Rock analysis, low-pressure HF digestion

Low pressure acid dissolution advantages:

- The concentration of rock in the analytical solution can be several times higher than for the flux fusion method, with rock/solution proportions of up to 1:1000. This gives detection limits that can be better than the flux method.
- The setup is cheap compared to high-pressure acid dissolution, comparable to $LiBO_2$ fusion without the messy graphite.
- You *don't* have to fiddle with a dangerous hot furnace and molten glass.
- You will probably have lower blanks because there is no contamination from flux, crucibles, or furnace. Contamination from the acids is usually very low.
- Faster, in the sense that you do not have to attend to the samples every minute; the samples just sit by themselves most of the time.

Low pressure acid dissolution disadvantages:

- Zircon, chromite, and some other minerals may not completely dissolve (see below).
- You *do* have to fiddle with dangerous HF.
- Silicon, boron, and some other elements that form volatile fluorides are lost and cannot be analyzed.
- Slower, in the sense that samples take ~4 days of processing before they are ready for analysis.

What will and will not dissolve with this method

Most minerals <60 mesh dissolve completely, including:

- amphiboles
- feldspars
- garnet
- hematite
- ilmenite
- kyanite
- magnetite
- micas
- monazite
- olivine
- pyroxenes
- quartz
- rutile
- staurolite
- tourmaline

A few minerals do not readily dissolve, and if they are of importance in your samples this acid digestion procedure will probably not be completely effective even after a month of dissolution.

- **Zircon:** About 50% of zircon from Paleozoic granites dissolves in this procedure, somewhat more for old, radiation damaged zircon, and much less for young zircon. In experiments lasting up to 30 days, I found that zircon continues to dissolve at a decreasing rate that

somewhat resembles an exponential decay curve. Up to 10% of zircon remains after 30 days at 120°C in 50% HF. Dissolution rates were unaffected by the amount of HF (1 vs. 10 ml) with 10 mg of crushed zircon (<60 mesh), indicating that the slowing of the dissolution rate was not due to an approach to saturation. More likely, some parts of the zircon are more soluble than others because of differences in chemical composition and in the amount of radiation damage. Under the conditions described here, $HClO_4$, HNO_3 and HCl *slow* zircon dissolution proportional to the amount the HF is diluted. Note that this is contrary to some rock dissolution lore that $HClO_4$ solves all dissolution problems. The bottom line is that these strong acids behave exactly like water as far as zircon is concerned.

- **Chromite:** Chromite (<60 mesh) seems to be little affected by HF/HCl/HNO_3 mixtures at 120°C for periods of up to a week. $HClO_4$/HF mixtures etch chromite slowly. It may be that chromite will dissolve faster if the sample is first oxidized at high temperature (~1000°C), but I have not tried it.
- **Topaz:** Acids don't seem to faze this stuff at all.

WARNING! At elevated temperatures the closed Teflon vessels are under pressure (a few bars)! The containers *are not guaranteed by anyone* under these conditions, and they may fail catastrophically! Ours have never failed catastrophically, but take heed because the possibility remains and a rupture could have awful consequences if you ignore safety precautions. Containers must be heated and cooled in a closed drying oven in a hood. Don't even peek at them unless they are at room temperature! Take adequate safety precautions, and use these methods at your own risk! These containers WILL leak at 120°C unless in a retainer clamp.

Note The Teflon containers have numbered bases and lids. Always match lid and base numbers.

Dish washing (if needed)

Clean enough 17 ml (or other size) Savillex® containers for all necessary blanks, standards, and samples, taking into account necessary replicates. With the normal dissolution procedure, each container will hold enough solution to prepare 14 final analytical solutions.

1. Clean an appropriate number of 17 ml Teflon containers by boiling in 20% reagent grade HNO_3. Cool to room temperature and rinse in DI water.
2. Rinse in tap water (no detergent) an appropriate number of retainer clamp assemblies. Dry them in air on a paper towel.
3. Fill the Teflon containers 60% full with a mixture of 75% water, 20% HNO_3, and 5% HF. Securely tighten the covers and clamp them in retainer clamps in sets of 2 to 5. Put the clamped containers in a drying oven *in the hood* overnight at 120°C.
4. In the morning, turn off the oven and let the samples cool to room temperature before opening the oven door.
5. Remove the retainer clamp, discard the acid mixture, and thoroughly rinse the containers, including caps, with DI water.

Internal Standard Solution

To a 100 ml volumetric flask add 4 ml each of the 1000 µg/ml internal standard solutions for Rh, In, Re, and Bi. Add 3.5 ml of high-purity HNO_3 and dilute to volume. This internal standard solution is enough for up to 500 samples, and has the following concentrations:

HNO_3	5%
Internal standards	40 ppm

Dissolution Procedure Part 1

1. Weigh 0.1000 +/-0.0002 g of sample into a Teflon container. Wipe any dust off the rim of the vial and screw on the cap.
2. Add 2 ml of HF and 1 ml of HNO_3, and 0.1 ml of the internal standard solution. Cap the vials, clamp them into retainers, and heat in an oven at 120°C overnight (oven must be in the hood!). This step decomposes most silicates and glass and volatilizes most silica. This drastically lowers the silica activity in the second step and so aids dissolution of hard-to-dissolve silicates like tourmaline and kyanite.
3. Cool and remove vessels from the retainers, and evaporate to dryness. We have a home-made Teflon drying oven for this purpose.

Dissolution procedure Part 2

1. Add 3 ml of HF. Cap the vials, clamp them into retainers, and heat in an oven at 120°C overnight again (oven must be in the hood!).
2. Cool the samples, remove vessels from the retainers, and evaporate to dryness.
3. Add 3 ml of HNO_3 and evaporate the samples to dryness. This step decomposes most insoluble fluorides and drives off excess fluoride as HF. Enough fluoride remains to keep Ti, Nb, Ta, and similar elements in solution.

Dissolution procedure Part 3

1. Mix a solution containing high-purity acids by volume: 25% HNO_3 and 5% HCl, 0.1% HF. For example, to a 500 ml bottle add 125 ml HNO_3, 25 ml HCl, and 0.5 ml HF, and quickly fill the rest with DI water.
2. Add 15 ml of this to each sample container.
3. Cap the vials, clamp them into retainers, and heat in an oven at 100°C overnight (shake once after 1 hour; oven must be in the hood!). This solution has:

Dissolved solids assuming no silica lost	0.65%
Dissolved solids assuming 50% silica lost	0.33%
Dissolved solids assuming 75% silica lost	0.16%
Internal standards	261 ppb

Dilution Procedure

Take 0.5 ml of the solution from the Teflon vial and transfer it to a 13 ml plastic autosampler test tube. Add 12 ml of 1% HNO3 solution, cap, and shake. This analytical solution contains:

Dissolved solids assuming no silica lost	0.026%
Dissolved solids assuming 50% silica lost	0.013%
Dissolved solids assuming 75% silica lost	0.007%
HNO_3	1.4%
Internal standards	10.5 ppb

Note that the counting times on the internals standards can be short. Also, the concentrations of some elements in common rocks may be >100 ppb in this solution (e.g., Sr, Ba, LREE, V, Cr, Ni). This means you should do the detector cross calibration, analyze low abundance isotopes, or dilute the sample more.