Standard Operating Procedure

Procedure: Proximate Analysis of Solids by NAVAS Thermogravimetric Analyzer (TGA)

Department: Bioeconomy Institute

Building/ Room Number: Biorenewables Research Laboratory (BRL) 1114

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Procedure Overview: The thermogravimetric analyzer (TGA) uses a furnace and a scale to perform proximate analysis measurements of solid samples such as biomass, biochar and coal. This model CANNOT test liquid samples. The NAVAS TGA 1000 can analyze up to 19 samples of up to 10 g (typically 1 g) simultaneously. The instrument can be programmed to measure moisture, volatiles and ash content at temperatures between 50-1000°C, under nitrogen or air atmospheres, with specified temperature ramp rates, and for specified periods of time or until samples reach constant weight.

Health and safety information for materials used: Compressed air and nitrogen cylinders are under high pressure. Ground biomass and biochar may be fine powders that can create dust hazards.

Hazard Control Measures:
- Safety glasses
- Lab coat
- Latex or nitrile gloves (for handling samples)
- OSHA Toes or steel-toed shoes (for moving compressed gas cylinders)

Waste Disposal Procedures: Biomass, char, coal, ash and unburned residue can be placed into the non-hazardous waste garbage.

Decontamination Procedures: None

Spill Containment and clean up procedures: Biomass, biochar, coal, and ash can be swept up or wiped with a wet cloth and disposed of in the garbage.

Using substances requiring special procedures: No

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Detailed procedures, operation instructions, maintenance, and emergency contact information list is attached.
Equipment Description

The Navas TGA-1000 (thermogravimetric analyzer) is used to measure changes in weight associated with changes in temperature. The most common measurement performed on the TGA is proximate analysis: determining the moisture, volatile matter, fixed carbon, and ash content of a substance. Moisture content is the mass lost above 100°C; the instrument generally maintains a temperature around 105°C until sample weight remains constant. Volatile matter is the mass lost upon heating to high temperatures in an inert environment (here nitrogen). Ash content is the mass that remains after heating the sample to high temperatures in the presence of air. Fixed carbon content is determined by difference.

The TGA consists of three main parts: the compressed gas cylinders, the instrument with blower, and the computer with software to operate the instrument. The compressed gas cylinders include a compressed air tank used for the oxygen source, a nitrogen tank, and a compressed air tank shared with the bomb calorimeter and used to power the TGA pneumatics. The cylinders are secured on the north side of the fume hood and are connected to the instrument through ports in the back (compressed air is connected at the oxygen port).

The relevant parts of the main instrument (Figure 1) include: lid, sample crucibles, carousel, side panels, flow meter, test weight button, compressed gas plumbing, blower, and vent tubing. The majority of the instrument’s operation is controlled through the software. Lid height is controlled through pneumatics and has several levels including fully open, closed and partially open (for cooling). Reusable ceramic crucibles are used to hold the samples. The ceramic carousel consists of 20 slots that hold the reference and sample crucibles, and can be raised to rotate or lowered to place a sample on the weighing pedestal. “Home position” for the carousel is at the front of the instrument and is where the scale pedestal is located; it is labeled with an arrow on the white insulating material. The side panels (Figure 2) are fastened down by one screw and can be removed for maintenance and repair. The flow meter is on the front of the instrument (see Figure 3) and indicates the gas flow rate in L/min. The “test weight button” is the red button seen in Figure 3. It is used during sample loading and unloading to lower and/or rotate the carousel.

The software is located on the desktop and under “Navas Instruments TGA.” Instructions for using the software are located in the “Instrument Operation” section of this manual.

Pre-Analysis Checklist

The following checklist is to be performed before using the TGA:

- Samples to be tested are solids, not liquids.
- Computer is on and the instrument software is open.
- Printer is on and has sufficient paper.
- Compressed air cylinder for pneumatics is open and set to 80 psi.
- Compressed air and nitrogen cylinders are open and set to approximately 60 psi and 50 psi, respectively.
- Fume hood is functioning as indicated by a green light on the upper right of the hood (Figure 4). If the red light is illuminated, make sure that hood sash is at the proper height and that the key switch located on the lab’s east wall is set to “on”.
- The vent tubing outlet is venting into the fume hood and is held in place by the fume hood sash (Figure 4).
- Listen for leaks in the connections and inside the instrument. If leaks may be present, see Maintenance for a leak check procedure.
- Instrument lid is open.
- All crucibles have been removed from the carousel and cleaned.
- Material should be in small enough particle sizes to fit completely inside provided crucibles. The scale can read up to 4 decimal places and the heaviest sample size allowed is 10 grams.

**Instrument Operation**

1. Click Options<Programs located on the toolbar at top. Choose appropriate program. If program does not exist, create it (see Create a New Program).
2. Once program is chosen, click Configuration <Diagnostics on the toolbar. The diagnostics window will pop up.
3. Without any crucibles in the carousel, click Close under Lid menu; once the lid is closed, click the Tare button to zero out the scale.
4. Click on Weight icon. When prompted, enter the number of samples to be tested (not including the empty reference crucible). Carousel positions will appear to fill in carousel diagram indicating which slots are to be used in this analysis.
5. If the carousel is not already in home position, it will rotate there. Place the empty reference crucible in home position.
6. Press the red test weight button or click OK to rotate the carousel to the next position to be filled. Place an empty sample crucible in that position.
7. Repeat until all needed carousel positions are filled with empty crucibles. After the last empty crucible has been placed, the lid should close automatically to measure and record the empty crucible weights, and then reopen so that the samples can be loaded.
8. A window will now open where sample information can be entered.
9. For the first sample, create a new sample identifier by entering an alphanumeric name in the prompt box. A good sample identifier is “analyst’s last name, sample number, replicate number”.
10. Before clicking OK, remove sample crucible from carousel in the home position and fill it with the desired amount of sample.
11. Put the sample crucible back on the carousel and press the red test weight button; this will lower the carousel, setting the crucible on the balance pedestal. The current weight of sample will be displayed.
   a. To change the mass of sample, remove crucible from carousel and add/remove appropriate amount; return sample to on top of the pedestal to reweigh (do not press red button again as this will move on to the next sample).
   b. If the weight is unreasonable or varying widely, move the sample around on top of the pedestal so that the sides of the crucible are no longer touching the sides of the carousel.
12. When the amount of sample is correct, press ENTER key to move on to the next sample.
13. Repeat until all samples are identified and loaded.
14. Press ENTER key to continue.
15. The instrument will close the lid and reweigh the samples.
16. Once the samples have been reweighed with the lid closed and the analysis is ready to run, click the Execute (traffic light) icon.
17. A message will be displayed asking to regulate air flow. Adjust the flow meter on the front of the instrument to be between 4 and 6 L/min, and click okay.
18. The instrument will now run through the selected analysis program (may take several hours).
   a. Check on TGA periodically in case error messages appear and pause testing.
      i. An error in gas flow could mean the tank is closed, the tank is empty, the gas flow meter is set too low, or there is a leak.
      ii. An error about sample weight is most likely to occur if the crucible is set in the carousel such that the crucible is still touching the carousel when lowered onto the scale pedestal.
19. If the analysis was successful, the computer will automatically print the data in the preset format selected when creating the program, as well as any requested graphs. The lid will gradually raise and the blower/internal fans turn on and off to complete an automated cooling cycle.
20. Only when the lid is completely open and the furnace has cooled to 40°C should crucibles be removed for cleaning.
21. Crucibles can be cleaned simply by emptying the ash into the non-hazardous waste and wiping out the crucible with a Kim-wipe. Crucibles can also be washed in soap and water, as long as they are rinsed with distilled water and allowed to dry before being used again.

Create a New Program
1. Click Configuration Tab< Configuration to bring up list of programs. Blank program spots are labeled by a single placeholder letter such as “B”.
2. Select a program spot and enter a new program name. Generally, this is the only step need in the Configuration tab.
3. After naming program, go to Options Tab<Programs and select program to be modified.
4. Click on. Configuration Tab<Slope Settings. A window will pop up with parameters that can be changed (see Slope Screen Shot). The top of the window has eight available Slope tabs and an LOI Formulas tab. Generally, only Slope 1, Slope 2, and Slope 3 are used for moisture, volatiles and ash, respectively.
5. For each slope, check the Analyze This Slope box and type an appropriate type into the Name box such as “Moisture”, “Volatiles”, or “Ash” for that slope.
6. For all slopes, make sure the Place Covers box is not checked. This TGA does not use crucible covers.
7. In the General Parameters section, enter desired final temperature in degrees Celsius. This is the primary hold temperature for the current slope. Enter desired ramp rate. If Automatic Control button is checked instead, the maximum ramp rate will be used until the furnace reaches the High Power Limit Temperature entered, at which point, the furnace heating rate will level off (this is done to avoid overshotting the final temperature).
8. In the Analysis Type section, there are several options to determine when the instrument will move on to the next slope. The following are most commonly used.
a. By Constant Weight—furnace will maintain final temperature until sample reaches a constant weight (as determined by the Plateau Deviation setting).
b. By Time—furnace will maintain final temperature for a specified time (in days, then hours: minutes: seconds).
c. By Plateau deviation or Hold Time—furnace will maintain final temperature until sample reaches a constant weight or the specified hold time is reached, whichever comes first.

9. For all slopes, check the following boxes:
   a. Reference crucible weighed every rev...
   b. This box should be checked for normal operation...
   c. Slower results, increase precision. (Do not check this box for volatiles slopes.)
   d. When marked results are presented only with zero or positive sign.

10. In the Gas Type section, select nitrogen or oxygen (compressed air) for inert or oxidizing atmospheres, respectively.

11. In the Start Before Analysis or After Analysis section, options are available to change the furnace temperature without recording any data; these options would be used if pre/post-heating/cooling is needed in the protocol.
   a. In the case of some volatiles slopes, the furnace needs to be cooled before the ashing step begins. This can be done by checking Execute End Cycle Before Analysis and entering the desired temperature, ramp rate and hold time parameters.

12. In Type of Results section, check the desired result type (Result = .... is not commonly used in proximate analysis).

13. In Samples Results Modifications section, Results Modification as Dry box should not be checked, and set Multiplication Factor = 1 and Addition = 0.

14. Save program.

Instrument Shutdown

1. Instrument lid should be open and furnace temperature should be cooled down to room temperature.
2. Sample crucibles should be removed from carousel and cleaned.
3. Place clean crucibles in the drawer directly under instrument.
5. Turn off the computer and printer.
6. Close compressed air and nitrogen tanks. Do not move pressure setting valve on regulator or close compressed air tank that is shared with the bomb calorimeter.
Maintenance

For problems with the pneumatics, check that the compressed gas tank is open, set to 80 psi and that there are no leaks in the connections. If a leak is suspected, use soap solution spray bottle to check all connections (if soap solution bubbles continuously, gases are leaking out of that connection). To check for leaks inside the instrument, remove the side panel by removing the single screw and lifting the panel off. Leaks have been known to occur around the connections to the internal regulator (inside right side panel) and at the T-connection with the bomb calorimeter.

To recalibrate the scale, see page 20 of the Navas Instruments operating manual.

The compressed air and nitrogen tanks are leased from the ISU Chemistry Stores and must be returned as soon as possible after all usable pressure has been utilized. Used tanks should be closed, the In Use portion of the tag removed (so that it reads Empty), and the tanks taken to the outdoor cylinder rack behind the BRL building near the dumpster. New air tanks can generally be picked up from Chemistry Stores whenever it is opened, though they may need to be ordered ahead.
Emergency Contacts

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