

Using the Bruker Tracer III-SD Handheld X-Ray Fluorescence Spectrometer using PC Software for Data Collection

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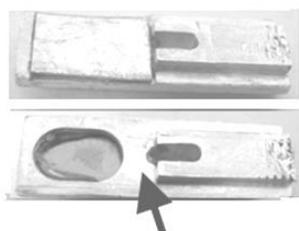
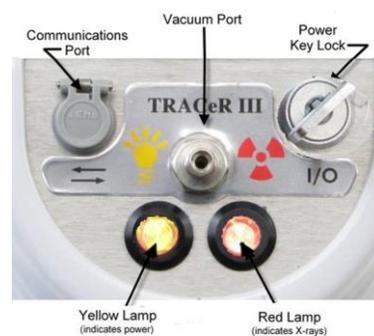
For assistance in the X-ray lab, contact Charles Settens
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<http://prism.mit.edu/xray>

This SOP guides you through collecting X-ray Fluorescence (XRF) data using a PC to operate the Bruker Tracer III-SD handheld XRF. Data can also be collected using a PDA- this mode of operation is covered in another SOP.

Prepare the Instrument

1. Make sure that the cable from Communications Port to the computer is connected.
2. If doing low mass elements (Mg to Cl), connect the vacuum system to the Vacuum Port. Do not turn it on yet.
3. Use the Power Key to turn the instrument on. Turn the key all the way clockwise. The yellow lamp should illuminate.
4. Put the desired filter in the filter slot (brass screw). See Appendix A for guidance choosing a filter.



This side toward instrument



brass knurled screw



filter insertion

5. Turn on the vacuum pump. The vacuum gauge should read below 15—if it does not, contact SEF staff to replace the vacuum window.

- Place the sample on the sample table. Put the sample shield over the sample. If your sample is too large for the sample shield, or you need to hold the instrument to the sample for measurement, then see SEF Staff for assistance.



The Sample Table



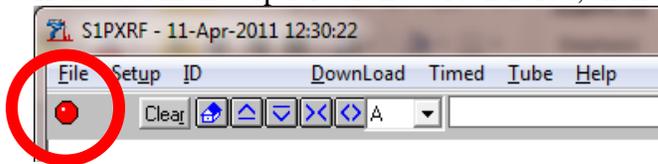
The Sample Shield

Start the Software

- Make sure that the XRF unit has been turned on for at least 1 minute before you start the software.
- Start **S1PXRF**
- In the menu *Download > Baud Rate*, make sure that the Baud Rate is set to 115200
- In the menu *Download > Port*, make sure that the Port is set to the port listed on the data collection computer.
- Select the menu item *File > PDZ Preview*.
- In the PDZ Preview dialogue window, select **Path**. Choose a previously collected *.pdz file. It does not matter which *.pdz file you select. This step configures several communication parameters.

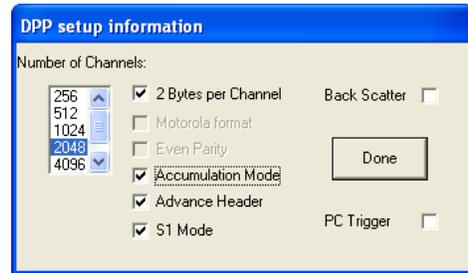


- If the dot in the top left of the screen is red, then click on it once so that it will turn green.

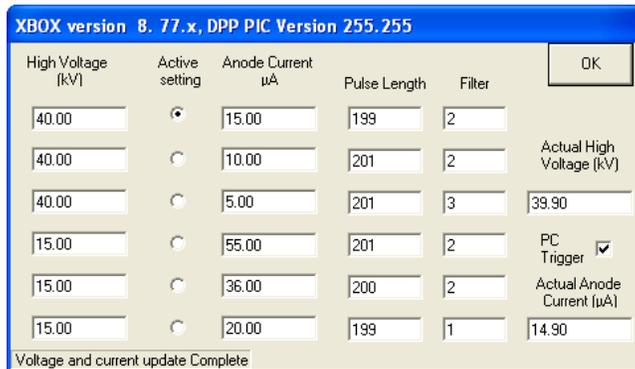


8. Select the menu item *Setup > Instrument Setup*

9. In the Instrument Setup dialogue box
- Ensure that **Back Scatter** and **PC Trigger** are both unchecked
 - All other options should be checked.
 - Number of channels should be 2048.
 - Click **Done** to close the window.



10. Select the menu item *Tube > KTI Tube > Read*.



11. In the KTI Tube window dialogue

!! You must have a sample in place before doing this step. If your sample does not fit conveniently on the sample table, then use a dummy sample (one of the XRF calibration standards) !!

- Select the desired voltage and current. See Appendix A for guidance choosing voltage and current.
- Check the box **PC Trigger**.
- Watch the values **Actual High Voltage** and **Actual Anode Current**. Ensure that they go to the correct values.
- When they stabilize at the correct values (+/- 1%), uncheck the box **PC Trigger**.
- Click **OK** to close this window

12. Select the menu item *Setup > Instrument Setup*.

- This time, make sure that **PC Trigger** is checked
- Back Scatter** should still be unchecked.
- All other options should be checked.
- Number of channels should be 2048.
- Click **Done** to close the window.

Collect Data

There are two options to collect data, the manual data collection and the timed assay. The timed assay is very useful for comparing scans from different samples, since it makes sure that the data collection time was the same for all measurements.

MANUAL DATA COLLECTION

1. In the Navigation Bar in the top left of the data window, click on the **Start** button. Data will begin collecting.



2. When enough counts have accumulated, then click the **Stop** button in the navigation bar.
3. To save the file, select the menu item *File > Save As*. Save the file in *.pdz format

TIMED ASSAY DATA COLLECTION

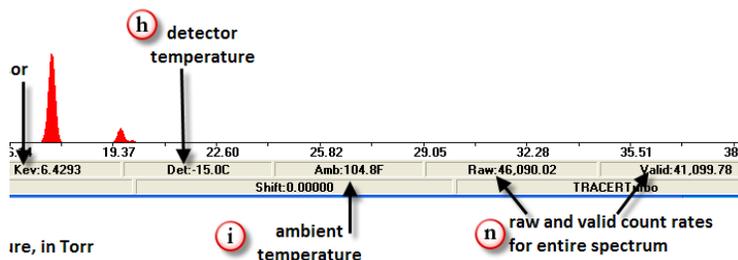
1. Go to the menu *Timed > Timed Assay*
2. Enter the data collection time in seconds (typically 120 seconds)
3. Make sure that the **PDZ** File Types checkbox is checked
4. Make sure that **Autosave** is checked
5. Make sure that **FWHM** is 150
6. Click **OK** to start data collection for the specified amount of time.



!!! FOR BOTH METHODS OF DATA COLLECTION, YOU MUST MONITOR THE COUNT RATE

Make sure that the count rate is less than 200,000 cps. The count rate is found in the lower right corner of the S1PXRF program (shown below). If the count rate exceeds 200,000 cps, then:

- a. Stop the measurement by clicking on the **Stop** button in the navigation bar.
 - b. Select the menu item *Tube > KTI Tube > Read*.
 - c. Select an option with the same voltage but a lower current.
 - d. Click **OK** to close the window.
 - e. Restart the data collection.
- * *You can also use a lower current to reduce the intensity of sum peaks*



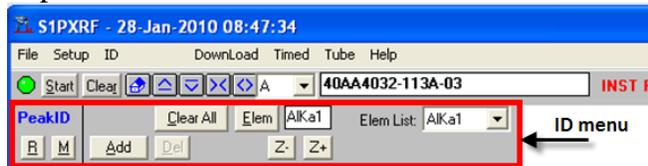
Analyze Data

You can do some basic data analysis with S1PXRF, the data collection software. The data analysis software, Spectra, provides more functionality.

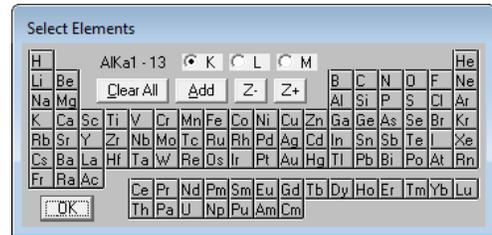
Identifying Elements with S1PXRF

The document S1PXRF User Guide provides a more detailed reference for how to use the program S1PXRF. A link to this user guide can be found on the desktop of the data collection computer.

1. Select the menu item *ID*.
 - a. This opens the **ID menu**



2. To see the fluorescence lines for an element of interest:
 - a. Click on the **Elem** button in the ID menu. The Select Elements window opens.
 - b. Select the element that you want to display
 - c. Use the radial button to select the K, L, or M lines (you can only add one set of lines at a time).
 - d. If you want to permanently label the peaks from that element in the spectrum, click on the **Add** button.
 - e. Use the **Z-** or **Z+** buttons to scroll through the elements, viewing the fluorescence lines for each in turn.
 - f. Click **OK** to close the Select Elements dialogue.
3. To get quantitative information about the fluorescence peaks:
 - a. Select the menu item *Setup > Get ROI Data*
 - b. The Intensity Data window will open, which contains the energy and channel limits for each element. Chan-Counts records the total counts within the channel limits for each element.
 - c. You can Copy or Print this list



The "Intensity Data" window shows a table with columns: Copy, Print, Ratio Mode, Energy1, Energy2, Chan-Start, Chan-End, Chan-Counts, and ROI. The table contains data for various elements and their peaks.

	Copy	Print	Ratio Mode	Energy1	Energy2	Chan-Start	Chan-End	Chan-Counts	ROI
205									
AlK.				1.4128	1.5606	70.7659	78.1693	19500.34	0.001257
S K				2.2287	2.3870	111.6316	119.5641	53751.25	0.003468
RhL				2.6152	2.7783	130.9920	139.1630	88739.78	0.005720
PdL				2.7562	2.9210	138.0554	146.3119	84118.66	0.005422
SnL				3.3580	3.5299	168.2006	176.8117	34173.44	0.002203
CaK				3.6043	3.7790	180.5372	189.2893	62194.17	0.004009
CrK				5.3181	5.5113	266.3810	276.0569	5257922.54	0.338964
FeK				6.3023	6.5053	315.6789	325.8474	9327670.23	0.601330
NiK				7.3716	7.5847	369.2356	379.9133	496471.38	0.032008

4. To change the view in the S1PXRF window
 - a. In the Navigation Bar:
 - i. The series of buttons () expands, shrinks, compresses, and broadens the spectra for easier viewing.
 - ii. The  icon restores the spectrum to its original dimensions.
 - b. You can left-click and drag in the window to expand, shrink, compress, and broaden the spectra as well.
 - c. To change the colors and display
 - i. Select the menu item *Setup > Display and Color*
 - ii. Select the radio button for an item listed, and then you can change its color and font
 - iii. The **Flood Fill** option will toggle between filling the spectra with a solid color or just showing the spectra as an outline.
5. To save the analysis results
 - a. Save the file as a *.pdz to record the analysis as well as the spectrum
 - b. Select the menu item *File > Copy to Clipboard* to capture the image of the spectrum on the screen so that you can insert it into another document (such as a MS Word document).

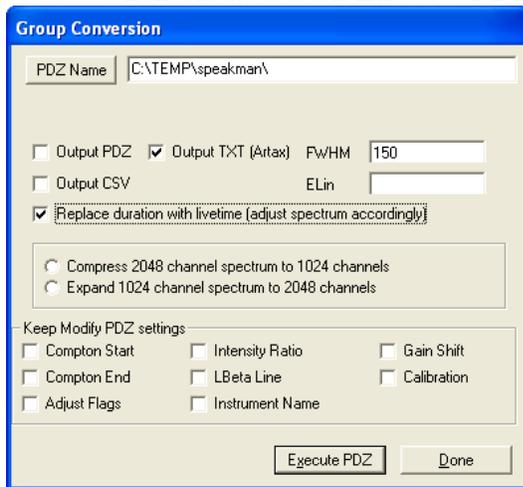
Analyzing Data in Spectra

The document Spectra User Guide provides a more detailed reference for how to use the program Spectra. A link to this user guide can be found on the desktop of the data collection computer.

Spectra can be used to collect data with some instruments. However, we only use it to analyze data—so ignore all references in the user manual related to collecting data with Spectra.

Before you can open data in Spectra, you must convert the data into a *.txt format

1. In S1PXRF, go the menu *Setup > Group Conversion*
2. Click on the button **PDZ Name** and select one file in the folder that you want to convert. All files in that folder will be converted.
3. Check **Output TXT (Artax)**
 - a. The **FWHM** should be 150
4. Check **Replace duration with livetime (adjust spectrum accordingly)**
5. Click on the button **Execute PDZ**



To Start Spectra

- 1) Select the **Spectra** shortcut from the desktop or start menu
- 2) A window will ask for a password. Leave the password field blank and click **OK**.
- 3) You will get two error messages as Spectra starts up. Ignore the error messages and just click **OK**.

To Open Data in Spectra

- 1) Go to the menu *File > Open Spectrum*
- 2) Select the *.txt files that you want to open
- 3) Click **OK**

To Manipulate the View of Data in Spectra

To scroll and zoom the data view, you left-click and drag the mouse while holding down different keys on the keyboard. The program also behaves differently depending on where the cursor is positioned.

- **To zoom the y axis:** left-click and drag on the y-axis, to the left of the data window
- **To zoom the x and y axis:** hold down the CTRL key and left-click and drag within the data window
- **To scroll the x axis:** left-click and drag on the x-axis, below the data window
- **To zoom out:** double-click outside the data window (to the left or below the data window)
- **To change the scan color:**
 - In the toolbar, use the drop-down menu (circled in red below) to select a spectrum
 - Click on the color box to the left of the scan name and select a new color.

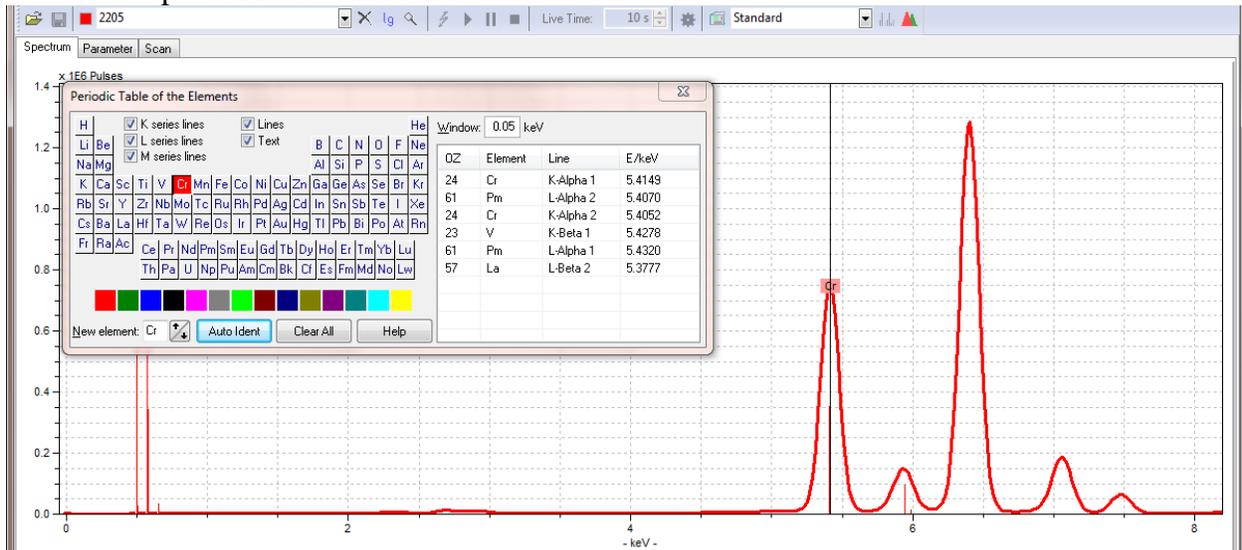


To change line widths or fonts sizes, go to the menu *Options > Display Options*.

Many other view options can be accessed by selecting the *Options* menu or right-clicking on the data.

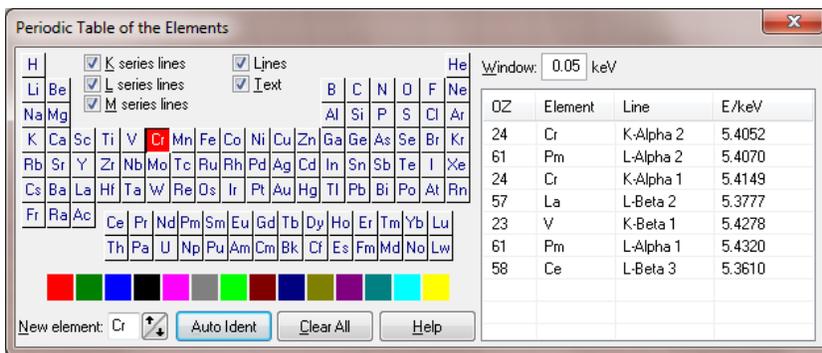
To Identify Elements

- 1) Select the menu *Analyze > Periodic Table*
- 2) The window “*Periodic Table of the Elements*” will open
- 3) Left-click on a peak in the spectrum
 - i) A line will be drawn at the position where you clicked
 - ii) Within the *Periodic Table of the Elements* window, all elements that will create a spectral line at that energy will be listed
 - iii) If you left-click on an element, either in the periodic table or in the list, then it's spectral lines will be drawn in the data window



Within the window *Periodic Table of the Elements*, you can control how spectral lines are shown and labeled

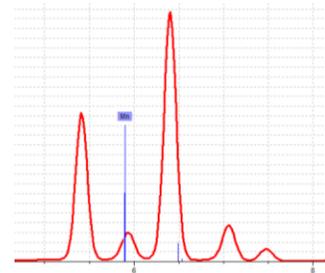
- All of the spectral lines for an element will be drawn only if the **Lines** option is checked
- The K-alpha 1 spectral line is labeled if **Text** is checked.
 - If the **Lines** option is not selected, then the **Text** label will be placed at the maximum of the K-alpha peak.
 - If the **Lines** option is selected, then the **Text** label and height for the K-alpha lines for all elements will be the same height.
- The **K**, **L**, and **M** series of spectral lines can be shown or hidden by checking the corresponding options
- To change the color used for the lines of an element, select a color box from the row at the bottom of the window and drag it to the element on the periodic table.



Advice for Elemental Identification

Use the K-alpha and K-beta peak combinations to identify the elements present in a sample. If an element is present, both the K-alpha and K-beta peaks will be produced. The K-alpha peak will usually be substantially more intense than the K-beta peak.

In the spectrum to the right, Mn could produce peaks near the observed peaks of 5.9 and 6.4 keV. However, the K-beta peak at 6.4 keV would be much weaker (based on the peak heights shown by the blue line markers).

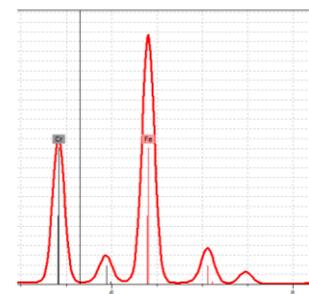


Labeling the peaks as Cr and Fe does a better job of matching the observed peak positions and the relative intensities of the peaks.

In this spectrum, it would be very difficult to identify a trace amount of Mn, because:

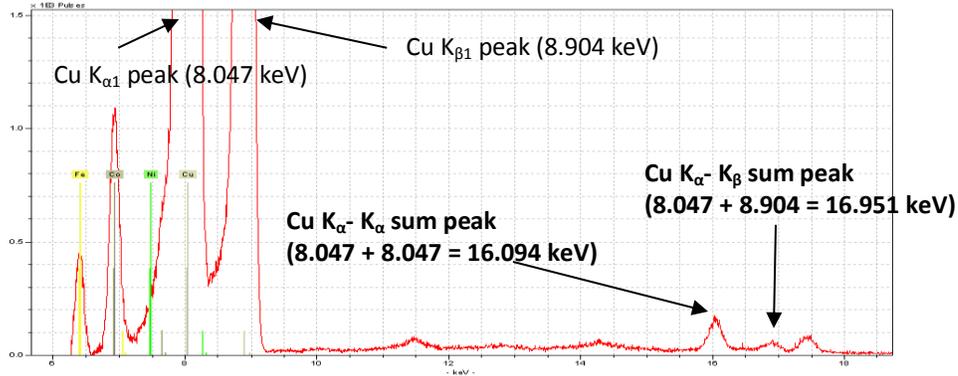
- the Mn K-alpha peak overlaps the Cr K-beta peak
- The Mn K-beta peak overlaps the Fe K-alpha peak

The best way to determine the presence of Mn would be reference to calibration spectrum or peak deconvolution (described on page 11)



Sum Peaks

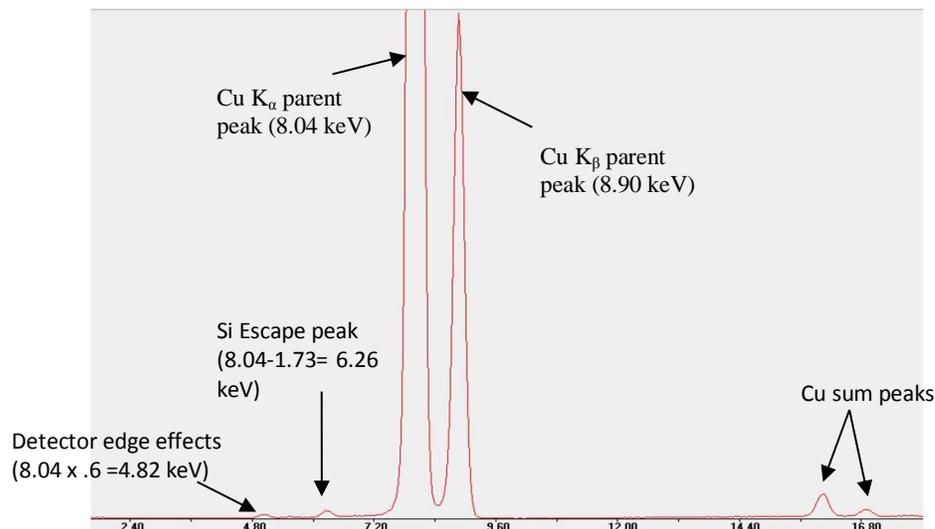
When two or more x rays enter the detector at the exact same time they are read and converted into one pulse with energy (e.g. amplitude) equal to the two pulses combined. Sum peaks appear on a spectrum when this occurs enough times to create a visible peak, as seen in **Error! Reference source not found.** and **Error! Reference source not found.** In theory, sum peaks can appear in any combination of characteristic energies, but they are most commonly found as double K_{α} - K_{α} , K_{α} - K_{β} and K_{β} - K_{β} because the higher rate of occurrence of these x rays leads to a higher probability of a sum event being recorded. Although sum peaks are small, they may be mistaken as trace elements and cause spectral interference with other characteristic peaks



ESCAPE PEAKS

While most characteristic x-rays entering the detector are converted into pulses which are processed by the digital pulse processor, an incoming x-ray can excite and cause fluorescence in an atom in the detector. If the x-ray entering the detector has an energy greater than the absorption edge of an element in the detector (for the TRACeR: Silicon), then fluorescence in the detector may occur. The inbound x ray will lose the amount of energy required to fluoresce the detector atom, leaving the x ray with an energy $E' = E_{\text{inbound}} - E_{\text{Characteristic energy of detector}}$, thus causing the detector to read the x ray as having an energy of E' .

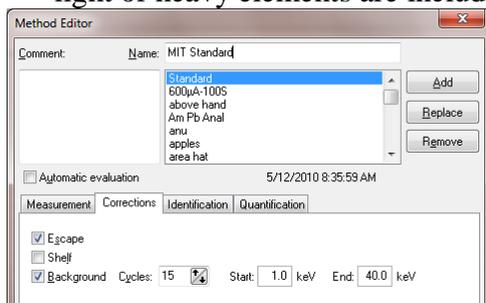
Escape peaks are much less intense than the characteristic peaks from which they are derived. Several escape peaks can occur in one spectrum. In the case of a Si based detector, escape peaks will appear approximately 1.74 keV lower than a characteristic peak because silicon has a K_{α} absorption edge. **Error! Reference source not found.** shows the escape peak from the Cu K_{α} peak. This figure also shows detector edge effect, which occurs at approximately 60% of the total K_{α} parent peak energy. Escape peaks can be automatically corrected by computer algorithms and software.



Spectrum Deconvolution

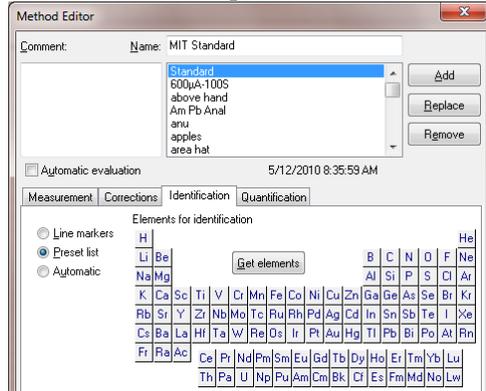
Based on typical profile intensities, the experimental data can be fit. Use this method:

- 1) Identify all of the elements in your sample.
- 2) Select the method that you would like to use or create a new method.
 - a) Go to the menu *Measurement > Method*. The **Method Editor** will open.
 - b) Select or create new method.
 - i) To select a method, at the top of the **Method Editor** window you should select the method that you want to use. Click **OK** to close the Method Editor window and proceed to step 3.
 - ii) To edit a method, at the top of the **Method Editor** window you should select the method that you want to use. Then follow steps c through h below.
 - iii) To create a new method, type in a new **Name** at the top of the **Method Editor** window. Then follow steps c through h below.
 - c) Use the four tabs, Measurement, Corrections, Identification, Quantification to define the method.
 - d) Measurement tab: this tab is not used for our instrument. You do not need to change anything in this tab.
 - e) Corrections tab:
 - i) Check the **Escape** correction
 - ii) Check the **Background** correction
 - iii) Define the number of **Cycles** that you want to use for deconvolution. This should be 10 to 15.
 - iv) Define the **Start** and **End** of the energy range that you want to refine. The maximum useful range for our instrument is 1 keV to 40 keV. This range can be trimmed if no light or heavy elements are included in the analysis



- f) Identification tab:
 - i) Check Line Markers to use the elements that you manually identified in step 1.
 - ii) Check Preset List if you would like to create a standard list of elements that you expect to always be present as you analyze similar samples. If you have identified the elements in the current spectrum, you can click the button **Get elements** to populate

the list with the elements you have identified. Alternatively, you can manually select elements from the periodic table.



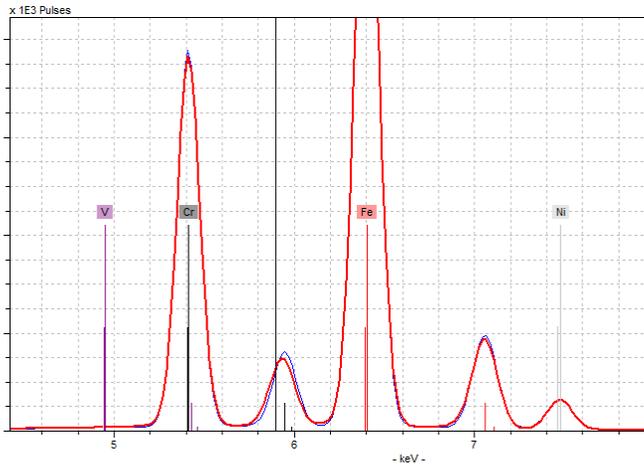
g) Quantification tab:

- i) If you have created a calibration curve, you can reference it in this tab. This will allow you to quantify the concentration of each element present.
- ii) Check **Calculate concentration**
- iii) Load the **Calibration file** that you created previously.

h) Once all tabs are filled out, click **Add** to create a new method or click **Replace** to edit the current method. Then click **OK** to close the Method Editor.

3) To deconvolute the spectrum,

- a) Go to menu *Analyze > Evaluation*
 - i) The spectrum will be fit using the Bayes method.
- b) Compare the calculated spectrum to the observed spectrum. Slight mismatches may indicate elements that were not properly identified



The mismatch of the calculated (blue) spectrum to experimental (red) spectrum at 5.9 keV may indicate that some Mn is present. Mn has a peak at 5.9 keV and would account for the shoulder to the left of the Cr K-beta peak in the observed data.

c) The Results tab will list the calculated intensities for the primary peaks of each element.

Appendix A: Guide to Selecting Filters and Tube Powers

The Bruker Tracer III-SD uses a Rh X-ray source and Pd slits. This means that Rh and Pd lines will always be present in your spectra, unless they are removed. The Rh and Pd L-lines can obscure the presence of elements such as Cl and S.

Filters can be used to remove the Rh and Pd L-lines from your spectra. Combinations of tube power and different filters can also make the instrument more sensitive to certain elements. The current filters and settings available to us are listed below. We can also develop custom filters to enhance the sensitivity to certain elements in your sample if necessary.

GENERAL ANALYSIS

This setting allows X-rays from 1 to 40 keV to reach the sample. All elements from Mg to Pu will be excited and produce a fluorescence signal. Rh and Pd lines from the source will be present in the spectrum. This will prevent observation of Cl and S lines.

Settings:

- Do not use a filter.
- Set the voltage to 40 kV
- Use the lowest possible current for metallic samples and the highest possible current for non-metallic samples
- Use the vacuum

ANALYSIS OF LIGHT ELEMENTS (Cu and below, except S and Cl)

This setting allows X-rays from 1 to 15 keV to reach the sample. The elements Mg, Al, Si, and P to Cu will be excited. The Rh and Pd lines will be present, so you will not be able to observe Cl or S lines. Because the Rh L lines are reaching the sample, elements with their absorption edge below 2.3 keV will be strongly excited—this includes Mg, Al, and Si.

Settings:

- Do not use a filter
- Set the voltage to 15 kV
- Set the current to 55 μ A
- Use the vacuum

ANALYSIS OF LIGHT ELEMENTS, (Fe and below, except for Ti and Sc but including S and Cl)

This setting allows X-rays from 3 to 12 keV to reach the sample. The Ti filter absorbs many of the Rh L-lines and fluoresces Ti K-lines. This removes the Rh and Pd lines from the spectrum and will strongly excite element with their absorption edge below 4.5 keV. However, Ti lines will be present in the spectrum, so this would not be appropriate in measuring for Ti content.

Settings:

- Use the **Blue** filter (which is Ti metal)
- Set the voltage to 15 kV
- Set the current to 55 μ A
- Use the vacuum

ANALYSIS OF METALS (Ti to Ag and W to Bi)

This setting allows X-rays from 12 to 40 keV to reach the sample. There is little sensitivity to elements below Ca.

Settings:

- Use the **Yellow** filter (Ti and Al)
- Set the voltage to 40 kV
- Start with the current at 10 μ A; lower it if the count rate is too high
- Do not use the vacuum

ANALYSIS OF HEAVY METALS (higher Z elements such as Hg, Pb, Br, As)

This setting allows X-rays from 14 to 40 keV to reach the sample. This setting is most sensitive to As and Pb. There is little sensitivity to elements below Ca.

Settings:

- Use the **Red** filter (Ti, Al, and Cu)
- Set the voltage to 40 kV
- Set the current to 15 μ A
- Do not use the vacuum

ANALYSIS OF HIGHER Z ELEMENTS (Fe to Mo) in ceramics

This setting allows X-rays from 17 to 40 keV to reach the sample. This will excite elements from Fe to Mo. This setting is optimized for Rb, Sr, Y, Zr, and Nb. There is little sensitivity to elements below Fe.

Settings:

- Use the **Green** filter (Cu, Ti, Al)
- Set the voltage to 40 kV
- Set the current to 15 μ A
- Do not use the vacuum