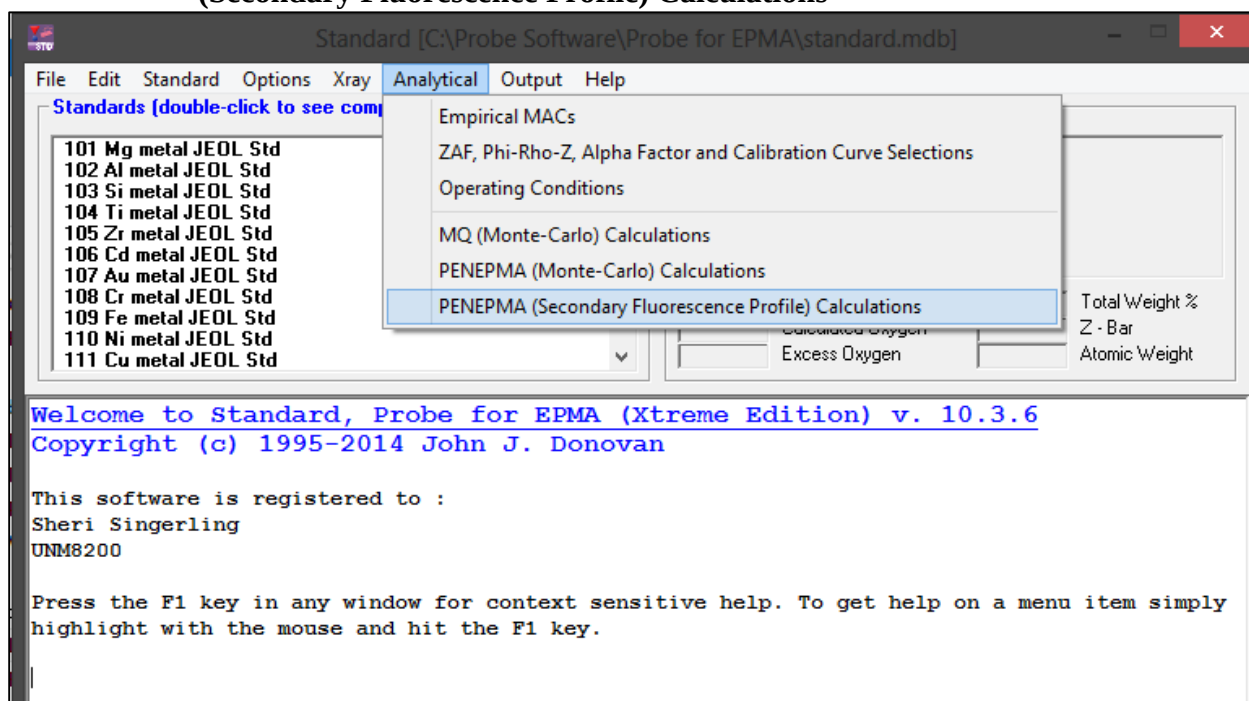


PENEPMA Instructions (.geo files):

*additional information for these procedures is available on the PFE forum:

<http://www.probesoftware.com/smf/index.php>

1. Open the **Standard.exe** ( Standard) file with the following path: C:\Probe Software\Probe for EPMA
2. Choose the default **STANDARD.MDB** file
3. Check to see if there is a **secondary fluorescence (SF) problem** with the phases and corresponding elements of interest by running the Fanal. If you already know that an SF problem exists, skip to 4.
 - a. In the Standard.exe program, click the **Analytical tab** → **PENEPMA (Secondary Fluorescence Profile) Calculations**



- b. To run the program, you will have to **create .PAR and .MAT files** for your phases. You do this on the left side of the screen.
 - i. **.PAR files** take ~10 hours to run, so **make sure adequate files don't already exist in the penfluor folder** with the following path:
C:\UserData\penepma12\penfluor
 - ii. Here are **links on the PFE forum** for PAR files as they are **updated periodically**:
<http://probesoftware.com/smf/index.php?topic=13.msg23#msg23>
<http://probesoftware.com/smf/index.php?topic=119.msg1638#msg1638>

Primary Intensity Calculations (create .PAR files for one or all .MAT files) (~10 hours each at 3600 sec)

Create Material Files in PENEPA_Path

Mat. A:

Mat. B:

Mat. B Std:

Time (in seconds per simulation, x10):

Number of Simulations (in electrons, x10):

Run Penfluor and Fitall for ALL three materials (generate .PAR files)

Run Penfluor/Fitall for Material A Only

Run Penfluor/Fitall for Material B Only

Run Penfluor/Fitall for Material B Std Only

iii. **.MAT files** can be created using the **lists** provided or by entering in a **formula**

1. Make sure the **density is accurate** for your .MAT files. Before typing in the formula for the phase, make sure you have entered the correct density.

PENEPA Material Files (create .MAT files)

Select Material A (beam incident material)	Select Material B (boundary material)	Select Material B Std (primary standard) (must contain the measured element)
101 Mg metal JEOL Std 102 Al metal JEOL Std 103 Si metal JEOL Std 104 Ti metal JEOL Std 105 Zr metal JEOL Std 106 Cd metal JEOL Std 107 Au metal JEOL Std 108 Cr metal JEOL Std 109 Fe metal JEOL Std 110 Ni metal JEOL Std 111 Cu metal JEOL Std 112 Mo metal JEOL Std	101 Mg metal JEOL Std 102 Al metal JEOL Std 103 Si metal JEOL Std 104 Ti metal JEOL Std 105 Zr metal JEOL Std 106 Cd metal JEOL Std 107 Au metal JEOL Std 108 Cr metal JEOL Std 109 Fe metal JEOL Std 110 Ni metal JEOL Std 111 Cu metal JEOL Std 112 Mo metal JEOL Std	101 Mg metal JEOL Std 102 Al metal JEOL Std 103 Si metal JEOL Std 104 Ti metal JEOL Std 105 Zr metal JEOL Std 106 Cd metal JEOL Std 107 Au metal JEOL Std 108 Cr metal JEOL Std 109 Fe metal JEOL Std 110 Ni metal JEOL Std 111 Cu metal JEOL Std 112 Mo metal JEOL Std
Density Osc. Strength Osc. Energy 8.96 0 0	Density Osc. Strength Osc. Energy 8.9 0 0	Density Osc. Strength Osc. Energy 8.9 0 0
Oscillator strength (F _{cb}) and Oscillator energy (W _{cb}) of the plasmon should be zero for insulators		
Create PENEPA Material A From List	Create PENEPA Material B From List	Create PENEPA Mat. B Std From List
Create PENEPA Material A From Formula	Create PENEPA Material B From Formula	Create PENEPA Material B Std From Formula
Density of V equals 5.8 Density of Cr equals 7.19 Density of Mn equals 7.43 Density of Fe equals 7.86 Density of Co equals 8.9 Density of Ni equals 8.9 Density of Cu equals 8.96	Density of Sc equals 3 Density of Ti equals 4.5 Density of V equals 5.8 Density of Cr equals 7.19 Density of Mn equals 7.43 Density of Fe equals 7.86 Density of Co equals 8.9	Density of Sc equals 3 Density of Ti equals 4.5 Density of V equals 5.8 Density of Cr equals 7.19 Density of Mn equals 7.43 Density of Fe equals 7.86 Density of Co equals 8.9

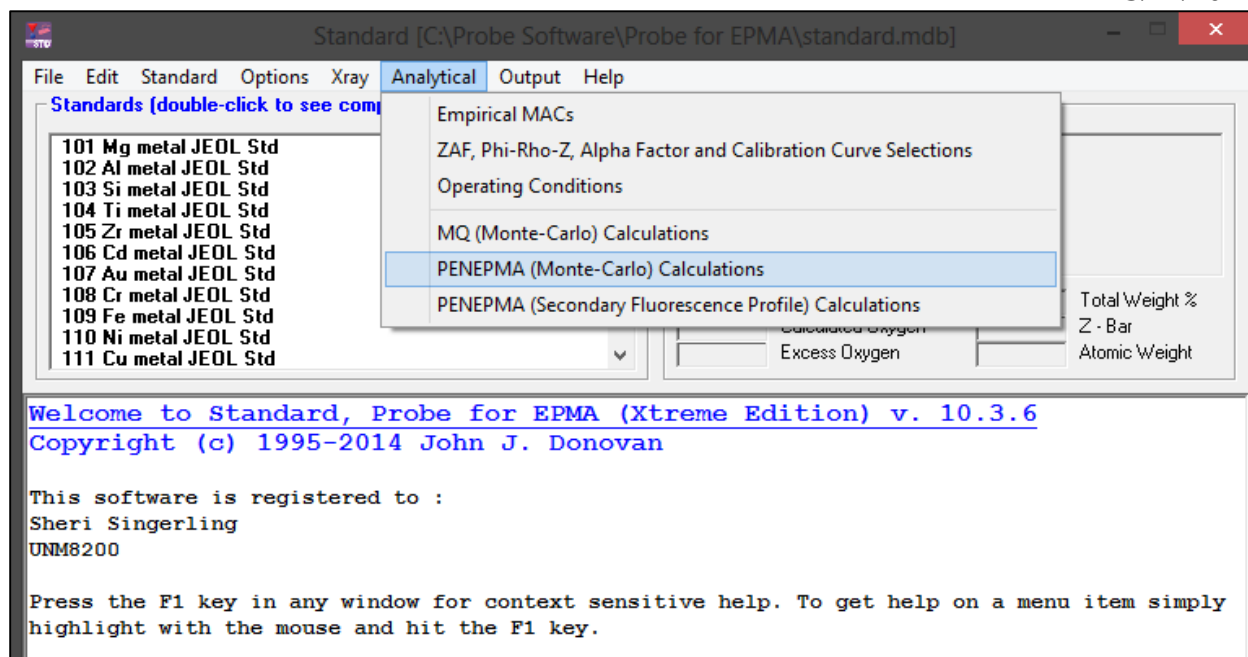
iv. You will need to create **.PAR and .MAT files** for **the phases of interest and the standards** you will use on the probe for elements likely affected

by SF (e.g., ~1 micron spherical inclusions of Fe,Ni-metal in pyrrhotite grains)

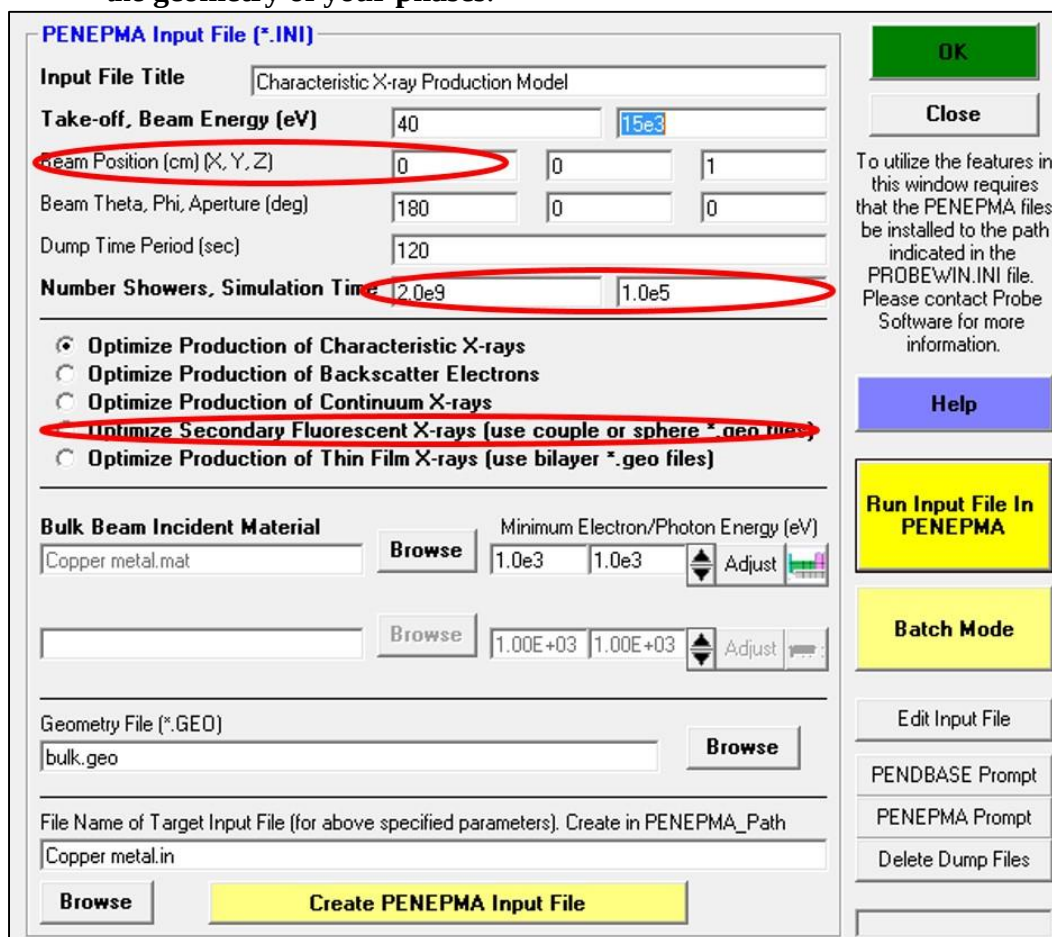
1. Material A = incident beam phase (e.g., Fe,Ni-metal)
 2. Material B = boundary phase (e.g., pyrrhotite)
 3. Material B std = primary standard (e.g., pyrite for S, Fe metal for Fe, Ni metal for Ni)
- c. After the .PAR and .MAT files have been created, you can **run the program** to determine if SF is an issue for your materials. You do this on the right side of the screen.

The screenshot shows the PENEPM software interface. At the top, there are buttons for 'Help' (blue), 'Take-off' (set to 40), 'KeV' (set to 15), and a green 'OK' button. Below these are buttons for 'PENDBASE Prompt', 'PENEPM Prompt', 'Penfluor Prompt', 'Fanal Prompt', 'Binary Calculations', and a 'Close' button. The main section is titled 'Calculate Secondary Fluorescence Profiles For the Specified Element and X-ray'. It states 'Parameter Files are created in PENEPM_Root\Penfluor'. There are three rows for material selection: 'Material A (beam incident)' with 'Cu.par', 'Material B (boundary)' with 'Co.par', and 'Material B Std (primary std)' with 'Co.par'. Each row has a 'Browse' button. Below these are dropdowns for 'Element' (set to Co) and 'X-Ray' (set to ka), and input fields for 'Microns' (50) and 'Points' (50). A large yellow button reads 'Run Fanal (generate k-ratio file for couple boundary)'. To its right are checkboxes for 'Send To Excel' (unchecked), 'Use Log Scale' (unchecked), and 'Use Grid Lines' (checked). A 'Copy To Clipboard' button is also present. At the bottom right, there are two input fields for numerical values, both set to .000000, and a 'Zoom Full' button.

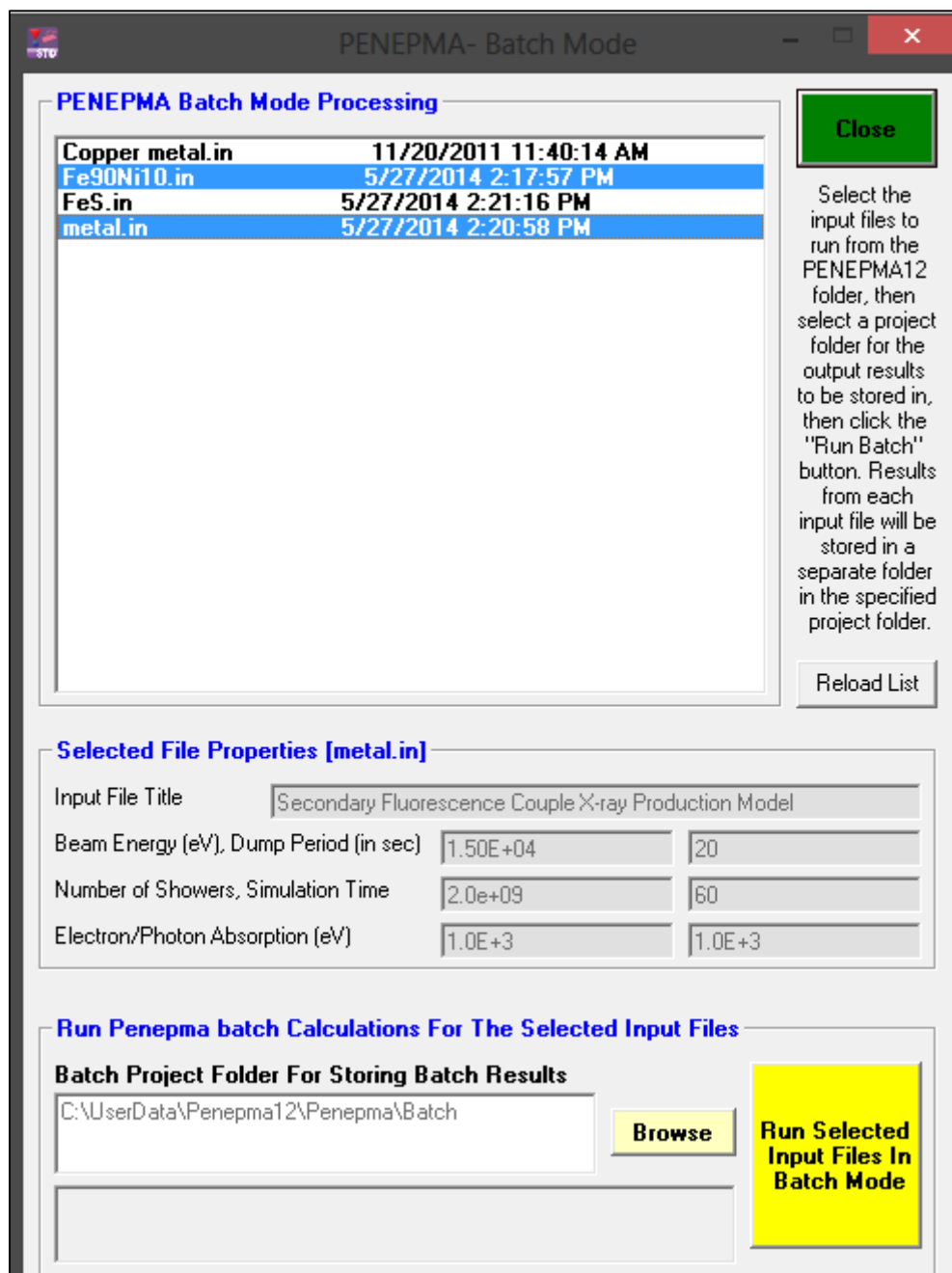
- i. Enter in all the required information making sure **Material B std includes the element** you are running the program for
 - ii. Click “**Run Fanal (generate k-ratio file for couple boundary)**” button
 - iii. You can extract the resulting plot by clicking the “**copy to clipboard**” button and pasting it into an appropriate program like MS paint, Adobe photoshop, or MS powerpoint
 - iv. If any of your elements show a SF issue near the boundary between the two phases of interest, proceed. Otherwise, no additional corrections to microprobe data are required
4. Since SF is a problem with at least one element your analyzing for, you will need to **generate corrections for this effect**
- a. In the Standard.exe program, click the **Analytical tab** → **PENEPM (Monte Carlo) Calculations**



- b. To generate corrections, you have to **create .IN files** for your incident beam phase with the boundary phase and any standards. This program also takes into account the **geometry of your phases**.



- i. You will likely want to **decrease the simulation time** as the default is ~27 hours. Go with whatever will give to low uncertainties (I usually do 3600 s).
- ii. Choose the “**Optimize Secondary Fluorescent X-rays (use couple or sphere *.geo files)**” option
- iii. **Load your .MAT files** for the beam incident phase and adjacent phase using the browse buttons
 1. *You want to make sure to **avoid using the Taylor series premade .MAT files**. These do not seem to work when you try to make .IN files for them.*
- iv. **Load the correct geometry file** using the browse button (1mic_sphere.geo). Note that this file must have the following path: C:\Probe Software\Probe for EPMA\penepma12\Penepma. There are many geometry files in the penepma12 folder, but you have to move the one you want into the Penpma folder within. *Changing this will change the beam position's x value to a non-zero value. Make sure to change it back to 0.*
- v. Make sure that the “**minimum electron/photon energy**” boxes include **the x-ray lines you are measuring for**. Sometimes the values in these boxes change when you are inputting all your parameters and may exclude the x-ray lines you are interested in. **Keeping it at the default value of 1.0e3 is a safe bet.**
- vi. Name your .IN file and click “**Create PENEPM Input File**”.
 1. You must **do this for the incident beam phase which includes the boundary phase and any standards used for the elements of interest.**
 2. For the **standard .IN files**:
 - a. Choose the “**Optimize Production of Characteristic X-rays**” option
 - b. Use the **bulk geometry file**
 - c. Since PENEPM does not distinguish the intensity produced from SF and the intensity produced from the actual sample, you will need to run a **bulk geometry for your incident phase** as well
 - i. In an example where both the inclusion and the surrounding phase have a given element, like Fe in Fe,Ni-metal and FeS, the emitted intensity for Fe can be both characteristic x-rays or secondary fluoresced x-rays. This bulk run will allow you to tease apart the two intensities.
- c. After you have created all your .IN files, you are ready to **run the program for k ratio corrections**
 - i. Still in the same window, click the “**Batch Mode**” button on the far right
 - ii. In the new window that pops up, **highlight all .IN files** you will use



- iii. Choose an appropriate location for the results to be saved to using the browse button or leave it as the default
- iv. Click the **"Run Selected Input Files In Batch Mode"** button
- v. Once the simulations are complete, the console window that pops up will close and you will be able to see the files wherever you saved them to (C:\UserData\penepma12\Penepma\Batch)
- d. Your **intensities** can be found in the **T column** of the **"pe-intens-01.dat"** files in each of your folders (the most common transitions are K L3 (Ka), K M3 (Kb), L3 M5 (La), L2 M4 (Lb))

i. PFE forum link:

<http://probesoftware.com/smf/index.php?topic=202.msg1506#msg1506>

```
# Results from PENEPA. Output from photon detector # 1
#
# Angular intervals : theta_1 = 4.500000E+01, theta_2 = 5.500000E+01
#                      phi_1 = 0.000000E+00, phi_2 = 3.600000E+02
#
# Intensities of characteristic lines. All in 1/(sr*electron).
# P = primary photons (from electron interactions);
# C = fluorescence from characteristic x rays;
# B = fluorescence from bremsstrahlung quanta;
# TF = C+B, total fluorescence;
# unc = statistical uncertainty (3 sigma).
```

#	IZ	S0	S1	E (eV)	P	unc	C	unc	B	unc	TF	unc	T	unc
16	K	L2		2.3067E+03	3.297587E-06	1.56E-06	1.333990E-07	2.31E-07	1.660507E-07	1.66E-07	2.994497E-07	3.96E-07	3.597036E-06	1.58E-06
16	K	L3		2.3079E+03	5.332268E-06	2.12E-06	8.893268E-08	1.89E-07	3.632790E-07	2.42E-07	4.522117E-07	4.31E-07	5.784479E-06	2.15E-06
16	K	M3		2.4641E+03	3.508071E-07	4.70E-07	4.446634E-08	1.33E-07	3.761546E-08	7.97E-08	8.208180E-08	2.13E-07	4.328889E-07	4.94E-07
26	K	L2		6.3910E+03	1.791501E-05	2.75E-06	3.112644E-07	3.52E-07	6.365442E-07	3.33E-07	9.478086E-07	6.85E-07	1.886282E-05	2.79E-06
26	K	L3		6.4040E+03	3.613636E-05	4.15E-06	2.667980E-07	3.26E-07	1.288797E-06	4.73E-07	1.555595E-06	7.99E-07	3.769196E-05	4.18E-06
26	K	M3		7.0582E+03	4.720356E-06	1.40E-06	8.893268E-08	1.89E-07	1.128464E-07	1.38E-07	2.017791E-07	3.26E-07	4.922135E-06	1.42E-06
26	K	M2		7.0582E+03	2.471344E-06	1.04E-06	8.893268E-08	1.89E-07	1.881374E-07	1.95E-07	2.770700E-07	3.83E-07	2.748414E-06	1.07E-06
28	K	L2		7.4610E+03	1.422923E-06	7.45E-07	0.000000E+00	0.00E+00	1.886779E-08	5.66E-08	1.886779E-08	5.66E-08	1.441791E-06	7.47E-07
28	K	L3		7.4783E+03	2.401182E-06	9.58E-07	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	2.401182E-06	9.58E-07
28	K	M3		8.2648E+03	4.446634E-07	4.20E-07	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	4.446634E-07	4.20E-07
28	K	M2		8.2648E+03	4.001971E-07	3.99E-07	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	0.000000E+00	0.00E+00	4.001971E-07	3.99E-07

5. To **correct your concentrations** (in wt.%) from microprobe data, you will need to convert the SF **intensities into wt.%** for each element which involves several steps. Here is an abbreviated version:

a. $I_A^{\text{geometry}} - I_A^{\text{bulk}} = I_A^{\text{unknown}}$

b. $(C_A^{\text{std}}/[ZAF]_A^{\text{std}}) \times (I_A^{\text{unknown}} / I_A^{\text{standard}}) = K \text{ ratio}_A$

c. $K \text{ ratio}_A \times 100 = K \text{ ratio}_A \% \text{ and } (K \text{ ratio}_A \%) \times ([ZAF]_A^{\text{unknown}}) = C_A^{\text{unknown}}$

- a. Tease apart the **SF contribution to intensity from the total intensity**

i. This is why you ran a “bulk” geometry file for your incident beam phase in 4.v.b

ii. Simply subtract the intensity of your incident beam phase from the bulk geometry (i.e., Fe90Ni10 with bulk.geo) from your incident beam phase with the correct geometry (i.e., Fe90Ni10 with 1mic_sphere.geo)

$I_A^{\text{geometry}} - I_A^{\text{bulk}} = I_A^{\text{unknown}}$ (where A is your element)

- b. Generate the **k-ratio**

i. If you used a pure element standard, simply divide the intensity from a. by the intensity from your standard (which is from the in-tens-01.dat file for your standard)

$K \text{ ratio} = I_A^{\text{unknown}} / I_A^{\text{standard}}$ (where A is your element)

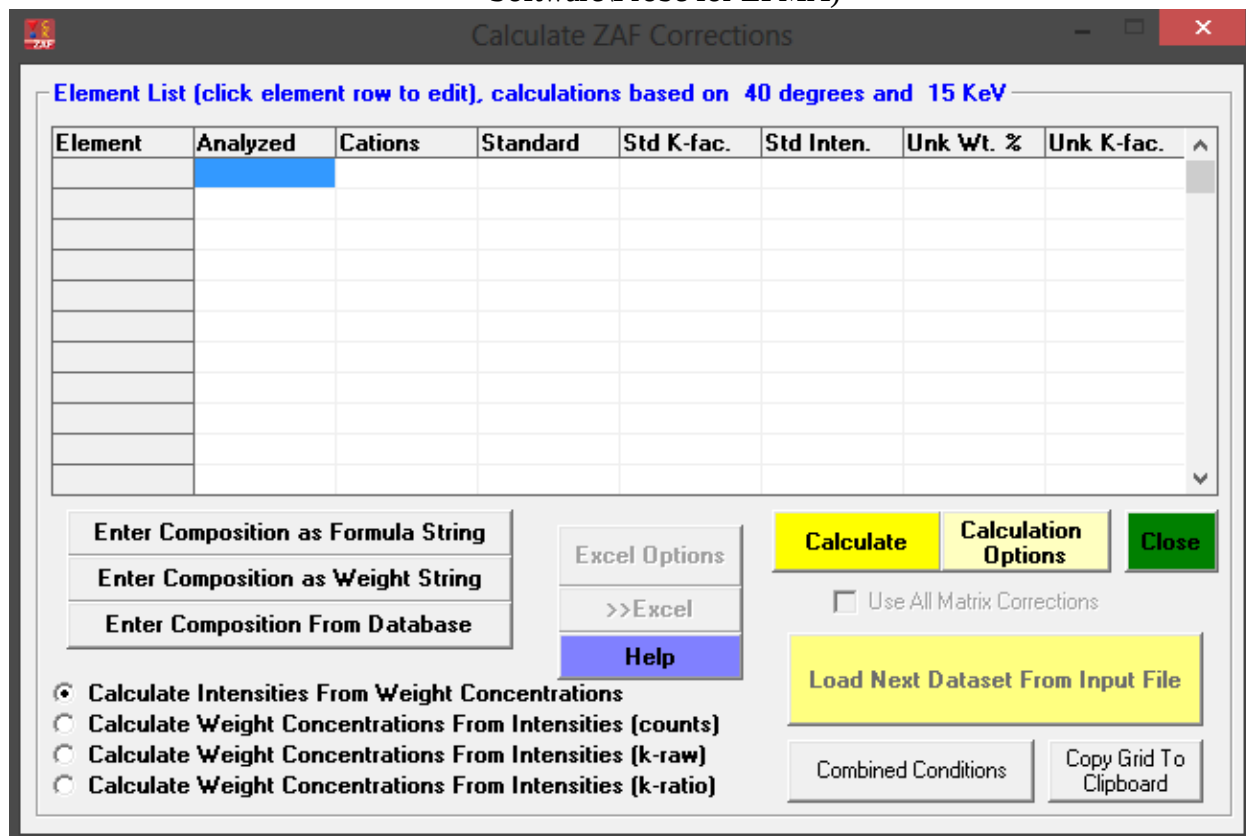
ii. If you **did not use a pure element standard**, you must take into account that your **k-factor does not equal 1**.

1. **K factor** = $C_A^{\text{std}}/[ZAF]_A^{\text{std}}$ (where C is the fraction of your standard that is the element A and [ZAF] is the ZAF correction for element A for the standard). In pure element standards, both of these terms equal 1.

2. **Determine C** by simply looking at the formula for your standard. For example if you used pyrite FeS₂ as your standard for S, C for sulfur is 2/3.

3. **Determine [ZAF]** by using CALCZAF.

- a. Open the **CalcZaf.exe** (with the following path: C:\Probe Software\Probe for EPMA)



- b. You can either **enter the elements manually or type in the mineral formula** for your non-pure element standard.
 c. Click the “**Calculate**” button
 d. The output screen displays the [ZAF] for each element under the “**ZAFCOR**” column

under the ZAFCOR column

File	Edit	Standard	Xray	Analytical	Run	Output	Help			
Z-LINE	X-RAY	Z-ABSOR	MAC							
Ni	ka	Ni	5.7825e+01							
Ni	ka	Fe	3.6228e+02							
Fe	ka	Ni	8.9300e+01							
Fe	ka	Fe	6.8270e+01							
ELEMENT	ABSFAC	ZEDFAC	FINFAC	STP-POW	BKS-COR	F(x)e				
Ni ka	1.0119	4.3419	4.3935	.2135	.9269	.9883				
Fe ka	1.0157	4.3900	4.4588	.2087	.9161	.9846				
SAMPLE: 32767, ITERATIONS: 0, Z-BAR: 26.20918										
ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(x)u	Ec	Eo/Ec	MACs
Ni ka	1.0577	1.0000	.9880	1.0450	.9943	.9937	.9344	8.3330	1.8001	330.438
Fe ka	1.0005	.9866	1.0015	.9886	1.0006	1.0009	.9841	7.1120	2.1091	70.4694
ELEMENT	K-RAW	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	FORMULA	KILOVOL			
Ni ka	.00000	.10009	10.459	-----	10.000	.100	15.00			
Fe ka	.00000	.90576	89.541	-----	90.000	.900	15.00			
TOTAL:			100.000	-----	100.000	1.000				

4. Now simply **divide C by [ZAF]** to get the K-factor.

5. Multiply your K-factor by the intensity of the unknown over the intensity of the standard

$$\mathbf{K\ ratio_A = (C_A^{std}/[ZAF]_A^{std}) \times (I_A^{unknown} / I_A^{standard})}$$

- c. Convert the **k ratio into concentration**

- i. You must have the k ratio in wt.% to apply the correction to your microprobe data.
- ii. To convert from k ratio to wt. %:

1. Turn the k ratio into k ratio % by multiplying it by 100

$$\mathbf{K\ ratio_A \times 100 = K\ ratio_A\ \%}$$

2. Turn k ratio % into wt.% by multiplying it by $[ZAF]_A^{unknown}$

- a. Again, use CALZAF to determine $[ZAF]$ for the element of interest or even use the actual ZAF corrections provided in the output of your microprobe data (excel spreadsheet)

$$\mathbf{(K\ ratio_A\ \%) \times ([ZAF]_A^{unknown}) = C_A^{unknown}}$$

- d. You now have the **concentration of the element of interest (in wt.%) due to SF**. To correct your microprobe data, simply subtract this concentration to your microprobe data.

$$\mathbf{C_A^{unknown_microprobe} - C_A^{unknown_SF}}$$