Application Note

Equilibrated versus Scanning Porosimetry

The porosity of solids and powders is frequently characterized by mercury intrusion porosimetry. This technique provides detailed information on pore volumes, density, and pore-specific surface area, while also yielding information that can be used to characterize the shape and structure of pores.

To perform mercury intrusion porosimetry, various levels of pressure are applied to a sample immersed in mercury (a nonwetting liquid). As mercury is forced into the sample's pores, pore size is calculated using as constraints mercury's contact angle and surface tension. The pressure required to force mercury into the sample's pores is inversely proportional to the diameter of the pores (when it is assumed that the pores are right circular cylinders).

Mercury intrusion porosimeters apply pressure to the sample in one of two ways:

- **Scanning**: pressure increases continuously

- **Equilibration**: pressure is held at each data-collection point for a specific time period or until the rate of intrusion decreases below a value pre-selected by the user

All of Micromeritics' mercury porosimeters offer both scanning and equilibrating by time. The AutoPore Series also offers equilibration by rate. At the present time, no known competitive instrument provides all of these capabilities.

Equilibrated analyses, particularly those equilibrated by rate, provide detail-rich, comprehensive, accurate porosity data. Scanning analyses are quicker, and produce highly repeatable data, but accuracy may be reduced. Scanning tends to show smaller intrusion volumes and smaller pore sizes, so it is best-suited for applications in which repeatability is more important than accuracy, such as certain types of quality-control sampling.

Understanding why scanning and equilibrated data may differ significantly is useful when selecting a method.

Pore filling is a process

Intrusion is not instantaneous; mercury begins entering a pore opening at the moment the pressure exceeds the value required for the pore opening's diameter, but the time required for the mercury to fill the pore is dependent upon its volume and shape. The equilibration mode of operation holds pressure steady while the pores fill. Depending on the extent of equilibration the user specifies, pore volume readings taken using this type of analysis show the complete pore volumes. If equilibration is not allowed, filling may be incomplete when the instrument takes the volume reading, then moves on to the next pressure point.

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This causes scanning data to show:

- *Smaller-than-actual pore volumes*: If the pores are not yet completely filled when the reading is taken, the volume read is smaller than the actual volume (when the pores are completely filled).

- *Combined pore volumes*: Any amount of mercury that fills the pores *after* a reading is taken is included in the next pressure reading. If there is an intrusion at that pressure, that intrusion's volume includes some of the lower-pressure volume, but it may also exclude some of its own volume, if the reading is taken before filling is complete.

- *The presence of smaller pores than actually exist*: Any amount of mercury that fills the pores *after* a reading is taken is included in subsequent pressure readings. If there is no new intrusion at these subsequent pressures, this volume appears to indicate the presence of pores of a smaller diameter.

Factors that affect the filling rate

Pore size is calculated using the Washburn equation, which assumes that pores are right circular cylinders. This equation provides a useful model for determining pore diameters, although few pores are cylindrical in reality. In fact, the flow of mercury into porous media is similar to that into a highly complex network of channels. Mercury intrusion porosimetry is a technique which is rate limited, as predicted by the Darcy Equation, which describes the general function of pressure drop vs. flow rate:

$$\frac{p_1 - p_2}{L} = \frac{\alpha \mu V}{g_c}$$

where

p_1	=	the upstream pressure
p_2	=	the downstream pressure
L	=	the media thickness (or pore length)
$1/\alpha$	=	the permeability coefficient
μ	=	the fluid viscosity
V	=	superficial velocity of fluid (based on total cross section)
g_c	=	a dimensional constant.

The velocity of flow of a viscous liquid, such as mercury, is proportional to the pressure drop and inversely proportional to the length and surface area of the pore. Hence given a specific limited flow velocity, the complete filling of a porous network will be a function of time. The larger the volume of pores, the more time is required to fill the total pore volume completely. The continuous pressure increase used in the scanning method may not allow time enough for the flow-limited filling of small pores to occur. Therefore, mercury intrusion porosimetry curves are most accurate if they are obtained when a pore is completely filled, i.e., at equilibrium.

Illustrative data

All data were obtained using a Micromeritics AutoPore high pressure mercury porosimeter.

The data in the following figures clearly show that mercury intrusion porosimetry is a rate-limited technique. Figure 1 illustrates an experiment in which five samples of a single material (porous alumina extrudate) were analyzed using different equilibration routines. Scanning was used for Sample 1. Samples 2, 3, and 4 were equilibrated by time for 2, 10, and 30 seconds, respectively. Sample 5 was equilibrated by rate at 0.001 µL/g-sec.
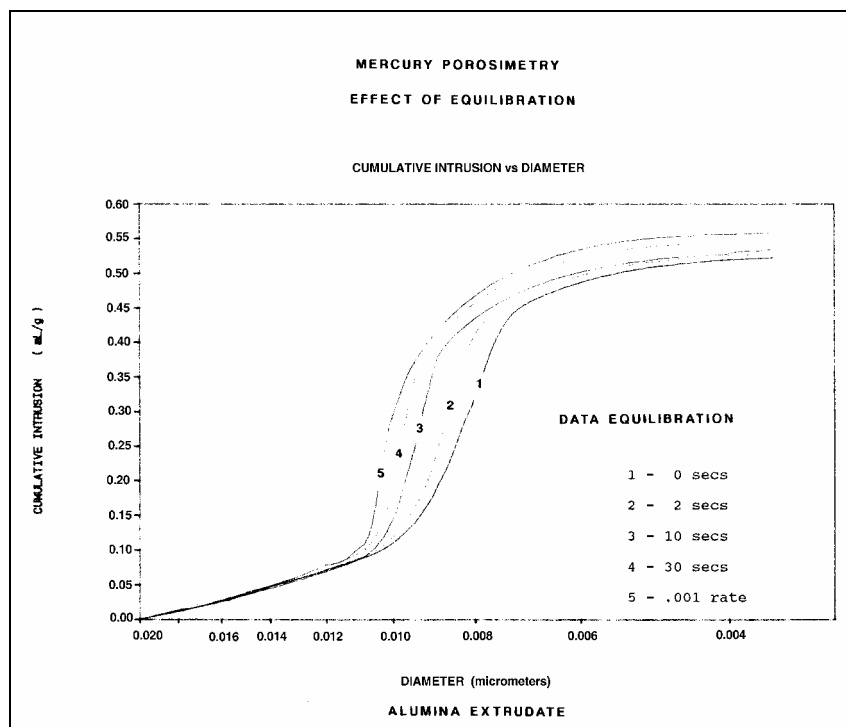
Figure 1. Cumulative intrusion vs. pore diameter for five analyses of alumina extrudate using different equilibration routines. The graph illustrates the effect of equilibration on pore size distribution.

The data obtained in the scanning analysis yielded the smallest pore volume and the smallest pore diameter. The data obtained in the equilibrating-by-rate analysis yielded the highest total pore volume and the largest pore diameter. Equilibrating by time gave intermediate results, with quality of results correlating with the amount of time allowed.
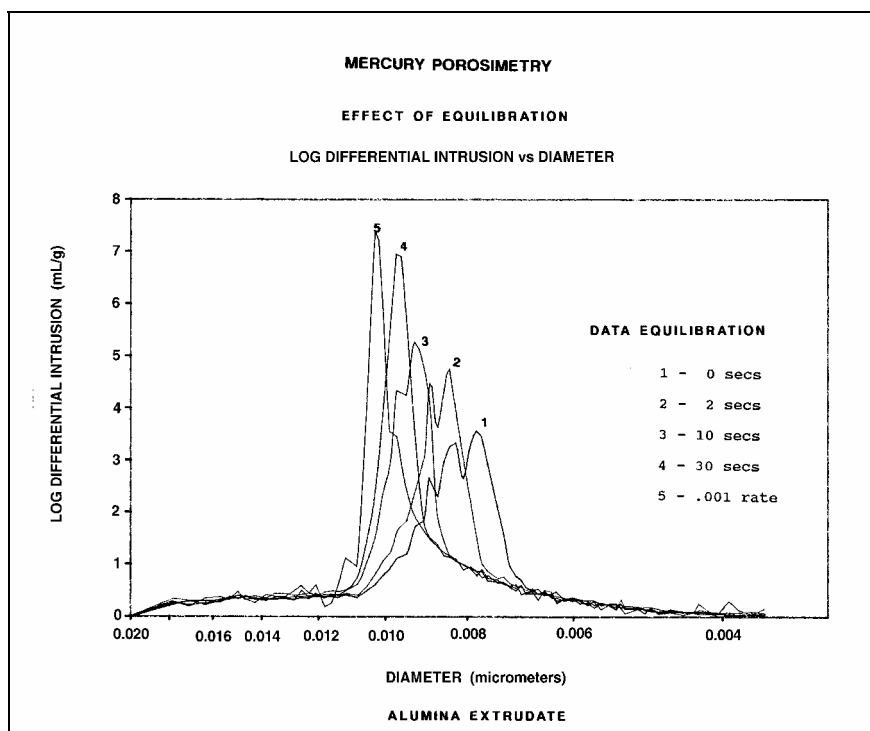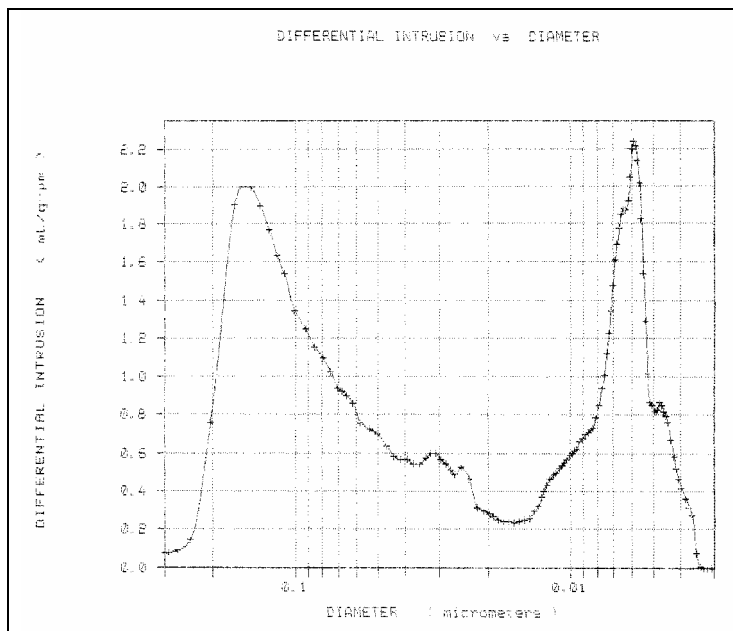
Figure 2. Log differential intrusion vs. pore diameter for five analyses with alumina extrudate using different equilibration routines. The graph shows the effect of equilibration on the log differential pore size distribution.

Figure 2 presents the log differential intrusion vs. diameter for all five equilibration routines. In conjunction with the table shown below, these data demonstrate the rate-limited filling of the pores by mercury under pressure. There is a clear progression to a larger median pore diameter as the equilibration time is lengthened for each data point. The data obtained in the equilibration-by-rate analysis yielded the largest median pore diameter.

Equilibration	Total Pore Volume (cc/g)	Median Pore Diameter (microns)
0 seconds	0.582	0.0081
2 seconds	0.5938	0.0089
10 seconds	0.5939	0.0095
30 seconds	0.616	0.0098
0.001 µL/g-sec	0.6210	0.0102

Figures 3 and 4 illustrate the differences in population distribution data obtained by performing equilibrated and scanning analyses on a catalyst.

Figure 3. Differential intrusion vs. pore diameter for a bimodal catalyst powder. All data points were obtained on the AutoPore using equilibration by a rate of 0.008 µL/g-sec.
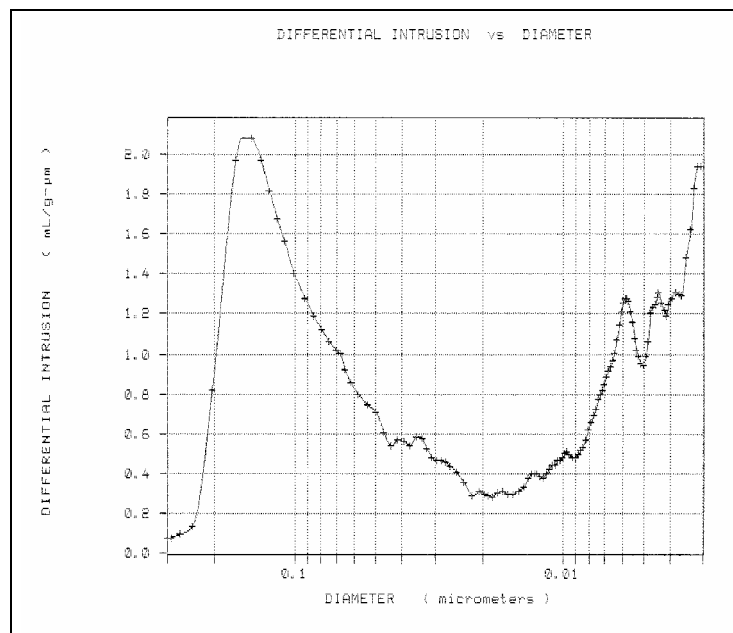
Figure 4. Differential intrusion vs. pore diameter for a bimodal catalyst powder. The data were obtained using the AutoPore in scanning mode (no equilibration; the pressure was increased continuously).

Figure 3 shows data obtained using equilibration by rate. Pressure was held at specified pressure points until the rate of intrusion fell below 0.008 µL/g-sec. After equilibration was achieved at each point, the intrusion volume was recorded. Two groups of pores were observed, centered at 0.170 and 0.006 micrometers.

Figure 4 shows data collected using the scanning method. The same material was analyzed, but all data points were recorded under continuously increasing pressurization.

The intrusion of mercury into larger pores is not as flow-limited as that into the smaller pores, so the large pore structure data obtained by scanning generally agree with the equilibrated data. However, when equilibration is not allowed, the flow-limited filling of the small pores may not be complete when a reading is taken. For this reason, Figure 4 indicates the presence of smaller pores than the equilibrated data reveal. Also, the scanning data show less fine structural detail of the 0.006 micrometer pores than the equilibrated data do.

Selecting a method

Some rate-independent samples yield similar data regardless of the method used. Whether a sample is rate-independent can be determined by comparing data from scanning and equilibrated tests on that material.

Continuously increasing pressure during porosimetry (scanning) yields reproducible data and is quicker than allowing equilibration by either rate or time. Although they are highly reproducible, data collected without equilibration are less accurate. Therefore, analyses using the scanning method may be very useful in quality control applications where the data values are less important than consistency.

Applications requiring both repeatability and very high accuracy should employ one of the equilibration methods. Mercury intrusion data collected using equilibration by time, or better yet by rate, may take longer, but it is extremely accurate and reproducibly determines the pore structure of materials for the pore diameter range of 360 micrometers to as low as 3 nanometers.