

SURFACE AREA OF FRESH AND REGENERATED CATALYST

UOP Method 944-96

SCOPE

This method is for determining the surface area of fresh and regenerated alumina-supported catalyst. The method describes the standard procedure for analysis and data collection using a Quantachrome Autosorb-1 or Autosorb-6 analyzer.

OUTLINE OF METHOD

The sample is degassed using heat and vacuum. After weighing, it is cooled in liquid nitrogen. The amount of nitrogen gas adsorbed on the sample is measured at various predetermined pressures. The built-in computer processes the data and calculates surface area based upon a five-point adsorption isotherm. The results are printed and/or plotted as desired.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg, high weighing chamber to accommodate 270-mm cells, Sartorius Model No. BA210S, Thomas Scientific, Cat. No. 1352-N75

Cells, pellet, 4-mm ID stem, 25-mm spherical bulb, Quantachrome Corp., Cat. No. 74028

Regulator, helium, two-stage, Matheson Gas Products, Model 3122-580

Regulator, nitrogen, two-stage, Matheson Gas Products, Model 3122-580

Sorption analyzer, automatic, Quantachrome Corp., Autosorb-1 or Autosorb-6. The designations-1 and -6 refer to the number of analytical stations on the instrument.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Stem inserts, glass rod, void volume reducers for 4-mm ID stem, Quantachrome Corp., Cat. No. 74029

Stoppers, rubber, micro, Thomas Scientific, Cat. No. 8751-K20

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water, except where noted.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Boiling stones, silicon carbide, Thomas Scientific, Cat. No. 1590-D33

Helium, 99.995% minimum purity

Nitrogen, gas, 99.997% minimum purity

Nitrogen, liquefied

PROCEDURE

Install and initialize the instrument according to the directions in the Autosorb Operation manual¹. The instructions in the manual are essential for correct operation of the instrument and should be fully understood before any attempt is made to analyze samples on the Autosorb-1 or Autosorb-6.

Sample Cell Tare Mass Determination

1. Attach clean, empty cells (with stem inserts if desired) to the degas positions of the instrument.
2. Place the manual-auto switch, on the degas manifold control panel, in the "AUTO" position. The "READY" light should be on.
3. Press the "LOAD" button and then the "SELECT" pushbuttons on the individual stations holding the cells to be evacuated. The indicator lights should be illuminated on the pushbuttons.
4. Press the "START" button to start the degas procedure.
5. Evacuate the empty cells for 5 ± 1 minutes. It is not necessary to heat the cells.
6. Press the "REMOVE" button at the end of the evacuation period and then the selector buttons for the stations containing the empty cells. All the pushbuttons should light.
7. Backfill the cells with helium by pressing the "START" button.
8. Remove the cells and stopper immediately after the backfill operation is completed (see *NOTE*).
9. Record the mass of the helium-filled cell, stopper and stem insert to the nearest 0.1 mg. This is the sample cell tare mass. Use the same stopper and stem insert for the subsequent run.

Sample Pretreatment

1. Place a representative portion of the sample in the tared cell.
 - The amount of sample to be used varies with the expected surface area of the material. The manufacturer recommends adjusting the sample mass so that between 20 and 50 m² of surface are present in the cell. Therefore, the greater the expected surface area, the less sample required. For most catalysts, 0.20 ± 0.02 g is a good approximation.
2. Place heating mantles around each cell and hold them in place with the metal clips.
3. Attach the cell to port on the degas manifold. Repeat for any additional cells.
4. Press the “LOAD” button and then the “SELECT” pushbuttons for the stations loaded. All selected pushbuttons should light.
5. Set the pretreatment temperature at 300°C on the digital temperature dials above the stations. The degas temperature should be clearly stated on the printout.
 - A lower temperature is to be used only for samples that may degrade at 300°C.
6. Turn on the toggle switch for the heater power.
7. Press the “START” button to begin the degassing procedure.
 - The computer will automatically reduce the pressure in the cell slowly and activate the heater at the appropriate time.
8. Check the sample, after a minimum of two hours, to ensure that degassing has been completed by pressing the “TEST” button and the “SELECT” pushbutton for the cell to be tested. Then press the “START” button. All other stations are isolated from the manifold and the manifold connection to the vacuum pump is closed. If the manifold pressure is stable or rises very slowly (less than two millitorr/min), the sample is adequately degassed and may be analyzed. If not, repeat the degassing procedure, beginning at Step 2.
 - Where possible, pretreatment overnight is preferred.
9. Turn off the heater toggle switch and remove the heating mantle from the cell. Allow the cell to cool to room temperature.
10. Press the “REMOVE” button and the “SELECT” pushbuttons for the cells to be removed. Press the “START” button and allow each sample cell to be backfilled with helium before removing from the manifold.
11. Remove the cell from the manifold and stopper each cell immediately with the same stopper used during the tare mass determination.
12. Weigh the cell, stopper, stem insert and degassed sample to the nearest 0.1 mg. Subtract the tare mass to obtain the degassed sample mass.

Sample Analysis

Some Autosorb-6 instruments require a separate saturation vapor pressure measurement station. The Autosorb-1 and later models of the Autosorb-6 do not. If a separate station is required, place a clean, empty cell on one of the analysis stations. Station 6 is normally used as the reference station but any station can be used.

1. Unstopper the sample cells (from Step 12, *Sample Pretreatment*) and quickly connect them to the stations.
2. Fill the Dewars with fresh liquid nitrogen and add a few beads of high surface area material (catalyst spheres or silicon carbide boiling stones) to the Dewars as boiling chips. The level and age of the liquid nitrogen used on all stations including the P_0 station must be the same, or errors in the determination can be introduced.
 - The large Dewars hold enough liquid nitrogen for an analysis time of 60 hours and *should not* be refilled during analysis.
3. Select the command “P” from the main menu. The P_0 menu will be displayed. Select option “2”, the P_0 station. Select the leak test option and set the time for five minutes. Answer the last question with “Y” (Yes).
 - The instrument will fill the empty cell with nitrogen. A small amount of the nitrogen in the cell is liquefied and the pressure of the vapor above the liquid is used as the reference pressure.
4. Select the command “I” (Initialize) from the main menu on the terminal to start the analyses. Select an available analysis station. Enter the sample identification information (limit 50 characters); for example:

Requester, Sample ID Number, Test Number, Date, Pretreatment Temperature; i.e., HALLORAN 5331-34 TEST 2345 03/06/96 300C
5. Enter the degassed sample mass previously obtained (Step 12, *Sample Pretreatment*).
 - If the instrument has been upgraded with the PC software package, the following instructions (Steps 6 through 10) can be set as default conditions in a separate program. Follow the manufacturer's instructions for preparing and using this program.
6. Enter “Y” for leak test option and specify five minutes.
7. Select “Y” in answer to “FAST PUMPDOWN Y/N”.
8. Select “3” in response to the “SELECT EQUILIBRATION TIME” option.
 - The answer to this query sets the analysis parameter used by the instrument to determine how long the pressure must be stable (1 to 5 minutes) before the instrument collects the data and starts adding nitrogen for the next point.
9. Select “3” in response to the “SELECT P/ P_0 TOLERANCE” option.
 - This determines how closely the actual pressure points will be to the preset table values. A value of “3” (+0.012 or -0.004) is a satisfactory compromise between speed and precision.

10. Answer the final query, "ALL SELECTIONS OK Y/N", "N" if errors were made in answering any of the preceding options. This will erase all prior entries so that they can be corrected (beginning at Step 3). An answer of "Y" will display the analysis menu. After a "Y" answer, proceed to Step 11.
11. Move the cursor to "5 POINT BET (.10, .15, .20, .25, .30)" and press "RETURN". This selects the five-point surface area option.
12. Enter "X" to exit the analysis menu.
13. Enter "Y" in answer to the "START ANALYSIS ON STATION n (Y/N)" query to begin the analysis.
 - An "N" answer will return the display to the main menu and all data entered to that point will be lost.
14. Repeat Steps 4 through 13 for any additional samples.
 - If PC software is used with the instrument, the PC should be left in data acquisition mode. Follow the manufacturer's instructions.
 - Once started, the computer will control all operations for complete data collection under normal circumstances. Abnormal circumstances, such as power failure or instrument malfunction, will cause error messages to be displayed on the terminal and activate an audible alarm. Refer to the manufacturer's instruction manual for suggested troubleshooting procedures.

Instrument Maintenance

The following is a schedule of routine maintenance for the instrument:

1. Check gas pressures daily.
2. Empty Dewars and refill with *fresh* liquid nitrogen every three days.
3. Drain moisture traps from compressor weekly.
4. Check o-rings on all stations for powder build-up every two weeks. Do this more often if primarily running powders.
5. Change filter gaskets on all stations every three months or sooner if large volumes of powders are run.
6. Change pump oil every three months.

CALCULATIONS

All calculations are performed by the computer and the results displayed on the terminal. These results can be subsequently printed or plotted as desired. If the instrument has been equipped with PC software, follow the manufacturer's instructions for report and graphics printing.

The surface area of the material is calculated by application of the Langmuir² and BET³ (Brunauer, Emmett and Teller) equations. Five points in the range of 0.1 to 0.3 P/P_0 are used in the analysis. A correlation coefficient "CORR" is reported for both equations. The equation whose correlation coefficient is closer to 1.000 is the better fit for the data. A negative value for the "C" constant in the BET report is another indication that the Langmuir is the more correct equation.

Type "D" at the main menu and specify a station number. The "DATA REDUCTION MENU FOR STATION n" message will then be displayed on the terminal. Select "3" (EDIT) option to display the points selected for the "M" (multipoint BET) and "L" (Langmuir) calculations. Ensure that the same five points are selected for both calculations (.10, .15, .20, .25, .30). Return to the Data Reduction menu and select "4" to generate reports. Once in the Report menu, move the cursor by using the up and down arrow keys and press "RETURN" to select the following options: "MULTIPOINT BET," "LANGMUIR SURFACE AREA," "ISOTHERM" and "LANGMUIR ISOTHERM". Print these data tables by answering "X" (to exit) and "Y" (Yes) to the questions.

All remaining data reports are generated in the same manner. Before starting new analyses, ensure that all data have been printed out. Without a PC data acquisition package, data stored on a station is erased when the station is initialized for another run.

REPORT

An example of a typical data report is given in the *APPENDIX*. The first several lines of the printout consist of the station number, sample identification and mass, and instrumental parameters for the analysis, including the total elapsed time. The next section contains the summary properties of the material, including the multipoint BET and Langmuir surface area. The isotherm printout appears next, listing the actual pressure points taken and the normalized amount (cc/g) of gas adsorbed. This table contains the same data that are used in the isotherm plot.

NOTE

If a second helium source, apart from the instrument, is available, an alternative procedure can be used to fill the cells. Insert a thin piece of tubing, connected to a helium source, to the bottom of an inverted cell. Displace the air in the cell by flushing with helium for approximately 30 seconds. Remove the tube and immediately stopper the cell.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab) and using data collected from each of three laboratories, the within-laboratory estimated standard deviation (esd) was calculated for Surface Area for two types of catalysts, at the levels listed in the Table. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable difference shown in the Table at the levels listed (95% probability).

Reproducibility

Two tests performed in different laboratories by different analysts on different days should not differ by more than the allowable difference shown in the Table at the levels listed (95% probability).

Table

Surface Area, m ² /g	Repeatability		Reproducibility	
	Within-Lab esd	Allowable Difference	Between- Lab esd	Allowable Difference
680	7.2	22	11.1	68
180	1.8	5	3.0	18

The surface area of the higher surface area catalyst was calculated according to the Langmuir equation; the lower, according to the BET equation. However, the precision stated applies regardless of which equation is used.

TIME FOR ANALYSIS

The elapsed time for an analysis varies with the degree of macroporosity of the sample. Typical elapsed times for catalyst samples are in the range of 4 to 6 hours. The labor requirement is 1.0 hour per sample.

REFERENCES

1. Autosorb-1 or Autosorb-6 Instrument Manual, Quantachrome Corp., supplied with instrument
2. I. Langmuir, *Journal of the American Chemical Society*, **40**, 1361 (1918)
3. S. Brunauer, P. Emmett and E. Teller, *Journal of the American Chemical Society*, **60**, 309 (1938)

SUGGESTED SUPPLIERS

Matheson Gas Products, P.O. Box 96, Joliet, IL 60434 (815-727-4848)
 Quantachrome Corp., 1900 Corporate Dr., Boynton Beach, FL 33426 (407-731-4999)
 Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-6099 (609-467-2000)

APPENDIX

Typical Instrument Printout

REPORT FOR STATION 4

SAMPLE ID LOG#21525 3-8305 7458-33-R-132 4/3/96 300C

SAMPLE WEIGHT = .3614 g

P/P₀ TOLERANCE = 3

EQUILIBRATION TIME = 3

ANALYSIS TIME = 221.3 MINUTES

MULTI POINT BET

P/P ₀	VOLUME (cc/g)	1/(W(P ₀ /P-1))
.102	44.08	.20526E+01
.151	48.25	.29501E+01
.203	52.24	.39004E+01
.252	55.97	.48195E+01
.303	59.87	.58126E+01

AREA = .18561E+03 SQ M/g

SLOPE = .18623E+02 INTERCEPT = .14176E+00 CORR = .9999 C = .13237E+03

LANGMUIR SURFACE = .31859E+03 SQ M/g CORR = .99658

ISOTHERM

P/P ₀	VOLUME (cc/g)	P/P ₀ OLERANCE	EQUILIBRATION TIME
.10160	44.07856	3	3
.15104	48.24877	3	3
.20298	52.23630	3	3
.25215	55.96949	3	3
.30314	59.87241	3	3

LANGMUIR SOTHERM

P/P ₀	P/P ₀ /W
.102	.18440E+01
.151	.25045E+01
.203	.31087E+01
.252	.36043E+01
.303	.40506E+01

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