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APPLICATION NOTE, APPN-01

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The WSI POROMETER gas displacement models (**3G**, **3Gz**, **micro**, ***macro*** and ***nano***) monitor the expulsion of a wetting liquid from the pores of a specimen with increasing pressure. Flow rate and pressure are measured and pore flow and number and other distributions are measured in the overall size range of approximately 500 diameter down to 0.04 µm diameter or < 2 nm if instead of gas, a liquid is used to displace the wetting fluid. The exact range depends on model. This application note gives details of both gas displacement and liquid displacement Porometry.

GAS DISPLACEMENT METHOD

The specimen to be analyzed is immersed and wetted preferably in a liquid with low surface tension, low vapor pressure and low reactivity. WSI POROFIL™, a specially selected and filtered fluorinated hydrocarbon, is the preferred liquid, although water and other liquids may be used if desired. The specimen is placed in a sample holder assembly and subjected to increasing pressure and flow of dry air (or liquid). The wetting liquid is expelled from the pores of the specimen when the pressure is great enough to overcome the capillary attraction of the liquid in the pores. Monitoring the initial fluid flow (i.e. the bubble point; at which gas or liquid is first seen to pass through the specimen) allows the calculation of the maximum pore size. Continuing the pressure increase allows a pressure/flow curve with 256 or other number of data points to be obtained. When all of the pores are emptied, the pressure/flow curve will have the same slope as that obtained with a dry (non-wetted) specimen, or in the case of a flowing liquid, without the wetting fluid present in the pores. The pressure is then automatically reduced to that of atmospheric pressure and the flow reduces to zero. The pressure is then automatically increased again and a 'dry' curve is obtained on the same specimen, establishing the pressure/ flow characteristics of the dry specimen. The two runs (wet and dry curves) allow the pore distribution to be calculated.

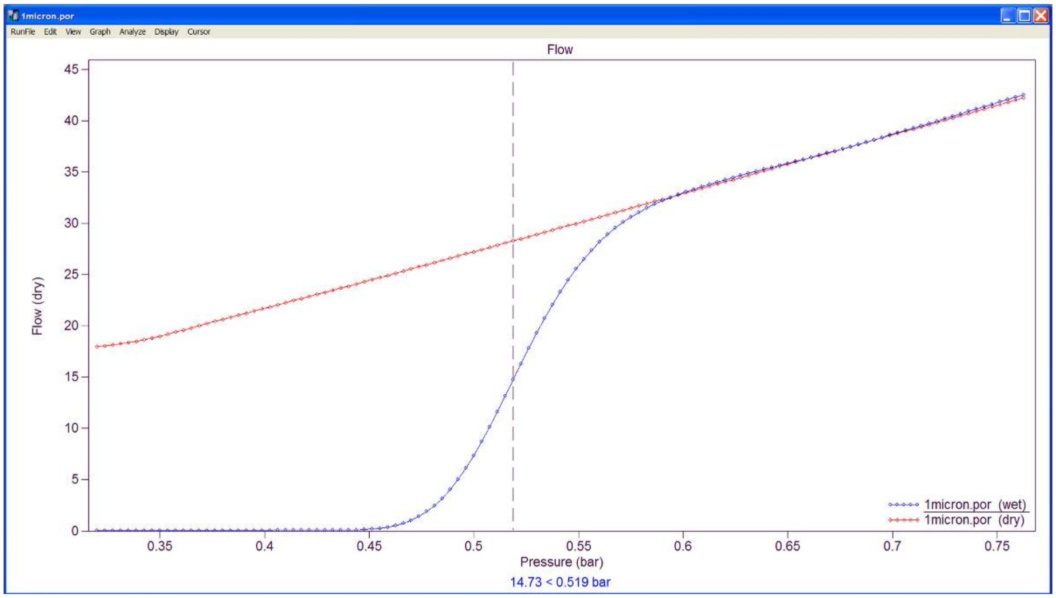

Fig. 1 Run screen showing completed data set for gas displacement

LIQUID DISPLACEMENT METHOD

The use of a liquid to displace the wetting fluid has some advantages, the most significant being that for a given pressure liquid measures smaller pore sizes than gas. The run data obtained is similar to that of gas, however the flow rates are significantly lower and run time is somewhat longer. To perform this type of analysis, a liquid flow sensor is required and this is available as an option with the Porometer nano. Although a gas pressure is used to displace the liquid and flow rate can be detected on the gas flow sensors, a true liquid flow sensor gives more stable data due to fluctuations caused by gas compression.

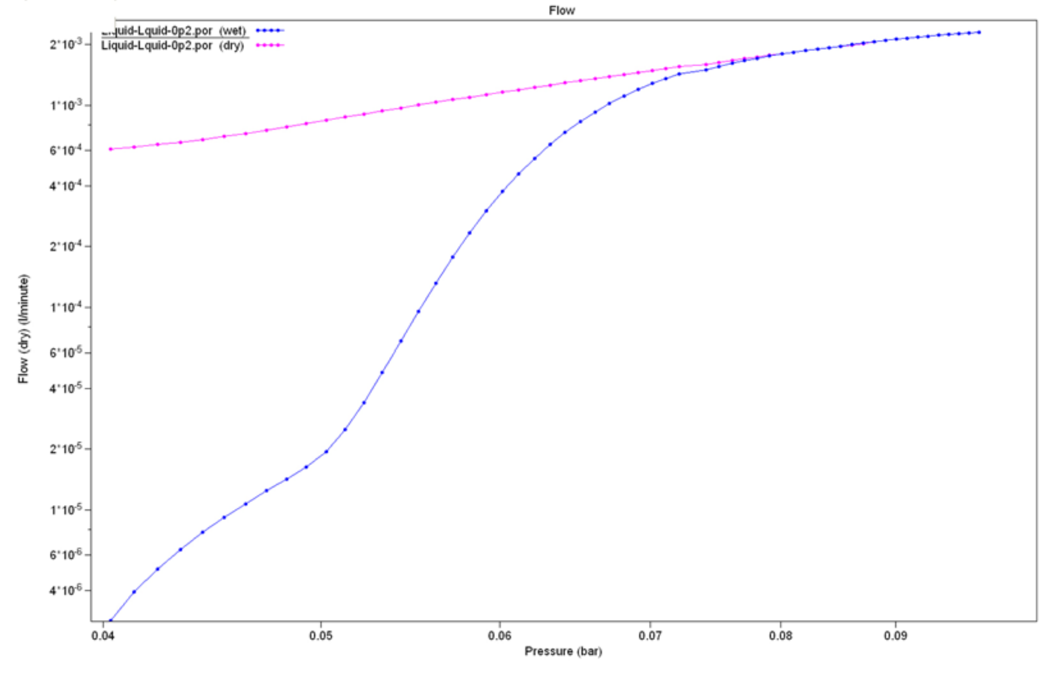

Fig. 2 Run Screen showing Liquid-Liquid Example for 200 nm membrane

The liquid-liquid data set shown in Fig. 2 is of a 200 nm membrane. To compare this data with the same run data sample set from the gas displacement method, two additional Figures are included. Fig. 3 shows the gas set and Fig 4. shows a log-log plot of both gas and liquid data. The log scale is necessary to be able to visualize the differences between them. The calculated pore size data is given later in this application note.

The WSI POROMETERS are microcomputer controlled and use a menu driven Windows program user interface. The operator enters sample identification, any changes in system parameters and pore size range to be evaluated. A real time plotted display of pressure versus flow is presented on the Visual Display with the pressure axis converted to pore sizes (pore diameter) assuming a parallel wall cylinder model. At the completion of the wet run, 256 data points are stored in memory. The instrument then resets and the dry run is performed automatically. After the end of the run cumulative and differential plots of pore size distribution, together with maximum, minimum and mean flow pore sizes are displayed on the Visual Display. All data displayed on the Visual Display may be printed on a Windows identified printer and saved to a data file. It is possible to measure the dry run first, rather than the wet.

The pressure control is achieved with a computer controlled pressure regulator system. Regulated air flows via the temperature controlled mass flow sensor to the sample holder and the pressure sensor module. A typical pressure sensor module comprises a 0-16 bar sensor, a 0 1.0 bar sensor and a relief valve. During initial pressurization, the 0-1 bar sensor is operative. At the end of the useful range of this sensor, the 0-16 bar sensor is enabled. The gas/liquid separator traps liquid on the downstream side of the specimen holder. At the start of the analysis, the bubble point detection algorithm monitors mass flow.

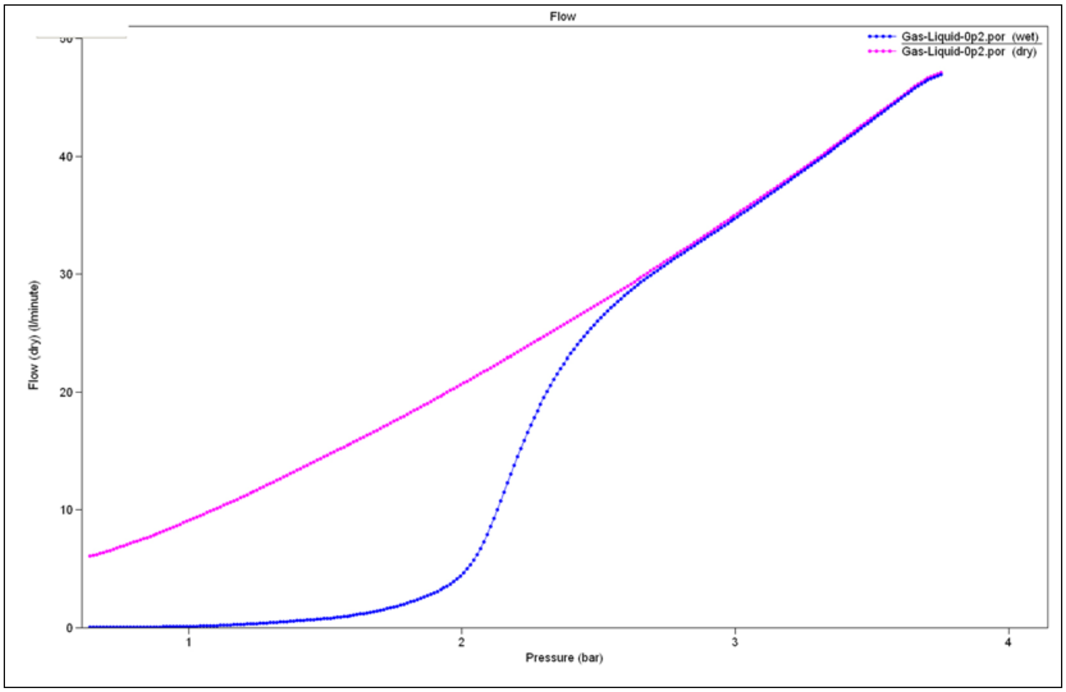

Fig 3 Gas Displacement data for 200 nm membrane sample

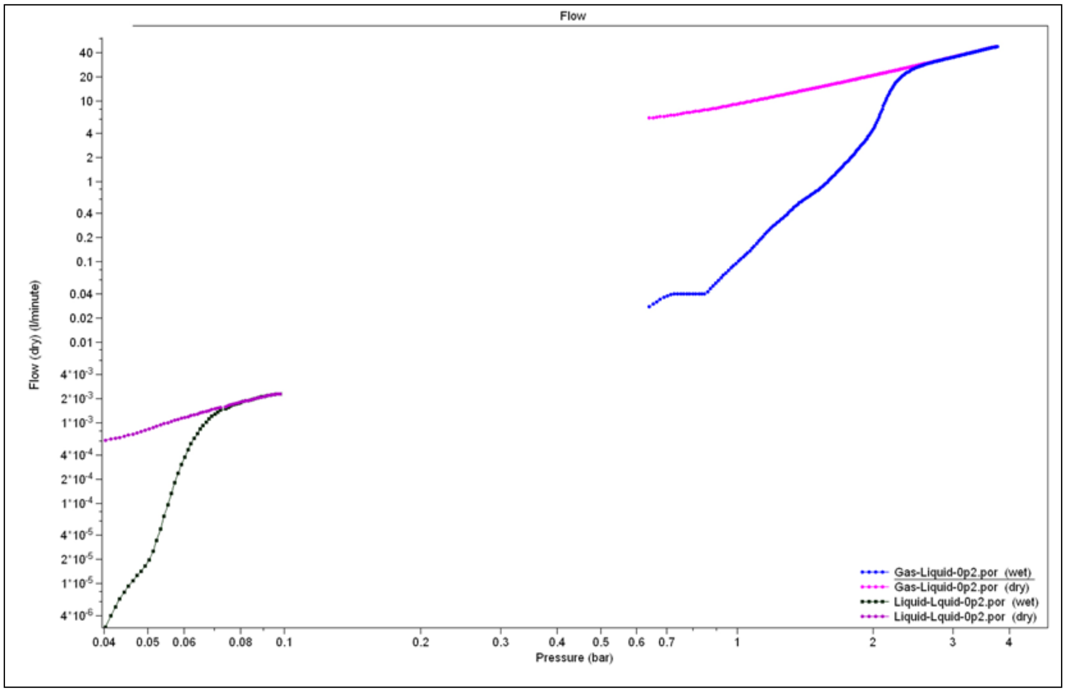

Fig. 4 Overlay of Liquid and Displacement Data for 200 nm membrane

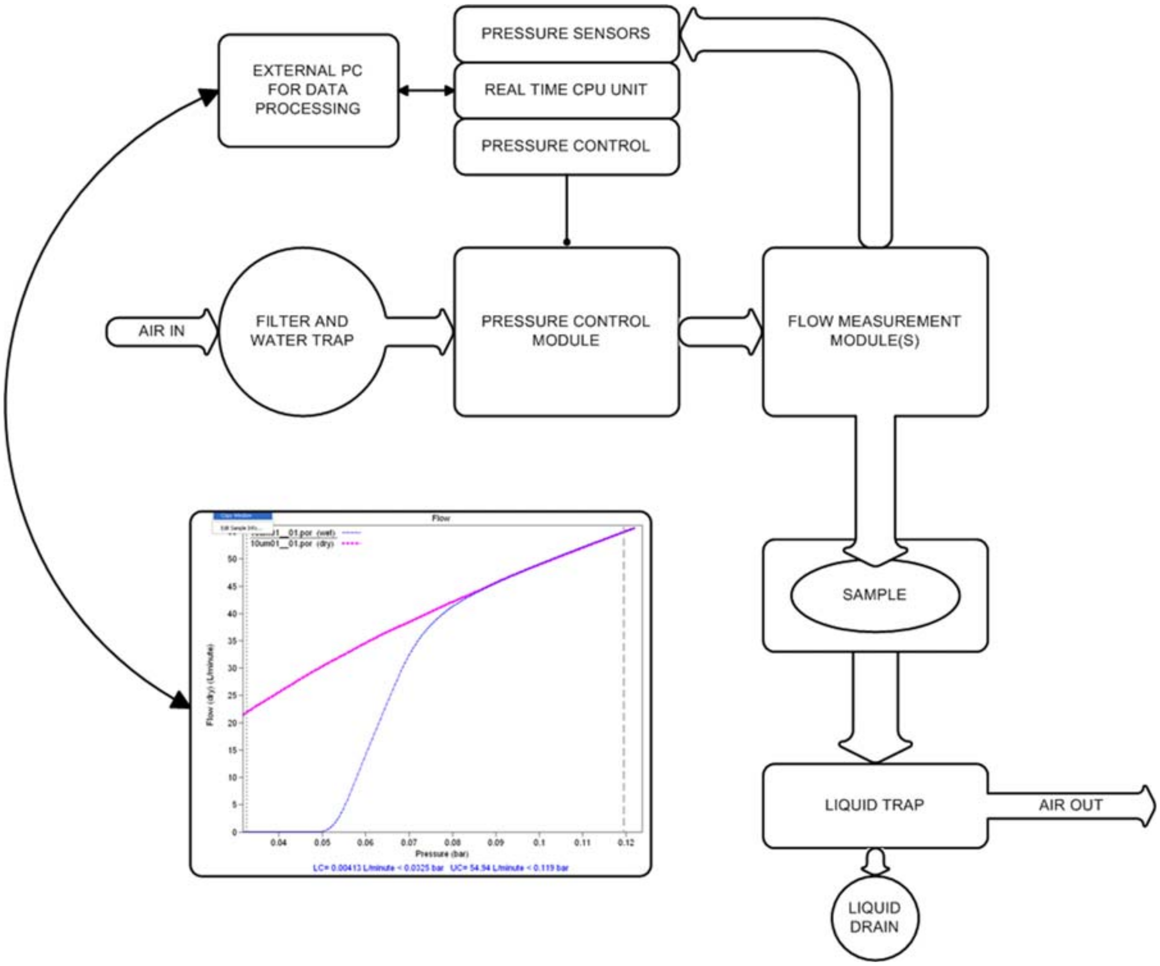

Fig. 5 WSI Porometer 3Gz Block Diagram

Pore Size Analysis, Basic Theory

The WSI POROMETER models use a liquid displacement technique to measure the pore size distribution of a sample. The sample is first thoroughly wetted with liquid of low surface tension and low vapor pressure, e.g. WSI POROFIL, such that all of the pores have been filled with the liquid. The wetted sample is subjected to increasing pressure, applied by a gas source. As the pressure of gas increases, it will reach a point where it can overcome the surface tension of the liquid in the largest pores and will push the liquid out. Increasing the pressure still further allows gas to flow through smaller pores, until all of the pores have been emptied. By monitoring the pressure applied to the sample and the mass flow through the sample the while the wetting liquid is being expelled, a 'wet' run is obtained for the sample. If the sample is then tested 'dry' without wetting fluid in its pores, a 'dry' run is obtained. By comparing the flows on the 'wet' run with those from the 'dry' run, the pore size distribution can be calculated.

The method depends upon the capillary rise created by surface tension. A wetted capillary or pore immersed in a liquid draws liquid up the capillary until equilibrium with the force of gravity is obtained.

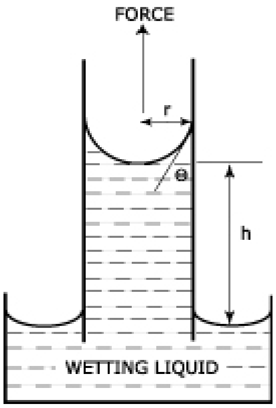

Fig. 6

The equilibrium conditions can be expressed as:

$$2\pi\ r\ \gamma \cos\theta = r^2\ \pi\ h\ \rho\ g \ldots\ldots\ldots\ldots \text{(Eq. 1)}$$

Where:

r= radius of the capillary (or pore)
h= height of column of liquid
γ= surface tension of liquid
ρ= density of liquid
θ= contact angle between the liquid and capillary wall
g= acceleration due to gravity

and since pressure (P) = $h\rho g$, equation 1 becomes

$$Pr = 2\ \lambda \cos\theta \ldots\ldots\ldots\ldots \text{(Eq. 2)}$$

If the liquid does not wet the capillary, the contact angle formed between the specimen pores (capillaries) and the liquid in use is greater than 90 degrees.

However, if the liquid (e.g. POROFIL) is used, it fully wets the capillary and assuming a zero contact angle, i.e. cos r = 1, equation (2) may be restated as

$$\text{Pore diameter } (\mu m) = \frac{40\ \lambda\ (mN/m)}{\text{Pressure (mbar)}} \ldots\ldots\ldots\ldots \text{(Eq. 3)}$$

Thus, by measuring the pressure of gas required to force the liquid out of the capillary (or pore), the diameter of that capillary (or pore) can be obtained. For Porofil, Equation 3 simplifies to Pore Diameter (µm) = 0.64 / Pressure (bar), where the constant 0.64 is K. This equation assumes a cylindrical pore. Alternative pore shapes may be assumed. To implement alternative pore shapes, the size conversion factor must be changed. This factor is applicable for gas displacement of the wetting fluid, however if a liquid is used to displace the wetting fluid, the constant K, shown as 0.64 above becomes much lower, since by using another liquid the Interfacial Contact angle between the two liquids becomes relevant, rather than the gas / liquid / sample Surface Tension. The term Interfacial Tension is used her to distinguish the two systems; it is essentially the same as Surface Tension. An example Interfacial tension for a Water-based system is, It should be noted that water is only very slightly soluble in Isobutanol:

Wetting Liquid	*Flowing Liquid*	*Interfacial Tension, nM/m*
Water	Isobutanol	1.7

This yields a size factor of 0.068 as compared to 0.64 for Porofil and a gas system. Other liquid choices provide different interfacial tension values. The system used with the example shown in Fig. 5 is 0.05 assuming zero contact angle.

In operation, the sample is wetted with WSI POROFIL (or other liquid) and an increasing pressure of air (or liquid) applied. A mass flow versus pressure curve is obtained (as in Fig. 7, blue curve, the 'wet' curve) between the starting and ending pressure points. This example is for gas displacement of the wetting fluid. If a liquid is used as the displacing medium, the surface tension / contact angle of the wetting fluid with gas is no longer valid. With a liquid-liquid system, the Interfacial Tension becomes important (this termed is used to help distinguish the difference between the gas system and liquid system). Here Interfacial Tension is assumed to refer to that between the wetting liquid and the flowing liquid.

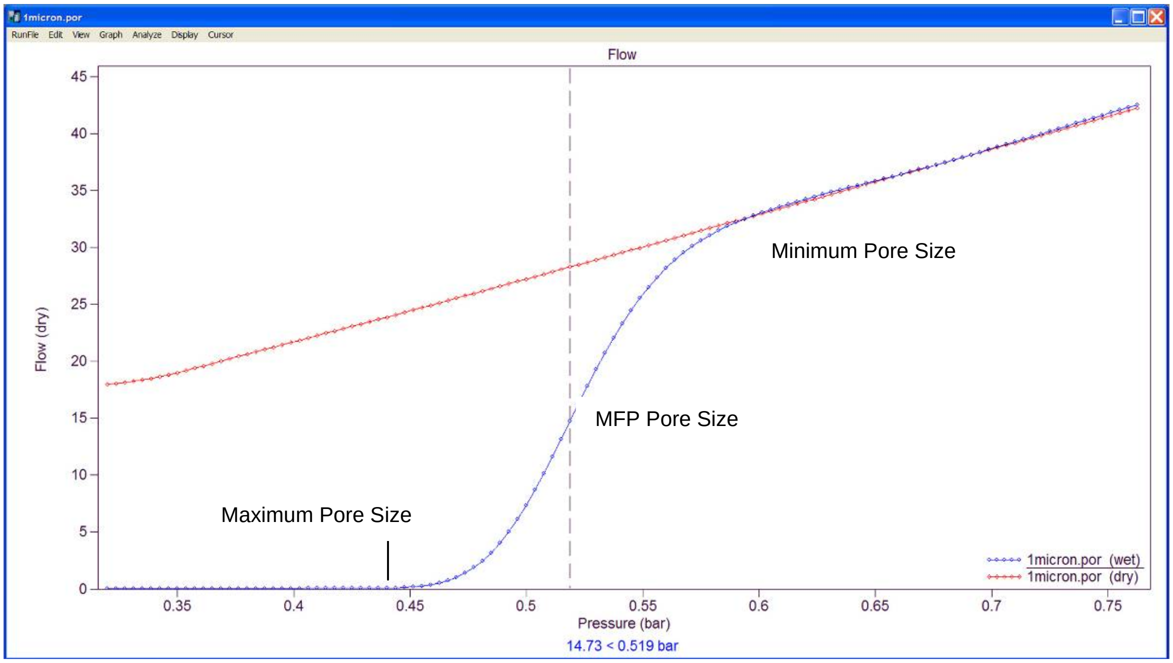

Fig. 7 Annotated run Screen for gas displacement

The system pressure is then automatically reduced to the starting pressure and then increased again to the end pressure thereby deriving the red line (the 'dry' line).
The vertical mark applied to the wet curve is that of the first detectable flow of air through the wetted sample and corresponds to the Maximum Pore Size (often called the bubble point). The size at which the wet flow has reached 98% of its maximum flow is defined as the Minimum Pore Size. The Mean Flow Pore Size is the value where 50% of the 'dry' curve crosses the 'wet' curve. This refers to the gas system, however a similar situation occurs with the liquid system.

256 data points (or more or less) of flow and pressure values) are obtained, from which the following size distributions are calculated, if required, and are plotted against equivalent pore diameter (the diameter of a straight cylindrical pore of equal properties; the theory is based on a cylindrical pore model).

A Liquid – Liquid system is essentially the same except at much lower flow rates. With a liquid system, the liquids used must be filtered with smaller pores than that of the sample to be measured.

Bubble Point (Maximum Pore Size)

The definition for ‘bubble point is the pressure (or equivalent pore size) at which the first continuous stream of bubbles is detected. The detection of the first bubble is not necessarily the same as the bubble point. Another way to look at the bubble point is the transition point between diffusion flow and bulk gas flow through the sample.

To be compatible with the ASTM methods of measuring bubble point, the rate of rise of pressure should be controlled. If the pressure is increased too quickly, the correct bubble point may be missed (bypassed), and if the pressure is raised too slowly, diffusion or transverse flow may be incorrectly identified as the bubble point. Use of an absolute flow rate determination may be a good way to identify the “largest pore size” of a series of samples; however the data will vary with sample permeability and sample area.

The older manual ways of identifying bubble point with observation of the “the first stream of bubbles” or “first bubble”, “third bubble” or other similar method is somewhat operator dependent.

To determine the bubble point (or maximum pore size) with an automatic instrument a method that is not dependent upon the sample area and the sample permeability must be used. The correct way should use a consistent and carefully controlled pressure increase rate as specified in the original bubble point test methods.

The automatic bubble point mode in the WSI Porometer 3G (and earlier Coulter Porometer and Porometer II units) produces consistent data regardless of the measured sample area. The exact algorithms used are proprietary and therefore are not explained in detail.

Mean Flow Pore Size (MFP)

The Mean Flow Pore Size is calculated from the pressure intersection point of half the dry flow value with the wet flow data pressure point. It often corresponds to the peak of the differential pore flow size distribution, but only if the pore size distribution is mono-modal.

Minimum Pore Size

The Minimum Pore Size is calculated at the pressure where the wet and dry data plots converge. The automatic software determination of this convergence point is difficult and not as repeatable as the 98% value that was introduced with the Coulter Porometer and used with the WSI Porometer 3G.

Cumulative Flow Distribution

$$\text{Cumulative flow (CF(n))} = \frac{\text{Wet Flow (n)}}{\text{Dry Flow (n)}} \quad \text{(Eq. 4)}$$

for n = 0 to 255 data points

Differential Flow Distribution

$$\text{Differential Flow (DF(n))} = \frac{\text{CF(n+1) - CF(n-1)}}{2} \quad \text{(Eq. 5)}$$

for n = 0 to 255 data points

Number Distribution Calculations

The following number distribution calculations are implemented on the Porometer models.

The Hagen-Poiseuille Equation (Eq. 4.8) determines the flow rate ***Q*** of a fluid (air) with viscosity η, and differential pressure, ***ΔP*** through a number of cylindrical pores, ***N*** of radius ***r*** and length, ***l*** :

$$Q = \frac{N\pi r^4 \Delta P}{8\eta l} \qquad \text{. . . . . (Eq. 8)}$$

Tortuosity is a user input value and its value is 1 for cylindrical pores. Tortuosity is defined in the following way:

Pore Length, *l* = Sample Thickness .Tortuosity . . . .(Eq. 9)

For a very tortuous pore, a value of 5 or more should be used for the Tortuosity. There are no real guidelines to follow; this should largely be an empirical determination. Use of a Tortuosity value of 1 for all samples in a series will still give comparable pore number distributions; however only for true cylindrical pores will a value of 1 give true number values.

Example Pore Size Distributions

The following plots show differential pore size distributions for the nominal 200 nm membrane using both gas and liquid Porometry methods. This data is based upon different channel widths, and so direct comparisons other than distribution location are not obvious, but they do illustrate the ability of the liquid-liquid method to give comparable data to the gas-liquid method at much lower pressures.

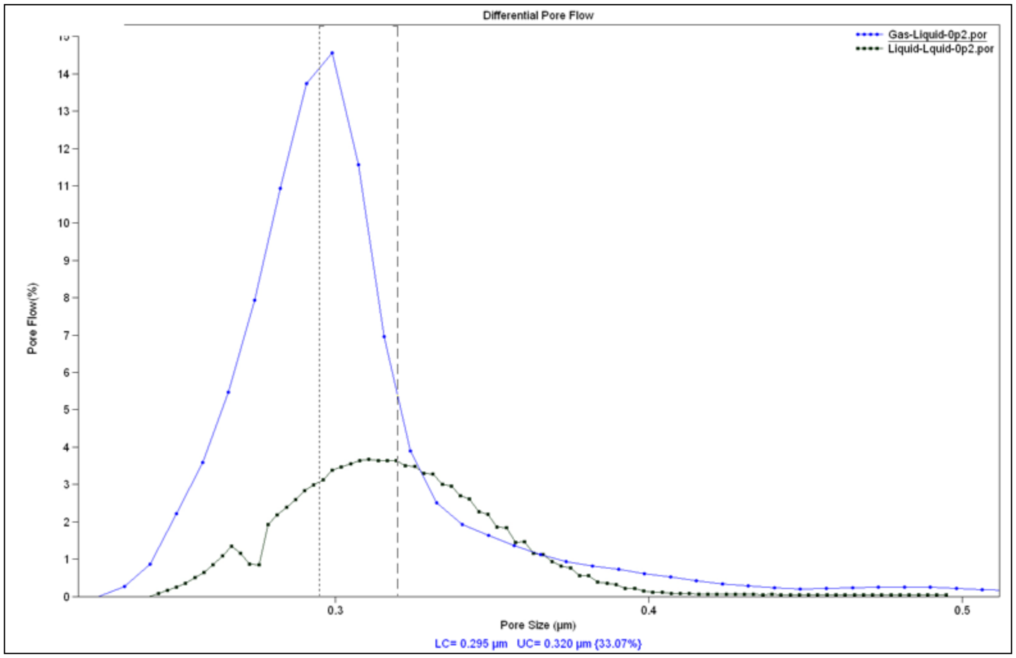

Fig. 8 Differential Flow % Distributions for Liquid – Liquid and Gas – Liquid systems for the nominal 200 nm sample

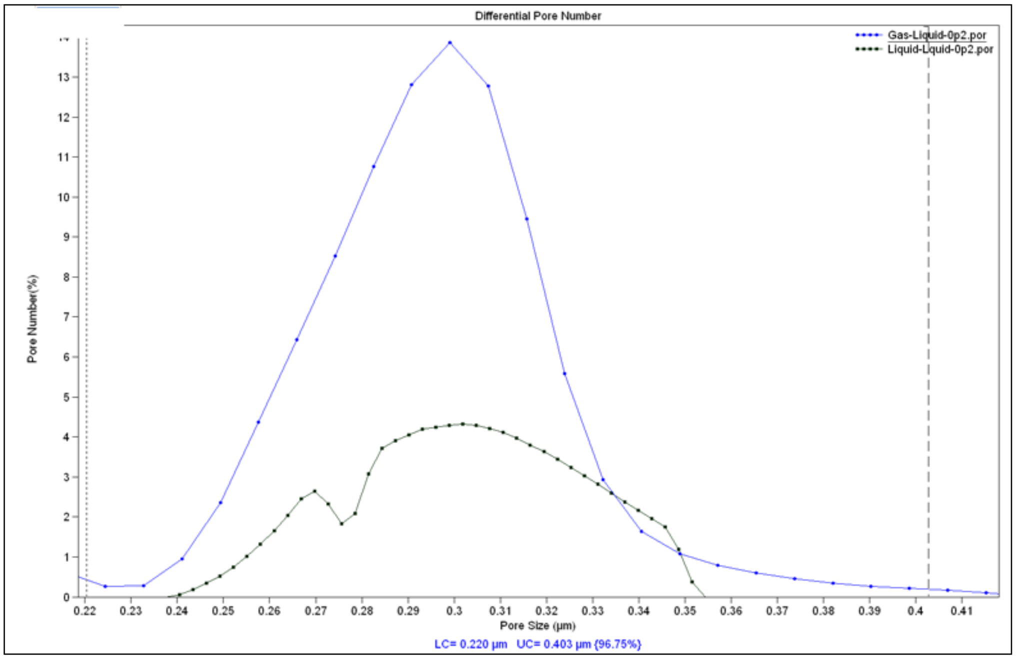

Fig. 9 Differential Pore Number % Size Distributions for Liquid - Liquid and Gas – Liquid systems for the nominal 200 nm membrane sample