Picotrace system: standard rock dissolution procedure

This procedure has been tested and seems to work fine on a wide variety of metamorphosed igneous rocks that have not been annealed within the past 200 million years. Radiation damage is important for hastening zircon dissolution, and this procedure may not work so well for zircons in young or recently annealed rocks. For this reason, your samples should not be heated to high temperatures prior to dissolution! This procedure works perfectly for amphiboles, feldspars, garnet, hematite, ilmenite, kyanite, magnetite, micas, monazite, olivine, pyroxenes, quartz, rutile, staurolite, tourmaline, and, with caution, zircon*. It does not completely dissolve corundum. High TiO_2 samples may leave a residue, though Ti-rich minerals will be completely decomposed**. Chromite is not completely decomposed***.

Pre-clean the sample vessels

In general, samples rinse out extremely cleanly and this step isn't necessary. However, if the vessels were left open, or if they were used to dissolve mineral separates, or if they are new, or if you don't trust the last user to have left them clean, you may want to clean them. When in doubt, clean them out! Note: the vessels do not need to be dried between uses.

1. Put vessels and lids in DI water spiked with 2% Citranox® acidic detergent solution. Bring to a boil and let cool.
2. Load samples with 6 ml water, 1 ml HF, and 1 ml HNO_3.
3. Run the samples with the cleaning program. Let cool.
4. Empty vessels and rinse with DI water. Don't worry about drying them.

Prepare the sample blocks

Like the cleaning step, block preparation does not need to be done every time. The main thing is to wash off potentially contaminating dust, and to keep the vessel wells and threads coated with Teflon spray.

1. Gently wash the large holes in each sample block with DI water and a clean, wet cellulose sponge.
2. Rinse the sample block clean.
3. Air dry. Be sure the thermocouple wells are empty of water.
4. Spray the big holes with Teflon spray. Spray in a hood from at least two angles to make sure all large hole surfaces are coated. Let these dry.
5. Also squirt some of the spray into the threaded bolt holes.

Final dissolution solution

To a 500 ml bottle add:

1. 125 ml of high-purity HNO3.
2. 25 ml of high-purity HCl.
3. 0.5 ml of high-purity HF.

4. 0.3 ml of each of the 1000 ng/ml stock internal standard solutions (usually Ru, In, Re, Bi).
5. Fill as full as possible with DI water, and shake.

Diluting solution

To a 1 liter bottle add:

1. 14 ml of high-purity HNO_3.
2. Fill with DI water.

Dissolution procedure

1. Note that 1 or 2 Teflon vessels will remain empty for blanks, and some will also be for standards. Use this form to keep track of your work.
2. Weigh 0.2000 ±0.0002 g of powdered sample into each vessel. Take great care not to get any rock powder onto the vessel rim. Wipe it off with a damp Kimwipe if you do.
3. Add 3 ml of HF (50%).
4. Install the vessels in the pressure block and run the dissolution program. For typical zircon-bearing rocks, old rock dissolution takes four days. Probably one day is a minimum, but if you have young or annealed zircons, or maybe chromite, you can heat them for longer times.
5. Turn off the heating program and cool the vessels.
6. Install the evaporation lid, lid filters, and aspiration bottles.
7. Turn on the aspirator and make sure you see a continuous stream of bubbles coming through the bottles.
8. Start the evaporation program. Note, this evaporation will take ~8–12 hours and should be run overnight. The temperature in the vessels should never exceed the acid boiling point.
9. Turn off the heating program and cool the vessels.
10. Add 15 ml of HNO_3 to each sample. The purpose of this is to decompose low solubility fluoride salts and drive off the fluoride as HF vapor. Because of its low boiling temperature (120°C), 70% HNO_3 is not so efficient at driving off fluorides as acids with higher boiling temperature, like perchloric and sulfuric acids.
11. Put back the evaporation lid, lid filters, and aspiration bottles, and run the evaporation program again. Note, this evaporation will take ~18 hours and should be run overnight.
12. Turn off the heating program and cool the vessels.
13. Add 15 ml of the final dissolution solution (see above) to each sample vessel.
14. Put the pressure lids back on the vessels and run the final solution program.
15. Turn off the heating program and cool the vessels. Analyze them as soon as possible.

Dilution procedure

Sample test tubes are 10 ml, blank and standard tubes are 50 ml.

1. To the sample tubes add 10 ml of the diluting solution and 0.20 ml of the sample vessel solutions.
2. To standard and blank tubes add 5*10 ml of the diluting solution and 5*0.20 ml of the sample vessel solutions.

This solution contains 1.2% HNO_3, 0.027% dissolved rock (minus silica, which evaporated as SiF_4), and 10 ppb of each internal standard element. Analyze as soon as possible.

Notes on dissolution

* Because of the slow rate of zircon dissolution, users MUST confirm for themselves that zircon is dissolved for each sample at the end of each run. This can be done after the analyses are complete by first transferring all unused sample solutions from the digestion vessels into conical-bottom test tubes. Pipette off most of the solution and add DI water to the tubes to dilute the acids. Pipette off most of the solution again, and transfer anything left at the tip of the tube bottom onto a watch glass. Swirl the watch glass to gather all particles to the center, and examine under a petrographic microscope. Zircons generally appear white in oblique incident light, because of light scattering from the many solution pits along decay particle tracks. In transmitted light zircons appear dark gray, frequently nearly opaque, for the same reason. High birefringence and parallel extinction may be observed. Any sample with remaining zircon must be digested again, and for a longer time. This is obviously not an issue for rocks that don't contain zircon. I have analyzed many hundreds of metamorphosed igneous rock samples (felsic and mafic, last heated at least 250 million years ago) with up to 620 ppm Zr, and have not seen any undissolved zircons.

** This procedure has worked fine for rocks with up to 6% TiO_2, as determined by the lack of residue after dissolution, and by comparison of many hundreds of samples analyzed for TiO_2 by this procedure, and by a commercial lab that analyzed major elements using lithium borate fusion and ICP-OES spectroscopy. However, I have also analyzed rutile and titanite mineral separates (chunks 1-2 mm across) and found that some white titanium residue was left using this procedure. Therefore, this procedure works fine on rocks with 0-6% TiO_2, but does not result in 100% dissolution samples with more. TiO_2 recoveries (i.e., TiO_2 in solution) calculated for the mineral separates indicated that ~6% TiO_2 in a rock is about the limit for this standard procedure. The rutile and titanite mineral separates were completely decomposed, however, leaving only pure white powder as the residue. Recoveries of other elements are probably close to 100%. For TiO_2-rich samples, modify this procedure by using less sample or more HF in the final dissolution step. Don’t dissolve your sample introduction system, though.

***This procedure was tested on 20 mg of NIST-103a, chromite refractory. Note that 20 mg is 1/10 that used for normal rock analysis. Some chromite remained after the normal procedure given above. The residue was not weighed, but by eye the residue was 4 or 5 mg (20-25%), based on comparison with 20 mg of the standard. It seems likely that an 8 day dissolution step would dissolve the chromite. Roasting of the sample in air, with oxidation of the chromite, may make it more soluble. Note that roasting should not be done on zircon-bearing samples because it anneals decay particle tracks and so makes the zircon much more difficult to dissolve.