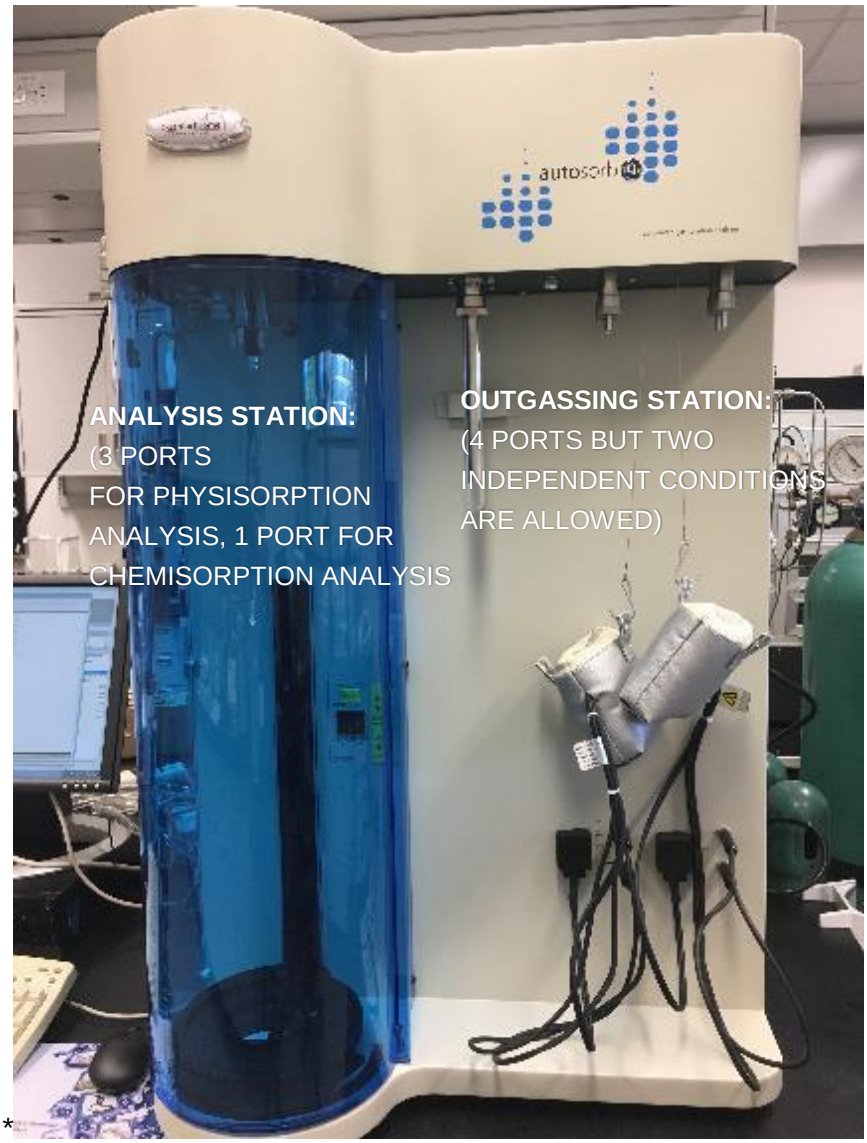
Standard Operating Procedure (SOP) – Quantachrome Autosorb iQ3

Instrument:	Autosorb iQ3	**Computer password:**	paic2012
Building/Room:	222	**Effective Date:**	02/12/2020
NRF Staff in charge:	Kristy Schepker Gary Scheiffele	**SOP prepared by:**	Ana C. Bohórquez and Kristy Schepker



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1. Circumstances of Use:

- To characterize porous materials by multi-point BET surface area determination (range from ~0.0005 m^2/g to no known upper limit).
- To determine pore size distribution range ~3.5 Å -5000 Å (0.35 nm – 500 nm). Being able to collect data at relative pressures from 1 x 10^{-7} when using nitrogen gas at 77 K (or argon gas at 87 K).
- For ultra-low surface area measurements Krypton gas is required. Krypton cylinder (99.99% high purity) is provided by the RSC. We will take care of the installation of the cylinder.
- For zeolites characterization, Argon (99.99% high purity) should be used. Argon is supplied by the RSC.
- Carbon dioxide (99.99% high purity) should be use for activated carbon characterization.
- At the RSC our equipment possesses a software (Windows® based ASiQWin™) foir instrument control, data acquisition, and data reduction software providing all classical surface area and pore size measurement models (BET, t-plot, STSA, BJH, DA, DR, HK, SF, etc.) as well as the most comprehensive DFT library (NLDFT, QSDFT, GCMC).

2. Preventive Maintenance (RSC Staff):

- Cleaning bulkhead filters (outgas and analysis stations).

- Cold trap maintenance.
  Whenever the liquid nitrogen in cold trap Dewar is allowed to evaporate completely, any contaminants (oils, water, etc.) trapped in the cold trap tube can back stream into the outgas manifold, as well as into the vacuum pump lines. If the cold trap Dewar cannot always be kept filled, it is recommended that the cold trap tube be cleaned frequently. If no significant sample degassing or outgas exposure to high levels of contaminants has taken place since the latest cleaning, the cold trap Dewar can be safely allowed to run out of liquid nitrogen. Please, ***always maintain the Autosorb iQ and its vacuum pumps turned ON to maintain the outgas system in a clean state between runs****.*

- Checking/ adjusting flow rates.
  For all gasses, the input pressure should be set between 8-10 psig.

3. Sample Preparation

Every sample should be degassed by flow or vacuum before analysis. Sample preparation for PHYSISORPTION ANALYSIS involves the optimization of several key variables including:

- Sample cell selection.
- Outgas temperature selection.
- Outgas time.
- Unloading sample cell / use of backfill gas.
- Minimization of elutriation.

Elutriation, or loss of powder out of the sample cell, is caused by too rapid a gas flow out of the cell. It is most problematic for low-density samples. Wider stems and larger bulbs can be beneficial in reducing elutriation.

a) *Wider stems reduce the velocity of the gas leaving the cell when evacuation begins and thus it is less likely to entrain powder particles and transport them upwards and out of the cell.*
b) *The presence of a filler rod significantly increases gas velocity because of the narrowing of the internal dimensions and can exacerbate elutriation. In problematic cases, the filler rod may be dispensed with during analysis, but some loss of resolution and/or sensitivity may result.*

4. General things to check prior use:

- **SHARE BETWEEN OUTGASSING AND ANALYSIS.** Because the outgassing station and the analysis system share common resources, frequent use of the outgassing options while an analysis is running will increase analysis time. Please do not begin an outgassing routine while another user is performing an analysis.

- **GAS CONNECTIONS.** The autosorb iQ instrument has seven gas input fittings on the right side of the instrument. The port closest to the front of the instrument is dedicated to helium and it is connected to a helium supply for all measurements, as the cell void volume measurement is performed using helium during each run (analysis station – physisorption measurements). The port furthest to the back is for the backfill gas. The gas connected to this port is used to backfill the sample cell after degassing. *Normally either helium or nitrogen is used here, but it can be any gas desired; nitrogen is recommended as it introduces effectively no buoyancy errors when weighing freshly outgassed samples.*

Currently, at the RSC we have installed the following gases:

- Port 1: Nitrogen (supplied by NRF system).
- Port 2: Hydrogen for chemisorption analysis (cylinder 99.99% purity).
- Port 3: Argon77 for physisorption analysis (cylinder 99.99% purity).
- Port 4: Krypton for low surface area physisorption analysis (cylinder 99.99% purity).
- Port 5: Carbon dioxide (CO_2) for physisorption analysis (cylinder 9.99% purity).

Helium – Use to calculate the cell void volume.
Nitrogen – Use for sample backfilling.

- **REGULATORS GAS DELIVERY.** The regulator (s) should be set to deliver 8-10 psig (~60 kPa) for any gas except for hydrogen for which the regulator should be set to 5–6 psig (~35 kPa).

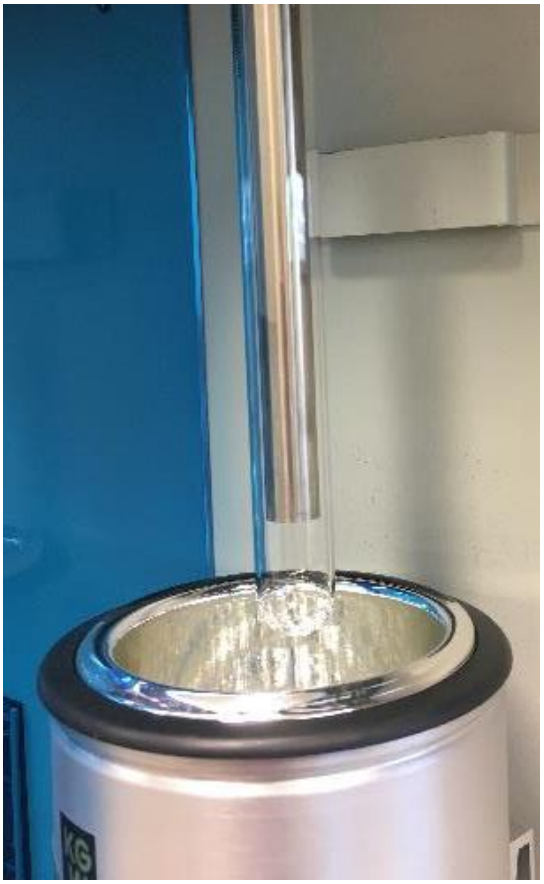
- **MAIC DEWAR, COLD TRAP DEWAR AND ANALYSIS DEWAR.**
RSC staff will refill the Dewar upon request, or as needed and indicated by logout notes. If you will be running the autosorb afterhours be sure to request a dewar refill prior to your session.
    - a) The autosorb iQ instrument is supplied with a 3 L Dewar Flask for analysis which is placed on the lift-drive base. The dewar flask holds the coolant, usually liquid nitrogen (but is equally suitable for liquid argon), used for the analysis. *The analysis dewar flask should not be filled beyond the bottom of its neck. Fill the dewar prior to each analysis.* **The 3 L dewar holds sufficient liquid nitrogen to run up to 90 hours under normal conditions.** If the analysis will take longer than this, the reservoir will need to be refilled. See Section I.5.7 for refilling instructions in the autosorb iQ and ASiQwin GAS SORPTION SYSTEM OPERATING MANUAL.
    - b) A smaller Cold Trap Dewar Assembly is provided for the outgassing stations.

Users with after-hours access will need to request staff refill the MAIC dewar noting the time of their anticipated use.

- **FINE/COARSE VACUUM CONTROL.** When evacuating the sample cell during loading, it is first evacuated slowly using a *fine vacuum* for a minimum time and then, once the pressure is low enough, the *course vacuum* is opened. The pressure at which the switch between fine and course vacuum is made is specified as the *evacuation Cross-over Pressure.* When evacuating the sample cell, the instrument will pump for the minimum time and then continue to pump until the pressure is below the specified pressure, and then switch to coarse vacuum. There are four modes from which to choose in cross-over pressure:
    - **User Entered:** a pressure > 0 but ≤ 76 Torr may be entered along with a minimum Time of less than 10 minutes.
    - **Fine Powder:** Crossover pressure is set to 3 Torr with a minimum time of 6 minutes.
    - **Powder:** Crossover pressure is set to 20 Torr with a no minimum time.
    - **Pellet:** Crossover pressure is set to 50 Torr with no minimum time.

Increasing velocity

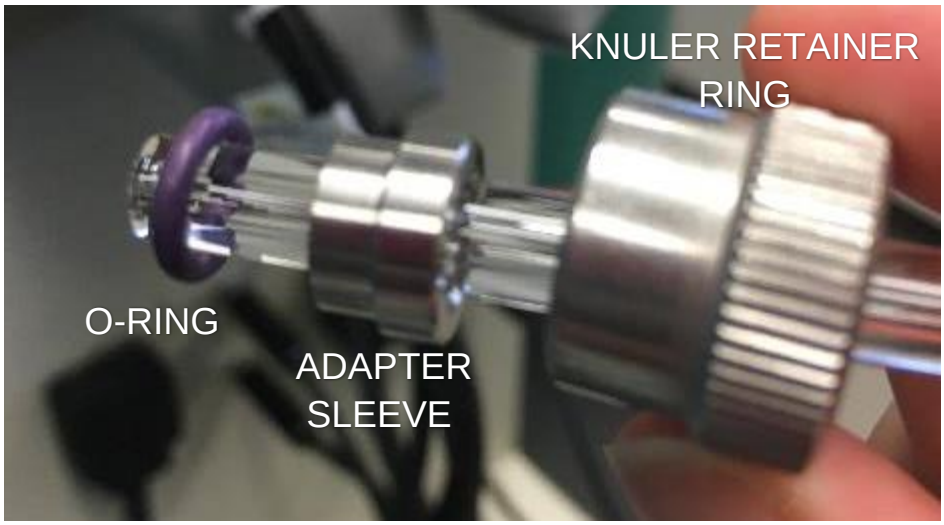
- **COLD TRAP CELL**. A cold trap is used for two reasons (i) to permit continued removal of condensable "products" of degassing even when heated samples are not connected to active vacuum, (ii) to maintain the highest possible vacuum levels for degassing and (iii) to prevent diffusion of condensable vapors into the degas manifold. The cold trap also prevents water vapor produced by heated samples from deactivating the for line trap media which is installed on these units to reduce the back streaming of oil vapor from an oil pump into the system. The glass cold trap tube is inserted into the cold trap fitting in the same manner as the sample cells (using O-rings, adapter sleeve and a Knuler retainer ring). *The cold trap Dewar flask should be filled with liquid nitrogen and mounted on the front panel by inserting the hook into the bracket*. Take care not to break the tube. The liquid nitrogen coolant does not need to be of a high quality for this purpose: indeed, it is convenient to use "old" LN2 from the analysis Dewar for this purpose.



- **SAMPLE CELLS.** Sample cells are available with outside stem diameters of 6, 9, and 12 mm (internal diameters of 4, 7, and 10 mm respectively). Each cell should be used with the appropriate glass filler rod during analysis. **Each user should buy their own sample cell for experiments.** The RSC is not responsible for samples cells. For very low surface area samples, it is recommended to use a sample cell with large bulb to accommodate a larger amount of sample. Please, check in the manual on the **Appendix 8 Accessories**, the product number for standard physisorption cells, chemisorption cells and specialty cells.

- **FILLER RODS** Filler rods are available for users to borrow from the RSC upon request. Filler rods should not be used during outgassing, but may be used to reduce the amount of gas needed during an analysis.

- **CELL BULKHEAD FITTINGS.** The fittings for holding the sample cells use adapter sleeves and O-rings and are designed to accept 6, 9, and 12 mm size cells (see Figure C.7 in the user's manual). The correct size O-ring and adapter must be used with each corresponding cell. Be sure to use only one O-ring when installing a cell into the fitting. Two O-rings (of any size) are likely to cause a leak leading to erroneous results. When changing from one size cell to another, be sure to remove the O-ring, which may be stuck inside the bulkhead fitting. A dowel rod of the appropriate size is useful for this purpose.



- **HEATING MANTLES FOR OUTGASSING.** The heating mantles used for samples outgassing are equipped with three cables and plugs. One is for power and the other two are thermocouples for controlling the temperature of the mantle. Plug the power into the corresponding socket for the respective station. One thermocouple plugs into the control socket (heating mantle symbol with degas station number identifier) and the other into the over-temperature (O/T) socket. The thermocouples are identical, so it doesn't matter which is plugged into which socket of the same mantle station. The mantle temperature is controlled by software and can be set to a constant temperature or programmed with a ramp and soak profile. DO NOT REMOVE FROM THE OUTGASSING STATION THE HEATING MANTLES.

- **VENT CONNECTIONS.** If the instrument will be used with hazardous gasses, the vent ports on the left side of the instrument will need to be connected with a suitable hose and hose clamp to the lab's exhaust system. The vent port labeled "SAMPLE CELL" discharges gases which flow through a chemisorption cell. The vent port labeled "VAC PUMP" discharges those gases which are pumped out of the system by the internal vacuum pumps (no external vacuum pump is required in this port). The vent port labeled "CAL LOOP" discharges those gases which flow through the titration loop of the Cal Loop option (TPX option only).

5. Procedures:

This section will be described in three modules:

- Physisorption analysis (outgassing and analysis)
- Vapor sorption analysis
- Chemisorption analysis
- TCD

Before starting to analyze your samples, we encourage each user to check scientific publications to look for outgassing conditions and analysis conditions (pressure points and data analysis) to understand your material. For example, high outgassing temperatures could collapse porous structures in certain type of rearrangements. In this case, low temperatures are needed with long outgassing times (long as 24 hours).

Other materials with microporous structures could need elevated temperature and short times. Either is your case you need to back up your outgassing conditions with a proper literature search. Alternatively, call Quantachrome or Micromeritics and see what they suggest.

For more details and references please check the user manual:

E. SAMPLE PREPARATION CHAPTER – PAGES: 82 – 92

F. INSTRUMENT OPERATION CHAPTER

Physisorption Analysis Setup on PAGES: 104 – 121
Vapor sorption Analysis Setup on PAGES: 201 – 208
Chemisorption Analysis Setup on PAGES: 121 - 145
TPX option for TPR/TPD/TPO Setup on PAGES: 209 - 239

<u>Powers outgassing suggestions (by Gill Brubaker):</u>

1. Metal oxides: 150°C for 6 hours unless porous then 180°C for 12 hours.
2. Metals: 150°C for 6 hours unless a coinage metal, soft or low melting point, nanosizes (then room temperature for 12 hours) under vacuum.
3. Organics: depends but usually no higher than 50°C. Check melting point and vapor pressure in CRC if necessary.
4. Micro porous carbon black/ zeolite materials need longer outgassing.
5. If BET curve and isotherm formed is not linear or has low R^2 may not be totally outgassed - If desorption curve crosses over repeat outgassing conditions and make sure you weight out your sample correctly.
6. Lower SSA does not necessarily mean you lost sample - maybe you lost ice frosted or solvent crystals.
7. Silica 100°C to 150°C 6 hours (overnight).

5.1 PHYSISORPTION ANALYSIS

a) Outgassing

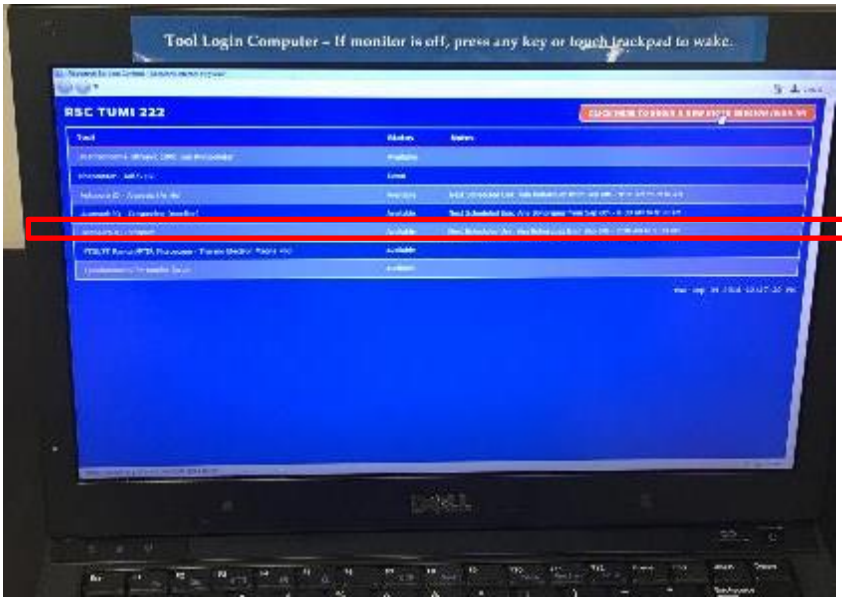
- Sample outgassing using Autosorb iQ3 is performed using the two dedicated outgassing stations on the front of the instrument (left and right stations are called Station 1 and 2, respectively). Each station is split into two ports for allowing to outgas two samples at the same time in each station. These additional ports will still be controlled as Stations 1 and 2 respectively. Two independent outgassing conditions can be set in each outgassing station.

- Because there is a valve at each Station but not a valve preventing exposure to atmosphere at each of the four substations, it is necessary to plug a dowel rod (metal pin) in the substations that are not being use while running outgassing stations.

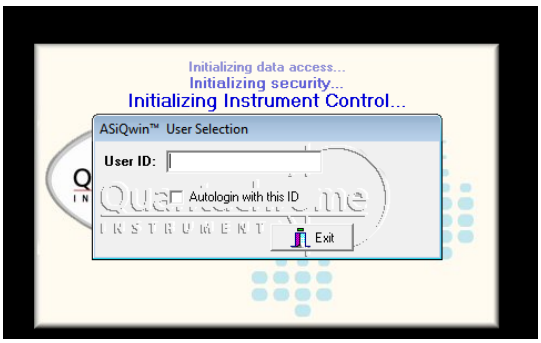
- **DO NOT USE FILLER RODS DURING OUTGASSING PROCEDURES. FILLER ROD ARE USED ONLY FOR ANALYSIS**.

STEPS DURING OUTGASSING:

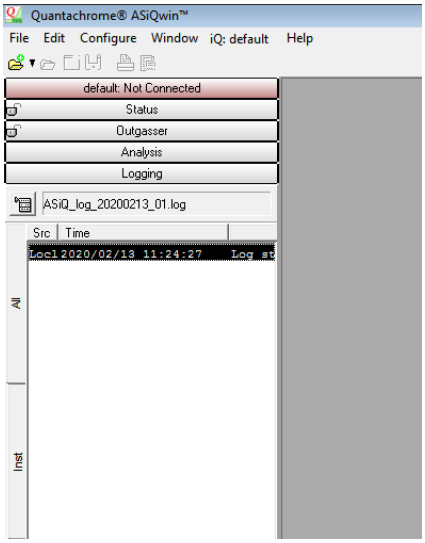
1. Sign IN into the TUMI computer in room 222. Sign in for “Outgassing” (monitor).
   - Note: **Charges apply only when logged into the analysis station**. There is no charge for the use of the software or the monitoring station.

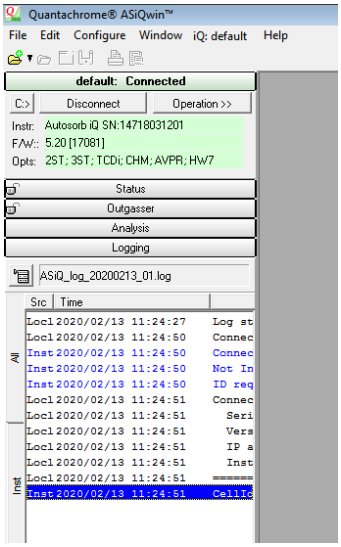


2. In the Desktop click on the ASiQwin software and log into the application using your full name.

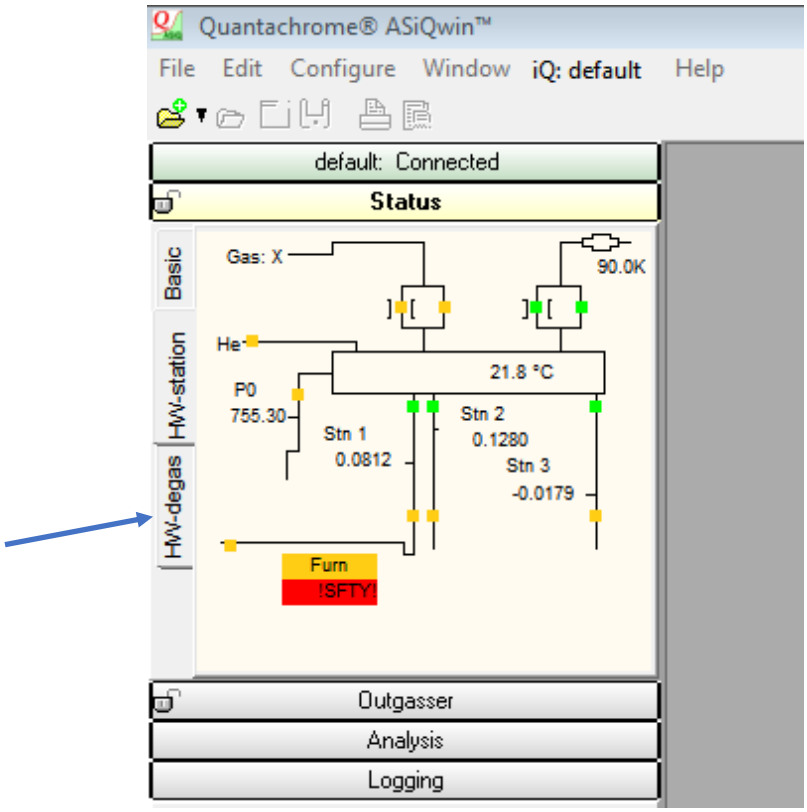


3. Connect PC to the Autosorb iQ3 software (ASiwin) by start ASiQwin by double-clicking on its icon on the desktop or from the Start menu. Once the instrument has completed its initialization, click on the Connect button and begin using the instrument. If the connection is successful, the status bar will turn from pink to green and say “Connected.”





4. Verify that the valve to the outgassing station to be used is closed by clicking on the HWdegas tab on the Status display in the Asiwin software.



5. Prepare your sample as follows:

    - Weight out empty cells (at least three times to avoid reproducibility errors). First, make sure the weighting balance is ON and the level centered (Room 222 is equipped with two weighting scales). Then place a clean and dry sample holder inside the weighting balance and tare it. Following, place the empty sample cell and cover it to avoid air fluctuations during measurement.

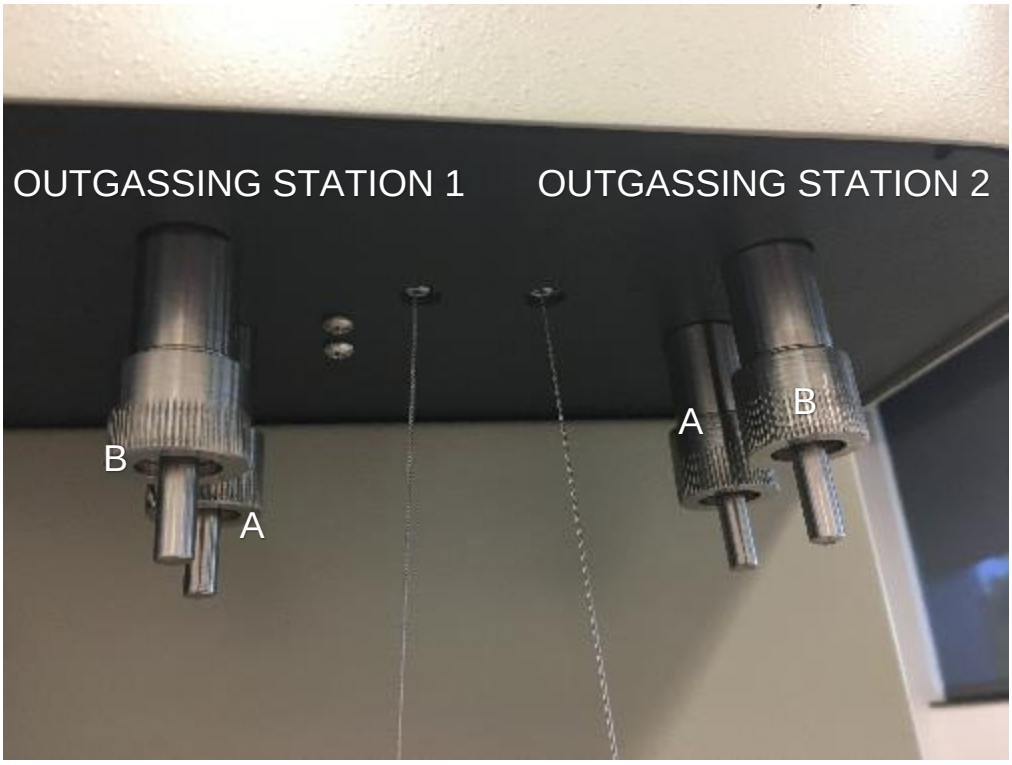
- If fluctuations are predominant while weighting out your samples, use the Viper static neutralizing blow-off gun to produce a blast that neutralizes static charges and to blow away dust and dirt outside the sample holder.

- Remove cover, and load sample into the sample cell. Make sure there is enough material to perform the measurements (sufficient for 2-50 m^2 total area) and place the cell cover AGAIN. Weight out empty cell + sample (three times).

- Calculate the average of weight for empty cell and empty cell + Sample. Keep a table to record sample weights as shown:

Mass, g	Measure 1, g	Measure 2, g	Measure 3, g	Average, g
Empty cell				
Cell + Sample				

6. Remove the dowel pin from the outgassing port by first turning the knuler retainer ring counterclockwise until the metal pin can be easily removed. Be careful in not dropping the adapter sleeve and O-ring, which may be stuck inside the bulkhead fitting. A dowel rod of the appropriate size is useful to remove the O-ring without damaging.



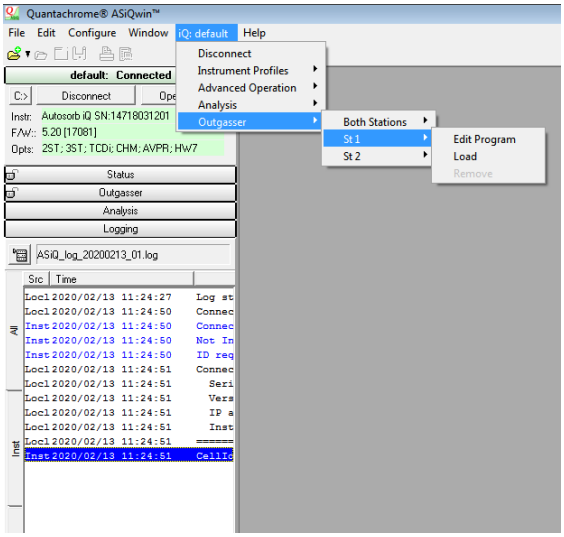
7. Place on the top of the sample cell the appropriate knuler retainer ring, adapter sleeve and O-ring (in that order), and insert the cell into the outgassing station port fitting. Make sure that the cell is engaged in the port and gently tightened. Do not attempt to over tighten the knuler ring. This can cause a leak in the outgassing station port. Finger tight is fine, cell may wiggle side to side, but should be firm vertically.

8. Place the sample cell in the pouch of the heating mantle carefully.

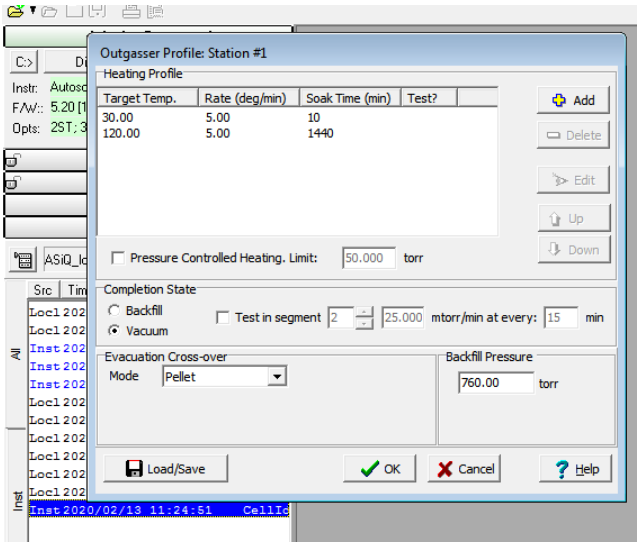
9. Remove empty cold trap Dewar from the outgassing station and fill cold trap Dewar with liquid nitrogen (use cryogenic gloves and face shield for safety precautions).

10. Place cold trap Dewar slowly until it engages the bracket in the outgassing station.

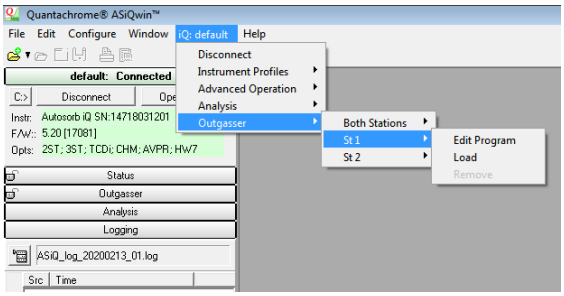
11. In the Quantachrome ASiQwin software:



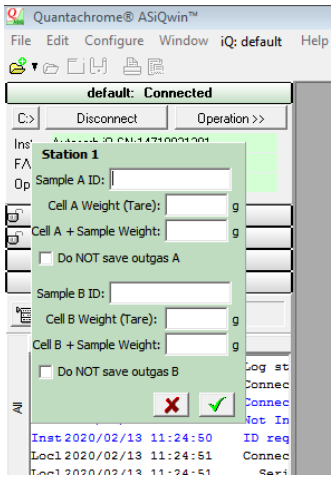
- Create a sequence for outgassing (degas temperature and degassing time).
    - It is generally good practice to start the profile with a 10 minute soak at room temperature (set to 27, heaters cannot be cooled), to allow time to establish a good vacuum. The temperature can be slowly increased to the desired temperature or increased in steps with soak periods to give time for excessive moisture to be removed gently.



Click on Load in the menu for that station. If loading both stations, they can both be inserted and the Load All in the ALL submenu selected. The instrument will first equalize the pressure in the manifold with the sample pressure to avoid elutriation of the sample and then evacuate the sample. When the crossover pressure is reached, and the course vacuum is opened, the heating profile loaded will begin.



- Identify your samples and add the cell weight and the cell + sample weight (average) and click green check bottom to continue with the outgassing procedure.



12. When the outgassing is completed the mantle will turn off and cool automatically. **Allow the sample cell to cool.** You want to avoid moisture going into the sample cell.

13. Reweight the sample after degassing as follow:

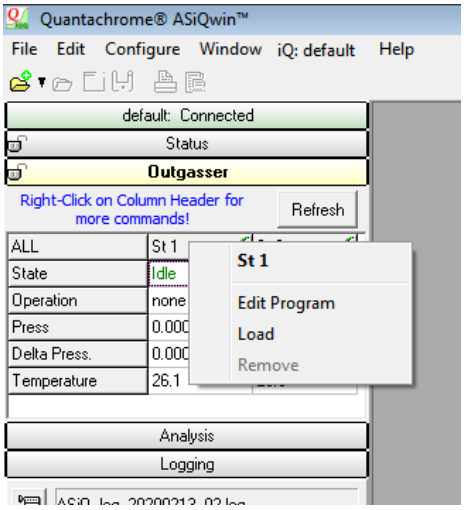
    - Select Remove from the station menu being unloaded (or Remove All from the ALL menu).

    - The sample will be backfilled if selected and prepare the station for the sample

to be removed (backfilled to reach atmospheric pressure).

- When ready the Status display will indicate the outgasser is in idle state, at which time it is safe to remove the sample.

- **Always check the status of the valves before physically removing sample cells or dowel pins.**



- Unhook the mantle from the support hook provided at the outgassing station to allow the mantle to be removed.

- Loosen the ultra-torr fitting by turning counterclockwise and slide the sample tube out.

- Replace the dowel pin into the outgasser until it is ready to be used again.

STEPS DURING ANALYSIS:

1. Check that Helium levels are above 500 psi in the Helium cylinder.

2. Check that nitrogen flow is between 8-10 psi.

3. Make sure that you transfer your samples to the analysis Remove samples from the outgassing station (see above).

4. Weight out dry empty cell + Sample after outgassing (three times).

5. Averaged weight for empty cell + Sample.

Mass, g	Measure 1, g	Measure 2, g	Measure 3, g	Average, g
Empty cell				
Cell + Sample				
Cell + Sample After Outgassing				

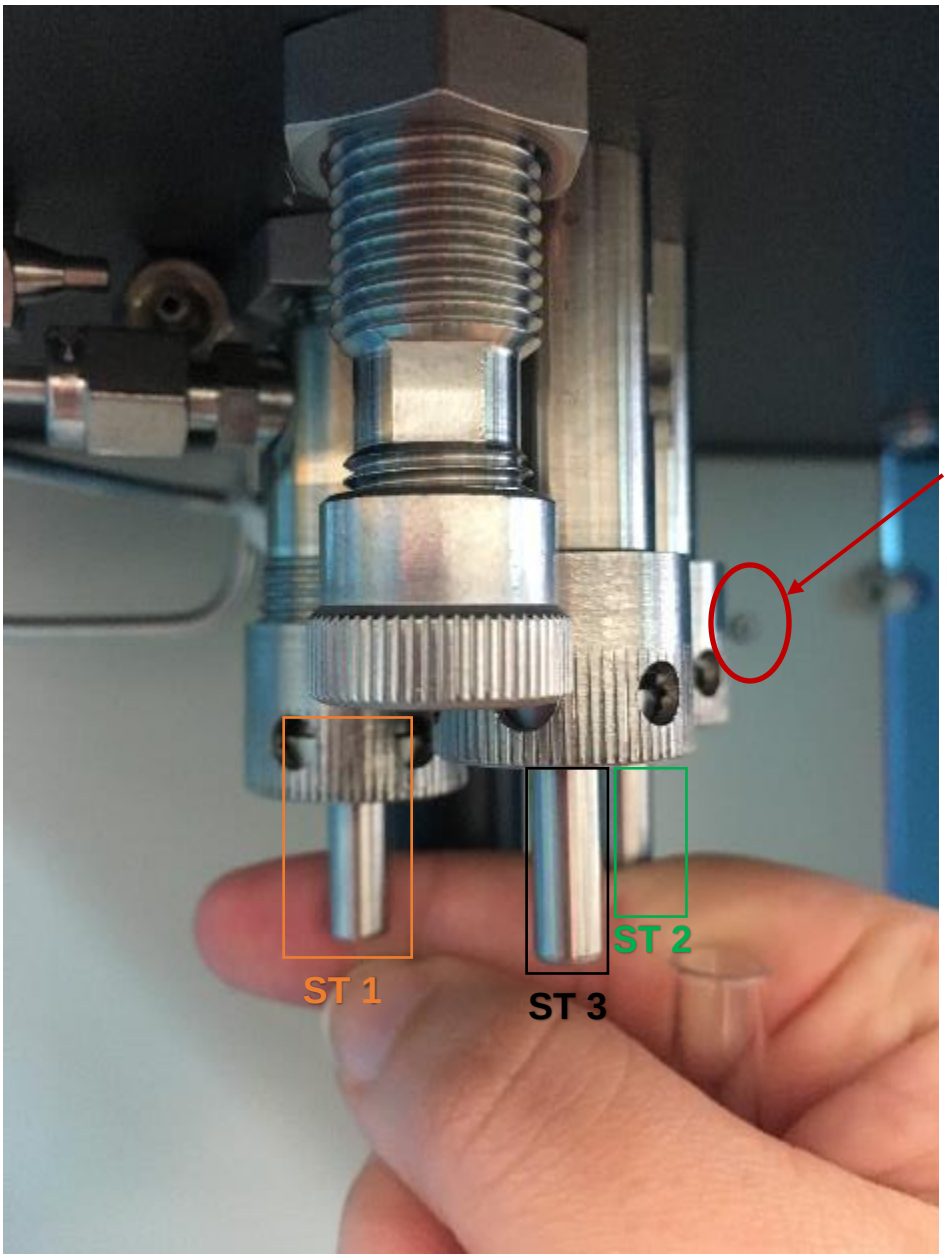
6. Optional - Place filler rod carefully in the sample cell (do it horizontally).

7. Place sample in the station 1, station 2, or station 3 properly as shown in the picture.

    a. Station 1 (ST1): Port in the left back of the analysis station.

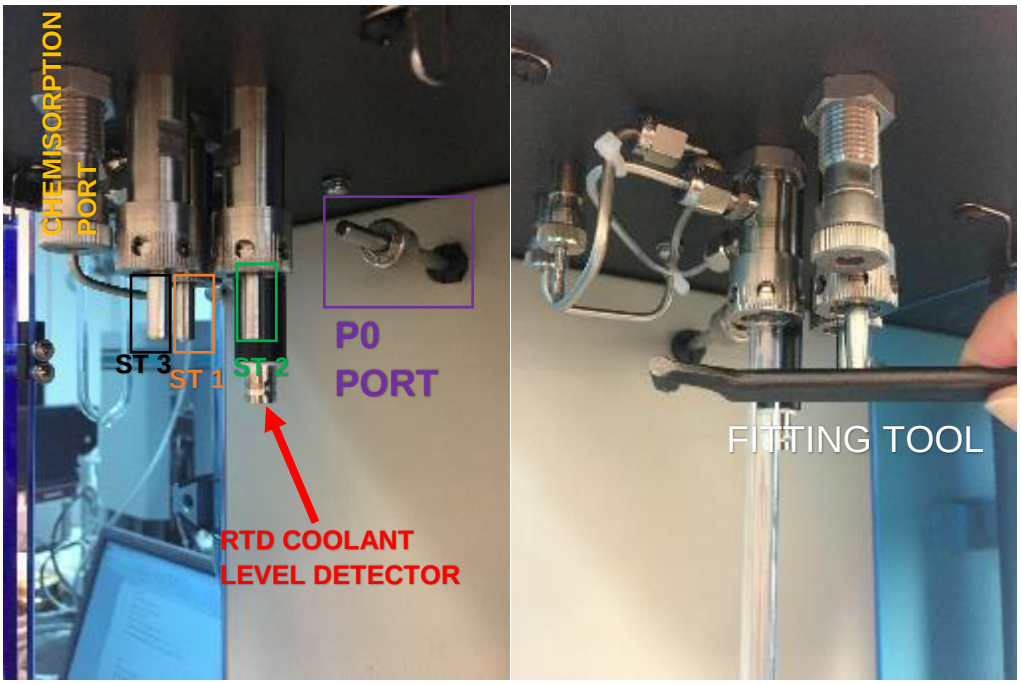
    b. Station 2 (ST2): Port in the right back of the analysis station.

    c. Station 3 (ST3): Port in front, the closest port in from od the operator.



If this blue light is on during setup, instrument needs to be serviced by staff

Light indicates thermometer is in liquid nitrogen.



8. Engage the coolant level sensor (RTD) in the analysis station.

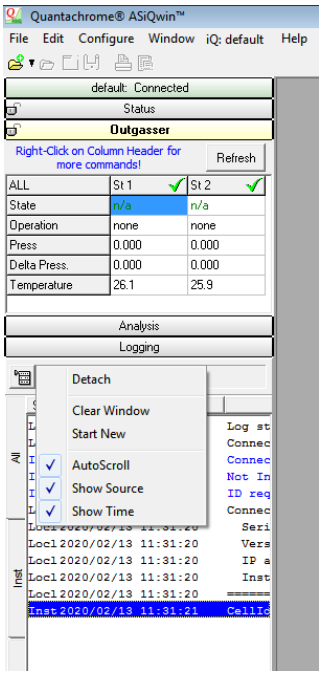
9. Remove metal pin from the P0 port, then attach Po in the analysis station. P0 cell is used to measure the saturated vapor pressure of adsorbate, or substance adsorbed, during an analysis (e.g. Nitrogen).

10. Fill in the liquid nitrogen Dewar for the analysis station as follow.

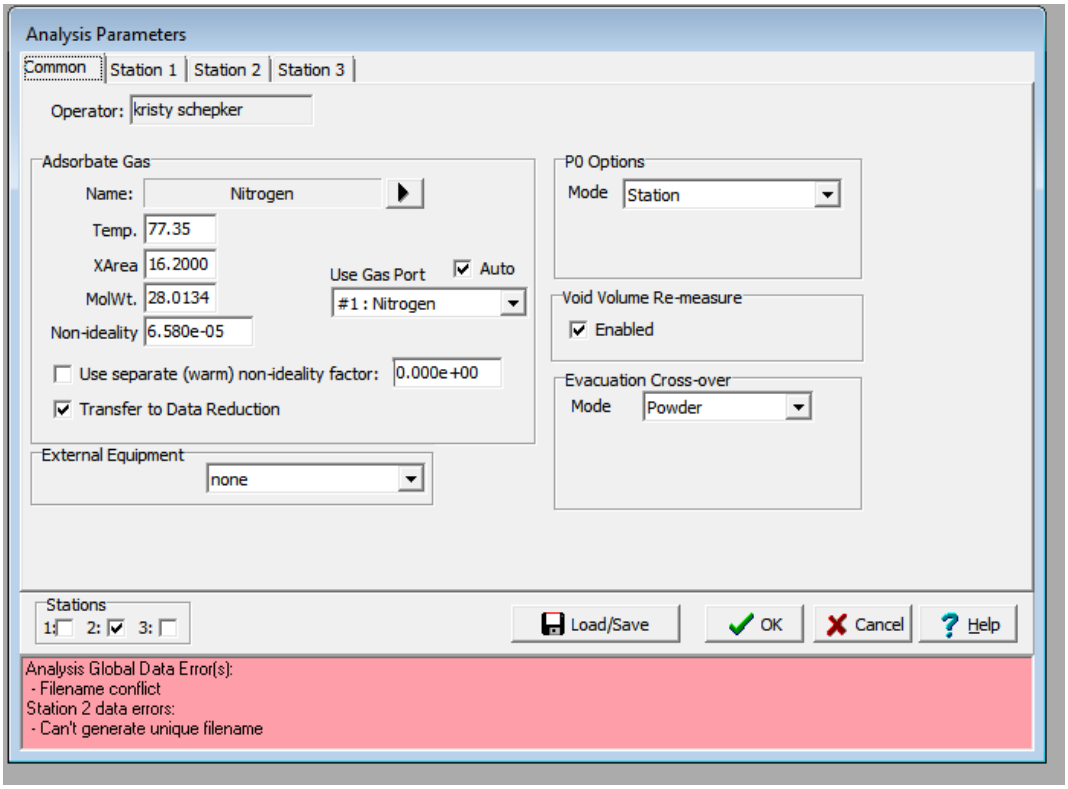
Screw with arrow should be facing the machine, not the window.

11. Sign ON the TUMI computer in room 222. Sign ON for “Analysis” This will allow to activate Helium, Argon and carbon dioxide valves. Nitrogen will be always open.

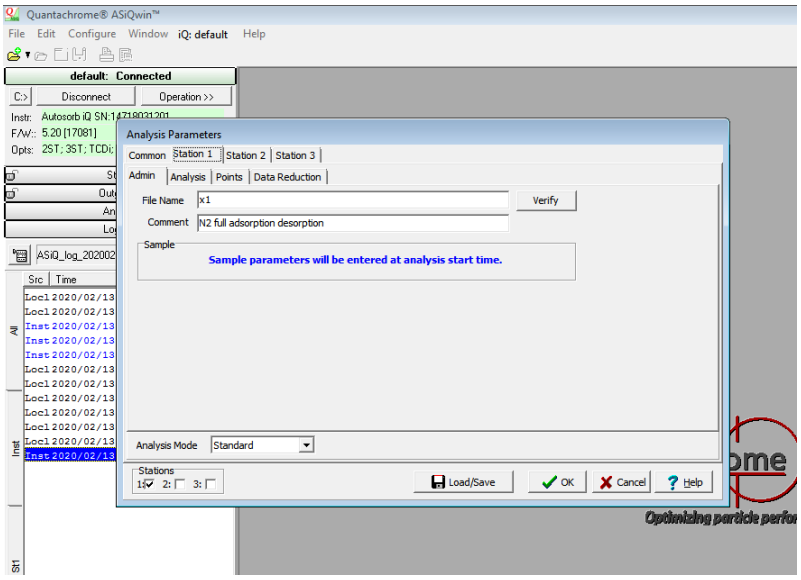
12. Create a new log for your measurement. This will allow to avoid long log files which will be easy to handle in case an error in the system.



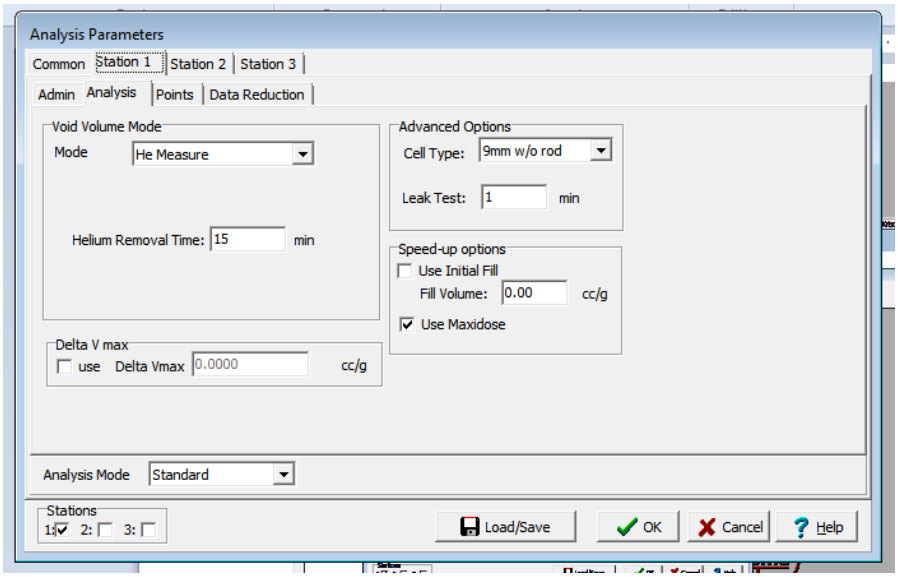
13. You will need to edit the analysis parameters. **Open iQ default> Analysis > Edit parameters**. To define common feature per analysis procedure (See common tab). Adjust as needed depending on your type of analysis. Here you can change the adsorbate to nitrogen, argon, krypton or carbon dioxide. You can change P0 as station or user defined. P0 will be user defined for adsorption measurements in Argon, Krypton or carbon dioxide. Also, define which analysis station you will be using. Finally, evacuation cross-over can be change to power or fine.



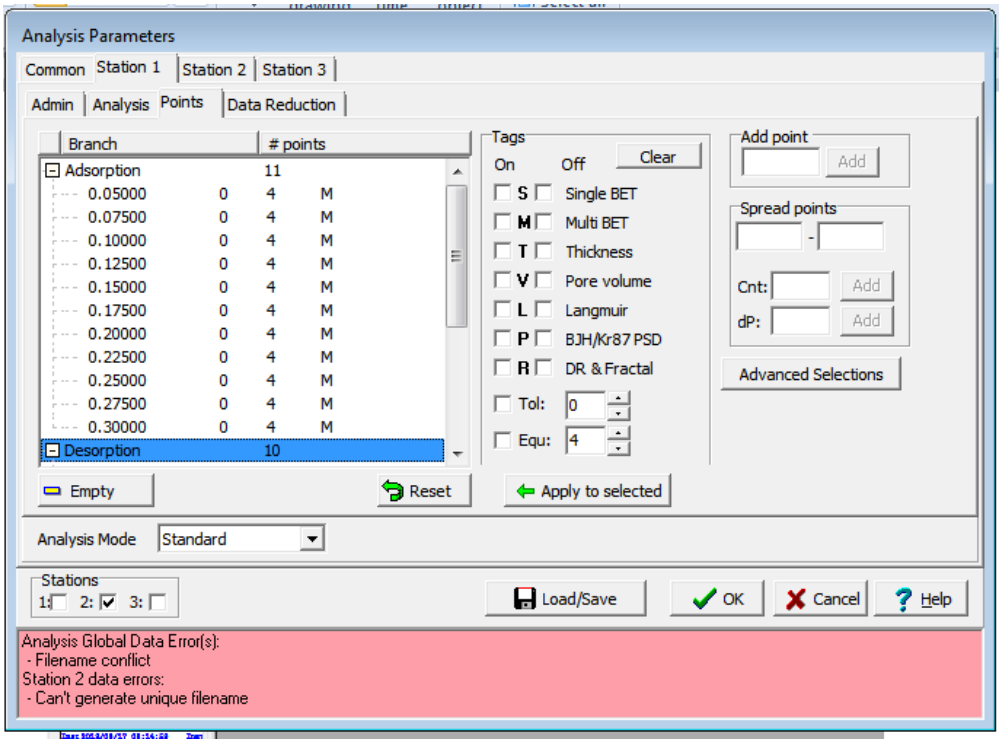
14. Define an analysis procedure per analysis station (see in station tabs, Admin, Analysis and Points tabs). Adjust as needed depending on your type of analysis. Here you can change the adsorbate to nitrogen, argon, krypton or carbon dioxide. Also, you can change P0 as station or user defined. P0 will be user defined for adsorption measurements in Argon, Krypton or carbon dioxide. Finally, evacuation cross-over can be change to powder or fine.
    - In the Admin tab add sample name.



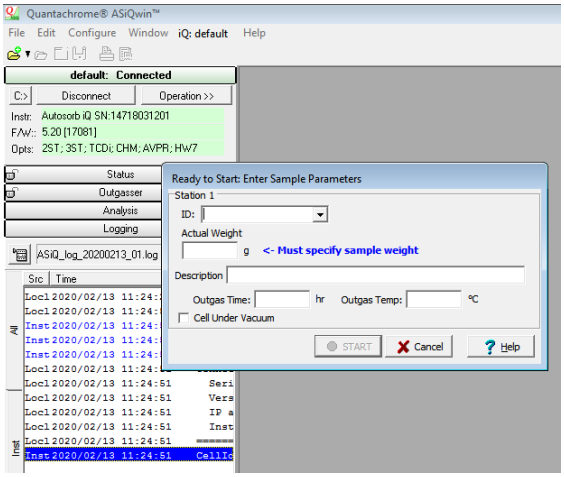
- In the Analysis tab select cell type (6 mm, 9 mm, 12 mm or without rod (w/o rod) cells). Always use Maxidose.



- In the Points tab select the adsorption and desorption point that you would like to collect during analysis. Remember to choose the right tolerance and equilibration time per data point.



15. Start analysis in iQ default menu.



16. Wait until bath rises to ensure the fan cover is in place (should remain in place always) and then verify the analysis begins without errors. It can take up to 30 min.

----------Common errors preventing analysis from beginning ----------
Each connection will be leak tested before the analysis begins, and if any port fails the leak test the analysis will not run. When a port fails the leak test, a yellow error with “leak test failed” text is added to the log, and the instrument will return to a standby state. You will need to check the seal of any port that fails, generally by removing the cell or dowel pin, inspecting the O-ring, and reinstalling the cell or dowel pin. Retaining rings should hold the pieces snug, but should not be overtightened. Loose or overtightened retaining rings can both cause failed leak tests.

17. After analysis is completed, open blue door from analysis station and remove analysis Dewar. Discard liquid nitrogen or re-use liquid nitrogen in the cold trap for outgassing. `

18. Remove P0 cell from bulkhead fitting of analysis station and plug port with a dowel pin and place it in the drawer.

19. Remove RTD from BNC connection on analysis station and place it in the drawer.

20. Insert a stainless steel dowel rod in the sample station, P0 and each outgassing station

21. Remove sample and discard or store it properly. Clean the cell with water and soap and isopropanol as a final wash and place it in the oven at 110°C to dry. Please leave a note indicating ownership of cells left in dryer.

5.2 VAPORSORPTION ANALYSIS

For vapor sorption analysis it is required to prepare the instrument overnight and then to

prepare a vapor source (e.g. distillated water).

1. Flip the toggle (pump ballast valve) switch from GAS to VAPOR position.
2. Turn on (push up) the circuit breaker to manifold heating system.
3. Allow enough time for the temperature in the manifold to stabilize to 50°C (overnight). The manifold temperature is displayed on the status display in the software.
4. Fill the vapor generator glassware to just below the top of the bulb with liquid.
5. Remove the dowel and install vapor generator glassware. Make sure that the sources do not have air bubbles.
6. Do not use a level sensor. For vapor sorption analysis it is required a floating sensor. Since the bath will rise to the upper limit switch as long the vapor sorption analysis option is selected.
7. P0 cell must be removed and User Entered P0 option must be selected.
8. Use a Dewar (+ circulator bath) filled with water to assure optima temperature stability. In this case, the water should cover as much of the sample as possible (to minimize the effect of ambient air currents to the sample cell).
9. The bath temperature must be held below room temperature (5 °C minimum difference) to complete a full isotherm (otherwise P/P0 range is limited).
10. USE TOLERANCE ZERO.
11. DO NOT USE A ROD IN THE CELLS.
12. In the case of water vapor, the lowest possible P/P0 is 10^{-3}.
13. Prepare full isotherms of adsorption and desorption with at least 20 points or higher each.
14. Return the unit to Gas Mode after vaporsorption analysis, and clean the system as follows:
    a. Maintenance from the iQ menu:
        i. Advance operation Menu
        ii. Click on cleanup after vapor sorption operation
        iii. Leave manifold heater “ON”
        iv. Vapor/Go switch in the “VAPOR” position – 25 torr/mph
15. During cleaning all ports must remain closed (outgassing and analysis stations), Heater should remain on, and switch in vapor mode.
16. When the vacuum levels are correct, switch to _____, and turn off heaters.

5.3 CHEMISORPTION ANALYSIS

We are not currently including training for chemisorption in the general training sessions, if you require this analysis please discuss your needs with RSC staff.

5.4 TCD

Please discuss with RSC Staff if needed.