CONSIDERATIONS FOR GPC ANALYSIS USING LITHIUM BROMIDE MODIFIED DIMETHYLFORMAMIDE AS MOBILE PHASE

Authors: Kaveh Amini, Elom Pedanou, Paula Hong
Affiliations: Waters Corporation, Milford, MA, USA

INTRODUCTION

While GPC is commonly performed with DMF as a mobile phase, this mobile phase can pose challenges for instrumentation. For example, DMF is a highly viscous mobile phase, necessitating higher column temperatures to reduce the viscosity and provide improved resolution of polymer strands. Furthermore, polymers may be prone to aggregation or polar interactions under DMF conditions – making accurate GPC analysis challenging. To reduce these non-specific interactions, LiBr or a salt is added to DMF as a modifier.

Given these considerations, instrumentation for these types of separations must meet methods conditions, including a system capable of handling highly viscous/corrosive mobile phases as well as providing the necessary column temperature for the required banks of columns, typically ≥70 °C. In this poster, the Arc™ HPLC System equipped with a strong solvent kit and a CM30S column heater will be used to perform the separation. Specifically, poly(methyl methacrylate) (PMMA) samples were analyzed on an Arc HPLC System with DMF/0.05M Lithium Bromide (LiBr) as the mobile phase. The results obtained showed high precision for the retention times and good correlation of the calculated molecular weight values for the PMMA sample.

METHOD

Sample Description (Standard Solutions)

Polymethylmethacrylate (PMMA) Mid MW Standards Kit, (p/n: WAT035706) was obtained from Waters Corporation. The kit contains standards with Mp between 10600 and 990000 Da.

The standards were prepared at the concentrations specified in the table.

Mp	Concentration (mg/mL)
99000, 76600, 53300, 271000	0.05
17400, 55100, 33000	1
10600	2

To prepare the standards, 5.0 mg of the standard was weighed in a scintillation vial and 10 mL of DMF containing 0.05 M LiBr was added. The vials were capped and left for at least 12 hours in the fume hood for standards to dissolve without any vigorous shaking. The solution was filtered through 0.45 µm syringe filters and then diluted using DMF containing LiBr to appropriate concentration.

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS

METHOD (CONT'D)

Method conditions:

System	Arc HPLC System with CM-30S column manager and strong
Mobile Phase:	N,N-Dimethylformamide with 0.05M Lithium Bromide
Columns:	All columns 7.8 x 300 mm with 5 µm: Styragel™ HR 5 Column, 100,000 Å, in DMF, 50K - 4M Styragel HR 4 Column, 10,000 Å, in DMF, 5K - 600K Styragel HR 1 Column, 100 Å, in DMF, 100 - 5K
Column Temp.:	70 °C
Detection:	2414 Refractive Index (RI) ,Sampling rate: 2 pts/sec, Polarity:
Injection volume:	100 µL
Flow rate:	1.0 mL/min
Vials:	LCMS Certified Clear Glass 12 x 32 mm Screw Neck Total Re-
Sample Temp.:	25 °C
Wash solvents:	Purge Solvent: N,N-Dimethylformamide Needle wash: isopropyl alcohol
Chromatography Data Software:	Empower™ 3.8.0 CDS with GPC option

RESULTS AND DISCUSSION

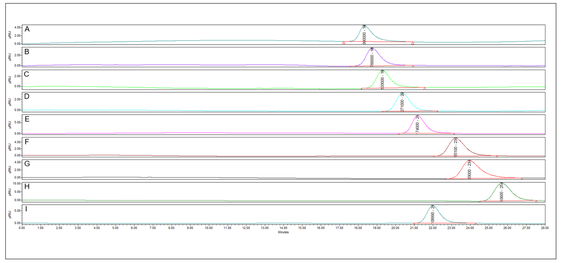

Figure 1. GPC analysis of narrow PMMA standards (A) Mp 990000 Da, (B) Mp 766000 Da, (C) Mp 533000, (D) Mp 271000 Da, (E) Mp 174000 Da, (F) Mp 55100 Da, (G) Mp 33000 Da, (H) Mp 10600 Da and (I) the broad PMMA sample (10800 DA) obtained on the Arc HPLC System equipped with strong solvent kit.

- GPC with DMF necessitated higher temperatures (70 °C) to reduce viscosity and improve resolution.
- To prevent non-specific binding and any polar interactions between the analyte and columns, lithium bromide (LiBr), at a concentration of 0.05M, was added to the DMF.
- Reliability and reproducibility of GPC analysis was confirmed by RSD%s of retention time and peak area obtained for different standards.
- Analysis of the sample showed good correlation with the expected values.

RESULTS AND DISCUSSION (CONT'D)

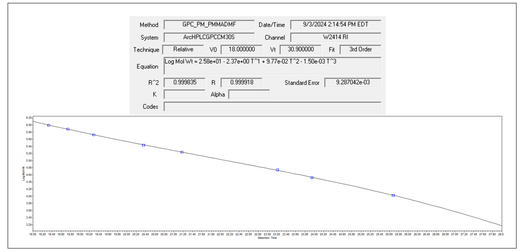

Figure 2. Calibration curve and data for GPC analysis of PMMA, using Empower 3.8 CDS with GPC option.

Mp (Da)	RT (min)	RT RSD%	Peak Area	Peak Area RSD%
990000	18.33	0.01	225959. 69	5.28
766000	18.74	0.01	196226.02	2.86
533000	19.30	0.00	191896.29	5.01
271000	20.35	0.02	180158.22	1.02
174000	21.18	0.00	399406.80	1.75
55100	23.21	0.01	347705.54	1.40
33000	23.95	0.01	342672.64	0.57
10600	25.08	0.00	713904.61	0.29

Table 1. Repeatability of PMMA standards (n=3) on Arc HPLC System with strong solvent kit

	RT (min)	Area	Mp	Mn	Mw	PDI [Mw/Mn]
Obtained (%RSD)	21.98 (0.00)	367457.07 (0.93)	108993.50 (0.10)	98063.70 (0.60)	104025.8 (0.20)	1.06 (0.40)
Expected	NA	NA	108000	104000	107000	1.03

Table 2. Calculated results for PMMA sample (average of n=3) and comparison to expected results.

CONCLUSION

- **The Arc HPLC System using DMF/0.05M Lithium Bromide (LiBr) as the mobile phase was successfully used to perform GPC analysis of PMMA.**
- **The CM30S provided adequate temperature control of the bank of columns at required temperatures (70 °C).**
- **The results obtained showed acceptable accuracy and precision with molecular weight (Mp, Mn and Mw) values within 6% of the expected value.**

Reference

Empower GPC Software Getting Started Guide, Waters Corporation User Guide, 71500031303
Reproducibility and Reliability of GPC Analysis of Polystyrene on the Arc™ HPLC System, Waters Application Note. 720008479. 2024.

720009088EN