

Calculations used in porometry

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A porometer measures gas flow as function of an applied pressure. Typical curves for the wet and dry curve for a filter or membrane are shown in figure 1 below. The wet curve is measured to determine the pore sizes, the dry curve is needed for the calculation of both the mean flow pore size, smallest pores and the gas permeability.

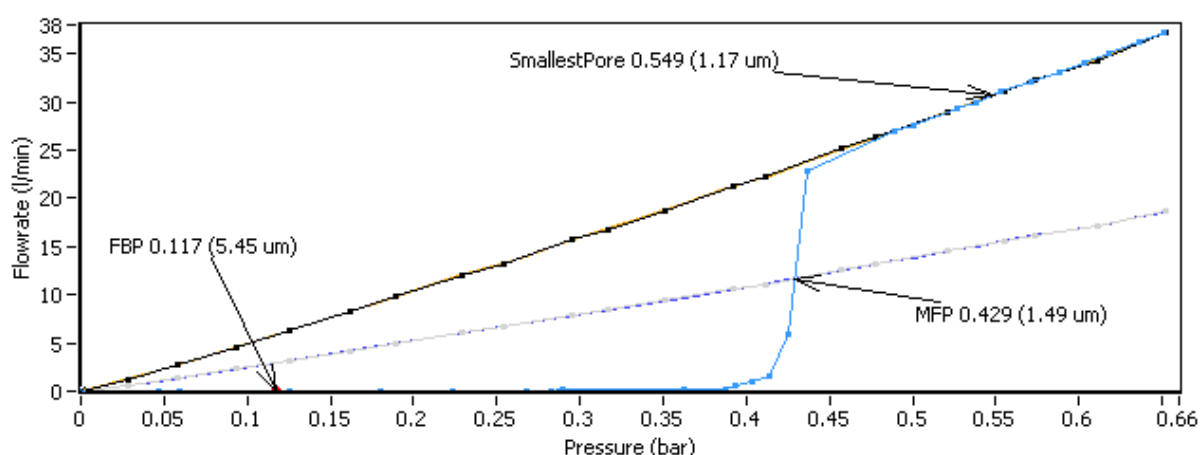


Figure 1: Typical example of a porometer measurement on a filter

As one can read in the application note about the determination of the first bubble point, there are several ways to determine this important parameter. The mean flow pore size or MFP is calculated by the intersection of the wet curve (blue line in figure 1) and the so-called “half dry” curve. This “half dry” curve (the grey dotted line in figure 1) is the mathematical half of the dry curve. Usually this coincides with the most populated fraction of pores within a filter. The smallest pore is calculated as the pressure where the dry curve (black line in figure 1) meets the wet curve.

To recalculate these pressures towards a pore size value, the Washburn equation is used. The Washburn equation expresses the mathematical link between pressure and pore diameter, using surface tension and contact angle of the wetting liquid:

$$D = 0.04 \gamma \cos \theta / P$$

With D the pore diameter in μm , γ the surface tension in dyn/cm, θ the contact angle between the wetting liquid and the substrate and P the pressure in bar.

When a wetting liquid is fully wetting, no contact angle (figure 2) should be observed. A good wetting liquid completely disappears into the pores. The choice of a good wetting liquid with almost no contact angle is essential for a good measurement and it simplifies the Washburn equation as the cosine of a zero angle equals one. Thus for a proper wetting liquid, the Washburn equation can be rewritten as:

$$D = 0.04 \gamma / P$$

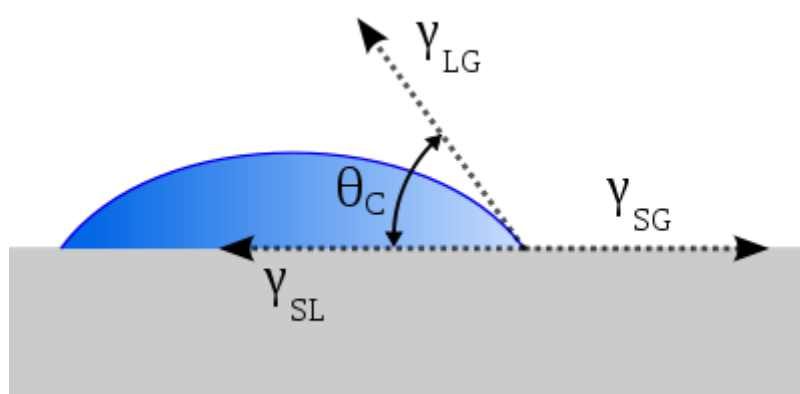


Figure 2: Definition of the contact angle θ (source: Wikipedia)

The surface tension is usually generalized to the surface tension between the liquid and air or any other inert gas. For water this value is around 72 dyn/cm, for the well-known wetting liquid group of perfluoroethers, this value is around 16 dyn/cm. The Washburn equation assumes all pores are cylindrical and straight. Thus other parameters that can be of influence are the shape and the tortuosity. Therefore sometimes (linear) correction factors such as shape factor and tortuosity factor can be found used.

One of the key advantages of porometers using stability routines for pressure and flow, is that they offer the possibility to overcome the effects of shape and tortuosity: if the pressure is kept stable long enough, eventually all pores with the same diameter will open. Moreover, by changing the stabilization algorithms one can get a good idea about the complexity of the pores in the material (see also application note on influences of shape factor). Porometers without stability routines (pressure scan porometers) don't offer this possibility. Therefore corrections for shape factor and tortuosity can be taken into account.

Besides the first bubble point, mean flow pore size and smallest pore, information about the pore size distribution can be obtained (similar to porosimetry and particle sizing). These calculations are described in ASTM F 316-03. From the wet and dry curve, three other curves are derived from the measured datapoints. The differential curve or DIF shows the percentage of pores present at a certain pressure. The cumulative curve is the sum of all differential values between 0 and 100 %.

However, as the pressure is inversely proportional to the diameter ($P \sim 1/D$), an equal pressure step at low pressure results in a larger pore size step than the same pressure step for smaller pores. For example assume a pressure of 0.1 bar with a 0.05 pressure step. In terms of pore size (if a wetting liquid with 16 dyn/cm is used), this means 6.4 μm (0.1 bar) and 4.3 μm (0.15 bar). At 2 bar the same pressure step of 0.05 bar represents 0.32 μm (2 bar) and 0.31 μm (2.05 bar). To take these differences into account, the DIF curve is recalculated by dividing each fraction with the difference in pore size. This curve is called the corrected differential curve or CDIF. This CDIF curve is often regarded upon as the pore size distribution. Because we only use measured data points, we do not use histograms for the pore size distribution graph.

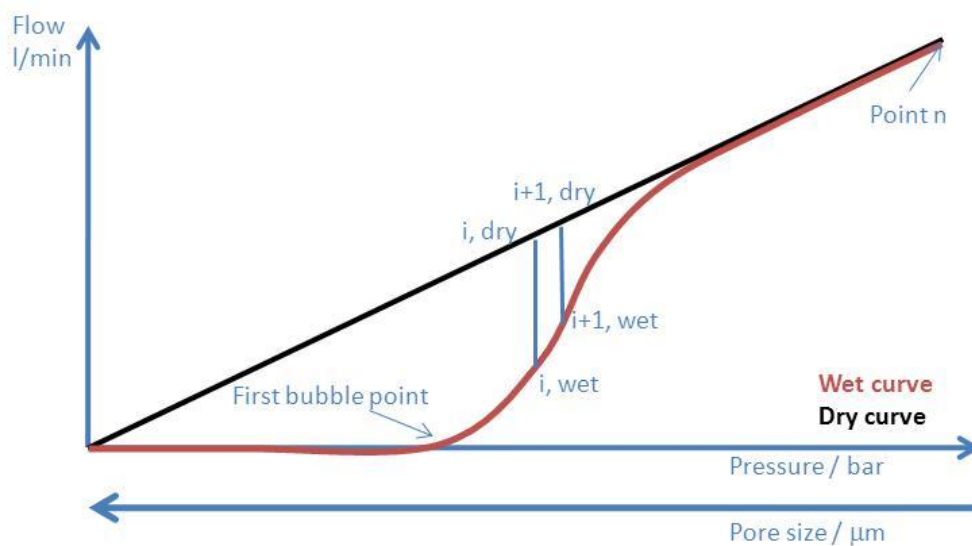


Figure 3: Theoretical wet and dry curve

$$[DIF]_i = \left\{ \frac{\left(\frac{flow\ i + 1, wet}{flow\ i + 1, dry} - \frac{flow\ i, wet}{flow\ i, dry} \right)}{\sum_{j=0}^n \left(\frac{flow\ j + 1, wet}{flow\ j + 1, dry} - \frac{flow\ j, wet}{flow\ j, dry} \right)} \right\} * 100$$

$$[CUM]_i = \sum_{j=0}^i [DIF]_j$$

$$[CDIF]_i = \left\{ \frac{\frac{[DIF]_i}{pore\ size\ (i) - pore\ size\ (i + 1)}}{\sum_{j=0}^n \left(\frac{[DIF]_j}{pore\ size\ (j) - pore\ size\ (j + 1)} \right)} \right\} * 100$$

Figure 4: Mathematical equations for the calculus of the differential, cumulative and corrected

differential curves

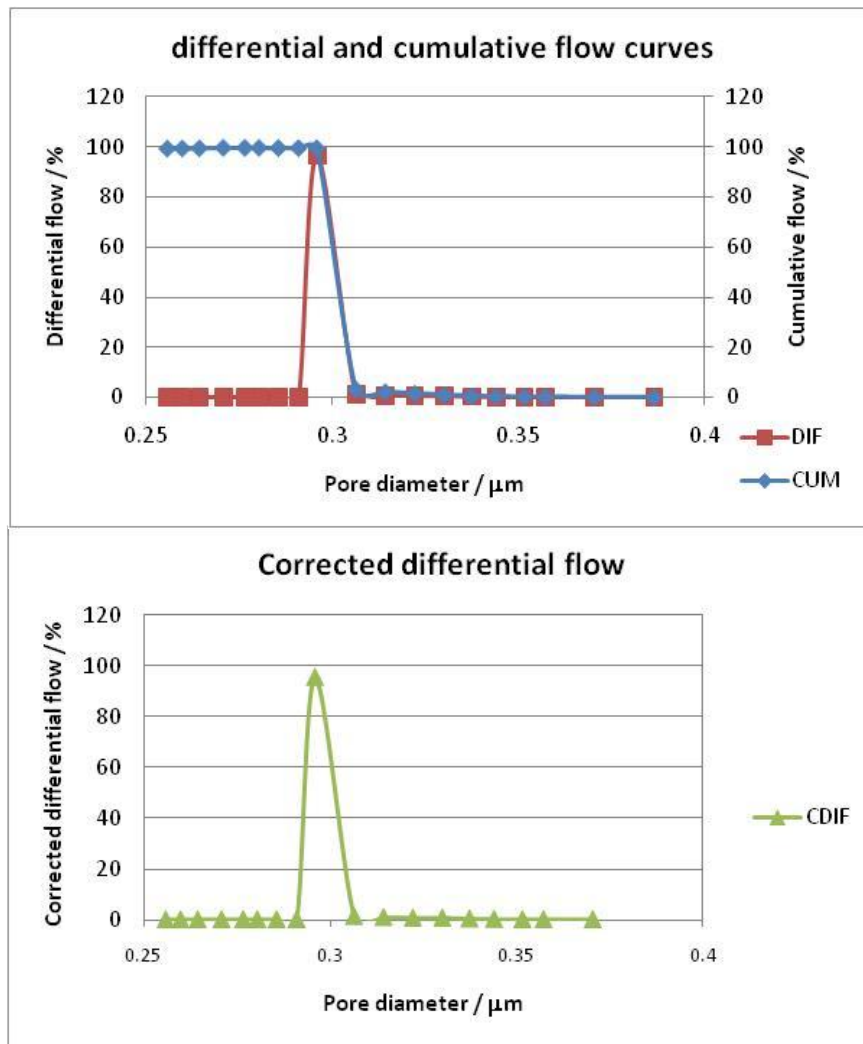


Figure 5: DIF, CUM and CDIF curves of actual measurements.

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