

BET

Standard Operating Procedure (SOP)

Surface Area & Pore Size Distribution Analyses

Name: **BET - Autosorb-1C**

Model #: **AX1C-MP-LP**

Manufacturer: **Quantachrome Instruments**



Annotated Figure of Autosorb-1

Miscellaneous – About Pore Size (from IUPAC)

Microporous – pore size smaller than 2 nm;

Macroporous – pore size larger than 50 nm;

Mesoporous – pore size between 2 to 50 nm.

Preparations for Sample Analysis

1. Take liquid nitrogen from Chemical Department (Next building) (Just write the volume – 4L, and write Biswas on the log notebook)
2. Fill **Cold Trap Dewar** with liquid nitrogen (3/4)
3. Cold trap dewar is then mounted to **Autosorb-1**
4. Open He and N₂ cylinder valves and ball valves located after pressure regulators. Confirm cylinder pressure regulators are set to **10 psi**
5. Operator must sign in log book

Degassing Samples Prior to Analysis

1. Choose appropriate cell size for sample (6, 9 or 12mm)
* We only have one cell (9 mm) with fill glass rod for sample.
2. Using a 5-place analytical balance, weigh and record the weight of the empty sample cell with fill glass rod.
(Weigh 3 times for each sample and then calculate the average)
Record this as the **initial weight**.
3. Remove fill glass rod and insert sample (powders) into the glass cell using a **funnel** (½ to full volume of the cell will be appropriate)
4. Replace the fill glass rod into cell
5. Weigh the sample cell with the glass rod and sample
(Weigh 3 times and then calculate the average)
Record this weight as the **Weight before Degassing**.
Calculate the sample weight by subtracting the **initial weight** from the **Weight before Degassing**.
6. Put the cell into a **heating mantle** (pinch mantle to open the mouth) using a **clamp** to secure cell into mantle.
7. Attach the cell and mantle to the sample preparation station (There are two stations. We are now using **Station 2**)
 - a. First remove the **Knurled retainer ring, plunger with o-ring, and cell adapter** from the sample preparation station.
(Be careful! **Don't leave system open any longer than necessary!**)
 - b. Place ring, adapter and o-ring onto sample cell
 - c. Insert the cell into the station hole and tighten the nut gently (**Tighten by hand only!**)
8. **Set temperature manually** (200 °C is normally used. 120 to 350 °C for water evaporation)
Turn heat on by lifting the **toggle switch** to the **up position**. (The green light is NOT ON at this moment. It starts to blink after degassing has been started.)
9. Degassing may take more than **1-2 hrs** depending on your sample conditions

Computer Set Up for Degassing

1. On Tool bar click <OPERATIONS>
2. From the drop down menu click <OUTGASSER>
3. From pop up menu click on **Station 2**
4. Click <LOAD>
5. Click <OK>; This begins the sample outgas routine.
6. Record the start time in log book.
7. After 20 minutes, go the <OUTGASSER> again
8. Click <TEST>
9. The Outgass test continues to show failing information until it passes (usually will take more than **30 minutes** or **even longer** to reach the goal: **10 micron/min.**

[NOTE: This value is a user-definable “outgas pressure rise limit”. The purpose of this value is only to provide a reference value that indicates the response expected of a clean and leak-free outgassing system. Typically, a clean AUTOSORB degassing system can itself out gas (release gaseous contaminants) slightly, thereby leading to pressure rise of up to 2-3 micron/min (0.002 mmHg/min) when the degassing stations are plugged with dowel pins or loaded with empty sample cells. Therefore, the “outgas pressure rise limit” is set by default at 5 micron/min (0.005 mmHg/min). This value should be altered if there is any reason to suspect that the internal cleanliness of the AUTOSORB may have changed. But since its use is for reference purpose only, it should be noted that the actual value used will not influence the effectiveness of the outgassing operations in any way]

About **DEGAS**:

Temperature – Samples should be degassed at the highest temperature (up to 350 Cel) that will not cause a structure change to the sample. This will accelerate the degassing process.

Time – Time for complete degassing, that is complete removal of unwanted vapors and gases adsorbed on the sample surface, can only be properly determined by conducting a degas test which is built into the AUTOSORB software. As a general guideline however, **three hours** should be considered a reasonable minimum. IUPAC recommend no less than **16 hours**, which can be achieved overnight. Samples that require low temperatures generally require the longest outgas times.

A sample can be considered ready for analysis when the sample passes degas test of no more than 10 mcirons Hg per minute.

10. When Outgassing is complete, remove sample by going to <OUTGASSER> again, then press <REMOVE>
11. Turn off the heat by putting toggle switch to the down position. (It will take approximately 20 – 30 min for sample cell to cool.)
12. When the temperature display is back to room temp, and the **LED indicator** on the selected port turns **orange**, the sample is ready to transfer.
13. Remove the cell and mantle from the sample preparation station, **and then** carefully remove the heating mantle from the cell.
14. Move the **Knurled retainer ring, plunger with o-ring, and cell adapter** from the analysis port to the degassing port.
(Be careful! **Don't leave system open any longer than necessary!**)
15. Quickly but carefully attach the sample cell to the analysis port, using the same procedure as that during degassing. (**Tighten by hand only. Don't touch the temperature probe!**)

Sample Testing

1. Fill the **Sample Cell Dewar** at least half full with liquid nitrogen;
2. On the computer, go to the <ANALYSIS> <PHYSISORPTION ANALYSIS PARAMETERS>
3. Input the following
 - Sample ID (such as TiO₂-SiO₂-400)
 - File ID: enter operators initials, e.g. **07012010-PW**
 - Operator: Your name
 - Bath T: enter temp (**77.35 K**) (This is the temp of liquid nitrogen)
 - Adsorbent: **Nitrogen** or Krypton (Usually we use Nitrogen)
 - Leak test: **1 min for nitrogen** and 1 min for Krypton
 - Maxi-dose: (**ON**) for nitrogen and (**OFF**) for Krypton
 - Outgas time: Enter your recorded time
 - Outgas temperature: enter outgas temp, e.g. 200 °C
 - Po parameters: **P₀ Station** for Nitrogen and (User Entered Po for Krypton)
 - User Po/Ambient: **760 mmHg** for Nitrogen and (2.63 mm Hg for Krypton)
 - Cell type: enter **the bulb size used** (6, **9**, or 12 mm) select with rod option
NOTE: Generally, 6 mm is for fine powder, 9 mm for larger particles/small pellet, and 12 mm for large pieces that cannot reduce their size.
 - Analysis points: **11-point analysis for nitrogen** (This is a simple standard multi point Brunauer-Emmett-Teller (BET) measurement selection to analysis surface area. In fact, you can choose other methods, such as Single Point BET, 3 point BET, Five Point BET, and Seven Point BET. The standard multi point BET measurement requires a minimum of **three points**. For single point BET, you should choose a relative pressure as high as possible, yet still in the linear region of the BET plot. For all except microporous samples, a P/P₀ of about **0.3** is preferable. If you want to analysis pore size distribution (either Density Function Test (DFT) or Barrett, Joyner and Halenda (BJH) analyses), you need to choose 20 Point Adsorption/Desorption or 40 Adsorption/Desorption. First, go to Analysis Points page to change **Tolerance** as **0**, set **Equilibration** as **3 min**; then go to Analysis Points page to click on **20 Adsorption** and **20 Desorption** (total **39 points**) or **40 Adsorption** and **40 Desorption** (total **79 points**) if you want to get detailed information/figures with higher resolution. In addition, you should also check corresponding **tags** if you need analysis **pore size distribution, BET, and other information together**. 39 points analysis will typically take 3-5 hours, and 79 points analysis can take over 10 hours to complete the task.

**NOTE: DFT is mainly for micropore analysis, while BJH is for whole range analysis, from microporous to mesoporous, even macroporous range. It is normally accepted that the desorption isotherm is more appropriate than the adsorption isotherm for evaluating the pore size distribution of an adsorbent. The desorption branch of the isotherm, for the same volume of gas, exhibits a lower relative pressure,*

resulting in a lower free energy state. Thus, the desorption isotherm is closer to true thermodynamic stability.

- Sample weight: Enter the weight you measured before
 - Evacuation: select the **Fine** option
 - Temp comp: Make sure this box is **NOT** checked
4. After parameters are entered, press <START> to begin analysis. Click <OK> to remove the Physisorption screen
 5. The Dewar does not rise at the first 30-40 min, which then rises to the sample cell position. (**Be careful to align the reference cell, the temperature probe and the sample cell so the Dewar rises without touching them!**)
 6. When the analysis is complete, an information label “Upload complete. Data Saved” flashes on the screen. And after around 30 min, the Dewar starts drop down automatically. Then remove the cell from the sample port and close the port using a **Knurled retainer ring, plunger with o-ring, and cell adapter immediately!**
(**Caution should be paid on NOT dropping the plunger into the Dewar!**)
 7. **Re-weigh** to obtain the degassed weight (Record this as **Actual Weight**)
 8. Finally, an Isotherm graph appears on the screen. Enter correct weight into the software by going to the menu <DATA REDUCTION> <SELECT MULTIPLE TABLES>
 9. Select the <MULTIPLE BET> option and press <View>. The data table with the analysis will appear
 10. The correlation coefficient should be greater than **0.999**. If the line is bending at the end, remove the first and last data points to correct the correlation. This is done with the menu <DATA REDUCTION> <EDIT RAW DATA AND TAGS>. Select the first and last points listed and press <DELETE SELECTED POINTS>. Typically coefficients of 0.9997 + are obtained.
 11. After checking the correlation coefficient, examine the “C” value, which indicates whether the BET analysis is valid for this sample. Ideally the number should be close to or greater than **100**. If it is less than **2**, the BET theory is **NOT valid** for the sample.
 12. Save the data to the hard drive and transfer to USB.

Shut Down

1. Empty powder from sample cell and save for other analysis or dispose of properly
2. Clean cell by sonication with DI water. Dry with acetone or methanol.
3. Store cell upside down to insure it is dry for the next user.
4. Make sure heater switch is in the down position (OFF)
5. Make sure that all of the ports are sealed with dowel plugs.

THEORY

The BET method is the most widely used procedure for the determination of the surface area of solid materials and involves the use of the BET equation.

$$\frac{1}{W((P/P_0)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0} \right)$$

in which W is the weight of gas adsorbed at a relative pressure, P/P_0 , and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The term C , the BET C constant, is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent/adsorbate interactions.

The BET equation requires a linear plot of $1/[W(P/P_0)-1]$ vs P/P_0 . which for most solids, using nitrogen as the adsorbate, is restricted to a limited region of the adsorption isotherm, usually in the P/P_0 range of **0.05 to 0.35**. This linear region is shifted to lower relative pressures for microporous materials.