Blank And Sample Compression Corrections for Mercury Porosimetry   11/14/2000

"Baseline" errors in mercury porosimetry data are errors that occur even when no sample is placed in the sample bulb and when a zero intrusion or extrusion volume of mercury would be expected as the pressure is increased to 60,000 psia and then decreased again.   The material which follows relates the causes of these errors and discusses ways to minimize and compensate for them when maximum accuracy is required.

Baseline Errors

When the AutoPore series of mercury porosimeters applies pressure (up to 60,000 psia) to the mercury, penetrometer, and surrounding high pressure oil, compression occurs.

Compressibility effects account for a substantial portion of the baseline errors. The penetrometer bulb and capillary are made of glass which decreases in linear dimensions by about 0.8% and in volume by 2.3% at 60,000 psia. If the mercury were incompressible, a typical penetrometer having a 400 microliter capillary and a 5 milliliter bulb would experience a rise of mercury in the capillary of about 124 microliters or 31% of the capillary. Fortunately, mercury compresses also, but slightly more than glass such that the capillary actually falls some as the pressure is increased. The compressibility amounts to about 150 microliters in this example leaving a net fall of 26 microliters or about 6% of the capillary. The oil which surrounds the penetrometer and transmits the pressure to the mercury compresses at more than 10 times the rate of the mercury and occupies only 3/4 the original volume at 60,000 psia. Some of the oil is in the electric field of the capacitor, especially around the sample bulb and its connection to the exterior. The dielectric constant of the oil increases with its density. This contributes an increasing capacitance which cancels some of the decrease due to the net fall of mercury with compression.

Other effects caused by compression arise from the plastic insulators which are used on the penetrometer bulb base to prevent an electrical short circuit.   Not only does the plastic compress almost as much as the oil, but it lags behind and only slowly assumes its final density. This is especially pronounced upon release of pressure where the plastic may continue to increase in dimensions for almost an hour. It also tends to increase the dielectric constant and capacitance with increasing pressure. The pressure vessel expands as the internal pressure is increased and, like the plastic, requires considerable time to stabilize. The resulting changes in spacing from the sample bulb to the walls and bottom causes a decrease in capacitance. Micromeritics has minimized this effect by making the initial spacings as large as is practical.

Another effect, and the one most difficult to predict, arises from the similarity of the penetrometer to a thermometer. This would not be troublesome if its temperature could be maintained constant, but compression of the surrounding oil causes a temperature rise of nearly 50°C in the oil and a smaller change in the glass and mercury. How quickly this heat is transferred to the mercury depends upon how

rapidly the pressure is being increased, the relative amounts of oil and mercury present, and how recently the vessel has been previously cycled and the metal and oil warmed relative to the penetrometer. Release of the pressure causes the inverse effect, chilling the oil and setting up a reversal of the heat flow. The thermal gradient across the glass of the penetrometer may be considerable such that little benefit may be derived from precisely equalizing the temperature coefficients of the mercury and glass. As might be expected this problem is worst when the sample bulb is large and the capillary volume small. Choosing the right penetrometer helps minimize this effect.   Make sure the sample nearly matches the size of the sample bulb and that the capillary volume is large enough to satisfy intrusion.

An Approach to Error Compensation

Situations arise where the typical errors of about 1.0% of capillary volume are significant or where the errors exceed this level due to unfavorable sample characteristics. Most commonly, this happens when one of the following is encountered: 1) The amount of sample available is so limited that the intrusion volume is only a small fraction of the smallest diameter capillary; 2) adequate sample is available but the porosity is so low that a limited amount of the smallest capillary is used even though the largest sample bulb is filled; 3) the sample is of small or moderate porosity and its compressibility or thermal properties differ considerably from those of mercury; 4) accuracy and reproducibility specifications have been imposed at levels tighter than the typically expected levels for mercury porosimetry. In such cases "blank corrections" may be used to advantage.

To apply blank correction, the operator should run a blank run, store the results using the exact run conditions and penetrometer type to be used for the real sample, and subtract this result from other runs. This technique has been found to be extremely useful. Examples of correction by subtracting a blank run file are shown in Figures 1 and 2.

CUMULATIVE INTRUSION vs DIAMETER
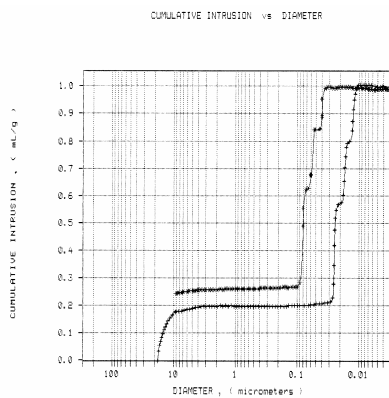
CUMULATIVE INTRUSION vs PRESSURE