Personal comments on the Picotrace system

After having used the Picotrace system for some years, I have a few observations regarding the system. First, my primary interest is dissolving igneous and metamorphosed igneous rocks, ranging from basaltic to granitic compositions. Naturally, zircon dissolution is a primary concern. First a bit of history.

- Our old low-pressure HF dissolution procedure, at 120°C, failed to dissolve zircons over digestion times up to a month. It was useful only for zircon-free mafic rocks.
- Our old $LiBO_2$ fusion method worked fine, of course, but when we got our new ICP-MS instrument we banned this method because Li and B contamination would compromise our water analysis programs.
- We also tried microwave digestion at temperatures up to 240°C, but with disappointing results. Part of the problem was that, with our (then) state-of-the-art system, digestions could be run at 240°C for only half an hour before cooling was required to protect plastic structural components. The 24 or so hours that might be needed for zircon dissolution would be difficult to achieve. Dissolution experiments up to 5 hours, requiring 10 half hour runs, were insufficient to dissolve zircons, similar to the findings of others. We also had numerous problems with vessel leaks, damage to the Kevlar reinforcing sleeves, and venting incidents during heating. We ascribe these problems principally to running the system at its pressure and temperature limits.

So, with this background we tried the Picotrace system.

Hot plate

The Picotrace hot plate is entirely made of or coated with Teflon. No metal parts are exposed. It seems very well designed and works exactly as described in the Picotrace literature. We run our hot plate in a hood, with the sash closed, but the hood fan off.

Hot plate controller

This is the programmable controller that monitors and controls the hot plate and sample temperatures. It can ramp temperature up over time, hold temperature for long periods, and turn the hot plate off after a set time. Operating the controller is not obvious, but the instructions are reasonably clear. After some practice, programming for normal runs is easy. After a power failure, however, the system woke up in the mode for changing the many system settings. It took a few minutes with the manual to figure out how to get it back to the normal run mode. There are a great many system settings and I wouldn't look forward to having to reset them all.

Sample blocks, vessels, and pressure plates

The two sample blocks are Teflon coated aluminum, each with 16 drilled, round-bottomed holes for the sample vessels. The vessels are machined, white Teflon, with the interiors "densified" by some process. To remove surface porosity, I suppose. The normal lids for dissolution fit over each vessel individually. The sealing surfaces are flat, and the seal is usually very effective. Each

lid is held in place by a Teflon-coated aluminum pressure disk, which is pressed down onto the vessel with a hand-tightened bolt threaded through an overlying plate. Bolt tightness is critical: too loose and the vessel vents, too tight and vessel expansion during heating can bend the pressure disks against the bolts. Other than that, there were some issues we had to resolve.

1. We had difficulties getting the sample blocks to reach their maximum operating temperature. See here for our solution.
2. The Teflon-coated aluminum block was supposed to have been quite resistant to corrosion. We found corrosion starting after four 24-hour runs at 175°C using only HF. The Teflon coating on the aluminum block is very thin, like that of the pressure disks, but not like the thick coatings on the hot plate. Corrosion manifests as the appearance of white crystalline salts on the surface of the black Teflon coating, and bubbling up of the coating. Detachment of the coating is supposed to occur after a while, but 4 runs seemed a bit soon. We clean the holes after each run with DI water and gentle scrubbing with a wet cellulose sponge. We also store the blocks in a desiccator to avoid continued corrosion. Before dissolutions we usually coat the vessel holes with Teflon spray. That seems to slow the corrosion rate tremendously. I suspect that the Teflon spray coating is laterally porous, which allows acid vapors coming through the sample vessel walls to diffuse away.
3. The Teflon-coated aluminum pressure disks each have a hole in the middle that is not coated. The purpose of the holes is unclear. Corrosion in the holes, and at the tip of the pressure bolt that presses down on the hole, started immediately from acid vapors diffusing through the Teflon lids. When the pressure plates are removed after a run, white aluminum and brown stainless steel corrosion products fall out onto the sample vessel lids. After a few runs the, Teflon coating on the disks on the side against the vessel started to bubble up as corrosion products formed under the coating. The Teflon coating is very thin. Teflon spray (dry film lubricant) does not seem to help reduce corrosion in the holes. We made a set of 6 mm thick Teflon disks, and put them between the pressure plates and vessel lids. This extra thickness of Teflon dramatically reduces corrosion of the pressure disks, though alignment of the pressure plates with the pressure bolts requires some care.
4. One pressure disk stuck to the Teflon lid because I used the wrong Teflon spray, and part of its Teflon coating tore away when it was pried off. This gave me the idea that the wrong Teflon spray could be used to glue the pressure disks and 6 mm Teflon spacers together. It worked, so now we just leave them stuck together all the time.

The sample blocks look like they will last a long time, though slow corrosion will take its toll. The pressure disks aren't so robust, and we are on our third set. What finally wrecks them is not corrosion, but overtightening the pressure bolts. When the vessel expands during heating, the plates bend under the bolt. Don't overtighten. Always use Teflon spray in the sample block holes, and I recommend 6 mm Teflon disk spacers between the aluminum pressure disks and the vessel lids. It may be that the sample blocks can be recoated with Teflon. There are many shops that claim to be able to do this around the U.S., though I have my doubts.

Teflon-coated aluminum pressure disk (black) shown with the 6 mm Teflon spacer we always use to reduce corrosion. The hole in the pressure disk has to be cleaned out periodically to remove dust-producing corrosion products. The corrosion products come from both the aluminum disk (white powder) and from the tip of the pressure bolt (dark-brown powder). This is an old photo. We've switched to graphite-filled Teflon disks, which have reduced corrosion even more than the white Teflon did.

Same as above, upside down, to show that there is no fancy machining. Aligning the two disks between the sample vessels below and the pressure bolts above can be a pain. Fortunately, after a run or two the two disks tend to stick together, especially if you use the sticky Teflon spray. We just leave them stuck together.

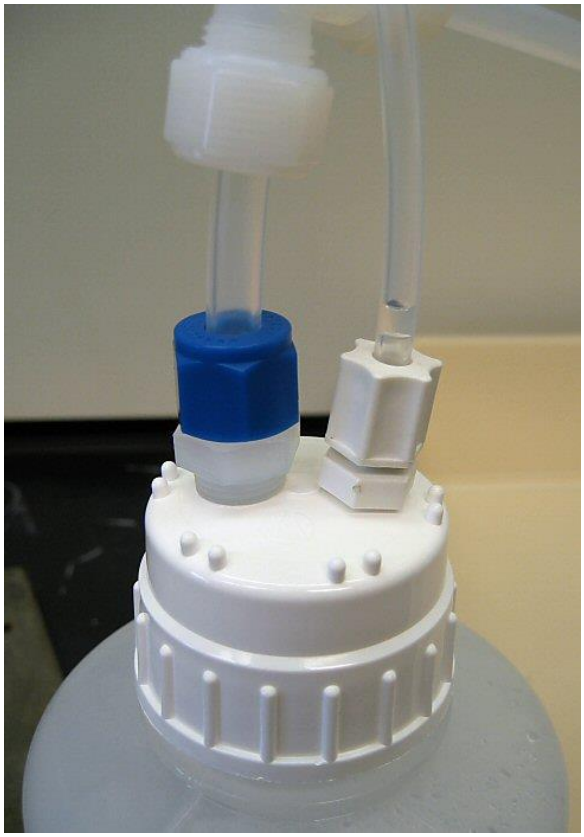
Drying cover and sparging bottles

The sub-boiling drying cover is made of a machined Teflon slab that covers all 16 sample vessels on a block. Each slab is connected to two 0.2 µm filters at one end, and an aspirator–neutralization system at the other. The cover works well, though it is very important to be patient. I became impatient one day and heated the samples too much. The samples boiled and I ended up with boiling splatters all over the insides of the vessels and the drying cover. Some vessels dry faster than others.

Two pairs of 2-liter plastic sparging bottles with tubing are supplied, used to neutralize the acid vapors that come off the samples as they dry. The bottles are supposed to contain NaOH solution to neutralize the acids. The bottles each have a Teflon top plug and supplied tubing. The PVC tubing supplied is large diameter and stiff, making it difficult to handle and difficult to keep the bottles upright.

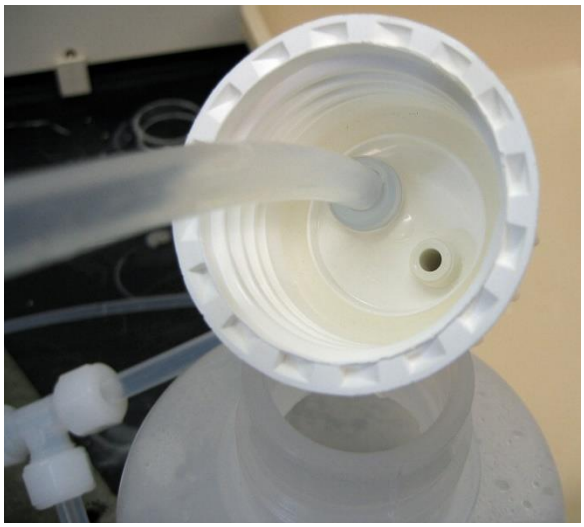
We built a plastic box that holds the two bottles upright despite the tubing pulling in different directions.

The aspiration rate through the bottles supplied with the system was difficult to control. Either vapors were not drawn through the bottles at all, because of leaks around the PVC tubing where it passes through the bottle top plugs, or the bottles collapsed under the vacuum. There was little middle ground.



We made our own neutralization system out of non-collapsible bottles (Nalgene 2126-2000 plastic vacuum bottles).The Picotrace plugs won't fit, so we had to drill and tap the caps that come with the Nalgene bottles.

This is an outside view of our drilled and tapped Nalgene bottle top. Note that we used the Picotrace-supplied fitting for the large-diameter Teflon tubing (left) that comes from the sample vessel drying cover, but used our own 6 mm OD tubing and fitting for the tube that goes to the aspirator (right).



Inside view of our drilled and tapped Nalgene bottle top. Our threads were quite tight so we didn't bother using Teflon tape to seal the threads.

Neutralizing solution

The sparging bottles are supposed to capture and neutralize acid evaporated from the samples, preventing the acids from contaminating the vacuum system, which may be aspirator water going down the drain, or a closed-loop system. Picotrace recommends NaOH for neutralization, which will certainly work. I cleverly decided to use Na_2CO_3 instead, which is cheaper and less corrosive to skin. This was a big mistake. It seemed to work fine for dozens of runs. Then, one fine day, I saw a big drop of acid run down from the samples into the bottle. There arose an eruption of foam that shot back up the tubing into the samples, ruining the batch. Luckily, our box of Na_2CO_3 had a very odd trace element composition (very high La but very little of the other REEs, high Cr, high Co, low Ni, etc.) that permitted us to determine which samples of all previous runs were contaminated. Fortunately, it was only two batches. Two batches ruined. Live and learn. Now we just use tap water in the sparging bottles, and dispose of the acid water as we do our other dilute acid wastes.

We had another problem with the Na_2CO_3 neutralizer during HF evaporation, that may also be a problem with NaOH. NaF crystallized around the end of the tube that brought condensed acid drops into the first sparging bottle. This NaF crust gradually slowed air flow, and sometimes prevented overnight evaporation of the acid. Yet another reason to use just tap water.