CalcZAF X-ray Analysis Program: ZAF and Φ(ρz) 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 Φ(ρz) 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:

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 Kα and the Au Lα 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
Cu20-Au80	Cu Kα	19.83	0.2462
	Au Lα	80.15	0.7525
Cu40-Au60	Cu Kα	39.64	0.4634
	Au Lα	60.36	0.5286
Cu60-Au40	Cu Kα	59.92	0.6622
	Au Lα	40.10	0.3323
Cu80-Au20	Cu Kα	79.85	0.8401
	Au Lα	20.12	0.1570

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:

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 Cu20-Au80 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 Kα analytical line, and the k-ratio of 0.2464; the element is analyzed relative to a pure element standard:

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

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 Cu20Au80 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:

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

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 Kα 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 Kα 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 Kα and Au Lα, is not significant. The use of Cu Lα 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 Lα line can fluoresce Cu Kα, resulting in a higher emitted intensity of Cu Kα 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 Kα intensity is due to fluorescence by Au Lα. 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 Kα exciting Fe Kα) 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 Kα by Au Lα since that line is generated at 20 keV. There is no fluorescence correction for Au Lα since there are no x-ray lines with sufficient energy to generate Au Lα 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 Lα 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 stochiometry
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 Φ(ρz) Correction			0(CITZAF) 0(Hein. 66)	0(CITZAF) 2(Hein. 86)	1(Orig.ZAF) 2(H86)	2(Frame) 2(H86)	3(LS-I) 2(H86)
Mass Absorption Coefficient							
Alloy	**Element**	**NIST Certified**					
20	Cu	**19.83**	19.93				
	Au	**80.15**	80.29				
	Sum	**99.98**	100.22				
40	Cu	**39.64**	39.57				
	Au	**60.36**	60.10				
	Sum	**100.00**	99.68				
60	Cu	**59.92**	59.67				
	Au	**40.10**	40.13				
	Sum	**100.02**	99.80				
80	Cu	**79.85**	79.77				
	Au	**20.12**	20.10				
	Sum	**99.97**	99.87				
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) 2(H86)
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 $\underline{200}$, 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_4Si_5, Ir_3Si_4, Ir_2Si_3, Ir_3Si_5, Ir_4Si_7, $IrSi_2$, and $IrSi_3$. 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_4Si_5 (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 Ir₃Si₅ that we will use in the second part of the exercise. We will use the CalcZAF option of calculating a composition from k-raw 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:
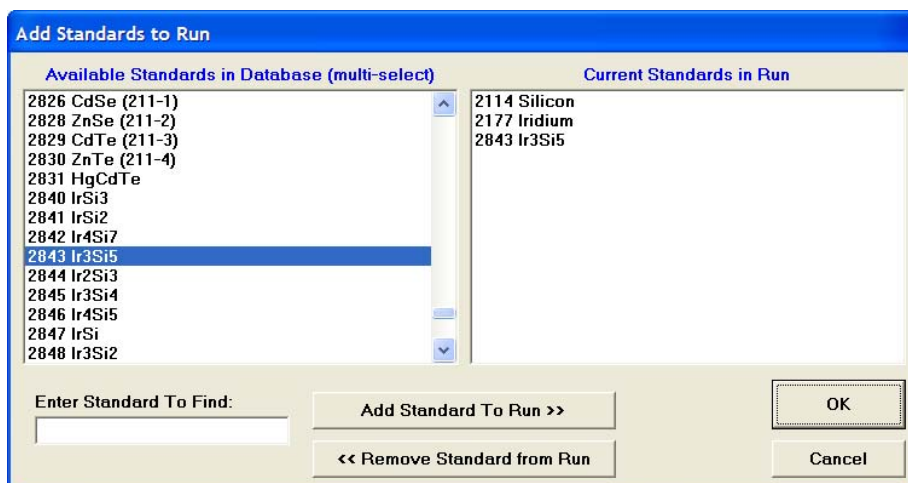
Next we set up for analysis of Si and Ir at 20 keV and 40 degrees takeoff using the Analytical -- Operating Conditions menu selection. We are now ready to set up CalcZAF for the calculation of Si Kα and Ir Lα data. Note that we have set up Ir Lα with the k-ratio relative to Ir metal, and we have selected the standard for Ir from the menu at the lower left of the window (these are the standards that we added to the run):
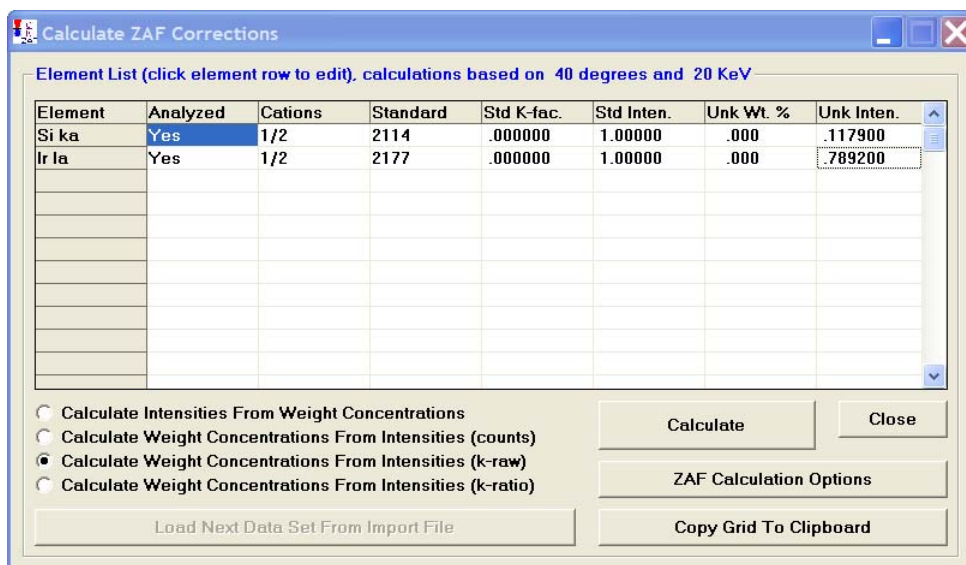
We can now calculate the corrected data using the Calculate button. The results are:

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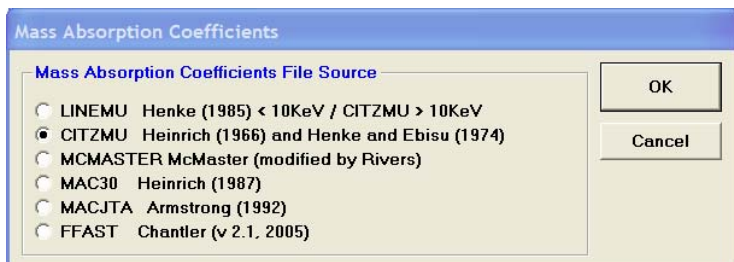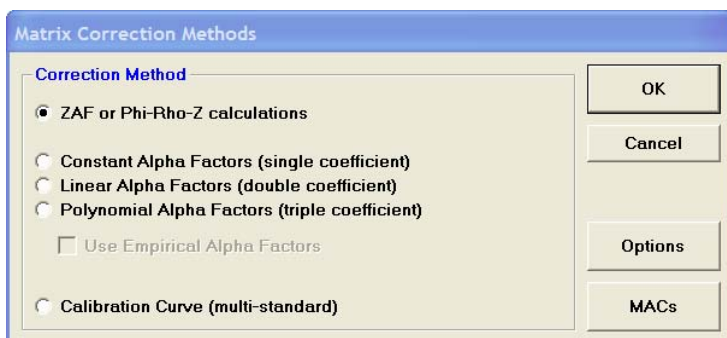
The total is not impressive. This result is obtained using the Armstrong Φ(ρz) and Henke mac data set. If we select the CITZMU mac data set (Heinrich 1966 macs), using the Analytical – ZAF Selections menu, followed by MACs button, we can select the CITZMU option:

163

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)
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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
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The analysis results look good. The composition agrees well within 1% relative of that for Ir4Si5. 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 Ir4Si5 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	87.25	12.75	100.00	0.500	0.500
Ir4Si5	84.55	15.45	100.00	0.444	0.556

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(ρz)	H66	84.66	15.48	100.14	0.444	0.556
PDR ZAF	H66	86.95	12.56	99.50	0.503	0.497
Heinrich	H66	84.98	13.74	98.72	0.525	0.475
LS I	H66	84.47	13.68	98.15	0.474	0.526
LS II	H66					
PackBrwn	H66	84.37	11.92	96.28	0.509	0.491
Bastin Phi	H66	86.27	15.02	101.29	0.456	0.543
Proza	H66	84.32	14.64	98.96	0.457	0.543
PAP	H66	84.70	13.74	98.44	0.474	0.526
XPP	H66	84.44	13.51	97.95	0.477	0.523
Arm Φ(ρz)	FFAST	84.08	13.32	97.40	0.480	0.520
PAP	FFAST	84.09	12.00	96.08	0.506	0.494

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 Ir3Si5 (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_3Si_5 and enter the k-raw values that were measured. The results are shown here for the Armstrong $\Phi(\rho z)$ and Heinrich 1966 mac's:

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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...
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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_4Si_5. 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 Kα 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 Kα in SiC is an excellent example. Using CalcZAF to calculate the expected k-ratio of C Kα and Si Kα 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 Kα 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 Kα is 0.05, meaning that only 5% of the generated C Kα x-rays are emitted from SiC at 15 keV and 40 degree takeoff. There is a 1000% absorption correction for C Kα as a result. In comparison there is essentially no fluorescence or atomic number correction. The C Kα 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 Kα 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 Kα and Ni Kα 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 Kα x-rays with an energy of 7.47 keV can efficiently excite Fe Kα x-rays where the excitation energy of Fe Kα 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 Kα x-rays generated by beam electrons are then partly absorbed by Fe atoms in the sample, reducing the emitted intensity of Ni Kα, and increasing the emitted intensity of Fe Kα 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
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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
```

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 Kα 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 Kα 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 Φ(ρz) 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 Kα in a C matrix, or Zn Kα in ZnO. Fluorescence corrections always result in a decrease in corrected x-ray intensity.

Atomic Number Correction – Cu Kα in CuAu and Si Kα 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.