UVM Cosmogenic Laboratory - Quartz Purity Testing

Purpose: This method details how we test the purity of quartz mineral separates. We have designed the method to facilitate rapid, safe dissolution of 30 samples at a time using an acid cocktail of 48% HF/ 1%H_2SO_4. The H_2SO_4 is added so that upon evaporation, the sample does not go to dryness. The H_2SO_4 also provides the matrix acid for ICP analysis. The method is performed in the meteoric laboratory. After testing, samples will either move to the in-situ lab (placed in drawers by the door) if they are deemed pure enough for analysis or will return to the mineral separation laboratory (placed in box for samples requiring for another week-long etch) if they are not sufficiently pure.

Hazards: The primary hazard associated with this method is exposure to concentrated HF. HF's unique properties make it significantly more hazardous than many of the other acids (See attached MSDS and read information on the lab wall). Secondary hazards include working near an active hot plate at temperatures near and above boiling (110C).

Personal Protective Gear: Gloves (double-glove when handling HF, use thin nitrile, latex, or PVC under thicker neoprene), goggles, face shield (when handling HF), rubber gown (when handling HF), rubber lab shoes.

Decontamination procedures before leaving the Lab:
-Rinse outer Neoprene gloves with DI water and hang them over the counter sink (outside the hood).
-Remove inner gloves and place in trash.
-Hang smock in corner and goggles on hooks before exiting the lab
-Wash hands thoroughly before leaving the vestibule.

Safety Signage: For the safety of people both inside and outside the lab, it is imperative that proper signage be used both on the hood itself (Plexiglas labels on Velcro) and on the vestibule door. Please read and implement signage instructions provided in the detailed methods that follow.

Important Notes

1. For the sanity of all involved, the 30 flat-bottom beakers need to be kept separate from the 30 round-bottom beakers. Flat-bottom beakers go in the green trays and round-bottom beakers go in the black trays.
2. Double check that you are using the right batch number by looking on the meteoric lab computer and checking for the last batch completed in the folder "quartz testing".

Getting ready

Select 30 samples to test and bring them into the meteoric lab. Note that it is important not to mix different types of samples together; high-level samples should not be tested in the same batch as low-level samples. This segregation helps minimize the chance of sample cross-talk from spilled quartz. If doing a mixed batch of samples, mass in the low level samples first to reduce the chance of cross talk. OPEN ONLY ONE TUBE AT A TIME.

Preparing your data sheet [10 minutes]

1. Turn on keyboard and mouse.
2. Open the folder on the desktop entitled "quartz testing"
3. Open file "quartz_test_template"
4. Save the file (select type *.xlsx*) remembering to the change the word "template" to your batch number. The file name format should be "quartz_test_*N*", where *N* is your batch number. Save the file in the folder "quartz testing batch sheets".
5. Fill in the information at the top of the sheet (name, date, and batch).
6. Organize your samples in alphabetical order. This is a key step.
7. Add all your samples ID's to the spreadsheet (in alphabetical order!) and double check them against your tubes.

Loading your samples [45 minutes]

1. Take out 30 quartz testing beakers in their plastic trays and one weigh boat (we use these to keep quartz from spilling into the balance which damages the mechanism).
2. Add the weigh boat to the balance, close the lid, and tare.
3. Weigh about 0.250 g of sample into the weigh boat; do this by holding the tube near horizontal and gently tapping the tube. DO NOT wear gloves as gloves increase the static charge. If you pour out too much sample, discard the quartz. DO NOT put it back in the tube because doing so risks sample cross talk and contamination.
4. Close the lid of the balance and record the weight in the spreadsheet. Remember to save the document after EVERY sample is massed!
5. Open a beaker and carefully pour the sample in (this is usually easiest if the weigh boat is folded loosely in half). Close the beaker tightly. You may need to tap the weigh boat to get the last of the sample into the beaker.

6. Clean the weigh boat with your fingers. Place it on the balance. If the mass reading is not zero, check for quartz, clean and then re-tare.
7. Repeat for the next 29 samples until all 30 are weighed into beakers. Check every time to make sure you have recorded the weight and that you are aliquoting from the right sample. Remember to save the document after EVERY sample is massed!
8. After you are done, use the lab vacuum to clean up any and all spilled quartz. The vacuum lives under the target packing box.
9. Print the "lab data entry" worksheet on the printer in the write-up room, punch it, and add it to the quartz testing binder. Use this sheet for recording any issues with samples or the weigh-in/dissolution process.

Adding Acid [15 minutes]

1. Put on yellow rubber smock, goggles, face shield, and double glove (thick over thin gloves).
2. Take out the repeat pipettor, the 50 ml reservoir for HF, the 250 ml Nalgene beaker, the bottle of HF/H_2SO_4 quartz testing solution, and a spill tray. The quartz testing solution should be kept in the spill tray at all times in case of a spill.
3. Place first Teflon-coated sample tray near the front of the hotplate. Remove lids and flip them over onto tray. Make sure that the beakers are towards the interior of the hotplate.
4. Decant about 175 ml of the quartz testing solution into the 250 ml Nalgene beaker. Set pipettor volume to "5 ml". Fill reservoir with 50 ml of quartz testing solution and discard first shot back to the beaker. CHECK that the pipette is not dripping (note that dripping is likely to happen if there is excess air space in the reservoir, so make sure that the pipette tip is completely submerged in liquid before filling). If the tip is dripping, empty the solution back into the beaker, rinse the tip inside and out three times, and discard replacing with new. Keep the gray top adaptor.
5. Prop your elbow on your hand to steady your arm. Add 5 ml of quartz testing solution to each beaker, working from back to front. Refill the reservoir after every 5 beakers to avoid running out of solution, and always discharge the first shot to the waste beaker after filling since the volume of the first shot is not accurate. Release the liquid SLOWLY and GENTLEY to prevent splashing. If there is HF left after all the samples have been filled, it should be poured back into the bottle (this is the ONLY time we do this).
6. Cover each beaker with a watch glass. Make sure that every watch glass is CONCAVE UP and make sure that the watch glasses are centered. Again, work from back to front.
7. Slide the tray to roughly 10 cm from the back of the hot plate. Repeat for the next two trays (the trays should end up in the middle of the hot plate).
8. Add little the plexiglass label to hood sash so everyone knows what's going on - "**HF Digestion**".
9. Turn hotplate on and set the temperature to 95C.
10. After at least 60 minutes, raise the temperature to 105C.

11. For complete digestion, the samples must cook for AT LEAST 8 hours at 105C.
12. When leaving the lab, place the "HF Digestion" sign on the lab door.

Pulling Lids and Evaporating [45 minutes]

1. After at least 8 hours, turn off the hotplate and let cool for 30 minutes.
2. Put on yellow rubber smock, goggles, face shield, and double glove (thick neoprene over thin gloves).
3. Take out the plastic container for the watch glasses and fill half way with DI water.
4. Gently tap each watch glass three times (Lee's magic number) to remove drops of acid condensate.
5. Remove watch glasses one tray at a time from back to front holding your arm with your hand for stability. Slide watch glasses sideways over the Teflon beakers trying to remove as much acid condensate as possible. If you drop a watchglass, don't try and pick it up, just leave it and the acid will evaporate over night during the dry off.
6. As each watch glass is removed, place it in the watch glass container.
7. Put watch glasses into 2 liter wash jug with 1 liter of 1% Nitric Acid (HNO3). Rinse the watch glass container thoroughly. Place the jug in the ultrasound and sonicate for at least several hours. Once sonication is finished, remove the jug, dump out the acid into the sink with the colander in place, rinse several times with DI water shaking the jug each time and then dump out the watch glasses, rinse them with the spray nozzle and place them back in the watch glass box.
8. Turn hotplate on to 110C and put the "**HF Evaporating**" label on the hood sash. Make sure to close the sash completely and DO NOT perform any other work in the hood during the HF evaporation process.

Labeling ICP Tubes [10 minutes]

1. Take out 30 new purple ICP tubes, put them in a rack, and number them with the test # and position (1-30) using a sharpie.
2. Put the tubes in a rack in order.

Tubing and beaker cleaning [45 minutes]

1. Turn off the hot plate and let it cool to less than 60 degree.
2. Put on goggles, inner gloves (PVC or nitrile), and a lab coat or smock.
2. Get out a 250 ml Nalgene beaker, repeat pipettor, and 50 ml DI reservoir. Fill the 250 ml Nalgene beaker with Milli-Q water.
3. Add 6 ml of Milli-Q water to each beaker, working from back to front. Refill the reservoir after every 6 or 7 beakers to avoid running out of solution, and always discharge the first shot to waste after filling since the volume of the first shot is not accurate.
4. Cap all beakers TIGHTLY.

5. One at a time, vortex each sample for 5 seconds. Invert the beaker before and after vortexing to ensure that the viscous H_2SO_4 gets mixed in. It's best to vortex the beakers twice. Once right side up, the second time, upside down.
6. Transfer each sample to its labeled tube and cap tightly. As each sample is transferred, but the beaker and its lid in a washing bottle. Place the 15 ml tubes in order in a rack.
7. Clean the Teflon-coated sample trays with 1% nitric squirt bottle and then rinse very thoroughly with DI water. Dry them in the oven.
8. Sonicate the beakers and lids in 1% Nitric acid for at least 8 hours. Remove the wash bottle from the sonicators, drain the acid to waste down the sink in the hood, and rinse the beakers with DI water several times shaking the bottle with the beakers between each rinse. Dump the beakers into the colander in the sink. Hand rinse each beaker and each lid with DI water. Push the beakers into their racks and rinse them one for time before inverting the entire rack with beakers in it into one of the slotted trays in the oven. Place the rinsed lids in a slotted tray too. The lids and beakers will be dry by morning.

ICP analysis

1. Take green plastic racks out the vestibule and transfer samples (in order) to red or purple racks. Only red or purple racks should leave the vestibule and move back and forth to the ICP. The use of specific racks is designed to reduce the change of boron contamination in the lab. Return the green rack to the Meteoric lab and wash it with Micro90 and DI water before drying in the oven.
2. Take the samples and the bin of standards to the ICP room. Bring the red clipboard with the load list to the ICP lab. You will use this list to record any issues that arise during analysis.
3. Turn on the Argon, the ICP, the chiller, and the ICP computer, and attach the tubing around the pump. Allow the instrument to warm up for 5 minutes (this allows the gas lines to purge and makes starting the plasma easier). Start the ICP JY program.
4. While the gas is flowing, transfer the sample tubes to the ICP sample rack double checking that they are in order and in the correct positions as indicated on their labels (refer to the diagram in the JY software for the correct positions).
5. Move the sample rack into the ICP vented cabinet. Make sure that the vented cabinet is turned on. One by one, remove the caps from the tubes, placing the caps in order and upside down in rows on the bottom of the vented cabinet. When all the caps have been removed, transfer the rack to the autosampler making sure it is properly seated and in the right location.
6. In the ICP vented cabinet, fill each standard tube with between 40 and 45 ml of the matching standard. Cap and shake the tube gently to mix the new and old standard. Place the tubes in the 50 ml sample rack on the

autosampler in order of concentration starting with the blank (again, refer to the diagram in the JY software for the correct positions).
7. Ignite the plasma and open the "Bierman_Quartz_Purity_Template" method. Enter the sample names in the run list where there the cells say "uk" (unknown), and rename the method with the quartz test batch number ("qtz_N"). Begin the run by clicking the "Play" button.
8. After the calibration is complete, check that the instrument calibrated correctly and make sure that the check standards are within 5% of nominal values. If all is well, allow the run to continue. Running 30 samples will take about 2 hours.

Data Importation

1. When the run is complete, open the "Analysis Results" menu, select ONE batch worth of samples (include calibrations and check standards), select the "Custom Report" option, and click "Preview". Print this report from the computer and add it into the binder in the write-up room under the appropriate batch number.
2. Click on the "Export" button (it looks like an envelope) and select the "Excel 5.0" format. Save the file to the "Bierman" folder on the desktop using the format "qtz_N". Use the memory stick to transfer the file to the mac mini in the Meteoric laboratory. Copy the file to the subfolder "ICP_data".
3. Open both the batch sheet and the matching ICP results sheet for the batch of data you seek to reduce. With both sheets open, check that the order of the data is identical in both by comparing LINE by LINE, the sample names. THIS IS A CRITICAL STEP. If the data and samples are not in the same order, the analytical results will not be meaningful. If you find that the samples are in a different order on the batch sheet and on the ICP data, then move the entire analysis until the order is correct.
4. Once you have matched LINE by LINE the results and the batch sheet, copy the ICP data including the standards and the sample names and paste it into the worksheet entitled "Paste ICP Data Here".
5. Do one final check that the import of data is correct. In the batch sheet, open the worksheet named "Paste ICP Data Here". There will be two columns of sample names. Scan down the columns and make sure LINE by LINE that the names are the same.

Label Printing -- Quartz Tubes

1. Open the "quartz testing" folder on the desktop and open the subfolder called "print labels from here".
2. Open the document called "Quartz_tube_labels" and click OK to bypass the security risk message that pops up.
3. When the "Open Workbook" window pops up, use the drop-down menu to select "Quartz tube label data" (note that this may NOT be the default) and click OK.

4. A Word document will open and the "Mail Merge Manager" toolbar should automatically appear. If it doesn't, or if it gets closed by mistake, re-open the toolbar under the "Tools" tab of the Microsoft Word menu.
5. Under the "Select Recipients List" heading of the "Mail Merge Manager" toolbar, use the "Get List" drop-down menu to select "Open Data Source". Navigate to the excel file for the correct batch (i.e. "qtz_text_*N*.doc"). Select it and click "Open". Click OK to bypass the security risk message.
6. When the "Open Workbook" window pops up, use the drop-down menu to select "Quartz tube label data" (note that this may NOT be the default) and click OK.
7. Under the "Preview Results" heading of the "Mail Merge Manager" toolbar, click the button on the left with the "ABC" symbol. This will generate a preview of the labels. Check the preview carefully.
8. Add a single sheet of LARGE labels to the printer in the write-up room and print the labels.
9. Find your original 30 tubes of quartz and stick on the labels.

Quartz Evaluation and Sample Disposition

We strive for quartz containing less than 100 ppm Al and less than a few tens of ppm of other impurities such as Ca, Na, and K. Levels of Fe and Ti are often similar to those of Al. Judging whether a sample is "clean" enough involves several steps. If the sample is very small, very high in ^{10}Be (i.e., we don't need to dissolve much), or no more material is available, then Al values > 200 ppm might be OK. Or, if many similar samples have been processed from the same geographic area and all give high total cation loads despite repeated etching (this seems to be a quartzite problem at times) then high values may also be acceptable. In general, if there is a correlation between high Al and high K, Na, and/or Ca the culprit is likely feldspar which can be removed by an additional week-long etch in very dilute HF/HNO_3.

If a sample is deemed "clean", then the small label is attached to it and "re-etch" is struck through with a sharpie. The sample is placed in a drawer just inside the in situ lab.

If a sample is deemed "dirty" then, then the small label is attached to it and "clean" is struck through with a sharpie. The sample is returned to the mineral separation lab for an additional week of weak acid etching.

This is for doing back to back quartz digestions……
Morning [total time, about 2 hours]

Turn off hotplate 15-30 minutes ahead to let samples that were drying (Batch 1) cool a bit [15-30 min]

After 30 minutes, add 7 ml milli-Q water to the dried-off samples using a 7 ml shot from the repipetor (do this gently and slowly to prevent splashing), cap each sample tightly, vortex, transfer to pre-labeled tubes (Batch 1). Set these aside for ICP analysis. [45 min]

Rinse now-empty beakers and lids with 1% nitric acid; place in 1% nitric acid in 2 liter jar, sonicate for an hour or more (Batch 1) [10 min]

Remove watch glasses from sonicator, add DI water to plastic 2-liter jar, cap, shake, repeat. Dump watch glasses (Batch 1) into colander, wash with spray gun. Return to small plastic box [5 min]

One tray at a time, add 5ml HF acid to quartz already weighed into beakers (perhaps while the hot plate is cooling or the night before, Batch 2) and start digestion (95 C) after placing wet watch glasses from small plastic box on them [15 min]

Label ICP tubes for Batch 2 [5 min]

Dump Batch 1 beakers into colander, wash with spray gun. Wash each Batch 1 beaker and lid individually with DI water. Place lids downside up on white plastic tray to dry, place beakers in racks, turn upside down over plastic tray in oven. Dry overnight. [10 min]

Raise hotplate to 105 C after 60 minutes.

YOU MUST ALLOW ≥8 HOURS FOR DIGESTION OF 250 mg OF 250-850 um QUARTZ

Evening [total time, about 55 min]

Turn off hotplate and let cool 15-30 minutes. This is a good time to take the beakers from the last batch off the ultrasound and wash them and set them to dry.

Tap watch glasses and remove by sliding sideways. Work back to front taking care to minimize drip. Put the acid-covered watch glasses in water.[10 min]. Turn hotplate back on to 110C. Evaporate off (Batch 2) HF over night.

Wash watch glasses in DI water in their labeled plastic box, then, dump into colander and rinse with spray hose, then sonicate over night in 1 liter of 1% nitric in a 2 liter wash container [15 min].

Weigh Batch 3 into now-dried beakers. [40 min]