High Temperature Gel Permeation Chromatography System using Dual Flow Differential Refractive Index Detector

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Objective

- To demonstrate the characterization of polymers using high temperature (up to 220 ºC) gel permeation chromatography (GPC) coupled to a dual flow refractive index (RI) detector.
- To make evident how the dual flow design of the RI detector significantly improves the accuracy and precision of molar mass averages and distributions of polymers determined using peak position calibration involving standards of known molar mass and chemistry.
- To highlight the multiple applications of high temperature GPC for the analysis of natural and synthetic polymers.

Introduction

- Since its inception the main utility of ambient and high temperature GPC has been to extract quantitative information in the form of molar mass averages and distributions of both synthetic and biopolymers with accuracy and precision.[1]
- Synthetic polymers, as well as most natural polymers, possess a distribution of molar masses.
- The ability to accurately and precisely characterize the molar mass distribution and averages is essential, as the shape and the breadth of a polymer's molar mass distribution will dictate the end-use properties of the polymer, such as hardness, tear strength, impact resistances, wear, etc.
- One of the most highly used tools for characterizing the molar mass of polymers is GPC coupled to RI detection.

Introduction

- Traditionally, molar mass averages and distributions of polymers obtained by GPC/RI are determined using peak position calibration involving polymer standards of known molar mass and chemistry.
- The repeatability and reproducibility of the molar mass averages obtained by GPC/RI are directly dependent on the baseline stability of the RI detector.
- Here we show the repeatability, reproducibility, and baseline stability of a dual flow RI detector coupled to a high temperature GPC through the determination of molar mass averages via peak position calibration for various synthetic polymers.

Experimental

Instrumentation:

EcoSEC® High Temperature GPC System (HLC-8321GPC/HT) with a dual flow refractive index detector

Experimental Continued

A dual flow RI detector, such as that in the EcoSEC High Temperature GPC System, is constructed in such a way that there are two sides:

1. a reference side, consisting of a flowing stream of pure solvent

2. the sample side, containing a flowing stream of analyte in the same solvent as in the reference side

Experimental Continued

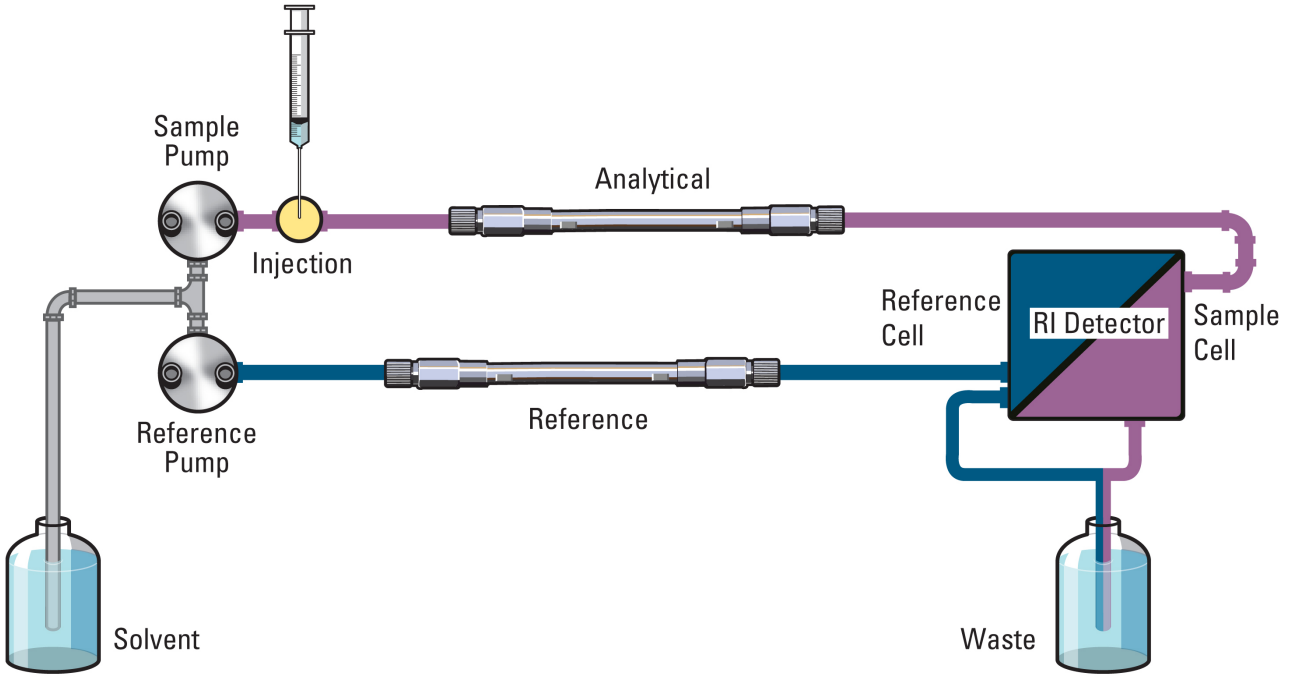

Figure 1: Depiction of the flow paths in the EcoSEC High Temperature GPC System, showing the dual flow RI detector flow cell when the contents of the reference and sample sides have different refractive indices as each other.

Experimental Continued

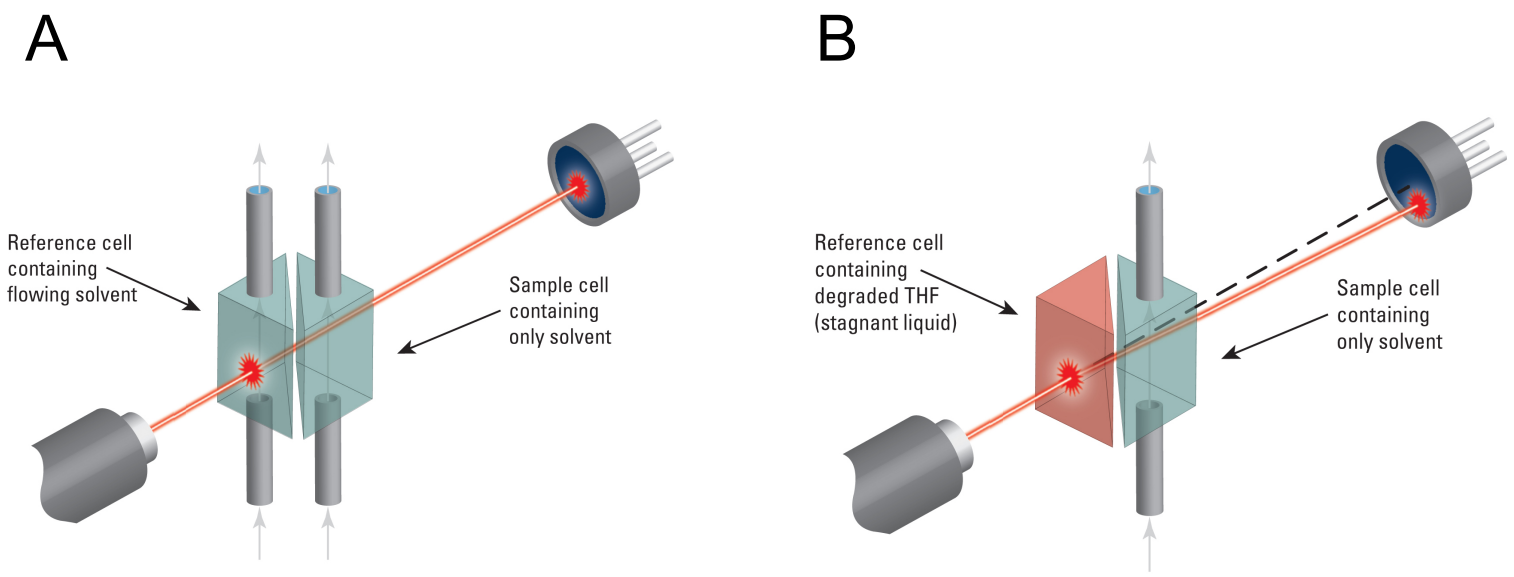

Figure 2: Depiction of a dual flow RI detector flow cell (A) and a conventional RI detector flow cell (B) showing the compensation of the changes in refractive index of the solvent over time.

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High Temperature Gel Permeation Chromatography

High Temperature Gel Permeation Chromatography

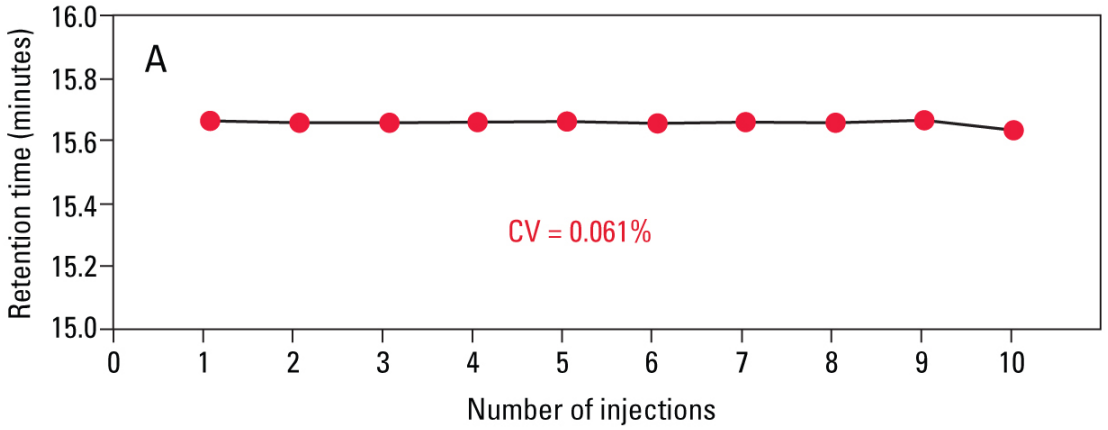
- The analysis of some polymers by GPC/RI require extremely high temperatures due to solvent compatibility and solubility issues.
- High temperature GPC is used for the same types of applications as ambient GPC and requires an instrument that delivers reliable and reproducible results.

High Temperature Gel Permeation Chromatography

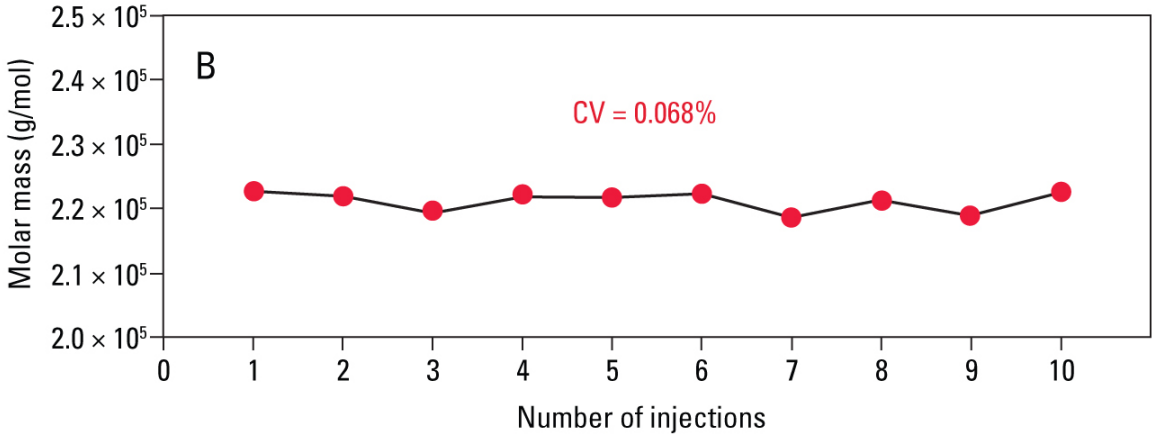
- Peak position calibration is used to determine molar mass averages and distributions, to compare batches or lots of a given polymer, to monitor reaction processes, to determine variations in molar mass averages obtained through different synthesis routes, and to distinguish between polymers with the same chemical compositions but different end-use properties.

- GPC coupled to a dual flow RI detector for the analysis of polymers at elevated temperature has shown to increase the reliability and reproducibility of molar mass averages and distributions.

Figure 3: High Temperature GPC Accuracy and Precision



Reproducibility of retention times for 10 successive injections.



Reproducibility of molar mass for 10 successive injections.

Figure 3 Conclusions

- The dual flow RI detector design is shown to compensate for any changes in the refractive index of the solvent over time by continuously flowing pure solvent through the reference side of the flow cell, thus significantly increasing baseline stability of the RI detector and the repeatability and reproducibility of the molar mass averages.

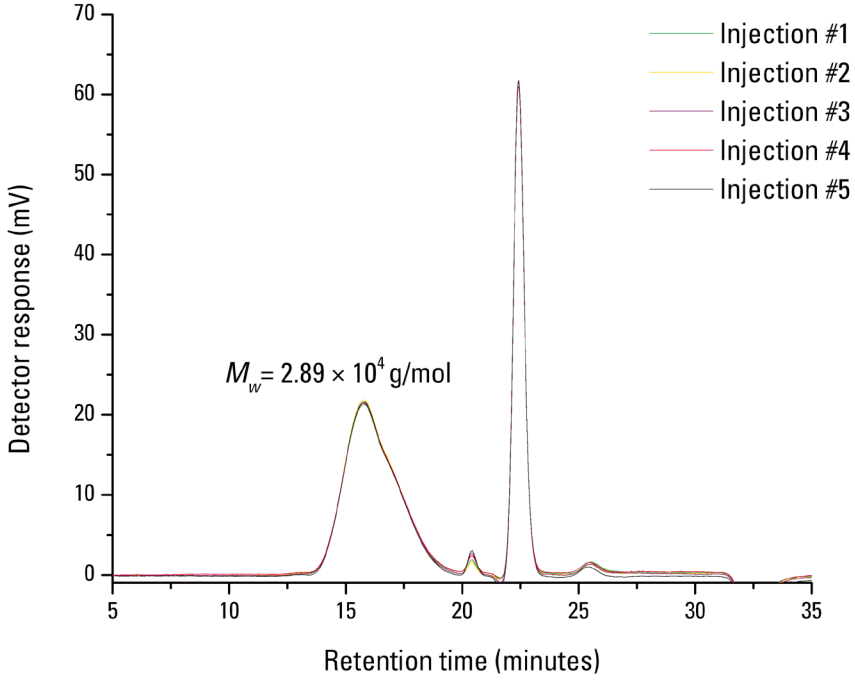
- The dual flow refractive index detector results in a high degree of reproducibility of retention times and molar mass determination. The intraday coefficients of variation for retention time and weight-average molar mass are well below 1% for successive injections.

Polyethylene and Polypropylene

- Due to their ruggedness, polymers such as polyethylene and polypropylene can only be analyzed by high temperature GPC.

- The end-use properties of polyethylene and polypropylene are dictated by the molar mass averages and distributions of the polymers. High temperature GPC/RI measurements provide molar mass averages and distributions via peak position calibration with polystyrene standards.

Figure 4: GPC elution profiles and molar mass averages of low density polyethylene (LDPE)

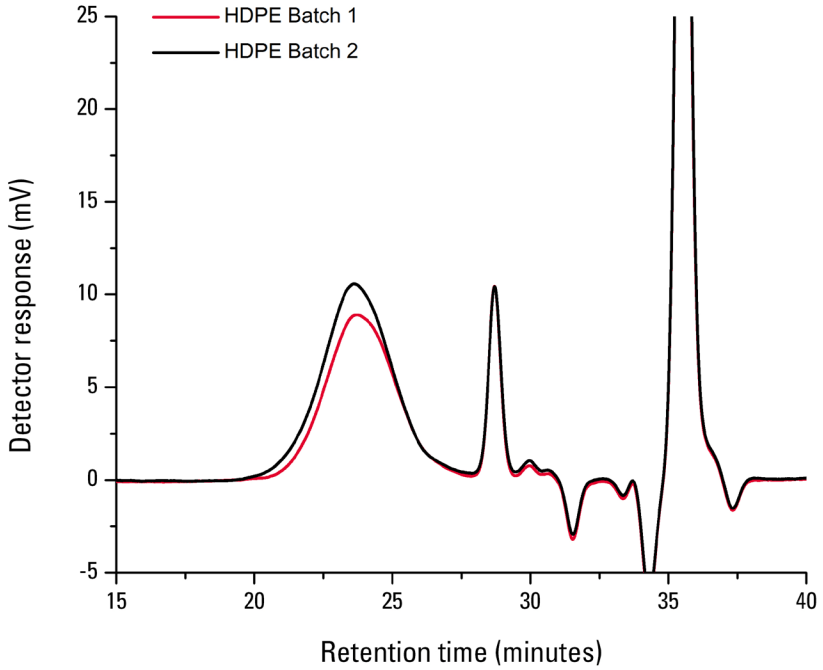


Column:	TSKgel GMH$_{HR}$-H(S) HT2, 13µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	ODCB w/ 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	low density polyethylene

Figure 4 Conclusions

- Figure 4 shows the RI GPC elution profile of multiple dissolutions of the same LDPE sample obtained using the EcoSEC High Temperature GPC System.
- The dual flow RI detector in the EcoSEC High Temperature GPC System results in a high degree of reproducibility of retention times and molar mass determination as the coefficients of variation for the weight-average molar mass, M_w, are well below 1%.

Figure 5: GPC elution profiles for high density polyethylene (HDPE)



Column:	TSKgel GMH$_{HR}$-H(S) HT2, 13µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	ODCB w/ 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	high density polyethylene

Table 1: Molar mass averages and polydispersity of two HDPE samples

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
HDPE Batch 1	4.48×10^4	1.18×10^5	2.95×10^4	2.638
HDPE Batch 2	3.66×10^4	1.03×10^5	2.64×10^4	2.803

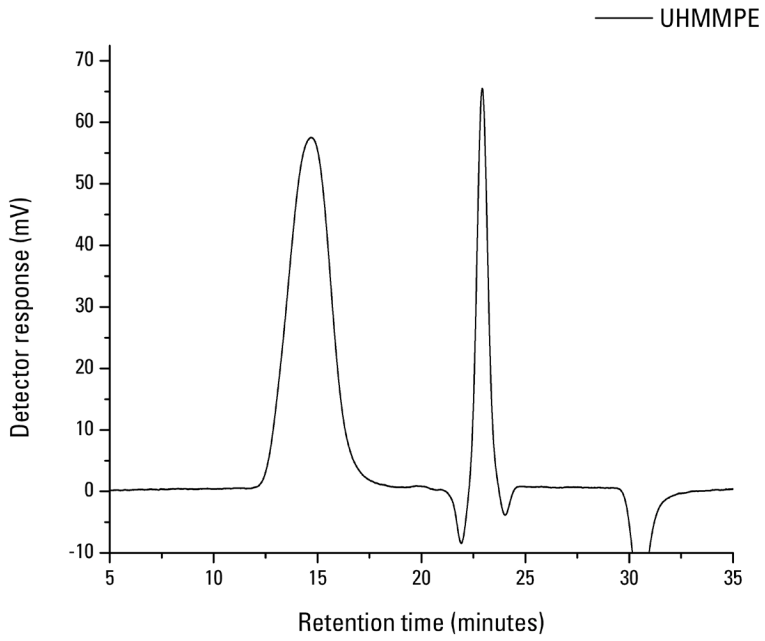
[a] $PDI = M_w/M_n$

Figure 5 and Table 1 Conclusions

- Figure 5 compares the GPC elution profiles of two different batches of a HDPE. Batch 2 extends slightly further in the larger polymeric size, shorter retention time direction of the GPC elution profile than Batch 1.

- The slight variation in the GPC elution profile results in an approximately 15% difference in the polystyrene relative molar mass averages between the two batches, Table 1. The difference in molar mass averages between Batch 1 and Batch 2 may or may not affect the end-use properties. Additionally the polydispersity index, *PDI*, between the two batches varies.

Figure 6: GPC elution profiles and molar mass averages of ultra high molar mass polyethylene (UHMMPE)

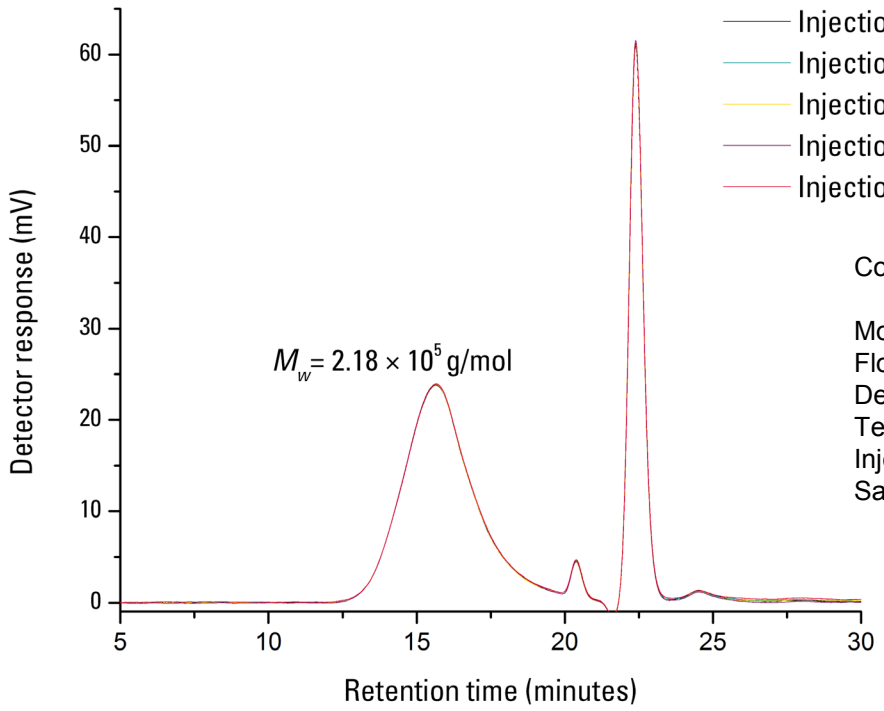


Column:	TSKgel GMH$_{HR}$-H(S) HT2, 13µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	1-CN
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	220 °C
Injection vol.:	300 µL
Sample:	low density polyethylene

Figure 6: Conclusions

- The GPC elution profile obtained using the dual flow RI detector in the EcoSEC High Temperature GPC System for ultra high molar mass polyethylene is shown in Figure 6.

Figure 7: GPC Elution Profile of Polypropylene



Column:	TSKgel GMH$_{HR}$-H(S) HT2, 13µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	ODCB w/ 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	low density polyethylene

Figure 7: Conclusions

- Figure 7 shows the RI GPC elution profile of consecutive injections of a polypropylene sample obtained using the EcoSEC High Temperature GPC System.

- The dual flow RI detector in the EcoSEC High Temperature GPC System results in a high degree of reproducibility of retention times and molar mass determination, as the coefficients of variation for the weight-average molar mass, M_w, are well below 1%.

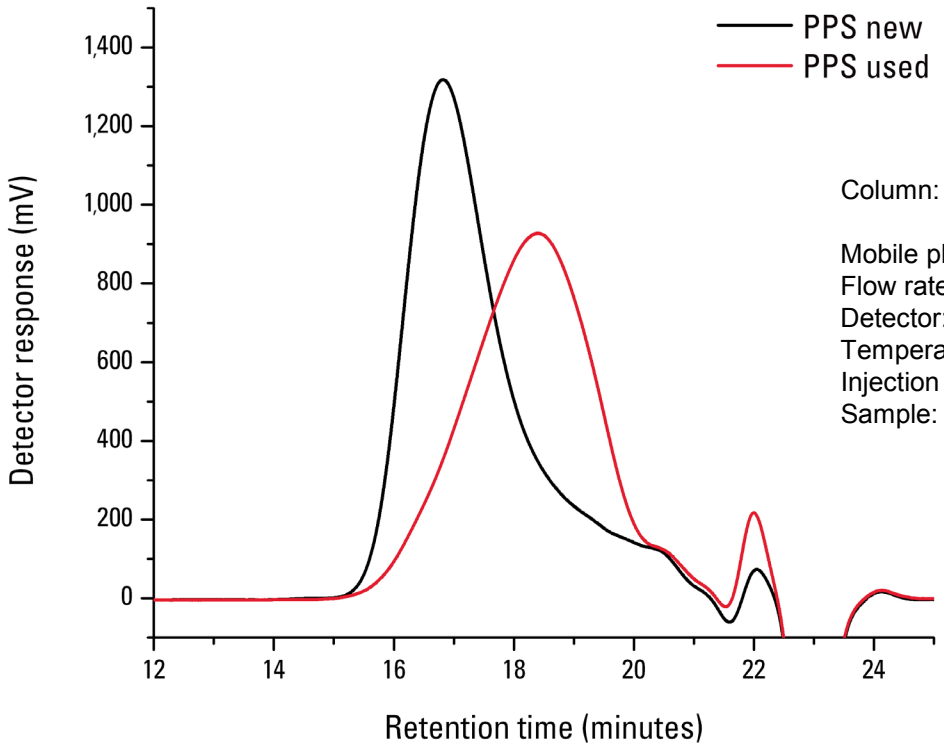
Polyphenylene Sulfide (PPS)

- High temperature GPC is a fast, accurate and reliable method for the comparison of polymers exposed to various conditions. For example, the GPC elution profiles and molar mass averages of a virgin product and a product exposed to extreme environmental conditions can be compared to determine how the products performance may be altered due to exposure to those conditions.

- The ability to characterize the molar mass averages and distributions of PPS is essential as these properties play a vital role in the determination of mechanical, bulk and solution properties of the processing and end-use properties of a given material.

- Analysis of PPS using high temperature GPC is traditionally difficult as the analysis must be performed in 1-CN at 220 ºC. 1-CN is a difficult solvent to use for analytical experiments as the solvent ambers over time and can cause havoc for detection methods such as refractive index.

Figure 8: GPC elution profiles of two PPS samples introduced to different conditions



Column:	TSKgel GMH$_{HR}$-H(S) HT2, 13µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	1-CN
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	220 °C
Injection vol.:	300 µL
Sample:	polyphenylene sulfide

Figure 8 Conclusions

- The new PPS sample elutes prior to the used PPS sample. The shorter retention time of the new PPS sample indicates that the new PPS sample is larger in polymeric size than the used PPS sample; as the elution order in GPC is that of an “inverse-sieving” technique, larger analytes sample a smaller pore volume than smaller analytes resulting in the larger analytes eluting from the GPC column prior the smaller analytes.

- The GPC chromatogram for the used PPS sample is shifted considerably towards the longer retention time, smaller polymeric size, compared to that of the new PPS sample.

Table 2: Molar mass averages and polydispersity index of two PPS samples introduced to different conditions

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
PPS new	5,790	3.91×10^4	7.19×10^4	6.746
PPS used	3,176	1.62×10^4	5.54×10^4	5.106

[a] $PDI = M_w/M_n$

Table 2 Conclusions

- Differences observed in the molar mass averages is important in any product failure investigation as the molar mass averages dictate the end-use properties of a product, such as tensile strength, elongation, brittleness, hardness, toughness, etc.

- The approximately 20 to 50% decrease in the molar mass averages observed between the new PPS and the used PPS is potentially enough evidence to determine that after a predetermined amount of time the end-use product(s) made with this PPS sample will begin to fail or will no longer be able to perform to standards.

Figure 9: Overlay of Cumulative and Differential Molar Mass Distributions of New and Used PPS

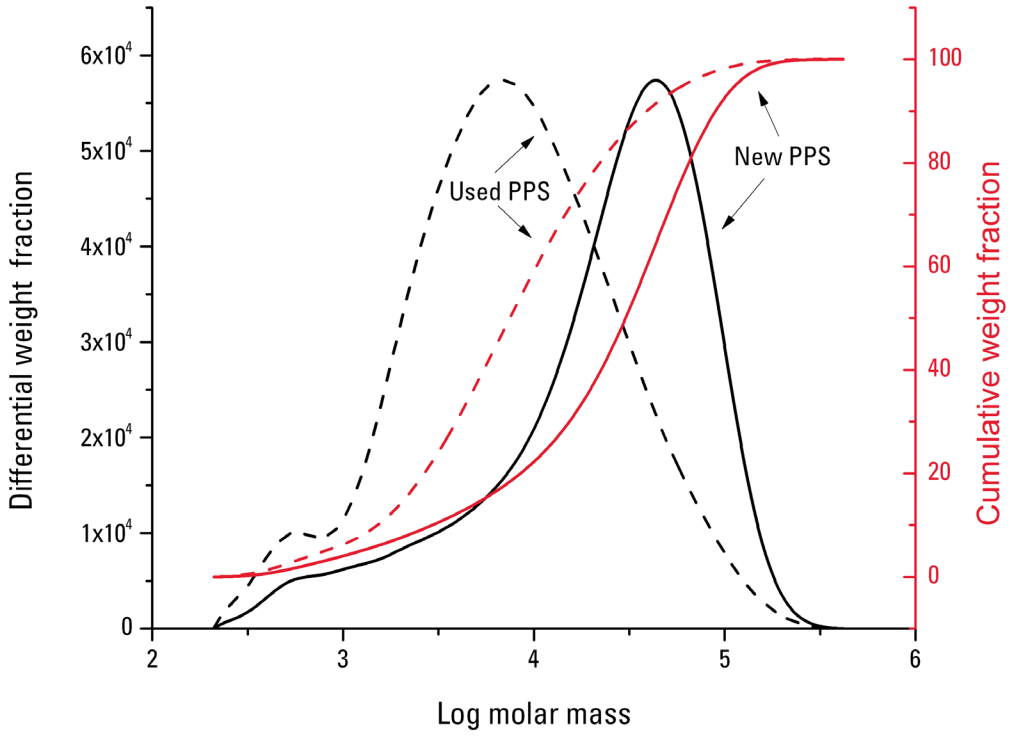


Figure 9 Conclusions

- The differences in the molar mass averages observed between the new and the used PPS samples can also be observed through the molar mass distributions, MMD.

- The new PPS sample MMD extends significantly further in the high and low molar mass directions than the used PPS sample. The used PPS sample has a considerably higher quantity of low molar mass species than the new PPS sample.

- The decreased breadth of the molar mass distribution of the used PPS sample compared to the new PPS sample can also be seen through the polydispersity index values, *PDI*. The *PDI* of the new PPS sample is 25% greater than that of the used PPS, an indication that usage of the PPS results in a significant change in the molar mass distribution of the product.

Conclusions

- The utilities of ambient and high temperature GPC are numerous, as the size base mechanism of the technique and the ability to determine molar mass averages and distributions allow for various experimental goals. To name a few: peak, position calibration GPC/RI can be successfully used for synthesis monitoring, failure analysis, lot-to-lot or batch-to-batch variations, and exposure analysis.

- A dual flow RI detector increases the reliability and reproducibility of molar mass averages obtained using peak position calibration for both ambient and high temperature GPC.

References

[1] Striegel, A.M.; Yau, W.W.; Kirkland, J.J.; Bly, D.D. *Modern Size Exclusion Liquid Chromatography, 2nd edition;* Wiley: New York, 2009.