

# **Pulse ChemiSorb 2705**

## **Operator's Manual**

**275-42801-01**

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## **Operator's Manual**

**275-42801-01  
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# **CHAPTER 1**

## **GENERAL INFORMATION**

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- Organization of the Manual
- Conventions
- Equipment Description
- Specifications

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## GENERAL INFORMATION

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This manual describes how to install and operate the Pulse ChemiSorb 2705.

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### Organization of the Manual

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The manual is divided into the following chapters:

**Chapter 1 - General Information.** Describes the components of the Pulse ChemiSorb 2705 System and lists its specifications.

**Chapter 2 - Installation.** Describes how to unpack, inspect, and install the Pulse Chemisorb 2705.

**Chapter 3 - General Operating Instructions.** Describes how to use the analyzer's front and rear panel controls.

**Chapter 4 - Performing Analyses.** Provides instructions for preparing samples and performing analyses.

**Chapter 5 - Troubleshooting.** Provides instructions for troubleshooting hardware problems.

**Appendix A - Chemisorption.** Describes the theory behind chemisorption analysis.

**Appendix B - Relative Thermal Conductivity of Gases.** Lists the relative thermal conductivity of gases.

**Appendix C - Physisorption.** Describes the theory behind physisorption analysis.

**Appendix D - Data Reduction Programs Using the IBM Personal Computer.** Provides results from a data reduction program.

**Appendix E - Other Gases and Compositions.**

**Appendix F - Sample Tubes.** Describes and pictures the various types of sample tubes used in 2705 analyses.

**Appendix G - Technical References.**

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## Conventions

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This manual uses the icons shown below to identify notes of importance, cautions, and warnings.



Notes contain information which will help you operate the instrument more effectively.



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



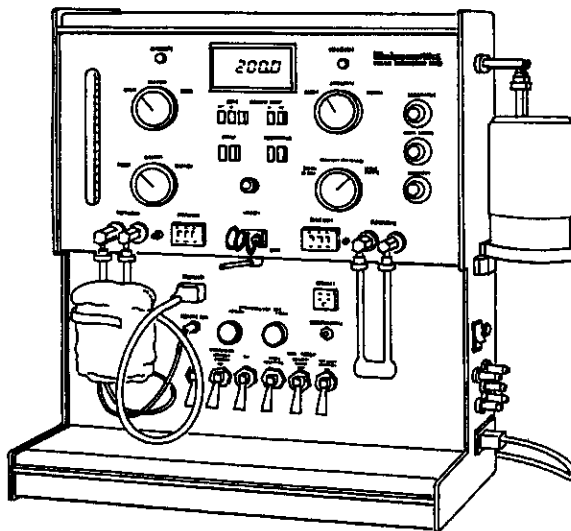
Warnings contain information to help you prevent actions which could cause personal injury.

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## Equipment Description

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The front and right side panels of the Pulse ChemiSorb 2705 are shown in the following illustration. A schematic diagram is shown in Figure 1-2. All operating controls, except the power switch, are on the front panel. Utility connections are on the lower right panel and exhaust ports are on the left panel.



*Figure 1-1. The Pulse ChemiSorb 2705*

The Pulse ChemiSorb 2705 provides an economical means for conducting either chemisorption or physisorption tests. In the former, a reactive gas is induced to bond with active sites on a catalyst surface at an elevated temperature. Measuring the amount of the gas so bonded permits determining active site density and dispersion of the active metal. Attaching the TPD/TPR 027 Option for the Pulse ChemiSorb to the unit permits it to perform temperature-programmed desorption, reduction, and oxidation analyses. The system also provides two locations — one before and one following its internal detector — for attachment of a mass spectrometer.

The surface area of catalysts, catalyst supports, or other unrelated solids can be determined with the unit through a physisorption (physical adsorption) test. In this test, a single molecular layer of an inert gas is formed on the surface of the catalyst, catalyst support, or solid. Surface area is then deduced from the quantity of gas required to form this monolayer. Total sample pore volume is established by continuing adsorption until condensed gas fills the pores at cryogenic temperature; the volume of the condensed liquid is then

equal to that in the pores. Pore volume distribution is determined near saturation.

Fuller development of the pertinent theory behind all operations of the Pulse Chemisorb 2705 is found in the Appendices.

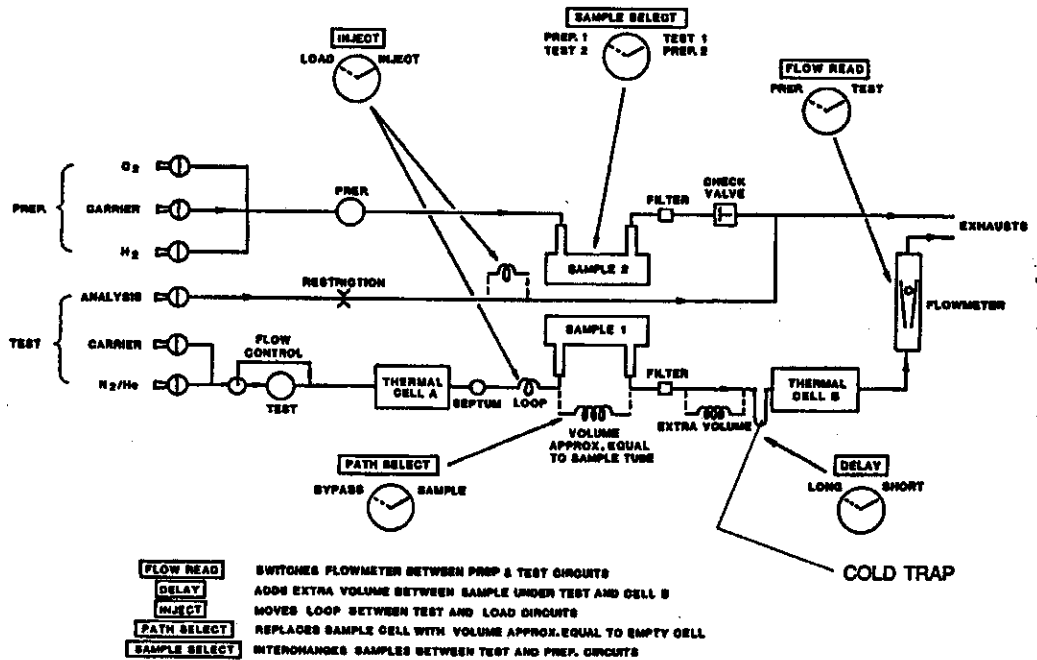


Figure 1-2. Schematic Diagram

## Specifications

| Characteristics                      | Specifications   |
|--------------------------------------|--|
| ————— SAMPLE PARAMETERS —————        |  |
| Minimum Active Volume:               | 0.001 cm <sup>3</sup>  |
| Maximum Active Volume                | Greater than 100 cm <sup>3</sup>                               |
| Minimum Active Specific Volume:      | 0.0001 cm <sup>3</sup> /g                                      |
| Maximum Active Specific Volume:      | Greater than 20 cm <sup>3</sup> /g                             |
| Minimum Surface Area:                | 0.2 m <sup>2</sup>   |
| Maximum Surface Area:                | 280 m <sup>2</sup>   |
| Minimum Specific Surface Area:       | 0.02 m <sup>2</sup> /g   |
| Maximum Specific Surface Area:       | Limited only by weighing accuracy of smallest sample           |
| Pore Volume                          |  |
| Minimum:                             | 0.0001 cm <sup>3</sup>   |
| Maximum:                             | 0.15 cm <sup>3</sup>   |
| Sample Holder volume:                | 1 cm <sup>3</sup> standard; larger and smaller sizes available |
| Throughput:                          |  |
| Active Volume:                       | Depends on injection steps; typically 1 to 2 hrs per sample    |
| Surface Area:                        | Typically 30 min per sample                                    |
| Total Pore Volume:                   | Typically 45 min per sample                                    |
| Preparation Temperature:             | 35-500°C with quartz mantles                                   |
| ————— ACCURACY/REPRODUCIBILITY ————— |  |
| Active Volume:                       |  |
| Low and Moderately Low:              | Typically better than ± 2.0% 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         |
| Pore Volume:                         | Typically better than ±3%                                      |

| Characteristic                                  | Specification  |
|---|--|
| <b>UTILITIES/SUPPLIES</b>                       |  |
| Accommodates to standard power mains worldwide. |  |
| Voltage:  | 100, 120, 220 or 240 VAC $\pm$ 10%   |
| Current:  | 1.4 A (100/120 VAC);<br>0.8 A (220/240 VAC)  |
| Frequency:                                      | 50/60 Hz   |
| Gases:  |  |
| Active:   | Hydrogen, oxygen, carbon monoxide, sulfur dioxide, ammonia, nitrous oxide, etc.  |
| Inactive:                                       | Helium, argon, nitrogen, etc.  |
| Surface Area and Pore Volume:                   | Helium, nitrogen, and mixtures thereof   |
| Coolant (Surface Area and Pore Volume):         | Liquid nitrogen recommended  |
| <b>EXPOSED MATERIALS</b>                        |  |
| To Active Gases:                                | Stainless steel, borosilicate glass, Buna-N, tungsten, fluorocarbon-filled polyimide (injection loop valve seal), PEEK (Poly Ether Ether Ketone) |
| To Inactive Gases:                              | Copper, brass, stainless steel, borosilicate glass, Buna-N, tungsten   |
| <b>ENVIRONMENT</b>                              |  |
| Temperature:                                    | 15-32°C (59-90°F) operating;<br>0-50°C (32-122°F) storage and shipping   |
| Humidity:                                       | 20-80% relative (non-condensing)   |
| <b>CABINET</b>                                  |  |
| Dimensions:                                     | 46.5W x 53H x 30.5D cm<br>(18.3W x 20.9H x 12D in.)  |
| Color:  | Beige with brown panels and rust highlights  |
| Weight:   | 20 kg (44 lbs)   |

## **CHAPTER 2**

### **INSTALLATION**

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- Visual Inspection
- Selecting the Location
- Electrical Requirement
- Gas Supply
- Cold Bath
- Strip-Chart Recorder
- Sample Attachment and Selection





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## INSTALLATION

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### Visual Inspection

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The Pulse ChemiSorb 2705 and its accessories should be visually inspected as soon as unpacked to ensure that all items have been received and none has sustained physical damage. The carrier and your local Micromeritics representative, or the factory, should be notified immediately if shipping damage is found. An inspection report must be obtained from the carrier for insurance purposes.

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### Selecting the Location

---

The instrument performs best in a regulated temperature environment. It should be installed on a workbench 75 to 90 cm (30-36 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 on it.

Provide working space of at least a square meter (10 ft<sup>2</sup>) of free space to one side and leave a clearance of a few centimeters to the rear of the instrument. Ready access to an analytical balance capable of weighing 50 g with 1-mg resolution 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 cylinders will be necessary. Nearby location of a strip-chart recorder can be helpful.

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## Electrical Requirement

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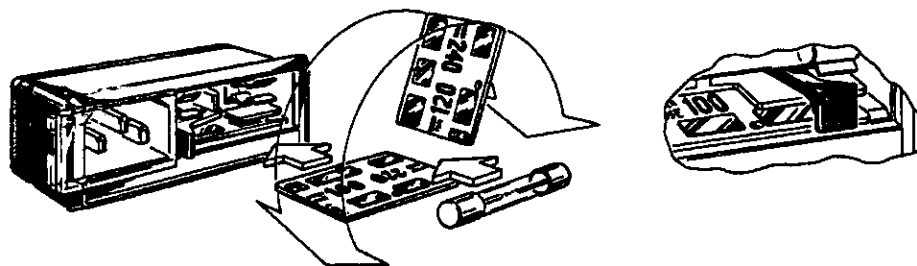
The Pulse ChemiSorb utilizes either 100, 120, 220, or 240 VAC at 50/60 Hz, selectable by means of a universal power connector located low on the right panel. Current requirements are 1.4 A maximum at supply voltages of 100 or 120 VAC and 0.8 A maximum at supply voltages of 220 or 240 VAC.

All instruments leave the factory set for 120 VAC and with the line fuse removed. The correct setting of the universal power connector must be checked and the appropriate fuse installed before the unit can be operated.

Next to the power cord plug at its point of attachment in the right instrument panel is a small clear plastic window. Inside the window will be visible the number 120 since the instrument is set to operate with this voltage.

The supply voltage setting is readily changed. With the power cord unplugged from the instrument, slide the plastic cover to the left, and remove the small printed circuit card. Orient this card so that the appropriate voltage will be visible when the card is reinserted. Reinsert the printed circuit card. The fuse just above the card must also be appropriate for the voltage. Install a slow-blow fuse rated 2.0 A if the new voltage is either 100 or 120 VAC, and 1.0 A if the voltage is to be 220 or 240 VAC.

Finally, slide the plastic cover to the right and install the power cord. The following figure further defines the power selection process.



#### HOW TO SELECT OPERATING VOLTAGE

1. Open cover door and rotate fuse-pull to left.
2. Select operating voltage by orienting PC Board to position desired voltage on top left side. Push board firmly into module slot.
3. Rotate fuse-pull back into normal position and re-insert fuse into holders, using caution to select correct fuse value.

|          | Voltage   | Fuse Value       |
|----------|-----------|------------------|
| 50/60 Hz | 100 Volts | 2.0 A, Slow Blow |
|          | 120 Volts | 2.0 A, Slow Blow |
|          | 220 Volts | 1.0 A, Slow Blow |
|          | 240 Volts | 1.0 A, Slow Blow |

*Figure 2-1. Voltage and Fuse Selection*

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## Gas Supply

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A variety of gases may be used in chemisorption analysis. As a minimum, cylinders of hydrogen and oxygen will likely be desired for catalyst conditioning prior to analysis. One or more of the following additional gases — ammonia, nitric oxide, carbon monoxide, carbon dioxide, hydrogen sulfide, helium, or argon — will also be needed for analysis. Surface area measurement may be made quickly with a mixture of 30% nitrogen and 70% helium or with mixtures provided by a Dual Channel Flow Controller (P/N: 230-62806-00), operating from two separate cylinders of pure nitrogen and pure helium. Total pore volume measurement requires a premixed gas and a pure gas. Complete pore distribution evaluation requires either mixed gases produced by the Dual Channel Flow Controller or premixed gases.

Whatever the gas, 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. Some commercial regulators incorporate a lubricant that can migrate and contaminate downstream systems. These types must be avoided. Regulators suitable for most gases are available from Micromeritics. Refer to Product Bulletin No. 74 for more information on gas regulator choices. When requested, Micromeritics will recommend the appropriate regulator for the more reactive gases where its offering is not satisfactory. Micromeritics includes rolls of 1/8-in. copper tubing with fittings in the accessory kit. Do not use rubber or plastic tubing; both are susceptible to leaking, and the release of plasticizers into the gas stream can cause erratic results.

Some tests require the syringe injection of gas. This gas is conveniently supplied through a septum in the line between instrument and tank. One or more of these accessories (P/N: 230-25833-00) will be found very convenient.



**It is easy to overtighten metal tubing fittings. Doing so can collapse the tubing, damage the fitting, and cause a leak. Tighten each fitting by hand and then add one-quarter turn with a wrench.**

Micromeritics recommends the use of research grade gases. If unobtainable, the highest purity gas conveniently available will probably prove satisfactory for surface area and total pore volume determinations. Since the same gas is used 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  $-67^{\circ}\text{C}$  ( $-88^{\circ}\text{F}$ ) should be sought. Use of an external cold trap is mandatory when gas with a dew point of at least  $-67^{\circ}\text{C}$  ( $-88^{\circ}\text{F}$ ) is unavailable.

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

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## Cold Bath

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Liquid nitrogen is the most frequently used cryogen in surface area and total pore volume analyses. Provision for a source of supply and a suitably large storage reservoir must be provided by the user when these tests are anticipated.

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## Strip-Chart Recorder

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The detector-display of the Pulse ChemiSorb 2705 gives the integrated volume of each peak of a chemisorption titration, hence a plot of the peaks is unnecessary. However, a strip-chart recorder connected through the jack on the right side panel may be desired by some users. The recorder should be capable of responding to a signal of up to  $\pm 10$  V full scale from instruments with serial numbers above 200.

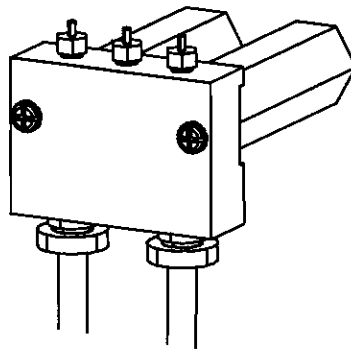
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## Sample Attachment and Selection

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Samples in any one of a variety of glass sample holders — hereafter called simply tubes — are attached at either of two places designated SAMPLE 1 and SAMPLE 2. The two stems of the tube are inserted into screw connectors which seal by means of compressed O-rings. To install a tube, first partially unscrew both connector nuts, push in the tube stems until a rigid stop is encountered, then tighten the connector nuts.

Each sample attachment component bears three connectors. Use these connectors with the TPD/TPR 027 Option unit or when you wish to connect a mass spectrometer directly downstream from the sample. The outermost connectors are plugged off in other tests.



*Figure 2-2. Preparing and Attaching Sample Tube to Analysis Port*

## **CHAPTER 3**

# **GENERAL OPERATING INSTRUCTIONS**

---

- Sample Attachment and Selection
- Gas Flow and Regulation
- Test Gas Injection
- Path Selection
- Delay
- Heating and Cooling
- Display
- Zeroing and Calibrating
- Cold Trap





## GENERAL OPERATING INSTRUCTIONS

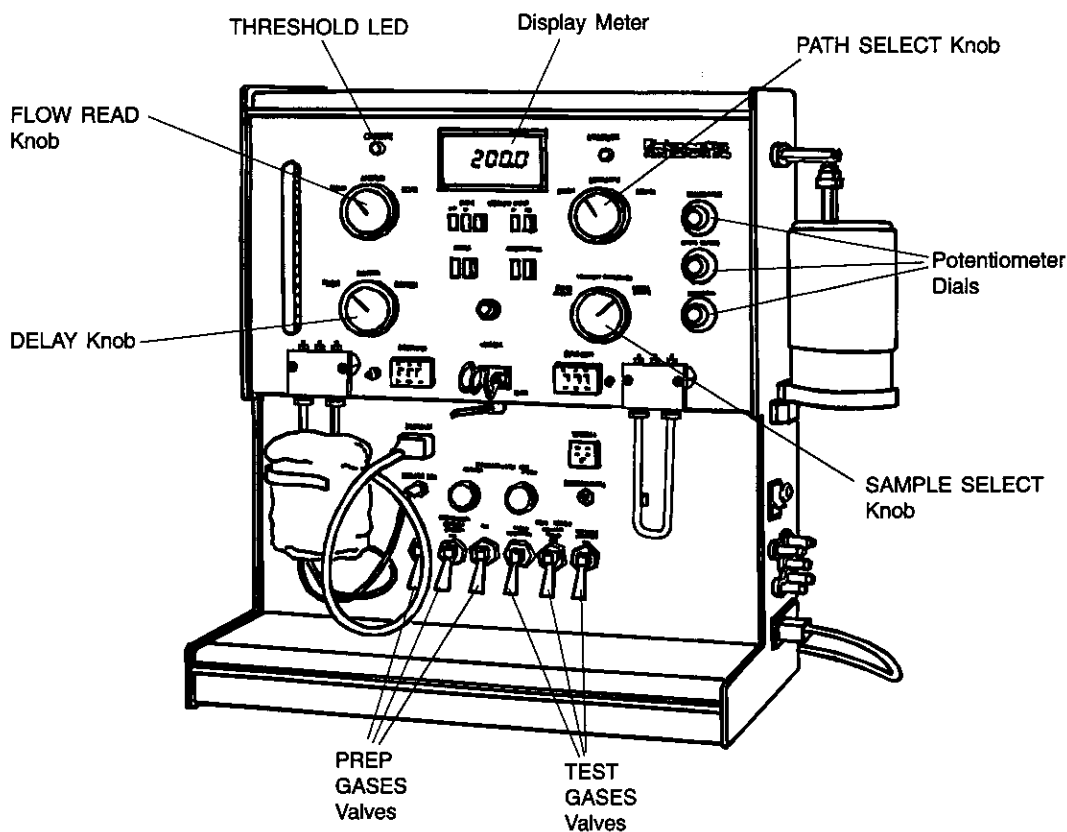


Figure 3-1. The Pulse ChemiSorb 2705

### Sample Attachment and Selection

The Pulse ChemiSorb is designed so that catalysts or other samples can be prepared and analyzed while remaining at one position. Samples thus not subjected to recontamination, which might occur if they were moved from a preparation port to an analysis port. The intention also is that one sample is prepared for analysis while another is evaluated. On initial start-up with two unprepared samples, a choice has to be made as to which will be prepared first. The SAMPLE SELECT knob, the lower right of the four large knobs, permits this choice. For example, if SAMPLE 2 is selected for initial preparation, SAMPLE 1 could be analyzed if it were ready. Turning the SAMPLE SELECT knob to PREP.1/TEST 2 after the sample at SAMPLE 2 has been readied starts the normal, intended sequence of operations.

---

## Gas Flow and Regulation

---

Valves for turning gases on and off are arranged in a row low on the front panel. Gas flow occurs when a handle is lifted to point horizontally outward; "flow off" requires the handle to aim downward. Two flow rate adjustment control knobs are centrally located just above the on-off valves, and a flow rate indicator is at the upper left. The on-off valves and adjustment controls are designated either PREP. or TEST. The flow rate indicator responds to either of these two categories as selected by the large, upper left knob labeled FLOW READ, i.e., the flow rate of a preparation gas is indicated when this knob is on PREP. and of a test gas when on TEST. Gas flow continues and the flow adjustment controls are operational irrespective of which particular flow category is being indicated.

The numbers on the flowmeter are for reference only as it responds somewhat differently to each gas used. Mid-scale, however, corresponds approximately to 30 cm<sup>3</sup>/min.

The flowmeter indicates the combined ANALYSIS (ACTIVE) and PREP. gas flows when the FLOW READ knob is set to PREP.

---

## Test Gas Injection

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Centrally located on the front panel are two means for injecting a controlled quantity of test gas, a septum, and a loop. Use of the septum requires a precision syringe with needle. The syringe needle (P/N: 004-61602-01) should have a side-entry port for maximum septum (P/N: 004-32602-00) life. Only the gas labeled ANALYSIS (ACTIVE) is injected by means of the loop. The loop is filled when the ANALYSIS (ACTIVE) on-off valve is on and the loop handle is to the left. The contents of the loop are inserted into the carrier gas stream when the handle is shifted to the right. Loop volume changes are accomplished by changing the size of the loop. Loops having volumes of approximately 50, 100, 200, 500, and 1000  $\mu$ L (P/N's: 270-62800-00, -01, -02, -05, and -10, respectively) are included as accessories. Each loop is attached by two readily accessible nuts.

---

## Path Selection

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The large knob at the upper right designated PATH SELECT serves to pass to the detector system either the gas stream coming from the sample undergoing a test or the gas stream from the septum and loop. Ordinarily, this knob will be on SAMPLE. However, the knob should be set on BYPASS to calibrate or to determine the volume of a loop.

---

## Delay

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The large knob at the lower left labeled DELAY, when turned to LONG, adds an extra volume in the gas system downstream of the sample under test. This extra volume is needed only in physisorption investigations. It serves to delay the arrival of desorbed gases at the detector system long enough for the flow rate to recover from the rapid desorption of adsorbed gases created by removal of the cryogenic liquid.

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## Heating and Cooling

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Sample heating is accomplished with a mantle mounted about the sample tube and plugged into the nearby outlet for power and with its thermocouple connector inserted into the jack just below for temperature control. The mantle is held securely about the sample tube with a clip pushed laterally around the mantle. The push button selector designated TEMP. SET (1 or 2) permits selecting mantle temperatures up to 500°C. The mantle will not heat unless the thermocouple is plugged into the jack. The LED (light emitting diode) beside the temperature selector alternates on and off showing power is being applied to attain or hold the desired temperature. Quartz mantles must be used to attain 500°C safely.

The display meter (upper center of front panel) registers the mantle temperature when the push buttons immediately below labeled TEMP. 1 and TEMP. 2 are pressed. The 1, of course, refers to SAMPLE 1 and the 2 to SAMPLE 2. A flashing display indicates a sample temperature beyond the 500°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 either sample tube. A beaker of water may suffice to achieve near room temperature conditions. A Dewar is required for cryogenic liquids. A simple stand of bent sheet metal provides a platform of about 5 cm (2 in.) height and is included in the accessory kit to hold the liquid container well up and about the sample. Slide the stand under the container once it has been brought up about the sample.

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## Display

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The display meter in the upper center of the front panel indicates sample temperature as noted above. It indicates the detector output signal when the DET. push button immediately below is pressed. When the instrument is calibrated as described in Chapter 4, it indicates one of the following:

- The integrated peak area of injected gas passing the catalyst under test
- The total surface area of a sample in a mixed gas BET evaluation
- The volume of adsorbed or desorbed gas in a multipoint surface area or pore volume test

The LED indicator labeled THRESHOLD to the left of the meter indicates by its flashing when signals greater than the threshold level are being accumulated. The faster the flashing the greater the magnitude of the signal. The system is set to begin indicating the accumulation of signals at a positive detector output of between 6 and 7 mV (maximum signal of 10 V) with the push button directly below the meter labeled X1 depressed. It stops indicating when the signal falls to between 3 and 4 mV. When the X10 push button is selected, the corresponding voltages are 10 and 11 mV and 8 and 9 mV. Negative polarities are never integrated.

Whether the display indicates a positive or a negative signal when detecting gas composition depends on the relative thermal conductivities of the carrier and analysis gases. When the analysis gas is more conducting than the carrier gas, pressing the +REL.COND. push button below the meter results in a positive display. Alternately, when the analysis gas is the poorer conductor, selecting the -REL.COND. push button gives a positive display. **Appendix B** lists the relative conductivities of a number of gases.

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## Zeroing and Calibrating

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The three potentiometric dials arranged vertically to the right on the front panel are, as their designations indicate, for zeroing and calibrating the instrument. Details of their use are given in Chapter 4.

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## Cold Trap

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As noted in Chapter 4, surface area and total pore volume determinations can be significantly altered by water vapor in a mixed gas such as nitrogen and helium. Gas with a specified dew point of  $-67^{\circ}\text{C}$  ( $-88^{\circ}\text{F}$ ) or lower is desirable.

Total pore volume and pore area and volume distribution tests require essentially pure nitrogen gas. A bath of liquid nitrogen and isopropyl alcohol ( $\text{LN}_2/\text{IPA}$ ) is recommended in this case. The temperature of such a bath ( $-80^{\circ}\text{C}$ ) is sufficiently low to remove water vapor but not nitrogen.



## **CHAPTER 4**

### **PERFORMING ANALYSES**

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- Introduction
- Intended Use and Precautions
- Chemisorption
- Physisorption
- Shutdown





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## PERFORMING ANALYSES

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### Introduction

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The Pulse ChemiSorb 2705 permits making a variety of measurements and you may be interested in performing only some of these. If so, you may not need to become familiar with the entire remainder of this manual. It is written with separate sections for each type of test with reference made to other tests where appropriate. Shortened, step-by-step guides are also provided that are intended to prompt an operator once basic familiarity with the instrument and the test to be performed is gained.

Each section presumes that appropriate electric power, gas sources regulated to required pressures, exhaust gas take-off lines, a recorder, and the like, are attached as specified previously. Necessary accessories and supplies, such as heating mantles, extra sample tubes, or liquid nitrogen, are also taken as on hand. Further, each section assumes that power is turned on, samples are in place, and testing is ready to be initiated.

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### Intended Use and Precautions

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#### Intended Use

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The Pulse ChemiSorb 2705 measures the quantity of active sites on the surface of a catalyst. It measures this so-called active site dispersion by the technique of surface titration using any of a number of reactive gases such as ammonia, carbon dioxide, carbon monoxide, hydrogen, nitrous oxide, oxygen, and hydrogen sulfide.

If the TPD/TPR 027 Option is added to the Pulse ChemiSorb 2705, the system will perform temperature-programmed desorption, reduction, and oxidation analyses. The system detects TPD/TPR activity as changes in the concentration of a gas mixture flowing over a sample surface while the sample temperature increases linearly. During TPD analyses, pre-adsorbed chemisorptive gas desorbs from the surface at a critical temperature indicative of the strength and number of active sites on the surface of the sample. During TPR analyses, hydrogen is consumed by reducible species on the sample surface as a function of temperature and indicates the total surface area of the reactive metal.

You can attach a mass spectrometer either immediately downstream of the sample (see **Sample Attachment and Selection** in Chapter 3) or at the exhaust port of the instrument for more detailed analysis of reaction products.

The instrument also permits measuring the total surface area of catalysts as well as of any granular or powdered solid using an inactive gas like nitrogen. In addition, the total pore volume can be determined with the Pulse ChemiSorb.

The Temperature-Programmed Desorption/Temperature-Programmed Reduction (TPD/TPR) furnace and controller system is available as part number 027-00000-00. This option consists of a 1100°C furnace and a ramp and soak temperature controller. A built-in signal conditioner amplifies the 2705 bridge signal and the sample temperature thermocouple signal. Temperature ramps and TCD bridge signals can be plotted on a chart recorder.

## Precautions

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### General

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The potential for creating explosive conditions or hazardous atmospheres always exists where reactive gases are employed. Take time to consider the consequences of any situation before moving into it. Ask yourself these questions:

- What could happen if connections were not made completely or if a leak developed?
- Are the gases I'm using explosive in any proportions?
- Have I provided for adequate ventilation?
- Are there coworkers nearby to whom I can turn if the unexpected happens?
- Can extremely toxic gases such as carbonyls of metals be formed?

Gases are employed in quite small quantities in the Pulse ChemiSorb unit, but safety considerations must never be overlooked.

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 left side of the instrument as one faces it. Conduits should always be attached here to carry these streams to external vents or neutralizing devices. Also be sure an injection loop and both sample holders are securely in place before starting a test.

Sample preparation and analysis gas flows are carefully separated in the instrument so that the detectors will not be exposed to pure oxygen, for example, if gas sources are connected to the Pulse ChemiSorb 2705 in accordance with inlet port labels and prescribed procedures are followed. Be sure to adhere to these designations when connecting gases. It is to be noted that oxy-

gen can be employed as an analysis gas because the procedure permits it to be injected only in small quantities within an inert carrier gas.

For long-term stability, the Pulse ChemiSorb 2705 should be purged of oxygen from the atmosphere by flowing the inert carrier gas (TEST GASES) 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 are likely to 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. Remove water vapor from instruments with serial numbers less than 200 by positioning a Dewar of liquid nitrogen or other cryogen (such as isopropyl alcohol and liquid nitrogen) about the cold trap. On instruments with serial numbers above 200, remove water vapor by positioning the Dewar about a loop of the gas delivery tube before the tube enters the instrument. Be sure to use this cold trap unless there is no question of sufficient gas dryness.

Unplug the power cord before removing the rear panel for any reason. Connections carrying potentials as great as 240 V can be encountered inside.

## Dewar

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We recommend the following be observed when handling Dewars containing liquefied gases:

- Protect yourself by wearing 1) goggles (or a face shield), 2) an insulated or rubber apron, and 3) insulated gloves.
- When pouring liquefied gases from one container to another: 1) cool the receiving container gradually to minimize thermal shock, 2) pour the liquefied gas 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 liquefied gases (or other materials of extremely low temperature). Do not use a glass or metal stirring rod unless it is coated with some type of protective coating.

- Do not remove the mesh covering from the Dewar flask. This covering is in place to minimize the risk of flying particles if the Dewar is accidentally knocked over or dropped and broken.
- Do not handle heavy objects above the Dewar. If unavoidable, place a protective cover over the Dewar's opening. If an object of sufficient weight is accidentally dropped into the Dewar, shattering may occur.

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## Chemisorption

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### Sample Preparation and Set-Up

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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 opening the appropriate gas inlet valve, placing the FLOW READ knob on PREP., and adjusting the gas flow with the FLOW SET, PREP. valve.



CAUTION: Do not mix oxygen and hydrogen in the flowmeter. Oxygen and hydrogen combined in air and can release tremendous amounts of heat.

The DELAY valve should always be on SHORT during chemisorption work. Shift the FLOW READ valve to TEST, open the CARRIER (INERT), TEST gas valve, and adjust the gas flow to the desired rate using the FLOW SET, TEST valve. Note the gas flow rate because it is important to maintain it at the same value throughout the test. Once the flow rate is set, do not change the FLOW SET, TEST knob for the remainder of the test for that sample. Now press the DET. push button and set the display meter to zero using the COARSE and FINE ZERO dials. The FLOW READ valve should be left on TEST during sample heating to prevent possible moisture collection in the flowmeter.

The temperature is established by installing a heating mantle about the sample tube and setting the temperature with the TEMP. SET (1 or 2) register. If starting with two unprepared samples, first one and then the other is treated by shifting the SAMPLE SELECT valve as appropriate. Bring the sample to be tested to the desired temperature with the TEMP. SET register. The temperature is displayed by pressing the TEMP. and TEMP. 1 or 2 push buttons.

Fill the loop with analysis gas by being sure the INJECT lever is toward LOAD and opening the ANALYSIS gas valve for approximately 30 seconds. This flow is restricted to a relatively low value and is not adjustable. The exhausted analysis gas passes through the flowmeter when the FLOW READ knob is on PREP.; its rate is thus added to that coming from whatever preparation is underway and thus can be estimated if so desired. The analysis gas flow must be closed before injection to allow the pressure to equilibrate in the loop.

## Performing the Test

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Before starting the initial analysis, the pressure in the test loop must be at least 200 psig. Pressure less than 200 psig may cause the sample to be inadequately saturated, resulting in inaccurate initial determination of analysis.

Be sure the loop is loaded with analysis gas, the carrier flow rate is as set before, and the SAMPLE SELECT knob is oriented to TEST for the required sample. Press the display push buttons labeled PEAK AREA and X1 (X10 in some cases). Clear the display by pressing CLEAR DISPLAY. Set the CALIBRATE knob fully clockwise to gain maximum sensitivity. Now make the first injection to the catalyst sample by moving the INJECT lever from LOAD to INJ. If the sample chemisorbs the entire quantity of injected gas, there will be neither change in the display meter indication nor peak registered on an attached strip chart recorder. 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 loop if none of the injected gas is taken up by the sample. The desired situation, of course, is the uptake of all the analysis gas by the catalyst for at least the first few injections. 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 loop has been chemisorbed by the sample. Clear the display by pressing the CLEAR DISPLAY push button.

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 (and the peaks on any recording are identical, or nearly so). 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

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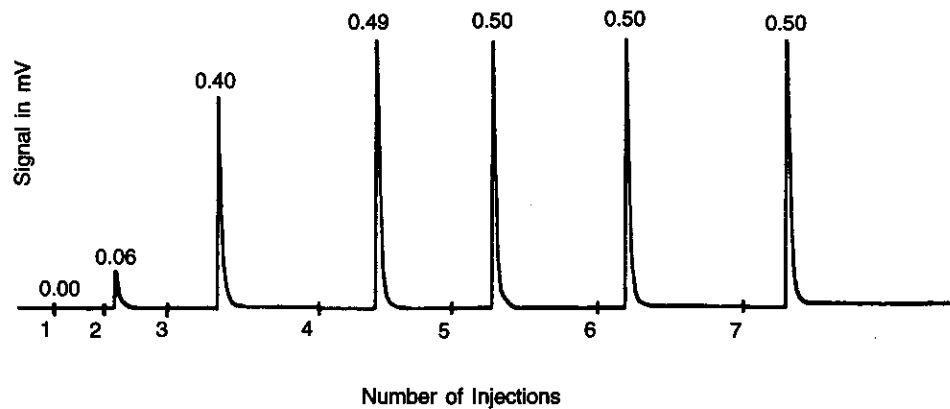
The complete record of results might be like that given in Table 4-1 and Figure 4-1. These particular results pertain to the chemisorption of hydrogen on a platinum-alumina catalyst. They were obtained using a loop with 0.0891 cm<sup>3</sup> of volume.

**Table 4-1. Chemisorption Data on Platinum-Alumina Catalyst**

| Injection Number | Quantity of Hydrogen Injected | Output 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                 |

\*Loop volume  
\*\*Peak area

The catalyst sample weighing 0.8353 g was first reduced at 450°C with a stream of hydrogen flowing over it at approximately 15 cm<sup>3</sup>/min for two hours. It was then cooled to 35°C in a stream of argon, and hydrogen injections were made at about three-minute intervals. The tests were conducted with the REL.COND.+ push button pressed. Ambient temperature was 22°C and atmospheric pressure was 740 mmHg.

**Figure 4-1. Recorded Chemisorption Peaks**



No more hydrogen was chemisorbed after the 4th injection. The latter display meter readings (0.50) indicate the peak area corresponding to the loop 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

$$k = \frac{0.0891}{0.50} = 0.1782$$

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

$$\begin{aligned} \text{1st inj., } 0.0891 - 0 &= 0.0891 \\ \text{2nd inj., } 0.0891 - (0.06 \times 0.1782) &= 0.0784 \\ \text{3rd inj., } 0.0891 - (0.40 \times 0.1782) &= 0.0178 \\ \text{4th inj., } 0.0891 - (0.49 \times 0.1782) &= 0.0018 \\ &\hline &0.1871 \text{ cm}^3 \end{aligned}$$

Converting this quantity to standard conditions of temperature and pressure yields

$$0.1871 \times \frac{273}{295} \times \frac{740}{760} = 0.1686 \text{ cm}^3 \text{ (STP)}$$

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 hydrogen molecule attaches to two platinum atoms, meaning there are twice the platinum atoms exposed as there are molecules of hydrogen sorbed. It is also generally assumed that the support on which platinum is dispersed does not sorb 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; the sample weighed 0.8353 g; the stoichiometric factor is 2; the atomic weight of platinum is 195.09 g/g-mole; one gram-mole of a gas at STP occupies 22414 cm<sup>3</sup>; and the volume of hydrogen chemisorbed was measured to be 0.1686 cm<sup>3</sup> STP. Thus

$$\text{Percent Dispersion} = \frac{0.1686 \text{ cm}^3 \times 195.09 \text{ g/gmole} \times 2}{0.8353 \text{ g} \times 22414 \text{ cm}^3/\text{gmole} \times 0.005} \times 100 = 70.3\%$$

This result means that 70.3% 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.

## **Establishing Loop Volume**

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Injection loops obtained from Micromeritics are labeled as to volume. They were calibrated on the injector of your instrument at a particular temperature and with a certain flow rate. Your conditions may be slightly different, so, for precise results, it may be advisable to re-calibrate them for your laboratory.

Whenever a loop is removed, reinstall it in the exact same orientation. The swaged ferrules on the connectors may be located at slightly different distances for the tubing ends because of injector machining differences. You might, for example, make sure the volume label on the loop can always be read as you face the instrument.

Small volume loop calibration may be conducted with the X10 range rather than the X1, provided the audible alarm does not sound, indicating amplifier saturation. The steps below apply to the X1 range, hence, when calibrating small loops using the X10 range, adjust the syringe to 0.10 cm<sup>3</sup> in Step 7 and adjust the display to 0.100 in Step 10.

1. Assuming the loop to be calibrated is properly installed, set the INJECT lever to LOAD.
2. Use helium as the carrier gas and establish flow at 1/4 to 1/2 of full scale on the flowmeter.
3. Use nitrogen as the active gas; open its valve so that it will be flowing through the loop while Steps 4 through 11 are being carried out.
4. Fill a 1-cm<sup>3</sup> syringe with nitrogen from an auxiliary septum connected to a nitrogen cylinder. Do not allow your hands to warm the syringe.
5. Press the DET. push button and adjust the display to zero with the ZERO knobs.
6. Press the PEAK AREA push button and clear the display with the CLEAR DISPLAY push button.

7. Adjust the syringe to exactly 1 cm<sup>3</sup>.
8. Press the DET. push button and inject the gas in the syringe into the septum just above the loop.
9. In a few minutes, the passage of a peak will occur. Wait for the display to return to zero.
10. Press the PEAK AREA push button and adjust the display reading to 1.00 using the CALIBRATE knob.
11. Clear the display by pressing the CLEAR DISPLAY push button.
12. Close the analysis gas valve and allow the pressure to equilibrate in the loop.
13. Press the DET. push button and inject the nitrogen in the loop by shifting the INJECT lever to INJ.
14. Again in a few minutes a peak will pass. Wait for the display to return to zero.
15. Press the PEAK AREA push button. The number on the display is the loop volume in cubic centimeters.

### **Abbreviated Step-By-Step Procedure**

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1. Prepare sample by reducing with hydrogen, or alternately oxidizing and reducing, at elevated temperature.
2. Set carrier gas flow rate.
3. Set display meter to zero.
4. Fill loop with analysis gas.
5. When sample is at desired analysis temperature, make first loop injection to sample. Record volume of gas chemisorbed.
6. Continue injecting gas and recording results until sample completes uptake.
7. Compute volume of chemisorbed gas, active site dispersion, etc.

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## Physisorption

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### Single Point Surface Area

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Surface areas measured by a single point physisorption determination are less precise than those established by the multipoint procedure but the saving in time and effort may justify the practice for many applications. Single point measurements are accomplished using a 30% N<sub>2</sub>/70% He gas mixture. Liquid nitrogen is the cryogenic liquid in most instances. Only nitrogen gas is physically adsorbed at liquid nitrogen temperature, the helium serving as an inert carrier.

As developed in **Appendix C, Physisorption**, 1.0 cm<sup>3</sup> of nitrogen gas at 22°C and 760 mmHg represents a single layer of nitrogen molecules physically adsorbed on a surface of 2.84 m<sup>2</sup>. Thus when the instrument is adjusted to indicate 2.84 m<sup>2</sup> of sample surface for every 1.0 cm<sup>3</sup> of gas adsorbed, it displays directly the total sample surface area. Small ambient temperature deviations from 22°C are relatively insignificant, but a value differing considerably from 2.84 may be more appropriate in some locations far removed from sea level elevation. This point is pursued further as appropriate in what follows.

### Calibration

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Before beginning calibration, ensure that:

- at least one empty sample holder is in place
- the SAMPLE SELECT knob is set to TEST for that location
- the DELAY knob is on LONG
- the PATH SELECT knob is on SAMPLE
- a Dewar of liquid nitrogen or other cryogen is positioned about a loop of the gas delivery tube if the dryness of the 30% N<sub>2</sub>/70% He gas is questionable.
- the N<sub>2</sub>/He gas is flowing such that the flowmeter indicates 16. (This value was selected because experience shows that it is most favorable for the majority of cases. Other components also have been adjusted to this condition. It is only important to the user because calibration and testing need to be conducted at identical conditions; this is the one chosen.)
- the DET., X1 and -REL COND. push buttons are pressed.

1. Fill the 1-mL precision syringe with nitrogen gas by holding the needle tip immediately above the level of liquid nitrogen in a Dewar, the evaporating liquid providing an atmosphere of pure nitrogen. Flush the syringe a few times to be sure of obtaining a proper fill. Wipe the needle tip free of accumulated frost and lay the syringe aside, perhaps on the rubber mat of the instrument, allowing the gas inside the syringe to reach room temperature.
2. Zero the instrument display using, as appropriate, the COARSE and FINE ZERO knobs. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved. The two primary factors leading to excessive instability are instrument warm-up, which may require up to 30 minutes after initial power application, and the progression of the residue from a previous analysis, which also can require as much as 10 minutes for elimination. Be sure these situations do not exist when setting the zero. Once set, the zero should not be readjusted unless a sustained change beyond  $\pm 0.02$  units occurs.
3. Press the PEAK AREA and the CLEAR DISPLAY push buttons.
4. Adjust the syringe to the 1-mL mark and insert the needle in the septum at INJECT, being sure to push it all the way in. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.

The Threshold light will begin flashing and the indicator will start accumulating surface area information after approximately 5 minutes. The rates of flashing will increase and then decrease. When the THRESHOLD light registers no flash for 15 to 20 seconds, which will typically occur after about 3 minutes, the accumulation may be considered complete. Another check for completeness is the number displayed when the DET. push button is pressed; it should be 0.02 or less.

The number displayed by the indicator with the PEAK AREA button pressed is now set with the CALIBRATE control knob beside the indicator to read the value for S as calculated using equation (7) of Appendix C. The value of S is 2.84 when room temperature is approximately 22°C, atmospheric pressure is near 760 mmHg, and a gas composition of 30% N<sub>2</sub> and 70% He is being used. The value of S can vary significantly for conditions considerably different from the above.

The instrument is now calibrated. Confirmation of calibration is established as deemed necessary by making repeat injections. Reproducibility should be within  $\pm 0.02$  units on the display meter.

## Sample Preparation

Surface areas can be measured reliably with a total sample surface of as much as 280 m<sup>2</sup> but results are both rapidly and accurately determined if sample quantity is adjusted to give 12.5 to 25 m<sup>2</sup>. Sample quantity should therefore be adjusted to fall in the vicinity of 12.5 to 25 m<sup>2</sup> when practical. This will likely not be possible 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 results as a specific surface area, i.e., in terms of square meters per gram. True weight is most reliably determined after the sample has been freed of whatever gases and vapors (most especially water vapor) it may have picked up from the atmosphere or from prior chemisorption tests. This means the weight is best established after the measurement is completed. The glass 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.

Except for the warning in the Intended Use and Precautions section against contaminated and decomposing materials that may give off corrosive or condensing vapors, sample pretreatment, or outgassing, is readily accomplished on the Pulse ChemiSorb. It is true, however, that samples which have been predried, perhaps in a vacuum oven, will clean up faster. Preconditioning of sample is recommended whenever possible.

Pour the powder to be analyzed into a dry, clean sample tube, being careful to leave some free space horizontally above the sample for the unimpeded flow of gas. Install the tube securely in a holder and attach the holder to the instrument at one of the connectors labeled SAMPLE (1 or 2). Set the SAMPLE SELECT knob so that PREP. 1 or 2 is selected as appropriate for the sample location.



Place a heating mantle about the sample tube and plug in both its power cord and thermocouple lead. Set the push button selector marked TEMP. SET (1 or 2) to the desired temperature. 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. switch and the appropriate TEMP. 1 or 2 push button.

Heating to the highest temperature consistent with the thermal stability of the sample gives the most rapid outgassing. In actual practice, degassing at 200 to 250°C for 15 to 20 minutes is often adequate. Some catalysts require higher temperatures and longer times.

Repetitively adsorbing and desorbing nitrogen 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, a series of tests may need to be conducted varying either time of treatment or temperature or, perhaps, both to establish degassing conditions.

There may be a tendency for a portion of some very fine, fluffy powders to be carried from the sample bulb by the gas passing over the sample. This problem can be overcome by one of a number of procedures. Since such a fine powder is likely to exhibit a comparatively great surface area, the quantity of sample can usually be reduced without penalty; this increases the free space above the sample and reduces the gas velocity over it. A bit of glass wool can be inserted in the exit stem of the glass sample tube to confine the sample; the exit stem is to the right as one faces an installed sample holder. Finally, the gas flow rate can be reduced; the only significant effect here is a lengthening of analysis time. Select a lower number on the flowmeter graduations, say 10, and adopt this as the standard mark. Note that both calibration and testing must still be carried out at the same flowmeter setting, viz. 10. Make the test in all other respects as before.

A liquid nitrogen and isopropyl alcohol slurry can be used about the cold trap to remove water vapor from the nitrogen gas if you suspect the nitrogen of being contaminated with water vapor. This slurry should be maintained by periodic, partial refreezing. Again, try to make these additions in the interval between a calibration run and a test or between tests.

## Performing the Test

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100% during the analysis and the multiplier is set on X1. If the multiplier is set on X10 and the sample is not adequately degassed, resulting in incomplete and premature termination of analysis.

Materials with unknown characteristics are always best tested with the multiplier set on X1. Only samples having less than 3.5 m<sup>2</sup> of surface area are advantageously tested with a setting of X10 and then primarily only when the sample is a slow desorber, perhaps due to long or tortuous passageways within the sample itself. Tests of excessively large surface area samples with the X10 push button pressed may overload the signal processing circuit and result in some error. Should this occur, a high-pitched audio tone will be heard above the normal clicking sound.

When the sample is deemed degassed, remove its heating mantle and shift the SAMPLE SELECT knob so that the sample is on TEST. Another sample can now be installed at the other sample connector. The position of the SAMPLE SELECT knob will automatically be such that the new sample is on PREP. Install a heating mantle about it and set its degassing temperature as described above. Wait for passage of the preparation gas if it is other than the test N<sub>2</sub>/He gas mixture. Clear the display by pressing the PEAK AREA and CLEAR DISPLAY push buttons.

Press the REL. COND. + push button. Raise a Dewar of liquid nitrogen about the sample just degassed. Put the bent metal stand under the Dewar to hold it well up about the sample tube. The level of liquid nitrogen should be maintained as nearly constant as possible about 2 to 4 cm (0.8 or 1.6 in.) below the Dewar lip. A further guide to proper liquid level is that frozen condensate does not build up on any metal portion of the sample holder. The liquid nitrogen/isopropyl alcohol slurry 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. Try not to add slurry 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 slurry in the cold trap is allowed to evaporate below the level of the cold trap tube. The same precautions are necessary for the external gas supply cold trap, when used.

The THRESHOLD light will begin blinking and the indicator will start accumulating data approximately 5 minutes after the cold bath is placed about the sample. The float of the flowmeter must have returned to its normal position before data accumulation begins, i.e., before the THRESHOLD light starts blinking. If it has not, the test will have to be repeated using a lesser quantity of sample.

In 5 or 10 minutes, this activity will subside. When the blinking is no more frequent than once in 15 to 20 seconds (or the indication with DET. pressed has returned to 0.02 or less), the adsorption of nitrogen gas may be safely considered complete. The value displayed may or may not be recorded as desired. It is the sample surface area in square meters as 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 when the reference potentiometer is properly adjusted as described in Appendix E. The desorption procedure may be dispensed with when this is found to be the case. Clear the display by pressing CLEAR DISPLAY in preparation for registering the desorption information. Press the REL. COND. - push button.



The desorption peak is now obtained by removing the Dewar of liquid nitrogen and bringing the sample to room temperature. Immersing the sample tube in a beaker of room temperature water is frequently appropriate. Special sample tubes such as those having ground glass joints must be warmed with care as they are more subject to stress development which can lead to breakage. Continue the warming procedure until the flowmeter float returns essentially to its normal level. As with adsorption, the THRESHOLD light will blink and the display accumulate for several minutes. It will be necessary to reduce the sample quantity and start again if the threshold light begins blinking before the float returns to its normal level. The value displayed is the sample surface area when THRESHOLD blinking is no more frequent than once every 15 to 20 seconds (or the DET. indication has returned to 0.02 or less). It should be recorded along with sample descriptive information and weight. The indicated number divided by the sample weight in grams is the sample specific surface in square meters per gram.

### **Abbreviated Step-By-Step Procedure**

The following condensed instructions are intended as a ready reference to guide operators who have gained familiarity with the Pulse ChemiSorb 2705 by following and understanding the detailed operating procedures given immediately above. A beginning operator may find them deficient.

### **Calibration**

1. Establish gas flow with empty sample tube in place.
2. Fill 1-mL syringe with nitrogen gas and lay aside.
3. Set on LONG DELAY.
4. Set REL. COND. to -.
5. Be sure flowmeter float level is as desired.
6. Press DET. and X1 push buttons.
7. After equilibration, zero display using COARSE/FINE ZERO.
8. Press PEAK AREA push button.
9. Clear peak area display.
10. Inject 1 mL of gas. Refill syringe if confirmation test is desired.

11. After counting ceases, set CALIBRATE knob so display shows number calculated by equation (7), Appendix C.
12. Repeat to confirm calibration.

### **Test**

1. Prepare sample with SAMPLE SELECT on PREP.
2. Shift SAMPLE SELECT from PREP. to TEST. (Wait for passage of preparation gas if other than test N<sub>2</sub>/He mixture.)
3. Adjust level of liquid nitrogen about cold trap, if necessary.
4. Set REL. COND. to +.
5. Press PEAK AREA push button.
6. Place liquid nitrogen about sample and adjust its level to desired point.
7. Press CLEAR DISPLAY push button to clear display of adsorption result when counting ceases.
8. Set REL. COND. to -.
9. Remove liquid nitrogen and promptly warm sample to room temperature using beaker of water.
10. Be sure gas flow rate has returned to normal before counting begins.
11. After counting ceases, record value displayed as sample surface area.

## Multipoint Surface Area

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The startup and sample preparation procedures are identical with the single point method. However, a series of premixed gases must be acquired or a Dual Channel Flow Controller (P/N: 230-62806-00) must be used to provide the several gas compositions. Incorporation of a Multigas Manifold (P/N: 230-62804-00) in the incoming gas system is very helpful if you are using several premixed gases.

### Calibration

---

The calibration procedure preparatory to a multipoint analysis is accomplished essentially as described above for single point testing with a few exceptions. The steps must be repeated for each of the gas mixtures to be used and a different CALIBRATE knob setting must be determined for each gas composition. Making a single point calibration as well as a single point test prior to undertaking multipoint work is recommended as a means of gaining familiarity with the operation.

The procedure described here presumes use of premixed gases and a manifold. The output of the manifold is connected to the Pulse ChemiSorb at the N<sub>2</sub>/He inlet.

The instrument is first flushed with the lowest N<sub>2</sub> composition gas having, for example, a composition of near 5% N<sub>2</sub> with the remainder helium. This is achieved by opening the appropriate valve on the manifold and the N<sub>2</sub>/He MIXTURE valve on the instrument. Set the flow to the desired rate (usually ball at 16 on the flowmeter). The DELAY knob should be on LONG and the SAMPLE SELECT knob to the TEST position to be employed later in sample analysis. Set REL COND. push button to – (negative).

Now, in order and as described in the Abbreviated Step-by-Step Procedure, Calibration section above, draw pure nitrogen into a 1-mL precision syringe and momentarily lay it aside; zero the instrument; press the PEAK AREA and CLEAR DISPLAY push buttons; adjust the syringe to 1 mL; and inject the nitrogen. After the THRESHOLD light ceases to register counts (approximately 5 minutes) adjust the CALIBRATE knob so that the display reads the volume of gas at standard conditions as detailed in Appendix C. For example, if ambient temperature is 22°C and atmospheric pressure is 740 mmHg, the CALIBRATE knob should be adjusted such that the display indicates

$$1.00 \times \frac{273.2}{295.2} \times \frac{740}{760} = 0.90$$

as calculated by equation (8), Appendix C.

This means that 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. The CALIBRATE knob reading should be recorded for subsequent use.

The Multigas Manifold is provided with an erasable tab in front of each valve as a convenient readily accessible place for recording this calibration information. It is suggested, further, that the nitrogen composition of the cylinder connected to each valve also be recorded on the tab. Doing so then provides essential information where it can be conveniently recalled as needed.

Appropriate CALIBRATE knob settings are now determined and recorded for the other gas mixtures in an identical manner. A few minutes will be needed after shifting manifold valves from one gas to another to allow the previous gas to be flushed out. The display meter with DET. pressed will cease registering a change as soon as the new gas has thoroughly swept through the instrument. The setting appropriate for each gas mixture is recorded in a convenient place for subsequent availability. Perhaps this place is the manifold tabs as suggested above. The numbers will fluctuate somewhat from instrument to instrument and they will vary, of course, with gas composition. Typical numbers appear in Table 4-2. Do not use these data; they are illustrative only.

*Table 4-2. Typical Calibration Numbers*

| Gas Composition (% N <sub>2</sub> )                | CALIBRATE Knob Setting |
|--|------------------------|
| 4.999  | 91                     |
| 9.997  | 101                    |
| 14.993   | 111                    |
| 22.006   | 124                    |
| Do not use these data; they are illustrative only. |                        |

## Sample Preparation

---

Surface areas can be measured reliably with a total sample surface of as much as 280 m<sup>2</sup> but results are both rapidly and accurately determined if sample quantity is adjusted to give 12.5 to 25 m<sup>2</sup>. Sample quantity should therefore be adjusted to fall in the vicinity of 12.5 to 25 m<sup>2</sup> when practical. This will likely not be possible 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 results as a specific surface area, i.e., in terms of square meters per gram. True weight is most reliably determined after the sample has been freed of whatever gases and vapors (most especially water vapor) it may have picked up from the atmosphere or from prior chemisorption tests. This means the weight is best established after the measurement is completed. The glass 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.

Except for the warning in the Intended Use and Precautions section, earlier in this chapter, against contaminated and decomposing materials that may give off corrosive or condensing vapors, sample pretreatment, or outgassing, is readily accomplished on the Pulse ChemiSorb. It is true, however, that samples which have been predried, perhaps in a vacuum oven, will clean up faster. Preconditioning of sample is recommended whenever possible.

Pour the powder to be analyzed into a dry, clean sample tube, being careful to leave some free space horizontally above the sample for the unimpeded flow of gas. Install the tube securely in a holder and attach the holder to the instrument at one of the connectors labeled SAMPLE (1 or 2). Set the SAMPLE SELECT knob so that PREP. 1 or 2 is selected as appropriate for the sample location.



Make sure the appropriate PREP. button is selected.

Place a heating mantle about the sample tube and plug in both its power cord and thermocouple lead. Set the push button selector marked TEMP. SET (1 or 2) to the desired temperature. 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. switch and the appropriate TEMP. 1 or 2 push button.

Heating to the highest temperature consistent with the thermal stability of the sample gives the most rapid outgassing. In actual practice, degassing at 200 to 250°C for 15 to 20 minutes is often adequate. Some catalysts require higher temperatures and longer times.

Repetitively adsorbing and desorbing nitrogen 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, a series of tests may need to be conducted varying either time of treatment or temperature or, perhaps, both to establish degassing conditions.

There may be a tendency for a portion of some very fine, fluffy powders to be carried from the sample bulb by the gas passing over the sample. This problem can be overcome by one of a number of procedures. Since such a fine powder is likely to exhibit a comparatively great surface area, the quantity of sample can usually be reduced without penalty; this increases the free space above the sample and reduces the gas velocity over it. A bit of glass wool can be inserted in the exit stem of the glass sample tube to confine the sample; the exit stem is to the right as one faces an installed sample holder. Finally, the gas flow rate can be reduced; the only significant effect here is a lengthening of analysis time. Select a lower number on the flowmeter graduations, say 10, and adopt this as the standard mark. Note that both calibration and testing must still be carried out at the same flowmeter setting, viz. 10. Make the test in all other respects as before.

A liquid nitrogen and isopropyl alcohol slurry can be used about the cold trap to remove water vapor from the nitrogen gas if you suspect the nitrogen of being contaminated with water vapor. This slurry should be maintained by periodic, partial refreezing. Again, try to make these additions in the interval between a calibration run and a test or between tests.

## Performing the Test

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 (Appendix C) to yield the surface area. The calibration procedure was designed to set the instrument to register adsorbed gas volumes. Now the purpose is to determine adsorbed gas volumes for a specific sample.

A multipoint analysis can be conducted as a series of single-point steps (refer to **Single-Point Surface Area**), progressing from lower to higher nitrogen gas concentrations. Adsorption proceeds less rapidly at lower relative pressures, therefore a longer than usual time will be required for equilibration of the first points. After each concentration is established, the instrument CALIBRATE knob 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 once three to five measurements are completed.

Determine the sample weight once all the mixed 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 in Table 4-3.

Now compute the sample specific surface area following the method given in the following section, **Calculating the Result**, or using the program (P/N: 230-33609-00) available from Micromeritics written for an IBM personal computer (see Appendix D).

*Table 4-3. Example Adsorption Data*

| Gas Composition<br>(% N <sub>2</sub> ) | Specific Adsorbed Volume<br>(cm <sup>3</sup> /g, STP) |
|--|---|
| 4.999                                  | 15.16   |
| 9.997                                  | 17.39   |
| 14.993                                 | 19.16   |
| 22.006                                 | 21.46   |

## Calculating the Result

Appendix C gives the basic theory and pertinent equation of the multipoint calculation. Table 4-4 formalizes the procedure beginning on the left with the experimental data of the previous section and proceeding to the right.

*Table 4-4. Example BET Calculation*

| Gas composition (%N <sub>2</sub> ) | Specific Surface Volume V (cm <sup>3</sup> /g @ STP) | $V(1/P) - V$ | $V(1/P)$ | $V(1/P) - V$ | $V(1/P) \times V$ |
|------------------------------------|--|--------------|----------|--------------|-------------------|
| 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           |

$$(*) \frac{\%N_2}{100} \times \frac{740}{755} = \frac{\%N_2}{100} \times 0.980 = \%N_2 \times 0.00980$$

A plot of the sixth versus the third column is shown in 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 is thus

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

The result computed by the program described in Appendix D is  $76.2 \pm 0.54 \text{ m}^2/\text{g}$ . The example printout is also included there. For purposes of comparison, a single-point specific surface area of  $73.8 \text{ m}^2/\text{g}$  was obtained for this same material using a gas composition of 30.017% N<sub>2</sub> and the remainder helium.



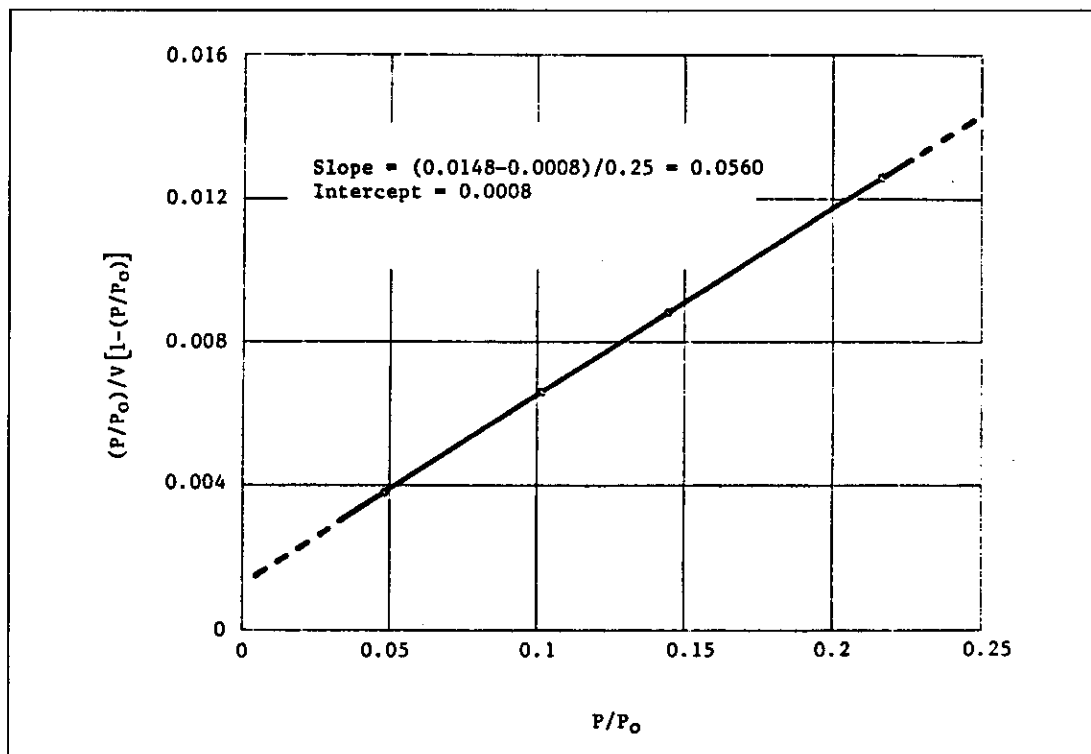


Figure 4-2. Example Plot

## **Abbreviated Step-By-Step Procedure**

The following condensed instructions are intended as a ready reference to guide operators who have gained familiarity with the Pulse ChemiSorb 2705 by following and understanding the detailed operating procedures given immediately above. A beginning operator may find them deficient.

### **Calibration**

1. Establish gas flow with empty sample tube in place.
2. Install empty sample tube at one sample position.
3. Fill 1-mL syringe with gas and lay aside.
4. Set on LONG DELAY.
5. Set REL. COND. to -.
6. Press DET. and X1 push buttons.
7. After equilibration, zero display using COARSE/FINE ZERO.
8. Press PEAK AREA push button.
9. Clear peak area display.
10. Adjust syringe to 1 mL and inject gas. Refill syringe for next test.
11. After counting ceases, set CALIBRATE knob so display shows number calculated by equation (8), Appendix C.
12. Record CALIBRATE dial reading on manifold tab.
13. Repeat steps 9-12 if confirmation test is desired.
14. Establish flow of next gas.
15. Repeat steps 6-14 until all gas calibrations are done.

**Test**

1. Set SAMPLE SELECT valve to appropriate sample.
2. Press DET. push button.
3. Select gas with lowest nitrogen content.
4. Set CALIBRATE dial to factor for selected gas.
5. Set REL. COND. to + to see integrated adsorption peak.
6. Place liquid nitrogen about sample and fill Dewar to desired level.
7. Wait for counting to cease then adjust display, if needed, to zero with FINE ZERO knob.
8. Return REL. COND. to -.
9. Press PEAK AREA and CLEAR DISPLAY push buttons.
10. Remove liquid nitrogen and promptly warm sample to room temperature using beaker of water.
11. Be sure gas flow rate returns to normal before counting begins.
12. After counting ceases, record value displayed as cubic centimeters of adsorbed gas (STP) versus nitrogen gas percentage.
13. Select next gas.
14. Repeat steps 4-13 until all gases have been run.
15. Compute sample surface area.

## Total Pore Volume

---

The volume of liquid condensed in pores from a condensible gas at greater than 95% of its saturation vapor pressure is generally accepted to correspond to the pore 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<sub>2</sub> 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<sub>2</sub>/2% He mixture of gases are required. A Multi-gas Manifold (P/N: 236-62804-00) makes shifting from one gas to the other convenient. The outlet from the manifold should be connected to the Pulse ChemiSorb at the connector labeled N<sub>2</sub>/He MIXTURE. 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 of the Pulse ChemiSorb is accomplished with 98% N<sub>2</sub>/2% He gas serving as the carrier. Inject a 10-cm<sup>3</sup> volume of pure nitrogen in a stream of 98% N<sub>2</sub>/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°C and 740 mmHg, equation (11), Appendix C, shows the liquid volume equivalent of 10 cm<sup>3</sup> 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.

1. Attach at least one sample tube and set the SAMPLE SELECT valve at TEST for the port to which the sample is attached. The DET. and X2 push buttons are pressed; the DELAY knob is on LONG; the PATH SELECT is on SAMPLE; FLOW READ is on TEST; and REL. COND. is to -. The cold trap Dewar is either installed with a liquid nitrogen and isopropyl alcohol slurry in it or it is left off, depending on gas purity as explained in Chapter 3.
2. Replace the needle on the 10-mL precision syringe with the shorter needle on the 1-mL syringe. Fill the syringe by holding its needle tip immediately above the level of liquid nitrogen in a Dewar, the evaporating liquid providing an atmosphere of pure nitrogen. This syringe requires more careful filling than the 1-mL syringe because of its greater volume and the small inlet hole in the needle. Withdraw the plunger slowly and be sure to hold the needle just above the liquid nitrogen for a period of time after withdrawal to allow complete pressure equilibration within the syringe barrel. Flush the syringe several times to be sure of obtaining a proper fill. Wipe the needle tip free of accumulated frost and lay it aside, perhaps on the rubber mat of the Pulse ChemiSorb, for it to come to temperature equilibrium with the room.
3. While the syringe is equilibrating, regulate the nitrogen-helium flow through the instrument such that the flowmeter float is at the 16 mark.
4. Zero the instrument display using, as appropriate, the COARSE and FINE ZERO knobs. Observe the display for a few minutes to establish system stability. A change of no more than 0.01 should be achieved. The two primary factors leading to excessive instability are instrument warm-up, which may require up to 30 minutes after initial power application, and the progression of the residue from a previous analysis, which also can require as much as 10 minutes for elimination. Be sure these situations do not exist when setting the zero. Once set, the zero should not be readjusted unless a sustained change beyond  $\pm 0.02$  unit occurs.
5. Press the PEAK AREA and the CLEAR DISPLAY push buttons.
6. Adjust the syringe to precisely 10 mL and insert the syringe needle in the septum at INJECT. Inject the gas at a moderate rate. Withdraw the needle when the syringe is completely discharged.

The THRESHOLD light will begin flashing and the indicator will start accumulating information after approximately 5 minutes. The rate of flashing will increase and then decrease. When the THRESHOLD light registers no flash for 15 to 20 seconds, which will occur after about 10 to 12 minutes, the accumulation may be considered complete. Another check for completeness is the number displayed when the DET. push button is pressed; it should be 0.02 or less.

The number to be displayed by the indicator with the PEAK AREA button pressed is now set with the CALIBRATE knob to read the value calculated at the beginning of this procedure multiplied by 100. In the example above, 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  $\pm 0.02$  unit.

### **Sample Preparation**

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Prepare the sample for analysis as described in the Sample Preparation section for Singlepoint Surface Area except use pure nitrogen gas in this case. Be sure control settings during and upon completion of this step are as follows:

- FLOW READ knob on TEST
- DELAY knob on SHORT
- PATH SELECT knob on SAMPLE
- SAMPLE SELECT knob on the appropriate TEST (1 or 2) for the sample location
- INJECT lever on LOAD
- DET. and REL. COND. – push buttons pressed

## Performing the Test



Before starting the analysis, make sure the flow pressure for the gas is at least 200 psig. Be sure to follow the instructions on the sample to be analyzed and the quantity available in the current data termination of analysis.

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

The sample was prepared for analysis with nitrogen gas only flowing over it at an elevated temperature. As soon as it cools to near room temperature, place a Dewar of liquid nitrogen about the sample tube and wait for at least 15 minutes for nitrogen to condense in all pores (and even in some interstitial spaces). The level of liquid nitrogen should be maintained as nearly constant as possible about 2 to 4 cm (0.8 or 1.6 in.) below the Dewar lip. A further guide to proper liquid level is one such that frozen condensate does not build up on any metal portion of the sample holder. The COLD TRAP Dewar, if one is used, should also be maintained with liquid nitrogen and isopropyl alcohol slurry. It is advisable to replenish it periodically, perhaps before each pore volume determination. Replenishment can cause a short-term change in gas flow rate which can induce errors if done while counting is in progress.

After the wait for condensation is over, set the DELAY knob to LONG and shift from pure nitrogen to 98% N<sub>2</sub>/2% He. Set the REL. COND. push button to - and press the DET. push button. The display will begin registering counts. When the display has returned to within 0.02 of zero, press the PEAK AREA and CLEAR DISPLAY push buttons. Adjust the CALIBRATE knob to its appropriate setting as determined in Total Pore Volume, Calibration.

The total pore volume is now obtained by removing the Dewar of liquid nitrogen and bringing the sample to room temperature. Immersing the sample tube in a beaker of room temperature water is frequently appropriate. Special sample tubes such as those having ground glass joints must be warmed with care as they are more subject to stress development which can lead to breakage. Continue the warming procedure until the flowmeter float returns essentially to its normal level. As before, the THRESHOLD light will blink and the display accumulate for several minutes. The float of the flowmeter must have returned to its normal position before data accumulation begins, i.e., THRESHOLD light blinking. If it has not, the test will have to be repeated using a lesser quantity of sample. The value displayed is 100 times the sample total pore volume when THRESHOLD blinking is no more frequent than once every 15 to 20 seconds (or the DET. indication has returned to 0.02 or less). Divide the displayed value by 100 to obtain total pore volume. This lat-

ter 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.

### **Abbreviated Step-By-Step Procedure**

---

The following condensed instructions are intended as a ready reference to guide operators who have gained familiarity with the Pulse ChemiSorb 2705 by following and understanding the detailed operating procedures given immediately above. A beginning operator may find them too abbreviated.

### **Calibration**

1. Establish flow of 98% N<sub>2</sub> and 2% He through instrument.
2. Press DET. and X1 push buttons; select DELAY, LONG, and install a Dewar of liquid nitrogen/isopropyl alcohol on COLD TRAP if needed.
3. Set REL. COND. to –.
4. Fill 10-mL syringe with nitrogen and lay aside.
5. Zero display using COARSE/FINE ZERO.
6. Press PEAK AREA and CLEAR DISPLAY push buttons.
7. Be sure flowmeter float level is correct.
8. Adjust syringe to precisely 10 mL and inject gas. Refill syringe if confirmation test is desired.
9. After counting ceases, set CALIBRATE knob so display shows number calculated by equation (11), **Appendix C**.
10. Record CALIBRATE dial reading for future use in testing.
11. Repeat from Step 5 onward to confirm calibration.



**Test**

1. Establish a flow of pure nitrogen through instrument.
2. Note flowmeter float level.
3. Press DET. and X1 push buttons.
4. Add a liquid nitrogen/isopropyl alcohol slurry to the cold trap, if used and if necessary.
5. Place liquid nitrogen about sample and adjust its level.
6. Set DELAY on LONG and press X1.
7. When DET. stabilizes at less than  $\pm 0.02$  and flowmeter returns to the level noted in Step 2, establish flow of 98% N<sub>2</sub>/2% He through instrument.
8. When display restabilizes at less than  $\pm 0.02$ , press PEAK AREA, CLEAR DISPLAY and REL. COND. – push buttons.
9. Set CALIBRATE knob to value appropriate for gas.
10. Adjust flowmeter float level to that of calibration, if necessary.
11. Remove liquid nitrogen and promptly warm sample to room temperature using beaker of water.
12. Be sure gas flow rate has returned to normal level before counting begins.
13. After counting ceases, value displayed is 100 times sample total pore volume. Divide displayed value by 100 to obtain total pore volume of sample.
14. Divide total pore volume value by sample weight to get total specific pore volume.

---

## Shutdown

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Any time the Pulse ChemiSorb is expected to be operated within the next few days, it is recommended that it be left with the CARRIER (INERT) gas flowing at one-quarter its normal rate and that power also be left ON. The gas loss and power drain are very low and the instrument will be immediately ready for use.



Should the instrument, after having been used for several days or longer, be left unattended for a period sufficiently long for the liquid nitrogen in the liquid nitrogen/saturated alcohol slush about the cold trap to evaporate, this U-tube should be removed. Otherwise, its collection of impurities are released into the system from which they must subsequently be removed. As soon as the U-tube is removed, replace it with a clean dry one, taking another clean and dry the U-tube thoroughly before replacing it.

Whether the Pulse ChemiSorb is to be completely shut down or left in a standby state as suggested above, keep sample tubes at both SAMPLE positions, a U-tube at the cold trap, and gas inlet valves not in use closed. This ensures the integrity of the system and retards the infusion of water and other undesirable vapors.



## **CHAPTER 5**

### **TROUBLESHOOTING**

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- Port Filter Cleaning
- Sticking Flowmeter Float
- Detector Drift
- Low Results on X10 Range
- Erratically High Results
- Non-Reproducible Calibrations
- Peak Area Display Not Clearing to Zero
- Preparation Temperature Controller Fails to Function
- Display and Indicators Fail to Illuminate
- Substantial Difference Between Adsorption and Desorption



## TROUBLESHOOTING

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The user is encouraged to make the checks and tests described in this section before seeking further assistance. The local serviceman or the factory should be contacted only then if unsuccessful in resolving the difficulty.

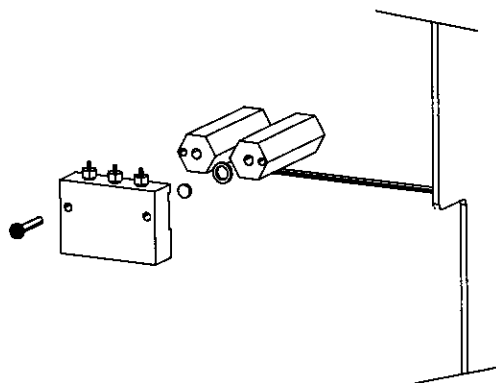
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### Port Filter Cleaning

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Should a decrease in gas flow be noted, the 10- $\mu$ m pore size filters just downstream of each sample tube should be cleaned or replaced. These filters are flat, disk-shaped elements of stainless steel (P/N: 004-27052-00) sealed in place with Buna-N O-rings (P/N: 004-25466-00) or Kalrez™ O-rings (P/N: 004-25465-00). They are accessible from the front of the instrument by removing the two screws holding each flat plate just above the sample tube attachment nuts. Inspect the filters to see if they are encrusted with accumulated debris. If so, remove them, perhaps using a pointed, but not sharp, aid. They can generally be cleaned in an ultrasonic bath. Be sure they are dry before attempting to reinstall them.

When installing new or cleaned filter elements, be sure they are pressed firmly inside their O-rings and that the O-rings are positioned in their recesses. Replace each plate, securing it tightly in place with its two screws.



*Figure 5-1. Inspecting the Port Filter*

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## Sticking Flowmeter Float

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Accumulated vapor deposition or, rarely, a fine particle that escapes filter entrapment can cause the ball float to stick in the glass tube of the flowmeter. The flowmeter must be cleaned to eliminate this problem. Wear an anti-static wrist strap during this procedure.

Unplug the power cord and then remove the rear panel. A circuit board will be found blocking free access to the flowmeter mounts. The board is snap-mounted to the side wall. Slip it off its mounting pins. Now disconnect the tubes that lead to the inlet and outlet of the flowmeter. Remove the two lock nuts that secure the flowmeter to the front panel.

The tube is removed by loosening one hexagonal socket screw in its upper end once the flowmeter is out of the instrument. Being careful not to lose the ball float, flush the tube with water and detergent. Should an organic solvent be necessary to remove all the deposit, be sure the clear front window of the flowmeter or other elements are not attacked by the solvent. Now dry the tube and float, reassemble the flowmeter, and reinstall it by following in reverse the removal steps.

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## Detector Drift

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

The most likely cause of detector instability is condensible vapors arising either from sample clean-up operations or from impure input gases. Drifting is particularly severe with water vapor as noted elsewhere in this manual. Use the built-in cold trap when making physical adsorption measurements; it may be advisable to incorporate such a trap in gas lines with chemisorption tests also. Let dry gas flow through the detector for an hour or so to see if this will not correct this problem.

Surprisingly small amounts of impurities from other sources can also cause drift problems. 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.

Some detector drift, which will be most rapid during the first few minutes after turning on the power, is to be expected. It is due to the detector system coming to its regulated temperature. This drift should disappear in about 30 minutes. The instrument is generally usable after 10 minutes if it has been properly purged of air.

Incompletely degassed samples will cause detector drift and offset as contaminants can still be flushed from them at room temperature. Such drift and offset will cease once a sample is immersed in liquid nitrogen as in physical adsorption testing.

Leaks caused by a worn septum, loose plumbing connections, and missing or damaged sample tube O-rings may allow the entry of air with deleterious effects. Always use a good septum and undamaged O-rings. Replace the septum periodically, perhaps after every 100 injections using the conical tipped, side port needle provided with the 1-mL syringe, or more frequently if another needle style or the larger needle of the 10-mL syringe is employed. If it should be necessary to tighten plumbing connections, be sure they are not overtightened as overtightening can easily damage small copper tubing and lead to the very problem seeking to be eliminated.

---

## Low Results on X10 Range

---

The X10 range (10 times increase in detector sensitivity) is provided for use with those samples which produce less than a 10% enrichment in the carrier gas stream. The detector signal can be truncated when this 10% limit is exceeded which results in a lowered peak area value. The operator is alerted to the possibility of a somewhat misleading result by a special high-pitched audio tone when this occurs.



---

## Erratically High Results

---

Adding liquid nitrogen/isopropyl alcohol slurry 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 will be a somewhat greater surface area value than would otherwise have been achieved.

The liquid nitrogen/isopropyl alcohol slurry should only be replenished between tests.

---

## Non-Reproducible Calibrations

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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.

The syringe should next be tested for gas tightness and freedom from obstructions in the needle. Immersing the needle tip under water and pressing the plunger should result in a steady stream of bubbles and no unusual resistance to motion from the plunger. If this underwater test is made, be careful not to draw water into the syringe and to dry the needle thoroughly.

The flow rate should be monitored by observing the flowmeter float to see that it is constant. If it does not maintain a steady position, check the gas regulator setting for its recommended 15 psig setting, check the flow control knob for smooth operation, and check for gas leaks about the septum, the sample tubes and holders, the gas inlet connection, and, finally, internal plumbing connections.

---

## Peak Area Display not Clearing to Zero

---

Temperature changes and aging of components may cause the peak area display to register a number slightly different from zero when it is cleared. To correct this condition, remove the rear panel of the instrument. Being careful not to contact any of the electrical leads in the lower portion of the instrument, locate the circuit board mounted beneath the top panel of the instrument and immediately above the display. The rightmost potentiometer (R2, Display Zero Adjust) located at the righthand end of the circuit board and just above the edge of the display meter should then be adjusted with a small bladed screwdriver until the display registers zero. The display RESET button should be held down while this is done.

---

## Preparation Temperature Controller Fails to Function

---

A flashing temperature display indicates that either the thermocouple is not connected or that a temperature of at least 500°C has been reached. Plug the thermocouple in or, if this has already been done, examine its leads for evidence of broken connections. If the thermocouple is intact, examine the temperature setting to determine if 500°C or higher has been selected and reduce any such setting. Circuitry inside the instrument protects the operator, the sample tubes, and the heating mantles by limiting the temperature to 500°C regardless of the setting chosen by the operator.

The thermal characteristics of the heating mantles permit temperature regulation to a precision of approximately  $\pm 10^\circ\text{C}$ . 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 indicated initially but subsequently will vary less due to the moderating effects of the glass 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 thereafter intervening by reducing the setting to the desired temperature when the desired temperature is reached.

---

## Display and Indicators Fail to Illuminate

---

Verify first that the electrical outlet is energized by plugging in another appliance and verifying that power is available. Unplug the Pulse ChemiSorb and examine the fuse and the voltage selector circuit board. Should the problem persist when these are replaced, again unplug the instrument and remove the back panel. Examine all connectors to be sure that they are firmly engaged. Check also for broken wires, especially in the lower areas of the instrument near the power entrance, power switch, and power transformer. In addition, check the push button circuit breaker mounted to the power supply. (The power supply is located on the side panel near the exhaust gas ports.) Press the button; then apply power to the instrument. If problems persist, contact your Micromeritics service representative.

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## **Substantial Difference Between Adsorption and Desorption**

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

# **APPENDIX A**

## **CHEMISORPTION**



## CHEMISORPTION

---

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 is generally conceded to occur 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  $N_{\text{Active}}$  to the total number of metallic atoms incorporated in the catalyst  $N_{\text{Total}}$ , i.e.,

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

Chemisorption testing reveals  $N_{\text{Active}}$ . The totality of metal atoms  $N_{\text{Total}}$  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.

Pre-qualification 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<sub>2</sub>O<sub>3</sub> in relation to thiophene conversion reactions. The chemisorption technique was employed using NO. Other chemisorption studies (2-7) employed O<sub>2</sub> and MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The amount of chemisorbed O<sub>2</sub> 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 MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> and ESCA measurements. Here the unknown was the availability (relative surface exposure) of the Mo in a CoMo/Al<sub>2</sub>O<sub>3</sub> 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.

## **APPENDIX B**

# **RELATIVE THERMAL CONDUCTIVITY OF GASES**

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## RELATIVE THERMAL CONDUCTIVITY OF GASES

| Name             | Chemical Formula                                 | Conductivity<br>(Relative to Air) |
|------------------|--|-----------------------------------|
| Air              |  | 1.0                               |
| Ammonia          | NH <sub>3</sub>                                  | 0.92                              |
| Argon            | Ar   | 0.68                              |
| Butane           | C <sub>4</sub> H <sub>10</sub>                   | 0.60                              |
| Carbon Dioxide   | CO <sub>2</sub>                                  | 0.62                              |
| Carbon Monoxide  | CO   | 0.97                              |
| Ethane           | C <sub>2</sub> H <sub>6</sub>                    | 0.79                              |
| Helium           | He   | 5.84                              |
| Hydrogen         | H <sub>2</sub>                                   | 7.07                              |
| Krypton          | Kr   | 0.37                              |
| Methane          | CH <sub>4</sub>                                  | 1.29                              |
| Neon             | Ne   | 1.87                              |
| Nitric Oxide     | NO   | 0.99                              |
| Nitrogen         | N <sub>2</sub>                                   | 1.00                              |
| Nitrogen Dioxide | NO <sub>2</sub> or N <sub>2</sub> O <sub>4</sub> | 1.51                              |
| Nitrous Oxide    | N <sub>2</sub> O                                 | 0.65                              |
| Oxygen           | O <sub>2</sub>                                   | 1.02                              |
| Sulfur Dioxide   | SO <sub>2</sub>                                  | 0.38                              |
| Water Vapor      | H <sub>2</sub> O                                 | 0.67                              |



## **APPENDIX C**

### **PHYSISORPTION**

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## PHYSISORPTION

---

One form of the well-known BET equation (10) that describes the physical adsorption of a gas upon a solid surface is

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

where V is the volume at standard temperature and pressure (STP) of gas adsorbed at pressure P, P<sub>o</sub> the saturation pressure which is the vapor pressure of liquified gas at the adsorbing temperature, V<sub>m</sub> the volume of gas (STP) required to form an adsorbed monomolecular layer, and C a constant related to the energy of adsorption.

The surface area S of the sample giving the monolayer adsorbed gas volume V<sub>m</sub>(STP) is then calculated from

$$S = \frac{V_m A N}{M} \quad (2)$$

where N is Avogadro's number which expresses the number of gas molecules in a mole of gas at standard conditions, M the molar volume of the gas, and A the area of each adsorbed gas molecule as given in **Appendix E**.

### 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

$$\frac{\frac{P}{P_o}}{V \left[ 1 - \frac{P}{P_o} \right]} = \frac{1}{V_m} \left[ \frac{1}{C} + \frac{P}{P_o} \right] \quad (3)$$

Now if P/P<sub>o</sub> ≫ 1/C, equation 3 can be further represented by

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

which rearranges to

$$V_m = V \left[ 1 - \frac{P}{P_o} \right] \quad (5)$$

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 give also

$$V_m = V \left[ 1 - \frac{P}{P_o} \right] \quad (5)$$

Substituting equation 5 into equation 2 yields

$$S = VAN \left[ \frac{1 - \frac{P}{P_o}}{M} \right] \quad (6)$$

from which the sample surface area is readily determined once the volume  $V$  of gas adsorbed (or desorbed, which must 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 Pulse ChemiSorb 2705 is calibrated is injected at room temperature and the prevailing atmospheric pressure. This volume must thus be multiplied by the ratios  $273.2/(Rm. Temp., K) \times (Atm. Press., mmHg)/760$  to convert it to standard conditions ( $0^\circ C$  and 760 mmHg).

Avogadro's number  $N$  is  $6.023 \times 10^{23}$  molecules/g-mole.

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

The presently accepted value for the area  $A$  of a solid surface occupied by an adsorbed nitrogen molecule<sup>(2)</sup> is  $16.2 \times 10^{-20} \text{ m}^2$  (=16.2 Angstroms<sup>2</sup>).

$P$  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.  $P_o$ , 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<sub>2</sub>/70% He mixture adsorbed at liquid nitrogen temperature when room temperature is 22°C and atmospheric pressure is 760 mmHg is the expression

$$S = v \left[ \frac{273.2}{\text{Rm. Temp}} \right] \left[ \frac{\text{Atm. Press.}}{760} \right] \left[ \frac{6.023 \times 20^{23} \times 16.2 \times 10^{-20}}{22.414 \times 10^3} \right] \left[ \frac{1 - (\%N_2/100) \times \text{Atm. Press.}}{\text{Sat. Press.}} \right] = v \cdot \text{constant} \quad (7)$$

where S is the surface area in square meters.

For calibration purposes, this means that a syringe injection of  $v = 1.00 \text{ cm}^3$  of nitrogen at 22°C and 760 mmHg results in a constant having a value 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°C and 760 mmHg, pressure changes having relatively more effect than temperature. Another value should then be calculated. For example, suppose the gas was 29.33% N<sub>2</sub>, the laboratory was 25°C, atmospheric pressure was 710 mmHg, and the saturation pressure was measured to be 735 mmHg, the value, instead of being 2.84, should be 2.67.

## 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/Po)] 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<sub>2</sub> with the remainder He. Equation 1 shows then that the slope and intercept of this line are, respectively, (C-1)/V<sub>m</sub>C and 1/(V<sub>m</sub>C) and that both the values of V<sub>m</sub> and C can be determined.

The Pulse ChemiSorb 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

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



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

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

or simply

$$S = \frac{4.353}{\text{slope} + \text{intercept}} \quad (10)$$

## Total Pore Volume

---

The scientist, L. Gurvitsch<sup>(11)</sup>, noted many years ago that the volume of liquid condensed in the pores of a porous solid from a condensable 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<sup>(12)</sup>, 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 Pulse ChemiSorb 2705 thus requires determining the volume of gas which, condensed as a liquid, is extracted by a sample from a 95-98% N<sub>2</sub>/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<sup>3</sup> and gaseous nitrogen 22414 cm<sup>3</sup> which is a ratio of 0.00155. Designating the calibrating gas volume by  $v$ , the equivalent total pore volume  $V_{tp}$  is thus

$$V_{tp} = \frac{273.2}{\text{Room Temp.}} \times \frac{\text{Atm. Press.}}{760} \times 0.00155 \times 100 \times v \quad (11)$$

This value of  $V_{tp}$  is inserted into the Pulse 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<sup>3</sup> (=v) at ambient conditions is recommended which results in a total pore volume measured in cubic centimeters. Dividing the total pore volume (cm<sup>3</sup>) by sample weight (g) yields the specific total pore volume (cm<sup>3</sup>/g).



## **APPENDIX D**

# **DATA REDUCTION PROGRAM USING THE IBM PERSONAL COMPUTER**

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## Data Reduction Program Using the IBM Personal Computer

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On the next pages are presented typical results from a data reduction program, available from Micromeritics under P/N: 230/33609/00 which computes surface area parameters from Pulse ChemiSorb 2705 data.

The program computes values by the BET and/or Langmuir method. In addition, the user can request a plot of the calculated BET/ Langmuir data to be displayed on the monitor.

This program runs on an IBM Personal Computer and is written in Microsoft® Basic. The system hardware/software listed below are required to execute the program:

- An IBM Personal Computer equipped with one disk drive (single or double sided) and 192K bytes of memory.
- An IBM monochromatic monitor.
- Any system compatible printer (optional).
- IBM DOS Version 2.1 (with IBM BASICA).

This program should work on IBM-compatible systems distributed by other vendors. However, Micromeritics has tested the above programs only on the IBM PC and ISI 5160 computer systems, and cannot support them on other vendor systems. Further system information, complete documentation, and a BASICA listing are supplied with each program diskette.

## MICROMERITICS INSTRUMENT CORPORATION

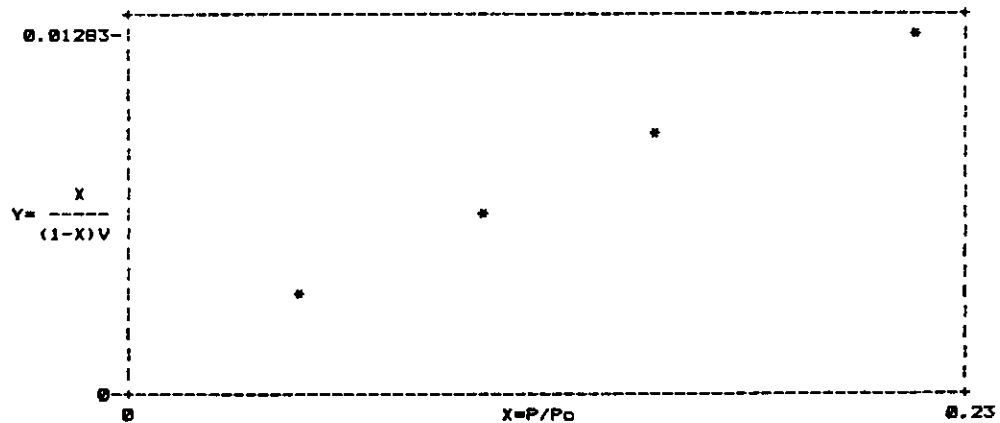
BET SURFACE AREA ANALYSIS  
REPORT DATE: 4/15/85

SAMPLE I.D.: ALUMINA  
 SAMPLE WEIGHT: 0.6180 g  
 MOL. CROSS-SECTIONAL AREA: 0.162 nm<sup>2</sup>  
 SAMPLE TEMPERATURE: 0.00 C

ADSORBATE: Nitrogen  
 BARMETRIC PRESSURE: 760 mmHg  
 SATURATION PRESSURE: 775 mmHg

| EXPERIMENTAL DATA (%) | (VOL) | VOL ADSORBED (cm <sup>3</sup> /g AT STP) | X=P/P <sub>0</sub> | Y=X/[(1-X)V] |
|-----------------------|-------|--|--------------------|--------------|
| 4.999                 | 9.37  | 15.16                                    | 0.0490             | 0.00340      |
| 9.997                 | 10.75 | 17.39                                    | 0.0980             | 0.00625      |
| 14.993                | 11.84 | 19.16                                    | 0.1470             | 0.00900      |
| 22.006                | 13.26 | 21.46                                    | 0.2158             | 0.01283      |

BET SURFACE AREA: 76.22 +/- 0.54 m<sup>2</sup>/g  
 SLOPE: 0.0564 +/- 0.0004  
 INTERCEPT: 0.0007 +/- 0.0001  
 C<sub>i</sub>: 84.80  
 V<sub>m</sub>: 17.51 cm<sup>3</sup>/g  
 CORRELATION COEFFICIENT 1.0000



## SPECIFIC SURFACE AREA

|                          |            |     |               |
|--------------------------|------------|-----|---------------|
| BET SURFACE AREA:        | 173.4344   | +/- | 2.6988 SQ M/G |
| SLOPE:                   | 0.025203   | +/- | 0.000386      |
| INTERCEPT:               | -0.000103  | +/- | 0.000058      |
| C:                       | -244.0489* |     |               |
| Vm:                      | 39.8407 CC |     |               |
| CORRELATION COEFFICIENT: | 0.9999     |     |               |

|                          |            |     |               |
|--------------------------|------------|-----|---------------|
| LANGMUIR SURFACE AREA:   | 242.8726   | +/- | 5.1480 SQ M/G |
| SLOPE:                   | 0.017924   | +/- | 0.000380      |
| INTERCEPT:               | 0.000398   | +/- | 0.000058      |
| B*P <sub>0</sub> :       | 45.0719    |     |               |
| Vm:                      | 55.7917 CC |     |               |
| CORRELATION COEFFICIENT: | 0.9998     |     |               |

RELATIVE PRESSURE RANGE: 0.0500 TO 0.2100

\*A negative BET "C" value means the BET model is not appropriate for this sample; the alternate is the Langmuir model which agrees well here.





## **APPENDIX E**

### **OTHER GASES AND COMPOSITIONS**



## OTHER GASES AND COMPOSITIONS

---

Although nitrogen in helium (30/70) with liquid nitrogen as the sample cold bath provides the most frequently used conditions for physisorption measurements, there are occasions where it may be desirable to employ a different set of circumstances. For example, some investigators favor a 20/80 nitrogen-in-helium mixture when analyzing carbon blacks; carbon dioxide in helium is sometimes preferred when surveying coals; and n-butane permits analysis at ice water temperature, a convenience at some sites.

The instrument should be adjusted when using mixtures significantly different from the 30/70 nitrogen-in-helium mixture to ensure linearity of response. This is accomplished by pressing the REL. COND., DET. and X1 push buttons, and turning both the FINE and COARSE ZERO controls fully clockwise until the stops are encountered. Establish a stable flow of the differing gas mixture through the instrument and adjust the small screwdriver-adjusted potentiometer on the right panel near the gas inlet until the display indicates the percentage of nitrogen known to be contained in the mixture. Use equation (7) of **Appendix C** to compute a new calibration factor for the mixture and then proceed otherwise as with the 30% mixture.

The user should be aware that one-to-one surface area value correspondance with nitrogen values or among the other gases is unlikely when using these other gases. The area occupied by their molecules on solids is less investigated and apparently varies more widely depending on the nature of the solid.

The proper concentration of a gas other than nitrogen for single point surface area measurement is selected on the basis of what concentration produces a relative pressure  $P/P_0$  of approximately 0.3. For example, if argon as listed in Table E-1 is to be used in combination with helium, the result is

$$\text{Ar concentration} = \frac{250 \text{ mmHg} \times 0.3}{760 \text{ mmHg}} \times 100 = 9.9\%$$

since the vapor pressure of argon at liquid nitrogen temperature is 250 mmHg and the saturation pressure of liquid nitrogen is taken to be 760 mmHg for purposes of this illustration.

Table E-1 also lists basic physical property information as required in arriving at the appropriate constant in equation 6 for a number of gases at selected temperatures. By way of illustration, suppose 30 mole % n-butane mixed with 70 mole % helium were to be used at ice water temperature to measure surface area. The numerical constant in equation 7 (Appendix C) would be

$$\frac{273.2}{295.2} \times 6.023 \times 10^{23} \times \left( 46.9 \times \frac{10^{-20}}{22414} \right) \times \left[ 1 - \left( \frac{0.3 \times 760}{1060} \right) \right] = 9.15$$

The Pulse ChemiSorb 2705 may require other adjustments to render it applicable under the new conditions. Contact your service representative or the factory for further information.

*Table E-1. Physical Property Data*

| Gaseous Adsorbate | Approximate Bath Temperature (°C) | Approximate Vapor Pressure at Bath Temperature (mmHg) | Approximate Area Occupied by Adsorbed Molecule at Bath Temperature (m <sup>2</sup> x 10 <sup>-20</sup> ) |
|-------------------|-----------------------------------|---|--|
| Nitrogen          | -195 (LN <sub>2</sub> )           | 760   | 16.2 (18)  |
| Argon             | -195 (LN <sub>2</sub> )           | 250   | 16.7 (12)  |
| Carbon Dioxide    | -80 (IPA/LN <sub>2</sub> )        | 793   | 19.1 - 20.6 (12)   |
| n-Butane          | -80 (IPA/LN <sub>2</sub> )        | 30  | 37.5 (12)  |
| n-Butane          | 0 (Ice Water)                     | 1060  | 46.9 (12)  |

## **APPENDIX F**

### **SAMPLE TUBES**

---



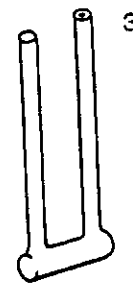
## SAMPLE TUBES



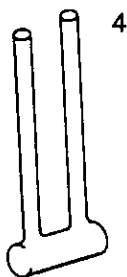
Cold Trap  
P/N: 230-61001-00



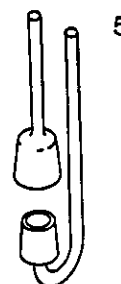
Cylindrical (standard)  
P/N: 230-61002-00



Capillary  
P/N: 230-61003-00



3/4 Cylindrical  
P/N: 230-61004-00



Monolith  
P/N: 270-61005-00

Tube 1 doubles as a cold trap and a holder for sample quantities up to a bulk volume of  $0.1 \text{ cm}^3$ . Because its use increases the gas velocity across the sample, it minimizes the creation of thermal gradients. Thermal gradients cause the separation of mixed gases and are evidenced by the presence of shoulders on recorded adsorption and desorption peaks. Such shoulders give distorted results. Low specific surface materials, perhaps as low as  $0.1 \text{ m}^2/\text{g}$ , which might be thought best measured using a large quantity of sample in the more common tube, are sometimes more accurately analyzed using a much smaller sample in this tube.

Tube 2 has an internal sample space of  $1.5 \text{ cm}^3$  and is used with bulk sample volume of up to approximately  $1 \text{ cm}^3$ . It is the primary general purpose sample holder.

Tube 3 has the same internal dimensions as Tube 2. Its outlet stem has a smaller internal diameter to increase gas velocity and turbulence and, hence, to diminish thermal gradient effects.



Tube 4 has an internal sample space of 7.0 cm<sup>3</sup> and is usable for sample bulk volumes up to 4.7 cm<sup>3</sup>.

Tube 5 is designed for monolithic samples. It will accommodate cylinders up to 2 cm in diameter and 3 cm long. Its use requires heating mantle P/N: 230-26002-00 which, however, is designed for 400°C max.

## **APPENDIX G**

### **TECHNICAL REFERENCES**



## TECHNICAL REFERENCES

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