

Low Temperature Ashing (LTA) for removal of organic matter from coal and shale

1. Introduction

This low-temperature ashing (LTA) procedure is used for sample preparation only, specifically for X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) studies. It is used to concentrate the mineral component of organic-rich samples for XRD studies, and to have organic-free samples for SEM and FTIR analyses. In this procedure, the resultant ash has minimal alteration of the original minerals' crystal structure due to the low temperature of ashing. However, the LTA process can form byproduct minerals from the liberation of elements and their recrystallization, for example calcium; iron; Ca and ammonium sulfates (bassanite, sabieite, and godovikovite). In addition, the dehydration of hydrated minerals can also occur, for example gypsum and clays (montmorillonite).

The ashing of the organic material is done with a highly reactive oxygen plasma. This reacts with the surface of the organic particles, oxidizing it several molecules deep. The oxidation occurs at approximately 66 °C. This is done by energizing oxygen with radio frequency (RF) energy at 13.56 MHz and 110 watts power in a vacuum at 0.3 to 0.5 torr. As the sample is ashed, it is stirred daily to re-expose the surface of the un-ashed organic matter. The process is repeated until all of the organics are removed.

XRD samples for LTA must be ground to their final size before ashing. In addition, 6 grams (g) of coal (one sample per dish) will usually produce enough ash for XRD analysis. If it is necessary to know that all of the organic has been ashed, then the weight of the samples must be monitored during the ashing process, as described in the procedure below. The samples must be weighed daily before and after stirring then the % ash calculated. Ashing will be continued until the % ash is constant. Note that there are losses due to stirring and the weight may decrease by about 0.1 % per day due to this factor. Ashing time varies depending on the rank of the organic matter in the sample; the lower the rank, the longer it takes to ash.

2. Interfaces with Other Methods

- a. EGL Method 25 – Method for Sample Login, Control, and Disposition
- b. EGL Method 26 – Method for Inorganic Sample Preparation
- c. EGL Method 29 – Calibration of Laboratory Scales and Analytical Balances
- d. EGL Method 30 – Preparation of Whole Rock Materials for the Acquisition of Semi-quantitative X-ray Powder Diffraction Patterns

3. Materials and Equipment

- a. Branson/IPC¹ 4155/2 plasma asher with associated equipment and gases
- b. 8" (inch) watch glasses (strain free, fire polished edges)
- c. 5" agate mortar and pestle

¹ Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

- d. 6×6 inch weighing papers
- e. 20 mL sample vials
- f. Small antistatic brush
- g. Box of Kimwipes¹
- h. Washbottle of alcohol
- i. Nitrile surgical gloves (4 mils thick)
- j. Analytical balance (0.001 g resolution)
- k. Indicator desiccant (“Drierite¹” CaSO₄)
- l. Dust mask

4. Procedure

A) Instrument start-up

1. Fill out the “LTA logbook;” operator, EGL lab number for the samples, number of samples, and time and date the equipment is started.
2. Turn "On" the RF Generator's power (switch lever is up).
3. Wait for the "Ready" light to come on, about 3 minutes.
4. Turn "On" the LTA controller's power (switch lever is up).
5. Open the main tank valves on the oxygen and nitrogen cylinder gas.
6. Open the needle valves on the cylinder gas regulators. The flowing downstream regulator pressure for the oxygen is ~10 psi and for nitrogen is 35 to 45 psi, adjust as necessary.
7. Turn "On" the vacuum pump using the wall switched outlet.
8. There is a vacuum line "Shut-off" valve just before the vacuum pump, track the light gray power cord back to the plug, and plug it into a 110 v AC outlet.
(Note, this is the "isolation" shut off valve for the vacuum line to the prevent vacuum pump oil from being sucked into the asher's chamber during a power failure.)
9. If there is a vacuum in the chamber, see the torr/vacuum meter on the controller, then turn the "Purge" switch to "On" (switch lever is up).
10. Open the Purge valve (counter clockwise).
11. Unlatch LTA door, but do not open it; the doors will open when the chamber reaches atmospheric pressure.
12. When the door opens, close the purge valve (clockwise).
13. Turn the "Purge" switch to "Off" (switch lever is down).

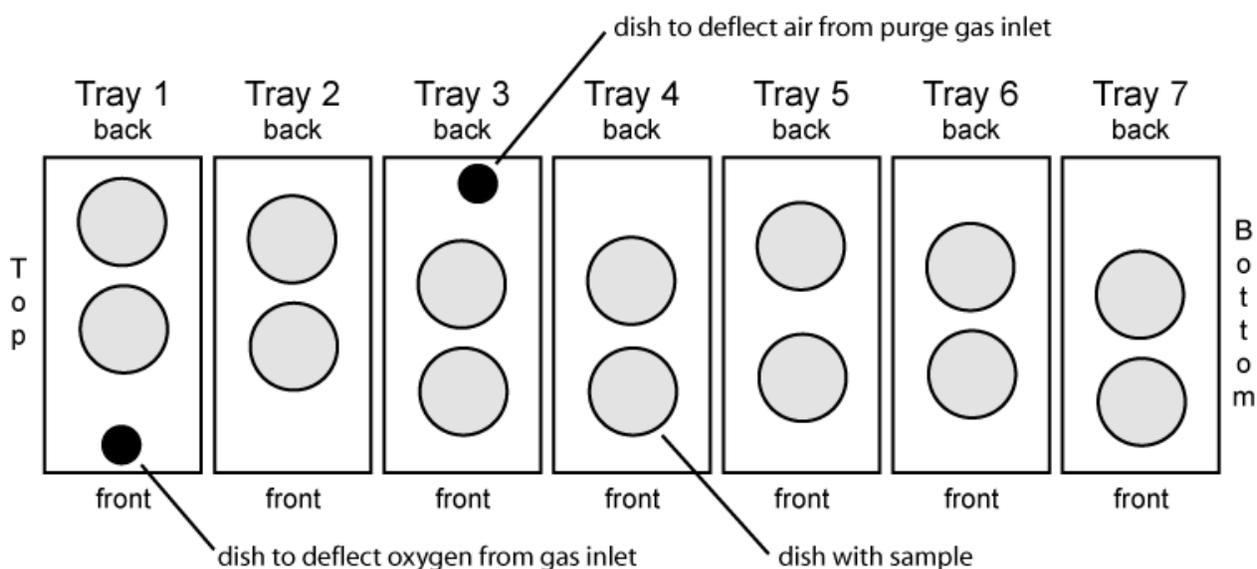
B) Ashing samples

14. Start with 14 clean, numbered, 8” watch glasses.
15. If not already done, label the watch glasses 1 thru 14. The numbers must be engraved into the watch glasses, on the underside, because a marker or a china pen will be ashed off of the surface of the glass after they have been exposed to the plasma.
16. Create a spreadsheet for the data.
17. Record the weight of the watch glass in the spreadsheet, and the lab/sample number. (Note, recording the weights and calculating the ash % is optional, and is only for checking the performance of the method, unless requested by the sample submitter.)
18. While the watch glass is on the balance, add approximately 5-6 g of sample to the watch glass in a thin even layer. If needed, brush the sample from the sides of the numbered watch glass so there is about 1” of space between the edge of the watch glass and the sample, then

clean the brush. Record the dish with sample weight in the spreadsheet. Calculate the original sample weight in spreadsheet, using the formula:

(weight of dish with sample) - (dish weight) = (original sample weight).

19. Put the watch glass on the ashtray (take note of Steps 20 through 22).
20. There are 7 trays in the LTA chamber. Put two (2) watch glasses per tray after the samples are added.
21. Be aware of the location of the inlet and outlet vents in the chamber, and place the watch glasses on the trays to prevent dust/sample cross-contamination due to gas or air circulation (see figure below). Tray 1 is placed in the top of the chamber with each successive tray placed below the previous tray until Tray 7 is on the bottom.
22. To help reduce sample cross-contamination it is recommended to place an upside-down small watch glass on Tray 1, located at the center front, under the oxygen gas inlet in the top of the chamber. Also, place a right-side up, straight-sided evaporating dish at the back and slightly to the right of center on Tray 3, in front of the purge gas inlet in the back of the chamber (see figure below).



23. Repeat steps #17 through 22 for all 14 watch glasses.
24. Once all of the trays are placed inside the chamber, close and latch the chamber door.
25. Open the Slow Vacuum valve (counter-clockwise) very slowly.
26. Slowly evacuate the chamber, until the vacuum meter reads 2 torr.
27. Turn the main Vacuum switch to On (switch lever is up).
28. Close the Slow Vacuum valve (clockwise).
29. When the vacuum meter reads 0.2 to 0.3 torr, turn "Gas 2" to On (switch lever is up). The operating pressure of the oxygen plasma is approximately 0.3 to 0.5 torr. Use the "Gas 2" needle valve, located at the top of the flowmeter, to adjust the pressure (oxygen flow rate) based on the vacuum meter's pressure reading. Note, check the downstream pressure gauge on the oxygen regulator, it should be ~10 psi. **Do not let the oxygen flow rate go below 0.2 torr.**
30. Turn the RF Power switch to On (switch lever is up).

31. Make sure RF meter's RF switch, directly below the meter, is switched to FWD (lever is down).
32. Turn RF Power Level knob clockwise until the RF meter reads 50 watts on the top scale, pause for a few seconds, and then turn to 100-110 watts.
33. Wait a few minutes and then turn off the lights in the room. Look through the window in the chamber door and make sure the plasma is bright light blue in color. If dark blue, adjust the gas levels to achieve this light blue color (0.3 to 0.5 torr, see Step #29). (Note, if nitrogen is in the system the color will be pink or pinkish, this is caused by air that has not been removed from the chamber. First try getting the air out of the system by turning the plasma off and waiting half an hour, then go to Step 30 and restart the plasma. If air is leaking in, maintenance maybe required.)
34. Let the LTA operate for at least 1 day. Note, the samples should be stirred daily.
35. Turn RF Power Level knob counter-clockwise to 0 watts.
36. Turn the RF Power switch to Off (switch lever is down).
37. Turn "Gas 2" to Off (switch lever is down).
38. Turn the main Vacuum switch to Off (switch lever is down).
39. Turn the Purge switch to On (switch lever is up).
40. Very very slowly at first, open the Purge valve (counter clockwise). Make sure to watch the torr gauge while opening the Purge valve. The torr gauge is a reflection of the amount of room air entering the chamber. The location of the inlet port inside the chamber is a potential location of cross contamination. If opened too quickly the sample will be blown off the weigh dishes. Note, the purge gas (room air) is pulled through a gas dryer using indicator desiccant.
(Note, when "Drierite" CaSO_4 is used; blue is dry, violet is moist, red is wet. When approximately 70% of the Drierite has turned red and/or violet, replace it.)
41. Unlatch LTA door, but do not open it; the doors will open when the chamber reaches atmospheric pressure.
42. Keep the door open for approximately 10 minutes or until your sample trays have cooled.
43. Close the "Purge" valve (clockwise).
44. Turn the "Purge" switch to "Off" (switch lever is down).
45. Take out a tray, starting with the top tray, and set it on the counter. Move down one tier with each cycle of steps #45 through 53.
46. If total organic removal is requested, weigh the sample and dish before stirring and record in the spreadsheet. Take one of the samples and empty it out into a mortar. You can use a soft antistatic brush to direct the sample into the mortar. Optionally, empty the sample onto a clean 8" watch glass or a 6×6" weighing paper as a narrow pile, and then into the mortar.
47. Use the pestle as a stirring rod to lightly stir the sample to a uniform color. Do not grind the sample.
48. Empty the sample from the mortar onto an empty, clean 8" watch glass or the watch glass from step #46.
49. Take the watch glass with sample and hold it over the numbered watch glass that the sample was on and tap the sides while distributing evenly. This will disperse the sample evenly back onto the watch glass. If needed, brush the sample from the sides of the numbered watch glass so there is about 1" of space between the edge of the watch glass and the sample. Put the watch glass back on the tray.

50. Lightly clean the brush used above with compressed air, then wipe clean the mortar and pestle and un-numbered 8" watch glass, from step #49, with alcohol wet Kimwipes, until clean.
51. Repeat steps #45 through 50 for each of the other samples. Stir the samples every work day – stirring is not required over weekends.
52. Rotate the trays every work day. For example move Tray 1 down to the second tier, Tray 2 to the third tier and so forth until Tray 7 is now where Tray 1 was the previous day.
53. Repeat steps #21 through 52 until the samples are a uniform color. Ash until there is no further change in sample color. If total organic removal is requested, weigh the samples and dish after stirring and record in the spreadsheet, repeat steps #19 through 52 until there is no change in weight. For coals, ash for at least 7 days or more; shales usually require at least 5 days (the lower the rank the longer the time).
54. When the samples are completely ashed, weigh them.
55. Weigh the ashed sample and dish together and enter this into the spreadsheet. Calculate the final sample weight in spreadsheet, using the formula:
(weight of dish with sample) – (dish weight) = (final sample weight).
56. Bottle the ashed samples. Empty the sample onto a 6×6" weighing paper, using a brush to get the excess sample off the dish. Then transfer the sample into a labeled 20 mL vial/bottle. Clean the brush between samples.
57. Calculate the % Ash in spreadsheet, using the formula:
((final sample weight) / (original sample weight)) × 100 = (% Ash in the sample).
58. Clean the watch glasses with warm soapy water and a soft scrubbing pad, rinse with deionized water and let them dry in a drying rack for reuse.
59. If you have another ashing job, go to step #14.

C) Instrument Shut-down

60. When there are no more samples to ash, shut-down the asher.
61. Put all of the trays in the asher chamber.
62. Close and latch the chamber door.
63. Open the Slow Vacuum valve (counter clockwise) quickly.
64. When the vacuum meter reads 5 torr, turn the main "Vacuum" switch to "On" (switch lever is up).
65. Close the Slow Vacuum valve (clockwise).
66. When the vacuum meter reads < 0.5 torr, turn the main "Vacuum" switch to "Off" (switch lever is down).
67. There is a vacuum line "Shut-off" valve just before the vacuum pump, track the light gray power cord back to the plug, and unplug it from the 110 v AC outlet.
68. Turn "Off" the vacuum pump using the wall switched outlet.
69. Close the main tank valves on the oxygen and nitrogen cylinder gas.
70. Close the needle valves on the cylinder gas regulators.
71. Turn "Off" the LTA controller's power (switch lever is down).
72. Turn "Off" the RF generator's power (switch lever is down).
73. Fill out "LTA logbook," add notes on total time run, any problems, and maintenance needed or performed.

D) Outline/short version for experienced users.

Inst. start-up

1. Logbook
2. RF Generator "On"
3. Controller "On"
4. Gas cylinders open.
5. Vacuum pump "On"
6. Plug in downstream vacuum solenoid valve
7. Main-vac, "Off"
8. Slow-vac closed.
9. Purge solenoid "On"
10. Purge valve open.

LTA Operation

11. Weigh out samples & load asher.
12. Purge solenoid "Off"
13. Purge valve closed.
14. Slow-vac, open.
15. Pump to 2 torr.
16. Main-vac, "On"
17. Slow-vac closed.
18. Pump to 0.2 to 0.3 torr.
19. Gas-2 "On" (0.3-0.5 torr).
20. RF "On" (110watts).
21. Check plasma.
22. Ash ~24 hrs.
23. RF "Off"
24. Gas "Off"
25. Main-vac, "Off"
26. Purge solenoid "On"
27. Purge valve **slowly** open.
28. Remove tray and stir ash.
29. Reload asher with trays rotated by one shelf.
30. Repeat steps 12-29 until samples are fully ashed.
31. Weigh ashed samples, then bottle.
32. Clean dishes.

Inst. shut-down

33. Purge solenoid "Off"
34. Purge valve closed.
35. Main-vac, "On"
36. Pump to <0.5 torr.
37. Main-vac, "Off"
38. Unplug downstream vacuum solenoid valve.
39. Vacuum pump "Off"
40. Gas cylinders closed.
41. Controller "Off"
42. RF Generator "Off"
43. Logbook

5. Calibration and Quality Control Samples

- a. Samples are weighed and recorded to the nearest milligram (0.001 g).
- b. The balance used for weighing must be inspected and certified yearly, and have a visible certification sticker.
- c. Check to see if the power setting is correct, the correct vacuum is achieved, and the O₂ is set at the correct flow rate. If not, reset controls or perform service to the equipment (see equipment's manual).
- d. Look in the chamber window to see that the plasma is a light blue color and evenly distributed. If not, check the control settings and/or perform service to the equipment (see equipment's manual). Note: if the plasma is uneven, the electrical contacts with the trays need to be cleaned and/or the oxygen flow rate reduced, do not let the flow rate go below 0.2 torr or above 1 torr. If the plasma is pink, there is N₂ in the system indicating an air leak; this may be due to a cracked door or window seal gasket.

6. Limits, Precautions, and Interferences

A. Personal Protection Equipment:

1. Heat resistant gloves.
2. Nitrile surgical gloves.
3. Dust mask

B. Special Precautions:

1. Samples are ashed at approximately 66 °C, let them cool before handling.
2. Exposure to alcohol, wear nitrile gloves.
3. Do not touch the metal vacuum pipe at the back of the ashing chamber, there is some radio frequency (RF) emitted from the chamber down the vacuum pipe and there is a RF shock hazard. This is especially important at the vacuum pipe direct behind the chamber, it is RF hot for a short distance, this is under the wood cover.
4. All of the control instruments, the chamber, and the vacuum pipe must be grounded together and to an "earth ground" to prevent shock at the vacuum pipe listed in "c" above, and for proper instrument operation.
5. When cleaning inside the chamber wear a dust mask and surgical gloves, as needed.

7. Acceptance of Data

This method does not generate data for the LIMS.

8. Data Handling and Transfer

Not applicable.

9. References

GaSonics International, 1988, 4X55 Plasma Treatment System: GaSonics International, San Jose, CA.

10. Attachments

None.

11. History of Changes

R0: Initial Issue

R1: Missing instruction lines (inst. # 35-36) were added, setting for oxygen feed rate reduced, added details in the procedure, revised figure, added the logbook steps, "Introduction" partially rewritten for clarification of the method, and an outline/short version written for experienced users.