IMPORTANT NOTICE: The current official version of this document is available via the Sandia National Laboratories WIPP Online Documents website. A printed copy of this document may not be the version currently in effect.

ACTIVITY/PROJECT SPECIFIC PROCEDURE

SP 12-33
CALIBRATION, USE AND MAINTENANCE OF THE ACCELERATED SURFACE AREA AND POROSIMETRY SYSTEM (ASAP 2020)
Revision 0

Effective Date: June 21, 2012

Author:	Leslie Kirkes	*Original signed by Leslie Kirkes*	*6/21/12*
	(printed name)	(signature)	(date)

1.0 Purpose and Scope

This procedure prescribes the Sandia National Laboratories (SNL) Waste Isolation Pilot Plant (WIPP) process for the calibration, operation, and maintenance of the Micromeritics ASAP 2020 as part of the laboratory geochemistry research activities in the support of the Waste Isolation Pilot Plant (WIPP) Project.

This procedure is applicable only for the Micromeritics ASAP 2020, Physisorption mode. If the Chemisorption mode is used in the future this SP will need to be revised. This document is concise, and is not meant to substitute for, or reproduction of the manufacturers' instruction manuals for the ASAP 2020 (i.e., ASAP 2020 Operator's Manual V3.04, May 2010). The user is responsible for reading and understanding the appropriate manuals (see references).

Acronyms and definitions for terms used in this procedure may be found in the Glossary located at the Sandia National Laboratories (SNL) WIPP Online Documents web site.

1.1 Instrument Description

The ASAP 2020 is equipped with two vacuum systems- one for sample preparation and one for sample analysis. This means that sample preparation (de-gassing) and sample analysis can occur simultaneously. During the sample analysis, the sample tube containing the sample will be evacuated and then cooled to cryogenic temperatures. Then the analysis gas will be introduced into the tube at precisely controlled pressures (usually Nitrogen). With each incremental pressure increase, the number of gas molecules adsorbed on the surface of the sample increases. The pressure at which adsorption equilibrium occurs is measured and the universal gas law is applied to determine the quantity of gas adsorbed. The below poster, describes the theory behind gas adsorption to particles, and surface area and porosity measurements. The link above the poster will take you to a larger view.

© 2012 Sandia Corporation

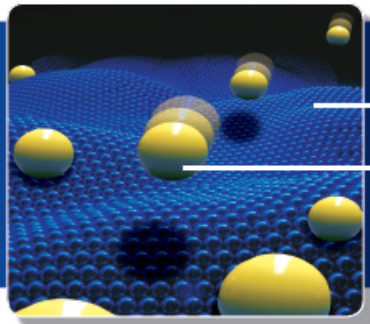
http://www.micromeritics.com/Repository/Files/Gas_Adsorption_Theory_poster.pdf

Gas Adsorption Theory

Presented by Micromeritics Instrument Corporation

Adsorption Defined

Similiar to surface tension, adsorption is a consequence of surface energy. Most atoms that make up a solid are bound on all sides by other atoms in the bulk of the solid. The atoms on the surface of the solid, however, are incompletely bound. Due to van der Waals forces of interaction, these surface atoms are more reactive and they attract gas, vapor, and liquids to satisfy the imbalance of atomic forces.

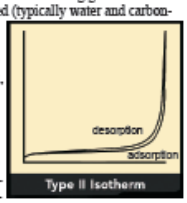


These surface molecules (in blue) are experiencing a bond deficiency, thus it is energetically favorable for them to adsorb molecules. (in yellow).

Stage 1 in diagram below.

Surface Area

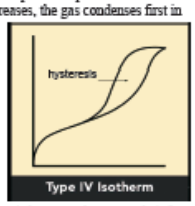
Surface area helps determine such things as how solids burn, dissolve, and react with other materials. To determine the surface area, solid samples are pretreated by applying some combination of heat, vacuum, and /or flowing gas to remove adsorbed contaminants acquired (typically water and carbon-dioxide) from atmospheric exposure. The solid is then cooled, under vacuum, usually to cryogenic temperature (77 k, -195 °C). An adsorptive (typically nitrogen) is dosed to the solid in controlled increments. After each dose of adsorptive, the pressure is allowed to equilibrate and the quantity adsorbed is calculated. The quantity adsorbed at each pressure (and temperature) defines an adsorption isotherm, from which the quantity of gas required to form a monolayer over the external surface of the solid is determined. With the area covered by each adsorbed gas molecule known, the surface area can be calculated.



Type II Isotherm

Porosity, Pore Sizes and Pore Distributions

Surface area determinations involve creating the conditions required to adsorb an average monolayer of molecules onto a sample. By extending this process so that the gas is allowed to condense in the pores, the sample's fine pore structure can be evaluated. As pressure increases, the gas condenses first in the pores with the smallest dimensions. The pressure is increased until saturation is reached, at which time all pores are filled with liquid. The adsorptive gas pressure then is reduced incrementally, evaporating the condensed gas from the system. Evaluation of the adsorption and desorption branches of these isotherms and the hysteresis between them reveals information about the size, volume, and area.



Type IV Isotherm

Chemisorption Determinations

Chemisorption is used to determine the percent metal dispersion, active metal surface area, size of active particles, and surface acidity of catalyst materials. The dispersion is the ratio of active sites to total sites on a catalyst.

Active Metal Dispersions

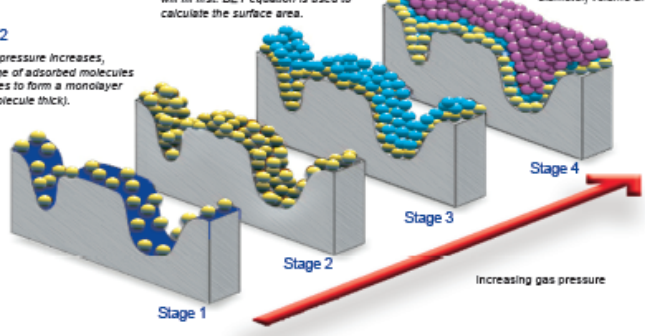
Chemisorption is the interaction of an active gas and a solid surface, involving the sharing of electrons between the adsorptive molecule and the solid surface. It is generally assumed that a chemisorbed layer will not exceed a single molecule in thickness. The efficiency of a catalyst in promoting a chemical reaction is related directly to the density of active sites on is surface.

Stage 1
Isolated sites on the sample surface begin to adsorb gas molecules at low pressure.

Stage 2
As gas pressure increases, coverage of adsorbed molecules increases to form a monolayer (one molecule thick).

Stage 3
Further increasing gas pressure will cause the beginning of multi-layer coverage. Smaller pores in the sample will fill first. BET equation is used to calculate the surface area.

Stage 4
A further increase in the gas pressure will cause complete coverage of the sample and fill all the pores. The BJH calculation can be used to determine pore diameter, volume and distribution.



Data Reduction Methods

Langmuir
provides a means of determining surface area based on a monolayer coverage of the solid surface by the adsorptive.

BET
the method of Brunauer, Emmet, and Teller is employed to determine surface area on a model of adsorption which incorporates multilayer coverage.

BJH
the method of Barrett, Joyner, and Halenda is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. It applies only to the mesopore and small macropore size range.

deBoer t-Plot
is most commonly used to determine the external surface area and micropore volume of microporous materials. It is based on standard isotherms and thickness curves which describe the statistical thickness of the film of adsorptive on a non-porous reference surface.

MP-Method
is an extension of the t-Plot method. It extracts micropore volume distribution information from the experimental isotherm.

Dubinin Plots
relate the characteristic energy of adsorption to micropore structure.

Medek
uses Dubinin plots to determine micropore volume distributions by pore size.

Horvath-Kawazoe Technique
provides a means by which the micropore volume distribution by size is extracted from the experimental isotherm. The original H-K method is based on slit-shaped pores, however additions by Saito-Foley and Cheng-Yang extend the method to apply to cylindrical and spherical pores, respectively.

Deconvolution by Classical Model Fitting
this method determines the best fit (in a least squares sense) of a set of single-mode model isotherms to the experimental isotherm. The solution set represents the pore volume distribution by size for the solid on which the isotherm was developed.

DFT Plus
density functional theory provides a method by which the total expanse of the experimental isotherm can be analyzed to determine both microporosity and mesoporosity in a continuous distribution of pore volume in respect to pore size.

micromeritics®
The Science and Technology of Small Particles™

www.micromeritics.com

For a great video about understanding the Physisorption technique, go to the following website:

http://www.micromeritics.com/Product-Showcase/ASAP-2020-Physisorption-Analyzer/ASAP-2020-Technique-Overview.aspx

2.0 Implementation Actions

2.1 Safety

The activities described in this SP shall conform with SNL Environmental Safety and Health programs (ES&H). This document does not address ES&H issues. Laboratory ES&H procedures and specific instrument hazards are described in laboratory-specific TWDs and JSAs, which can be found at the listed website: http://pob.sandia.gov/WIPP_ESH/

2.2 Responsibility

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure, is responsible for implementing the requirements of this procedure.

The Laboratory Technician, or designee, is responsible for performing the calibrations and measurements following the requirements of this procedure, documenting calibrations, and assuring that the latest revision of this document is followed.

2.3 Controls

Controls are established by written procedures or instructions prepared in accordance with NP 5-1, *Implementing Procedures* of the SNL WIPP Quality Assurance Program. Procedures are issued in accordance with NP 6-2, *Document Control Process* of the SNL WIPP Quality Assurance Program.

2.4 Standards

A standard curve cannot be made for this instrument; however there is a reference standard material that can be used to perform a quality check on the instrument. It is recommended that the Silica Alumina pellets (Catalog # 004/16821/00) reference standard material be used for the quality check for most applications. However, other checks may be purchased if desired. The expected surface area and pore values for each material purchased are LOT dependent. Each material will come with a certificate of analysis, which the user should use to determine tolerance and acceptance limits.

Silica-Alumina Example Values:

Multiple Point Specific Surface Area:	214 ± 6 m^2/g
Total Pore Volume at Po 0.9990 to 0.998:	0.62 ± 0.08 cm^3/g
Average Pore Diameter:	115 ± 15 Å
Single Point Specific Surface Area:	208 ± 6 m^2/g

2.5 Quality Control

If the results of the calibration and QC samples are not within the acceptance/tolerance limits (described in subsequent sections), all samples shall be flagged on the data report, and corrective action will be documented in the scientific notebook.

2.6 QC Sample Criteria

A quality check should be performed prior to sample analysis on a weekly schedule when the instrument is in use. The check should agree within the certified values listed for the reference material. The reference material will be used to verify that the ASAP 2020 is appropriately measuring surface area and pore: diameter, volume and size. Each material will come with a certificate of analysis, which the user should use to determine tolerance and acceptance limits.

2.7 Sample Preparation

Cleaning:

It is very important that the sample vials, filler rods and seal frits be clean and dry before use. The following cleaning procedure should be followed:

1. Measure out 5 grams of alconox (or suitable detergent) per 500mL of DI water (if a film develops on the vials, use less alconox).
2. Pour this mixture into the ultra-sonicator.
3. Allow the alconox to dissolve thoroughly (if there is a heating option on the sonicator, it is recommended to be used).
4. Carefully place the sample tubes, filler rods and seal frits into the sonicator bath (you may wish to fill the sample tubes with water before you place them into the bath).
5. Allow the sonicator to run for a minimum of 15 minutes.
6. When finished, using gloves, remove the sample tubes, filler rods and seal frits from the sonicator.
7. Rinse all, with DI water at least 3 times, then place them in the drying oven.
   (NOTE: A variation of this procedure can be found in the Micromeretics ASAP 2020 Physisorption manual on pages 4-16 to 4-18).
8. CAUTION: once the sample vials, filler rods and seal frits are clean and dry DO NOT touch them with your bare hands. Always handle them with gloves, once clean. Oil from your fingers can be transferred to the sample ware which can alter results or create degassing problems.

Sample Preparation:

Use gloves for this entire sample preparation procedure. Filler rods can be used to increase the accuracy for low surface area samples, by reducing the free-space volume. It is usually a good idea to use a filler rod for samples with a total surface area less than 100 square meters. The weight measurements at each of the following steps are very important for the accuracy of the sample determination. Three major weights will be taken: Before Degas weight with the sample vial empty, Before Degas weight with including the sample and the After Degas weight. An After Analysis weight can also be taken to ensure that no problems occurred during analysis.

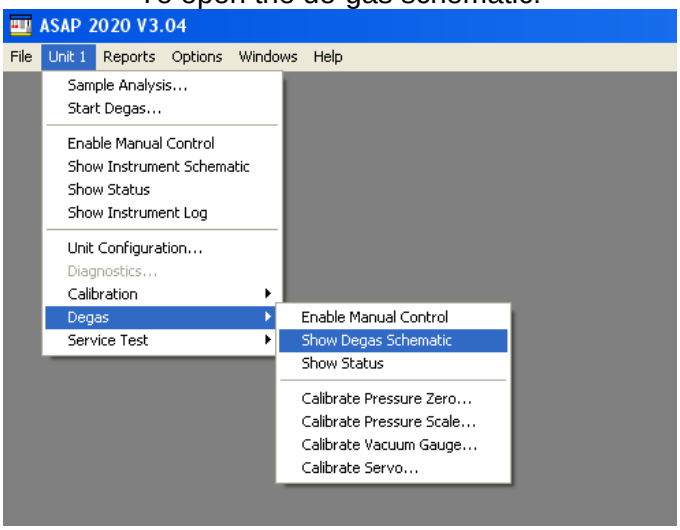
1. After cleaning and drying, allow the sample vial, filler rod and seal frit to adjust to room temperature.
2. Once cool, place the filler rod inside the sample vial and place the seal frit in the lid opening.
3. The empty vial weight will need to be determined. It is very important that this weight is accurate. Use the worksheet in Appendix A to record all of the weights for each sample. Tare the doughnut holder provided, then carefully determine the empty vial weight. Record this weight on the worksheet under Number 1.
4. Remove the seal frit and filler rod (if used), use a long funnel to place the desired amount of sample into the sample tube.
   NOTE: A good sample weight to start with is 0.2g, however if a low surface area is expected a sample weight of up to 3.0g may be necessary for proper analysis.

5. Replace the filler rod and seal frit in the sample tube. Then tare the doughnut holder, and determine the weight of the sample tube and sample. Record this weight in the worksheet under Number 2.
6. The sample is now ready for de-gassing

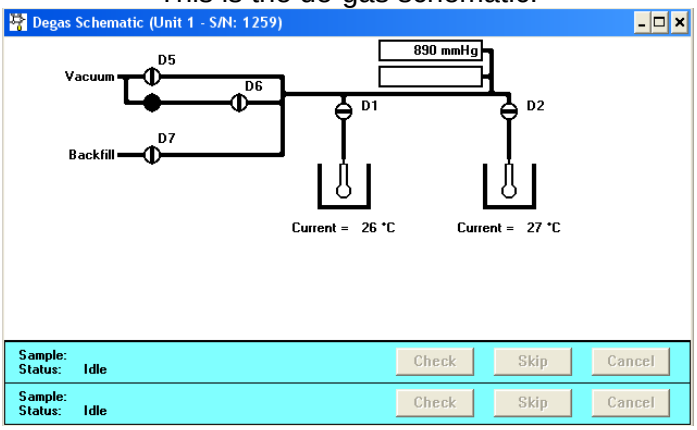
2.8 Instrument Set-up

The de-gassing process and the sample analysis are controlled utilizing computer controlled valves and pumps. The operation of the valves can be viewed in the two different schematics. It is a good idea to leave both schematics open during the operation of the instrument, so that the positions of the valves can be monitored for each schematic.

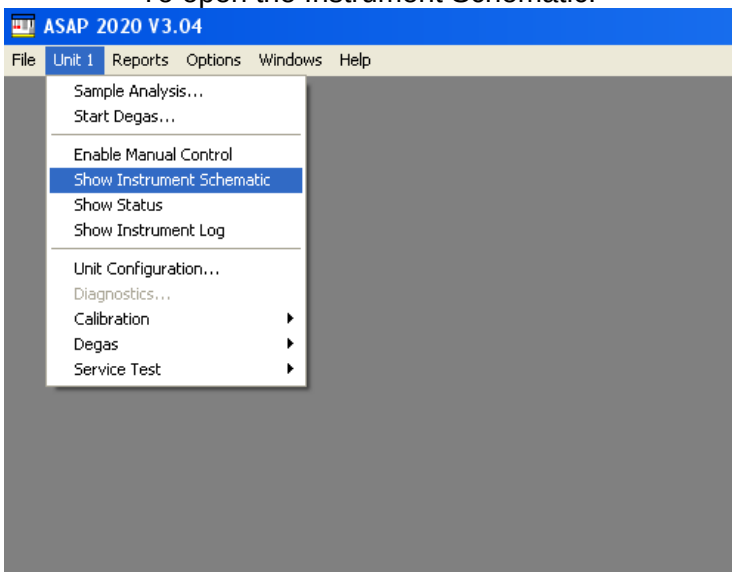
To open the de-gas schematic:



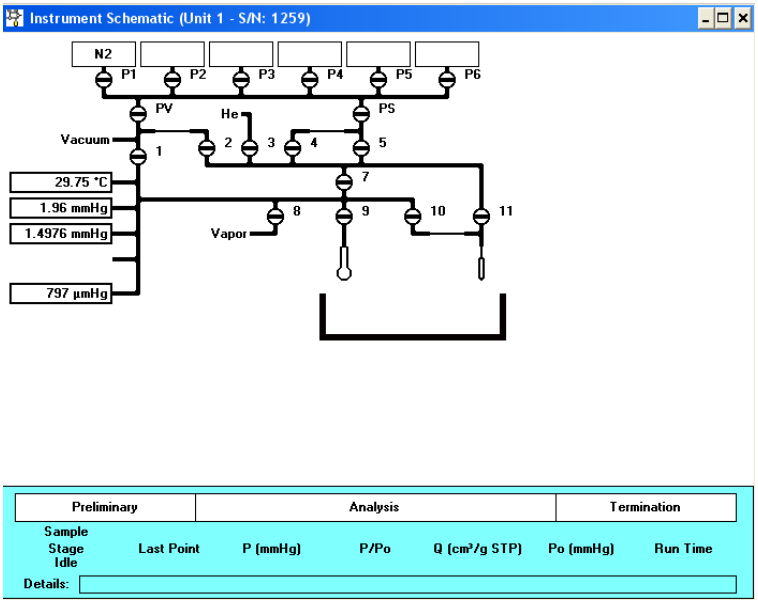
This is the de-gas schematic:



To open the Instrument Schematic:



This is the Instrument schematic:



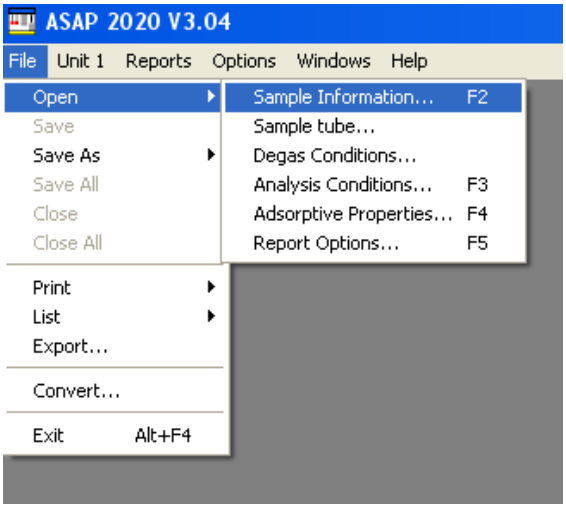
Fill Dewars:

Before starting a sample for de-gassing or sample analysis make sure that the cold trap dewar and the sample analysis dewar are full. See pages 4-25 to 4-27 of Micromeretics ASAP 2020 Physisorption manual for information on filling and installing the dewars properly.

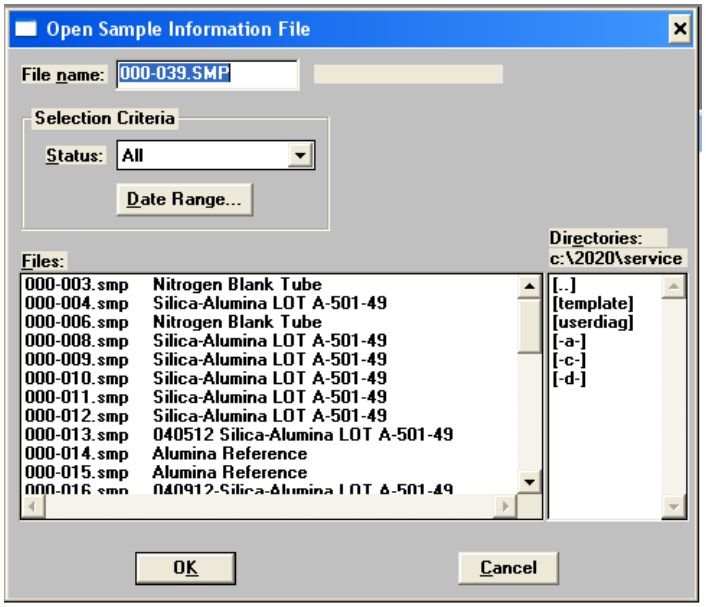
CAUTION: Liquid Nitrogen may splash, always use the proper PPE (i.e. face shield, thermal gloves) when working with liquid nitrogen.

2.9 Creating a Sample File

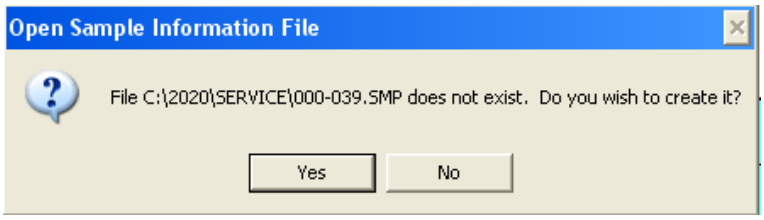
A sample file must be created before an analysis can be started for degassing. To create a new sample file, follow the diagram below.



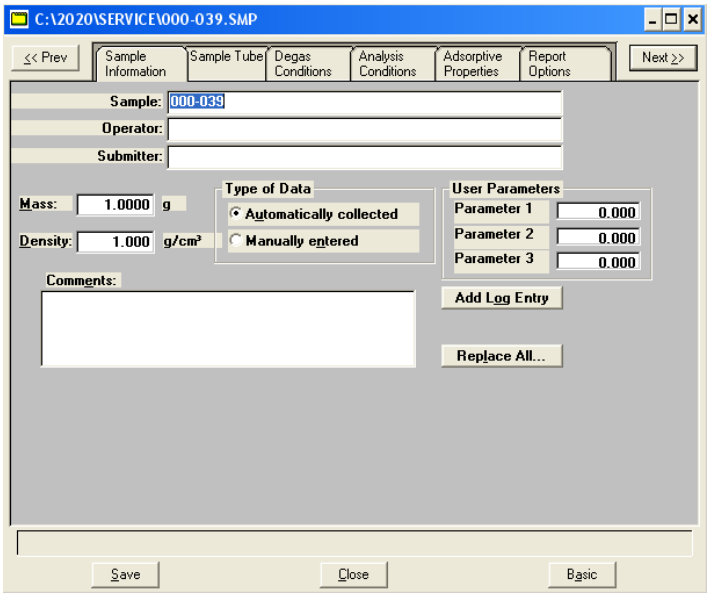
Clicking on sample information will take you to the following screen. This window contains all of the existing samples stored in the computer. You want to create a NEW sample. Do not click on one of the existing samples or you will over-write the data. The new sample number is displayed in the File Name box. For this example the new sample being created is Sample 000-039. NOTE: Do not change the name of the sample here. Once the new file is created you can re-name the sample with a new name.



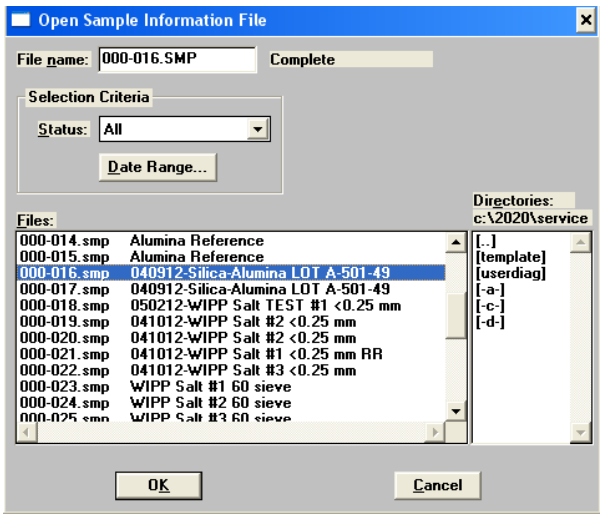
After you click ok, a new box will appear asking you if you want to create a new sample. Click Yes.



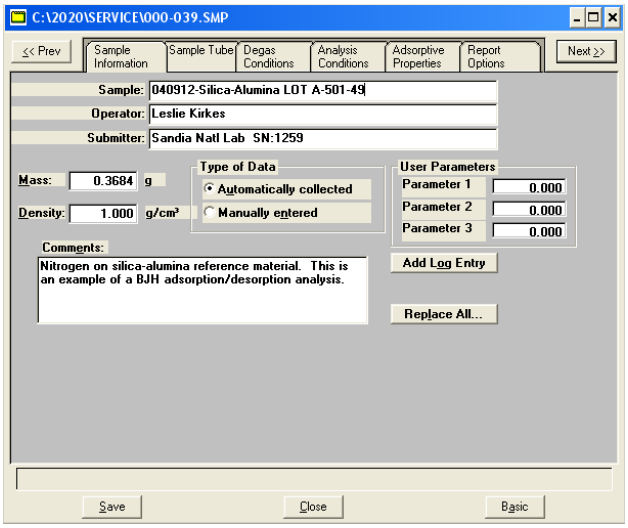
The parameters for analysis can now be entered, along with the sample name and weight. Go through each tab and set up the desired parameters. For more information on setting up the proper parameters refer to the Micromeretics ASAP 2020 Physisorption Manual.



Once a sample profile is created with all of the desired analysis parameters, it can be easily loaded in to the new sample file by clicking Replace All. If you are running many samples that need the same analysis parameters the easiest thing to do is use the Replace All button. After clicking Replace All, a browse window will come up asking you which sample information you would like to load into your new sample file. Click the sample information that you would like to upload, then press OK.

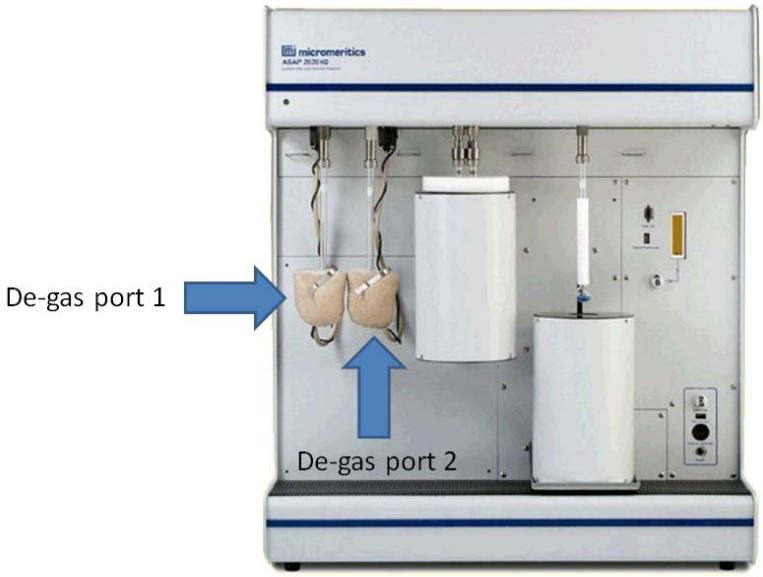


Once you have uploaded the sample information you will need to change the name of the sample, operator and also the weight to reflect your current NEW sample. Once you have made your new sample file, you are ready to start the de-gas procedure.



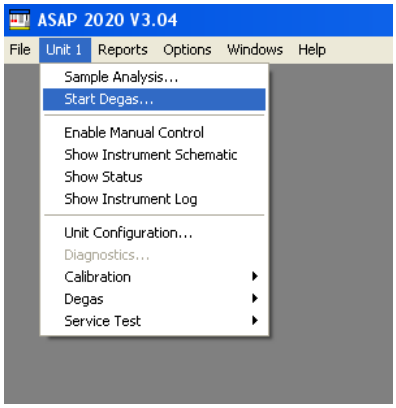
2.10 De-gas Procedure

The ASAP 2020 is equipped with two de-gas ports. De-gas port 1 and De-gas port 2 (as shown in the diagram below). A de-gassing procedure can be run on both ports at the same time. Securely, attach the sample tube to the desired de-gas port.

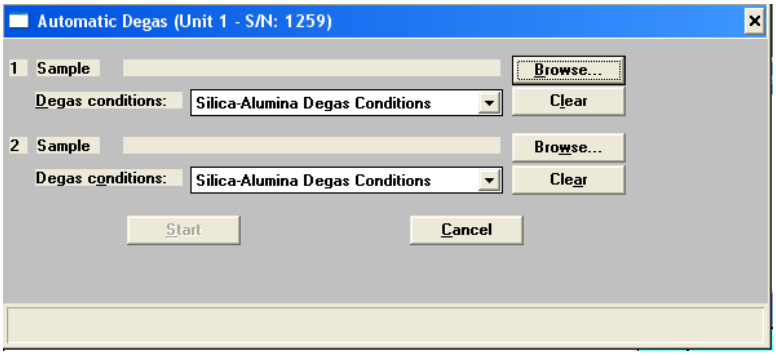


Picture modified from: http://www.micromeritics.com/repository/files/ASAP_2020_Brochure_3.pdf

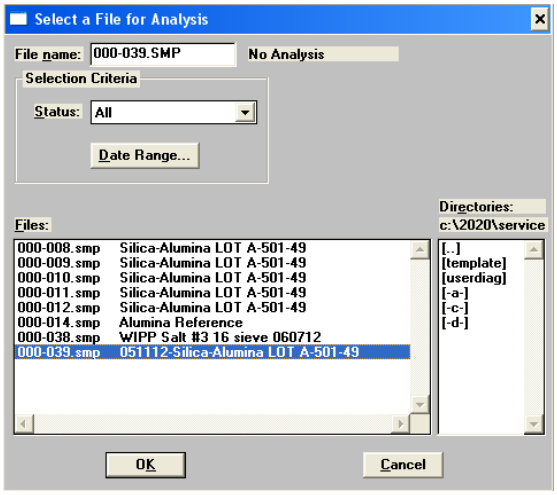
1. Place the degas port connector nut, ferrule, and O-ring onto the sample tube set as show in the figure on page 4-21 of the Micromeretics ASAP 2020 Physisorption Manual.
2. Place the heating mantle over the bulb of the sample tube and secure the mantle in place with the mantle clip.
3. Start the de-gas.



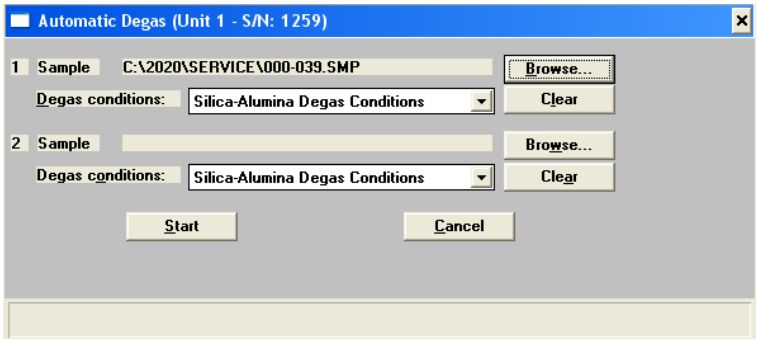
After clicking Start De-gas, a window will appear asking you to browse for the sample that you wish to start the de-gas on. The 1 is representative of De-gas port 1 and the 2 is representative of De-gas port 2. Click Browse next to the port in which your sample is inserted.



Clicking browse will take you to a list of samples that still need to be de-gassed. Click on your sample file that you created earlier then press OK. (Our example was sample 000-039).



Once you have selected your sample it will appear in the 1 box (De-gas port 1). Click Start when you are ready to begin the analysis. If you would like to de-gas another sample at the same time, repeat steps 1-3 on port 2.

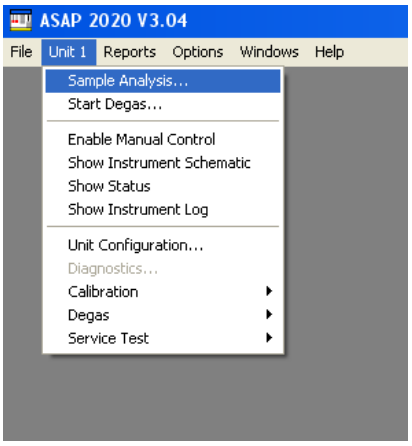


If using the Silica-Alumina Degas Conditions (which is the recommended method) the degassing procedure will take approximately 6 hours.

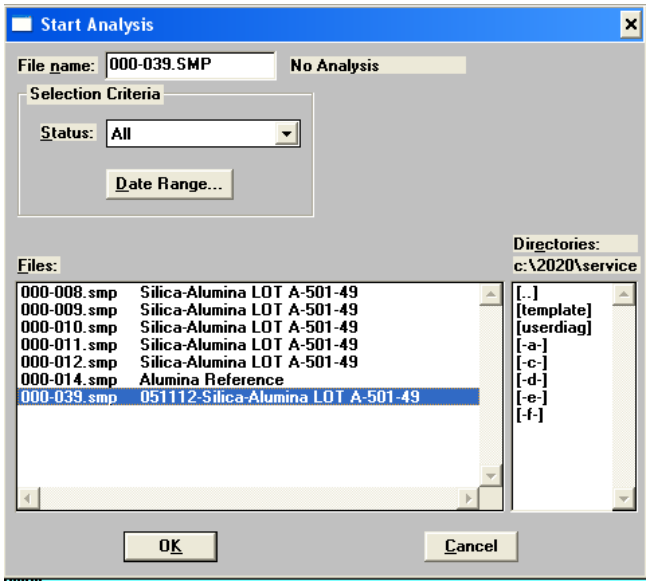
2.11 Sample Analysis

After the De-gas procedure has been completed. You are now ready to begin the Sample Analysis. Wear gloves for all of the following steps.

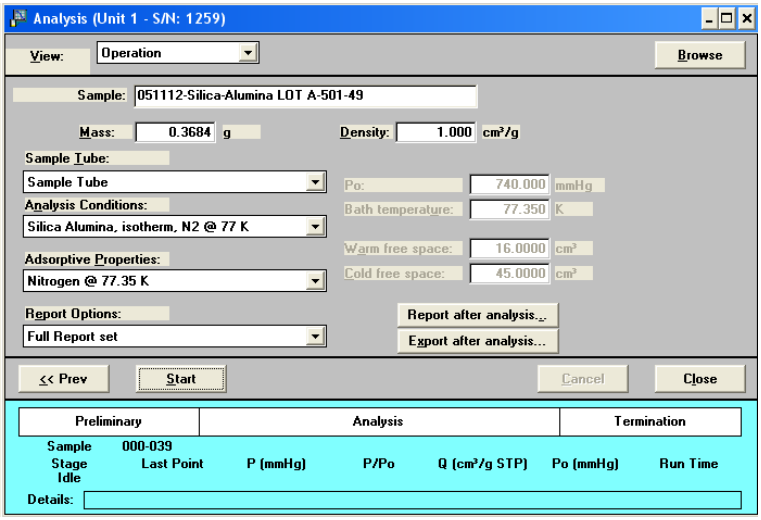
1. Remove the sample tube from the De-gas port.
2. Tare the doughnut holder, and record the weight for the sample tube. Record this weight on the worksheet under the After Degas section, Number 4.
3. Place the isothermal jacket around the sample tube neck, slide it down until it touches the bulb.
4. Carefully attach the sample tube to the analysis port. For more information see page 4-23 of the Micromeretics ASAP 2020 Physisorption manual.
5. Place the sample tube Dewar cover over the sample tube stem just above the isothermal jacket.
6. Start the Analysis



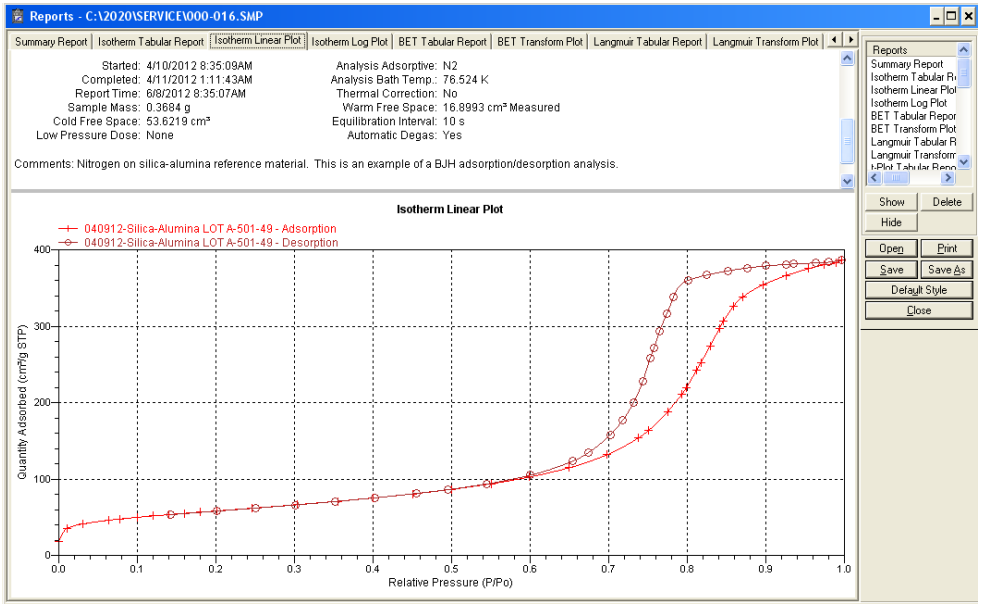
After clicking Sample Analysis, this window will appear. Click on the sample which you wish to start the analysis for, and then click OK. (Our example was 000-039)



After clicking Ok, type in the new calculated weight (from Appendix A worksheet #5) then press Start.



When the sample is completed, the isotherm for your sample should look similar to this:

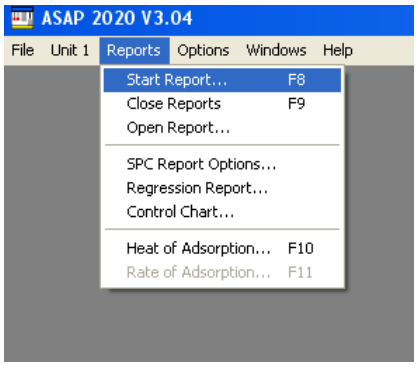


The amount of time that it takes for a sample analysis varies depending upon the surface area and porosity of the sample. If the sample has very low surface area the sample analysis will take approximately 3 hours, however if the sample has very high surface area the sample analysis can take 4-8 hours.

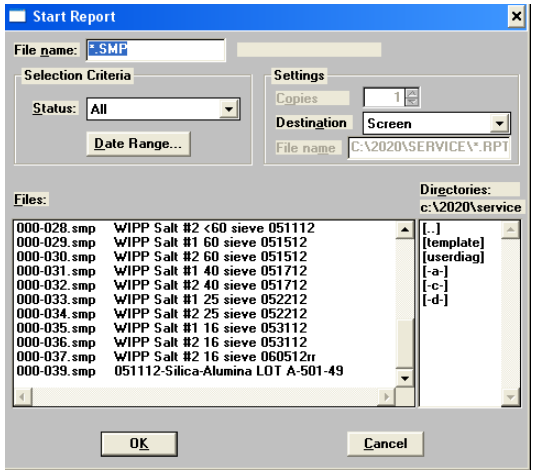
2.12 Data Collection/ Reports

Hard copies of the data collection and check printouts will be stored in a scientific notebook or scientific notebook supplement. Electronic copies will be stored in the ASAP 2020 computer.

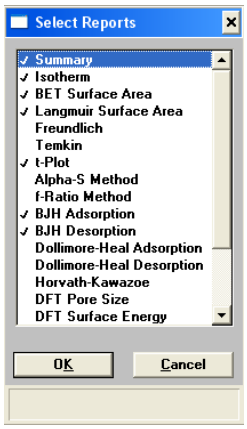
1. To create a report:



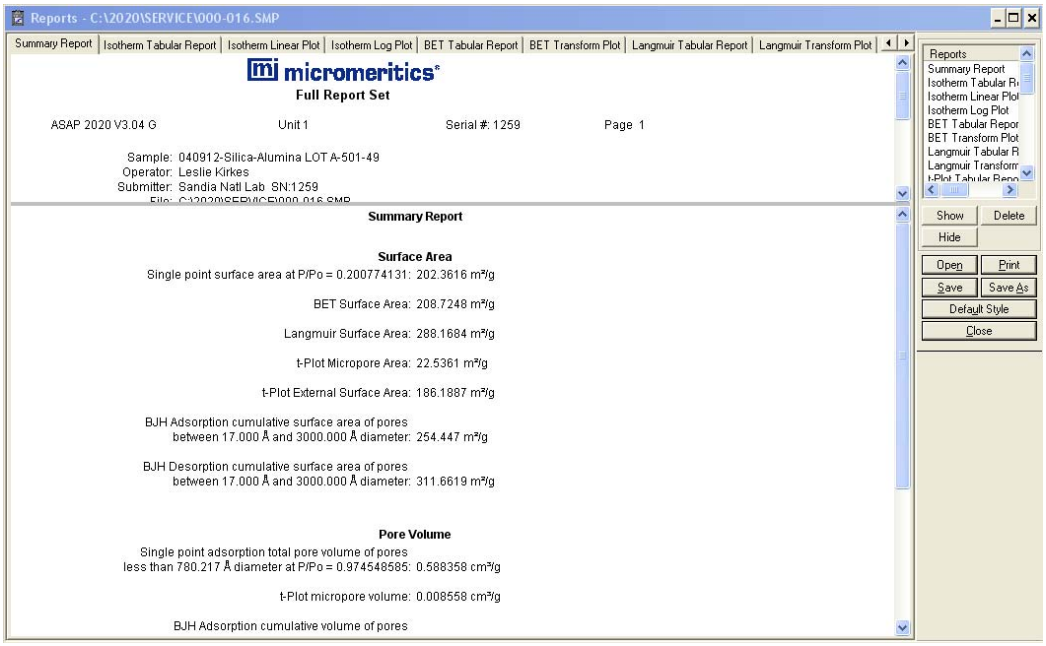
2. Select the sample that you would like to make a report for:



3. Select the Report Options:



4. Select OK and View and Print desired portions of Report:



2.13 Maintenance

Refer to Chapter 9 of the Micromeritics ASAP 2020 Physisorption Manual for trouble shooting and maintenance.

2.14 References

Micromeritics. ASAP 2020: Accelerated Surface Area and Porosimetry System. Operator's Manual. V3.04. 202-42801-01. May 2010.

3.0 Records

The following QA records, generated through implementation of this procedure, shall be prepared and submitted to the WIPP Records Center in accordance with NP 17-1 (Records):

QA Record

- Scientific Notebook Supplement
- Scientific Notebook

4.0 Appendices

Appendix A: ASAP 2020 Sample Data Worksheet

Appendix A
ASAP 2020 Sample Data Worksheet

Sample Name: _____
Analyst: _____
Degas Date: _____
Analysis Date: _____

Before Degas:

1. Mass of empty sample tube:
   - A_____ (g)
   - B_____ (g)
   - C_____ (g)
   - Average=_____ (g)
2. Mass of sample tube + sample:
   - A_____ (g)
   - B_____ (g)
   - C_____ (g)
   - Average=_____ (g)
3. Mass of Sample (Step 2 - Step1): _____ (g)

After Degas:

4. Mass of sample tube + sample:
   - A_____ (g)
   - B_____ (g)
   - C_____ (g)
   - Average=_____ (g)
5. Mass of sample (Step 4 – Step 1): _____ (g)

After Analysis:

6. Mass of sample tube plus sample:
   - A_____ (g)
   - B_____ (g)
   - C_____ (g)
   - Average=_____ (g)
7. Mass of sample (Step 6 – Step 1): _____ (g)

Compare the sample mass obtained after analysis (Step 7) with the sample mass after degas (Step 5). These two values should be close in range. If a significant difference is noted, analysis problems may exist or the sample may have been improperly degassed.

This work of authorship was prepared as an account of work sponsored by an agency of the United States Government. Accordingly, the United States Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so for United States Government purposes. Neither Sandia Corporation, the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by Sandia Corporation, the United States Government, or any agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of Sandia Corporation, the United States Government or any agency thereof.

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Parties are allowed to download copies at no cost for internal use within your organization only provided that any copies made are true and accurate. Copies must include a statement acknowledging Sandia Corporation's authorship of the subject matter.