DiscovIR-LC™

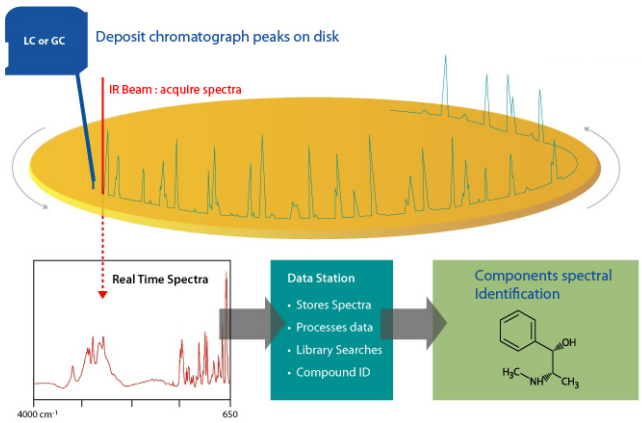
Deposition and Detection System

Application Note 027

June 2008

GPC COLUMN CALIBRATION USING THE DISCOVIR-LC

The DiscovIR-LC is a powerful new tool for materials analysis. When connected to the outlet of an LC column, the DiscovIR deposits the solvent-free LC eluants as a continuous track on an infrared transparent substrate. The built-in interferometer simultaneously captures a set of time-ordered infrared spectra from the deposited track. The result is a map of molecular structure of all sample components.



SUMMARY

This application note demonstrates technique and performance of the DiscovIR-LC system in the calibration of GPC columns. This note demonstrates the utility of FTIR in establishing calibration curves for GPC columns/column sets. Two examples show performance both with high resolution GPC and fast, broad-range column configurations.

The results show that:

- GPC-FTIR can be used for direct calibration, without need for additional mass sensitive detectors
- Elution times correlate closely to traditional liquid detectors
- There is no significant band broadening generated in this FTIR method
- FTIR is applicable to virtually all polymer separations.

Spectra Analysis

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EXPERIMENTAL

Polystyrene Standards Calibration

Calibration with polystyrene standards was performed on a set of four columns.
Columns: Jordi DVB 500Å. 4 – 50 cm X 10 mm ID.
The polystyrene standards were dissolved in CHCl3 at a concentration of 0.5 mg/ml.
Mobile phase: THF, 1 ml/min
Standards samples: 0.5 mg/ml each, 100µl injection, Jordi FLP Catalog # STD20000

Polymethyl methacrylate Standards Calibration

The polymethyl methacrylate (PMMA) standards were used to calibrate a single Jordi mixed bed w5 cm X 10 mm ID column.
PMMA standards were dissolved in CHCl3 at a concentration of 0.5 mg/ml.
Mobile phase: THF, 1 ml/min
Standards samples: 0.5 mg/ml each, 10µl injection, Jordi FLP Catalog # STD20200

Column eluant passed through a UV detector (254 nm), and thence to the DiscovIR-LC, where the eluant was deposited as a solvent-free track on a rotating Zn-Se disc. Residual standards solvent ($CHCl_3$) generated perturbation at the column elution volume, and post-run IR scanning was employed to eliminate this artifact.

RESULTS

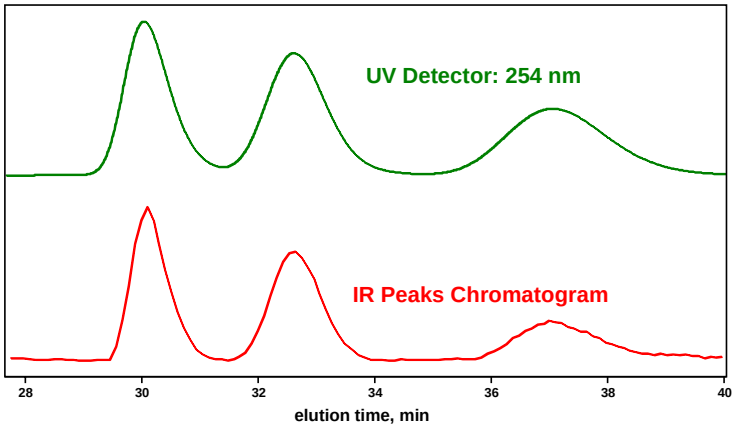

Figure 1 Comparison of the UV detector and IR data

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Figure 1 compares the elution profile of polystyrene standards as measured by a flow-through UV detector and the DiscovIR. As can be seen there is good agreement between the UV detector trace and the infrared chromatogram of the DiscovIR deposit track. Solute entering the DiscovIR is deposited on the collection disc within one second, and the infrared spectrum is acquired 30 seconds later. The system software automatically compensates for this time lag in generating the elution time of each acquired IR spectrum. The band-spreading contribution of the DiscovIR-LC is generally insignificant for polymer GPC separations. Flow injection experiments (no HPLC column) have shown that the DiscovIR operating under normal conditions has the ability to base-line resolve a series of pulsed solute injections of polystyrene at 6 -8 pulses/minute. (Sigma, the standard deviation of the peak width, was measured at 1.5 seconds. Optimizing the DiscovIR-LC operating conditions to minimize bandspreading gave a sigma of 0.8 seconds with polystyrene.) There is no evidence of additional band broadening of the DiscovIR deposits in GPC applications.

When generating a calibration curve, an additional low molecular weight standard was added to the three displayed above. The resulting IR chromatogram is shown in Figure 2. The polymerized individual oligomers of this material are well resolved by the column set. Methyl stretch frequencies are evident in spectra of the oligomer peaks, which are attributed to the polymerization catalyst utilized being incorporated as chain terminal groups in the synthesis.

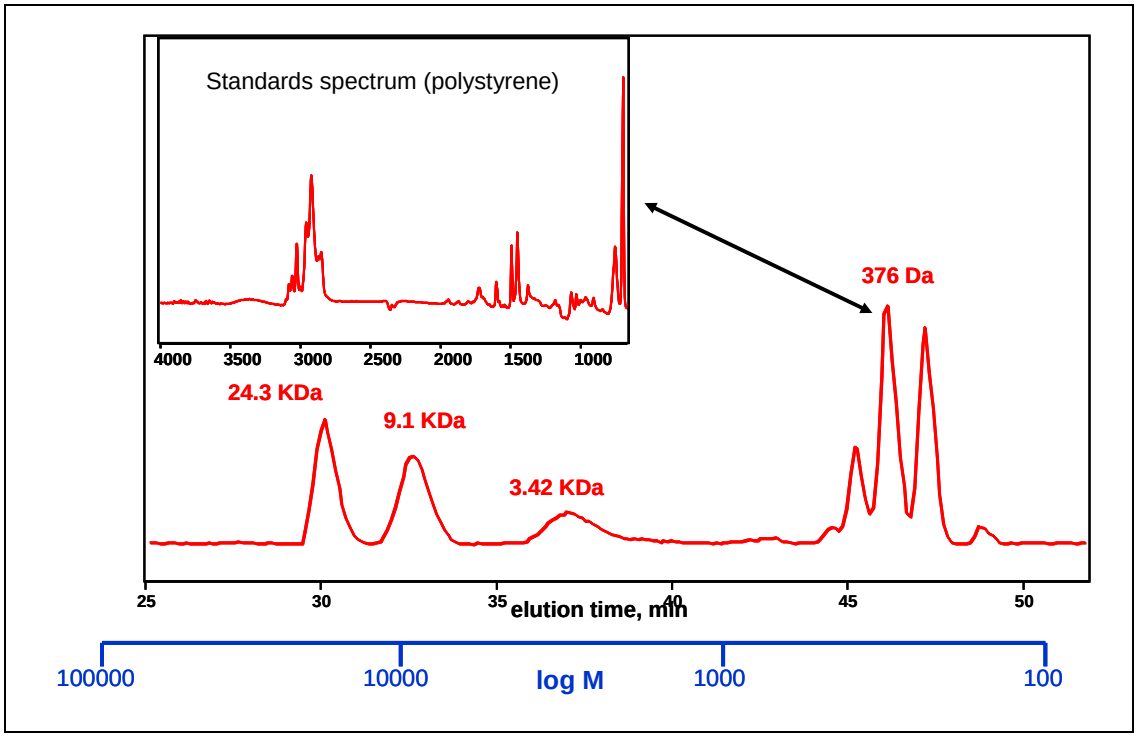

Figure 2 Elution profile of polystyrene standards

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The peak elution times and stated molecular weights of the standards were entered into a Microsoft Excel® spreadsheet. A scatter plot of time/volume vs. the $\log_{10}$ of molecular weight was generated. A linear regression line was then generated as the calibration curve (see Figure 3). This calibration curve was used to define the blue scale shown below the elution time axis in Figure 2.

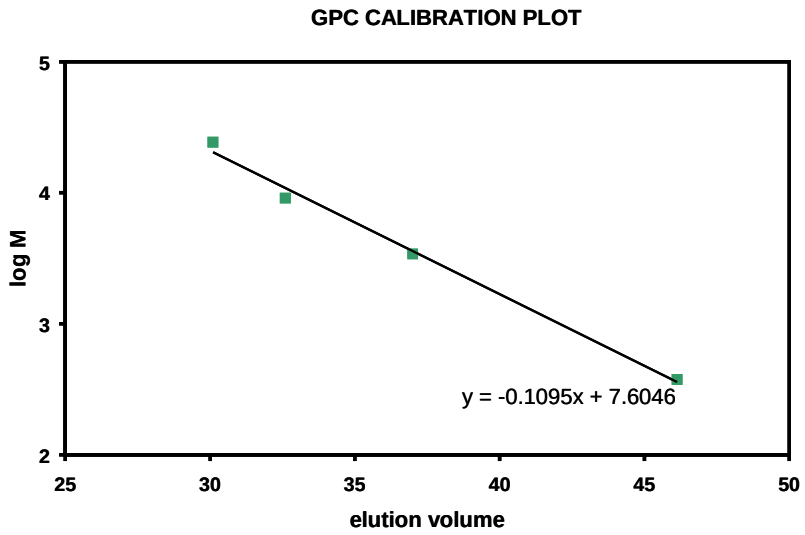

Figure 3 Column calibration plot of polystyrene standards

The set of PMMA standards encompassed a broader molecular weight range. We utilized a mixed bed column that would cover a broader distribution in a relatively short elution time. Results from this calibration experiment are shown in figures 4 and 5.

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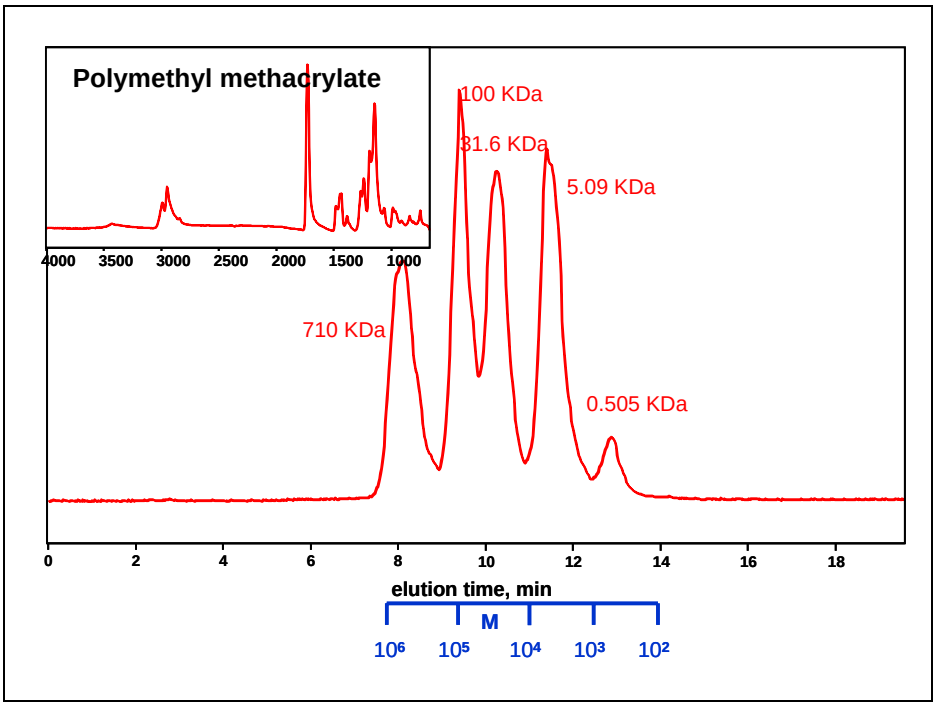

Figure 4 Elution profile of PMMA standards

UV data was unsatisfactory, as PMMA has minimal absorbance in a useful UV range. Virtually all polymers possess satisfactory IR absorbance.

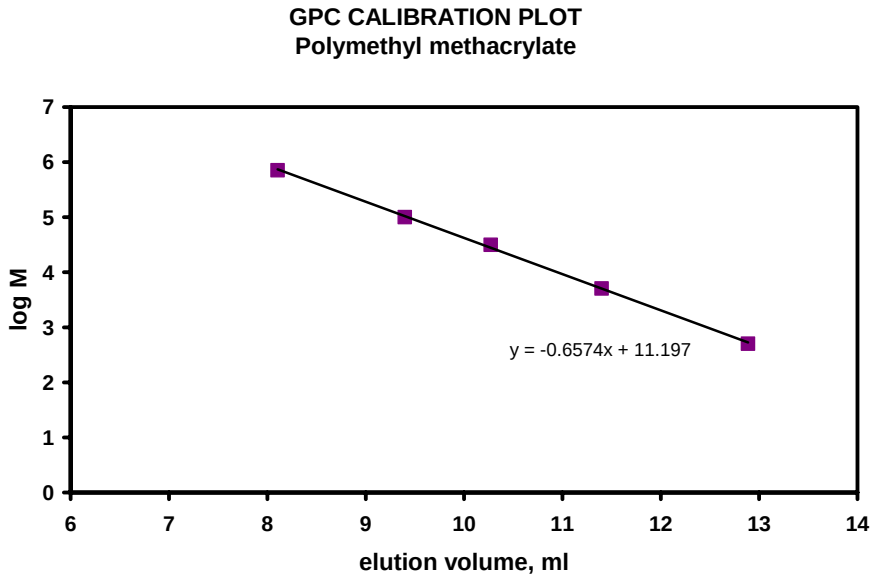

Figure 5 Calibration plot of PMMA standards

CONCLUSIONS

GPC polymer separations can be readily performed with non-specialized HPLC laboratory equipment and the DiscovIR-LC. This equipment setup generates insignificant time offsets to elution profiles and no effective band broadening. FTIR is essentially a universal detector for polymer systems.

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