micromeritics®

ChemiSorb 2720

Operator's Manual

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April 2009

WARRANTY

MICROMERITICS INSTRUMENT CORPORATION warrants for one year from the date of shipment each instrument it manufactures to be free from defects in material and workmanship impairing its usefulness under normal use and service conditions except as noted herein.

Our liability under this warranty is limited to repair, servicing and adjustment, free of charge at our plant, of any instrument or defective parts when returned prepaid to us and which our examination discloses to have been defective. The purchaser is responsible for all transportation charges involving the shipment of materials for warranty repairs. Failure of any instrument or product due to operator error, improper installation, unauthorized repair or alteration, failure of utilities, or environmental contamination will not constitute a warranty claim. The materials of construction used in MICROMERITICS instruments and other products were chosen after extensive testing and experience for their reliability and durability. However, these materials cannot be totally guaranteed against wear and/or decomposition by chemical action (corrosion) as a result of normal use.

Repair parts are warranted to be free from defects in material and workmanship for 90 days from the date of shipment.

No instrument or product shall be returned to MICROMERITICS prior to notification of alleged defect and authorization to return the instrument or product. All repairs or replacements are made subject to factory inspection of returned parts.

MICROMERITICS shall be released from all obligations under its warranty in the event repairs or modifications are made by persons other than its own authorized service personnel unless such work is authorized in writing by MICROMERITICS.

The obligations of this warranty will be limited under the following conditions:

1. Certain products sold by MICROMERITICS are the products of reputable manufacturers, sold under their respective brand names or trade names. We, therefore, make no express or implied warranty as to such products. We shall use our best efforts to obtain from the manufacturer, in accordance with his customary practice, the repair or replacement of such of his products that may prove defective in workmanship or materials. Service charges made by such manufacturer are the responsibility of the ultimate purchaser. This states our entire liability in respect to such products, except as an authorized person of MICROMERITICS may otherwise agree to in writing.
2. If an instrument or product is found defective during the warranty period, replacement parts may, at the discretion of MICROMERITICS, be sent to be installed by the purchaser, e.g., printed circuit boards, check valves, seals, etc.
3. Expendable items, e.g., sample tubes, detector source lamps, indicator lamps, fuses, valve plugs (rotor) and stems, seals and O-rings, ferrules, etc., are excluded from this warranty except for manufacturing defects. Such items which perform satisfactorily during the first 45 days after the date of shipment are assumed to be free of manufacturing defects.

Purchaser agrees to hold MICROMERITICS harmless from any patent infringement action brought against MICROMERITICS if, at the request of the purchaser, MICROMERITICS modifies a standard product or manufactures a special product to the purchaser's specifications.

MICROMERITICS shall not be liable for consequential or other type damages resulting from the use of any of its products other than the liability stated above. This warranty is in lieu of all other warranties, express or implied, including, but not limited to, the implied warranties of merchantability or fitness for use.

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Table of Contents

1 GENERAL INFORMATION

Introduction

This manual describes the installation and operation of the ChemiSorb 2720; its contents are organized as follows:

Chapter 1	**General Information.** Provides a general description of the ChemiSorb 2720, its features, safety precautions, and specifications.
Chapter 2	**Installation**. Describes how to unpack, inspect, and install the ChemiSorb 2720.
Chapter 3	**Operation.** Provides instructions on operating the ChemiSorb 2720.
Chapter 4	**Troubleshooting**. Provides troubleshooting information.
Chapter 5	**Ordering Information**. Provides ordering information for accessories and components available for the ChemiSorb 2720.
Appendix A	**Chemisorption Theory.** Describes the theory behind chemisorption analyses.
Appendix B	**Relative Thermal Conductivity of Gases**. Lists the relative thermal conductivity of gases.
Appendix C	**Physisorption Theory.** Describes the theory behind physisorption analyses.
Index	Provides quick access to subject matter.

Conventions

Symbols

This document uses the symbols shown below to identify notes of importance, cautions, and warnings.

✏ **Notes contain a tip or important information pertinent to the subject matter.**

❗ **Cautions contain information to help you prevent actions which could damage the instrument.**

⚠ **Warnings contain information to help you prevent actions which could cause personal injury.**

Precautions

General

Certain catalysts, particularly if previously used, when heated and exposed to reducing or oxidizing gases can give off noxious and corrosive gases. These effluents, as well as the efflux from all input gases, are directed to two exhaust ports on the right side of the instrument. Conduits (with suitable chemical compatibility) should always be attached here to carry these streams to external vents or neutralizing devices.

It is to be noted that oxygen can be employed as an analysis gas if the procedure permits it to be injected only in small quantities within an inert carrier gas. For long-term stability, the ChemiSorb 2720 should be purged of oxygen from the atmosphere by flowing the inert carrier gas for 5 minutes when the instrument is initially installed or after it has been stored for a period of time.

Impurities in any analysis gas employed for catalyst evaluation may have very deleterious consequences on chemisorption results. Use of reagent-grade gases is always recommended. Impurities can be a troublesome source of error in total surface area or pore volume determinations. Water vapor may be present in significant quantities in some commercial gases.

Cleanup of unusually contaminated samples should be accomplished prior to installation on the instrument, when possible.

While liquid nitrogen is the most commonly employed as the vapor trap coolant, it is possible to use liquid argon and a variety of slush baths involving organic solvents. These latter require special precautions. Be sure that no hot or burning combustible material comes near flammable solvents.

Unplug the power cord before removing the rear panel to gain access to internal components. Connections carrying potentials as great as 240 V may be encountered.

Hot Sample Tubes

Use protective gloves or be very careful to touch heated sample tubes only near their open end.

Heating mantles and the sample tubes within may become very hot in normal operation.

Dewar

Always handle Dewars with care. Any product incorporating a vacuum is a potential safety hazard and should be treated with caution. Always observe the precautions listed below.

We recommend that the following be observed when handling Dewars containing cryogenic liquids:

- Protect yourself by wearing 1) safety glasses (or a face shield), 2) an insulated or rubber apron, and 3) insulated gloves.
- When transferring cryogenic liquids from one container to another: 1) cool the receiving container gradually to minimize thermal shock, 2) pour the cryogenic slowly to prevent splashing, and 3) vent the receiving container to the atmosphere.
- Use a plastic stirring rod when stirring substances in a Dewar containing cryogenic liquids (or other materials of extremely low temperature). Do not use a glass or metal stirring rod.
- Do not handle heavy objects above the Dewar. If this is unavoidable, place a protective cover over the Dewar's opening. An object of sufficient weight that is accidentally dropped into the Dewar may shatter the Dewar.

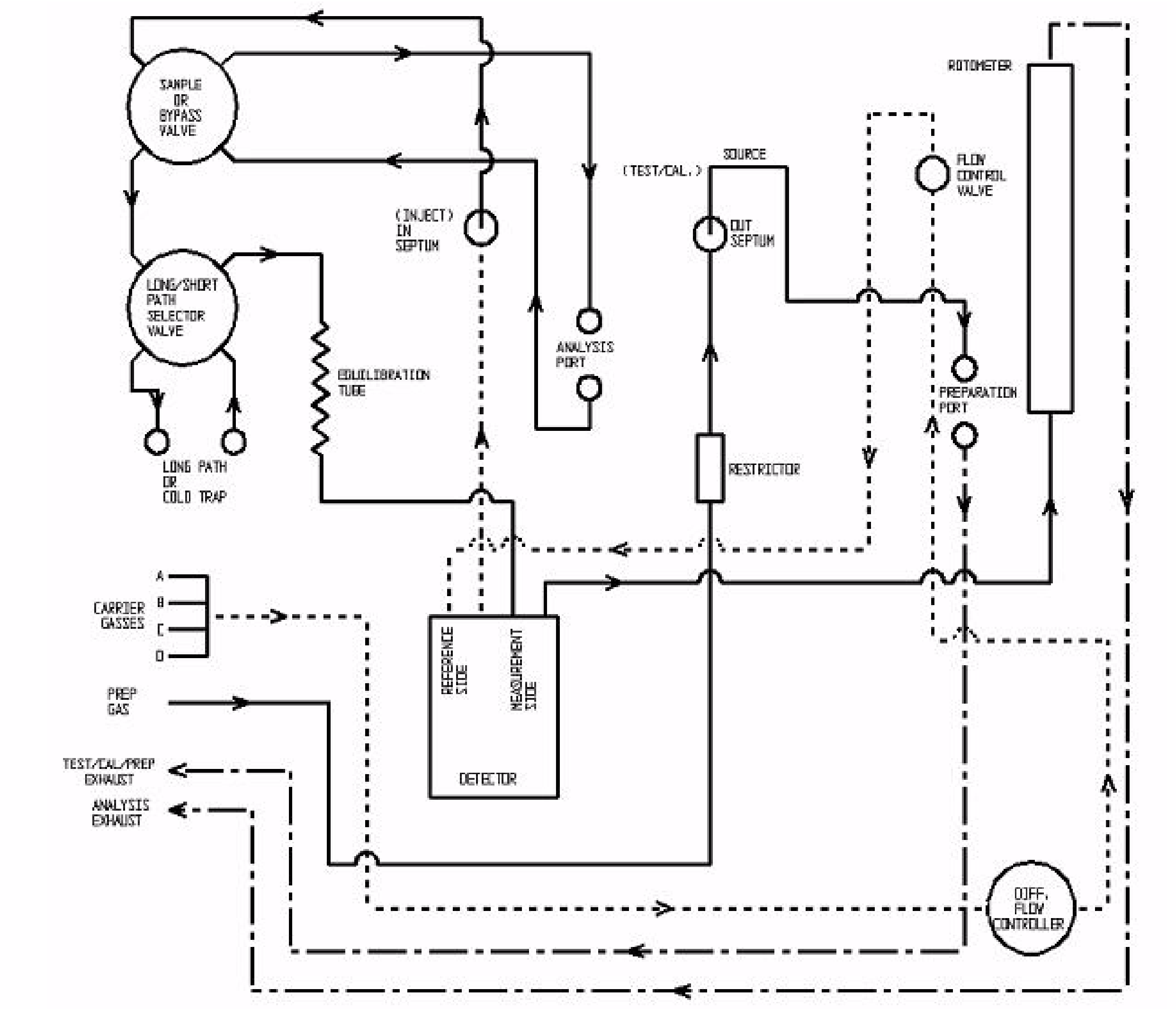
Description

The ChemiSorb 2720 provides an economical means for conducting chemisorption analyses. In chemisorption tests, a reactive gas sorbs to active sites on a catalyst surface. Measuring the amount of the gas sorbed permits determining active site density and dispersion of the active metal.

Attaching the ChemiSoft TPx Option permits the ChemiSorb to perform temperature-programmed desorption, reduction, and oxidation analyses at temperatures up to 1100 ^{o}C. Refer to **Chapter 5 - Ordering Information** for the part number or contact your Micromeritics sales representative for additional information about the option.

In addition, the surface area of catalysts, catalyst substrates, and granular and powdered materials can be determined with the unit through a physisorption (physical adsorption) test. In this test, typically nitrogen and krypton adsorb on the surface of the catalyst, catalyst substrate, or solid. Surface area is then deduced from the quantity of gas required to form a monolayer. Total sample pore volume is established by continuing adsorption until condensed gas fills the pores at cryogenic temperature; the volume of the condensed gas is then equal to that in the pores. Pore volume typically is determined near saturation.

The instrument contains two sample ports: one for degassing a sample and one for analyzing a sample. This design enables users to prepare one sample while another sample is being analyzed.



Legend

———————— Stainless

——-——-—— Teflon

- - - - - - - - - - - - Copper

ChemiSorb 2720 Schematic Diagram

Fuller development of the theory behind all operations of the ChemiSorb is found in the Appendices.

Principle of Operation

The ChemiSorb 2720 is designed primarily for measuring the quantity of active sites on the surface of a catalyst.The quantity of active sites may then be used to calculate the dispersion. The dispersion is the ratio of active sites to total theoretical sites. The active site dispersion is determined by surface titration using any of a number of reactive gases such as ammonia, carbon monoxide, hydrogen, nitrous oxide, and oxygen.

Making this test is accomplished by injecting small quantities of the reactive gas into an inert gas stream that is passing over the catalyst and determining the quantity of reactive gas that is eluted. The test is typically performed with the sample at ambient or elevated temperature so that only chemisorption and not physisorption occurs.

When the optional programmable system (ChemiSoft TPx) is added and the sample temperature is linearly increased, the ChemiSorb 2720 is capable of revealing at what temperature a previously chemisorbed component is desorbed (TPD), oxidized (TPO), or reduced (TPR).

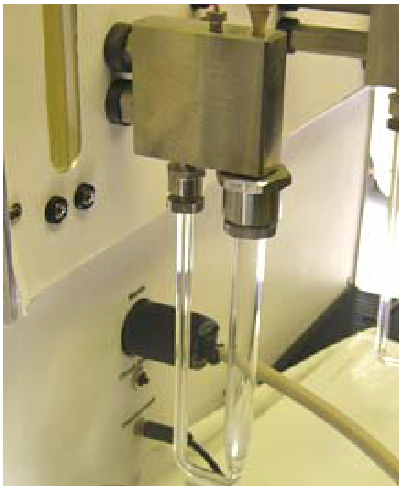
In addition to chemisorption analyses, surface area can also be determined using the ChemiSorb 2720. The specific surface area of granulated and powdered solids or porous materials is measured with the instrument by determining the quantity of a gas that adsorbs as a single layer of molecules (monomolecular layer) on a sample. Under specific conditions, the area covered by each gas molecule is known within relatively narrow limits. The area of the sample is thus calculable directly from the number of adsorbed molecules, which is derived from the gas quantity at the prescribed conditions, and the area occupied by each.

Components and Controls

This section provides a brief description function and use of major components and controls of the ChemiSorb 2720.

Sample Tube

Quartz, flow-thru tubes are used for chemisorption analyses. Borosilicate tubes are used for physisorption analyses. Borosilicate tubes are designed so that the sample resides in the bottom portion of the tube, ensuring that the sample remains below the liquid nitrogen level in the Dewar. A sample tube is attached to the instrument using knurled nuts and a seal is achieved via a compression O-ring. Chapter 2 provides instructions on how to install a sample tube.



This example shows a Quartz sample tube installed.

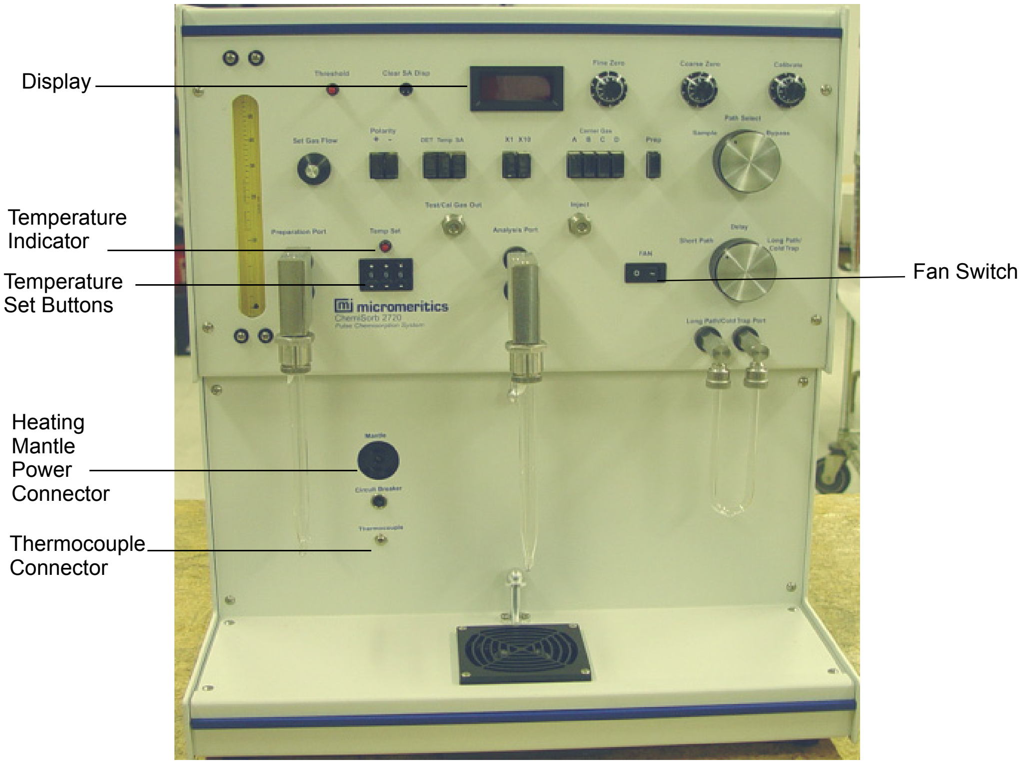
Heating and Cooling

The sample may be heated with a mantle mounted about the sample tube and plugged into the power connector on the front of the instrument, along with the thermocouple connector just below for temperature control. The mantle is held securely about the sample tube with a clip pushed laterally around the mantle. The button selector designated **Temp Set** allows the user to specify m4antle temperatures up to 400 ^{o}C. The mantle will not heat unless the thermocouple is connected to the instrument. The indicator above the temperature selector flashes on and off showing power is being applied to attain or hold the desired temperature.

Refer to Chapter 2 for instructions on properly installing a heating mantle.

The display meter (upper center of front panel) registers the mantle temperature when the **Temp** button is pressed. A flashing display indicates a sample temperature beyond the 400 ^{o}C limit, an unplugged thermocouple, or a defective thermocouple circuit.
Sample cooling is accomplished by immersing the sample in an appropriate liquid and

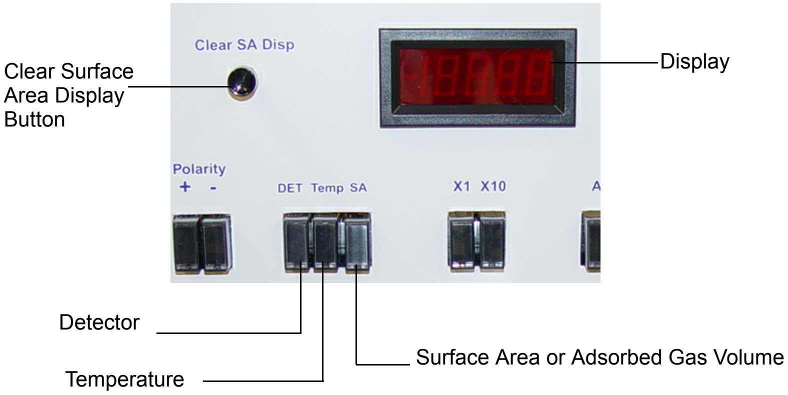
bringing the liquid container up and around the sample tube. A beaker of water may suffice to achieve near room temperature conditions. A built-in fan may also be used to cool samples. The fan is activated by a switch on the front panel of the instrument. A Dewar is required for cryogenic liquids. A pedestal is included in the accessory kit to elevate the Dewar up and about the sample.



Instrument Display

A single, multifunction display meter in the upper center of the front panel serves to display the following (selected by buttons below the display):

- detector signal
- temperature during degas or chemisorption analyses
- total surface area of a sample in a single-point surface area analysis
- integrated volume of each peak of injected gas passing the catalyst under test
- volume of adsorbed or desorbed gas in a multipoint surface area or total pore volume analysis



The signal chosen for display can be shifted at any time in any sequence without detriment to the other signals. Surface area information and gas volume data, whether displayed or not, are retained after a test is completed until the **Clear SA Disp** button to the left of the meter is pressed.

Surface area and adsorbed gas volume are displayed in terms of the quantity of sample contained in the sample tube. This means the displayed number must be divided by the sample weight to convert it to specific surface area (m^2/g) or specific volume (cm^3/g).

The temperature is displayed as degrees Celsius.

Threshold

The **Threshold** indicator lamp to the left of the display meter flashes when the detector signal is greater than the threshold level. The more rapid the flashing, the greater the magnitude of the signal.

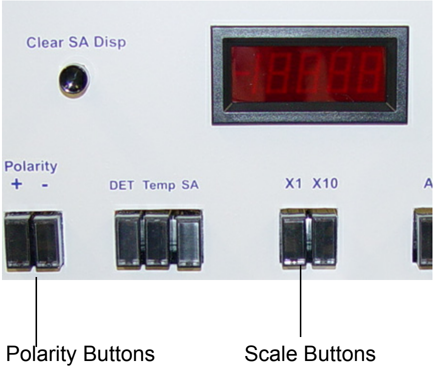
This lamp is designed to begin indicating accumulation of signals as follows:

X1 scale: between +0.06% and +0.07% nitrogen. It stops indicating when the signal falls between +0.03% and +0.04% nitrogen.

X10 scale: between +0.010% and +0.011% nitrogen. It stops indicating when the signal falls between +0.008% and +0.009% nitrogen.

Whether the display indicates a positive or a negative signal while gas composition changes depends upon the relative thermal conductivities of the carrier and analysis gases.

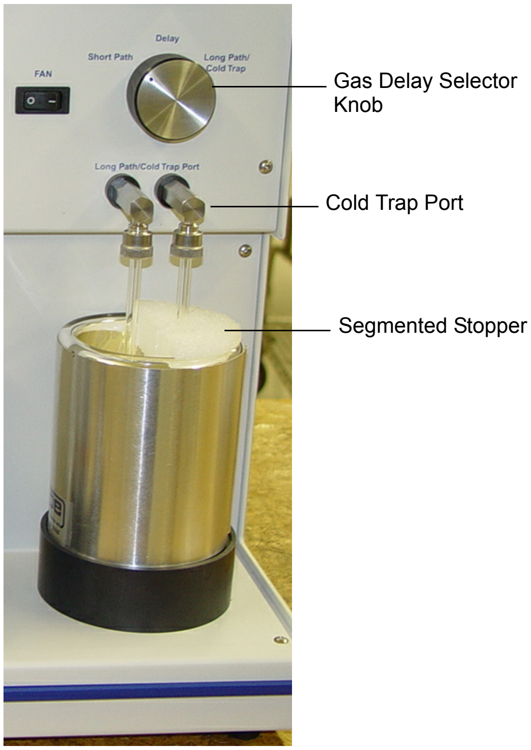
When the analysis gas has a higher relative thermal conductivity than the carrier gas, pressing the positive polarity (**Polarity +)** button below the meter results in a positive display. Alternately, when the analysis gas is the poorer conductor, selecting the negative polarity (**Polarity –)** button gives a positive display. Appendix B lists the relative conductivities for a number of gases.



Path Selection

Two gas paths are provided: **Sample** and **Bypass**. When **Sample** is selected, gas flows through the entire system. When **Bypass** is selected, gas flow circumvents the sample tube. During degas, the knob is set to **Bypass**; during analyses, it is set to **Sample**.

Cold Trap



A **Cold Trap** is provided for the removal of water of reaction or other reaction products that might otherwise interfere with the operation of the thermal conductivity detector or to remove impure vapors in the analysis gas stream, especially water vapor. These types of impurities tend to be present in small amounts in commercial gases and can detrimental to both chemisorption and surface area evaluation.

A Dewar with a segmented stopper and a U-tube are provided for this use. The stopper is designed to encase snugly the U-tube stems. The stopper is segmented so that the Dewar can be initially filled and refilled in place by removing only one half of the two-part stopper.

The Dewar is normally filled with liquid nitrogen when making surface area tests although other coolant baths can be used with special gases.

Gas Delay Setting

Two gas flow paths, labeled **Short Path** and **Long Path/Cold Trap**, are provided downstream of the Sample Analysis position. The purpose of both is to delay the arrival at the detector of sudden gas concentration changes long enough for the flow rate to return to normal. The Short Path is used for chemisorption testing and is usually sufficient for physisorption testing. However, high surface area materials may desorb large quantities of gas over a short period of time. In this case, the Long Path should be used.

Fine Zero, Coarse Zero, and Calibration Settings

Lever,
press up to
turn and set
position, and
down to lock
position

The **Fine Zero** and **Coarse Zero** knobs enable you to zero the instrument. Once system stability is achieved, a change of no more than 0.01 should be observed in the Display Meter.

The **Calibrate knob** enables you to set the surface area or gas volume at standard conditions.

The Fine Zero, Coarse Zero, and Calibrate knobs have a lever on the left side that must be pressed up to turn the knob and zero the instrument, and pressed down to lock the setting once established.

Septum

Calibration or pulse chemisorption are accomplished by means of a septum (labeled **Inject)** through which known volumes of gas are injected with a precision syringe. Gas to be injected can be withdrawn from the system using the **Test/Cal Gas Out** septum.

Any septum will leak after some number of penetrations. The supplied syringe needles have side-entry ports which greatly extend this life. Nevertheless, a septum will require replacement periodically. Refer to Chapter 4 for instructions on replacing a septum.

The knurled nut retaining the septum should be finger-tightened. Insufficient or excessive tightening may cause damage to the septum and leakage.

Detector

The Display shows the integrated area of each peak during a chemisorption titration, hence a plot of the peaks is unnecessary. However, if you wish to connect a recorder or data system to the instrument, you may do so using the connector labeled **Detector Signal Out** located on the side panel of the ChemiSorb. The signal level is between +7.5 volts and -7.5 volts.

Specifications

The ChemiSorb 2720 has been designed and tested to meet the following specifications.

Feature	Specification
SAMPLE PARAMETERS	
Minimum Active Gas Volume:	0.001 cm^3
Maximum Active Gas Volume:	Greater than 10 cm^3
Minimum Active Specific Volume:	0.0001 cm^3/g
Maximum Active Specific Volume:	Greater than 20 cm^3/g
Minimum Surface Area:	0.2 m^2
Maximum Surface Area:	199.9 m^2
Minimum Specific Surface Area:	0.02 m^2/g
Maximum Specific Surface Area:	Limited only by weighing accuracy of sufficiently small sample
Pore Volume:	
Minimum:	0.0001 cm^3
Maximum:	0.15 cm^3
Sample Size:	Up to 1 cm^3 diameter x 3 cm^3 length
Sample Ports	One dedicated analysis port and one dedicated preparation port
Throughput:	
Active Volume:	Depends on injection steps; typically 1 to 2 hours per sample
Surface Area:	Typically 12 minutes per sample
Total Pore Volume:	Typically 45 minutes per sample
Preparation Temperature:	35 - 400 °C with heating mantles

Feature	Specification
ACCURACY/REPRODUCIBILITY	
Active Volume:	
Low and Moderately Low:	Typically better than ± 2% with ± 0.5% reproducibility
High:	Typically better than ±1.5% with ± 0.5% reproducibility
Surface Area:	
Low and Moderately Low:	Typically better than ±3% with ± 0.5% reproducibility
High:	Typically better than ±2% with ± 0.5% reproducibility
ELECTRICAL	
Voltage:	100, 120, 220 or 240 VAC ± 10%
Operating Current:	1.25 A (100/120 VAC) 0.75 A (220/240 VAC)
Frequency:	50/60 Hz
SUPPLIES	
Gas:	Ammonia, carbon monoxide, hydrogen, nitrous oxide, and oxygen. Mixtures, with helium, of nitrogen, argon, krypton, ethane, n-butane, and other non-corrosive gases. A mixture of 30% N_2 and 70% He is recommended for single-point analyses. Mixtures of He and approximately 5, 12, 18, and 24% N_2 are suggested for multipoint use.
Coolant:	Liquid nitrogen or argon, solvent slush baths, ice water as appropriate for adsorbate
EXPOSED MATERIALS	
Sample Tube:	Quartz (Chemisorption); Borosilicate (Physisorption)
Exposed Materials:	Stainless steel, borosilicate glass, Buna-N, rhenium passivated tungsten filament, PEEK, Teflon, nickel, silicone (septum). Brass and copper for inert gas paths.

Feature	Specification
	ENVIRONMENT
Temperature:	15-35 °C (59-95 °F) operating; 0-50 °C (32-122 °F) storing and shipping
Humidity:	20-80% relative (non-condensing)
	CABINET
Dimensions:	46.5W x 53H x 30.5D cm (18.3W x 20.9 H x 12D in.)
Weight:	18 kg (40 lbs)

2 INSTALLATION

Introduction

This chapter describes how to

- unpack and inspect the equipment
- select an appropriate location for the ChemiSorb 2720
- install the ChemiSorb 2720

Unpacking and Inspecting the Equipment

The ChemiSorb 2720 instrument and its accessories should be visually inspected after unpacking to ensure that all items have been received and have not sustained physical damage.

When you unpack the shipping cartons, carefully compare the packing list with the equipment actually received. Be sure to sift through all packing materials before declaring equipment missing.

It is very important to save the shipping cartons when equipment is to be declared as damaged or lost. The inspector (or claim investigator) must examine the cartons prior to completion of the inspection report.

Equipment Damage or Loss During Shipment

When equipment is damaged or lost in transit, you are required to make note of the damage or loss on the freight bill. The carrier, not the shipper, is responsible for all damage or loss. In the event of equipment damage or loss during shipment, contact the carrier of the equipment immediately.

Equipment Return

Micromeritics strives to ensure that all items arrive safely and in working order. Occasionally, due to circumstances beyond our control, equipment is received which is not in working condition. When it is necessary to return equipment (damaged either during shipment or while in use) to Micromeritics for repair or replacement, the following procedure should be followed:

1. Pack the instrument in its original shipping carton if possible. If the original carton is unavailable, for a nominal fee Micromeritics can provide another carton for your use.

Failure to package your instrument properly may result in shipping damage.

2. Tag or identify the defective equipment, noting the defect and circumstances, if any, under which the defect is observed.
3. Reference the sales order or purchase order, and provide the date that the equipment was received.
4. Notify the Micromeritics Service Department of the defect and request shipping instructions. The service department will assign a Returned Materials Authorization (RMA) number. Write the RMA number on the outside of the shipping carton.

Selecting the Location

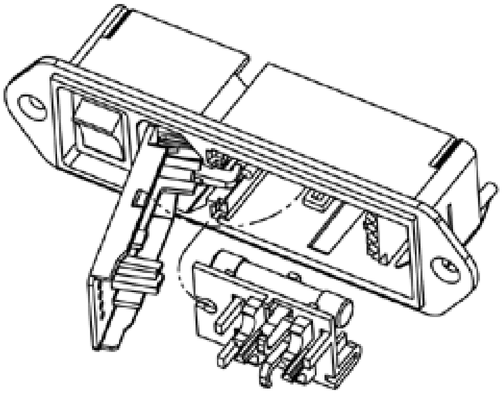
The instrument performs best in a regulated temperature environment. It should be installed on a workbench 75 to 90 cm (30 to 36 in.) high in a location free of drafts from either a forced-air heating or cooling system. It should not be located near a window through which sunlight may periodically fall.

A square meter (10 ft^2) of free space to one side at least and a few centimeters to the rear of the instrument should be provided for working space. Ready access to an analytical balance and a drying oven, preferably a vacuum oven, for sample preparation is advantageous. Space near the instrument in which to mount securely the appropriate gas cylinder, or cylinders, is also required.

Selecting the Input Power and Installing the Fuse(s)

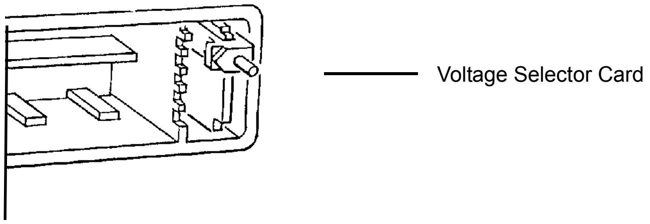
All instruments are initially configured for 120 VAC and with the line fuse removed. The correct setting of the universal power entrance must be checked and the appropriate fuse installed before the ChemiSorb 2720 can be operated. The ChemiSorb 2720 is designed to operate with 100, 120, 220, or 240 VAC at 50 or 60 Hz. Voltage selection and fusing are made at the power connector, which is located on the side panel of the unit.

1. Make sure the power cord is not connected to the ChemiSorb 2720. The cover of the input power connector cannot be opened when the power cord is installed.
2. Check the voltage setting on the cover of the power entrance.
   - If the voltage is correct:
     a. Open the cover by prying the left side of the cover open with a pointed object, then swinging the cover to the left.
     b. Remove the fuse block.

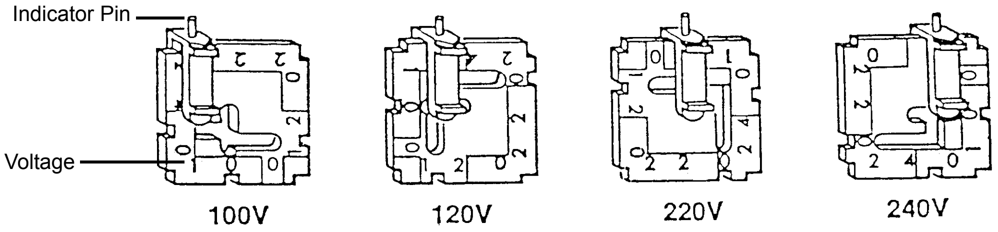


     b. Proceed to Step 6.
   - If the voltage is incorrect, open the cover and remove the fuse block as described above, then proceed to Step 3.

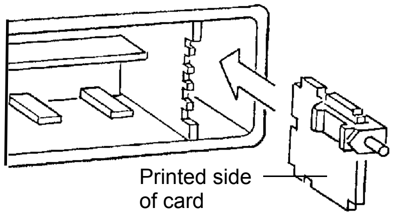
3. Using needle-nose pliers, pull the voltage selector card straight out of the power connector housing.



4. Orient the voltage selector card so that the desired voltage is indicated at the bottom. Orient the indicator pin so that it points upward as shown in the following illustration.



5. Insert the voltage selector card into the power connector housing with the edge containing the desired voltage first and with the printed side to the left.



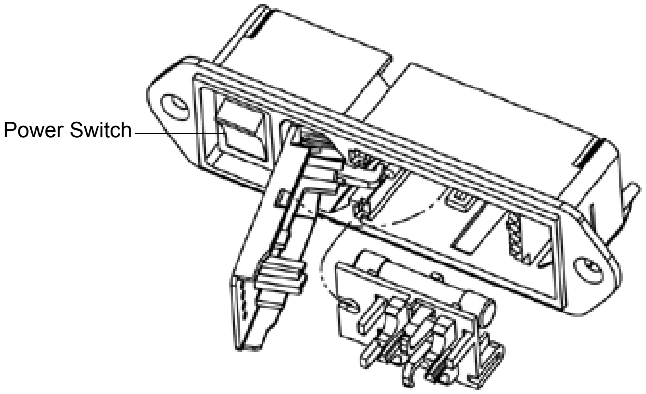
6. Fuse the input power line according to local safety practices. The input power connector can be used with either a single-fuse arrangement (100-120 VAC) or a double-fuse arrangement (200-240 VAC).

The fuses used in the ChemiSorb 2720 must be identical in type and rating to those specified. Use of other fuses could result in electrical shock and/or damage to the ChemiSorb 2720.

Insert the appropriate fuse(s) for the input power source. Refer to the chart below for the appropriate fuse rating.

Power Source	Fuse
100-120 VAC	2.0 Amp (slow-blow), type 3AG
200-240 VAC	5 x 20 mm, 1 Amp (slow-blow), type T

7. Insert the fuse block into the input power connector (as shown in the following illustration).
   - If the single-fuse arrangement is desired, the fuse block is positioned so that the side with the single-fuse slot and the jumper bar is away from the cover.
   - If the double-fuse arrangement is desired, the fuse block is positioned so that the side with the double-fuse slots is away from the cover.



When using the double-fuse arrangement, the fuse block will not snap into place. Simply position the fuse block properly. When you close the cover, the fuse block will seat properly.

8. Snap the fuse block into place, then close the cover. Once the fuse block and cover are in place, the position of the indicator pin shows the input power selected.
9. Connect the power cord to the power connector and to an appropriate power source.
10. Place the power switch on the side panel of the ChemiSorb in the ON (|) position.

Connecting the Gas Supply

A variety of gas mixtures may be used in chemisorption analyses. As a minimum, cylinders of 10% hydrogen in argon and 2 to 5% oxygen in helium will likely be desired for catalyst activation prior to analysis. One or more of the following additional gases — nitrous oxide, carbon monoxide, helium, or argon — may also be needed for analysis. Low concentration mixtures of ammonia may be used as the injected active gas but the exposure must be limited to avoid possible corrosion.

The most common gas for single-point surface area evaluation is a mixture of 30% nitrogen and 70% helium. Several mixtures containing between approximately 5 and 24% nitrogen are required when making multipoint surface area analyses. Pre-mixed gases are conveniently employed for single-point and multipoint surface area measurements. Total pore volume measurement requires a premixed gas and a pure gas.

Regulators

Whatever the gas mixture or its source, it should be regulated to a pressure of at least 0.11 MPa (15 psig) by a reliable, leak-tested regulator. Suitable regulators are available from Micromeritics (refer to Chapter 5 for ordering information).

Some commercial regulators incorporate internally a lubricant that can migrate and contaminate downstream systems. These types must be avoided.

One dual-stage regulator is required to make single-point tests. As many as four can be used to make multipoint analyses with pre-mixed gases. Micromeritics uses and recommends the use of research-grade gases. If unobtainable, the highest purity gas conveniently available will probably prove satisfactory. Since the same gas is employed in calibration as in making measurements, small proportions of such gases as argon, carbon dioxide, carbon monoxide, and methane will have an insignificant effect on results. Water vapor, however, is particularly degrading; gas having a dew point of at least -67 °C (-88 °F) should be sought.

Dual-stage regulators must be used for all gas supplies.

Guidelines

Use these guidelines when installing regulators and gas lines:

- Ensure that all required gases are available and near the instrument. If the gas bottles are not located near the instrument, you will have to use gas line extenders, which may negatively affect gas quality and pressure.
- Carefully route the gas lines from the bottle to the analyzer, avoiding overlapping or entangling gas lines. This will ensure the correct gas pressure and make maintenance easier.
- Label both ends of the gas lines before connecting for ease in identification and maintenance.
- Ensure that all gas bottles are closed before connecting them to the analyzer.

Gas Connections

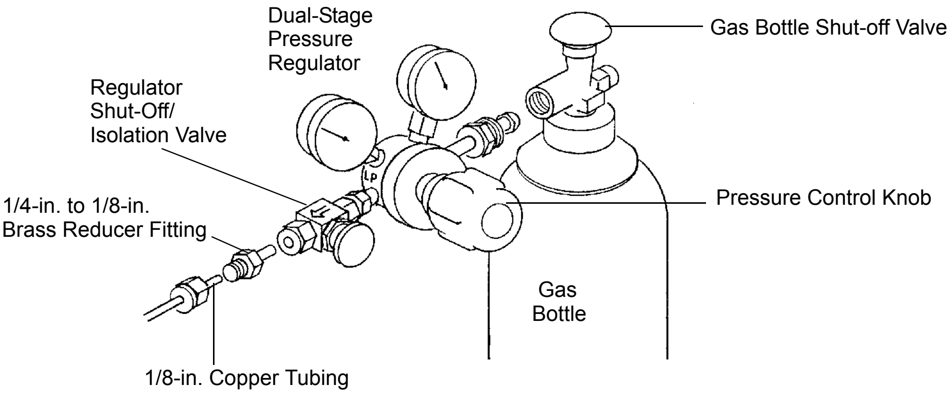
The instructions below describe a typical installation. Some configurations require additional components, such as regulator expansion kits.

Copper tubing sets with brass reducer fittings and one stainless steel tubing set are supplied with the analyzer.

Typically gas streams containing ammonia, nitric oxide, and nitrous oxide require the use of stainless-steel gas regulators and gas supply lines. If additional stainless-steel tubing sets are required, they may be ordered from Micromeritics (refer to Chapter 5).

Connect the gas supply as follows:

1. Attach an appropriate dual-stage regulator to the first gas supply bottle you want to connect and tighten with a wrench. Leave the gas bottle shut-off valve closed until instructed otherwise.



2. If the regulator has a 1/8-in. outlet, proceed to the next step. If the regulator has a 1/4-in. outlet, attach the reducer fitting to the outlet of the regulator shut-off/isolation valve and tighten the valve nut with a 9/16-in. wrench.

Do not overtighten the fittings. Doing so could collapse the brass fitting and cause a leak.

3. Attach the gas inlet line(s) to the regulator or reducer fitting and tighten with a wrench.
4. Purge the regulator as follows:

It is important to purge the regulator before proceeding. This will prevent contamination of the analysis gas.

a. Close the regulator shut-off valve by turning it fully clockwise.

b. Turn the pressure regulator control knob fully counterclockwise.

c. Slowly open the gas bottle valve by turning it counterclockwise, then quickly close the gas bottle valve.

d. Observe the gas bottle pressure gauge.

- If the pressure decreases, tighten the nut connecting the regulator to the gas bottle.
- If the pressure is stable, proceed to step e.

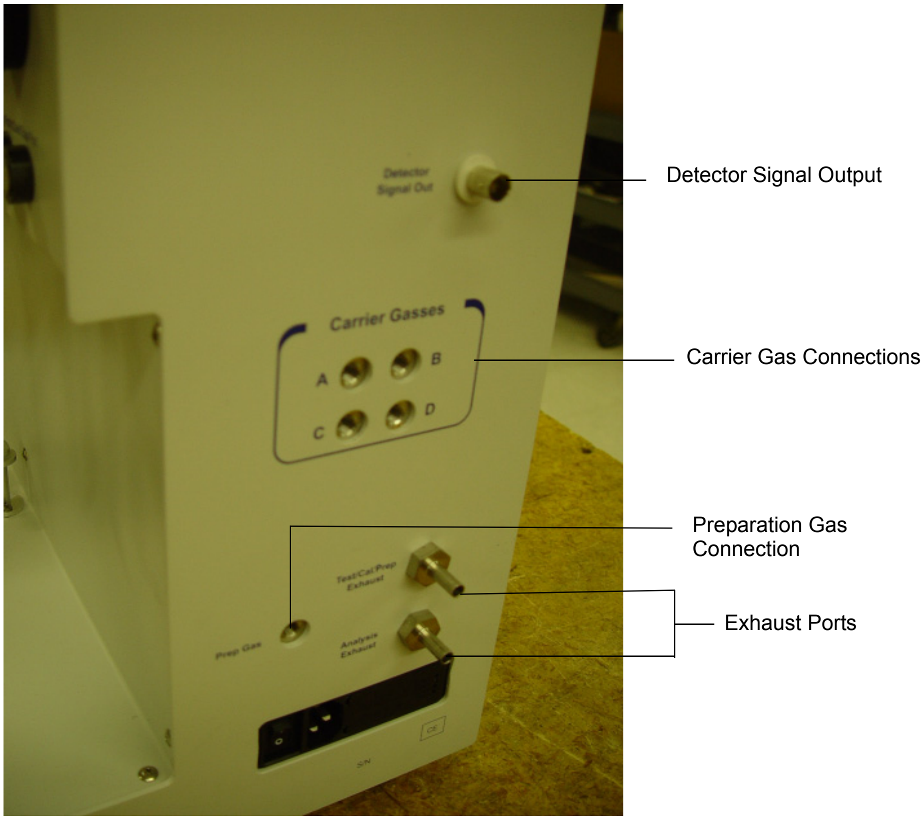
If you are using hazardous gases, make sure the gas supply equipment is adequately vented to prevent purging the regulator and tubing into the lab atmosphere in the following step.

e. Turn the pressure regulator control knob clockwise until the outlet pressure gauge indicates 0.11 MPa (15 psig). Open each regulator shut-off valve by turning it counterclockwise. Open the gas bottle shut-off valve. Flow gas for 10 to 30 seconds, then close each valve. These actions purge the regulator and gas inlet tubing.

f. Ensure that the gas bottle valve is completely closed.

5. Attach the other end of the copper tubing to the gas fitting on the side of the instrument and tighten the fitting.

   Analysis gas or gases are attached to the fittings labeled **Carrier Gases A**, **B**, **C**, or **D**. Preparation gas is attached to the fitting labeled **Prep Gas**.

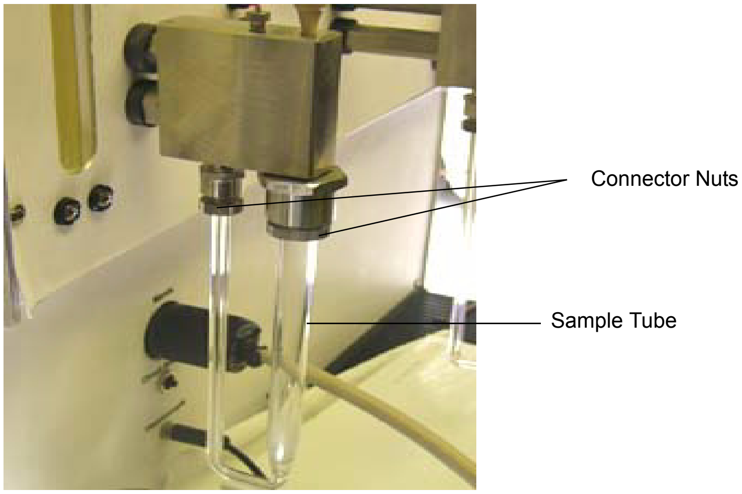


6. Repeat steps 1 through 5 for each gas supply bottle to be attached to the analyzer.

Safety demands that pressurized gas cylinders be securely fastened to a rigid support.

Installing and Removing a Sample Tube

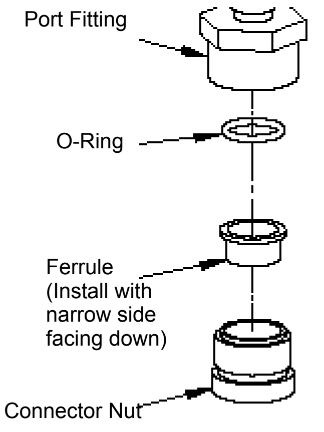
Quartz, U-shaped sample tubes are used to hold the sample for chemisorption analysis. Borosilicate tubes are used for physisorption analysis. Borosilicate tubes are designed so that the sample resides in the bottom of the tube, ensuring that the sample remains below the liquid nitrogen level in the Dewar. Sample tubes are installed into the Preparation and Analysis Ports for degassing and testing as described below.



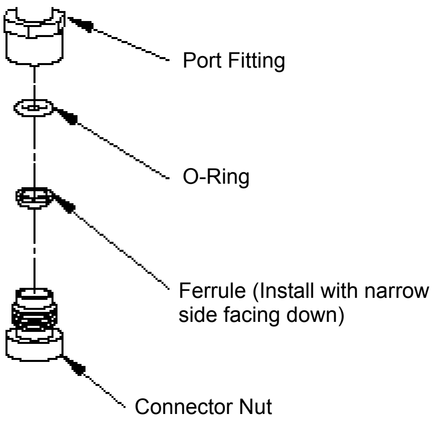
Install the sample tube assembly as follows:

1. Loosen the connector nuts on the sample port.
2. Insert the stems of the sample tube fully into the port; then tighten the connector nuts.

The connector nuts are sealed to the port fittings by means of an O-ring and ferrule. If these components become dislodged when connecting sample tubes, make sure they are inserted into the connector nut and fitting as shown below.



Sample Port
Front Connection



Sample Port
Rear Connection

Remove the sample tube assembly as follows:

1. While holding the sample tube with one hand, loosen the connector nuts on the sample port.
2. Gently slide the sample tube out of the port.

Installing a Heating Mantle

A heating mantle is used on a sample tube to assist in maintaining a specified temperature. Heating mantles are used on samples being degassed (on the Preparation port) or during chemisorption analyses (on the Analysis port).

1. Slide the heating mantle upward around the sample tube.
2. Holding the mantle in place with one hand, gently push the clip around the mantle as shown below.

Heating Mantle

Clip

Plug in heating mantle power and thermocouple cords

3. Plug the heating mantle power cord and the thermocouple plug into their appropriate connectors. Internal electronic circuitry limits the maximum temperature attainable to 400 ^{o}C. Attempts to exceed this limit will result in a flashing display if you press **Temp** on the front panel.

Using a Cold Bath

Liquid argon, liquid oxygen, dry ice and acetone, ice water, and various other slush baths prepared from low melting point liquid solvents partially frozen by mixing with liquid nitrogen may be employed. Liquid nitrogen is most frequently employed. Provision for a source of supply and a suitable storage reservoir must be provided by the user.

Verifying Operation

To verify that the instrument is operating properly, perform a reference material test according to the instructions in the Reference Material Kit supplied with the instrument.

3 OPERATION

Purging the System

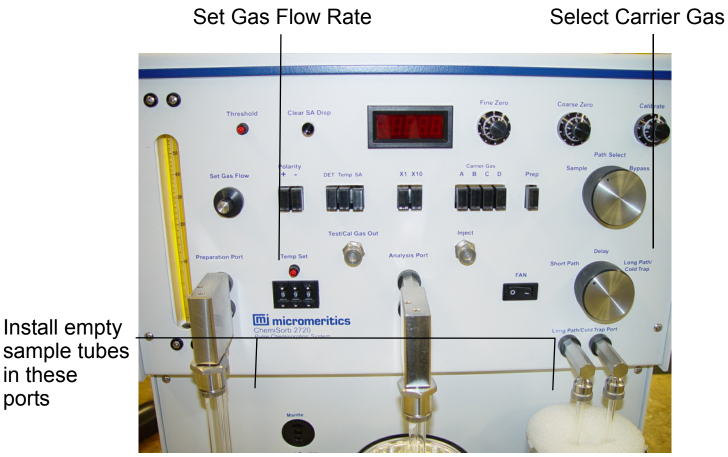
For best results, the ChemiSorb 2720 should be free of air before performing analyses. It is not necessary to purge air from the system before every analysis. Purging should be performed when:

- the ChemiSorb 2720 is initially put into operation
- the ChemiSorb 2720 has been idle for several days

These instructions assume the ChemiSorb 2720 has been installed as described in **Chapter 2, Installation**.

Remember to use caution when handling Dewars. Refer to "Precautions" in Chapter 1 for a list of recommended precautions.

1. Install empty sample tubes in the **Analysis Port** and the **Preparation Port**, making sure that each is fully inserted and properly fastened. (Refer to "Installing a Sample Tube" in Chapter 2.)



2. If not installed, install a U-tube in the **Long Path/Cold Trap** port, being sure both stems are fully inserted and securely sealed.
3. Press the **Carrier Gas A**, **B**, **C,** or **D** button to select the gas to be used for purging.
4. Using the **Set Gas Flow** knob, adjust the flow until the float is near or at the 20 SCCM mark on the flowmeter. If you are unable to accomplish this, the gas supply pressure is maladjusted. Readjust the supply pressure to approximately 0.11 MPa (15 psig) (refer to "Gas Supply" in Chapter 1).

5. Turn the **Delay** knob to the desired position to begin the purging process.

Short Path requires 5 to 10 minutes
Long Path/Cold Trap requires 20 to 25 minutes

Both paths should be purged.

6. Allow an additional 30 minutes of purging for complete temperature equilibration and operational stability.

Performing a Pulse Chemisorption Analysis

Sample Tube and Filler Rod

When performing a chemisorption analysis the following sample tube and filler rod (if required) should be used:

Item	Part Number
Sample tube	272-61702-00
Filler rod	236-61705-00

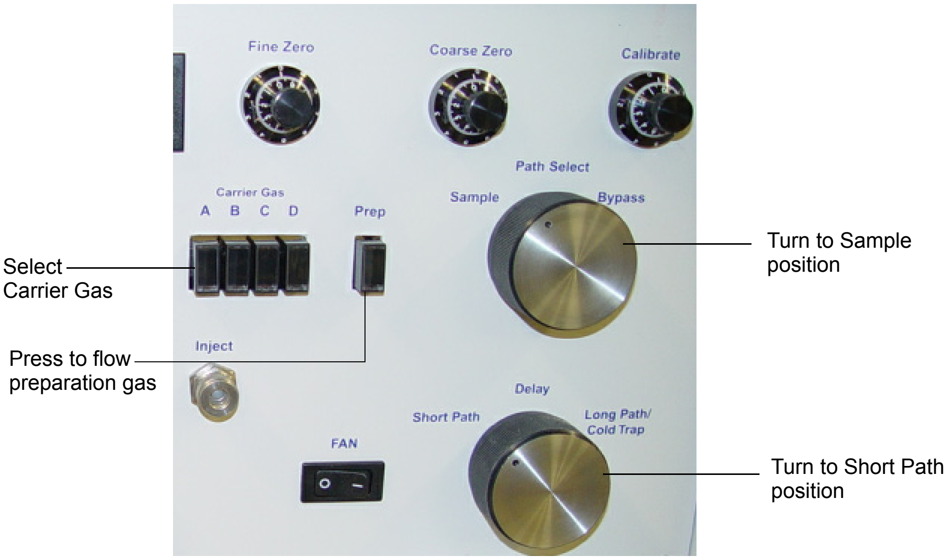
Preparing and Setting Up the Sample

Sample preparation procedures depend greatly on the type of catalyst and on user requirements. Therefore, no attempt will be made to specify details. Typically, a catalyst is flushed with hydrogen at an elevated temperature and then flushed with helium. It may or may not then be flushed with oxygen, helium, and hydrogen. These processes are carried out by selecting the appropriate gases using the gas valve buttons, and adjusting the gas flow with the **Set Gas Flow** knob.

Make sure you flush the catalyst with helium or argon when switching between oxygen or hydrogen. Oxygen and hydrogen combined in the unit can release tremendous amounts of heat.

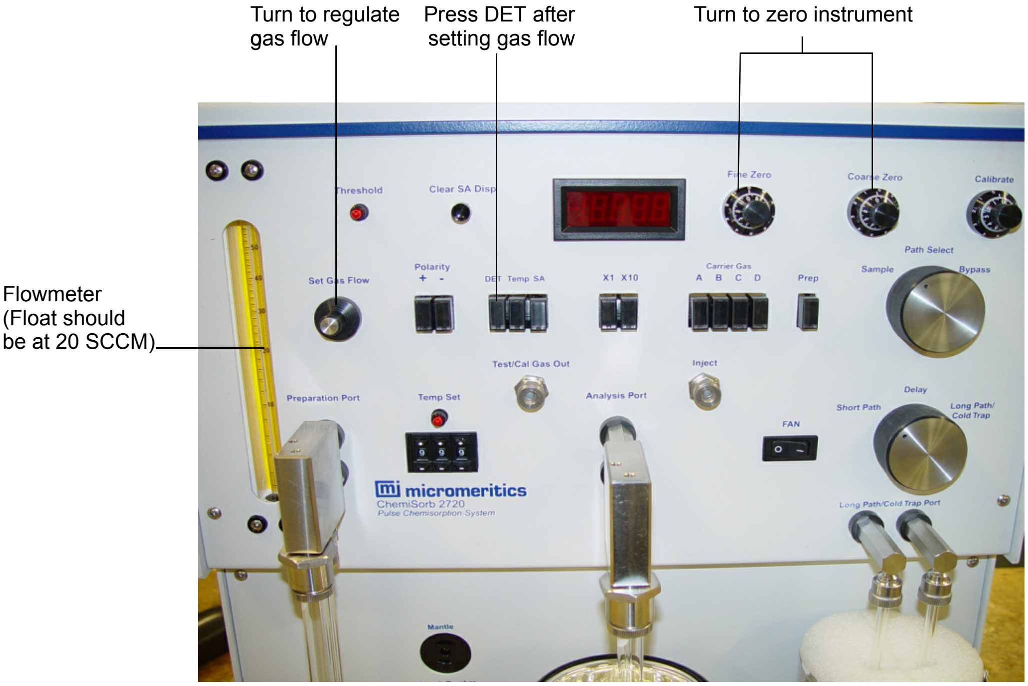
1. Turn the **Delay** knob to the **Short Path** position.
2. Turn the **Path Select** knob to the **Sample** position.
3. Select the negative polarity (**Polarity** –) button.
4. Select the **X1** or **X10** button.

5. Open the appropriate carrier gas valve (usually argon for H_2 pulse chemisorption) by pressing the **Carrier Gas A**, **B**, **C**, or **D** button.



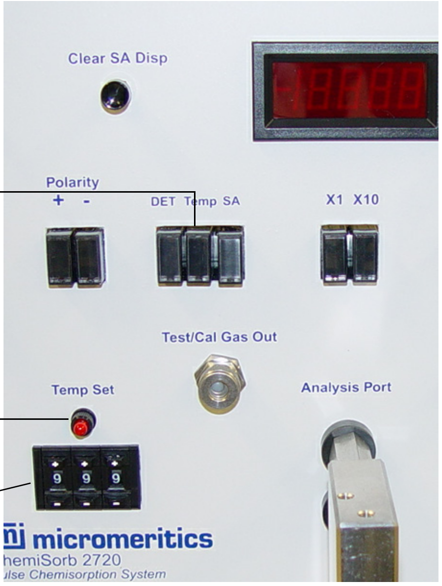
6. Press the **Prep** gas button to flow preparation gas.

7. Adjust the **Set Gas Flow** knob to regulate the gas flow through the instrument so that the flowmeter float is at the 20 SCCM mark.



8. Press the **DET** button.

9. Use the **Fine Zero** and **Coarse Zero** knobs to zero the instrument. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved.
10. Install a sample tube with sample in the **Analysis Port**.
11. Place a heating mantle around the sample and secure with a heating mantle clip.
12. Plug the heating mantle power cord and thermocouple into their appropriate connectors.
13. Specify the desired temperature using the **Temp Set** dials. The actual temperature to which the sample is being subjected at any time thereafter can be read on the instrument meter by pressing the **Temp** button just below the instrument display.



Press Temp to display temperature

Temperature Indicator illuminates when heat is applied

Set temperature in degrees Celsius

14. Fill a 1-mL precision syringe to 1 mL with nitrogen gas using one of the following methods:
    - Using the **Test/Cal Gas Out** septum on the instrument:

      a. Insert the syringe in the **Test/Cal Gas Out** septum and fill with gas.

Insert syringe and fill with gas

      b. Flush the syringe if needed to obtain 1 mL.

      c. Lay the syringe aside so that the gas can equilibrate to room temperature

- Using Liquid Nitrogen:
  - a. Fill a cold trap Dewar with liquid nitrogen. The evaporating liquid provides an atmosphere of pure nitrogen gas.
  - b. Hold the needle tip immediately above the level of liquid nitrogen and fill the syringe. Flush the syringe a few times to be sure of obtaining a proper fill.
  - c. Wipe the needle tip free of accumulated frost and lay the syringe aside, allowing the gas inside the syringe to reach room temperature.

Alternately, you can fill the syringe from an auxiliary septum attached to a gas cylinder. An auxiliary septum may be ordered from Micromeritics. Refer to Chapter 5, Ordering Information for the part number.

15. Proceed to "Performing the Analysis".

Performing the Analysis

To ensure that the tank contains enough gas for an analysis, make sure the tank pressure for the gas regulator is at least 200 psig. Tank pressures less than 200 psig may have excessive background levels of stray gases that may negatively affect the analysis.

1. Make sure the **Path Select** knob is set to **Sample**.

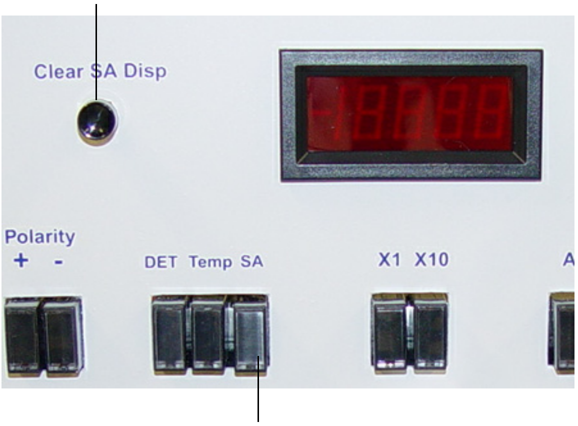
Turn to Sample position

Select Multiplier

Select Short Path

2. Press the **X1** button, unless you know from experience that you will need the X10 scale.
3. Make sure the **Delay** knob is set to **Short Path.**
4. Press the **SA** and **Clear SA Disp** buttons.

After pressing the SA button, press to clear display



Press to select SA (Peak Volume)

5. Turn the **Calibrate** knob fully clockwise to gain maximum sensitivity.
6. When the sample is at the desired temperature, insert the syringe needle fully into the **Inject** septum.

Insert the syringe and inject gas

Hold the syringe at the rear flange so that body heat does not affect the gas volume contained by the syringe barrel.

7. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.

   If the sample chemisorbs the entire quantity of injected gas, there will not be a change in the display meter indication.

   There will be an indication on the display meter and a peak evident on the recording if some of the injected gas is chemisorbed and some passed beyond the sample. The display will indicate the full volume of the injection if none of the injected gas is chemisorbed by the sample.

The desired situation, of course, is the chemisorption of all the analysis gas by the catalyst for the first injection. Allow at least 5 minutes to pass before concluding that none of the injected quantity has escaped reaction with the catalyst. At this point make note of the fact that one injection has been made and that a volume of gas equal to that of the injection has been chemisorbed by the sample.

8. Clear the display by pressing the **Clear SA Disp** button.
9. Make a second injection of analysis gas and treat the results as before, again making note of the step and the quantity of gas injected. Again, clear the display. Continue making injections and recording their input until the display meter indication is the same (or nearly so) for three or four injections. Make note of the fact of every injection and beside it record the display meter reading which represents the portion of the injected gas not chemisorbed by the sample.

Example

The complete record of results might be like that given in the table below. These particular results pertain to the chemisorption of carbon monoxide on a platinum-alumina catalyst. They were obtained using injections with 0.1 cm^3 of volume at 25 ^{o}C and 740 mmHg.

Table 3-1. Chemisorption Data on Platinum-Alumina Catalyst

Injection Number	Quantity of Carbon Monoxide Injected*	Display Meter Reading**
1	0.0891	0.00
2	0.0891	0.06
3	0.0891	0.40
4	0.0891	0.49
5	0.0891	0.50
6	0.0891	0.50
7	0.0891	0.50
*Injection volume **Peak area		

The catalyst sample weighing 0.8353 g was first reduced at 350 ^{o}C with a stream of hydrogen flowing over it at approximately 15 cm^3/min for two hours. The carrier gas was changed to helium and the sample was purged for 90 minutes at 350 ^{o}C. It was then cooled to 35 °C in a stream of helium, and carbon monoxide injections were made at about three-minute intervals. The tests were conducted with the **Polarity +** button pressed. Ambient temperature was 23 °C and atmospheric pressure was 740 mmHg.

No more carbon monoxide was chemisorbed after the 4th injection. The latter display meter readings (0.50) indicate the peak area corresponding to the injection volume and thus define a calibration factor k by which prior readings can be converted to true chemisorbed gas volumes. Its value for this test is

$$k = \frac{0.1}{0.5612} = 0.1782$$

The total carbon monoxide volume (at ambient conditions) chemisorbed at 250 °C is calculated from the injections showing chemisorption, i.e.,

1st inj., 0.1 - 0 = 0.100

2nd inj., 0.1 - (0.06 x 0.1782) = 0.088

3rd inj., 0.1 - (0.40 x 0.1782) = 0.020

4th inj., 0.1 - (0.49 x 0.1782) = 0.002

0.2110 cm^3

Converting this quantity to standard conditions of temperature and pressure yields

$$0.2110 \times \frac{273}{296} \times \frac{740}{760} = 0.1895\mathrm{cm}^3(\mathrm{STP})$$

There is some degree of uncertainty in how chemisorbed species bind to the atoms of a solid. In strong chemisorption on platinum as is the case here, it is generally accepted that each carbon monoxide molecule attaches to a platinum atom. It is also generally assumed that the support on which platinum is dispersed does not sorb carbon monoxide at the elevated temperature employed here. These assumptions being accepted, the percent dispersion may be calculated.

The total percentage of platinum by weight on the example catalyst is 0.5%, or 0.005 g/g; the sample weighed 0.8353 g; the stoichiometric factor is 1; the atomic weight of platinum is 195.09 g/g-mole; one gram-mole of a gas at STP occupies 22414 cm^3; and the volume of carbon monoxide chemisorbed was measured to be 0.1895 cm^3 STP. Thus

$$\text{Percent Dispersion} = \frac{0.1895\mathrm{cm}^3 \times 195.09\mathrm{g/gmole}}{0.8353\mathrm{g} \times 22414\mathrm{cm}^3/\mathrm{gmole} \times 0.005} \times 100 = 39.5\%$$

This result means that 39.5% of the platinum atoms are accessible on the support surface. The rate of decrease of this value with time of service as determined by successive tests would provide a guide to practical catalyst lifetime, for example.

Performing a Physisorption Analysis

Sample Tube and Filler Rod

When performing a physisoption analysis, the following sample tube and filler rod should be used:

Item	Part Number
Sample tube	272-61703-00
Filler rod	004-61701-02

Degassing the Sample

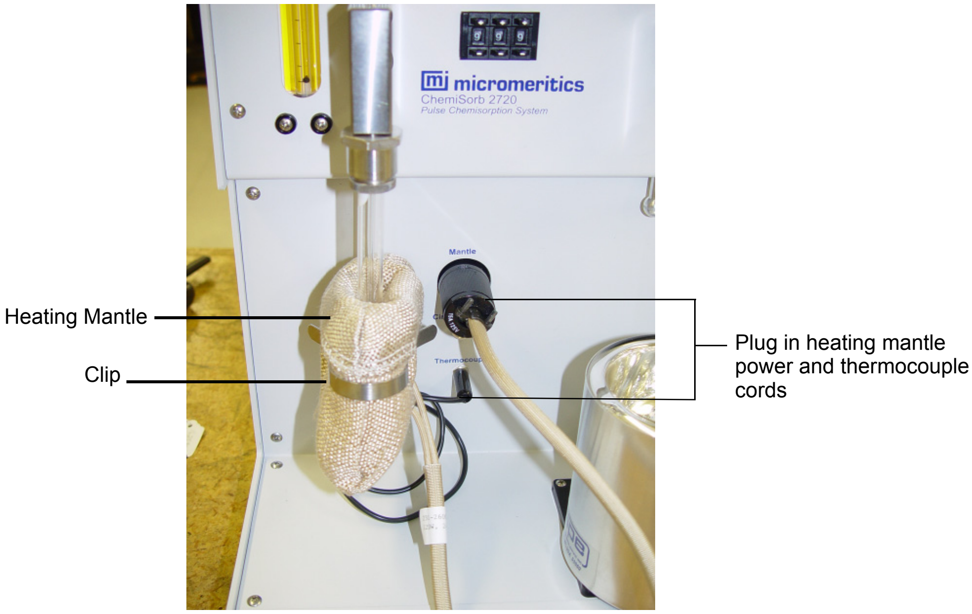
Surface areas can be measured reliably with as little as 0.1 m^2 of total sample surface or as much as 199 m^2. However, results are most accurately and quickly determined if sample quantity is adjusted to fall within 0.5 to 25 m^2 range. This usually is unlikely on the first attempt with a new material. On subsequent analyses, however, sample quantity may be optimized.

Sample weight must be established to express the final result as a specific surface area (square meters per gram) or the amount of gas adsorbed as specific volume (cubic centimeters per gram). True weight is most reliably determined after the sample has been freed of whatever gases and vapors — especially water vapor — it may have picked up from the atmosphere. This means the weight is best established after the measurement is completed. The sample tube stems should be stoppered as soon as the tube is removed. The tube, sample, and stoppers can then be weighed on an analytical balance and the sample weight established by subtracting the weights of the tube and stoppers as determined either before or subsequent to the main weighing.

Except for the warning in the **Precautions** section in Chapter 1 against contaminated and decomposing materials that may give off corrosive or condensing vapors, sample pretreatment (or outgassing) is readily accomplished on the ChemiSorb. However, samples which have been predried, perhaps in a vacuum oven, will degas faster. Preconditioning of samples is recommended whenever possible.

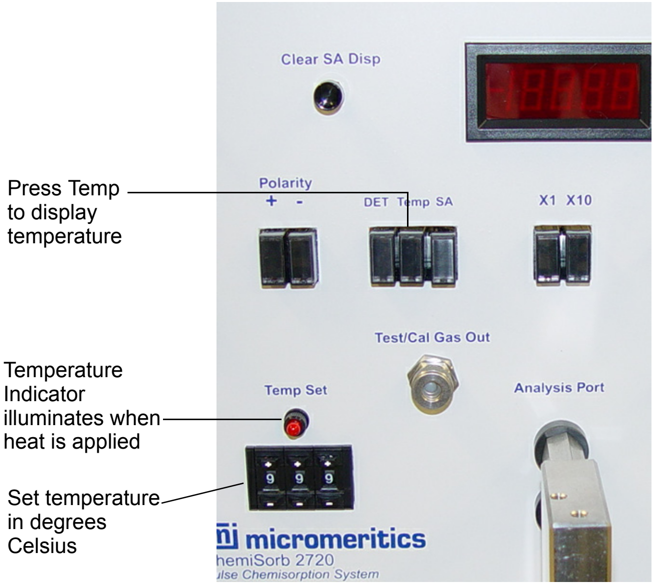
1. Pour the sample into a clean, dry sample tube; be sure to use borosilicate for physisorption.
2. Install the tube securely in the **Preparation Port**
3. Turn the **Path Select** knob to **Bypass**.

4. Place a heating mantle around the sample (refer to "Installing a Heating Mantle" in Chapter 2).



5. Plug the heating mantle power cord and thermocouple into their appropriate connectors.

6. Specify the desired temperature using the **Temp Set** dials. The actual temperature to which the sample inside the heating mantle is being subjected at any time thereafter can be read on the instrument meter by pressing the **Temp** button just below the instrument display.



7. For temperature and duration recommendations refer to “Degassing Considerations” on page 3-14.

Degassing Considerations

Heating to the highest temperature consistent with the thermal stability of the sample gives the most rapid degassing. The upper limit of the heating mantle is about 400 °C. Degassing at 200 to 250 °C for 15 to 20 minutes usually is adequate. Many materials degas well at 120 to 150 °C.

Repetitively adsorbing and desorbing nitrogen at the **Analysis** position can be employed as a degassing means for those materials that cannot tolerate elevated temperature degassing.

There is only one sure way to establish degassing requirements. A sample is adequately degassed when further treatment results in no increase in measured surface area. With unfamiliar materials, you may wish to perform a series of tests varying either time of treatment or temperature or, perhaps, both to establish degassing conditions.

Cold Trap Considerations

The level of the liquid nitrogen in the Cold Trap during surface area measurements should be held more or less constant by replenishing it as necessary every 20 to 30 minutes, preferably between analyses. Avoid adding liquid nitrogen while an analysis is in progress. The small, temporary flow rate change thereby introduced may slightly alter results. Rapid and disruptive detector drift may occur if the liquid nitrogen in the cold trap is allowed to evaporate below the level of the cold trap tube.

Performing a Single-Point Surface Area Analysis

Calibration

The ChemiSorb 2720 should be calibrated at the start of each 8-hour operational period or when you change analysis gas. Calibration is accomplished by injecting a precise volume of a pure gas or a known composition gas mixture into the instrument through a septum using a syringe and needle. Side-port needles are supplied to prolong septum life; sharp-edge needles should be avoided. The septum requires periodic replacement, nevertheless. Replacement is required more frequently when using the larger needle of the 10 mL syringe (approximately after 20 injections) than with the smaller needle of the 1 mL syringe (approximately after 100 injections). Refer to Chapter 5 for ordering information.

As discussed in **Appendix C, Physisorption Theory,** 1.0 cm^3 of nitrogen gas corresponds to 2.84 m^2 of sample surface in the ChemiSorb 2720 when employing a mixture of 30 mole % N_2 and 70 mole % He. Liquid nitrogen is used to set the adsorbing temperature when ambient conditions are 22 °C and 760 mmHg. Procedurally the steps are identical for other gases and conditions with the exception that another constant is applicable and some electronic adjustments may be required.

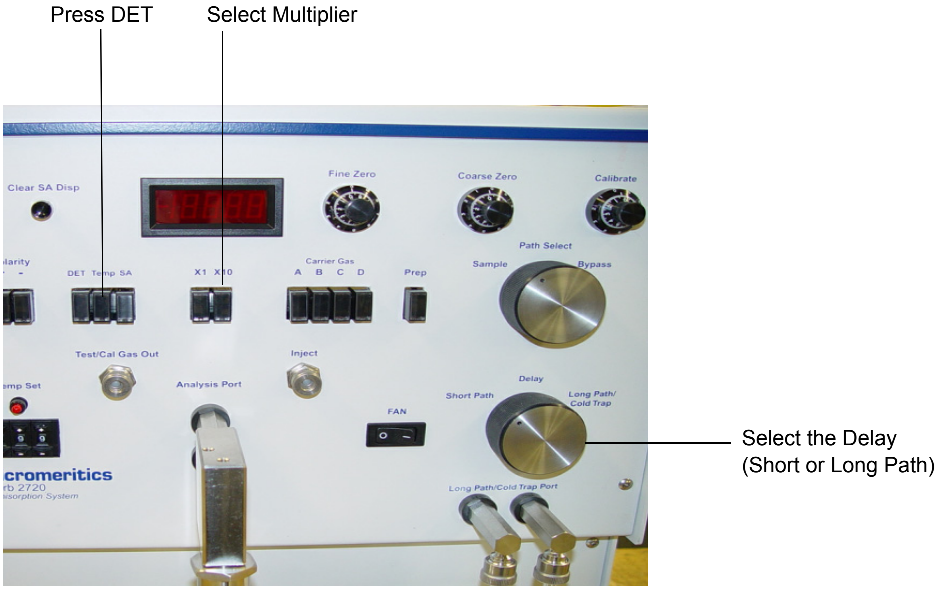
Small ambient temperature deviations from 22 °C are relatively insignificant, but a calibration value differing considerably from 2.84 may be required in some localities far removed from sea-level elevations. Perform the calibration as follows:

1. Insert empty sample tubes into the **Preparation Port** and the **Analysis Port**.
2. Turn the **Path Select** knob to **Bypass**.

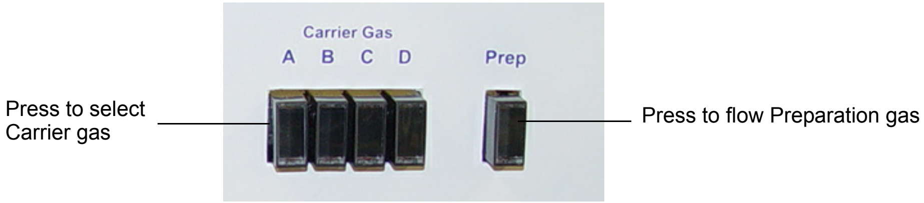
Select Bypass

Install empty sample tubes in these ports

3. If the cold trap is to be used:
    a. If it is not already installed, install the U-tube on the **Long Path/Cold Trap** port.
    b. Slide a Dewar under, then up around the Cold Trap U-tube.
    c. Place the Dewar pedestal beneath the Dewar.
    d. Place one half of the stopper on top of the Dewar.
    e. Pour liquid nitrogen into the Dewar through the open space until the liquid is within a centimeter (0.5 in.) of the stopper surface, then place the other half of the stopper on top of the Dewar.
4. Press the **DET** button.



5. Select the **X1** button.
6. Select the negative polarity (**Polarity** –) button.
7. Turn the **Delay** knob to the **Short Path** or **Long Path/Cold Trap** position (whichever is appropriate for the sample to be analyzed subsequently).
8. Press the **Prep** button to select the preparation (generally nitrogen) gas.
9. Press the **Carrier Gas A**, **B**, **C**, or **D** button to select the carrier gas (for physisorption, a mix of nitrogen in helium).



10. Fill a 1-mL precision syringe to 1 mL with nitrogen gas using one of the following methods:

    - Using the **Test/Cal Gas Out** septum on the instrument:

      a. Insert the syringe in the **Test/Cal Gas Out** septum and fill with gas.

Insert syringe and fill with gas

      b. Flush the syringe if needed to obtain 1 mL.

      c. Lay the syringe aside so that the gas can equilibrate to room temperature

    - Using Liquid Nitrogen:

      a. Fill a cold trap Dewar with liquid nitrogen. The evaporating liquid provides an atmosphere of pure nitrogen gas.

      b. Hold the needle tip immediately above the level of liquid nitrogen and fill the syringe. Flush the syringe a few times to be sure of obtaining a proper fill.

      c. Wipe the needle tip free of accumulated frost and lay the syringe aside, allowing the gas inside the syringe to reach room temperature.

Alternately, you can fill the syringe from an auxiliary septum attached to a gas cylinder. An auxiliary septum may be ordered from Micromeritics. Refer to Chapter 5, Ordering Information for the part number.

11. While the syringe is equilibrating, use the **Set Gas Flow** knob to regulate the gas flow through the instrument so that the flowmeter float is at the 15 SCCM mark.

Turn to regulate gas flow

Turn to zero instrument

Flowmeter (Float should be at 15 SCCM)

12. Use the **Fine Zero** and **Coarse Zero** knobs to zero the instrument. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved.

13. Press the **SA** and the **Clear SA Disp** buttons.

After selecting the SA button, press to clear the display

Press SA

14. Hold the syringe at the rear flange so that body heat does not affect the gas volume contained by the syringe barrel.

15. Insert the needle fully into the **Inject** septum.

Insert the syringe and inject gas

16. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.
17. After approximately one minute (five minutes for Long Path), the **Threshold** light begins to flash and the indicator starts to accumulate surface area information. When the flashing slows to no more than once in 15 to 20 seconds (approximately after three minutes), the accumulation may be considered complete. Completeness may be confirmed by pressing the **DET** button; it should be 0.02 or less.

Displays Surface Area Data

Use the Calibrate Knob to set surface area

Threshold indicator flashes during data accumulation

When Threshold indicator stops flashing, press DET to confirm completion

18. Use the **Calibrate** knob to set the surface area value (**S**); this is the number shown on the instrument display when **SA** is pressed (refer to equation (7) of Appendix C).

    The surface area value is 2.84 when room temperature is approximately 22 °C, atmospheric pressure is near 760 mmHg, and a gas composition of 30% N_2 and 70% He is being used. The surface area value can vary considerably for conditions different from the above. Should you be unable to reach 2.84, reduce the gas flow rate 20% and try again.

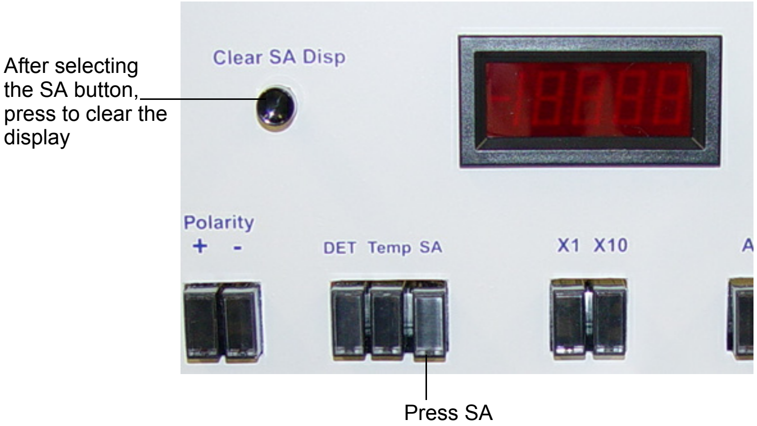
The ChemiSorb 2720 is now calibrated. Confirmation of calibration is established as deemed necessary by making repeat injections. Reproducibility should be within ±0.02 units on the display meter.

Analysis

Materials with unknown characteristics are best tested with the multiplier set on X1. Only samples having less than 3.5 m^2 of surface area are ever advantageously tested with a setting of X10 and then only when the sample is a slow desorber (perhaps due to long or tortuous passageways within the sample itself). Using the X10 setting for excessively large surface area samples may overload the signal processing circuit and result in some error. Should this occur, a high-pitched tone will be heard above the normal clicking sound. Select the X1 or X10 scale and the Short or Long Path as appropriate for the sample (and as employed during calibration).

1. Degas the sample as described in "Degassing the Sample" on page 3-12.
2. When adequately degassed, transfer the sample from the **Preparation Port** to the **Analysis Port**.

   A small amount of air is introduced during the transfer process. Press the **DET** button so that the display reveals the passage through the system of this air pulse (occurring within a minute or so after sample transfer).
3. When the display returns to within 0.02 of zero, press the **SA** and the **Clear SA Disp** buttons to clear the display.



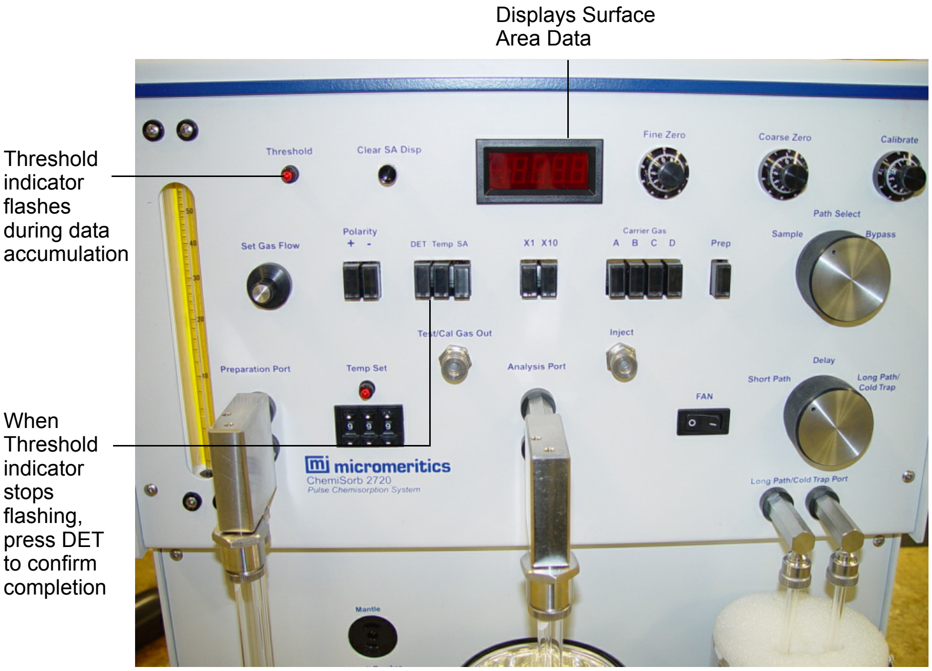
If desired, you may start degassing another sample after transferring the current sample to the Analysis position.

4. Turn the **Path Select** knob to **Sample**.
5. Turn the **Delay** knob to either **Short Path** or **Long Path/Cold Trap**.

   Short Path requires 5 to 10 minutes. (The Short path bypasses the Cold Trap.)
   Long Path/Cold Trap requires 20 to 25 minutes.
6. Select the positive polarity (**Polarity** +) button.
7. If the Cold Trap is used:
   a. Slide a Dewar under, then up around the Cold Trap U-tube.
   b. Place the Dewar pedestal beneath the Dewar.
   c. Place one half of the stopper on top of the Dewar.
   d. Pour liquid nitrogen into the Dewar through the open space until the liquid is within a centimeter (0.5 in.) of the stopper surface, then place the other half of the stopper on top of the Dewar.
8. Prepare a Dewar of liquid nitrogen for the sample to be analyzed. Fill the Dewar about half full. If a long analysis is to be performed, you may need to top off the liquid nitrogen after placing the Dewar about the sample.
9. Allow the liquid nitrogen in the Dewar to equilibrate for 30 minutes.
10. Slide the Dewar of liquid nitrogen under, then up around the sample.
11. Place the Dewar pedestal beneath the Dewar.

- After approximately one minute (five minutes for the Long Path) the **Threshold** light begins to flash and the instrument display shows data accumulation.

- Ensure that the flowmeter float returns to its normal position before data accumulation begins (**Threshold** light flashing). If it does not, wait until the analysis finishes (flashing ceases) and restart the analysis using the LONG path or a lesser quantity of sample.
- When the flashing slows to no more than once in 15 to 20 seconds (approximately three or four per minute), or the indication with **DET** pressed has returned to 0.02 or less, adsorption is complete.



12. Record the value if desired. This value represents the sample surface area in square meters obtained from the adsorption of nitrogen gas. The adsorption peak is not as sharp and clean as the desorption one and cannot be integrated with quite the precision of the latter. However, surface areas obtained by adsorption and desorption are virtually identical for many materials.The desorption procedure is unnecessary when this is found to be the case.
13. Press **SA**, then press the **Clear SA Disp** button to clear the display for registration of the desorption value.
14. Select the negative polarity (**Polarity** –) button.
15. Remove the Dewar of liquid nitrogen; allow the sample to equilibrate to room temperature so that desorption data can be calculated.

    To facilitate warming you can:

    - Place the **FAN** switch in the **ON** position, or
    - Immerse the sample tube in a beaker of room temperature water.

16. Continue the warming procedure until the flowmeter float returns to its normal level.
    - As with adsorption, the **Threshold** light flashes and the display accumulates data for several minutes.
    - When the flashing slows to no more than once in 15 to 20 seconds (or the **DET** indicator has returned to 0.02 or less), the sample surface area is displayed.
17. Record this value along with sample descriptive information and weight. This number divided by the sample weight in grams is the sample specific surface area in square meters per gram.

Performing a Multipoint Surface Area Analysis

Calibration

Calibration should be performed at the start of each 8-hour operational period. It is accomplished as described for single-point testing with a few exceptions.

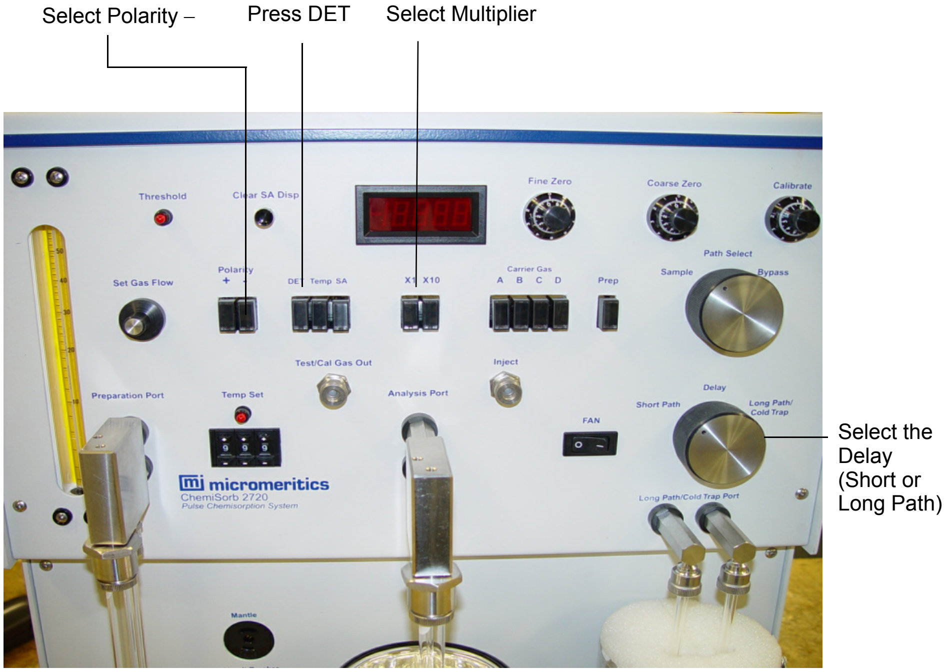
- Repeat all the calibration steps for each gas mixture used.
- Determine a different number for each gas composition.
- Calibrate the instrument in actual standard cm^3 of nitrogen.

The gas flow rate may be temporarily increased, if desired, when shifting from one gas composition to another to save time. Care must be taken in doing so to prevent sample discharge from the increased flow. If you suspect this may be a problem with your sample, you can temporarily substitute an empty sample tube. After purging is complete, the flow must be restored to the operating level; i.e., the 15 SCCM mark on the flowmeter and the **DET** zero confirmed.

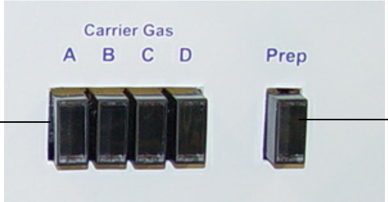
The ChemiSorb 2720 must be properly flushed with an appropriate gas having a certified composition of, for example, approximately 5% N_2 and 95% helium.

1. Insert empty sample tubes into the **Preparation Port** and the **Analysis Port**.
2. Turn the **Path Select** knob to **Bypass**.

3. If the Cold Trap is used:
    a. Slide a Dewar under, then up around the Cold Trap U-tube.
    b. Place the Dewar platform beneath the Dewar.
    c. Place one half of the stopper on top of the Dewar.
    d. Pour liquid nitrogen into the Dewar through the open space until the liquid is within a centimeter (0.5 in.) of the stopper surface, then place the other half of the stopper on top of the Dewar.
4. Press the **DET** button.



5. Select the **X1** button.
6. Select the negative polarity (**Polarity** –) button.
7. Turn the **Delay** knob to the **Short Path** or **Long Path/Cold Trap** position (whichever is appropriate for the sample to be analyzed subsequently).
8. Press the **Prep** button to select the preparation (generally nitrogen) gas.
9. Press the **Carrier Gas A**, **B**, **C**, or **D** button to select the carrier gas (for physisorption, a mix of nitrogen in helium).



Press to select Carrier gas

Press to flow Preparation gas

10. Fill a 1-mL precision syringe to 1 mL with nitrogen gas using one of the following methods:
    - Using the **Test/Cal Gas Out** septum on the instrument:

      a. Insert the syringe in the **Test/Cal Gas Out** septum and fill with gas.

Insert syringe and fill with gas

      b. Flush the syringe if needed to obtain 1 mL.

      c. Lay the syringe aside so that the gas can equilibrate to room temperature

    - Using Liquid Nitrogen:

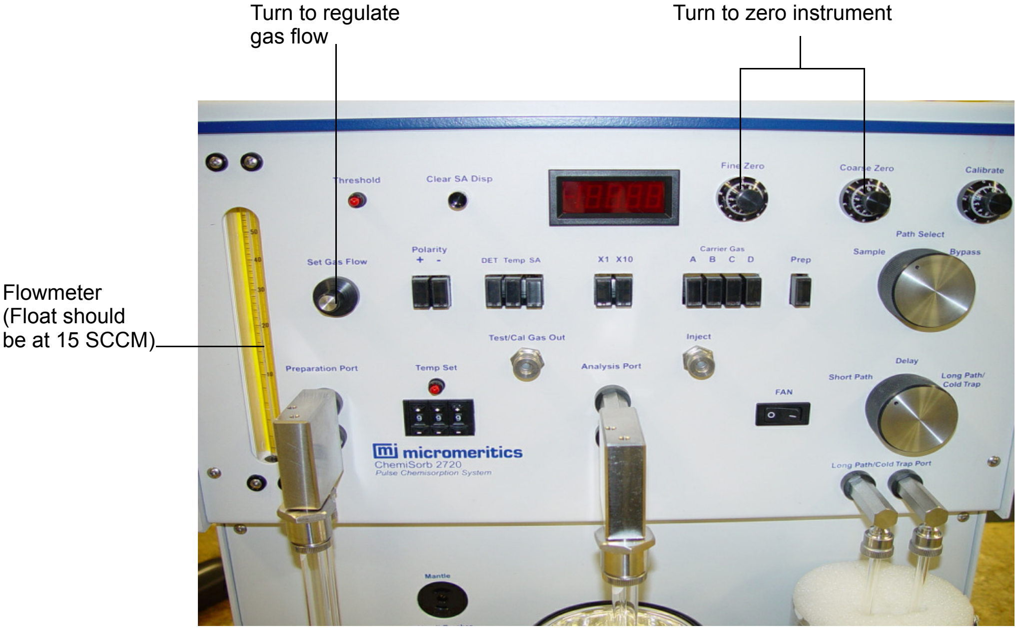
      a. Fill a cold trap Dewar with liquid nitrogen. The evaporating liquid provides an atmosphere of pure nitrogen gas.

      b. Hold the needle tip immediately above the level of liquid nitrogen and fill the syringe. Flush the syringe a few times to be sure of obtaining a proper fill.

      c. Wipe the needle tip free of accumulated frost and lay the syringe aside, allowing the gas inside the syringe to reach room temperature.

Alternately, you can fill the syringe from an auxiliary septum attached to a gas cylinder. An auxiliary septum may be ordered from Micromeritics. Refer to Chapter 5, Ordering Information for the part number.

11. While the syringe is equilibrating, use the **Set Gas Flow** knob to regulate the gas flow through the instrument so that the flowmeter float is at the 15 SCCM mark.



12. Use the **Fine Zero** and **Coarse Zero** knobs to zero the instrument. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved.

13. Press the **SA** and the **Clear SA Disp** buttons.

After selecting the SA button, press to clear the display

Press SA

14. Hold the syringe at the rear flange so that body heat does not affect the gas volume contained by the syringe barrel.
15. Insert the needle fully into the **Inject** septum.

Insert the syringe and inject gas

16. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.
17. After approximately one minute (five minutes for Long Path), the **Threshold** light begins to flash and the indicator starts to accumulate surface area information. When the flashing slows to once in 15 to 20 seconds (approximately after three minutes), the accumulation may be considered complete. Completeness may be confirmed by pressing the **DET** button; it should be 0.02 or less.
18. Use the **Calibrate** knob to set the gas volume at standard conditions (refer to Appendix C). For example, if ambient temperature is 22 °C and atmospheric pressure is 740 mmHg, set the gas volume as 0.90

    $$1.00 \times (273.2/295.2) \times (740/760) = 0.90$$

    as calculated by equation 8, Appendix C.

    Hereafter the instrument will indicate the adsorbed gas volume (STP) instead of the equivalent surface area of an adsorbent as in the single-point procedure.
19. Record the reading for subsequent use.

20. Repeat the calibration procedure for each gas mixture and record calibration information accordingly. Wait a few minutes after shifting from one gas to another to allow the previous gas to be flushed from the instrument. The instrument display with **DET** pressed will cease registering a change as soon as the new gas has thoroughly flushed from the instrument.

    The numbers will fluctuate somewhat from instrument to instrument and will vary, of course, with gas composition. Typical numbers are shown in the following table and are for illustrative purposes only.

Table 3-2. Typical Calibration Numbers

Gas Composition (% N_2)	Calibrate Setting
4.999	91
9.997	101
14.993	111
22.006	124
Do not use these data; they are illustrative only.	

Analysis

The objective in multipoint surface area analysis is to obtain the volume of adsorbate (nitrogen, usually) at STP taken up by the sample at a series of relative pressures and to treat these data in accordance with the BET equation (refer to Appendix C) to yield the surface area. The calibration procedure for multipoint analysis was designed to set the instrument to register adsorbed gas volumes. Now the purpose is to relate adsorbed gas volumes to conditions for a specific sample.

A multipoint analysis can be conducted as a series of single-point steps using the ChemiSorb 2720, progressing from lower to higher nitrogen gas concentrations. After each concentration is established in the ChemiSorb, the instrument is adjusted appropriately for the new gas mixture, and the adsorbed gas volume is measured. The sample surface area is computed in accordance with the BET equation after three or four measurements are completed.

If not previously obtained, determine the sample weight after all gases have been employed and the data collected. Divide the measured adsorbed volumes by the sample weight to obtain specific adsorbed volumes. As an example, the data might be as shown in the following table.

Table 3-3. Example Adsorption Data

Gas Composition (% N_2)	Specific Adsorbed Volume (cm^3/g, STP)
4.999	15.16
9.997	17.39
14.993	19.16
22.006	21.46
Do not use these data; they are illustrative only.	

Now compute the sample specific surface area following the method given in "Calculating the Result".

Calculating the Result

Appendix C gives the basic theory and pertinent equation of the multipoint calculation. The table below formalizes the procedure beginning on the left and proceeding to the right using the experimental data in Table 3-3.

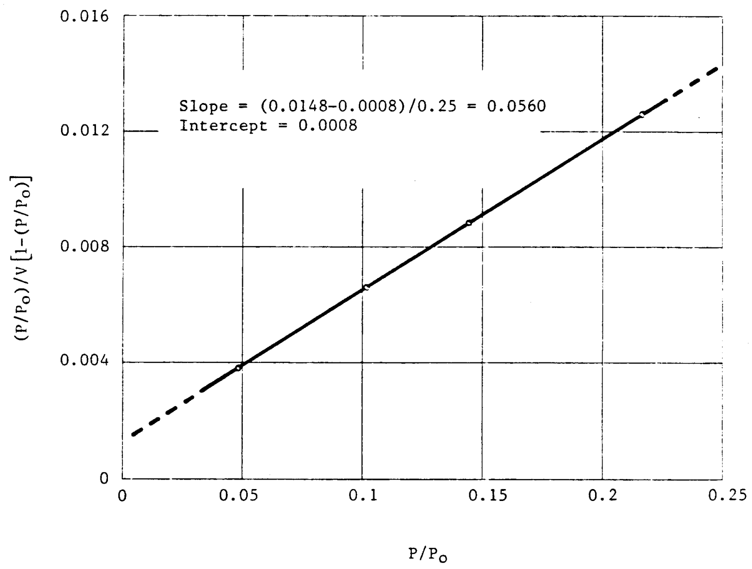
Table 3-4. Example Bet Calculation

Experimental Data		(*) P/Po	1-(P/Po)	V[1-(P/Po)]	(P/Po)/V[1-(P/Po)]
Gas Composition	Specific Gas Volume (V)				
4.999	15.16	0.0490	0.9510	14.42	0.00340
9.997	17.39	0.0980	0.9020	15.69	0.00625
14.993	19.16	0.1471	0.8529	16.34	0.00900
22.006	21.46	0.2158	0.7842	16.83	0.01282
(*) ($\%N_2/100$) x 760/775 = ($\%N_2/100$) x 0.981 = $\%N_2$ x 0.00981					

A plot of the sixth versus the third column is given by the following figure. The slope of the plotted line is 0.0560 and the intercept is 0.0008. From equation 10 of Appendix C, the sample specific surface area **(S)** is thus calculated as:

$$S = \frac{4.353}{0.0560 + 0.0008} = 76.6 m^2/g$$

For purposes of comparison, a single-point specific surface area of 73.8 $m^{2/}g$ was obtained for this same material using a gas composition of 30.017% N_2 and the remainder helium.



Performing a Total Pore Volume Analysis

The volume of liquid in pores from a condensible gas at greater than 95% of its saturation vapor pressure is generally accepted to correspond to the total mesopore plus micropore volume. However, users, drawing on their own experience and beliefs, tend to differ on the exact percent saturation to be employed. The following presumes analysis at 98% saturation for purposes of illustration, but the procedure is equally as applicable to one degree of saturation as another.

A caution to be noted is that 100% saturation does not represent a reliable, obtainable point. Any material held truly at 100% saturation will continue to accumulate condensed phase as long as it remains at this condition, eventually resulting in flooding of the sample space. The procedure given here exposes the sample to 100% N_2 to ensure pore filling but then reduces the gas composition to permit excess condensate to escape. In other words, it finds the 98% point on the desorption isotherm.

Pure nitrogen and a 98% N_2/2% He mixture of gases are required. When basic gas purity is uncertain, the cold trap Dewar should be used with a liquid nitrogen/isopropyl alcohol slurry as the cryogen; this will adequately freeze out whatever water vapor may be present.

Calibration

Calibration for total pore volume analysis is accomplished with 98% N_2/2% He gas serving as the carrier. Inject a 10-cm^3 volume of pure nitrogen in a stream of 98% N_2/2% He at ambient conditions and set the instrument to indicate the true volume of this gas when condensed as a liquid, the state in which it exists when filling the pores of a sample under these conditions. If, for example, ambient conditions are 22^{o}C and 740 mmHg, equation (11), Appendix C, shows the liquid volume equivalent of 10 cm^3 of gas is

$$\frac{273.2}{295.2} \times \frac{740}{760} \times 0.00155 \times 10 = 0.0140\text{cm}^3$$

This number multiplied by 100 is then set on the display meter using the **Calibrate** dial. The number will vary with locality and time due to differences in atmospheric pressure and temperature. The first step in the calibration procedure is thus to calculate the appropriate constant for conditions prevailing where the instrument is being used.

Perform the calibration as follows:

1. Insert empty sample tubes into the **Preparation Port** and **Analysis Port**.
2. Turn the **Path Select** knob to **Bypass**.

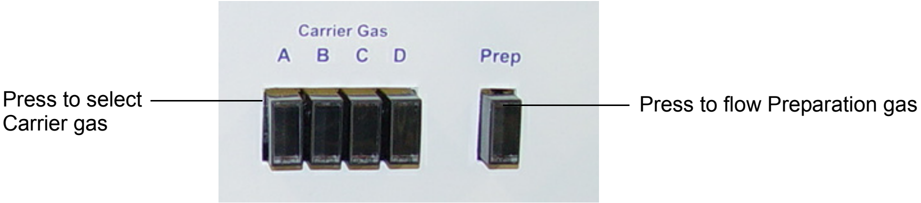
Select Bypass

Install empty sample tubes in these ports

3. If the Cold Trap is used:
   a. Slide a Dewar under, then up around the Cold Trap U-tube.
   b. Place the Dewar pedestal beneath the Dewar.
   c. Place one half of the stopper on top of the Dewar.
   d. Pour liquid nitrogen into the Dewar through the open space until the liquid is within a centimeter (0.5 in.) of the stopper surface, then place the other half of the stopper on top of the Dewar.
4. Press the **DET** button.

5. Select the negative polarity (**Polarity** –) button.

6. Select the **X1** button.
7. Turn the **Delay** knob to the **Long Path/Cold Trap** position.
8. Press the **Prep** button to select the preparation gas.



9. Press the **Carrier Gas A**, **B**, **C**, or **D** button to select the carrier gas.

10. Fill a 1-mL precision syringe to 1 mL with nitrogen gas using one of the following methods:

    - Using the **Test/Cal Gas Out** septum on the instrument:

      a. Insert the syringe in the **Test/Cal Gas Out** septum and fill with gas.

      b. Flush the syringe if needed to obtain 1 mL.

      c. Lay the syringe aside so that the gas can equilibrate to room temperature

    - Using Liquid Nitrogen:

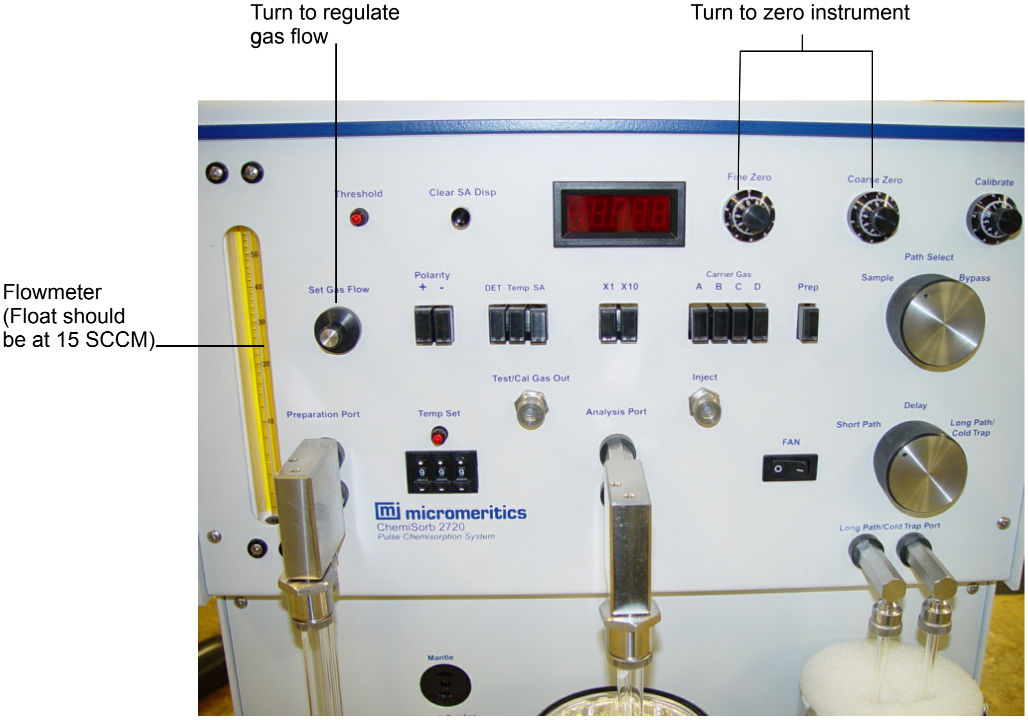
      a. Fill a cold trap Dewar with liquid nitrogen. The evaporating liquid provides an atmosphere of pure nitrogen gas.

      b. Hold the needle tip immediately above the level of liquid nitrogen and fill the syringe. Flush the syringe a few times to be sure of obtaining a proper fill.

      c. Wipe the needle tip free of accumulated frost and lay the syringe aside, allowing the gas inside the syringe to reach room temperature.

Alternately, you can fill the syringe from an auxiliary septum attached to a gas cylinder. An auxiliary septum may be ordered from Micromeritics. Refer to Chapter 5, Ordering Information for the part number.

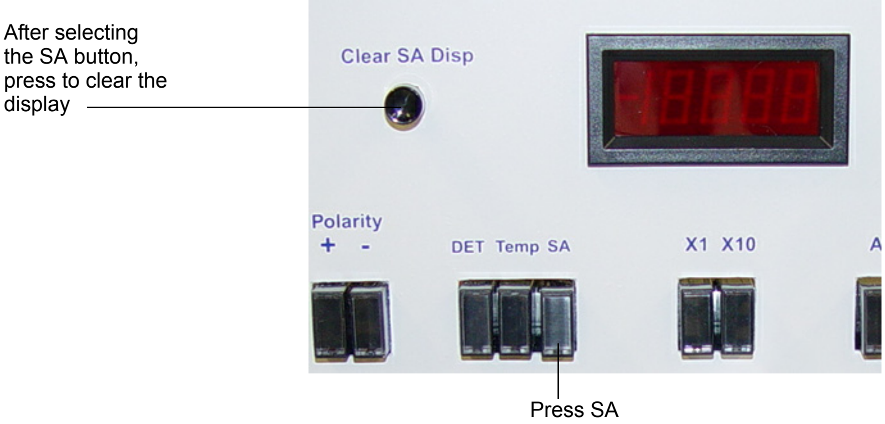
11. While the syringe is equilibrating, use the **Set Gas Flow** knob to regulate the gas flow through the instrument so that the flowmeter float is at the 15 SCCM mark.



12. Use the **Fine Zero** and **Coarse Zero** knobs to zero the instrument. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved.

Once set, the zero should not be readjusted unless a sustained change beyond ±0.02 units occurs.

13. Press the **SA** and the **Clear SA Disp** buttons.



14. Hold the syringe at the rear flange so that body heat does not affect the gas volume contained by the syringe barrel.
15. Insert the needle fully into the **Inject** septum.

Insert the syringe and inject gas

16. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.
17. After approximately five minutes, the **Threshold** light begins to flash. When the flashing slows to once in 15 to 20 seconds (approximately after three minutes), the accumulation may be considered complete. Completeness may be confirmed by pressing the **DET** button; it should be 0.02 or less.

Use Calibrate knob to set calibration value

When Threshold indicator stops flashing, press DET to confirm completion

18. Use **Calibrate** knob to set the display to the value calculated at the beginning of this procedure multiplied by 100. In the example shown in this section, this would be 1.40.

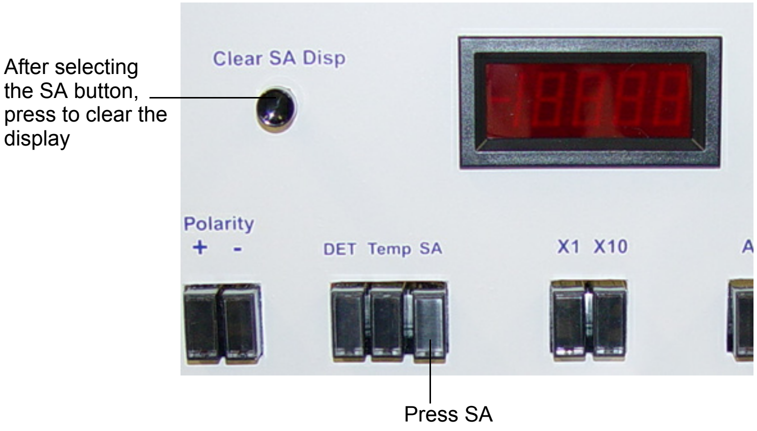
The instrument is now calibrated. Confirmation of calibration is established as deemed necessary by making repeat injections. Reproducibility should be within ± 0.02 unit.

Analysis

To ensure that the tank contains enough gas for an analysis, make sure the tank pressure for the gas regulator is at least 200 psig. Tank pressures less than 200 psig may have excessive background levels of stray gases that may negatively affect the analysis.

1. Degas the sample as described in “Degassing the Sample” on page 3-12.
2. When adequately degassed, transfer the sample from the **Preparation Port** to the **Analysis Port**.

   A small amount of air is introduced during the transfer process. Press the **DET** button so that the display reveals the passage through the system of this air pulse (occurring within a minute or so after sample transfer).
3. When the display returns to within 0.02 of zero, press the **SA** and the **Clear SA Disp** buttons to clear the display.



If desired, you may start degassing another sample after transferring the current sample to the Analysis position.

4. Prepare a Dewar of liquid nitrogen for the sample to be analyzed. Fill the Dewar about half full. If a long analysis is to be performed, you may need to top off the liquid nitrogen after the Dewar is placed about the sample.
5. Allow the liquid nitrogen in the Dewar to equilibrate for 30 minutes.
6. If the cold trap is used, check the level of the Cold Trap Dewar; replenish if necessary. Avoid replenishing the Dewar during analysis.

7. Slide the Dewar of liquid nitrogen under, then up around the sample.
8. Place the Dewar pedestal beneath the Dewar.

9. Wait for at least 15 minutes for nitrogen to condense in all pores. The level of liquid nitrogen in the Dewar should remain nearly constant. After the wait for condensation is over, turn the **Path Select** knob to **Sample**.
10. Turn the **Delay** knob to **Long Path**.
11. Select the appropriate **Carrier Gas** (**A, B**, **C,** or **D**) button for a 98% N_2/2% He.
12. Select the negative polarity (**Polarity** –) button.
13. Press the **X1** button.

    Total pore volume measurements should be conducted using the multiplier of X1. The X10 setting can be used when the tested material has a low pore volume, but it is still better to use a greater sample quantity and the X1 multiplier.

14. Press the **DET** button.

15. The display will begin registering counts. When the display has returned to within 0.02 of zero, press **SA**, then press the **Clear SA Disp** button to clear the display for registration of the desorption value.

16. Adjust the **Calibrate** knob to the setting determined during calibration. See "Calibration" on page 3-30.

17. Remove the Dewar of liquid nitrogen from the sample; allow the sample to equilibrate to room temperature.

    To facilitate warming you can:

    - Place the **FAN** switch in the **ON** position, or
    - Immerse the sample tube in a beaker of room temperature water.

18. Continue the warming procedure until the flowmeter float returns to its normal level. When it returns to normal, the **Threshold** light flashes and the display shows data accumulation for several minutes.

    When the flashing slows to no more than once in 15 to 20 seconds, the accumulation may be considered complete.

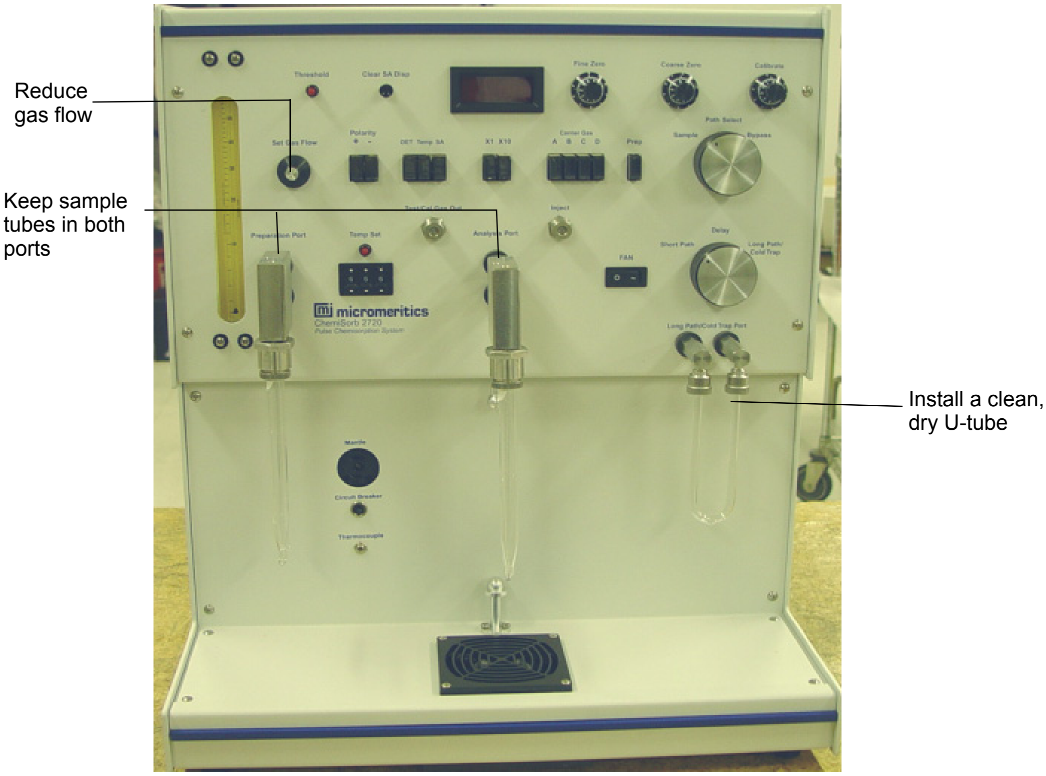
19. Observe the value in the Display.

    The value displayed is 100 times the sample total pore volume.

    Divide the displayed value by 100 to obtain total pore volume. This latter number should be recorded along with sample descriptive information and weight. The final number divided by the sample weight in grams is the sample specific total pore volume in cubic centimeters per gram.

Preparing the ChemiSorb 2720 for Idle Periods

If the ChemiSorb 2720 is to be inoperative or unattended for a period long enough for the liquid nitrogen in the Cold Trap Dewar to evaporate (or the dry ice to evaporate from the dry ice acetone slurry), remove the Dewar and U-tube so that impurities are not released into the system. Install a clean, dry U-tube after removing the current one. If additional U-tubes are unavailable, clean the current tube and allow to dry; then reinstall at the **Long Path/Cold Trap** port.



If the ChemiSorb 2720 is going to be idle only for a couple of days, reduce the gas flow to approximately one-quarter of its normal value and leave power ON. The gas loss and power drain are very low and the instrument will be immediately ready for use.

Regardless of how long the ChemiSorb 2720 is to be idle, keep a sample tube installed at both the Preparation and Analysis ports. This ensures the integrity of the system for gas flow and prevents infusion of water and other vapors.

4 TROUBLESHOOTING AND MAINTENANCE

Introduction

This chapter contains:

- common problems that may occur when operating the ChemiSorb, and how you can resolve them
- instructions on replacing the septum

Contact your local Micromeritics service representative if additional assistance is required.

Troubleshooting

Detector Drift

Some detector drift when first turning on the power is normal and to be expected. This type of drift is due to the detector system coming to its regulated temperature and should disappear in approximately 30 minutes. The instrument is generally usable after 10 minutes if it has been properly purged of air.

There are several likely causes for the detector indication (when on X1) not returning to zero within ±0.02 following a sample or calibration test with the **DET** button pressed.

1	During physisorption analyses, using contaminated gas mixtures along with failure to keep the cold trap properly submerged in liquid nitrogen. A decided shift of the detector baseline occurs between the adsorption and desorption modes when the gas contains impurities and the cold trap is ineffective. Surprisingly small amounts of impurities can cause detector drift. A contaminated pressure regulator, unclean metal connecting tubing, and unclean non-metal tubing and connectors can contribute impurities to an otherwise clean gas stream. Be sure one or more of these factors is not responsible before proceeding further.
2	Using atmospheric air to perform calibrations can cause detector drift because of its water vapor content which travels slowly through the system. Using atmospheric air is discouraged and the procedure described in "Single-Point Calibration" in Chapter 3, is recommended.

3	Using too much liquid nitrogen in the Cold Trap Dewar. Too much liquid nitrogen cools the metal fittings supporting the glass trap causing moisture from the atmosphere to freeze. This leads to erratic gas cooling. The liquid nitrogen level should be approximately 1 cm (0.5 in.) from the top of the Dewar.
4	Incompletely degassed samples cause detector drift and offset because contaminants can still be flushed from the sample at room temperature. Such drift and offset will cease once the sample is immersed in liquid nitrogen.
5	Leaks caused by a worn septum; always use a good septum. Replace the septum periodically; after approximately 100 injections when using the 1-mL syringe and approximately 20 injections when using the 10-mL syringe. Refer to "Replacing the Septum" in this chapter.
6	Leaks caused by loose plumbing. If it becomes necessary to tighten plumbing connections, be sure not to overtighten them. Overtightening can easily damage small diameter tubing.
7	Leaks caused by missing or damaged sample tube O-rings. Discard cracked or chipped sample tubes to avoid leaks and avoid damaging the O-rings.

Low Results On X10 Range

The X10 range (10 times increase in detector sensitivity) is provided when analyzing samples that produce less than a 10% enrichment for nitrogen in the gas stream. The detector signal is truncated when this 10% limit is exceeded which results in a lowered surface area value. A high-pitched audio tone is sounded if the possibility of misleading results occurs.

Erratically High Results

Failure to reset the surface area display to zero after passage of the air peak is often responsible for an apparently high result.

Air peaks or peaks due to other gases passing through the Long path may be forgotten due to their extended transit time and add to a subsequent surface area. You should be particularly aware of this possibility when a Short path adsorption followed by a Long path desorption is employed to save time.

Adding liquid nitrogen to the Cold Trap while a surface area result is accumulating can cause gas flow to decrease or even to stop momentarily. This will extend the time of gas passage and violate the assumption of constant flow rate upon which the surface area accumulation technique is based. The result is a somewhat greater surface area value than would otherwise have been achieved. The liquid nitrogen supply should only be replenished between tests or while awaiting air peak passage.

Non-Reproducible Calibrations

A damaged and leaking septum should be eliminated as the first possible cause of non-reproducible calibrations. Replace the septum with a new one if there is any doubt as to its integrity. (Refer to "Replacing a Septum" in this chapter.)

The knurled nut which retains the septum should be finger-tightened. Insufficient or excessive tightening may cause system leakage.

Check the syringe for gas tightness and freedom from obstructions in the needle. Immerse the needle tip under water and press the plunger; this should result in a steady stream of bubbles with no resistance to motion from the plunger. When performing this check, be careful not to draw water into the syringe. Allow the needle to dry thoroughly before using for calibrations.

Monitor the flow rate by observing the Flowmeter float to see that it is constant. If it does not maintain a steady position, check the following:

- the gas regulator setting for its recommended 15 psig setting
- the flow control knob for smooth operation
- gas leaks about the septum, the sample tubes and holders, the gas inlet connection, and internal plumbing connections

Also refer to "Detector Drift" in this chapter.

Heating Mantle Temperature Fails to Function Properly

A flashing temperature display indicates that either the thermocouple is disconnected or that a temperature at or above the maximum limit of 400 °C has been reached. Ensure that the thermocouple is plugged into its receptacle. If the thermocouple is plugged in, unplug the thermocouple and examine its leads for broken connections. If the thermocouple is intact, check to see if a temperature of 400 °C higher has been specified; if so, specify a lower temperature. Circuitry inside the instrument protects the operator and the heating mantles by limiting the temperature to 400 °C regardless of the setting chosen by the operator.

The thermal characteristics of the heating mantles prevent temperature regulation to a precision better than approximately 10 °C. Normal operation is cyclical with the temperature oscillating about the chosen temperature by several degrees, the initial overshoot will be the largest. The actual temperature at the sample will be somewhat lower than initially indicated and will vary less due to the moderating effects of the quartz wall of the sample tube and the flowing stream of gas.

The temperature control circuitry has been designed to require about 20 minutes to reach the desired setting regardless of how high the setting may be. This controlled ramping of temperature is intended to minimize destructive changes in the sample, especially those due to the boiling off of moisture. Faster heating may be achieved by setting to a much higher temperature than desired, and then reducing the setting to the desired temperature when that temperature is reached.

Substantial Difference in Adsorption and Desorption Result

Generally there will be little difference between indicated adsorption and desorption data (surface area in the case of single-point analysis and gas volume in multipoint testing). Substantial and persistent differences can be indicative of a leak somewhere in the system.

Lodged Flowmeter Float

Fine particles that escape filter entrapment, as well as accumulated vapor deposition can cause the ball float to become lodged in the glass tube of the flowmeter. Contact your local Micromeritics service representative if this occurs.

Replacing a Sample Port Filter

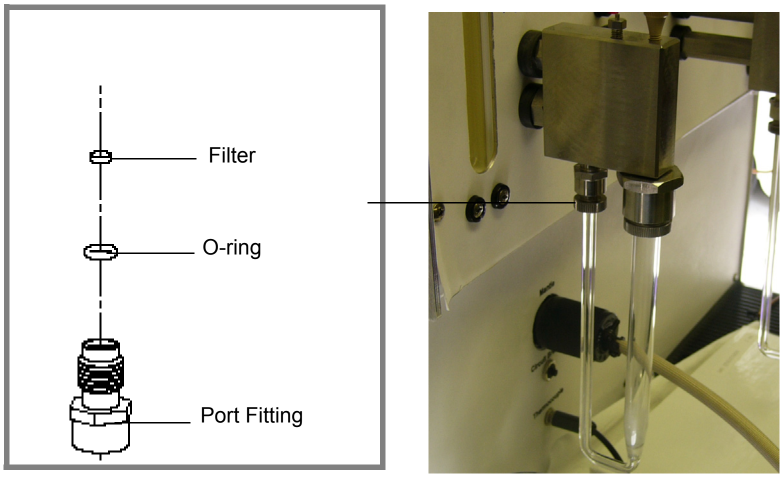
A filter frit is used to protect the analyzer internal components from contaminants that may elutriate from the sample tube during an analysis. However, as the analyzer is used, the filter may gradually become clogged with trapped particles. If the filter does become blocked, it must be replaced.

The filter is located in the rear port fitting.

1. Remove the sample tube from the port.

The sample tube and nearby components may be hot. Make sure you allow the sample tube to cool before removing it. Use gloves to protect your hands.

2. Remove the rear sample port fitting from the manifold. Use a small diameter probe to remove the O-ring and filter from the sample tube fitting.



Rear Sample Port

3. Install a new filter in the sample tube fitting.
4. Inspect the O-ring for cracks or cuts. If the O-ring is damaged, replace it. Otherwise, clean the O-ring you removed, dry it, and place it in the sample tube fitting. Make sure the O-ring is securely in place.
5. Place the sample tube fitting back into position and tighten it.

Replacing a Septum

A septum is installed at the **Test/Cal Gas Out** port and the **Inject** port. Each septum is held into place by a knurled nut.

A septum usually requires replacing after approximately 100 injections when using the 1-mL syringe and approximately 20 injections when using the 10-mL syringe. Refer to Chapter 5 for ordering information.

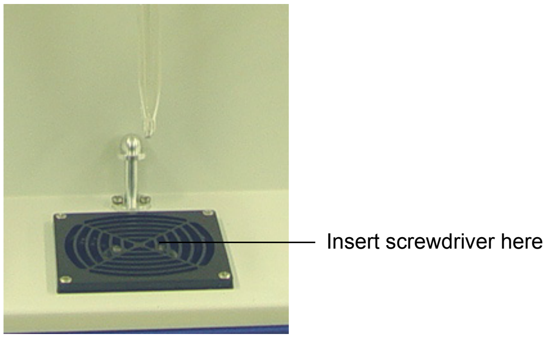
Replace a septum as follows:

1. Turn the knurled nut counterclockwise and remove it from the injection port.
2. Tap the nut into the palm of your hand to remove the septum; discard the used septum.
3. Place a new septum into the knurled nut. If the washer came out when you removed the used septum, be sure to place it into the knurled nut first.
4. Place the knurled nut back onto the injection port; turn the nut clockwise to finger-tighten.

Cleaning an Air Filter

The two fans on the front lower portion of the instrument contain air filters. These filters may accumulate dust over time, and should be cleaned on a yearly basis, or more often if required. To clean a filter:

1. Insert a pointed object, such as a flat-head screwdriver, into the center portion of the retaining cover, then pop off the cover.



2. Remove the filter and rinse it off.
3. Allow the filter to dry thoroughly.
4. Replace the filter, then replace the cover.

5 ORDERING INFORMATION

Introduction

Components and accessories can be ordered by:

- contacting our Customer Service Department at 770/662-3636
- accessing our web site at http://www.micromeritics.com

When ordering, please use the information provided in this chapter.

Part Numbers and Descriptions

Part Number	Description
021-00000-00	Model 021 LN_2 Transfer System, allows easy filling of sample Dewars
231-26001-00	Heating mantle, 24V, 120W, Type J
230-25808-00	Clip, for heating mantle
004-61617-00	Dewar, 350 mL
272-25833-00	Pedestal, for Dewar
272-31801-00	Dewar cover, for standard Dewar
272-31801-01	Dewar cover, for cold trap Dewar
004-32602-00	Septum, for Test/Cal Gas Out or Inject port
004-54805-00	Tool, stuffing extractor
004-61604-00	Syringe, 10 mL
004-61604-01	Needle, for 10-mL syringe
004-61602-00	Syringe, 1 mL
004-61602-01	Needle, for 1-mL syringe
003-60101-00	Power cord, IEC 10A
003-51131-00	Fuse, 2.0 Amp, Slow Blow, Type 3AG
003-51130-01	Fuse, 5 x 20 mm, 1 Amp Slow Blow, Type T
290-25846-00	Gas inlet line assembly, copper
201-25818-00	Gas inlet line assembly, stainless steel
004-62230-32	Gas regulator, 2-stage, CGA 320 fitting, 30 psig (CO_2)
004-62230-35	Gas regulator, 2-stage, CGA 350 fitting, 30 psig (CO, H_2)
004-62230-54	Gas regulator, 2-stage, CGA 540 fitting, 30 psig (O_2)

Part Number	Description
004-62230-58	Gas regulator, 2-stage, CGA 580 fitting, 30 psig (N_2, He, Ar, Kr)
004-62230-59	Gas regulator, 2-stage, CGA 590 fitting, 30 psig (ultrapure air)
004-25318-00	Reducer, 1/4-in. stub x 1/8-in. tubing
004-25549-00	Reducer, 1/8-in. tube x 1/4-in. tube
004-25034-00	O-ring, -008 70 Duro Buna-N
004-25044-00	O-ring, -013 70 Duro Buna-N
004-25466-00	O-ring, -010 70 Duro Buna-N
004-27056-00	Frit filter, 20 micron, for 1/4 in. sample port
272-25805-00	Ferrule, for 1/2 in. sample port
275-25803-00	Ferrule, for 1/4 in. sample port
004-32164-01	Quartz wool, 4-in. x 6-in. bag
272-61702-00	Sample tube, flow-thru, quartz; for chemisorption analysis
272-61703-00	Sample tube, flow-thru, borosilicate; for physisorption analysis
236-61705-00	Filler rod, for chemisorption analysis
004-61701-02	Filler rod, for physisorption analysis
004-32604-08	Cap, for 1/4 inch side of sample tube
240-32000-00	Cap, for 1/2-in. side of sample tube
930-54601-00	Brush, 0.059 diameter stem, for capillary side of sample tube
004-54609-00	Brush, 30 mm diameter, for sample side of sample tube
230-61001-00	U-tube, for cold trap
240-25853-00	Funnel, for pouring sample into sample tube
004-27047-01	Air filters, for fans
004-16825-00	Reference Material, Pt on alumina
004-16836-00	Reference Material, Silver Oxide
230-25833-00	Gas extraction assembly (auxiliary septum, attaches to gas cylinder)
290-25842-00	Gas extraction assembly with toggle valve (auxiliary septum, attaches to gas cylinder)
028-00000-00	ChemiSoft TPx Option, furnace, accessories, and software for temperature-programmed analyses and data reduction.
272-42801-01	ChemiSorb 2720 Operator's Manual

A CHEMISORPTION THEORY

Chemisorption Theory

Chemisorption is the term applied to the interaction of solid surfaces and gases when there is a sharing of electrons between the adsorbate molecule and the surface, i.e., when a chemical, valency bond is formed. A chemisorbed layer thus cannot exceed a single molecule in thickness. The chemisorption process proceeds rapidly, but, because an activation energy is required, it usually proceeds with increasing rapidity as temperature rises. The energy released by chemisorption is like that of any other chemical reaction; it normally is greater than 20 Kcal/mol. Chemisorption is not easily reversed; an energy input somewhat greater than that initially released is required for reversal.

Chemisorption occurs on heterogeneous catalysts at metallic-atom, active sites on the surface. Hence, much can be learned about the nature of a heterogeneous catalyst by chemisorption measurements.One obvious example is the density of active sites, called the dispersion, on the catalyst surface. Another is the relative activity among several catalysts for promoting particular chemical reactions such as hydrodesulfurization, hydrogenation, oxidation, and the like.Still another is catalyst poisoning by impurity deposition. And finally, the degradation with time of use of a heterogeneous catalyst can be established by chemisorption tests. More information about these uses is given subsequently.

Heterogeneous catalyst dispersion is especially important in the economics of any catalytic process. Active sites usually are formed by one or more of the noble metals. A platinum-alumina catalyst, for example, typically contains from 0.5 to 1.0% by weight platinum, which is by far the most expensive component. If sufficient site density, or dispersion, is attained with the lesser value, then the catalyst cost is essentially one-half what it otherwise would be. Dispersion information is also of great importance to any scientist wishing to follow the kinetics of a catalytic reaction. The number of active sites as measured with different gases gives a relative measure of the activity of a catalyst for different reactions.

The technical definition of dispersion D is the ratio of active metal atoms exposed on the catalyst surface N_{Active} to the total number of metallic atoms incorporated in the catalyst N_{Total}, i.e.,

$$D = \frac{N_{Active}}{N_{Total}}$$

Chemisorption testing reveals N_{Active}. The totality of metal atoms N_{Total} has to be computed from knowledge of the mass of metal incorporated in the catalyst.

Other techniques, such as X-ray diffraction, electron spectroscopy for chemical analysis (ESCA) and electron microscopy, are quite valuable in evaluating catalysts. One advantage of utilizing chemisorption is the lower price of the equipment, hence low cost per analysis. A primary advantage, however, is that chemisorption involves only the surface layer where actual chemical reactions take place. The other techniques either analyze multiple surface layers or cannot focus strictly on the active sites.

Prequalification of a heterogeneous catalyst for a particular use and the selection of potentially useful catalysts from among several possibilities are truly jobs for chemisorption. Topsoe, *et al* (1), for example, studied the activity of bimetallic catalysts such as $CoMo/Al_2O_3$ in relation to thiophene conversion reactions. The chemisorption technique was employed using NO. Other chemisorption studies (2-7) employed O_2 and MoO_3/Al_2O_3 catalysts.The amount of chemisorbed O_2 correlated well with catalytic activity for the propylene hydrogenation reaction. Ramachadran and Massoth (8) used the chemisorption of CO in evaluating the dibenzothiophene hydrodesulfurization reaction by reduced $CoMo/Al_2O_3$catalysts.Other researchers such as Yunes, *et al* (9), have shown that there is a very good correlation between the chemisorption of CO, NO, and O_2 and ESCA measurements. Here the unknown was the availability (relative surface exposure) of the Mo in a $CoMo/Al_2O_3$ catalyst to be employed in sulfidation and reoxidation reactions.

Catalysts inevitably undergo degradation with use, leading eventually to total deactivation. The phenomenon is sometimes due to coke formation and simple physical blockage; sometimes to active site poisoning due to such impurities as sulfur, iron, or vanadium in the feedstock; and sometimes to active site clustering as a result of temperature sintering. Chemisorption tests directly reveal the occurrence of any active site density changes, although, unfortunately, not the cause. Using a catalyst after its effectiveness has decayed beyond some point is wasteful of both processing time and raw materials. Periodic chemisorption testing supplies a key bit of the information needed to devise the optimum economical schedule for catalyst replacement or regeneration.

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B RELATIVE THERMAL CONDUCTIVITY OF GASES

Relative Thermal Conductivity of Gases

Name	Chemical Formula	Conductivity (Relative to Air)
Air		1.0
Ammonia	NH_3	0.92
Argon	Ar	0.68
Butane	C_4H_{10}	0.60
Carbon Dioxide	CO_2	0.62
Carbon Monoxide	CO	0.97
Ethane	C_2H_6	0.79
Helium	He	5.84
Hydrogen	H_2	7.07
Krypton	Kr	0.37
Methane	CH_4	1.29
Neon	Ne	1.87
Nitric Oxide	NO	0.99
Nitrogen	N_2	1.00
Nitrogen Dioxide	NO_2 or N_2O_4	1.51
Nitrous Oxide	N_2O	0.65
Oxygen	O_2	1.02
Sulfur Dioxide	SO_2	0.38
Water Vapor	H_2O	0.67

C PHYSISORPTION THEORY

Physisorption Theory

One form of the well-known BET equation(1) that describes the adsorption of a gas upon a solid surface is

$$\frac{\frac{P}{Po}}{V\left[1-\frac{P}{Po}\right]} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\left(\frac{P}{Po}\right) \qquad (1)$$

where

V = the volume (at standard temperature and pressure, STP) of gas adsorbed at pressure P

Po = the saturation pressure which is the vapor pressure of liquified gas at the adsorbing temperature

V_m = the volume of gas (STP) required to form an adsorbed monomolecular layer

C = a constant related to the energy of adsorption

The surface area S of the sample giving the monolayer adsorbed gas volume V_m(STP) is then calculated from

$$S = \frac{V_m A}{mM} \qquad (2)$$

where

N = Avogadro's number which expresses the number of gas molecules in a mole of gas at standard conditions

m mass of sample

M = the molar volume of the gas

A = the area of each adsorbed gas molecule

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1 Brunauer, S., Emmet, P.H., and Teller, E., *J. Am. chem. Soc. 60*, 309A (1938)

Single-point Surface Area

The constant C of equation 1 is typically a relatively large number, i.e., C>1, from which equation 1 reduces very nearly to

$$\frac{\frac{P}{Po}}{V\left[1-\frac{P}{Po}\right]}=\frac{1}{V_m}+\left[\frac{1}{C}+\frac{P}{Po}\right] \tag{3}$$

Now if P/Po>>1/C, equation 3 can be further represented by

$$\frac{\frac{P}{Po}}{V\left[1-\frac{P}{Po}\right]}=\left(\frac{1}{V_m}\right)\left(\frac{P}{Po}\right) \tag{4}$$

which rearranges to

$$V_m= V\left[1-\frac{P}{Po}\right] \tag{5}$$

Another way of arriving at the same result is by recognizing that the term $1/(V_m C)$ of equation 1 is generally small. Taking it as insignificant changes the slope, and hence the value of V_m and the sample surface area as calculated by equation 2, only a small amount. Equation 1 can be rearranged with the contribution of the intercept term taken to be vanishingly small to also yield equation 5.

Substituting equation 5 into equation 2 yields

$$S= VAN\left[\frac{1-\frac{P}{Po}}{M}\right] \tag{6}$$

from which the sample surface area is readily determined once the volume V of gas adsorbed (or desorbed, which must theoretically be identical) is measured and appropriate values for the other terms are incorporated.

For nitrogen gas adsorbed from a mixture of 30 mole % nitrogen and 70 mole % helium using a liquid nitrogen bath, the values are arrived at as follows:

The volume V of gas with which the instrument is calibrated is injected at ambient temperature and atmospheric pressure. This volume must thus be multiplied by the ratios 273.2/(Rm. Temp., K) x (Atm. Press., mmHg)/760 to convert it to standard conditions (0 ^{o}C and 760 mmHg).

Avogadro’s number N is 6.023 x 10^{23} molecules/g-mole.

The molar volume M of a gas at standard conditions is 22414 cm^3/g-mole.

The presently accepted value for the area N of a solid surface occupied by an adsorbed nitrogen molecule$^{(2)}$ is 16.2 x 10^{-20} m^2 (=16.2 Angstroms^2).

P is 0.3 x the atmospheric pressure in millimeters of mercury since the gas mixture is 30% nitrogen and adsorption takes place at atmospheric pressure. Po, the saturation pressure of liquid nitrogen is typically a small amount greater than atmospheric due to thermally induced circulation, dissolved oxygen, and other factors. With fresh, relatively pure liquid nitrogen, the saturation pressure is typically about 15 mmHg greater than atmospheric pressure. It can be 40 to 50 mmHg greater if the liquid nitrogen is relatively impure. The saturation pressure should be determined by other means in the latter event.

The result for a 30% N_2/70% He mixture adsorbed at liquid nitrogen temperature when room temperature is 22 ^{o}C and atmospheric pressure is 760 mmHg is the expression

$$S= v\left[\frac{273.2}{\text{Rm. Temp.}}\right]\left[\frac{\text{Atm. Press}}{760}\right]\left[\frac{6.023 \times 20^{23} \times 16.2 \times 10^{-20}}{22.414 \times 10^{3}}\right] \tag{7}$$

$$\left[\frac{(1- \%N_2 / 100) \times \text{Atm. Press.}}{\text{Sat. Press.}}\right]= v\cdot \text{constant}$$

where S is the surface area in square meters.

For calibration purposes, this means that a syringe injection of V = 1.00 cm^3 of nitrogen at 22 ^{o}C and 760 mmHg should produce an indicated surface area of 2.84, assuming the saturation pressure is 775 mmHg.

The value of S from equation 7 changes when ambient conditions differ significantly from 22 ^{o}C and 760 mmHg, pressure changes having relatively more effect than temperature. Another value should then be calculated. For example, suppose the gas were 29.33% N_2, the laboratory were at 22 ^{o}C, atmospheric pressure were 710 mmHg, and the saturation pressure were measured to be 735 mmHg, the value, instead of being 2.84, should be 2.67.

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2 Roberts, B. F., *J. Coll. Interface Sci. 23*, 266 (1967).

Multipoint Surface Area

A straight line usually results between P/Po values from about 0.05 to 0.25 when experimental data are plotted as (P/Po)/V[1-(P/P0)] on the ordinate against P/Po as the abscissa. Relative pressures within this prescribed range are typically obtained with gas compositions between about 5% and 25% N_2 with the remainder He. Equation 1 shows then that the slope and intercept of this line are, respectively, $(C-1)/V_mC$ and $1/(V_mC)$ and that both the values of V_m and C can be determined

The instrument is calibrated by injecting into it an accurately measured volume of each gas mixture at ambient conditions, calculating the volume of this gas at standard conditions, and setting the instrument to indicate thereafter adsorbed and desorbed gas volumes at standard conditions. When 1 mL of gas mixture is injected, its volume V at STP is given by

$$V = 1.00 \times \frac{273.2}{\text{Rm. Temp}} \times \frac{\text{Atm. Press.}}{760} \tag{8}$$

The sample specific surface area S in square meters per gram is calculated from equation 2 using appropriate constants and slope and intercept values once the plot is made. Using the constants given above, this relationship becomes

$$S = 6.023 \times 10^{23} \times 16.2 \times \frac{10^{-20}}{22414(\text{slope} + \text{intercept})} \tag{9}$$

or simply

$$S = \frac{4.353}{\text{slope} + \text{intercept}} \tag{10}$$

Total Pore Volume

The scientist, L. Gurvitsch(3), noted many years ago that the volume of liquid condensed in the pores of a porous solid from a condensible gas near its saturation vapor pressure is equivalent to the volume of the pores. This finding is now generalized into the "Gurvitsch Rule" and restated to apply typically at 0.95 relative pressure, a mass of data having accumulated confirming the general validity of the rule. (Some users prefer 0.98 relative pressure.) A total pore volume measurement with the instrument thus requires determining the volume of gas which, condensed as a liquid, is extracted by a sample from a 95-98% N_2/5% He gas mixture at liquid nitrogen temperature.

It must be noted that this technique, as well as all other gas-based measures of pore volume, does not distinguish between the gas condensed within pores and that adsorbed on surfaces external to the pores. The assumption is merely made that the adsorbed gas quantity is small relative to that condensed. Such an assumption is quite good with moderately-to-highly porous catalysts and adsorbents that are the primary materials for which pore volume is an important physical property.

The volume of gas with which the instrument is calibrated must first be converted to standard conditions and then to its equivalent liquid volume. A factor of 100 is included in the computation to permit entry of all significant figures into the instrument. The molar volume of liquid nitrogen is 34.670 cm^3 and gaseous nitrogen 22414 cm^3 which is a ratio of 0.00155. Designating the calibrating gas volume by v, the equivalent total pore volume V_{tp} is thus

$$V_{tp} = \frac{273.2}{\text{Rm. Temp}} \times \frac{\text{Atm. Press.}}{760} \times 0.00155 \times 100 \times v \tag{11}$$

This value of V_{tp} is inserted into the ChemiSorb as the calibrating factor.

A result subsequently obtained with a sample, divided by 100, is the total volume of pores in the sample in whatever units the original calibrating gas volume was measured. A syringe containing 10 cm^3 (=v) at ambient conditions is recommended which results in a total pore volume measured in cubic centimeters. Dividing the total pore volume (cm^3) by sample weight (g) yields the specific total pore volume (cm^3 /g).

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3 Gurvitsch, L., *J. Phys. Chem. Soc.* Russ. 47, 805 (1915).

D CALCULATIONS

Volume of Active Gas Injected From a Syringe

$$V_{inj} = V_{syr} \times \frac{T_{std}}{T_{amb}} \times \frac{P_{amb}}{P_{std}} \times \frac{\%A}{100\%} \tag{D-1}$$

where:

V_{syr}	=	syringe volume injected	________	cm^3
T_{amb}	=	ambient temperature	________	°C
T_{std}	=	standard temperature	273	K
P_{amb}	=	ambient pressure	________	mmHg
P_{std}	=	standard pressure	760	mmHg
%A	=	% active gas	________	%
RESULT				
V_{inj}	=		________	cm^3

Example: Volume Injected Using 10% Active Gas

V_{syr}	=	syringe volume injected	0.5	cm^3
T_{amb}	=	ambient temperature	22	°C
T_{std}	=	standard temperature	273	K
P_{amb}	=	ambient pressure	743	mmHg
P_{std}	=	standard pressure	760	mmHg
%A	=	% active gas	10	%

$$V_{inj} = 0.5\,cm^3 \times \left(\frac{273K}{22 + 273K}\right) \times \frac{743mmHg}{760mmHg} \times \frac{10\%}{100\%} = 0.0453\,cm^3$$

Calculating Volume Chemisorbed

$$V_{ads} = \frac{V_{inj}}{m} \times \sum_{i=1}^{n} \left(1 - \frac{A_i}{A_f}\right) \qquad \text{D-2}$$

where:

V_{inj} = volume injected ________ cm^3

m = mass of sample ________ g

A_i = area of peak i ________

A_f = area of last peak ________

RESULT

V_{ads} = ________ cm^3

Example: CO Chemisorption on 0.5 wt % Platinum on Alumina

V_{inj} = volume injected 0.0453 cm^3

m = mass of sample 1 g

A_f = area of peak last peak 0.00648

Peak	A_i	$1-A_i/A_f$	V^i_{ads}	ΣV^i_{ads}
1	0	1	0.0453	0.0453
2	0	1	0.0453	0.0906
3	0.00024	0.9300	0.0436	0.1342
4	0.00113	0.8256	0.0374	0.1716
5	0.00518	0.2006	0.0091	0.1807
6	0.00609	0.0602	0.0027	0.1834
7	0.00639	0.0138	0.0006	0.1840
8	0.00638	0.0154	0.0006	0.1847
9	0.00648	0	0	0.1847

$$V_{ads} = 0.1847 cm^3/g$$

% Metal Dispersion

$$\%D = S_f \times \frac{V_{ads}}{V_g} \times \frac{m.w.}{\%M} \times 100\% \times 100\% \tag{D-3}$$

where:

S_f	=	stoichiometry factor	________	
V_{ads}	=	volume adsorbed	________	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
m.w.	=	molecular weight of the metal	________	a.m.u.
%M	=	% metal	________	%
RESULT				
%D	=		________	%

Example: % Dispersion of 0.5 wt % Platinum on Alumina

S_f	=	stoichiometry factor, CO on Pt*	1	
V_{ads}	=	volume adsorbed	0.1803	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
m.w.	=	molecular weight of the metal	195.078	a.m.u.
%M	=	% metal	0.5	%

*Typical stoichiometry factors: 2 for H_2 on most metals and 1 for CO on Pt.

$$\%D = 1 \times \left(\frac{0.1803\,cm^3/g}{22414\,cm^3/mol} \right) \times \left(\frac{195.078}{0.5\%} \right) \times 100\% \times 100\% = 31.4\%$$

Active Metal Surface Area (per gram of sample)

$$MSA_s = S_f \times \frac{V_{ads}}{V_g} \times N_A \times \sigma_m \times \frac{m^2}{10^{18} nm^2} \qquad \text{D-4}$$

where:

S_f	=	stoichiometry factor	________	
V_{ads}	=	volume adsorbed	________	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
N_A	=	Avogadro's number	6.023×10^{23}	molecules/mol
σ_m	=	cross-sectional area of active metal atom	________	nm^2

RESULT

MSA_s = ________ m^2/g_{sample}

Example: Active Metal Surface Area (g/ sample) 0.5 wt % Platinum on Alumina

S_f	=	stoichiometry factor, CO on Pt	1	
V_{ads}	=	volume adsorbed	0.1803	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
N_A	=	Avogadro's number	6.023×10^{23}	molecules/mol
σ_m	=	cross-sectional area of active metal atom	0.08	nm^2

$$MSA_s = 1 \times \frac{0.1803 cm^3/g}{22414 cm^3/mol} \times \left(6.023 \times 10^{23} \frac{molecules}{mol}\right) \times 0.08 nm^2 \times \frac{m^2}{10^{18} nm^2} = 0.388 \frac{m^2}{g_{sample}}$$

Active Metal Surface Area (per gram of metal)

$$MSA_s = S_f \times \frac{V_{ads}}{V_g} \times \frac{100\%}{\%M} \times N_A \times \sigma_m \times \frac{m^2}{10^{18}nm^2} \qquad \text{D-5}$$

where:

S_f	=	stoichiometry factor, CO on Pt*	____________	
V_{ads}	=	volume adsorbed	____________	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
%M	=	weight percent of the active metal	____________	%
N_A	=	Avogadro's number	6.023×10^{23}	molecules/mol
σ_m	=	cross-sectional area of active metal atom	____________	nm^2
RESULT				
MSA_s	=		____________	m^2/g_{metal}

Example: Active Metal Surface Area (g/metal) of 0.5 wt % Platinum on Alumina

S_f	=	stoichiometry factor	1	
V_{ads}	=	volume adsorbed	0.1803	cm^3/g
V_g	=	molar volume of gas at STP	22414	cm^3/mol
%M	=	weight percent of the active metal	0.5	%
N_A	=	Avogadro's number	6.023×10^{23}	molecules/mol
σ_m	=	cross-sectional area of active metal atom	0.08	nm^2

$$MSA_m = 1 \times \frac{0.1803cm^3/g}{22414cm^3/mol} \times \frac{100\%}{0.5wt\%} \times \left(6.023 \times 10^{23}\frac{molecules}{mol}\right) \times 0.08nm^2 \times \frac{m^2}{10^{18}nm^2} = 77.52\frac{m^2}{g_{metal}}$$

Average Crystallite Size

$$d = \frac{F_g}{\rho \times MSA_m} \times \frac{m^3}{10^6 cm^3} \times \frac{10^9 nm}{m} \qquad \text{D-6}$$

where:

F_g = crystallite geometry factor (hemisphere = 6, cube = 5) _______

ρ = specific gravity of the active metal _______ g/cm^3

MSA_m = active metal surface area per gram of metal _______ m^2/g_{metal}

<u>RESULT</u>

d = _______ nm

Example: Average Crystallite Size of 0.5 wt % Platinum on Alumina

F_g = crystallite geometry factor (hemisphere = 6) 6

ρ = specific gravity of the active metal 21.09 g/cm^3

MSA_m = active metal surface area per gram of metal 77.52 m^2/g_{metal}

$$d = \frac{6}{21.09 g/cm^3 \times 77.52 m^2/g} \times \frac{m^3}{10^6 cm^3} \times \frac{10^9 nm}{m} = 3.67 nm$$

Calculations Summary Sheet

Sample:______________________________ T_{amb}:______________________ °C

mass:________________________________ P_{amb}:_____________________ mmHg

Date:________________________________

Volume Dosed

Equation D.1

$$\underset{V_{syringe}}{\boxed{}} \times \frac{273}{\underset{T_{amb}}{\boxed{}}} \times \frac{\overset{P_{amb}}{\boxed{}}}{760} \times \frac{\overset{\%\ \text{active}}{\boxed{}}}{100\%} = \underline{\qquad\qquad}$$

Volume Chemisorbed

Equation D.2

Peak	$\mathbf{A_i}$	$1-\frac{A_i}{A_f}$	$\frac{V_{inj}}{m} \times \left(1-\frac{A_i}{A_f}\right)$	$\sum\left(\frac{V_{inj}}{m} \times \left(1-\frac{A_i}{A_f}\right)\right)$
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				

RESULT

V_{ads} = ________________________ cm^3/g

% Metal Dispersion

Equation D.3

$$\underset{S_f}{\boxed{}} \times \frac{\overset{V_{ads}}{\boxed{}}}{22414} \times \frac{\overset{\text{m.w.}}{\boxed{}}}{\underset{\%M}{\boxed{}}} \times 100\% \times 100\% = \underline{}$$

Active Metal Surface Area (per gram of sample)

Equation D.4

$$\underset{S_f}{\boxed{}} \times \frac{\overset{V_{ads}}{\boxed{}}}{22414} \times 6.023 \times 10^{23} \times \overset{\sigma_m}{\boxed{}} \times \frac{m^2}{10^{18}\ nm^2} = \underline{}$$

Active Metal Surface Area (per gram of metal)

Equation D.5

$$\underset{S_f}{\boxed{}} \times \frac{\overset{V_{ads}}{\boxed{}}}{22414} \times \frac{100\%}{\underset{\%Metal}{\boxed{}}} \times 6.023 \times 10^{23} \times \overset{\sigma_m}{\boxed{}} \times \frac{m^2}{10^{18}\ nm^2} = \underline{}$$

Average Crystallite Size

Equation D.6

$$\frac{\overset{F_g = 6 \text{ or } 5}{\boxed{}}}{\underset{\rho_{metal}}{\boxed{}}\ \underset{MSA/g_{metal}}{\boxed{}}} \text{ x } \frac{m^3}{10^6 cm^3} \text{ x } \frac{10^9 nm}{m} = \underline{\hspace{3cm}}$$

Atomic Weights and Cross-Sectional Areas for Selected Materials

Metal	Symbol	Atomic Weight (g/mole) (m.w.)	Cross-Sectional Area (sq nm) (σ_m)	Density (g/mL) (ρ_{metal})
chromium	Cr	51.996	0.0635	7.19
cobalt	Co	58.933	0.0662	8.9
copper	Cu	63.546	0.0680	8.96
gold	Au	196.967	0.08696	18.9
hafnium	Hf	178.490	0.0862	13.3
iridium	Ir	192.220	0.0769	22.4
iron	Fe	55.847	0.0613	7.86
manganese	Mn	54.938	0.0714	7.43
molybdenum	Mo	95.940	0.0730	10.2
nickel	Ni	58.710	0.0649	8.8
niobium	Nb	92.906	0.0806	8.57
osmium	Os	190.220	0.0629	22.6
palladium	Pd	106.400	0.0787	12.0
platinum	Pt	195.090	0.0800	21.4
rhenium	Re	186.207	0.0649	21.0
rhodium	Rh	102.906	0.0752	12.4
ruthenium	Ru	101.070	0.0613	12.4
silver	Ag	107.868	0.0869	10.5
tantalum	Ta	180.947	0.0800	16.6
thorium	Th	232.038	0.1350	11.7
titanium	Ti	47.900	0.0741	4.54
tungsten	W	183.850	0.0741	19.3
vanadium	V	50.942	0.0680	6.11
zirconium	Zr	91.220	0.0877	6.51

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