Measurement of Concentration Dependence of Refractive Index
to Confirm Gel Permeation Chromatography Parameter
Application Note
November 2019 by Gabor Kiss

Background

One of the workhorse techniques for polymer characterization is Gel Permeation Chromatography (GPC) which is used to measure molecular weight, molecular weight distribution, degree of branching, radius of gyration, solvent power, etc. The instrument relies on small changes in refractive index due to the presence of polymer in a solvent (called the “mobile phase”) to generate an “elution curve” as solution is pumped through a porous medium. The determinant parameter is the change of refractive index with concentration, called dn/dC. This parameter varies widely among polymer/solvent systems and the GPC analysis software provided with the instrument is provisioned with dn/dC values for common polymer/solvent systems.

It is valuable to confirm the provisioned value by direct measurement, in order to increase confidence in the accuracy of calibration and analysis results. The Rudolph Refractometer offers two approaches.

Problem Statement

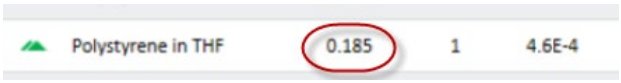
The most common solvent used for GPC is tetrohydrofuran (THF) which is a cyclic ether $(CH_2)_4O$. Polystyrene is a common industrial material used for a huge variety of applications. It is available as narrow molecular weight fractions with Mw/Mn on the order of 1.1 over a wide range of molecular weights.

Typically, GPC instruments and replacement columns are shipped with THF already imbibed into the gel as the mobile phase. Then various narrow distribution fractions are injected and the instrument constants are calculated using the known concentration, MW, and dn/dC values. The more precisely these are known, the more precise the calibration. After determining the instrument constants, the mobile phase is often replaced with a different solvent, but the instrument constants are carried over into the new polymer/solvent system.

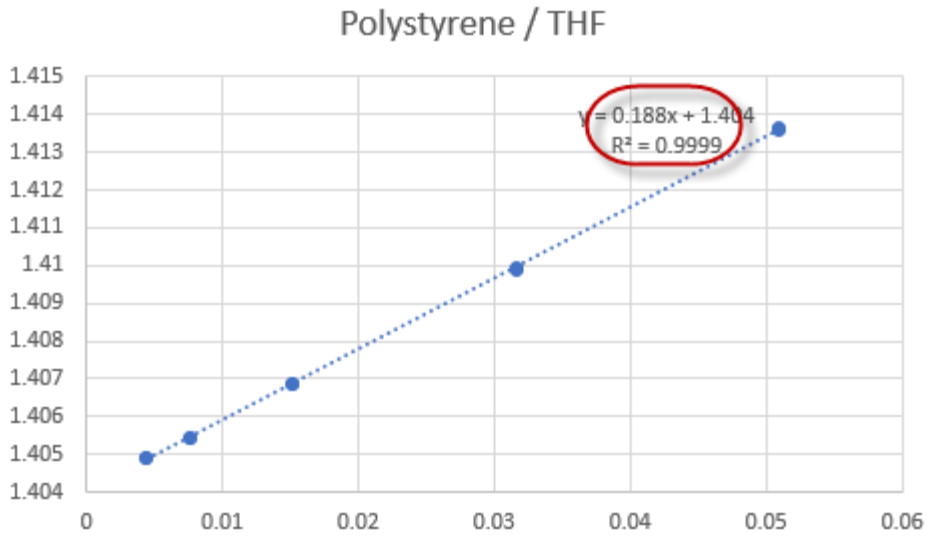
Thus, an independent confirmation of the dn/dC value for PS/THF is desirable to maximize confidence in the calibration and subsequent measurements.

The Measurement and Results

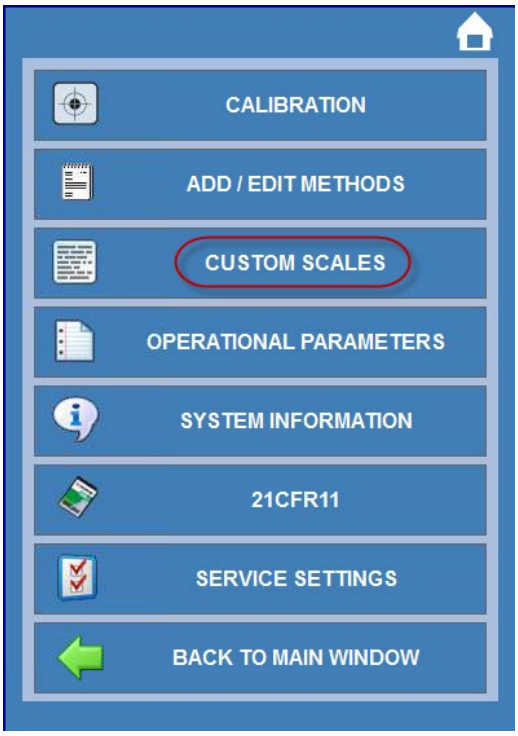
The dn/dC value provisioned into the Malvern OMNISEC software for PS/THF is 0.185

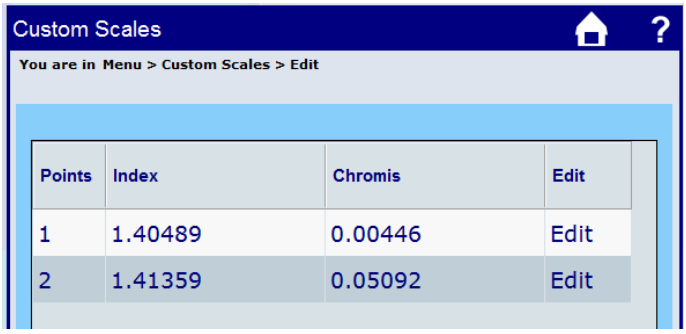


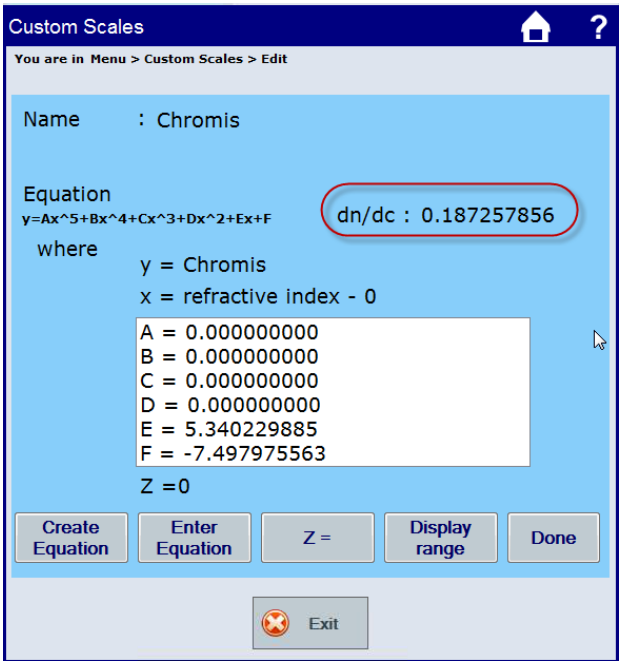
The refractive index for a series of 5 concentrations of polystyrene provided by Malvern was measured with a Rudolph J457 Refractometer. The results are shown below. The results are nearly perfect, with a correlation coefficient of 0.999 and a measured value of 0.188, or 1.6% higher than the provisioned value.



In fact, the Rudolph x57 Series Refractometer has a built-in feature to calculate dn/dC. Using the Custom Scales feature and inputting only two points gives the following result:







This method gives the identical result as the more laborious plotting of multiple points, and both agree with the value published by the GPC vendor, namely 0.187 and 0.188 vs 0.185.

Conclusion

By using the Rudolph Refractometer, a GPC user can easily and quickly obtain the data required to confirm the key dn/dC parameter required for initial setup and calibration of an instrument, and to give increased confidence in the accuracy of subsequent measurements.

Anyone using Gel Permeation Chromatography (GPC) would benefit from this approach.