

# Microanalysis Tools for the Analyst

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## Software Tools for Microanalysis

A number of increasingly sophisticated software tools are available as freeware for the microanalyst. These tools should be used in order to better understand the analytical problem that the analyst is confronted with, and can be used to study the analytical volume that results from electron scattering as well as the x-ray production volume that is used for quantitative analysis. These tools can also be used to study structures that are increasingly complex. The value of these tools is important in several aspects. First, these tools serve as educational tools to study microanalysis and will improve your global understanding of issues that pertain to analysis. Secondly, the tools can be used to simulate samples that have been studied in the past in order to determine if the results are accurate. The tools can be used to evaluate an analysis as it is being conducted or developed, in order to fine tune the procedure or determine if the proposed experiment is working as expected. Most importantly, the tools should be used as a first step in evaluation of an experiment that is being proposed.

There are many analytical problems that one must ultimately deal with. Your reputation as a scientist, and the reputation of the community at large as a support network for you all depend on the intelligent practice of the technique.

Here are some example problems that will be used in the discussion of the use of these tools.

1. What are the dimensions of the electron scattering volume and x-ray analytical volume for a sample, and how do these volumes compare for the analysis of electron images and specific x-ray lines?
2. What is the appropriate accelerating potential for use in the analysis of a sample, and how does the choice of this parameter affect sampling and x-ray analysis?
3. For a stratified sample such as a thin film on a substrate, how does the behavior of the thin film sample compare to a bulk material? How can thin film and bulk materials be discriminated using microanalysis?

4. How does a simulated EDS spectrum compare to the equivalent experimental spectrum, and why are there differences? How can simulated X-ray spectra be used to plan and troubleshoot experiments?
5. What is the extent of secondary x-ray fluorescence in a given sample, and how does the production of SF compare to primary excitation?
6. How do the x-ray correction parameters contribute to the total x-ray correction for the analysis of a sample, and how do these parameters vary with composition in a binary, ternary, etc. system?
7. How do different x-ray correction procedures compare in the analysis of given samples, and to what extent does the selection of mass absorption coefficients affect the analysis?
8. How does one evaluate the accuracy of microanalysis?

This list can go on, but when you think about it, there are several central themes in analysis. These are issues regarding the best methods for *measurement* of a signal in bulk vs. complex materials such as thin films and particles, how these materials are variably *sampled* during the measurement process, the appropriate *correction* of these measurements to concentration values, and an assessment of the *precision* and *accuracy* of these methods.

You may wish to ponder the degree of built-in bias that we all have based on what information is known or provided concerning a sample, and how we treat that sample based on the provided information. The requested list of elements, whether the sample is a stratified structure, etc. implies how we approach the analysis of a sample.

Here are some examples.

You are presented with a sample that is either a bulk sample of homogeneous Fe<sub>3</sub>C, or it is a piece of pure Fe with a 22.5 nm layer of carbon on top – the nice person giving you the sample can't remember the pertinent information. So, which is it, a bulk material or a thin film? What analytical procedure would you use and how would you conclusively prove it with supporting data? Tools: Casino, GMRfilm

What is the expected k-ratio for Mg using the K $\alpha$  X-ray line for MgO relative to a pure Mg metal standard (assume 15 keV and 40 degree takeoff)? If the emitted X-ray intensity from the Mg metal standard is 1000 cps, what is the count rate expected from MgO? Tools: CalcZAF

What is the simulated EDS spectrum for a 250 nm Ni sphere on a Fe substrate at 15 keV and 40 degrees takeoff angle? What is the smallest sphere that results in negligible generation of Fe K $\alpha$  X-rays? Tool: DTSA-II

The performance of your EDS detector needs to be evaluated after an attempt to observe light element X-rays has failed. What is the expected ratio of the Ni L $\alpha$  to Ni K $\alpha$  lines on a pure Ni metal standard obtained at 15 keV and 40 degree X-ray takeoff angle? Tool: DTSA-II

## Monte Carlo Simulation Software

Monte Carlo simulation codes are conceptually very simple. The trajectory of an electron is followed as it enters the sample, and we keep track of the energy and position of the electron in discrete scattering events that make use of random numbers to determine the scattering angle at each step in the simulation. When the energy of the electron is high, the scattering angle is low and the trajectory is not changed dramatically; conversely, when the energy is low the scattering angle tends to be large with large changes in direction of the electron and decreasing distance between steps. At each step in the calculation the electron energy is known and if it is greater than the excitation energy for elements in the sample, then a characteristic x-ray can be produced. The probabilities for electron scattering and x-ray production are evaluated using probability functions. Because these calculations are numerically intensive, historically there have been two models for Monte Carlo simulation, a multiple scattering model where the electron energy loss is averaged over a number of steps (these models run like a scared bat), and single scattering models where the energy is evaluated at each step (these models run more slowly, like a careful bat).

The advantages of Monte Carlo models is that they are simple codes that can be modified to accommodate very complex structures such as multiple layered samples, particles of complex geometry, rough surfaces, and so on. The Casino and WinXray programs also do an excellent job of calculating the x-ray signal from the analytical volume, and these results compare favorably enough with experimental measurements to be useful as a calculation tool. On the other hand, these programs calculate x-ray production from primary excitation only, and do not treat secondary fluorescence from either characteristic or continuum x-rays. That said, they are powerful tools for visualization and simulation of samples.

## Casino Monte Carlo Program

The Casino Monte Carlo Program is discussed in the references:

P. Hovington, D. Drouin and R. Gauvin (1997), “Casino: A New Era of Monte Carlo Code in C Language for Electron Beam Interaction, Part I: Description of the Program”, Scanning, Vol.19, pp. 1-14

D. Drouin, P. Hovington, R. Gauvin (1998) “CASINO: A New Monte Carlo Code in C Language for Electron Beam Interactions--Part II : Tabulated Values of the Mott Cross Section”, Scanning, Vol.19, pp. 20-28

P. Hovington, D. Drouin, R. Gauvin, D. C. Joy, N. Evans (1997) “CASINO: A New Monte Carlo Code in C Language for Electron Beam Interactions--Part III : Stopping Power at Low Energies”, Scanning, Vol.19, pp. 29-35

Casino can be acquired at: <http://www.gel.usherbrooke.ca/casino/index.html>, and an on-line tutorial can be used to help explore the program.

## Creating a Casino Simulation

The following instructions are modified from the Casino web site tutorial, and outline how to set up a new simulation.

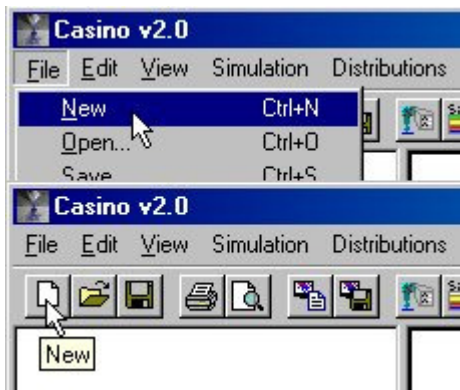

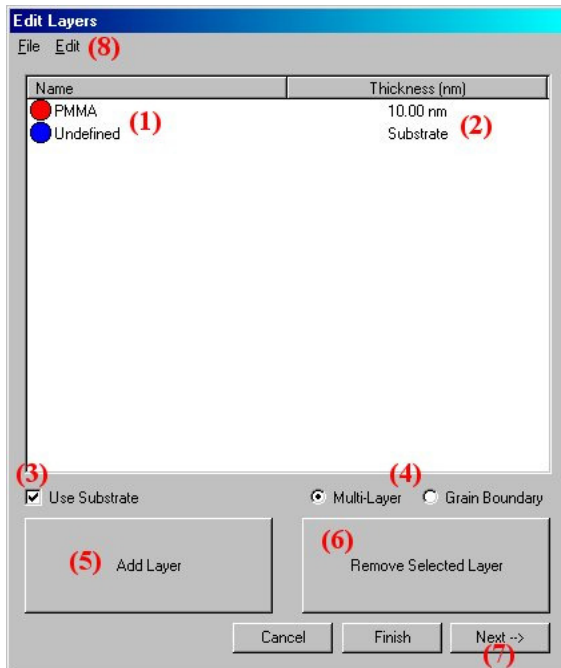


Figure 1 Create a new simulation by selecting from File menu or the New icon.

### Step 1: Creating the Simulation

To create a new simulation, select File/New from the menu or click of the  icon. The NEW SIMULATION wizard will appear on the screen.



**Figure 2** The Edit layer dialog box. Here you add a new layer, and edit each layer by clicking on the name (1) in order to edit the composition, and (2) to edit the thickness. Checkbox (3) is used for materials with a substrate, and radio button (4) is used to define horizontally layered vs. vertically layered structures. Option (6) is used to remove a layer if necessary. Complex samples can be created, then saved or loaded using (8) from sample definition files, and the Edit menu can be used to cut and paste layers.

## Step 2: Creating Layers

The first dialog box will be the EDIT LAYERS dialog. In this dialog you will create the layers of your sample. Casino is set up to simulate a number of layers on a substrate. If you are simulating a bulk material, then the substrate is the bulk material.

To begin, you will add a layer, by clicking the ADD LAYER button (5). If you add too many layers, you can remove them by selecting them and pressing the REMOVE SELECTED LAYER button (6) or by pressing DEL on the keyboard.

The NAME and CHEMICAL COMPOSITION of each layer can be defined by double-clicking the names of the layers (1). This will bring up the LAYER CHEMICAL COMPOSITION DIALOG which is described in Step 3.

If you wish to define the last layer as a substrate, make sure the USE SUBSTRATE checkbox (3) is checked.

Item (4) is used to define samples that have horizontal layers or vertical layers (such as a grain boundary). If your sample has multiple horizontal layers, select MULTI-LAYER (4), else if you sample is composed of vertical layers select GRAIN BOUNDARY (4).

The default thickness of the layer is 10 nm. To change the thickness of the layers simply click on the current thickness (2) and type in the new thickness.

You can copy and paste layers by selecting them and using the EDIT menu (8), and you can load and save complex layer assemblies using the File menu. These assemblies are saved as sample files.

When your sample is completed you can press Next--> (7) to move on to the next dialog MICROSCOPE AND SIMULATION PROPERTIES which is explained in Step 4.

Element	Z	Weight Fraction	Atomic Fraction
✓ C	6	0.599848	0.333333
✓ O	8	0.319614 (5)	0.133333
✓ H	1	0.080538	0.533333

**Figure 3 Layer Chemical Composition dialog box. The name identifier and composition fields are used to define the label and chemistry of the layer. In this example a polymethylmethacrylate layer is abbreviated as PMMA and the composition is actually C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>, but the composition has been entered as a nominal COH and will need to be edited manually. The calculated density is shown in (4) and can be updated by the user with more accurate data. User defined density and distribution data is identified by checking item (7). A complex sample chemistry with appropriate density data can be added to the library by using (3). This adds the layer composition to the “Userlayers.txt” file in the Casino folder.**

### Step 3: Editing Layers

This dialog box will let you give a name and a chemical composition to a layer. The name is a text label that is used to summarize that layer, and is also used to look up the material in the “Userlayers.txt” file so that you do not have to enter the compositional information every time for repeated materials. For this reason you should carefully choose the identifying label and keep a record of it.

The composition string is parsed by Casino to calculate the elemental composition of that layer. Start by entering the chemical composition in the COMPOSITION field (1). The elements must be written in Uppercase for the first letter and lowercase for the other, example (Fe2O3). This is important! Casino will automatically calculate the composition of the material if you enter the formula correctly. Try several test formulae (i.e., SiO2, CaAl2Si2O8, etc.). Then give the layer a name (2), if no name is given, the composition will be chosen as the name.

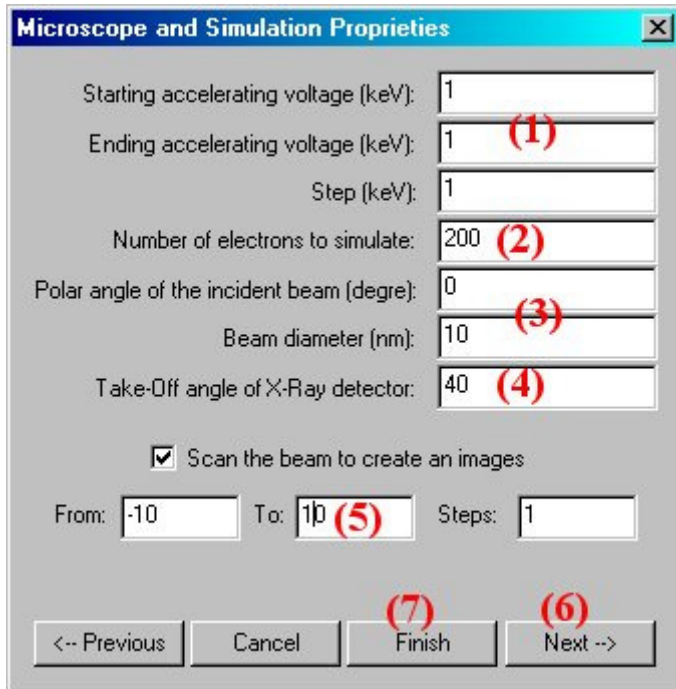
The density (4) will automatically be calculated from the atomic weight and the weight fraction of each element. This means that the calculated density may not be accurate because Casino cannot determine the structure for any phase (consider polymorphs for example), and you must enter the correct density if you have that information. The implications of using calculated density values rather than actual are twofold. First, the dimension of the scattering volume depends on an accurate value for the material density, and secondly, the mass-density dimension for  $\Phi(\rho z)$  data is density normalized and also depends on an accurate value for  $\rho$ .

If you wish to change the atomic fractions or weight fractions manually then simply click (5) on the value you wish to change. To autocomplete an element as the remainder of the composition simply press the AUTO-COMPLETE ELEMENT FRACTIONS button (6) after selecting the element.

To save an element for future use, give it a name and press ADD TO LIBRARY button (3). This will store the information (name, composition, density, and user distribution, if all provided) so that next time you enter a name for a layer and it exists in the library it will set the layer to the saved layer.

To reset values to their automatically calculated states, just uncheck the boxes USER DEFINED DENSITY AND DISTRIBUTION (7).

Repeat Step 3 for each layer and then move on to Step 4.



**Figure 4 The Microscope and Simulation Properties settings**

#### Step 4: Setting up the Microscope and Simulation

This dialog lets you select the parameters of your simulation.

First, enter the electron beam energy used for your simulation (1). The first box is where you set your starting beam energy, the second is the energy where you want to stop the simulation and the third box contains the step in KeV between each simulation. For example, if you need to simulate the scattering behavior of a thin film at 30, 20, and 10 KeV, then you enter 30 as the starting voltage, 10 as the ending voltage, and 10 as the step voltage. If the ending energy is smaller or equal to the starting, then the step will be ignored and only one simulation at the starting energy will be done.

Second, enter the number of electrons you want to simulate (2). Casino runs very fast in Monte Carlo simulation mode, and can easily accommodate runs that have  $10^5$  electrons. You should use a small number of electrons for initial runs or to visualize the scattering volume. A larger number of electrons should be used for more precise results and where x-ray intensities are needed. In general, remember that electron scattering has a significantly higher probability than x-ray production. Suggested values are 10,000 for quick runs, and 100,000 for x-ray intensities.

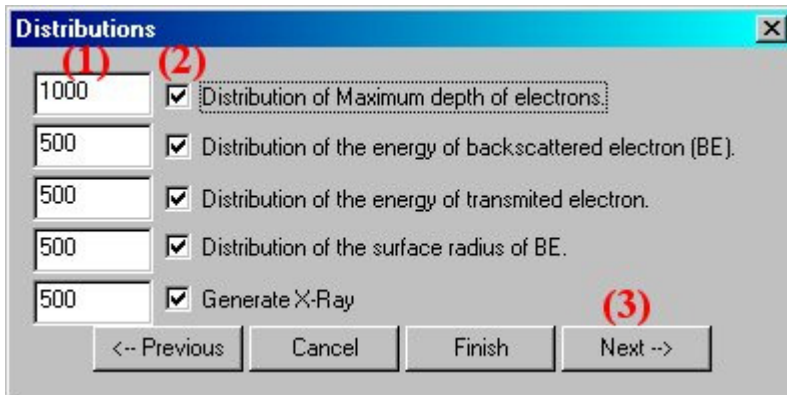
Third is the beam parameters (3), the first box represents the angle the electrons will be fired into the sample and the second box contains the width of the beam.

Fourth, define the angle of your X-Ray detector (4) with the positive X-axis of the sample being 0 and moving counterclockwise towards the negative X-axis being 180.



Finally, set the limits of your scan (5). The sample is centered at 0 nm. The step is in nanometers. If you do not wish to scan your sample, uncheck the box SCAN BEAM TO CREATE AN IMAGE. The FROM box then contains the position of the beam on the sample.

At this point you can already press FINISH (7) and move on to Step 8, but you can continue through the rest of the options by pressing NEXT--> (6) and moving on to Step 5.

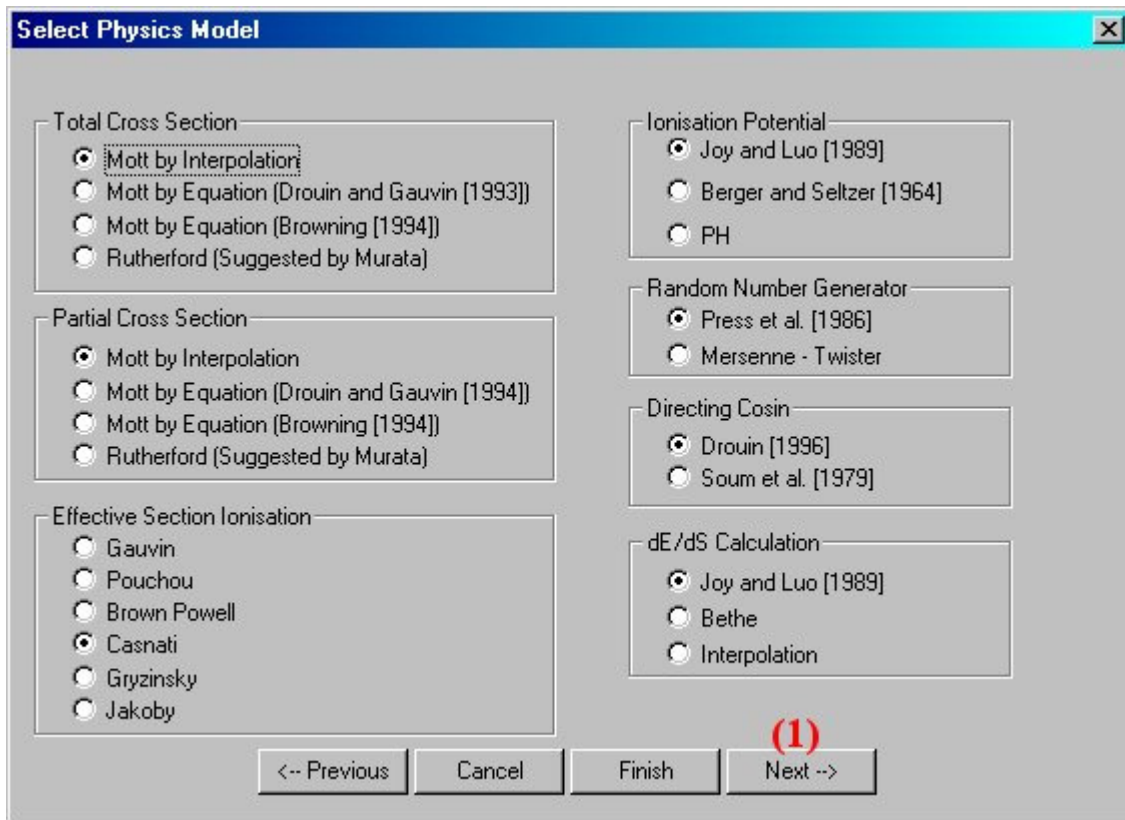


**Figure 5 Distribution selections**

### Step 5: Selecting Distributions

The Distributions dialog box allows you to turn the generation of electron and x-ray distribution plots on or off (checkboxes), and to select the number of divisions that are used for the range of values calculated by Casino. For example, the maximum depth distribution of electrons is selected with 1000 divisions for plotting. Check the box for each distribution you wish to see after calculations (2). Enter the number of points you want each distribution to have (1). One important note is that you should not have a large number of divisions coupled with a short run where too few electrons have been simulated, as this produces noisy and statistically invalid data. The default values are good for most runs, but you can adjust the values for your own purposes.

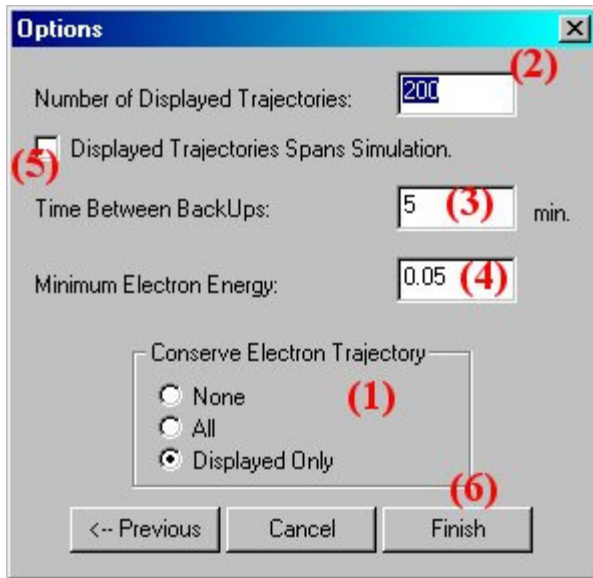
Move on to the next step (3).



**Figure 6 Physics Model Selections**

### Step 6: Choosing Physical Models

Casino provides you with the option of changing the physical models used in the simulation. If you do not know much about this, leave these set to the default values (Mott by interpolation, and the Casnati ionization cross-section – these are excellent choices for simulations). Unless you know which model does what, skip to the next step (1).



**Figure 7 Trajectory options**

#### Step 7: Options

The Options dialog box allows you to select the number of displayed electron scattering trajectories, the time between data backups to the hard drive, and the storage of the electron trajectory data. It is possible to generate very large files if you select conservation of trajectories, as this will write the detailed trajectory data to the file. You need this only if you plan to replot the distribution data in another program.

(1): Conserving the trajectories takes up a lot of memory. Conserving NONE will not save any trajectories to memory which means that there is no way to view the trajectories after they have been calculated. DISPLAYED ONLY will only keep the trajectories that have been displayed on the screen, this option is good if you want to see the trajectories and change some of their viewing parameters and ALL is used if you want to keep all the trajectories in memory, display a selected few during calculation but after calculations it will display all of them.

(2): Number of electron trajectories to display on the screen during calculations. This is the subset of total trajectories that will be displayed. This number should be relatively small or the plot will lose the interesting details of trajectory variation with electron energy.

(3): Minimal time between backups which are used to continue simulation in case of accidental termination of the simulation or computer lockup, etc.

(4): The minimal energy, in KeV, at which a trajectory is terminated. Be aware that many calculation steps become necessary at low energies due to large changes in scattering direction and energy. In general, Monte Carlo simulations should be terminated at a high enough energy to simulate what you are studying, in order to not spend time tracking low energy interactions.

(5): If checked the trajectories will be displayed at regular intervals during the simulation, otherwise the first trajectories are displayed.

(6): Press FINISH when your simulation is ready to be calculated on go to Step 8.

#### Step 8: The End

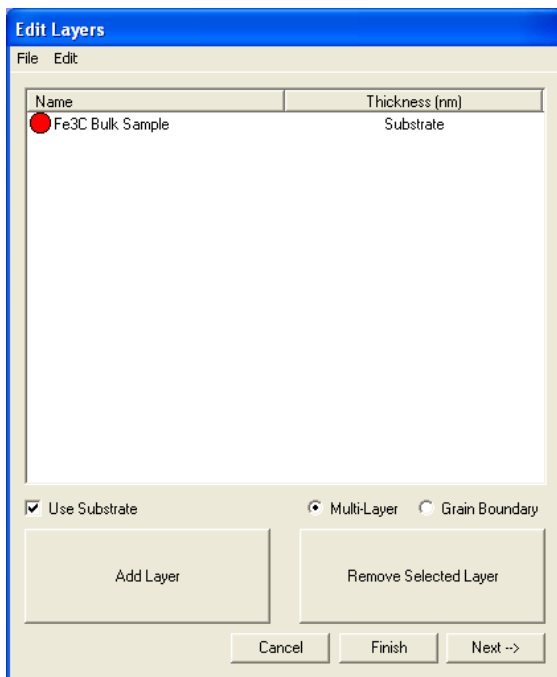
After pressing FINISH you will be asked if you want to begin the simulation, press YES if you wish to otherwise press NO.

Pressing Yes starts the Casino Monte Carlo Simulation.

## Application of Casino to Analytical Problem

The proposed analytical problem is how to differentiate between a bulk sample of  $\text{Fe}_3\text{C}$  and a thin film sample of 22 nm carbon on a pure Fe substrate. This is to demonstrate the study of a material that may or may not be layered, and to determine the structure and thickness of the layer if present.

To study this problem let's begin by simulating the bulk  $\text{Fe}_3\text{C}$  sample at multiple energies. You can use this problem to help get used to using the Casino program and with this problem we will demonstrate the type of analytical data that can be obtained with the program.



**Figure 8** Layer definition for  $\text{Fe}_3\text{C}$  bulk sample, where the  $\text{Fe}_3\text{C}$  is the substrate (no layers are present).

**Layer Chemical Composition**

Name:

Composition:

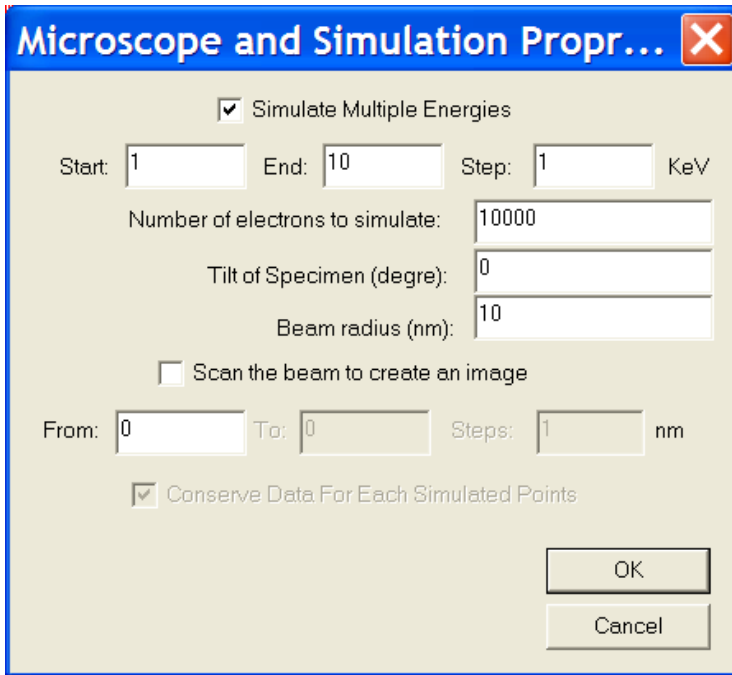
Density:

Element	Z	Weight Fraction	Atomic Fraction
✓ Fe	26	0.933106	0.750000
✓ C	6	0.066894	0.250000

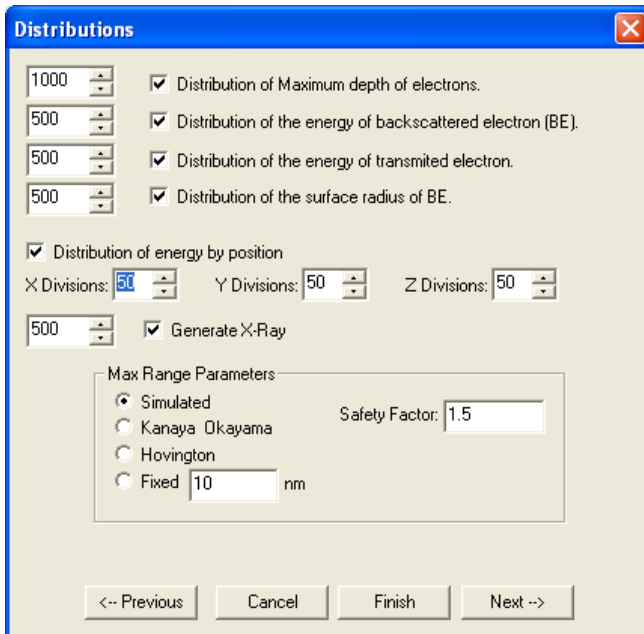
User Defined Density

User Defined Distributions

**Figure 9 Layer Chemical Composition data for Fe<sub>3</sub>C bulk sample. The composition was entered as “Fe3C” and Casino correctly calculates the weight fraction of Fe and C. The density of Fe<sub>3</sub>C is that value calculated by the weight fraction and densities of the elements Fe and C, which is not likely to be correct, and should be replaced with a better value. For this example problem it is not important.**

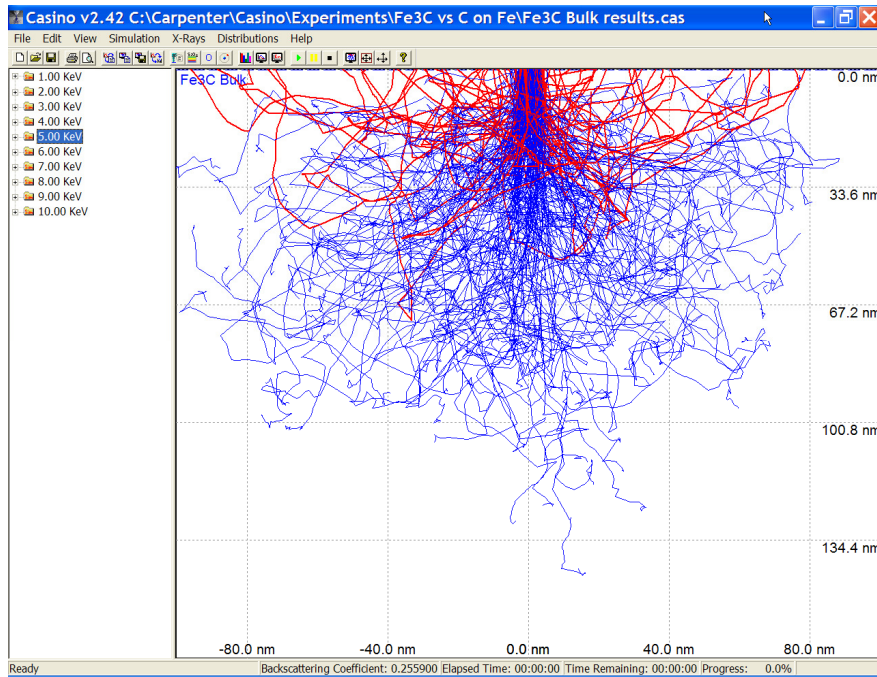


**Figure 10 Microscope and Simulation Properties for Fe<sub>3</sub>C bulk sample. Here we will simulate multiple energies from 10 KeV to 1 KeV in 1 KeV steps, and will run 10,000 electron trajectories at each energy.**



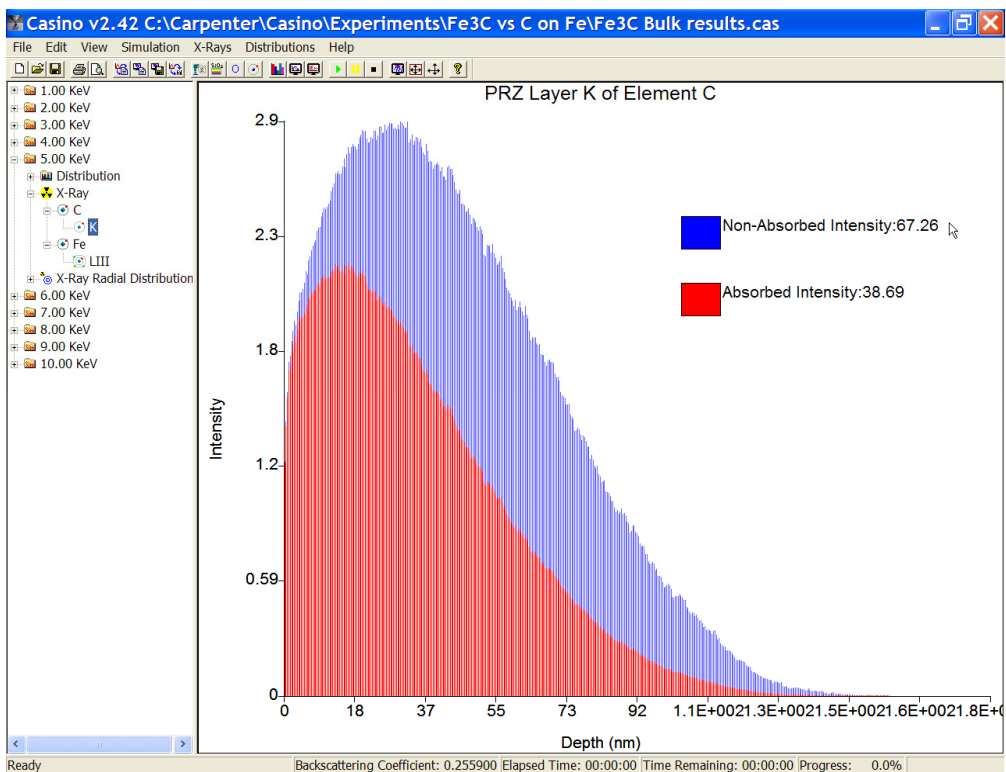
**Figure 11 Distributions Dialog box. The default settings are shown and are acceptable. In particular we want to have Casino determine the maximum range using Monte Carlo simulation, as we are interested in the behavior of the Fe-C system with varied accelerating potential, which translates into depth of sampling.**

Now run the simulation. The results from this run will look like the following figure, where the 5 KeV scattering plot has been selected.



**Figure 12 Casino Monte Carlo scattering plot for Fe<sub>3</sub>C sample at 5 KeV. Backscattered electron trajectories are shown in red, and electrons that do not backscatter are colored blue. Note the scattering volume samples approximately 100 nm at 5 KeV, so that the analytical volume is roughly 4 times deeper than expected for a carbon film of 22.5 nm on an iron substrate.**

Next we select the x-ray intensity data for each x-ray produced at the appropriate accelerating voltage. Shown in the figure below is the x-ray intensity data (both generated and emitted intensities) for C K $\alpha$  in the Fe<sub>3</sub>C bulk sample.



**Figure 13** X-ray  $\Phi(\rho z)$  data for Fe<sub>3</sub>C bulk sample at 5 KeV, showing intensity data for C K $\alpha$ , with blue curve indicating generated C K $\alpha$ , and red curve indicating emitted C K $\alpha$  intensity. The integrated intensities are listed next to the color keys, so that the generated intensity is 67.26, and emitted intensity is 38.69.

The next step is to run two other bulk sample simulations for pure carbon and pure iron at the same conditions as for the Fe<sub>3</sub>C sample, i.e., a total of 3 Casino runs is necessary to produce the necessary data for the Fe<sub>3</sub>C sample, one run on Fe<sub>3</sub>C, one run on pure carbon, and one run on pure iron. This allows us to calculate the k-ratio, or relative intensity, for the x-rays produced at each voltage. The k-ratio for C K $\alpha$  is calculated from the ratio of the intensity of C K $\alpha$  in Fe<sub>3</sub>C divided by the intensity of C K $\alpha$  in pure carbon from runs at each voltage. Using the 5 KeV data, the k-ratio is  $38.69/641.58 = 0.0603$ , that is, ~6% of the emitted C K $\alpha$  x-ray intensity should be observed on the Fe<sub>3</sub>C sample relative to a graphite standard.

The data from these runs is summarized in Table 1, which lists the x-ray intensities for C K $\alpha$ , Fe L $\alpha$ , and Fe K $\alpha$  in the Fe<sub>3</sub>C, pure C, and pure Fe. These emitted intensities are used to calculate the k-ratios for each x-ray at each accelerating voltage. It is important to calculate the *relative* x-ray intensity (i.e., relative to a pure element standard or the working standard of choice), instead of the *absolute* intensity, at each accelerating voltage. It is the relative intensities that we will compare to the thin film sample with a carbon layer on an iron substrate. Also note in this case that due to the low overvoltage, the Fe K-line can only be simulated at voltages in excess of the excitation energy, and that we should be wary of using data that are at an overvoltage of less than 1.5 for quantitative analysis.

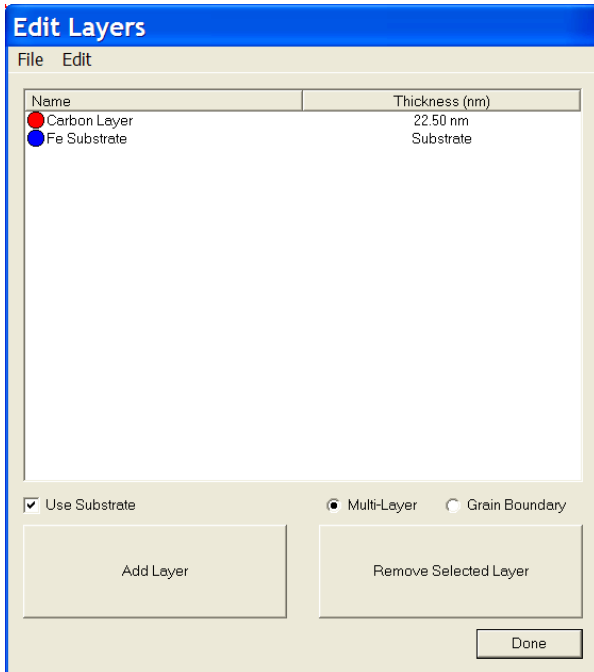


Table 1. Casino X-ray Intensity Data for Fe<sub>3</sub>C Bulk Sample, Pure C, and Pure Fe

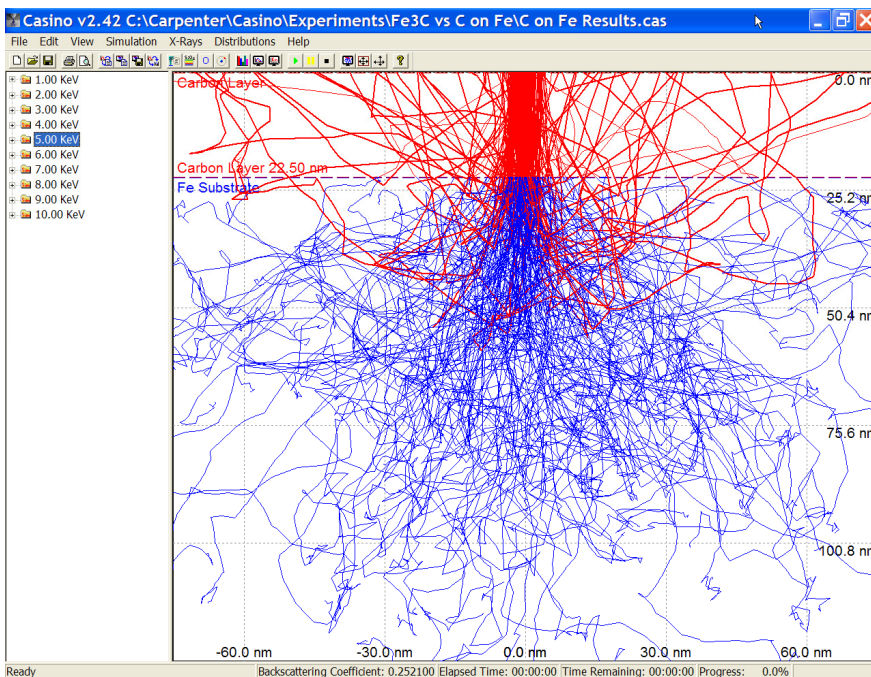
<b>KV</b>	<b>C K<math>\alpha</math> Fe<sub>3</sub>C</b>	<b>C K<math>\alpha</math> Graphite</b>	<b>Fe L<math>\alpha</math> Fe<sub>3</sub>C</b>	<b>Fe K<math>\alpha</math> Fe<sub>3</sub>C</b>	<b>Fe L<math>\alpha</math> Bulk Fe</b>	<b>Fe K<math>\alpha</math> Bulk Fe</b>	<b>K- ratio C K<math>\alpha</math></b>	<b>K-ratio Fe L<math>\alpha</math></b>	<b>K-ratio Fe K<math>\alpha</math></b>
1	5.17	48.63	7.70		8.71		0.1063	0.8840	
2	16.37	181.24	97.06		106.92		0.0903	0.9078	
3	26.23	335.15	213.31		233.03		0.0783	0.9154	
4	33.57	491.65	320.84		345.91		0.0683	0.9275	
5	38.69	641.58	411.17		438.86		0.0603	0.9369	
6	40.65	778.15	468.28		494.33		0.0522	0.9473	
7	40.97	902.07	502.95		530.62	0.00	0.0454	0.9479	
8	41.02	1015.05	528.93	17.30	544.76	19.08	0.0404	0.9709	0.9067
9	39.28	1102.94	529.36	74.81	547.19	82.46	0.0356	0.9674	0.9072
10	37.47	1170.38	522.61	166.75	544.37	183.80	0.0320	0.9600	0.9072

Next we need to turn our attention to the thin film sample which has a 22.5 nm layer of carbon on a substrate of iron. This is very easy to set up in Casino, so we create a sample with a layer of pure carbon 22.5 nm thick on an iron substrate, and then run the same model using the conditions we set up for the Fe<sub>3</sub>C bulk sample (i.e., 1 KeV to 10 KeV in 1 KeV steps). Be sure to use the same settings for the thin film run, because we will be using the Casino intensity data for pure carbon and pure iron to calculate the k-ratios in the thin film sample. The number of electrons must be the same since this represents the probe current used for the intensity measurement.

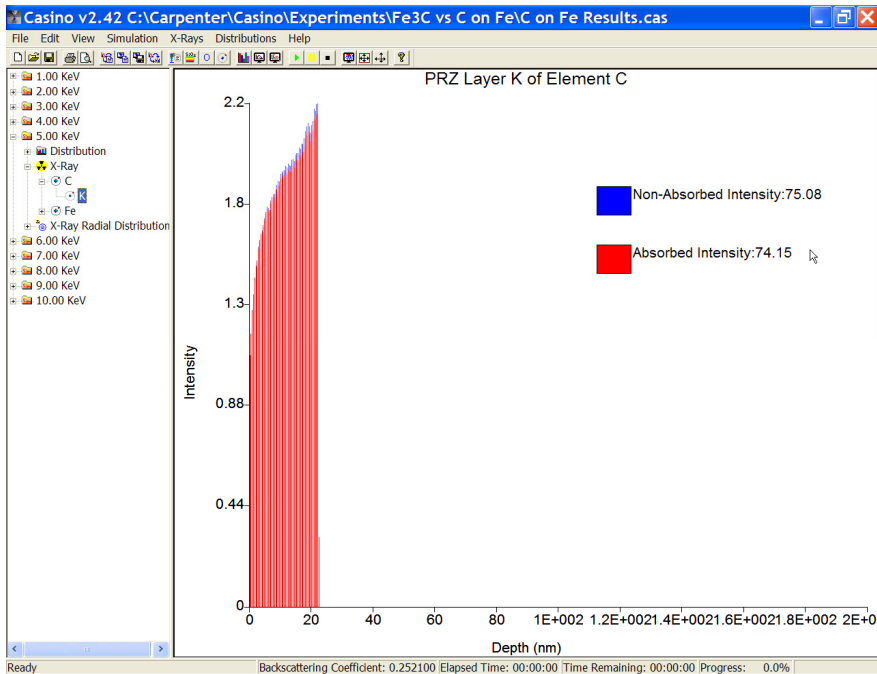
The Edit Layers dialog box shows the setup for the thin film sample:



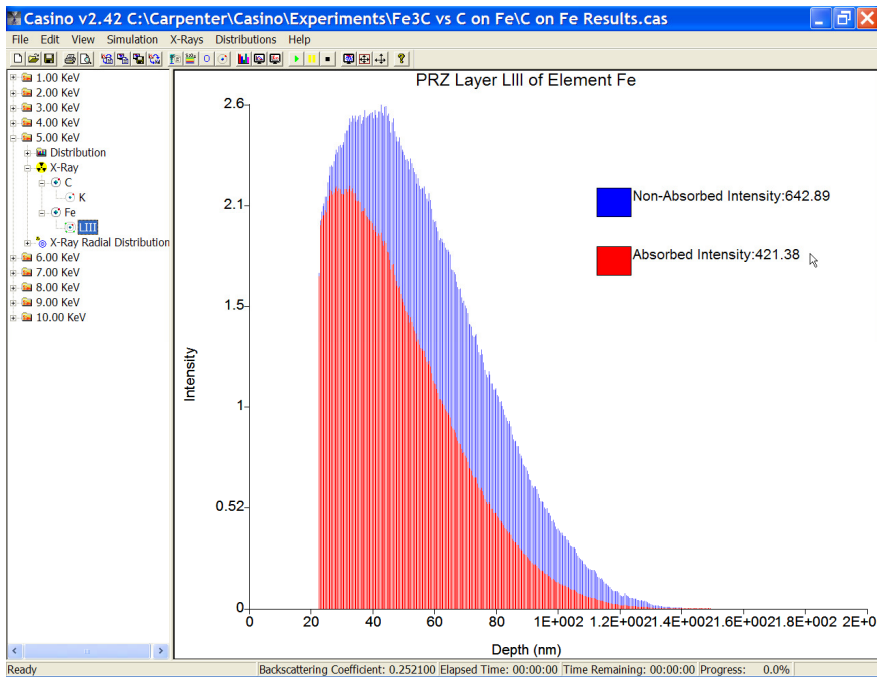
**Figure 14** Sample setup for the thin film sample with a 22.5 nm layer of carbon on an iron substrate.



**Figure 15** Casino scattering plot at 5 KeV for thin film sample with 22.5 nm carbon layer on iron substrate. Scale is the same as for the Fe<sub>3</sub>C bulk sample. Note the qualitative difference in the scattering plot compared to the bulk sample. This diagram should be a clue to the answer of this problem: There should be an accelerating voltage low enough so that all electrons are scattered within the carbon thin film, and no Fe x-rays are produced.



**Figure 16** X-ray  $\Phi(\rho z)$  data for thin film sample at 5 KeV, showing intensity data for C  $K\alpha$ , with blue curve indicating generated C  $K\alpha$ , and red curve indicating emitted C  $K\alpha$  intensity. The integrated intensities are listed next to the color keys, so that the generated intensity is 75.08, and emitted intensity is 74.15. Note the dramatic difference compared to the bulk sample. Here C  $K\alpha$  x-rays are generated only in the thin film layer, and little x-ray absorption occurs.



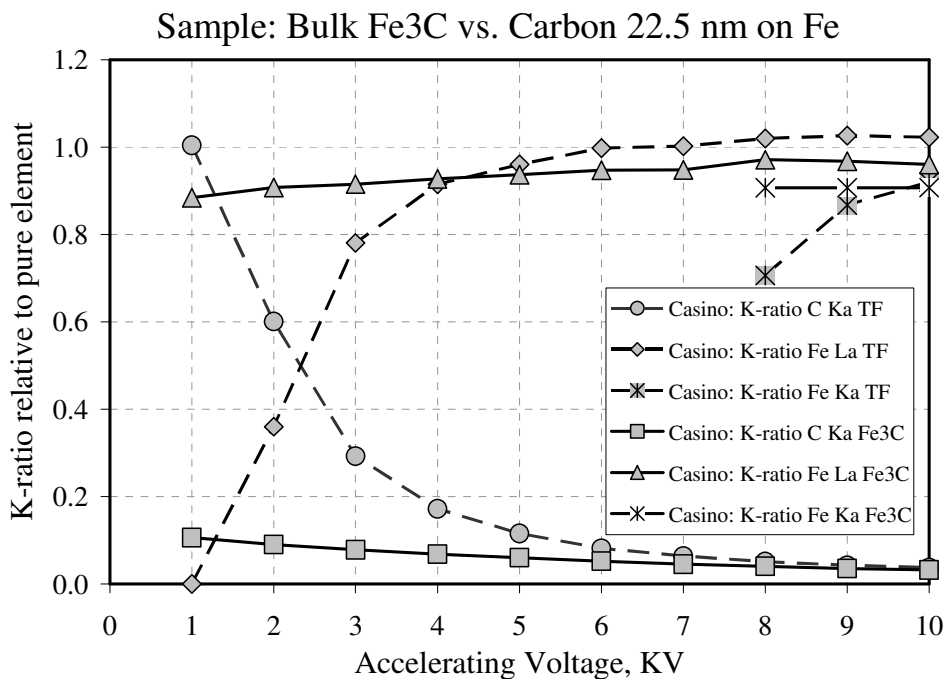
**Figure 17** X-ray  $\Phi(\rho z)$  data for thin film sample at 5 KeV, showing intensity data for Fe  $L\alpha$ , with blue curve indicating generated Fe  $L\alpha$ , and red curve indicating emitted Fe  $L\alpha$  intensity. The integrated intensities are listed next to the color keys, so that the generated intensity is 642.89, and

emitted intensity is 421.38. Note again the dramatic difference compared to the bulk sample. Here Fe K $\alpha$  x-rays are generated only in the substrate layer, and moderate x-ray absorption occurs.

Table 2. Casino X-ray Intensity Data for Thin Film Sample (TFS), Pure C, and Pure Fe

<b>KV</b>	<b>C K<math>\alpha</math> TFS</b>	<b>C K<math>\alpha</math> Graphite</b>	<b>Fe L<math>\alpha</math> TFS</b>	<b>Fe K<math>\alpha</math> TFS</b>	<b>Fe L<math>\alpha</math> Bulk Fe</b>	<b>Fe K<math>\alpha</math> Bulk Fe</b>	<b>K- ratio C K<math>\alpha</math></b>	<b>K-ratio Fe L<math>\alpha</math></b>	<b>K-ratio Fe K<math>\alpha</math></b>
1	48.83	48.63		8.71			1.0041	0.0000	
2	108.90	181.24	38.50	106.92			0.6009	0.3601	
3	98.07	335.15	181.92	233.03			0.2926	0.7807	
4	84.71	491.65	316.49	345.91			0.1723	0.9149	
5	74.15	641.58	421.38	438.86			0.1156	0.9602	
6	63.76	778.15	493.30	494.33			0.0819	0.9979	
7	57.78	902.07	531.74	530.62	0.00	0.00	0.0641	1.0021	
8	52.06	1015.05	555.59	544.76	13.48	19.08	0.0513	1.0199	0.7065
9	47.59	1102.94	561.67	547.19	71.51	82.46	0.0431	1.0265	0.8672
10	43.91	1170.38	556.64	544.37	169.06	183.80	0.0375	1.0225	0.9198

We now have the necessary data to compare the Casino simulations for the two samples in a quantitative manner. When the k-ratio data for the Fe<sub>3</sub>C and thin film samples are plotted together as a function of accelerating voltage, several features of bulk vs. thin film analysis are evident.



**Figure 18 Comparison of Casino data used to calculate k-ratios for the Fe<sub>3</sub>C bulk sample vs. the thin film sample with 22.5 nm carbon on iron substrate. The 1-4 KeV region is most diagnostic for discriminating bulk vs. thin film structure, since the scattering and analytical volumes are constrained by the physics to remain within the thin film layer. The k-ratios for the bulk Fe<sub>3</sub>C do not change as the voltage is decreased, but at reduced voltage the k-ratios for the thin film sample approach that of pure carbon as it is the surface layer. The complementary nature of the C K $\alpha$  and Fe L $\alpha$  data provide supporting evidence for the existence of a thin film structure, if present.**

This figure clearly illustrates the need to use relative intensity data to discriminate bulk vs. thin film structures. The posed problem is challenging because one cannot simply reduce the voltage and acquire a spectrum that indicates the presence of carbon since it is possible that carbon was deposited, accumulated, or contaminated the surface of the sample.

## **Win X-ray Monte Carlo / $\Phi(\rho z)$ Program**

The Win X-ray program is an extension of the Casino program, and allows one to calculate the x-ray intensity data for a simulated sample, and produces both  $\Phi(\rho z)$  data and EDS spectral data. Experience with the program by users indicates that, like Casino, excellent results can be obtained in comparison to experimental data measurements.

The details of the physics and algorithms used in Win X-ray are discussed in the reference:

R. Gauvin, E. Lifshin, H. Demers, P. Horny and H. Campbell (2003), "Win X-ray, a New Monte Carlo Program that Computes X-ray Spectra Obtained with a Scanning Electron Microscope", *Microsc. Microanal.* 12, 49-64, 2006

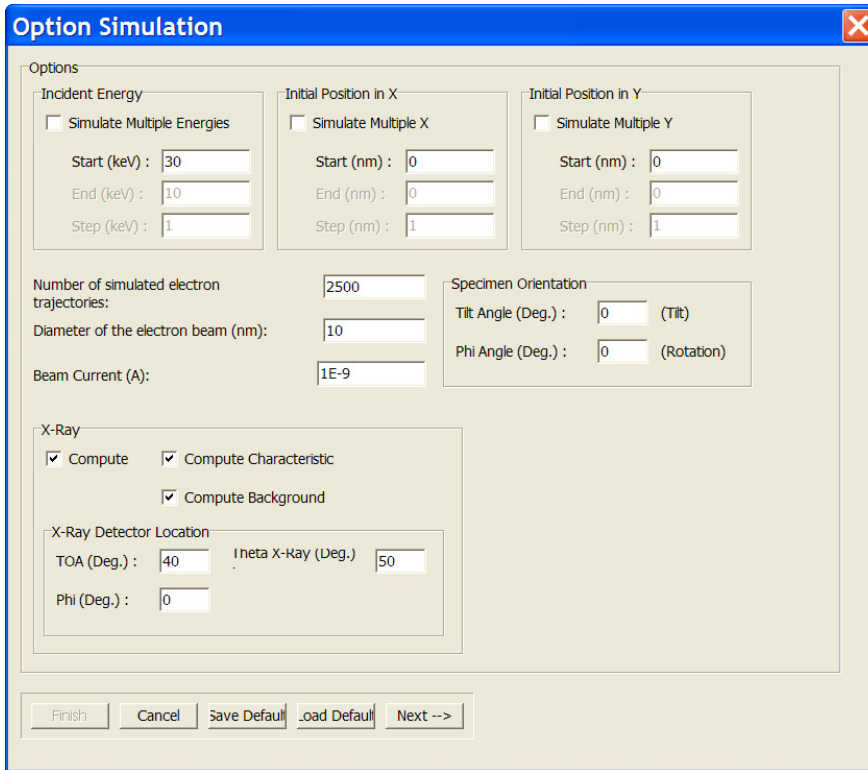
The advantages of the Win X-ray program are similar to those of Casino. Win X-ray can be used to calculate the x-ray intensity data for a multi-element sample, with the important data output that includes  $\Phi(\rho z)$  and EDS spectral data. The sample configuration will include the capability to model thin film and more advanced geometries. The program runs more slowly than Casino, but this is necessary as more complex calculations are being performed compared to Casino. A simulation of 10,000 electrons is sufficient to simulate typical samples, and typically requires about 20 minutes on a PC. The output from Win X-ray is graphically available and can be plotted from the numerous data files that are produced by the program.

## **Creating a Win X-ray Simulation**

Setting up a simulation in Win X-ray is similar to the procedure used for Casino. We will use an example to show how a Win X-ray run can be performed.

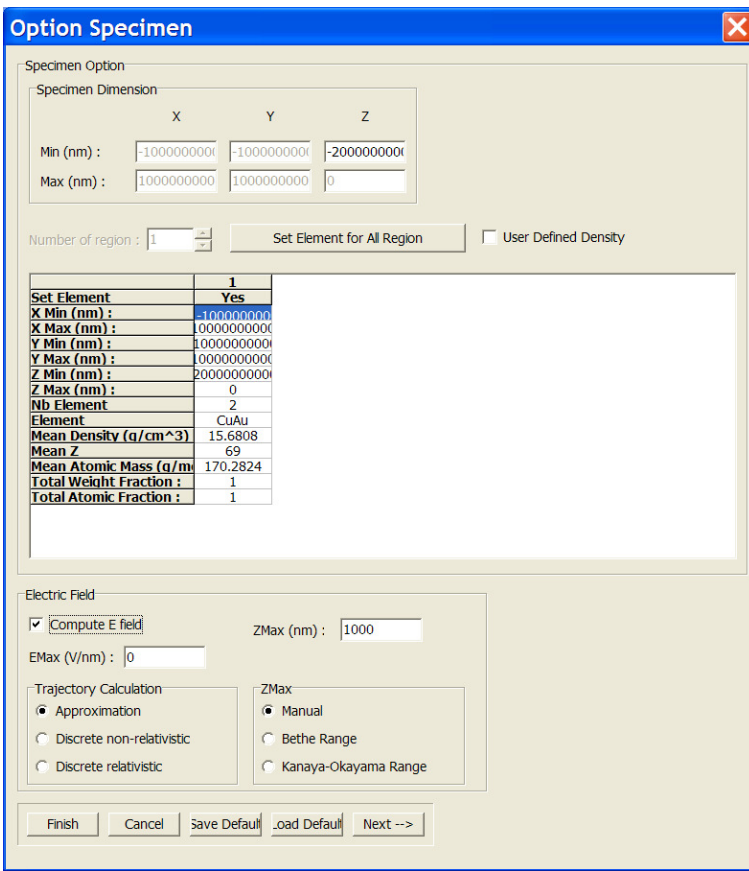
## **Win X-ray Sample Problem**

We will use Win X-ray to simulate the EDS spectrum of a  $\text{Au}_{80} - \text{Cu}_{20}$  alloy at 30 KeV. This will highlight the procedure used to set up the run and to show the output data. Begin by selecting File New, which will open up the Option Simulation window. This simulation will use one accelerating potential, 30 KeV, 2500 simulated electrons, x-ray data generation, and an x-ray takeoff angle of 40 degrees. Note that several accelerating potentials can be used, and multiple X and Y positions can be used to simulate a line profile across an interface.

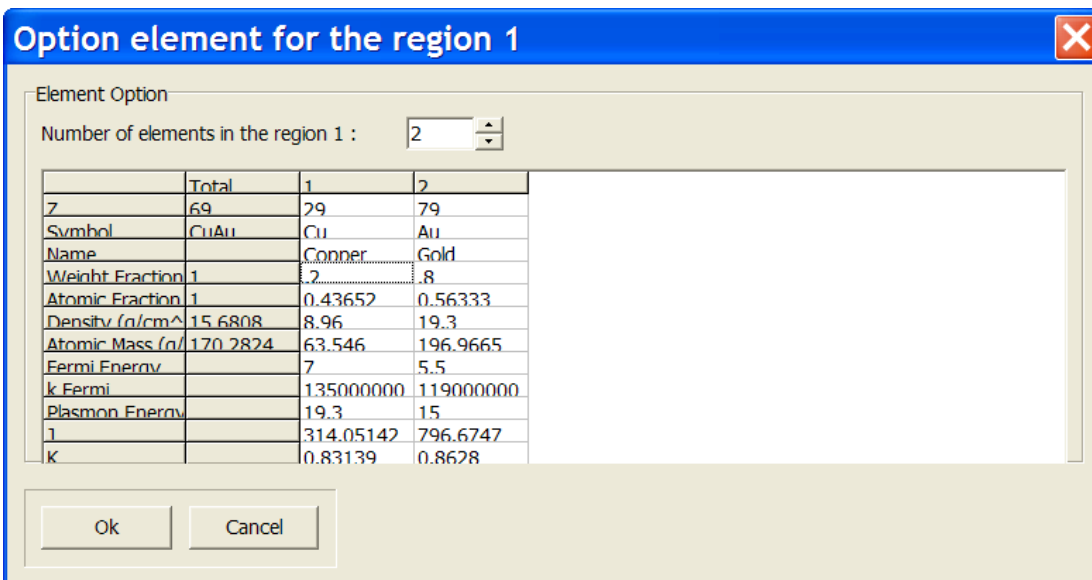


**Figure 19** The Option Simulation window. The accelerating potential used is entered in the incident energy fields and multiple energies can be used in the simulation. Note that selection of a large number of electrons will result in run times that are significantly longer than for Casino.

The next window is the Option Specimen dialog window, where clicking on Set Element for All Region is used to enter the number of elements, their atomic numbers, and the weight fraction of each element. The next figures show these windows and the results for entry of the weight fractions for Cu (Z 29, weight fraction 0.20) and Au (Z 79, weight fraction 0.80).



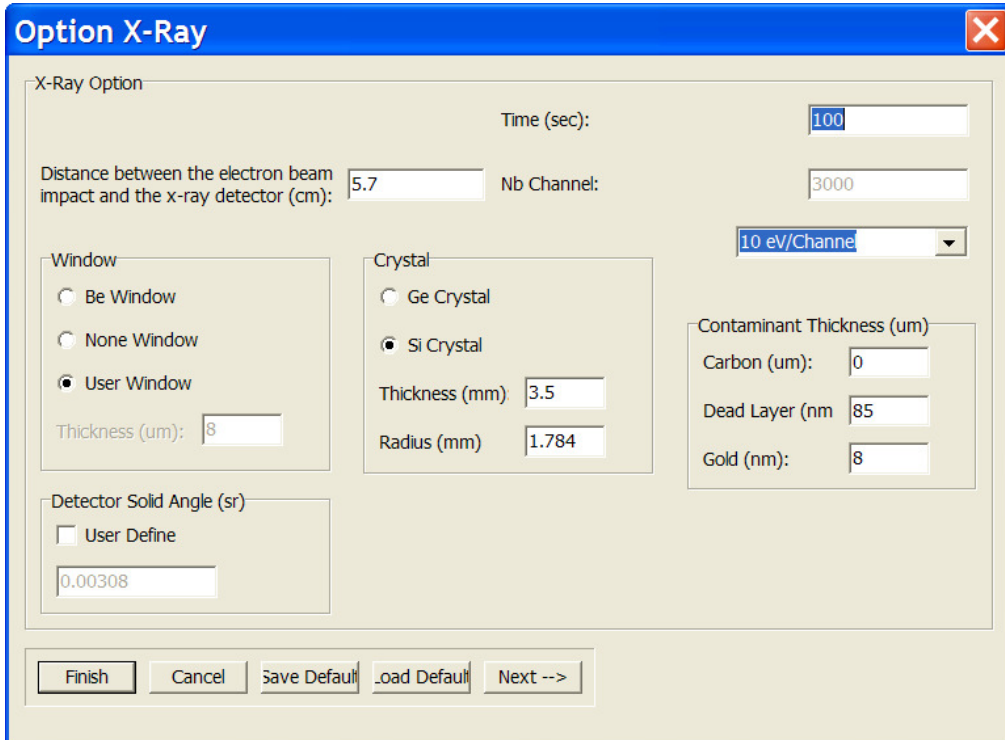
**Figure 20** The Option Specimen dialog box. The Set Element for All Region button is clicked to open the next dialog box for entry of the elements and their weight fractions and other parameters. Calculation of the electric field has been selected for this simulation.



**Figure 21** The Option Element dialog box. This dialog box is used to enter the compositional data for the sample. The number of elements in the sample, the atomic number, and weight fraction data are entered here and used by the program to calculate x-ray data.

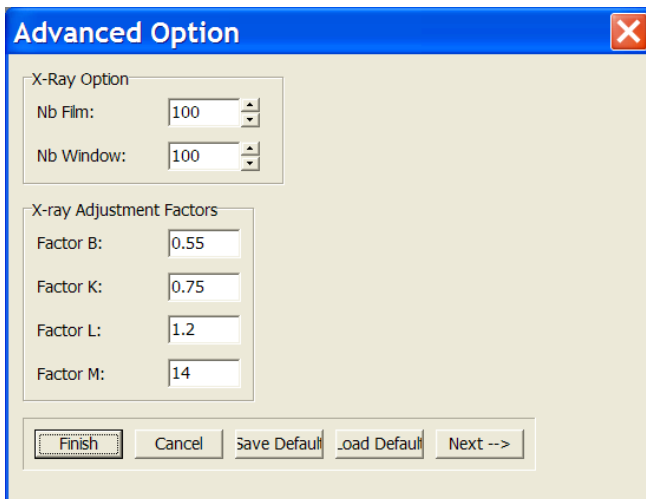


Next the Option X-ray dialog box is used to enter details concerning the EDS detector, including the detector distance, counting time, window material, detector crystal composition, contamination layer thickness, and detector solid angle.



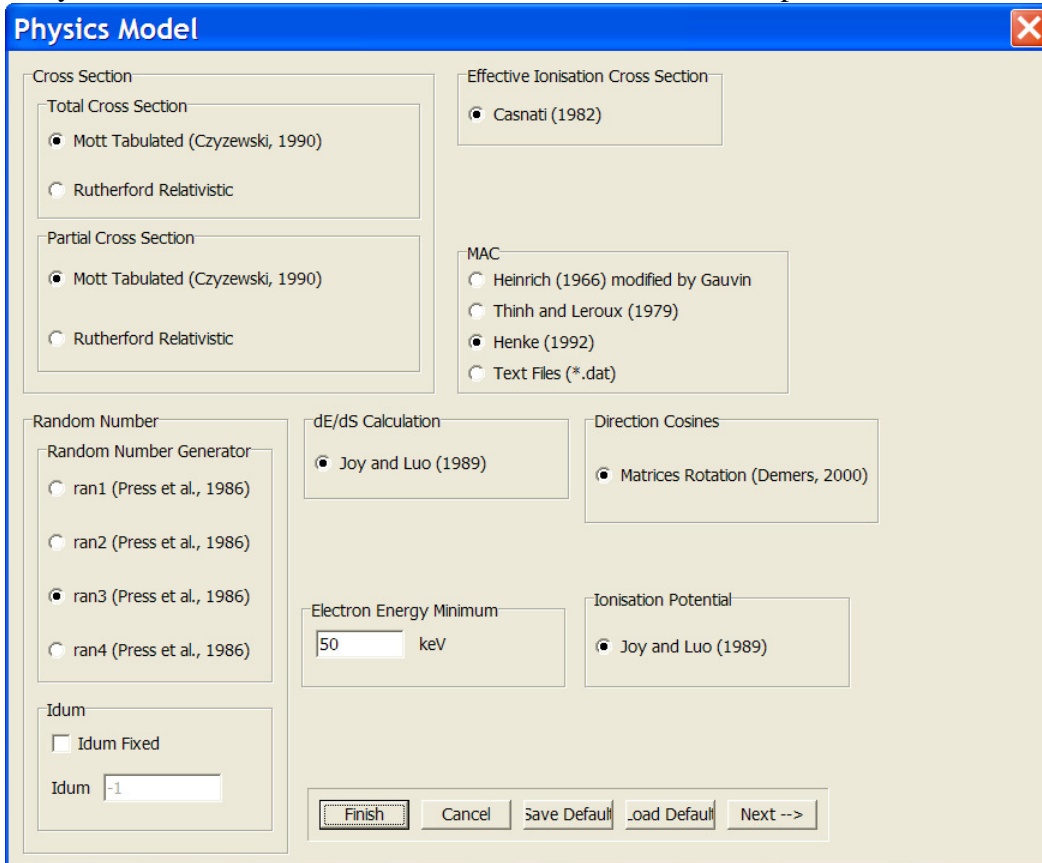
**Figure 22 Option X-ray dialog box. Details of the EDS detector are entered here.**

The Advanced Option dialog box is used to enter factors for the number of film and window parameters, and adjustment factors for x-ray scaling adjustment. These topics are covered in the Win X-ray paper.



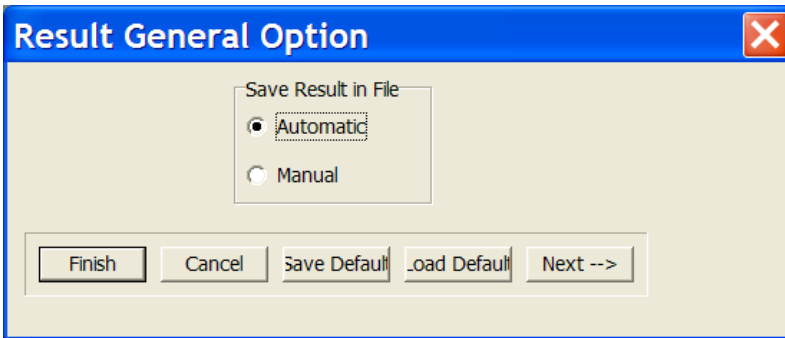
**Figure 23 Advanced Option dialog box. X-ray options and adjustment factors are entered here.**

The Physics Model dialog box is used to set the scattering parameters and cross-sections for electron scattering and x-ray generation functions. The electron energy minimum value is used to terminate the calculation at a sufficiently low energy, and for high energy x-rays this value could be raised to increase the calculation speed.



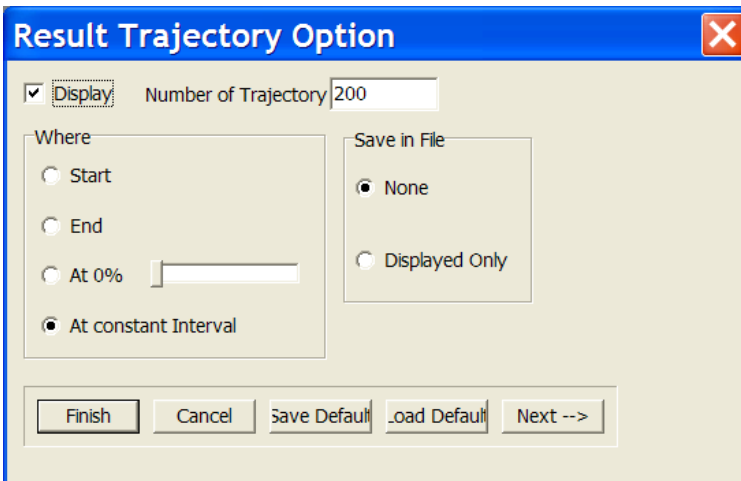
**Figure 24** Physics Model dialog box. The cross-section functions and other parameters for electron and x-ray generation are entered here.

The Result General Option dialog box is important, and you should select Automatic to save results in the text files at the end of the run. Otherwise you must manually save the data. You will lose data if you quit from Win X-ray and have not manually saved or automatically saved your data.



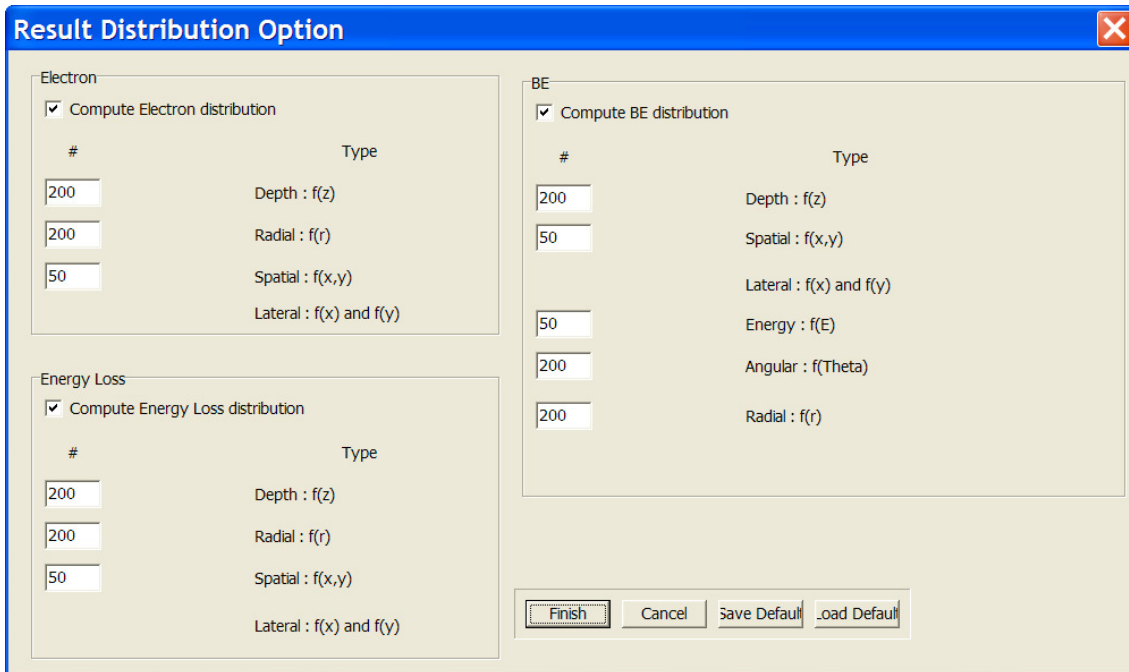
**Figure 25** Result General Option dialog box. Automatic vs. manual saving of run results is selected here.

The Result Trajectory Option dialog box is used to select the number of trajectories to display, and whether the trajectories are displayed only at the start, end, or intermediate stage of the simulation. The trajectories can also be saved into a results file.



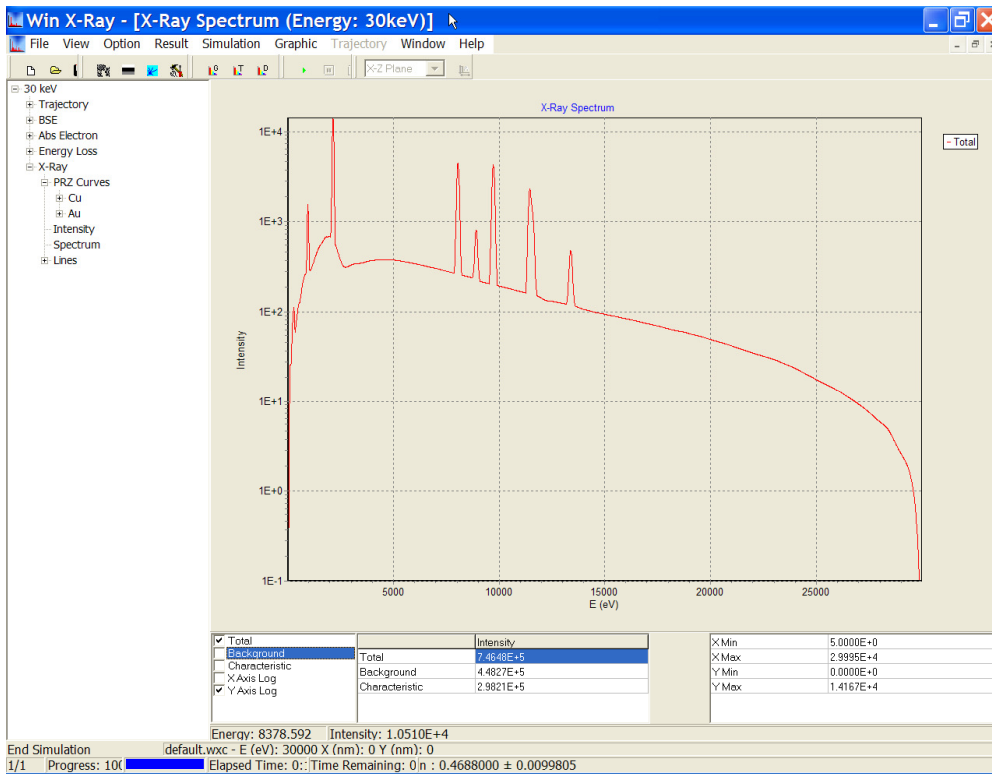
**Figure 26** Result Trajectory Option dialog box. Selection of display options and save options for electron scattering trajectories.

The Result Distribution Option dialog box is used to select the distributions for scattered primary electrons, backscattered electrons, and energy loss parameters for the simulation.



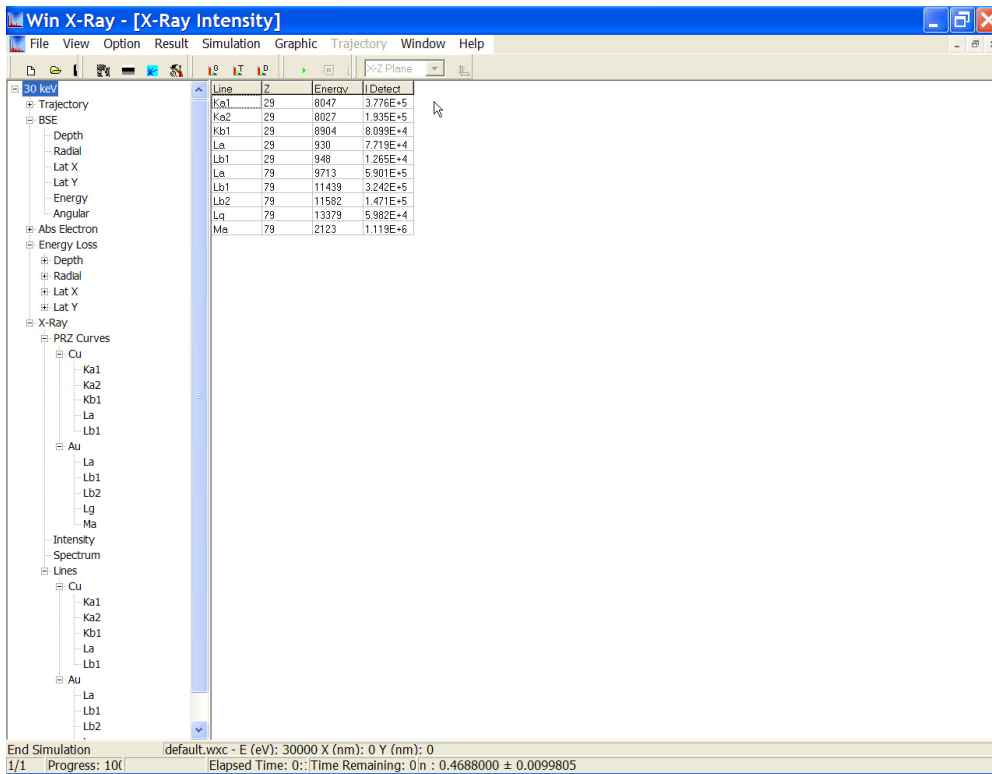
**Figure 27 Result Distribution Option dialog box. Primary, backscattered, and energy loss electron parameters are set in this box.**

After the Finish button is clicked, the simulation begins running, and the progress is indicated with a progress bar at the bottom of the screen. The screen shown below is the EDS spectrum for the Au<sub>80</sub> – Cu<sub>20</sub> alloy that was simulated. The characteristic x-ray peaks (from low energy to high energy) are Cu L $\alpha$ , Au M $\alpha$ , Cu K $\alpha$  and K $\beta$ , and the Au L-family lines, and these are superimposed on the continuum x-rays. The data to be plotted is selected from the left panel in the main Win X-ray window. This includes the electron trajectory plot, backscattered and absorbed electron data, energy loss data, and the x-ray data.



**Figure 28** Final spectrum display of simulated EDS spectrum. Spectrum shown is Au<sub>80</sub> – Cu<sub>20</sub> alloy at 30 KeV with Cu L and K lines, and Au M and L lines.

The figure below shows the intensity values for the characteristic peaks produced by Win X-ray. These intensity values can be used to calculate k-ratios in the same way that this was done with Casino. This requires that appropriate standard spectra are simulated. For example, to produce k-ratios for Cu and Au in the alloy, it is necessary to run a simulation for pure Cu and pure Au, then ratio the intensities for Cu and Au in the alloy relative to those intensities in the pure element.



**Figure 29** X-ray intensity data for Cu and Au peaks in the CuAu alloy.

# CalcZAF X-ray Analysis Program: ZAF and $\Phi(\rho z)$ Algorithms

CalcZAF is a public domain program written by John Donovan of Probe Software, which is based on the CITZAF core distribution of ZAF and  $\Phi(\rho z)$  correction algorithms developed by John Armstrong.

CalcZAF can be used to perform a wide range of computations, including the following:

1. Calculation of emitted x-ray intensity relative to pure element or specified standard compositions.
2. Calculation of concentration for measured k-ratios relative to either pure element or specified standards.
3. Evaluation of the effect of different correction algorithms on generated and emitted x-ray intensities for chosen systems.
4. Evaluation of mass absorption coefficient and other data set parameters on x-ray intensities for chosen systems.
5. Inspection of x-ray data such as x-ray line and edge energies, mass absorption coefficients, and other data

## Setting up CalcZAF

Launch the CalcZAF program. Two windows are opened up, the main window with log file output, and the data entry window that has a grid layout:

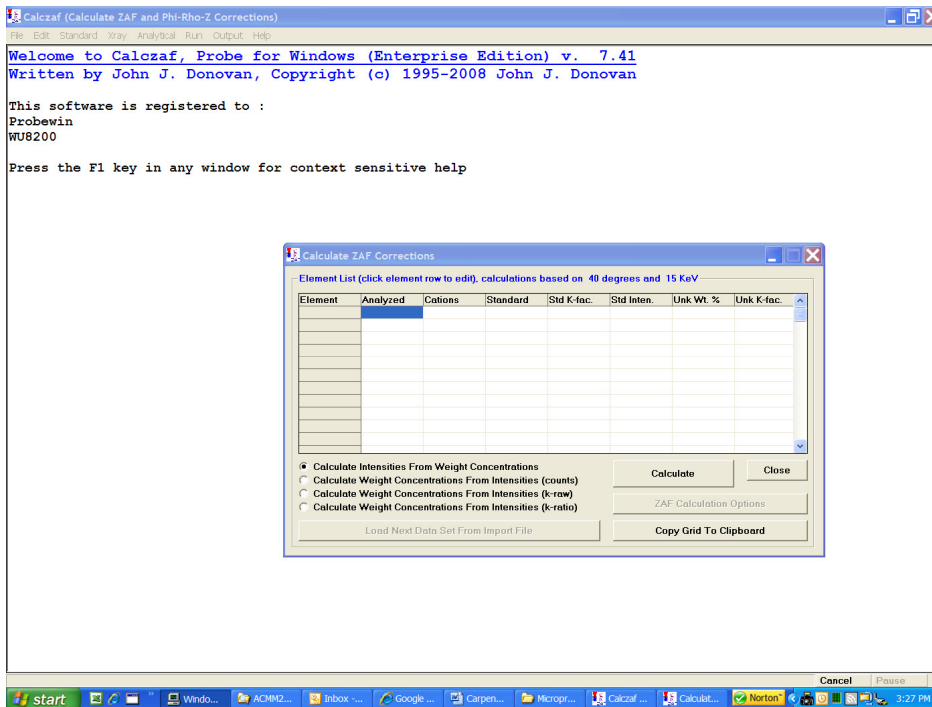


Figure 30 CalcZAF Program

The CalcZAF program has a help file accessed from the Help menu, and also has context-sensitive help that is brought up using the F1 key at any point.

We will use the following exercise to show how CalcZAF can be used to process k-ratios collected on the set of NIST Cu-Au microanalysis standards.

### ***Cu-Au alloys***

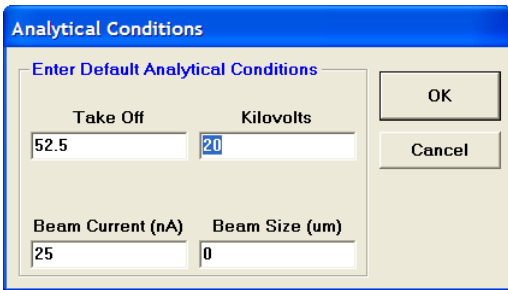
The first exercise in this laboratory is how to correct a set of published analytical data of the NIST Cu-Au microanalysis standards. We shall see how the calculated compositions vary when using different ZAF and  $\phi(\rho z)$  correction procedures and how these compare to the NIST-certified compositions. (Note: These Cu-Au standards are a good set of materials to use for repetitive analyses to demonstrate quality control on your instrument.)

The data that will be analyzed in this first exercise was published in the NIST documentation for these standards. Electron microprobe analyses were performed at 20 keV on an instrument with a 52.5° take-off angle. Two elements were analyzed--Cu and Au. The Cu K $\alpha$  and the Au L $\alpha$  x-ray lines were used. Pure Cu metal and Au metal were used as standards. K-values relative to the pure element standards were reported (background-subtracted measured x-ray intensity in the sample divided by the corresponding background-subtracted x-ray intensity for the pure element standard). Four different samples were measured, each a different alloy composition. The NIST-certified standard compositions for the four materials and their measured k-ratios are given below:

Sample	Element and Line	Conc. wt%	k value
<b>Cu20-Au80</b>	<b>Cu K<math>\alpha</math></b>	<b>19.83</b>	<b>0.2462</b>
	<b>Au L<math>\alpha</math></b>	<b>80.15</b>	<b>0.7525</b>
<b>Cu40-Au60</b>	<b>Cu K<math>\alpha</math></b>	<b>39.64</b>	<b>0.4634</b>
	<b>Au L<math>\alpha</math></b>	<b>60.36</b>	<b>0.5286</b>
<b>Cu60-Au40</b>	<b>Cu K<math>\alpha</math></b>	<b>59.92</b>	<b>0.6622</b>
	<b>Au L<math>\alpha</math></b>	<b>40.10</b>	<b>0.3323</b>
<b>Cu80-Au20</b>	<b>Cu K<math>\alpha</math></b>	<b>79.85</b>	<b>0.8401</b>
	<b>Au L<math>\alpha</math></b>	<b>20.12</b>	<b>0.1570</b>

The first step is to enter the Analytical conditions, using the Analytical Menu and selecting Operating Conditions. These data were acquired on an ARL microprobe which had a takeoff angle of 52.5 degrees, and an accelerating voltage of 20 KeV:



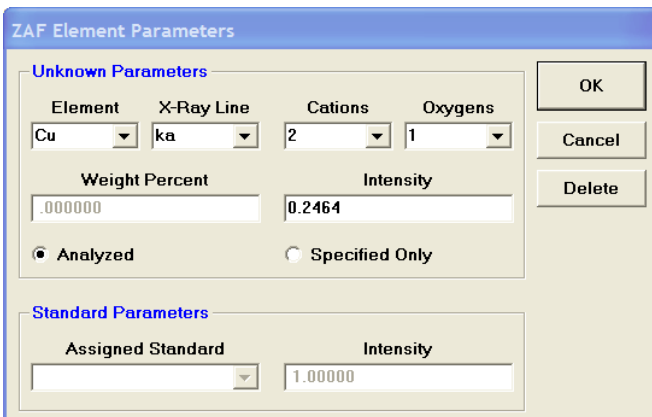


**Figure 31 Analytical Conditions**

For this exercise we will be processing k-ratio data to produce the calculated concentrations for the elements in our sample. This is the last radio button on the Calculate ZAF Corrections window.

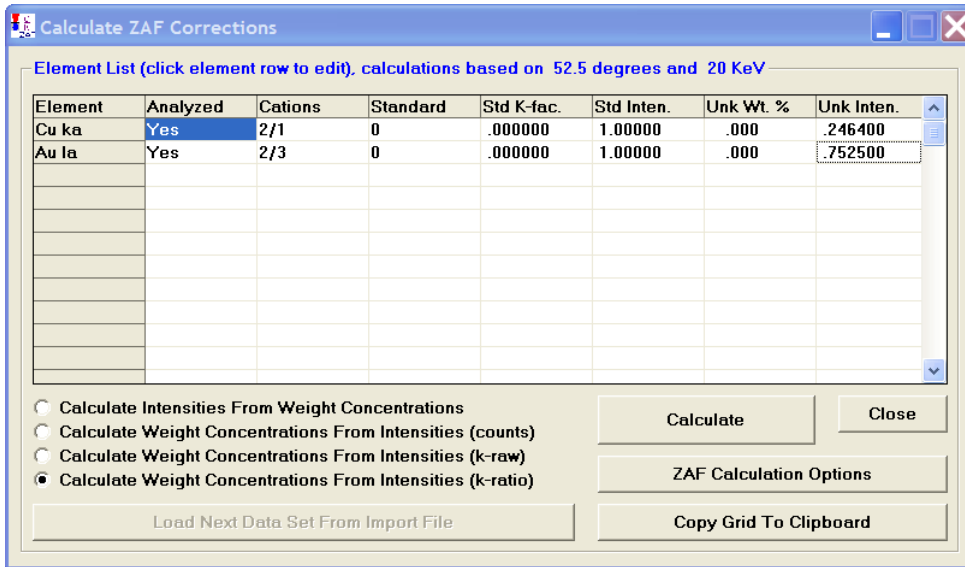
Next we enter the elements, the x-ray lines used for analysis, and the k-ratio for each element relative to the pure element standard used

For the Cu<sub>20</sub>-Au<sub>80</sub> standard, the data for Cu is entered by clicking on the first row of the grid in the window. Here we enter the element symbol for Cu, the K $\alpha$  analytical line, and the k-ratio of 0.2464; the element is analyzed relative to a pure element standard:



**Figure 32 Element Entry Window**

The same procedure is used to enter the data for Au using the L $\alpha$  line, and a k-ratio of 0.7525. When we have completed data entry, the window looks like this:



**Figure 33 Calculate ZAF Corrections Window**

We are now ready to calculate the concentrations for Cu and Au in the alloy. The Calculate button is used to perform the correction, and the results are displayed in the log window as shown here:

```

Correction Method:
ZAF or Phi-Rho-Z calculations
LINEMU Henke (1985) < 10KeV / CITZMU > 10KeV

Current ZAF or Phi-Rho-Z Selection:
Armstrong/Love Scott (default)

Correction Selections:
Phi(pz) Absorption of Armstrong/Packwood-Brown 1981 MAS
Stopping Power of Love-Scott
Backscatter Coefficient of Love-Scott
Backscatter of Love-Scott
Mean Ionization of Berger-Seltzer
Phi(pz) Equation of Love-Scott
Reed/JTA w/ M-Line Correction and JTA Intensity Mod.

Calculating All Standard K-factors...
Standard K-factors Calculated

CalcZAF Sample at 52.5 degrees and 20 keV

SAMPLE: 0, ITERATIONS: 3

ELEMENT K-VALUE ELEMWT% OXIDWT% ATOMIC% KILOVOL
Cu ka .24640 19.975 ----- 43.546 20.0
Au la .75250 80.268 ----- 56.454 20.0
TOTAL: 100.243 ----- 100.000

ELEMENT ABSCOR FLUCOR ZEDCOR ZAFCOR STP-POW BKS-COR F(CHI)
Cu ka 1.0484 .9294 .8320 .8107 .7329 1.1351 .9392
Au la 1.0040 1.0000 1.0625 1.0667 1.0949 .9704 .9556

```

The output lists the default correction algorithm, which is the Armstrong  $\Phi(\rho z)$  algorithm, and the mass absorption coefficient data set LINEMU. How do the results compare with the accepted concentrations for the CuAu alloys? The calculated values for Cu and Au are 19.97 and 80.26 wt%, and the accepted values are 19.83 and 80.15 wt%, respectively.

Inspection of the ZAF factors is important to understand the nature of correction in the CuAu system. It is the most powerful capability of CalcZAF and the CITZAF program on which it is based. Let's explore the ZAF correction using the Cu<sub>20</sub>Au<sub>80</sub> alloy, with a mind towards the dominant correction in this system.

### ***Discussion of ZAF Factors***

Remember that the basic relation for x-ray measurement and correction is from:

$$C = k * ZAF$$

where k is the k-ratio determined from the background-corrected peak intensity measured on the sample, divided by the same quantity measured on the standard:

$$k = (P-B)^{\text{sample}} / (P-B)^{\text{standard}}$$

and the ZAF factors represent the correction calculated for the effects of (Z) atomic number (electron retardation and backscattering), (A) x-ray absorption within both the sample and standard, and (F) characteristic x-ray fluorescence within both the sample and standard. Note that these factors treat the differential quantities between sample and standard, in addition to those within the sample and standard. In the normal presentation of ZAF factors, the individual Z, A, and F factors are multiplied and presented as the total factor "ZAF". In the CuAu example shown above, the measured k-ratio for Cu K $\alpha$  relative to pure Cu is  $k = 0.2464$ , the calculated ZAF factor is 0.8107, and the calculated weight fraction of Cu is  $C = k * ZAF = 0.2464 * 0.8107 = 0.1998$  or 19.98 wt%. The ZAF factors are calculated iteratively since they are a function of composition, and it is necessary to iterate using the k-ratio as an initial estimate of C. When we talk about running a ZAF program "in reverse" it means that we begin with the known values for C and calculate the ZAF factors in order to produce the calculated k-ratio that would be measured relative to the pure element standard. The k-ratio would be calculated from  $k = C/ZAF$  in this manner.

Note that the value of each ZAF factor is presented as a number greater or less than unity in order to compensate for the effect of that parameter. For example, an absorption factor of 1.10 represents the necessary correction to account for a 10% loss due to x-ray absorption within the target, a fluorescence correction of 0.90 represents a correction to account for a 10% increase in x-ray intensity due to characteristic x-ray fluorescence by a

matrix element, and an atomic number correction of 0.95 represents a correction for a 5% enhancement of x-ray intensity due to electron retardation and backscattering, while an atomic number correction of 1.05 represents a 5% loss of intensity due to the same effects.

### Absorption Correction

The absorption correction A (column ABSCOR) is formed by the ratio of the f(chi) for the CuAu alloy relative to the pure element standard. For both Cu and Au, f(chi) is close to 0.95 which means that 95% of the generated x-rays are emitted from the sample and 5% of the generated x-rays are absorbed within the sample. Absorption takes place within the pure element standard as well. The absorption correction A is the ratio of f(chi) for the standard (obtained by running in verbose mode) by f(chi) for the sample. For Cu this is  $0.9594/0.9392 = 1.0484$ . This means there is a 4% correction due to absorption of Cu  $K\alpha$  in the sample relative to the standard. Remember that x-ray absorption is a function of the mass absorption coefficient for an x-ray emitter due to absorption by the elements in the matrix, as well as the x-ray takeoff angle that the emitted x-rays are measured at. For this example the mac's are from the LINEMU data set and are:

```
Current Mass Absorption Coefficients From:
LINEMU Henke (1985) < 10KeV / CITZMU > 10KeV
```

Z-LINE	X-RAY	Z-ABSOR	MAC
Au	la	Au	1.3232e+02
Au	la	Cu	2.3420e+02
Cu	ka	Au	2.1412e+02
Cu	ka	Cu	5.0035e+01

These values are all similar and are of the order of 50-250. X-rays that have significant absorption have mac's in the 1000-10000 range. The absorption correction for Cu and Au in the CuAu binary, using Cu  $K\alpha$  and Au  $L\alpha$ , is not significant. The use of Cu  $L\alpha$  would result in a much larger absorption coefficient. There is effectively no absorption correction for Au in this alloy.

### Fluorescence Correction

The fluorescence correction F (column FLUCOR) represents the correction required when one or more characteristic x-ray lines of matrix elements fluoresce the line of interest. In the CuAu binary, only the Au  $L\alpha$  line can fluoresce Cu  $K\alpha$ , resulting in a higher emitted intensity of Cu  $K\alpha$  compared to the intensity due solely to generation by electron excitation. The fluorescence factor for Cu is 0.9294 which means that about 7% of the Cu  $K\alpha$  intensity is due to fluorescence by Au  $L\alpha$ . Note several aspects of the fluorescence correction. First, x-ray fluorescence is most important for the case of a K-line exciting a K-line of another element (i.e., Ni  $K\alpha$  exciting Fe  $K\alpha$ ) when the exciter line is just above the excitation energy of the absorber. Less important is fluorescence by L-lines and M-lines. Remember that the fluorescent yield is the important parameter in assessing x-ray fluorescence. Secondly, even if the Au  $Ma$  line was used for analysis of Au, it would still be necessary to correct for fluorescence of Cu  $K\alpha$  by Au  $L\alpha$  since that line is generated at 20 keV. There is no fluorescence correction for Au  $L\alpha$  since there are

no x-ray lines with sufficient energy to generate Au L $\alpha$  x-rays. Note that no correction is made for fluorescence by continuum x-rays. This is a complicated calculation that is not historically included in ZAF algorithms.

### Atomic Number Correction

The atomic number correction Z (column ZEDCOR) represents the combined effects of stopping power via electron slowing down (column STP-POW) and electron backscattering (column BKS-COR). The stopping power and backscatter corrections are inversely related, such that stopping power increases with lower Z while backscattering increases with higher Z, the result being that the two effects somewhat counteract to reduce the total correction. In the CuAu alloy example, the Z correction for Cu is 0.8320 which represents a 17% correction for the combined effects of electron retardation and backscattering. Conversely, the Z correction for Au L $\alpha$  represents a loss of intensity for this x-ray line due to the reduction of x-ray generation because a lower atomic number element Cu is in the matrix compared to a pure Au target.

CalcZAF allows you to load a file with k-ratio or concentration data in order to conveniently process analyses and explore the effect of changing the correction algorithm and mass absorption coefficient data sets. For our CuAu alloy example, if you select the menu File – Export CalcZAF Input Data File. Doing so will produce a file that has the following structure (this output shows the data for calculation of concentrations using k-ratios relative to the standards for Cu and Au which have standard numbers 2129 and 2179):

```
2, 2, 20, 52.5, ""
0 "" "" 0 "" "" 0
"Cu" "ka" 2 1 2129 0 0.2462 1
"Au" "la" 2 3 2179 0 0.7525 1
```

This capability allows you to generate an input file for CalcZAF from your own data. This procedure is discussed next.

### Importing Concentration or Intensity Data From a Disk File

The following information describes how to use a file with data to be corrected by CalcZAF. See the CalcZAF manual for more information.

CalcZAF allows the user to create ASCII files for importing concentration or intensity data from a disk file. An example file is supplied which is called CALCZAF.DAT. See the File | Open and File | Close menu for loading input data from file. Click the Calculate button to perform the calculations and click the Load Next Dataset from Input File button to load the next data set.

Each data set in the input file consists of 3 or more lines. The first line contains the calculation mode (defined above), number of analyzed and specified elements, operating voltage and takeoff angle. The second line contains the oxide or elemental calculation flag (1=oxide,2=elemental), the element by difference, element by stoichiometry to

stoichiometric oxygen, the stoichiometric ratio, the element by stoichiometry relative to another element, the element to which the stoichiometry is calculated relative to and the relative ratio. The third (and subsequent lines) are the element data for each element including the element symbol, the x-ray symbol ("ka", "kb", "la", "lb", "ma", "mb" or " " for a specified concentration), the number of cation atoms, the number of oxygen atoms, the standard number assigned as the primary standard (from the Probe for Windows STANDARD.MDB default database), the concentrations (for intensity calculations), the unknown intensity and the standard intensity (if required). This structure is repeated as often as desired for each data set. The program will automatically detect if the last data set has been reached.

The structure is shown below in pseudo-code:

```
' Read calculation mode (0, 1, 2, or 3), number of elements, kilovolts and
takeoff, (optional sample name)
Input #3, CalcMode%, LastChan%, Kilovolts!, Takeoff!, (SampleName$)

' Read oxide/elemental mode, difference, stoichiometry, relative
Input #3, OxideOrElemental%, DifferenceElement$, StoichiometryElement$,
StoichiometryRatio!, RelativeElement$, RelativeToElement$, RelativeRatio!

' Loop on each element
For i% = 1 To LastChan%
Input #3, Elsyms$(i%), Xrsyms$(i%), NumCat%(i%), NumOxd%(i%), StdAssigns%(i%),
ElmPercents!(i%), UnkCounts!(i%), StdCounts!(i%)
next i%

Note:
CalcMode% = 0 for calculation of k-ratios from concentrations
CalcMode% = 1 for calculation of concentrations from unknown and standard
intensities
CalcMode% = 2 for calculation of concentrations from "raw" k-ratios (no
standard intensities necessary)
CalcMode% = 3 for calculation of concentrations from "normalized" k-ratios (no
standards necessary)

Note:
OxideorElemental%=1 calculate oxide output based on stoichiometry
OxideorElemental%=2 calculate as elemental output (default)
```

Note: all strings (element symbols, etc.) must be in double quotes, elements not analyzed (specified concentrations or calculated) are indicated by a blank (empty double quotes) x-ray line string. If the element is a specified concentration, be sure to give the concentration in elemental weight percent for the "ElmPercents!(I%)" parameter and leave the count intensity fields zero.

An example of a CalcZAF input file demonstrating each calculation mode is shown here:

```
0,2,15,40., "MgO K-ratio" ' 1st dataset (calculates MgO intensities)
2, "", "", 0.0, "", "", 0.0
"mg", "ka", 1, 1, 0, 60.0, 0.0, 0.0
"o", "ka", 1, 0, 0, 40.0, 0.0, 0.0
```

```

1,3,15,40., "Fe2SiO4" ' 2nd dataset (calculates concentrations from unk and std
intensities)
2, "", "", 0.0, "", "", 0.0
"fe", "ka", 1, 1, 895, 0.0, 7568.1, 10265.7
"si", "ka", 1, 2, 14, 0.0, 1329.4, 5268.2
"o", "ka", 1, 0, 895, 0.0, 2519.6, 2498.1
2,3,15,40., "Fe2SiO4" ' 3rd dataset (calculates concentrations from "raw" k-
ratios)
2, "", "", 0.0, "", "", 0.0
"fe", "ka", 1, 1, 895, 0.0, .96283, 0.
"si", "ka", 1, 2, 914, 0.0, .00003, 0.
"o", "ka", 1, 0, 895, 0.0, 1.09972, 0.
3,2,20,40., "MgO" ' 4th dataset (calculates concentrations from normalized k-
ratios)
2, "", "", 0.0, "", "", 0.0
"mg", "ka", 1, 1, 0, 0., .418853, 0.0
"o", "ka", 1, 0, 0, 0., .190763, 0.0

```

Returning to our CuAu alloys, we now can generate a file that has all the k-ratio data for the 20 keV, 52.5 degree takeoff measurements:

```

2, 2, 20, 52.5, ""
0 "" "" 0 "" "" 0
"Cu" "ka" 2 1 2129 0 0.2462 1
"Au" "la" 2 3 2179 0 0.7525 1
2, 2, 20, 52.5, ""
0 "" "" 0 "" "" 0
"Cu" "ka" 2 1 2129 0 0.4634 1
"Au" "la" 2 3 2179 0 0.5286 1
2, 2, 20, 52.5, ""
0 "" "" 0 "" "" 0
"Cu" "ka" 2 1 2129 0 0.6622 1
"Au" "la" 2 3 2179 0 0.3323 1
2, 2, 20, 52.5, ""
0 "" "" 0 "" "" 0
"Cu" "ka" 2 1 2129 0 0.8401 1
"Au" "la" 2 3 2179 0 0.1570 1

```

These data can now be processed sequentially in CalcZAF, and the output from the log window shows all four alloys:

```

CalcZAF Sample at 52.5 degrees and 20 keV
SAMPLE: 1, ITERATIONS: 3
ELEMENT K-VALUE ELEMWT% OXIDWT% ATOMIC% KILOVOL
Cu ka .24620 19.958 ----- 43.526 20.0
Au la .75250 80.265 ----- 56.474 20.0
TOTAL: 100.223 ----- 100.000
ELEMENT ABSCOR FLUCOR ZEDCOR ZAFCOR STP-POW BKS-COR F(CHI)
Cu ka 1.0484 .9294 .8319 .8106 .7329 1.1351 .9392
Au la 1.0040 1.0000 1.0624 1.0666 1.0948 .9704 .9556

```

CalcZAF Sample at 52.5 degrees and 20 keV

SAMPLE: 2, ITERATIONS: 3

ELEMENT	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	KILOVOL
Cu ka	.46340	39.614	-----	67.185	20.0
Au la	.52860	59.973	-----	32.815	20.0
TOTAL:		99.588	-----	100.000	

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(CHI)
Cu ka	1.0348	.9472	.8721	.8549	.7981	1.0926	.9515
Au la	1.0080	1.0000	1.1256	1.1346	1.1908	.9452	.9518

CalcZAF Sample at 52.5 degrees and 20 keV

SAMPLE: 3, ITERATIONS: 3

ELEMENT	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	KILOVOL
Cu ka	.66220	59.690	-----	82.213	20.0
Au la	.33230	40.028	-----	17.787	20.0
TOTAL:		99.718	-----	100.000	

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(CHI)
Cu ka	1.0224	.9649	.9137	.9014	.8649	1.0564	.9631
Au la	1.0121	1.0000	1.1902	1.2046	1.2888	.9235	.9480

CalcZAF Sample at 52.5 degrees and 20 keV

SAMPLE: 4, ITERATIONS: 2

ELEMENT	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	KILOVOL
Cu ka	.84010	79.784	-----	92.507	20.0
Au la	.15700	20.030	-----	7.493	20.0
TOTAL:		99.813	-----	100.000	

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(CHI)
Cu ka	1.0108	.9824	.9563	.9497	.9322	1.0259	.9741
Au la	1.0160	1.0000	1.2557	1.2758	1.3875	.9050	.9443



The values from the above printout have been transferred to the following table.

ZAF or $\Phi(\rho z)$ Correction		0(CITZAF)	0(CITZAF)	1(Orig.ZAF)	2(Frame)	3(LS-I)	
Mass Absorption Coefficient		0(Hein. 66)	2(Hein. 86)	2(H86)	2(H86)	2(H86)	
Alloy	Element	NIST Certified					
20	Cu	19.83	<b>19.93</b>				
	Au	80.15	<b>80.29</b>				
	Sum	99.98	<b>100.22</b>				
40	Cu	39.64	<b>39.57</b>				
	Au	60.36	<b>60.10</b>				
	Sum	100.00	<b>99.68</b>				
60	Cu	59.92	<b>59.67</b>				
	Au	40.10	<b>40.13</b>				
	Sum	100.02	<b>99.80</b>				
80	Cu	79.85	<b>79.77</b>				
	Au	20.12	<b>20.10</b>				
	Sum	99.97	<b>99.87</b>				
Alloy	Element	4 (LS II) 2(H86)	5 (PB) 2(H86)	6 (Bast 1) 2(H86)	7 (Proza) 2(H86)	8(PAP) 2(H86)	9 (XPP)
20	Cu						
	Au						
	Sum						
40	Cu						
	Au						
	Sum						
60	Cu						
	Au						
	Sum						
80	Cu						
	Au						
	Sum						

## *Si-Ir alloy*

In the CuAu alloy example, the goal was to determine the composition of the alloys relative to the pure element standards that were used. The variation in calculated composition of the alloys was only a function of the correction algorithm chosen. How does one determine the accuracy of analysis in the CuAu binary? For that example we have the known compositions that were determined using wet chemistry. There are no intermetallic compositions in the CuAu binary that one could use as a standard to improve on the accuracy of analyses within the binary. The SiIr alloy example shows how critical it is to have such a material that can be used as a primary standard.

The silicides of transition metals such as Ir and Pt form a series of refractory compounds ranging in chemical bonding from covalent to metallic. Some of these compounds are of particular interest for microelectronic and thermoelectric applications. The phase diagrams for a number of these systems are quite complex and have not been fully determined. For example, at least nine different silicide phases have been reported by different investigators for the Ir-Si system, but the phase diagram for this system is not fully known. The grain sizes of a number of these phases in synthetic samples are too small to be isolated for bulk analysis, but are of adequate size for quantitative electron microbeam analysis.

In a study of silicon-rich iridium silicide compounds reported by Allevato et al. (*J. Alloys and Compounds* 200, 99-105, 1993) a series of alloy samples synthesized at the Jet Propulsion Laboratory were analyzed at the Caltech electron microprobe laboratory using the CITZAF correction program. Possible phases to be identified included IrSi, Ir<sub>4</sub>Si<sub>5</sub>, Ir<sub>3</sub>Si<sub>4</sub>, Ir<sub>2</sub>Si<sub>3</sub>, Ir<sub>3</sub>Si<sub>5</sub>, Ir<sub>4</sub>Si<sub>7</sub>, IrSi<sub>2</sub>, and IrSi<sub>3</sub>. Clear identification of these phases from each other and from phase intergrowths requires quantitative analyses of an accuracy approaching 1% relative.

In one particular sample in this study, the analyst needed to identify whether a individual 'crystal' in a polished section of an experimental run product was IrSi (50:50 atom %, 87.25 wt. % Ir, 12.75 wt. % Si), or Ir<sub>4</sub>Si<sub>5</sub> (44.4:55.6 atom %, 84.55 wt. % Ir, 15.45 wt. % Si). Quantitative electron microprobe analysis was performed using wavelength dispersive spectrometers. Data was collected having a measurement relative precision of better than 0.3%. The only standards available were pure Si and Ir metals. K-ratios were determined relative to these standards. The Si K $\alpha$  and Ir L $\alpha$  lines were measured. (Ir L was chosen in preference to Ir M in order to minimize the absorption correction for Ir and because, in general L-line matrix corrections have less uncertainty than M-line corrections.)

An accelerating potential of 20 keV was chosen (in order to have an adequate overvoltage for the Ir L line without having too great an overvoltage for the Si K line). The instrument had a spectrometer take-off angle of 40°. (Paul Carpenter performed the analyses while at Caltech) Typical measured k-ratios were: 0.7892 for Ir and 0.1179 for Si. Correction procedures employed were the Armstrong CITZAF correction [no doubt,

in part due to the fact that it was Armstrong's laboratory] and the 1966 Heinrich mass absorption coefficients. Now we have all the information we need to duplicate their results and see which answer they got.

For this CalcZAF example we need to set up standards for the analysis of Si and Ir in the alloy. Use the Standard.exe program to create three standards, pure Si, Pure Ir, and the standard  $\text{Ir}_3\text{Si}_5$  that we will use in the second part of the exercise. We will use the CalcZAF option of calculating a composition from k-rat values relative to the chosen standards. First we need to add the standards that were set up in the standard program to the "run" that we are using to process the Si and Ir data:

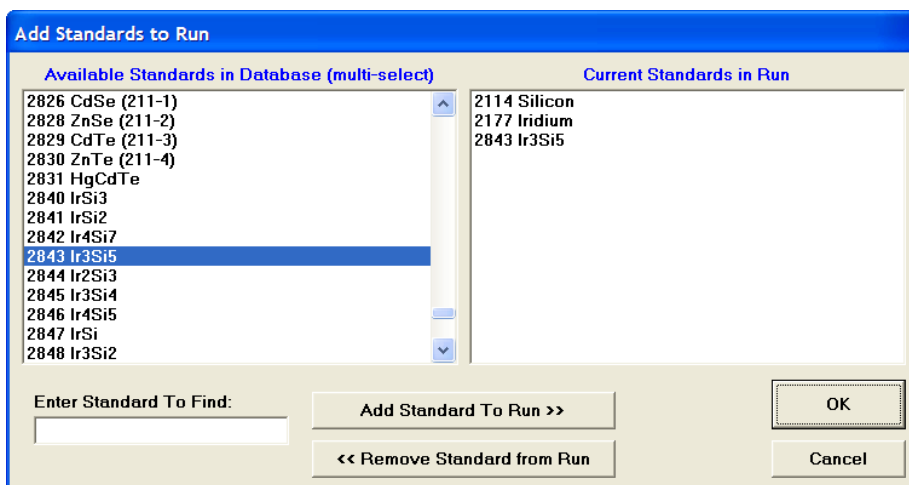


Figure 34 Add Standards to Run Window

Next we set up for analysis of Si and Ir at 20 keV and 40 degrees takeoff using the Analytical -- Operating Conditions menu selection. We are now ready to set up CalcZAF for the calculation of Si  $K\alpha$  and Ir  $L\alpha$  data. Note that we have set up Ir  $L\alpha$  with the k-ratio relative to Ir metal, and we have selected the standard for Ir from the menu at the lower left of the window (these are the standards that we added to the run):

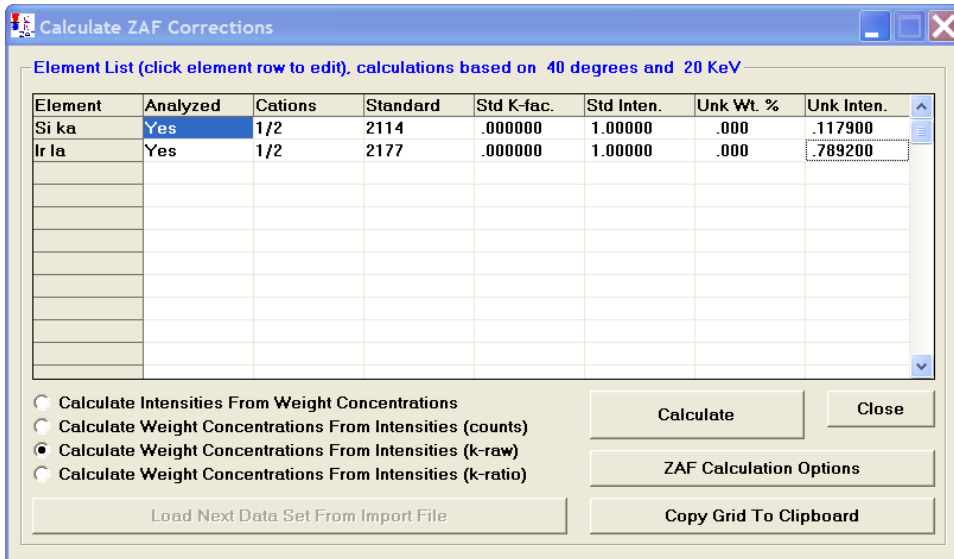


Figure 35 Setup for SiIr

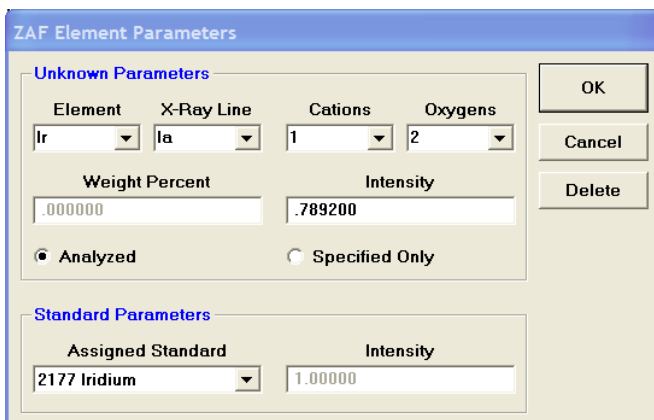


Figure 36 Entry of k-ratio for Ir

We can now calculate the corrected data using the Calculate button. The results are:

```

Correction Method:
ZAF or Phi-Rho-Z calculations
LINEMU  Henke (1985) < 10KeV / CITZMU > 10KeV

Current ZAF or Phi-Rho-Z Selection:
Armstrong/Love Scott (default)

Correction Selections:
Phi(pz) Absorption of Armstrong/Packwood-Brown 1981 MAS
Stopping Power of Love-Scott
Backscatter Coefficient of Love-Scott
Backscatter of Love-Scott
Mean Ionization of Berger-Seltzer
Phi(pz) Equation of Love-Scott
Reed/JTA w/ M-Line Correction and JTA Intensity Mod.

Calculating All Standard K-factors...
Standard 2114 Silicon
  
```

CalcZAF Sample at 40 degrees and 20 keV

SAMPLE: 0, ITERATIONS: 3

ELEMENT	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	KILOVOL
Si ka	.11790	14.360	-----	53.810	20.0
Ir la	.78920	84.354	-----	46.190	20.0
TOTAL:		98.714	-----	100.000	

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F (CHI)
Si ka	1.5832	.9894	.7776	1.2180	.5787	1.3437	.5371
Ir la	.9910	1.0000	1.0786	1.0689	1.1228	.9606	.9545

The total is not impressive. This result is obtained using the Armstrong  $\Phi(\rho z)$  and Henke mac data set. If we select the CITZMU mac data set (Heinrich 1966 macs), using the Analytical – ZAF Selections menu, followed by MACs button, we can select the CITZMU option:

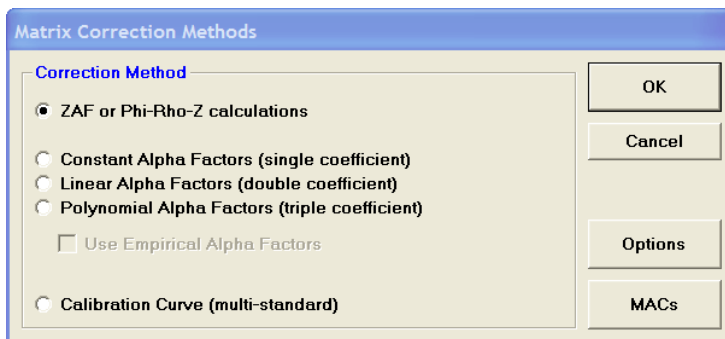


Figure 37 Matrix Correction Selection Window

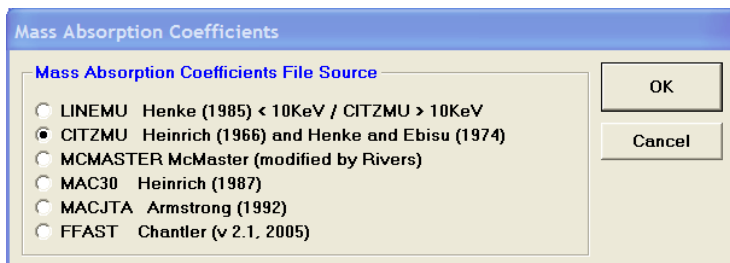


Figure 38 Mass Absorption Coefficient Selection

After doing so, rerun the analysis using the Calculate button, and you will get the following results:

```
Correction Method:
ZAF or Phi-Rho-Z calculations
CITZMU Heinrich (1966) and Henke and Ebisu (1974)

Current ZAF or Phi-Rho-Z Selection:
Armstrong/Love Scott (default)
```

```

Correction Selections:
Phi(pz) Absorption of Armstrong/Packwood-Brown 1981 MAS
Stopping Power of Love-Scott
Backscatter Coefficient of Love-Scott
Backscatter of Love-Scott
Mean Ionization of Berger-Seltzer
Phi(pz) Equation of Love-Scott
Reed/JTA w/ M-Line Correction and JTA Intensity Mod.

```

```

Calculating All Standard K-factors...
Standard 2114 Silicon
Standard 2177 Iridium
Standard 2843 Ir3Si5
Standard K-factors Calculated

```

CalcZAF Sample at 40 degrees and 20 keV

SAMPLE: 0, ITERATIONS: 4

ELEMENT	K-VALUE	ELEMWT%	OXIDWT%	ATOMIC%	KILOVOL
Si ka	.11790	15.325	-----	55.332	20.0
Ir la	.78920	84.662	-----	44.668	20.0
TOTAL:		99.987	-----	100.000	

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F(CHI)
Si ka	1.6848	.9899	.7794	1.2998	.5824	1.3382	.5098
Ir la	.9906	1.0000	1.0829	1.0728	1.1296	.9587	.9548

The analysis results look good. The composition agrees well within 1% relative of that for Ir<sub>4</sub>Si<sub>5</sub>. But is the calculated composition correct? Now change the correction procedure to the conventional ZAF correction of Philibert/Duncumb-Reed. Next choose the 1966 Heinrich mass absorption corrections. Compare with the previous results. Next try the other corrections in the same fashion (using the Heinrich 1966 mass absorption coefficients) and write the results down. Finally, use one of the corrections with the Heinrich 1986 mass absorption coefficients and copy the results.

What is your conclusion? Can you distinguish between IrSi and Ir<sub>4</sub>Si<sub>5</sub> with the uncertainty shown by variations using the different correction procedures?

Compositions of the possible phases analyzed are:

Compound	Ir wt. %	Si wt. %	Total	Ir (atom)	Si (atom)
IrSi	<b>87.25</b>	<b>12.75</b>	<b>100.00</b>	<b>0.500</b>	<b>0.500</b>
Ir <sub>4</sub> Si <sub>5</sub>	<b>84.55</b>	<b>15.45</b>	<b>100.00</b>	<b>0.444</b>	<b>0.556</b>

Here are the results using CalcZAF and the various correction algorithms and mac data sets:

Correction #	MAC	Ir wt. %	Si wt. %	Total	Ir (atom)	Si (atom)
Arm Φ(pz)	<b>H66</b>	<b>84.66</b>	<b>15.48</b>	<b>100.14</b>	<b>0.444</b>	<b>0.556</b>
PDR ZAF	<b>H66</b>	<b>86.95</b>	<b>12.56</b>	<b>99.50</b>	<b>0.503</b>	<b>0.497</b>

<b>Heinrich</b>	<b>H66</b>	<b>84.98</b>	<b>13.74</b>	<b>98.72</b>	<b>0.525</b>	<b>0.475</b>
<b>LS I</b>	<b>H66</b>	<b>84.47</b>	<b>13.68</b>	<b>98.15</b>	<b>0.474</b>	<b>0.526</b>
<b>LS II</b>	<b>H66</b>					
<b>PackBrwn</b>	<b>H66</b>	<b>84.37</b>	<b>11.92</b>	<b>96.28</b>	<b>0.509</b>	<b>0.491</b>
<b>Bastin Phi</b>	<b>H66</b>	<b>86.27</b>	<b>15.02</b>	<b>101.29</b>	<b>0.456</b>	<b>0.543</b>
<b>Proza</b>	<b>H66</b>	<b>84.32</b>	<b>14.64</b>	<b>98.96</b>	<b>0.457</b>	<b>0.543</b>
<b>PAP</b>	<b>H66</b>	<b>84.70</b>	<b>13.74</b>	<b>98.44</b>	<b>0.474</b>	<b>0.526</b>
<b>XPP</b>	<b>H66</b>	<b>84.44</b>	<b>13.51</b>	<b>97.95</b>	<b>0.477</b>	<b>0.523</b>
<b>Arm <math>\Phi(\rho z)</math></b>	<b>FFAST</b>	<b>84.08</b>	<b>13.32</b>	<b>97.40</b>	<b>0.480</b>	<b>0.520</b>
<b>PAP</b>	<b>FFAST</b>	<b>84.09</b>	<b>12.00</b>	<b>96.08</b>	<b>0.506</b>	<b>0.494</b>

Inspecting these corrected results, there are analyses with good and bad totals, and analyses that seem to point to either SiIr composition, but no clear agreement.

To sort out the uncertainty in the Ir-Si alloy analyses, depending on what correction procedure was used, we substituted an intermetallic compound in the system that was closer in composition to the unknown. The compound chosen was Ir<sub>3</sub>Si<sub>5</sub> (80.41 wt. % Ir, 19.59 wt. % Si). It was used as a standard for both Ir and Si. Typical k-values (relative to the compound standard) of 1.0720 for Ir L and 0.7792 for Si K were measured under identical analytical conditions as were used for the pure element standards.

In CalcZAF, change the standard used for both Si and Ir from pure elements to Ir<sub>3</sub>Si<sub>5</sub> and enter the k-rw values that were measured. The results are shown here for the Armstrong  $\Phi(\rho z)$  and Heinrich 1966 mac's:

```

Correction Method:
ZAF or Phi-Rho-Z calculations
CITZMU Heinrich (1966) and Henke and Ebisu (1974)

Current ZAF or Phi-Rho-Z Selection:
Armstrong/Love Scott (default)

Correction Selections:
Phi(pz) Absorption of Armstrong/Packwood-Brown 1981 MAS
Stopping Power of Love-Scott
Backscatter Coefficient of Love-Scott
Backscatter of Love-Scott
Mean Ionization of Berger-Seltzer
Phi(pz) Equation of Love-Scott
Reed/JTA w/ M-Line Correction and JTA Intensity Mod.

Calculating All Standard K-factors...
Standard 2114 Silicon
Standard 2177 Iridium
Standard 2843 Ir3Si5
Standard K-factors Calculated

CalcZAF Sample at 40 degrees and 20 keV

ELEMENT K-VALUE ELEMWT% OXIDWT% ATOMIC% KILOVOL
Si ka .11905 15.468 ----- 55.573 20.0
Ir la .78839 84.623 ----- 44.427 20.0
TOTAL: 100.091 ----- 100.000

```

ELEMENT	ABSCOR	FLUCOR	ZEDCOR	ZAFCOR	STP-POW	BKS-COR	F (CHI)
Si ka	1.6835	.9899	.7797	1.2993	.5830	1.3373	.5102
Ir la	.9906	1.0000	1.0836	1.0734	1.1307	.9584	.9549

Correction #	MAC	Ir wt. %	Si wt. %	Total	Ir (atom)	Si (atom)
Arm $\Phi(\rho z)$	H66	84.62	15.47	100.09	0.444	0.556
PDR ZAF	H66	83.75	15.09	98.85	0.448	0.552
Frame	H66	84.45	15.21	99.66	0.448	0.552
LS I	H66	84.52	15.36	99.88	0.446	0.554
LS II	H66					
PackBrwn	H66	84.38	15.33	99.71	0.446	0.554
Bastin Phi	H66	84.76	15.32	100.08	0.447	0.553
Proza	H66	84.34	15.40	99.73	0.444	0.555
PAP	H66	84.35	15.32	99.68	0.446	0.554
XPP	H66	84.39	15.31	99.70	0.446	0.554
Arm $\Phi(\rho z)$	FFAST	84.58	15.37	99.95	0.446	0.554
PAP	FFAST	84.31	15.23	99.54	0.447	0.553

The result of using a standard closer to the sample in composition is dramatic in the SiIr binary system: the concentrations of Ir and Si, the analytical total, and the atomic proportions all demonstrate a significant improvement in agreement compared to using the pure element standards. These results clearly indicate that the sample is Ir<sub>4</sub>Si<sub>5</sub>. Failure to use the appropriate standard, or lack of availability thereof, would result in an erroneous assignment of the phase chemistry. This is an excellent example of the importance of appropriate standards and the shortcomings of correction algorithms and mass absorption coefficient data sets.

### *Compositional Systems Representing Key Analytical Issues*

It is helpful to illustrate the nature of analytical problems in compositional systems that highlight key components of the ZAF correction and a discussion of problems and potential solutions.

#### *Absorption Correction – C K $\alpha$ in SiC*

The dominant correction for all materials analyzed by electron beam methods is the absorption correction, i.e., the correction for absorption of x-rays by all elements in the sample. X-rays are generated in the scattering volume by electrons and also by secondary x-ray fluorescence, and all x-rays are attenuated along the path to the detector; we measure the emitted x-ray intensity but must know the generated intensity as a part of the ZAF correction. The x-rays of light elements (Be, B, C, N, O, F) and of low energy L and M-family x-rays have large mass absorption coefficients and are absorbed to a greater degree in the sample. The analysis of C K $\alpha$  in SiC is an excellent example. Using



CalcZAF to calculate the expected k-ratio of C K $\alpha$  and Si K $\alpha$  in SiC relative to pure C and Si standards at 15 keV and 40 degree takeoff angle, and using the default Armstrong  $\Phi(\rho z)$  with Henke mac's, we get the following (edited) output:

```

Takeoff = 40, Kilovolts = 15

Current Mass Absorption Coefficients From:
LINEMU Henke (1985) < 10KeV / CITZMU > 10KeV

  Z-LINE  X-RAY  Z-ABSOR      MAC
  C      ka      C    2.3412e+03
  C      ka      Si   3.6660e+04
  Si     ka      C    4.5462e+02
  Si     ka      Si   3.5048e+02

ELEMENT K-VALUE  ELEMWT%  OXIDWT%  ATOMIC%  KILOVOL
  C ka   .03088  29.950  -----  49.994   15.0
  Si ka  .67722  70.050  -----  50.006   15.0
  TOTAL:          100.000  -----  100.000

ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR  STP-POW  BKS-COR  F(CHI)
  C ka   10.3467  .9999  .9376  9.6997  .9045  1.0366  .0499
  Si ka  1.0099  1.0000  1.0243  1.0344  1.0443  .9808  .8967

```

Inspection of the numbers shows that the mac for C K $\alpha$  by Si is 36,660 (very high) which is an indication that Si is a problem matrix for the analysis of C, and indeed the f(chi) for C K $\alpha$  is 0.05, meaning that only 5% of the generated C K $\alpha$  x-rays are emitted from SiC at 15 keV and 40 degree takeoff. There is a 1000% absorption correction for C K $\alpha$  as a result. In comparison there is essentially no fluorescence or atomic number correction. The C K $\alpha$  line happens to be close to the Si L edge and suffers extreme absorption.

There are two solutions to this problem that analysts should always try to pursue. First, using a SiC primary standard will at least decrease the dependence of the correction algorithm and mac values on using pure element standards; however, this does not reduce the dramatic absorption of C K $\alpha$  x-rays. The second strategy is to use a lower accelerating potential for analysis – this is an option that should always be considered because a reduction in voltage will reduce the absorption path length for emitted x-rays. The down side of using a low accelerating voltage is that x-ray analysis parameters were not measured at low keV and their use is uncertain. If we run the same example in CalcZAF by changing the analytical conditions to 5 keV, the results are as follows:

```

ELEMENT K-VALUE  ELEMWT%  OXIDWT%  ATOMIC%  KILOVOL
  C ka   .13088  29.950  -----  49.994   5.0
  Si ka  .67376  70.050  -----  50.006   5.0
  TOTAL:          100.000  -----  100.000

ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR  STP-POW  BKS-COR  F(CHI)
  C ka   2.4846  1.0000  .9210  2.2883  .8841  1.0417  .3577
  Si ka  1.0012  1.0000  1.0384  1.0397  1.0526  .9865  .9853

```

A factor of 3 reduction in accelerating voltage results in a factor of 4 reduction in the absorption correction, and coupled with the use of a SiC primary standard is an excellent approach to the analytical problem. Another strategy is to measure Si and calculate C by stoichiometry.

### ***Fluorescence Correction – Fe K $\alpha$ and Ni K $\alpha$ in FeNi Alloys***

The fluorescence correction is most important for the case of a K line with an energy just above the edge energy of a K line. Fluorescence depends on the ionization cross-section for excitation of the line of interest, as well as the fluorescent yield which determines the probability of emission of a photon. This process is most important for K by K fluorescence, and less so for L by L and M by M fluorescence. Practically speaking this restricts us to the first row transition elements, and elements found in steel alloys are the most well known examples. An example system is the FeNi binary, where Ni K $\alpha$  x-rays with an energy of 7.47 keV can efficiently excite Fe K $\alpha$  x-rays where the excitation energy of Fe K $\alpha$  is 7.11 keV. In general, candidates for x-ray fluorescence can be identified by comparison of the line energy of the exciting element with the edge energy of the excited element. Ni K $\alpha$  x-rays generated by beam electrons are then partly absorbed by Fe atoms in the sample, reducing the emitted intensity of Ni K $\alpha$ , and increasing the emitted intensity of Fe K $\alpha$  due to fluorescence. The most important compositions are Ni-rich alloys, since Fe atoms would be surrounded by Ni atoms and efficient fluorescence would be expected. Using the CalcZAF program to calculate the expected k-ratios relative to pure Fe and Ni standards, for an alloy with 10 wt% Fe and 90 wt% Ni at 15 keV and 40 degrees, the (edited) results are:

```

Takeoff = 40, Kilovolts = 15
WARNING in ZAFFLU- the ka line of Fe is excited by the ka line of Ni

Current Mass Absorption Coefficients From:
LINEMU  Henke (1985) < 10KeV / CITZMU > 10KeV

  Z-LINE  X-RAY  Z-ABSOR      MAC
  Fe      ka      Fe      6.8270e+01
  Fe      ka      Ni      8.9300e+01
  Ni      ka      Fe      3.6228e+02
  Ni      ka      Ni      5.7825e+01

ELEMENT  K-VALUE  ELEMWT%  OXIDWT%  ATOMIC%  KILOVOL
Fe ka    .12615   10.000   -----  10.459   15.0
Ni ka    .89563   90.000   -----  89.541   15.0
TOTAL:           100.000   -----  100.000

ELEMENT  ABSCOR  FLUCOR  ZEDCOR  ZAFCOR  STP-POW  BKS-COR  F(CHI)
Fe ka    1.0039  .7792  1.0134  .7927  1.0055  1.0078  .9808
Ni ka    1.0063  1.0000  .9986  1.0049  .9994  .9993  .9821

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Inspection of the ZAF factors for this FeNi alloys shows that the absorption and atomic number corrections are not significant, as both x-ray lines are energetic, the mass absorption coefficients are relatively small, and the electron scattering is similar due to

the similarity in atomic number of Fe and Ni. The fluorescence correction (FLUCOR) for Fe shows a 22% fluorescence contribution from Ni  $K\alpha$  x-rays; Ni does not show a correction since there are no characteristic x-rays with energy higher than the edge energy for Ni. There is a small absorption correction for Ni since Fe atoms are absorbing the Ni  $K\alpha$  x-rays.

What can be done to minimize the dependence on the fluorescence correction? Again, the use of a primary standard will result in fluorescence occurring in both the standard and the sample. A change in accelerating voltage does not help, as that affects the absorption correction. In general, the fluorescence correction is important in materials such as steels, and the use of well characterized steel reference standards is important for accurate microanalysis.

Here we emphasize that this correction treats fluorescence by characteristic x-rays, and the ZAF and  $\Phi(\rho z)$  algorithms do not generally treat fluorescence by continuum x-rays. Continuum fluorescence is important for energetic x-ray lines generated in a low Z matrix. An example is Cu  $K\alpha$  in a C matrix, or Zn  $K\alpha$  in ZnO. Fluorescence corrections always result in a decrease in corrected x-ray intensity.

### ***Atomic Number Correction – Cu $K\alpha$ in CuAu and Si $K\alpha$ in IrSi***

The atomic number correction Z corrects for the difference in electron retardation and backscattering between the sample and standard. The CuAu and IrSi examples both illustrate the importance of the Z correction, and in general, any system where a large difference in Z between the standard and sample will have a large correction for atomic number effects. Referring back to the CuAu data, the Z factor for Cu is 0.96 (Stopping power factor S 0.93 and backscatter factor R 1.03), and the Z factor for Au is 1.26 (stopping power S 1.39 and backscatter R 0.91). For the IrSi data, the Z factor for Si is 0.78 (stopping power S 0.58 and backscatter R 1.34) and the Z factor for Ir is 1.08 (stopping power S 1.13 and backscatter R 0.96). In these examples, the correction for Cu and Si is to reduce the intensity due to increased x-ray production in a higher-Z matrix with Au and Ir, respectively. The Cu and Si atoms experience a greater number of ionizations due to the backscattering from Au and Ir. Conversely, the Au and Ir atoms experience a lower ionization due to the presence of Cu and Si atoms, respectively, that do not have a high backscatter coefficient.

There is no change in analytical conditions that can be used to reduce the atomic number correction. Selection of a standard closer in composition and atomic number to the sample will result in both standard and sample having the same electron scattering characteristics. This was dramatically illustrated by using  $Ir_3Si_5$  in the IrSi system. For the CuAu system there is no stoichiometric intermetallic that has a defined composition.