Accurate and Reproducible Polymer Analysis with High Speed GPC

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Abstract

Traditionally, the analysis of polymers by Gel Permeation Chromatography, (GPC), has been carried out using column sets most commonly consisting of three or four columns of approximately 7.8mm internal diameter with a length of 30cm each. Three and four-column banks have generally been chosen in order to obtain sufficient pore volume to provide adequate resolution for accurate and reproducible determination of molecular weights and molecular weight distributions of polymeric samples, however, the use of these large column banks results in analysis times of 45-60 minutes per injection. In addition, the higher volume column banks minimize the negative effects of system bandspreading and the less reproducible solvent delivery of older technology chromatographic pumps. With the advent of higher performance solvent management systems, many polymers can now be analyzed accurately and reproducibly utilizing lower volume columns resulting in total analysis times of seven minutes or less.

This paper demonstrates the use of high-speed GPC columns, namely Waters new HSPgel™ offerings, for obtaining accurate and reproducible molecular weight distributions in under seven minutes.

Alternative data processing techniques for calibration may be utilized that will allow for the high-speed measurement of molecular weights and distributions with accuracy and precision approaching that obtained from conventional column sets. With the combination of the high-speed chemistry, the alternative data technique, and high performance solvent delivery technology, high-speed GPC may be used with many polymers for accurate molecular weight analysis, and not merely as a screening tool.

Conditions and Instrumentation

System: Waters 2695 Separations Module with In-line Degasser and Column Heater Module (35°C)

Detector: Waters 2414 Differential Refractive Index Detector (35°C)

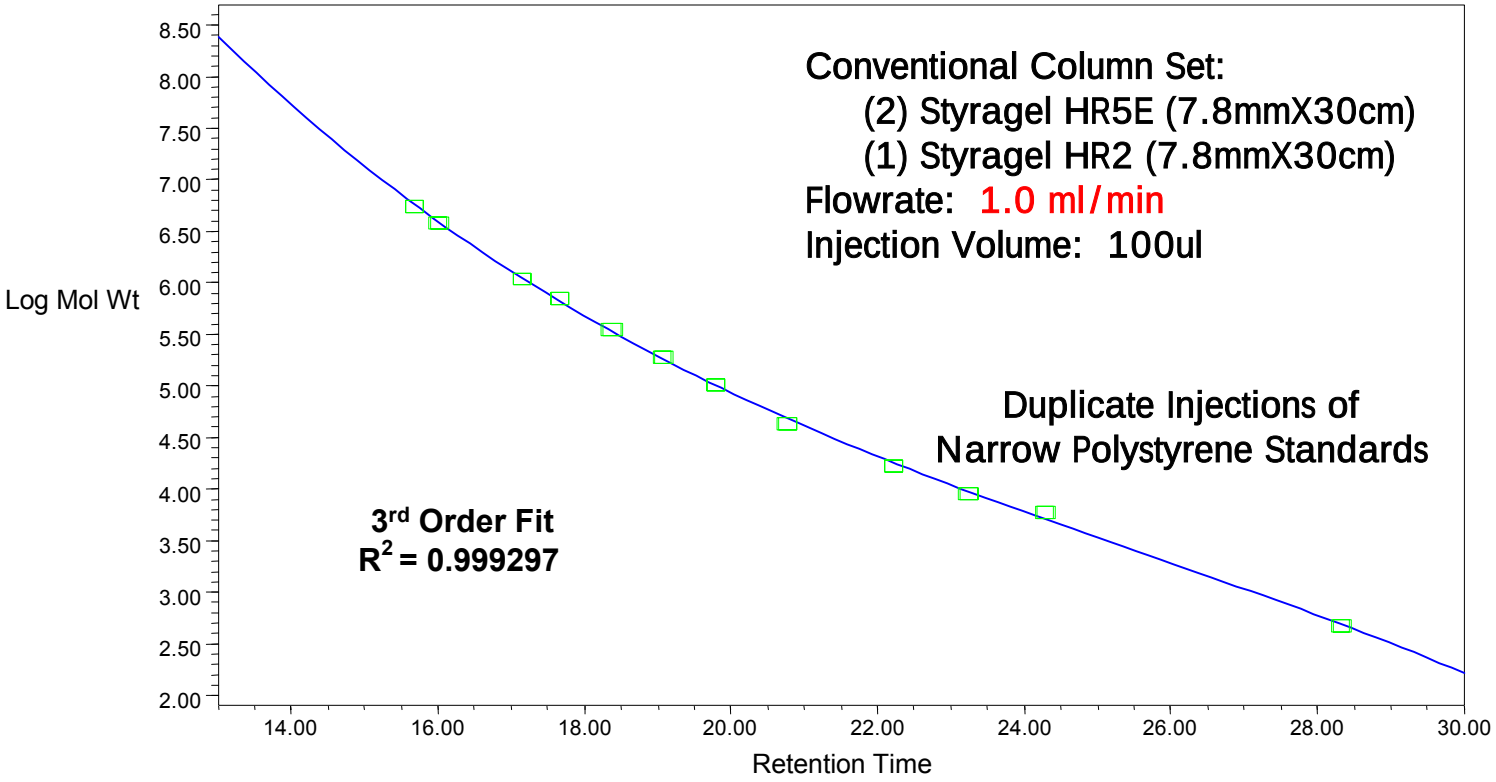
Data: Waters Millennium^{32} Chromatography Manager

Eluent: Tetrahydrofuran (THF), stabilized

Columns and Flow Rate were varied

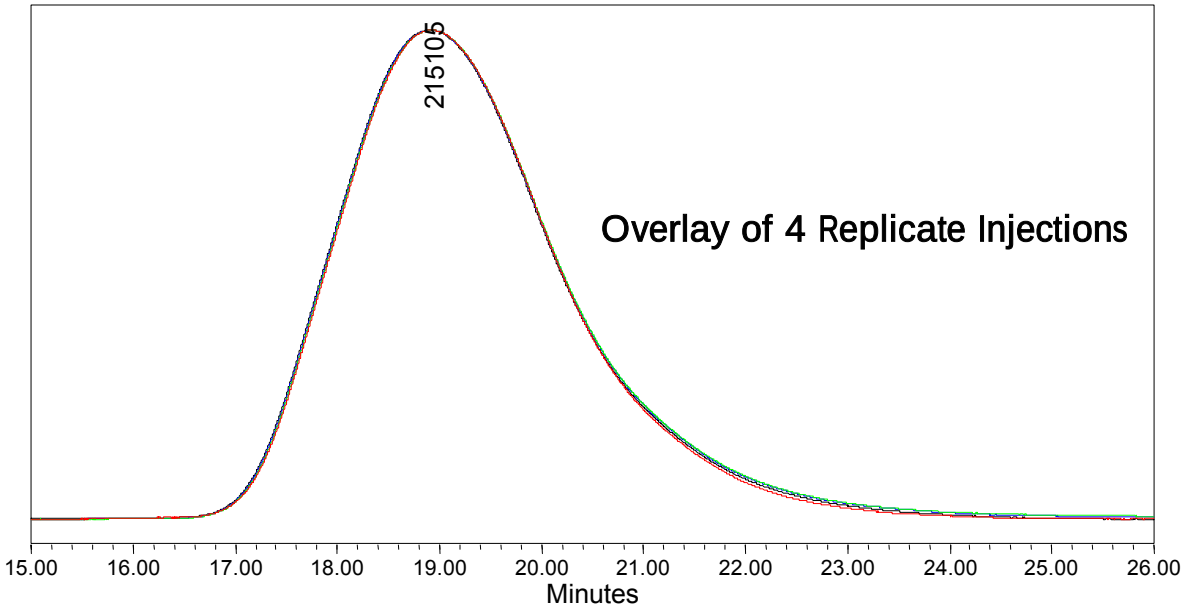
Waters Alliance® HPLC/GPC System

Conventional Column Set – Calibration Curve



When running Conventional GPC, the column set is most commonly calibrated with a series of narrow standards. Here, narrow polystyrene standards were injected in duplicate for calibration. The calibration curve was generated with a 3rd order polynomial (cubic) resulting in a good fit with the data (correlation coefficient = 0.9993) as would be expected.

Conventional Column Set – Broad Polystyrene



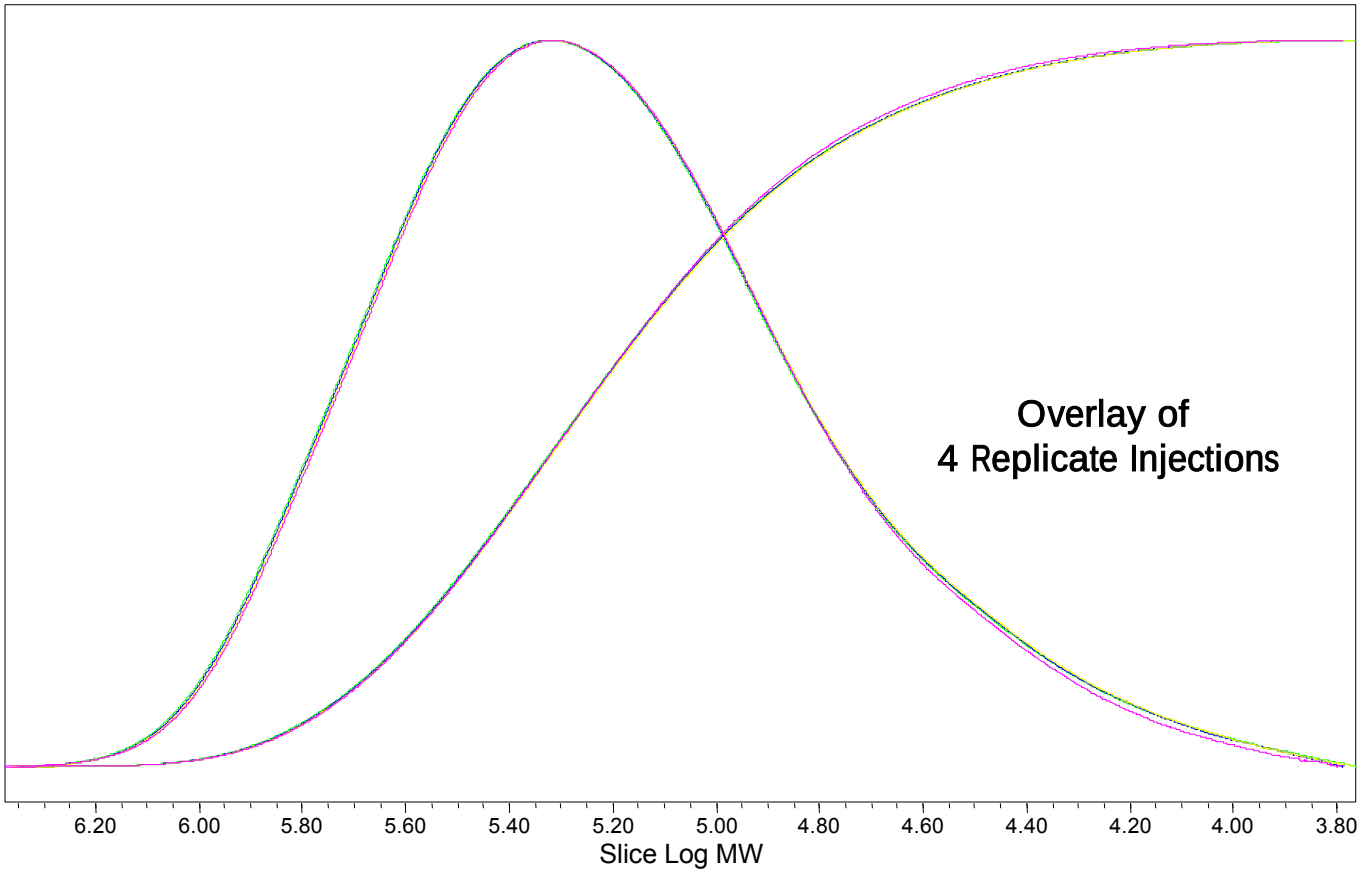
Total Run Time
~40 minutes

Component Summary Table

	Sample Name	Mn	Mw	Mz	Mz+1	Polydispersity
1	Broad PS	101518	238858	421733	618746	2.352855
2	Broad PS	97299	237695	422293	616095	2.442944
3	Broad PS	98149	239409	425387	620564	2.439230
4	Broad PS	98099	241219	429838	629094	2.458944
Mean		98766	239295	424813	621125	2.42
% RSD		1.9	0.6	0.9	0.9	2.0

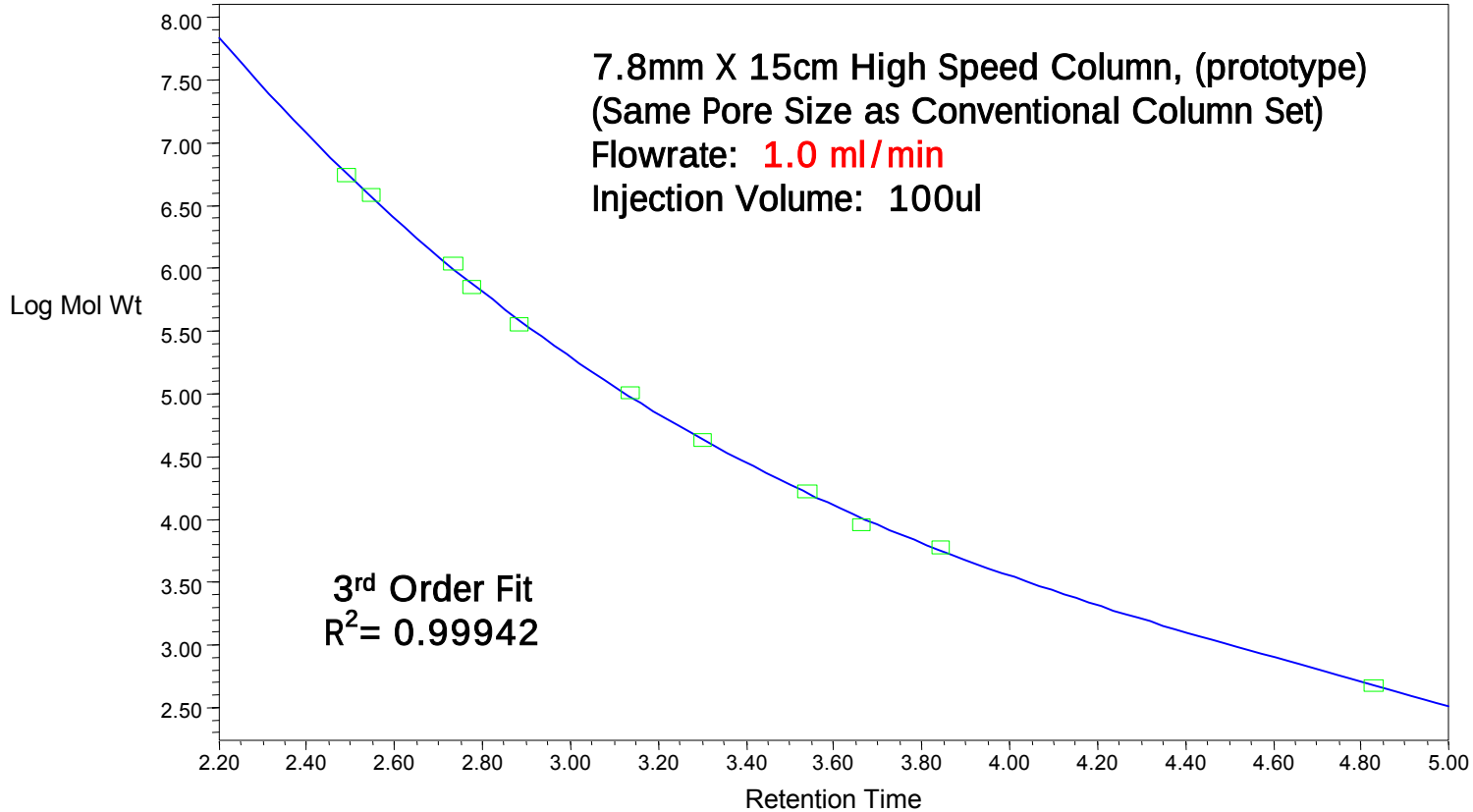
Using the previous calibration curve for quantitation, a broad polystyrene sample was injected in quadruplicate. The overlays and tabulated results demonstrate the typical reproducibility that is expected with this chromatographic system with conventional columns without the use of any Flow Marker or Reference Peak correction. The only disadvantage to this analysis is the long analysis time of 40-45 minutes which is required to ensure complete elution of the solvent/impurity peaks.

Conventional Column Set
MW Distribution for Broad Polystyrene



The molecular weight distributions obtained with Conventional Columns should be highly reproducible as shown here for 4 injections of a broad polystyrene sample.

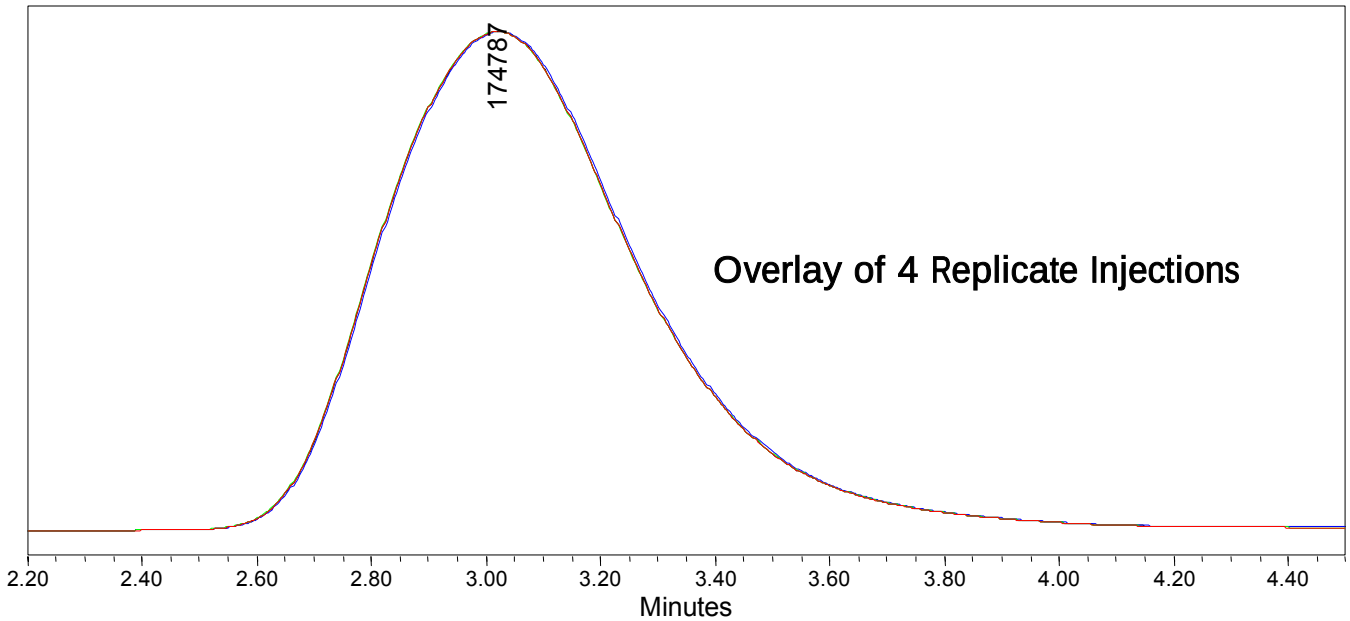
7.8mm x 15cm High Speed Calibration Curve



Candidates for High Speed GPC Column geometries were selected based upon a desired goal of 5-6 minutes for total run time. 15cm long High Speed Columns were prepared with internal diameters of 4.6mm, 6.0mm, 7.8mm, and 19mm. By running each at an appropriate flowrate, linear velocities, and therefore run times, could be kept generally constant.

Here, a narrow polystyrene standard calibration curve was obtained using a 7.8mmX15cm prototype High Speed GPC Column. The data was fitted to a 3rd order polynomial resulting in a correlation coefficient of > 0.9994

7.8mm x 15cm Column – Broad Polystyrene



Total Run Time

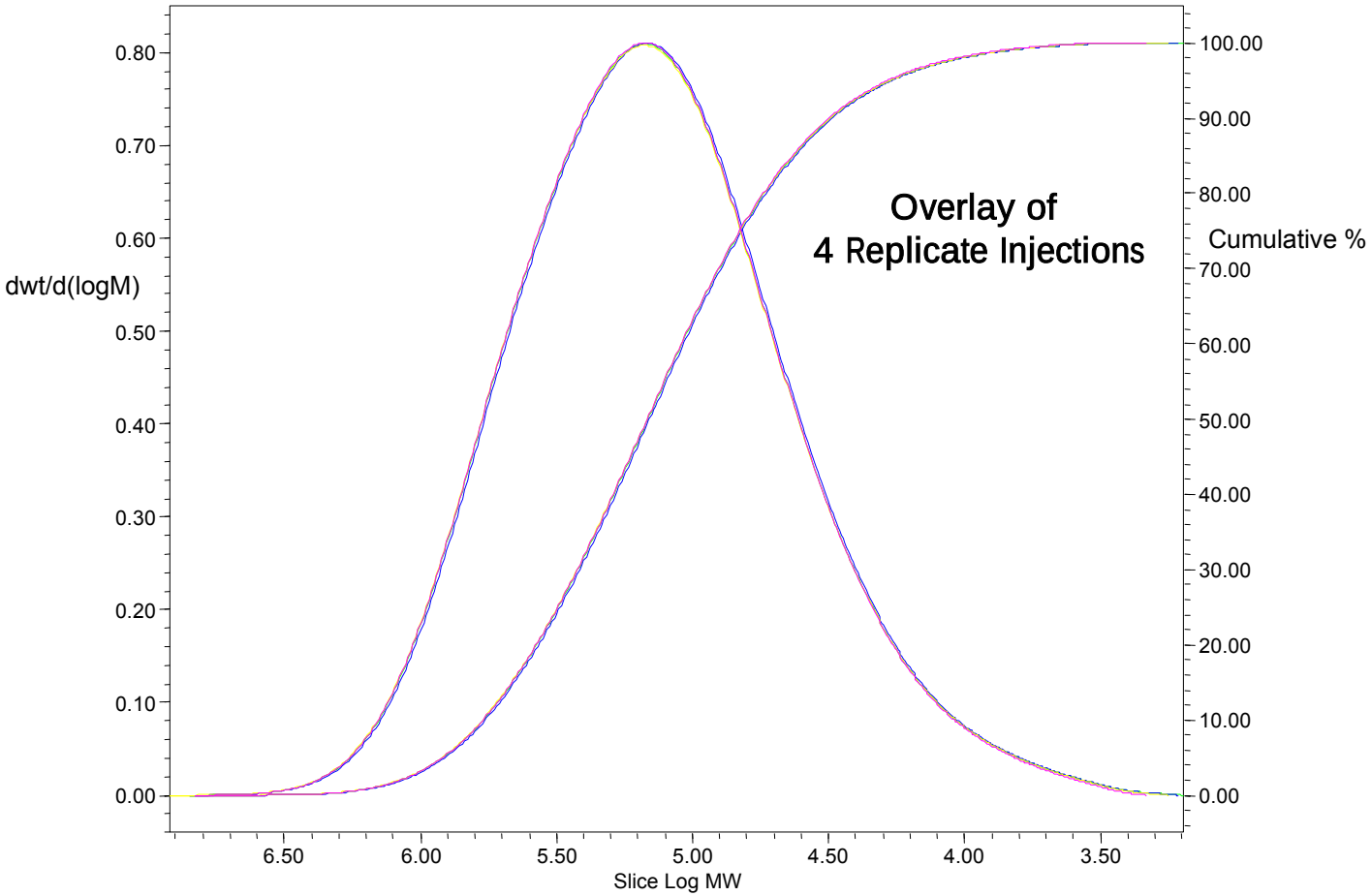
~6.5 minutes

Component Summary Table

	SampleName	Mn	Mw	Mz	Mz+1	Polydispersity
1	Broad PS	67762	247898	623697	1189815	3.658381
2	Broad PS	66396	249087	637121	1264190	3.751547
3	Broad PS	64897	242982	615918	1195875	3.744129
4	Broad PS	65694	247167	624571	1201755	3.762417
Mean		66187	246783	625327	1212908	3.73
% RSD		1.8	1.1	1.4	2.8	1.3

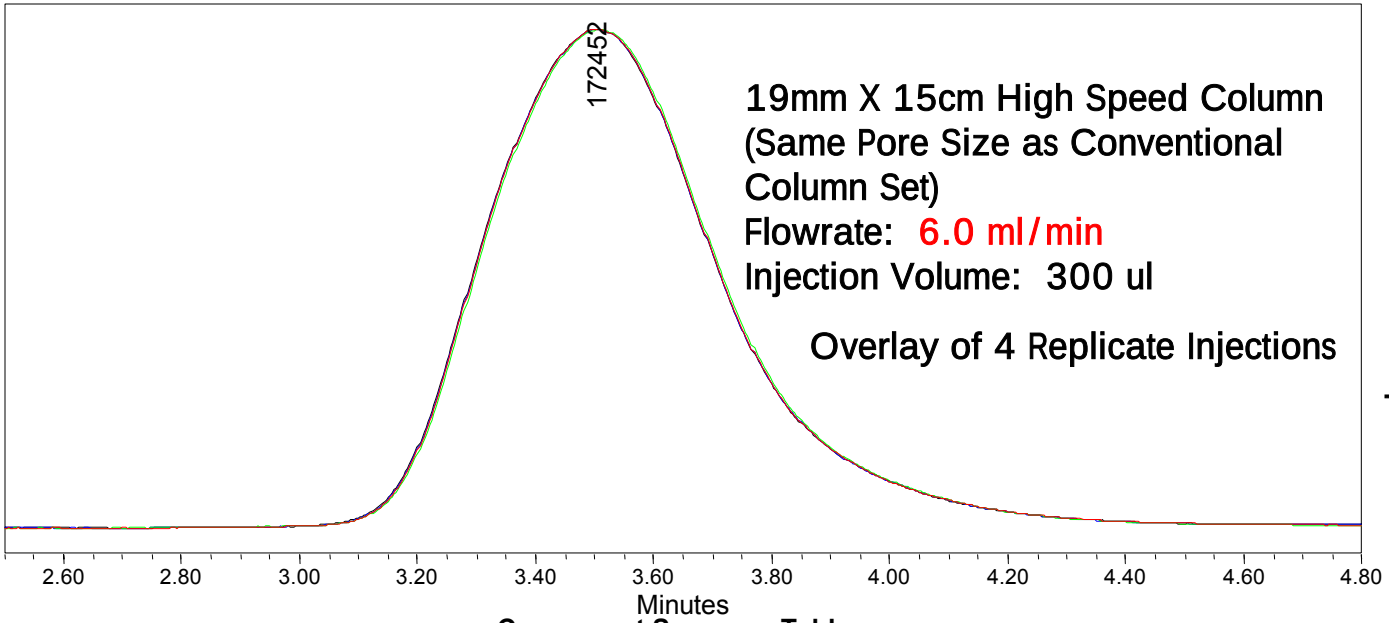
Using the same High Speed Column, a broad polystyrene sample was injected 4 times and the overlay of the chromatograms is displayed here along with the molecular weight results. Even with a total run time of only 6.5 minutes, the chromatograms are nearly exact overlays and the calculated molecular weight values exhibit only ~1-2% RSD's. The Mw is very close to that obtained with the conventional column set, however, the Mn, Mz, and polydispersity have a significant error due to the greater relative peak spreading with the High Speed Column.

7.8mm x 15cm High Speed Column MW Distribution for Broad Polystyrene



The molecular weight distribution obtained for the broad polystyrene sample with the 7.8mm X 15cm High Speed Column is extremely reproducible but is significantly broader than that obtained with the Conventional Column Set.

19mm x 15cm Column – Broad Polystyrene



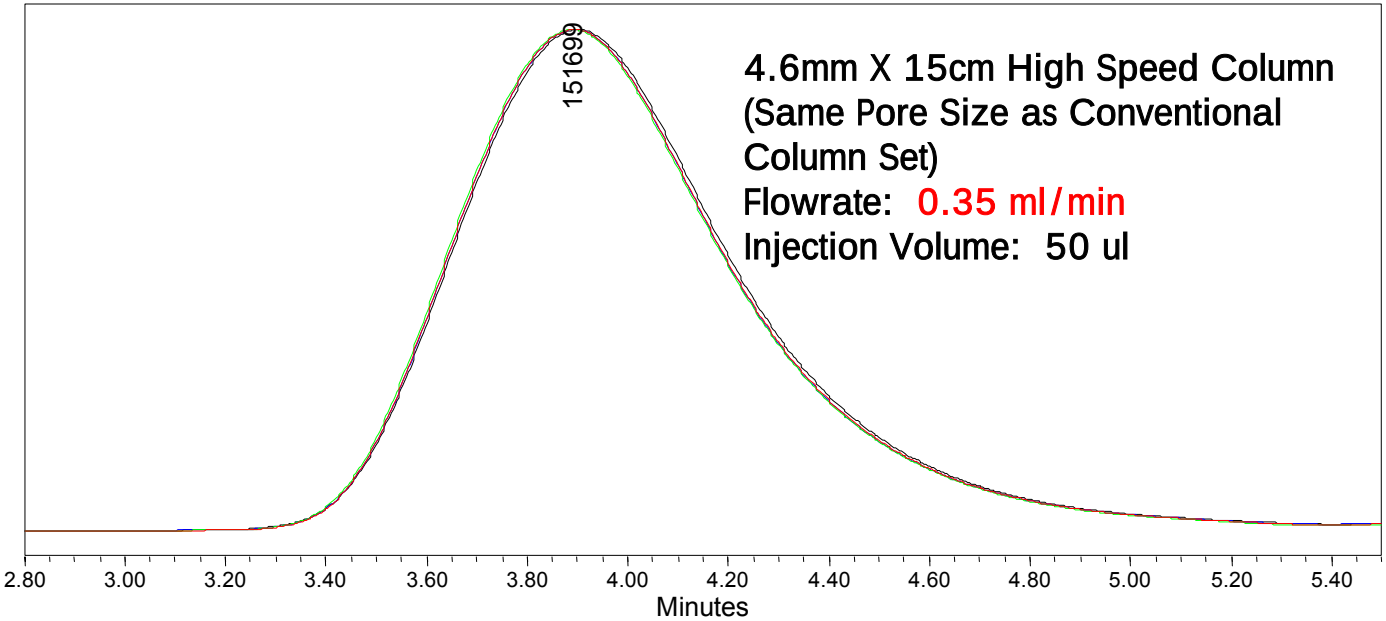
Total Run Time
~6.5 minutes

Component Summary Table

	SampleName	Mn	Mw	Mz	Mz+1	Polydispersity
1	Broad PS	78047	232809	510528	968145	2.982924
2	Broad PS	81957	238569	527827	1029491	2.910916
3	Broad PS	81239	241151	547496	1138681	2.968403
4	Broad PS	81296	237270	522951	1017288	2.918604
Mean		80635	237450	527201	1038401	2.95
% RSD		2.2	1.5	2.9	6.9	1.2

The same broad polystyrene sample run on a 19mm x 15cm High Speed Column obtained similar results to the 7.8mm ID High Speed Column. The Mw obtained was approximately the same as the result from Conventional GPC columns and the other MW averages exhibited significant error from the expected values. The larger pore volume column column did show more resolution between the sample peak and the solvent peaks, but this column configuration did require a flowrate of 6.0 ml/min to achieve the same analysis time as the 7.8mm ID configuration.

4.6mm x 15cm Column – Broad Polystyrene



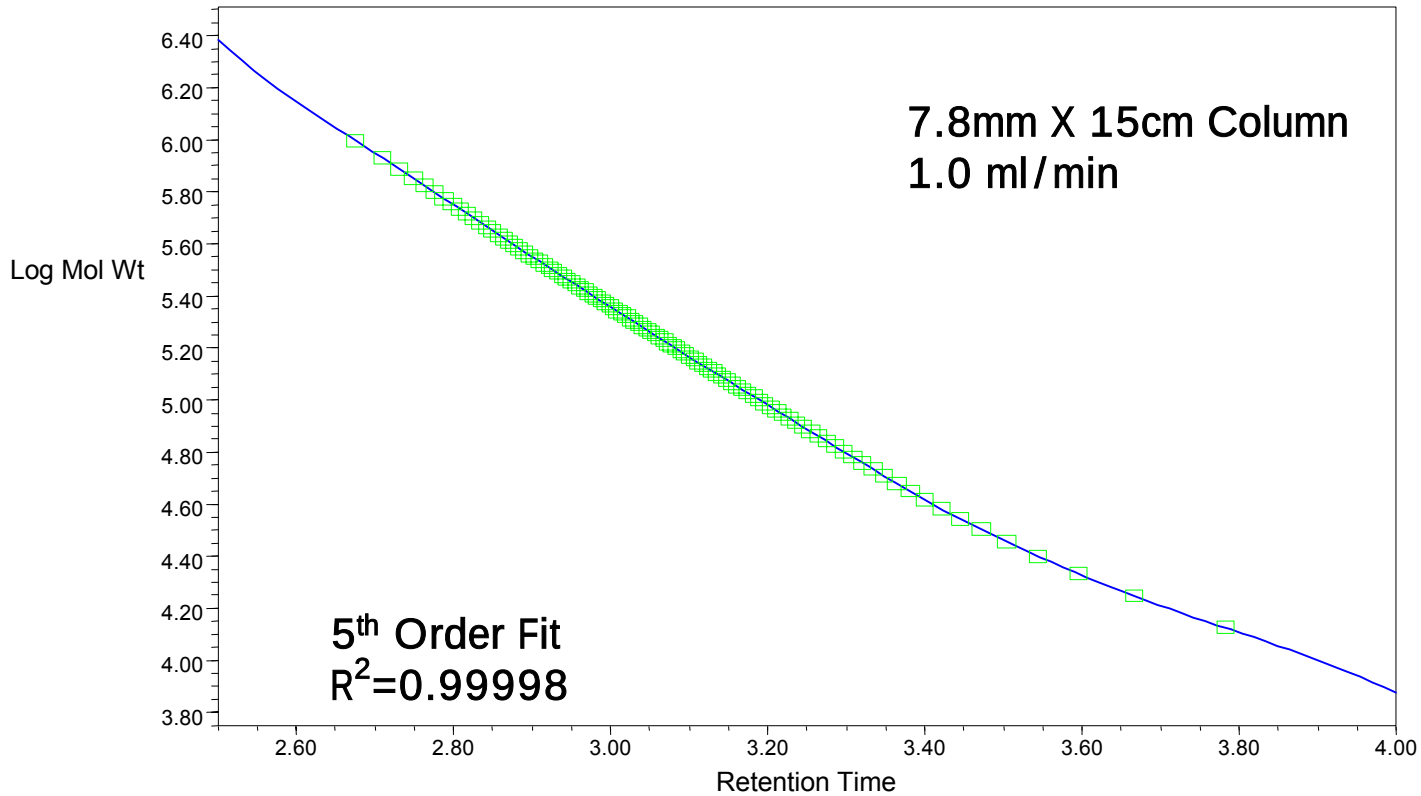
Total Run Time
~7.5 minutes

Component Summary Table

	SampleName	Mn	Mw	Mz	Mz+1	Polydispersity
1	Broad PS	48446	237293	825538	1955121	4.898089
2	Broad PS	48973	244091	883806	2287006	4.984172
3	Broad PS	48740	238726	850865	2144707	4.897976
4	Broad PS	47508	235895	904557	2566203	4.965321
Mean		48417	239001	866191	2238259	4.94
% RSD		1.3	1.5	4.0	11.5	0.9

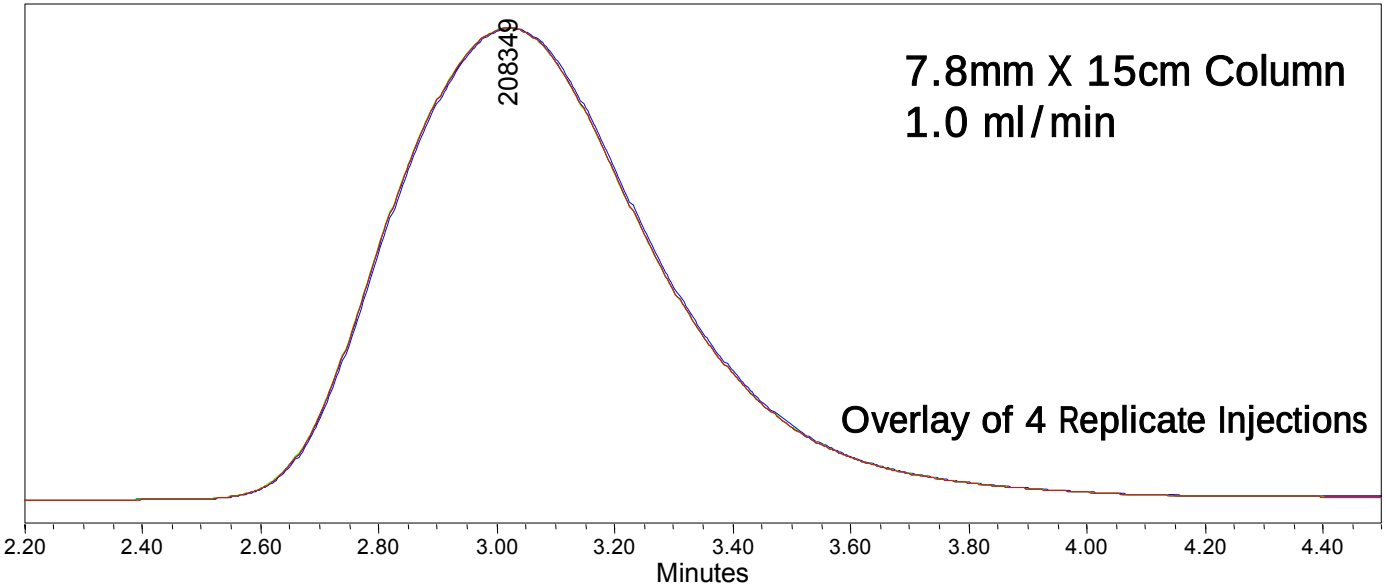
Switching to a 4.6mm ID High Speed Column resulted in worse results due to the greater effect of system bandspreading on the separation. The overall peak is much broader with significantly more peak tailing than the other column configurations. In addition, less resolution was available between the sample peak and the solvent/impurity peaks.

High Speed GPC – Calibration Curve with Cumulative Matching



A simple means to achieve correct molecular weight results for moderate molecular weight polymer samples is through the use of Cumulative Matching Calibration routines. This is accomplished by running a broad sample on a Conventional Column Set and determining a molecular weight distribution for the sample. The same sample can then be run on the High Speed Column and the previously determined molecular weight slice data is used to generate a calibration curve consisting of 100 data points that cover the entire molecular weight range of the broad standard as shown in the calibration above for a 7.8mm ID High Speed Column. Additional narrow standards may be added to extend the range of the calibration curve.

High Speed GPC – Broad Polystyrene with Cumulative Matching



Total Run Time
~6.5 minutes

Component Summary Table

	SampleName	Mn	Mw	Mz	Mz+1	Polydispersity
1	Broad PS	100677	241773	429299	630199	2.401465
2	Broad PS	100965	242625	431605	635701	2.403058
3	Broad PS	99387	238436	424417	625958	2.399064
4	Broad PS	100752	241626	429023	630492	2.398235
Mean		100445	241115	428586	630587	2.40
% RSD		0.7	0.8	0.7	0.6	0.1

Using this Cumulative Matching calibration curve for quantitation, the broad polystyrene sample shown above resulted in the same molecular weight results and precision as those obtained with the Conventional Column Set. Similar correlations were also found for bimodal polymer blends.

Traditional GPC vs High Speed GPC
Broad Polystyrene Sample

		Mn	Mw	Mz	Mz+1	Polydispersity
Conventional GPC	Mean	98,800	239,000	425,000	621,000	2.42
	%RSD	1.9%	0.6%	0.9%	0.9%	2.0%
7.8mm x 15cm High Speed GPC With Cumulative Matching	Mean	100,000	241,000	429,000	631,000	2.40
	%RSD	0.7%	0.8%	0.7%	0.6%	0.1%
% Variance		1.21%	0.84%	0.94%	1.61%	0.83%

The table above demonstrates the excellent correlation between molecular weight results obtained with Conventional GPC columns and those obtained with 7.8mm x 15cm High Speed GPC columns processed using the Cumulative Matching calibration routine. A percent variance of less than 2% was obtained for all molecular weight averages and polydispersity values for the two methods which can be considered to be essentially identical.

New High Speed GPC Chemistries

HSPgel™ HR (high resolution)

HSPgel™ RT (room temp.)

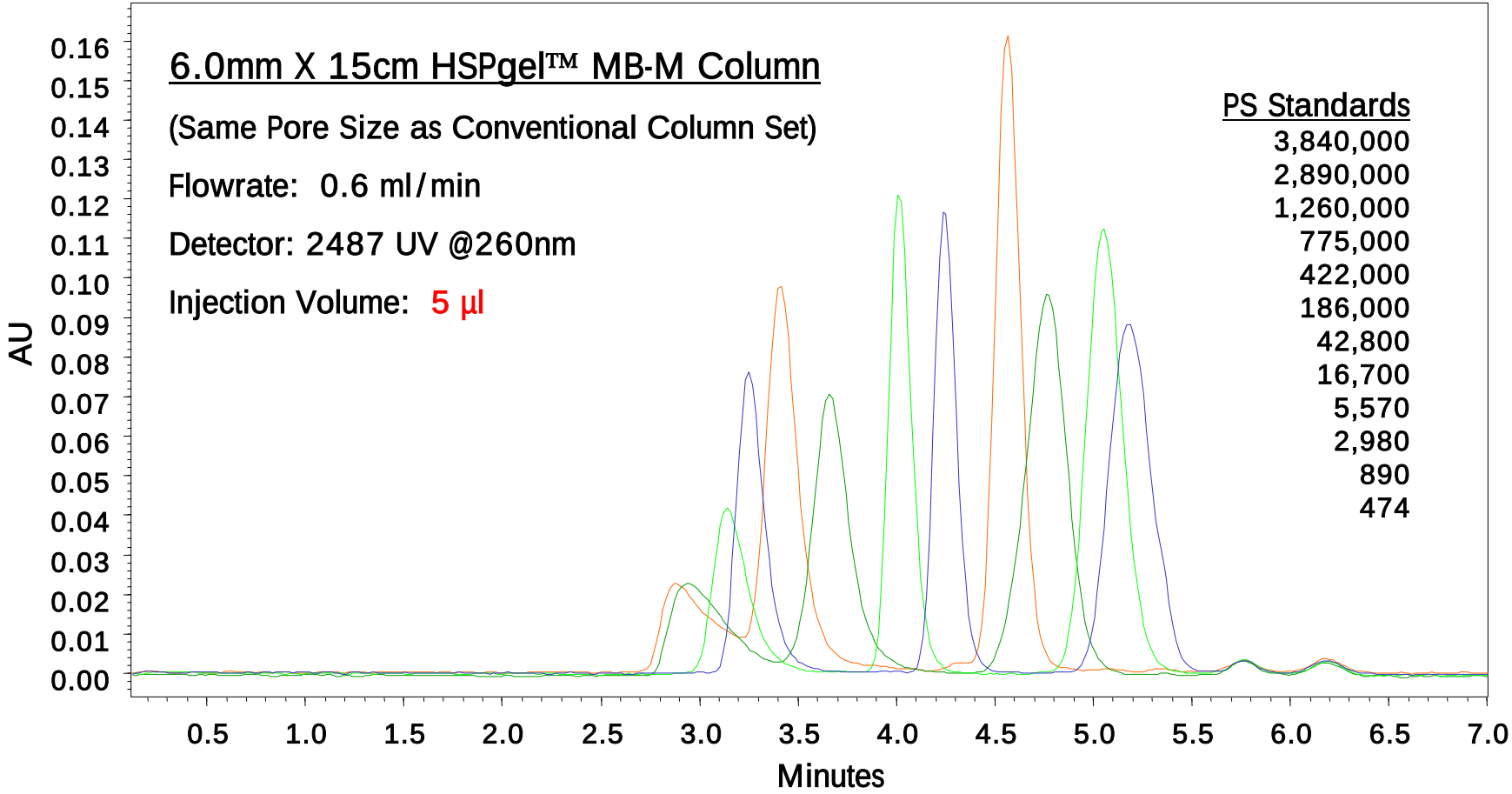
HSPgel™ HT (high temp.)

HSPgel™ AQ (aqueous GPC)

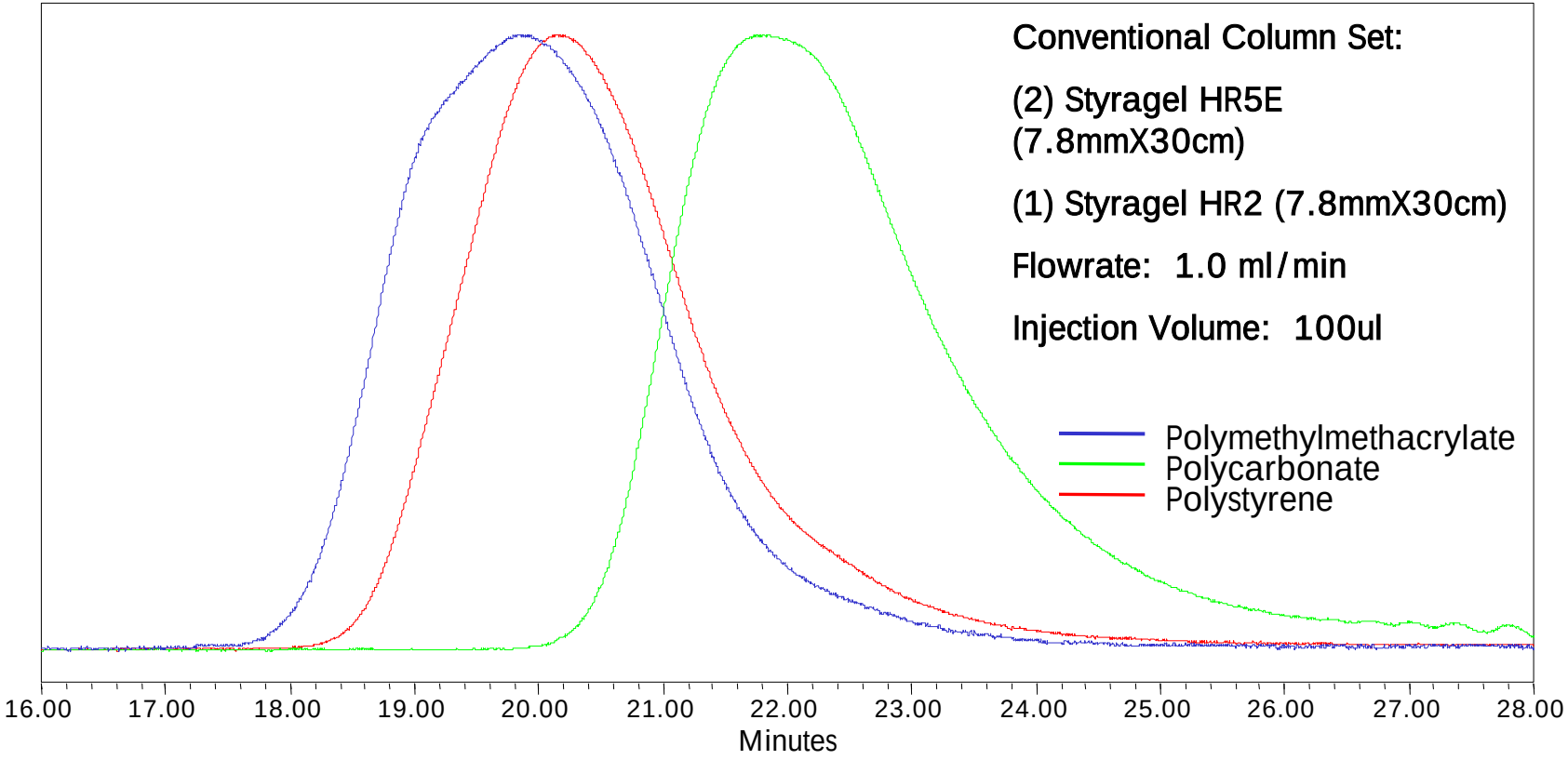
6.0mm x 15cm

After the 4.6mm, 7.8mm, and 19mm x 15cm high-speed prototypes were evaluated, new columns of dimensions 6.0mm x 15cm were evaluated, and proved to give the most accurate and reproducible molecular weight distributions. The HR, RT and AQ High-speed columns are available now, with the HT version available later in October '02.

High Speed GPC of Polystyrene Standards
UV Detection at 260nm

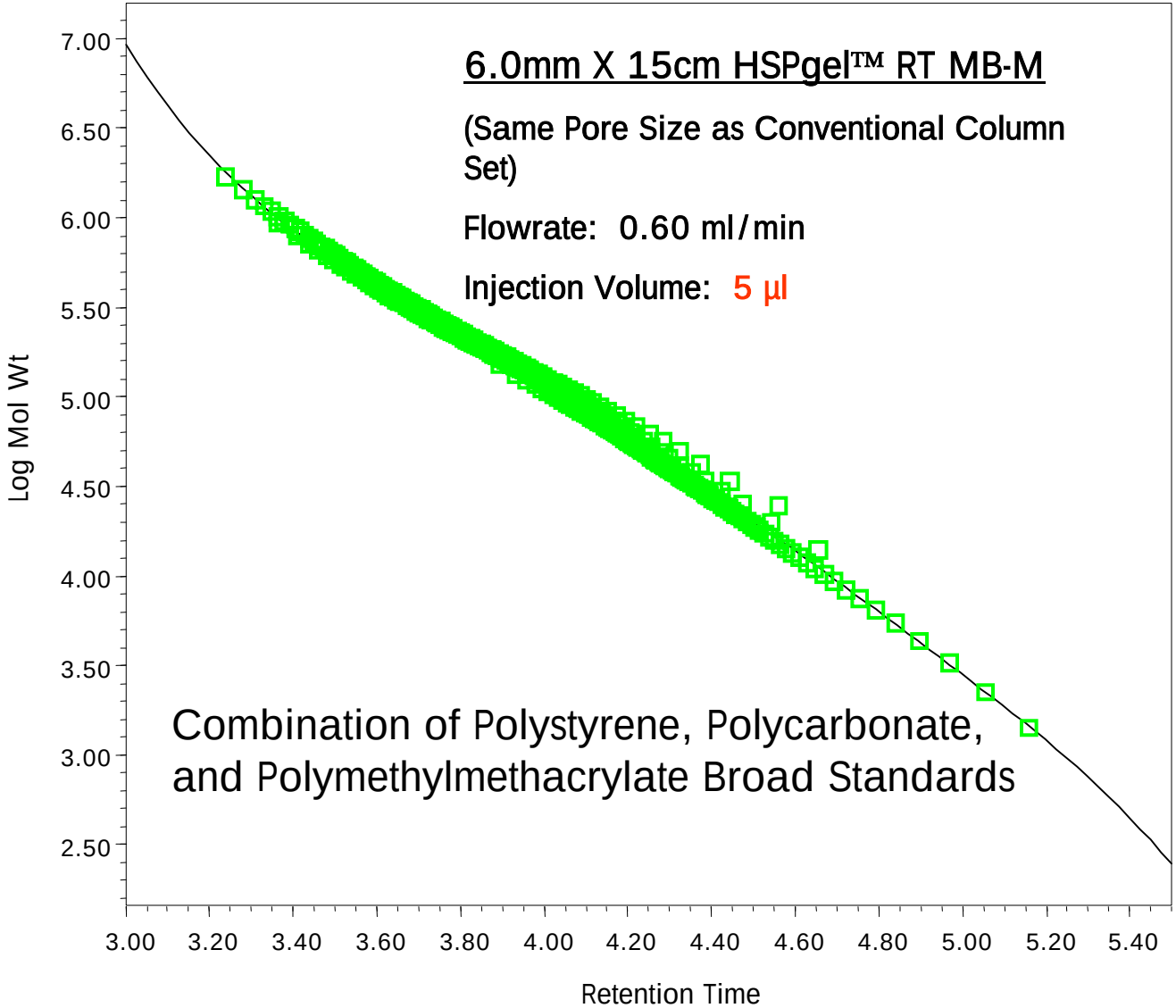


Broad Standards for Cumulative Matching Calibration

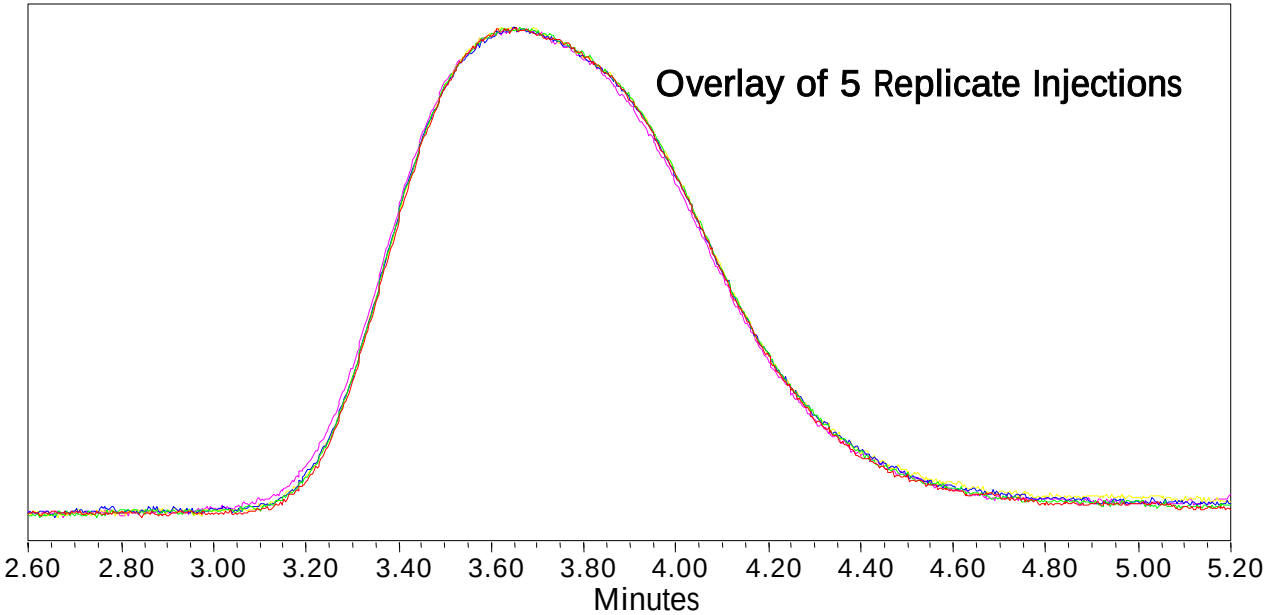


This represents an overlay of three broad standards, PMMA, PC, and Polystyrene, run on the conventional Styragel HR 3-column set. The molecular weight distributions are determined for each via a narrow standard calibration curve (polystyrene in this case). The known distribution for each is used to create the cumulative matching broad standard calibration curve (300 points)

Combination of Three Broad Standards in Cumulative Calibration Curve



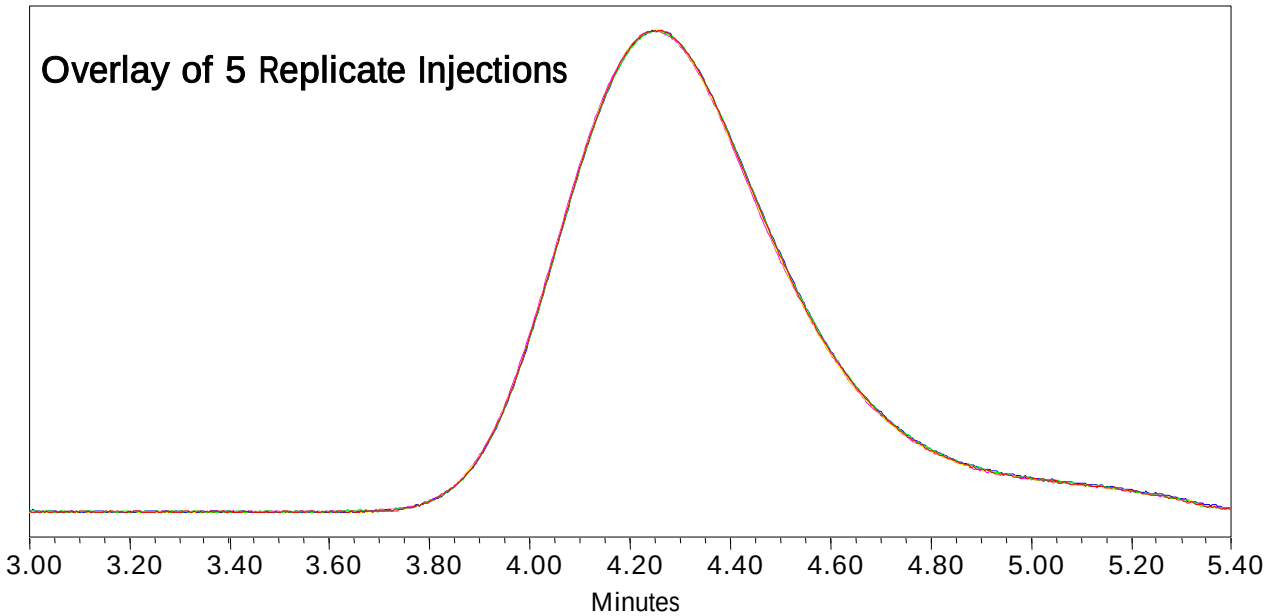
RT MB-M Column - Polymethylmethacrylate



	SampleName	Inj	Mn	Mw	Mz	Mz+1	Polydispersity
1	PMMA	1	152517	371781	705923	1166511	2.437636
2	PMMA	2	156169	374127	709927	1159176	2.395659
3	PMMA	3	163961	378182	718382	1197269	2.306540
4	PMMA	4	158032	376581	719791	1201028	2.382935
5	PMMA	5	165376	389073	767407	1358269	2.352665
Min			152516.9	371780.8	705922.5	1159176.0	2.3
Max			165375.5	389073.1	767407.2	1358268.8	2.4
Mean			159210.9	377948.8	724285.8	1216450.7	2.4
% RSD			3.4	1.8	3.4	6.7	2.1

The table above lists the % RSD's for the MW averages for the PMMA broad standard run on the RT MB-M high-speed column using the cumulative matching calibration.

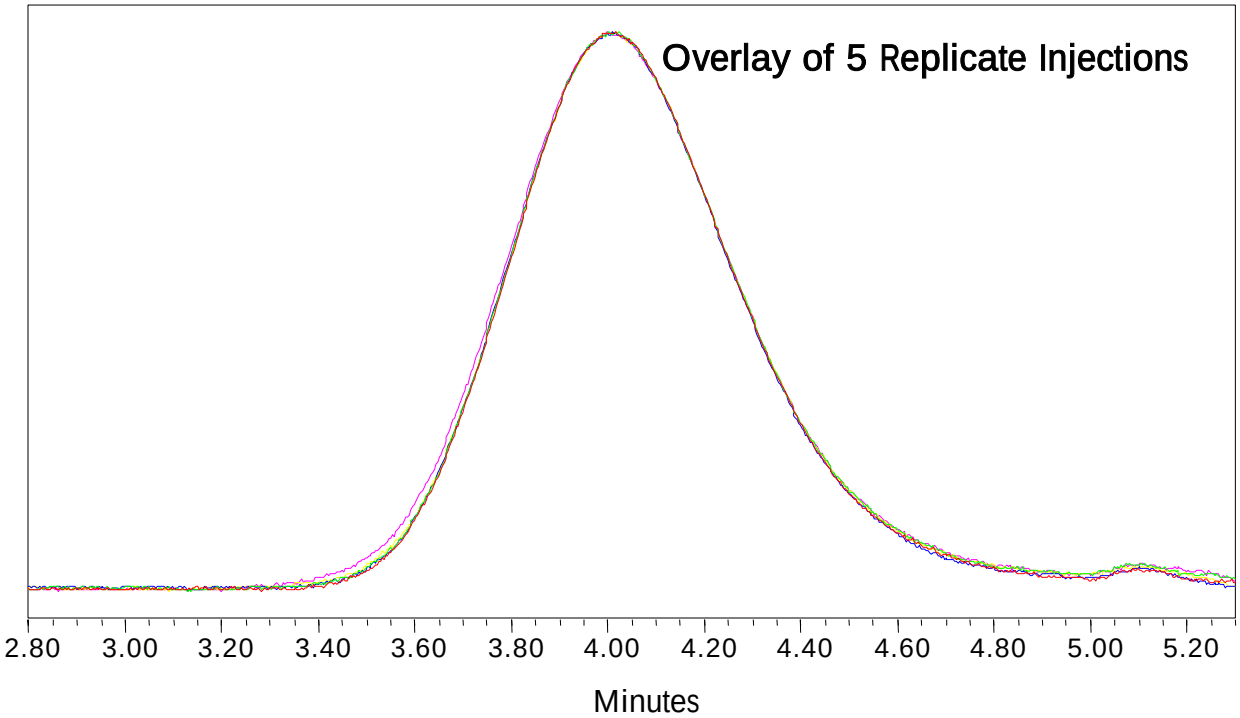
RT MB-M Column - Polycarbonate



	SampleName	Inj	Mn	Mw	Mz	Mz+1	Polydispersity
1	PC	1	18287	50062	76822	100816	2.737583
2	PC	2	18437	50106	77339	102455	2.717624
3	PC	3	17901	49793	76609	100721	2.781589
4	PC	4	17996	50255	77405	102064	2.792505
5	PC	5	18100	50603	78155	103678	2.795660
Min			17901.0	49793.2	76609.4	100720.8	2.7
Max			18437.3	50602.5	78154.8	103678.2	2.8
Mean			18144.4	50163.7	77266.1	101947.0	2.8
% RSD			1.2	0.6	0.8	1.2	1.3

RSD's for the Polycarbonate run on the high-speed column, using cumulative matching calibration

RT MB-M Column - Polyvinylchloride



	SampleName	Inj	Mn	Mw	Mz	Mz+1	Polydispersity
1	PVC	1	64599	126827	196036	270940	1.963298
2	PVC	2	67046	126896	193695	264112	1.892680
3	PVC	3	67214	127761	195929	269380	1.900809
4	PVC	4	67974	127995	197066	272697	1.882998
5	PVC	5	66490	131148	208040	297255	1.972452
Min			64598.9	126826.9	193695.0	264112.3	1.9
Max			67973.9	131147.9	208039.9	297254.8	2.0
Mean			66664.6	128125.5	198153.2	274876.8	1.9
% RSD			1.9	1.4	2.9	4.7	2.2

Accuracy of Traditional GPC vs High Speed GPC

	PMMA		Polycarbonate		Polyvinylchloride	
	Average Mn	Average Mw	Average Mn	Average Mw	Average Mn	Average Mw
Conventional Columns	166,600	381,700	17,680	46,900	67,580	123,100
RT MB -M Column	159,200	377,900	18,140	50,160	66,660	128,100
% Variance	4.44%	1.00%	2.60%	6.95%	1.36%	4.06%

*Determined using Cumulative Calibration Curve containing Three Broad Standards

Conclusions

- High Speed GPC with Cumulative Matching Calibration allows for the determination of molecular weights and molecular weight distributions using Refractive Index detection with accuracy and precision equaling that of Conventional columns for many Gaussian polymer samples of moderate to high molecular weight
- The new 6.0mm x 15cm HSPgel™ High Speed GPC columns give overall good results with a good balance between accuracy, precision, and resolution
- Bimodal samples such as polymer blends may suffer from lack of resolution, however, accurate Mw values may still be obtained for screening purposes with narrow standard calibration
- High Speed GPC is an excellent tool for rapidly obtaining accurate molecular weight results especially for QC labs routinely running many samples of similar MW range