Extraction of Beryllium from Quartz Method

Version: This version was created by Peter Strand, September 2016. It is an adaptation of the following two procedures, modified for the University of Maine Cosmogenic Isotope Laboratory:
1. John Stone's Be-10/Al-26 method (http://depts.washington.edu/cosmolab/chem) as modified by Brenda Hall.
2. Roseanne Schwartz's Lamont Doherty Be-extraction method (http://www.ldeo.columbia.edu/cosmo/methods).
Where applicable, I've included notes from the two methods.

The method that follows is used to separate Beryllium from pure quartz for AMS measurement.

John says: The procedure described below will cope with up to ~10 mg of Fe and 3-5 mg of Ti, assuming the total amount of Al, Be and other metals is less than 3-5 mg. It can be modified to accommodate larger samples by increasing the size of vessels, ion exchange columns, etc.

"ICP" Aluminum check for quartz purity:

John says: Check the trace-element content of the quartz separate before dissolving it for ^{26}Al-^{10}Be analysis. It is important to obtain low concentrations of Al, Ti, Mg, Ca and alkalis. High Al levels decrease the ^{26}Al/^{27}Al ratio and limit the number of ^{26}Al ions that can be counted. This will reduce the statistical precision of the measurement. High levels of Ti and other trace elements may complicate the chemical separation described below.
Careful quartz clean-up usually (though not always) results in Al and Ti concentrations of <100 ppm. Higher levels of Al may indicate the presence of impurities such as feldspar, muscovite, garnet, or sparingly soluble fluorides from the HF treatment. Note, a 99.5% pure quartz separate containing ~0.5% feldspar still has an Al concentration of ~1000 ppm.

"ICP" Al-Check

- Select and label a set of small, 8ml Teflon ICP beakers, one for each sample.
- Weigh and record the weight of each beaker with lid on.
- With a clean spatula, transfer 0.05-0.35g of sample into the beaker. (0.1 g of sample is a good target) *Doing this in front of the anti-static machine helps keep quartz grains from being flung about by static.*
- Weigh and record the weight of the beaker and sample with lid on.
- Add a small amount of 1% HNO_3 with squirt bottle, enough to wet the grains, then cap the beaker.
- Thoroughly clean the spatula with isopropanol and a KimWipe after each sample.
- Uncap ICP beakers and place on the large hotplate in the fume hood.
- Don the HF safety gear and get a clean 100 ml Teflon reagent beaker. Carefully pour enough concentrated HF into the reagent beaker for 2-3ml for each ICP-check beaker.
- Add 2-3 ml of this HF to each sample with a disposable pipette.
- Add 1 ml of 8% H_2SO_4 to each beaker and set hotplate to ~275 °F. The samples will dry down to a droplet of H_2SO_4 overnight.
- Cool the samples.

John says: Check the samples for solid material. An opaque, white, crystalline material indicates that the quartz is not clean enough for Be/Al chemistry. Fluffy white bits may indicate garnet. Samples may have a dark material which is probably illmenite or organic material, both of which can be HF-resistant. Illmenite or organic material can be ignored as they will not interfere with the chemistry and will only slightly contribute to the total error via an overestimation of the quartz weight.

- Add 5 ml of 1% HNO_3 to each beaker with the repeat pipettor, and then cap beakers. The solutions are now ready for ICP analysis, and should be not be weighed and recorded until immediately before being sent for ICP analysis.
- Weigh and record the weight of the beaker and solution with lid on.
  Solution weight = weight of beaker w/ solution - beaker tare weight
- Transfer to cleaned and labeled ICP-check centrifuge tubes once weighed.

To get ppm of sample, take measured ppm of solution and multiply by weight of solution (here, ~5.1 g). Divide by g in sample.
i.e., 3.6 ppm Al in ICP solution x 5.1 g of ICP solution = ~18 micrograms of Al in ICP solution, obtained from dissolving 0.1 g of rock. Thus, ~180 ppm Al in rock.

To calculate mg in sample, take ppm of sample (from above) and multiple by weight of quartz to be dissolved for chemistry. Divide by 1000.
i.e. 180 ppm Al in sample x 8 g quartz weight = 1.44 mg in sample

Sample Weighing, Spiking & Blank Preparation

- Determine the amount of quartz and carrier needed for each sample.

- For a batch of 6-11 samples of similar size, prepare 1 process blank.

- Label Jars with tape or Teflon marker.
  Select a Savillex jar large enough so you only fill the beaker 1/2 full. Estimate space for 5mls HF per gram of sample, the sample itself, and some water.
  Roseanne says: samples <10g use 90ml Savillex, samples ≥10g use 180ml+ Savillex.
  Use the same size beaker for the blank as for the samples. Name the blank based on the batch number (check the master book): B25, B26, etc.

- To reduce static, wrap Al foil around the beakers and use anti-static gate.

- If you are not using the entire sample, make sure the sample is well mixed so that the split taken is representative of the entire sample.

Weighing Sample

METHOD 1: *Weighing directly into Savillex jar. (For a sample size < 25g and Savillex jar < 180ml.)*
- Place a clean labeled Teflon jar wrapped w/ Al foil on the analytical balance (the Al foil reduces static).
- Tare the balance.
- Add desired amount of sample to the jar with clean spatula. Record the weight to 4 decimal places.
- Remove the jar from the balance and cover grains with MQ-water.

Optional weighing method:
METHOD 2: Weight by difference. (If the Savillex beaker + Sample will be > 200g.)
- *Wrap the Savillex jar w/ Al foil.*
- *Weigh the entire sample in its storage container. Record this weight as "Sample + Tare wt.".*
- *Empty the entire contents of the container into the Savillex jar.*
- *Weigh the empty container. Record this weight as "Tare wt."*
- *You will calculate your sample weight – "Sample + Tare" – "Tare".*
- *Cover the sample w/ MQ-water.*

Be very careful not to spill any sample in this transfer, since your sample weight is being determined by weighing the amount removed from the sample container.

  - Clean your spatula and work area between samples!

Adding Carrier (^{9}Be)

Since the natural concentration of ^{10}Be in rock is too low to be detected by AMS we add a known amount of ^{9}Be to each sample.

Record the initial weight of the working carrier bottle confirm that it is equal the final weight from the previous use. Remove all the Parafilm before weighing the bottles and invert the bottles a few times to homogenize the solution. When you are finished spiking all your samples, record the final weight of the carrier bottle.

Everyone's work depends on the integrity of the carrier. NEVER RISK CONTAMINATING THE CARRIER!

- We calculate the amount of carrier added to a sample by weighing the carrier bottle before and after each addition to a sample, rather than directly weighing the amount delivered to the sample.

- Tare the balance.

- Invert carrier bottle a few times to homogenize the solution. Be sure drops of condensation around the lid are taken up and mixed in. Weigh the carrier bottle and confirm that it equals the final weight from the previous use. Record this weight in both the log and your notebook.

- Remove the cap and pipette ^{9}Be carrier into your sample. Use the “Carrier only” 100 – 1000µL pipette and <u>MAKE SURE THE PIPET IS SET AT THE CORRECT VOLUME!</u>

- Immediately recap the carrier bottle and reweigh it. Work quickly, but carefully. Do not leave the carrier bottle open longer than necessary. We want to reduce evaporation as much as possible.

- Check the pipette tip to ensure that the entire amount removed from the bottle, which is what we are weighing, is delivered to your sample and no drops were left behind in the tip.

- If a drop remains in the pipette tip, remove the pipette tip and rinse it out with some MQ-H_2O directly into the sample beaker. Discard the tip and use a new tip.

- Reweigh the carrier bottle and record the weight. Calculate the amount of carrier added to your sample as you go along to ensure you have added the amount of carrier you think you have added.

- When finished, check that the carrier bottle cap is screwed on firmly and seal with Parafilm.

- Record all final weights in the Log Book and in your notebook. Record which carrier you used.
- All of the necessary data (sample and carrier weights) must end up in the database and a printed copy should be taped into the lab book.
- Print the chemistry tracking sheet and tape it to the bench in the Al-Be lab.

Blanks

Roseanne says:
The primary use of blank is to correct the sample ^{10}Be concentration for any ^{10}Be contamination occurring during the sample preparation.

As a general rule, prepare 1 blank per 8-10 samples if all samples are of similar size and are spiked with the same amount of carrier and you expect they will go through the exact same column chemistry. If sample weights should vary by a factor of 3, make up 2 blanks, one to represent small samples and one for large samples, or if you know or even just suspect some of your samples will require more column chemistry, prepare an extra blank.

The blanks are treated exactly like a sample. Use the same size Savillex jar as you used for your samples, rinse the sides down w/ MQ-water as you did for the quartz, and add the carrier in the exact same manner. Prepare blanks at the same time you weigh out and spike samples.

Sample Dissolution

***SAFETY INFORMATION**: You will be using very large volumes of concentrated HF in this step. Follow all safety precautions. Do not work alone in the lab while pouring large volumes of HF. The sample may react upon addition of concentrated HF, so add the HF slowly and use extra caution with a large sample. Do not swirl your samples for a few hours.*

Don gloves, sleeve guards, face shield, and apron. Weighed and spiked samples are taken to the hood. In the fume hood, for each sample:

- Add ~5 ml HF per gram of quartz from the bottle-top dispenser. (Reagent A.C.S. grade is ok)

- Screw the caps on the beakers, loosely at first, to allow for any release of gas if the samples are reactive. After a few hours, tighten the lids.
  Roseanne says: If quartz is clean, samples will not react when HF is added.

- If you have the time, just let the samples sit until they're dissolved, rather than putting them on a hotplate. It's the easiest and cleanest way to handle them. You eliminate having to deal with condensation on the lids, and the deposition of silica and fluoride salts on the lid. *A 5 gram sample will dissolve in about a day while a 50 gram sample will need several days. Swirling them several times/day helps. Make sure the caps are on tightly! Wear full protective gear including face shield when handling the bottles*

You can speed the dissolution up with heat, but first allow the samples to sit overnight before placing them on the hotplate. You can heat them initially with the lids off and at a very low temperature (~125 °F) for a few hours so you are sure they won't react violently. Then, put the lids on tightly and turn the heat up to ~300 °F. It is the combination of heat and pressure that really speeds things up. It is important that you used a large enough jar so there is enough headspace to accommodate the buildup of pressure.

Note: Savillex Teflon melts at 260 °C (500 °F). Keep the temperature below 220 °C (420 °F).
(The pancake griddles should not get this hot)
DO NOT put Savillex containers on the ceramic hotplate

If you are measuring Al, this is where you would take a split for stable Al measurement. Otherwise, continue with the dry down.

Evaporation & Dry Down

Once the samples have dissolved, or are nearly dissolved, you will evaporate off all the HF. Fe, Ti, Al, Be, and other ions are left as chloride salts ready for anion exchange clean up. Drying down the solutions eliminates F^- *and Si via the reactions:*

$H_2SiF_6(l) \rightarrow(\text{heating})\rightarrow SiF_4(g) + 2HF(g)$ *and* $HF(l) \rightarrow(\text{heating})\rightarrow HF(g)$

CAUTION: Perchloric acid is a very strong mineral acid and when heated above 150 ºC. becomes a strong oxidizer and can react violently with many oxidizable substances, such as paper and organic solvents, causing fire or explosion.
Do not have any paper or organic solvents in the hood!

- Open beakers, rinse droplets off of lids into jars with MQ-water

- Add ~ 0.5 – 1.0 ml conc. $HClO_4$ to each jar, using a disposable pipette. Place on a hotplate at 150 – 200 ºC to evaporate. You can set them on the pancake griddle hotplates overnight at the lower temp. It can take more than 24 hours for a large sample to completely evaporate.
  Perchloric acid is thick and drippy. Use a disposable pipette and keep a plastic beaker close by to put the pipette in.

- Place the vessels on the hotplate and evaporate at ~400 °F
  If leaving overnight, turn hotplate down to ~300 °F

- Dry them down completely, and then add another 0.5 ml conc. $HClO_4$ to each jar. Swirl them to get everything into solution and evaporate to dryness. If needed, use a little MQ-H_2O to rinse the sides down.

- Repeat once more. You will have done a total of 3 additions of $HClO_4$.

Perchloric acid will fume characteristically dense white fumes when the temperature is hot enough.

VERY IMPORTANT! Until the sample is completely dissolved, do not spill a drop! If you lose any solution at this point you are preferentially losing ^{9}Be (the carrier). Once the sample has completely dissolved, ^{9}Be and ^{10}Be are in equilibrium, and a spill will not affect the 10/9 ratios.

Small vessels that contain < 100 ml will dry down in a day. Larger volumes may take two days or more. Sometimes there are minerals that won't dissolve which you'll centrifuge out later. Place a sign on the front lab door indicating that a HF evaporation is in progress.

Chloride Conversion

- Once all HF and perchloric acid is evaporated, remove the Savillex jars from the hotplate and cool slightly before adding HCl.
  Note: HCl tends to splatter when added to a very hot beaker.

- Add ~2-3 ml 6M HCl (amount not critical). Wet all sample and dry down again at ~275 °F.
  Use the larger amount for samples with a very large residue. Rinse down the sides of the beaker with the HCl addition and/or a little MQ-water. The residue should re-dissolve almost instantaneously.
  Samples can be moved to recirculating hood after first HCl conversion

- Repeat the HCl addition (using ~2-3 ml 6M HCl) and evaporation step 2 more times
  You will have done a total of 3 additions of HCl

- Cool the samples completely. Then add 2 ml 6M HCl to each sample. Close the lid and allow them to dissolve.

Roseanne says: The final solution may be a deep yellow-green color due to $FeCl_3$*. Some samples may also have thrown a fine, powdery white precipitate that will not re-dissolve. This is probably* TiO_2*. No Al or Be is co-precipitated with the Ti and it can be removed by centrifuging before the anion exchange.*

Anion Exchange Columns

- Rinse 15-ml centrifuge tubes w/ MQ-water and label them w/ sample ID and “Anion”

- Transfer the samples to the labeled centrifuge tubes. You can pour it in, or transfer with a disposable pipette. If the sample is thick, sticky and full of residue it is easier with a pipette.

- Add another 1 ml of concentrated 6M HCl to the jar as a rinse and transfer to the centrifuge tube. There should be 3 ml in the tube. Samples are now ready for Anion columns.

The anion exchange columns remove Fe^{III} *(and some Ti) in the sample.*

Resin = AG-1 X8 200-400# mesh. This procedure uses 3 ml of resin (=filled to the 4cm mark)

The anion columns can be reused many times. Inspect the columns before use. When the anion resin gets too old it will take on a darker color and/or contains bubbles in it. If you need to repack columns, follow the procedure for column packing (see Appendix).

**You can reuse the Savillex jars you dissolved your sample in if they are 90 ml or smaller, and if they are clean. Sometimes the digestion leaves black residue behind. This can be wiped out w/ a KimWipe, but should then be followed by a quick leach w/ some dilute HCl or HNO3 (~5% is fine) on the hotplate. Use a new clean KimWipe for each jar.*

Prep SAMPLES:

- Centrifuge the samples for 10 minutes at 3500 RPM to remove solids.

Prep COLUMNS:

- Place waste containers under columns and drain water from columns. Discard water

- Examine resin for bubbles and look on top for dirt from previous samples

- Add 15 ml 1.2M HCl (fill headspace 1 ½ times). This washes the resin

- Add 9 ml 6M HCl (fill headspace 1x). This conditions of the resin

Anion Exchange Columns

COLLECT Beryllium fraction:

- Place labeled 30 ml Savillex vials (or 90ml Savillex) under columns.

- Load samples with disposable pipette. Use a new pipette for each sample. Drip the solution down the column wall, reaching as far as possible into the column with the pipette. Do NOT pour the sample into the column. Try not to disrupt the top surface of the resin. Allow them to drain through completely.

(Elute the Beryllium fraction with a total of 9 ml 6M HCL added in 3 aliquots – 3x resin volume, allowing the acid to drain through before the next addition.

- Add 1 ml 6M HCL
- Add 4 ml 6M HCL
- Add 4 ml 6M HCL

Clean columns:
Strip of Fe & Discard (you don't need to keep this)

- Replace waste containers
- Add 9 ml 1.2M HCl
- Add 9 ml MQ-water
- fill columns with MQ-water, cap, and store

John says: In strong HCl, Fe(III) forms a range of anionic Cl^- *complexes* $FeCl_4^-$, $FeCl_5^{2-}$ *and* $FeCl_6^{3-}$*, which bind tightly to the anion exchange resin. These will form a yellow-brown band at the top of the resin column. Al and Be do not form strong* Cl^- *complexes and elute from the column with the HCl. Some Ti in the form of* $Ti^{(IV)}Cl_6^{2-}$ *will bind, but most will drain through as cationic or neutral species, ending up with the Al + Be.*

Sulfate Conversions

- Add 1 ml of **0.5M H_2SO_4** to each Be/Al fraction and dry-down at ~275 °F. This will take ~ 4-6 hours. NEVER EXCEED THIS VOLUME OF H_2SO_4! *The dried residue from this step may turn an alarming dark-brown to black color due to organics which bled from the anion resin. Don't worry - it will disappear over the next couple of steps.*
  Note: Do NOT add peroxide with the sulfuric acid in this step as it will form Cl gas!

- Once dried down, cool the beakers and add 2 drops of **~2% H_2O_2** (hydrogen peroxide) (if using 30% H_2O_2, just use the smallest drop you can – though note that 30% H_2O_2decreases strength rapidly with time - we used 2 drops of 30% for a year-old bottle). Then add **2-3 ml of MQ-water** with disposable pipette. *The cakes will begin to dissolve, taking on an amber/gold - red color ($TiO[H_2O_2])^{2+}$) if Ti is present. Reheat the vials. The black charry material will disperse and disappear after a while. Dry the samples down again. Red may creep up walls.*

- Cool, repeat the **H_2O_2/water** (**2 drops ~2% H_2O_2+ 2-3 ml of MQ-water)** addition, and dry the samples a second time. At the end of this procedure, the samples should end up either as compact white cakes or small, syrupy droplets of involatile H_2SO_4. *Samples may be slightly yellow. If they remain charry or dark-colored, repeat the peroxide/water addition and dry them down a third time.*

- Take the samples up in **4 ml of MQ water**, containing a couple drops of **30% H_2O_2**or trace of 2% H_2O_2. *Warm them a little if necessary to get them back in solution. Don't risk evaporating too much water - keeping the acid strength low for column loading gives a sharper elution and cleaner Ti-Be cut. The samples are now in ~0.2 M H_2SO_4, ready for loading on the cation exchange columns. They can be stored indefinitely in this form.*

John says: Ca^{2+} can be problematic during sulfate conversion (before cation columns) because crystalline calcium sulfate ($CaSO^4$ – same composition as gypsum) may form, which is difficult to re-dissolve. Also, during cation exchange, Ca^{2+} (and other cations) compete for adsorption sites with other cations and causes cations to elute faster (e.g. Ti may elute with only 4-5 ml of acid rather than 10 ml, and Be elutes right after Ti).

John says: The cation column separates Al, Be and Ti. The column procedure using 2 ml of resin can handle 3-5 mg of Ti, if the total amount of Al and other metals is less than 3-5 mg. The method easily scales up and the volume of resin can be doubled or tripled.

Cation Exchange Columns

COLUMN SETUP

If reusing columns, simply setup and drain, if not reusing columns, follow below:

- *Place waste collection cups. Using a disposable pipette, add 2 ml of* <u>*DOWEX-50 X8 200-400#*</u> *cation exchange resin to each column. Fill the column with a little MQ-water and before it drains, slurry in a thin suspension of resin. This will immediately slow the dripping, and you can keep the column full with water while you slowly add more resin to the 2 ml mark. Tapping the column can help to get the dripping started. Be very careful not to trap air bubbles.*

STRIPPING & CONDITIONING RESIN:

- Strip the resin by filling each column headspace with 3 M HCl (This is 9 ml, equal to 4-5 resin-bed volumes.) Allow it to drain completely.

- Condition first with 9 ml 1.2 M HCl. Drain completely.

- Make up a beaker of 0.2 M H_2SO_4 containing a few drops of 30% peroxide (or trace of 2% H_2O_2.) This is 4 parts 0.5 M H_2SO_4 to 6 parts MQ water
  (**75 ml MQ-water + 50 ml 0.5M H_2SO_4 + 3 drops H_2O_2** works well)
  John says: Can use roughly 50-50 solution. *Accurate volumes are not important; the aim is to match roughly the acid strength of the sample solution.*

- Condition the columns by filling the headspace (9 ml) with above solution. Allow it to drain through.

- Discard any leftover conditioning acid in the waste container, and replace it with **0.5 M H_2SO_4 containing a dash of 2% H_2O_2.** (about 0.5 ml peroxide to 50 ml acid). Remove waste containers and discard waste in acid-waste container.

Cation Exchange Columns

ELUTE Ti:

- Place labeled 30 ml Nalgene ("Ti/Al Fraction") bottles under columns. *Use 60 ml Nalgene bottles if doing "double" (4ml) cation columns*

- Load each sample onto its column using a clean disposable pipette. Ti will form a narrow brown band at the top of each resin bed, and then begin to move down the columns. Allow the sample to run into the resin completely.

- Add 1 ml of **0.5 M H_2SO_4 w/ trace 2% H_2O_2** to each beaker as a rinse. Swirl the beakers to pick up any droplets of the original solution left over from the first load. Add the rinse solutions to the columns after they have drained. Allow this to run in completely.

You will add 10 ml (5 bed volumes) of **0.5 M H_2SO_4 w/ trace 2% H_2O_2** to each column in three additions (4 ml + 4 ml + 2 ml). If Ti is present, you can see the Ti band move down the resin and elute from the columns. For samples containing Ti but very little Al, the Ti will elute slower and it may be necessary to add another 1 – 4 ml to completely remove Ti.

- Add 4 ml **0.5 M H_2SO_4 w/ trace 2% H_2O_2**.
- Add 4 ml **0.5 M H_2SO_4 w/ trace 2% H_2O_2**. Allow first 8 ml to drain through completely.
- Add 2 ml **0.5 M H_2SO_4 w/ trace 2% H_2O_2**. Drain.
- Add additional **0.5 M H_2SO_4 w/ trace 2% H_2O_2** in 1 ml increments to completely remove Ti.
- Repeat above step until columns are no longer dripping yellow and eluate is clear

Roseanne says: You can safely elute until the eluate is clear. If the drips are immediately yellow, the column is probably overloaded with Al. Take note of this, but continue on. You will probably have to do a second column to clean up the sample. If you suspect an overload, still add 10 ml of 0.5 M H_2SO_4 w/ trace 2% H_2O_2 to the columns.
John says: 12 ml of the sulfuric acid eluent can be run through the columns without risk of losing Be. Yellow drips start with the first Ti - this shouldn't be immediate upon adding the acid. Drip will go clear when Ti is gone. Do not add >14 ml.

Make a note in your notebook how many mls is took to elute the Ti, how dark or light, narrow or broad the Ti band is, and when it started dripping yellow.

- Remove Ti/Al Fraction bottles

Cation Exchange Columns

ELUTE Be:

- Place 30 ml labeled Savillex teflon vials under each column. Reuse from before.
- Add 10 ml (5 bed volumes) of 1.2 M HCl ("10%" HCl). This will have to be added in 2 lots. There is no need to allow the first to drain completely before adding the second. Allow it to drain through completely.
- Elute Blanks with 12 ml 1.2 M HCl (2 additional mls). With no other ions "pushing" the Be through the column, it takes a little more to get the Be out.

ELUTE Al:

- Replace 30 ml Nalgene ("Ti/Al Fraction") bottles under columns.
- Elute Al from the columns with 6 ml (~3 bed volumes) of 3M HCl.

Clean Columns:

- Flush columns with MQ-water
- Fill columns with MQ-water, cap, and store.

Tip: make sure there are clean centrifuge tubes for the next step. Tubes should be washed in dilute nitric - sit about a week, rinsed twice with water and dried in oven.

Beryllium Recovery

Dry down

- Add ~5 drops of 7.5 M HNO_3 to each Be sample and dry on a hotplate at 275 °F (dry down will take approx. 5 hrs after 2ml columns. After 4ml columns will take ~8-10 hrs. If drying overnight, put hotplate at 200 °F (~100 °C)

Roseanne says: Do not exceed 300℉ during dry down. Time your dry-down so you can remove vials soon after completion. Drying on high heat, or with excessive time "cooking" the droplet of H_2SO_4 after evaportation may lead to the cristilization of beryllium-sulfate ($BeSO_4$), which is difficult to dissolve in the next step.

- Once the Be fractions have dried, cool and remove them from the hotplate. The Be fraction should have contracted to a tiny, clear droplet of concentrated H_2SO_4.
  Occasionally they will form a small white cake. This usually indicates the presence of either Ti or Al

John says: If the Be sample is troublesome to dissolve, even with heat, additional acid can be added as an aid. A lot of precipitate that won't dissolve implies a problem, likely calcium sulfate. Intractable samples usually can be dissolved with the addition of a lot of extra acid and heat. Such samples almost certainly will need to go back through cation columns again. Check the Ca ppm in the original ICP check. If the original Ca was low, this problem should never materialize.

Transfer to Centrifuge Tubes

- Label cleaned 15-ml screw cap centrifuge tubes for each sample.

- Pipette 2 ml of 1% HNO_3 (TM-grade) into each vial. If pure, the Be fractions will dissolve freely. If they don't, you can warm the vials for a few minutes on the edge of the hotplate with the lid on, or just wait a few hours.

Make sure your Be fractions are completely dissolved before moving on to the next steps

- Carefully pour the solution into a labeled centrifuge tube. Don't worry if a last drop clings to the floor of the Be beaker, but if its large, you can pick it up w/ a disposable pipette.

- Immediately add another 2 ml of 1% HNO_3 into the vial as a rinse, and transfer to the c-tube.

Brenda says: Precipitate, ignite, and pack Al and Be samples shortly before the accelerator run in which they will be measured. Superstition among practitioners hold that Al-and Be-oxides slowly rehydrate if left for weeks or months after baking and will produce lower beam currents. Cathodes packed in advance of a run (or cathodes which have to be stored after a cancelled run) should be stored in the desiccator cabinet in the Al-Be lab.

Beryllium Hydroxide $Be(OH)_2$ Precipitations & Washes

You will precipitate the samples two times, and do 3 washes with a pH adjusted water. This step cleans up your sample and gets rid of Boron contamination. You will see your samples get more clear and translucent with each step.

- Add ~ 250 µl NH_4OH to the centrifuge tube, cap it, and mix well on the vortex mixer. You should see the white $Be(OH)_2$ precipitate swirling around. Using a clean pipette tip for each sample, remove ~ 1 µl to check the pH. It should be close to 9. If the pH is below 8.5, add more NH_4OH (add ~30 µl at a time until you reach the correct pH).
  Roseanne says: If you overshoot and the pH is 10, leave it. It's better a little high than low.

- Centrifuge for 10 minutes at 3500 RPM.

- LOOK AT YOUR SAMPLES CAREFULLY AT THIS POINT and compare the sample Be to the blank Be. They should all be the same size.
  Roseanne says: If the samples are larger than the blank, it indicates Al and you probably need to do a second cation column. If the sample is smaller than the blank, you may have lost Be. But, before you make this assumption, check the pH of the supernatant. If it is just pH 8, try adding more NH_4OH and bring the pH to 9. Centrifuge again. If it is still small, just proceed to the 2nd precipitation. This always improves the clarity and often the size of the precipitate. If the precipitate is still too big (indicating that there is probably Al in the Be fraction) go to the section on preparing a sample for a second column (Appendix).

- Pour supernatants back into labeled 30-ml Savillex Teflon. Be careful not to pour out any precipitate.

- Do a 2nd precipitation: Add 100µl of 7.5M HNO_3 to all your samples. Swirl on the vortex mixer until precipitate has dissolved completely. Bring the volume up to 5-ml with MQ-water. Swirl again on vortex mixer. Re-precipitate $Be(OH)_2$ by adding ~100µl TM NH_4OH. Mix well on the vortex mixer.

- Centrifuge for 10 minutes again at 3500 RPM. Decant supernatant into same rinse bottle.

Roseanne says: After precipitating the $Be(OH)_2$, do not let the samples sit around. Always centrifuge and pour off the supernatant immediately. Impurities in the supernatant may precipitate out of the solution over time, defeating the purpose of precipitation and wash steps.

pH 8 RINSES:

Roseanne says: This step presumably gets rid of any Boron-10 contamination, an isobar of ^{10}Be.

- Bring solution volume up to 5 ml with the pH 8 adjusted water (pH8 water is MQ-water w/ few drops NH_4OH). Swirl on the vortex mixer, centrifuge, LOOK!, and decant the supernatant into the rinse bottles. Do three pH 8 rinses in total.

$Be(OH)_2$ Combustion

Transfer Samples to Quartz crucibles

- Set up clean crucibles in the Quartz sled, and on the sled, write the sample ID next to the crucible. If possible, do not fill all 10 positions on the sled, and make a diagram in your notebook with the position of each sample in the sled. *Samples located over sled legs may take slightly longer to dry-down on hotplate.*

- Dissolve the $Be(OH)_2$ in the C-tubes with 25 µl 7.5M HNO_3.
  Good place to pause overnight or longer.

- Swirl on the vortex mixer.

- Bring up to speed in centrifuge (3500 RPM @ 0 seconds) to ensure all liquid is collected.

- Transfer to the crucible using the 200 µl pipette.
  Reach all the way into crucible with pipette tip, try not to get liquid on sides of crucible

- With another pipette, add another 25 µl 7.5M HNO_3 as a rinse. Pick this up w/ the same pipette you used for the sample transfer, and add this to the crucible. Use a new pipette tip for each sample. Cover all crucibles with lids except the one into which sample is being transferred.

Hotplate Dry-Down

After all samples have been transferred to the crucibles, place the sled on ceramic hotplate in the fume hood with crucible and sled covers off. Begin with a low temperature. You want the sample to dry on the bottom of the crucible and heating it too fast can result in it drying around the sides making it more difficult to get the sample out of the crucible after its been combusted. Suggested times:

- 200 °C for 15 minutes
- 250 °C for 75 minutes
- 300 °C for 150 minutes
- 350 °C for ~30+ minutes (until dry)
- 400 °C for 15 minutes (once dry)

Samples will likely form small white cakes at the bottom of crucible. Samples may dry-down without forming white cakes, in which case the sample is very difficult to see. Don't worry, it is not lost! Assuming all transfers went well, the $Be(OH)_2$ *will appear after combustion.*

Cobust Samples

- Fetch a propane torch from the flammable cabinet,
- Set up torch, ring stand, and crucible tongs in the fume hood
- Light the torch.
- After removing the crucible covers from the vial, grasp the vial with the tongs about halfway up. Wave the crucible through the flame cautiously at first (if not completely dry, sample may sputter and bubble up if heated too fast). Once the sample begins to glow orange, hold it in the flame for 30 to 40 seconds more. Some samples never glow, in which case 2 minutes is more than sufficient. Remove it from the heat and place it back in the same spot in the quartz sled in the hood to cool.
- Once cool enough to handle, cover with labeled crucible covers, and store in the glove box for loading. Samples should be loaded as soon as possible after combusting.

Tip: make sure your cathode loading tools are clean for the next step. The cleaning procedures are on the following page.

Loading Cathodes for LLNL

Equipment List

- Cathodes
- Drill Rods, #55
- Stainless Spatulas (scrapers)
- Quartz rods
- Niobium powder
- Scooper
- Cathode holder/stand
- Hammer
- Dust Mask
- Ionizer

Be extremely careful when working with beryllium metal (oxide form). Beryllium is a known health risk and all precautions must be followed when working with it. Always work in the glovebox, and wear a dust mask.

- **Label Cathodes**
  - Make sure you are using cathodes that have been cleaned, and check each cathode to make sure the hole is centered, and is the correct size. We occasionally get cathodes with holes that are too small. Check this with the drill rod.
  - Label the cathode with the sample number, full sample name and LLNL BE#.

- **Clean Drill Rods**
  - If you are starting with new drill rods, you only need to wipe them down with methanol. If you are reusing your drill rods, first wipe them off with methanol. You can rinse them with some water, but dry them off immediately, because they rust easily. Then, clean the ends off with some fine sandpaper (400 or 600 grit). Finally, rinse them off again and wipe them down with methanol.

- **Stainless Spatula's (Scrapers)**
  - These should be cleaned in a 10% nitric solution overnight. They should also get at least 1 hour in the ultrasonic bath. Pour off the cleaning acid into the 2nd spatula cleaning acid bottle, and then rinse the spatulas thoroughly. Wrap them well with KimWipes and dry them in the oven.

- **Quartz Rods**
  - These are cleaned in a 20% nitric solution. Follow the spatula instructions. They have their own teflon bottle labelled "glass cleaning".

SET UP IN THE GLOVEBOX

- Wipe down the glovebox with MQ-water thoroughly.
- Place ionizer in the glovebox
- Set up your tools on a clean KimWipe.
- Set up the cathode holder on a KimWipe.
- Set up the following waste containers:
  - Be-waste plastic bag for used crucibles, KimWipes, and gloves.
  - A waste cup with isopropanol for the used drill rods
  - A waste cup with MQ-water for the used spatulas, quartz rods
  - A waste cup with MQ-water for the used crucible covers
- You will need the tiny scoop and niobium powder and a hammer. Wipe off the hammer with some isopropanol first.
- Put on clean gloves and sleeves, and close the sample door from the inside. You'll be here for a while, so you might want to grab a stool.

LOADING THE CATHODE

- Place the cathode on the holder
- Fetch the next crucible and take the lid off.
- Add 2 level scoops niobium. You can adjust this up or down for larger and smaller samples.
- Using the quartz rod first, gently mix the niobium into the sample. Once the Niobium is mixed in, static is usually not a problem, but before that, the Beryllium can be rather flaky.
- Grind the Niobium and Beryllium together, as you would grind something up with a mortar and pestle.
- Using the stainless steel scraper, scrape together the mixture into the bottom.
- Repeat the quartz rod grinding and scraping a few times.
- When the sample is fully homogenized, use the scraper to collect it into the bottom. You can also tap the crucible on your work surface to get it to collect.
- Carefully tilt the crucible on the edge of the cathode, at a 45 deg. angle or so, and gently tap the crucible, and the cathode with the scraper. This will cause it to pour down onto the cathode. If it doesn't slide right into the hole, simply tap the sides of the cathode. It will.
- Using the drill rod, hammer the sample into the hole. Hammer hard for about 20 taps, then remove the drill rod, take the sample off the holder and tap it a few times on the holder. Then hammer another 20 pretty hard taps. Repeats the hammer followed by tapping a total 3 times, and finish off with about 10 more gentle taps. ~70 total hammer taps!
- You can gently turn the cathode upside down on the clean KimWipe to check that it isn't going to spill out.
- Store the cathode in a labeled storage vial, and double check that all your labels are correct.
- Wipe down your work area before loading the next cathode.
- Store samples in desiccator until they are shipped to LLNL.

Appendix

Preparing Resin and Packing Columns

Resin Preparation

- Soak the resin in 6M HCl in the designated bottle. After a few hours, decant the HCl into a waste container. Fill the bottle w/ MQ-water, shake and decant after the resin has settled. This will take a couple of hours. Do this 2-3 more times so that it is no longer strong acid.

Packing columns with resin

- Before filling the columns with resin, fill the column with water and make sure it drips. Usually tapping the column up and down a few times breaks the surface tension and it'll begin to drip. Or, squirt in a few drops of methanol before adding water.

- Then, fill the column with MQ-water and using a disposable pipette immediately add some resin from the batch soaking in MQ-water. The initial resin will settle onto the frit and immediately slow the water dripping through. Keep the water volume full while you add the resin. The resin should settle out gradually and evenly as it is added thus avoiding air bubbles getting trapped in the resin bed. Continue to add resin to the column until the proper volume is reached. If you do get air bubbles, fill the column with some water and suck up the resin with the pipette to re-suspend it and usually it will resettle without bubbles.

You've overloaded a column! Preparing samples for a 2nd Cation Column

- You still have to precipitate the sample. This is the only way to remove the sulfuric acid. So, do that, and note the volume of precipitate.
- Dissolve the BeOH precipitate in 2ml of 3M HCl and transfer it back to a Teflon beaker.
- Then follow the normal procedure for Sulfate Conversions.

Acid strengths:

Chemical	Molecular Formula	Approx. Strength of Concd. Reagent	Molarity of Concd. Reagent
Hydrofluoric Acid	HF	49.0 %	28.9
Hydrochloric Acid	HCl	37.2 %	12.1
Nitric Acid	HNO_3	70.4 %	15.9
Sulfuric Acid	H_2SO_4	96.0 %	18.0
Ammonium Hydroxide	NH_4OH	56.6 %	14.8

DOUBLE CATION COLUMN – (4ml resin)

- Use the larger columns.
- Fill w/ 4 ml resin. *Note, that the columns are marked w/ height in cm., and not volume. 4 ml is just under the 6 cm. mark.*

STRIPPING & CONDITIONING RESIN:

- ~ 18 ml 3 M HCl (Fill to the top twice.) Allow it to drain completely.
- ~ 18 ml 1.2 M HCl. Drain completely.
- ~ 18 ml 0.2 M H_2SO_4 containing a trace of 2% H_2O_2. Drain completely.

Remove waste trays and discard acid into waste containers.

ELUTE Ti:

- Place 60 ml rinsed and labeled Nalgene (“Ti/Al Fraction”) bottles under columns.
- Load each sample onto its column using a clean disposable pipette. YOU STILL LOAD in 4ml. Allow to soak into the resin completely.
- Add 1 ml 0.5 M H_2SO_4 containing a trace of 2% $H_2O_2$to each beaker as a rinse and add to the column. Drain completely.
- Add 18 ml of 0.5 M H_2SO_4 w/ trace 2% $H_2O_2$to each column. It may be necessary to add a further 4-5 ml of 0.5 M H_2SO_4 to completely remove Ti. Note how much you use.

ELUTE Be:

- Place 30 ml labeled Teflon vials under each column.
- Add exactly 20 ml of 1.2 M HCl.
- Elute Blanks with 22 ml 1.2 M HCl (2 additional mls). With no other ions “pushing” the Be through the column, it takes a little more to get the Be out.

ELUTE Al:

- Replace 60 ml Nalgene (“Ti/Al Fraction”) bottles under each column to collect the Al fraction.
- Add 12 ml of 3M HCl.

Clean Columns:

  - Flush columns with MQ-water
  - Fill columns with MQ-water, cap, and store.