Hugh McLaughlin, P.E.
151 Hill Road
Groton, MA 01450-1609

tel: 978-448-6414
cell: 978-302-3510
hsmclaughlin@verizon.net
file: GACS on a Budget V.doc

Version V, issued July 2016

GACS on a Budget

Gravimetric Adsorption Capacity Scan (GACS)
measurements for Biochars and Activated Carbons

Introduction: Biochar is a new use, as a soil amendment, for an old material, charcoal. As such, existing analytical methods that measure charcoal properties are typically inappropriate, and the resulting measurements close to useless at measuring relevant biochar properties and predicting biochar performance in agricultural applications.

Adsorption, the molecular level uptake of moisture and organic molecules, is one such property that is present to varying degrees in biochars and activated carbons. Adsorption, similar but different from absorption, involves the removal of an "adsorbate" from the fluid phase, liquid or vapor, and retention of that adsorbed species within existing available space inside the "adsorbent". Adsorption is hard to measure, since it is evidenced by only a small heat release and no external swelling of the absorbent. The most significant change is the increase in weight, but that is due to the additional weight of the adsorbed material, which can be minuscule in applications where the impact of the adsorption is still significant. In summary, we want to measure it, we need to measure it, and it is a challenge to measure.

Adsorption, represented by a capacity under a set of conditions, is measured by "challenging" the char with a known substance, usually an organic vapor, and measuring the extent of uptake via adsorption of the challenge gas under controlled conditions. The test is not a routine analytical method and the closest historic analytical method is the BET surface area assay. Unfortunately, the BET method is performed under conditions far removed from what occurs in the soil, with the BET method measuring the adsorption of nitrogen vapor in a partial vacuum at liquid nitrogen temperatures (minus 196 degrees Celsius). As such, BET measurements may not accurately predict, or even differentiate, the adsorption capacity of chars in typical biochar applications.

The recommended (by me) adsorption capacity assay is known as "GACS" or Gravimetric Adsorption Capacity Scan. The GACS method is similar to another esoteric method known as the GRPD test for activated carbon, recently renamed GAED, which was developed, in turn, from a test known as TACTIC (developed by Calgon Carbon Corporation to study activated carbons.) The GACS assay is performed on a custom-built modified TGA (Thermo-Gravimetric Analyzer) and measures all the adsorption behavior of chars and activated carbons over a wide range of adsorption conditions. For the purposes of comparing chars, it is sufficient to subject all

chars to the same conditions and measure the extent of adsorption, with more adsorption being better and the adsorption capacity being quantified as proportional to the weight gain at a specified temperature.

Unfortunately, GACS instruments are not commercially sold and adapting existing instruments, such as thermo-gravimetric analyzers, to measure the properties of biochars is expensive and labor-intensive. The purpose of this document is to detail how to assemble a GACS instrument capable of measuring adsorption properties of biochars and activated carbons "on a budget". Irrespective of the budget, the basic instrument is the same. The greater the budget, the better the quality of the data and the less labor-intensive the operation of the instrument. All designs are straightforward, if a bit tedious, to assemble and de-bug.

The budget tiers are $1000, $5000 and $10,000. In each design, the labor cost is "donated" – it is expected that anyone who builds one of these needs the data, irrespective of how long it takes to make or run the instrument. Anyone who is doing research, including the lowly graduate student, falls into this category. It also includes any organization that is selling or using biochar and desires to accurately know the adsorption properties of their material. That may or may not be good news, depending on the quality of the biochar.

Adsorption Capacity, as measured by GACS, is performed on pure biochar after it is made and before being blended or used for any application. If the biochar is wet, it can be dried and/or the GACS procedure will remove any residual moisture from the sample.

Skills needed to attempt this: While the skill set required assembling and de-bugging a GACS apparatus are not exhaustive, it is a task not recommended for everyone. Some power tools will make the tasks easier, but what is most important is that the builder can read these instructions and fill in the gaps in the guidance based on understanding the intent of the design. If these instructions make "no sense" to you, then don't attempt this without additional help from others that can read between the lines and ferret out the functional intent of specific details.

In addition to fabrication challenges, there is a "scientific method" being applied to running the actual assay. The GACS instrument measures something relatively difficult to measure, and one has to make sure that the desired measurement is both precise and accurate – and repeatable. The rigor and attention-to-detail utilized in passing an undergraduate science lab course is the right set of skills. So, if you hated science labs or flunked several, this may not be for you.

Subassemblies and their functions: The GACS instrument consists of an analytical balance that is modified to measure the weight of a small sample of biochar or activated carbon as the adsorption capacity is "scanned" from high (300C) to low (100C) temperature. In addition to the adsorption capacity, additional information, such as moisture content and relative volatile levels, are collected during the period of time when the sample is heated to the higher starting temperature of the scan.

The complete GACS instrument is shown in Figure 1.

Figure 1: Complete GACS Instrument (and additional lab equipment in background)

Figure 1 shows the major subassemblies of the GACS instrument:

- Vapor supply and flow control plus heating tape power (lower left)
- Vibration-isolating stand with analytical balance on top (middle)
- Heated chamber with sample inside (on lab jack below balance)
- Temperature controller with latching relay (optional – lower right)
- Data acquisition by displaying scale weight and sample temperature (right)

The subassemblies will be described in the order they are constructed, starting with the stand for the analytical balance. Figure 2 shows the basic balance stand without the upper red concrete block. The stand consist of a 4" x 8" x 16" solid concrete block on the bottom and a thinner (1.75") block on the top, with the supporting legs fabricated out of 2 pieces of 1.5" slotted angle (see www.mcmaster.com, p/n 896K24 – order one of 4664T61 and 8975K445 at the same time). The vertical legs are 18" and the remaining horizontal pieces are cut out of the second piece of slotted angle. The aluminum plate is adjustable from side to side and located 2.25" below the upper concrete block, as shown in Figures 1 & 2.

The aluminum plate has a hole in the middle – something like 5/16" is recommended, as shown in Figure 2 and 3. Figure 3 shows a small fan mounted to provide a laminar flow of sweep air between the aluminum plate and the top concrete block – to prevent any rising hot vapors from influencing the balance reading. The fan is a 12V fan running on a 5V transformer – to slow the fan down and allow laminar flow horizontally beneath the balance.

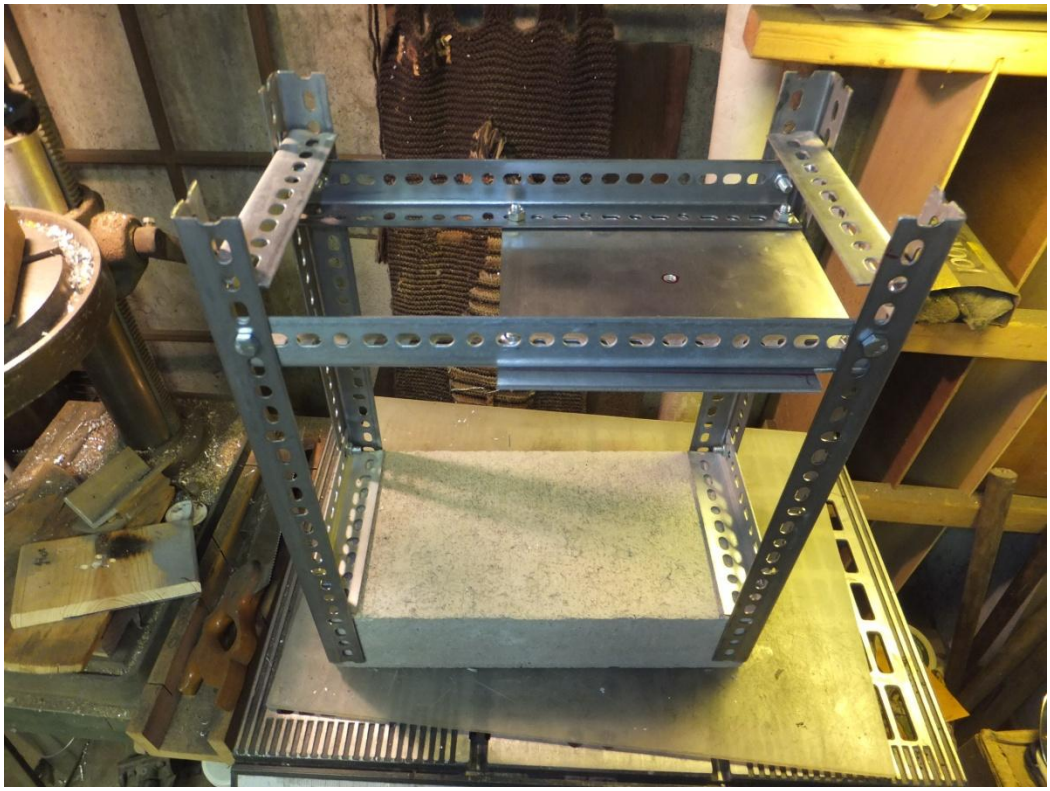

Figure 2: Vibration-isolating balance stand (without upper red concrete block)

Figure 3: Laminar flow fan mounted in balance stand, 5/16” hole in Al plate on left

The role of the balance stand is to hold the balance in a relatively vibration-free place and allow the biochar sample to be connected to the balance from BELOW, in order to hang a sample into the heated chamber as shown in Figure 1. This is a good time to discuss the specifics of the analytical balance.

The analytical balance has to have the "weigh below" feature, which is a little plug in the bottom of the balance that is removed and allows a thin wire to be connected to the internal weighing mechanism of the balance. It is traditionally used for density measurements, ala Archimedes, and the GACS instrument takes advantage of this feature. Not all balances have this capability and anyone building this instrument must be sure to get a balance that has "weigh below" – it cannot be added to a balance after the fact.

Because the balance is open at the bottom, it is important to close the top, as shown in Figure 4.

Figure 4: Faraday Cage sealing the top of the balance weighing mechanism

The cover for the top of the balance weighing mechanism does two things; it prevents heated air from rising through the balance, which would influence the measurement, and it eliminates any static charge around the balance internals – which is called a Faraday Cage in the world of electricity. It is basically a metal container, and a clean tin can works just fine as long as it does not touch anything connected to the weighing mechanism, such as the pan.

Because of the Faraday Cage, calibrating the balance in a GACS instrument is tedious and is not done that often. The nature of the adsorption capacity calculation is on a weight basis of the biochar or activated carbon, so the actual weight changes are "normalized" by the weight of the adsorbent. Because of this, small errors in the absolute calibration of the scale cancel out and the calculated adsorption capacity is not affected. However, the balance has to be reasonably calibrated and this means balances with "internal calibration" capability are quite convenient. If a balance is being purchased specifically for constructing a GACS instrument, the "internal

calibration" feature is recommended if it is available.

The final feature of the analytical balance is measurement accuracy or resolution – which basically determines the cost of the balance. The finer the balance resolution, the more it costs. For the GACS measurement, the minimum acceptable resolution is 0.1 mg, which is sometimes called the "maximum accuracy". This accuracy is a compromise between the cost of higher accuracy balances and the need to have sufficient resolution to measure the weight gain of biochars with relatively poor adsorption capacity.

The sample volume of the GACS instrument is about 2 cubic centimeters, with smaller sample volumes yielding better measurements. Since dry biochars weigh as little as 150 kg per cubic meter, the specific gravity is 0.150 and 2 cubic centimeters will weigh 300 milligrams. The maximum weight gain for relatively poor adsorbing biochars is only 2 weight percent at 100C, as will be discussed later. Thus, the total weight gain will be 2% of 300 milligrams or 6 milligrams total. For a balance with resolution of 0.1 mg, that corresponds to an increase of 60 units on the balance display. This is why a 1 mg balance will not suffice, since the entire measurement of adsorption capacity would only represent 6 digits on the right of the balance reading – making it very hard to distinguish between two chars, since each increment represents 16% of the adsorption capacity.

For this reason, analytical balances that have maximum accuracy of 0.01 mg are very nice when making GACS instruments, but they are expensive. A good 0.1 mg balance is about $1500 new and balances that resolve to 0.01 mg are in the $4000 to $9000 range. For this reason, used balances are often used, if they can be found. Ebay is an excellent resource, but there are issues with getting a balance that functions correctly. If buying off Ebay, get a balance that is working without concerns and preferably has been calibrated in the recent past. High quality balances last decades if cared for and acceptable quality electronics have been available for many years, so focus on the condition of the balance more than the absolute age of the unit.

Once the balance stand is completed and an appropriately accurate analytical balance found, a ½" hole is drilled in the top concrete block exactly under the "weigh-below" access port under the balance, with the balance resting securely on the top block. It may be necessary to have a flat surface to support the balance leveling feet on the concrete block if they extend to the edges of the upper block. It is very important to locate the balance on the stand and the stand in the room in a place where it can be accessed, but not be in the way. Once the GACS instrument is set up, it is never moved nor the balance turned off – the instrument takes too long to stabilize if disturbed.

So far we have created a stable balance with the ability to weigh "something" from below. That something is the small sample of biochar or activated carbon that is being subjected to the GACS assay. The sample is about two cubic centimeters in volume and is suspended in a temperature controlled chamber that is purged with vapors. Since the vapors will be interacting with the sample, the sample is contained in a small basket made of fine stainless steel screen (see www.mcmaster.com, p/n 9317T86 – 3" diameter works well) shaped into a basket, as shown in Figure 5. The wire screen disc is formed over the end of a broom handle by twisting the sides while pressing down, then the top edge trimmed even with scissors and a thin wire handle added. The handle is contoured to allow the basket to hang below the attachment point and provide reasonable access to introduce the sample into the basket.

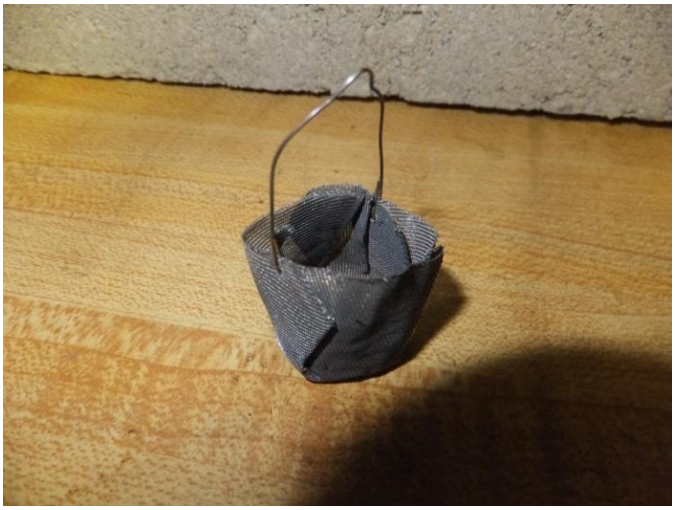

Figure 5: 100 mesh 304SS wire screen basket with stainless wire handle

The wire basket is suspended below the aluminum plate by a thin wire that connects the sample basket to the “weigh-below” attachment point of the balance. The thin connecting wire passes through the hole in the upper concrete block and through the hole in the aluminum plate, which are aligned exactly vertical so the wire does not touch anything. To align the heated chamber, three “pins”, made from threaded bolts tapped through the aluminum plate, are provided, as shown in Figure 6. Figure 6 also shows the thermocouple extending down through the aluminum plate and positioned in the middle of the wire basket at the top edge or slightly inside the wire basket. During the GACS assay, the vapors pass up the heated chamber, through the wire basket and the granular solids therein, and past the thermocouple above the sample. In this manner, the temperature of the vapor “downstream” of the sample is measured and used as the measurement of the sample temperature in the GACS assay.

Figure 6: Wire sample basket hung below aluminum plate with 3 aligning pins and thermocouple

The wire basket is enclosed by a heated chamber, shown in Figure 7. It consists of a 4” by 1.5” steel pipe nipple with a 1.5” pipe cap on one end. The capped pipe nipple is wrapped from the top down with a 1/8” copper tube that extends out to receive the vapor that purges the sample chamber. The 1/8” tube enters the capped nipple at the bottom, as shown in Figure 7.

After the 1/8” tubing is wrapped around the nipple, a heating tape is wrapped around the assembly. I recommend a 2’ by 1” high temperature heating tape, 208 watts/120 volts (http://www.heatingtapes.com/Duo_All.pdf - p/n AWH-101-020DM). The heating tape and the 1/8” copper tubing exit the top of the heated chamber as shown. The entire assembly is placed in an insulted container, with a 28 oz tomato products working well. The heated pipe assembly is wrapped in high temperature insulation and anchored to the bottom of the container by bolting through the bottom of the container into the pipe nipple.

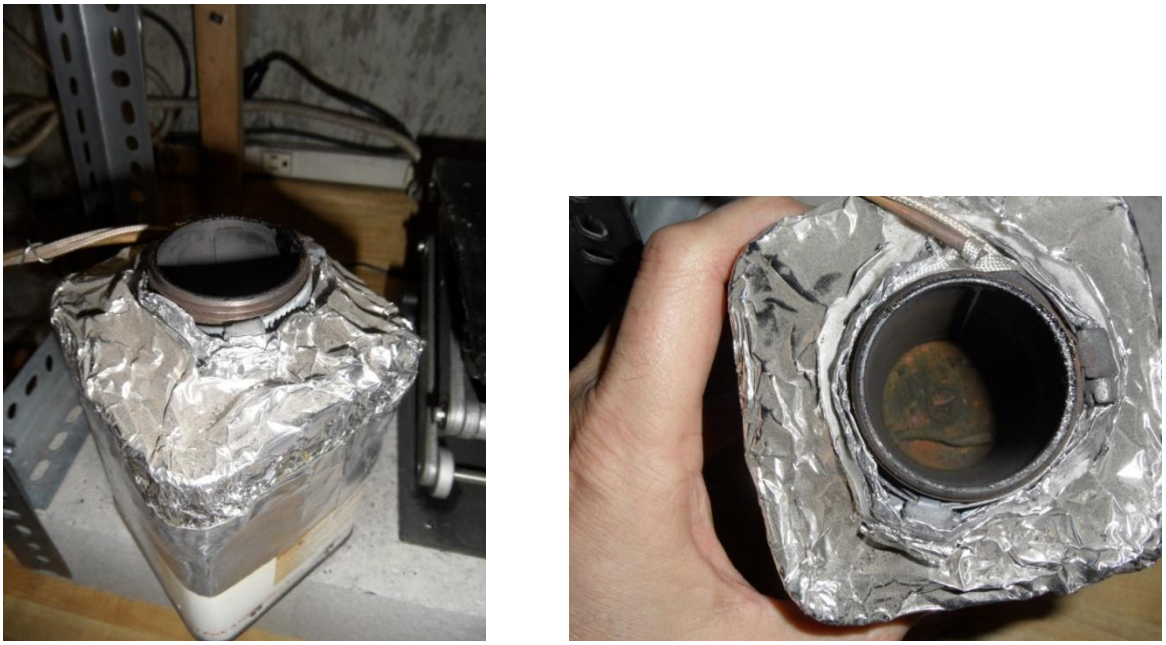

Figure 7: Two views of the heated chamber, with 1/8” vapor injection tube at bottom

The heated chamber has one feature that need to be appreciated: it needs to be insulated, but not too insulated. This is because the GACS assay heats the sample up to 300C, then turns off the heat and lets the sample coast down in temperature to 100C. If the sample does not have enough insulation, it either will not heat up or will coast down too fast. If it has too much insulation, the assay takes longer and the balance drifts, which affects the accuracy of the measurement. The preferred interval for the cooling down is about 45 minutes to one hour from 300C to 100C.

The heated chamber is held in place by a lab jack, as shown in Figure 8. As will be seen, the sample basket has to be accessed during the GACS assay, so it is important to make it relatively quick and easy to remove and reinstall the heated chamber and associated sample basket.

Figure 8: The insulated heated chamber sealed against the Al plate, held with a lab jack

The last assembled unit is the gas supply that provides a steady flow of either inert gas, typically nitrogen or helium, or the challenge gas, with 1,1,1,2-Tetrafluoroethane (R134a – the automotive air conditioning refrigerant) being the current preferred choice. Even butane can be used, but the lower molecular weight makes the detection of the extent of adsorption by the weight gain harder to accurately measure, as compared to the denser R134a. Figure 9 shows the gas supply components.

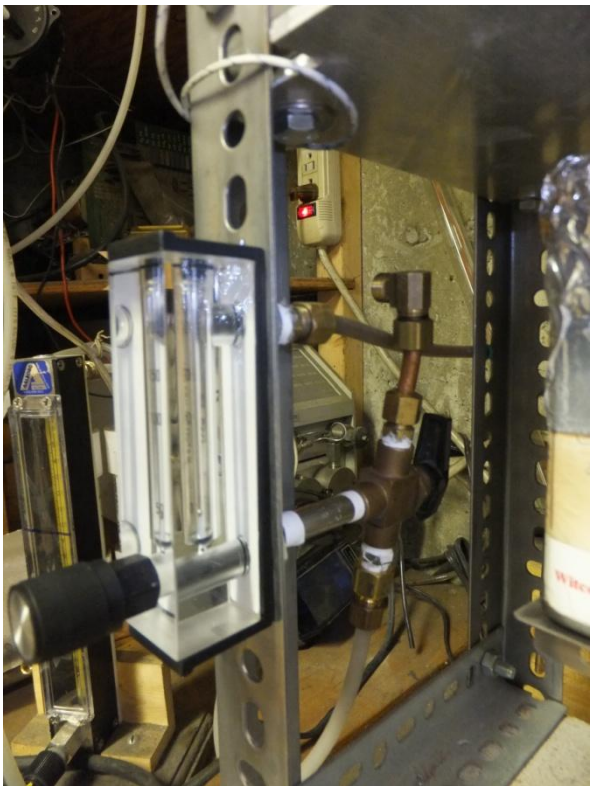

Figure 9: The gas supply, with 3-way valve leading to a rotameter with flow control valve

The gas supply consists of a source of inert gas, a source of challenge gas and the components to select and adjust the flow rate of gas being supplied to the heated chamber. The gas supplies need to be regulated, either by pressure regulators or flow control valves, to allow a steady controlled flow of either gas at a flow rate of 100 to 150 ml/min. The 3-way valve shown in Figure 9 allows the facile switching from the inert gas to the challenge gas during the GACS assay, as will be discussed in detail below.

The final subassembly is the "data acquisition" capability. This is the area where the most options exist at different costs. The data collected for the GACS assay is basically the pairs of data consisting of the sample temperature and weight, recorded often enough to plot the trend of weight gain as a function of temperature. As such, time actually drops out of the GACS assay, since the measurements are made at essentially thermodynamic equilibrium over the entire range of temperatures measured.

Figure 1 has the "bare-bones" data acquisition, where the balance reading and the temperature measurement are displayed. To capture the data set, someone manually records the data, striving to get the temperature and weight at the same time. This is hard to do, and a bit of technology really helps, in the form of a digital camera in video recorder mode, as shown in Figure 10. After the run, the video is scanned and the pairs of temp-weight data at input in a spreadsheet, then graphed. As will be discussed, the entire data acquisition electronic train can be automated, but this configuration gets one started and creates the same data set, after providing a little "sweat-equity" during the data reduction phase.

Automation of the data acquisition involves connecting the balance and the temperature measurement to a laptop and querying them periodically (I recommend every 30 seconds for a total data acquisition cycle of about one hour involving 120 relevant data sets). One configuration I have used historically, but not the only possibility, is to have the balance report the display every second to WinWedge (http://www.taltech.com/winwedge), then have WinWedge ask the temperature measurement for its value every thirty seconds, then write both the time, reported temperature and the most recent balance reading into a spreadsheet, advancing one row with each data set. It is a bit of an hassle to get everything talking to each other, but Tech Support at WinWedge is excellent at getting you to the end of the learning curve and justifies the cost of the software with every visit (by the way, you will need a registered copy of the software to get help, so don't steal the software and call up asking for help…..).

To preserve the option for upgrading the data acquisition system, build the initial configuration with a balance that has an RS-232 output (a common feature) and a temperature measurement meter that also has an RS-232 (less common in sub-$50 units, but routine for $100+ units and included with any unit with data logging capabilities). Ironically, older laptops running less invasive versions of Windows (XP and Win2000) seem to play "nicer" with the mundane task of data capture and recording, since they are less devoted to tracking your habits and porting them to "big brother". Do not have the data acquisition computer accessing the web during data acquisition – that is just asking for trouble.

Figure 10: “Automated” data acquisition, with temperature and balance weight being videoed

With the assembly of the data acquisition capability, the GACS assay can be run. The entire assay consists of a temperature ramp up from ambient to 300C with the heat tape energized and then descending back down to 100C with the heat tape turned off. Consecutive runs can be conducted starting at just below 100C, as will be seen. The GACs assay consists of the following phases:

1) Start the data acquisition of periodic temperature and balance weight data pairs
2) Heat and dry the sample basket to the temperature rises to 100C in the inert gas sweep
3) Tare the balance at 100C or note balance reading to correct challenge gas weight gains
4) Lower the heated chamber, remove the sample basket and load the char sample
5) Reseal the heated chamber and resume heating – heat tape is “on” while loading sample
6) Heat to 300C in a steady inert gas sweep; sample will lose moisture as it heats
7) **At exactly 300C, turn off the heat tape**
8) Switch to challenge gas at the same flow rate as inert gas, adjust as necessary until stable
9) Allow sample to cool to 100C under continuous challenge gas flow; collecting data pairs
10) Stop the challenge gas flow at 100C, empty sample basket
11) Tabulate the temperature-balance weight data pairs at even internals for the 300C to 100C period of data-logging, using at least 20 data points (every 10 degrees C or less)
12) Enter the data pairs into a spreadsheet; correct the 300C to 100C weight gain for the 100C sample basket weight (if not zeroed at step 3)
13) Calculate weight gain over minimum observed weight from 100C to the maximum temperature (slightly above 300C due to thermal overshoot of the heating tape) and weight percent gain by normalizing by minimum sample weight to create a data set of weight percent gain above the minimum weight versus temperature Celsius from 100C to 300C. Note that the first minute of data after the challenge gas is switched at 300C is disregarded due to buoyancy effects, as discussed below.
14) Plot weight percent gain versus temperature 100C to 300C with the weight gain in log scale to improve resolution of trends, temperature scale is linear in degrees Celsius

There are several other interesting metrics that can be extracted during the GACS assay, such as:

1) Sample weight loss from 100C to 300C in inert gas as percent of minimum sample weight – this is a measure of the "volatiles", consisting of water vapor up to 200C and low boiling "mobile matter" from 200C to 300C
2) Sample weight losses after 300C – some samples continue to lose weight after reaching 300C due to loss of mobile matter and residual carbonization. This is a strong indicator of a low temperature biochar or excessive volatiles. If the weight loss after 300C is significant, then the lowest weight recorded after 300C is used to normalize the weight gain measurements. The immediate weight loss when the gas supply is changed to the challenge gas at 300C is due to a temporary buoyancy effect of the denser challenge gas. Thus the first minute of the transition after switching vapor supplies is disregarded and the system equilibrates to the new vapor environment by the time the temperature reaches its maximum above 300C. Any char exhibiting significant weight loss after changing to the challenge gas is indicating a low temperature char which is often accompanied by low adsorption capacity over the entire range of 300C to 100C.
3) Interpolate the challenge gas uptake at 100C as a weight percent of the lowest sample weight below 300C – this is the best single number characterization of the GACS assay. Typical biochars exhibit 2 to 8 weight percent uptake of R134a at 100C, with most activated carbons being 10 to 20 weight percent at 100C. If a char exhibits less than 2 weight percent uptake at 100C, one should question whether "biochar" is the best use of the material, as opposed to charcoal, the cooking fuel, or perhaps a renewable fuel for co-firing with coal in utility applications.

In conclusion, the GACS method has proven to be a cost-effective and time-efficient method of characterizing the adsorption properties of microporous carbonaceous materials, including activated carbons and biochars. Like many measurements, it is used in comparison with known standards and a library of similar materials. In general, a GACS instrument cannot be absolutely calibrated against other instruments due to the accuracy of the temperature measurement and calibration, which may be off several degrees between identical thermocouples and may drift over time due to aging of the thermocouple. In addition, repeatability of consecutive runs is +/- 2 to 5 percent, so avoid "squeezing the data". However, the accuracy and insights of the GACS method are quantum leaps ahead of the alternative measurements of adsorption, principally because microporous adsorbents, and especially biochars, are so poorly behaved due to material heterogeneities (ie. Non-graphitic impurities providing interferences to isolating the adsorption phenomenon under the specific conditions of the assay: ref: BET-N2 versus BET-CO2 vs Butane Activity vs Iodine Number, et al.)

Finally, this guidance is my gift to you, but it does not include a seasons-pass on technical assistance. You are welcome to contact me for assistance, but be prepared to compensate me for the time involved. This is particularly relevant to what Garp called "Gradual Students": You are in Gradual School, where you gradually figure out you no longer want to be a student anymore. As such, suck it up and figure it out – the perseverance and techniques will serve your experimental career well in the future. Trust me, I have "been there and done that".

- Hugh McLaughlin, PhD, PE, CTO – NextChar.com