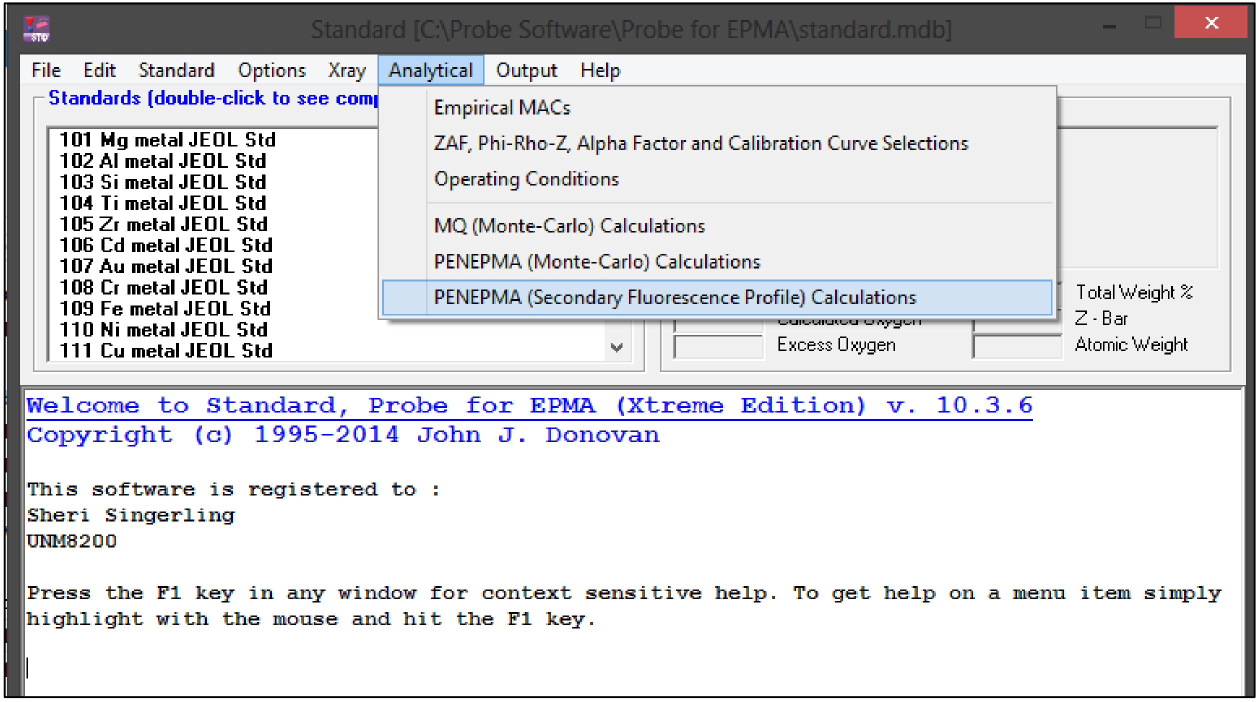
Sheri Singerling
v. 1.0
9/12/2014

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**



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

```
Welcome to Standard, Probe for EPMA (Xtreme Edition) v. 10.3.6
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Sheri Singerling
UNM8200

Press the F1 key in any window for context sensitive help. To get help on a menu item simply
highlight with the mouse and hit the F1 key.
```
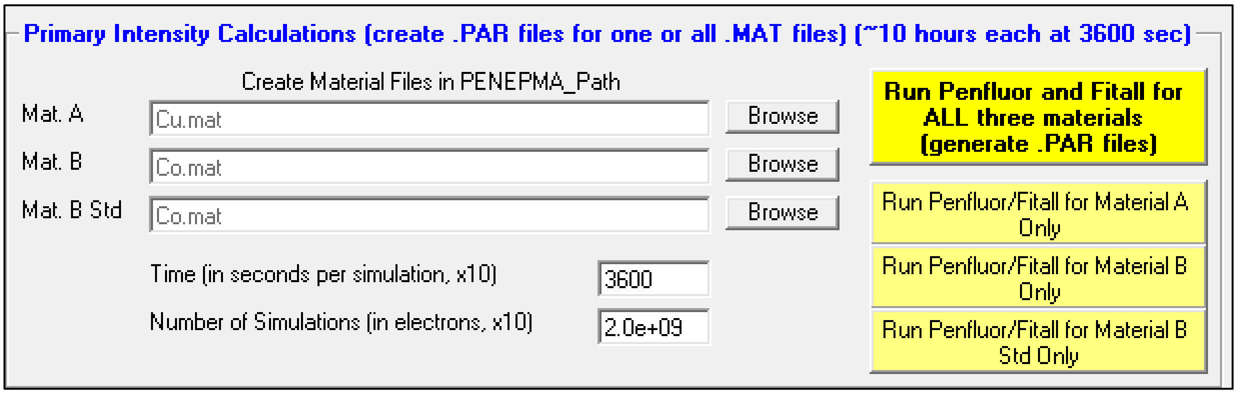
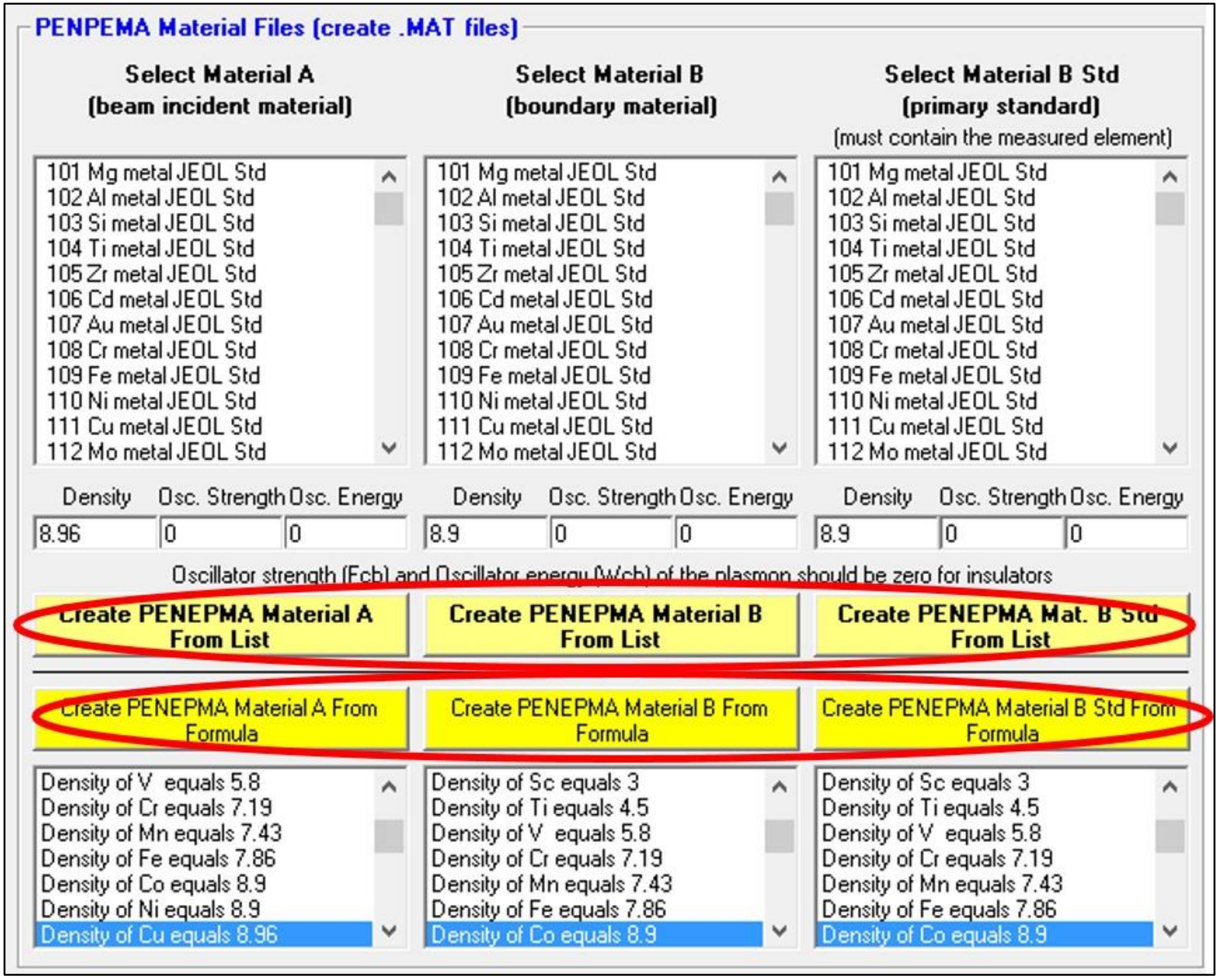

    - b. To run the program, you will have to **create .PAR and .MAT files** for your phases. You do this on the left side of the screen.
        - i. **.PAR files** take ~10 hours to run, so **make sure adequate files don't already exist in the penfluor folder** with the following path: C:\UserData\penepma12\penfluor
        - 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



Mat. A: Cu.mat
Mat. B: Co.mat
Mat. B Std: Co.mat
Time (in seconds per simulation, x10): 3600
Number of Simulations (in electrons, x10): 2.0e+09

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.

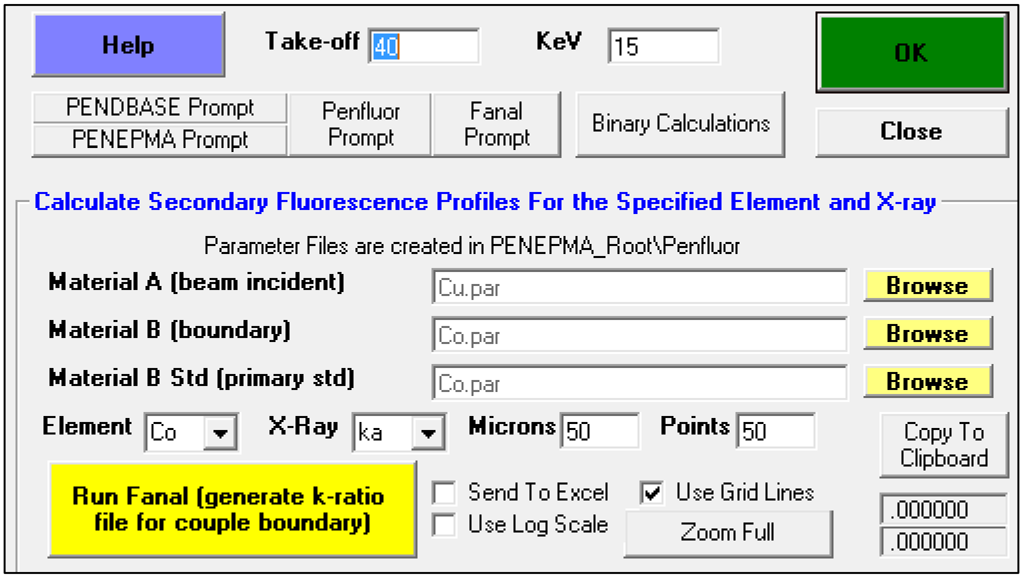


	Density	Osc. Strength	Osc. Energy
Material A	8.96	0	0
Material B	8.9	0	0
Material B Std	8.9	0	0

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.



Take-off 40
KeV 15

Calculate Secondary Fluorescence Profiles For the Specified Element and X-ray

Parameter Files are created in PENEPMA_Root\Penfluor

Material A (beam incident) Cu.par
Material B (boundary) Co.par
Material B Std (primary std) Co.par
Element Co
X-Ray ka
Microns 50
Points 50
☐ Send To Excel
☑ Use Grid Lines
☐ Use Log Scale
.000000
.000000

i. Enter in all the required information making sure **Material B std includes the element** you are running the program for

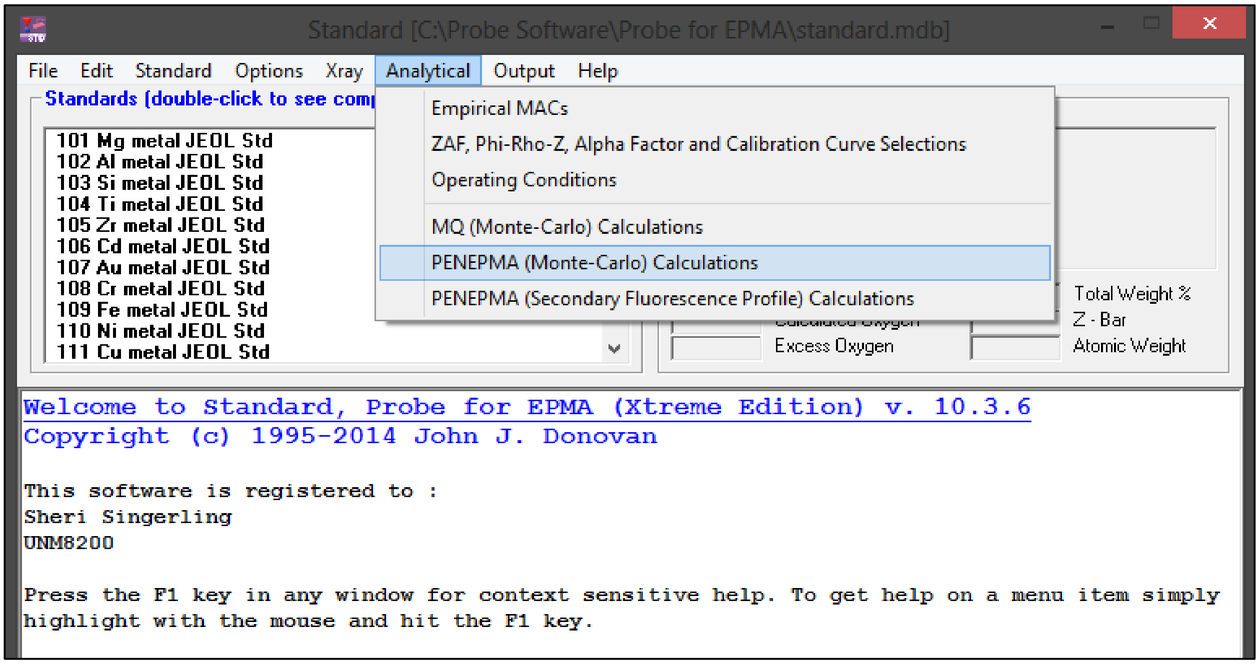
ii. Click **"Run Fanal (generate k-ratio file for couple boundary)"** button

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 → PENEPMA (Monte Carlo) Calculations**



Standards (double-click to see comp

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

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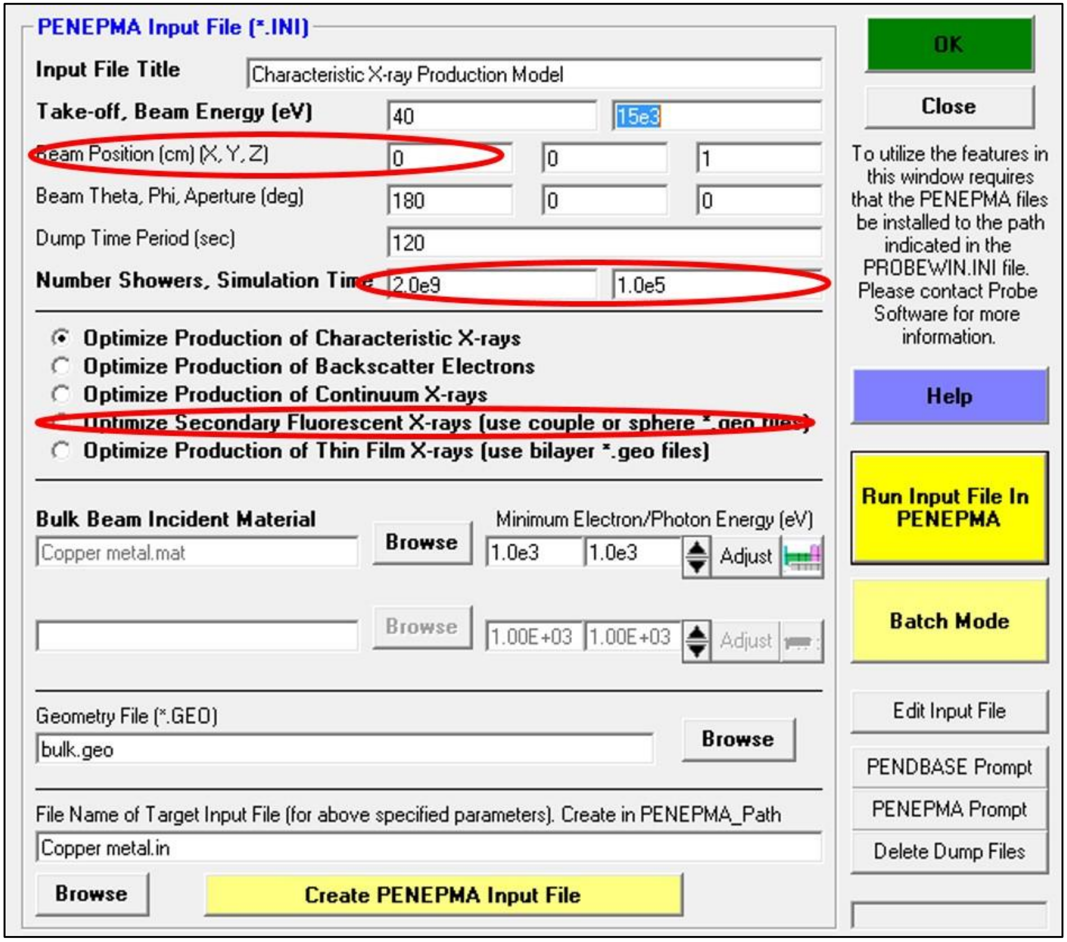
Press the F1 key in any window for context sensitive help. To get help on a menu item simply highlight with the mouse and hit the F1 key.

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**.



PENEPMA Input File (*.INI)

Input File Title	Characteristic X-ray Production Model		
Take-off, Beam Energy (eV)	40	15e3	
Beam Position (cm) (X, Y, Z)	0	0	1
Beam Theta, Phi, Aperture (deg)	180	0	0
Dump Time Period (sec)	120		
Number Showers, Simulation Time	2.0e9	1.0e5	

● Optimize Production of Characteristic X-rays
○ Optimize Production of Backscatter Electrons
○ Optimize Production of Continuum X-rays
○ Optimize Secondary Fluorescent X-rays (use couple or sphere *.geo files)
○ Optimize Production of Thin Film X-rays (use bilayer *.geo files)

Bulk Beam Incident Material: Copper metal.mat

Minimum Electron/Photon Energy (eV): 1.0e3 1.0e3

1.00E+03 1.00E+03

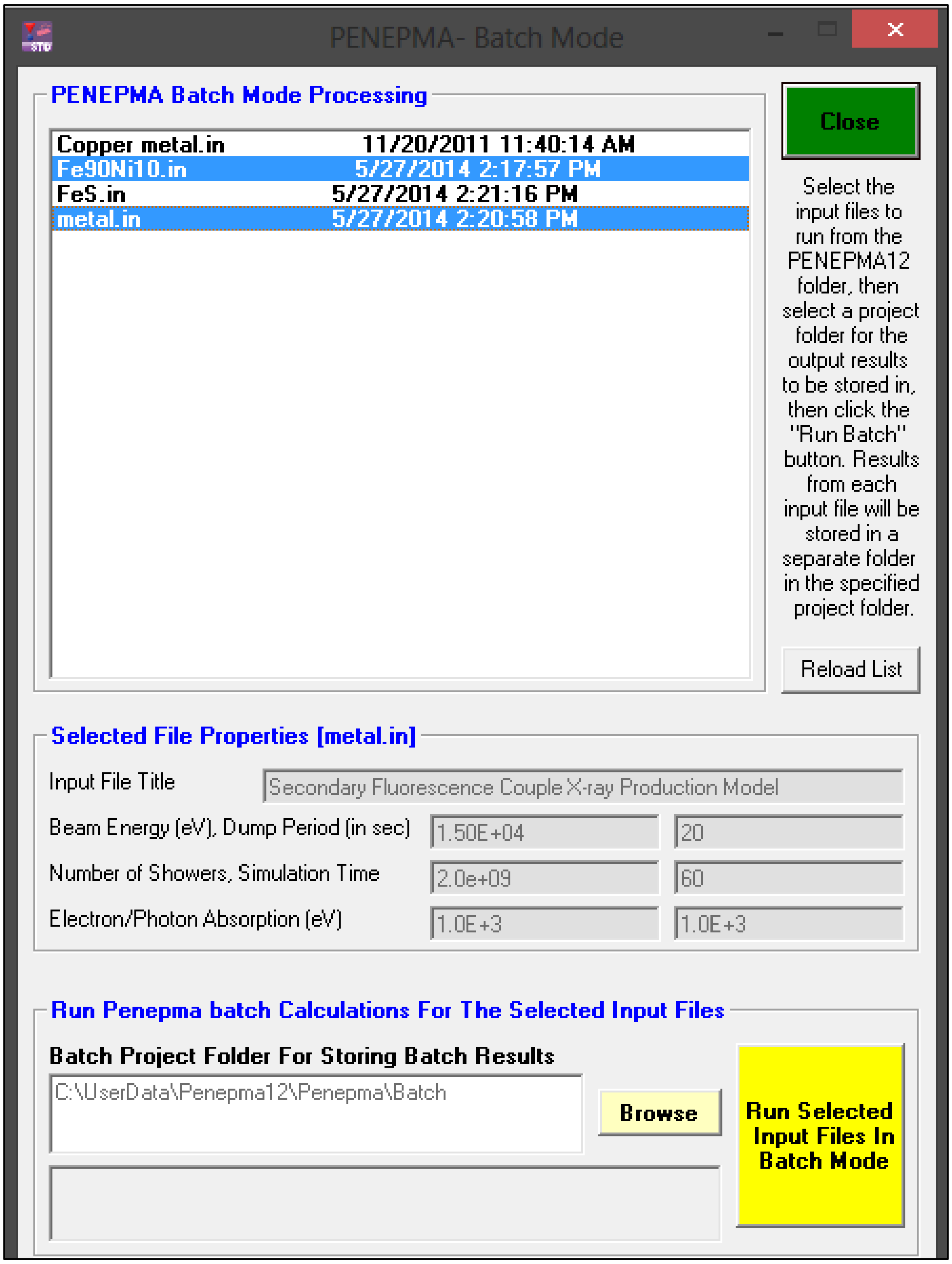
Geometry File (*.GEO): bulk.geo

File Name of Target Input File (for above specified parameters). Create in PENEPMA_Path: Copper metal.in

To utilize the features in this window requires that the PENEPMA files be installed to the path indicated in the PROBEWIN.INI file. Please contact Probe Software for more information.

    i. You will likely want to **decrease the simulation time** as the default is ~27 hours. Go with whatever will give to low uncertainities (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 PENEPMA 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 PENEPMA 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



Copper metal.in	11/20/2011 11:40:14 AM
Fe90Ni10.in	5/27/2014 2:17:57 PM
FeS.in	5/27/2014 2:21:16 PM
metal.in	5/27/2014 2:20:58 PM

Select the input files to run from the PENEPMA12 folder, then select a project folder for the output results to be stored in, then click the "Run Batch" button. Results from each input file will be stored in a separate folder in the specified project folder.

Input File Title: Secondary Fluorescence Couple X-ray Production Model

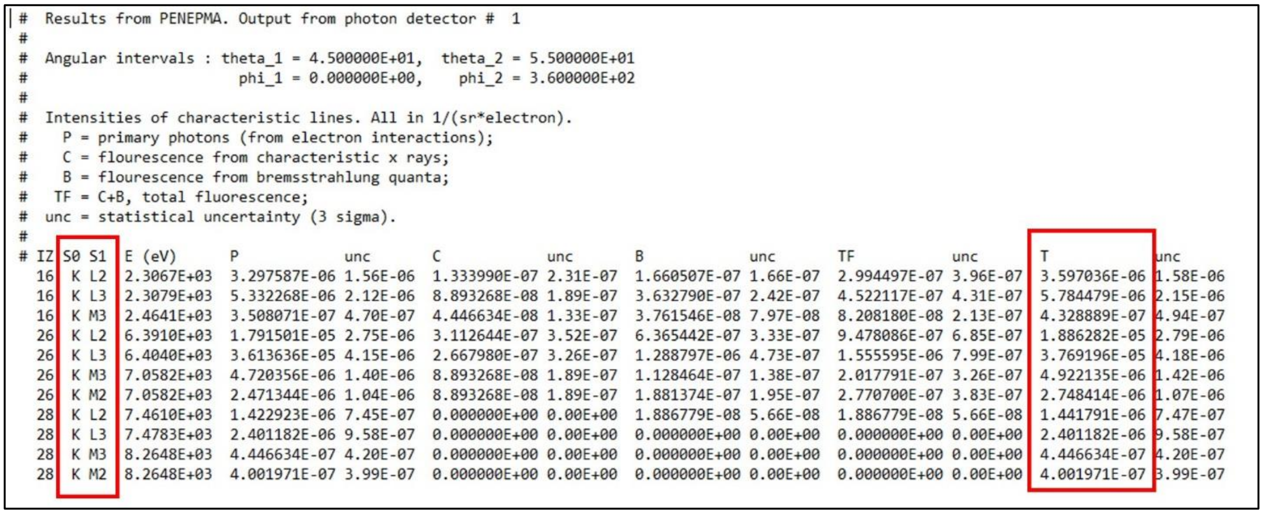
Beam Energy (eV), Dump Period (in sec)	1.50E+04	20
Number of Showers, Simulation Time	2.0e+09	60
Electron/Photon Absorption (eV)	1.0E+3	1.0E+3

Batch Project Folder For Storing Batch Results: C:\UserData\Penepma12\Penepma\Batch

   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))

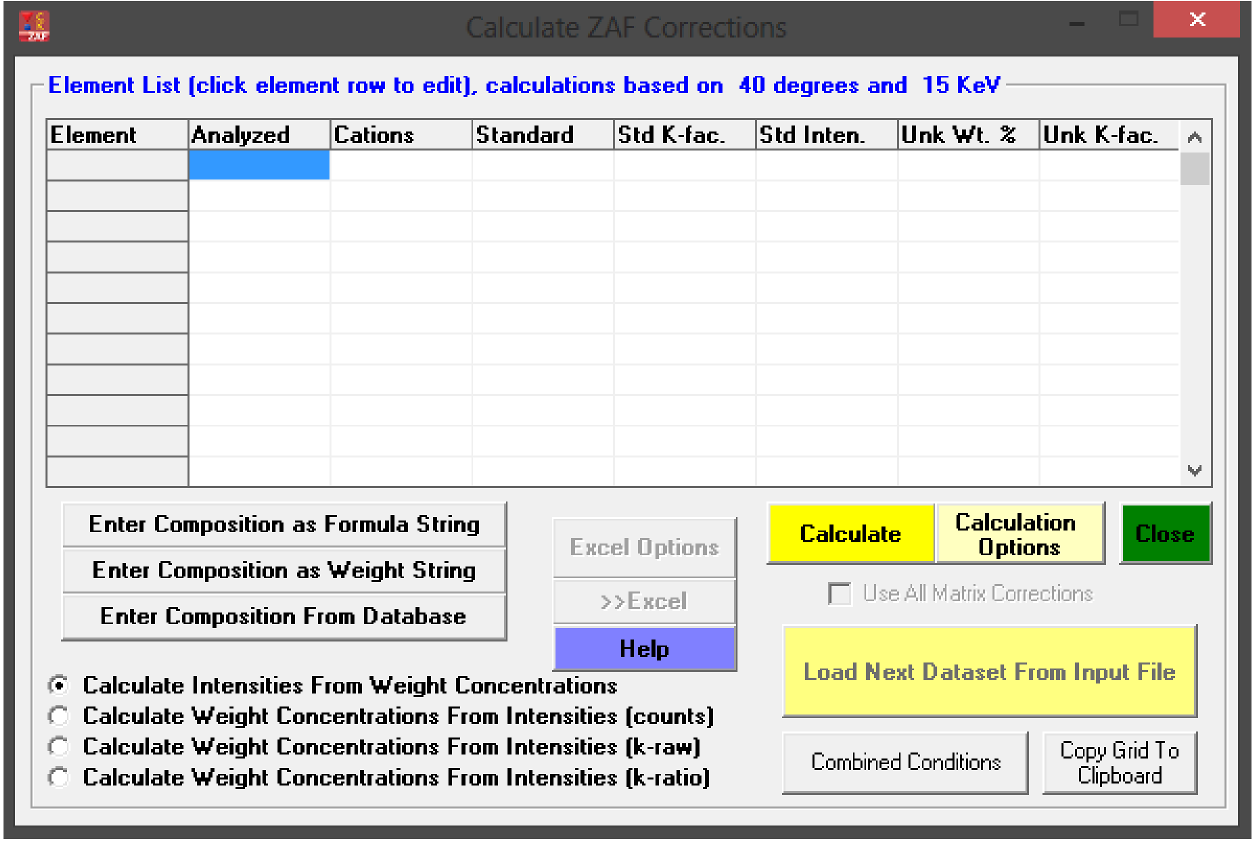
        i. **PFE forum link**: http://probesoftware.com/smf/index.php?topic=202.msg1506#msg1506



```
|#  Results from PENEPMA. 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 = flourescence from characteristic x rays;
 #    B = flourescence 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
```

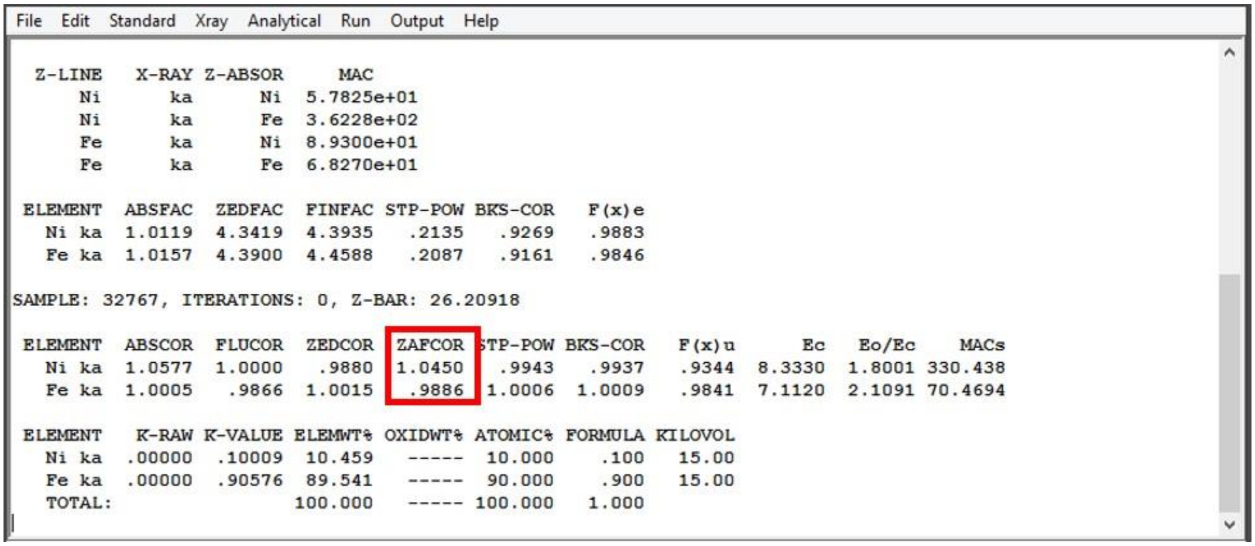
5. To **correct your concentrations** (in wt.%) from microprobe data, you will need to convert the SF **intensities into wt.%** for each element which involves several steps. Here is an abbreviated version:
   a. $I_A^{geometry} - I_A^{bulk} = I_A^{unknown}$
   b. $(C_A^{std}/[ZAF]_A^{std}) \times (I_A^{unknown} / I_A^{standard}) = K\ ratio_A$
   c. $K\ ratio_A \times 100 = K\ ratio_A\ \%$ and $(K\ ratio_A\ \%) \times ([ZAF]_A^{unknown}) = C_A^{unknown}$
    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)
       $I_A^{geometry} - I_A^{bulk} = I_A^{unknown}$ **(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)
       $K\ ratio = I_A^{unknown} / I_A^{standard}$ **(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** = $C_A^{std}/[ZAF]_A^{std}$ (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 FeS_2 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)



● Calculate Intensities From Weight Concentrations
○ Calculate Weight Concentrations From Intensities (counts)
○ Calculate Weight Concentrations From Intensities (k-raw)
○ Calculate Weight Concentrations From Intensities (k-ratio)

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



```
  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

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

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

$$\textbf{K ratio}_A \times 100 = \textbf{K ratio}_A\ \%$$

        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)

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

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.

$$C_A^{unknown}\_\text{microprobe} - C_A^{unknown}\_\text{SF}$$