Agilent 390-MDS Multi Detector Suite

Detector Options for GPC with the 390-MDS Multi Detector Suite

Technical Overview

Introduction

The Agilent 390-MDS can be fitted with a viscometer and/or a light scattering detector to perform all forms of gel permeation chromatography (GPC), greatly increasing the accuracy and information content of the analysis. These detectors probe different aspects of polymers in solution, and reveal how individual polymer chains interact with the solvent. Most importantly, the detectors permit determination of molecular weights that are independent of the chemistry of the standards used for calibration, allowing complex polymers to be analyzed with confidence.

Agilent 390-MDS

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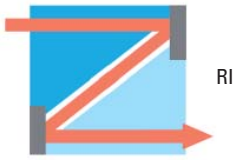
1 Option One - Conventional GPC analysis



Conventional GPC involves using a single concentration detector such as a refractive index detector. The detector simply measures the amount of material eluting from the column at any given time. Measuring when samples of interest elute from the column and comparing this to a column calibration generates the molecular weight values for the sample. The calibration itself is created by measuring the elution behavior of a series of standards of known molecular weight and plotting log M as a function of retention time.

Limitations of Conventional GPC/SEC

Despite its popularity as an analytical tool for the determination of the molecular weight distribution of polymers, conventional GPC does have some fairly major limitations.

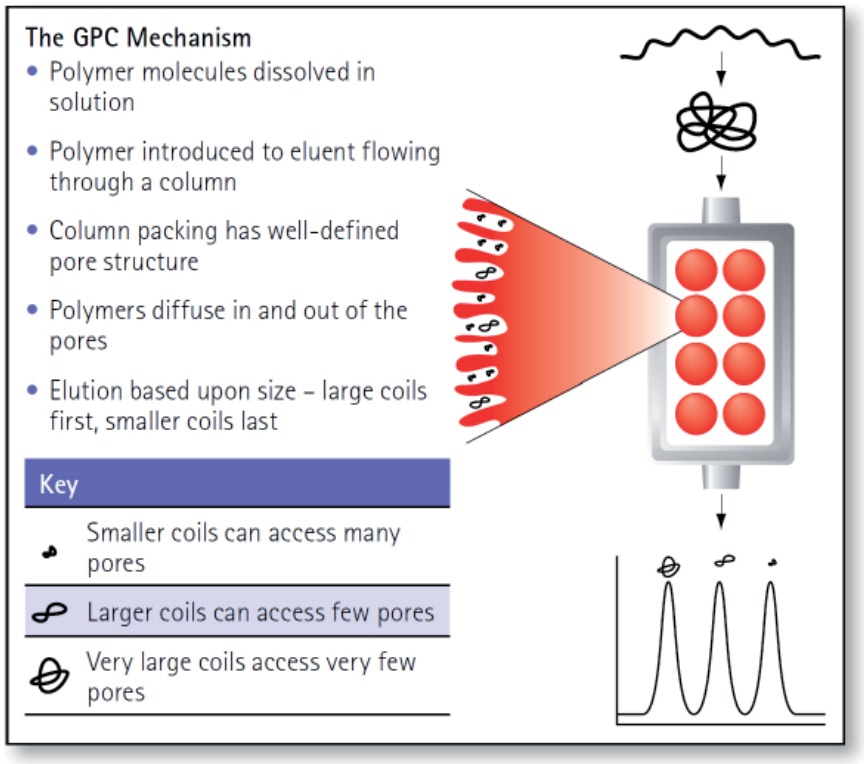
A comparative technique

Conventional GPC/SEC employing a single concentration detector is a comparative technique. During calibration, it is assumed that a series of polymer molecules elute from the GPC/SEC column at particular times based upon their molecular weights. However, the GPC/SEC mechanism separates polymer molecules on the basis of size in solution, not molecular weight. If the samples under analysis are of a different chemistry to the standards used in the calibration, they may have very different sizes at any given molecular weight due to differing degrees of solvation. As a result, the calculated molecular weights for those samples using the calibration will not be accurate but only relative to the standards used to create the calibration.

If the standards used in the calibration and the sample are of the same chemistry, then accurate molecular weights are obtained. However, if the standards and the sample differ chemically, the results are inaccurate. For some analysts, obtaining only relative molecular weights is sufficient, as differences between batches of product can still be observed. However, for other workers, the lack of accurate molecular weights can be a severe limitation of conventional GPC/SEC.

Information poor

Conventional GPC/SEC is relatively information poor. The column separates the polymer molecules on the basis of their size in solution, and the detector determines the concentration of the polymer molecules eluting from the column. No other information about the behavior of the polymers in solution is revealed, and their size, although crucial to the separation mechanism, is not measured in the analysis. Comparatively speaking, conventional GPC/SEC is not an information-rich technique.



GPC Separation Mechanism

Multi-detector GPC

It is possible to overcome the limitations of conventional GPC by performing multi-detector GPC. Data from the concentration detector are combined with data from another information-rich detector to greatly increase data quality and quantity from the analysis. Three forms of multi-detector GPC that can be performed using the Agilent 390-MDS are discussed on the next page.

2 Option Two - GPC viscometry analysis employing a concentration detector and a viscometer

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Use:
Measure accurate molecular weights
Measure molecular viscosities (related to density)
Measure polymer branching

Viscometer

Advantages:
Independent of polymer chemistry
Wide molecular weight range
Simple to use

Hydrodynamic volume α Molecular Weight x Intrinsic Viscosity
Plot of log (MW x Intrinsic Viscosity) vs Retention Time ≡
log (Hydrodynamic volume) vs Retention Time

Column separated and calibrated in terms of size
therefore universal calibration obtained

Equipping the Agilent 390-MDS with a viscometer allows analysis of polymers by GPC viscometry.

Alongside a concentration detector such as a refractive index detector, the viscometer gives accurate molecular weights for samples irrespective of the standards used for the column calibration, and reveals details of the structure and conformation of polymer molecules in solution.

Using GPC viscometry, molecular weights are determined using the universal calibration method. A plot of molecular size as log (molecular weight x intrinsic viscosity) vs. retention time is constructed for a series of narrow standards as shown in Figure 1.

This results in a size vs retention time calibration. Therefore, it does not matter what standards are used in the analysis; the same calibration is obtained as the column separates the molecules on the basis of size.

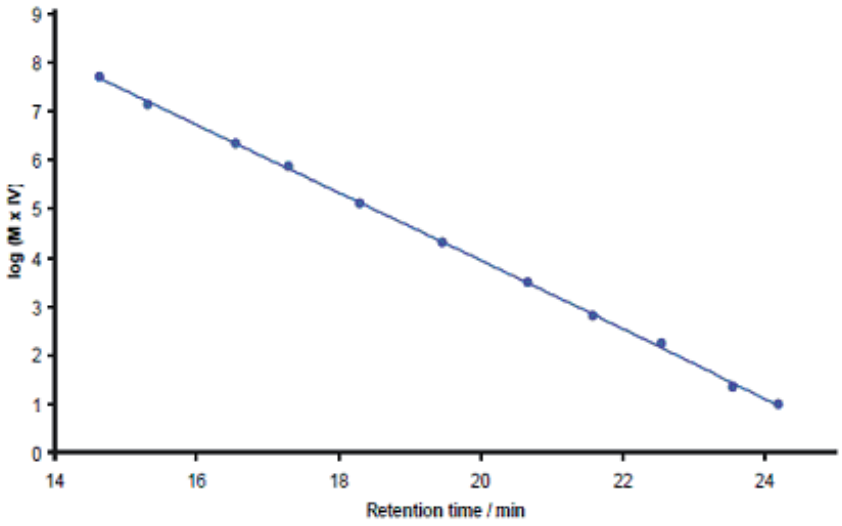


Figure 1. The universal calibration

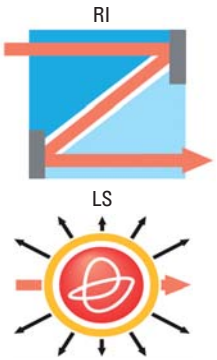
Molecular weights are then determined with reference to the universal calibration using the retention time and intrinsic viscosity data from the viscometer.

The universal calibration technique provides polymer molecular weights regardless of the calibrants used in the analysis. This allows cheaper calibrants such as polystyrene to be used but still delivers accurate polymer results.

Using this method:

- Intrinsic viscosities related to molecular density are measured from the viscometer and concentration detector
- Accurate molecular weights are calculated from the universal calibration
- Radius of gyration, an actual measure of molecular size, is calculated using a model for the polymer behavior in solution

3 Option Three - GPC light scattering analysis employing a concentration detector and a light scattering detector



Use:
Measure accurate molecular weights
Measure molecular sizes
Measure polymer branching

Advantages:
Independent of polymer chemistry
Sensitive to high molecular weight
No column calibration required

$$R_{(\theta)} = C\,M\,(dn/dc)\,P_{(\theta)}K_{(\theta)}$$

- $R_{(\theta)}$: Detector response
- $C\,M$: Concentration X Mass
- (dn/dc): Specific refractive index increment
- $P_{(\theta)}$: Particle scattering function
- $K_{(\theta)}$: Light scattering constant

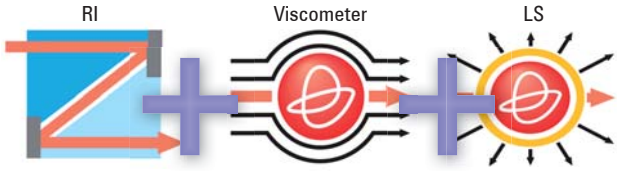
A dual-angle 90° and 15° light scattering detector may be housed inside the Agilent 390-MDS to allow analysis of polymers by GPC light scattering, employing the dissymmetry method. This detector irradiates the sample in a flow cell with laser light of fixed wavelength and measures the intensity of light scattered at different angles relative to the incident beam. Using GPC light scattering, accurate molecular weights are determined directly using the response of the light scattering detector with the intensity of scattered light described by the simplified expression above.

No column calibration is required; molecular weights are measured directly from the response of the light scattering detector. The particle scattering function describes how the intensity of scattered light changes, depending on the angle the scattering is measured at relative to the incident laser beam. If more than a single angle is used, as in the light scattering detector in the Agilent 390-MDS, data at the different angles can be correlated to determine the size of the scattering molecule in the cell.

Using this method:

- Molecular weights are calculated directly from the light scattering response, calculating the particle scattering function from the ratio of intensities at 15° and 90°
- Absolute molecular weights without the need for a column calibration
- Radius of gyrations are determined by the particle scattering by comparing the two angles, but only if the molecule is over ca. 10 nm in size and the scattering intensity shows angular dependence
- Intrinsic viscosity is calculated using a model for the polymer behavior in solution

4 Option Four - GPC triple detection using concentration, viscometry and light scattering data



In this technique, both viscometer and dual-angle light scattering detector are housed inside the Agilent 390-MDS along with a concentration detector. Using GPC triple detection, molecular weights are determined directly using the response of the light scattering detector as described above and intrinsic viscosities are provided by the viscometer.

Using this method:

- Molecular weights are calculated directly from the light scattering response, calculating the particle-scattering function from the ratio of intensities at 15° and 90°
- Most accurate molecular weights obtainable by GPC
- Radius of gyrations are determined from the particle scattering function by comparison of the two angles, but only if the molecule is over ca. 10 nm in size and the scattering intensity shows angular dependence
- Intrinsic viscosity is calculated from the viscometer trace
- Most powerful and versatile form of the GPC experiment

Comparisons Between Conventional GPC, GPC Viscometry, GPC Light Scattering and GPC Triple Detection

Conventional GPC using only a concentration detector generates molecular weights by comparison to a series of calibration standards. However, unless the standards and samples are of the same chemistry, and therefore the same size in solution at any given molecular weight, the results are only relative as the GPC column separates on the basis of size not molecular weight. Conventional GPC only gives accurate molecular weight results if standards of the same chemistry as the samples under investigation are used.

GPC viscometry and GPC light scattering or GPC triple detection can be used to determine 'absolute' molecular weights of samples, independent of the chemistry of standards used in the column calibration (GPC viscometry) or independent of column calibration entirely (GPC light scattering and GPC triple detection).

Of the multi-detector GPC methods, triple detection is the most powerful and the most versatile, as the technique makes use of all available methods of analyzing the molecules eluting from the GPC column. The data obtained may then be analyzed using any of the techniques discussed above, giving unique insights into the polymer under investigation.

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