$LiBO_2$ fusion method for rock and mineral digestion

Note! We no longer permit $LiBO_2$ fusion solutions into the ICP-MS, due to severe long-term contamination of the system with Li and B, and injector and torch damage. This information is left here for your general benefit, and in case we have to resort to $LiBO_2$ fusions again some future time.

Advantages of fusion digestion

- Does not require dangerous HF.
- Dissolves all common rock-forming minerals, *including* zircon and chromite.
- As far as we can tell, all elements are put into solution except those that volatilize.
- Silica can be analyzed.
- All samples can be processed as a batch through each step.
- Fast, in the sense that a large number of samples can be ready for analysis in a couple of days, including dish washing.

Disadvantages of fusion digestion

- Analytical solutions are dilute, with rock/solution proportions about 1:2500, so detection limits may be poorer compared to those from acid dissolution.
- Requires a dangerous hot furnace and molten glass.
- Possible contamination from the large amounts of flux used, from the large amounts of the crucible that is burned off, transferring any ash to your sample, and from furnace dust that falls in from the lining and door.
- You can forget about analyzing trace quantities of Li and B for months by ICP-MS, and for ultra-trace quantities of Li and B forever.
- Slow, in the sense that you have to sit there tending the samples every second while you are fusing. Very tedious, though you can listen to music or watch TV as long as you don't pay too much attention to them.

Dish washing

1. Wash an appropriate number of graphite crucibles, ideally one crucible for each sample, blank, and standard you weigh out. This usually means one or two of each sample and standard, and two to four of the blank. It is wise to wash several extra crucibles, if there is room. Put the crucibles in a large (1, 2, or 4 liters) glass beaker, open end up. Cover the crucibles with 20% reagent grade HNO_3, and cover the beaker with a large watch glass.
2. Put the beaker on a hot plate in a hood, with a couple of steel screens under the beaker to avoid thermal and weight stresses that can crack the beaker. Turn the hot plate to the highest setting or just below. Heat the acid on a hot plate to boiling.
3. Turn off the hot plate and let the acid cool to room temperature without moving it from the hot plate. Discard the acid and individually check that the crucibles are free of deposits on the inside. Remove any deposits by rubbing them with your finger (wear a vinyl lab glove). Crucibles still having glass stuck to the insides need to be boiled in acid again.
4. For the clean crucibles, replace the acid with DI water and heat on a hot plate to boiling again. Cool, drain, and repeat heating in DI water to boiling. Discard the water and dry the crucibles upside down on paper towels on a lab bench, in a drying oven, or on top of the hot furnace.

5. Wash an appropriate number of 1” x 1.5” snap-cap glass vials to hold the flux and rock powders prior to fusion. Remember that you will need flux vials for all unknowns, standards, and blanks and all replicates of these.

Weighing samples

1. Dry sufficient high-purity $LiBO_2$ flux in a *covered*, large fused silica crucible in a muffle furnace at 600°C for several hours.
2. Remove the flux from the furnace and cool 1/2 hour in a desiccator (keep the hot crucible away from plastic and glass!).
3. Using a clean plastic funnel, transfer the flux to the specially marked plastic flux bottle. Keep the bottle tightly capped and in a desiccator until used.
4. Into clean 1" x 1.5" snap-cap glass vials add 0.5800 ±0.0010 g of flux. If you weigh flux for all needed vials now, you only need one piece of weighing paper.
5. Into the glass vials with flux add 0.1200 ±0.0002 g of rock powder. Weigh out all unknowns and standards now. The blanks get no rock powder, of course.
6. Gently mix the contents of a flux vial by holding it at a 45° angle and rotating it to roll the powders around. 30 seconds to a minute usually mixes the powders thoroughly. If clumps won't break up this way, use a plastic rod to gently break them up. Try not to get any powder onto the lid.

Fusing the samples

1. Pre-heat the muffle furnace to 1000°C.
2. To a 250 ml plastic beaker add ~75 ml of DI water and 8 ml of concentrated, high-purity HNO_3. There are graphite-stained beakers for this purpose.
3. Add a small stirring bar to the beaker and cover with a watch glass to prevent contamination. Put the beaker on a magnetic stirrer.
4. Pour the powder from one of the glass vials into a dry graphite crucible, trying not to spill any onto the lip. Get as much out of the vial as you can by tapping it.
5. Put the crucible in the furnace and set the timer to 10 minutes. NOTE: you can actually fit *two* crucibles into the furnace at once. If you do this, be sure to have two beakers of acid on two stirrers. Unless you are smarter than you look, the two samples should be duplicates.
6. After 4 elapsed minutes, take the crucible out and swirl the contents for 5 seconds or so, and place it back in the furnace. Do this again after 7 minutes have elapsed.
7. Turn on the stirrer (medium-high setting, vigorous stirring without splashing).
8. When the timer reaches zero, first take the cover off the beaker. Then, take the crucible out of the furnace *while* tilting it about 45° to the side. Pour the molten glass bead into the stirring acid, taking care not to let the bead or the crucible touch the plastic. The bead will shatter, and should dissolve in about 5 minutes.
9. Quantitatively transfer the dissolved rock solution from the beaker to a 250 ml plastic volumetric flask. Bring the flask to volume and mix thoroughly. Take care not to pour the stirring bar into the flask.
10. Pour the contents of the volumetric flask into a plastic bottle (standards and blanks) or a small plastic test tube (unknowns). This solution contains:

HNO_3	2.2%
Total dissolved solids	0.28%

This whole procedure takes 20-25 minutes for each sample or sample pair, if one person is doing the work. If two people are doing the work, the time can approach 15 minutes.

Stock internal standard solution

1. To a 100 ml volumetric flask add 1 ml of each 1000 ppm single element solution for Rh, In, Re, and Bi.
2. To the same 100 ml volumetric flask add 2.9 ml of concentrated, high-purity HNO_3.
3. Dilute the volumetric flask to volume. This is your stock internal standard solution:

HNO_3	2.0 %
Rh	10 ppm
In	10 ppm
Re	10 ppm
Bi	10 ppm

Diluting solution

This recipe makes enough for ~100 test tubes, or approximately 40 samples in duplicate, not including blanks and standards. Prepare more of this diluting solution if you are going to have more than 100 test tubes.

1. To a 1000 ml volumetric flask add 12 ml of concentrated, high-purity HNO3, and 2 ml of the stock internal standard solution, above.
2. Dilute the volumetric flask to volume. This is your diluting solution:

HNO_3	0.84 %
Rh	20 ppb
In	20 ppb
Re	20 ppb
Bi	20 ppb

Sample dilution

To a 13 ml plastic test tube, add 9.5 ml of the diluting solution and 3.2 ml of the concentrated sample solution from the first dilution, above. Shake the test tube to thoroughly mix the contents. This is the sample you analyze. It contains:

HNO_3	1.05 %
Total dissolved solids	0.043%
Rh	17 ppb
In	17 ppb
Re	17 ppb
Bi	17 ppb

This solution is dilute enough to allow ICP-MS to run many hours without clogging the cones, and concentrated enough so that typical detection limits for many heavy elements are 0.01 ppm in the rock.