



High-throughput SEC analysis using semi-micro column packed with mono- disperse polystyrene particles which have a broad pore-size distribution

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Outline

- 1. Approach to High-throughput SEC**
- 2. Multipore Technology**
- 3. Latest High-Throughput SEC on multi-pore semi-micro short columns**



Our approach to high-throughput SEC

Conventional SEC

Columns

Smaller particle size
Semi-micro short column

Equipment

Low dead volume
High reproducibility

High-throughput SEC



TOSOH

TSK-GEL for size-exclusion chromatography in organic solvents

Year	Column	I. D. (mm)	Length (cm)	Particle size (um)	TP/30cm
1971	S	7.5	120	40	1,500
1972	H	7.5	60	10-13	6,000-8,000
1983	HXL	7.8	30	5-13	8,000-16,000
1987	NewHXL	7.8	30	5-10	14,000-16,000
1992	HHR	7.8	30	5-13	8,000-16,000
1993	SuperH	6	15	3	32,000
1996	MultiporeHXL-M	7.8	30	5	16,000
1999	SuperHZ	4.6	15	3	32,000
2000	SuperHZM	4.6/6.0	15	3-10	18,000-32,000
2005	SuperMultiporeHZ-M	4.6	15	4	32,000
2006	SuperMultiporeHZ-N	4.6	15	3	32,000



Comparison of Spec. and Operating Conditions between semi-micro and conventional column

	Semi-micro column	Conventional column
Particle size (um)	3 - 10	5 - 13
Column size (mmID x cm)	6.0 x 15 4.6 x 15	7.8 x 30
Theoretical plates/column	8,000 – 16,000	8,000 – 16,000
Std. flow rate (mL/min)	0.6 (6.0 x 15 column) 0.35 (4.6 x 15 column)	1.0
Analysis time/column (min)	6	12
Solvent consumption/column (mL)	3.6 (6.0 x 15 column) 2.1 (4.6 x 15 column)	12
Sample injection volume (uL)	5 (6.0 x 15 column) 2 (4.6 x 15 column)	50



The best selling GPC system in Japan

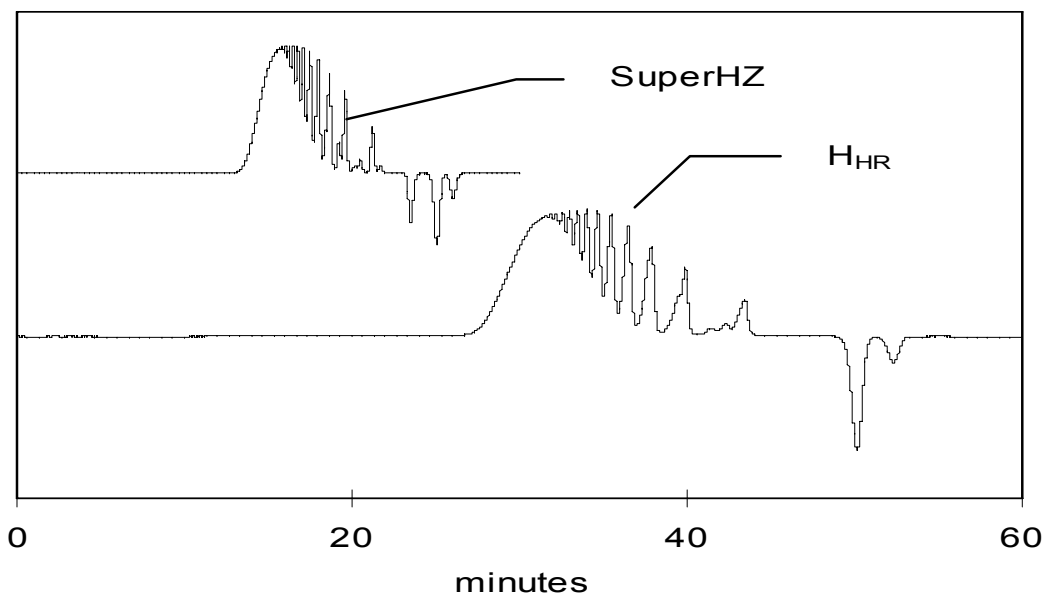
HLC-8220GPC is the 5th generation model of the Tosoh dedicated GPC systems, and it has the fundamental functions which are required by polymer researchers.





The features of HLC-8220GPC

Comparison of analytical time



<Condition>

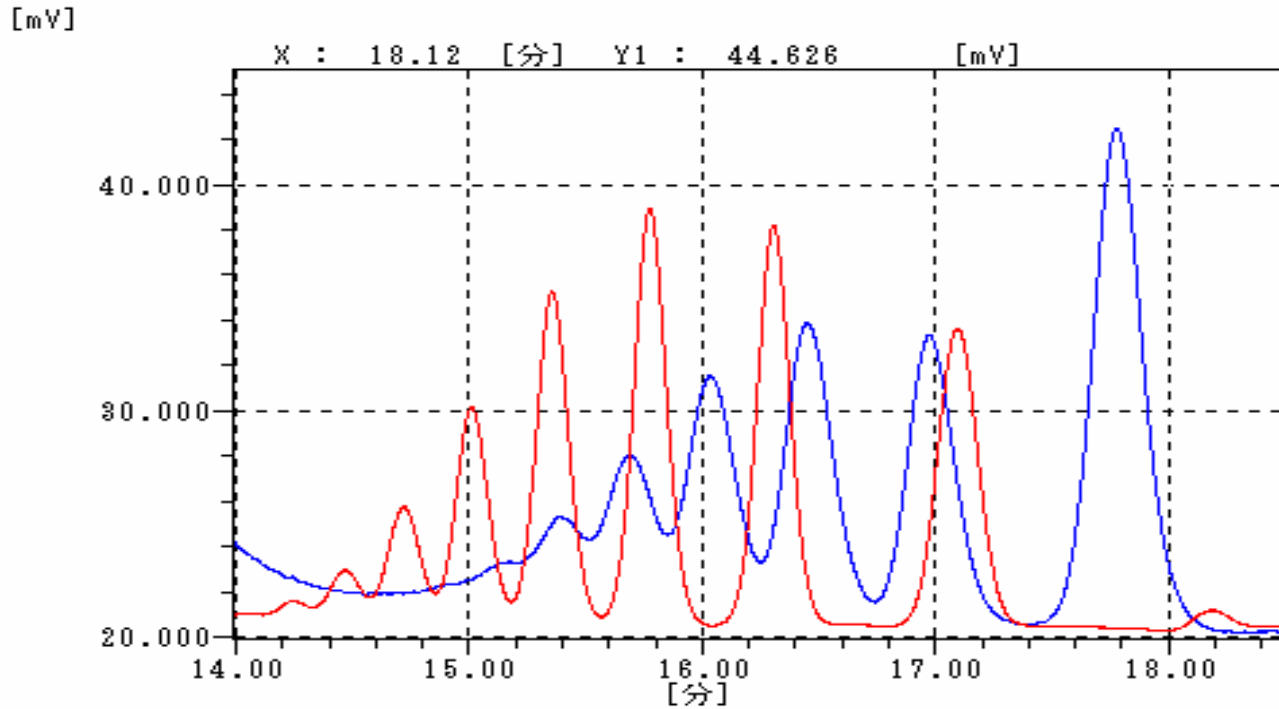
Flow rate: SuperHZ(0.35mL/min), HHR(1.0mL/min)

Dimension: 4.6mmID*150mm*4 (SuperHZ), 7.8mmID*300mm*4 (HHR)



The features of HLC-8220GPC

Effect of system dead volume

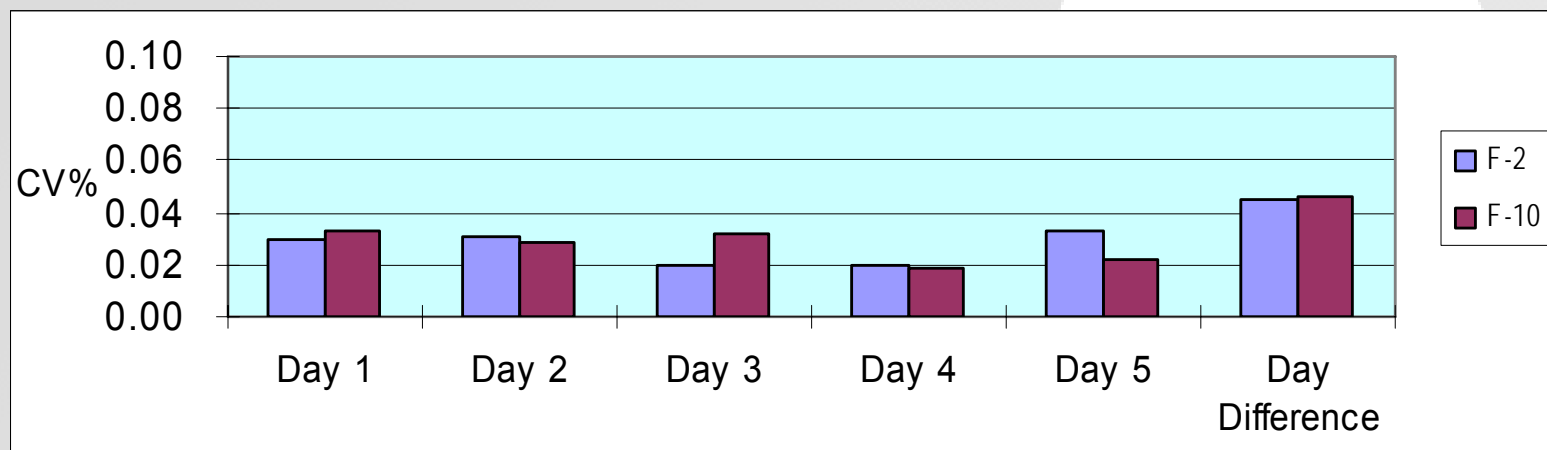


Red: 8220GPC Blue: Breeze



The features of HLC-8220GPC

Reproducibility of Retention Time



<Condition>

Column: SuperHM x 2

Solvent: THF

Flow Rate: 0.35 mL/min

of injection: 10/day

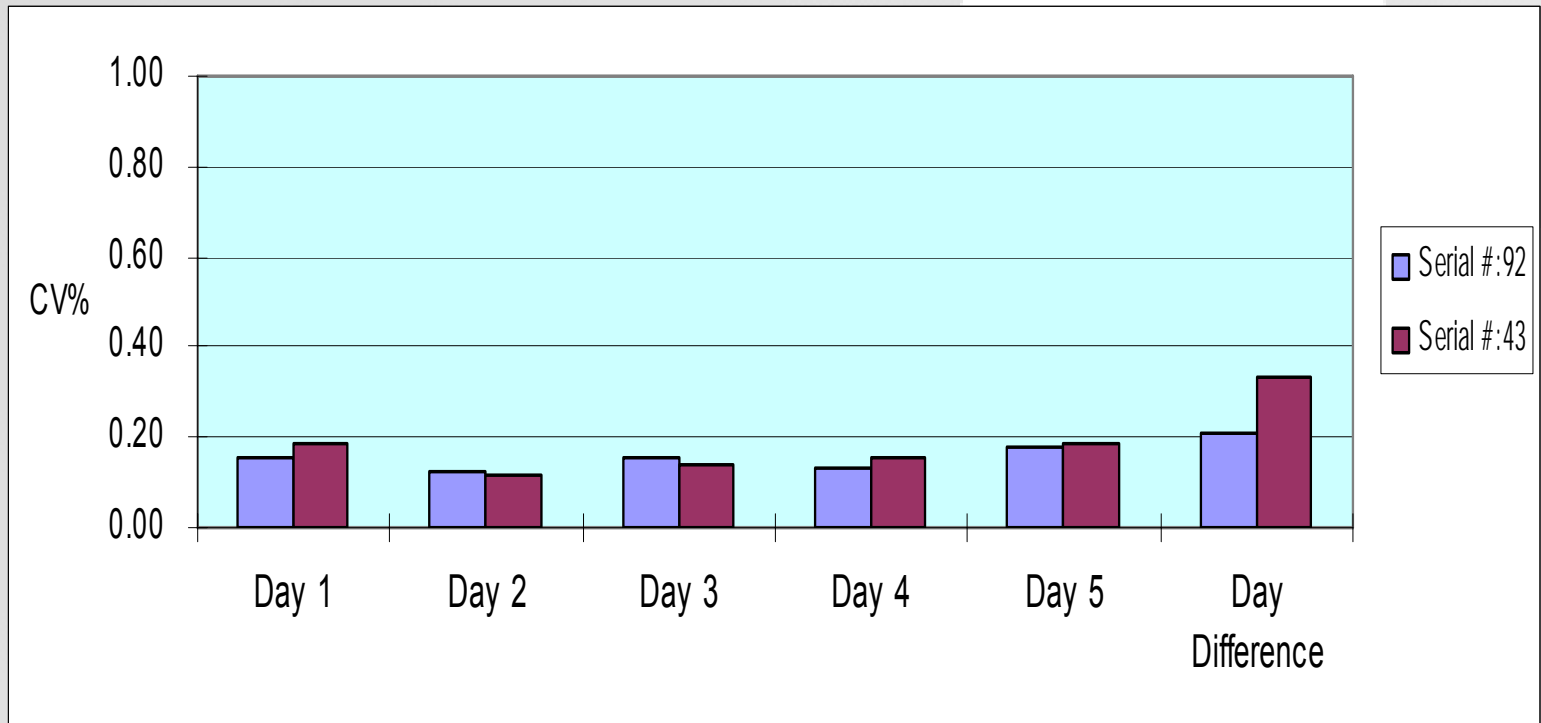
CV%: *Less than 0.04% within a day*

Less than 0.05% in different days



The features of HLC-8220GPC

Reproducibility of Molecular Weight



<Conditions>

Column: SuperHM x 2

Solvent: THF

Flow Rate: 0.35 mL/min

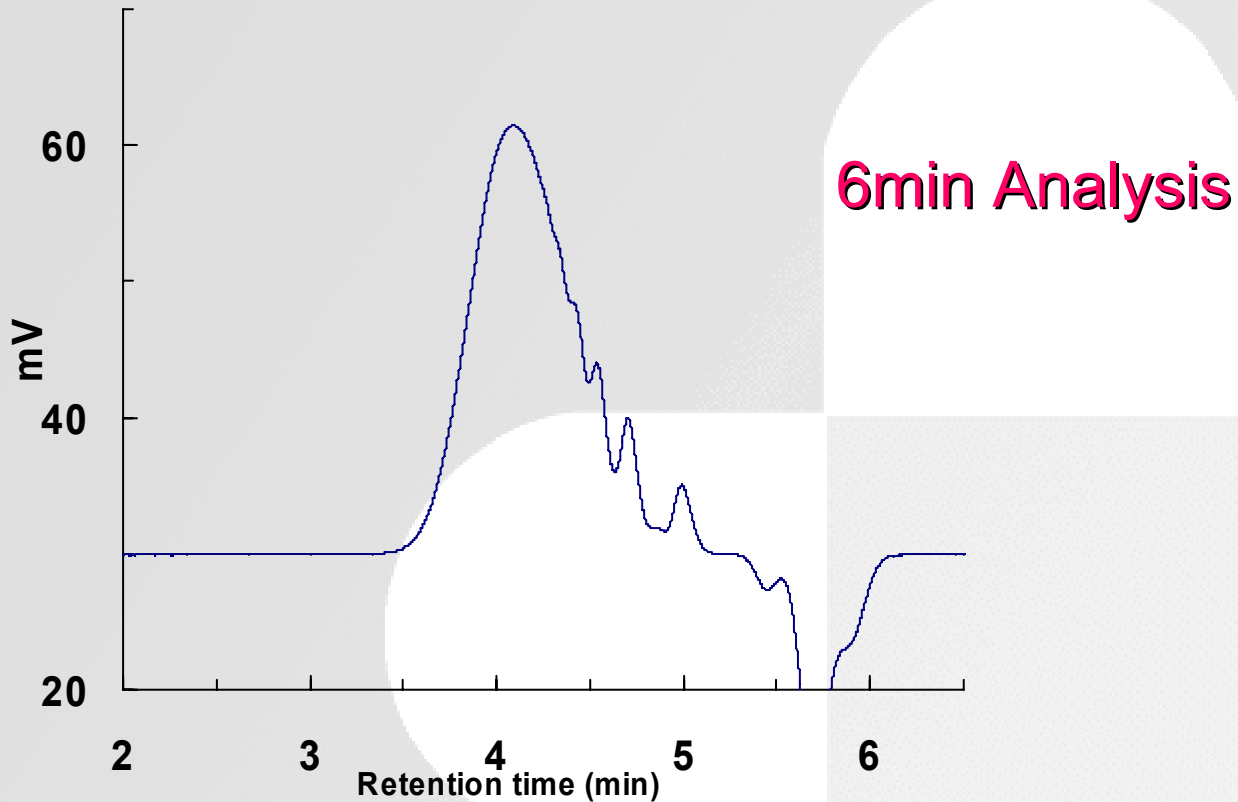
of injection: 10/day

CV%: Less than 0.2% within a day

Less than 0.4% in different days



Chromatogram of Epoxy Resin on SuperHZ



Conditions

Column ; TSKgel SuperH2M-N (4.6mm I.D. x 15cm)

Eluent ; THF

Flow rate ; 0.35mL/min

Sample ; Epoxy Resin

Temp. ; 40

Detection ; RI

Injection ; 5 μ L



Stability of measurement on SuperHZ

	Repeatability (n=6)			Reproducibility (n=3)		
	Mn	Mw	Mz	Mn	Mw	Mz
A.V.	2386	5414	8599	2368	5417	8629
S.T.D	14.5	5.6	7.5	17.0	30.3	37.9
CV (%)	0.61	0.10	0.09	0.72	0.56	0.44

Conditions

Column ;TSKgel SuperH2M-N (4.6mm I.D. x 15cm)
Eluent ;THF
Flow rate ;0.35mL/min
Sample ;Epoxy Resin

Temp. ;40
Detection ;RI
Injection ;5 μ L



Multipore Technology

- **Single pore column / Individual columns**
 - Limited separation range
 - Necessary to connect columns with different separation range
 - Inflection point
- **Mixed bed column / Linear column**
 - Wide separation range
 - Linear calibration curve
 - Inflection point
- **Multipore column**
 - Wide separation range
 - Linear calibration curve
 - No inflection point



The Feature of Multipore Packings

- **Identical particle size with wide pore size distribution**
 - Real linear calibration curve without inflection point for wide separation range
 - Accurate and smooth chromatogram
 - Possibility of single grade column measurement (no need to connect different grade nor mixed-bed column)

- **Large porosity**
 - Shallow calibration curve
 - Higher resolution especially for oligomeric region



TSKgel MultiporeHxl-M



TSK-GEL for size-exclusion chromatography in organic solvents

Year	Column	I. D. (mm)	Length (cm)	Particle size (um)	TP/30cm
1971	S	7.5	120	40	1,500
1972	H	7.5	60	10-13	6,000-8,000
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1987	NewHXL	7.8	30	5-10	14,000-16,000
1992	HHR	7.8	30	5-13	8,000-16,000
1993	SuperH	6	15	3	32,000
1996	MultiporeHXL-M	7.8	30	5	16,000
1999	SuperHZ	4.6	15	3	32,000
2000	SuperHZM	4.6/6.0	15	3-10	18,000-32,000
2005	SuperMultiporeHZ-M	4.6	15	4	32,000
2006	SuperMultiporeHZ-N	4.6	15	3	32,000



Semi-micro columns with multi-pore packings

- Identical particle size with wide pore size distribution
- High porosity

+

- Small particle with multi-pore
 - 3 or 4 μm in 4.6mmID x 15cm
 - High through-put GPC analysis



TSK-GEL SuperMultiporeHZ series

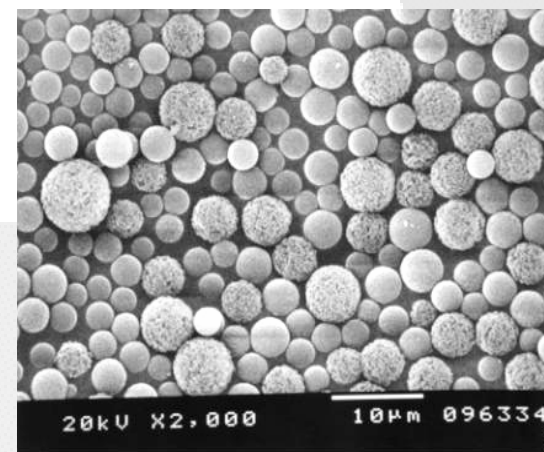
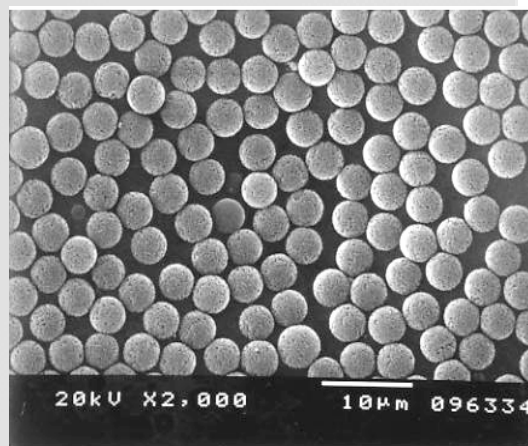
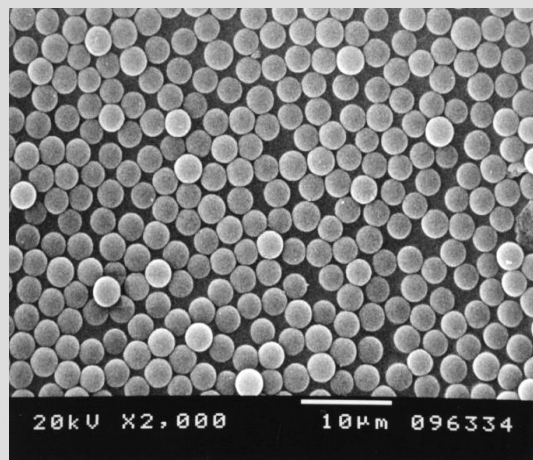


Physical properties of TSK-GEL SuperMultiporeHZ series

Parameter	TSKgel SuperMultiporeHZ-N	TSKgel SuperMultiporeHZ-M
Base material	Poly(Styrene/divinylbenzene)	
Particle diameter	3 micron	4 micron
Max exclusion limit MW	120,000	2,000,000
Mean pore size	8 nm	14 nm
Range of polystyrene sample	50,000 ~ 500	1,000,000 ~ 500
Theoretical plates	18,000/15cm	16,000/15cm
Column size(Analytical)	4.6mmID x 15cm	
Column size(Guard)	4.6mmID x 2cm	



SEM Photographs of TSK-GEL SuperMultiporeHZ series and Mix-bed type column



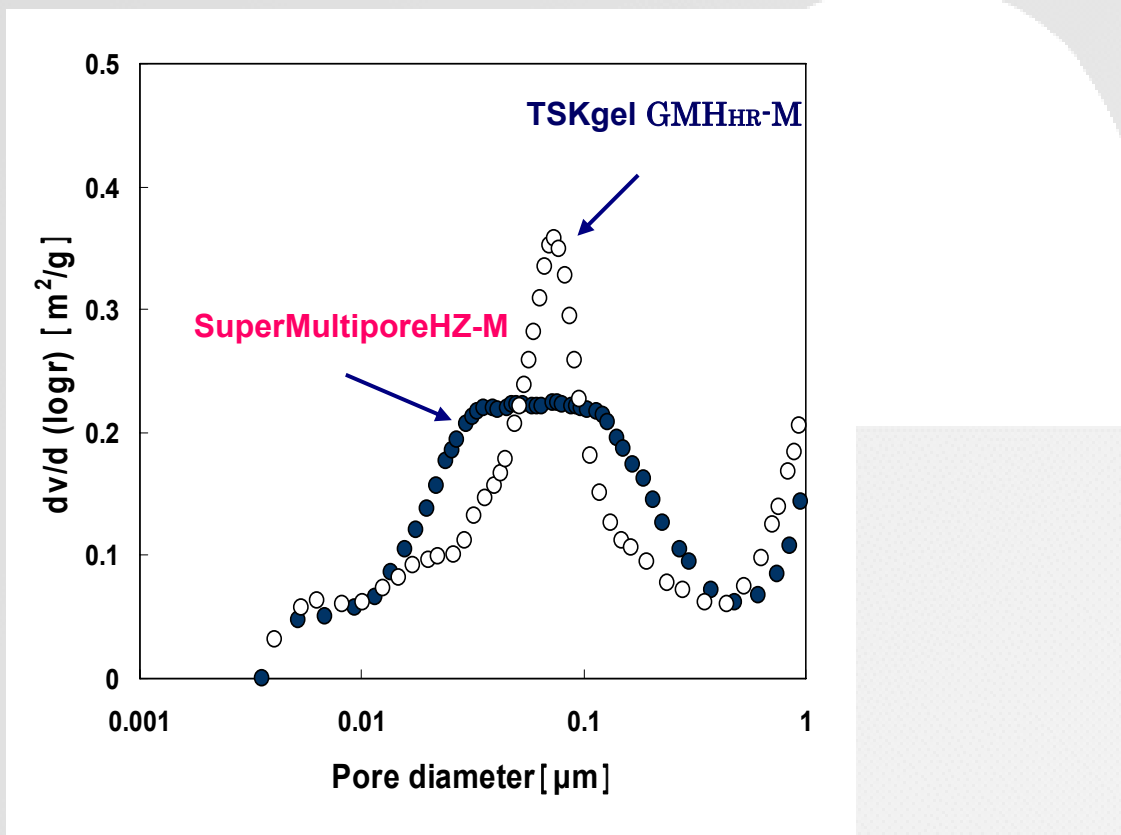
**TSKgel SuperMultiporeHZ-N
(3 micron)**

**TSKgel SuperMultiporeHZ-M
(4 micron)**

**TSKgel SuperHZM-M (mixed-bed)
(4-7 micron)**



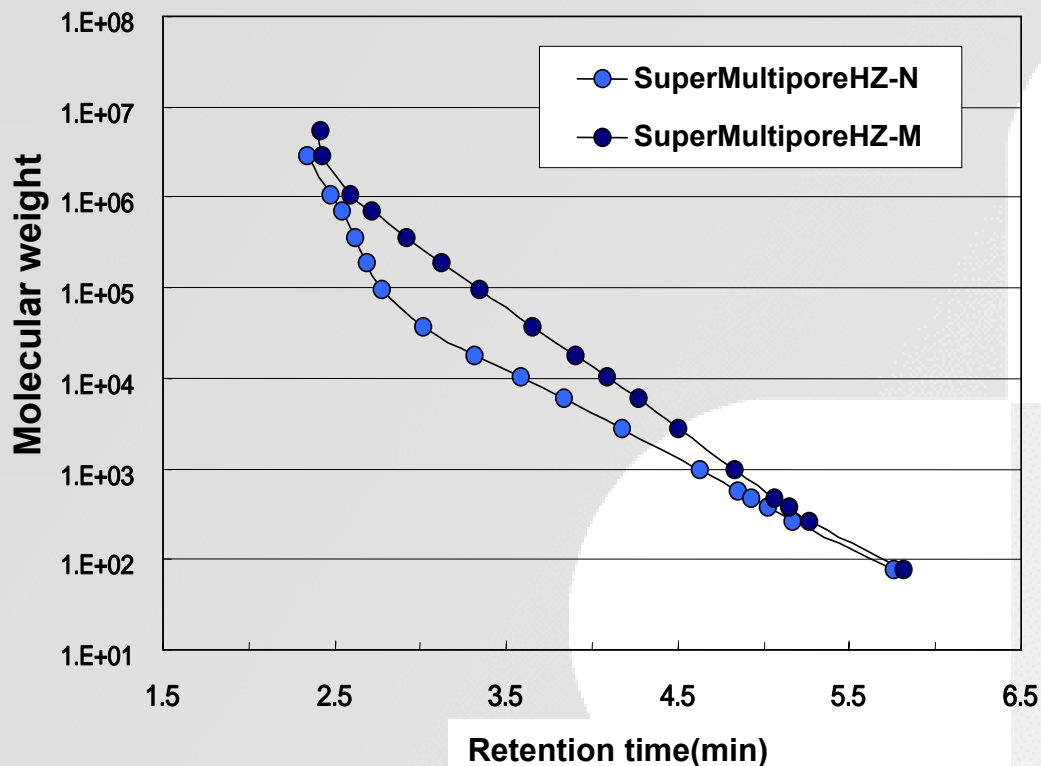
Pore size distribution of SuperMultipore column and mixed-bed column



	Linearity	Slope	Ex.Lim. M.W.	porosity (%)	pore diameter ()
SuperMP-M(041123M)	0.9999	-3.8412	2,120,000	71.5	142



TSK-GEL SuperMultiporeHZ series



Conditions

Column size: 4.6mmID*15cm
 Eluent: THF
 Flow rate: 0.35ml/min
 Temperature: 25C
 Detection: UV 254nm
 (UV-8020 microcell)
 Sample: std PS

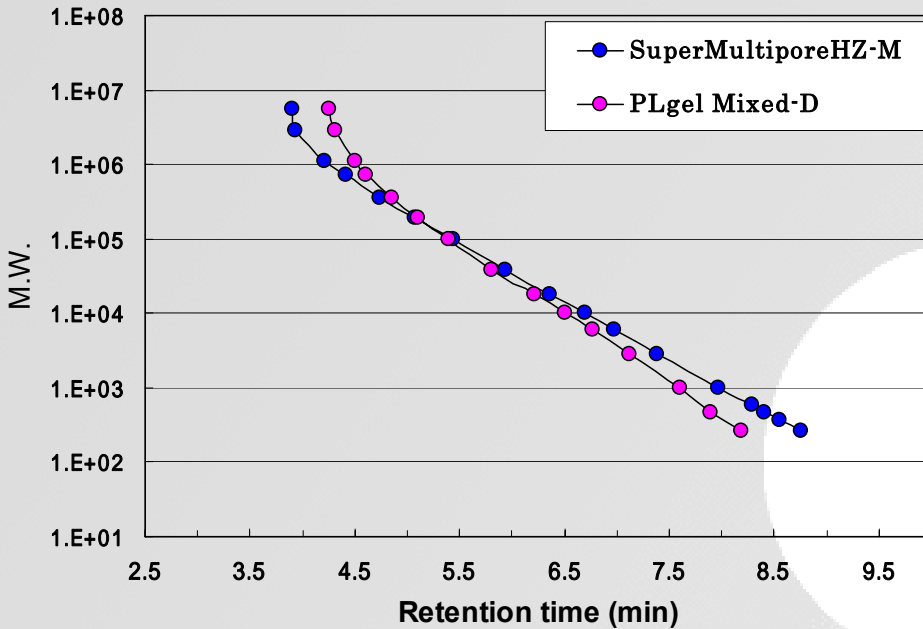
Column	Linearity	Slope	Max Exclusion Limit	Porosity(%)	Pore diameter(nm)
SuperMultiporeHZ-N	0.9996	-2.8131	125,000	70.3	8.2
SuperMultiporeHZ-M	0.9998	-3.8211	1,810,000	72.6	13.9



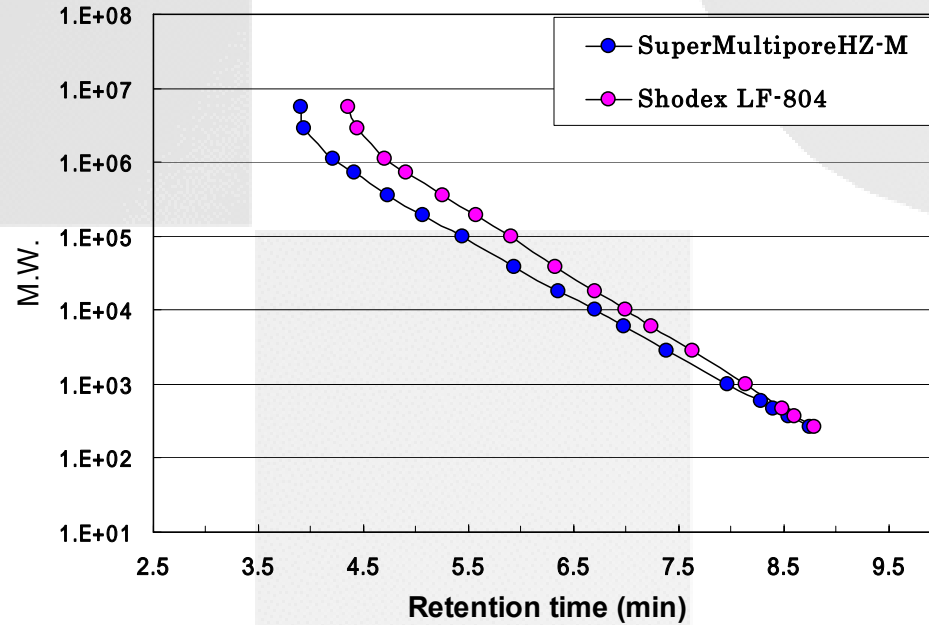
Comparison of calibration curves

- SuperMultiporeHZ-M vs. competitors -

TSK-GEL vs. Polymer Lab.



TSK-GEL vs. Shodex.



Conditions

Column size:4.6mmID*25cm

Eluent:THF

Flow rate:0.35ml/min

Temperature:25

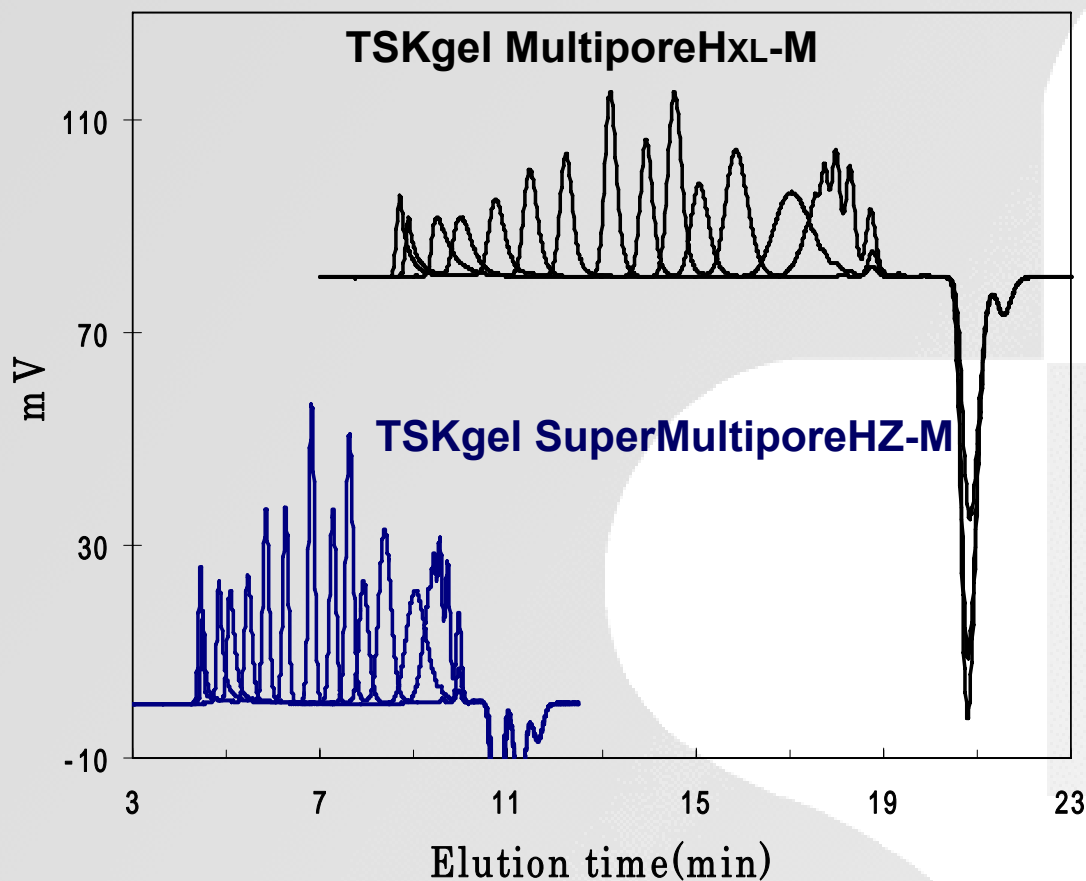
Detection:UV 254nm(UV-8020 microcell)

Sample:STD P.St.



Comparison of chromatograms of PS standards on SuperMultiporeHZ-M and current Multipore HXL-M

High Throughput



Conditions

Column:

(A) TSKgel MultiporeHXL-M
(7.8 mmID x 30 cm x 2)

(B) TSKgel SuperMultiporeHZ-M
(4.6 mmID x 15 cm x 2)

Eluent: THF

Flow rate: (A) 1.0 mL/min

(B) 0.35 mL/min

Temperature: 40

Detection: RI (HLC-8220GPC)

Sample: Polystyrene standards.

(A) 50 μ L (B) 10 μ L

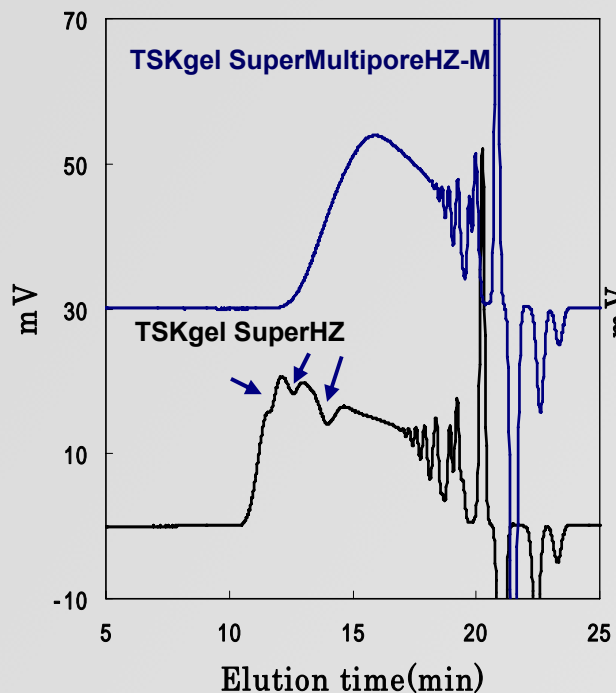


TOSOH

Comparison of chromatograms of synthetic polymers on SuperMultiporeHZ-M (x4) and SuperHZ 2000+2500+3000+4000

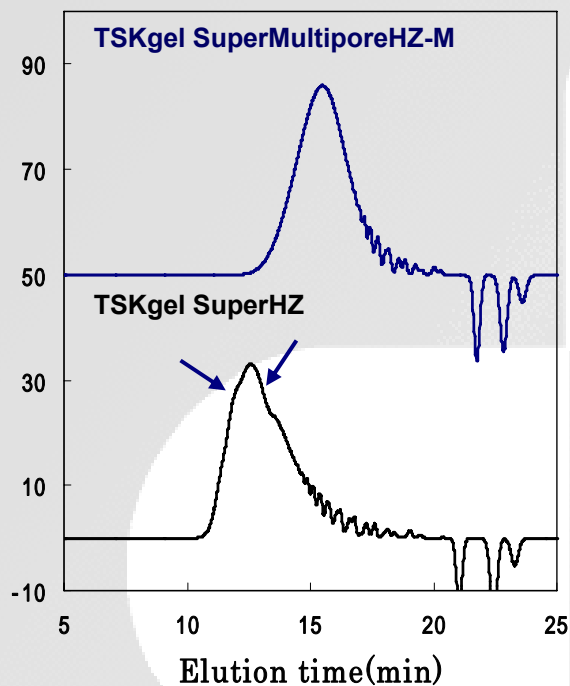
Smooth chromatogram

Phenolic resin



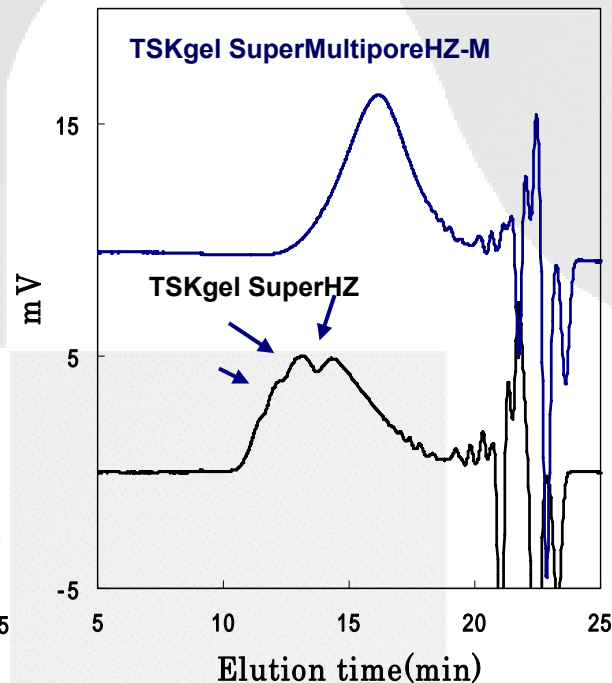
Sample: Phenolic resin (SD)
0.3% 10 μ L

Epoxy resin



Sample: Epoxy resin (Ep1009)
0.3% 10 μ L

Acryl resin



Sample: Acryl resin (KP)
0.3% 10 μ L

Conditions

Column: (A) SuperMultiporeHZ-M (4.6 mmID x 15cm x 4)
(B) SuperHZ4000,3000,2500 and 2000 (4.6 mmID x 15cm x 4)
Eluent: THF

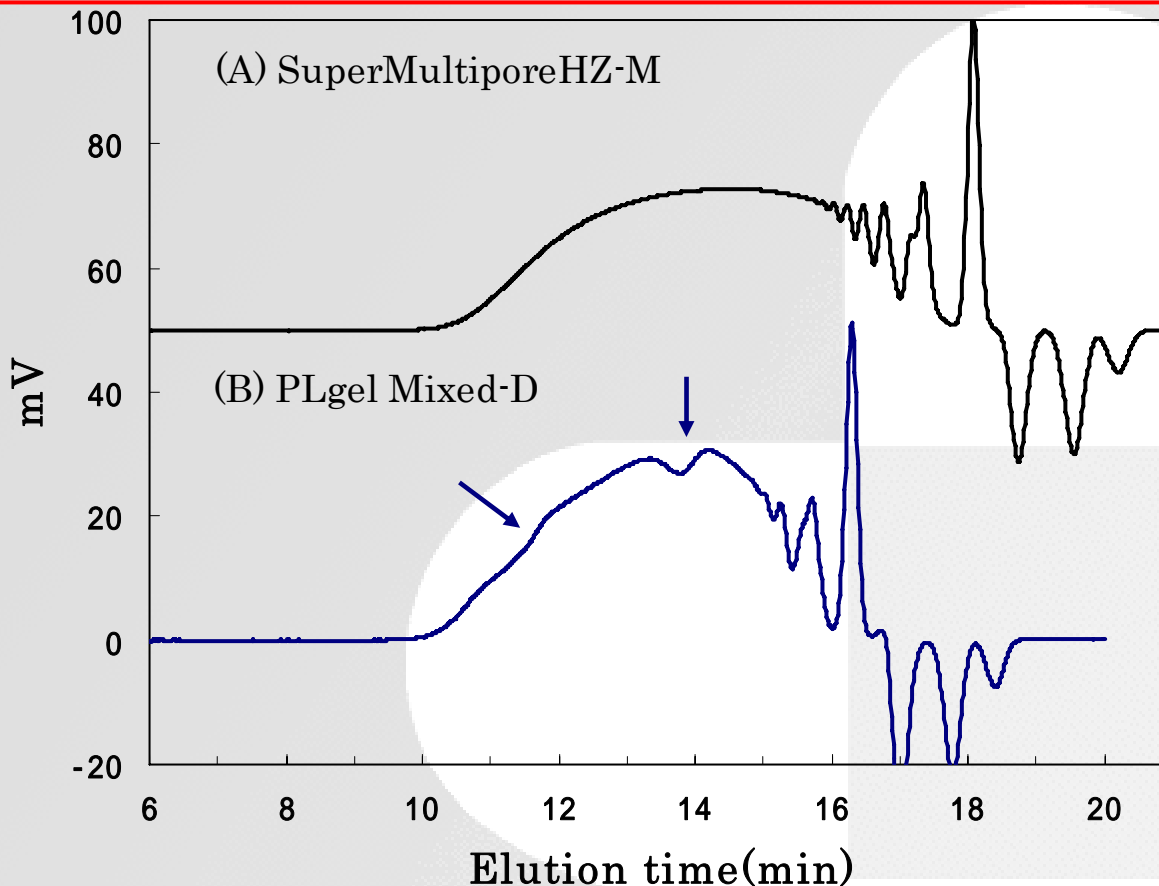
Flow rate: 0.35 mL/min
Temperature: 40
Detection: RI (HLC-8120GPC)



Comparison of chromatograms for phenolic resin

- SuperMultiporeHZ-M and Mixed-bed column -

Smooth chromatogram



Conditions

Column: (A) SuperMultiporeHZ-M(4.6mmID*25cmx2)

(B) PLgel Mixed-D(4.6mmID*25cmx2)

Eluent:THF

Flow rate:0.35ml/min

Temperature:40

Detection:RI(HLC-8120GPC)

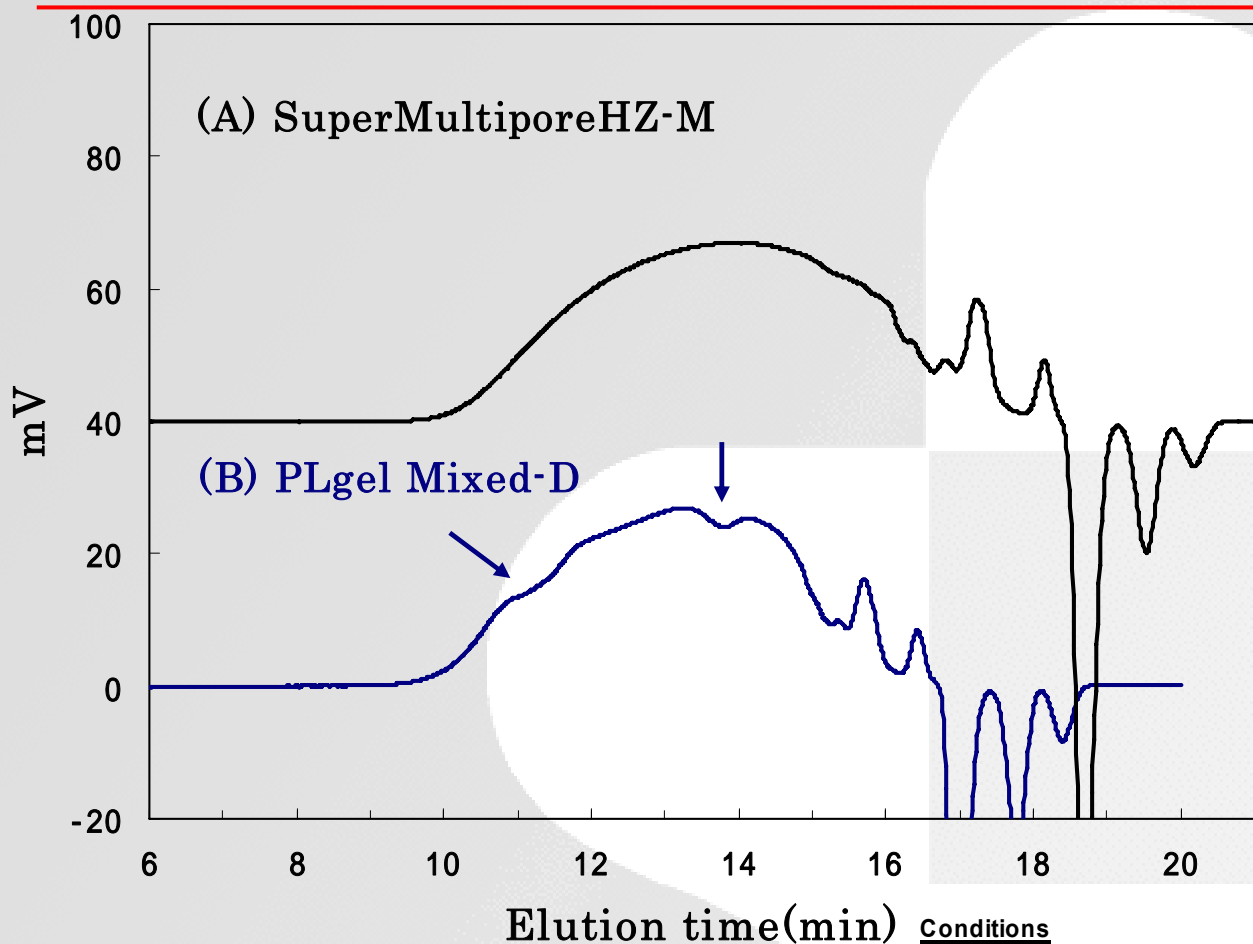
Sample:Phenolic resin(S.D.)(0.5%) 10 μ l



Comparison of chromatograms for alkyd resin

- SuperMultiporeHZ-M and Mixed-bed column -

Smooth chromatogram



Conditions

Column: (A) SuperMultiporeHZ-M(4.6mmID*25cmx2)

(B) PLgel Mixed-D(4.6mmID*25cmx2)

Eluent:THF

Flow rate:0.35ml/min

Temperature:40

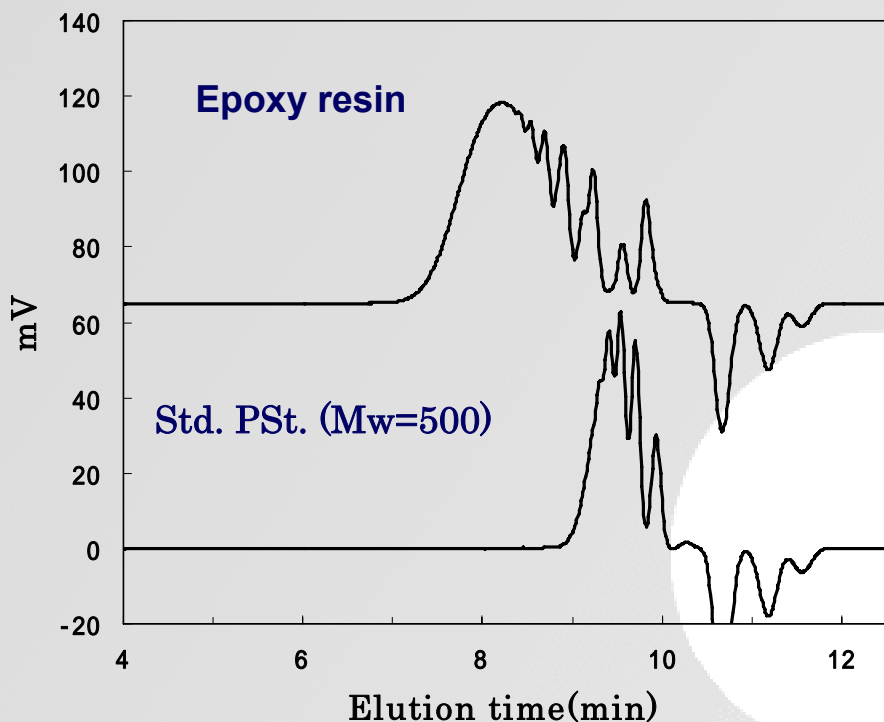
Detection:RI (HLC-8120GPC)

Sample:Phenolic resin(S.D.)(0.5%) 10 μ l



Comparison of chromatograms for alkyd resin - SuperMultiporeHZ-M and Competitor multi-pore column - High Resolution

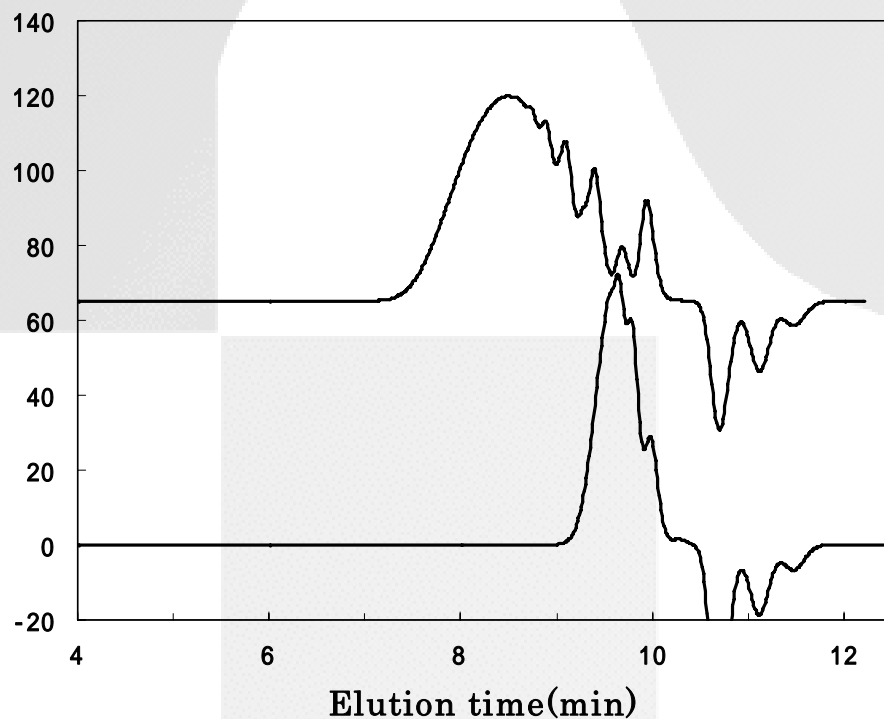
SuperMultiporeHZ-M



Conditions

Column size:4.6mmID*15cmx2
Eluent:THF
Flow rate:0.35ml/min
Temperature:40
Detection:RI(HLC-8120GPC)

Shodex LF-804



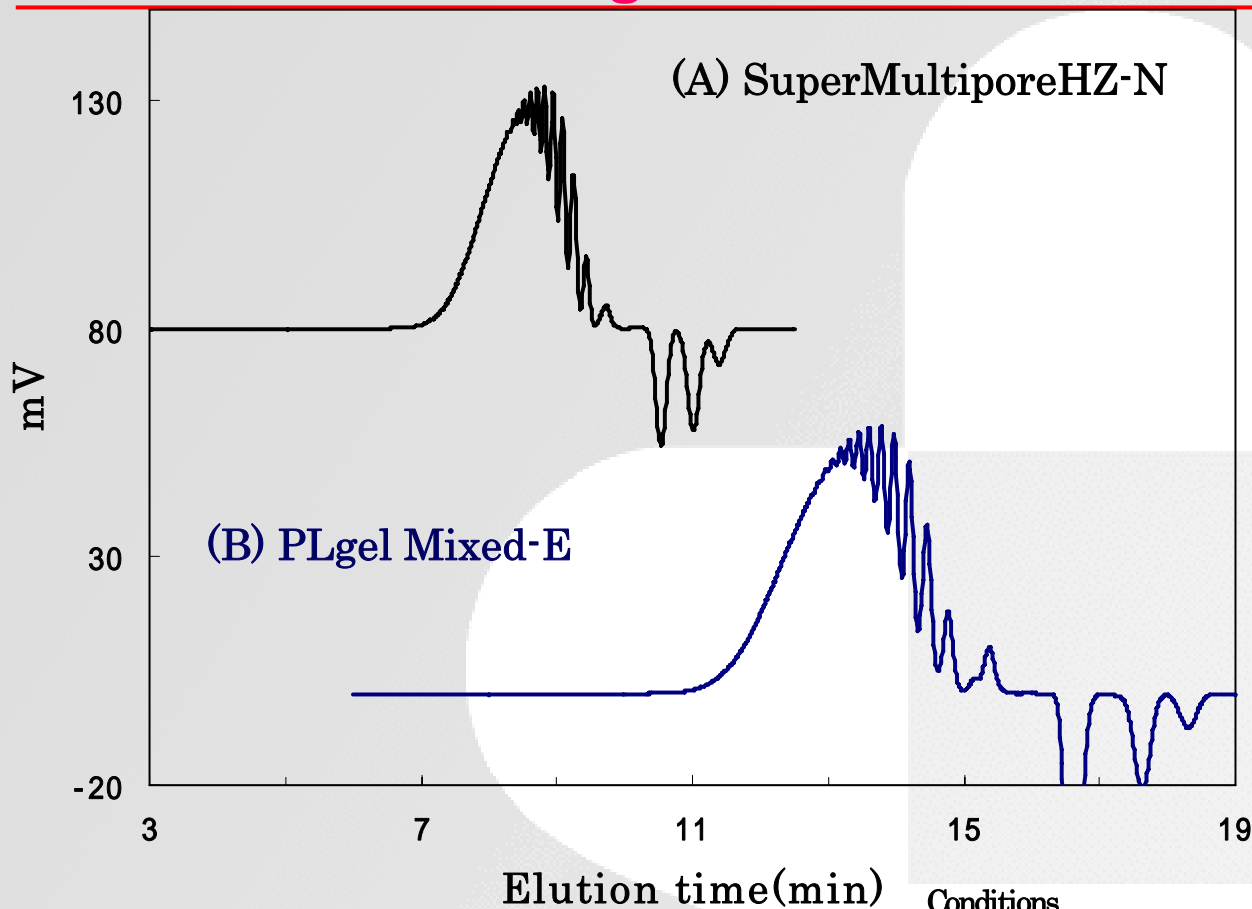
Conditions

Column size:6.0mmID*15cmx2
Eluent:THF
Flow rate:0.60ml/min
Temperature:40
Detection:RI(HLC-8120GPC)



Comparison of PTMEG profile on SuperMultiporeHZ-N and mixed-bed column

High Resolution



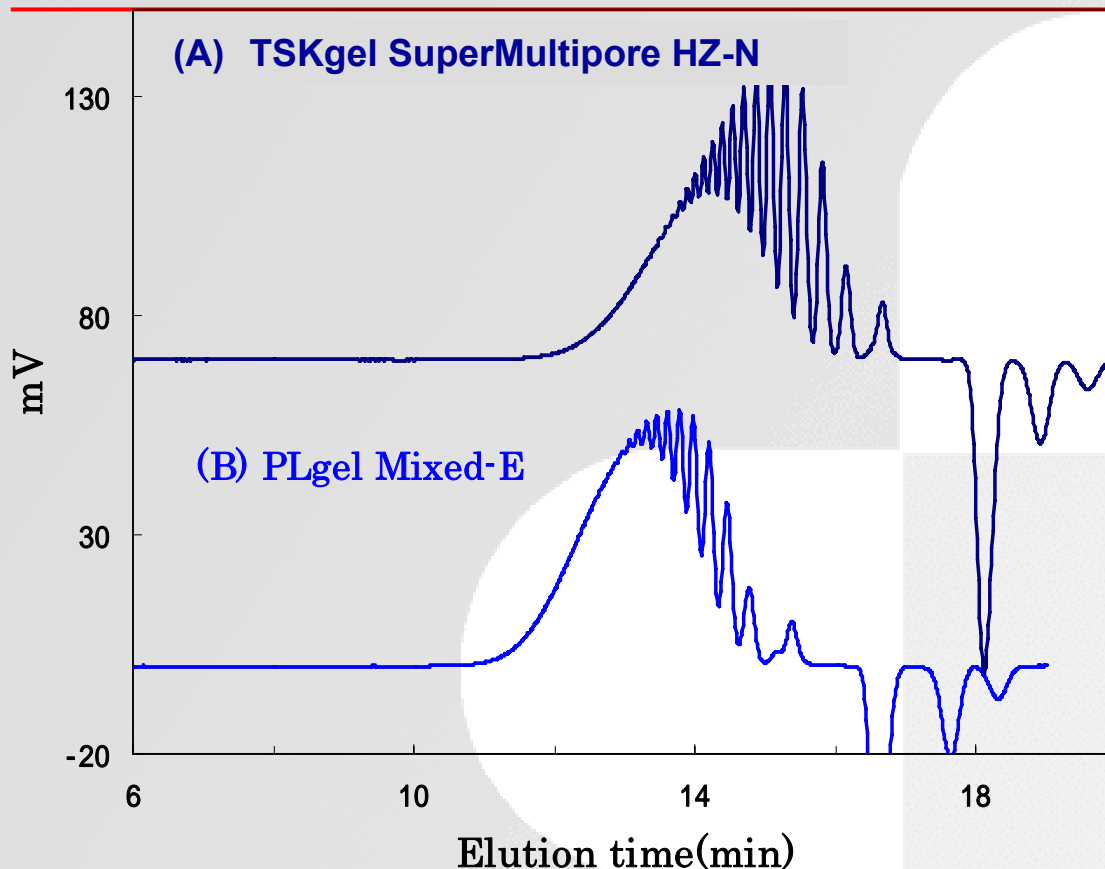
Conditions

Column (A) SuperMultiporeHZ-N(4.6mmID*15cmx2)
(B) PLgel Mixed-E(4.6mmID*25cmx2)
Eluent:THF
Flow rate:0.35mL/min
Temperature:40
Detection:RI
Sample:PTMEG 650(1.0%) 10 μ L



Comparison of PTMEG profile on SuperMultiporeHZ-N and mixed-bed column with the same column size

High Resolution



Conditions

Column: (A) SuperMultiporeHZ-N(4.6mmID*25cmx2)
(B) Commercial Mixed-bd column (4.6mmID*25cmx2)

Eluent:THF

Flow rate:0.35mL/min

Temperature:40 C

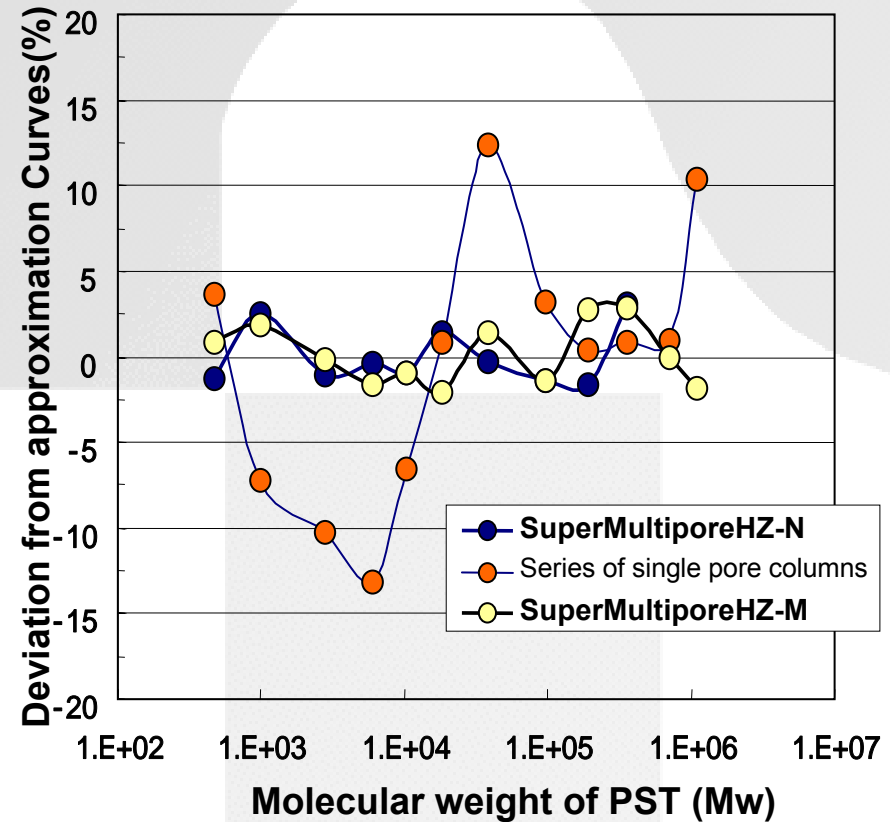
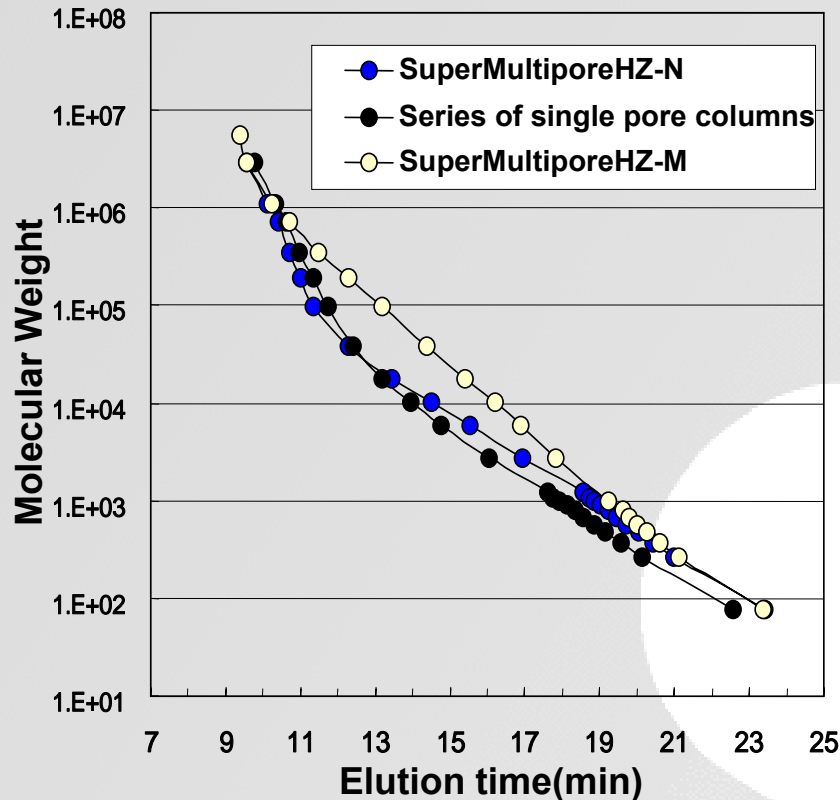
Detection: RI

Sample: PTMEG 650 (1.0%) 10uL



Error of the actual data point from calibration curve

Precise MW



Conditions

Column size:4.6mmID*15cmx4

Eluent:THF, Flow rate:0.35ml/min

Temperature:25 C

Detection:UV 254nm(UV-8020 microcell)

Sample:STD P.St. 10uL



Conclusion

Combination of
Dedicated GPC system

And

Semi-micro column with multi-pore packings
TSK-GEL Super Multipore HZ columns



**High Throughput GPC Analysis
with High Accuracy and Reproducibility**