## GMR Film Correction Program

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This document briefly explains how to use the GMR Film software to perform correction of stratified samples which have a structure that warrants use of thin film correction procedures.

This software is based on the original Fortran source code written by Richard Waldo at General Motors. The original paper is from the proceedings of the Microbeam Analysis conference:  
“An iteration procedure to calculate film compositions and thicknesses in electron-probe microanalysis”,  R. A. Waldo, Microbeam Analysis 1988, D. E. Newbury, ed., [MAS annual proceedings], p. 310-314.

A second paper covers the characteristic fluorescence correction in thin-film analysis:

“A Characteristic X-ray Fluorescence Correction for Thin-Film Analysis by Electron Microprobe”, R.A. Waldo, Microbeam Analysis 1991, D.G. Howitt Ed., 45-53.

### Thin film correction using the GMR Film program

The GMR Film software is a set of Fortran source code files that have been compiled using the gfortran compiler distributed with the Cygwin environment. The GMR.exe executable requires several Cygwin dll’s in order to run as a windows console application. These dll’s have been included with the GMR.exe executable program. There are also several text files that are required in order to run GMR Film, these are help files that provide information at stages in the program data input, and the standard.dat file which contains standard compositions that can be recalled once entered by the user.

All of these files need to be in the same directory. When GMR.exe is run, it will produce a text file with a name that is encoded with a time stamp. You can use a text editor to read and copy the data from this file.

The current version of the GMR.exe executable runs on 64-bit Window operating systems whereas the older executables do not.

The original Fortran source contained minor bugs related to array dimensioning available using the Intel Fortran compiler. There is a residual problem observed for processing of compositional data for bulk samples when atomic proportions are used (the program is put into an infinite loop which requires ctrl-C to exit). Also note that the calculated values are in some cases different from those obtained with the older version of GMR Film, and this may be due to testing in the mass absorption coefficient routine.

I am providing this version so that attendees of EPMA 2016 have an alternative to commercial thin film software.

### Thin Film Exercise 1 –Ni-Cr film on Fe-Gd-Pt layer on a Si metal substrate

Pouchou (1993) reported microprobe data from the analysis of a layered specimen composed of a Ni-Cr film over a Fe-Gd-Pt layer over a Si metal substrate. They analyzed the sample using Kα lines for Ni, Cr and Fe; Lα line for Gd; and Mα line for Pt. Analyses were performed at three different accelerating potentials—30, 25 and 20 keV—on an instrument with a spectrometer take-off angle of 40°. The NiCr film was estimated to have a density of 7.41 g/cm3; the Fe-Gd-Pt layer was estimated to have a density of 10.6 g/cm3. K-ratios were measured for each element relative to its pure element standards. The published raw data are reported below. (The author also made RBS measurements and processed his data through a commercial thin film correction program, STRATA, based on his thin film correction method.)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Eo | Layer 1 | | Layer 2 | | |
| k-Ni K | K Cr K | k Fe K | k Gd L | k Pt M |
| 30 | 0.0054 | 0.0299 | 0.0098 | 0.0052 | 0.0048 |
| 25 | 0.0084 | 0.0443 | 0.0147 | 0.0076 | 0.0058 |
| 20 | 0.0151 | 0.0744 | 0.0258 | 0.0123 | 0.0083 |

We now have all the data we need to process this analysis through the GMRFilm program and get a calculated estimate of both the film compositions and thicknesses. Start the GMR.exe program and you should get a console screen with the following output:

Type (H)elp for information on the program, otherwise hit Enter key: **🡨 [enter]**

(NOTE: The input for this program is almost ‘self explanatory’. The program instructions scroll on the screen as the program executes. Therefore, where possible in this section, brief comments will appear in bold italic type to the right of the screen display listing and the data you are inputting will appear in bold type after a bold left arrow ( “ **🡨** “) to the right of where you are asked to input data.)

Results are automatically saved to asci file “<filename depends on time code on your computer>”

Print primary and secondary x-ray intensity data (def=N)? **🡨 [enter]**

This is a film (F) or bulk (B) analysis (def.=F)?

**🡨 [enter] *(this is a multi-layer film)***

Include continuum fluorescence correction?

Note: Not recommended for Bastin Scanning ’86 (B)

or Packwood (P) phi(z) models (def.=Y)?

**🡨 y [enter] *(when high energy lines in a high-Z***

***film on a low-Z substrate are used,***

***answer ‘y’, then reprocess with ‘n’)***

To calculate k-ratios enter 'K' or 'k';

To calculate compositions enter 'C' or 'c' (def=C): **🡨[enter]**

Observe or change mass absorption coefficients (n)? **🡨 [enter]**

Note that we answered ‘y’ in this case for calculating a continuum fluorescence correction. When you are measuring high energy x-ray lines (> 5 keV) in a thin layer phase that has a high average atomic number, resting on a substrate that has a low average atomic number, the increased contribution of x-rays produced by the x-ray background continuum to the total x-ray emission may be significant. In such a case you should process the data with and without a continuum fluorescence correction and note the difference in results. (Because there are large uncertainties in the continuum correction, one should not just use it without comparison.) As you will see, it is very easy to reprocess the same data with and without this correction. Also note that we took option ‘C’ instead of ‘k’.

Next we are ready to start inputting analytical conditions and choose the correction procedure we wish to use, as is seen below.

Enter take-off angle (default=40 degrees) :

**🡨 [enter] *(Pouchou used 40°)***

Choices of phi(rz) models are :

Bastin's Scanning (1986) (b)

" Scanning (1990) (c)

***(Note: Default PAP is a very commonly used correction.***

Pouchou, Pichoir (PAP) Scanning (1990 (e)

or Packwood's MAS (1986) (p)

Choose (default=e): **🡨 [enter]** ***(PAP chosen)***

Is this a one condition (voltage) analysis (y)? **🡨 [enter]**

Enter beam voltage (Eo) in kV (def.=15):

**🡨 30 [enter] *(Let’s start out with that data.)***

Now we are ready to start inputting data about the nature of our samples.

Number of layers (count substrate as 1) :

**🡨 3 [enter] *(Ni-Cr, Fe-Gd-Pt, Si substrate)***

Number of elements in layer 1 : **🡨 2 [enter] *(Ni and Cr)***

Number of elements in layer 2 : **🡨 3 [enter] *(Fe, Gd and Pt)***

Number of elements in the substrate : **🡨 1 [enter] *(Si metal substrate)***

Now we’re ready to enter data on the elements we are analyzing and the input gets a bit more complicated. First you see the dialog.

Enter elements, x-ray lines, options. (e.g. FeKa,c)

Type He(lp) for detailed instructions; otherwise hit Enter key.

**🡨 he [enter]**

***(normally, you would just hit [enter]***

***however, we want to see the instructions on how to enter the data…)***

You then see on the screen the following set of instructions.

----------------------------------------------------------------------

Enter all element and x-ray data in format ELXRn,s.

Analytical lines supported: Ka, Kb, La, Lb, Lb2, Lb3, Lb4, Lg1, Lg2,

Lg3, Ma, Mb, Mg. La and Lb can also be input as La1 and Lb1.

Examples: CuKb b ka ,c NDLA ,d PtLb3,n

(An element determined by stoichiometry should be the last one entered

for the particular layer if this is a film (non-bulk) system.)

-----Switches:s,c,d,m,n------

s is an optional switch: s=s : This element determined by stoichiometry.

s=c : " " analyzed with a compound std.

Bulk analysis only ---> s=d : " " analyzed by difference.

If an element is present in more than one layer you may want to

calculate its composition in one of the layers from the total

experimental k-ratio for the element.

For this option use switch s=m or n: (s=m --> pure element standard

s=n --> compound standard).

Type he(lp) now for more information on this option.

---------------------------------------------------------------------

Symbol, x-ray for layer 1 element 1 :  ***(Don’t do anything yet!)***

You could type: **he [enter]** at this point and get information on how to handle an element that is present in more than one layer of the sample. We will not need that for this laboratory, so you are left to list it out on your own. Instead, we will now enter the information on the analyzed elements (each one relative to a pure element standard). This is shown in the dialog below:

Symbol, x-ray for layer 1 element 1 : **🡨 nika [enter] *(enter data from the informat***

Symbol, x-ray for layer 1 element 2 : **🡨 crka [enter] *information given above)***

Symbol, x-ray for layer 2 element 1 : **🡨 feka [enter]**

Symbol, x-ray for layer 2 element 2 : **🡨 gdla [enter]**

Symbol, x-ray for layer 2 element 3 : **🡨 ptma [enter]**

Symbol, x-ray for substrate element 1 : **🡨 sika [enter]**

Observe or change mass absorption coefficients (n)? **[enter] *(no need to change)***

Layer densities are used solely to convert thicknesses

in ug/cm^2 to Angstroms; they have no effect on the results.

Approximate layer 1 density (gm/cm^3): **🡨 7.41 [enter] *(taken from information above)***

Approximate layer 2 density (gm/cm^3): **🡨 10.6 [enter]**

Fix composition and thickness of layer 1? (n): **🡨 [enter] *(we wish to determine***

Fix composition and thickness of layer 2? (n): **🡨 [enter] *their composition and***

**thickness)**

Fix composition of substrate? (n) : **🡨 y [enter] *(substrate is known to be pure Si)***

Now comes the time to input the k-ratio data and calculate the composition. First, let’s enter the k-ratio data (taken from the table above):

k-ratio for layer 1 element Ni = 0.00000 new value : **🡨 .0054 [enter]**

k-ratio for layer 1 element Cr = 0.00000 new value : **🡨 .0299 [enter]**

k-ratio for layer 2 element Fe = 0.00000 new value : **🡨 .0098 [enter]**

k-ratio for layer 2 element Gd = 0.00000 new value : **🡨 .0052 [enter]**

k-ratio for layer 2 element Pt = 0.00000 new value : **🡨 .0048 [enter]**

As soon as this data is entered, the program goes into its calculation mode and you should see on the screen:

Layer 1 : Ni;Ka , Cr;Ka

Layer 2 : Fe;Ka , Gd;La1, Pt;Ma

Substrate: Si;Ka

" : The composition of the substrate has been fixed.

Composition Thickness K-ratio Fchar Fcont

Weight% Atom% ug/cm\*\*2 Angstrom Cmp.Std Pure El % %

======= ===== ======== ======== ======= ======= ===== =====

layer 1 Ni: 14.32 12.90 51.013 688.4 ------- 0.00540 0.06 -4.07

layer 1 Cr: 85.68 87.10 51.013 688.4 ------- 0.02990 0.51 -1.73

sum : 100.00

layer 2 Fe: 51.14 76.16 25.657 242.1 ------- 0.00980 0.17 -2.70

layer 2 Gd: 29.28 15.49 25.657 242.1 ------- 0.00520 0.10 -3.99

layer 2 Pt: 19.58 8.35 25.657 242.1 ------- 0.00480 0.00 -1.44

sum : 100.00

substrate Si: 100.00 100.00 ------- ------ ------- 0.75073 0.00 0.00

sum : 100.00

See file 'help4.dat' for explanation of 'Fchar' and 'Fcont'.

More k-ratios? (y): ***(Don’t do anything yet!!!!!)***

The output data is also stored in a data file on disk. The output is fairly self-explanatory. The program works by iterating its estimation of the various layer thicknesses until the calculated compositions from the measured k-ratios for each layer sum to 100%. Thus, if you have a missing element, if the layer has been charging, or if the beam current drifted without correction, you will have the corresponding error in the layer thickness (as well as that possibly in the calculated composition). The layer thicknesses are actually calculated in terms of mass thickness (e.g., as shown in the printout, μg/cm2). Therefore, if there is any uncertainty in the density, the more accurate figure to be quoted is the mass thickness, rather than the thickness.

If you had additional samples to measure under the same conditions (and to be corrected under the same conditions), you could just hit **[enter]** at this point and the program will ask for the next set of input k-values. If you type **n [enter]** (as we are about to do), you will be asked if you want to process another system. If you type **y [enter]** (as we are about to do, note the default is ‘no’), then you will first be asked if you want to reprocess the same data by any combination of: removing the continuum fluorescence correction (option ‘r’), including the continuum fluorescence correction (if you hadn’t already used it, option ‘i'), changing the thin film model used (option ‘m’), or changing the accelerating potential (option ‘e’). If you answer “no”, you start over from the beginning with the input data. However, if you answer with one of the option codes, you will see you previously input k-values, which you can just leave alone (e.g., to process the same data through a different combination of corrections) or change (e.g., when processing data with different accelerating potentials).

In our case, let’s first see the effect of not considering continuum fluorescence. Answer the questions as shown below:

More k-ratios? (y): **🡨 n [enter]**

Another system? (n): **🡨 y [enter]**

Change Eo (E), Model (M), and/or Remove Continuum correction (R);

Enter any combination (examples: M rm REM ); otherwise <CR> : **🡨 r [enter]**

k-ratio for layer 1 element Ni = 0.00540 new value : **🡨 [enter]**

k-ratio for layer 1 element Cr = 0.02990 new value : **🡨 [enter]**

k-ratio for layer 2 element Fe = 0.00980 new value : **🡨 [enter]**

k-ratio for layer 2 element Gd = 0.00520 new value : **🡨 [enter]**

k-ratio for layer 2 element Pt = 0.00480 new value : **🡨 [enter]**

Copy the results into the table on the next page. Next let’s include the continuum fluorescence correction, but change the thin film correction to that of Bastin (1986) (option ‘b’).

More k-ratios? (y): **🡨 n [enter]**

Another system? (n): **🡨 y [enter]**

Change Eo (E), Model (M), and/or Include Continuum correction (I);

Enter any combination (examples: M ei IEM ); otherwise <CR> : **🡨 im [enter]**

Choices of phi(rz) models are :

Bastin's Scanning (1986) (b)

" Scanning (1990) (c)

Pouchou, Pichoir (PAP) Scanning (1990 (e)

or Packwood's MAS (1986) (p)

Choose (default=e) : **🡨 b [enter]**

k-ratio for layer 1 element Ni = 0.00540 new value : **🡨 [enter]**

Copy the results into the table on the bottom of this page. Are they much different from the PAP correction? Finally, let’s change the correction back to PAP, the accelerating potential to 25 keV and then 20 keV, and then change the k-factors with the values in the table (Layer 1 and 2 k-ratio data for Cr, Fe, Ni, Gd, and Pt).

More k-ratios? (y): **🡨 n [enter]**

Another system? (n): **🡨 y [enter]**

Change Eo (E), Model (M), and/or Remove Continuum correction (R);

Enter any combination (examples: M rm REM ); otherwise <CR> : **🡨 me [enter]**

Choices of phi(rz) models are :

Bastin's Scanning (1986) (b)

" Scanning (1990) (c)

Pouchou, Pichoir (PAP) Scanning (1990 (e)

or Packwood's MAS (1986) (p)

Choose (default=e) : **🡨 [enter] *(PAP is the default)***

Enter beam voltage (Eo) in kV (def.=15): **🡨 25 [enter]**

k-ratio for layer 1 element Ni = 0.00540 new value : **🡨 .0084 [enter]**

k-ratio for layer 1 element Cr = 0.02990 new value : **🡨 .0443 [enter]**

k-ratio for layer 2 element Fe = 0.00980 new value : **🡨 .0147 [enter]**

k-ratio for layer 2 element Gd = 0.00520 new value : **🡨 .0076 [enter]**

k-ratio for layer 2 element Pt = 0.00480 new value : **🡨 .0058 [enter] *etc. …***

***(repeat for 20 keV data)***

**Thin Film Analysis Results**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Method** | **Layer 1** | | | **Layer 2** | | | |
| **Ni wt%** | **Cr wt%** | **T (Å)** | **Fe wt%** | **Gd wt%** | **Pt wt%** | **T (Å)** |
| RBS meas | 14.4 | 85.6 | 683 | 51.4 | 28.6 | 20.0 | 246 |
| Pouchou (1993)Strata | 14.7 | 85.4 | 671 | 52.0 | 28.7 | 19.3 | 242 |
| GMRF PAP w CF 30KV | 14.3 | 85.7 | 688 | 51.1 | 29.3 | 19.6 | 242 |
| PAP w/o CF 30 KV |  |  |  |  |  |  |  |
| Bastin ’90 w CF 30 KV |  |  |  |  |  |  |  |
| PAP w CF 25 KV |  |  |  |  |  |  |  |
| PAP w CF 20 KV |  |  |  |  |  |  |  |

### Thin Film Exercise 2 – Co-Pt and Mn-Bi thin films on SiO2 substrates

The previous example showed how different estimates of multi-layer sample compositions and thicknesses could be determined by measuring the same sample using different electron beam energies. Another way of getting different estimates is to simultaneously measure different x-ray lines of the same element (e.g., K and L or L and M). Our next exercise is an example of this.

Kyser and Murata measured Mn-Bi thin films on a SiO2 substrate. They measured three different alloy films on an electron microprobe using an accelerating potential of 20 keV and a take-off angle of 52.5°. Bulk, polished, pure element standards were used in determining the k-ratios. The authors determined their thin film thicknesses and compositions using RBS measurements and Monte Carlo calculations. The authors reported the film thickness in μg/cm2, since they did not know the density.

Their published raw data is as follows:

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | k-Mn K | k-Bi M | k-Bi L |
| X115-3 | 0.0226 | 0.0525 | 0.0771 |
| X115-5 | 0.0293 | 0.0220 | 0.0323 |
| X115-7 | 0.0329 | 0.00668 | 0.0099 |

We have all the data we need to process these films through GMR Film. Use the previous example as a template. At least start with the PAP correction procedure and the continuous fluorescence correction used. You have two layers. The SiO2 substrate should be fixed in thickness and composition. (When asked to fix the composition of the substrate, choose atom proportions—1 for Si, 2 for O.) You can use a typical density for the system of 8.6 (Mn is 7.4; Bi is 9.8), but tabulate your thicknesses in μg/cm2 to compare with the authors. You can save yourself some work by listing **3** (not 2) elements in layer 1 – ‘mnka’, ‘bima’, and ‘bila’. Then you can switch off putting a 0 for the k-value of Bi L when you enter a value for Bi M, and vice versa.

Fill the table on the following page with the results of your analyses. How do they compare with the RBS and Monte Carlo results reported by the authors? How do they compare with each other?

**Kyser & Murata (1974) Thin Film Analysis Results**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Sample:** | **X115-3** | | **X115-5** | | **X115-7** | |
| **Method** | **Mn wt%** | **T (g/cm2)** | **Mn wt%** | **T (g/cm2)** | **Mn wt%** | **T (g/cm2)** |
| K&M ’74 RBS | 26.6 | 48.2 | 53.5 | 33.0 | 80.1 | 26.2 |
| K&M Monte Carlo | 25.5 | 53.0 | 51.0 | 38.0 | 80.0 | 29.0 |
| GMR PAP w CF |  |  |  |  |  |  |
| Bi M |  |  |  |  |  |  |
| Bi L |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
| Bi M |  |  |  |  |  |  |
| Bi L |  |  |  |  |  |  |
|  |  |  |  |  |  |  |
| Bi M |  |  |  |  |  |  |
| Bi L |  |  |  |  |  |  |