Retention Volume and Resolution Dependence on Temperature and Pressure for High Temperature Gel Permeation Chromatography.

by

Eric A. Choudhary

A Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

MASTER OF SCIENCE

Major Subject: Chemistry and Chemical Biology

Approved:

_____

Dr. Chang Ryu, Thesis Adviser

_____

Dr. James A. Moore

Rensselaer Polytechnic Institute
Troy, New York

April, 2009
(For Graduation May, 2009)

ABSTRACT

Gel permeation chromatography (GPC) has long been in use as the dominant instrument in polymer analysis, despite having a long analysis time. In order to be able to keep up with the increased demand for speed and capacity, high temperature (HT) operation of GPC can help reduce analysis time by taking advantage of reduced mobile phase viscosity, allowing faster flow rates at a constant pressure. However the increased temperature causes the polymer stationary phase packing to become more susceptible to compression, which can compromise performance. Here, HT-GPC was evaluated for fast analysis with 11 polystyrene standards ranging in molecular weight from 370 to 371,100g/mol from room temperature up to 138 ^{o}C while varying the flow rate at each temperature. A flow rate dependence on retention volume was found at lower temperatures, with increasing flow rate yielding a higher retention volume, which is consistent with previous results due to compression of the mobile phase. It was found that at high temperatures however an increase in pressure leads to a decrease in retention volume to a certain point. This is opposite of the trend at lower temperatures. This is most likely due to compression of the gel pores, which would exclude a greater portion of solutes and cause them to elute sooner. At around 73 ^{o}C there is retention volume independence on flow rate and the two mechanisms cancel each other out.

It was found that analysis time can be cut by more than a factor of 4 using high temperature and faster flow rates, with the tradeoff being a decrease in resolution. The separation efficiency was compared and evaluated by calculating the theoretical plate heights from the chromatograms obtained. At 138 ^{o}C, with a flow rate of 4.0 mL/min, there is an 81% increase in theoretical plate height over a standard room temperature analysis at 1.0 mL/min. Even faster flow rates at the elevated temperature should further reduce analysis time and increase resolution. Faster flow rates will further reduce the effect of longitudinal diffusion and will introduce turbulent flow that will aid in speeding mass transfer. Even with some loss in resolution, the HT-GPC apparatus can be used quickly as a reliable first approximation technique. Another problem found with high temperature operation is a decrease in the working life of the column.