ICP Sample Preparation

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Introduction

Inductively Coupled Plasma Optical Emission Spectroscopy, ICP-OES, is a method to perform elemental analysis on a sample in solution (ODP Technical Note 29). This manual covers hard rock sample preparation for ICP-OES analysis. Hard rock samples are prepared via the 'flux fusion' approach. This technique ensures complete dissolution of sample allowing a full elemental analysis. Solutions are stable which allows further analysis, and involves no HF making. It is a safe and ideal method for shipboard analyses (ODP Technical Note 29).

Rock samples are crushed to a fine, talc-like powder using multiple cleaning, crushing and grinding procedures. After grinding, loss on ignition (LOI) is determined. Ignited material is fused with flux powder forming a glass sample bead. Fused beads are then dissolved in 10% HNO_3. This is further diluted and the resulting solution is processed by the ICP-OES machine.

The complete process (from sample table to ICP-OES machine) takes at least 4 days in the very best scenario:

- Day 1 involves: sampling, polishing on the Diamond Wheel, cleaning (sonic bath), and drying samples overnight.
- Day 2: Crushing in the X-Press, grinding in the Shatterbox, a pre-ignition (for LOI) weight, and placing samples in the muffle furnace overnight.
- Day 3-4: Taking a post-ignition (for LOI) weight, giving ignited samples to the chemistry technician to add sample to the pre-weighed flux, and fusing the sample bead. The beads are then handed back to the chemistry technicians to continue ICP analysis.

Wait until there are about six or more samples so you can prepare a 'batch' of six or more at a time.

Note: LOI determines the amount of alteration of the sample, generally, scientists use this to determine the 'freshness' of the ingenious rock being analyzed. Typically we use unignited powder in the bead preparation as that is what correlates to the certified values. However it is not always the case. Please speak to the geochemists regarding their preference of ignited or unignited powders in the bead preparation. There are many standards (both unignited and ignited) available for the geochemists to include in their dataset.

Apparatus, Reagents, & Materials

Laboratory Apparatus

General Laboratory Equipment

- Compensated Dual Analytical Balance System (Mettler Toledo balances)
- Drying ovens at 110°C and 60°C
- Muffle furnace
- Sonicating bath

Hard Rock Processing

- Splitting room saw
- Buehler grinder/polisher with 70 µm grit diamond grinding wheel
- Sonicator (with small water bath)
- X-Press crusher
- Spex Shatterbox with tungsten carbide (WC) grinding vessel
- Spex Mixer Mill with tungsten carbide or alumina canisters
- Retsch MM400 Mixer Mill

LOI/Bead-Making

- Fisher Ashing muffle Furnace
- Sample Bead Maker

Reagents

- 0.172 mM LiBr wetting agent (0.15 mg ultrapure LiBr in 10 mL DI water)
- 400mg of drew sighed lithium metabolite flux (weighed on shore)
- 10% nitric acid (143 mL concentrated nitric acid/L of solution). **Caution!** always add acid to water.
- Isopropyl alcohol, laboratory grade
- Deionized water (18.2 M/cm^2 laboratory water obtained from Chemistry Lab)

Materials

Grinding Samples

- Beakers
- Glass cleaner
- Tweezers
- Teflon spatula
- X-Press aluminum die
- Core liner pieces
- Delrin plugs
- Sample vials or jars
- Weighing paper, 6 x 6
- Kimwipes

LOI/Sample Bead

- Quartz or alumina ceramic crucibles
- Tongs
- Vials containing 400 mg lithium metaborate flux (preweighed on shore)
- Milligram calibration weighing set
- Weighing paper, 4 x 4
- Vials for excess ignited powder
- Agate mortar and pestle
- Pt-Ag crucibles

Preparing Rock Samples

Rock samples are prepared for ICP analysis using the following procedures on each sample:

1. Cut to size (see *Cutting Samples to Size below*)
2. Polish (see *Polishing Samples on Diamond Wheel below*)
3. Clean (see *Cleaning Samples below*)
4. Dry (see *Drying Samples below*)
5. Crush (see *Crushing Samples in the X-Press in XRD Sample Preparation Hard Rock*)
6. Grind (see *Grinding Samples in the Shatterbox in XRD Sample Preparation Hard Rock*)

Cutting Samples to Size

To cut samples for the X-Press, use the splitting room rock saws (located in the Core Deck) following these guidelines:

- Cut samples to ~1–2 cm in length and width. Avoid cutting irregular pieces; ideal samples are cubes
- Avoid veins, infilled vugs, etc
- Remove as much contaminated material as possible
- Contact the petrologist(s) if cutting reveals unexpected features

Notes about altered samples:

- It may be desirable to hand-pick and separate alteration material such as vesicles and/or veins from whole-rock basalt
- Sometimes veins/alterations do not become apparent until after cleaning and drying.
- Speak to the petrologist about that method if alteration is visible

Polishing Samples on Diamond Wheel

Polishing the samples remove contamination caused by drill bit, saw blade, or other unwanted material. Grind each surface (each outer side) on a high-speed, diamond disc.

Apparatus and Materials

- Buehler Grinder/Polisher
- Diamond grinding disc
- Sample Beaker

Each sample will correspond to one beaker; collect as many beakers as needed. Beakers need to be cleaned (DI water and isopropyl alcohol) and labeled (ex. 1, A, or sample label).
Next start the grinding process using the Buehler grinder located in the X-Ray preparation area of the Thin Section Lab (Figure 1).

Note: The diamond disc is attached to a magnetic disc which is then placed on the wheel plate. Diamond disks are located on the stud shelf in the ICP preparation area of the Thin Section Lab. Use the silver (125 µm mesh) or purple (220 µm mesh) diamond disc.

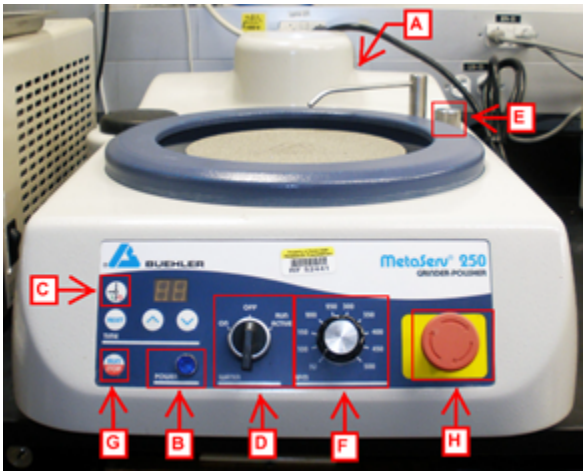

Figure 1: Buehler Grinder Polisher. A. On/Off switch B. Power Indicator light C. Timer On/Off button D. Water On/Off switch E. Water flow control knob F. Disc speed control. G. Stop/Start. H. Emergency Stop.

To start the polisher flip the 'On' switch in the back (Figure 1A). The power indicator light (Figure 1B) should illuminate. Press the timer on/off button (Figure 1C) to get continuous disc rotation. Turn the water on by flipping the 'Water' switch to the 'On' position (Figure 1D). The water flow can be adjusted by turning the knob shown in Figure 1E.

The rotation speed is controlled by the dial shown in Figure 1F. The range is 0 rpm to 500 rpm. 150 rpm is a good starting position. Adjust the speed if needed: faster for hard rocks and slower for softer rocks.
With the water on and the RPM adjusted press the 'Run' button (Figure 1G). Move the sample back and forth across the disc to prevent making a groove. If there is an emergency press the 'Emergency Stop' button (Figure 1H) to stop rotation and cut off the water. To enable the wheel again twist the knob until it pops back out.

Polish the rocks with a Buehler diamond disc (Figure 2) until they're completely smooth and round on all edges. The purpose of grinding on a diamond disc is to remove any possible contaminates caused by the drilling mud (or drill bit) or the rock saws in the splitting room. There should be no pits or jagged corners. Put the rock into a labeled beaker (Figure 3). Before polishing the next sample, clean the diamond disc with a dressing stone. Dressing stones are found in the Splitting Room of the Core Lab. Do this for all samples and then move on to 'Cleaning Samples'.

Figure 2. Buehler diamond discs for polishing (use either one).

Figure 3. Labeled beaker with polished rock inside.

Cleaning Samples

To remove contamination (oil, skin, and residue from the diamond wheel) wash the polished samples in 70% isopropyl alcohol and DI water. From this point onward, wear gloves when handling samples to avoid reintroduction of contaminants.

Apparatus and Materials

- Sonicator with basket
- Beakers
- 70% Isopropyl Alcohol
- Tray(s)

Place the basket in the sonic bath and fill to just above the wholes in the basket with DI water. Pour enough isopropyl alcohol (70%) into each beaker to cover the sample. DI water can also be used if the scientists prefer. Place the beakers in the sonic bath basket. There should be enough liquid in the beaker to keep the sample from floating in the basket (Sonic Bath without basket Figure 4).

Figure 4. Sonic Bath (without basket).

Sonicate the samples for 15 minutes. You should notice the isopropyl or water becoming cloudy from residue being shaken off the samples. Then follow the wash sequence below:

1. Decant as much of the liquid as possible
2. Sonicate again with DI water for 10 min
3. Decant liquid into the sink

Repeat the rinse cycle until the water is clear. If the samples are soft and/or clay rich, they will not reach the "clear water" state. Continuing to sonicate will only dissolve the sample. If after 3–4 washings, the water still isn't clear, go to the next step. After the final rinse, decant as much water from the beaker as possible.

Drying Samples

This step requires at least 12 hours and therefore should be done towards the end of your shift. Turn oven on (Figure 5) and adjust the dial to about 110°C (this is marked on oven, or you will have to turn on oven a couple hours before and use the thermostat inside to get the temperature correct. It is important to not overheat the sample as it may affect some minerals. Temperatures less than 110°C is ok, but it may take longer than 12 hours for the sample to dry.

Apparatus and Materials

- ICP Oven
- Samples

Note: The ICP oven should be kept clean at all times, as samples are left open and are susceptible to contamination. **The ICP oven should only be used for ICP samples.** If the oven shows any sign of rusting, please notify the ALO as a new oven will need to be ordered.

Place the beakers into the ICP Oven at 110°C for at least 12 hours (Figure 5). You can cover the beakers with a larger clean beaker if there is any possibility of rust or debris falling onto the sample.

Figure 5. The ICP Prep Oven located in the X-Ray lab. A. 'On/Off' Switch B. Temperature Setting C. Heating Indicator.

After 12 hours the samples should be dry, remove the beakers from the oven and place them inside the desiccator (Figure 6) while you prepare the X-press station.

Figure 6. Desiccators located in the X-ray lab

Crushing Samples in the X-Press

See XRD Sample Preparation Hard Rock

Grinding Samples in the Shatterbox

See XRD Sample Preparation Hard Rock

Determining LOI

Loss on Ignition, or 'LOI', compares a mass measurement taken before and after a sample is subjected to extreme heat. Petrologists use LOI as an indication of degree of alteration. Low LOI values suggest relatively fresh, unaltered basalt; whereas high LOI numbers suggest alteration (clay, alteration minerals, etc.). LOI is determined by weighing a small amount of the sample (~5 g) before and after ignition. Samples typically lose weight as water is driven off, though an iron-rich, water-poor sample may gain weight. 5g of sample is suggested to reduce the %LOI error to around 1% or less. Advise the scientists if they want less ignited.

LOI is not required for all types of ICP Preparation. Check with the science party to determine if LOI is a desired measurement. If the science party does not want an LOI measurement move on to the section Making the Sample Bead.

Loss on Ignition

Determining a sample LOI comprises three procedures:

- Pre-ignition weighing
- Igniting samples
- Post-ignition weighing

Advice on LOI Procedures (from Exp. 366 Methods, from Exp 393/Jeff Ryan)

Shipboard sample preparation and LOI determination procedures described in Murray (2000) and updated in recent *IODP Proceedings* volumes (e.g., Reagan et al. [2015] for Expedition 352) are appropriate for a range of sediment and rock compositions, but some care must be taken with unusual sample matrixes. As an example, attempting sample ignitions on carbonate-rich materials can lead to spurious results and issues with contamination if quartz crucibles are used for sample ignitions because carbonates will react with quartz upon heating to both devitrify and decompose the crucible. Alumina ceramic crucibles may be better for carbonates but risk contamination for Al and potentially other elements due to spallation over time. Putting carbonate rich samples or sediment in quartz crucibles ruins the crucibles and the LOI determination (consulted with Jeff Ryan on this, Exp 393). Consult with the scientists to be determine what crucible will be needed.

Maximum ignition temperatures of 1000°C and higher are appropriate for ultramafic and some mafic igneous materials but may result in sample sintering and/or sticking to some Si- or Ca-rich materials. Ignition temperatures of <850°C are inadequate to decompose carbonate minerals in sediment samples, even if samples are held at temperature for several hours. In general, igniting samples to at least 900°C as a maximum temperature is advisable to decompose all volatile-bearing phases and obtain reliable measures of LOI.

Pre-ignition Weighing

Apparatus and Materials

- Mettler Toledo Dual Balance
- Acid Washed Quartz or Alumina Ceramic Crucibles
- 4x4 Weigh Paper
- Reference Weights
- Thermolyne Muffle Furnace

Clean the balance area including the balance plates inside the balance. Any dust or particles on the plate could throw off the weight measurements. Before beginning make sure there are enough acid washed crucibles for your samples. The crucibles are located in the X-Ray lab in a plastic container labeled 'Acid Washed Crucibles'. Wear gloves while handling the crucibles.

Place a large sheet of paper in front of the balances and place supplies here. For each sample you need weigh paper (Figure 28A), a scoopula (Figure 28C), and a crucible set (Figure 28B). Clean the scoopula with isopropyl alcohol in between each sample as it has direct contact with the sample powder.

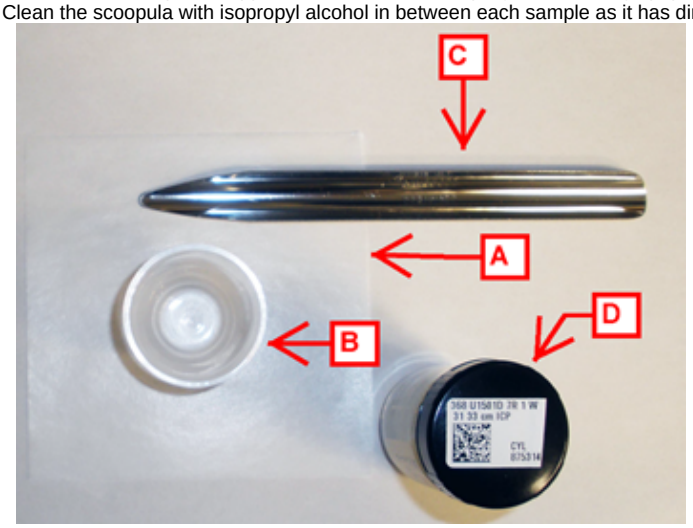

Figure 28. Materials needed for weighing LOI. A: Clean paper or kim wipe. B: Crucible set. C: Scoopula. D: Samples

Setting up the Mettler Toledo Balances

Samples are weighed on the Mettler-Toledo Dual Balance. The Dual balance uses two weighing stations to compensate for shipboard motion: one a 'known' reference weight (Figure 29A) and the other an 'unknown' sample weight (Figure 29B). The balance takes a series of measurements and uses the average value as the final weight (for a more in-depth guide refer to the Balance User Guide on Cumulus). Each balance has a control panel plate, which constantly records weight. These plates communicate with the "Mettler Balances" program.

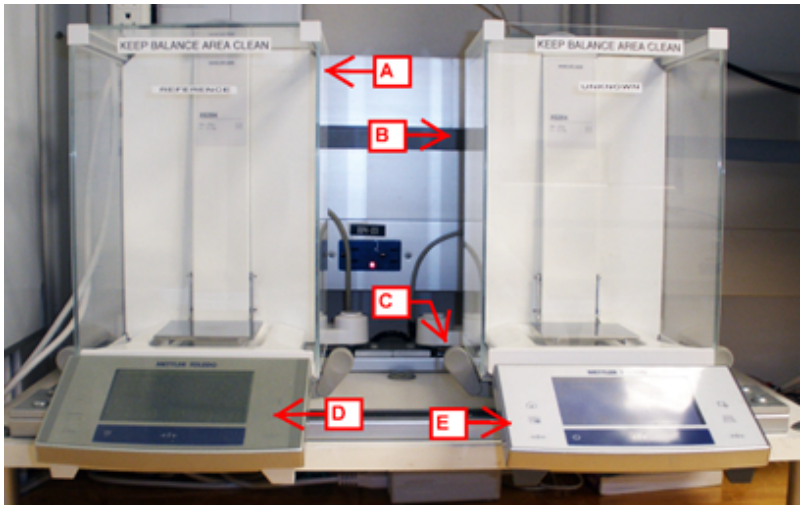

Figure 29. Mettler Balance Station located in the XRay lab. A: Reference balance. B: Unknown balance. C: Sliding door. D: Reference power module. E: Unknown power module.

Open the Mettler Balances program (Figure 30). There are multiple panes and parameters that are set before we start measuring.

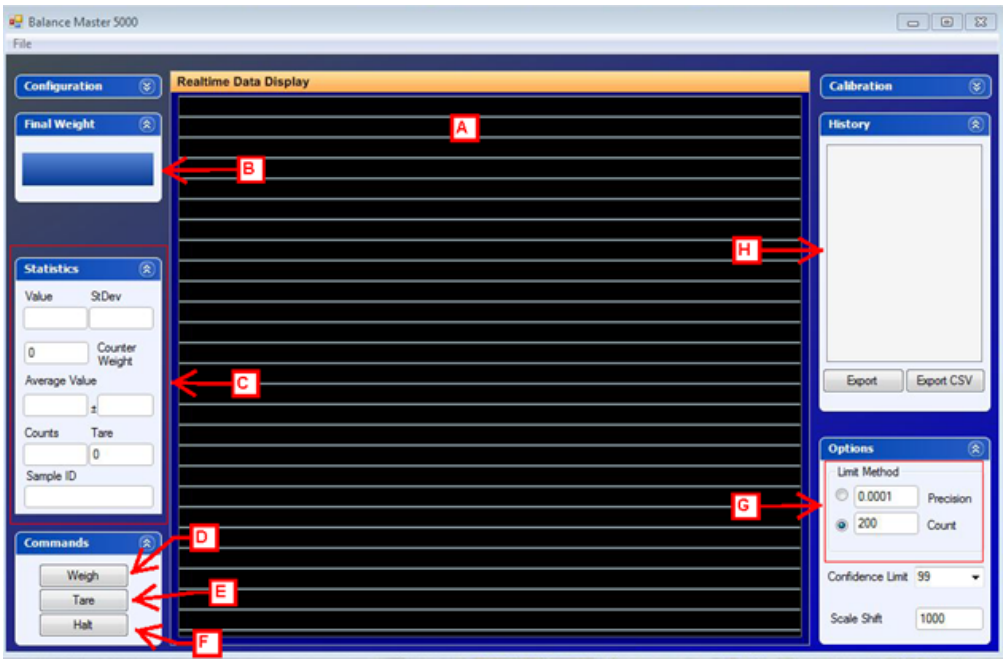

Figure 30. Mettler Balance program window. A: Graphical measurement window. B: Final weight panel. C: Statistics panel. D: Weigh. E: Tare. F: Halt. G: Options panel. H: History panel.

Graphical Measurement Window: Shows a line graph of the live-time measurement weight and the running average weight.
Final Weight Panel: Displays the Final Weight after all measurement counts have been made.
Statistics Panel: Shows the average weight adjusting with time.
Counter Weight: Enter in the reference weight

Counts: The elapsed amount of measurements
Tare: Shows and applies the tare or 'zero' value.
Sample ID: Name the sample being measured.
Commands Panel: Executable commands
Weigh: Starts measurement
Tare: Determines the 'zero' weight. This value is applied to the final weight.
Halt: Stops a measurement before it has gone through all counts
History Panel: Shows statistics on all measurements taken. This file can be exported into an excel file by using the 'Export' button. Note: The 'Export CSV' file does not work.
Options Panel: Editable measurement parameters. We measure using the 'Counts' feature. 'Counts' is active when the dot is blue. Change the number of counts or measurements the balance takes here.
At the beginning of a series of measurements, tare the balances. To do this first make sure that the 'Counter Weight' field is set to '0' and then set the 'Count' value. The 'Count' is dependent of the sea state: 600 for calm waters and 1000 counts for rough waters. If seas are too rough than wait until the weather settles before continuing to measure.
A rule of thumb is that the measurement of a known reference mass shouldn't have a larger deviation than the accuracy desired. For example, our accuracy is +/- 0.05 grams; weigh a reference mass in the unknown balance that is close to the masses you are measuring (e.g., 25 grams) and perform the measurement with the appropriate counterbalance mass in the reference balance pan. You should get a final mass of 24.95—25.05 grams.
Once parameters are set, select the 'Tare' button. When the tare is complete the 'Final Weight' Section turns orange and the 'History' Section updates (Figure 31).

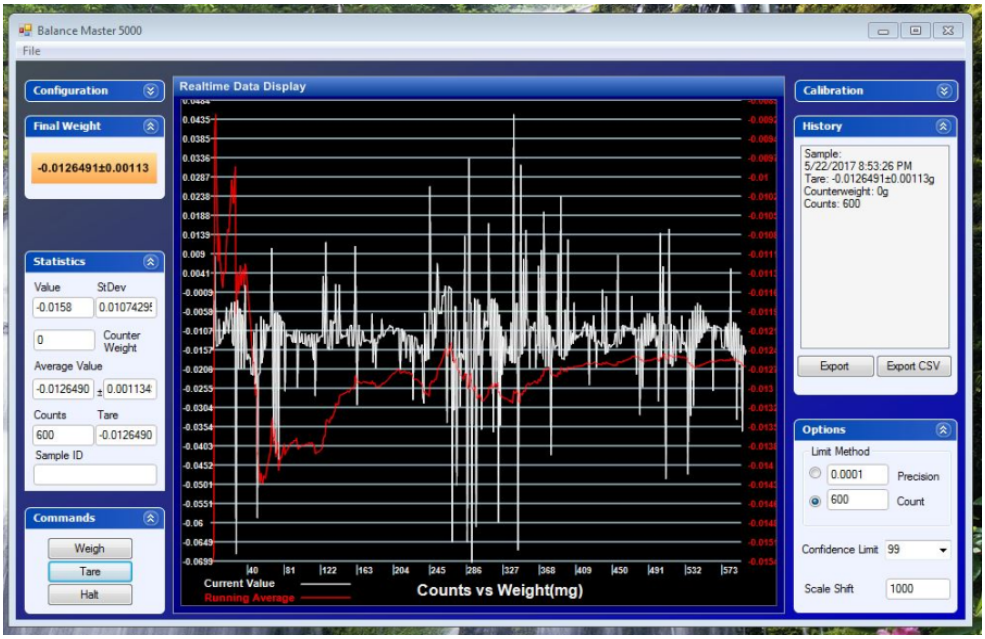

Figure 31. Mettler Balance program window showing a tare calculation.

Put in a reference weight into the "Reference' balance. With the tweezers, select the 20g weight and place it in the center of the 'Reference' balance (Figure 32). To have a more accurate measurement, the reference weight should be close to the expected 'Unknown' sample weight (roughly ~20g). Enter this reference weight into 'Counter Weight' in the Statistics panel.

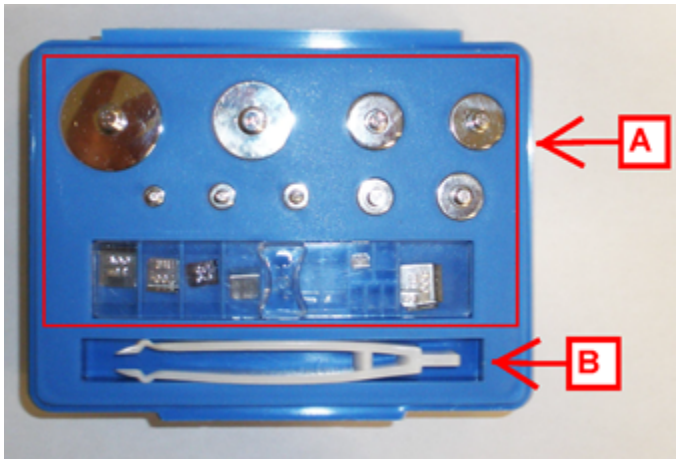

Figure 32. Reference weights. A: Weights. B: Tweezers.

Weighing Crucibles

The quartz crucibles have three sections: an outer (or large) crucible, an inner (or small) crucible, and a lid (Figure 33). If alumina ceramic crucibles are needed, as for carbonate rich samples or sediment samples, replace the inner quartz crucible with the ceramic crucible.

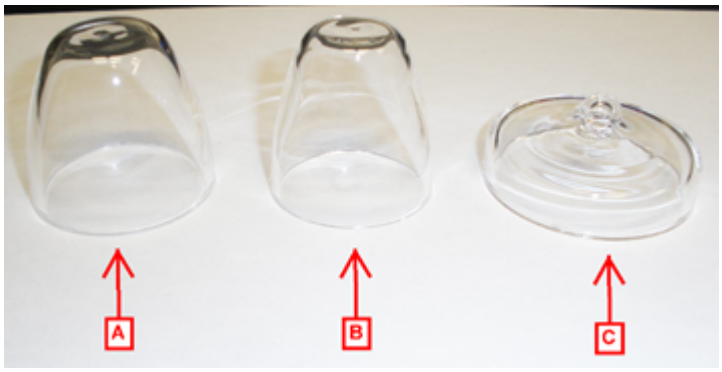

Figure 33. Crucible components. A: Outer (large) crucible. B: Inner (small) crucible. C: Lid.

The inner crucible holds the sample material and is the only piece that is weighed. They are assembled as seen below with the inner crucible inside of the outer crucible and the lid sitting over the entire unit (Figure 34). Crucible sets (large, small and lid) are engraved and lettered and should be kept as a set. For example, Crucible lid 'A' should always be run with large and small crucible 'A'. If a crucible is unlabeled use a diamond-tipped pen to etch in an unused lid.

Figure 34. Complete and assembled crucible unit.

Weight measurements are recorded in an excel spreadsheet which will be uploaded to LIMS at the end of an expedition (Figure 35). Open the excel spreadsheet titled 'LOI Template' found in Local Disk > DATA and save the spreadsheet in Local Desktop > XRD-ICP Prep Documents >LOI spreadsheets.

	A	B	C	D	E	F	G	H	I	J	K
1	X368										
2	SAMPLE NAME			CRUCIBLE ID	CRUCIBLE WT	CRU + FRESH SAMPLE WT	CRUCIBLE + IGN SAMPLE WT	SAMPLE WEIGHT	POST IGNITION LOSS	%LOI	COMMENTS
3	Hard Rock LOI at 1025 for 4 hours										
4	SITE	TEXT ID	CORE/SECT/INTERVAL								
5									0	#DIV/0!	

Figure 35. LOI spreadsheet.

The spreadsheet has multiple columns to fill in.'SITE', TEXT ID', 'CORE/SECT/INTERVAL', 'CRUCIBLE ID', 'CRUCIBLE WT', 'CRU+FRESH SAMPLE WT', and 'CRU+IGN SAMPLE WEIGHT'. 'SAMPLE WEIGHT', POST IGNITION LOSS', and '%LOI' are calculated values based on the weights entered in columns E – G.
The first measurement taken will be the initial weight of an empty crucible. To complete this measurement, open the side door and place an empty inner crucible in the center of the '*Unknown'* balance (Figure 36). Record the number or letter etched onto the crucible in the excel spreadsheet under 'Crucible ID.'

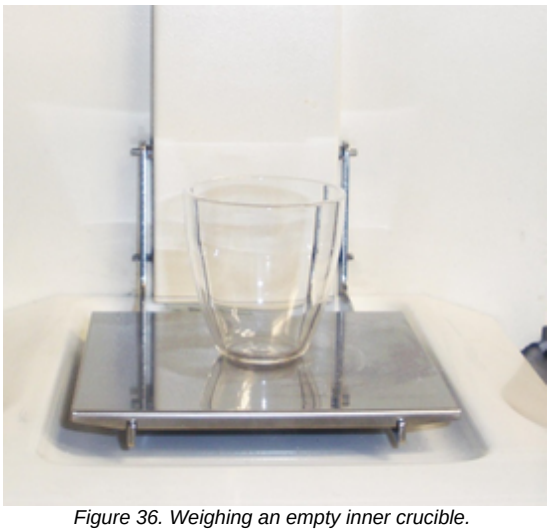

Figure 36. Weighing an empty inner crucible.

Close the door and click 'Weigh**'.** Wait for the counts to finish and then record the 'Final Weight' in the spreadsheet under 'Crucible Wt'.

Weighing Sample

Weigh out 5 grams of sample powder into the crucible within +/- 0.05g (Figure 37). The total weight should be the crucible weight + 5 grams within +/- 0.05 grams. For example, a crucible weighs 14.32g, thus the total weight plus the sample will be between 19.27 – 19.37g. We use 5g because it is a good representation of the sample, to decrease the %LOI error to about 1%, and it fills the crucible appropriately. You will find that you will loose some of the sample due to it sticking to the crucible when you are finished with the LOI.

Note: If there is only a small amount of material, you can use less but the %LOI error will be larger.

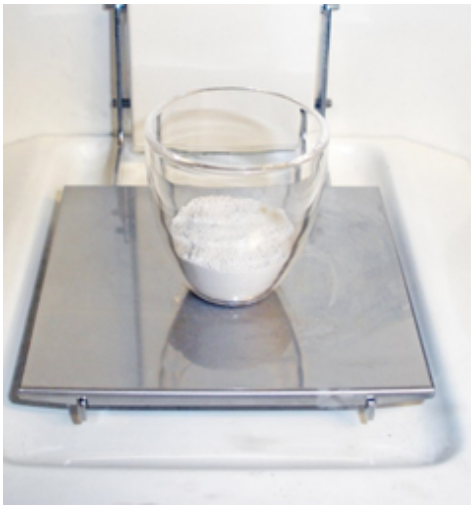

Figure 37. Crucible with approximately 5g of sample. Pre-ignition measurement

When the sample is close to this range click 'Weigh.' Press 'Halt' to stop the measurement and either add or remove sample if needed, and then click on 'Weigh' again to take a new measurement.

When a sample's final weight is within the allowable range, record the 'final weight' value into the spreadsheet under 'CRU + FRESH SAMPLE WT'.

Carefully remove your sample from the balance. Place your crucible into the larger quartz holder and cover with a lid (Figure 38). Repeat this process for all samples. After all samples have been weighed and recorded, take samples from the desiccator and bring over to the muffle furnace in the Chemistry Lab.

Figure 38. Complete crucible unit with sample, ready for ignition.

Igniting Samples

Samples are ignited in the Thermolyne Muffle furnace located in the Chemistry Laboratory. The entire ignition cycle takes approximately 20 hours to complete and cool down to ~200°C. After ignition, samples need to be taken out when they come down to ~ 50°C-200°C. If the samples sit for too long they will reabsorb moisture and the 'Post-Ignition Weight' will be inaccurate. Time this accordingly.

Using the Muffle Furnace

Bring crucibles over to the Muffle Furnace (Figure 39). There is a wooden tray to assist with the transfer of crucibles from one lab to the other. Turn the power switch on and the control panel will illuminate.

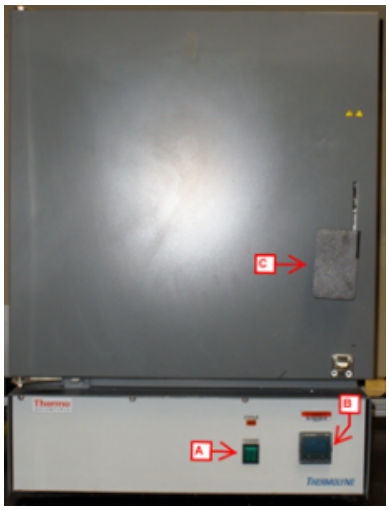

Figure 39. The Thermolyne Muffle Furnace. A: Power Switch. B: Control Panel. C: Door handle.

Confirm with scientists, what temperature and how long samples should be run for. Below is a quick reference guide:

Material	Ignition Time at °C
Basalts	4 or 5 hr at 1025°C
Si-rich sediments	4 or 6 hr at ~900°C
Samples with: • Muscovite • Biotite • Amphibole • Carbonates	6 hr or more at **XXX**°C

A common program is an increase in temperature of 3°C/min to a target temperature of 900°C and a hold of one hour. Then ramp up at a rate of 3°C/min to a target temperature of 1025°C and hold for four hours before cooling. This ramp cycle is already programmed into the furnace and corresponds to 'Program 1'.

Oven Programs: (Note: Once a program has finished, the temperature setting returns to room temperature, ~25°C.)

- Program 1: Ramp up to 900°C at 3°C/min and hold for 1 hour, then continue to 1025°C at 3°C/min and hold for 4 hours.
- Program 2: Ramp up to 950°C at 3°C/min and hold for 4 hours.
- Program 3: Ramp up to 550°C at 3°C/min and hold for 1 hour.

- Program 4: Ramp up to 900°C at 3°C/min and hold for 1 hour, then continue to 1025°C at 3°C/min, no hold.

To check or edit a program see additional guides attached to the furnace itself. It is also possible to run the furnace manually without a ramp up cycle. Discuss with scientists their preference.

Either enter the desired temperature manually or select your program. If you are running the furnace manually, enter the desired temperature; no other buttons or steps are needed. If selecting a program, press and hold 'Run' (Figure 40).

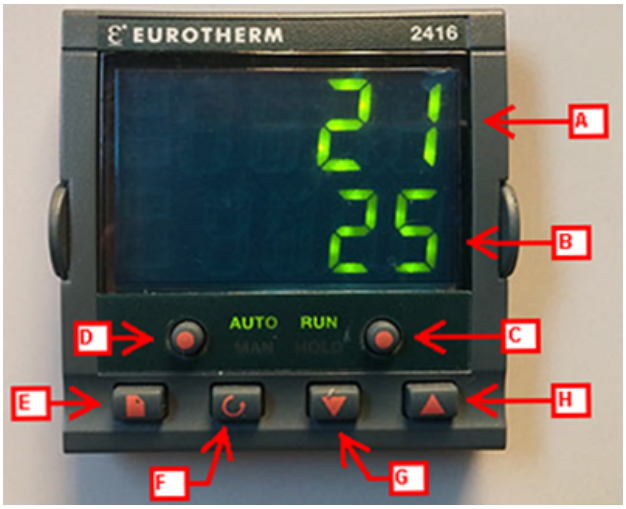

Figure 40. Control Panel on Thermolyne Muffle Furnace. A. Actual temperature. B. Desired/ Set temperature. C. Run/ stop button. D. Auto run button. E. Page button. F. Scroll button. G. Down button. H. Up button.

When the furnace finishes it's cycle and cools down to ~50°–200°C, remove the crucibles with tongs or the padded gloves (if cool enough). Put samples back into the wooden tray and store tray in the desiccator. Keep samples in the desiccator and remove one at a time while weighing. It is very important for the samples to not reabsorb moisture so begin weighing as soon as possible.

Post-Ignition Weighing

Post-ignition measurements should be taken soon (within an hour) after removing crucibles from the furnace. Failure to do so will disrupt the LOI values. Reweigh the crucible plus the ignited sample to determine how much weight was gained or lost. Follow the same weighing procedure as in ***Pre-ignition Weighing***.

1. Record the final weight in the excel spreadsheet under 'CRUCIBLE + IGN SAMPLE WT'. The spreadsheet will populate the columns 'Post Ignition Loss' and '%LOI'.
2. The formula used to calculate LOI is:

%LOI = 100 x (weight change during ignition)/ (fresh sample weight).

***Note**: By convention, weight lost during ignition is recorded as a positive LOI value; whereas weight gained is recorded as a negative LOI value. Report the results to 2 decimal places.*

Uploading LOI Data To LIMS

Open the Excel File **LOI_Spreadsheet** in **Local Disk > Documents > XRD > Sample and ICP Prep > LOI > LOI Spreadsheets > LOI_ExpXXX.xlsx**

The spreadsheet has three sheets:

- The first sheet is as follows:

SAMPLE NAME	SITE HOLE/CORE /SECTION/INTERVAL	CRUCIBLE ID	CRUCIBLE WT	CRU + FRESH SAMPLE WT	CRUCIBLE + IGN SAMPLE WT	SAMPLE WEIGHT	POST IGNITION LOSS	% LOI	Comments
QRND12345678	999A/1H/4/70-72	I	14.813	19.813	19.690	5.0000	0.123	2.46	

- The second sheet is for repeats.
- The third sheet is the format for uploading the data using the spreadsheet uploader (*Figure 41*).

Put your LOI information into the spreadsheet following the example format. Fill in the following:

- **Text ID**: e.g., WDGE11258831 (Note: capital letter matters)
- **Analysis**: LOI
- **Replicate:** leave blank, unless true replication (not just reanalyzing) of a sample, then begin replicate numbering with '0', then '1', then '2'.
- **crucible_number:** Crucible ID (e.g., A, B, F...)
- **crucible_preignition_mass:** crucible mass only (small inner crucible) (component unit: grams)

- **crucible_and_preignition_sample_mass:** inner crucible with fresh sample before ignition (component unit: grams)
- **crucible_and_postignition_sample_mass:** inner crucible with ignited sample after ignition (component unit: grams)
- **loi_percent:** LOI in % (component unit: none; the value is already a percentage)
- **reference_mass:** sample mass (calculated difference) (component unit: grams)
- **comment:** specify temperature and time used for LOI (e.g., 950 deg C for 4 hours; used during Exp 391)

Text ID	Analysis	Replicate	Instrument	Display Flag	Component Name	Component Value	Component Unit	Component Name	Component Value	Component Unit	Component Name
QRND12345678	LOI				crucible_number		NONE	crucible_preignition_mass		GRAMS	crucible_and_preignition_sample_mass

Component Value	Component Unit	Component Name	Component Value	Component Unit	Component Name	Component Value	Component Unit	Component Name	Component Value
	GRAMS	loi_percent	2.46	NONE	reference_mass		GRAMS	comment	950°C for 4 hrs

Figure 41. LOI Spreadsheet Upload Template

Open up the program **Spreadsheet Uploader** Pinned to the Taskbar (*Figure 42*).

Figure 42. Spreadsheet Uploader Icon.

Copy and paste your spreadsheet into that uploader. Click the 'Edit' button and 'Validate Sheet'. This checks and highlights any errors that need to be fixed. When the spreadsheet comes up clean, click 'Lims' and 'Upload'. The sheet will turn green when the measurements are successfully uploaded. The data is now in LIMS under Chemistry > ICP-AES Solids >Expanded LOI.

Cleaning the Quartz or Alumina Ceramic Crucibles

1. Wash the crucibles with DI water and a small piece of a scouring pad (no soap).
2. Rinse several times with DI water.
3. Place crucibles in a 10% HNO_3 bath for 12 hr. If in urgent need, the quartz crucibles can be soaked a minimum of 2 hours, but extra flux blanks will need to be made and added to batches that use these crucibles.
4. Rinse the quartz crucibles 3 times with DI water after the acid bath. For the ceramic crucibles, rinse 3 times with DI and then soak them in a large beaker of DI water for 4-6 hours to dilute the acid absorbed by the crucibles.
5. Dry the either type of crucibles in the oven at a maximum temperature of 60°C. For the ceramic crucibles, heat them to 800°C in the muffle furnace for 2 hours and allow to cool to room temperature before removing.

Some crucibles will develop a thin white or red cloudy film, become spotted, or start flaking. If any of these things happen discard the crucible in the sharps container. When the crucible undergoes one of those changes the quartz has started to react at high temperatures, and could start contaminating the samples.

Making the Sample Bead

- In a vial, mix 400 mg lithium metaborate flux (pre-weighed onshore) with either ignited or non-ignited powdered sample, check with the science party to determine which sample type should be used. Typically we use unignited powder as that is how our standard beads are prepared and what correlate to the certified values. This step is typically completed by the chemistry technicians.
- *Fuse both sample powder and flux into a glass bead* (Figure 43). Dissolve the bead in nitric acid. This solution will be further diluted and analyzed by the ICP.

Figure 43. Fused glass bead.

- An analytical procedural blank of Flux is prepared identically to the samples. The 0.4 g of flux (the pre-weighed flux) is fused with 10µL 0.172 mM of LiBr and dissolved. An additional 0.1 g of flux is NOT added to mimic the TDS of the 0.5 g mix of sample + flux because this would provide an inaccurate quantitation of the impurities introduced by the amount of flux used in preparation of the unknowns.

Weighing the Sample

Note: This process is typically done by the chemistry technicians.
Weighing the sample is a critical step. The sample weight should be as close to 100 mg as possible. Inaccuracies in the weight will show up in the analytical results. Print small labels for each sample and place on your small, clear capped vial. On the lid label a sticker with the core, section, and interval. Confirm with scientists what powder you will be using Fresh or Ignited.

1. Clean the countertop around the balance and the balance pans with isopropyl alcohol. Put sheets of white paper on all the working surfaces.
2. Arrange all supplies on the white paper: tweezers, scoopula, and a sheet of 6x6 weigh paper.
3. Ensure the following items are available and labeled for each sample.
    - 1 bottle of pre-weighed flux
    - 1 new, empty, acid-washed vial for the remaining ignited powder
4. Pre-label the bottles before weighing (one label each on the cap and the bottle).
5. Make two weigh boats. Cut a rectangular strip from your piece of weigh paper and fold up the two long sides. Put one on the 'Tare' Side and the other on the sample side. You will need to make a new boat for each sample. The tare boat will remain there for all of your samples.
6. Close the door of the balance and tare for 100 counts.
7. Remove a crucible of ignited powder (if using ignited powders) from the desiccator. If the powder has hardened from the furnace then transfer the sample from the crucible to a clean agate mortar and grind until it is a loose fine powder. If your sample is fine proceed to the next step. If using Fresh, use the vial of fresh powder that is provided by the XRay technician. Note if the fresh powder will be shared with XRF measurements. Once the 100mg is removed from the vial give back to the XRD technician for XRF analyses.
8. Keep your boat in the weigh pan and with your scoopula measure out 100 milligrams. Be careful not to spill your sample onto the pan. If you do, remove your sample boat and with a small brush wipe away the loose powder.
9. Close the door and weigh the sample, putting more sample on or off until you achieve a reproducible weight that is within ±0.00050 g of 0 (half a milligram).
10. When the sample weight is as close to 100 mg as you can get it (i.e., 0.0995–0.1005 g), open the labeled bottle with the pre-weighed flux and **car efully** pick up the paper with the sample powder on it and transfer all of the powder into the bottle containing the flux. Snap the paper a few times with a flick of your index finger to make sure everything goes in.
11. Homogenize the sample/flux mixture by holding the vial slightly off of vertical and rotating it. Tap it from time to time on the bench top as you rotate it to clear any powder from the sides of the vial. Avoid getting the sample/flux powder stuck around the cap.

Fusing the Sample into a Bead

The most critical aspect of bead-making is maintaining a constant sample to flux ratio. A ratio of 1:4 suffices in most situations. If samples are small (e.g., volcanic glasses), a sample mass <0.1 g may be used. However, the same ratio must be maintained between the samples and the calibration standards (otherwise the matrix will not match). For example, 0.05 g of sample requires 0.2 g flux.

Using the Beadmaker

Using the Bead Maker during rough seas is <u>not advised</u>, due to extra physical stress of the machine parts which could cause damage to the Bead Maker.

Collect platinum crucibles, platinum tipped tongs, 0.172 LiBr, and pipette tips from the safe above the Bead Maker (Figure 44). Get the 10-100ul pipette and teflon spatula from the drawer and clean with isopropyl alcohol. Have a tray of samples that need to be fused and an empty tray for finished beads.

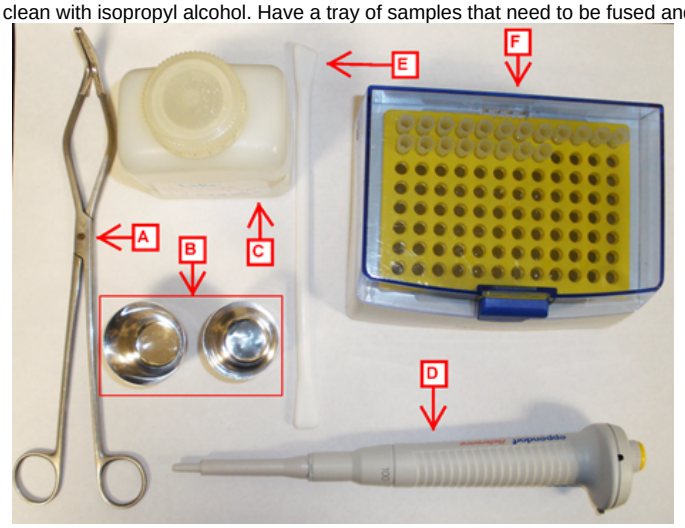

Figure 44. Bead making supplies. A: Platinum tipped tongs. B: Platinum crucibles. C: 0.172 Libr wetting agent. D: Pipette. E: Teflon spatula. F: Pipette tips.

Turn 'On' the Bead Maker (Figure 45; switch on the right side of the instrument).

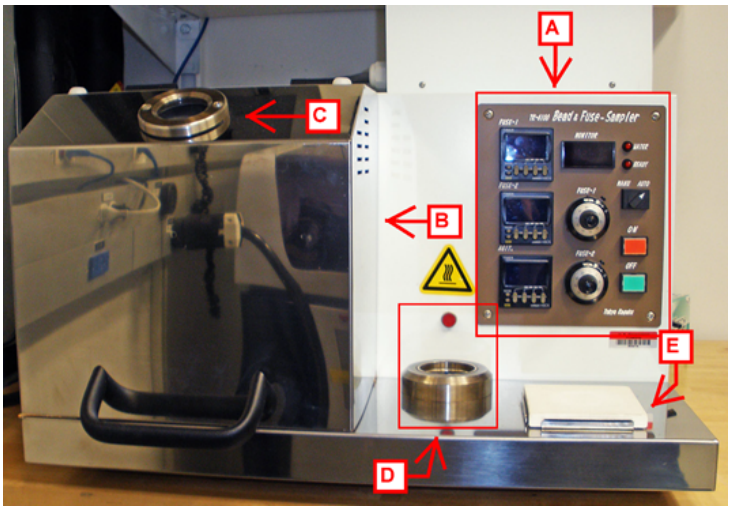

Figure 45. Beadmaker. A: control panel. B: Site of platinum crucible. C: View port window. D: Fan to cool platinum crucible. E: Ceramic plate used for dislodging the fused bead.

Next, turn on the water (Figure 46; 47). The handle is to the left of the machine on the wall. Raise the handle slightly to turn it on. You will hear a small click once it is in the 'on' position. Now the 'Water' and 'Ready' indicator lights should be on. Do not run any samples unless these lights are on.

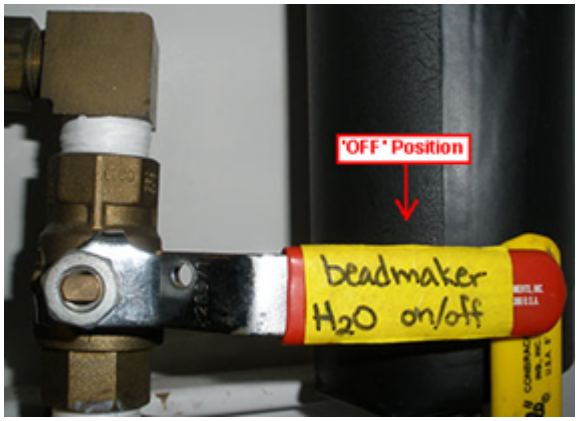

Figure 46. Water in off position.

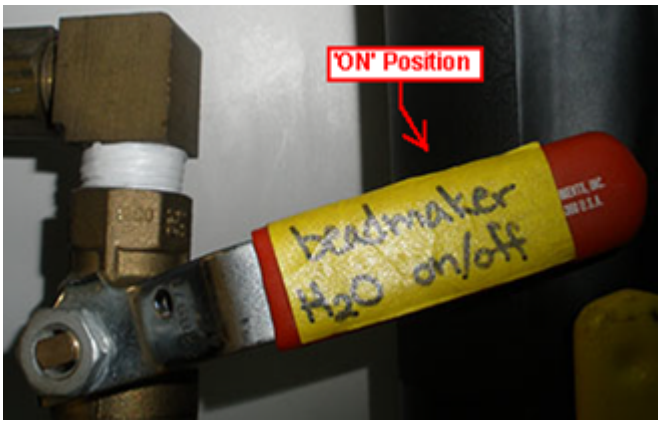

Figure 47. Water in on position.

1. Lay a large Kim wipe and a piece of weigh paper down next to the Bead Maker. Unwrap a platinum crucible and place it on the weigh paper. Pour the powder mix into the crucible. The sample should evenly cover the bottom.
2. Pipette 10 µL of 0.172 mM LiBr wetting agent into the center of the sample powder.
3. Open the Bead Maker lid and place sample inside the sample holder. The short wide crucible will fit directly; whereas, the tall narrow crucible will need an additional ceramic ring (no longer have these?).
4. Close the lid. Double check both indicator lights are on. Press 'On' to start the program. The process will take 12 minutes and the sample is heated in three stages:
    - Stage 1:700°C for 2 min

    - Stage 2:1050°C for 5 min,
    - Stage 3: 1050°C in agitation for 5 min.
5. Be prepared to remove the crucible as soon as the timer reaches 0. The material hardens very quickly so be ready with safety glasses, gloves, and the platinum tipped tongs before the final stage has finished.
6. With the Pt-tipped tongs, lift out the crucible and swirl the contents around to get the entire sample into one bead. **Wear eye protection!** The bead is very hot and rapid cooling can cause it to shatter and fly out.
7. Place the crucible on its cooling rack. When seated properly the red light behind it will start flashing. When the beadmaker beeps it should be finished cooling.
8. Place a sheet of 6x6 weigh paper on the ceramic plate. Take crucible from the cooling rack and prepare to flip it upside down on the paper to extract the bead.
9. With crucible in hand flip over and give it a firm whack on the weigh paper. The bead should pop off without much resistance. Put the bead back into the vial that contained the flux/sample mixture.
10. If there are small pieces of bead left behind you can use your Teflon spatula to try pry it off. Do not use too much force. The platinum is malleable and will get scratched and damaged if put under too much force. If it still remains, make a note of the sample number and inform the chemistry technician. The residue (if any) should come off during the cleaning process.
11. Repeat process for all samples.
12. Hand off all beads to the chemistry technicians to continue on with the ICP analysis.

Cleaning Platinum Crucibles

1. Rinse crucibles with DI water.
2. If beads are stuck to the bottom, sonicate with DI water for 30 min or more.
3. Place crucibles in HNO3 10% bath for 12 hr. If you notice any signs of residue, leave in the acid bath for longer. If the crucibles are in urgent need, a minimum cleaning time in the HNO3 10% acid bath is 2 hrs, however, extra flux blanks should be made with these crucibles for analysis to ensure there isn't leftover contamination.
4. Clean a Tupperware container with isopropyl alcohol. Lay down sheets of paper towel and large Kimwipes.
5. Take crucibles out of the acid bath and rinse with DI water 3 times. Place crucible in the container. If the crucibles require polishing, see ***Polishing the Platinum Crucibles.***
6. Cover all crucibles with a large Kimwipe and place in the drying oven in the Chemistry Laboratory. Leave overnight.
7. When dry remove crucibles and bring into the XRD laboratory. Wrap each crucible in a small Kimwipe and and place back in the safe. Lock the safe after all crucibles have been put back.

Polishing the Platinum Crucibles

It may be necessary to polish the crucibles to remove scratches. Do this no more than once per expedition because polishing thins the platinum and in time the crucible will crack. A polishing machine is located in the ICP prep area.

1. Wrap a silk cloth (like the cloth used to clean eyeglasses) around the polishing nozzle.
2. Apply a diamond paste (Grade 30, found in Thin Section Lab) to the front of the silk-covered nozzle and place the crucible over the nozzle.
3. Turn polisher on and polish the crucible bottom for ~30 s (the bottom will be shiny). Be careful because the crucible will get hot. Do not try to remove any deep scratches – the crucibles are not that thick. The least amount of polishing the better.
4. Clean the crucibles with isopropyl alcohol and put in 10% HNO3 bath for 12 hr.

Using the LOI Furnace to Make Sample Beads

If the bead maker breaks, use the LOI furnace to make beads.
Caution! Safety is a major issue with this procedure; use proper personal protection equipment and note where the nearest fire extinguisher is located.

1. Obtain the following safety equipment:
    - Welder's jacket (orange leather) and welder's gloves
    - Face shield
    - Long pants
    - Steel toed boots
2. Have a designated spotter in the room with you when placing samples in and taking samples out of the oven.
3. Heat furnace to 1020°C.
4. Pour the sample powder mix into a Pt-Au crucible.
5. Pipette 10 µL of 0.172 mM LiBr wetting agent into the sample powder.
6. Place each crucible into the oven slowly, one by one. Close the door in between samples. Six crucibles is an appropriate number. If you are not comfortable using the furnace, create beads in smaller batches.

Note: It is possible to put Pt-crucibles directly onto the furnace shelf; however, it is advised to use a sample holder swing custom made by the ET's. The swing goes into the furnace by the upper vent, and can be rocked back and forth (with the door closed) from the outside. This is advised, as it allows for complete mixing and fusing of the sample.

1. Wait until the temperature returns to 1020°C, then leave the samples in for 6 min.
2. Remove each sample crucible with the long tongs. When the sample is removed, turn the crucible 45° to one side.

Note: The furnace drops temperature extremely quickly each time the door is open. If you swirl the sample or tip the crucible from side to side; the bead will not flow together and will be smeared across the bottom of the crucible. If not using a sample holder swing, it is advised to simply tip the crucible to one side.

1. Place the sample crucible on a ceramic plate to cool. These crucibles are very hot and may burn anything near or under them. Take appropriate precautions.
2. Repeat this procedure until all samples are completed.

Credits

This document originated from Word document ICP_HR_Prep_UG_376.doc (see Archived Versions below for a pdf copy) that was written by H. Barnes & K. Bronk; later edited by N. Lawler & A. Armstrong. Credits for subsequent changes to this document are given in the page history.

LOI LIMS Component Table

ANALYSIS	TABLE	NAME	ABOUT TEXT
LOI	SAMPLE	Exp	Exp: expedition number
LOI	SAMPLE	Site	Site: site number
LOI	SAMPLE	Hole	Hole: hole number
LOI	SAMPLE	Core	Core: core number
LOI	SAMPLE	Type	Type: type indicates the coring tool used to recover the core (typical types are F, H, R, X).
LOI	SAMPLE	Sect	Sect: section number
LOI	SAMPLE	A/W	A/W: archive (A) or working (W) section half.
LOI	SAMPLE	text_id	Text_ID: automatically generated database identifier for a sample, also carried on the printed labels. This identifier is guaranteed to be unique across all samples.
LOI	SAMPLE	sample_number	Sample Number: automatically generated database identifier for a sample. This is the primary key of the SAMPLE table.
LOI	SAMPLE	label_id	Label identifier: automatically generated, human readable name for a sample that is printed on labels. This name is not guaranteed unique across all samples.
LOI	SAMPLE	sample_name	Sample name: short name that may be specified for a sample. You can use an advanced filter to narrow your search by this parameter.
LOI	SAMPLE	x_sample_state	Sample state: Single-character identifier always set to "W" for samples; standards can vary.
LOI	SAMPLE	x_project	Project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
LOI	SAMPLE	x_capt_loc	Captured location: "captured location," this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
LOI	SAMPLE	location	Location: location that sample was taken; this field is usually null and is unnecessary because any sample captured on the JR has a sample_number ending in 1, and GCR ending in 2
LOI	SAMPLE	x_sampling_tool	Sampling tool: sampling tool used to take the sample (e.g., syringe, spatula)
LOI	SAMPLE	changed_by	Changed by: username of account used to make a change to a sample record
LOI	SAMPLE	changed_on	Changed on: date/time stamp for change made to a sample record
LOI	SAMPLE	sample_type	Sample type: type of sample from a predefined list (e.g., HOLE, CORE, LIQ)
LOI	SAMPLE	x_offset	Offset (m): top offset of sample from top of parent sample, expressed in meters.
LOI	SAMPLE	x_offset_cm	Offset (cm): top offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset, converted to cm)
LOI	SAMPLE	x_bottom_offset_cm	Bottom offset (cm): bottom offset of sample from top of parent sample, expressed in centimeters. This is a calculated field (offset + length, converted to cm)
LOI	SAMPLE	x_diameter	Diameter (cm): diameter of sample, usually applied only to CORE, SECT, SHLF, and WRND samples; however this field is null on both Exp. 390 and 393, so it is no longer populated by Sample Master
LOI	SAMPLE	x_orig_len	Original length (m): field for the original length of a sample; not always (or reliably) populated
LOI	SAMPLE	x_length	Length (m): field for the length of a sample [as entered upon creation]
LOI	SAMPLE	x_length_cm	Length (cm): field for the length of a sample. This is a calculated field (length, converted to cm).
LOI	SAMPLE	status	Status: single-character code for the current status of a sample (e.g., active, canceled)
LOI	SAMPLE	old_status	Old status: single-character code for the previous status of a sample; used by the LIME program to restore a canceled sample
LOI	SAMPLE	original_sample	Original sample: field tying a sample below the CORE level to its parent HOLE sample
LOI	SAMPLE	parent_sample	Parent sample: the sample from which this sample was taken (e.g., for PWDR samples, this might be a SHLF or possibly another PWDR)
LOI	SAMPLE	standard	Standard: T/F field to differentiate between samples (standard=F) and QAQC standards (standard=T)
LOI	SAMPLE	login_by	Login by: username of account used to create the sample (can be the LIMS itself [e.g., SHLFs created when a SECT is created])
LOI	SAMPLE	login_date	Login date: creation date of the sample

LOI	SAMPLE	legacy	Legacy flag: T/F indicator for when a sample is from a previous expedition and is locked/uneditable on this expedition
LOI	TEST	test changed_on	TEST changed on: date/time stamp for a change to a test record.
LOI	TEST	test status	TEST status: single-character code for the current status of a test (e.g., active, in process, canceled)
LOI	TEST	test old_status	TEST old status: single-character code for the previous status of a test; used by the LIME program to restore a canceled test
LOI	TEST	test test_number	TEST test number: automatically generated database identifier for a test record. This is the primary key of the TEST table.
LOI	TEST	test date_received	TEST date received: date/time stamp for the creation of the test record.
LOI	TEST	test instrument	TEST instrument [instrument group]: field that describes the instrument group (most often this applies to loggers with multiple sensors); often obscure (e.g., user_input)
LOI	TEST	test analysis	TEST analysis: analysis code associated with this test (foreign key to the ANALYSIS table)
LOI	TEST	test x_project	TEST project: similar in scope to the expedition number, the difference being that the project is the current cruise, whereas expedition could refer to material/results obtained on previous cruises
LOI	TEST	test sample_number	TEST sample number: the sample_number of the sample to which this test record is attached; a foreign key to the SAMPLE table
LOI	CALCULATED	Top depth CSF-A (m)	Top depth CSF-A (m): position of observation expressed relative to the top of the hole.
LOI	CALCULATED	Bottom depth CSF-A (m)	Bottom depth CSF-A (m): position of observation expressed relative to the top of the hole.
LOI	CALCULATED	Top depth CSF-B (m)	Top depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
LOI	CALCULATED	Bottom depth CSF-B (m)	Bottom depth [other] (m): position of observation expressed relative to the top of the hole. The location is presented in a scale selected by the science party or the report user.
LOI	RESULT	crucible_and_postignition_sample_mass (g)	RESULT post-ignition crucible and sample mass (g): mass of the sample plus the crucible after ignition ("ashed")
LOI	RESULT	crucible_and_preignition_sample_mass (g)	RESULT pre-ignition crucible and sample mass (g): mass of the sample plus the crucible before ignition
LOI	RESULT	crucible_number	RESULT crucible number: number of the crucible used for this measurement
LOI	RESULT	crucible_preignition_mass (g)	RESULT crucible preignition mass (g): mass of the empty crucible before ignition
LOI	RESULT	loi_percent	RESULT loss on ignition (wt%): loss of material after ignition
LOI	RESULT	reference_mass (g)	RESULT reference mass (g): field for the reference mass used on the reference balance (not always populated)
LOI	RESULT	ssup_asman_id	RESULT spreadsheet uploader ASMAN_ID: serial number for the ASMAN link for the spreadsheet uploader file
LOI	RESULT	ssup_filename	RESULT spreadsheet uploader filename: file name for the spreadsheet uploader file
LOI	SAMPLE	sample description	SAMPLE comment: contents of the SAMPLE.description field, usually shown on reports as "Sample comments"
LOI	TEST	test test_comment	TEST comment: contents of the TEST.comment field, usually shown on reports as "Test comments"
LOI	RESULT	result comments	RESULT comment: contents of a result parameter with name = "comment," usually shown on reports as "Result comments"

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