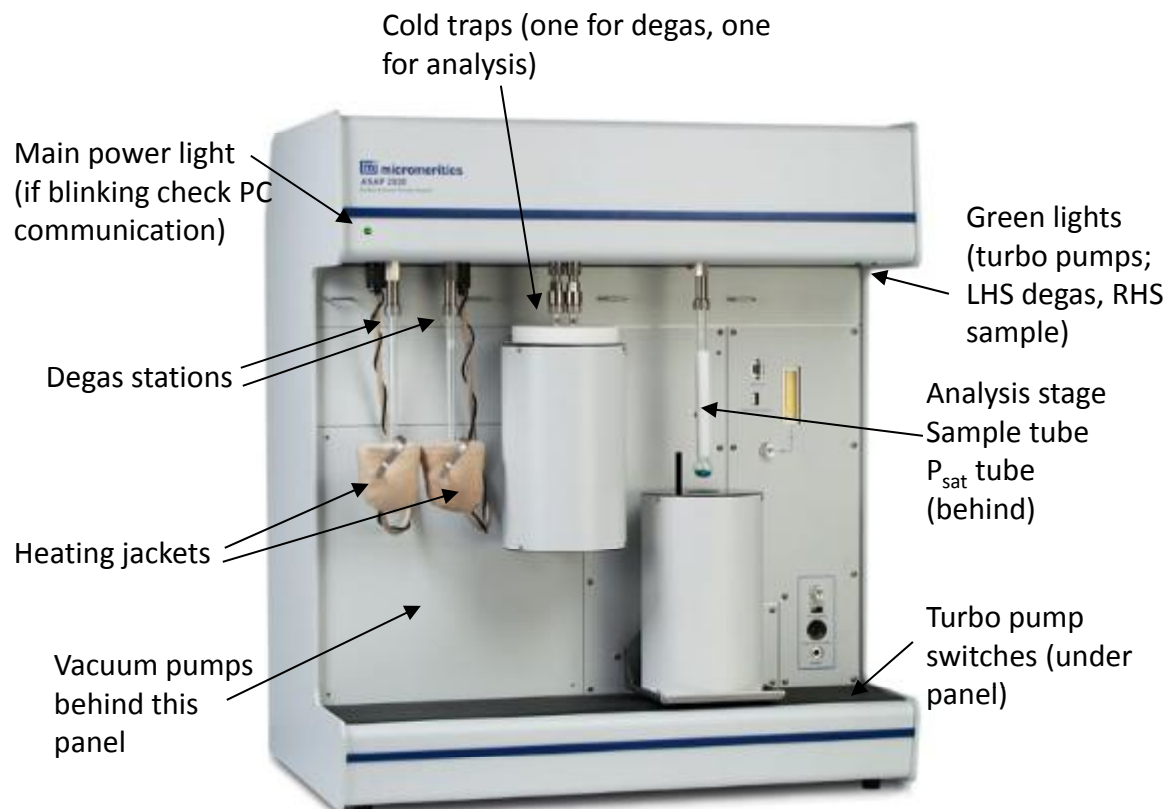# Surface Area and Porosity Analysis

Micromeritics ASAP 2020: Physisorption User notes

Lab C115, door code 3886

Introduction

Using the ASAP surface areas, pore sizes, shapes and distributions can be measured. The sample is first degassed to remove surface contamination and adsorbed species using vacuum, heat, and/or nitrogen. A probe gas (commonly nitrogen) is introduced at cryogenic temperatures; known aliquots are dosed up to saturation pressure, then a vacuum is applied and the gas is removed, which may result in hysteresis behaviour. The instrument measures values of pressure, temperature and volume. Various models are used to calculate the properties of the porous material from this data.

Cold traps (one for degas, one for analysis)

Main power light (if blinking check PC communication)

Degas stations

Heating jackets

Vacuum pumps behind this panel

Green lights (turbo pumps; LHS degas, RHS sample)

Analysis stage
Sample tube
P_{sat} tube (behind)

Turbo pump switches (under panel)

Surface area and porosity

Very low surface area < 0.01 $m^2\,g^{-1}$
Low surface area < 10 $m^2\,g^{-1}$
High surface area > 250 $m^2\,g^{-1}$

Micropores < 20 Å
Mesopores 20 – 500 Å
Macropores > 500 Å

Settings and maintenance

The dewars are designed to last for 72 hours. They should be emptied ~ weekly to remove ice which collects in the bottom.   Similarly the cold traps should be emptied and cleaned periodically, see page 9-14 in the manual for instructions.

Regulators should be set to ~ 10 psi, gases should be high purity (at least 99.999 %).

O-rings need to be replaced periodically, up to monthly with heavy use.

If the instrument is out of use for an extended period of time, pull everything down under vacuum, close all valves, then switch off.

Preparation

The free-space volume, *i.e.* that not occupied by the sample, needs to be known (see Micromeritics Application Note 1004). Errors in this are a common source of problems with measurements. The volume can be measured using helium before an experiment, but this is not suitable for some materials, *e.g.* zeolites, as the helium is very difficult to remove. For such materials the free-space can be calculated from a measurement on an empty sample tube, and this value can then be entered in the sample information file. This should be done for each sample tube and they should be labelled and used with the same seal frit each time.

Cleanliness of sample tubes is very important. Gloves should be used to avoid fingerprints as oils can take a day to evaporate under vacuum on the instrument. An accurate (4 figure) sample mass, both before and after degassing, is required.

Information on solvent/water loss and thermal stability is useful, for example from thermogravimetric analysis. The degas parameters can be based on this. Sample density is also required if calculated free space values are being used.

Software: Instrument Control

ASAP 2020 v3.03

Unit 1 → Show Instrument Schematic shows the current status of the instrument.

In normal use, analysis files are created which control all aspects of the experiment, and the user simply has to run these files. Occasionally manual control is needed; this should not be carried out unless the user fully understands the process. To manually open or close valves, use Unit 1 → Enable Manual Control. Right click on a valve to open or close, or left click to highlight then use the space bar. Disable manual control as soon as possible to prevent inadvertently opening or closing valves (this can happen when using the space bar in a different window).

Unit 1 → Degas → Show Degas Schematic and → Enable Manual Control work in the same way for the sample preparation section.
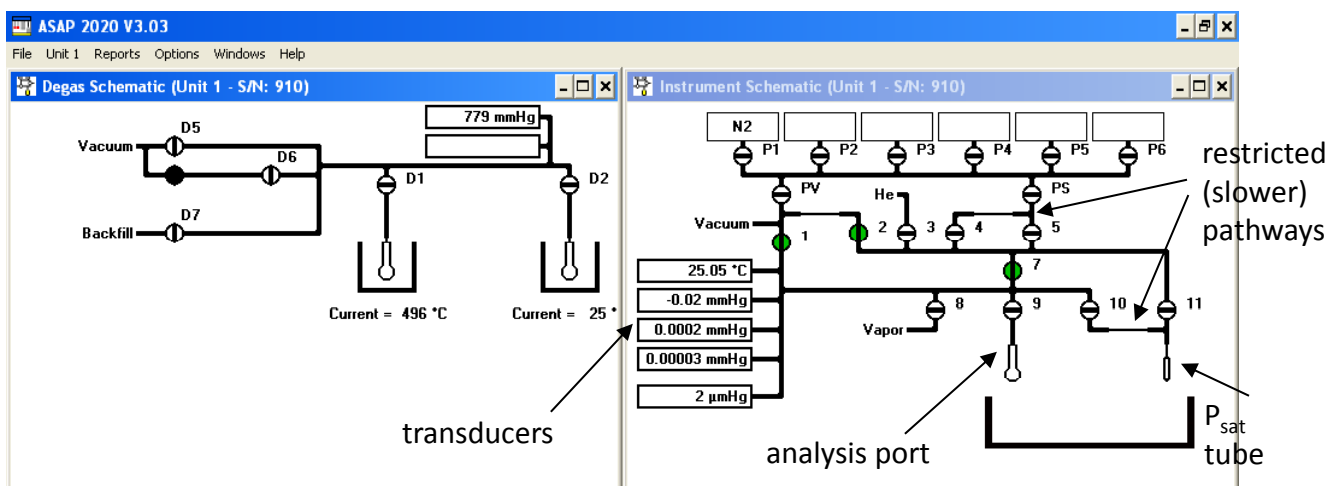
Software: Creating files

Files are located in C:\2020

Sample files, which contain all the parameters to run an experiment, are .smp type. Other file types which contain sections of data from a sample file can be saved, such as degas files, .deg. Once an experiment has been run a report file, .rep, can be saved. These can all be read only in the ASAP software.

Use File → Open to both open an existing file or create a new one. Files are auto-numbered by the software (000-xyz) and it is helpful to enter the file number as part of the sample name.

The easiest way to create a sample file is to copy the parameters from an existing one and edit as required. In the 'Sample Information' tab click on 'Replace All'. Existing files that can be used as templates are 000-008.smp BET template, 000-009.smp full adsorption template and 000-010.smp full adsorption and desorption, or use one from a previous sample.
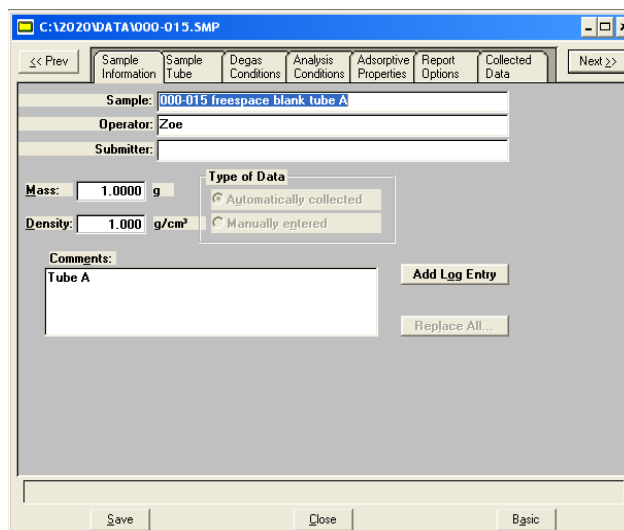
Edit/enter data as required in each tab.

The sample preparation or degas stage has two phases – evacuation and heating. The hold pressure is used if there is a sudden pressure increase (for example if water is given off) – the system will hold at this pressure until the release subsides. 'Backfill sample tube' will fill the tube with the backfill gas (nitrogen) to atmospheric pressure when degassing is complete, enabling removal of the tube.
Use File → Save As to save this as a .deg file.
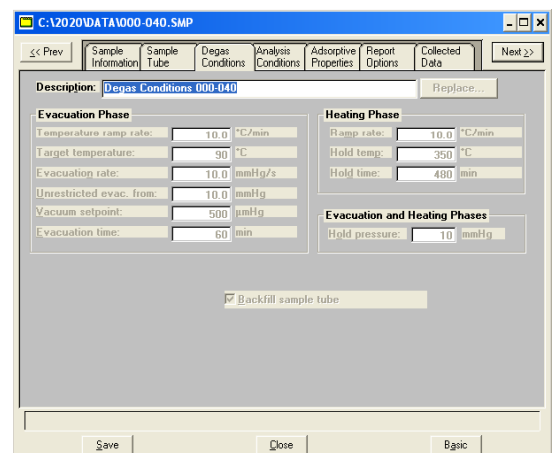
In the 'Analysis Conditions' tab the P/P_0 values are specified and the type of analysis is selected. Examples: total pore volume at 0.95, BET based on 0.03 – 0.3 (or 0.1 – 0.2 for microporous materials), and BJH adsorption 0.26 – 0.995. If desorption data is being collected, it should only go as far down as 0.1, as lower P/P_0 values will take a long time to achieve.

The buttons along the bottom contain further experiment parameters. If calculated free space values are being used they should be entered here, otherwise select 'measure'. Do not use the 'fast evacuation' option as this can suck powder up into the main manifold.
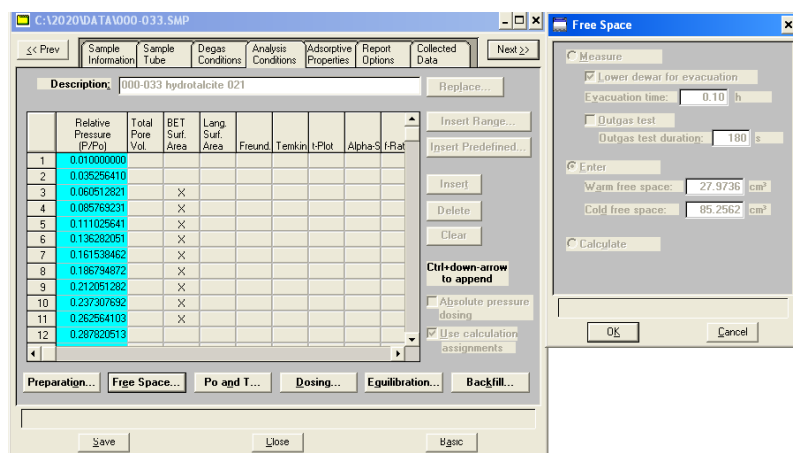
In 'Report Options' the types of analysis and calculations required can be selected and customised.

When all parameters have been entered or edited, save then close the file.

Running a sample: Degassing

The first stage usually takes place on one of the degas ports. Weigh the sample into a sample tube and fit a seal frit. A glass filler tube can be used to which minimise free space, however these should not be used for microporous materials. The optimal quantity of sample is that which has a surface area of approximately 30 m^2. Use the long funnel to prevent powder sticking to the sides of the sample tube.

Put the nut, collar and o-ring on the sample tube, then attach to the degas port. If heating, fit a heating jacket.

In the control software, go to Unit 1 → Start Degas. Making sure the correct port is selected (left hand is 1, right hand 2) browse to the appropriate sample and .deg file. Click on 'clear' if a port is not being used. Click 'Start' to begin the program. 'Check' will suspend the degas, 'Cancel' will stop it.

Running a sample: Analysis

When the degas stage is complete and the tube cooled, remove from the port and reweigh.

Fit the isothermal jacket and attach the tube to the sample port. Check that the jacket on the P_{sat} tube is at the same height as on the sample tube, and that the P_{sat} tube is in position for the dewar, alongside the sample tube.

Fill the sample dewar to the correct level and place on the platform:

Level of LN2 must be between these limits – dip in and breathe on to check
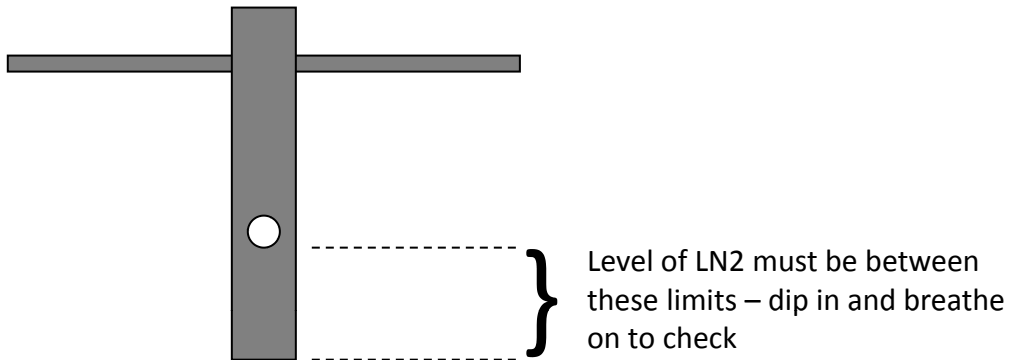
Start the analysis using Unit 1 → Sample Analysis. Select the file to be run and start.

Results

If the .smp file has run successfully a report will be generated and open in the software. It contains a number of tabs depending on which models have been selected for calculations. An example isotherm plot and BET surface area:
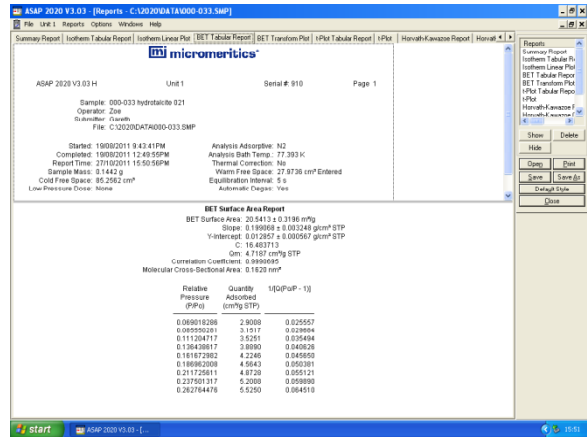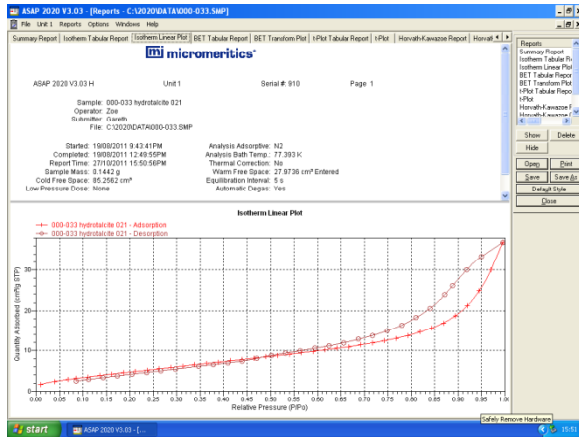
The isotherm should give an indication of the type of material and the quality of the data. If there is a hysteresis loop it should close by around 0.4 P/P_0 – if not the sample may not be degassed fully, or there may be a free space error.

The report is re-run each time it is opened and some parameters can be changed in the .smp file beforehand. Use Report → Start Report and select the appropriate file. It can be saved as a .rep file.

Right-click on a table of data to copy, then paste into Notepad for use in Excel or similar.