Technical Note:

A Few Facts Pertaining to the Low Pressure Performance of a Mercury Intrusion Porosimeter

- The Maximum Measurable Pore Size -

The low pressure range of a mercury porosimeter is used to characterize the larger end of the pore size range. Most manufacturers also use the low pressure module to initially fill the penetrometer sample cup with mercury. The first step (see Figure 1) is to evacuate the penetrometer, then mercury is allowed to enter and fill all accessible voids. Step 2 in Figure 1 shows the penetrometer stem filled and the sample cup filled sufficiently to float the sample material to the top of the cup, but the level of mercury supply has not yet risen to the level of the top of the cup.

In Step 3, mercury rises until it contacts a sensor, which activates a circuit that closes the mercury reservoir valve and, thereafter, maintains the level of mercury in the supply line at a specific height. After the cup is completely filled, the reference point for measuring mercury head pressure is the top of the sample cup. Being a liquid, the level of mercury in the sample cup will tend to equal the level of mercury in the supply line that contains the level sensor, and mercury will invade all interparticle voids and pores larger than some critical size (see inset in Figure 1, Step 3). The Washburn Equation can be employed to reveal the critical size and, therefore, the size range of voids that were filled during the penetrometer filling process.

Although pressure in the sample cup may have been pumped down to <<1 mmHg, there still will be a pressure gradient along the vertical extent of the liquid mercury due to head pressure. For example, mercury in a sample cup with a vertical dimension of 30 mm would have a pressure gradient ranging from 0 to 30 mmHg from the top to the bottom of the cup, respectively.

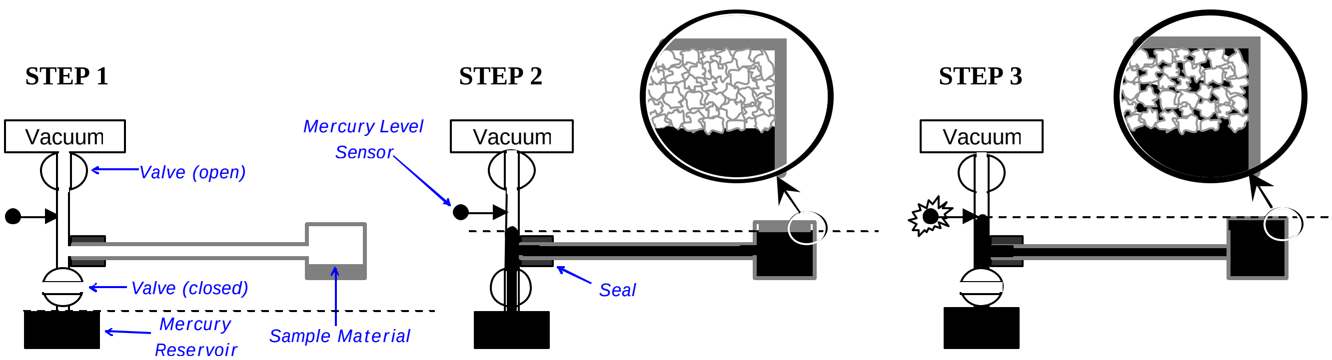

FIGURE 1. The initial filling of a penetrometer containing sample material. Mercury invades some of the larger voids and pores during the filling process.

Table 1 illustrates the effect of head pressure on pore filling at pressures; it also takes into account the effect contact angle has on the size void or pore being filled. The far left column is the pressure in mmHg, which corresponds to the depth at which head pressure is measured below the top of the cell.

The difficulties associated with characterizing large pore sizes by mercury porosimetry is illustrated in Figure 2. A monolithic, porous body (shown in cross-section) is enclosed in a sample cup with an inside diameter of 20mm. Assume the penetrometer has just been filled and the low pressure analysis is about to begin. Therefore, the figure illustrates the initial conditions of an analysis. For this example, the contact angle is taken to be 135°. Note that the size scale in the figure does not apply to the particle and pores, but only to the penetrometer. The particle and pore sizes are greatly magnified to illustrate the effect of head pressure on pore filling.

TABLE 1. Mercury Head Pressure and Pore Sizes Filled at These Pressures

Pressure Produced as a Function of Depth				Mercury-to-Solid Contact Angle (degrees)				
				125	130	135	140	145
Pressure mmHg	Pressure (psi)	Pressure dyne/cm^2	Pressure Pascals	Maximum Size Pore (µM) Unfilled at Current Pressure				
1	0.019	1.33E+03	133	8346	9353	10289	11147	11920
2	0.039	2.67E+03	267	4173	4677	5145	5573	5960
3	0.058	4.00E+03	400	2782	3118	3430	3716	3973
4	0.077	5.33E+03	533	2087	2338	2572	2787	2980
5	0.097	6.67E+03	667	1669	1871	2058	2229	2384
6	0.116	8.00E+03	800	1391	1559	1715	1858	1987
7	0.135	9.33E+03	933	1192	1336	1470	1592	1703
8	0.155	1.07E+04	1067	1043	1169	1286	1393	1490
9	0.174	1.20E+04	1200	927	1039	1143	1239	1324
10	0.193	1.33E+04	1333	835	935	1029	1115	1192
11	0.213	1.47E+04	1467	759	850	935	1013	1084
12	0.232	1.60E+04	1600	696	779	857	929	993
13	0.251	1.73E+04	1733	642	719	791	857	917
14	0.271	1.87E+04	1867	596	668	735	796	851
15	0.290	2.00E+04	2000	556	624	686	743	795
16	0.309	2.13E+04	2133	522	585	643	697	745
17	0.329	2.27E+04	2266	491	550	605	656	701
18	0.348	2.40E+04	2400	464	520	572	619	662
19	0.367	2.53E+04	2533	439	492	542	587	627
20	0.387	2.67E+04	2666	417	468	514	557	596
21	0.406	2.80E+04	2800	397	445	490	531	568
22	0.425	2.93E+04	2933	379	425	468	507	542
23	0.445	3.07E+04	3066	363	407	447	485	518
24	0.464	3.20E+04	3200	348	390	429	464	497
25	0.483	3.33E+04	3333	334	374	412	446	477
26	0.503	3.47E+04	3466	321	360	396	429	458
27	0.522	3.60E+04	3600	309	346	381	413	441
28	0.541	3.73E+04	3733	298	334	367	398	426
29	0.561	3.87E+04	3866	288	323	355	384	411
30	0.580	4.00E+04	4000	278	312	343	372	397
:	:	:	:	:	:	:	:	:
1.55E+06	30,000.	2.07E+09	2. 07E+08	0.0054	0.0060	0.0066	0.0072	0.0077
3.10E+06	60,000.	4.14E+09	4. 14E+08	0.0027	0.0030	0.0033	0.0036	0.0039

For the pressures shown in the left four columns, all pores larger than the sizes shown in right five columns are filled.

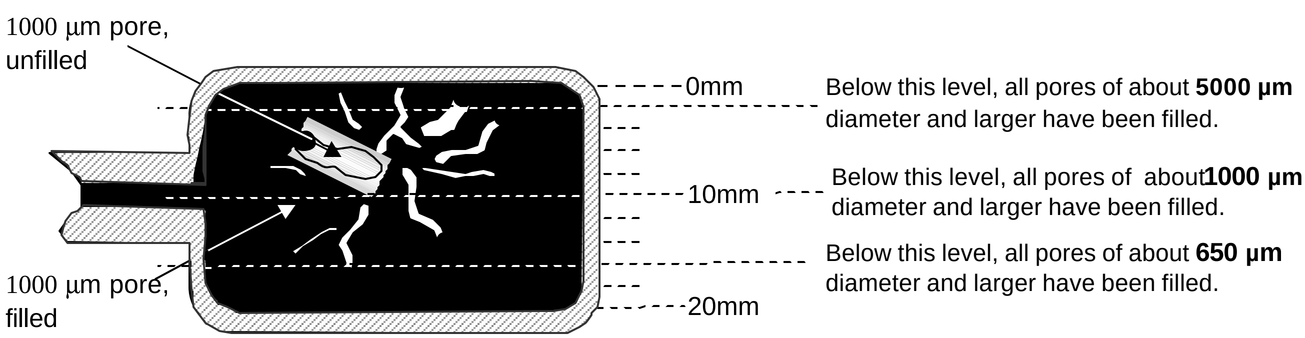

FIGURE 2. The effect of head pressure on pore filling. Note that pores of the same size are not filled toward the top of the sample cup, but are filled when at deeper positions. (Not to scale!)

The scale to the right of the penetrometer shows the depth of the sample below the top of the sample cup. Since the scale is in millimeters, it also depicts the head pressure gradient (mmHg) along the vertical axis of the volume of mercury contained in the sample cup. Therefore, the sample simultaneously is subjected along its vertical extent to a range of pressures from near zero to 18 mmHg. The result is that pores with openings at the upper side of the sample may be empty while pores of the same size located midway or higher on the sample (or, in the case of a powder, in the sample bed) may have already been filled.

The facts presented above invoke the question: ***How does an instrument manufacturer specify the upper pore size range that can be measured with their mercury porosimeter?***

If a manufacturer claims there product can characterize pores volume distribution up to pore sizes of 360 µm, what does this really mean? Assuming, again, a contact angle of 135°, one thing it implies is that the sample is located in a volume of the sample cup that is less than 30mm below the top of the sample cup (the top surface of the mercury), otherwise some quantity of the 360 µm pores will already be filled and their volumes will be accounted for during the next pressure step when the remaining pores of 360 µm are filled. The result will be an underestimation of pore volume for the size class.

As an example of the error this potentially causes, assume that 50% of the sample mass is located greater than 30mm below the top of the sample cup. This means that 50% of all pores larger than 360 µm have been filled. During the next pressure step when only pores of, say, 350 to 360 µm are assume to have been filled, the intrusion volume will be in error by about 50%.

Assume a manufacturer claims the maximum pore size range to be 1000 µm. To obtain a meaningful measurement of the pore volume associated with this pore size, the sample material must be no more than 10 mm deep in the sample cup. Since a 1000 µm pore is a 1 mm pore, to assure that all pore filling is accounted for in this particular case, the sample thickness would be only about 10 times the pore diameter.

Does all this mean that collecting valid data for pores in the size range from about 360 to 1000 µm cannot be accomplished? No, it simply means that the analyst must be aware of the severe limitations for taking measurements in that range and understand that if these are neglected, the measurement may very well be meaningless. If one analyzes samples that are within the limitations of the technique when applied at low pressures, then the data can be valid. However, one will soon discover that sample types appropriate for analysis in this size range are very limited.

The final question this discussion might raise is: ***What is the effect of head pressure in the high-pressure (minimum pore size) range?*** The same pressure offsets occur in the high pressure range, in fact, the head pressure affect is even greater because the penetrometer is positioned with the cup down and stem up, so the sample is perhaps 24 cm below the surface of the mercury (240 mm/Hg head pressure). If no correction were made to the pressure reading, it would have the potential to introduce as much as 10% pressure error at the low end of the high pressure range. However, Micromeritics' mercury porosimeters account for the mercury head pressure effect produced when the penetrometer is moved from the low- to high-pressure port. First, the instrument checks to assure that the low pressure analysis setup results in the analysis ending at a pressure equal to or greater than the head pressure that will be generated when the penetrometer is inverted. If it does not, the analyst is warned. Second, the operating program adjusts the readings from the high pressure transducers and reports the head-corrected pressure. The head-corrected pressure is the pressure that causes intrusion, not the pressure measured at the transducer.

As can be appreciated from the above discussion, understanding the details of what occurs during an analysis allows the analyst to understand the value of the reported data. Just because an instrument can produce a certain measurement does not mean that the quality of the measurement is the same under all circumstances. The analyst must assure that what is intended to be measured is actually what the instrument has measured.