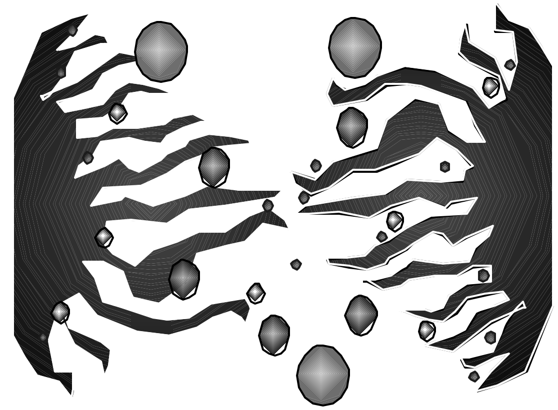
Tools For Polymer Characterization

Size Exclusion

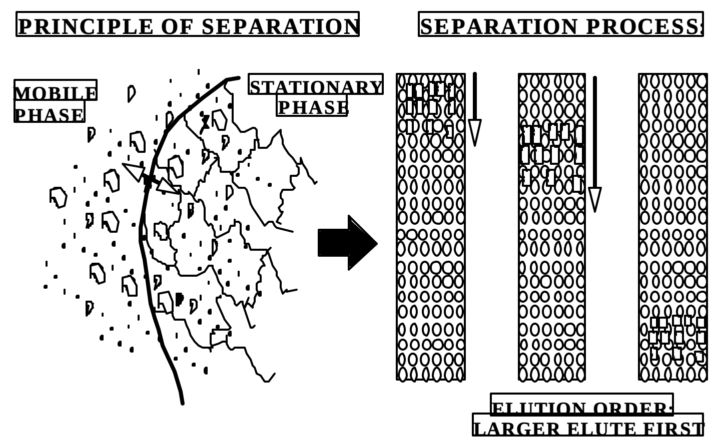


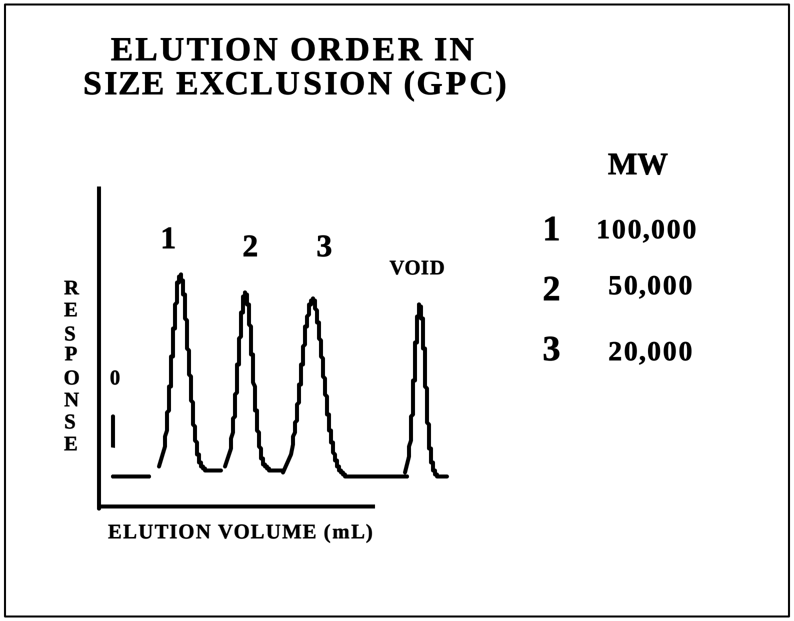
Gel Permeation / Size Exclusion / Gel Filtration - GPC / SEC / GFC

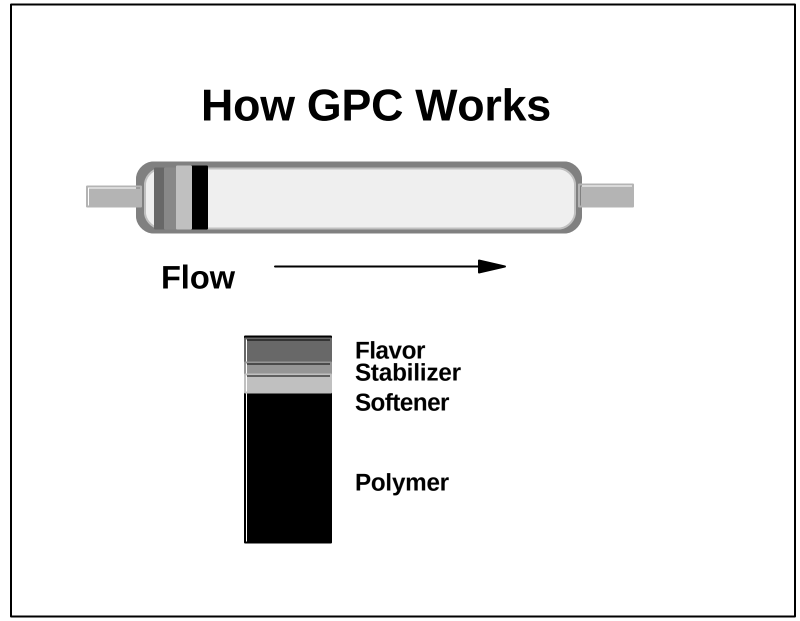
- GPC polymers
- SEC polymers & proteins
- GFC proteins

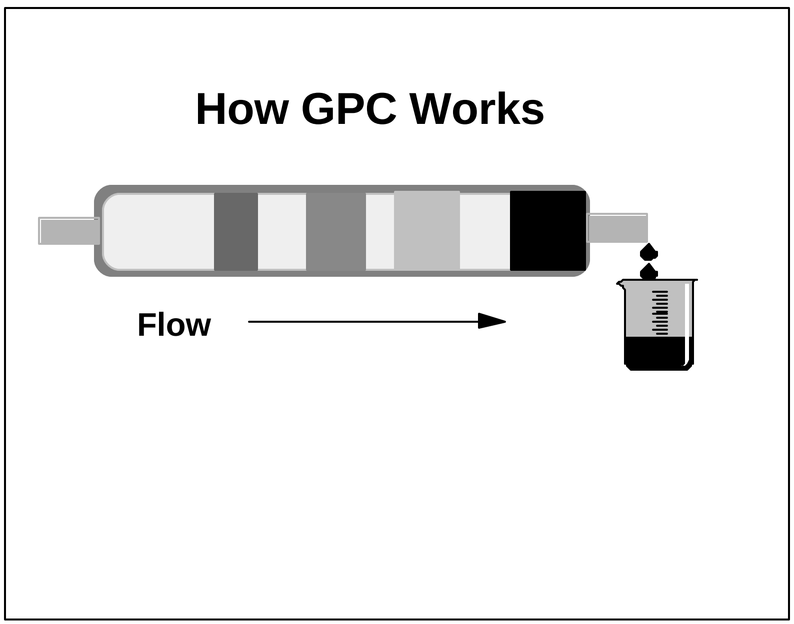
- Separation based on molecular size in solution
- Order of elution - larger < small
- Relatively low resolution method
- Very predictable chromatography
- If it can be dissolved, it can be analyzed

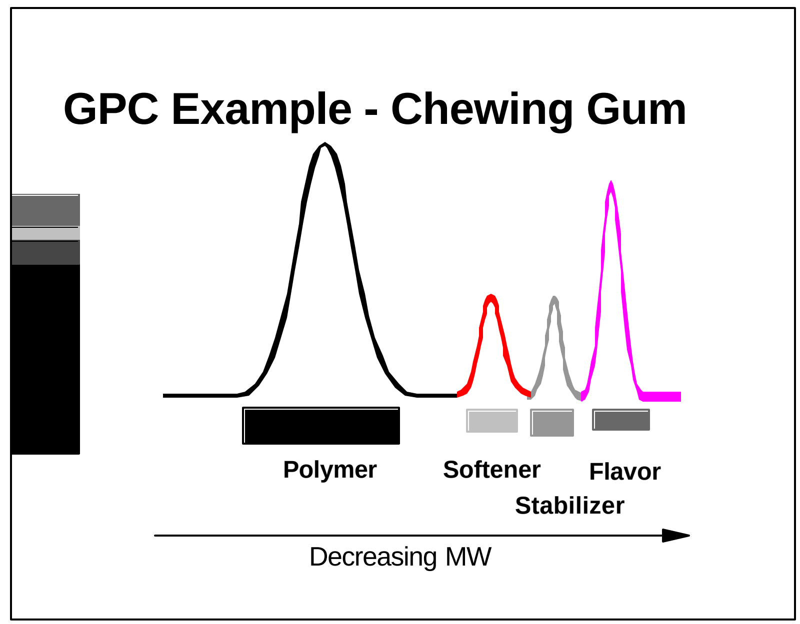
SIZE EXCLUSION CHROMATOGRAPHY




ELUTION ORDER IN
SIZE EXCLUSION (GPC)
RESPONSE
0
1
2
3
VOID
ELUTION VOLUME (mL)
MW
1 100,000
2 50,000
3 20,000


How GPC Works
Flow
Flavor
Stabilizer
Softener
Polymer

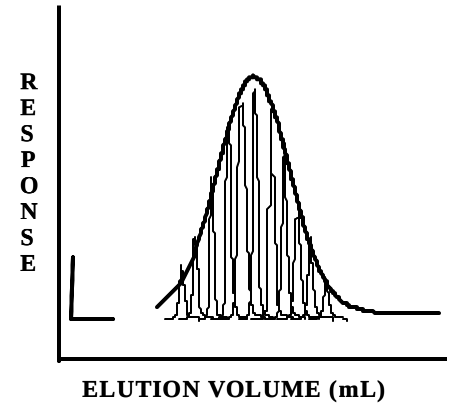

How GPC Works
Flow


GPC Example - Chewing Gum
Polymer
Softener
Flavor
Stabilizer
Decreasing MW

Molecular Weight Distribution

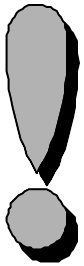
- Polymers have a distribution of various chain lengths, and, therefore, molecular weights.
- Monomers have a single molecular weight, and are monodisperse.
- This distribution of molecular weights results in an "Envelope" of elution from a column set.

MOLECULAR WEIGHT DISTRIBUTION



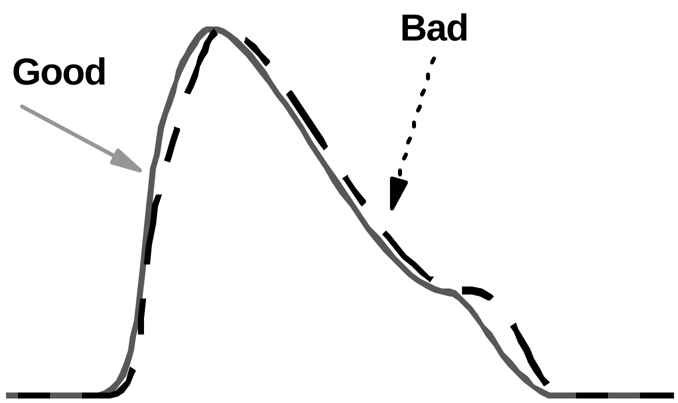
Why GPC?

"Molecular Weight Distribution correlates with virtually all key processing characteristics and performance properties of a material."

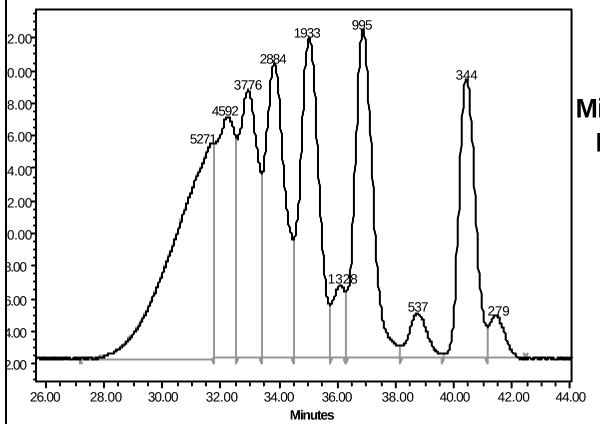


Plastics Technology, May 1986

Comparison of Results

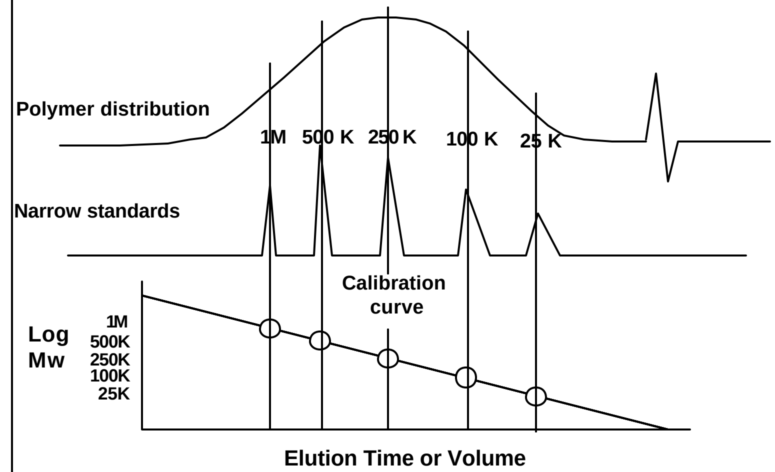


Millennium Integration Narrow Unknowns

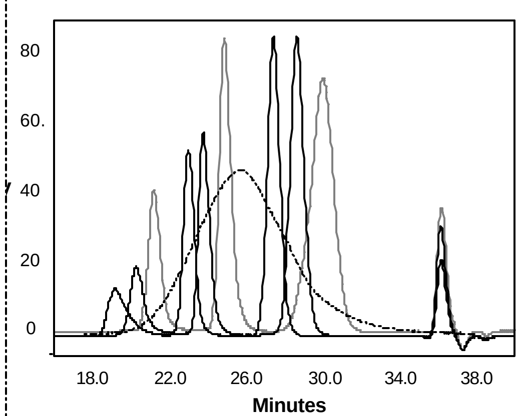


Mid to High MW Epoxy Resin

Gel Filtration/Size Exclusion/Gel Permeation



GPC Narrow Standards
+ Broad Sample

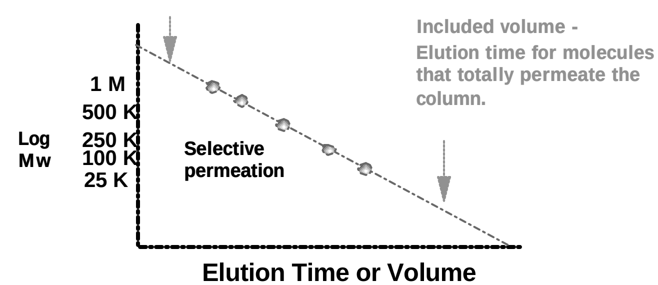


- ►3 Columns 7.8 x 300mm
- ►Flow: 1.00 mL/min
- ►RI Detector

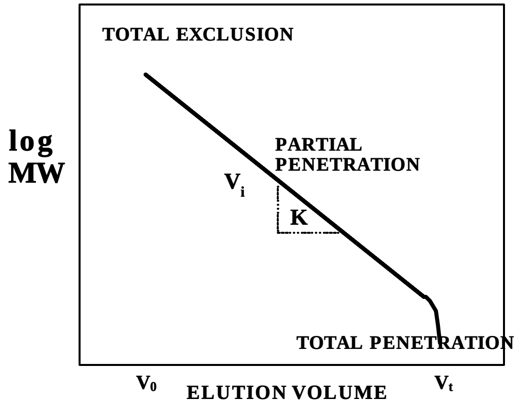
Gel Permeation/Size Exclusion/Gel Filtration

uded volume -
npound moves through the interstitial
me of column only. No penetration into
of the packing pores and no adsorption
he packing surface.

Calibration Curve



THEORETICAL CURVE OF THE STERIC EXCLUSION



$$\frac{V_i - V_0}{V_t - V_0} = K$$

$$0 <= K =< 1$$

Gel Permeation / Size Exclusion / Gel Filtration - GPC / SEC / GFC

- **There should be no interaction between the media surface and the sample.**
- **The same molecule can have different radii in different solvents.**

GPC/SEC Separations

GPC is a SIZE separation technique.

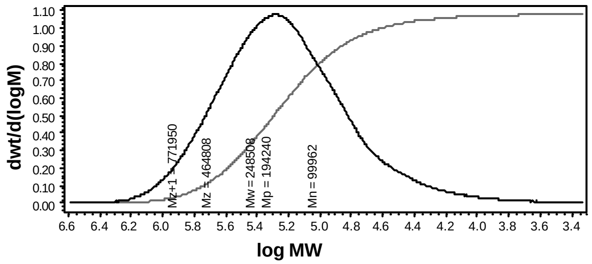
Separation is based on size in solution, not molecular weight.

Polymer size in solution is dependent on solvent and temperature.

Distribution Shapes

- Polymers may elute in many different shapes.
- Typical shapes are: Gaussian, Multi-Modal, Skewed-High, Skewed-Low.
- The various shapes may define important characteristics such as processing parameters and physical properties.

Molecular Weight Distribution



Slice Table - DOW 1683

#	Retention Time (min)	Adjusted RT (min)	Mol Wt (Daltons)	Log Mol Wt	Cumulative % (%)	Area	Outside Vo-Vt
1	19.550	19.550	1690819	6.228097	0.155	498	No
2	20.750	20.750	711461	5.852151	4.745	9695	No
3	21.950	21.950	294563	5.469178	28.585	29920	No
4	23.150	23.150	122389	5.087743	67.276	28261	No
5	24.350	24.350	52049	4.716409	89.878	10265	No

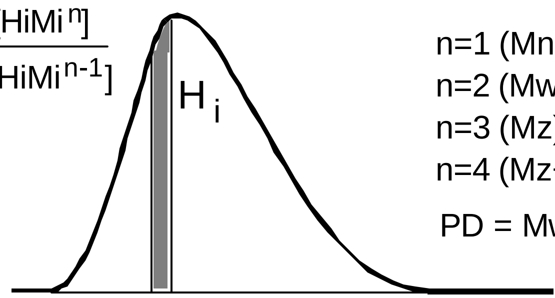
Calculation of MW Averages

- **Slices (heights, Hi) are drawn from the chromatogram baseline to the distribution curve, (usually >100).**
- **Slice heights are multiplied by the corresponding MW's, and summed, (e[HiMi])**
- **Statistical averages are then calculated to obtain each MW moment:**

  e[HiMi^n]/e[HiMi^n-1];
  Where n=1 is Mn, n=2 is Mw, n=3 is Mz.

Calculation of MW Averages

$$M_x = \frac{\Sigma[HiMi^{n}]}{\Sigma[HiMi^{n-1}]}$$



n=1 (Mn)
n=2 (Mw)
n=3 (Mz)
n=4 (Mz+1)

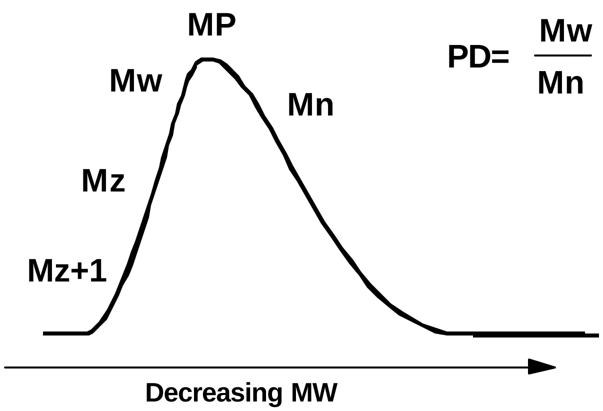
PD = Mw/Mn

Retention Time (or Volume)

Molecular Weight Moments

- 1st Moment = M_n (Number Average)
- 2nd Moment = M_w (Weight Average)
- 3rd Moment = M_z (Z Average)
- 4th Moment = M_{z+1} (Z+1 Average)
- M_w/M_n = Dispersity
- Moments are related to physical properties.

Molecular Weight Distribution



Physical Properties

- M_n is related to brittleness, flow properties, compression set.
- M_w is related to strength properties, (tensile, impact resistance).
- M_z is related to elongation and flexibility.
- M_{z+1} is related to die swell.

Importance of MWD

Property/Processs Parameter	Effect of High MW	Effect of Low MW
Impact Strength	↑	↓
Melt Viscosity	↑	↓
Processing Temp	↑	↓
Flex Life	↓	↑
Brittleness	↑	↓
Drawability	↓	↑
Softening Temp	↑	↓
Stress-crack Resistance	↓	↑
Melt Flow	↓	↑

Polymer Concentrations for GPC

- MW > 1,000,000 ________ 0.007 - 0.02%
- 500K - 1,000,000 ________ 0.02 - 0.07%
- 100K - 500K ________ 0.07 - 0.10%
- 50K - 100K ________ 0.10 - 0.13%
- 10K - 50K ________ 0.13 - 0.16%
- < 10K 0.16 - 0.20%

Sample Preparation

- Solvent must allow polymer chains to open up into the "most relaxed" conformation.
- Allow sufficient time for chains to unfold (>3 hours for some polymers).
- The greater the MW and crystallinity, the longer the time needed.
- High temperature, may be needed for highly crystalline polymers.

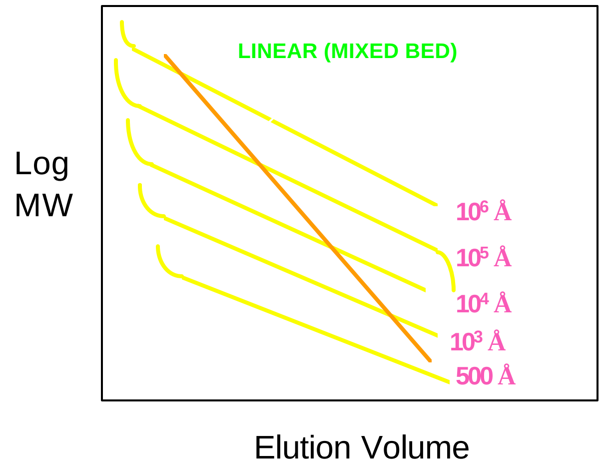
Sample Prep (cont'd)

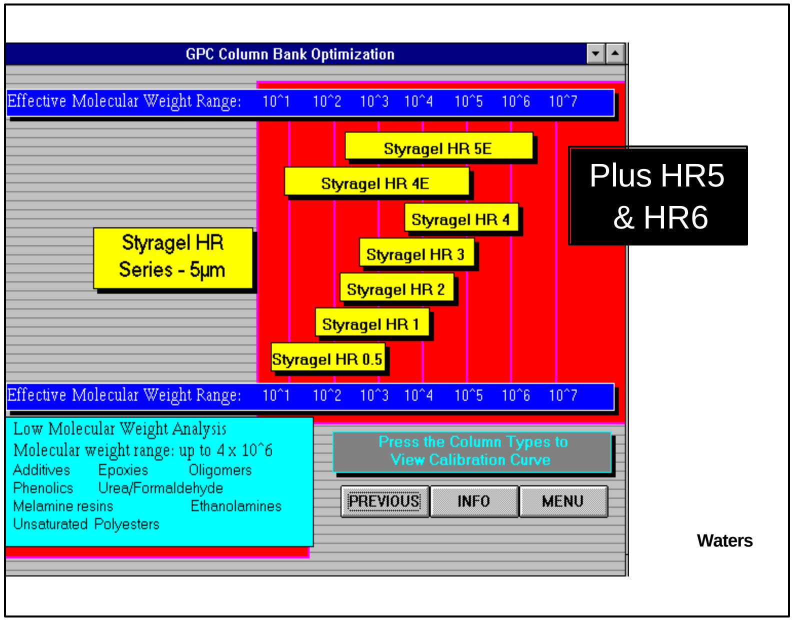
- The polymer solution should be filtered unless there may be a chance of shear.
- To enhance dissolution, some light swirling (no vigorous shaking) may be done.
- Narrow standard solutions need not be filtered, and high molecular weight standards should not be shaken at all.
- An in-line filter may be used, but a pre-column is not recommended.

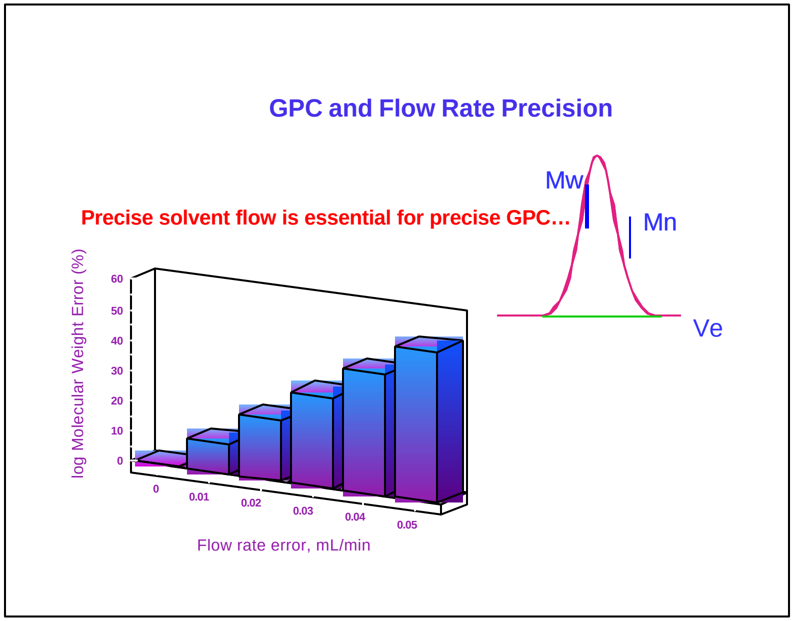
Column Selection

▶ MW 100 - 1,000	50A
▶ MW 250 - 2,500	100A
▶ MW 1,000 - 18K	500A
▶ MW 5,000 - 40K	10^3A
▶ MW 10K - 200K	10^4A
▶ MW 50K - 1M	10^5A
▶ MW 200K - >5M	10^6A
▶ 500K - ~20M	10^7A

ELUTION CURVES OF VARIOUS STATIONARY PHASES




GPC Column Bank Optimization
Effective Molecular Weight Range: 10^1 10^2 10^3 10^4 10^5 10^6 10^7
Styragel HR 5E
Styragel HR 4E
Styragel HR 4
Styragel HR 3
Styragel HR 2
Styragel HR 1
Styragel HR 0.5
Styragel HR Series - 5µm
Plus HR5 & HR6
Effective Molecular Weight Range: 10^1 10^2 10^3 10^4 10^5 10^6 10^7
Low Molecular Weight Analysis
Molecular weight range: up to 4 x 10^6
Additives Epoxies Oligomers
Phenolics Urea/Formaldehyde
Melamine resins Ethanolamines
Unsaturated Polyesters
Press the Column Types to View Calibration Curve
PREVIOUS
INFO
MENU
Waters


GPC and Flow Rate Precision
Precise solvent flow is essential for precise GPC…
Mw
Mn
Ve
log Molecular Weight Error (%)
60
50
40
30
20
10
0
0
0.01
0.02
0.03
0.04
0.05
Flow rate error, mL/min