GMRFILM is a research grade, shareware DOS program for thin film analysis (created by Richard Waldo of General Motors Research Labs [Microprobe Lab]). It can be used to estimate film thicknesses using the experimentally determined K-ratios, or to calculate compositions given known thickness and K-ratios. Thin films are increasingly important in the EPMA lab, e.g. as specific research objects (creating thin film superconductors), AND because many samples have either intentional (conductive) thin films laid down on them (carbon, gold, etc), or accidental ones (e.g. oxide coat).

You run it on an IBM compatible PC, in a DOS window ("console" in Windows).

You have two options: run the software is on the standalone computers in 306/308 (just above Obi-Wan in 306), or download from the class website and run on a PC computer. You should see many files: gmrfilm.abs is a short abstract and readme.1st file has info about the program. Click on **gmrfilm.exe** to run the main program (which will need access to the many files that were created when it all was unzipped). On the new Win7 computer in 306, it will say you cannot run full screen mode; click ignore and continue.

Given conditions: Generally take the defaults, but especially the following:
Film analysis   PAP phi rho z model $E_0 = 15$ kV
40° take off angle   K lines for O, Mg, Si, Ti; L lines for Zr, Hf; M line for Au

-- it will ask for an approximate density for layer. Use what you find in the literature, unless I give you something to use.
-- take defaults, EXCEPT *do* include the continuum fluorescence correction (Yes).
--there are two different ways to run the software: one is to enter K-ratios and get compositions. I prefer however to run it "backwards", to set up a geometry and a test composition, and then CREATE K-ratios which I then compare to actual data, and try to match the data with the simulation. This way I feel I have more control over the process and can see if things "make sense"
--Entering elements: for our examples here we can assume we have pure element standards for all elements, as we are doing a totally theoretical "what if" approach. So we will just enter the element followed by the line: 4 characters, first 2 for element, last 2 for line. For C, O, K, N etc, the second character is a blank space, ok? For using this software in the real world where you need to use real non pure element standards, there are "switches" that tell the software what to do—see the Appendix for those instructions.

Problems -- Do 2 of the 3 (or all 3 for extra credit)

1. You want to determine the thickness of an oxide coating (TiO_2) that has formed on your "pure" Ti standard (no carbon coat). Calculate the TiO_2 thicknesses from the experimental k-ratios:
Ti 0.9738   O 0 .0180   Assume TiO2 density is 4.2 g/cm3.

You will input guessed thicknesses of the thin film TiO2 coating (hint: somewhere between 10 and 1000 A), and then compare the resulting k-ratios with those you are given, trying to find the best match for each case, for both (Ti and O) k-ratios. Note: for the element that is in both layers (Ti), the program splits out the k-ratio for each layer (top+subtrate) separately, so you must sum them together.
The actual probe experimental k-ratio is the sum of both, so do NOT just look at the value of Ti K in the thin film, but immediately add BOTH Ti k-ratios together – **that sum is what you are trying to match**. You may not get both elements to exactly match the above k-ratios: give you best/closest estimate. (Use TiKa and O Ka [O space Ka] when it asks for element+line)

2. Calculate the **relative error** on each Mg, Si and O Ka (K-ratios) in an analysis of your unknown Mg2SiO4 if your standard has 250 A of Carbon whereas the unknown has 150 A (assume simple case elemental standards; assume C film density 1.6 g/cm3). This means, effectively, calculating the difference

in K-ratios for each element, between the 250 and 150Å cases, and then dividing by the value for the 150Å case, and multiplying by 100%. This is an analogy for differences in carbon coat thickness between a standard and an unknown. Which of the 3 elements (Mg Ka, Si Ka, O Ka) is most affected by differences in Carbon Coat thickness.

3. You have a zircon (ZrSiO4, with slight substitution of Hf for Zr) that has been ion probed, which means it has been gold coated. You want to do an EPMA analysis, but all you have are <u>your normal carbon coated zircon standards</u>. You go ahead, calibrate, and give the analysis a shot….and get an analysis with a total of **about 91 wt%**--which you know makes it look faulty

(below, numbers you can trust)

K-Ratio

	K-Ratio
Zr	0.3652
Hf	0.0066
Si	0.1316
O	.0802

Element	Wt %
Zr	43.73
Hf	0.95
Si	14.46
O	31.98
Total	91.12

(after **<u>normal</u>** matrix correction—which gives wrong values)[1]

Then you recall you have GMRFILM on your computer, and figure you'll plug in the k-ratios-<u>which you can trust</u>, with some guesses at the Au coating thickness, to see if you can extract a halfway decent chemical analysis. Can you? (answer….yes) **What is your estimation of the Au thickness (assume density of 19 g/cm3)?**

There are two ways to run to accomplish this

The 'K' Option	The 'C' Option
▼	▼
Selecting "K" option at start and input a nominal Zircon composition, use atomic %: Zr: 0.99, Hf: 0.01, Si: 1.0, O: 4.0	Selecting "C" option at start and input the experimental k-ratios above and trying to generate a "good" zircon analysis (appropriate stoichiometry, 100 wt% total). I suggest you try this second approach.
▼	▼
Try several iterations, with varying Au thickness, keeping the composition constant	Try several iterations, with varying Au thickness, keeping the K ratios constant
▼	▼
You will always get a sum total of 100% doing this method, but you need to get the K ratios to match the ones found above	You will always get the K ratios to match the ones found above, but the Weight % sum total will not be at 100% until the correct Au coating thickness is found

Additional Settings:

Fix film thickness and composition? Yes (you effectively have already fixed it by saying the top layer is Au Ma) and you will input guessed thickness.
Fix substrate composition? No. You will then input the element k-ratios.

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[1] These compositions result from using carbon-coated standards, and therefore if the unknown has a gold coat, can be significantly in error, as the gold both retards the incident HV electrons (lose energy) plus absorbs exciting x-rays, especially Zr La and O Ka. This is why we are using a thin film program to "salvage" otherwise useless probe data.

Appendix – Do Not Use for this homework BUT keep for future reference for real research

<u>"switches"</u>: You enter ELEMENT + XRAY LINE + SWITCH; where switch refers to HOW the standard for the element exists (or if the element is not measured, but "by stoichiometry", or some other aspect [determined by how the software was put together!];

--if the element is in more than one layer, use switch m -- if standard used is pure element

use n -- if standard used is a compound

but if the element is in only one layer, use c -- if standard is a compound

and

you can use switch s – for an element by stoichiometry (eg oxygen) BUT this is very tricky to use and you have to make sure you don't incorrectly define the material (i.e. for the other elements you have to be sure you don't have too many opposing valences)

use no switch if pure element standard

Enter all element and x-ray data in format ELXR,s where EL is the Element, XR is the Xray line, and s is the switch: e.g. TiKa or TiKa,m (both equivalent) with no spaces but for C Ka or O Ka,c you MUST put a blank space after a single letter element) <u>In most cases you can get away with just ELXR and no switch, unless doing O Ka by stoichiometry (e.g. O ka,s)</u>

Version history 12/7/04 11/14/06   11/26/07 4/18/2013 4/11/2014 (Thanks Mike!)