Name ___________________________

Lab 10 WDS4 Importance of Background Modeling for Trace Elements Analysis 4/8/14

The purpose of this exercise is to demonstrate a sometimes overlooked aspect relevant to trace element measurements by EPMA – evaluation of the background around the peak of interest by detailed wavescans.

Many people might just look at the equation that defines the "minimum detection limit" for an element, and calculate how many counts they need to reach some low level, by increasing current and increasing time. (I calculate these figures for this problem elsewhere—appendix, next page.) But I would argue that this approach is incomplete and can lead to errors.

The correct determination of trace element levels can be a time consuming process and users/customers must be educated to expect it to take longer, to be certain that any number reported is "real".

Fluorine in a volcanic glass at low levels: I received a query from a graduate student in Texas trying to measure F and Cl in melt inclusions. He had been told that he should look at Smithsonian basaltic volcanic glass standard VG2 which has .05 wt% F reported—but he could find no peak using TAP and PC1. So I decided to check this out for myself.

Approach

(1) Determine which spectrometers can be used: TAP (sp1), PC1 (sp2), PC0 (sp4)
(2) Locate a standard to peak on (F-topaz, UW std 1100), and peak and check PHA settings. Note: F on TAP is a little tricky setting up. Change the default peak scan settings to ±7000
(3) Locate standards with various low levels of F:
  a. KN18 obsidian (rhyolitic) glass with .64 wt% F (UW 933) --50 points, 2 sec
  b. KE12 obsidian glass with .42 wt% F (UW 932) – 30 points, 4 sec, narrower range[1]
  c. RLS-132 obsidian glass with .21 wt% F (UW 934) – 30 pts, 30 sec, same range[1]
(4) Do wavescans, one by one, using the above settings, and see what you can see starting with the higher levels of F—this is totally a visual exercise. You don't have to write down any numbers. **The point: do you see, at these higher levels of F, a peak at the F Ka peak position?**
  a. KN18: TAP?___ PC1?___ PC0?___
  b. KE12: TAP?___ PC1?___ PC0?___
  For RLS-132, you will write down data in the blank table on the next page.

	KE12	KN18	RLS	VG2
Si	32.9	34.9	35.4	23.8
Ti	.2	.1	.1	1.9
Al	4.0	5.6	6.1	7.4
Fe	6.5	2.8	1.7	9.2
Mg	0	0	0	6.7
Ca	.3	0	0	11.1
Na	5.4	4.2	3.9	2.6
K	3.5	3.6	3.8	.2
O	46	48	49	44
F	0.42	0.64	0.21	0.05

(5) Are there issues with interferences by other elements present? ____ Which ones? (Virtual WDS is helpful here)
____

(6) What element/line especially creates a big problem for basaltic glass compared to rhyolitic glass? ______

---

[1] SP1 TAP ±800; SP2 PC1 ±1000; SP4 PC0 +1100 and -2100

Note that RLS has the lowest amount of F, .21 wt % (2100 ppm). Looking at this 30 second scan, with the lowest amount of F, **you can graphically see what the minimum detection level is**.

For trace elements we use 3 sigma as a way to "be sure" that a count is above the statistical variation of the background, and thus, above detection level, at >99% confidence level.

The small peak on top of this background is 0.21 wt% F. You can calculate, using the total background counts, what 3 sigma is, and then calculate what this 3 sigma value translates to in wt%,. It's just a proportionality equation.

Fill in the blanks:	PC0 (sp4)	PC1 (sp2)	TAP (sp1)
1. Peak counts (cts/sec)			
2. Estimate the background (cts/sec)			
3. Multiply bkg (#2) x 30 secs (total cts).			
4. Take the square root (=1 sigma)			
5. Multiply by 3 (=3 sigma)			
6. Divide by 30 (= "minimum detect level" over the background in row #2 above)			
7. Subtract #2 from #1 (= F Ka)			
8. Divide #6 by #7 (=fraction of F that is detectable)			
9. Multiply #8 by .21 wt% F = detection level in wt%			

7. The scans above on a glass with .21 wt% F, at least for PC1 and PC0, clearly show a peak. We could conceivably believe that a peak half that high, representing .10 wt% F, could be detectible. But the numbers above (row 9) would make you believe that the detection level is ~half of that. I am not really convinced. So let us definitely create a detection level of .05 wt%, by increasing our counts by a factor of 4. Why 4? Square root of 4 is 2, so it halves the "observable" detection level to ~0.05 wt%. We do that by doubling the beam current (20→ 40 nA; 30→ 60 seconds/channel)

Now, run a wavescan for F, using the last settings (40 nA, 60 seconds, 30 points) on the VG2 glass. Defocus the beam if not done so before, to 20 or 25 microns. You can also 'bump' the stage 3-4 microns every 10 seconds, so there is less chance of 'beam damage' (element migration).

After running this LONG scan, do you believe there is 0.05 wt% F present? ______

Write up a summary of the "search for trace F" in volcanic glass; discuss what you think is a reasonable detection limit of F in the 4 glasses being examined, and particularly discuss the differences resulting from which crystal is used. If the MDL for F on TAP is .22 wt% for 30 second count, how long would you need to count to achieve an MDL of .05 wt% (at same current)? What would you tell the student about his ability to measure F in VG2 glass using PC1 or TAP.

Appendix (using traditional equation, i.e. in Goldstein)

MDL for F **using F-topaz**			
	PC0	**PC1**	**TAP**
peak cts	635	2547	81.2
bkg cts	16	185	2.3
p/b	40.7	14.8	36.3
		Minimum Detection Limits	
TIMES(SEC)			
2	0.2938	0.2435	0.8698
8	0.1469	0.1218	0.4349
30	0.0759	0.0629	0.2246

Version 11-25-08 12/1/09 4/9/13