

ICP Sample Digestion

Purpose:

To reduced complex oxides for use in ICP-OES by concentrated acid at high pressure and temperature. The Parr Bomb acts as a pressure cooker. As it is heated, it remains sealed and builds up very high pressure which greatly accelerates reactions.

Precautions (Warnings)

For the safety of the user and the equipment some precautions must always be followed

1. EXPLOSION HAZARD. Violent oxidation can occur, leading to high pressures. The higher pressure accelerates the reaction further and such a “runaway reaction” may cause an explosion.
 - a. Expected pressures do to acid and organic loads must be estimated before use and be lower than the maximum of 1800 Psi
 - b. The Oven Temperature must be checked regularly
2. All samples must be digested in an open beaker first to complete potentially explosive reactions.
 - a. For sintered and calcined samples 10 min in the teflon insert is sufficient
 - b. For carbonates or other carbon containing minerals a longer time and potentially the use of heat should be used to ensure oxidation of all carbons before continuing
3. Parr Bomb should be heated when there is minimal potential exposure
 - a. i.e. When almost no one is around
4. A note must be placed on the oven and Lab door stating it is in use
5. Parr Bomb must never be operated at temperatures greater than 250°C
6. Never stir in the liner - swirling is ok
7. Never pry the lid of the liner, only push and twist
 - a. If it does not come off let it sit for a few hours and try again
8. Wear a lab coat, gloves(vinyl??) and safety glasses when using or even touching the bomb or liners

Maximum inorganic sample 2 grams

Maximum organic sample 0.2 grams and 6 mL HNO₃

Maximum Pressure 1800 psig

Maximum Temperature 250°C

Set up:

The key to a safe and clean (minimal contamination) digestion is proper setup!!

1. Clean the space in the fume hood you intend to use
2. Place oven in the fume hood on the left side and plug in
 - a. This way the door can swing open with the sash down
3. Create a workspace a few paper towels thick
4. Place the HNO₃ and HF to the back of your workspace, Pipet and teflon insert to the front
5. Obtain 2 pipet nozzles and place with pipet
6. Fill a 250 mL beaker with water (I use DI) and place on workspace.

Procedure:

1. Mortar and Pestle sample into a fine powder
2. Weigh out about 50 mg of sample - Record value
3. **For carbon containing samples DO NOT PROCEED see appendix**
4. Add 50 mg of sample into Clean teflon insert
 - a. A quick pour from weight paper is best - you really don't want to get any on sides or lip
5. **Everything from here on must be done in the fume hood**
6. Using the pipet slowly add 5 mL of HNO₃
 - a. Reactions may occur so be careful
 - b. Do not get any acid on the lip of the teflon insert
7. Using the pipet (new nozzle) slowly add 2.5 mL of HF
 - a. Do not get any acid on the lip of the teflon insert
8. Gently swirl solution and let sit for 10 min
 - a. Oven can be turned on to begin heating at this point
9. Following Parr Bomb Manual carefully place teflon insert into the bomb and tighten lid
10. Place bomb into the oven set temp to max and wait for it to reach 230°C
11. Set timer for 2 hours
12. Monitor Oven temperature regularly
 - a. Adjust temp knob as needed to maintain 230°C
13. Once time is up turn off oven and allow to cool to 100°C
14. Remove bomb and allow to cool to room temp before opening (**Do not attempt to force cool**)
 - a. Follow Parr manual
 - b. Do Not pry teflon lid only push/twist - if wont open let sit for a few hours and try again
15. Complex with H₃BO₃ to prevent precipitation of digested species (No?) (dry down instead)
16. Empty teflon insert into proper container (not glass HF is still active and can eat glass)
17. Rinse teflon liner with DI (millipore)

H₃BO₃ Complexation (This in not enough according to OSU's lab man)

1. Add 1.5 g of H₃BO₃ powder to the solution in the teflon insert
2. Swirl
3. Following Parr Bomb Manual carefully place teflon insert into the bomb and tighten lid
4. Place bomb into the oven set temp to 200 and wait for it to reach 190°C
5. Set timer for 30 min
6. Monitor Oven temperature regularly
 - a. Adjust temp knob as needed to maintain 190°C
7. Once time is up turn off oven and allow to cool to 100°C
8. Remove bomb and allow to cool to room temp before opening (**Do not attempt to force cool**)
 - a. Follow Parr manual
 - b. Do Not pry teflon lid only push/twist - if wont open let sit for a few hours and try again
9. Empty teflon insert into proper container (not glass HF is still active and can eat glass)
10. Rinse teflon liner with DI (millipore)

Appendix

Notes for use with ICP:

1. Also, run one blank for every eight samples.

Note: Samples should be spiked, equilibrated and analyzed as soon as possible after completing the above digestion. Ideally, samples should be taken out of the oven just before you are ready to spike and analyze. If the samples sit around the results will be poor.

Using the pipet:

1. Set desired amount (most accurate between 1 mL and 5 mL)
2. Put nozzle on tip
3. Dip nozzle tip in liquid
4. Pull out and push trigger to first click
5. Dip back into liquid and slowly release trigger pulling in liquid
6. as you remove from liquid touch nozzle tip to side of container to remove excess liquid
7. In desired location slowly push trigger to first click and hold for 3 sec (small shakes may help)
8. In discard container empty nozzle with full trigger pull
9. Rinse nozzle with water with a few times
10. Discard nozzle in trash

Predigestion for carbon containing samples

18. **Pre-digest to oxidize labile, potentially explosive organics.** Add 3 mL of conc. HNO₃ (ACS Plus Grade) under the fume hood. Some samples containing carbonate minerals will foam strongly, so add carefully at first. Close beaker. Heat in a 90°C hot block for at least 3 hours.
19. **Replace any lost acid.** Check the volume of HNO₃ remaining in order to determine acid loss to evaporation. Add the volume of HNO₃ that has been lost, if any.
20. **Parr Bomb Digestion.** Transfer sample into the Parr Bomb Teflon cup

Honeywell

Partial Vapor Pressure of HF over
Aqueous Solutions of HF

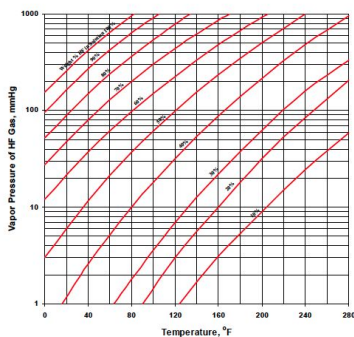


Table 4 Acids and mixtures of acids tested for the microwave-assisted dissolution of ceramic materials

Order	Acid or mixture of acids
1st	HCl
2nd	HNO ₃
3rd	H ₂ SO ₄
4th	HCl + HNO ₃ (3 + 1 v/v; <i>aqua regia</i>)
5th	(NH ₄) ₂ SO ₄ 20% m/v in H ₂ SO ₄
6th	HCl + HF
7th	HNO ₃ + HF
8th	H ₂ SO ₄ + HF
9th	HCl + HNO ₃ (3 + 1 v/v) + HF
10th	(NH ₄) ₂ SO ₄ 20% m/v in H ₂ SO ₄ + HF
11th	HNO ₃ + H ₂ SO ₄ + HF
12th	HCl + H ₂ O ₂
13th	HNO ₃ + H ₂ O ₂
14th	H ₂ SO ₄ + H ₂ O ₂
15th	HF + H ₂ O ₂

21.

Dry-Down

Notes from meetings:

Clean everything really really good before starting!!! Else contamination

To run samples, you have to drive off the HF with a series of dry-downs. Dry it down to viscous bead; take up in HCL, dry down; take up in HNO₃, dry down; take up in HNO₃, dry down; take up in 2N HNO₃. This last solution is then diluted with 1% (v/v) HNO₃ and run on the ICP. Not a 100% sure, but I think that the HCl is 6N, HNO₃ is 8N for the dry downs. Make sure that you have a method blank that you have taken through the same procedure.

Start at 110 C for 2 hrs then drop to 75-90C for a few hours

4. Dry down on hotplate with cap removed
 - a. Reduce temperature as you get close to complete evaporation to ensure gentle drying
5. Re-dissolve in 1mL 70% HNO₃
 - a. Check that sample is completely in solution- no visible particulates
 - b. If there are particulates, try further digestions with either more H₂O₂ or aqua-regia
6. Dry down on hotplate with cap removed
 - a. Reduce temperature as you get close to complete evaporation to ensure gentle drying
7. Re-dissolve in 1mL 36% HCl
8. Dry down on hotplate with cap removed
 - a. Reduce temperature as you get close to complete evaporation to ensure gentle drying
 - b. Sample is now ready for storage, or ready to be brought up in appropriate volume of acid for column chemistry
 - c. If sample is going to be split between aliquots for elemental analysis and aliquots for isotope work, more weighing steps are required. You'll need the initial empty weight of each Savillex vessel, the total weight of Savillex + solution at the time the aliquots are taken, and the weight of each aliquot.

The OES autosampler holds standards plus up to 88 samples at a time.

5mL of sample with solids loading to achieve acceptable ppb

10 - 20 mL of stds

highest concentration std needs 20 mL

You need a set of mixed stds usually 5 or 6 including a "0" standard and a method blank

Dilute in 1v/v%HNO₃

Element	Detection Limits [ppb]	Signal/Background
K	40	430
Na	100	500
Ti		7900

Bi		870
Mg		9999

Instrument take about 1hr to set up (calibration and such) then ~3min per sample
Get Nitric acid of higher purity than reagent grade...!!

Supplies:

Prices are from April 2016

Dry-Down Vessels and lids:<http://www.savillex.com/ProductDetail.aspx?ProductName=Vial-only-30-ml-rounded-inside-flat-outside-threaded-top> - \$19.40 ea<http://www.savillex.com/ProductDetail.aspx?ProductName=Closure-33-mm-plain-threaded> - \$7.45 ea**Auto sampler tubes:**https://us.vwr.com/store/catalog/product.jsp?catalog_number=60818-725 - \$204.50 - we bought a case of these**Acids:**High Quality Acids: HNO₃, HF, HCl - I will get VWR numbers once you have given the ok.HNO₃[71009-340](#)

HF

[AA10989-AC](#)

HCl

[JT9385-1](#)

Weight paper

https://us.vwr.com/store/catalog/product.jsp?catalog_number=12578-165**Mixed Standard:**

The quote I got was \$200 for 500mL we need 5 linear dilutions at 10-20mL each for each run. - 500mL should last us a while but would only be good for 1 composition e.g. 80BNT-20BKT

<http://www.scpscience.com/en/custom-standards/aqueous>http://solutionsguide.tetratec.com/index.asp?Page_ID=732&AQ_Magazine_Date=Current&AQ_Magazine_ID=2230**A mortar and pestle:**Al₂O₃ - Mortar - \$206 - <http://www.sigmaaldrich.com/catalog/product/aldrich/z282014?lang=en®ion=US>Pestle - \$91 - <http://www.sigmaaldrich.com/catalog/product/aldrich/z282065?lang=en®ion=US>

Other types:

Higher contamination:

Agate - MO-95 - \$110 <http://www.advaluetech.com/products/agate-mortar/agate-mortars-and-pestles>

Low contamination:

Zirconia - \$1,300 - <http://www.samaterials.com/laboratory-equipment/113-zirconia-mortars-pestles.html>Diamonite - \$\$\$\$ - <https://www.fishersci.com/shop/products/diamonite-mortar-pestle-sets-2/p-46023>VWR sells in 500 packs https://us.vwr.com/store/catalog/product.jsp?catalog_number=60818-703