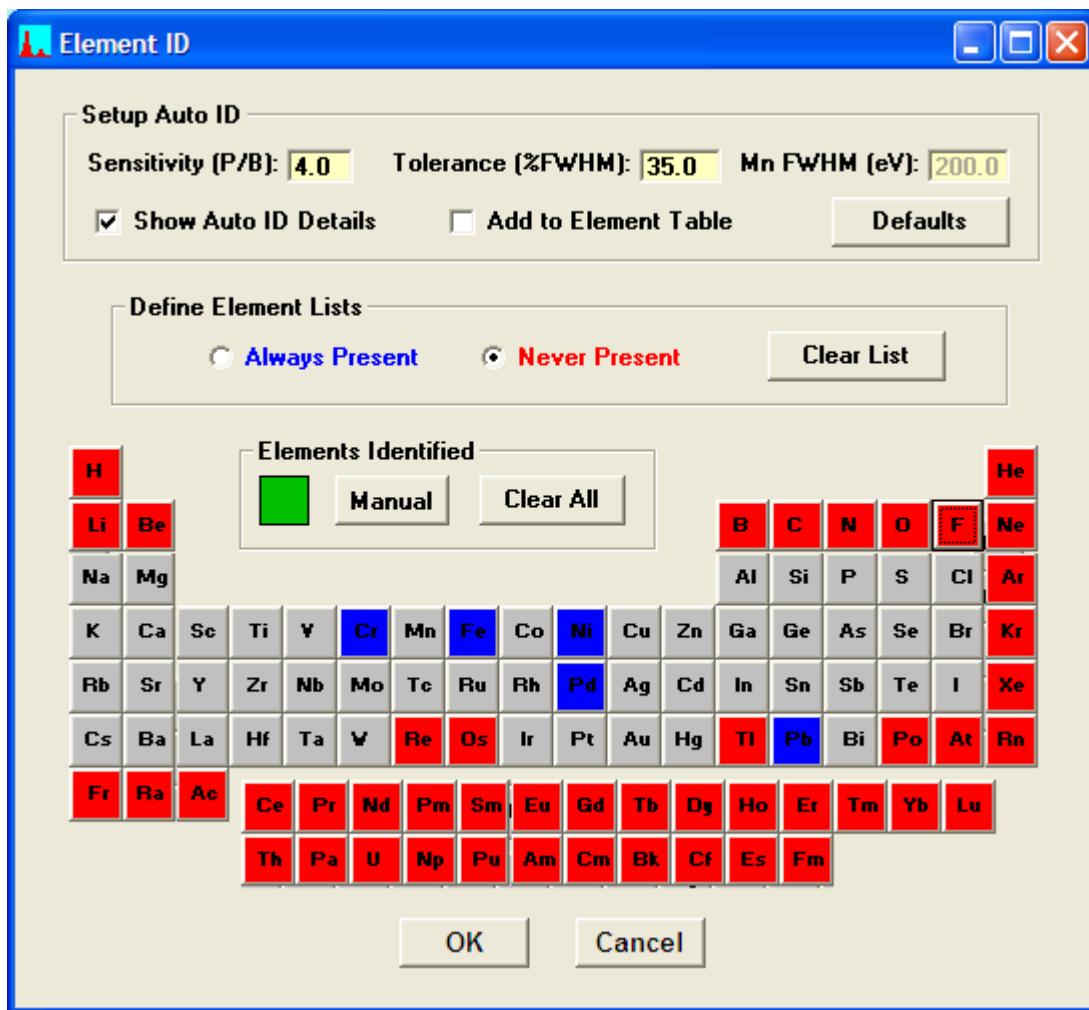
This option sets up the parameters before doing an Automatic Peak Identification (Process-AutoID). The panel for doing this will be like the following example, which shows the default settings:



The top part of the panel 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<sub>a</sub> FWHM is shown, but this parameter is entered elsewhere.

If the “Show Auto ID Details” option is checked then a list of peaks and x-ray line assignments are displayed at the end of the AutoID process. The “Add to Element Table” option selects whether you want to add the identified elements to the element list currently displayed in the Element Table in XRS-FP.

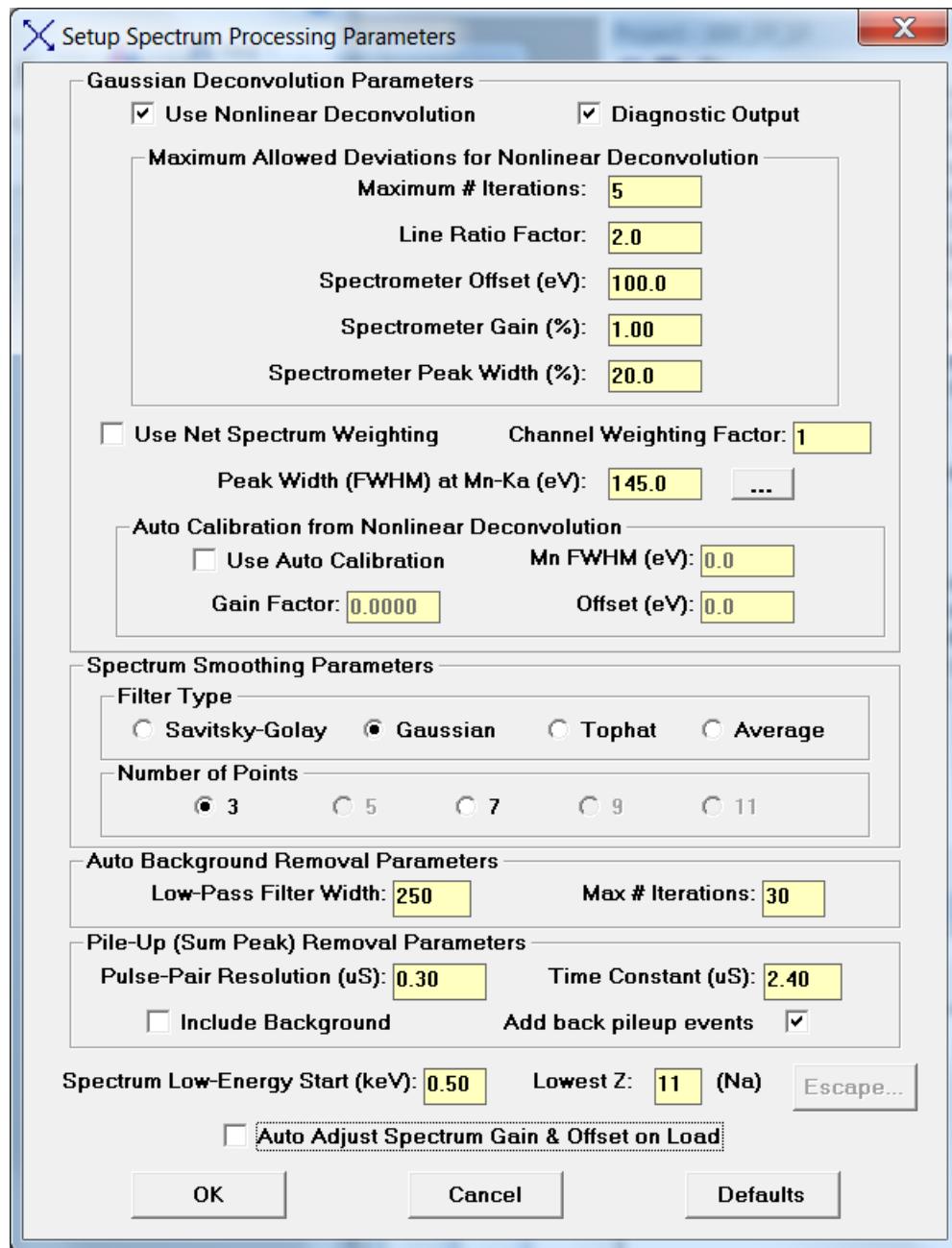
As this chart is displayed *all* elements will be included in the possible Auto-ID. Typically there are many elements that can be identified that are known not to be present. Likewise there are some that can be assumed to always be there. There are two options to assist with this knowledge – the **Always Present** and **Never Present** lists. After selecting the radio button for the specific list, clicking on the element buttons will add those elements to the specified list, as in the following example:



Elements identified as “Always Present,” or those that are added with the Manual button, are added to the spectrum display after each click.

## 12.4 Setup Processing

This panel contains the parameters used to setup the various spectrum-processing options.



There are 3 main sections: (a) the Gaussian Deconvolution parameters, used to extract net peak intensities from an XRF spectrum with overlapped peaks, (b) the Automatic Background removal parameters, which control the removal of the spectrum background, and (c) the Pile-Up (Sum Peak) removal parameters. In addition there is an additional parameter, the Spectrum Low-Energy Start, which is used for all spectrum methods to define the start of real spectral data, as opposed to low-energy noise events.

There are two options for the Gaussian method, which are the linear or nonlinear deconvolution. These parameters can be described as follows:

(1) Use 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 are effective.

(2) 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.

(3) 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).

(4) 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)).

(5) 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.

(6) 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.

(7) 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.

(8) 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.

(9) 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-Ka 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 user can select from a variety of different smoothing operators when using the Process-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.

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 subtracted 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-Ka 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.

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.

Since v.6.2.8 of XRS-FP, there are two more checkbox options available in XRS-FP and related libraries. First, you have option of subtracting the background *before* making the pile-up correction. This is done in behind the scenes, and the background is added back *after* the pile-up removal is complete. The purpose of this option is to allow the complete removal of the pile-up peaks *without* going below the background level or, in some cases, below the x-axis (i.e., this would produce negative counts except that they are truncated to zero counts).

If the processing is allowed to “chop” the background, or worse, this can cause problems with the later real background removal. By forcing the channels to not go below the background, “holes” do *not* appear in the background itself. Although this is an artificial restriction, it can often improve the quality of the pile-up removal. It works well when the total background counts are relatively low. It should be used with caution, especially if the background counts make up a large fraction of the total spectrum counts, as this would then distort the pile-up calculations which rely on an accurate estimate of the total spectrum count rate.

The second checkbox option controls whether the subtracted estimated pile-up events are added back to their parent peaks. It has been observed in certain unusual cases that the pile-up can be distorted and not follow the classical descriptions of the pile-up process. An example of this is when the input count rate varies substantially during the acquisition. This is an unusual artifact so this checkbox should normally be left checked.

There are several options for smoothing filters. The default is the 3-point Gaussian 1:2:1 filter, but you can select more points or use a Savitsky-Golay filter. They all produce similar results, except that a 5-point smooth is equivalent to running two 3-point smooths. The Tophat filter produces a bipolar spectrum with positive and negative lobes. It both smooths and removes the background at the same time. The Average filter tends to flatten out the spectrum, lowering the peak-to-background ratios and broadening the peaks. The Tophat and Average filters are only recommended for special applications.

The user can also select the lowest energy value (Spectrum Low-Energy Start) in the spectrum that will be used for processing (e.g., for the background and deconvolution operations). For standard detectors, with Be windows, the number of low-energy events will likely be very small so this parameter will not be useful. However, it could be important for spectra with significant peaks at or below about 0.7 keV.

Similarly, 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. The SIR-FP method can also be used to estimate the low atomic number fraction in a sample analysis.

The Auto-Adjust option should be checked if the acquired spectra are not adjusted so that the energy scale is exactly, 10, 20, 40 eV/channel, etc. This is complementary to the Auto-Adjust-Spectrum-on-Acquire option shown in the Setup-MCA/DPP panel, but works *after* the acquisition.

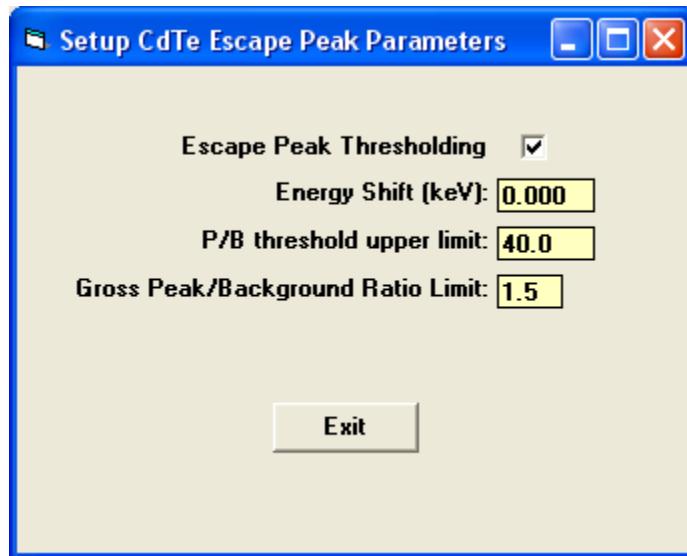
It is very important that you do not confuse the two parameters and, in particular, that you do not use them both together! The software has protection against this happening but it is still possible that this situation could arise if the XRS-FP.ini file is edited manually, for example.

If spectra are acquired manually, they are usually saved unadjusted. This means that when the file is re-loaded, the spectrum *must* be adjusted, assuming they are out of calibration. This is usually the case for the DP4, but with the DP5 or PX4 it is possible to calibrate the hardware to produce calibrated spectra at 10, 20, eV/channel, etc. When the Auto-Adjust parameter is set, spectra are adjusted when they are read from a disk file. During manual acquisition, though, the spectrum is not adjusted automatically. When using the automatic analysis (the Auto-Mode panel), the spectra are first adjusted and *then* saved (adjusted) to disk, before further spectrum processing. When the Auto-Adjust-Spectrum-on-Acquire option is checked, the spectra are already adjusted, so no further adjustment should be required on loading a spectrum from disk, etc.

If the detector is of the CdTe type, then there is a special panel that can be used to fine tune the escape peak correction for the Cd and Te K escape events, as shown below. The check box selects whether the escape peak correction is to be constrained at some level or not. One constraint is the upper limit for the Peak/Background ratio of the net spectrum and the original (gross) spectrum in any given channel. In other words 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.

Similarly, 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.



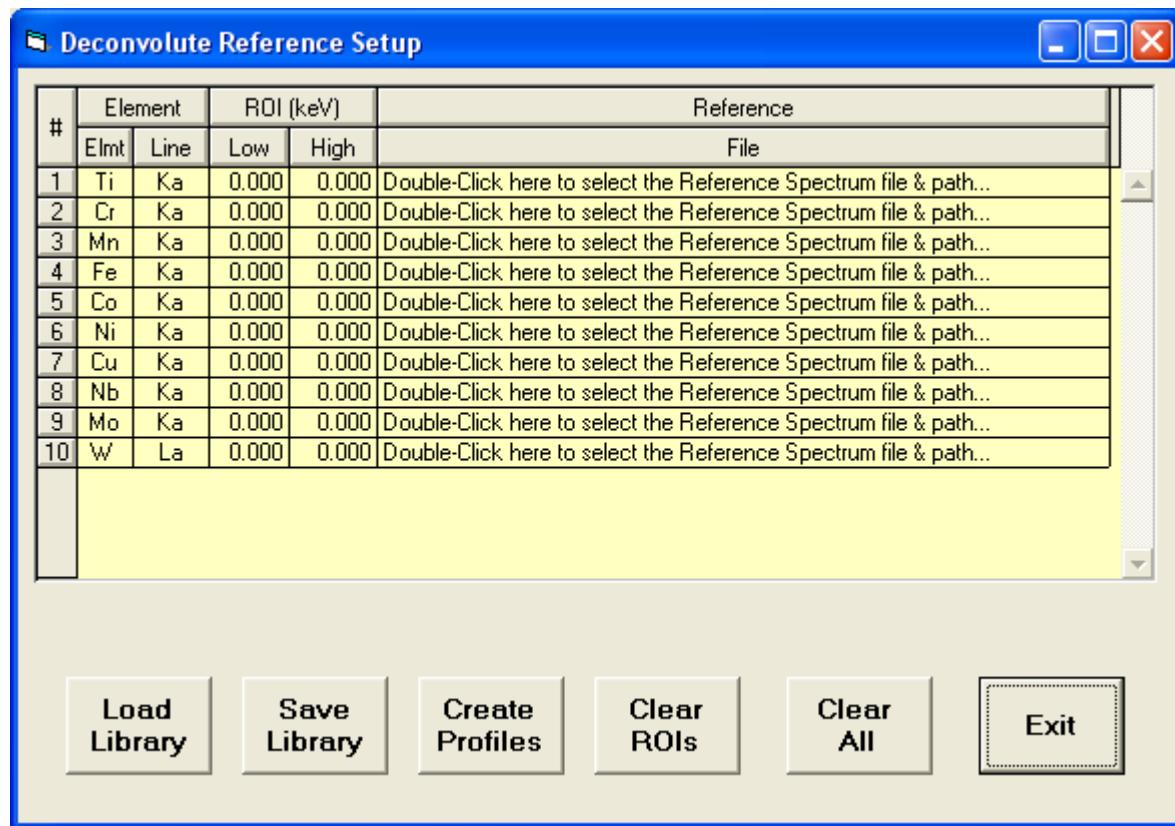
The final option on the Setup-Processing panel is to set or clear the Auto-Adjust option in the software. If this option is checked then any spectrum that is loaded into XRS-FP will be automatically adjusted. It is very important that this option be set correctly, and further details on the adjust procedures can be found in the next section.

## 12.5 Setup Reference

First the individual profiles must be extracted before any deconvolution can be performed. This requires the collection of a series of spectra, one for each element to be included in the deconvolution list. From each spectrum, a region will be extracted (known as the “deconvolution region”) and stored in memory. The profiles should be from spectra where there are no overlaps for the element-line series of interest. So the first step is to collect all these spectra. They will later be processed as you require, in the same way as the analyzed spectrum will be processed.

Once the reference spectrum files have been acquired and saved, then prepare the TFR file that will be used to process the FP or LSQ calibration standards and unknown samples. This will include all the processing steps such as escape peak and background removal.

After saving this TFR file, then click on the Setup-Reference menu item, and a screen such as the following will appear:

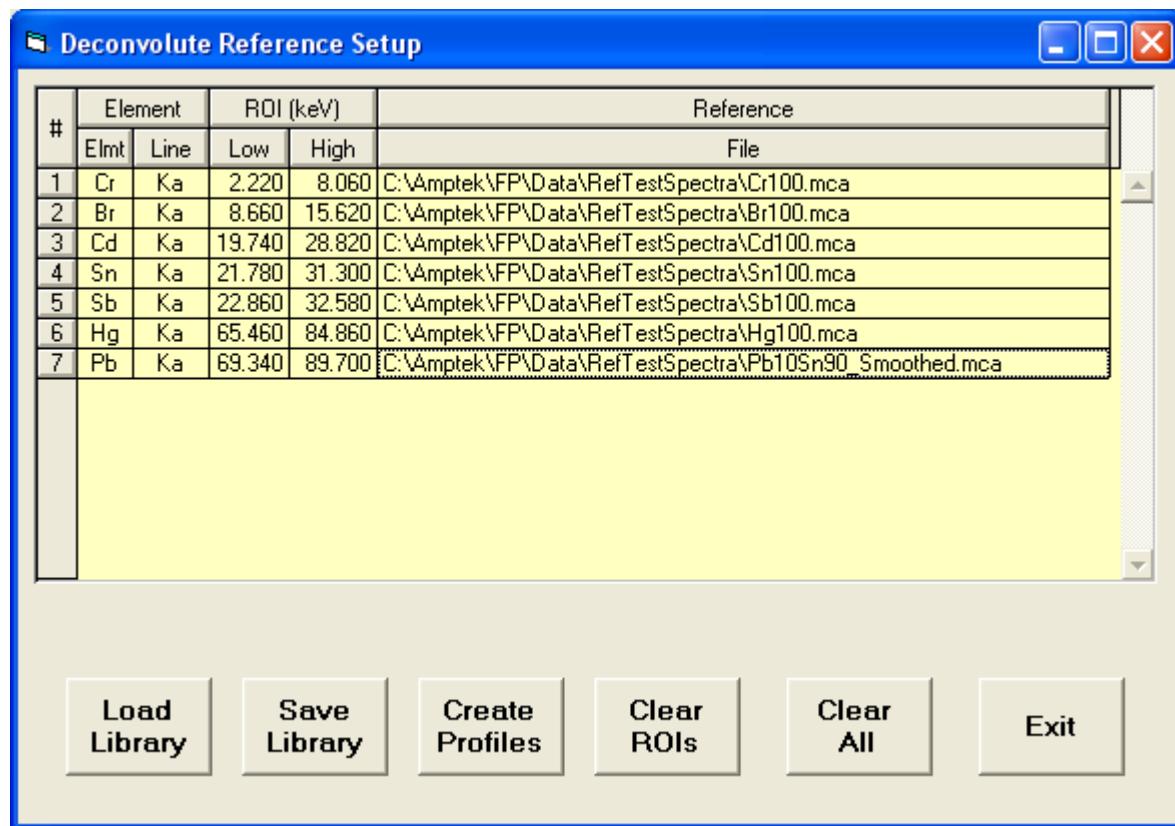


The list of elements and lines will correspond to those defined in the TFR file, with Reference selected as the Intensity method. So make sure to set these up correctly before starting the Reference Profile creation. Double-Click on each Reference File text box to load the appropriate spectrum file. After doing

this for each element, then click on the Create Profiles button to load each spectrum in turn, process the spectrum using the setup in the TFR file, and then “extract” a region of the spectrum (the “Deconvolution ROI”) that will be used in the later multi-element deconvolution of standards and unknown samples. This region is displayed in the foreground color/group, and the complete processed spectrum is shown in the compare group.

Note that the ROI is based upon the current value of the Mn FWHM of the detector, and is extended to about 3 times the FWHM below the lowest x-ray line in the series, and about 2 times the highest line. The reason that it is extended further at the lower energy is that this is typically where most of the tailing exists and this default should cover most of that area in the spectrum. Only when the ROI is clear (both energies set to zero) will the default values be calculated. Once there are ROI values these will not be changed except by the user or after the Clear ROIs button is pressed. If you wish to extend or contract the default ROI for any reason, simply enter your preferred energies and then click on the Create Profiles button again.

After the profiles have been created, then this panel should look like the following:



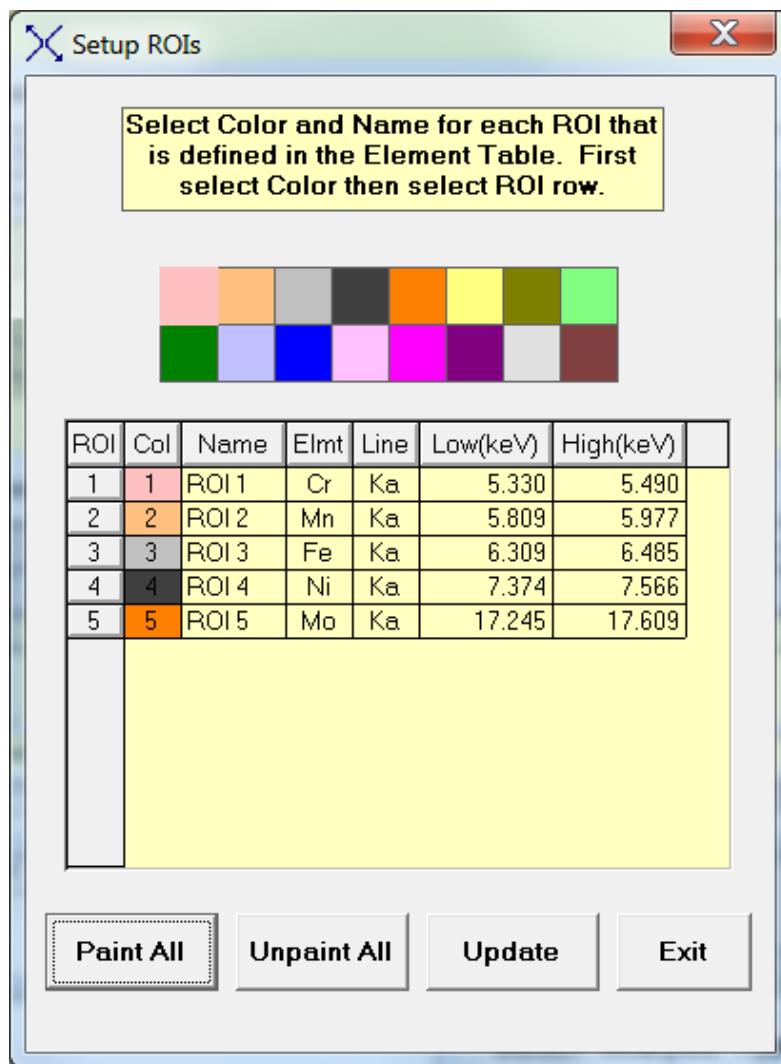
At this point you can save the library as an RFL file by clicking on the Save Library button. You can view this file, like any other file from this software, with a standard text editor such as Notepad or WordPad. You will see that this file just reflects what you see on the screen. The actual profiles are not saved in this

file at all, only the file names so they can be re-created. If you now save the TFR file it will include the name (only) of the current RFL library file, so that when the TFR file is re-loaded the RFL will be automatically invoked to re-create the Reference Profiles in memory for subsequent spectrum processing.

This re-creation must be done each time the TFR file is loaded but once created in memory it will remain until another TFR file (with the Reference method) is loaded or the software is shut down.

## 12.6 Setup ROI

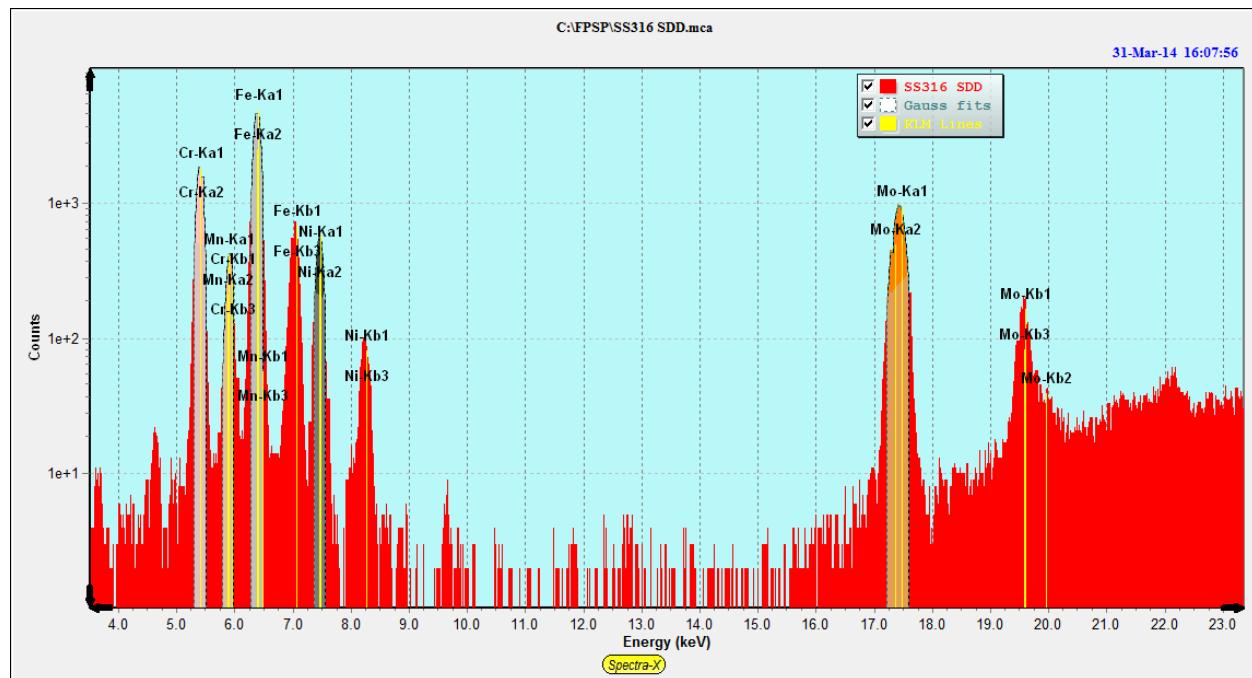
This function allows you to define and paint windows (ROIs) on the current spectrum in the Spectra-X panel. In version 5.6 this was changed from a single ROI to multiple ROIs, with the panel now that looks like the following:



This default list of ROIs is taken from the contents of the currently loaded TFR file. The ROI values are calculated, by default, on the Expert Panel to be 1.2x the calculated FWHM at the line energy of the analyte.

For example, in this table 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 All button to send the ROIs to Spectra-X (v.2.0.0.0 or later) and these ROIs will be displayed in the table in Spectra-X, and then shown on the spectrum, for example as shown below:



You can find out more about the handling of ROIs in the Spectra-X section towards the end of this manual. In the table above, default colors have been assigned to the ROIs, starting with color number 1 in the color chart above the table.

There is no way to save the information in the Setup ROIs panel, but the more informative ROI Table in Spectra-X can be saved using the Spectra-X File menu command.

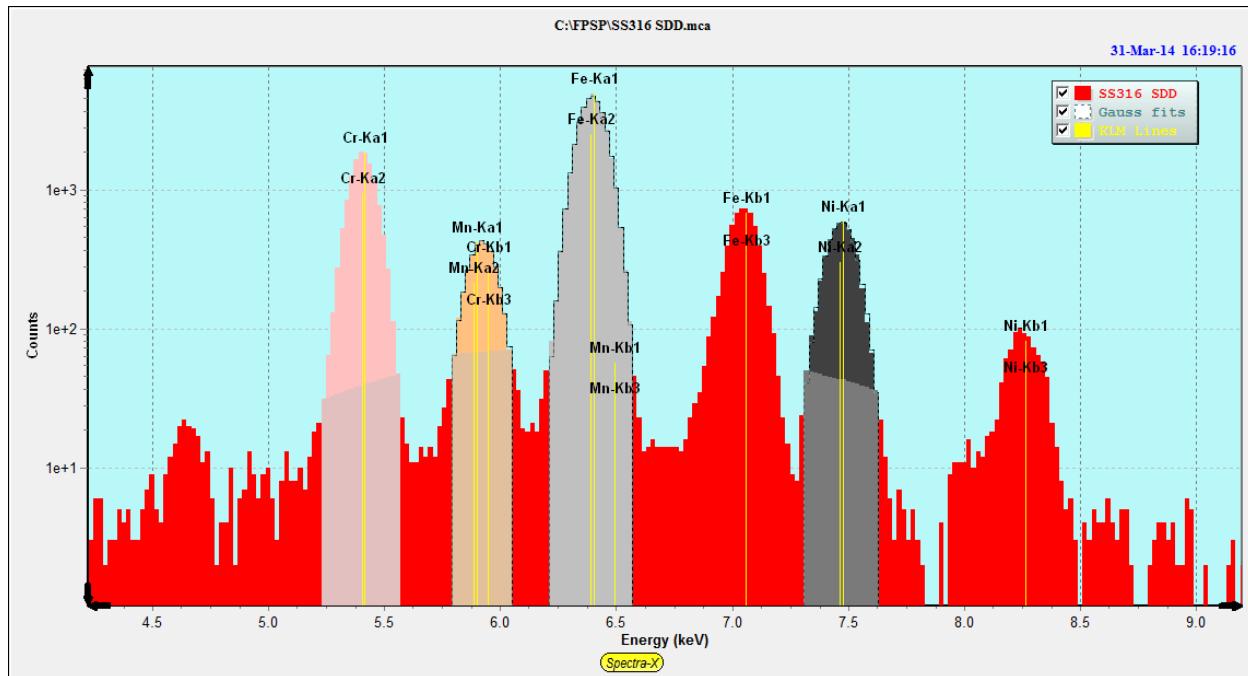
To change the color simply click on the color column in the appropriate ROI row, and then click on one of the colors in the color chart.

The ROI names are also arbitrary and can be changed by the user, as can the ROI widths, of course.

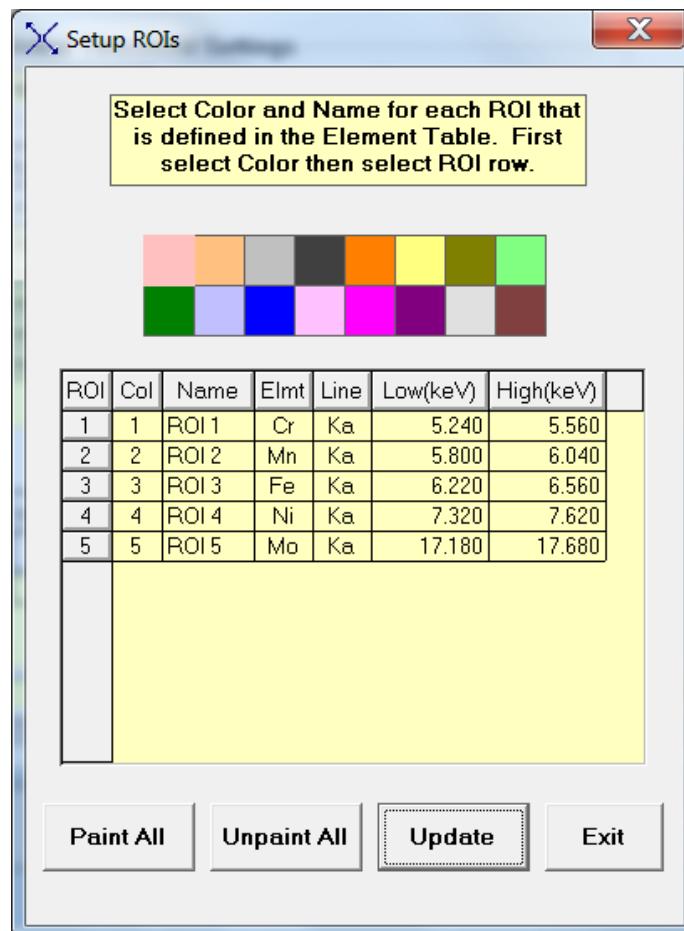
Clicking on the Unpaint All button erases all the painted ROIs in the spectrum in Spectra-X.

The Update button will read the ROI table in Spectra-X and loads the values into both the Setup-ROI panel, and also the Element Table in the Expert Panel.

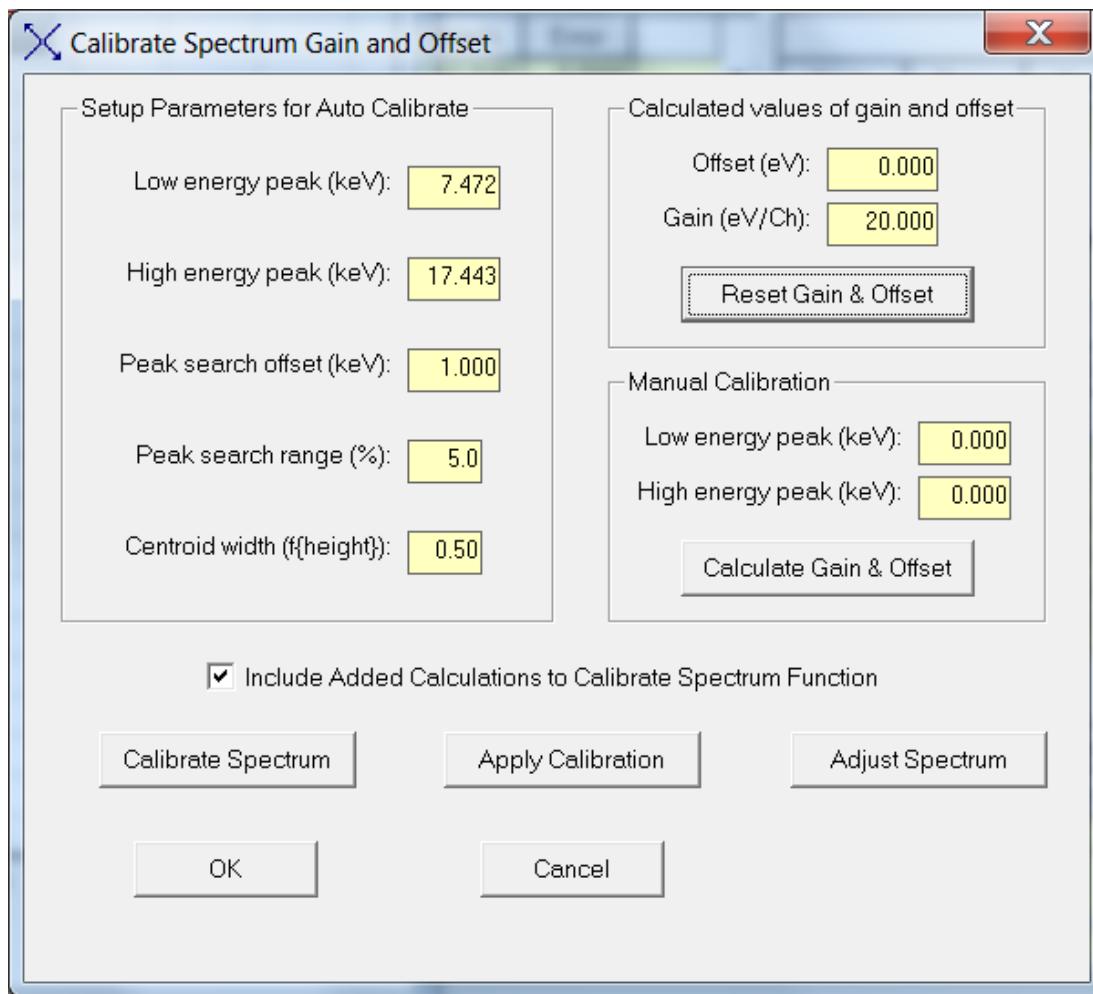
For example, after re-painting the ROIs in Spectra-X, as shown below:



The Update button gets the new ROIs and loads into the Setup-ROI table as shown below:



## 12.7 Setup Spectrum Adjust



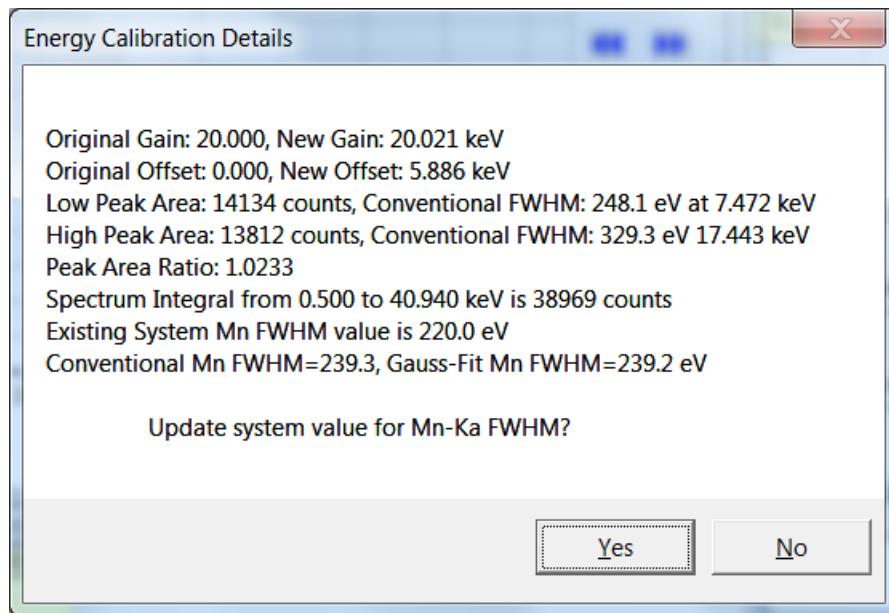
This panel provides functions to calibrate the gain and zero (offset) energy of a given spectrum, and to then “Adjust” subsequent spectra to bring them to a fixed calibration having a zero offset and an integer gain value such as 10, 20 or 40 eV/channel.

Although an XRF spectrometer is typically set to a zero offset value and a gain value that is 10, 20 or 40 eV/channel, in practice there may be small or large deviations from these nominal values.

Note that this procedure is also described in a step-by-step guide in Section 5.1, and also there are separate detailed tutorials available if you have a supported hardware platform.

In the XRS-FP software version 5.9.10, a new option was introduced, a check box that allows additional calculations to be made during the Calibrate-Spectrum action, and more information to be made available.

If selected then a message pops up after the Calibrate button is pressed, such as the one shown in the following example:



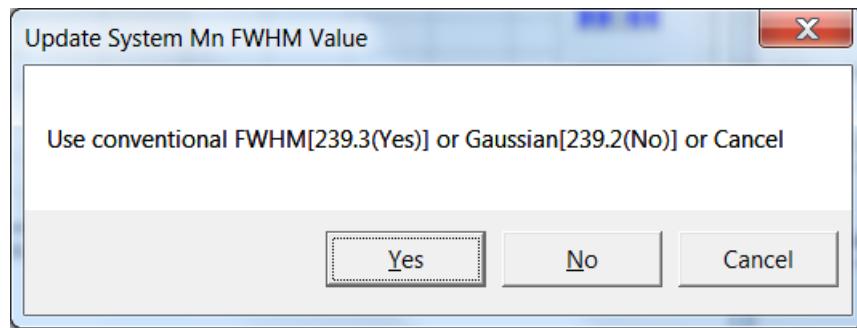
As noted in this example message, the existing and calculated values of the software gain and offset parameters are displayed in keV. Also, each peak is integrated both by simple channel-by-channel integration over an ROI that is twice the calculated peak FWHM at each energy, and by a single Gaussian peak fit.

Prior to these calculations (including the basic Calibrate action), the spectrum background is removed temporarily to avoid incorrect calculations of the FWHM values, and possibly even the centroid calculations, which can be affected by a sloping background (i.e., one that is not horizontal).

The FWHM is also calculated for each peak using the simple peak “walk” method that finds the fractional channels just at or below the FWHM height of the centroid channel. In addition, each Gaussian fit is also integrated over the same ROIs, and the FWHM calculated, but these details are not shown in the message, except for the Gaussian FWHM of the peak nearest to the Mn-Ka line energy.

Note that a single Gaussian fitted to a “peak” at higher energies is really being fit to at least 2 lines, which may be substantially separated in energy causing an incorrect value to be calculated for the FWHM. Conversely, in the Gaussian deconvolution function the Mn FWHM is used to calculate the FWHM of each line associated with the analyzed element, which can be several lines for each series selected.

You now have the option to update the so-called system (Mn) FWHM, which is calculated from the measured values by the two methods described above. If you select “Yes” to this option, then a second dialog is presented:



You can choose “Yes” to update the Mn system FWHM with a FWHM calculated from the conventional (peak-walk) method, or from the Gaussian peak-fit method, or leave the existing values as is. You can later check in the Setup-Processing or Setup-Detector panels for the current value of the Mn FWHM.

In addition, the ratio of the peaks is calculated (ideally, this should be close to 1, as shown in the above example), and the integral of the spectrum from 0.5 keV up to the maximum channel in the spectrum. These values are useful in judging the quality of the spectrum for calculating both the energy calibration factors and the FWHMs.

For the energy calibration, the assumption is made that the peak centroid positions can be described by a simple 2-parameter linear equation of the form:

$$\text{Energy} = \text{Gain} * \text{Channel} + \text{Offset}$$

and that any deviation from the nominal values will still result in a set of peak centroids that still fit this equation, where the gain is slightly different from the nominal value (e.g., 19.95 instead of 20.00), and that the offset is a non-zero value.

When this panel is first loaded, the screen parameters are obtained from the XRS-FP.ini file, if this file is present in the \Windows directory.

The main part of this panel is grouped into three distinct sections:

- (a) The 5 text boxes on the left-hand side, in the Setup Parameters for Auto Calibrate frame, contain the parameters to be used for spectrum calibration.
- (b) The 2 text boxes in the top right-hand corner describe the current values for the spectrometer offset and gain.
- (c) The Manual Calibration frame that can be used for calculating the starting values of the spectrometer offset and gain, if necessary.

The Setup Parameters for Auto Calibrate section provides the input parameters for the Spectrum Calibration, and the Calibrate Spectrum button activates the algorithm for calculating the effective offset and gain of the spectrometer. The method requires a spectrum that has two well-defined and unambiguous peaks that are well separated (at least 5, but preferably at least 10 keV apart). These two

peaks will have well-defined centroid values (in keV) and will be approximately Gaussian in shape. An example might be a binary mixture of Zr and Ti. A spectrum should be acquired for this sample such that the two peaks have comparable amplitudes, and reasonably good statistics (i.e., the typical acquire time would be at least 50 seconds). These two peaks should, ideally, be the ones in the spectrum with the highest amplitudes. The user should specify the centroid energy of these two peaks, e.g., 4.508 keV for Ti-Ka (i.e., weighted mean of the Ka1 and Ka2 peaks) and 15.746 keV for the Zr-Ka (weighted mean) peak centroid.

When the Calibrate Spectrum button is pressed the software will first find the nearest peak maximum to the specified centroid energies, and then calculate the peak centroids for these two peaks. The peak search extends over a range governed by two parameters. The first is the Peak Search Offset (keV), and the second is the Peak Search Range (%). The Offset is a fixed deviation above and below the input peak centroid value.

For example, for a value of 0.8 keV, the peak search for the Ti-Ka peak would extend from 3.708 through 5.308 keV. The Peak Search Range refers to a percentage of the peak centroid energy. Therefore, if the search range were 5.0%, then for a peak nominally at an energy of 20.0 keV, the search would extend from 19.0 through 21.0 keV. The larger of the two deviations is used in each peak search. Using the above examples, the absolute deviation value (0.8 at 4.508 keV) would be used for the lower-energy peak, and the percent range (1.0 at 20.0 keV) would be used for the higher-energy peak.

To calculate the centroids, a region of the peak is used, which is distributed evenly about the peak maximum channel. This region is set by the Centroid Width parameter, which is expressed in terms of a fraction of the peak channel height. In other words, for a width value of 0.5 the centroid calculation is made within and including channels that are equal or greater than 0.5 times the peak channel height. In this particular example, this is equivalent to the FWHM region.

The result of the Calibrate Spectrum operation is that new values of offset and gain are calculated. These new values are displayed in the top right-hand corner text boxes. If the spectrometer is too far from the required calibration (e.g., if the electronics cannot be further adjusted) then it may be necessary to perform a manual calibration. To do this, first ensure you have an unadjusted (raw) spectrum, then click first on the “Reset Gain & Offset” button to reset the values to their target ones (e.g., an Offset of 0 eV, and a Gain of 20 eV/channel). Next, use the cursor in the Spectra-X window to identify the centroid channels for the two peaks of interest, and then enter their displayed energy values in the Low and High energy peak text boxes in the Manual Calibration frame. Now click on the “Calculate Gain & Offset” button again to get approximate values for the Gain and Offset. Now click on the Calibrate Spectrum button and the automatic algorithm should refine these initial estimates of Gain and Offset.

Now at this point there are two ways to proceed. In the first method (not recommended), using the Apply Calibration button, the spectrum offset and gain values are simply changed in Spectra-X to change the actual energy scale on the horizontal axis. This operation will then display the peaks at their correct

energies, but the energy scale will not be in the required integer form, such as 10, 20 or 40 eV/channel, etc. Because of this, the second method (Adjust Spectrum) is preferred (see below).

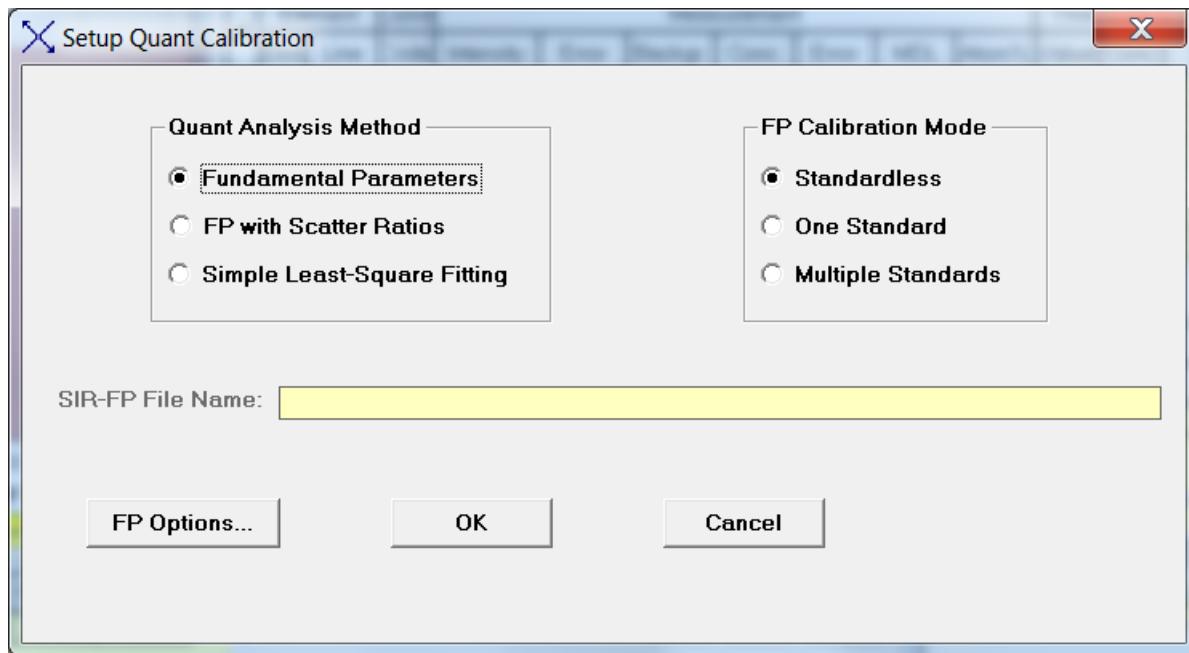
Since the spectrum processing algorithms require that the spectra must be obtained with a zero offset and integer gain value (10, 20 or 40 eV/channel), the spectra must actually be altered to make them "appear" as if it was collected with the expected values. This is accomplished by the Adjust Spectrum button and an internal software function. The new effective values of the spectrometer Offset and Gain must be retained for application to all future spectra, assuming they are all collected under similar conditions that do not cause any significant peak shifts (i.e., dead times and/or count rates are similar). This is accomplished when you exit this panel with the OK button. These two values are then saved in the XRS-FP.ini file and automatically loaded each time the software is loaded.

Once the spectrometer has been calibrated this way, you can simply perform the Adjust Spectrum step to bring the spectrum peaks into the expected positions. This is the preferred method in the XRS-FP software usage.

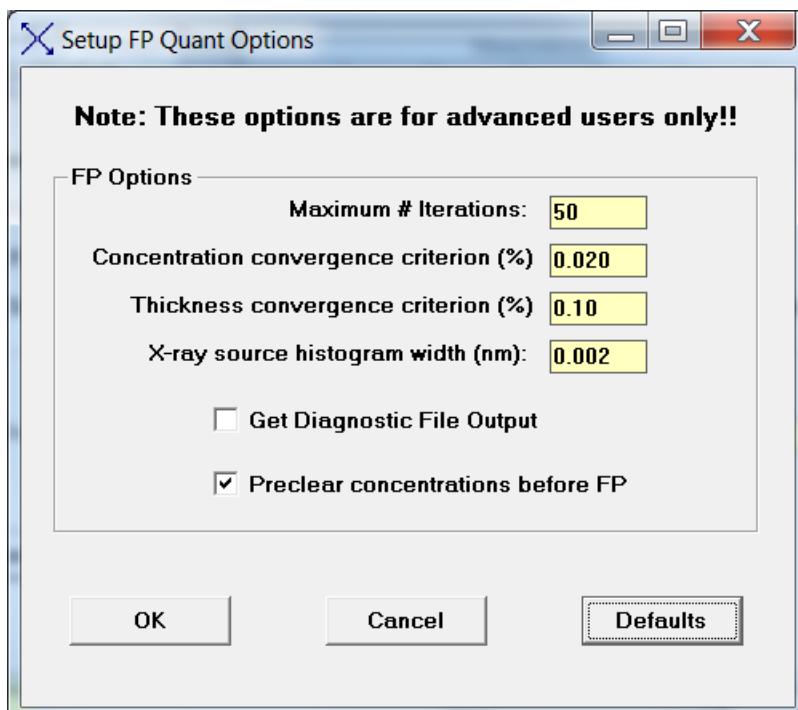
At the end of any operations in this panel, the OK button (if enabled) will save the new values of Gain and Offset in the XRS-FP.ini file, located in the XRS-FP software directory. Pressing the Cancel button will invalidate any changes, reverting to the status before this panel was invoked. Note that Gain and Offset values can also be entered manually in their respective text boxes.

After exiting this panel be sure to check one of two check boxes, in order to use the Adjust function as a routine automated method. In the first method you can check the "Auto Adjust Spectrum Gain & Offset on Load" option in the Setup-Processing panel. This will then enable any future spectrum files to be automatically adjusted when loaded with the appropriate gain and offset values. Alternatively, you can use the Auto Adjust Spectrum during Acquire button option in the Setup-MCA panel. If you have a live system, then this option will affect spectra as they are being acquired, and the spectra will be auto-adjusted so that the peaks are immediately shown in their correct locations.

## 12.8 Setup Quant



This panel includes quantitation methods other than FP analysis. Check the FP radio button as shown to select the standard FP analysis, and the Scatter Ratios option to use the SIR-FP method. The last Quant option is for a simple least-squares calibration using standards and analysis, where it is not necessary to analyze the complete sample, and inter-element effects are ignored. A new button has been introduced in v.5.9.3 of the XRS-FP software titled FP Options. This button to bring up the following panel:



As noted in the heading of the FP Options panel, these parameters are for advanced users and applications only. If in doubt use the default settings. The parameters setup in this panel are also saved in the XRS-FP.ini file in the [Processing] section:

```
; Set=1 to output FP Diagnostics file FPiters.txt. Default=False(0).
FPDiagnostics=0

; Maximum number of iterations for FP calculations. Default=50.
FPIterations=50

; Convergence criterion for all calculated concentrations using FP. Default=0.02%
FPConcConverge=0.020

; Convergence criterion for all calculated thicknesses using FP. Default=0.1%
FPThickConverge=0.10

; Histogram bin width for calculated x-ray source spectrum used for FP analysis. Default=0.002 nm.
FPDeltaLambda=0.002

; Flag to pre-clear concentrations prior to FP Quant. Default=1.
FPPreClear=1
```

The FPDiagnostics flag was always there in the INI file, but was not accessible through the XRS-FP GUI. If set 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.

The convergence criteria control when the software determines that convergence has been achieved – i.e., the results for each element (and/or layer thickness) are not changing by more than each criterion from one iteration to the next. The FPIterations parameter sets the limit on the maximum number of iterations during each FP quantitation. If convergence had not been reached then the soft error “Results Not Converged” will be returned by the FP library function.

The FPDeltaLambda 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 FPPreClear 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 set the PreClear option to 1, which was the previous default.

Note that there are now 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.

There are three different options in the right panel for FP. If the model is set to Standardless, then no standard calibration is required. However, the software must be setup accurately (see other setup panels), 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. However, in the later software there is also another option for multiple-standard calibration. This is an option in the software and may not be part of your configuration. The differences in these two methods will be briefly described.

In the original multiple-standard model, you could provide any number of standards, BUT only the last one for each element would be used. Typically this method was for use with a single standard (usually a pure element) for each element to be calibrated. Since there are no standards with the same element there is not a conflict for which coefficient to use. In the case where several standards have the same element, then only the last one in the sequence would be used. This may not be the intended choice when several multi-element standards are used together.

In the newer 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 Calibration section. For this method you should collect spectra of each standard and process each one, creating and saving a TFR file, as if it was a single-standard FP calibration.

The original multi-standard is described in some detail in the section 5.2 on a generalized calibration scheme. After setting the multiple-standard model in this Setup-FP panel, proceed to calibrate each standard in turn (with only the elements in the standard), and then run a typical unknown sample, making sure to define all elements of interest in this sample, which must correspond to all the elements that have been calibrated with the standards. At this point, as soon as the actual sample analysis is performed, the standards information is merged together resulting in a single set of calibration coefficients for the analysis.

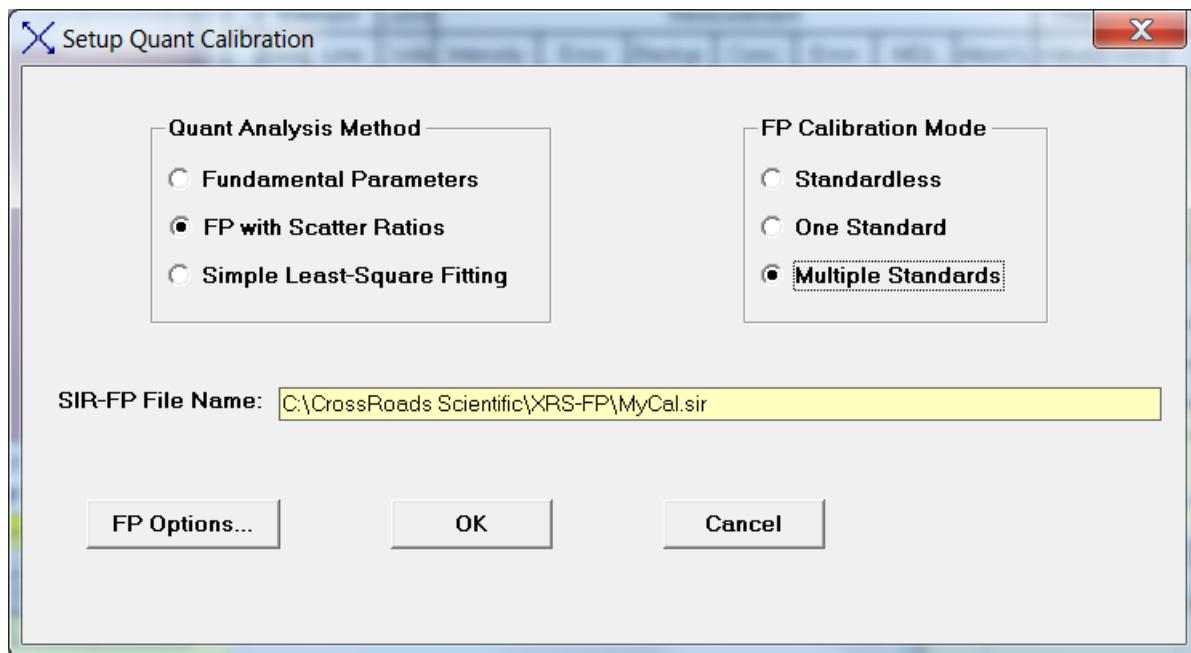
You can now optionally save this analysis report, complete with the merged calibration coefficients, as a "secondary" standard. In other words, future analyses can then be done with a "single" standard, where

the report file (\*.tfr) for this calibration is loaded (with its calibration coefficients), and the system is then immediately ready for subsequent analysis of unknown samples with this calibration.

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.

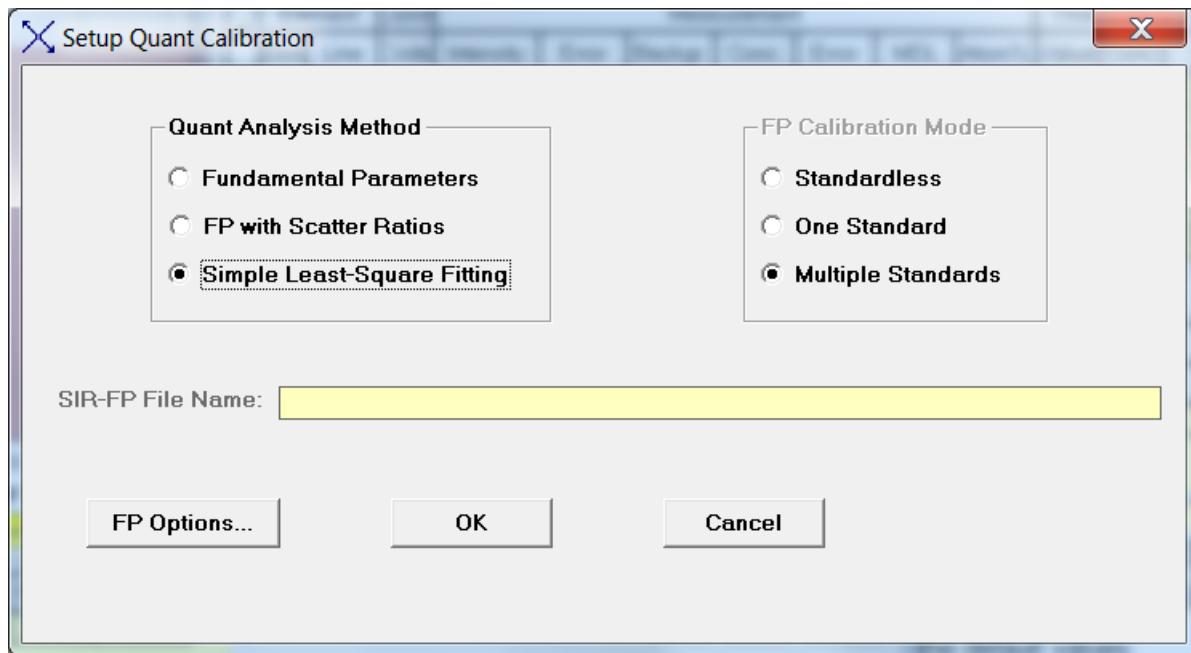
Note that this method should not be used in conjunction with the Peak-to-Compton method as these two would then be in conflict. This method is described further in the Process-Analyze and Calibration-SIRFP sections.

To select the SIR file (\*.sir) just double click on the SIR file name entry box and this will bring up a dialog to browse for a suitable file. After selecting such a file, then the Setup-FP dialog should look like the following example:



The last option under the Method frame is the Simple Least-Squares Fitting model. When this is selected, the Multiple Standards radio button is also selected automatically.

See later in this document for a description on applying (Calibrating) both the MLSQ (FP) and the LSQ models. This is done with the Calibrate-MLSQ menu item in each case, so it is important that the appropriate Quant model is chosen first by using Setup-Quant.

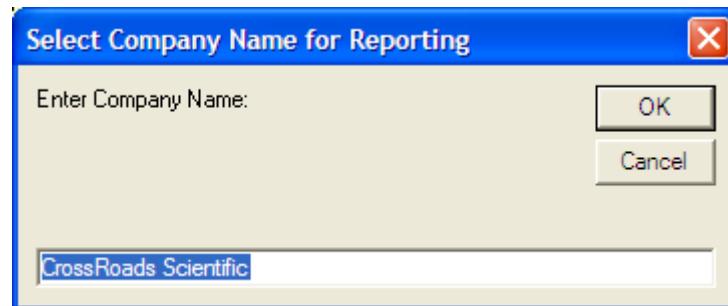
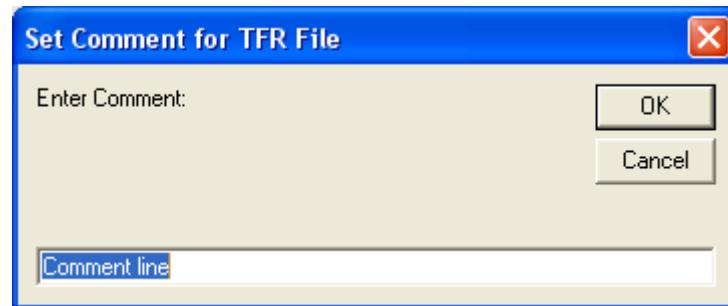


Further information about these quantitation methods can be found in the Process-Analyze section

## 12.9 Setup Reports

This is a simple 2 step process that allows the user to input both a Comment and a Company Name that will get used when the TFR reports are printed instead of the default names.

The following show the 2 screens with the default values:



## 13 CALIBRATE MENU

### 13.1 Calibrate Spectrum

This command loads the same dialog as the Setup Spectrum Adjust command, which was described in an earlier section.

### 13.2 Calibrate FP

After setting the appropriate FP mode (see above), this command “calibrates” each currently loaded report as a standard. This command cannot be used in the standardless mode of FP. For a single-standard calibration, this command takes the entered standard information, and the intensities derived from the current spectrum, and calculates the calibration coefficients for each element. These coefficients may be thought of as sensitivity factors, since all the inter-element corrections have been made, and these values should be the same whether the standard is a pure element or a multi-element standard.

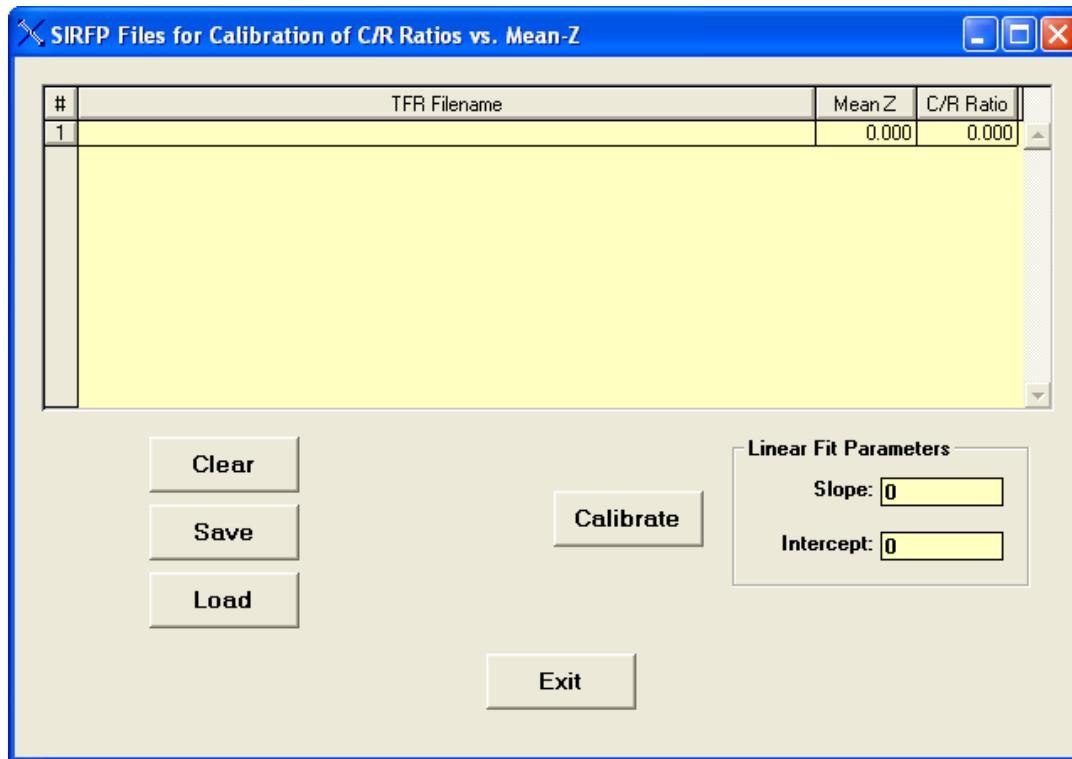
Of course, in practice there will be some variations from standard to standard, and from element to element, because the FP method does not always completely model the sample perfectly. Also, other errors, such as those from spectrum processing, may also contribute to uncertainties in the calculated coefficients. The calibration coefficients are displayed in the rightmost column of the Element Table section.

For the simple multiple-standard calibration, see the Setup-Quant section 12.9 above, and section 5.2 in the FP Calibration section of the manual. A more complex and newer version of multiple-standard FP calibration is described below in section 15.4.

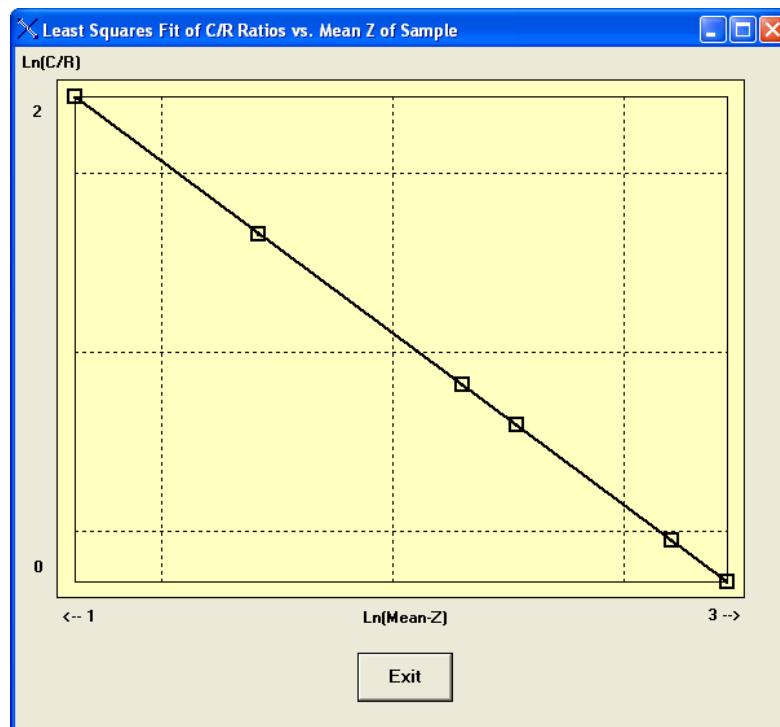
Note that there are now several tutorials available for calibrating and using the FP, MLSQ and SIR-FP methods. These contain example files and step-by-step instructions to performing calibrations.

### 13.3 Calibrate SIR-FP

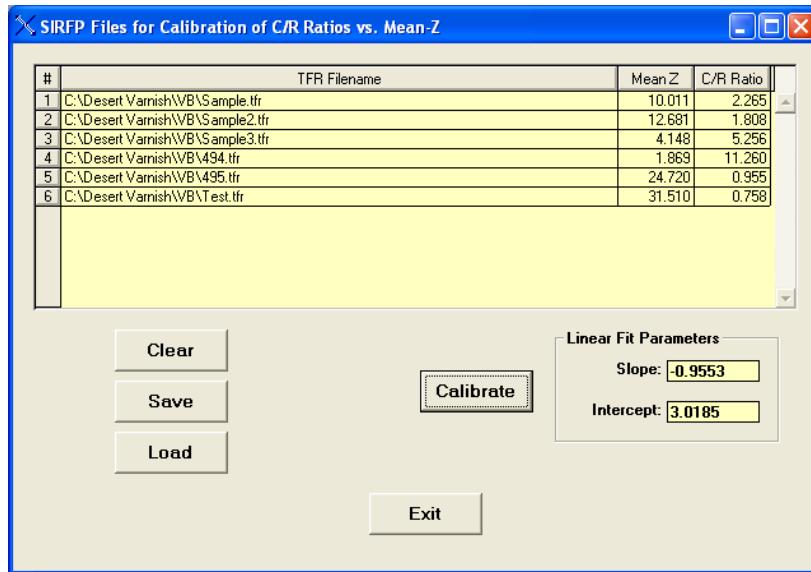
This option allows one to select a series of TFR files that have been created for low-Z (atomic number) standards. Each low-Z standard must previously have been created and processed with a matching spectrum, and the related Compton/Rayleigh scatter-peak information extracted (see the tutorial for more information). Then, once these standard files have been selected, the Calibrate button on the following panel calculates a least-squares fit of the C/R (Compton-to-Rayleigh) ratios as a function of the mean Z of the material. This is then plotted with the mean-Z on the ordinate (Y-axis) and the C/R ratio on the abscissa (X-axis). Initially, when first loaded, the panel will look like the following:



To select individual TFR files, double click on the TFR filename cell for each row. Additional standards (rows) may be added by using the down-arrow key. After each TFR file is loaded, the mean-Z and C/R ratio for that standard is displayed in appropriate columns. A previously created SIR calibration file can also be loaded instead of loading each TFR file in turn. After selecting several files, click on the Calibrate button to do the least-squares fitting of the two variables. You should have a plot like the following:



Each of the variables is actually converted to a log function so that the scope can cover a wider range in detail. It was also found that log-log plots produced better linear fits than the straight linear fitting. When you exit from the plot you will be left with the calibration parameters, such as:



The calibration can now be saved with the Save button. More details about the SIR-FP method can be found in the Process-Analyze section and the SIR-FP tutorial.

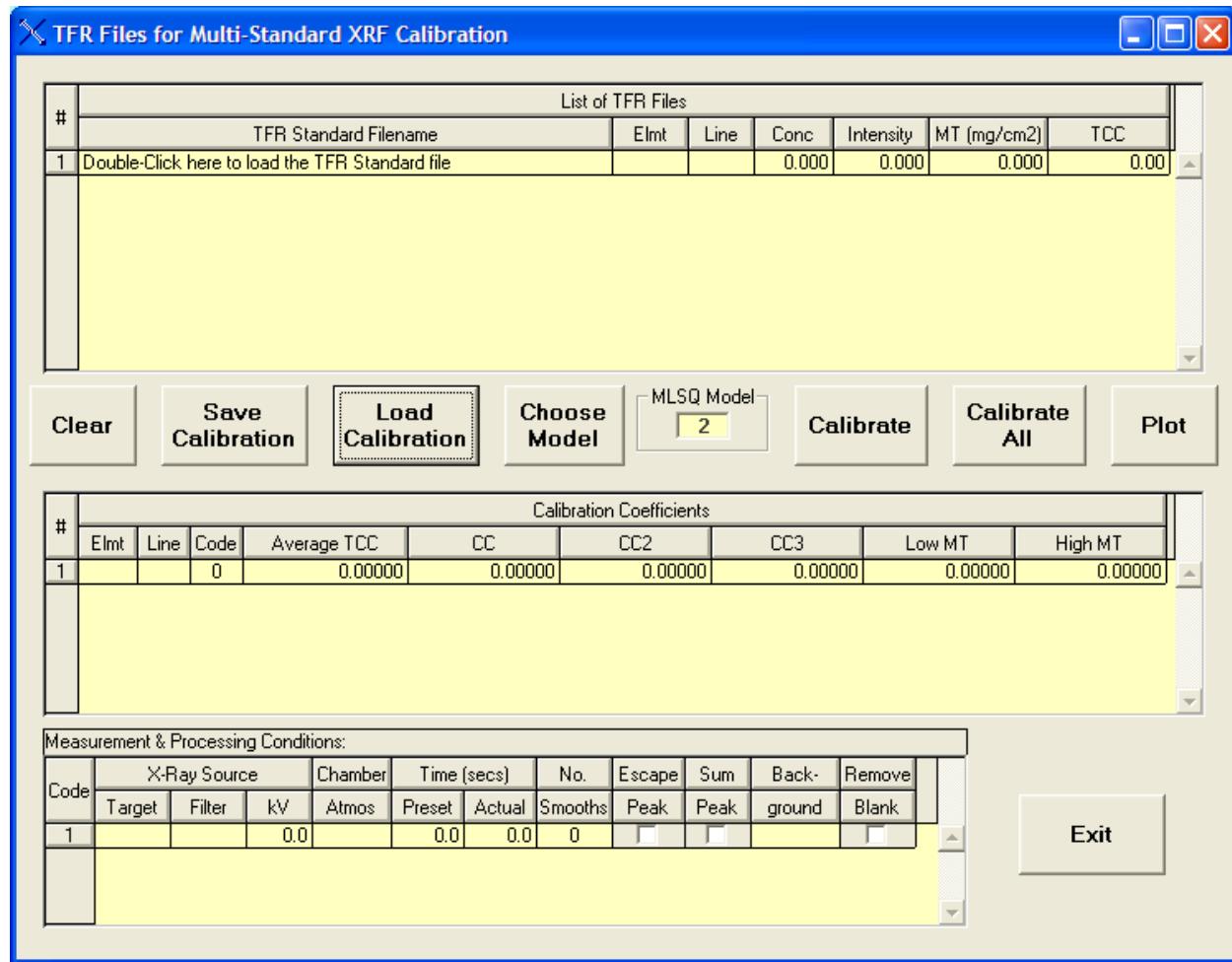
### 13.4 Calibrate MLSQ

This option in the software is only available with a HASP security plug that has been programmed with this option. There are two ways to use the (M)LSQ option – the first uses the FP method, and the second uses a simple Least-Squares fitting procedure of intensities vs. concentrations (LSQ). The appropriate Quant model (i.e. FP or LSQ) *must* have been chosen by using Setup-Quant *before* the Calibrate-MLSQ step can be performed.

As described earlier in the section on Setup-Quant, there are now two basic ways of using multiple standards for FP calibration. The original method typically used just one standard per element and so the calibration coefficient, for any given element, only came from one standard file. In this more complex version, calibration coefficients from ALL standards can be used together, choosing from several different models to allow various least-squares fits.

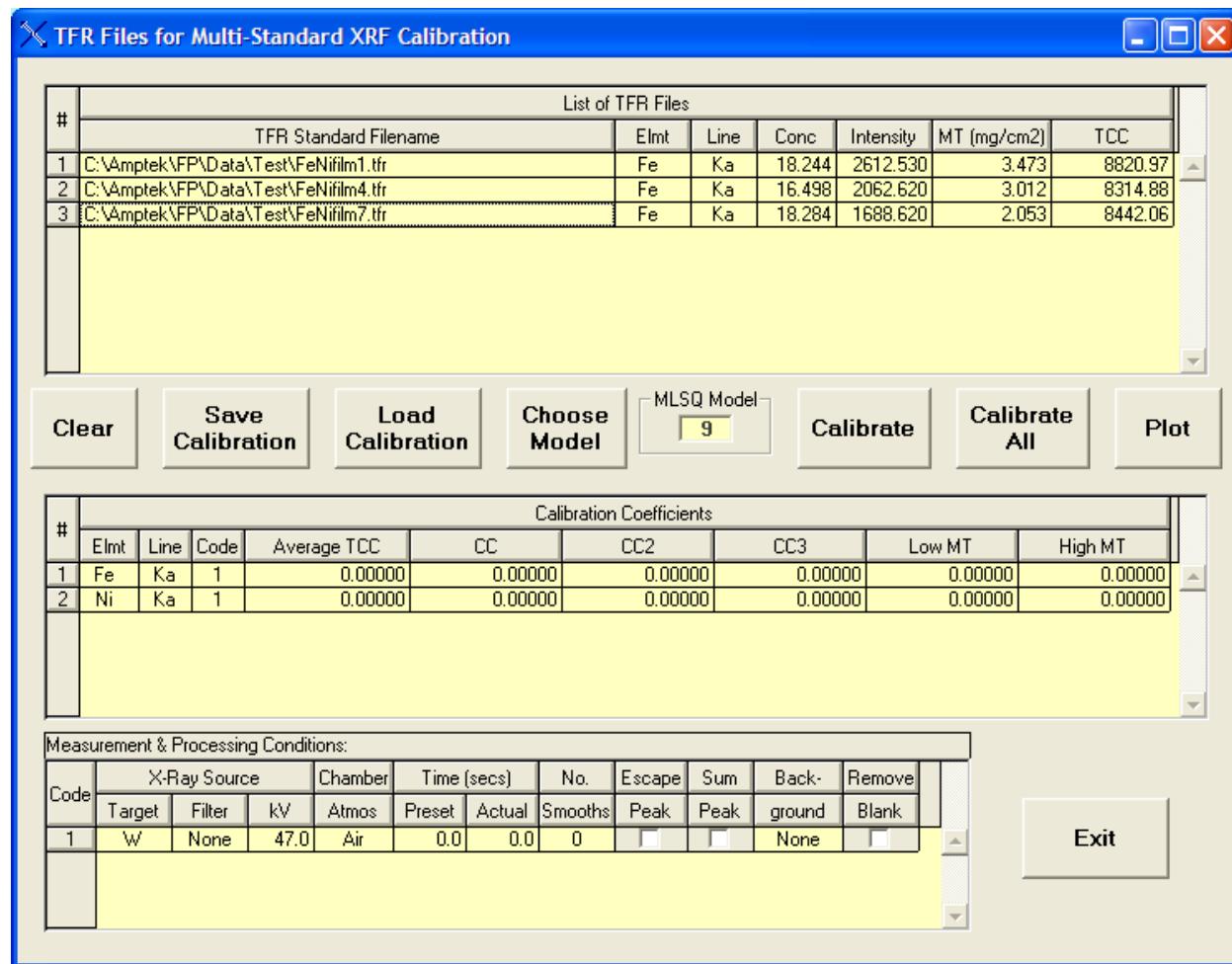
There is now a tutorial on how to setup and use the MLSQ option with the FP method, either with or without the SIR addition option.

Prior to using Calibrate-MLSQ, the user should have prepared a series of single-standard TFR calibration files, described in previous sections. Clicking on this menu item brings up the following panel:

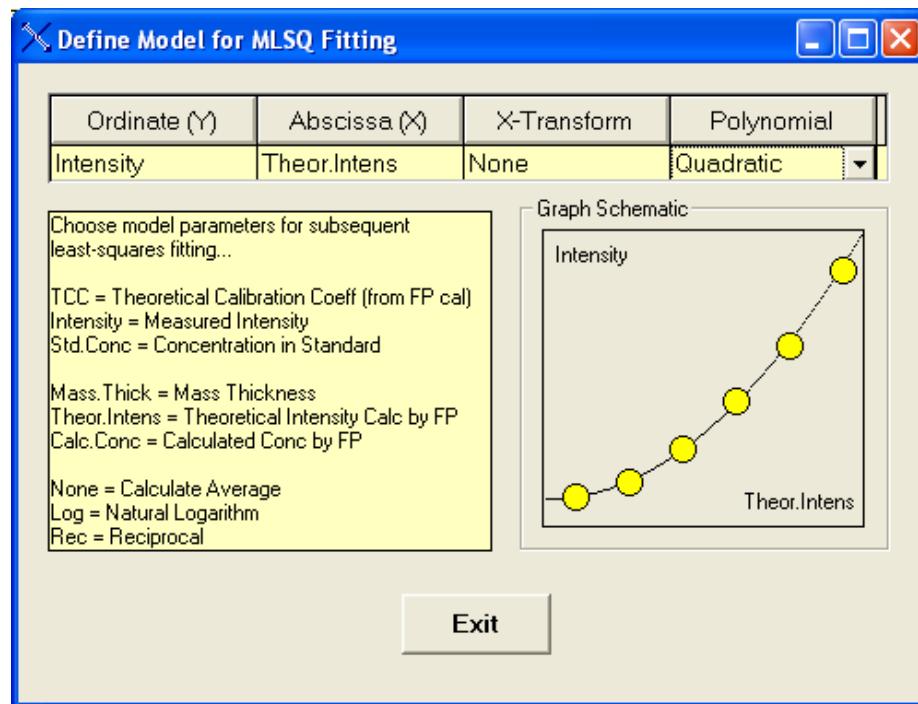


There are several key sections in this panel. The top section contains a table to show a list of TFR files to be selected. The center section will contain a list of merged calibration information, once the Calibrate button has been pressed. The lower section is a copy of the measurement conditions table from the first TFR file – all others MUST have been created using the exactly the same conditions, otherwise a warning message will result during the TFR file load.

To select a TFR file, double click on the row cell under the TFR Standard Filename column heading. This will load a File-Open dialog to allow you to select a file. After selecting 3 example files, this is how the panel could now look:



After selecting all the files of interest for a given application, then Choose the Model for the least-squares fitting. Something like the following panel will now be displayed, and you choose from several different options in each of the columns (in some cases the option is fixed, depending upon the other choices):



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

- (1) This is the simple single-standard FP calibration, which is not considered in this panel,
- (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.,  $\text{Log}(MT)$ , on the X-axis. This is also known as the Linear-Log model.
- (4) This is the same as (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 (3), except that a quadratic fitting equation is used.
- (7) This is the same as (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. Since v.5.0.1 of the XRS-FP software, the fits are now forced through a (0, 0) origin, which now avoids several instabilities observed with non-zero intercepts.

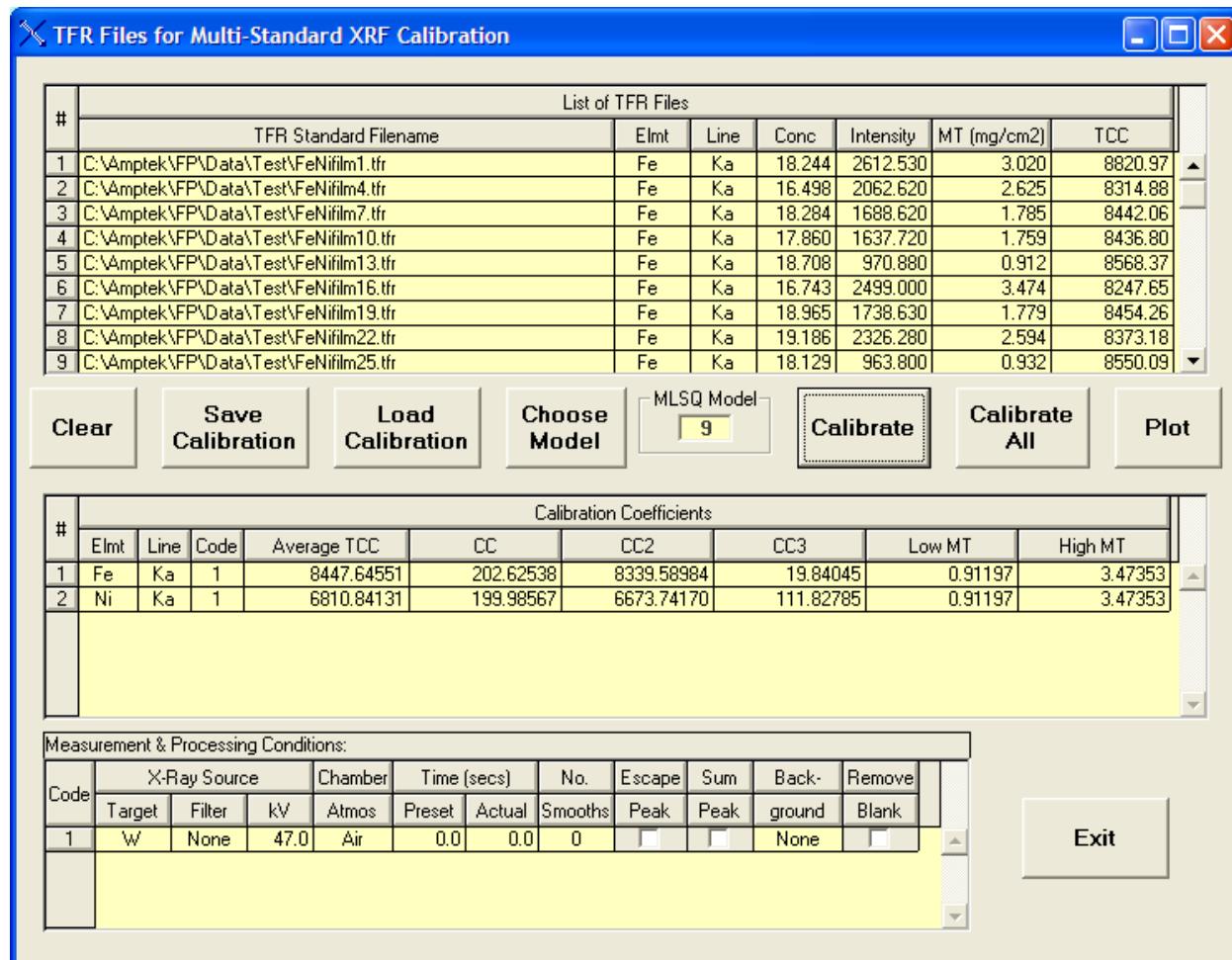
- (10) This is the same as (9) except that the fitting equation is a quadratic. As in (9) the fit is now forced through a (0, 0) origin.

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 (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.

This panel describes some of the options that may be chosen from each column – not all combinations are possible! The standard concentration model regression is not yet implemented. At the bottom right is a schematic diagram of how the final plot might look – it is NOT the actual plot!

Once the model has been chosen, you can then click on the Calibrate button, and the screen will look something like the following:

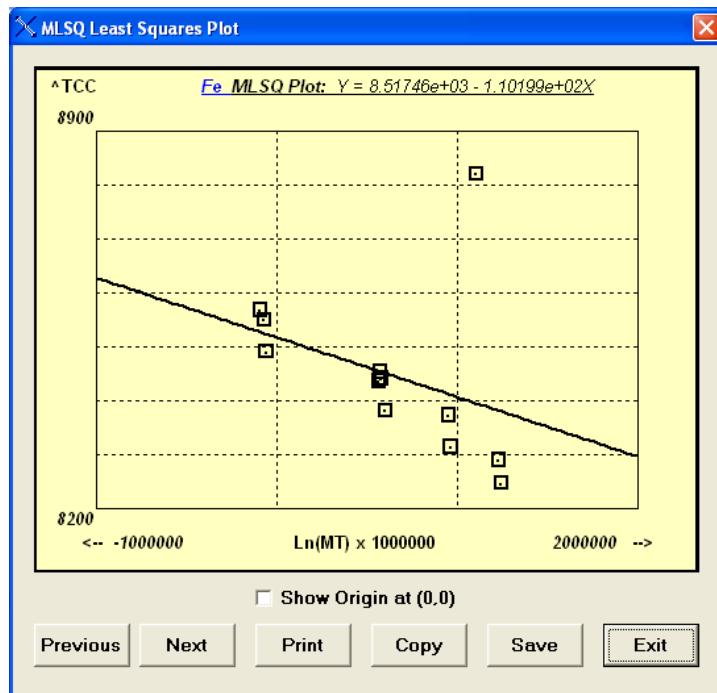


This shows all the initial TFR files in the top section, and the merged calibration coefficients in the middle section. The average TCC value is always shown for reference. The other columns are various secondary coefficients that are calculated from the respective least-squares fitting equation. Also shown are the low and high limits of the mass thickness, which will be used to constrain the later use of these coefficients during quantitative FP analysis.

Note that the Calibrate All button not only calibrates each TFR file (as does the Calibrate button), but also processes a matching spectrum with the same path and name (but different file extension, of course).

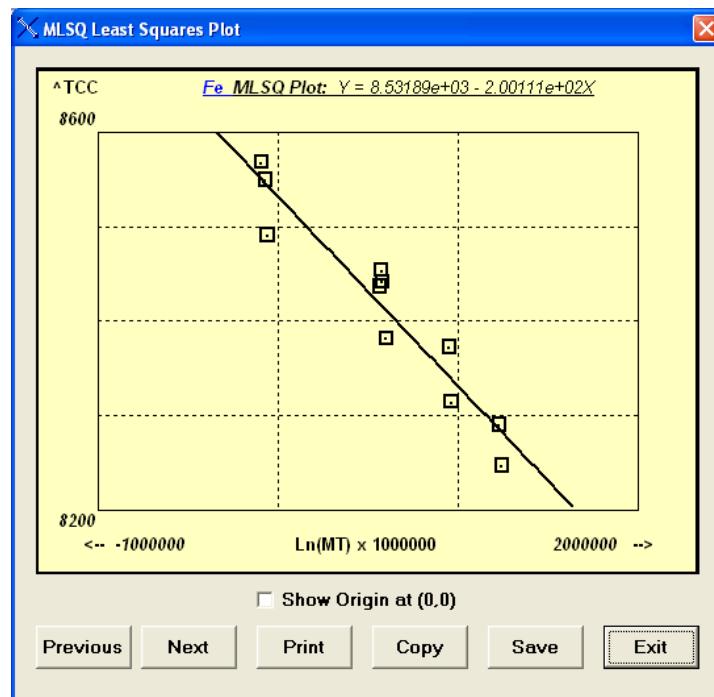
The average value of the TCC is used as the starting point for the analysis, and refinements of this are calculated during the FP quantitation. The latest values of intensities, mass thicknesses and concentrations (depending on the chosen model) are used to update the TCC value at the end of each iteration.

After the calibration you can show the fit by clicking on the Plot button. Depending on the model, you could see something like the following (for model number 2):

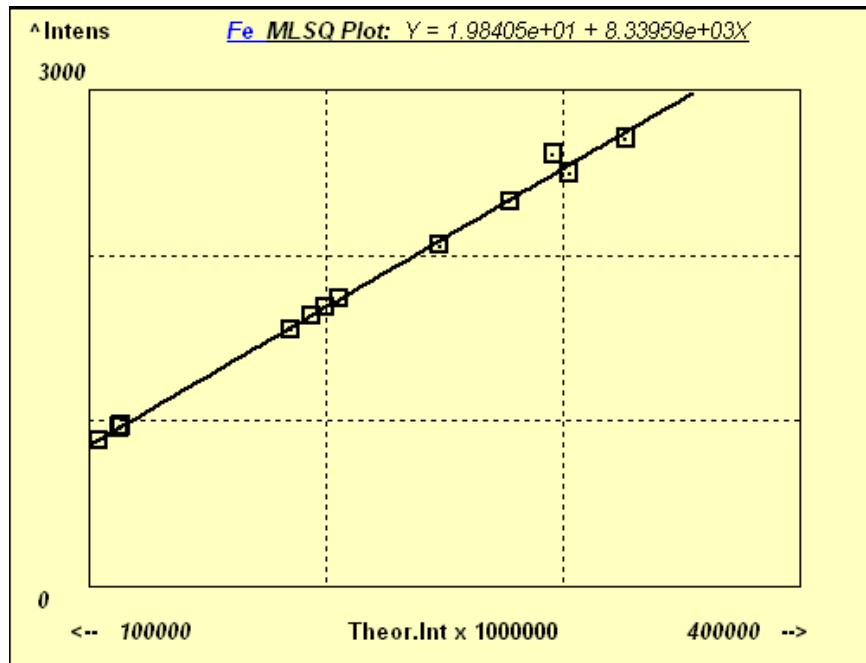


You can step through the plots for each element in turn by clicking on the Previous or Next buttons. You can also Print a copy of the plot to a printer, Copy it to the Windows clipboard (for pasting into other applications), or Save a copy of the plot as a bitmap (\*.bmp) file. The least-squares fitting equation is shown at the top of the screen with the element symbol. This particular plot has one point that is an outlier. By simply deleting the specific TFR standard from the calibration, and then recalibrating, you can see the improvement in the fitting:

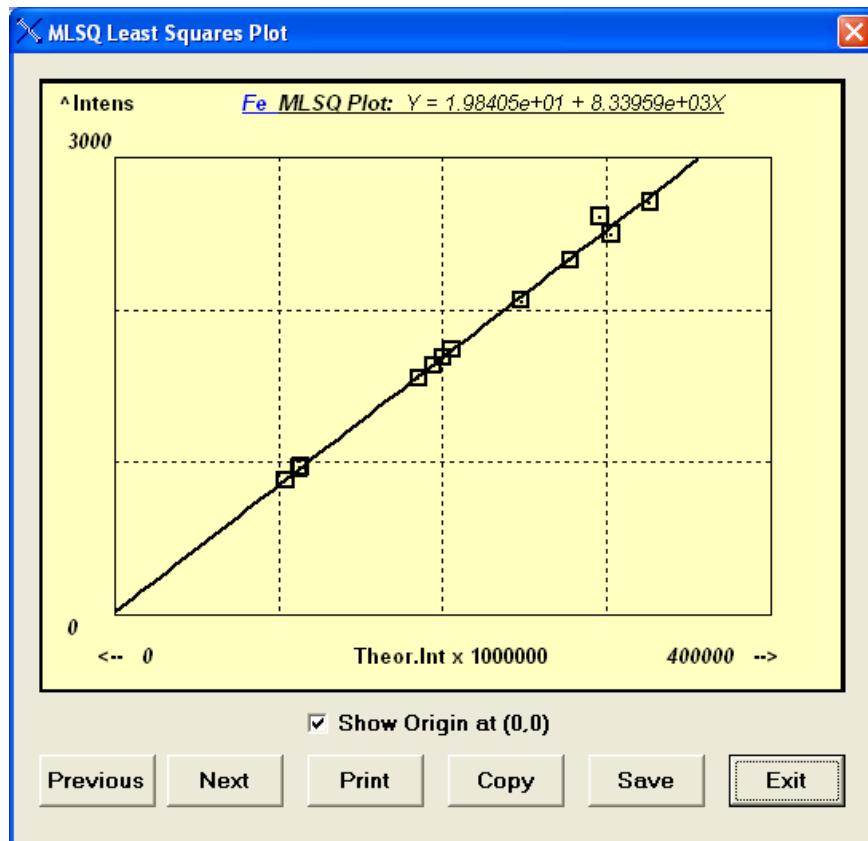
The following plot shows a much more evenly distributed set of points:



The following example uses model number 9, plotting the measured against the theoretical intensities:



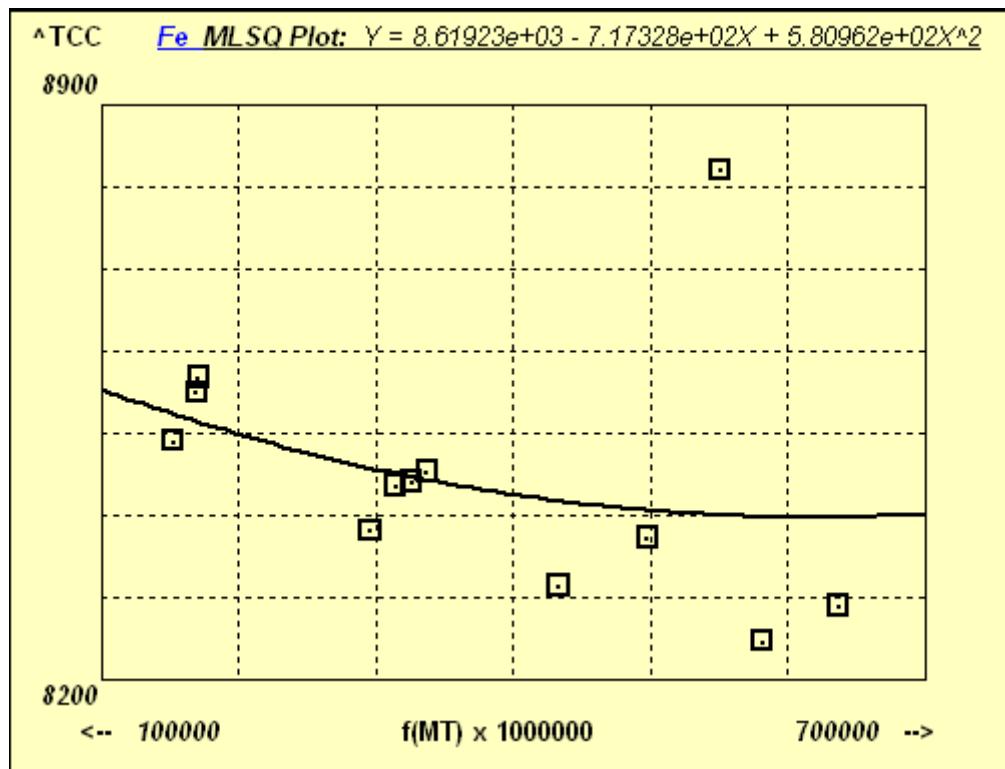
You can also click on the Origin check box to force the inclusion of a (0,0) origin in the plot. Note that this does NOT affect the actual least-squares fitting, just the display:



You can see from this example that this model produces a linear fit that passes very close to the origin.

Once you are satisfied with the model and fitting coefficients, save the Calibration as a least-squares calibration file (\*.lsq). Since this file just contains a list of TFR files to be used for the MLSQ calibration, the calibration itself *must* be re-done each time the \*.lsq calibration file is loaded, as all the secondary coefficient information is not currently saved in the file.

Here is another example of a least-squares fit, to the same set of data, using model number 8, with fits to partial mass thickness values. You can see the same outlier as in an earlier plot, and how this one point can affect the overall quality of the fitting model:



*Important Tips:*

The TFR file that was loaded prior to the MLSQ calibration will have been overwritten during the calibration process itself. This is because this file itself is not necessarily on the list of TFR files for calibration and may not be consistent with those files.

At the end of any MLSQ (FP or LSQ) calibration, the last file in the list will be the one displayed, and the coefficients will be part of this data set. At this time you should save this TFR data set as a new TFR file, with some generic name that describes the overall calibration, not the name of the last standard. Whenever this new TFR file is loaded, all the MLSQ coefficients will be loaded with it, along with the element and processing information as usual.

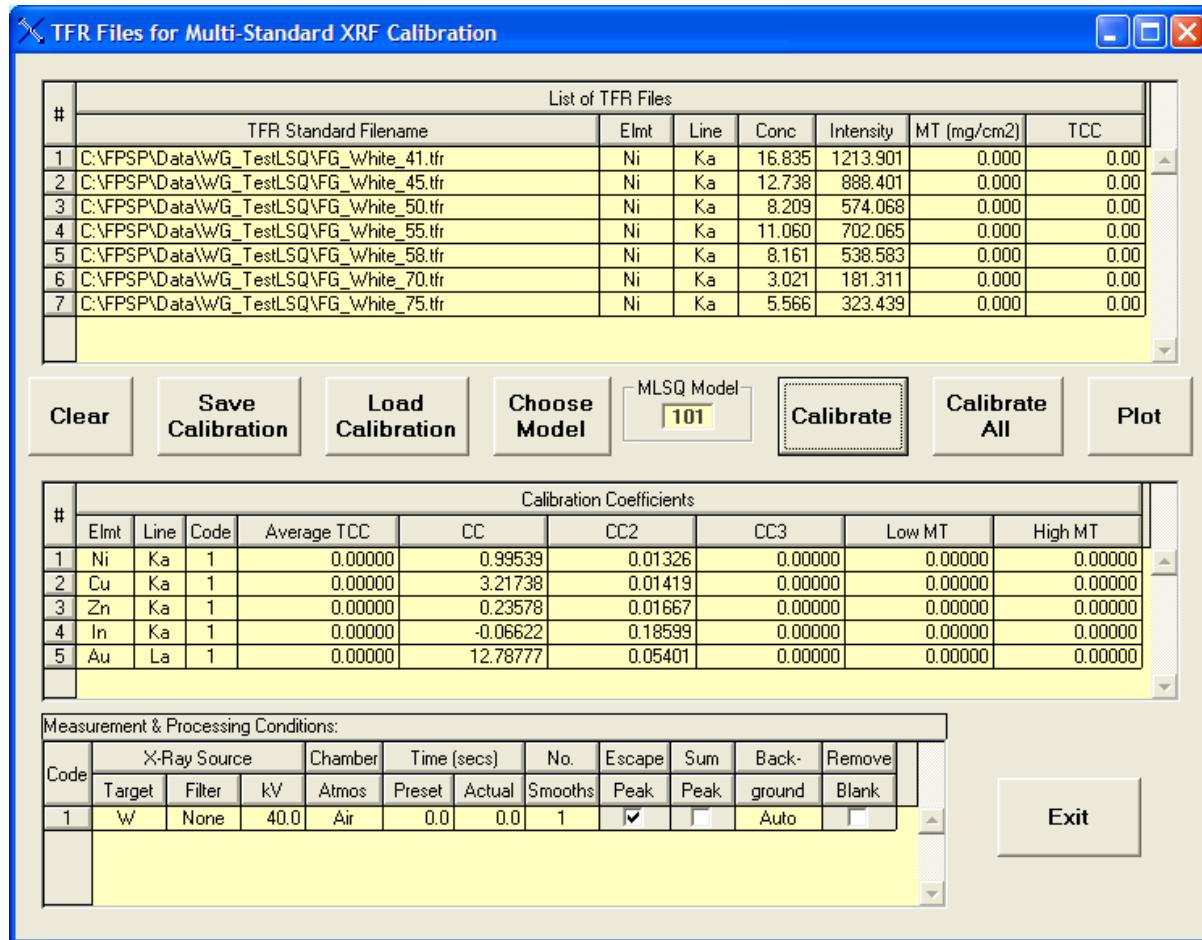
If there is an error during the calibration the original TFR file will then be re-loaded (it is saved as a scratch file SaveTemp.tfr) to return the software to the initial status quo.

The next example shows the application to the simple least-squares method (i.e. no FP matrix correction). For this method, set all the Quant methods to LSQ, and no previous calibration steps are necessary for each standard. The simple least-squares calibration procedure is very similar to the MLSQ one described above for the FP version, except that the individual TFR files are not calibrated – only the intensity and

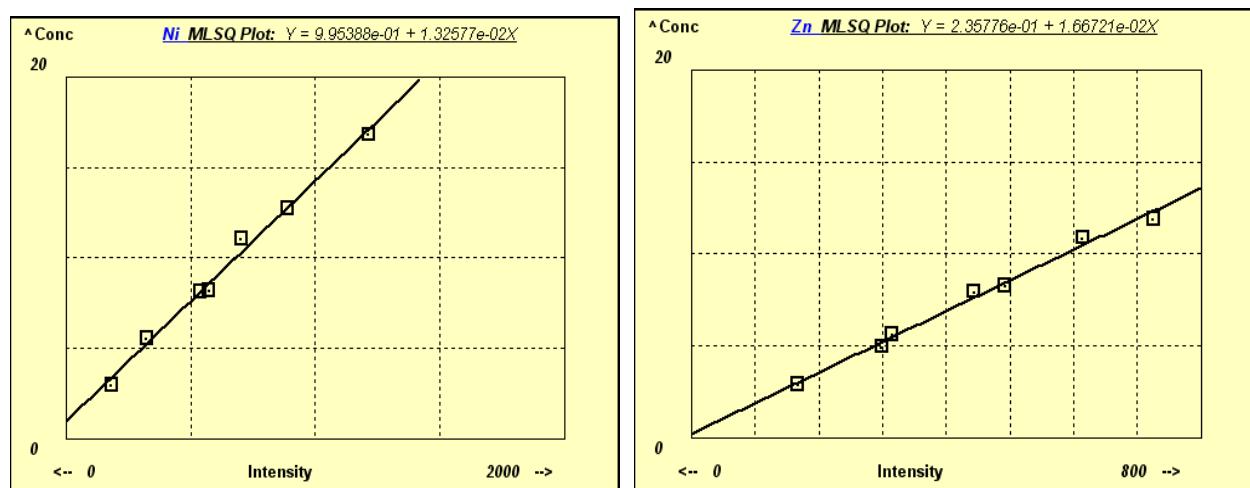
element data is used to form a matrix for the final least-squares calibration, with the resulting coefficients stored as above, but with the choice of only 1 model at present:

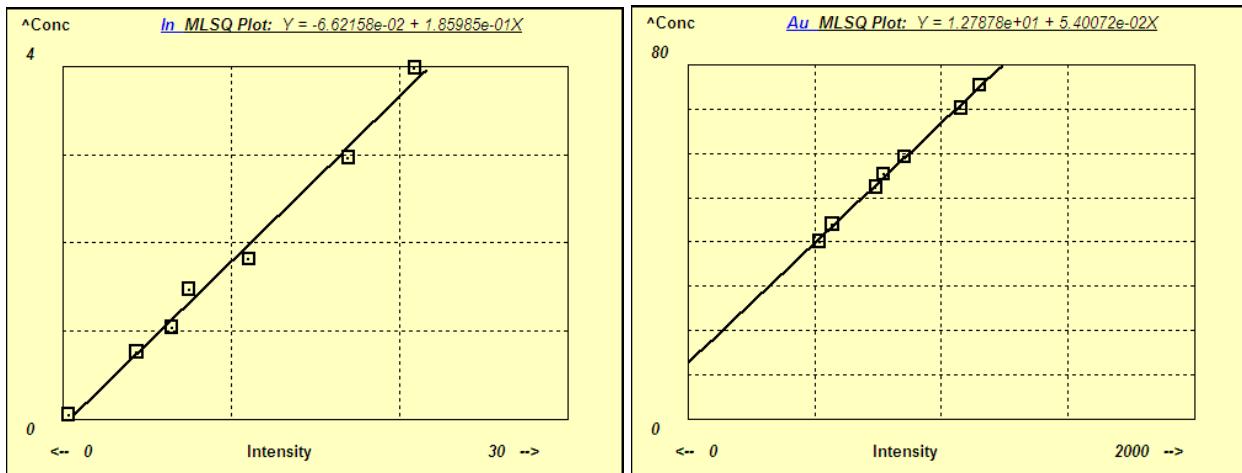
- (101) Linear fit with 2 coefficients (slope and intercept).

The first screen shows the results summary after the calibration of a series of White Gold standards.

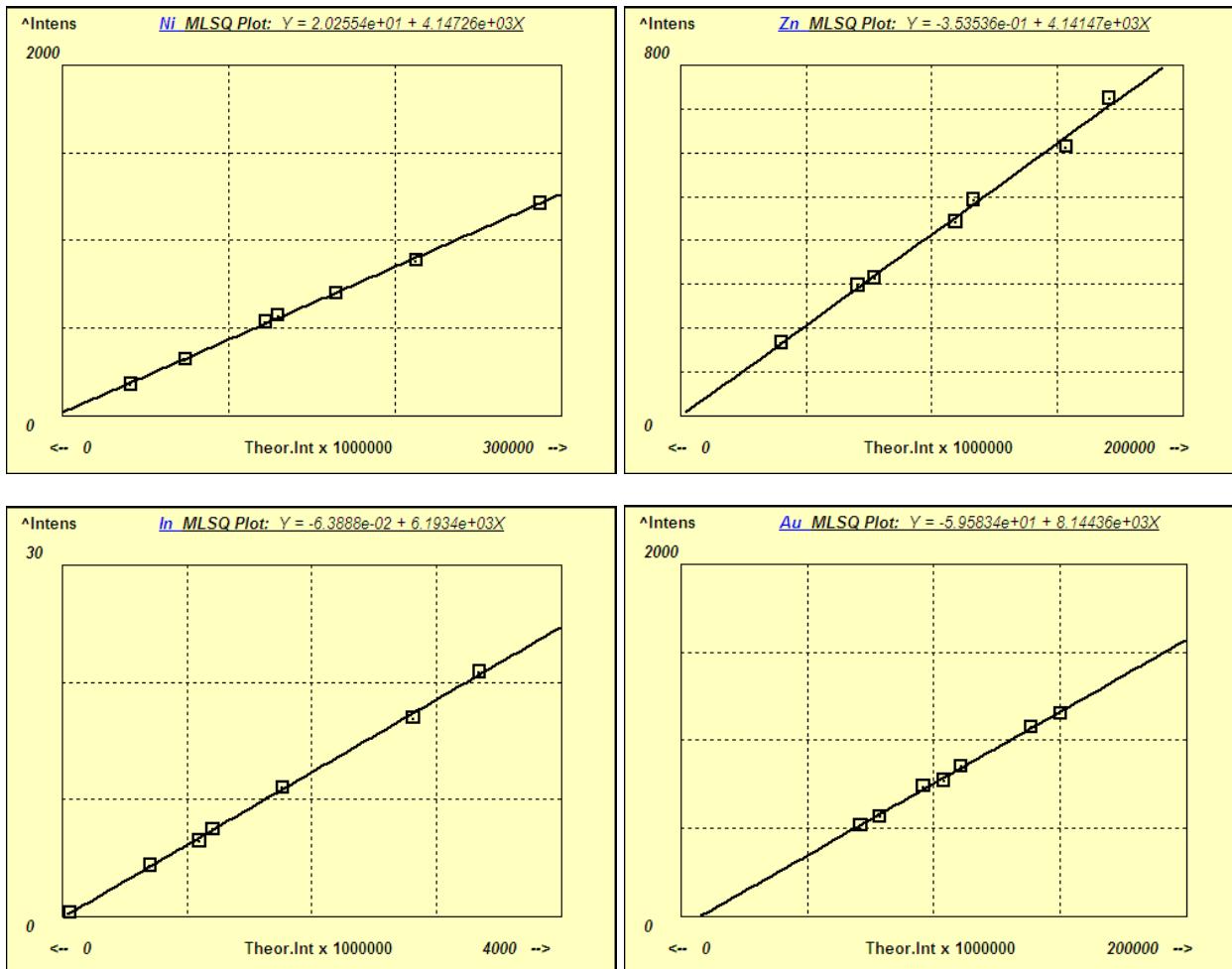


Here are some example calibration plots for Ni, Zn, In and Au.





Here is the same data set, but using the FP calibration method, with the MLSQ Intensity (Linear fit of Intensities vs. Theoretical Intensities) model:



Note that the fits are generally better for the FP version of MLSQ, but because these standards have very similar compositions, even the simple LSQ calibration is not bad, at least over the range of the standards.

## 14 PROCESS

### 14.1 Process Calculate

There are two options in this new menu item for 3.0.0 software and above.

#### 14.1.1 Process Calculate – Mole%

Sometimes it is useful to be able to calculate directly the Mole% values of components, without having to do a complete quantitative analysis, which normally calculates components on the basis of both Wt% and Mole%. If you enter the Wt% values of the components in the component table, then this option will calculate and display the Mole% equivalents

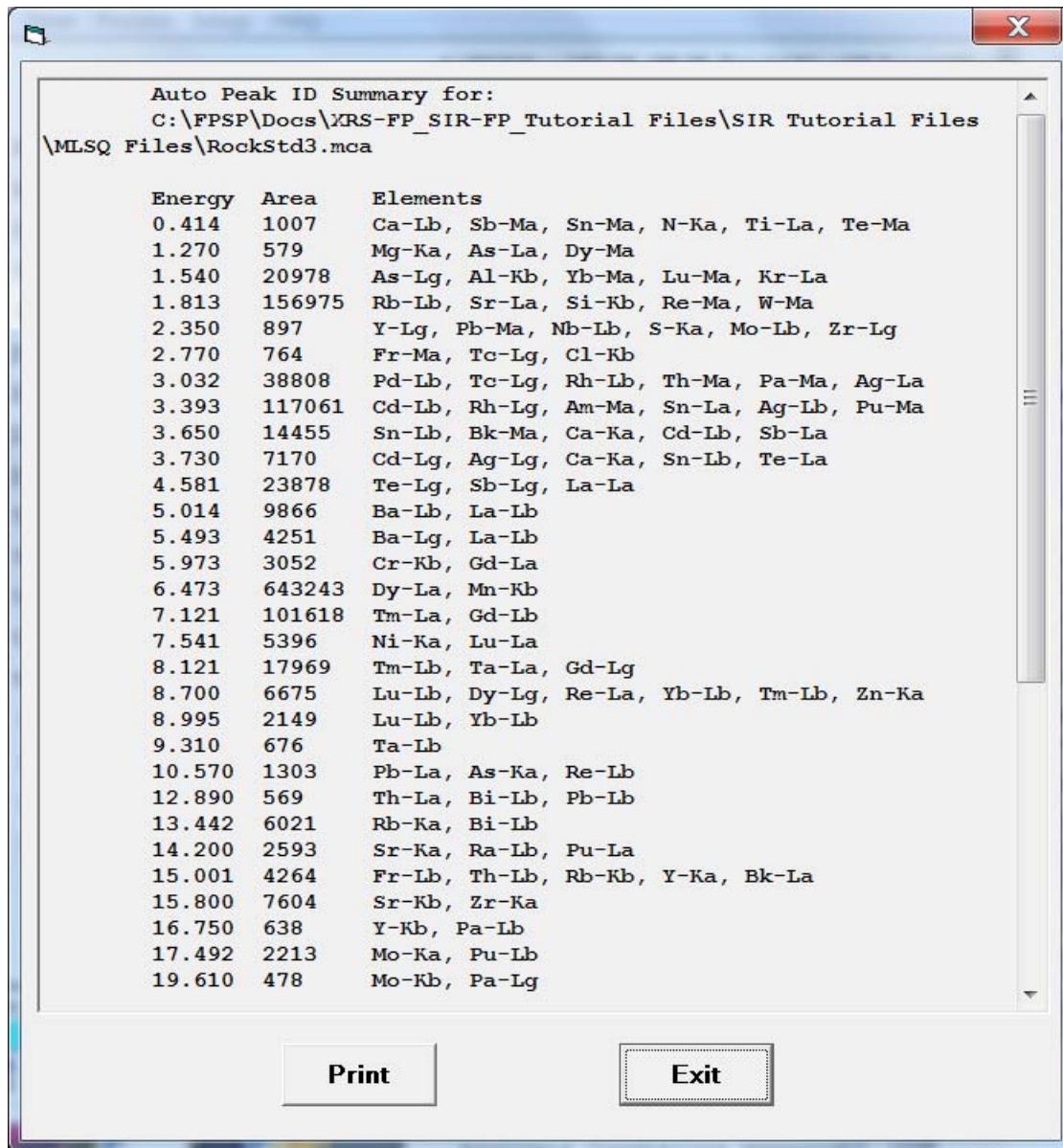
#### 14.1.2 Process Calculate – Wt%

More likely, one might want to enter the components in Mole% because the atomic or molecular ratios are known, but the Wt% values are not available. This option allows these values to easily be calculated, as shown in the following example where CaO and SO<sub>3</sub> were entered as 50-50%.

Specimen Component Table:						
#	Component	Type	Conc.	Error	Units	Mole%
1	CaO	Calc	41.190	0.000	wt.%	50.000
2	SO <sub>3</sub>	Calc	58.810	0.000	wt.%	50.000

## 14.2 Process AutoID

This operation will perform an Automatic Peak and Element ID as per the settings in Setup-AutoID. A typical output from this operation is shown in the figure below, and the identified elements can be added to the Sample and Element Tables if that option is checked in Setup-AutoID.

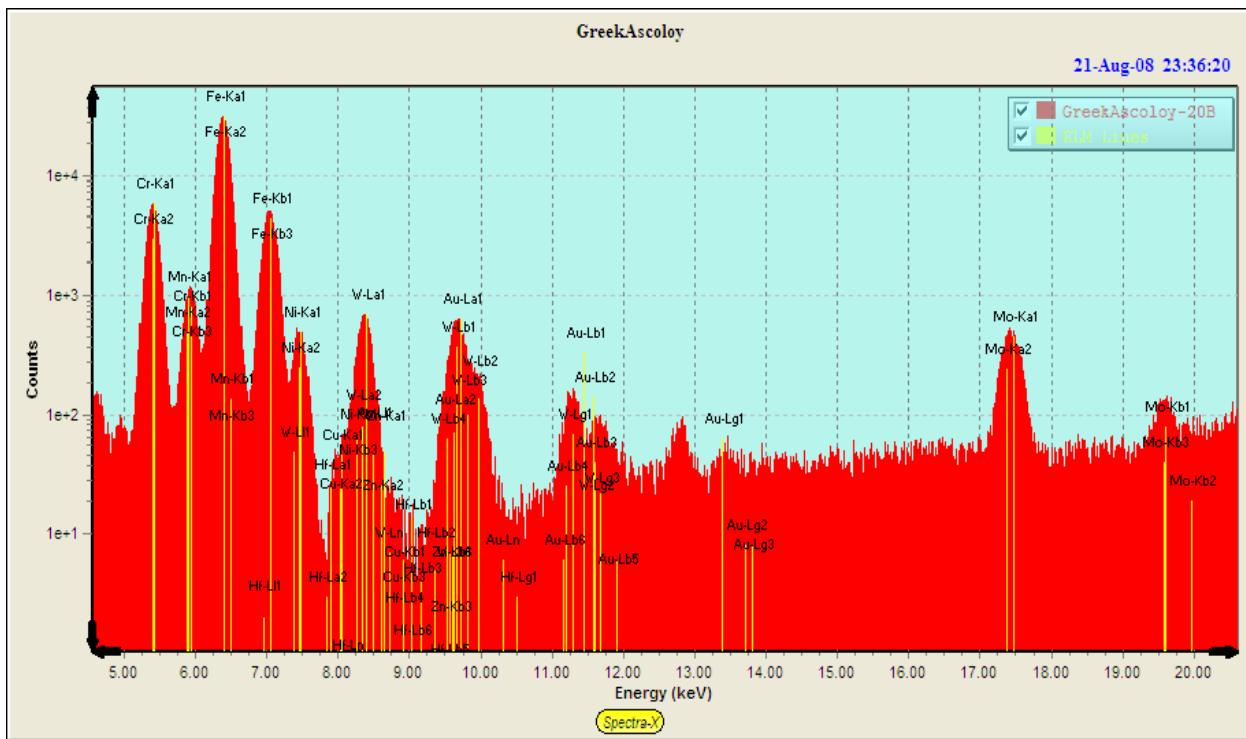


The dialog box displays a table of peak data:

Energy	Area	Elements
0.414	1007	Ca-Lb, Sb-Ma, Sn-Ma, N-Ka, Ti-La, Te-Ma
1.270	579	Mg-Ka, As-La, Dy-Ma
1.540	20978	As-Lg, Al-Kb, Yb-Ma, Lu-Ma, Kr-La
1.813	156975	Rb-Lb, Sr-La, Si-Kb, Re-Ma, W-Ma
2.350	897	Y-Lg, Pb-Ma, Nb-Lb, S-Ka, Mo-Lb, Zr-Lg
2.770	764	Fr-Ma, Tc-Lg, Cl-Kb
3.032	38808	Pd-Lb, Tc-Lg, Rh-Lb, Th-Ma, Pa-Ma, Ag-La
3.393	117061	Cd-Lb, Rh-Lg, Am-Ma, Sn-La, Ag-Lb, Pu-Ma
3.650	14455	Sn-Lb, Bk-Ma, Ca-Ka, Cd-Lb, Sb-La
3.730	7170	Cd-Lg, Ag-Lg, Ca-Ka, Sn-Lb, Te-La
4.581	23878	Te-Lg, Sb-Lg, La-La
5.014	9866	Ba-Lb, La-Lb
5.493	4251	Ba-Lg, La-Lb
5.973	3052	Cr-Kb, Gd-La
6.473	643243	Dy-La, Mn-Kb
7.121	101618	Tm-La, Gd-Lb
7.541	5396	Ni-Ka, Lu-La
8.121	17969	Tm-Lb, Ta-La, Gd-Lg
8.700	6675	Lu-Lb, Dy-Lg, Re-La, Yb-Lb, Tm-Lb, Zn-Ka
8.995	2149	Lu-Lb, Yb-Lb
9.310	676	Ta-Lb
10.570	1303	Pb-La, As-Ka, Re-Lb
12.890	569	Th-La, Bi-Lb, Pb-Lb
13.442	6021	Rb-Ka, Bi-Lb
14.200	2593	Sr-Ka, Ra-Lb, Pu-La
15.001	4264	Fr-Lb, Th-Lb, Rb-Kb, Y-Ka, Bk-La
15.800	7604	Sr-Kb, Zr-Ka
16.750	638	Y-Kb, Pa-Lb
17.492	2213	Mo-Ka, Pu-Lb
19.610	478	Mo-Kb, Pa-Lg

Buttons at the bottom: Print, Exit

You may print this panel to the printer with the Print button. The elements identified are also displayed in the spectrum display panel, as shown in the example below, which was the result from a different spectrum.

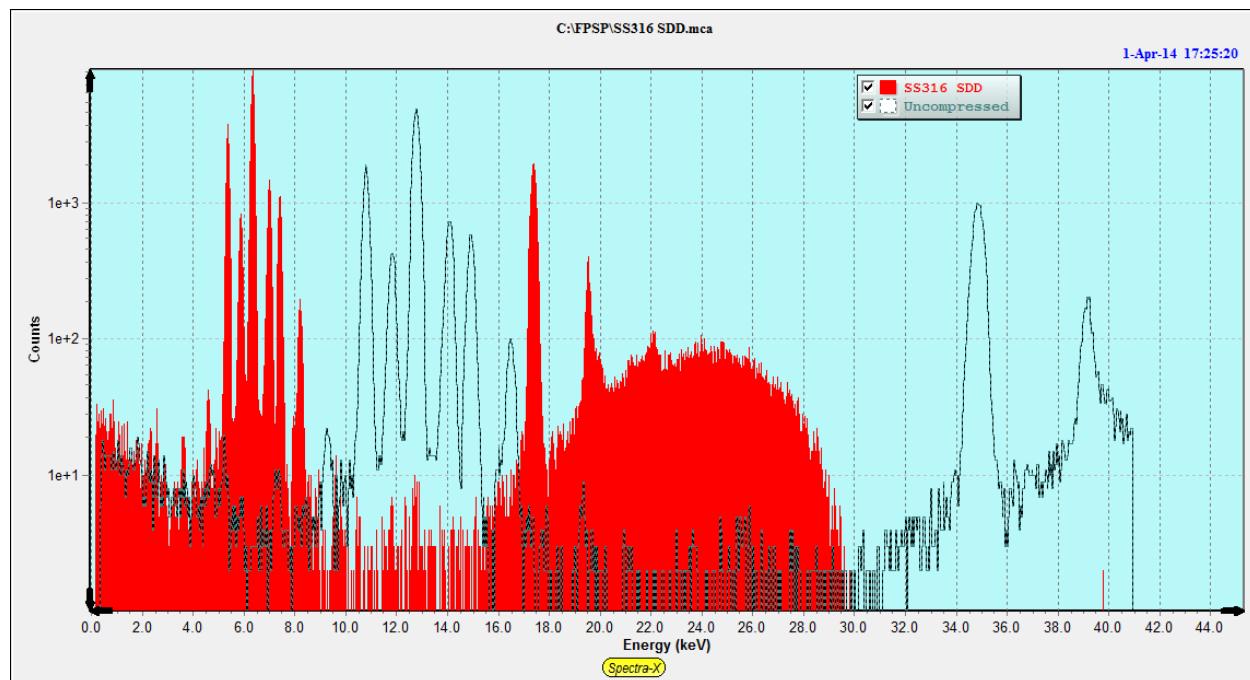


## 14.3 Process Spectrum

This set of commands control the various steps required in spectrum processing, such as spectrum smoothing, escape-peak removal, sum-peak removal, background removal and peak deconvolution (i.e., overlap correction). An additional choice “All” is also available, which performs all the operations, as specified (checked) in the current Condition Code in the Condition Table.

### 14.3.1 Process Spectrum – Compress

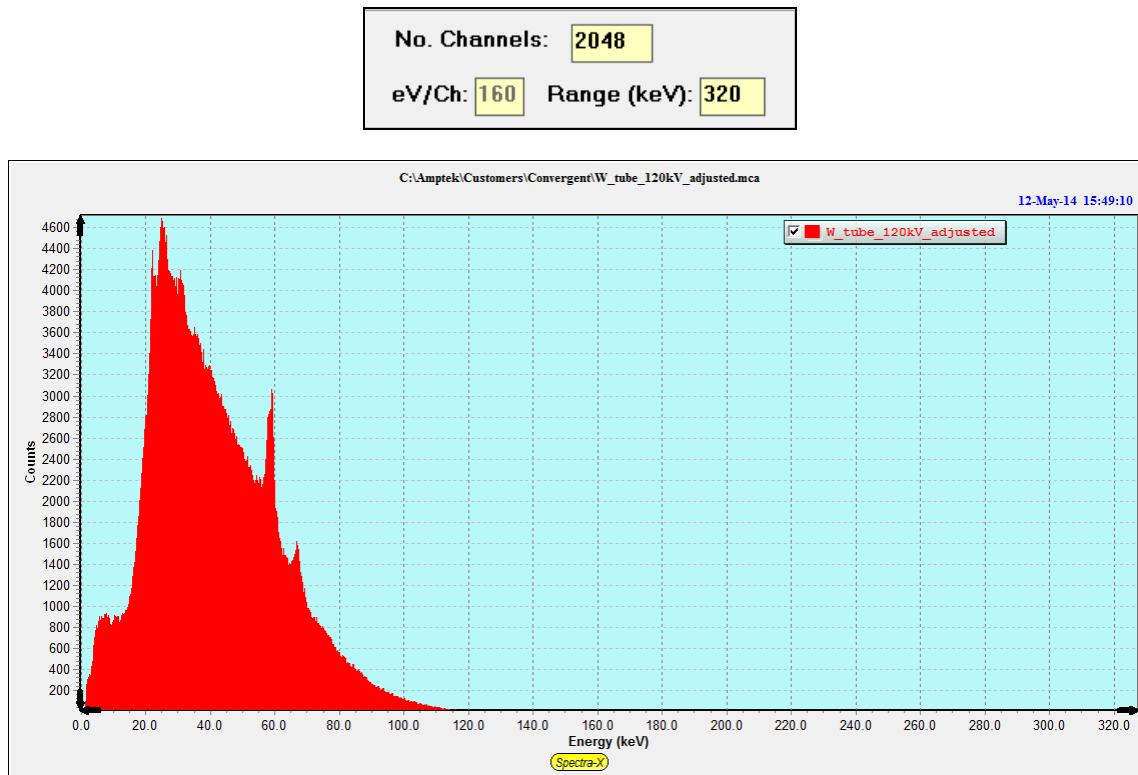
This function simply compresses the spectrum by a factor of 2 in the number of channels. The uncompressed original spectrum is shown in the Compare Group 1. The counts in each channel pair are added together so that the total number of counts in the spectrum should remain the same. Also the channel width in eV is doubled.



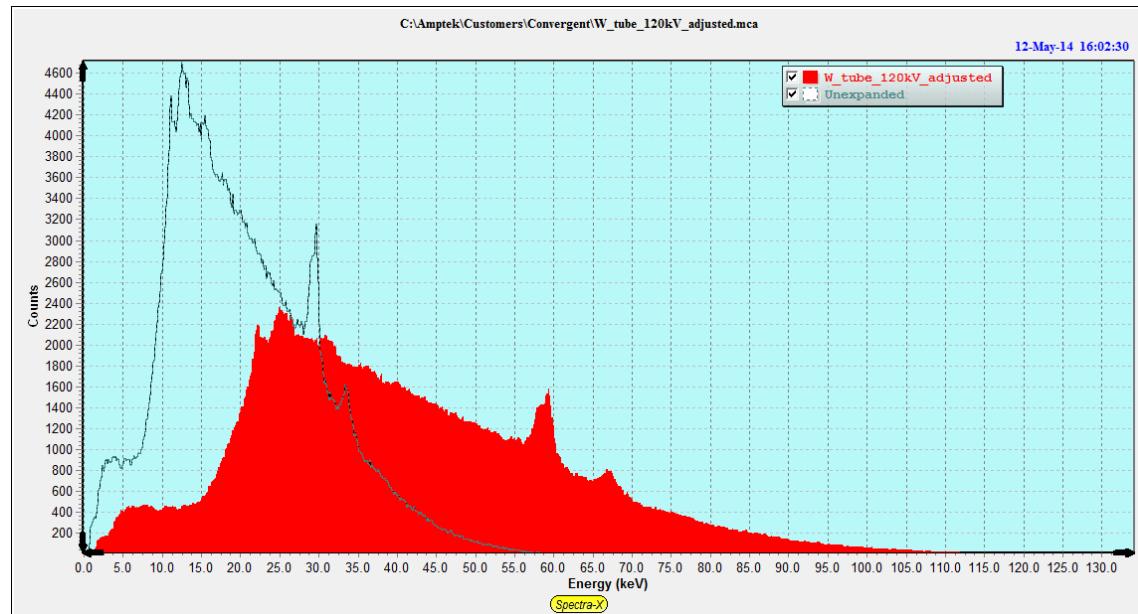
### 14.3.2 Process Spectrum – Expand

This function does the opposite of the Compression option above. The counts in each channel are divided by two, and the total number of channels doubled (up to a maximum of 4096). The channel width (in eV) is halved, so that the total number of counts is approximately the same, allowing for rounding errors.

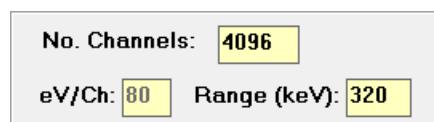
In the example below a spectrum with 2048 channels is read in with a channel width of 160 eV. The Setup-MCA panel shows the following details:



After the Process-Expand operation, the Spectra-X screen looks as follows, with the expanded spectrum in red bars and the original unexpanded spectrum as black dots:



The Setup-MCA screen now shows the following:



### 14.3.3 Process Spectrum – Efficiency Correct

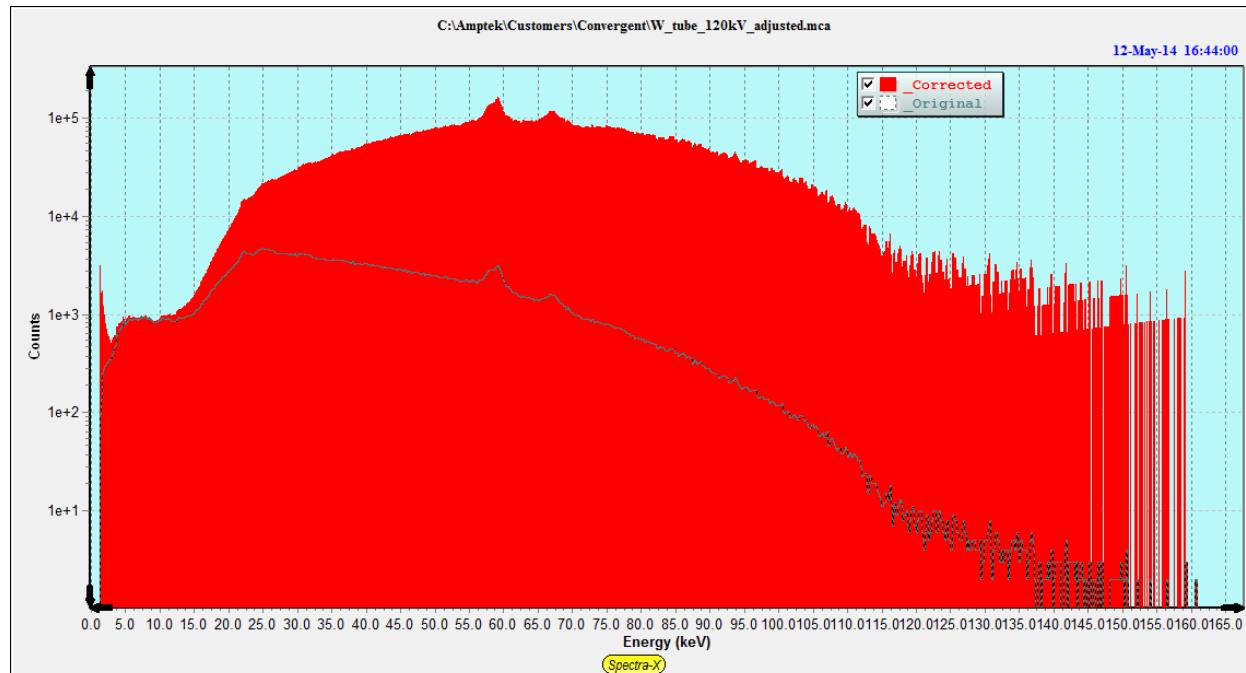
Beginning with version v.5.3.0.2 of XRS-FP.exe there is an option that will correct an x-ray spectrum for losses in intensity by air-path absorption and detector efficiencies that are less than 100% (window & detector contact layer absorption and/or x-rays passing completely through the detector, etc.). This option is designed for customers who are using the software to collect spectra directly from x-ray tubes.

To use this method you would first correct for sum and escape peak losses using those two commands. Then the second step corrects for the efficiency of x-ray detection by the detector and window. You should setup the system geometry and detector/windows parameters correctly as these parameters will be used for estimating this loss, and correcting the spectrum on a channel-by-channel basis. Note that there is no correction for an external filter on the detector - just the detector window (unless you express the filter as part of the window description).

Typically the high end of the x-ray tube spectrum will be increased noticeably after this correction. Also note that this correction can become very noisy when there are very few counts, so some limits have been put on the correction (i.e., no greater than 100,000 times increase).

A second part of this option is to correct for the x-ray loss in the atmosphere in the measurement chamber. The atmosphere should be set in the Condition Code table, typically for Code #1. The choices are Air, He or Vacuum. The critical distance to setup is the Sample-to-Detector distance in Setup-Geometry panel. With this second correction the values can very noisy at the low-energy end of the spectrum, so the same safety limit as in the previous paragraph is also used here.

The following shows a W tube spectrum that was taken by a Si pin diode detector, before (black dots) and after (red bars) the corrections for the detector and atmospheric absorption.



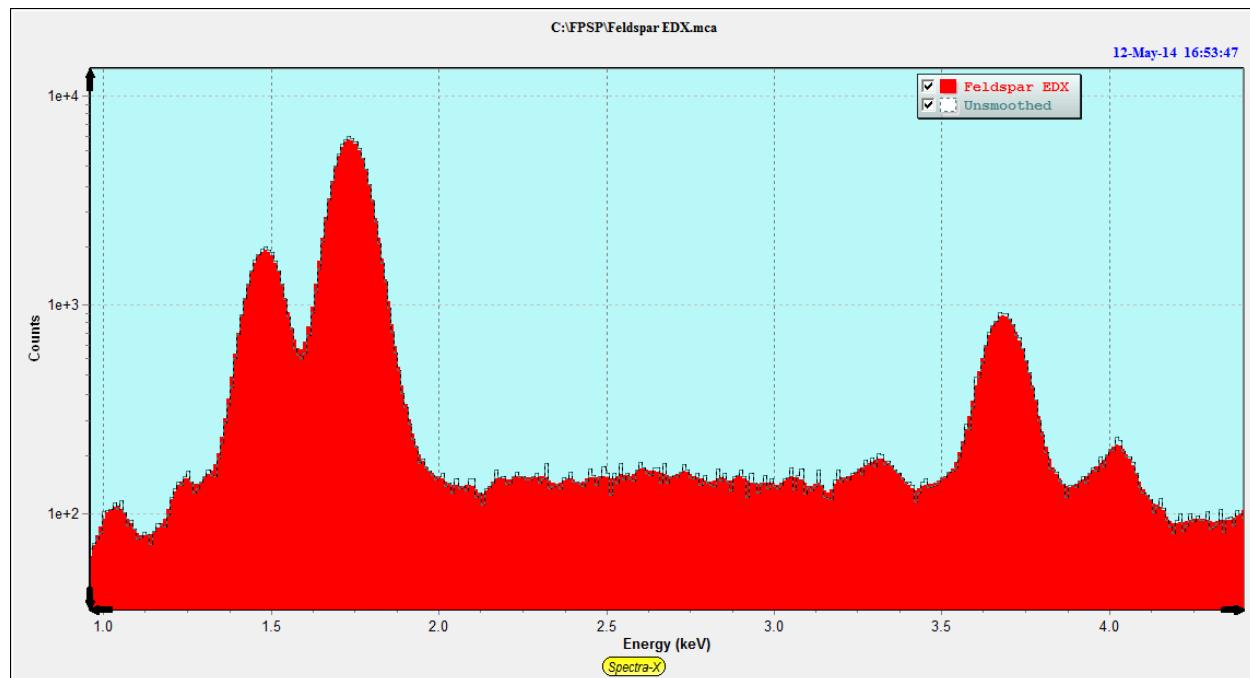
Note that after setting all these parameters you should re-save the Master.tfr file (or save to some other file) to make use of these values in the future. You could create many different TFR files for different setups, if necessary.

Warning - one last note is that this feature should NOT be used for normal XRF spectrum processing as these factors are also applied automatically during the FP quantitative analysis step.

#### 14.3.4 Process Spectrum - Smooth

This option performs a number of smooths on the spectrum loaded in the main group in Spectra-X. The default smoothing is the 3-point (1:2:1) Gaussian type, but there are other options as described in the Setup-Processing panel. The number of smooths is determined by the entry in the Condition Table (for the current condition). This option may be performed iteratively for an indefinite number of passes, each one being governed by the number of smooths in the Condition Table. It is not recommended that spectra be over smoothed – typically, 0 to 2 smooths should be sufficient. Too much smoothing tends to degrade the overall information content of spectra, and also slightly broaden the peaks. There are several other smoothing filters that can be used as shown in the Setup-Processing panel, but most give very similar results as multiple passes of the basic 1:2:1 smoothing.

After this option is completed, the original spectrum is displayed in the Compare group (Dots), and the smoothed spectrum is displayed in the original main group (Bars). The following shows one part of a spectrum after 4 smooths.

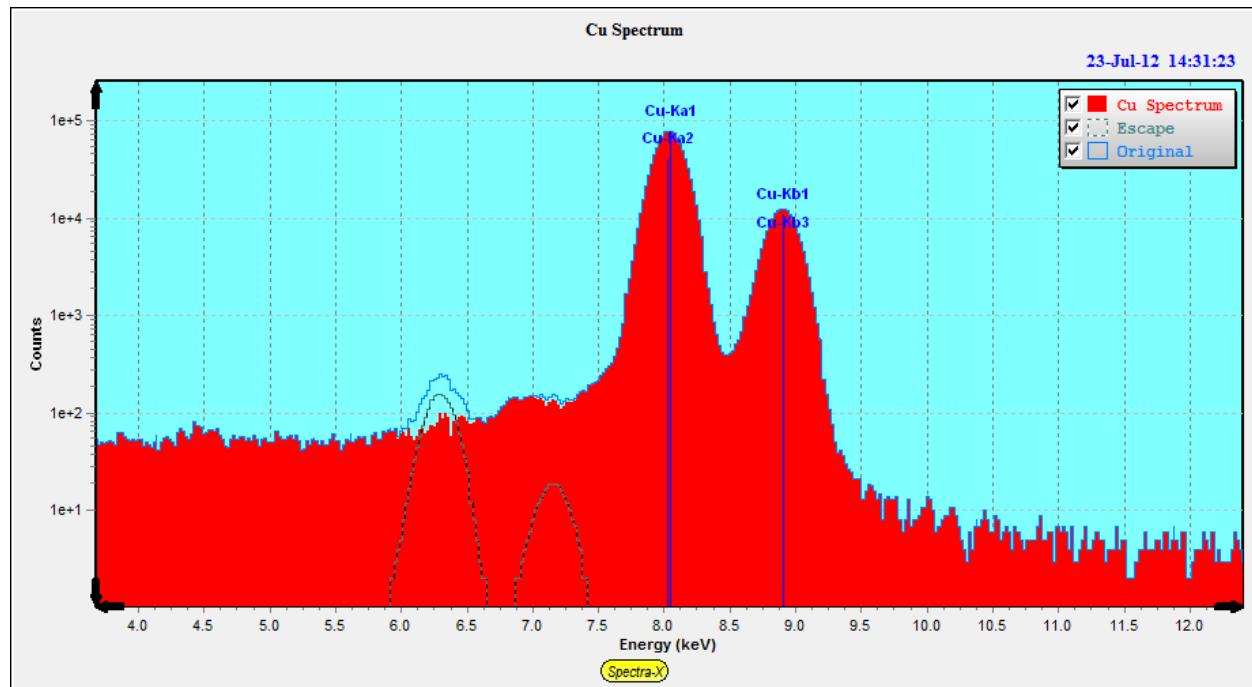


### 14.3.5 Process Spectrum - Escape Peaks

This option performs subtraction of the Si escape peaks (for Si detectors). The software uses an internal function to estimate the fraction of x-ray events (above the Si-K edge, for Si detectors) that will generate Si-K x rays that will escape from the front or backside of the detector. It is only intended (at present) for Si detectors.

After this option, the escape-peak processed spectrum is located in the main group (Bars), and the stripped escape events are shown in the Compare group (Dots). After the escape events are subtracted, they are added back to their parent peak. This operation may only be performed once on each spectrum, unless the spectrum is restored.

The following spectrum shows the original spectrum (in blue) and the processed spectrum (in red) after removing the Si escape peaks (black spectrum) from Cu.

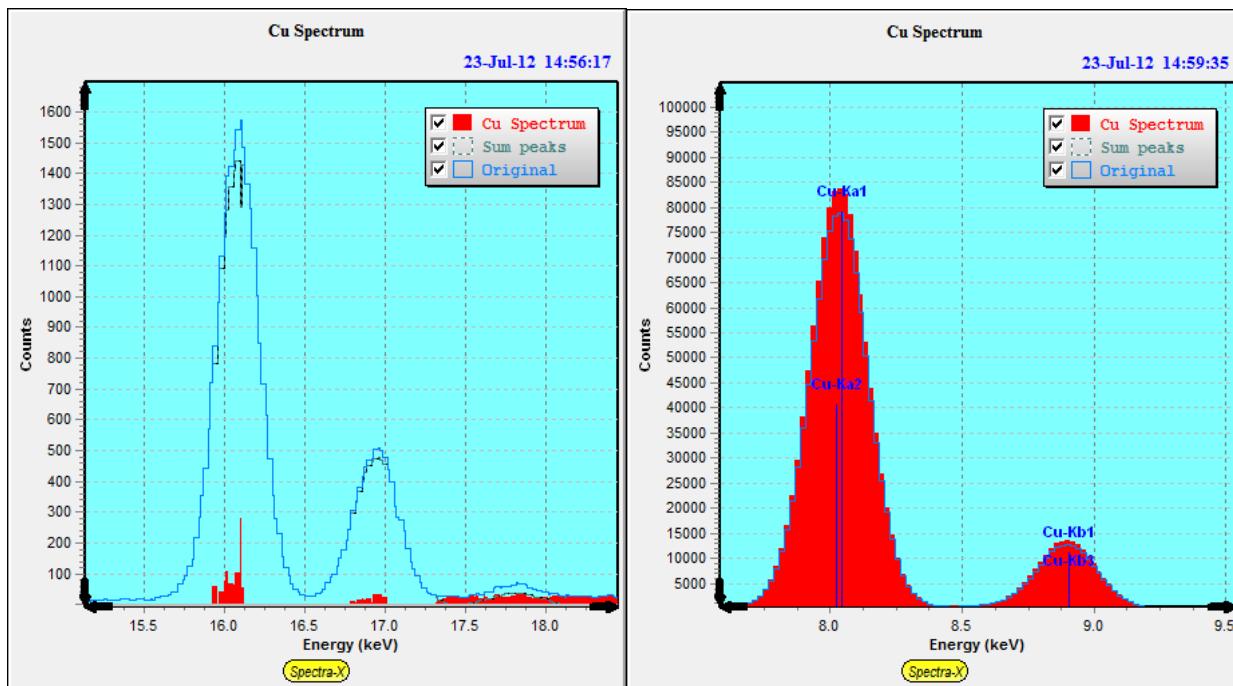


### 14.3.6 Process Spectrum - Pileup (Sum-Peak) Removal

This option performs subtraction of the pileup (sum) peaks. This option is only recommended for spectra where a high dead time is present. It is not normally required if the dead time is maintained below about 25%, except for low-energy (< 1keV) x-rays, where the pulse pileup discriminator is not effective, and even modest total count rates can result in peak pileup (sum peaks). This correction is generally not as accurate as the escape peak removal, and may leave some residual sum peaks in the spectrum.

After this option, the pileup-peak processed spectrum is located in the main group (Bars), and the stripped pileup events are shown in the Compare group (Dots). Critical to this routine is the knowledge about the pulse-pair resolution time (with a default value of 1 microsecond), and the time constant of the main channel for low-energy (<1 keV) x-ray photons. This operation also may only be performed once on each spectrum, unless the spectrum is restored.

The figures below show the removal of the escape peaks from a Cu spectrum. The left figure shows the calculated sum peaks, the original spectrum and the spectrum after the sum-peak removal. The right figure shows the sum peak events that were lost, added back to the parent (Cu-K) peaks.

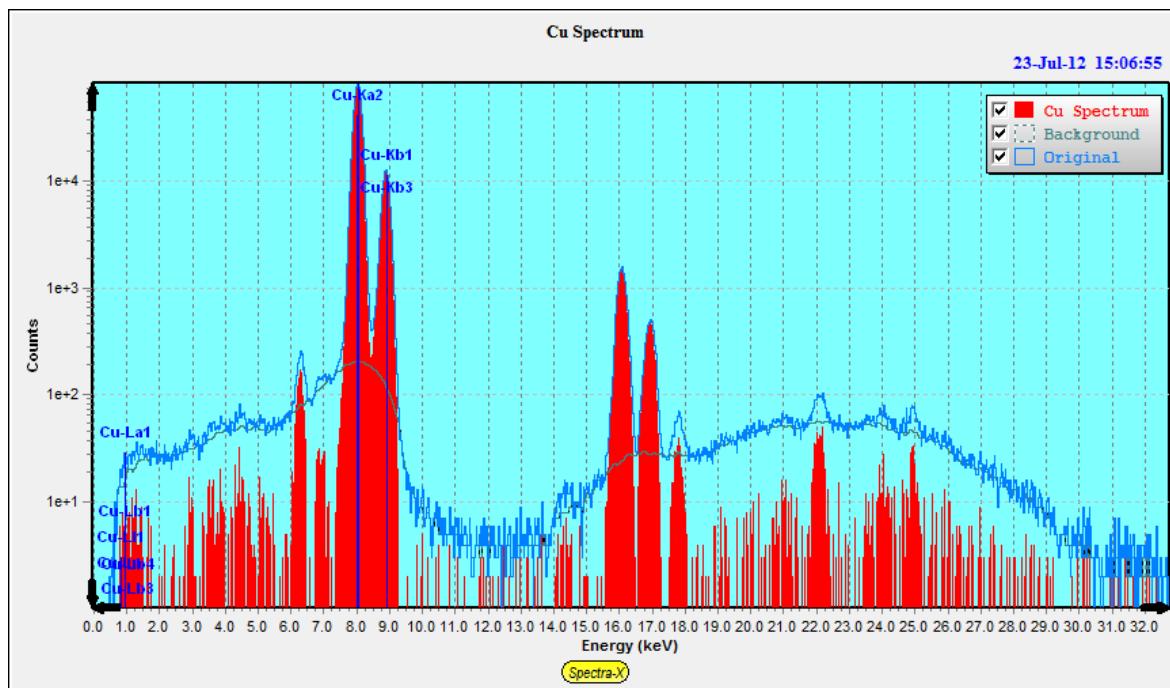


### 14.3.7 Process Spectrum - Background Removal

This option removes the background from the current spectrum. This can be removed using the Automatic method (the default), or by using a background spectrum file. The automatic method first performs an estimation of the background and then subtracts it from the spectrum in the main group. For more information on the background estimator, see the Setup-Processing parameters.

This option performs an iterative band-pass filter that removes rapidly changing regions (i.e., peaks) and leaves the slower-varying regions, which also determine the estimate of background below the peak regions. After this option is complete, the background-subtracted spectrum is loaded in the main group (Bars), and the background itself is displayed in the Compare group (Dots). This operation may only be performed once on each spectrum.

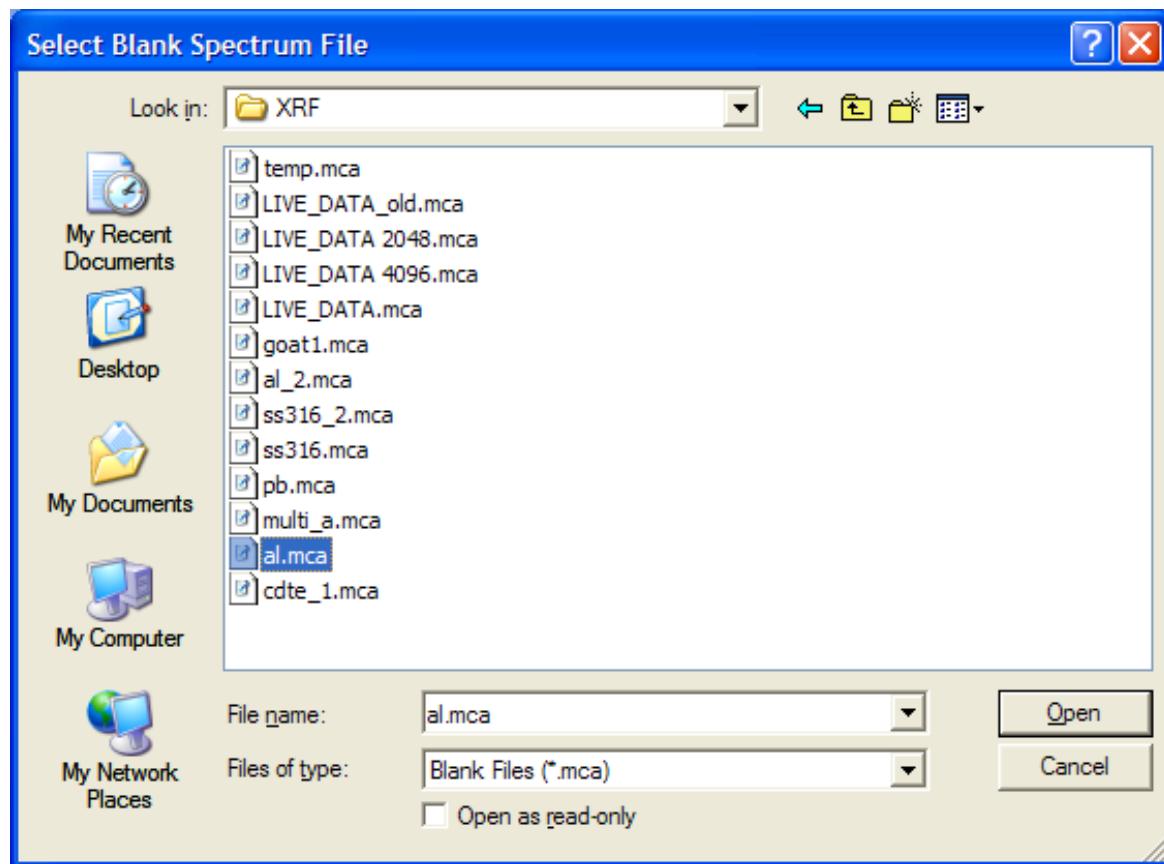
To view the background on the *unprocessed* spectrum, simply Restore the original spectrum in the main group, and this will leave the background in the Compare group and you can compare the two spectra in the background regions (by expanding the vertical scale if necessary) to judge visually the quality of the fit, as shown below where the subtracted and original spectra are shown with the estimated background.



The Background-File option requires a separate spectrum file that represents an estimate of the typical sample spectrum background. It works similarly to the Process Spectrum - Blank option, except that it is the background being subtracted rather than some artifact peaks. First select the File option in the Background column of the condition code and then double-click on the Background-File cell to bring up a dialog similar to the one for the Blank file selection (see below). Then, during the background removal process, the background file will be subtracted channel-by-channel from the current spectrum. The only normalization that is possible is the automatic use of the acquisition times for the 2 spectra.

#### 14.3.8 Process Spectrum – Blank Subtraction

This option is only available if the check box has been selected in the Processing Conditions has been set, and a blank (e.g., \*.mca) spectrum file has been defined. This can be done either by entering the filename and path directly, or by double-clicking on the Blank File cell, which will then bring up a dialog to select the \*.mca file, such as the following example:

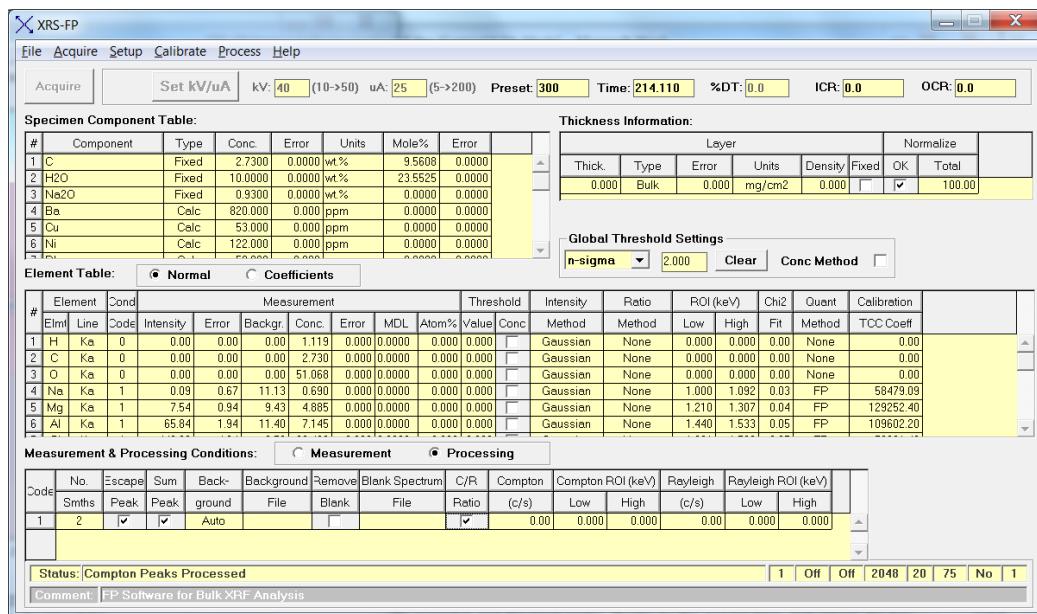


After selecting the require file, this name and path will be saved in the \*.tfr file (using the File-Save command). Blank subtraction is done to remove artifacts in the spectrum that cannot be handled with background removal or some other spectrum processing. It should be used with care, since it relies on there being a constant “blank” effect that does not very significantly from one spectrum to another. Examples where this might be useful include the removal of argon peaks from fluorescence of air, removal of tube scatter peaks, or removal of some contaminant peaks from the XRF system itself.

The software does a channel-by-channel subtraction of the blank counts from the matching counts in the spectrum being analyzed. There is no normalization or scaling done, except on the basis of acquisition times, so the blank should be acquired under the same conditions as used for the normal spectra (e.g., livetime, KV, etc.). The blank spectrum removal is done after the background removal step (in the Process Spectrum All command), so it would make sense to remove the background from the blank as well, and then store the processed spectrum (with smoothing, escape peak removal, etc.) as the blank spectrum.

### 14.3.9 Process Spectrum – Compton Peak

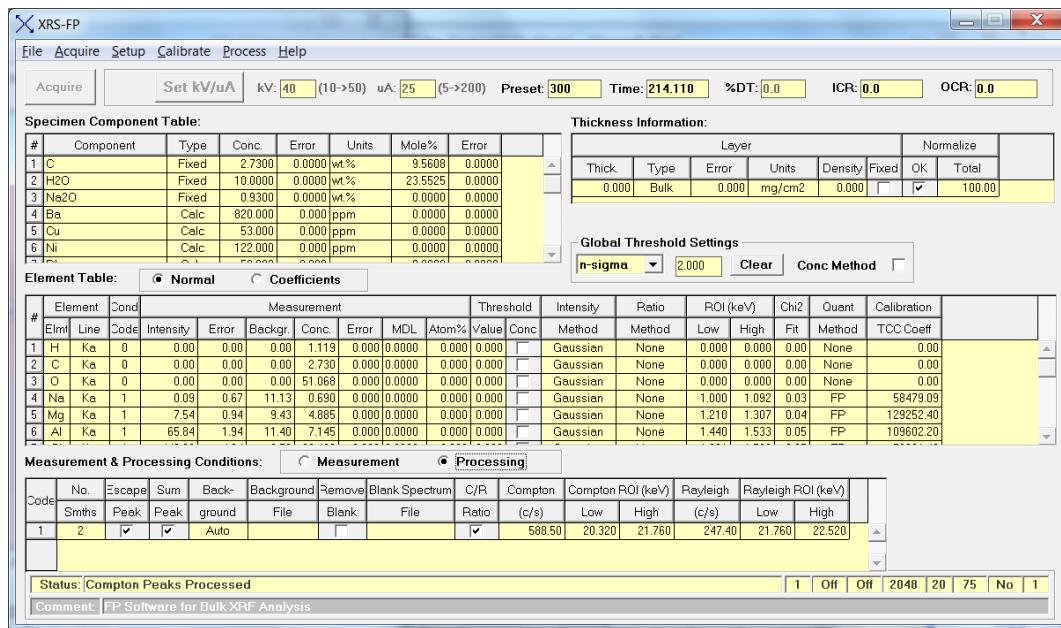
This feature allows peak intensities to be extracted for the Compton and Rayleigh scatter peaks. These values can be used to calculate Peak-to-Compton ratios, instead of simple peak intensities for analysis, or for Compton-to-Rayleigh peak ratios for the SIR-FP method, or simply for improving the overall spectrum fitting (deconvolution) there the scatter peaks might overlap other analyte peaks of interest. Only 1 condition code can be used for extracting scatter peak information, even though several conditions may be used in the overall analysis. In the following example the Condition Table had no scatter peak information entered and the C/R checkbox was unchecked. After selecting the C/R checkbox, the default ROI values are initialized to zero as shown below.



After clicking on the Process-Compton menu item, default ROI values are assigned in the following (simplified) way. First a “cut point” is found, which is at the minimum count value between the Compton and Rayleigh peak channels, after some local smoothing to reduce noise in the spectrum. The a high point is found by looking at the channels after the Rayleigh peak and finding a point where the spectrum channels start to increase again in value – perhaps because of the presence of a Compton Kb peak. Then a low cut point is made on the low side of the Compton peak. This cut point is no more than the distance between the Compton Ka peak channels and the mid-cut point. There are other internal checks done to avoid getting bad values, but this is the main part of the algorithm.

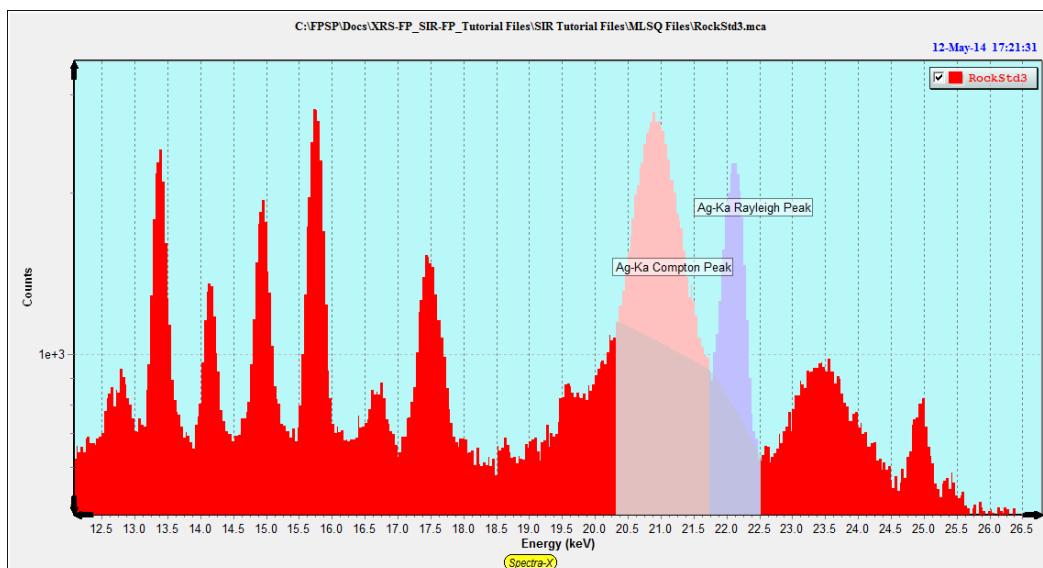
Prior to the steps outlined previously, the software will automatically allocate the initial peak positions based upon knowledge about the tube anode material and the geometry of the tube and XRF spectrometer. The former determines the energy location of the Rayleigh scatter peak, and the latter determines the energy offset for the Compton peak. Therefore, it is important that the Tube and Geometry parameters are set correctly.

After selecting the 3 cut points, the function integrates the Compton and Rayleigh peaks, divides by the acquire time, and reports the two intensities along with the Regions Of Interest (ROI) used for the peak integrations. In this example, the ROIs were set as below, with the calculated integrals (intensities).



The ROI's can manually be entered into the Condition Table, to override the regions calculated by the software. This is very useful when the geometry is not exactly known, or when there are peak overlaps, either between the Rayleigh and Compton peaks or with neighboring sample peaks.

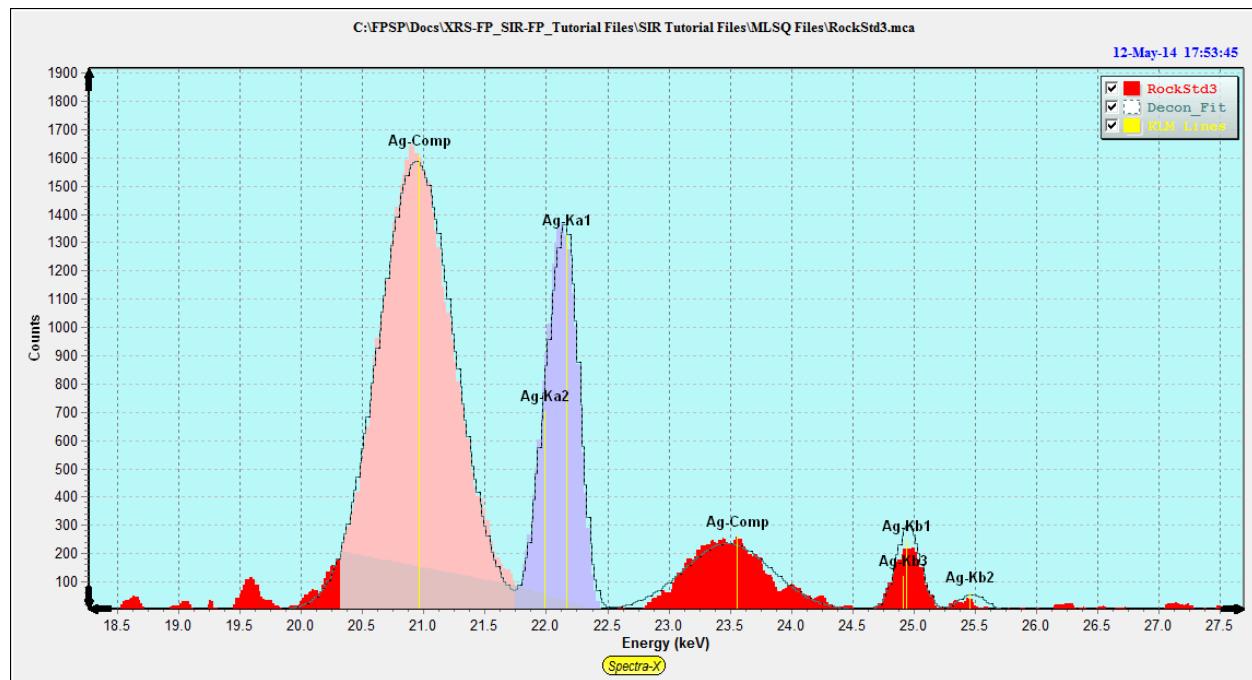
To clear all the current ROI's and intensities from the Rayleigh and Compton peaks, just click on the C/R Peaks check box to Uncheck the C/R option, and then re-check it again. Whenever the cells are first displayed they contain zeroes, and this ensures that the next Process – Compton command will calculate new ROI's and intensities from scratch. Of course, any manually entered ROI's will also be erased. The ROIs selected above are shown re-painted manually in the Spectra-X panel.



The Compton peak integral can also be used in the optional Peak-to-Compton ratioing method that is defined in the Element Table. Just select the Compton option in the Ratio column for the element, to ratio that element's intensity to the Compton peak intensity. This is a useful alternative method to analysis by FP. However do NOT use both methods together. The same can be done for ratioing to the Rayleigh scatter peak, which is useful in certain applications.

You should note that the default selections for Compton and Rayleigh scatter peak integrals are often only initial estimates. The better way for more accurate fitting of the scatter peaks is to include these peaks in the spectral deconvolution. If the C/R option is checked, this inclusion is automatic during the Gaussian deconvolution option, and this is done after all other spectrum processing, including background removal.

The following figure shows the result for the above spectrum after Gaussian deconvolution including the scatter peaks. Note that when the scatter peak fitting is done this way, the scatter peaks are fit with Gaussian functions in the same way as other analyte. However, the Compton peak width and location are allowed to vary considerably because of the uncertainty of the exact scatter angle and the density of the sample. Low density (i.e. low-Z) samples have a broader range of scatter angles and therefore the peak is broader, plus there is often multiple scatter in these materials.



### 14.3.10 Process Spectrum – Deconvolute

#### 14.3.10.1 General

The Process Spectrum Deconvolute option performs the extraction of net peak intensities using one of three methods. The first is simple peak integration across a fixed Region-Of-Interest (ROI) and is called the Integrate method. The second is using synthetic Gaussians to fit the spectral peaks, using a known database of line ratios and peak energies, etc., The third (and new in v.3.3.0) method is the Reference deconvolution, which uses stored profiles for each element to fit the peaks, instead of synthetic Gaussian profiles. Gaussian deconvolution is the default method and the setup parameters for this are described in the Setup Processing section. Note that *only* those elements (in the Element Table) that are defined with the Gauss option will get their peak intensities from the Gaussian deconvolution option, even though *all* elements will be included in the deconvolution process, to ensure correct spectral fitting. Other elements may be set to the Integrate or Reference option.

Note that these peak widths used in the Integrate method are usually significantly narrower than the “integration” regions used internally by the Gaussian peak deconvolution method, since the latter are integrated “mathematically” by an analytic function. However, note also that for severely overlapped spectra, the Integrate method could actually yield *higher* intensities, since overlap correction has *not* been performed.

When you are sure that there are no overlapping peaks (a somewhat unusual situation!), you can safely use Integrate for all the elements. There is one advantage in using the simpler Integrate method in that the repeatability, or precision, is typically better than that using other least-squares fitting methods, although the accuracy is likely to be reduced when overlaps are significant.

There are two different approaches to fitting the peaks by a least-squares method. The first uses linear fitting, where the peak ratios, energies and widths are fixed. This method is usually very fast. The second uses a nonlinear approach where these parameters are allowed to vary within certain constraints. This is described in more detail, for nonlinear Gaussian deconvolution in the Setup-Processing section. For Reference deconvolution only the linear method is available as the profiles are already fixed in advance, unless more advanced techniques are used (not yet available in this software).

Note that for a large number of elements (say, greater than about 15), the nonlinear method can become very slow, so be patient while this operation is in progress, or use the linear version.

#### 14.3.10.2 Gaussian Deconvolution

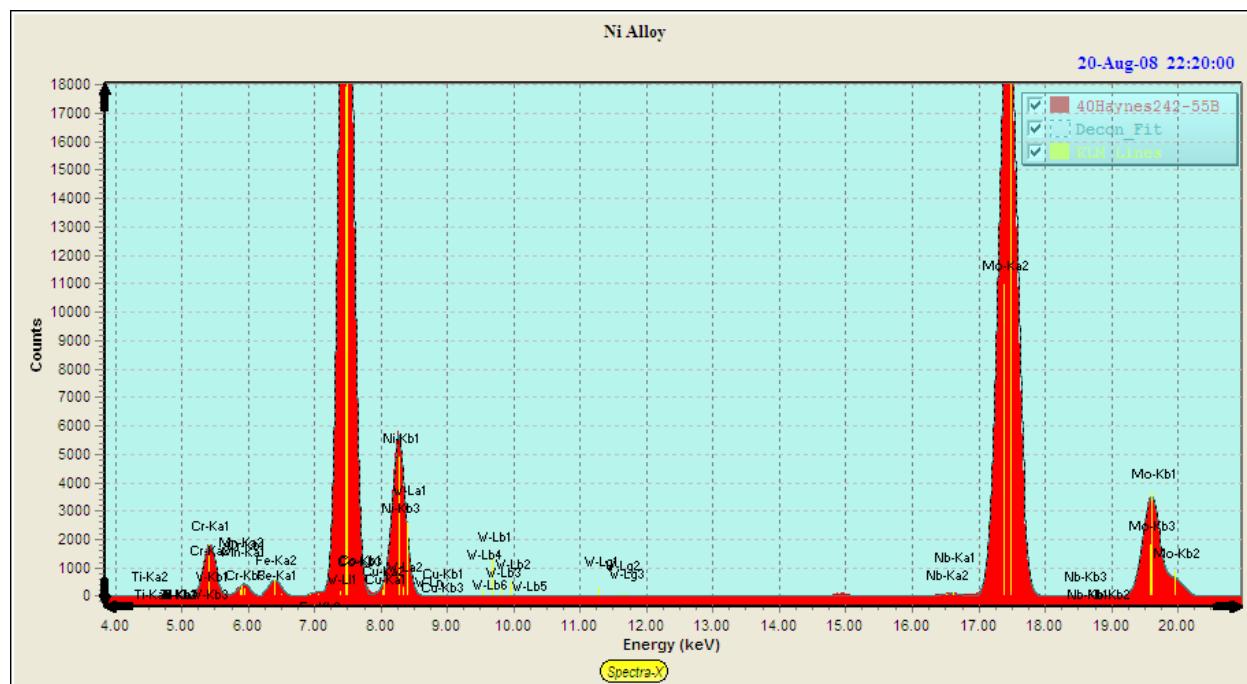
The next part of this guide describes the use of the Gaussian deconvolution method.

At the end of the Gaussian deconvolution, the spectrum in Group S1 (Bars) is untouched, and the synthetic Gaussian-fitted spectrum is displayed in Group S2 (Dots). After the fitting process, the elemental intensities are saved in the Report, in the Element Table. This command may be performed on

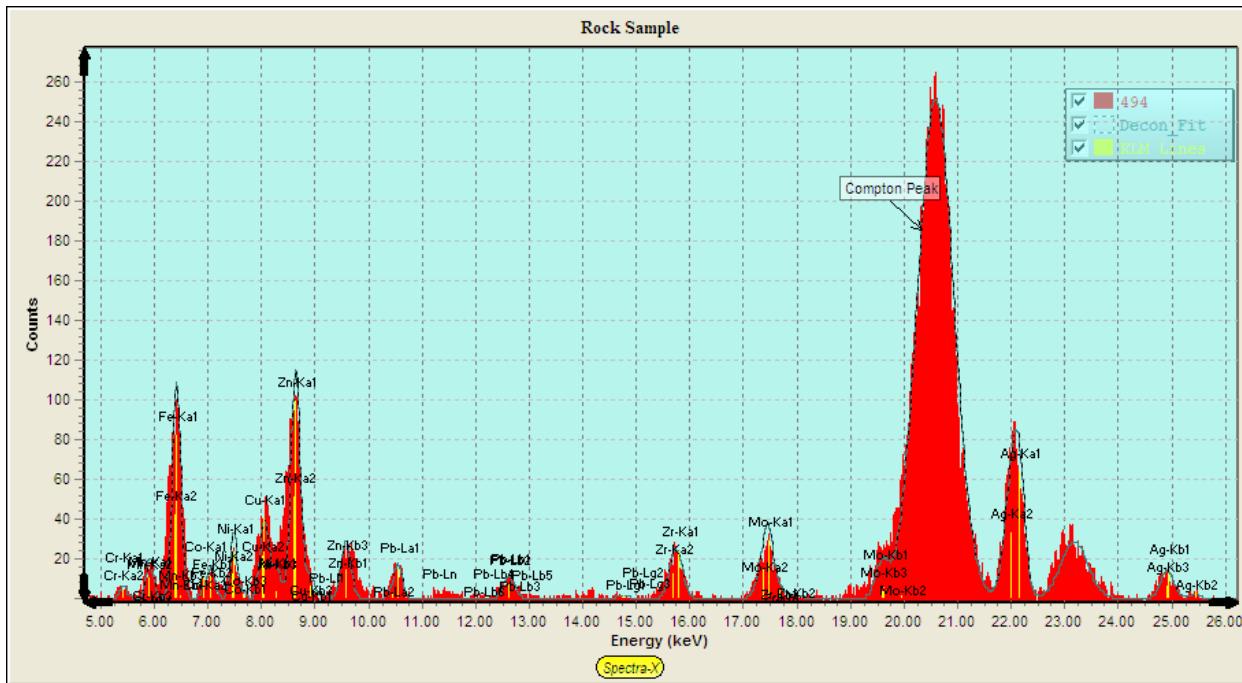
the same spectrum for an unlimited number of times (i.e., one can change the setup parameters, and redo the analysis).

A feature is available in the software has to do with including the Compton and Rayleigh peaks in the spectrum deconvolution. If the function Process - Compton Peak has been invoked, and the C/R ratio check box is checked, then the Compton and Rayleigh peaks are automatically included in the overall spectrum fitting. At the end of the procedure the Compton and Rayleigh peak intensities are updated with information derived from the overall spectrum fitting.

Remember that the previous Process - Compton Peak function just does simple integration of the peaks, without any overlap or energy correction. In the nonlinear deconvolution the Compton peak is allowed to move independently of the other analyte peaks in the spectrum, including the Rayleigh peak. This is because the Compton peak shape, and position, can vary significantly from one type of sample to another.



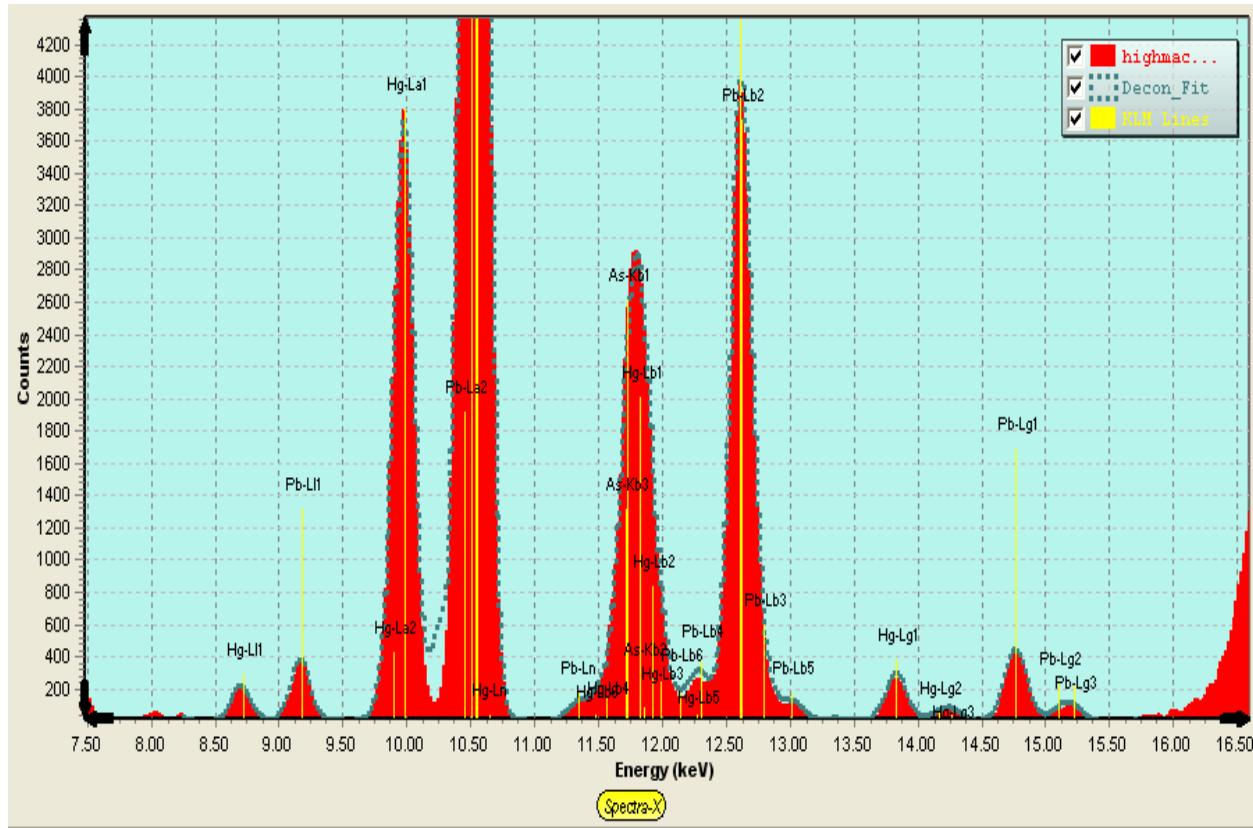
The example below shows the fitting to a rock sample spectrum, with fits to the Compton and Rayleigh peaks included in the display:



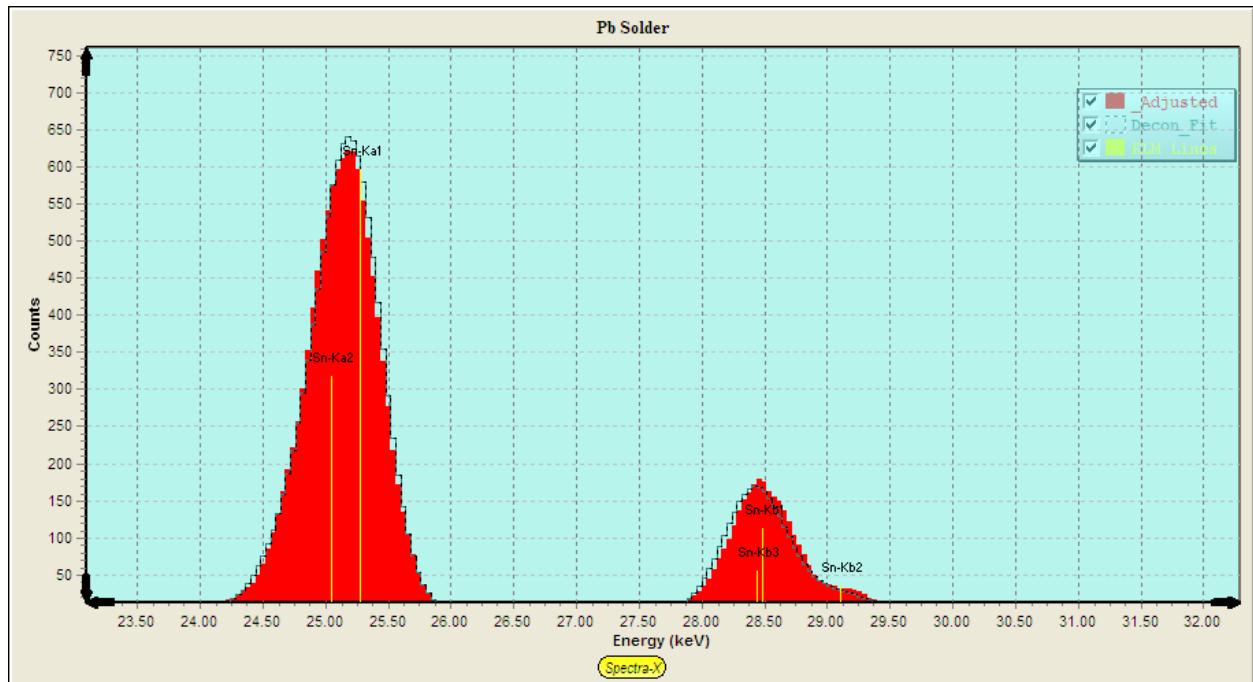
#### 14.3.10.3 Reference Deconvolution

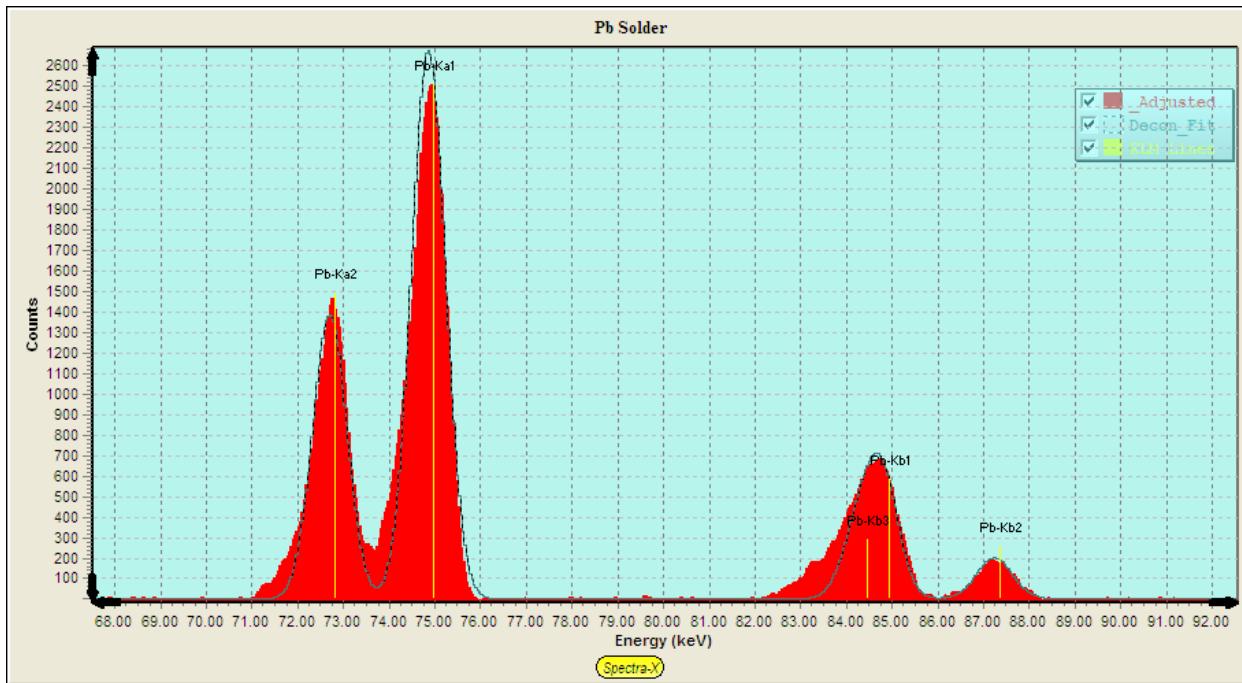
Now let's describe the use of the Reference deconvolution method, which is more complex to setup and use than the simpler Gaussian method, but may be useful in cases where the peak shapes deviate substantially from Gaussian shapes – this is usually in the form of low-energy tailing on the left side of peaks, such as is typically found with CdTe detectors. The details of the initial setup are described in the Setup-Reference section earlier in this manual.

After the reference library and profiles have been setup, you can use the software in exactly the same way as for the Gaussian deconvolution. A typical spectrum fit around the Pb-L, Hg-L, As-K peaks, using a reference library, is shown below:



It is interesting to compare this with a spectrum processed using nonlinear Gaussian deconvolution. This spectrum was taken with a CdTe detector, which has good Gaussian peaks for the Sn-K series, but much worse for the Pb-K peaks at higher energies, where there is severe hole tailing.





Both deconvolution methods can produce good fits. The nonlinear method allowed for peak shift, width and line ratio changes, but does not fit the low-energy tail region, for the Pb-K peaks.

As stated before, the Reference deconvolution, which is a linear process only, is good for modeling non-Gaussian peak shapes, but less tolerant to changes in peak shapes, positions and line ratios, although the latter may not always be the case if the Reference profile matches closely to the line ratios obtained in the typical samples to be analyzed.

#### 14.3.11 Process Spectrum - All

This option performs all of the spectrum processing steps selected in the Condition Table for the current condition, each step operating as described above.

#### 14.3.12 Process Spectrum - Restore

This option restores the original spectrum in the S1 group (Bars), before any spectrum processing had been performed (i.e., at the time the Load Spectrum was performed).

## 14.4 Process Analyze

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 commands, this command will convert the elemental intensities to composition using the FP library and other information described above.

After this command is finished (and it can take up to a minute or more for complex FP calculations), the elemental and component compositions will be updated, and the TFR report file can be printed and/or saved. The FP method itself is relatively straightforward at this point, producing the results using the calibration coefficients, or possibly standardless for samples with a known thickness.

An example of the output from a standardless analysis is shown below (note that all the calibration coefficients (TCC values) are set to zero for standardless analysis).

Specimen Component Table:										Thickness Information:							
#	Component	Type	Conc.	Error	Units	Mole%	Error			Layer	Normalize						
1	Cr	Calc	14.7405	0.2079	wt.%	31.9199	0.0000										
2	As	Calc	18.4087	0.1304	wt.%	27.6655	0.0000										
3	Pb	Calc	36.9889	0.4727	wt.%	20.0994	0.0000										
4	Cd	Calc	8.0696	0.8491	wt.%	8.0828	0.0000										
5	Hg	Calc	21.7923	0.3895	wt.%	12.2324	0.0000										

Element Table:										Global Threshold Settings							
#	Element	Cond	Measurement					Threshold	Intensity	Ratio	ROI (keV)		Chi2	Quant	Calibration		
#	Elmt	Line	Code	Intensity	Error	Backgr.	Conc.	Error	MDL	Atom%	Value	Conc	Method	Method	Low	High	Fit
1	Cr	Ka	1	565.39	7.97	2.19	14.740	0.208	0.0132	31.920	0.000	✓	Reference	None	5.308	5.521	0.24
2	As	Ka	1	2347.71	16.64	258.63	18.409	0.130	0.0430	27.666	0.000	✓	Reference	None	10.417	10.670	0.78
3	Cd	Ka	1	23.96	2.52	9.83	8.069	0.849	0.3604	8.083	0.000	✓	Reference	None	23.007	23.340	0.12
4	Hg	La	1	826.36	14.77	45.87	21.792	0.389	0.0610	12.232	0.000	✓	Reference	None	9.864	10.113	0.41
5	Pb	La	1	1384.67	17.69	258.63	36.989	0.473	0.1467	20.099	0.000	✓	Reference	None	10.425	10.678	0.38

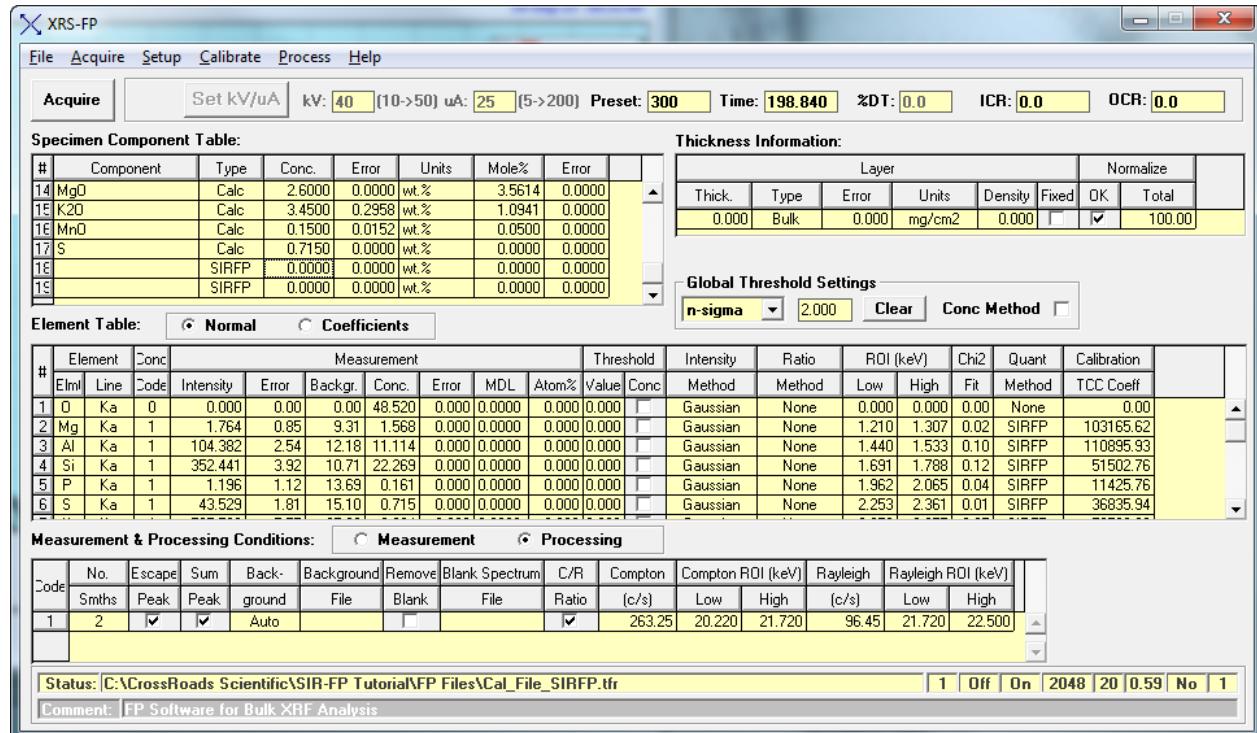
  

Measurement & Processing Conditions:										Processing							
Code	X-Ray Source				Detector				Chamber		Time (secs)		Monitor				
	Target	Filter	mg/cm <sup>2</sup>	KV	uA	Type	Filter	mg/cm <sup>2</sup>	Atmos	Preset	Actual	Intensity					
1	Ag	None	0.000	30.0	10.0	Sipin	None	0.000	Air	100.0	40.200	0.0					

The empirical LSQ quantitative method does not use all the information about a sample and only relies on simple calibration coefficients from the standards calibration. In particular the LSQ method does not care about the concentrations units, but just converts intensities using the empirical calibration coefficients. An example of the output when using the LSQ method is shown below, including the coefficients used to convert the intensities to concentrations in the Element Table.

#	Element	Cond	Measurement				Threshold	Quant	Calibration						
			Elmt	Line	Code	Intensity	Conc.	Value	Conc	Method	TCC Coeff	Coeff.Error	CC	CC2	CC3
1	Se	Ka	1	0.19235	0.390	0.000	□	LSQ	0.00	0.00	0.00000	0.00000	2.02544	0.00000	
2	Br	Ka	1	108.50100	202.431	0.000	□	LSQ	0.00	0.00	0.00000	0.00000	1.86571	0.00000	
3	Hg	La	1	0.00612	0.027	0.000	□	LSQ	0.00	0.00	0.00000	0.00000	4.48833	0.00000	
4	Tl	La	1	0.00386	0.016	0.000	□	LSQ	0.00	0.00	0.00000	0.00000	4.26114	0.00000	
5	Bi	La	1	0.00000	0.000	0.000	□	LSQ	0.00	0.00	0.00000	0.00000	3.74936	0.00000	

When using the SIR-FP method, estimates are made for the unanalyzed fraction of a sample by comparing the known fraction of analytes with the measured C/R ratio and ascribing the remainder to a pair of elements that bracket the estimated mean atomic number. You must either select those elements manually or let the software choose them, in which case you make blank entries in the Component Table.



During the SIR-FP calculations these elements are assigned automatically. In the next screen the elements O and F were assigned automatically during the SIR-FP analysis:

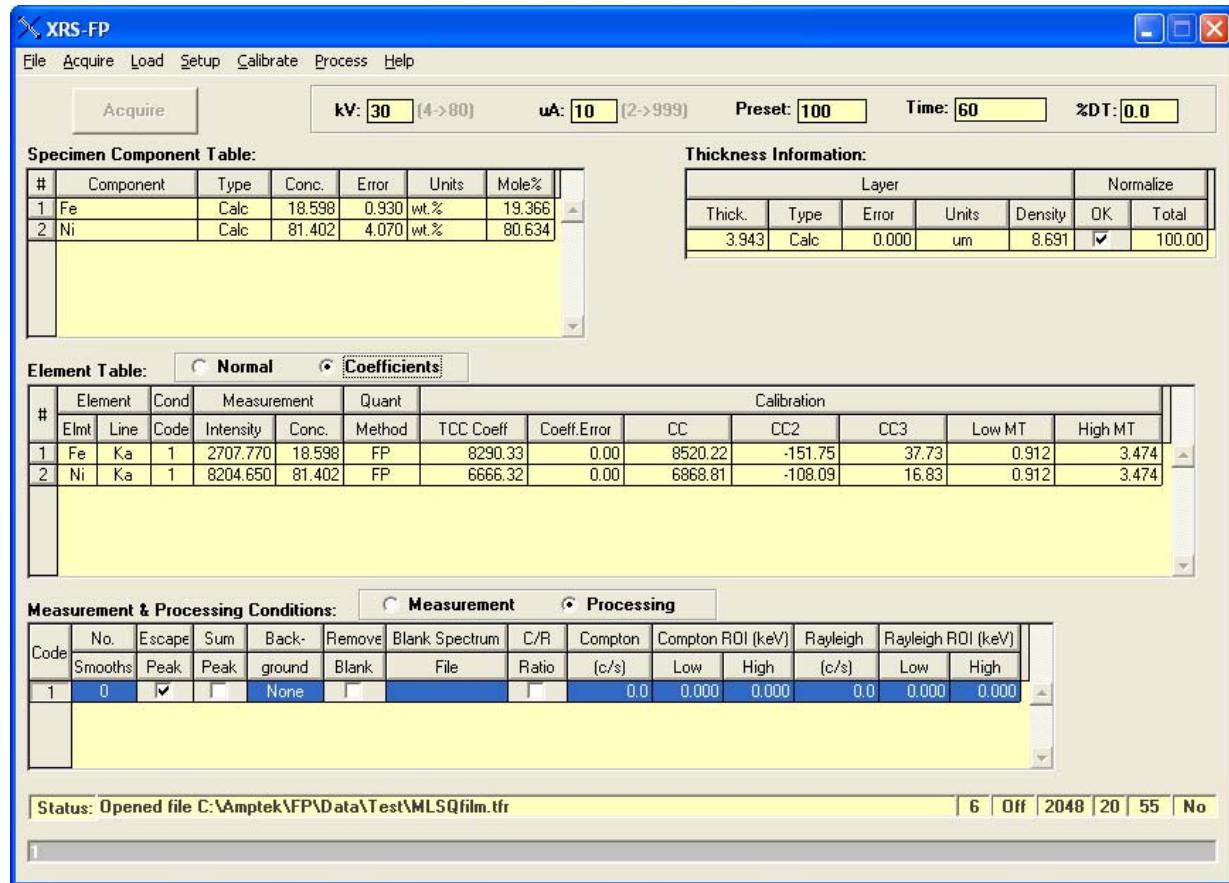
Specimen Component Table:								
#	Component	Type	Conc.	Error	Units	Mole%	Error	
14	MgO	Calc	2.6000	0.0000	wt.%	3.5614	0.0000	
15	K2O	Calc	3.4500	0.2958	wt.%	1.0941	0.0000	
16	MnO	Calc	0.1500	0.0152	wt.%	0.0500	0.0000	
17	S	Calc	0.7150	0.0000	wt.%	0.0000	0.0000	
18	O	SIRFP	0.0000	0.0000	wt.%	0.0000	0.0000	
19	F	SIRFP	0.0000	0.0000	wt.%	0.0000	0.0000	

In the next example, the sample was known to contain a residual matrix mostly of H and N, and so these 2 elements were added to the Component Table (fixed) before the SIR-FP analysis took place:

Specimen Component Table:								
#	Component	Type	Conc.	Error	Units	Mole%	Error	
14	MgO	Calc	2.5450	1.7366	wt.%	2.4630	0.0000	
15	K2O	Calc	3.3718	0.0540	wt.%	1.3962	0.0000	
16	MnO	Calc	0.1466	0.0056	wt.%	0.0806	0.0000	
17	S	Calc	0.6992	0.0412	wt.%	0.9505	0.0000	
18	H	SIRFP	0.0000	0.0000	wt.%	19.1803	0.0000	
19	N	SIRFP	0.0000	0.0000	wt.%	33.0062	0.0000	

In the final variation on FP analysis, the MLSQ calibration method may be used to analyze samples on a routine basis. Once a calibration has been performed (see Calibrate-MLSQ section), creating a TFR file with the MLSQ secondary coefficients embedded, then a subsequent sample analysis can be performed using this file in the same way that any other FP analysis is performed.

The next example shows a TFR file that was analyzed after Calibrate-MLSQ-FP and shows the various secondary calibration coefficients as well as the normal TCC coefficients.



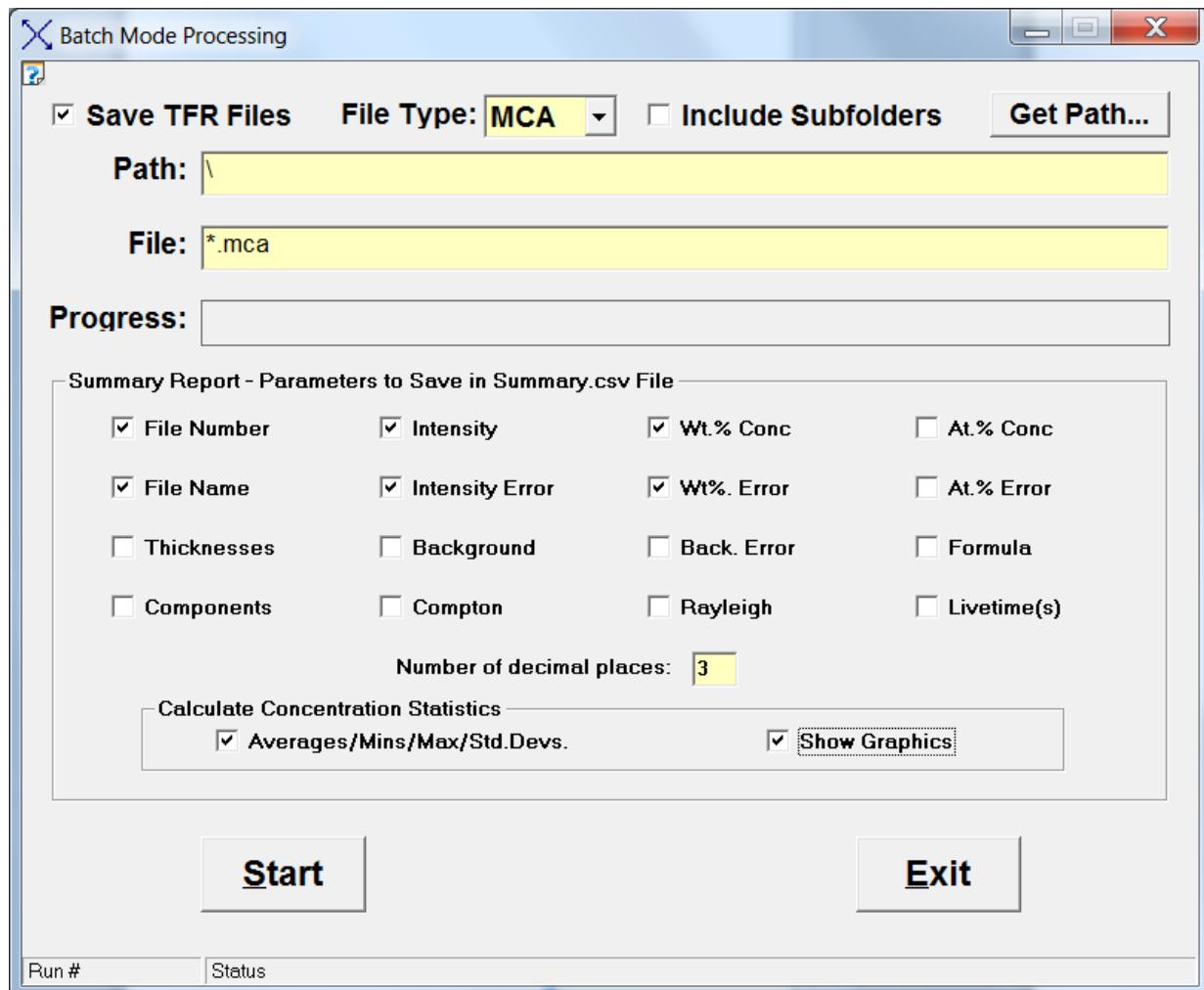
This example, calculated using model number 6 (see status bar), has all the secondary coefficients defined, along with the average TCC value for each element. In other words, this is a copy of the coefficients seen in the Calibrate-MLSQ-FP panel. Although these coefficients do not get saved in the LSQ calibration file for MLSQ, it is possible to save them in a TFR file by saving a TFR file after doing subsequent analysis.

## 14.5 Process Batch

This is a feature that allows for batch processing of existing spectrum files. An example of this screen is shown in the following figure and allows you to select various options for the results that are calculated, and whether you want a graphical display of those results. You must choose a path and folder that contains all the spectra for processing, and then choose the type of spectrum file (e.g., the file extension - \*.mca, etc.). Care should be used when using the \*.csv or \*.txt spectrum file types that all the files in the directory are true spectrum files.

The spectrum files will all be processed using the currently loaded TFR file, and a matching TFR file created and saved for each analysis, if the Save TFR option is checked, along with a summary of all the results in the summary.csv file.

A similar option (the Show Graphics checkbox) is available in the Auto-Mode analysis screen; except that in this case the spectra are collected live through the interface from XRS-FP to the acquisition electronics. If the TFR file type option is selected in Process-Batch, then only existing TFR files will be processed, and no spectrum processing is required.

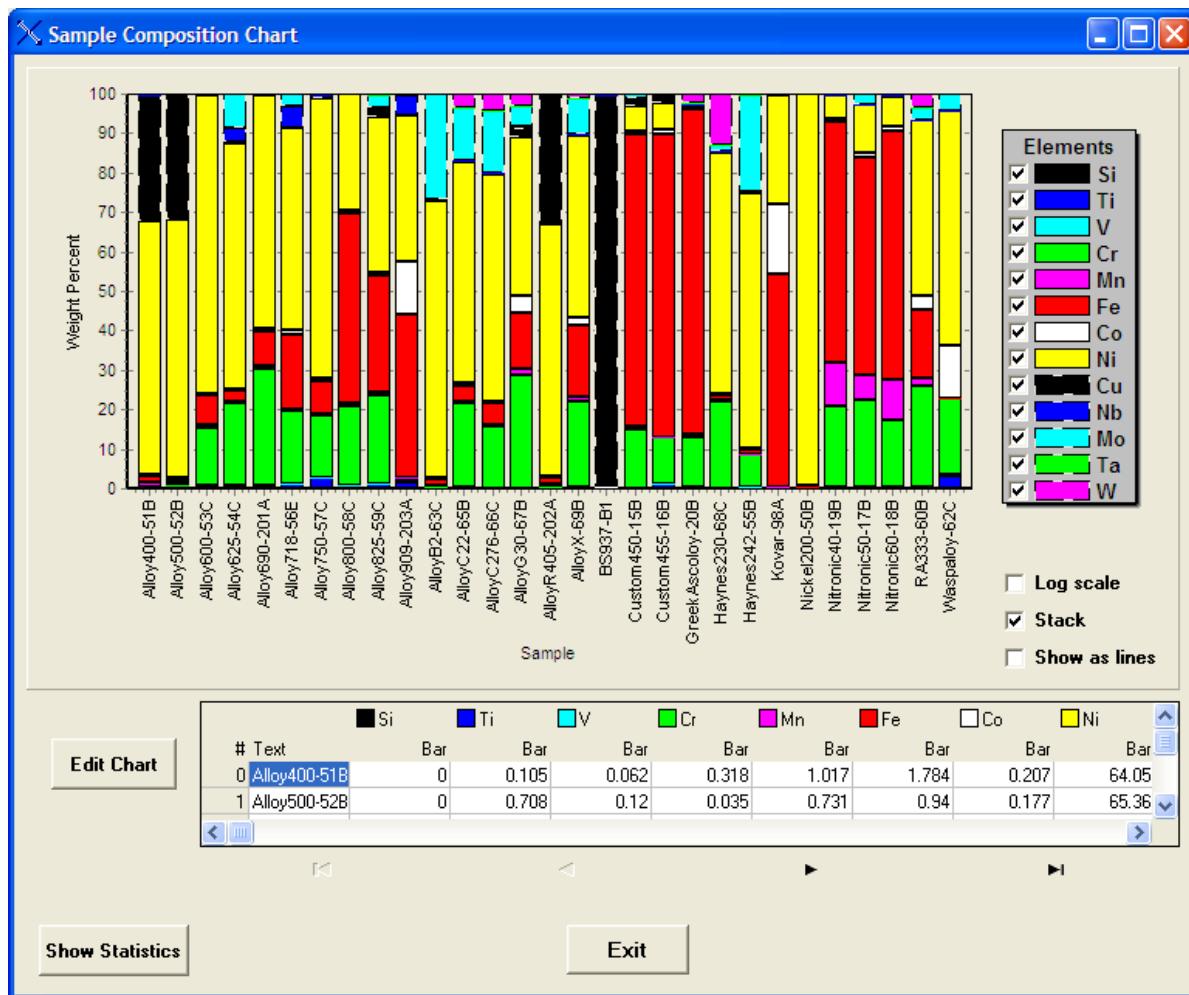


A new option in v.5.9.9 now allows the user to process a series of subfolders in the selected path instead of the files in the path folder itself. Each subfolder in the main path will be treated as a separate batch process. You should not have any files at the next level up or down as they will not be processed.

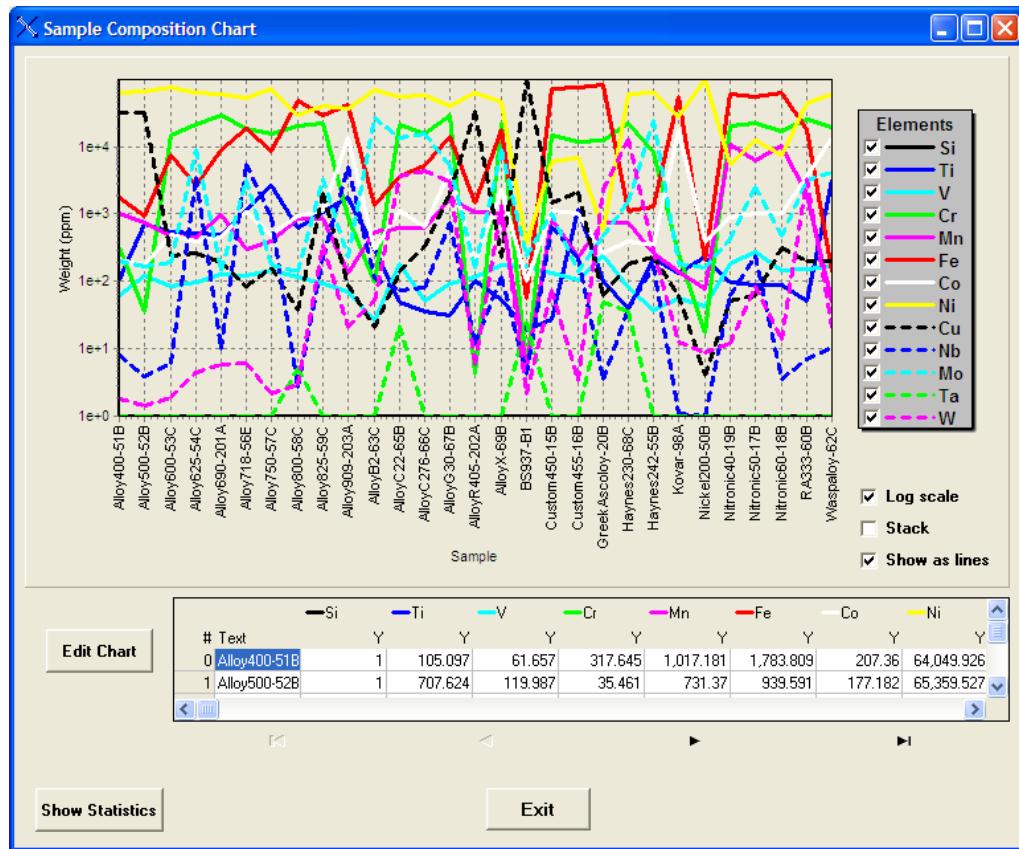
Conversely, if this option is NOT selected then the files in the selected path are processed as a group, as before. Each subfolder gets a separate summary.csv file.

There are various options (checkboxes) that can be selected prior to starting the Process-Batch (as shown above). When checked, each of these parameters is saved in file summary.csv. This file can be opened later in Excel or WordPad.

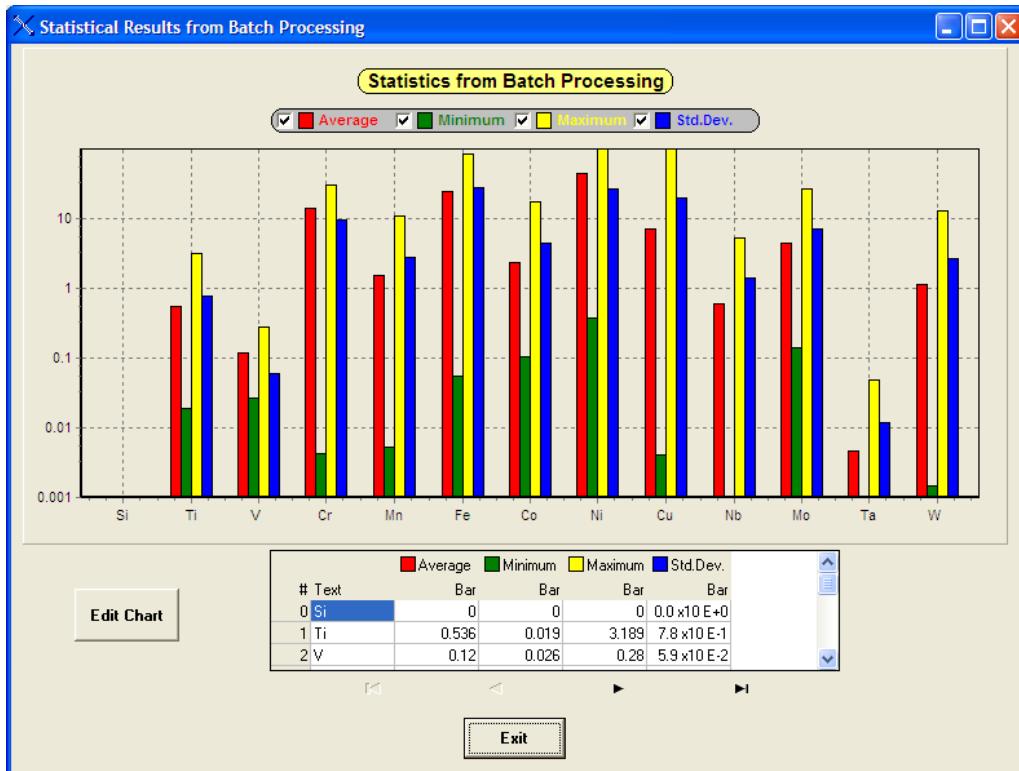
The Show Graphics option allows viewing after the batch processing of the results, directly in XRS-FP. An example of a stack composition chart from a Process-Batch run is shown in the following figure:



This chart may also be displayed in different ways. The following figure shows the same plot, but unstacked and on a log scale with lines instead of bars:



Clicking on the Show Statistics button produces a chart such as the following figure. The calculated Averages, Minima, Maxima and Standard Deviations are shown as histogram bars for each element.



The above chart shows the minimum, maximum, average and standard deviation of the composition for each element in the sample set. Both charts also show a table containing the contents of each chart, in row-column format.

An example of the summary file that is output in CSV format (summary.csv) is shown below, captured from WordPad. This was processed with the option to calculate the statistics, as shown above.

XRS-FP Summary Report										
#	Filename	Ti-Conc	Cr-Conc	Mn-Conc	Fe-Conc	Co-Conc	Ni-Conc	Cu-Conc	Nb-Conc	Mo-Conc
1	Alloy400-51B	7.36E-02	0.2839543	0.8279535	1.931415	0.69	25.792	27.45842	7.22E-02	4.20E-02
2	Alloy500-52B	1.025859	2.09E-02	0.6825395	0.9833888	0	70.87936	26.28168	0.0386139	3.22E-03
3	Alloy600-53C	0.471009	14.98413	0.3454793	7.854084	1.16E-02	75.96549	6.52E-02	0.2314932	4.38E-02
4	Alloy625-54C	0.1654543	13.4769	0.3199241	1.97157	3.43E-02	43.43568	5.37E-02	33.35575	7.159985
5	Alloy690-201A	0.5869228	29.60245	0.5882359	9.521832	3.99E-02	59.45134	7.11E-02	8.09E-02	7.08E-03
6	Waspaloy-62C	4.96296	19.8539	4.78E-02	4.19E-02	14.11048	56.74712	5.81E-02	6.56E-02	4.025675
Stat.1,Average:										
Stat.2,Minimum:										
Stat.3,Maximum:										
Stat.4,Std.Dev.:										

These results look like the following figure when imported and formatted in Excel:

XRS-FP Summary Report										
#	Filename	Ti-Conc	Cr-Conc	Mn-Conc	Fe-Conc	Co-Conc	Ni-Conc	Cu-Conc	Nb-Conc	Mo-Conc
1	Alloy400-51B	0.074	0.284	0.828	1.931	0.000	69.258	27.458	0.072	0.042
2	Alloy500-52B	1.026	0.021	0.683	0.983	0.000	70.879	26.282	0.039	0.003
3	Alloy600-53C	0.471	14.984	0.345	7.854	0.012	75.965	0.065	0.231	0.044
4	Alloy625-54C	0.165	13.477	0.320	1.972	0.034	43.436	0.054	33.356	7.160
5	Alloy690-201A	0.587	29.602	0.588	9.522	0.040	59.451	0.071	0.081	0.007
6	Waspaloy-62C	4.963	19.854	0.048	0.042	14.110	56.747	0.058	0.066	4.026
Stat.1	Average:	1.214	13.037	0.469	3.717	2.366	62.623	8.998	5.641	1.880
Stat.2	Minimum:	0.074	0.021	0.048	0.042	0.000	43.436	0.054	0.039	0.003
Stat.3	Maximum:	4.963	29.602	0.828	9.522	14.110	75.965	27.458	33.356	7.160
Stat.4	Std.Dev.:	1.705	10.464	0.259	3.606	5.252	10.824	12.642	12.395	2.777

Of course, further manipulation of this data in Excel is now possible.

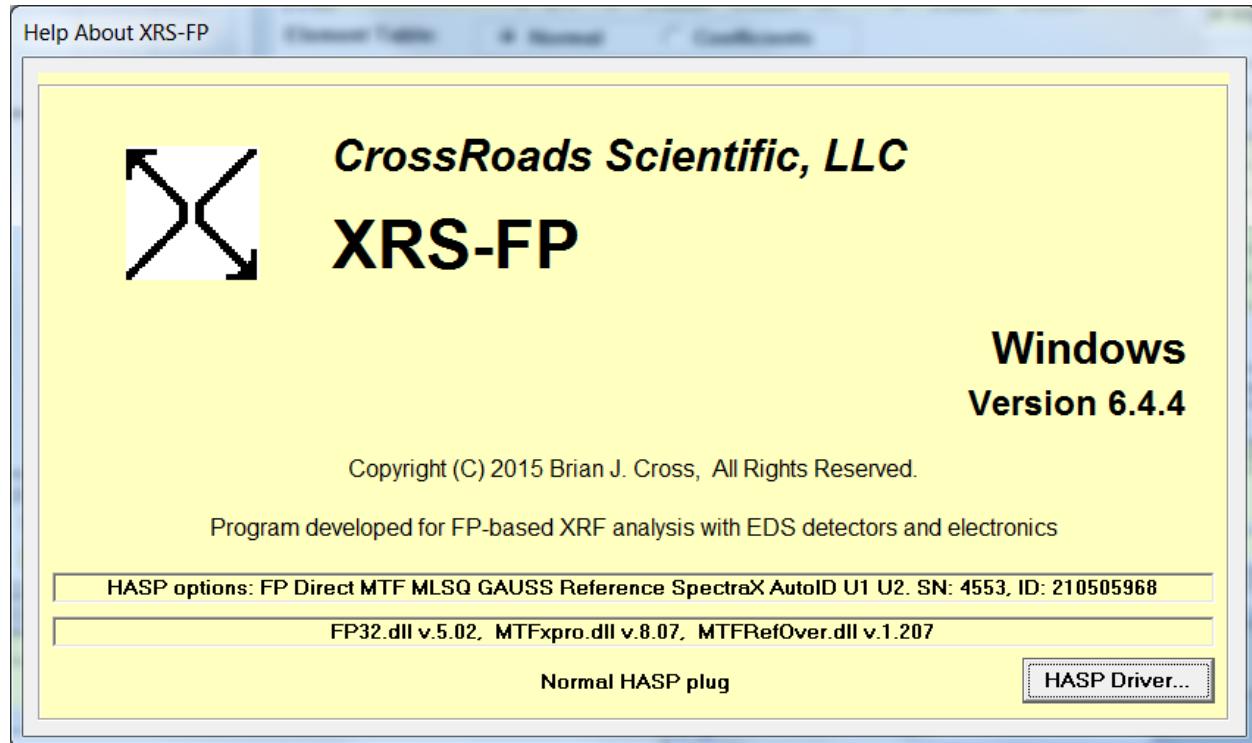
It is now possible to process multiple-condition analyses using the batch processing option. There are some necessary restrictions imposed on the filenames in order to make this work.

The "primary" filename is associated with condition code #1 - this is the default for single-condition analysis. Any other spectrum files must have 4 alphanumeric characters (\_CC2, \_CC3, etc.) appended to the root filename. For example, if you have a sample named Rock, then the default (CC1) spectrum would be named, say, "Rock.mca". Any additional spectra taken at different condition codes *must* be named "Rock\_CC2.mca", then "Rock\_CC3.mca", etc. Then these spectrum files are processed within a single TFR file and the final results analysis by the selected quantification method (e.g., FP).

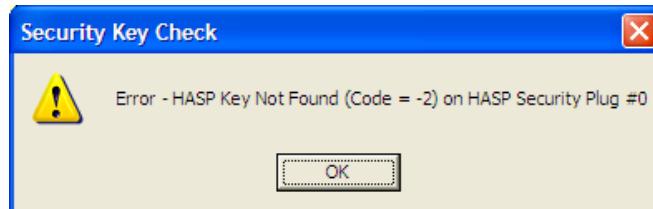
## 15 HELP ABOUT

This command shows the start-up “splash” screen, containing the version of the software and other information about the HASP security plug that is required in order to run the FP software.

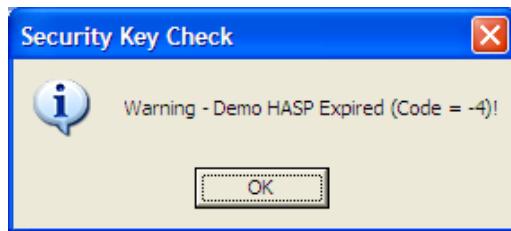
The HASP plug MUST be installed (see next section) to use the installed DLL's (FP32.dll, MTFxpro.dll, and MTFRefOver.dll). There are other options, such as the Spectra-X, MLSQ and MTFFP options that are only available in the software if the appropriate options are set in the HASP plug.



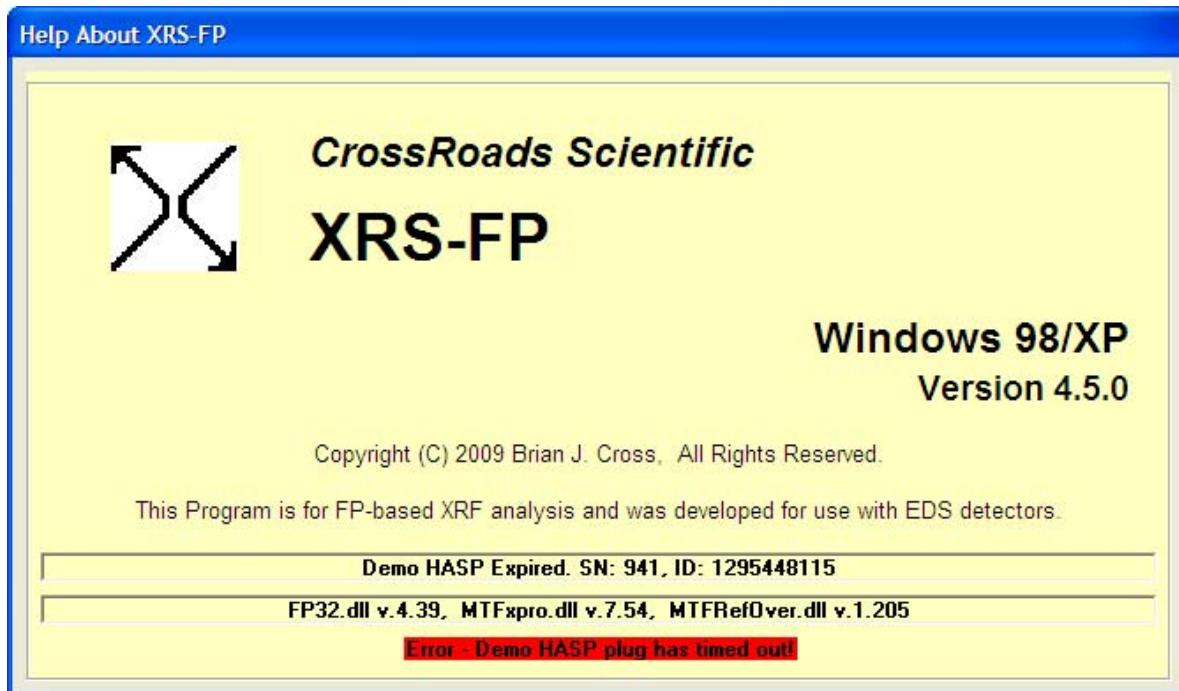
The Splash screen also shows the type of HASP plug (normal or demo, and whether it is a Net plug or not). If the HASP plug is bad or missing, then an error message such as the following will be displayed:



If the HASP is a demo plug then information will be displayed about the status of that plug, such as whether it is about to expire or not. If it has expired, you will get several warnings such as the following:

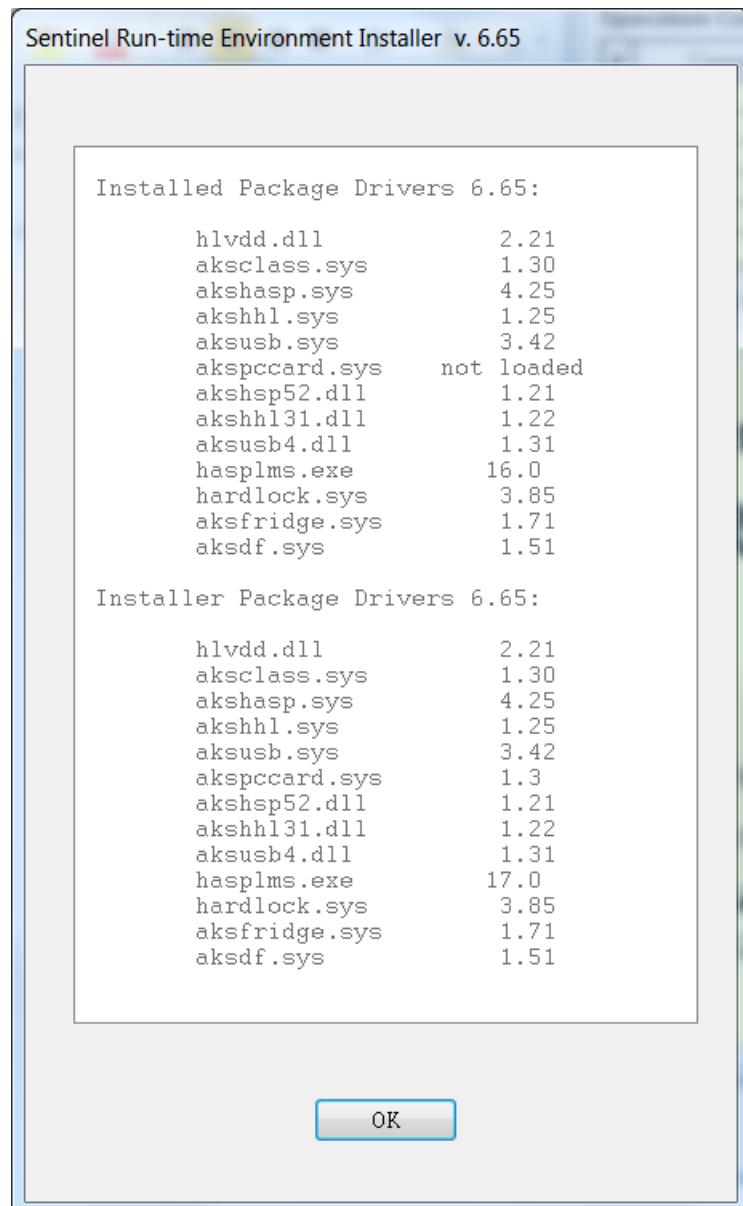


The Splash screen will then look like the following example:



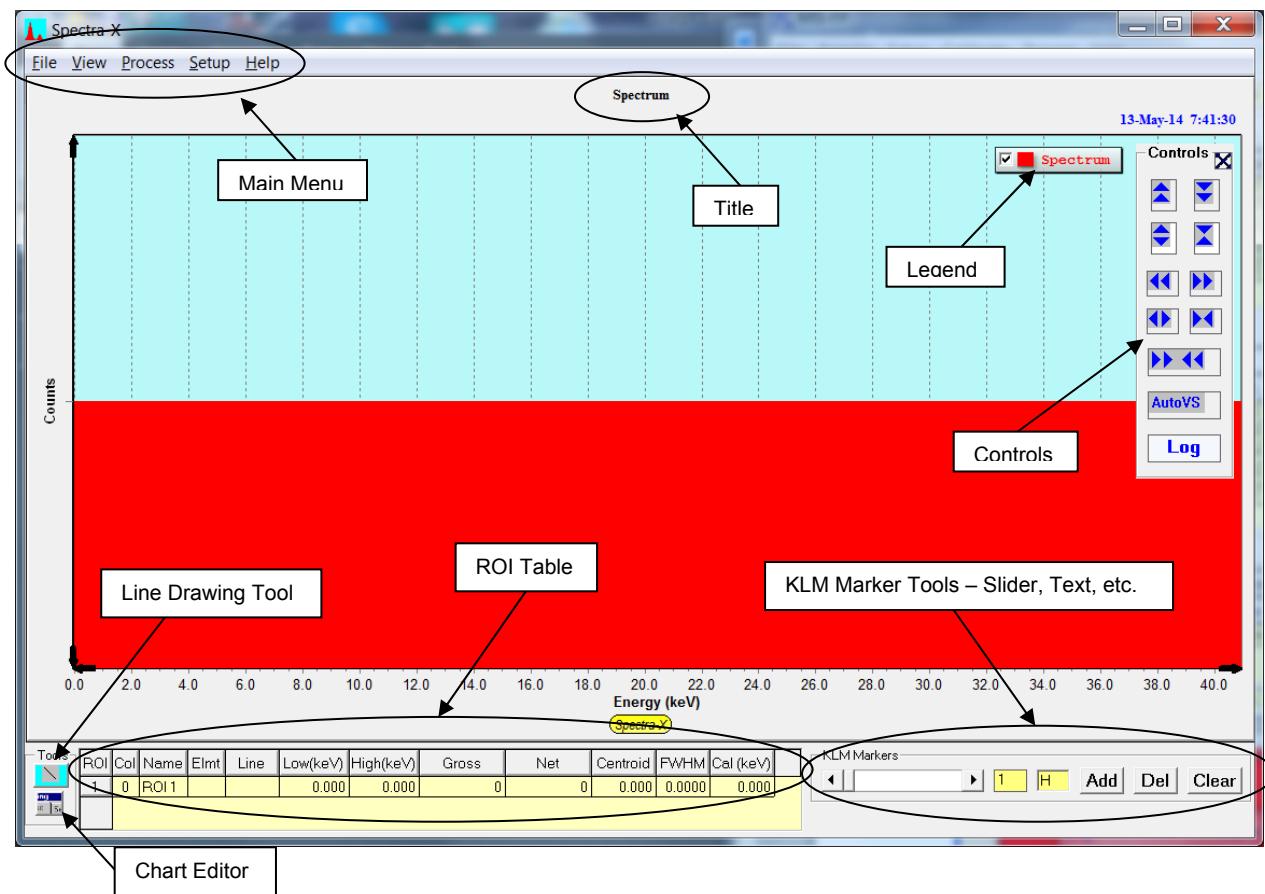
You should call your software supplier if you get any of these error messages.

Clicking on the "HASP Driver" button will check the HASP further and provide information about the current drivers, as shown below.



## 16 SPECTRA-X

Spectra-X is a separate Active-X DLL that has its own window and controls. This component is a slave to the main XRS-FP application and receives data from this host. This data is primarily spectral data, but can include formatting information and elemental information to allow the display of KLM markers, etc. The default screen on loading the software will be similar to the one shown as follows:



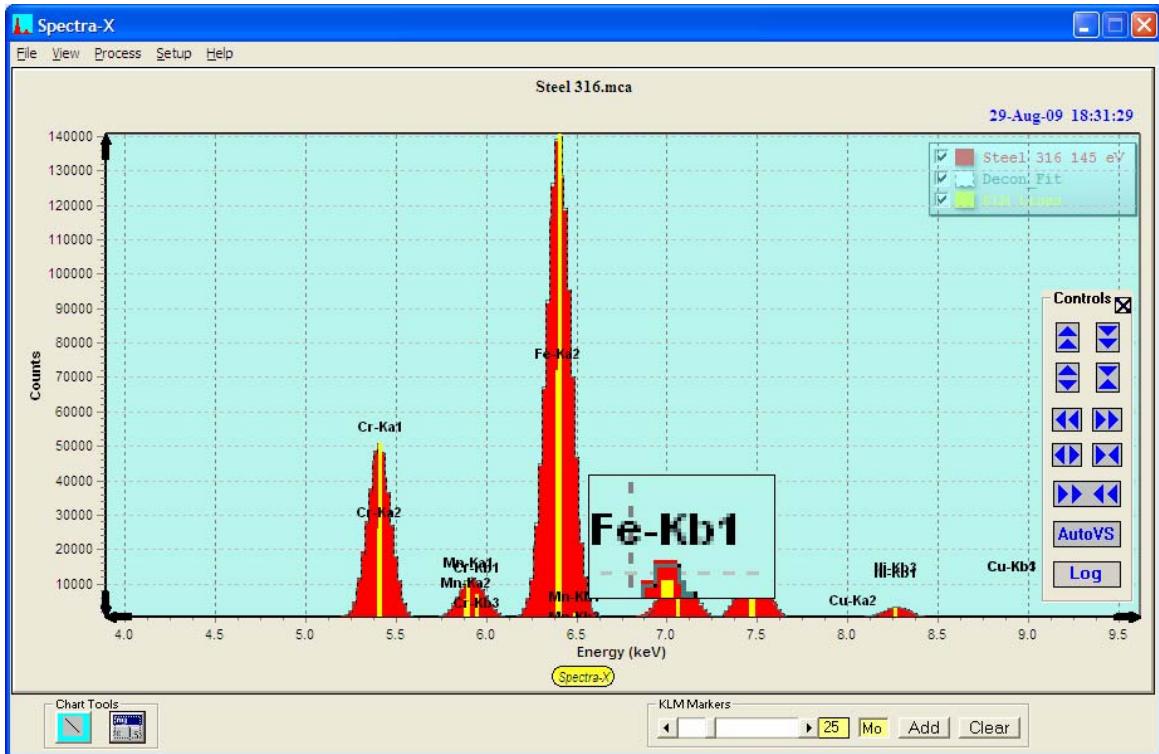
Several key areas are highlighted such as the Main Menu, the Spectrum Title, the Legend, the (Empty) Spectrum, the Line Drawing Tool, the Chart Editor, the ROI Table and the KLM Marker Tools. These will be described in more detail below. Note that the initial horizontal energy scale is setup and controlled by the host XRS-FP software, and so the number of channels and the energy scale must be setup in XRS-FP before reading spectrum files.

Each axis (horizontal and vertical) have controls that allow the spectrum to be scrolled in two ways. The black arrow keys move the display a small step at a time in the opposite direction to the arrow. Also you can click on either of the X or Y axis scales and drag the spectrum from side to side or up and down (do this slowly!).

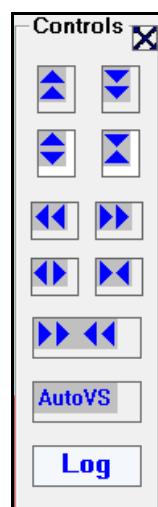
You can also draw a “rubber band” around an area of the spectrum you wish to expand by clicking in the chart area and dragging the cursor to the right and to the bottom. To unzoom the zoomed spectrum area,

simply reverse this rubber banding by dragging the cursor upwards and to the left, and then the complete spectrum will be re-displayed.

There is a magnifying glass tool that enables you to get a close-up view of a small part of the spectrum, as shown in the following example:

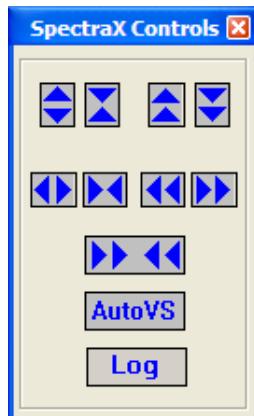


In addition, there is a floating control panel that is used to expand and contract the spectrum display in several ways, as shown below:

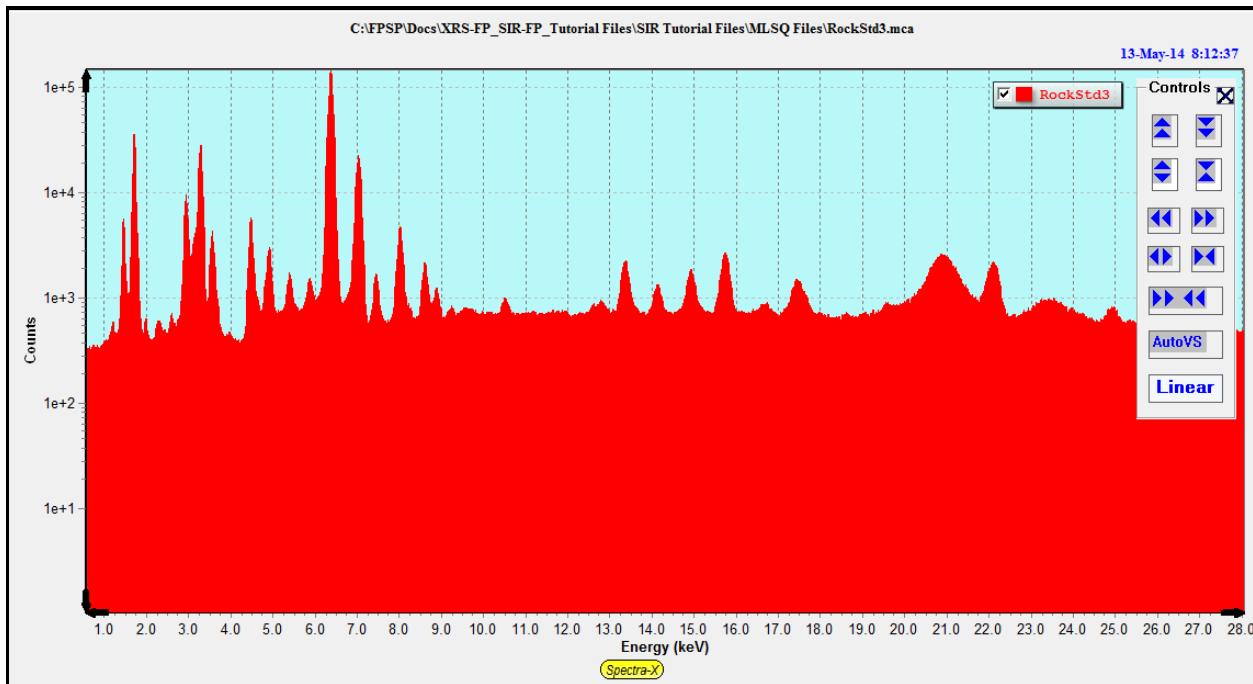


It can be dragged around the Spectra-X spectrum area.

Alternatively you can specify the Controls to be external to Spectra-X as shown below:

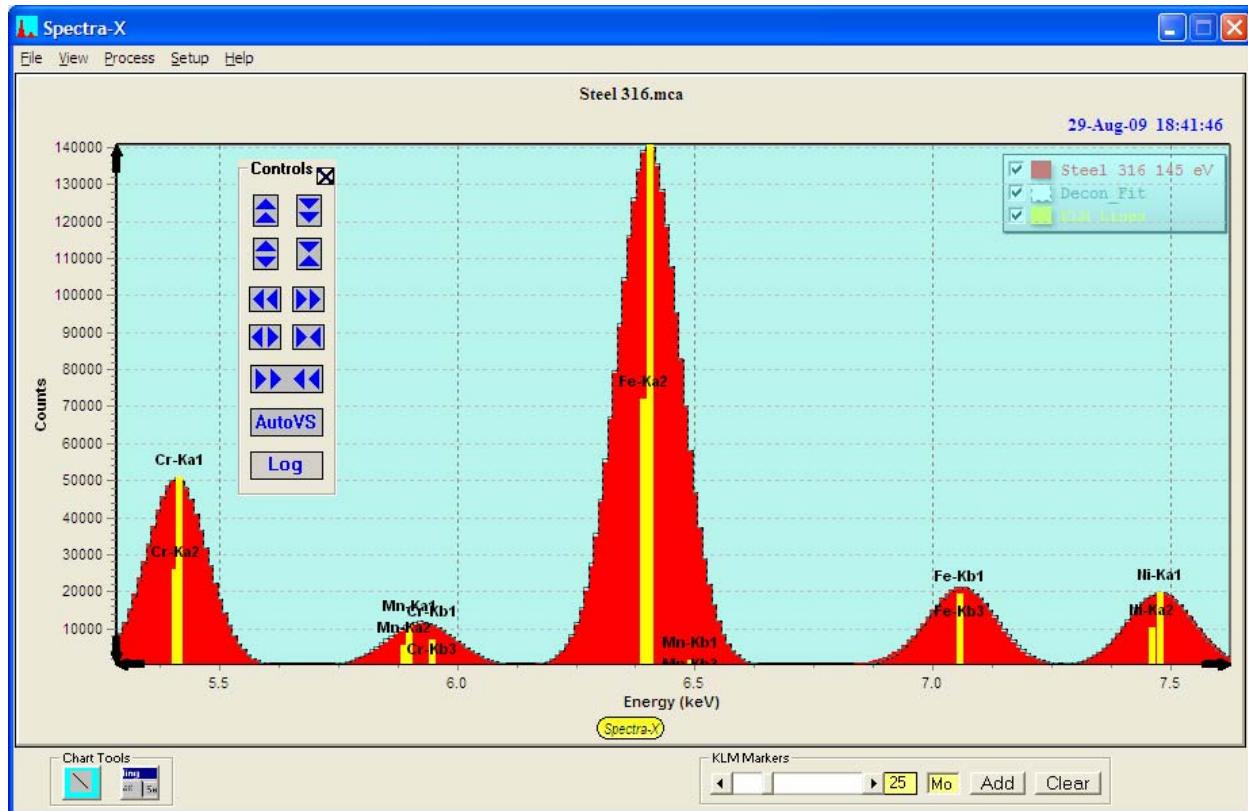


There are controls to expand and contract each axis, in either one or two directions, as well as the ability to scroll the horizontal axis, and to compress it to the maximum available. The AutoVS button displays the vertical axis so that the highest channel, in *any* spectrum, is shown on the chart. The AutoVS now toggles between scaling to the maximum channel in the spectra, to scaling to the maximum channel displayed, ignoring any channels not displayed on the panel. The Log button changes the vertical axis between to a log scale, as shown below:

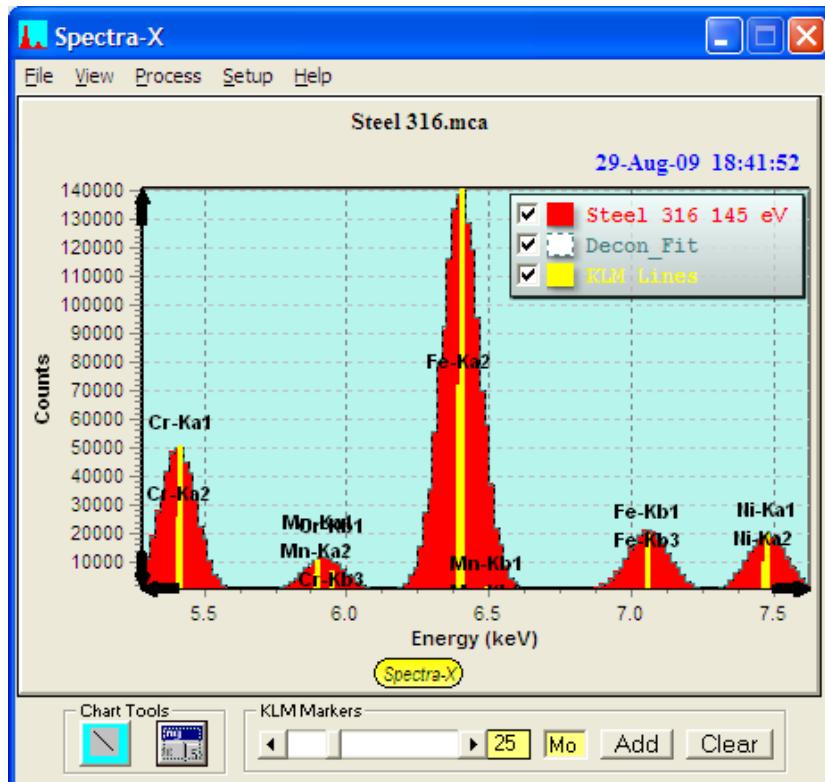


The button in the Controls panel changes to "Linear" and clicking the button again will return the spectrum display to a linear vertical scale.

The internal panel for the Spectra-X Controls can be placed anywhere on the spectrum chart area, as in the following example:



Both Controls can also be turned off. You can also resize the Spectra-X screen, as shown below:



## 16.1 File Menu

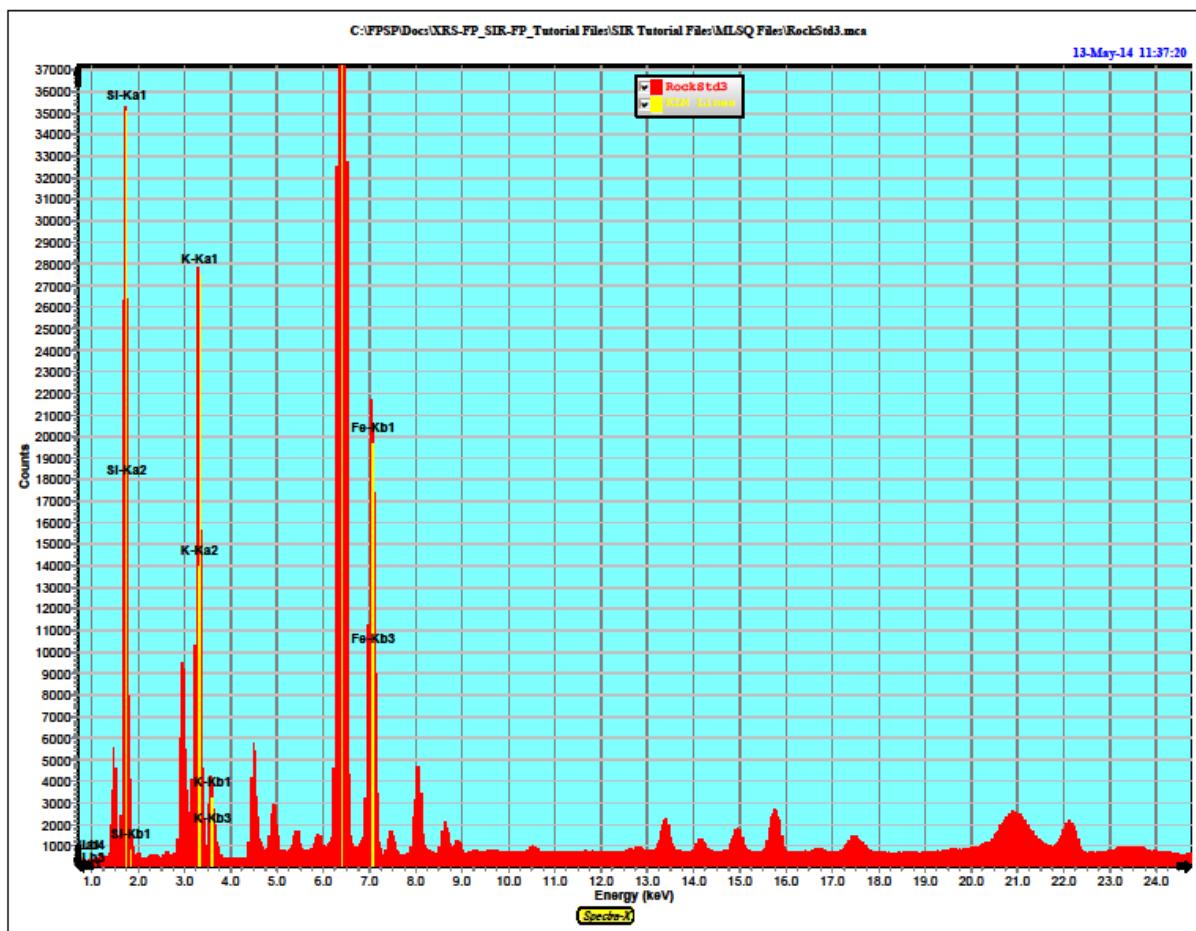
This section describes all the File menu options for the Spectra-X panel (not XRS-FP).

### 16.1.1 File-New

This command clears all currently loaded spectra and resets Spectra-X to its initial state, but with the x-axis set to Channels.

### 16.1.2 File-Print

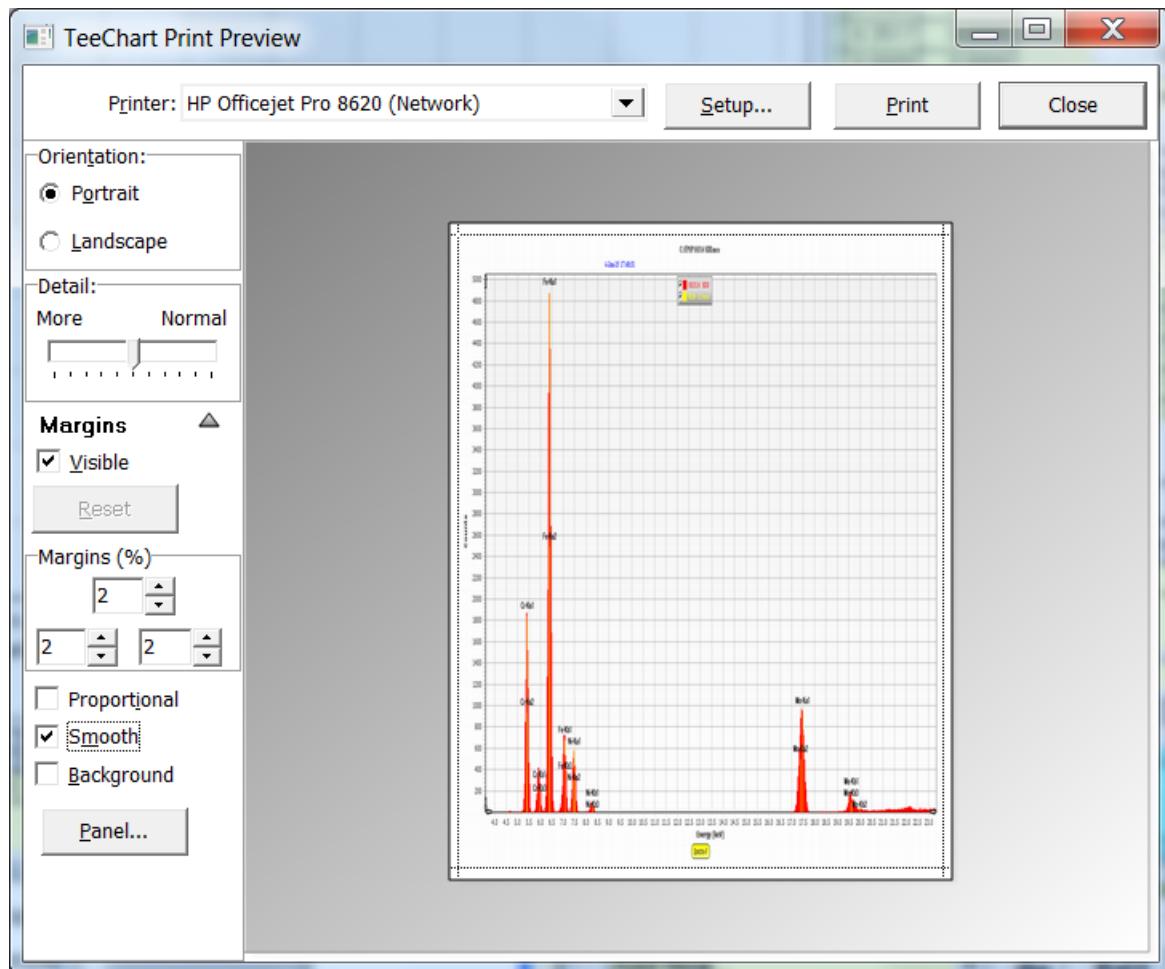
This option prints the current spectrum display to the default printer, using the default settings for the output. The printer properties should be setup in advance. The following example was printed to an Acrobat “printer” PDF file.



### 16.1.3 File-PrintPreview

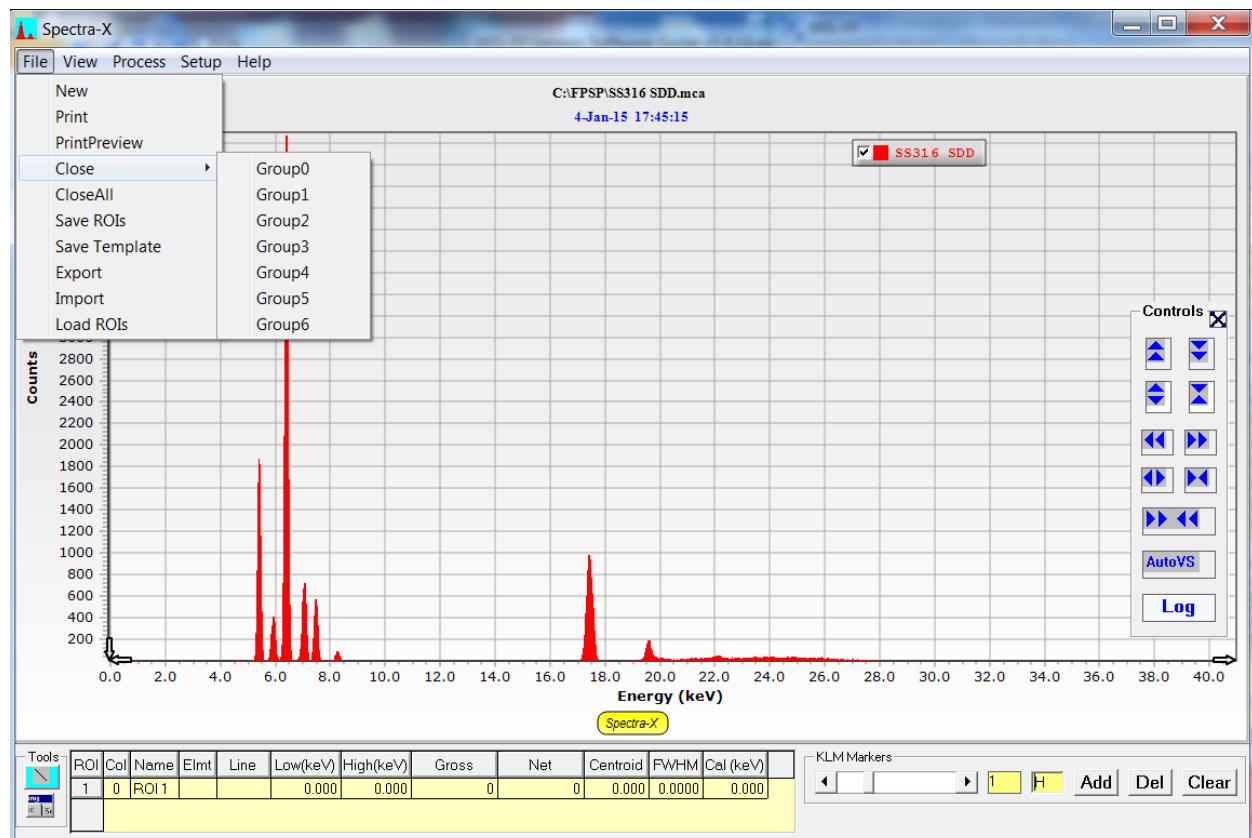
This option shows a miniature view of the spectrum display and allows the user to alter the settings such as the margins and print quality. This panel also allows the user to select and setup the printer to be used for subsequent printing.

The following is a typical dialog:



### 16.1.4 File-Close

This option allows the user to close any one of the groups. Group 0 is the Main group, and the others are the Compare groups. After being closed the group no longer has any spectral data in it, and the name is removed from the legend.



### 16.1.5 File-CloseAll

This option closes all of the spectral groups (0 through 6) and leaves a blank screen with a single empty spectrum.

### 16.1.6 File-SaveROIs

This option saves the contents of the current ROI Table to an ASCII text file. As an example, consider the ROI Table in the following spectrum panel (only some of which is visible):

ROI	Col	Name	Elmt	Line	Low(keV)	High(keV)	Gross	Net	Centroid	FWHM	Cal (keV)	
1	1	ROI 1	Ti	Ka	4.350	4.760	47870	34417	4.525	0.0980	0.000	▲
2	2	ROI 2	Cr	Ka	5.190	5.550	21016	5692	5.409	0.1488	0.000	▼
3	3	ROI 3	Mn	Ka	5.780	6.020	16084	3812	5.904	0.1186	0.000	

After saving this table information to a file, the file has the following contents:

```

ROI V1.00
"Number of ROIs",10
"ROI #","Color Index","Label","Elmt","Line","Low","High","Energy"
1,1,"ROI 1","Ti","Ka",4.35,4.76,0
2,2,"ROI 2","Cr","Ka",5.19,5.55,0
3,3,"ROI 3","Mn","Ka",5.78,6.02,0
4,9,"ROI 4","Fe","Ka",6.14,6.66,0
5,5,"ROI 5","Co","Ka",6.8,7.3,0
6,6,"ROI 6","Ni","Ka",7.371675,7.584724,0
7,7,"ROI 7","Cu","Ka",8.41,8.86,0
8,8,"ROI 8","Nb","Ka",15.42,16.06,0
9,9,"ROI 9","Mo","Ka",18.56,19.8,0
10,10,"ROI 10","W ","La",9.01,9.46,0
"Gauss Peak Fitting",1
"Net Channel Fitting",0

```

Each of the 10 rows in this table, contain the row number, color index (1-16), label, element, line, and the low and high energy of the ROI itself (in keV). The final column contains the theoretical energy of the ROI peak centroid if that has been defined (set by default to zero).

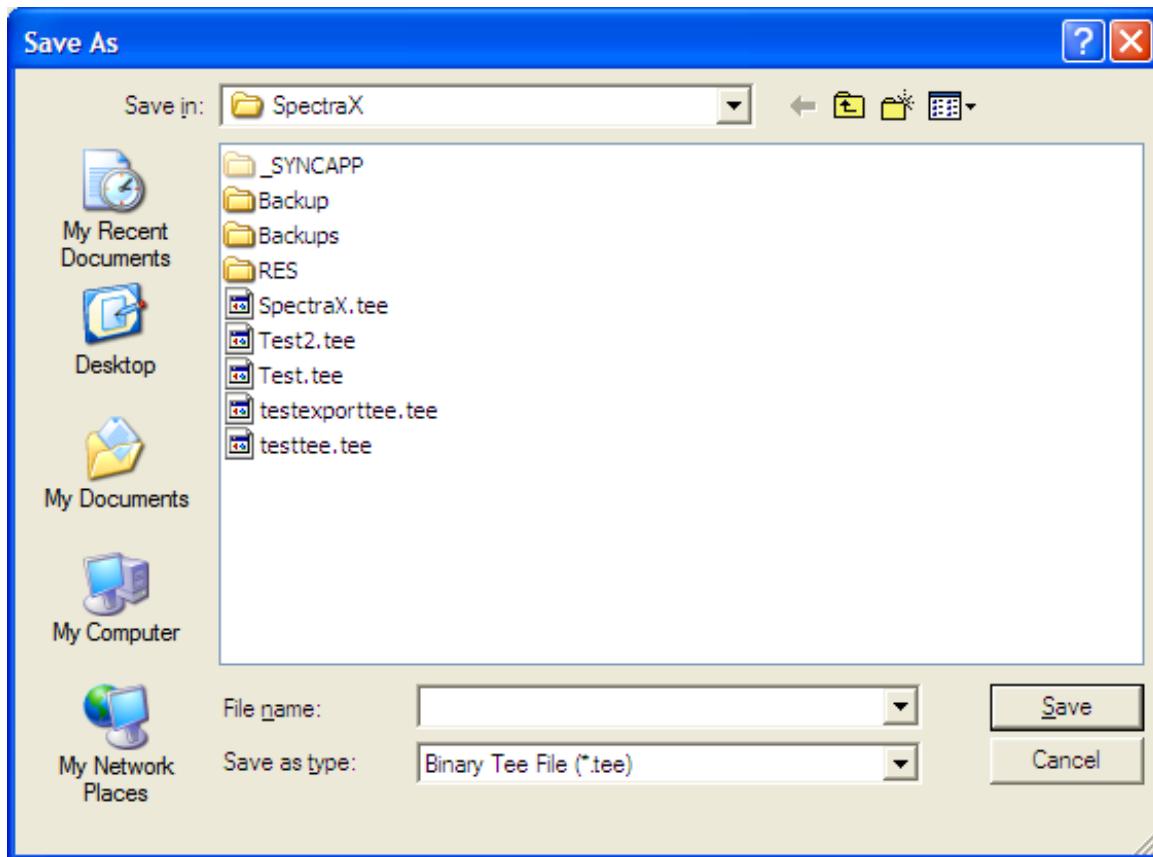
At the bottom of the file are two calculation method flags. The first item, when set to 1, instructs the Spectra-X panel to fit each ROI with a single Gaussian peak, and calculate the FWHM of that peak based on the Gaussian fit. If the flag is set to zero, then the FWHM is calculated by a simple centroid calculation using all the channels within the ROI.

The second item instructs the Spectra-X panel to use either the net channel counts (flag =1) or the gross channel counts (flag = 0), when calculating the FWHM value (using either the Gaussian or channel method).

### 16.1.7 File-SaveTemplate

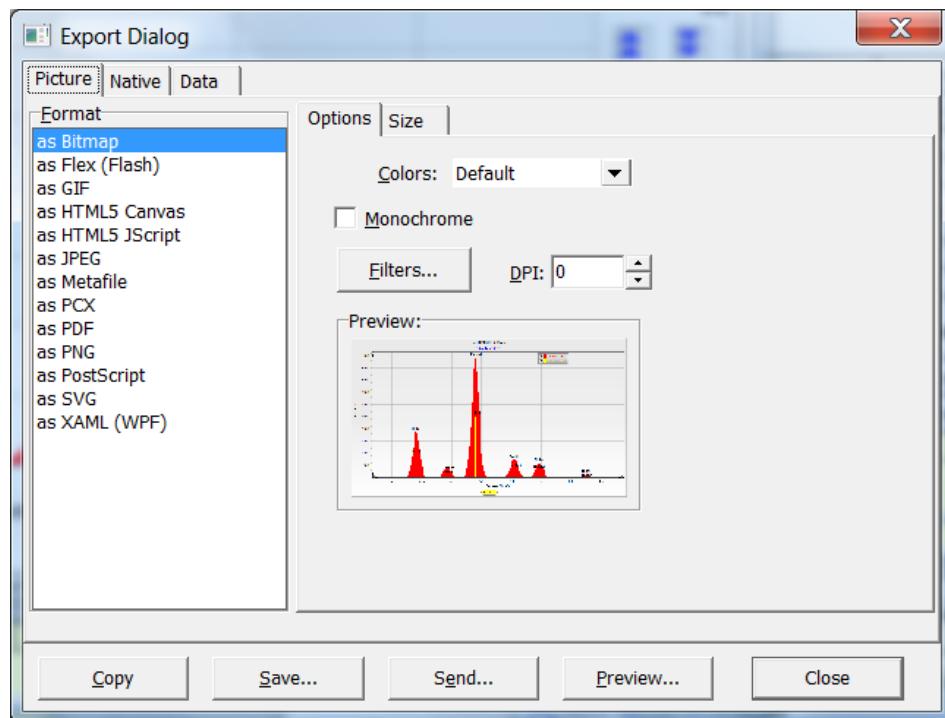
This option allows the user to define the look and feel of the Spectra-X panel, and then recall this template at a later date to setup the screen in the same manner. The default template is SpectraX.tee and it is created each time the software starts up, from the settings that are preprogrammed into the Spectra-X library.

The file type for the templates is the native \*.tee type. To re-load the saved template use the File-Import command (see below).

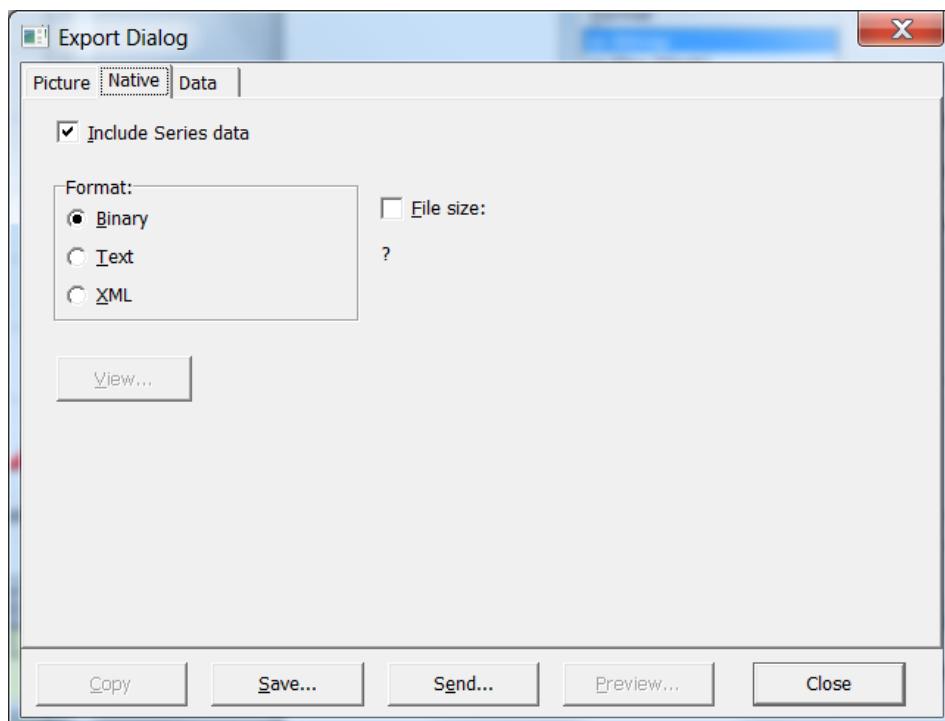


### 16.1.8 File-Export

This option allows you to export the spectrum display in many different formats, as shown below. This allows the creation of a graphics copy of the screen for inserting in documents, etc., or you can simply copy the graphic to the clipboard and then paste it directly into a suitable document (Word, etc.).

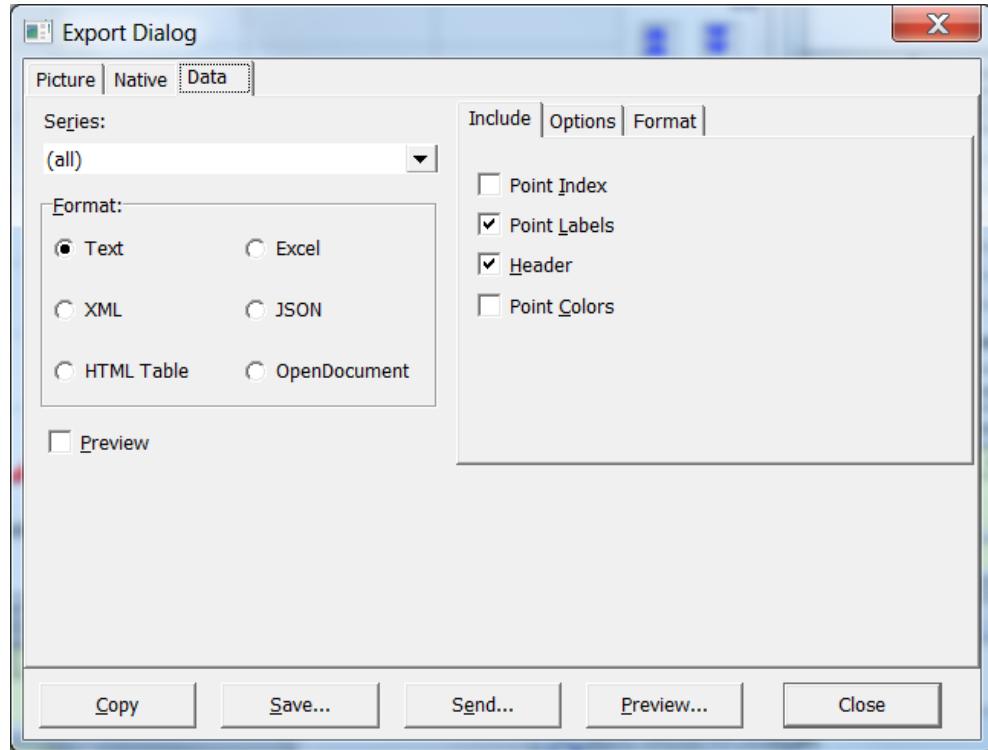


The Native tab provides a binary output form in TeeChart format, for the data displayed on the screen.



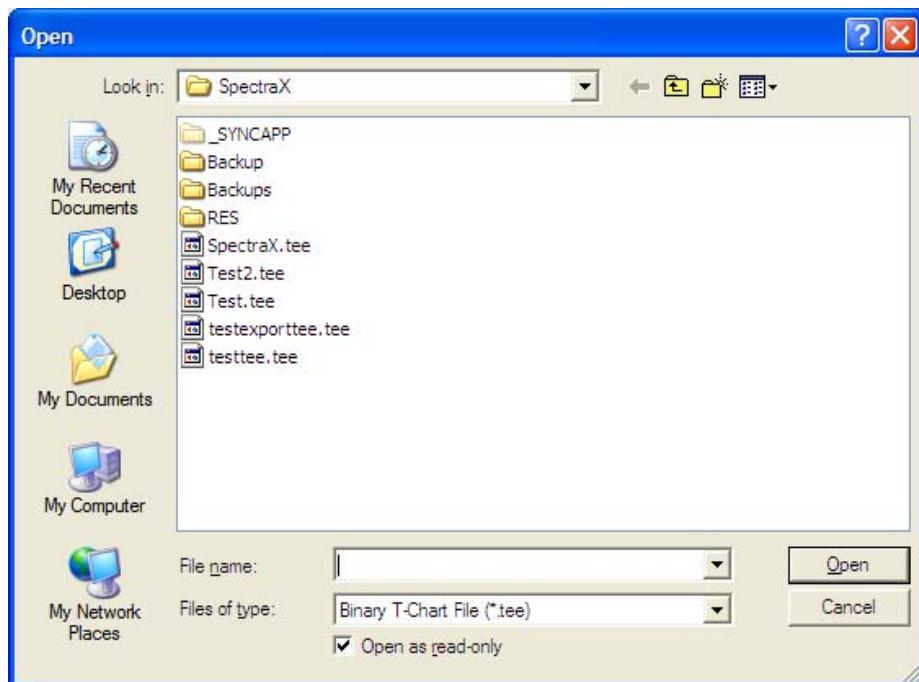
The native binary is the same as those created by the Save-Template command. There are 2 other types available, which are \*.txt and \*.xml files – these can be externally read and potentially edited (with care!).

Finally, the Data tab provides other options for exporting the complete spectra data in text and other formats:

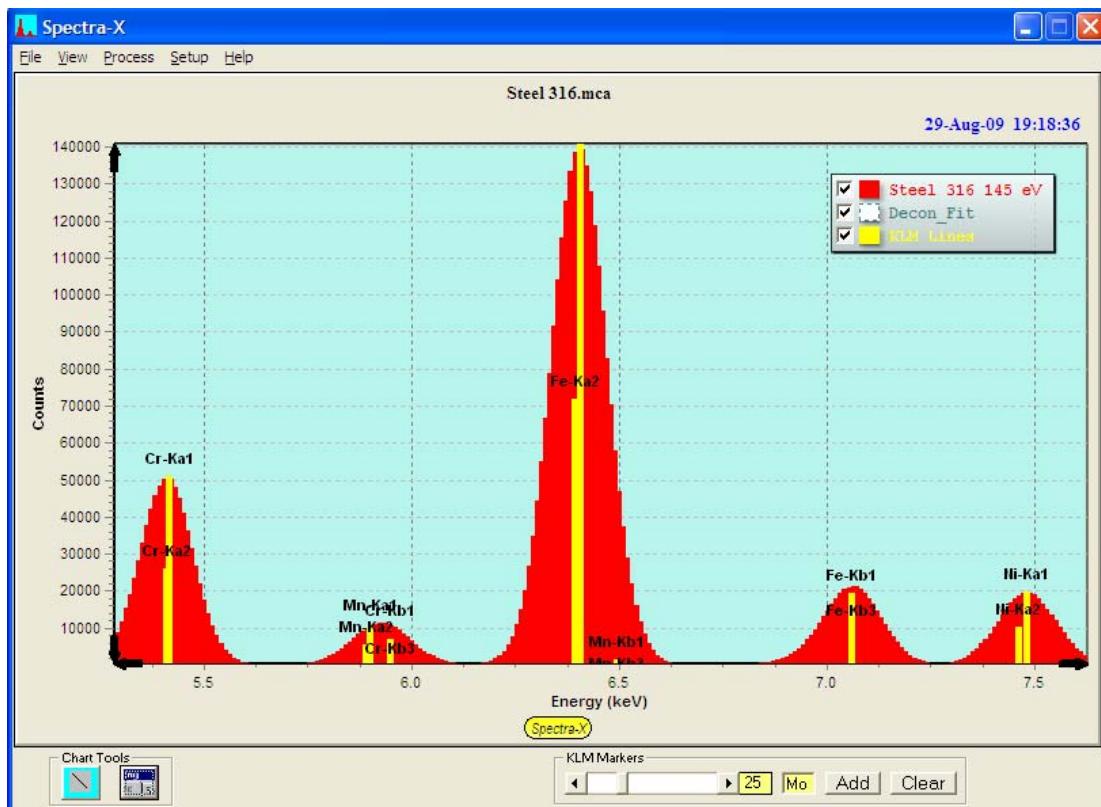


### 16.1.9 File-Import

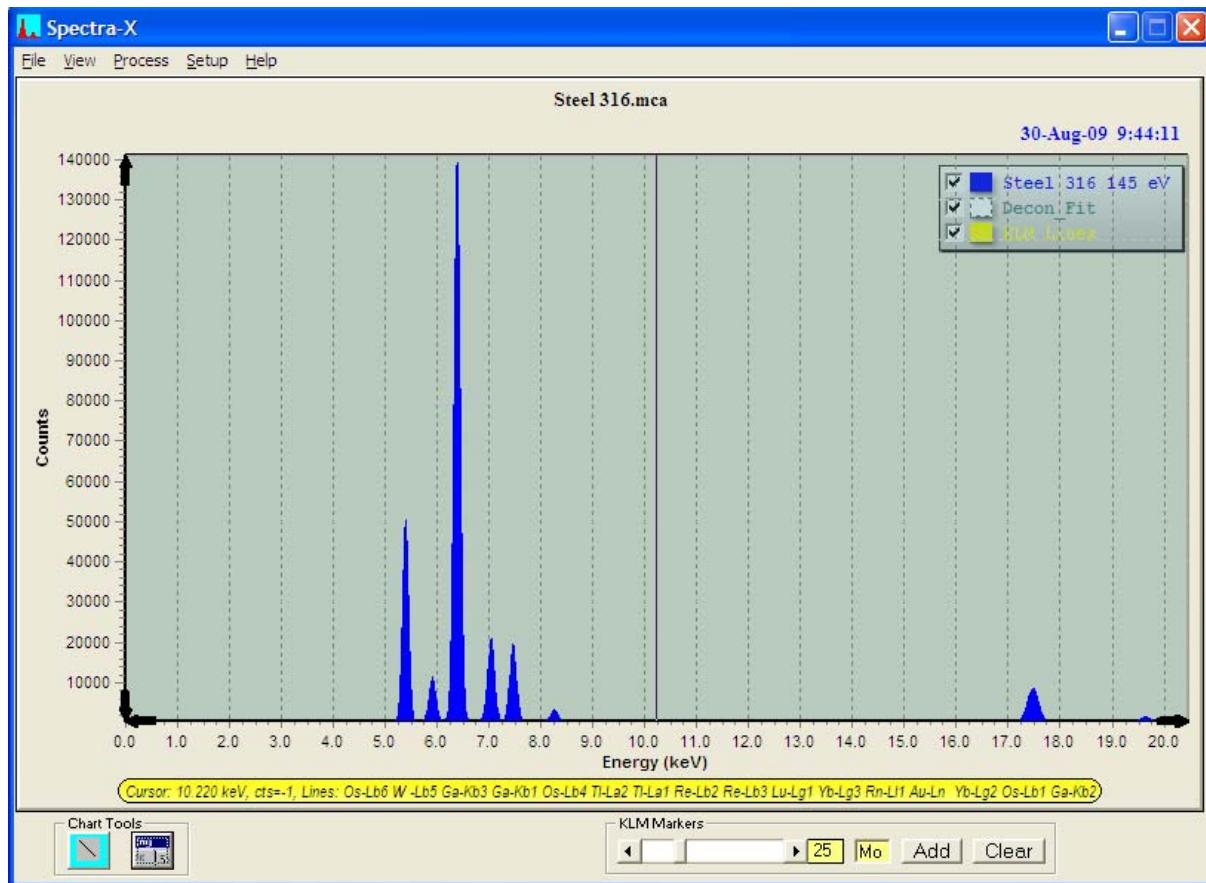
This feature is new in v.1.5.0 of Spectra-X. It enables the loading of previously saved template files that were saved with the File-Save-Template command (see above). An example of the displayed screen is showed below:



It is identical to the Save-Template panel except that it is a load (open) option. For example, the following screen is shown in the default (SpectraX.tee) style:



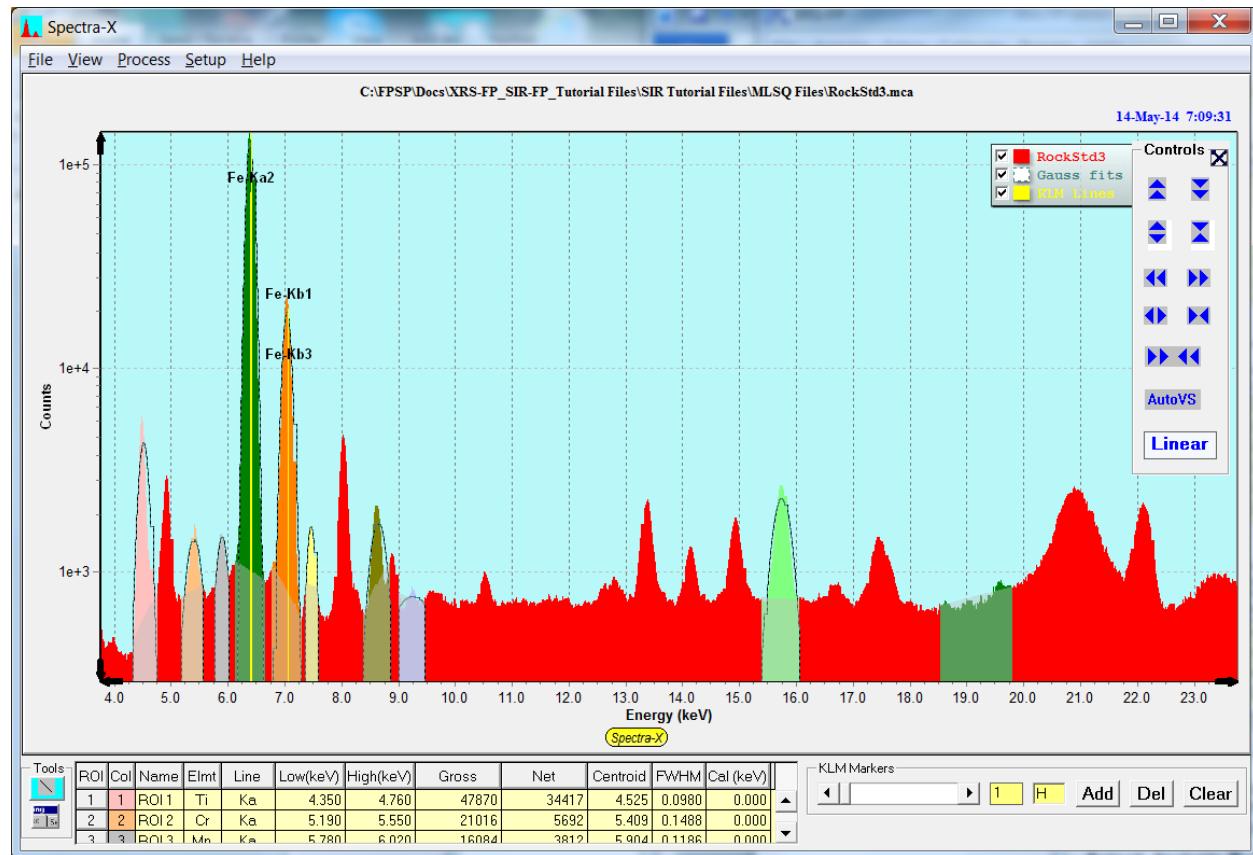
After loading a saved template file, the appearance changes to the following style:



Note that scale has been reset and the markers have been cleared. Note that the spectrum display appearance can be reset to the default by using the View – Reset Chart command (see below).

### 16.1.10 File-LoadROIs

This action loads the contents of a previously saved ROI Table, defined in Spectra-X. After loading the example file described in File-SaveROIs, the ROI table is reset to the contents of the file, and the ROIs are painted on the current spectrum in Group 0, as shown below.

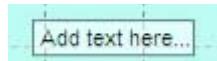


More details about defining and painting ROIs are provided later in this manual in the Tools section.

## 16.2 View Menu

### 16.2.1 View-Add\_Text

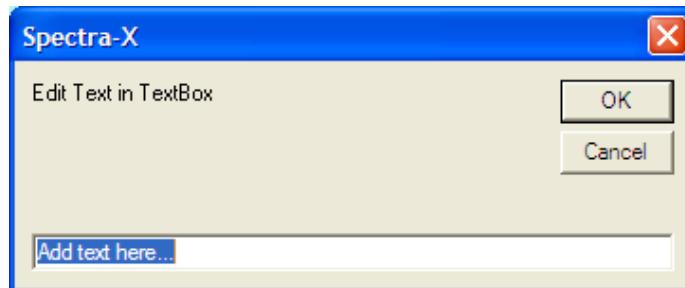
This option allows the addition of text boxes to annotate the spectrum display screen. Initially a default text box is displayed as follows:



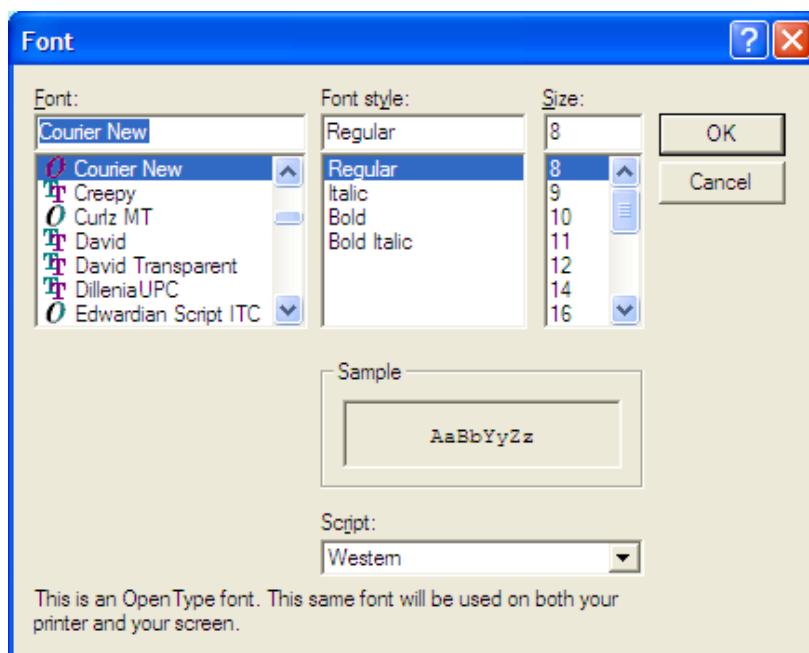
Then if you click with the right mouse button on the text box a popup menu appears:



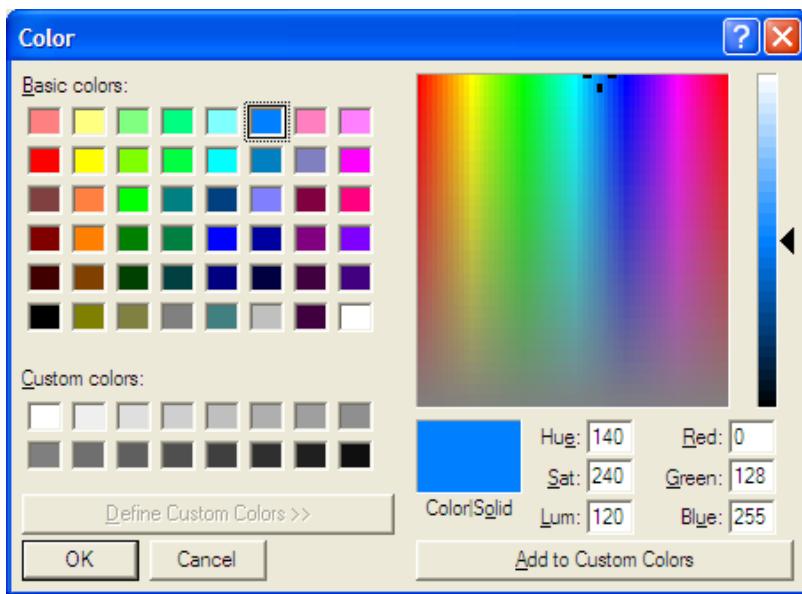
The first choice is “Edit Text” and selecting this will then display a simple text box for editing (v.1.5.0):



The second choice is “Edit Font” and this allows you to select the font type and size, as follows:

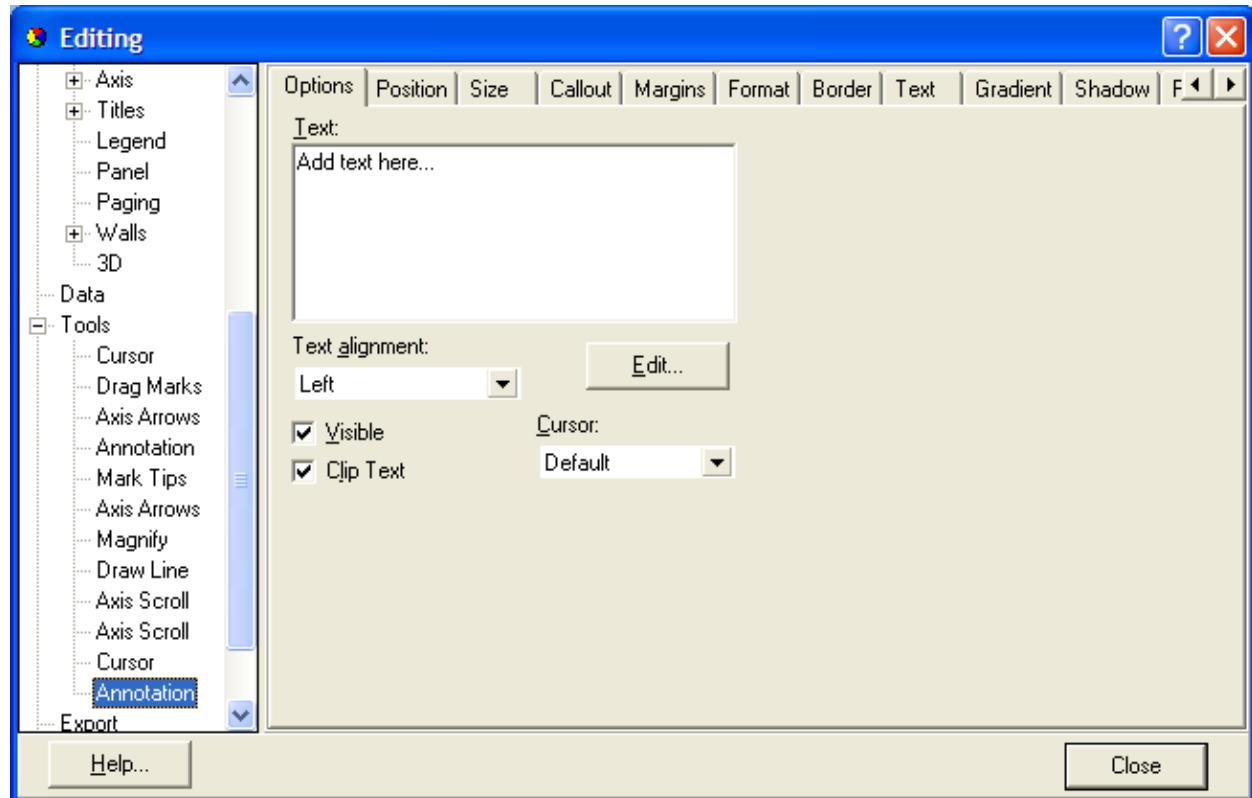


The third choice is "Edit Color" and this allows you to select the font color, as follows:

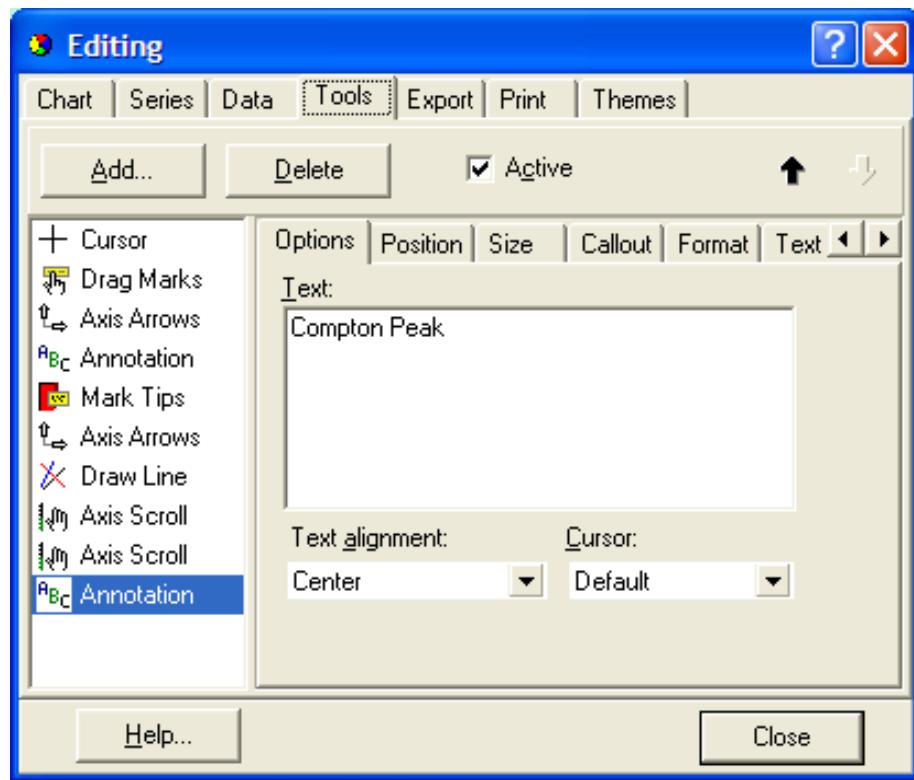


You can also delete and remove the text box with the Delete Text option.

You can also click on the TeeChart Editor tool (see below), then select and expand the Tools item and then select the annotation inserted at the bottom of the Tools list. This enables you to edit the text, as shown in the following display:



Now edit the Text area in this panel to put your custom text, such as "Compton Peak" as shown in the following example, where you can change any of the properties such as alignment, font size, transparency, etc.

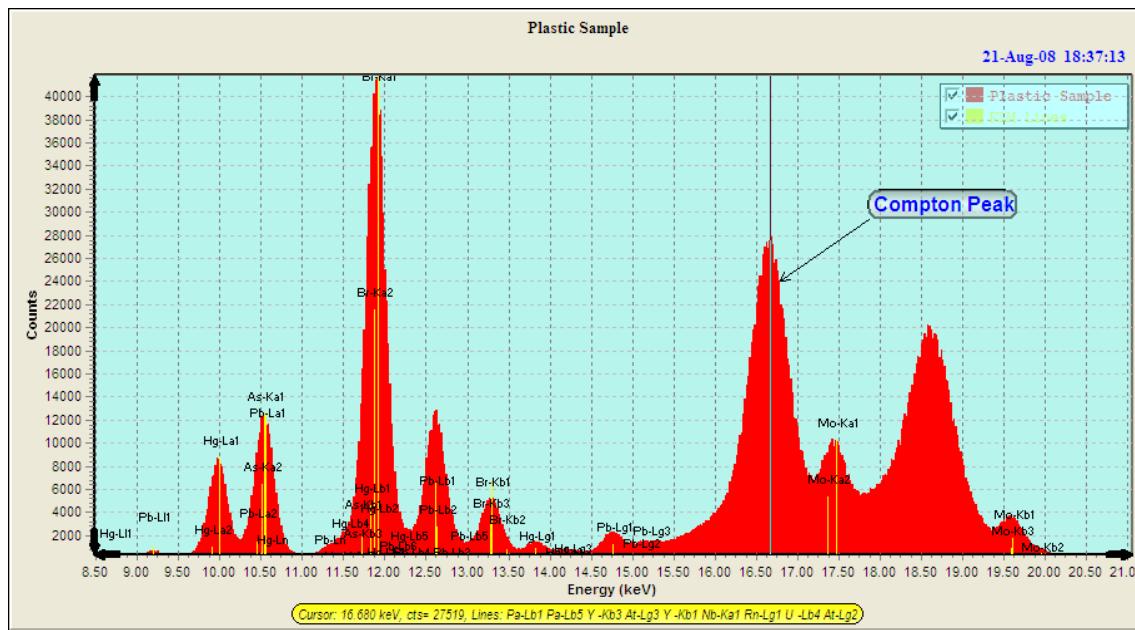


Now when you click on the Close button this text appears on the spectrum display, such as:



You can click with the left mouse button and drag this text box anywhere on the spectrum display. If you want to "attach" it some channel area then use the right mouse button to bring up the Callout menu and select Show and Active (if not set already) and an arrow will automatically be generated that connects the text box with the nearest channel.

If you position the text box carefully you then ensure that it points to the appropriate area of the spectrum, as in the following example where it highlights the channels that are part of the Mo-Ka Compton peak:



You can add any number of these text boxes to the spectrum display.

### 16.2.2 View-Cursor

This option turns on and off the vertical cursor. The cursor is shown in the figure above, and at the bottom of the screen there is a status line showing the cursor energy (keV), the counts in the channel, and possible x-ray lines that are close to the cursor energy. The latter helps identify unknown peaks.

### 16.2.3 View-Date

This option turns on and off the time of day and date shown in the second line from the top.

### 16.2.4 View-Legend

You can turn on and off the Legend with this option. The Legend is shown in the figure above. Note that it can also be re-positioned with the Chart Editor (see later).

### 16.2.5 View-Lines

You can turn on and off the display of lines that have been drawn on the spectrum display (see the Line Tool description).

### **16.2.6 View-Magnifier**

This tool was shown in an example at the beginning of the Spectra-X section. It allows you to zoom in on an area of the spectrum in more detail.

### **16.2.7 View-Reset Chart**

This was also described above in the section on templates. If you changed the appearance of the Spectrum Chart then you can reset it back to the default settings. Note that the scales will be reset and annotations lost.

### **16.2.8 View-ROI Table**

This command toggles between showing and not showing the ROI Table. See later in the ROI Table section (under tools) for more information about setting up the ROI Table.

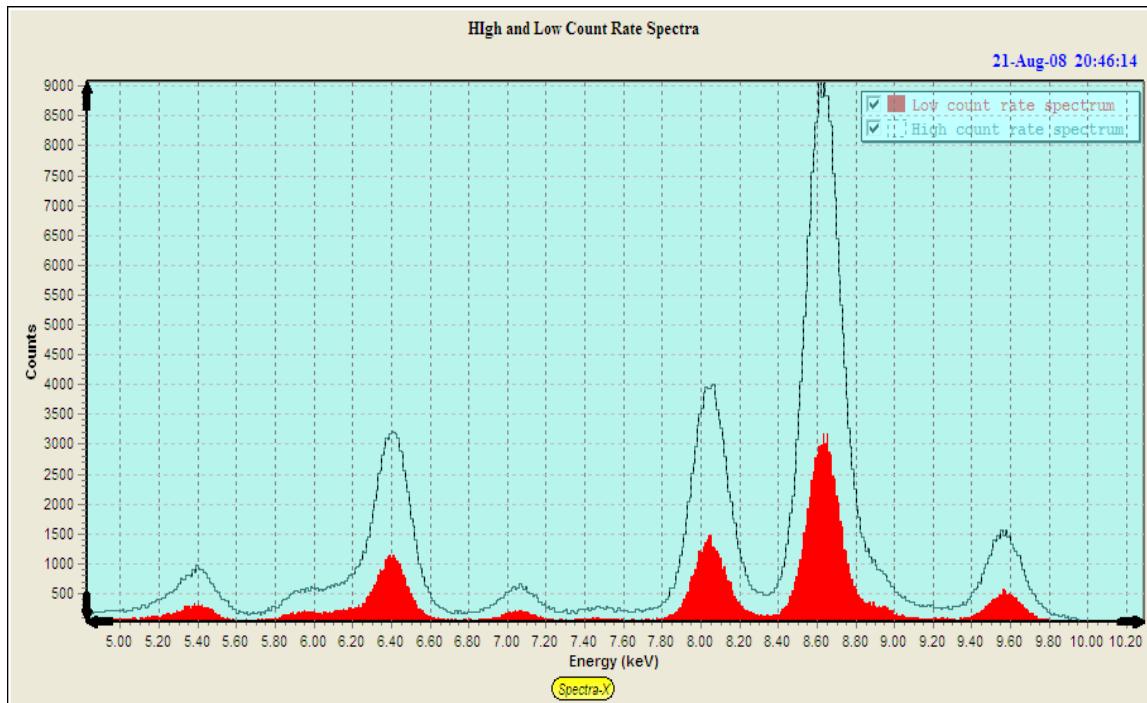
### **16.2.9 View-Status**

This turns the status line on and off. This line displays the cursor energy (keV), the counts in the channel, and possible x-ray lines that are close to the cursor energy.

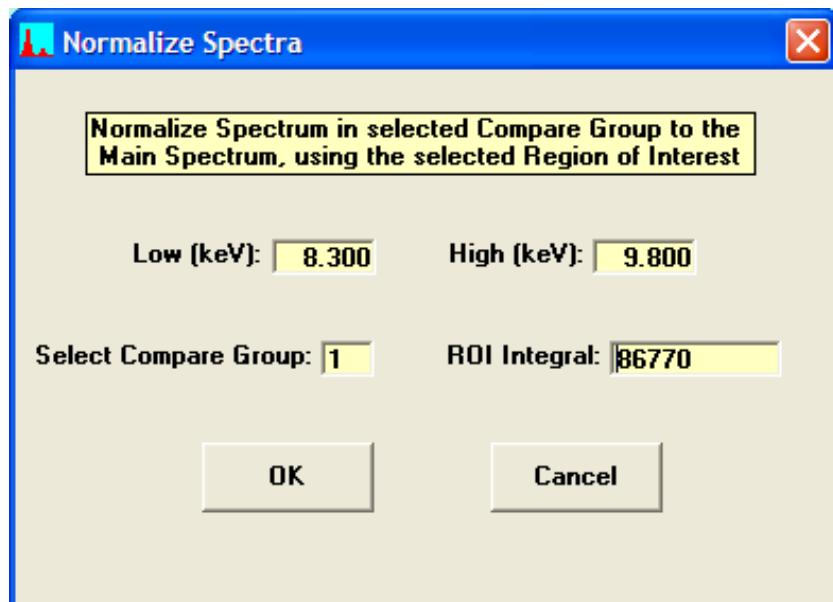
## 16.3 Process Menu

### 16.3.1 Process-Normalize

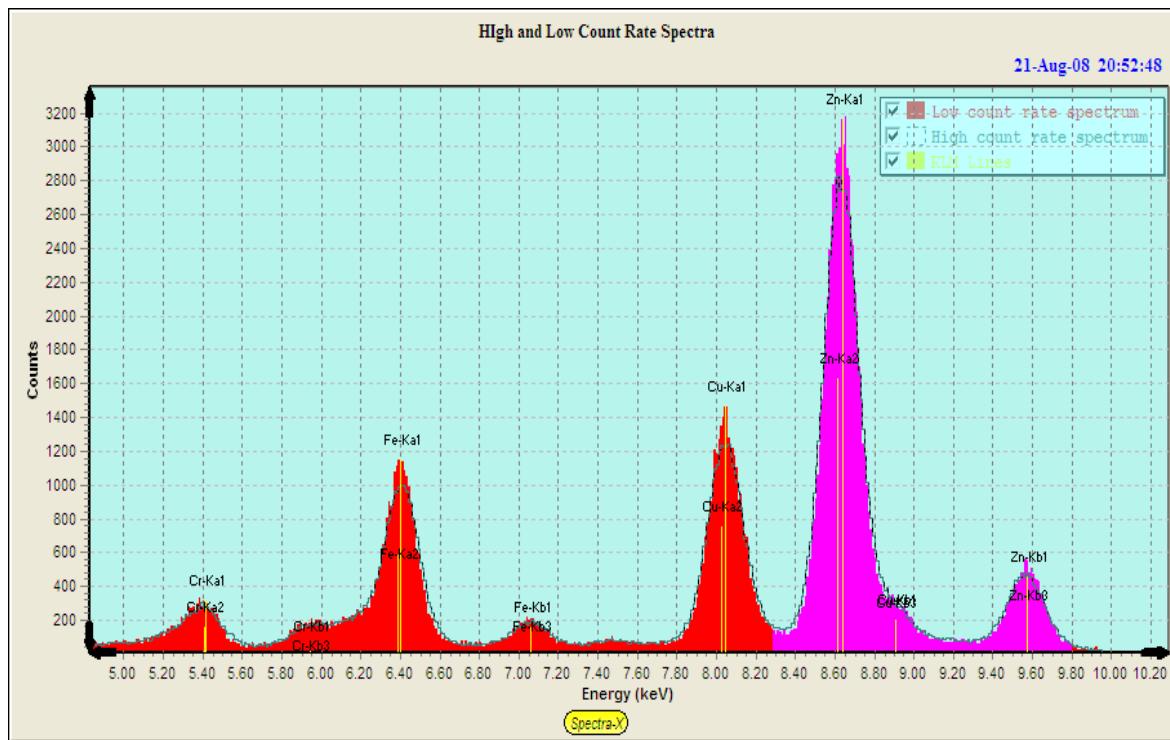
This option allows two spectra to be normalized so they can be compared more easily. This operation uses spectra in the Main group and, typically, Compare group 0 (although any group can be used). For example, the following figure shows 2 spectra collected from the same sample at 2 different count rates:



We can use Process-Normalize to scale the two spectra equally in the vertical axis, and this is done within a “Region-Of-Interest” or Window that is selected from the panel, as in the following example:



A ratio is calculated from the ROI counts in each spectrum, and then every channel in the compare spectrum is multiplied by this ratio so that within the ROI there will be the same number of counts. The result from this example is shown in the following figure:



### 16.3.2 Process–Paint ROIs

You can paint several windows (ROIs or Regions-Of-Interest) over different parts of the spectrum. This is now setup using the ROI table (see later). You can clear all of the ROIs with the Process – Unpaint ROIs command, and then re-paint them using the Process – Paint ROIs command. When the Gaussian fit option is set, the Paint operation also displays the Gaussian peak fits for each ROI in Compare Group 0.

See later in the ROI Table section (under tools) for more information about painting ROIs.

### 16.3.3 Process–Unpaint ROIs

This command clears all ROIs that have been painted. See later in the ROI Table section (under tools) for more information about painting ROIs.

### 16.3.4 Process–Clear ROI Table

This command clears all ROIs in the ROI Table. See later in the ROI Table section (under tools) for more information about painting ROIs.

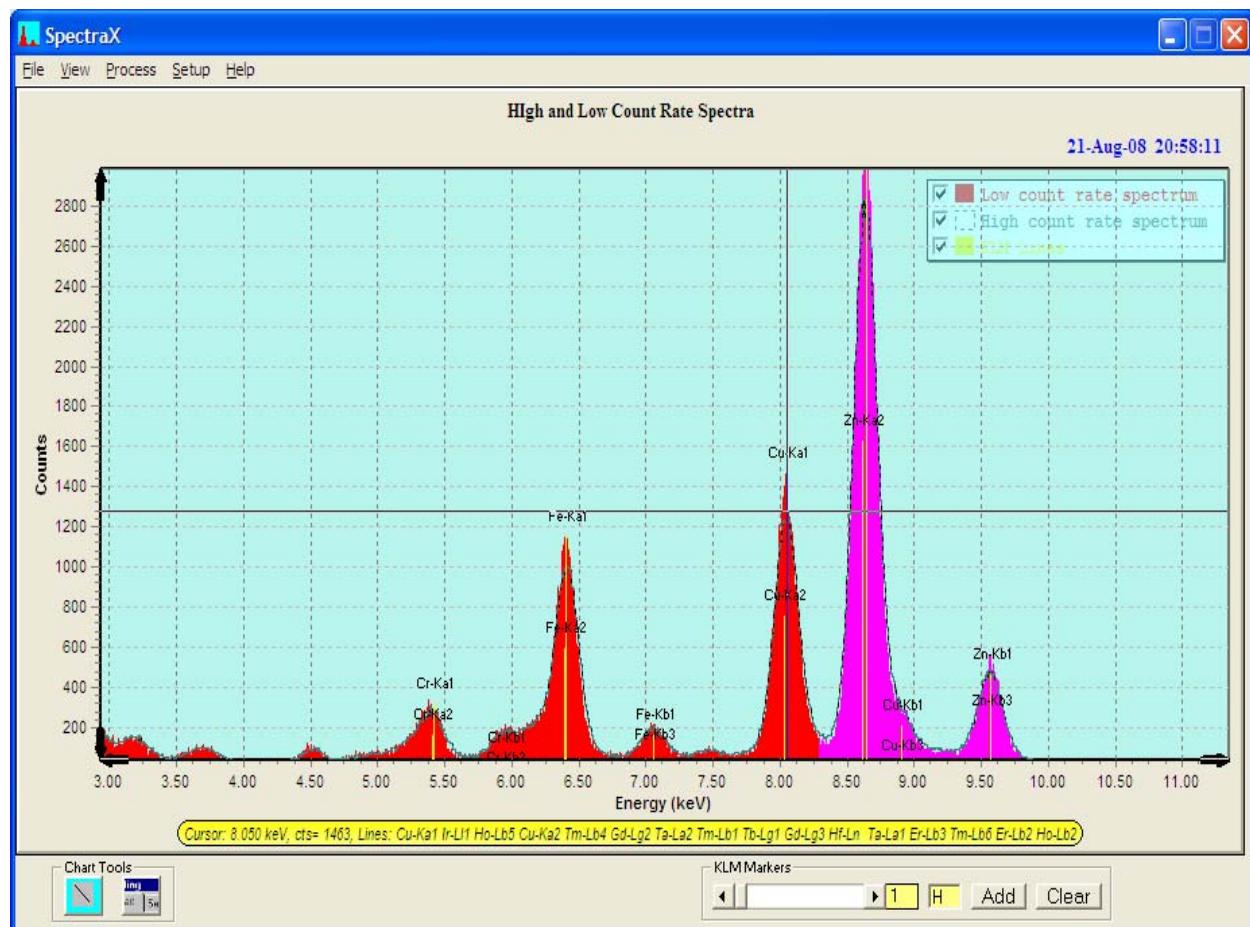
## 16.4 Setup Menu

### 16.4.1 Setup-Controls

This is a new feature in v.1.5.0. You can now either use the external form Controls for Spectra-X, as in previous versions, or switch to the internal panel, or turn them off completely.

### 16.4.2 Setup-Cursor

This option allows the user to select either or both a vertical and horizontal cursor. The following figure shows the spectrum with two cursors displayed:



### 16.4.3 Setup-KLM Markers

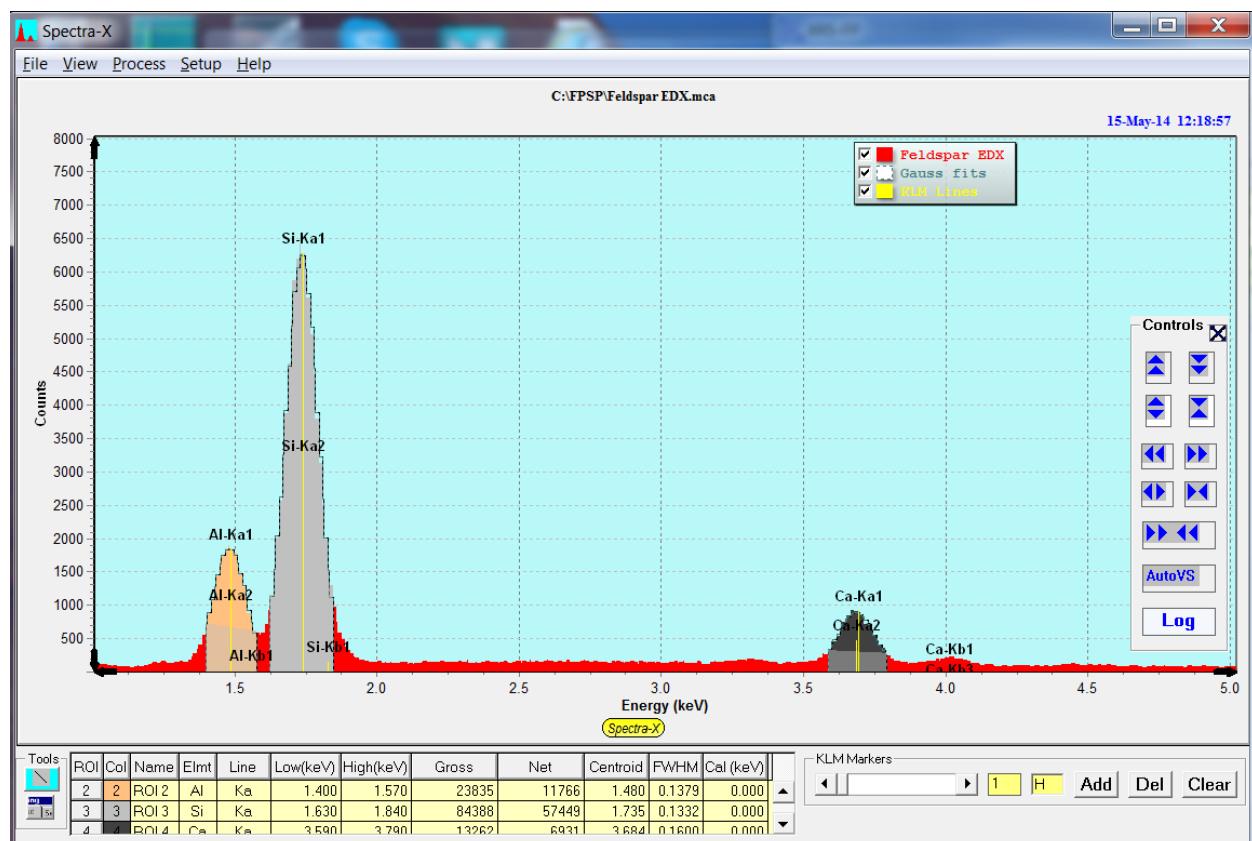
This option allows you to select between showing all the lines (up to 30) for each element selected by the KLM markers, or just the main centroid lines. Keep in mind that the latter may not always match exactly to the peaks.

## 16.4.4 Setup-ROI Calc Method

There are 2 sub options in this menu. For each ROI in the ROI Table, there are two column parameters – Centroid and FWHM. Each of these may be calculated in different ways as described in the next two options.

### 16.4.4.1 Setup-ROI Calc Method-Gaussian

The menu option instructs the calculation of the centroid and FWHM for each ROI to be done by fitting a single Gaussian peak (Gaussian flag checked), or by a simple channel-based method (Gaussian flag unchecked). When the Gaussian fit method is chosen, the Compare Group 1 shows the Gaussian fits for each ROI. For example, the two ROIs for Al, Si and Ca in the following spectrum show the Gaussian fits for those 3 elements, and the resulting Centroid and FWHM values in the ROI Table.

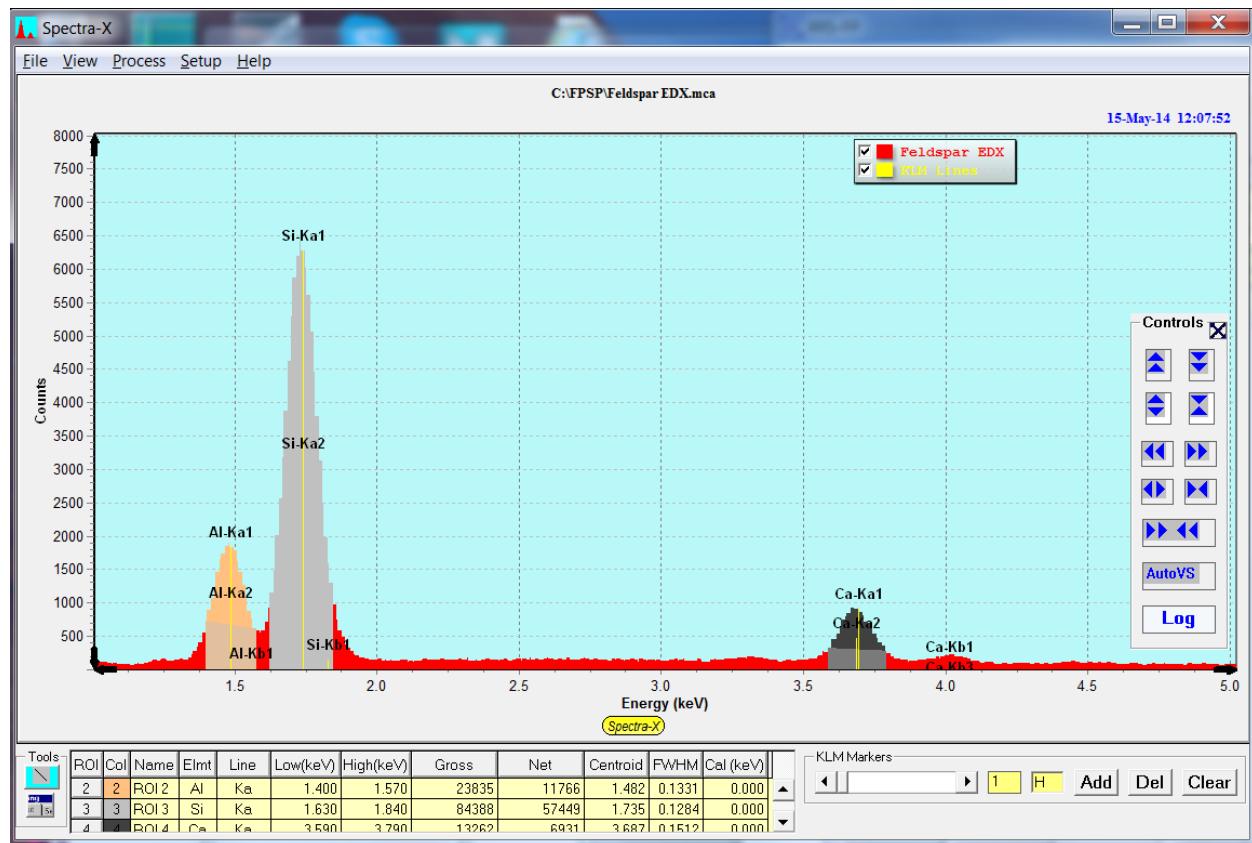


The Gross channel data was used for the fitting (see below).

After changing this option to use the channel-based method (simple weighting for centroid, and channel “walking” to find the FWHM points on either side of the centroid, then Unpainting and Painting the ROIs, the new values are calculated as shown below.

Note that any time the ROI values or setup parameters are changed you should Unpaint and Paint all the ROIs to update all the calculated values.

Note also that both these examples were calculated using the Gross channel counts data.

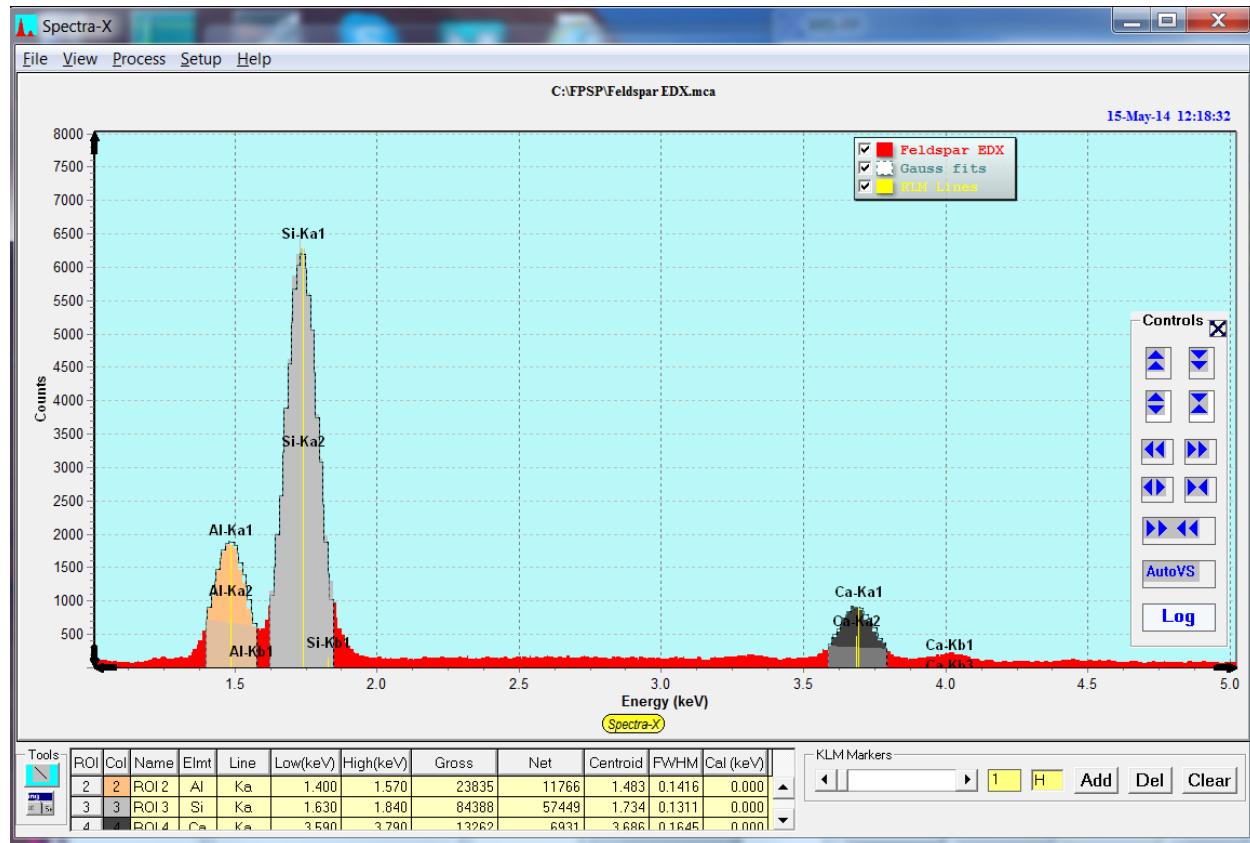


#### 16.4.4.2 Setup-ROI Calc Method-Net

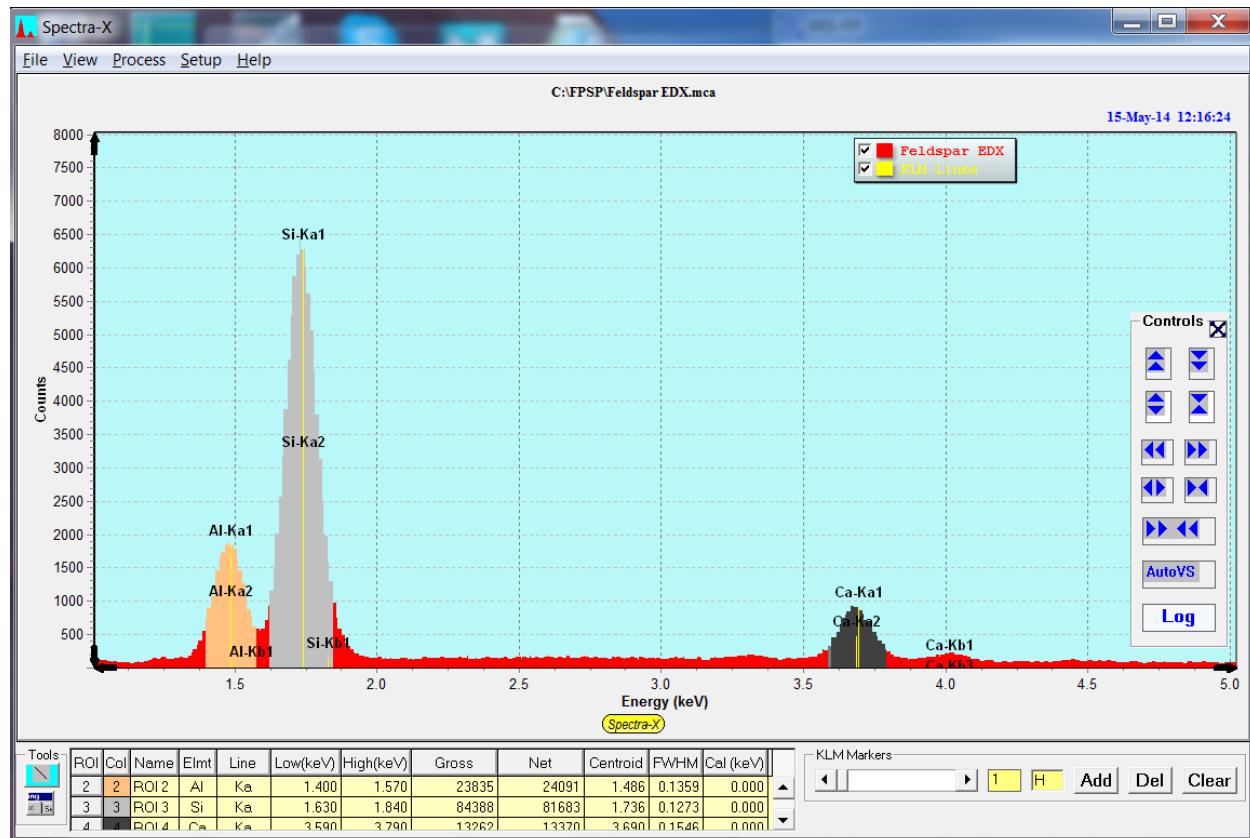
This menu option instructs the calculation of the centroid and FWHM (see above) to use either the net channel counts (Net flag checked) or the gross channel counts Net flag unchecked). The Gross counts are the actual contents of each channel.

The Net counts are calculated by subtracting a simple linear background away from the channel data in the ROI. I.e., a virtual line is drawn between the first and last channel in the ROI, and the intercepted values at each channel are subtracted from the actual (Gross) counts in that channel.

The effects of setting this option to Net on the examples above are shown below. The first example show the results after using the Gauss fitting method with the Net counts.



The second example shows the same thing with the Channel fitting calculations and Net counts.



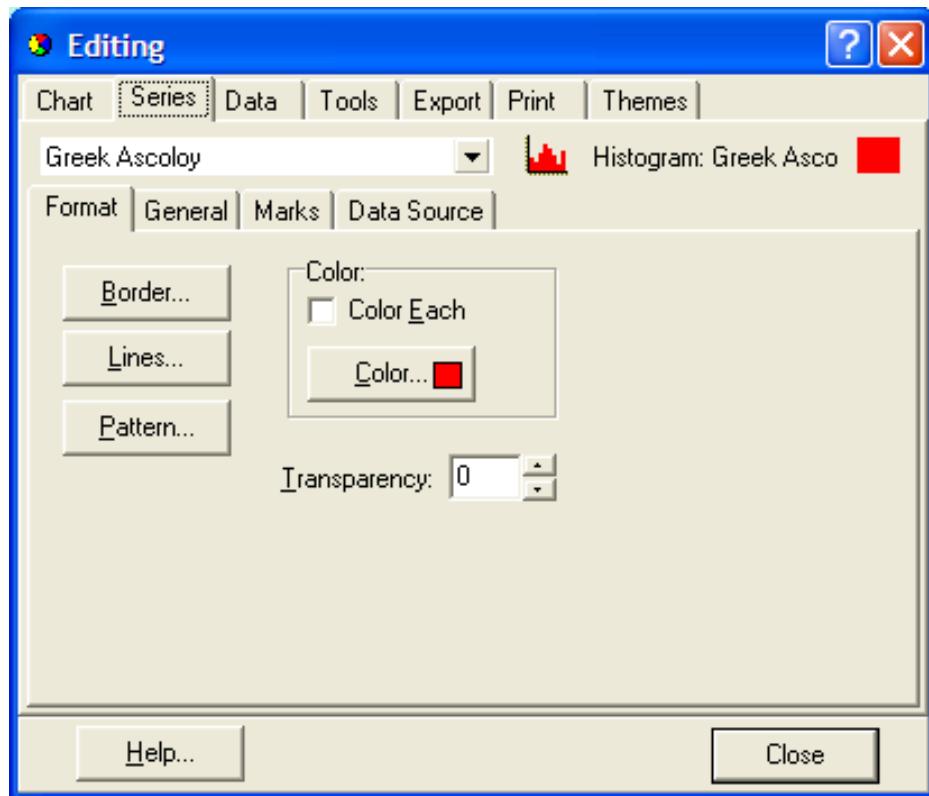
## 16.4.5 Setup-Spectrum

There are 3 sub options in this menu.

### 16.4.5.1 Setup-Spectrum-Chart

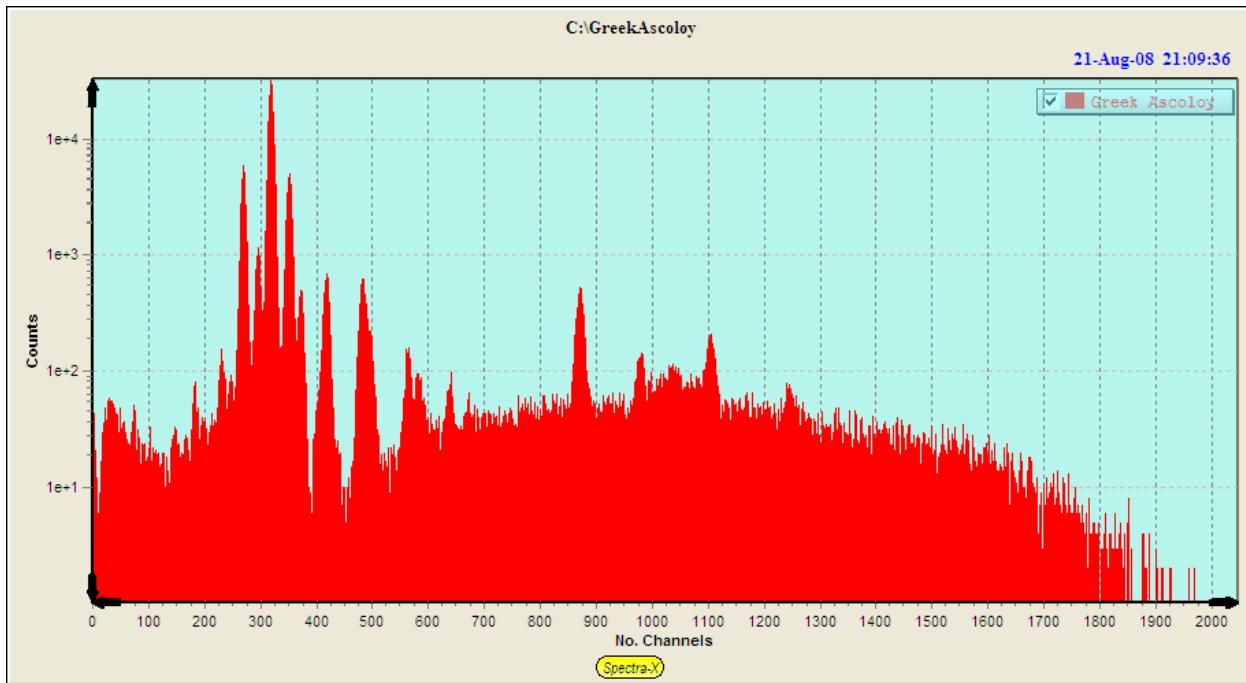
This option allows you to modify the chart properties of the various spectra in the spectrum display. Note that this is just a temporary change and the properties will be reset when Spectra-X is re-loaded. The histogram type and color can be changed, and many related parameters.

An example of this panel is shown below:



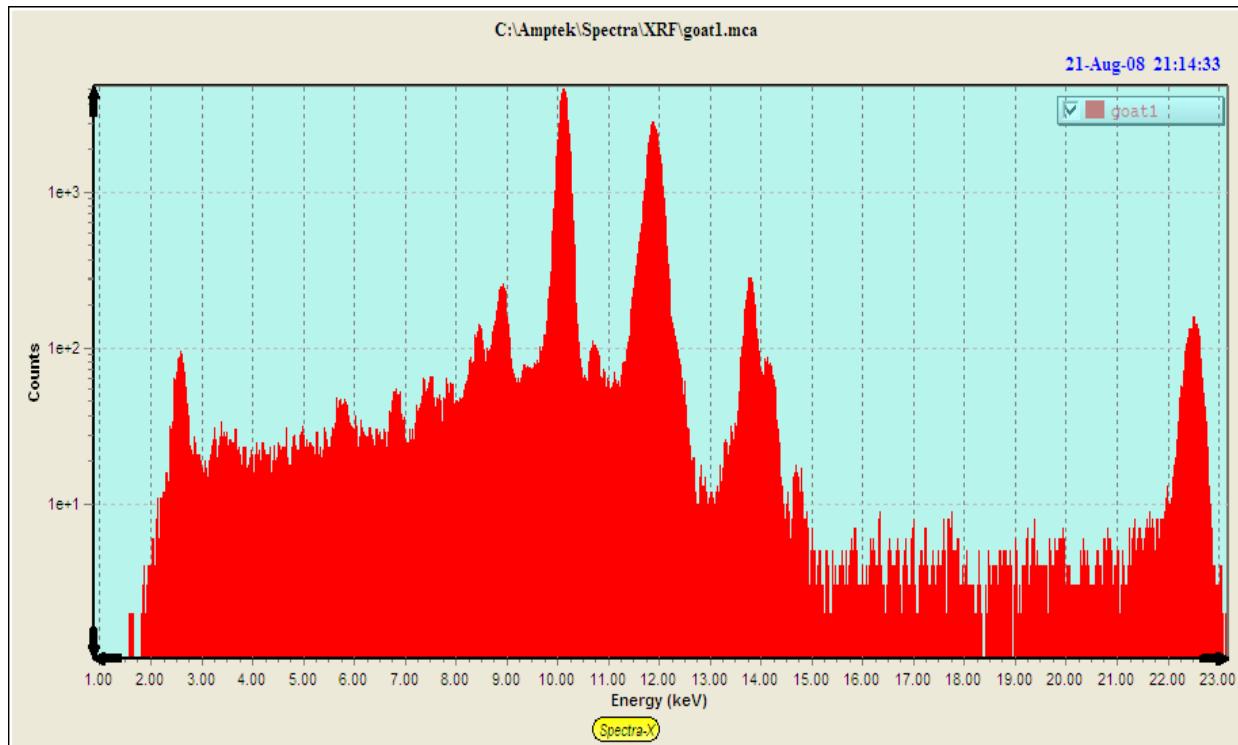
### 16.4.5.2 Setup-Spectrum-Energy

The default horizontal scale is in units of energy (eV/channel). As an option you can convert the scale to channels by turning off the default state, as shown in the following figure, which is also shown in log scale:

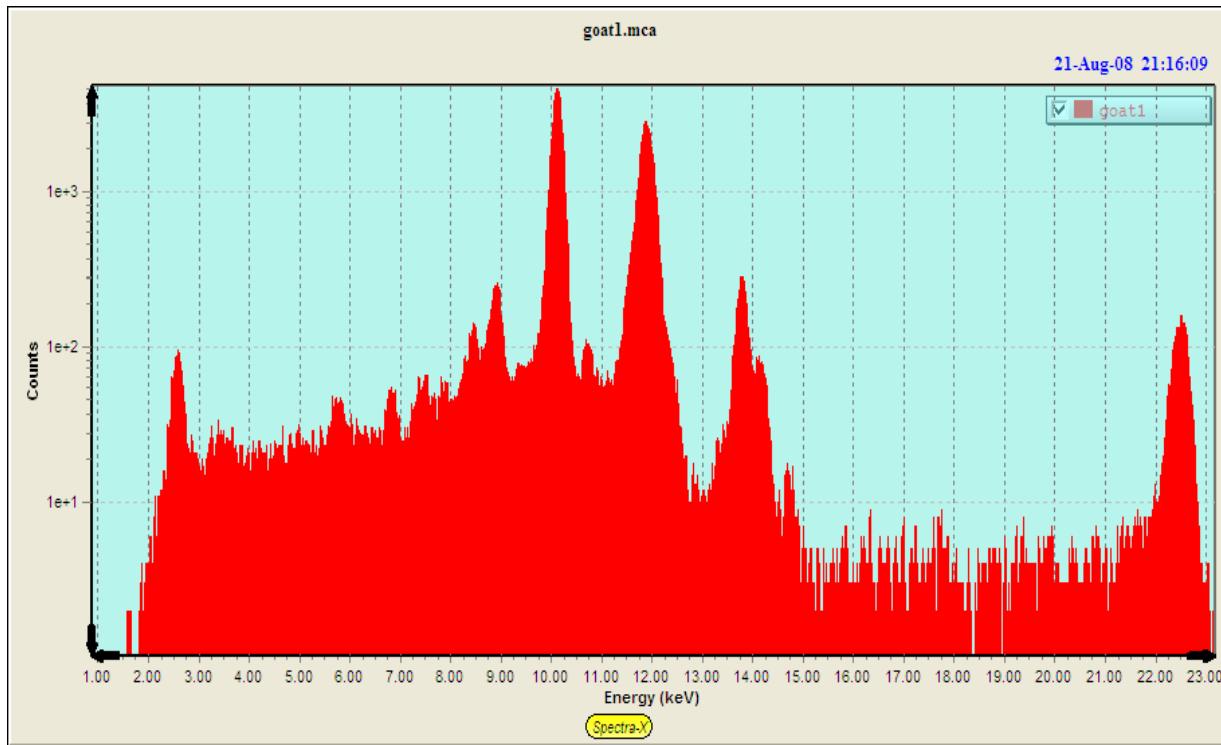


#### 16.4.5.3 Setup-Spectrum-Full Title

This option allows toggling between the full pathname, as shown in the next figure.



The next figure shows the short form of the title.



## 16.5 Spectra-X Tools

### 16.5.1 Lines

The Lines tool has the following icon:



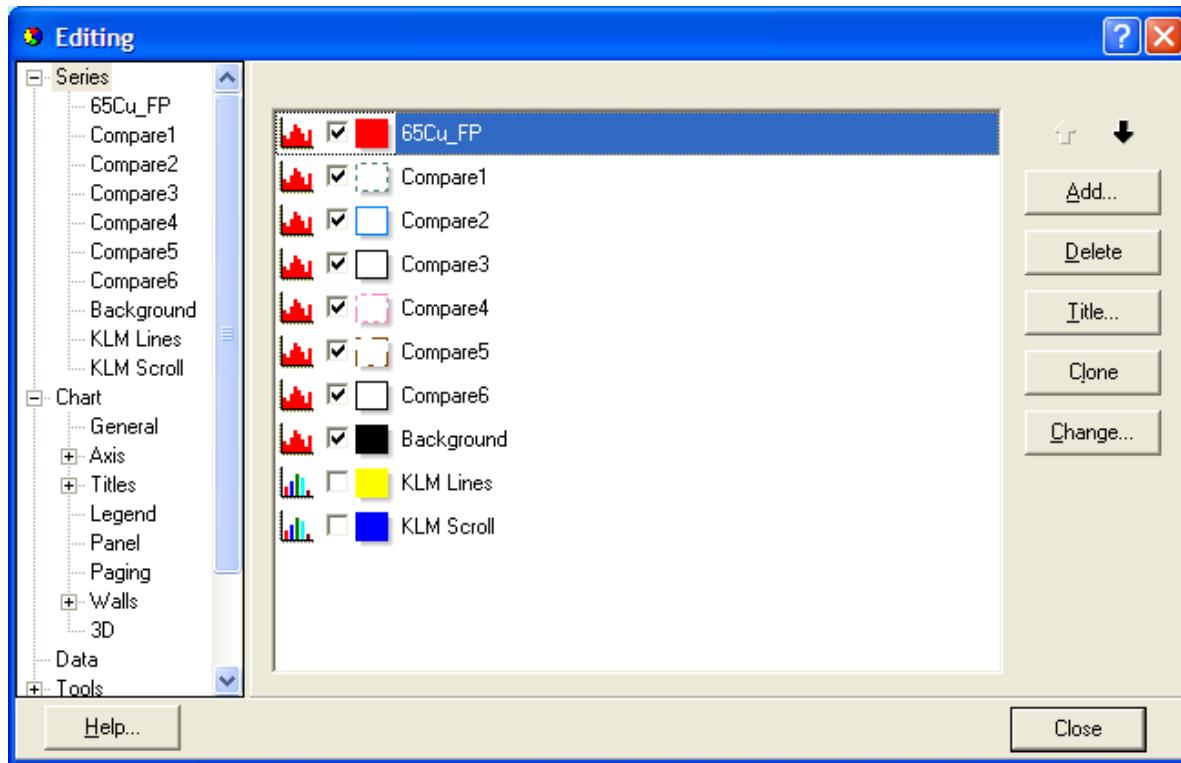
When clicked this turns on the Line Drawing tool and you can draw lines freely anywhere on the spectrum display. You can turn this off by clicking on the Lines tool again. You can also turn on and off the lines that you have drawn by using the View-Lines command (see above).

### 16.5.2 Chart Editor

The Chart Editor has the following icon:

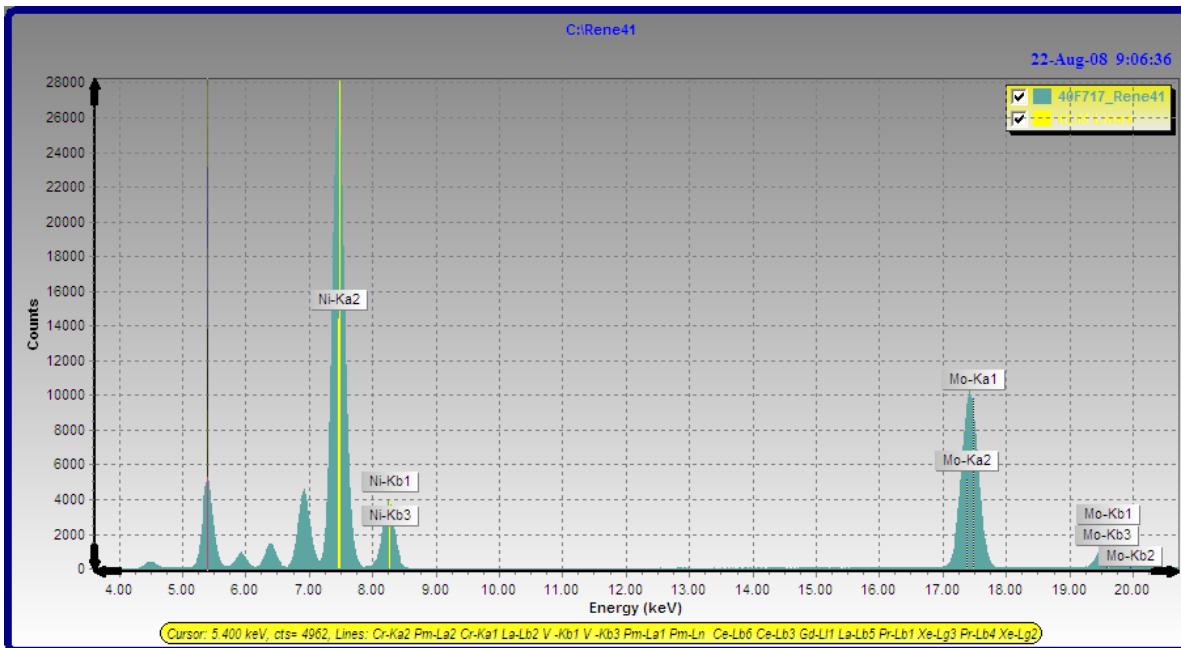


When clicked this shows the following dialog:



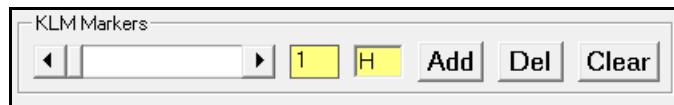
This allows you to change almost any property in the spectrum chart, including the style of the histograms in each of the groups.

You can also apply themes that change the overall appearance of the spectrum display. For example the application of the Business Theme produces the following type of display:



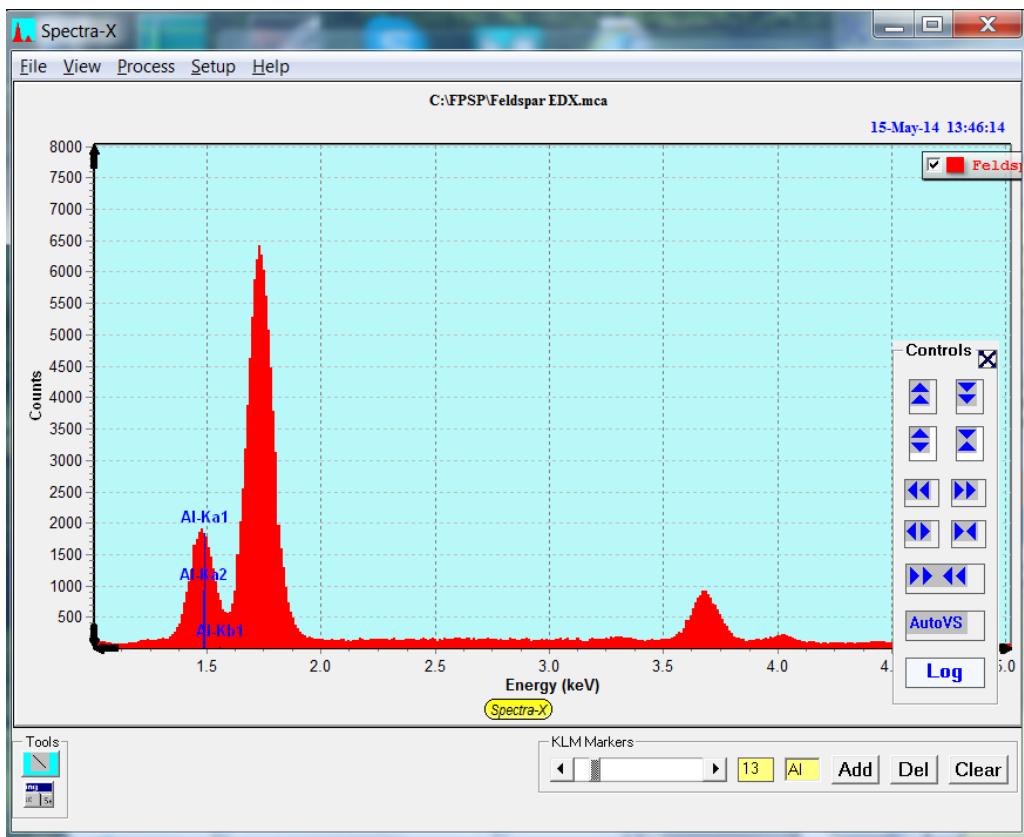
### 16.5.3 KLM Markers

The KLM markers' tools have the following layout:



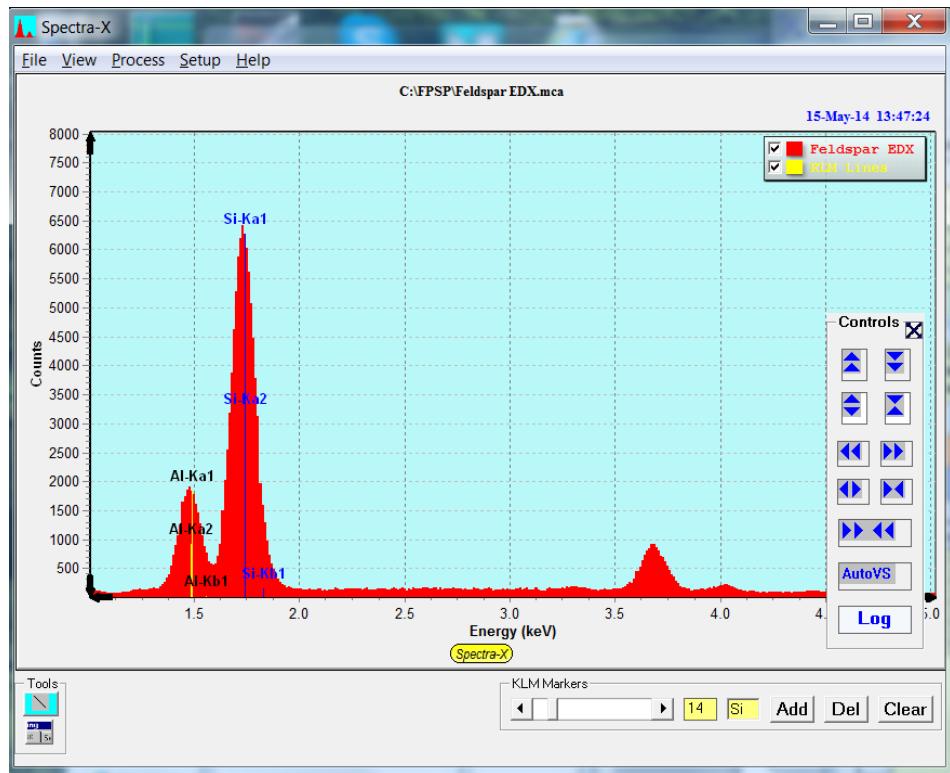
There is a horizontal scroll bar that moves the KLM markers up and down the energy scale in the spectrum, showing the atomic number of the current selection to the right of the scroll bar.

Further to the right is a text box where you can add an element symbol to select individual markers without using scroll bar. As each new element is selected, the KLM markers are shown in blue.

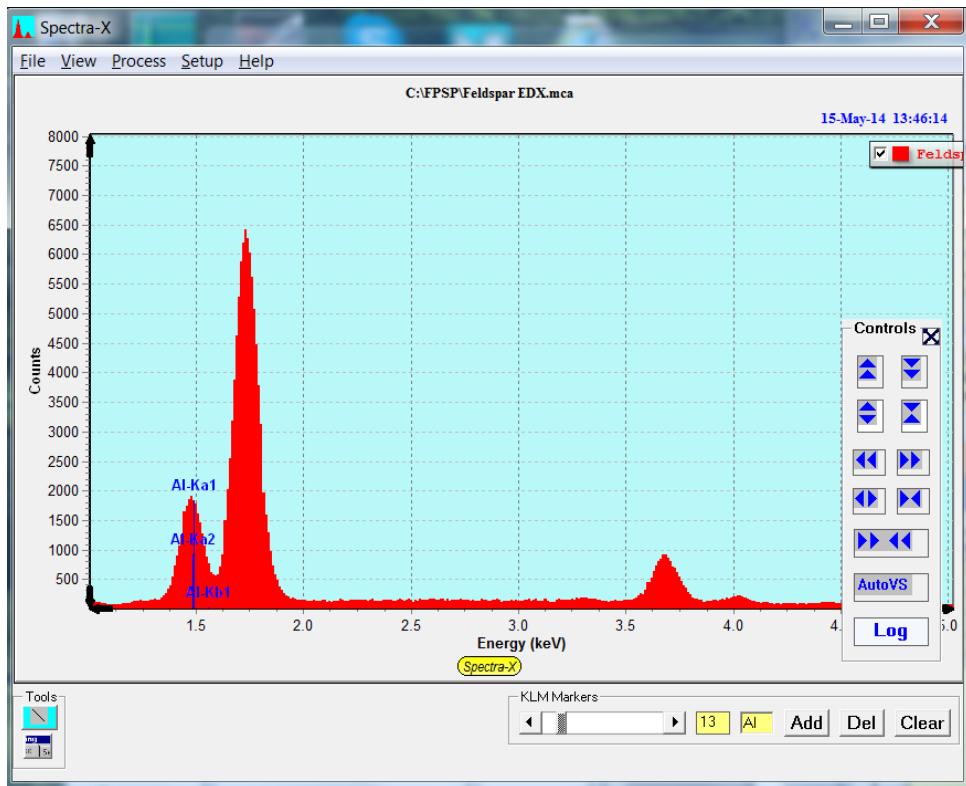


To add the markers, for the selected element to the spectrum, click on the Add button. This turns the markers from blue to yellow when the KLM markers are moved.

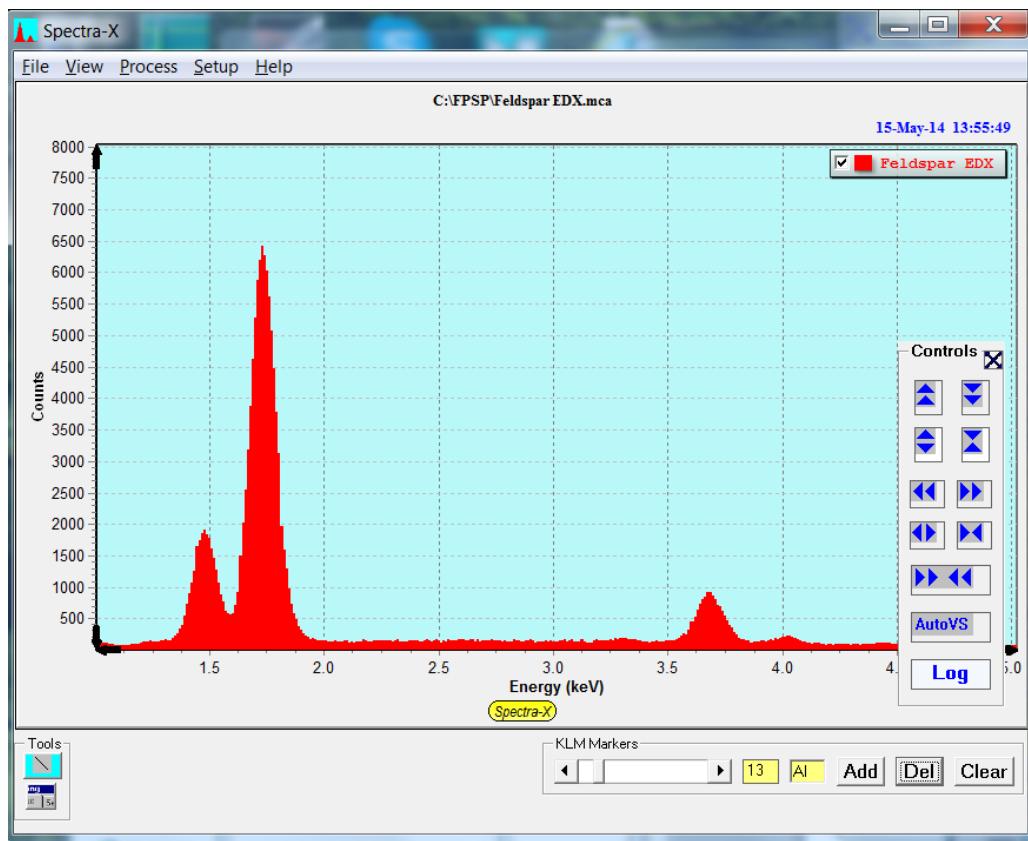
In the next figure the KLM markers have been moved one step to a higher Z, so Al is now yellow (after the previous Add), and the next element Si is shown with blue markers.



To delete KLM markers for a specific element click on the Del key while displaying the symbol for that element. For example, if the scroll bar above is scrolled down by 1 atomic number value, it now highlights Al again:



Now, after clicking the Del button, you can see that the AI markers have been deleted.



The Clear button clears *all* the markers from the spectrum.

The parent line in any (K, L or M) series will be scaled to the height of the channel where that line marker is located. All the other “daughter” lines in the same series are scaled to this parent by the line ratios in the FP database.

### 16.5.4 ROI Table

Some of the details about setting, adjusting and painting ROIs, are covered in other sections in this manual (both in the main XRS-FP section and Spectra-X).

A convenient way to initialize this table is to use the Setup-ROI menu item in the main XRS-FP panel. This option takes the ROIs defined in the current TFR file, copies them to the Setup-ROI panel thus allowing further changes including color selection, and then this table can be transferred to Spectra-X by clicking on the Paint All button.

Any non-zero ROIs are then painted on the spectrum in the main group of Spectra-X. Extra information is available in the ROI Table in Spectra-X, and this table can be defined independently of XRS-FP if desired.

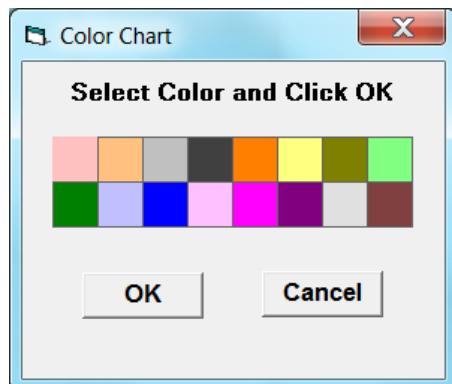
The contents can be Saved or Loaded to an \*.roi file, as outlined in the previous sections for Spectra-X. Note there is no way to save or load ROIs using the main XRS-FP panel.

A typical example of the ROI Table in Spectra-X is shown below.

ROI	Col	Name	Elmt	Line	Low(keV)	High(keV)	Gross	Net	Centroid	FWHM	Cal (keV)	
2	2	ROI 2	Al	Ka	1.400	1.570	23835	11766	1.480	0.1379	0.000	▲
3	3	ROI 3	Si	Ka	1.630	1.840	84388	57449	1.735	0.1332	0.000	▼
4	4	ROI 4	Ca	Ka	3.500	3.700	13262	6931	3.684	0.1600	0.000	▼

To view all the rows you must use the vertical scroll bar at the right of the table. The ROIS are numbered starting from 1, and there is no limit to the number of ROIs that can be defined. Default colors are assigned and shown in the "Col" column.

Along with the color is the color index from the following chart that is displayed when you double-click on any cell in the "Col" column.



You can change the color by click on any one of the 16 colors in this chart and then clicking the OK button.

It is not necessary, but can you define the element and analyte line (Ka, Kb, La, Lb, Lg or Ma) for each ROI. The Element column is a text field and the Line column is a dropdown list.

The Gross and Net columns represent the ROI integrals from both the Gross and Net count values for the currently displayed spectrum. The Net counts are calculated by subtracting a simple linear background away from the channel data in the ROI. I.e., a virtual line is drawn between the first and last channel in the ROI, and the intercepted values at each channel are subtracted from the actual (Gross) counts in that channel during the integration.

The Centroid and FWHM (Full-Width at Half Maximum) column values are calculated for the currently displayed spectrum using either Gaussian peak fitting for each ROI, or by a simple channel weighting calculation for the centroid and by “walking” down each side of the peak from the peak channel for the FWHM. If the half height is between two channels then the height is estimated from the two adjacent channels.

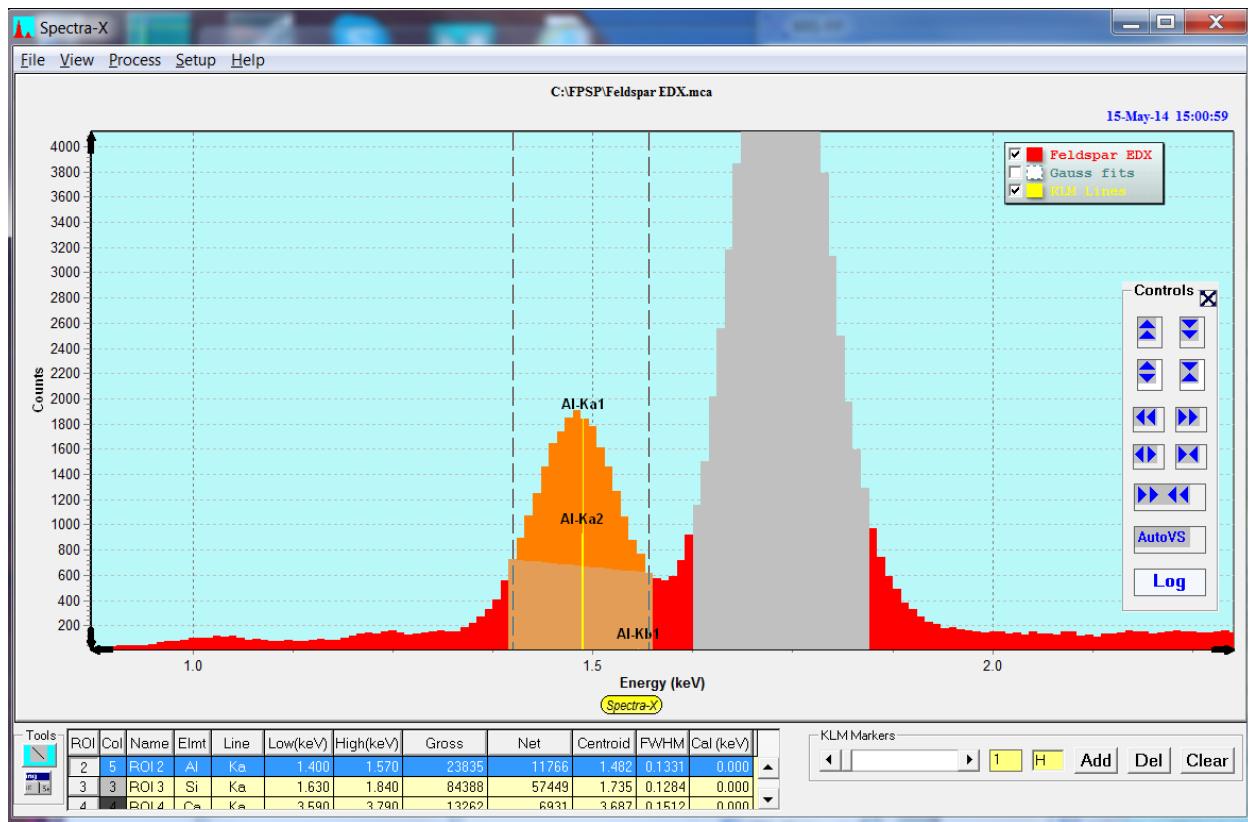
The final “Cal” column is for documentation of what the expected centroid is expected to be for the defined ROI. It is not used in the software – it is only there for documentation, and does get saved when the ROI Table is saved as an ROI file.

Of course you can define the ROIs simply by entering the Low and High energy values in keV. However, it is more intuitive to do this by cursor painting on the spectrum itself. This is done by highlighting one of the rows in the table – this is done by clicking on the ROI number cell (and unselected by repeating the operation a second time).

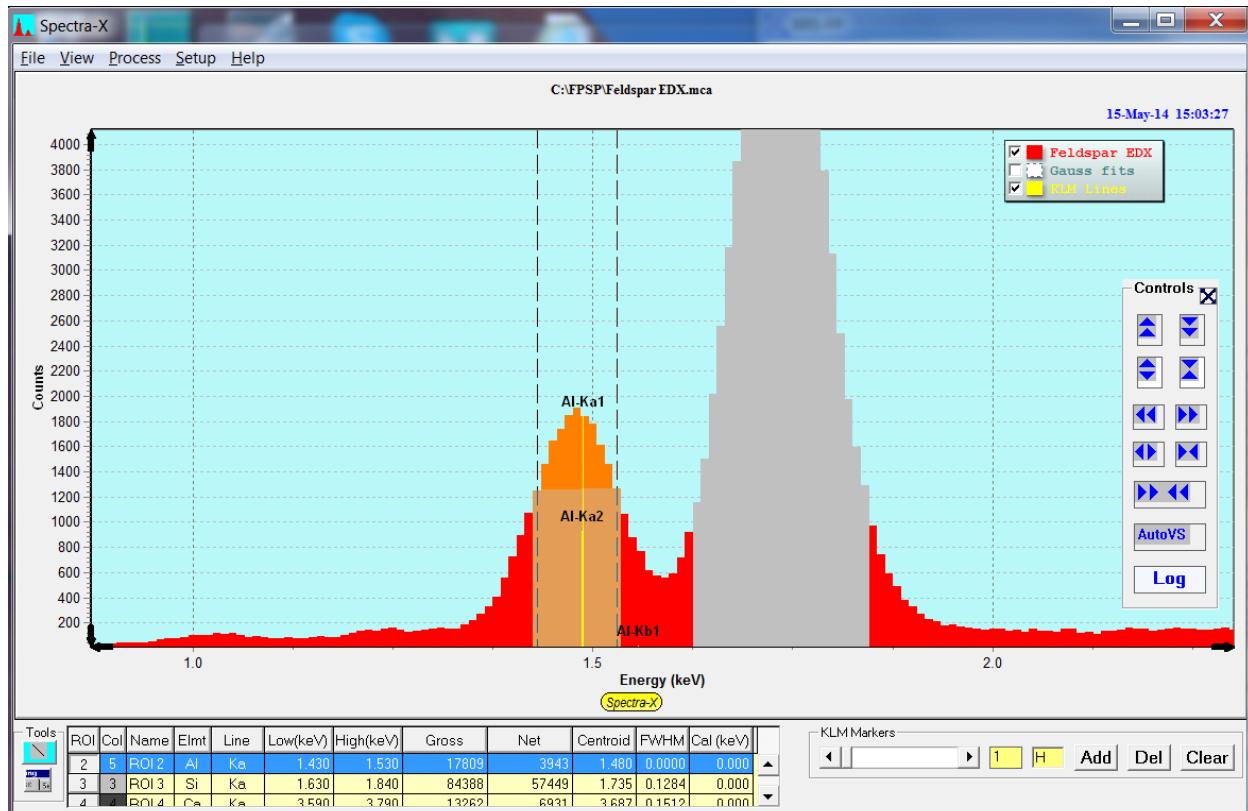
For example, clicking on the ROI #2 cell highlights row 2 as shown below.

ROI	Col	Name	Elmt	Line	Low(keV)	High(keV)	Gross	Net	Centroid	FWHM	Cal (keV)	
2	5	ROI 2	Al	Ka	1.430	1.530	17809	3943	1.480	0.0000	0.000	▲
3	3	ROI 3	Si	Ka	1.630	1.840	84388	57449	1.735	0.1284	0.000	▼
4	4	ROI 4	Ca	Ka	3.590	3.790	13262	6931	3.687	0.1512	0.000	

After clicking this row, the ROI is displayed on the spectrum with two cursors – both a low and a high one, as shown in the following figure around the Al-K peak.

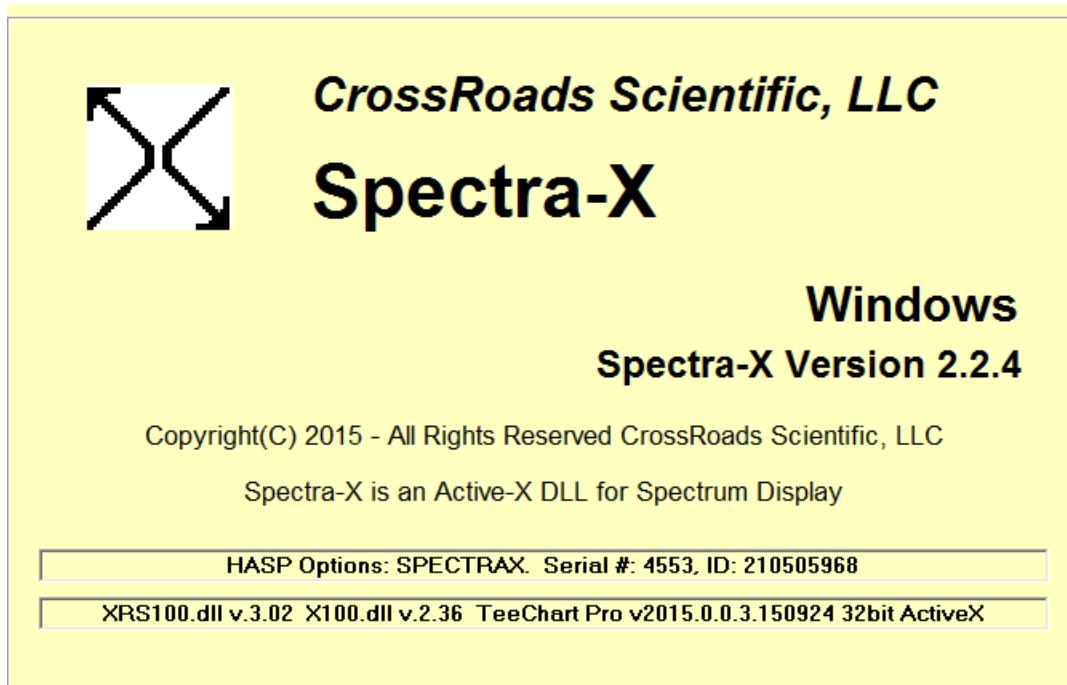


Now you can “grab” either one of these cursors and adjust their positions up or down in energy. For example, after reducing the width of the ROI #2 the spectrum looks like the following figure.



## 16.6 Help-About

The current splash screen for Spectra-X is shown below:



This screen shows the HASP security plug options relevant to Spectra-X, and the dependent DLL's that are used by Spectra-X. XRS100.dll and X100.dll are two x-ray libraries provided by CrossRoads Scientific, and TeeChart is a third-party charting component.

## 17 HASP SECURITY PLUG INSTALLATION

Supplied with your software is a HASP software copy protection device (or “Security Plug”), which must be installed in any of the parallel printer or USB ports on your Intel (or similar) PC. The parallel-port HASP is a “pass-through” plug for a Centronics parallel printer cable, and is transparent to printer operations. The USB HASP is NOT a pass-through plug – a USB hub can be used if extra USB ports are required.

**\*\*\* Warning \*\*\***

**Do NOT install more than one plug on the same computer – this will cause unpredictable results!**

You can make as many copies of the software as you like, for backup or running on other computers, but only when the Security Plug installed will the software function correctly.

The HASP plug is manufactured by SafeNet Inc. More information about the plug and the latest drivers (for various operating systems) can be found on their web site at:

<http://sentinelcustomer.safenet-inc.com/sentineldownloads/>

**\*\*\* Warning \*\*\***

**Make sure you download the HASP4 driver for the plugs and NOT the HL driver!**

Their generic driver installation program (Haspdinst.exe previously Hinstall.exe) will automatically install the correct driver for the operating system being used. You may obtain the latest driver from the SafeNet at any time if you suspect that your computer requires updating. Make sure you use the HASP4 driver, and NOT the HASP HL driver, unless you are using a NetHASP plug, which requires both drivers installed.

Note that starting with XRS-FP v.4.6.0, the older Hinstall HASP installer above has been replaced by a newer one that contains all driver types and is for all operating system. This installer is called Haspdinst.exe and installation syntax is the same. Instead of the command “Hinstall -i” the new command is “Haspdinst -i” and this can be done with the Windows Run command or from a DOS command prompt. This installer is supplied with the XRS-FP software.

*The parallel-port HASP plug should be installed as follows (for older PCs):*

- (1) First turn off power to your PC and printers.
- (2) Remove the printer cable to one of your parallel ports, unless you have a spare parallel port.  
Note: parallel port network adapters and tape drives should NOT be connected through the HASP4 plug.
- (3) Carefully align the male end of the 25-pin HASP plug with the female 25-pin parallel printer socket.

- (4) Screw the plug into the socket, being careful not to over tighten either of the screws.
- (5) Re-attach the printer cable (if removed) into the socket-end of the HASP4 and tighten.
- (6) Turn on power to your PC and printer, and check that both are functioning correctly.

Now run your Windows application software and verify that it is functioning correctly.

It is not advisable to access the plug while your computer is printing, as this can cause unpredictable results. Also, some bi-directional printers and parallel ports can cause problems in correctly accessing the security plug. If this is the case, try reconfiguring your Windows printer driver, the BIOS Setup for the parallel port, or the HASP4 driver itself.

If you encounter any problems with this installation, call your software supplier.

*The USB HASP4 or HL plugs can be installed as a standard Windows “Plug ‘n Play” device. Ensure that you have administrative privileges on your computer if necessary. The USB HASP plugs will illuminate a small LED when they are correctly installed, with an operational driver. Current installers now install all the driver packages, and these are updated by the Windows Update installer also, as an optional update.*

Note that for current software versions, 3 batch files are provided to install, uninstall and check the status of the HASP plug and its drivers. These are as follows:

- (1) Install HASP Driver.bat.
- (2) Uninstall HASP Drivers.bat
- (3) Check HASP Status.bat