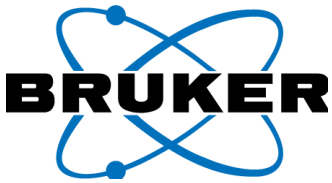
030.0023.01.0



Creating Empirical Calibrations

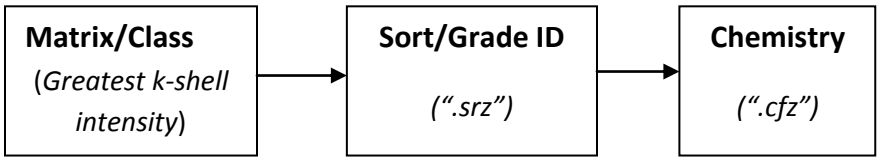
Spreadsheet Manual

Save Date: December 1, 2010

Table of Contents

1. Overview

1.1. It is important to understand the logical process of the S1 Bruker program on the Tracer's PDA. In order for the program to select the correct chemistry coefficient file, it must first identify the analyte matrix, then the alloy grade (or general composition). To do this, the program initially looks for the major K-shell peak intensity (the matrix element), and then places the analyte in a matrix category ("Class", e.g., Fe, Co, Ni). Next, the program analyzes the intensity ratios of the characteristic elements for the alloy matrix-set to determine Grade ID. For alloys, this is the 12-16 elements that the industry uses to identify a particular Grade ID (e.g., stainless steel 304 or 321). The program can then point to the correct chemistry coefficient file (".cfz") and calculate the chemistry composition of the sample.



1.2. When creating calibrations for other materials, you must decide the elements that are critical to differentiating one specimen from another. For field analysis, this will allow you to shoot a variety of samples without having to manually pre-select the calibration you wish to use. This is the "Sort" or "Grade ID" calibration ("*.srz").

1.3. Finally, when the program has detected sufficient data to classify the analyte, it will use the associated calibration coefficients stored in the, ***"*.cfz"*** file, to output quantitative chemistries for the elements of interest.

1.4.

Note
The default chemistry calibration uses Region of Interest (ROI). To use a Compton ratio, you must select Compton in the Chem model of the spreadsheet AND change columns "E" and "F" in the Alloy.csv file.

2. Enable S1 Calibration Macro

Note
• Enabling the S1 Calibration Macro adds a tab to the Excel menu bar. • The calibration spreadsheet provided on the CD has all of the original alloy calibration spectra files already loaded (over 250 assays). Spectra files have the extension, "**.pdz**". • The "Read PDZ" function is used strictly to perform the initial factory calibration and reads all 250+ pdz files into the spreadsheet.

2.1. For Use with Excel 2003 or Earlier

2.1.1. **OPEN** the calibration spreadsheet.

2.1.2. In the Excel menu bar, **CLICK** *Tools*.

2.1.3. **SELECT** *Add-ins*.

2.1.3.1. If the KTI Calibration Macro appears in the Add-in list, **ENSURE** box is checked.

2.1.3.2. If box is not checked, **CLICK** *Browse* AND THEN **SELECT** the file *C:\Program Files\KTICommon\S1CalMacros.xla* AND THEN **CLICK** OK.

2.2. **CLICK** OK on the Add-Ins box. The S1CalProcess item should appear in the Excel menu bar.

2.3. For Use with Excel 2007

2.3.1. **OPEN** the calibration spreadsheet.

2.3.2. **CLICK** the Microsoft Icon in upper left corner  .

2.3.3. **SELECT** Excel Options.

2.3.4. **SELECT** *Add-ins*.

2.3.4.1. If the KTI Calibration Macro appears in the Add-in list, **CLICK** OK.

2.3.4.2. If box is not checked, **CLICK** *Browse* AND THEN **SELECT** the file *C:\Program Files\KTICommon\S1CalMacros.xla* AND **ADD** Macro to list.

3. Getting Ready

Note
In order to add a new alloy to the calibration, you must have a sample of the new alloy and the laboratory analysis for chemistry of that sample (it is possible to add an alloy to the sort calibration without having the chemistry).

3.1. **ENSURE** the chemistry of the alloy fits within the currently existing calibration range of the instrument you are working on.

3.1.1. If the alloy is within the limits of the calibration, **PERFORM** an assay on the Tracer AND **MEASURE** the sample for at least 10 seconds.

3.1.1.1. If the assay results are acceptable, **ADD** the sample to the "Sort/Grade ID" calibration. (**Note:** If both the name and assay are correct, there is no need to add this alloy to the calibration).

3.1.1.2. If the assay is **NOT** acceptable, **ADD** this sample to both the Sort and Chemistry calibration.

3.2. **REVIEW** the chemistry of the alloy to be added AND **DETERMINE** the proper chemistry model to which it should be added. The existing assay models for the standard Alloy instrument include:

- TS1 Tool Steels
- NI1 Ni which are not included in Ni2 or Ni3
- NI2 Ni alloys with high Co
- NI3 Ni alloys with high Mo
- FE1 Low alloy Irons
- FE2 Stainless Steels (i.e., Fe based alloys with more than 5% Cr)
- CO1 All cobalt alloys
- CU1 All Copper Alloys
- TI1
- TI2
- TI3
- TI4

4. Measuring the New Sample

WARNING

- RADIATION HAZARD. X-RAYS EMITTED.
- BECAUSE THE SOFTWARE CONTROLS THE TRIGGER, IF THERE IS A SAMPLE ON THE INSTRUMENT AND THE IR SAFETY SENSOR IS COVERED, PXRF WILL START THE ASSAY.

Note

If the sample is an alloy, take a test assay in portable mode using the S1 Bruker program on the PDA. Note the matrix and alloy ID given. This will help to categorize and select the correct calibration method group. The actual calibration assays can also be taken in portable mode, but since the assays are long, it is usually easier to take them with the instrument in "Lab Mode", (connected to the PC and using PXRF). For instructions on taking timed assays, see the Tracer Series User Guide

4.1. **PLACE** the S1 Tracer in its stand with AC power or battery.

4.2. **TURN** the Tracer power switch on.

4.3. **CONNECT** the serial cable to the Tracer and PC.

4.4. **OPEN** the PXRF program on the PC.

4.5. **PLACE** the sample on the TRACER aperture

4.5.1. If the sample is small or low density, **COVER** sample with safety shield.

4.6. **SELECT** the desired instrument parameters from the "KTI Tube" menu. (Note: alternately, you may **SELECT** PC Trigger box, if available).

4.7. **SELECT** "Timed Assay" from the PXRF "Timed" menu.

4.8. **ENTER** the desired assay time. (The sample should be measured for at least 120 seconds (180 seconds is better), and for aluminums, 180 seconds is minimum.

4.9. Select "OK".

4.10. **ENTER** a file name designating the sample ID.

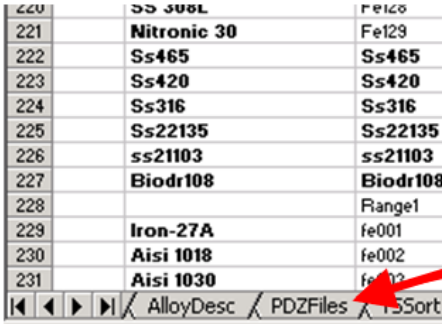


Figure 1

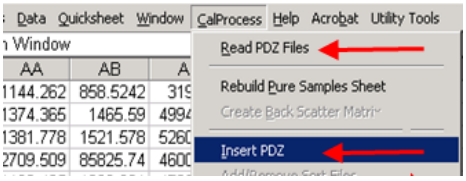


Figure 2

5. Adding New Standards to the PDZFiles Sheet

5.1. **OPEN** the "PDZ Files" tab (Figure 1).

5.2. **ENSURE** elements of interest are present on the list of elements.

5.2.1. If not, **SELECT** the last element column, **COPY** AND **INSERT** it as a new column at the end of the element columns.

5.2.2. **RENAME** the column to the desired element and atomic shell (e.g., BiLb1).

5.3. From the Excel menu bar, **SELECT** *CalProcess* (Figure 2*)*.

5.3.1. **SELECT** *Insert PDZ Files*. This will bring up the window with the serial number of the instrument (Figure 3).

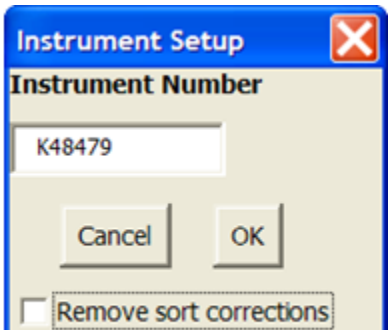


Figure 3

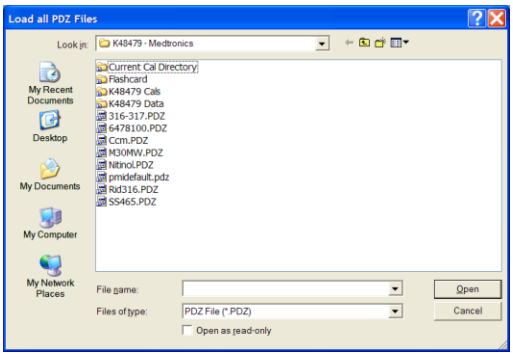


Figure 4

5.4. **ENSURE** serial number is the correct one for the instrument

5.5. **UNCHECK** *Remove sort corrections* (Figure 3).

5.6. **CLICK** OK. A file selection window opens (Figure 4).

5.7. **SELECT** all *.pdz files to be added and **CLICK** Open. The spreadsheet will automatically load all of the selected data.

6. Sort I: Adding or Removing an Alloy to an Existing Sort Calibration

Note
Even if your main interest is to add to the chemistry model, the new sample should be added to the Sort model.

6.1. In Excel, **SELECT** the Sort sheet appropriate for the matrix.

6.2. From the S1 CalProcess menu, **SELECT** *Add/Remove Elements* AND **CHANGE** the elements of interest as desired.

6.3. From the S1CalProcess menu, **SELECT** *Add/Remove Sort Files*. A window will open (Figure 5).

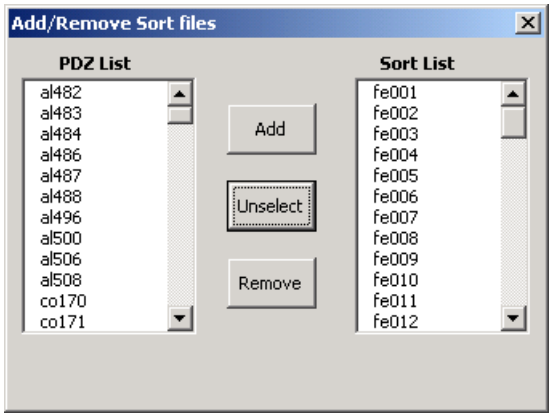


Figure 5

Notes
• At least one file must be available at all times so, first add files before removing files. • Available files (from PDZ sheet) that are NOT currently in use are listed on the left (see Figure 5); files currently in use are listed on the right. • Multiple files may be selected by holding down the Ctrl key.

6.4. **CLICK** on each file you want to ADD.

6.5. **CLICK** *Add*. A window will open *with* a Sigma value option.

6.6. **DO NOT CHANGE** the Sigma value (default is "2").

6.7. Click OK.

6.8. **SELECT** any files you wish to eliminate from the "Sort" model.

6.9. **CLICK** *Remove*.

6.10. **CLOSE** the Add/Remove window.

6.11. From the S1 Calibration menu, **SELECT** Create Sort File.

6.12. **SAVE** the file to the appropriate folder (this creates the *.srz file [e.g. Fe1.srz]. Each matrix has its own sort model).

6.12.1. If you receive a "Sort Range Error" showing overlapping alloys and you **DO** have all of the original calibration PDZ files, **CLICK** *Ignore.*

7. Chemistry I: Adding a New Sample to an Existing Chemistry Model

Notes
• If using a new sample, you will need the laboratory analysis for the sample. • If using a certified reference material, you will need the certificate. • Ensure that all of the tube settings in the new spectra are exactly the same as the original spectra used in the present model. (See PDZ Files sheet, columns "BA" to "BL").

7.1. Before adding a new alloy or sample to a Chemistry model, **ENSURE** all of the elements of interest are already in the model.

7.1.1. If all samples are **NOT** present, **GO TO** the PDZ file sheet and **ENSURE** the elements and lines are there.

7.1.1.1. If the element and/or line **IS NOT** in the list, **ADD** it to PDZfiles sheet as described in Appendix A).

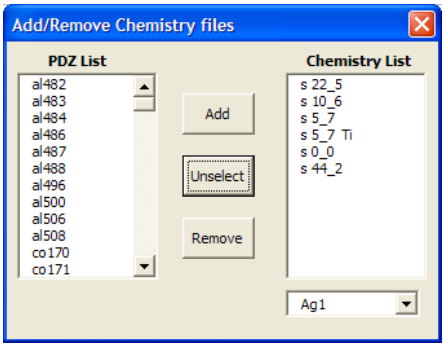


Figure 6

7.2. From the S1CalProcess menu, **SELECT** *Add/Remove Elements* .

7.3. **ADD** the new Element or line.

7.4. **SELECT** *Add/Remove Chemistry Files*. A window will appear (Figure 6).

7.5. **SELECT** the new sample from the *PDZ List* on the left.

7.6. Click *Add*.

Note
After adding the new "pdz" files (spectra) to the Chemistry model, you will automatically be shifted to the portion of the spreadsheet to enter the chemistry values (Lab results) for the new standard; if this does not happen, the area is located at the far right of the Chemistry sheet.

7.7. **ENTER** the laboratory assay value or certified value for each element as a wt% (without the "%") for alloys or appropriate unit of measure. (**NOTE**: These should be elemental concentrations, not oxides).

Note
Assay values may be added as each sample is added, or added later when other tasks are completed.

7.8. **ENTER** the assay values for the sample.

7.9. From the S1CalProcess menu, **SELECT** *Create Chemistry files.*

7.10. **SELECT** the appropriate chemistry calibration model (e.g., Cu1) (Figure 7, 1).

Note

When using Compton for Chemistry Intensity, use either the actual Compton energy range (Figure 7, 2), or select any energy range that provides optimal count rate and does not (and will not) have any element intensities.

7.11. **SELECT** the Chemistry Intensity (normalization method) (Figure 7, 3):

- **ROI** (Regions of Interest) is the default and recommended mode for alloys
- **Compton** is typically used for light element matrices and/or thin samples
- **Time** (Net Intensities: Time is not recommended as a normalization method)

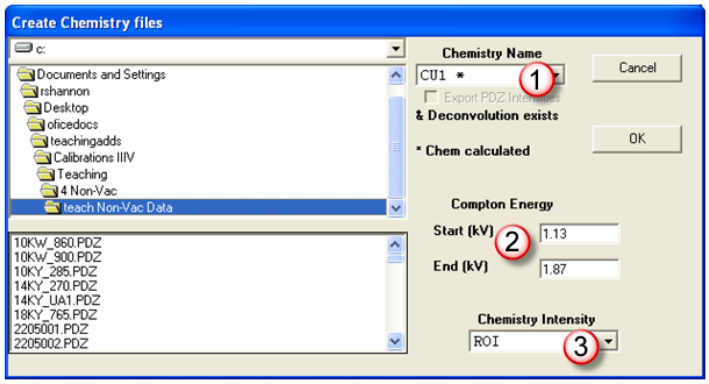


Figure 7

1 **Chemistry Model** 2 **Compton Range** 3 **Intensity Method**

7.12. **CLICK** OK. The Delta-I Model Selection window opens.

7.13. Understanding Delta Model Selection

7.13.1. The four columns (parameter options) on the left side of the Delta-Model Selection window (Figure 8) are used to create the regression equation (each element has its own separate coefficients):

- **Element** is the element currently being calculated/calibrated.
- **Slope** is selected for elements that may have an absorption/enhancement factor for the element of interest. This correction will be used in the regression to correct the concentration of the selected element. (To select or de-select an element, hold down the "Ctrl" key and click on the desired elements). **Note:** If you do not hold the "Ctrl" key, you will lose the previous selections.
- **BG S** (Background subtraction) provides a background/overlap correction for the element.
- **Omit Std** is used if a particular standard appears to be clearly a bad standard (or not appropriate for the calibration), select "Omit Std". **Note**: Be careful about omitting a standard. The problem is usually an interfering element. Omitting a standard in one calibration does not omit it from other elements' calibrations.

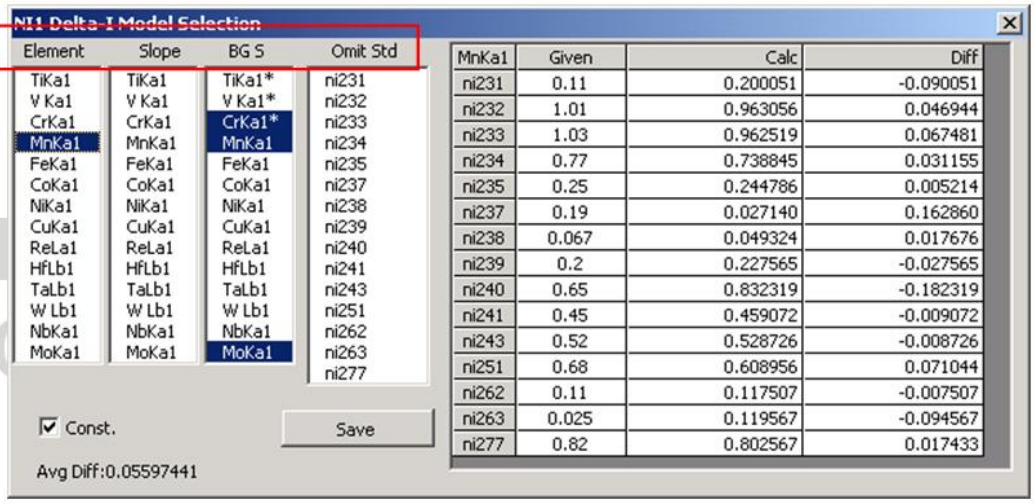


Figure 8

7.13.2. **MONITOR** the progress of the regression calibration by watching the *Ave Dev* at the bottom of the window. In general, a lower value is better.

7.13.3. **MONITOR** the error for each standard by observing the table at the right of the window.

7.13.4. **DO NOT SELECT** too many elemental corrections or terms for the regression, as this will cause the actual measurement to become unstable and impacts the precision of the measurements from one reading to the next. This is why the *Ave Dev* value is most important when creating a calibration model. *(If the Ave Dev is "Ø", then you have selected too many corrections.)*

7.13.5. Once the regression for an element has been completed, **SELECT** the next element in the list. After each element has been calibrated, an asterisk (*) will appear next to the element in the BG S column.

7.13.5.1. To change the correction for some elements, and to save the factory defaults, **USE** the arrow keys (↓↑) **TO SCROLL** through the elements after selecting one from the element list. All elements in the list should be addressed before saving the calibration.

7.13.5.2. Once all the elements have been satisfactorily regressed, **CLICK** *Save*. This will bring up a directory selection box.

7.13.5.3. **SELECT** the directory "*C:\……\Current Cal*".

7.13.5.4. **CLICK** *Save*.

8. PDZFile II: Adding New XRF Lines to PDZFile Sheet

Note

- You will most likely have new samples to use for calibration for this new matrix. It is best to add the new samples into the PDZFiles sheet before editing the *XXSort/XXChem* sheets.
- If you wish to add Element lines that are not already shown in the PDZFile Sheet, it is best to add them first.
- In the following examples, *XX* is a placeholder for the element of interest and/or its line (e.g., XXXX might be a placeholder for PbLb1). *Some date* is a placeholder for the date used in a filename.

8.1. To add an Element line, **INSERT** a column.

8.2. **TYPE** in the new line using the same naming convention (e.g., CrK, AsKb1, PbLb1).

8.3. From the S1CalProcess Menu, **SELECT** "Read PDZ File" This will bring up the window with the serial number of the instrument as shown.

8.4. **ENSURE** the serial number is correct for the instrument.

8.5. **UNCHECK** Remove sort corrections.

8.6. **CLICK** OK. A file selection window will then open.

8.7. **SELECT** the directory where the currently used data is located (e.g., the Non-vac Alloy data might be found on a CD in the directory "E:\K0XXXX *Some date* Tracer111LE\K0XXXX Non-Vac *Some date*\K0XXXX Non-Vac Data\").

8.8. **SELECT** *Read PDZ Files* to reorder all the element lines from lowest to highest energy and calculate the intensities for the added lines.

Note

At least one file must be available at all times so, first add files before removing files.

8.8.1. **SELECT** *Insert PDZ files* to add at least two of your new samples

8.8.2. **ADD** the samples into the XXSort and XXChem as described in Sections 6 and 7.

8.8.3. If the original data is not available, **DELETE** all the file names in the PDZfiles sheet (delete both Column B and A for good housekeeping).

9. Sort II: Adding a new Matrix

Notes

- In order for the macros to work properly, the Sort sheet must be created BEFORE creating the Chem sheet.
- There can be multiple calibrations in one chemistry sheet each labeled with the same two letters, defining the major element, and a sequential number to designate the different chemistry calibrations. It would be best to pick a sheet that has the number of chemistry calibrations you plan to make so that you do not need to add or remove calibrations.
- Adding multiple calibrations is described at the end of the Appendix.

9.1. To create a new sheet for the Class (i.e. CuSort/CuChem), **RIGHT CLICK** on an existing XXSort sheet AND **SELECT** *Move or Copy*.

9.2. **CHECK** the *Create Copy* box

9.3. Click OK.

9.4. **REPEAT** Steps 0 through 9.3 for the corresponding XXChem sheet.

9.5. **RIGHT CLICK** on existing tabs and **SELECTING** *Rename*.

9.5.1. **RENAME** each sheet with a two letter element name followed by Sort or Chem (e.g., CuSort/CuChem or "K Sort"/K Chem).

9.6. In the XXChem sheet, **GO TO** cell A2.

9.6.1. **SCROLL** to the right past the cell with "blank" typed in it and past the second set of XRF lines until you reach a cell with a two letter element designation followed by a number, the two letter designation should be both capital letters for example "AL1".

9.6.2. **CHANGE** the 2 letter designator to match the sheet, but the sheet has one capital and one lower case.

9.6.3. **CHECK** that you are changing a cell that has the text and not a link to a cell with the text.

9.7. **REOPEN** the XXSort sheet.

9.8. **ADD**/**REMOVE** sort files in accordance with Section 6.

9.9. **RENAME** the Base element column.

9.10. **ADJUST** the formulas to recognize the new Matrix or "Base" element.

9.10.1. In area labeled *Adjusted Windows* (below the first area), **RESET** the equations (e.g., if Cu is the new Base and is in column G, then the formulas in the *Adjusted Windows* section should be X/$G?).

9.10.2. **ENSURE** that the cell above the XRF line (i.e.CuKa1) (located to the right of the *Master Section* and below the *Adjusted Windows* section reads *Base* AND the cells over the XRF line read "If(xx=1000,"Base","""), where xx is the first cell in the matrix column just below the XRF line name.

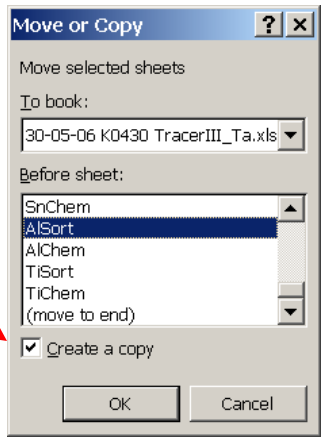
10. Creating a Flashcard Image

Several files must be updated in order to use the new calibrations on the PDA. The *Build PDA Image* macro will update these files automatically.

11. Transfer Modified Files to Flash Card.

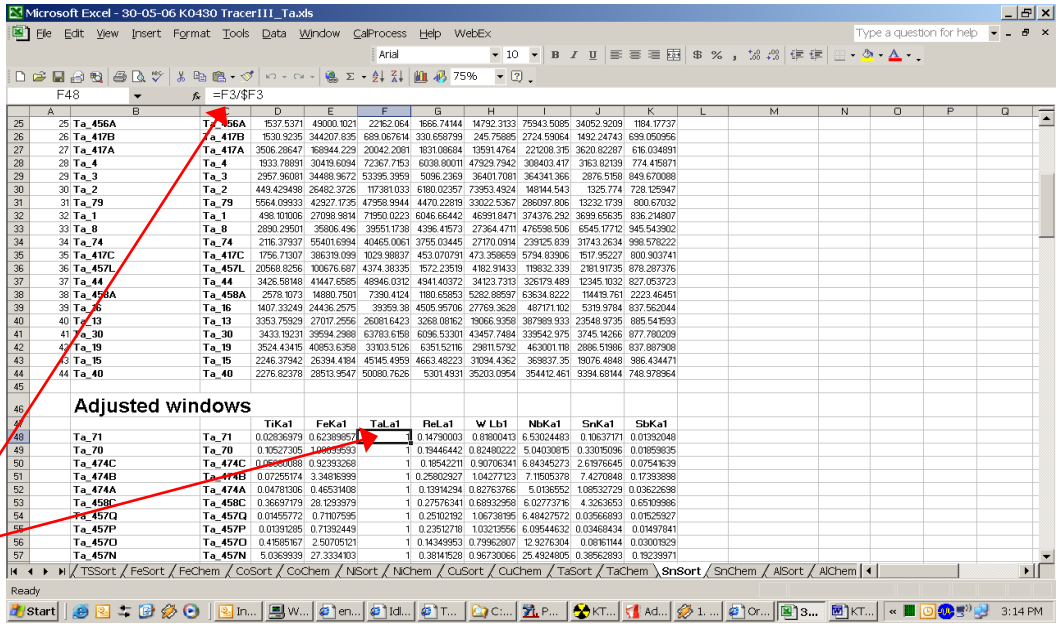
The *Build PDA Image* macro will create a new Flashcard image that contains both the Factory calibrations and the new calibrations.

Appendix A Creating a new Matrix Calibration



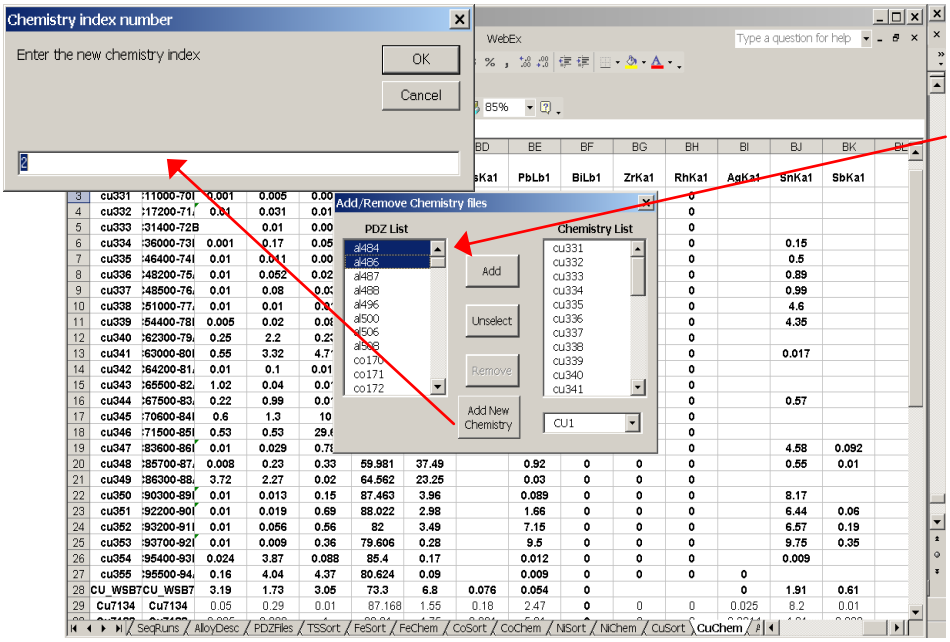
1. **SELECT** any existing "Sort" spreadsheet.
2. **SELECT** "Copy to New Sort Sheet" from the CalProcess Menu.
3. **SELECT** any existing "Chemistry" spreadsheet.
4. **SELECT** "Copy to New Chemistry Sheet" from the CalProcess Menu.
5. **RETURN** to the new "Sort" sheet.
6. **ADD** or **REMOVE** Elements from Chemistry spreadsheet.
7. **ADD** or **REMOVE** Elements from the sort files.
8. **ADJUST** the formulas to recognize the new Matrix or "Base" element (e.g., if Sn is the new Base and is in column J, then the formulas in the *Adjusted Windows* section should be X/$J. (**IMPORTANT**: **CHANGE** the old Base element column <u>first</u>.)

NOTE: **<u>YOU</u> <u>MUST</u>** "Create Sort" before using the Chem sheet. None of the Chemistry macros will work until you do so.



9. To the right of the “Master” section, there is another section which defines the base element. **GO TO** the column for your new matrix or “base” AND **EDIT** the cell over the line designation (SnKA1) formula to read, “If(xx=1000,”Base”,””), where xx is the first cell in the matrix column below line designation (SnKA1). Frequently the formulas lose a reference and need to be retyped.

10. **ADD** and **REMOVE** the chemistry files and **CREATE** the chemistry calibration (see Section 7).



To add a 2nd or 3rd Chemistry “Cfz” to an existing matrix set-- **SELECT** the Add/Remove Chem files”, then **SELECT** at least 2 new PDZ files from the left column

SELECT “Add New Chemistry” and **INSERT** the next index number.

Appendix B Building a Flashcard Image

1. From the *Instrument Info* tab, open the S1 Cal Process menu.
2. **SELECT** *Build PDA Image*.
3. **RIGHT CLICK** in Grey area to **ADD** new Calibration Method/or Group.
4. **ENTER** the Method name that should appear on PDA for user selection.
5. **SELECT** the associated Sort and Chemistry files (*.srz and .CFZ).
6. If using “Compton” ratio method, **SELECT** the Compton (eV) range.