

UNIVERSITY OF PENNSYLVANIA LABORATORY PROCEDURES FOR PREPARATION OF Be AND Al SAMPLES

I. PHYSICAL PRETREATMENT

A. Sample crushing and coarse grinding (In Geology Department)

1. Rock sample is crushed in jaw crusher, and ground using plate grinder, being careful not to grind the sample too fine.
2. Sample is sieved through 420 μ sieve. Plate grinder is readjusted and any material >420 μ is put through grinder and sieve again. This sequence is repeated until all rock material is \leq 420 μ .

B Fine Grinding (in DRL)

1. Sample is weighed.
2. Sample is sieved through 150 and 250 μ sieves.
3. Small quantities of rock material >250 μ (just enough to cover SiC balls in grinding chamber) are ground in Spex Wig-L-Bug mill for short periods of time (1 to 2 minutes depending on individual rock sample).
4. Material is stirred through 250 μ sieve. Material >250 μ is recycled through mill and sieve until all of sample is < 250 μ .
5. Sample is then sieved through 75 and 150 μ sieves. 75-150 μ fraction is weighed and bagged. 150-250 μ fraction is weighed and bagged. BY CAREFUL CONTROL OF GRINDING TIME, THE <75 μ FRACTION CAN BE MINIMIZED AND THE TWO LARGER FRACTIONS MAXIMIZED.

II. CHEMICAL PRETREATMENT - Deionized water and Teflon digestion vessels are used throughout procedures that follow. (Whenever something is weighed, the weight is recorded.)

A. Aqua Regia.

- 1. If 150 to 250 μ fraction is sufficient in size it is boiled in Aqua Regia for 2 hours. (If not large enough, combine with 75-150 μ fraction and boil in Aqua Regia.)**
- 2. Cool sample and allow to settle. Decant and save supernate (ALL SUPERNATES ARE LABELED AND SAVED).**
- 3. Sample is washed with H₂O, allowed to settle and supernate decanted. This is repeated until washes no longer have any yellow iron coloration and pH is ~ 3 to 4.**
- 4. Sample is dried in teflon beaker on hot plate and weighed. (If ICP analysis is not being done on preliminary fractions drying and weighing at this step can be omitted).**

B. HF Etch (helps to disaggregate any remaining compound grains).

- 1. Boil sample for 15 minutes with 1 H₂O : 2 HF. Decant supernate and wash sample with H₂O (very fine material will go with supernate).**
- 2. Sample is dried in teflon beaker and weighed.**
- 3. If using 150 to 250 μ fraction sieve through 150 μ sieve to remove any material < 150 μ after chemical pretreatment. If using combined 75 to 250 μ fractions, sieve through 75 μ sieve to remove any material < 75 μ .**

III. Heavy liquid Separation

A. Bromoform ($\rho \geq 2.70$)

- 1. Sample is added to 500 ml separatory funnel and heavy (usually dark) minerals are allowed to settle to bottom of funnel. Floating material is stirred until no additional trapped heavier particles settle out.**

2. Heavy fraction is removed through stopcock of separatory funnel onto filter paper in regular funnel. This and all subsequently removed fractions are washed with acetone repeatedly to remove bromoform (bromoform/acetone mixture is saved for recycling). This and all subsequently separated mineral fractions are air dried (covered with filter paper) and weighed.
3. Density of bromoform is lowered slowly with acetone until next fraction (usually "Q") begins to settle out. Remaining fraction (if sizeable) is stirred as in step A. 1. above.
4. "Q" fraction is allowed to drain into filter paper lined funnel. 10 ml of filtered solution is weighed in a volumetric flask to determine current density of bromoform and recorded.
5. "Q" can be put back into separatory funnel with bromoform of the same density and stirred to allow any grains of lighter material to float.

IV. MINERAL STAINING AND IDENTIFICATION

A. Mineral Staining

1. About 1 cc of "Q" fraction (or other desired mineral fraction) is placed in a small disposable plastic or teflon beaker. Conc. HF to just cover is added and allowed to stand for 1 minute, then decanted and discarded. Sample is rinsed with H_2O .
2. Sample is rinsed with $BaCl_2$, then with H_2O .
3. Sodium cobaltinitrite is added to sample for 1 minute and discarded, followed by a H_2O rinse.
4. Rhodizonate solution is added to sample for 1 minute and discarded, followed by a H_2O rinse.
5. Sample is air dried on filter paper.

B. MINERAL IDENTIFICATION

1. Dry sample is examined under microscope.
2. Orthoclase (K-spar) is stained yellow.

3. Plagioclase (> 3% An) is stained pink to red.
4. "Q" remains unstained, but may appear more or less frosted.
5. After staining and microscopic examination sample can be put back through bromoform for further separation if necessary.

V. CHEMICAL PREPARATION OF Al AND Be SAMPLES

Relinized water and Teflon digestion vessels are used throughout procedures that follow.
(Whenever weight is determined, said weight is recorded.)

A. Sequential dissolution of "Q" sample.

1. Fraction I dissolution:

25 g of "quartz" are dissolved with 30 ml of hydrofluosilicic acid on hot plate at 175 C; additional acid is added as needed. First "Q" fraction usually takes at least 24 hours to dissolve. Undissolved rock is monitored by measuring in a 50 ml centrifuge tube. (Volume of initial undissolved 25 g portion is approx. 20 ml.)

2. When it appears that sufficient rock has dissolved, remaining rock and solution are centrifuged. Supernate is decanted and saved as Fraction I. Sample is washed with H₂O, centrifuged, and decanted a total of 2 or 3 times. All washes are added to fraction I. Undissolved sample is dried on hot plate in digestion vessel, cooled and weighed.

B. Fraction II and/or III are prepared following Steps A.1. through A.2. above. The ultimate goal is to end up with between 5 to 10 grams of undissolved "quartz" sample.

C. Final Quartz Fraction

1. Combined Be - Al sample.

- a. Weigh 5 grams of quartz in disposable weighing pan on analytical balance.
- b. Add 1 ml of beryl carrier by pipetting onto sample and again weigh on analytical balance.
- c. Wash all quartz and carrier into digestion vessel with 10 ml of water.

- d. Add 20 ml conc. HF and dissolve sample on 100 C hotplate for a minimum of 14 hours with additional HF added as needed. When all sample is dissolved, evaporate to dryness.
- e. Add 10 ml conc. HCl and evaporate to dryness (to get rid of HF).
- f. Repeat step e.
- g. Dissolve dried sample in about 20-30 ml 0.5N HCl. Centrifuge and decant if there is any undissolved material remaining. Pour supernate into weighed 100 ml volumetric flask. Wash residue 2 to 3 times with 0.5N HCl centrifuge and decant into volumetric. Make volumetric up to 100 ml with 0.5N HCl and weigh on analytical balance.
- h. Pipette 5 ml of sample solution into each of 2 previously weighed 10 ml volumetric flasks labeled A & B.
- i. Weigh 100 ml volumetric flask after removing ICP samples. Add 1 ml Al carrier and weigh again.
- j. Weigh ICP sample added to each 10 ml volumetric flask. To B add 1 ml of Al "AA" solution with pipette and weigh flask again. Make each volumetric up to 10 ml with 0.5 N HCl. Shake well and transfer to labeled sample bottles for shipment to ICP laboratory.
- k. Pour the approx 90 ml of sample solution (with carrier added) back into same teflon vessel that it was dissolved in (after rinsing teflon vessel, wiping dark film out with kimwipe and again rinsing vessel). Evaporate solution to dryness on hotplate at 175 to 200 C. Dissolve in 10 ml of 0.5N HCl/2% NH₄Cl solution. Transfer to 15 ml centrifuge tube
- l. Using pH paper or appropriate mixed indicator to monitor pH, add 1:1 NH₄OH bring pH to 8. Allow to stand, recheck pH and add more NH₄OH if necessary. Add 2-3 drops of 4M NaOH to bring pH to 9. Centrifuge and save supernate as Supernate #1.

- m. Add H_2O to precipitate in centrifuge tube to bring up to 5 ml and vortex. Monitor pH with indicator or pH paper and bring pH to 5 with 2.5% HF and shake or vortex. Allow to stand briefly and adjust pH if necessary. Add 1:1 NH_4OH to bring pH back up to 8. Centrifuge and decant supernate into small digestion vessel. This is the Be fraction. The precipitate (Al sample) remaining in 15 ml tube is put aside until Be is finished being processed.

2. Be FRACTION.

- a. Be supernate is evaporated to dryness on 200 C hotplate. Dried sample is then re-dissolved in 10ml 2.5% HF and pH adjusted once again to 8 with 1:1 NH_4OH and centrifuged. The Be Solution is decanted back into the small teflon digestion vessel and once again evaporated to dryness on 200 C hotplate. Any precipitate from this step is saved to be combined with Al portion previously saved.
- b. White NH_4F residue is expelled at 200 C in a venting oven in a hood. (NH_4F can explode when combined with perchloric acid in the next step).
- c. 1ml conc. perchloric acid is added and evaporated to dryness on 200 C hotplate. This step is repeated once again to oxidize any organic matter suspected of being major source of ^{10}B interference in the accelerator.
- d. 1 ml Conc. HCl is added and evaporated to dryness on 200 C hotplate, to convert sample to $BeCl_2$. This residue is dissolved in 10ml 0.5N HCl (occasional minor turbidity caused by small amounts of Ti can be centrifuged away).
- e. Ultrapure NH_3 gas is bubbled through the final Be solution using disposable automatic pipetter tips attached to appropriate tubing. Resulting precipitate is centrifuged and supernate is decanted and saved as supernate #2. Precipitate is washed with water made slightly basic with ultrapure NH_3 gas, centrifuged and supernate added to supernate #3. This washing is repeated 1 more time. Add 0.5 ml of above ammoniated H_2O to resulting precipitate and use disposable micropipette to transfer $Be(OH)_2$ to alundum crucible. Sample is dried in oven at 110 C to remove H_2O . Sample is then converted to BeO in furnace at 800-850 C for 1 to 1 1/2 hours.

3. Al FRACTION

- a. Dissolve Al precipitate in 10 ml conc. HCl and transfer to hotplate.
- b. Add 10 ml conc. HCl and evaporate to dryness (to get rid of HF).
- c. Repeat step b.
- d. Dissolve in 10 ml 0.5N HCl/2% NH₄Cl solution. Heat. Adjust pH to 8 with 1:1 NH₄OH and let stand briefly. Centrifuge, decant and save supernate as supernate #3.
- e. Wash with ammoniated H₂O, centrifuge, and save supernate with supernate #3. Repeat washing once again.
- f. Transfer Al(OH)₃ sample to quartz crucible by pipetting in a similar fashion to that used for Be.
- g. Dry in oven at 110 C to remove H₂O.
- h. Convert to Al₂O₃ in furnace at 800-850 C for 1 to 1 1/2 hours.