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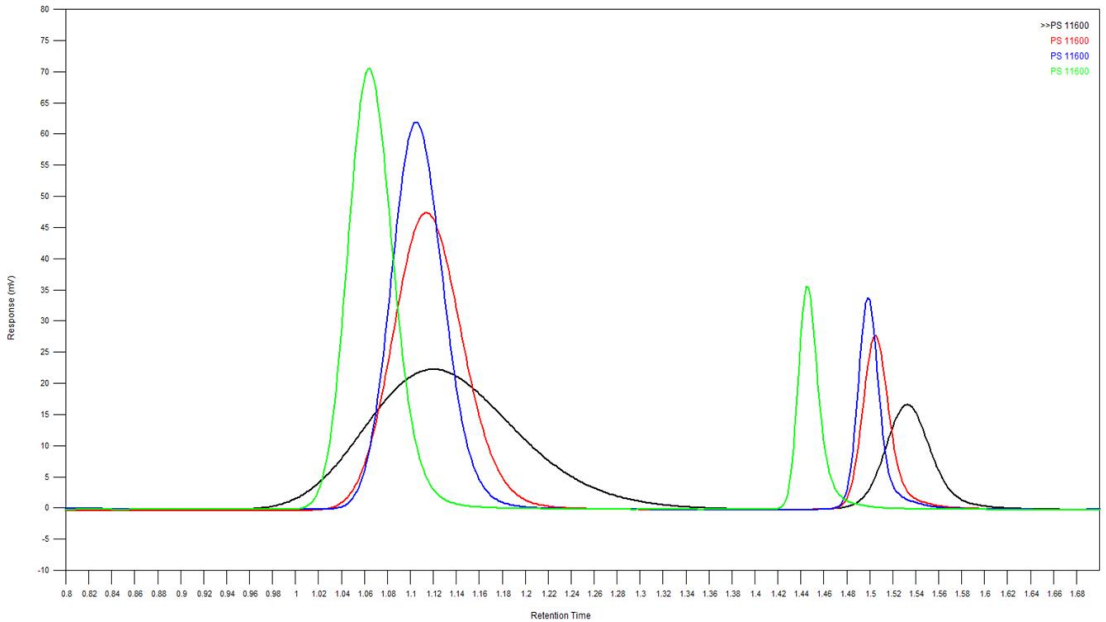
Introduction to GPC

Columns, Distributions, Sample Prep., Calibration, What's New



Polymer Analysis Techniques

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- High Performance Liquid Chromatography (HPLC) (mainly Size Exclusion Chromatography, SEC)
- Mass Spectroscopy (MS)
- Thermal Analysis (TA)
- Rheometry, Nuclear Magnetic Resonance spectroscopy (NMR), Fourier Transform Infrared spectroscopy (FTIR)

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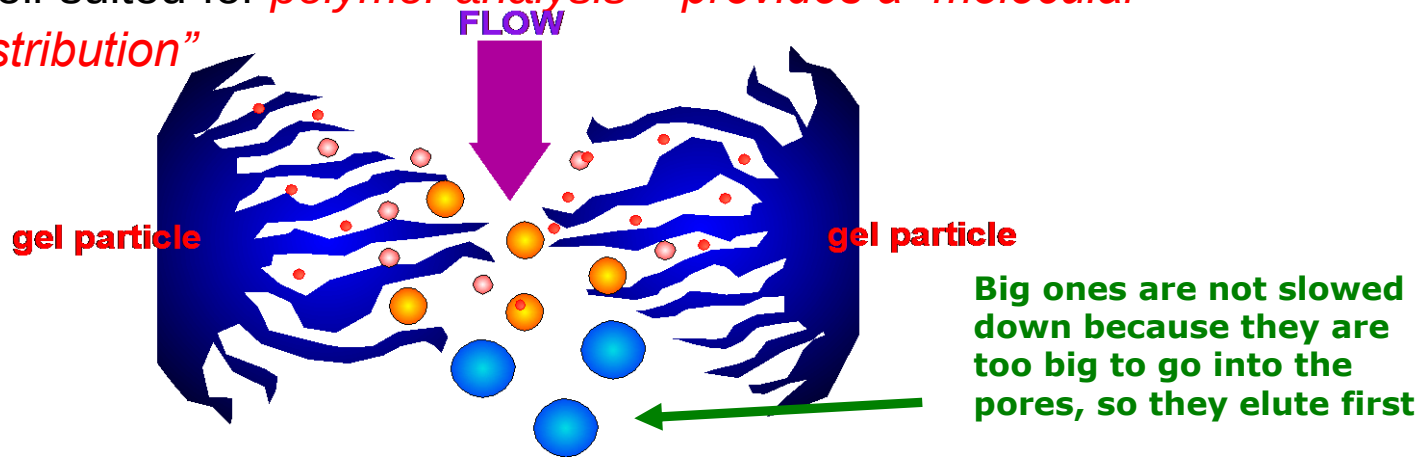
Outline

- What is GPC?
- GAP of Additives
- What's New?

What is GPC?

- Gel Permeation Chromatography (GPC) separates sample molecules based upon their *relative size in solution*
  - Size Exclusion Chromatography (SEC)
  - Gel Filtration Chromatography (GFC)
- GPC is an *isocratic* mode of separation
- GPC is well-suited for *polymer analysis – provides a "molecular weight distribution"*

Particles are Porous, rigid polymeric materials



Big ones are not slowed down because they are too big to go into the pores, so they elute first

What is GPC?

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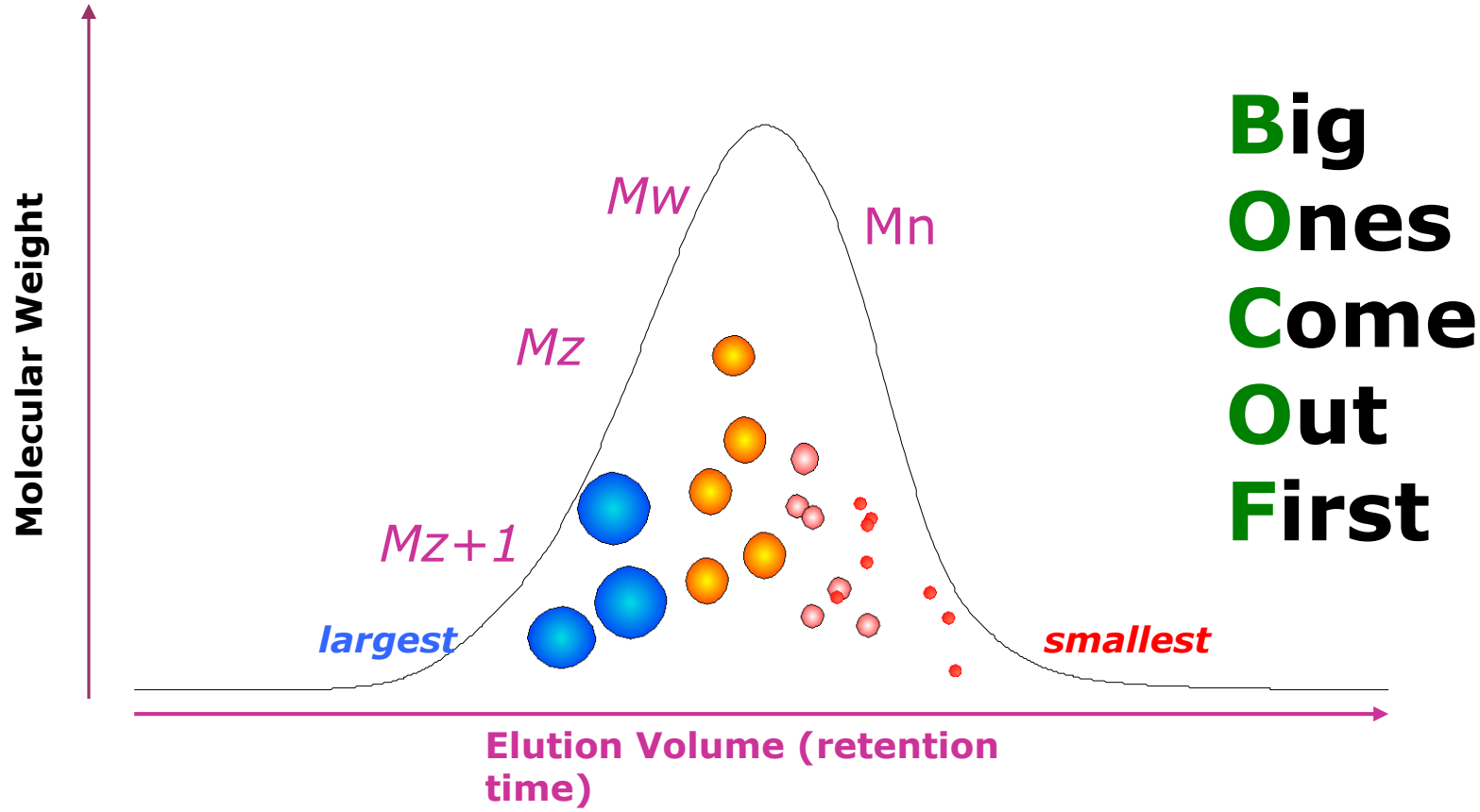
- The elution profile represents the *molecular weight distribution* based upon the relative content of different molecular weights…
- Based on size in solution



Big Ones Come Out First

Some definitions

- Molecular weight averages are used to provide numerical differences between samples
  - Mn: Number average molecular weight
    - At this point in the curve the *number* of molecules in the sample to left is equal to the number of molecules to the right
  - Mw: Weight average molecular weight
    - At this point in the curve the *weight* of the molecules to the left is equal to the weight of the molecules to the right
  - Mz and Mz+1: these values are calculated based on molecular weight and abundance (obtained by ultracentrifugation and GPC software computation)
    - The values are used for “comparison” purposes
      - Known samples to unknown samples
- These averages are statistical moments calculated from the molecular weight distribution curve

Molecular Weight Averages

GPC Delivers all MW information with one experiment

- GPC calculates the MW distribution of the polymer; this distribution can be measured for:
  - Mn can affect a polymer's brittleness, flow and compression properties.
  - Mw is related to strength properties, and impact resistance
  - Mz is related to elongation and flexibility, (Gumby - rubber)
  - Mz+1 is related to die swell, (extrusion parameter)

Molecular Weight/ Physical Property Correlations

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Properties of Polymers

GPC Process – Separates by Size in Solution

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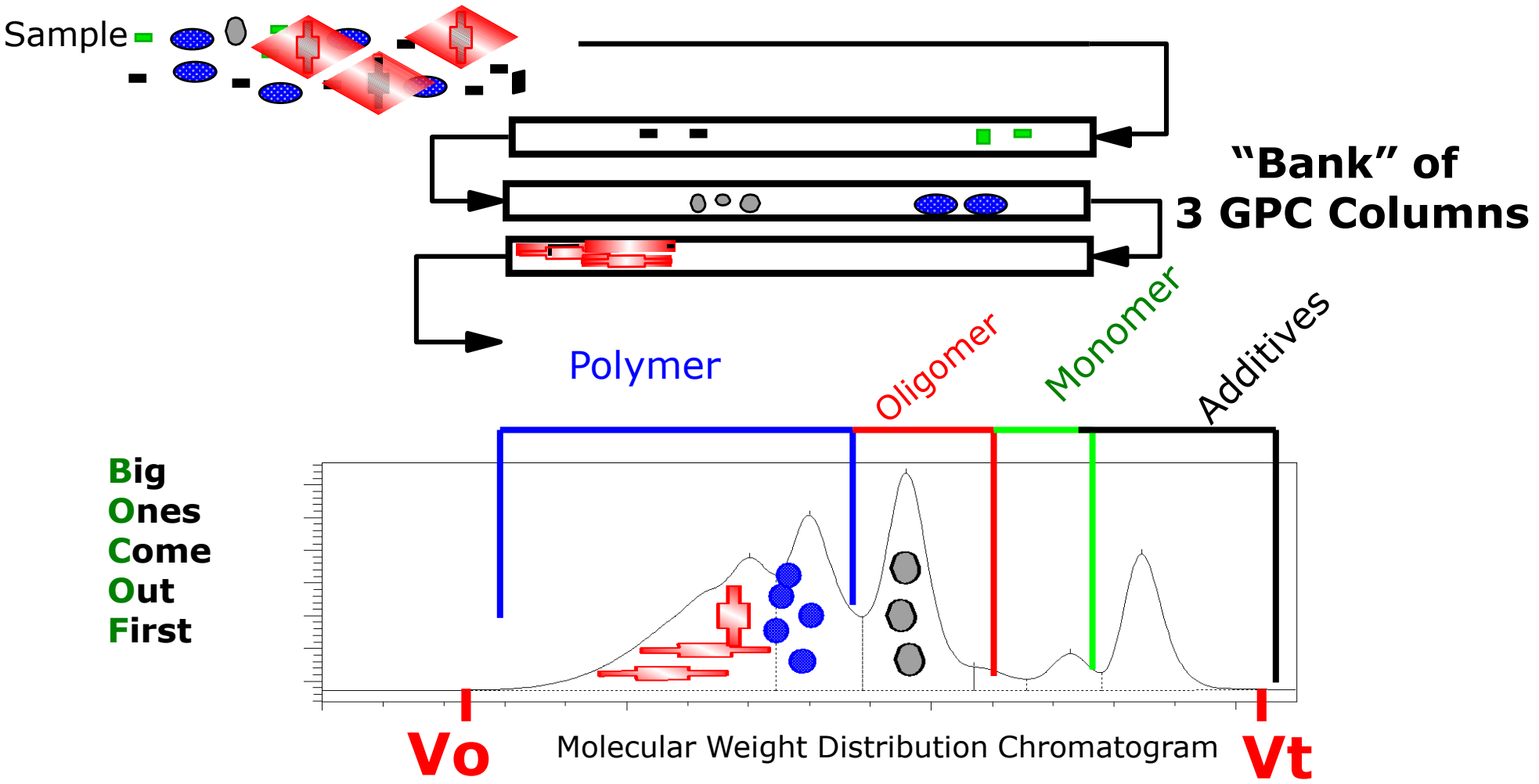
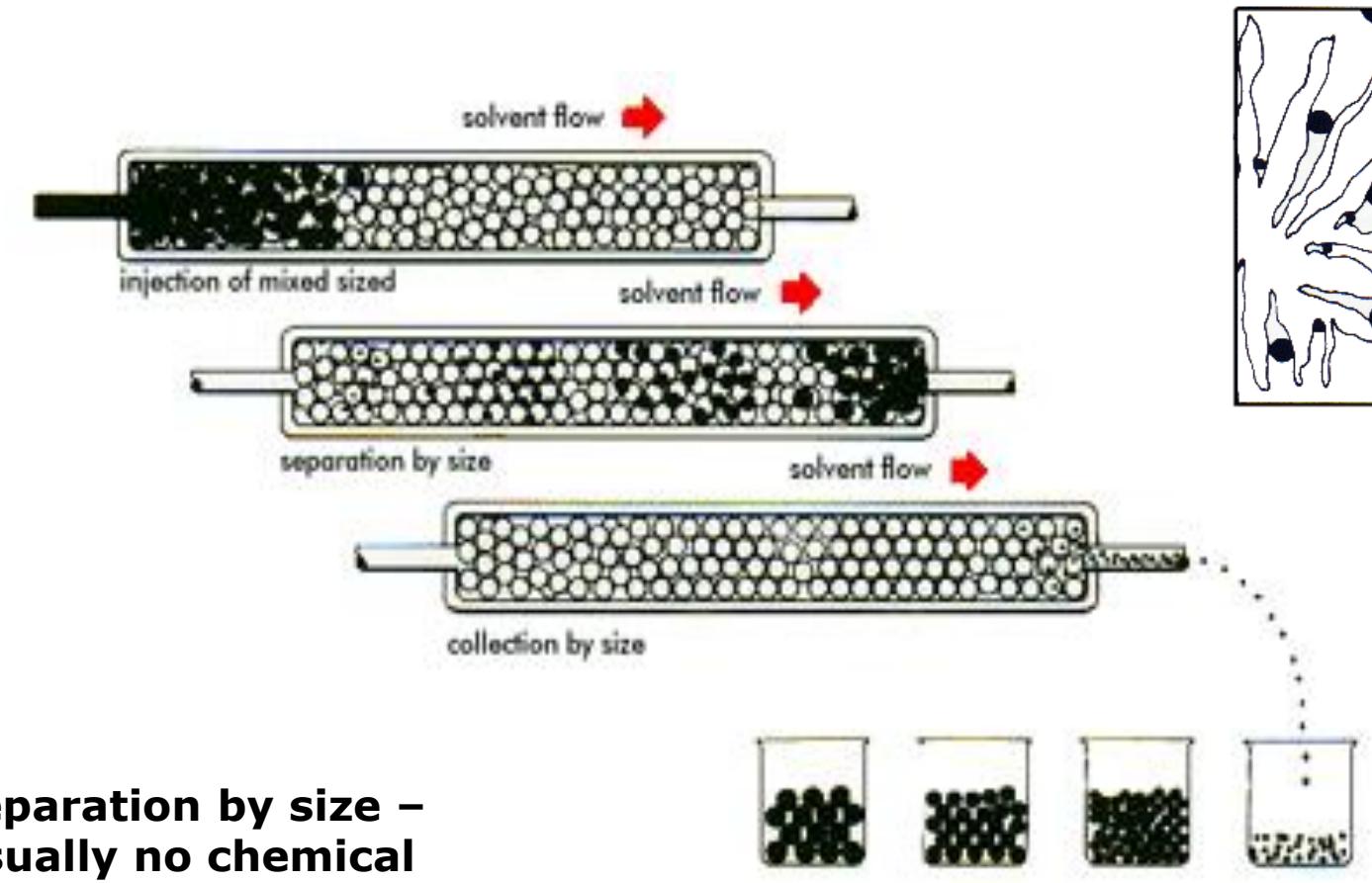
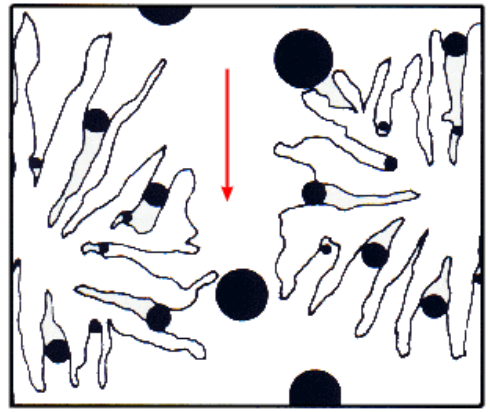


What is happening inside a column?





Separation by size –
Usually no chemical
Retention mechanism

BOCOF

Basic Column Information

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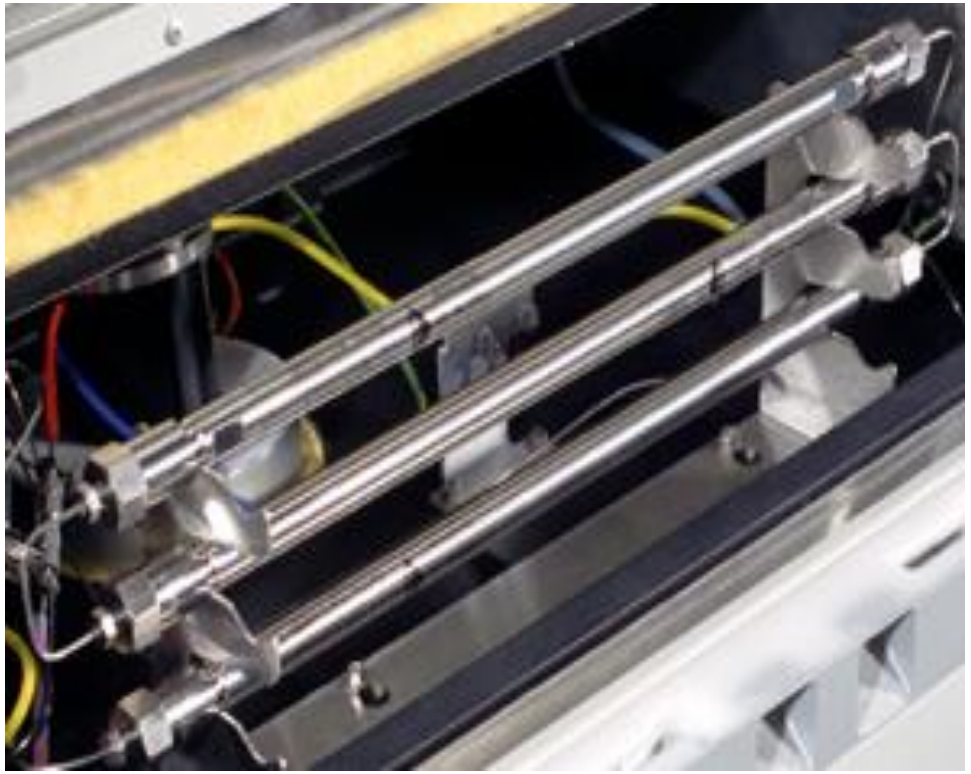
- Columns are put together in series to form a bank (>2)
- Always put the highest pore size column first (from the injector), and smallest pore size column last
  - This reduces back pressure on the most fragile column (LMW column)
- Ramp the flow up slowly – 0.1ml/minute – 1.0 ml/minute in small increments*
- Change over solvent at a 0.1ml/minute flow rate over night



Some applications at High Temperature >150˚ C

GPC Column Types

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- Organic vs. Aqueous GPC columns
- Different Pore Sizes
- Analytical vs. Preparative GPC columns
- Conventional vs. Solvent efficient, and High speed GPC columns.

Care and Use of GPC Columns

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- Basic GPC – typically a bank of 3 columns of different pore sizes to cover a broad MW range (as needed)
- Never use methanol or acetonitrile with Organic GPC columns because certain polar solvents will shrink the column, causing it to void
  - Note: Make sure to flush the complete system with solvent to be used before connecting the columns to the system
- Life time of the columns can be as long as ~ 1 year or more
- Store the columns in the solvent used with the column bank kept together
- Make sure that the end fittings on the column are tight to keep the column packing from drying out
- Be careful not to drop the columns, because they are fragile
- Filter sample solutions
- Prevent air bubbles from getting into columns

GPC Rules

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- Polymer is dissolved in a solvent at a low concentration (<0.10% w/v)
- Polymer solution passes through crosslinked, organic gel columns packed with controlled pore size particles.
- Larger molecules do not fit into pores (they are excluded) and elute first
- Vo : Exclusion volume
- Vt : Total volume or Permeation volume
- Exclusion principle assumes no adsorption of polymer molecules on packing material
- Every polymer will be eluted between Vo and Vt

Detectors in Polymer Chromatography

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- Concentration
  - Response ~ concentration, (C)
  - Refractometer; $\Delta N = (dn/dc)\ C$
- Structure-selective
  - UV/Vis Detector (Also can use as concentration detector if sample has UV response), Lambert-Beer Law
  - IR
- Molecular weight sensitive
  - Response ~ C x f(M)
  - Light scattering: f(M) = M; M(C)
  - Viscometer: f(M) = $[\eta] = kM\alpha$; $[\eta]C$
    - Where k, alpha are the Mark-Houwink constants
  - Mass Spec.: f(M) = 1/M; C/M

Refractive Index (RI) Definition

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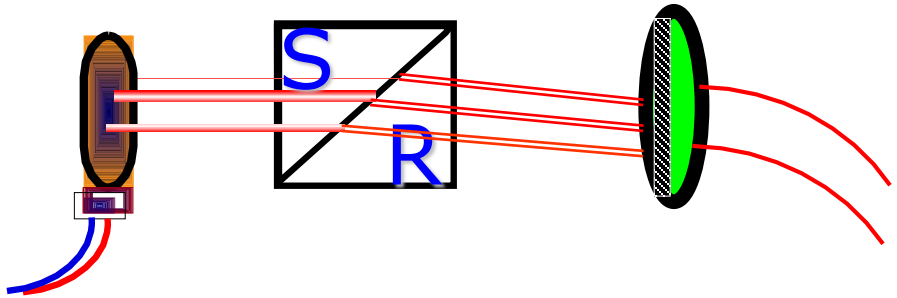
- RI's were among the first detectors used in LC/GPC, (late 1960's)
- Typically referred to as a "Universal Detector"
- Detects all dissolved solutes – "non-specific"
- Refractive index of any optical medium is defined as the ratio of the speed of light in a vacuum to the speed of light in the medium
- Detection based on the refractive index of a given analyte
- Measures the difference in RI from the eluent to the dissolved sample, (differential type)
  - The greater the dRI, the stronger the signal
- Sensitivity increase as RI difference increases



UV/Vis Detection

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- High Sensitivity
- High Selectivity
- Gain information on chemical composition
- Can be used in gradient mode
- Excellent for most polymer additives
- Linear response over a wide absorption range:
  - $A = \varepsilon \times l \times C$ (Beer/Lambert)
- Sometimes UV/Vis detection is used for
  - Higher detection sensitivity.
  - Copolymer analysis (usually coupled with RI detector)
  - Under gradient elution condition.

Polystyrene Standards
UV Detection at 260nm

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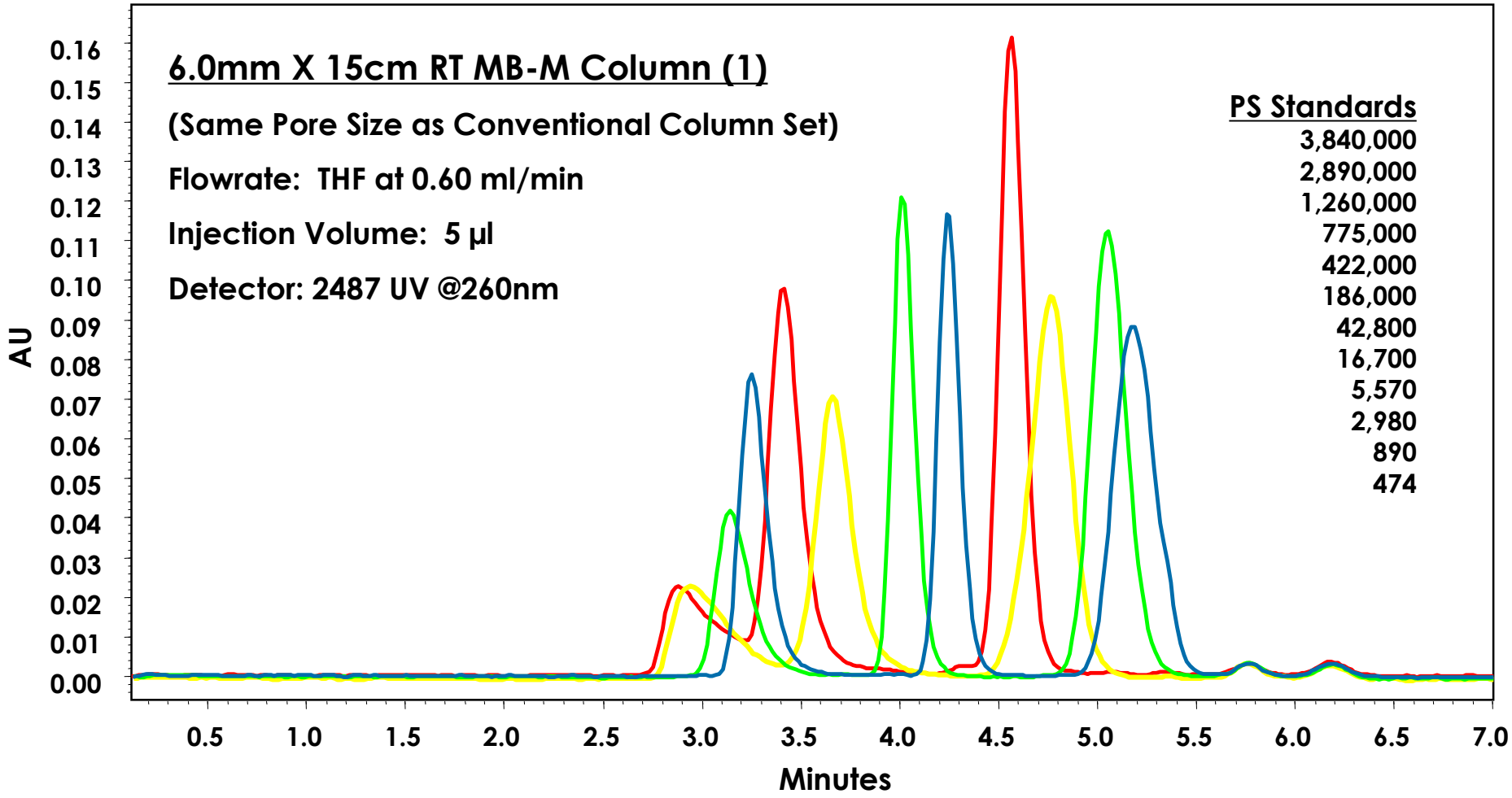

Evaporative Light Scattering Detector

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- Evaporative Light Scattering Detection for polymer characterization
  - ELSD is a concentration detector.
  - ELSD is not affected by solvent changes
  - Most appropriate detector for Gradient Analysis of Polymers (GAP) or Gradient Polymer Elution Chromatography (GPEC)
  - Good alternative to dRI for compounds having a low dn/dc
- Evaporative Light Scattering Detection for additives
  - ELSD is a universal detector
  - Compounds without UV-chromophore groups will be detected

Evaporative Light Scattering Detector

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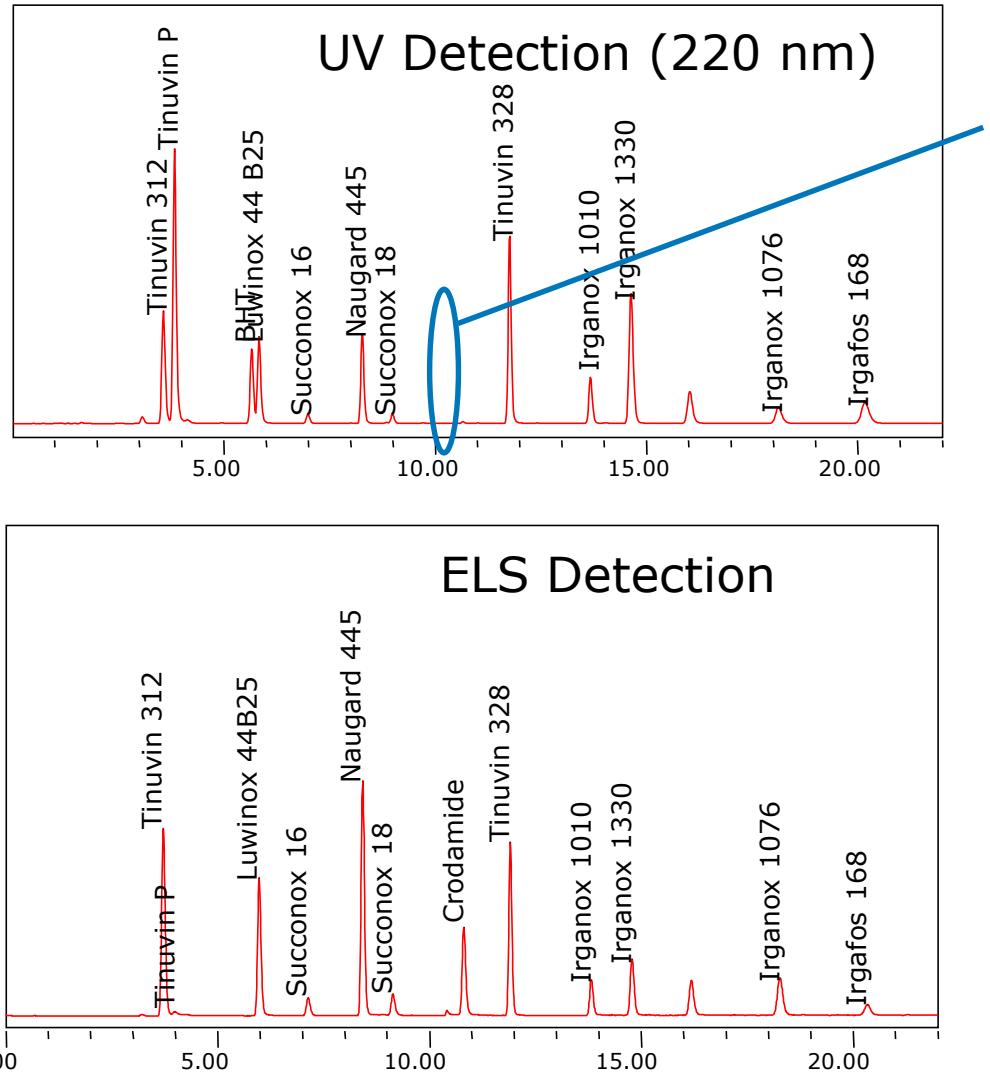
- Polymers are combined with low molecular compounds (0.1-3%)
- Additives have several key functions :
  - Protection : light stabilizers, antioxidants, anti-UV
  - Safety : flame retardants
  - Processing : plasticizers, slip agents
- Full characterization of synthetic polymers involves detection of additives
- Most of slip agents do not absorb UV light. ELS Detector is a good alternative to UV detection

Additives Mixture
Comparison of Detection Modes



Crodamide (oleamide) is not detected in UV mode

GPC Calibration - Narrow Standards

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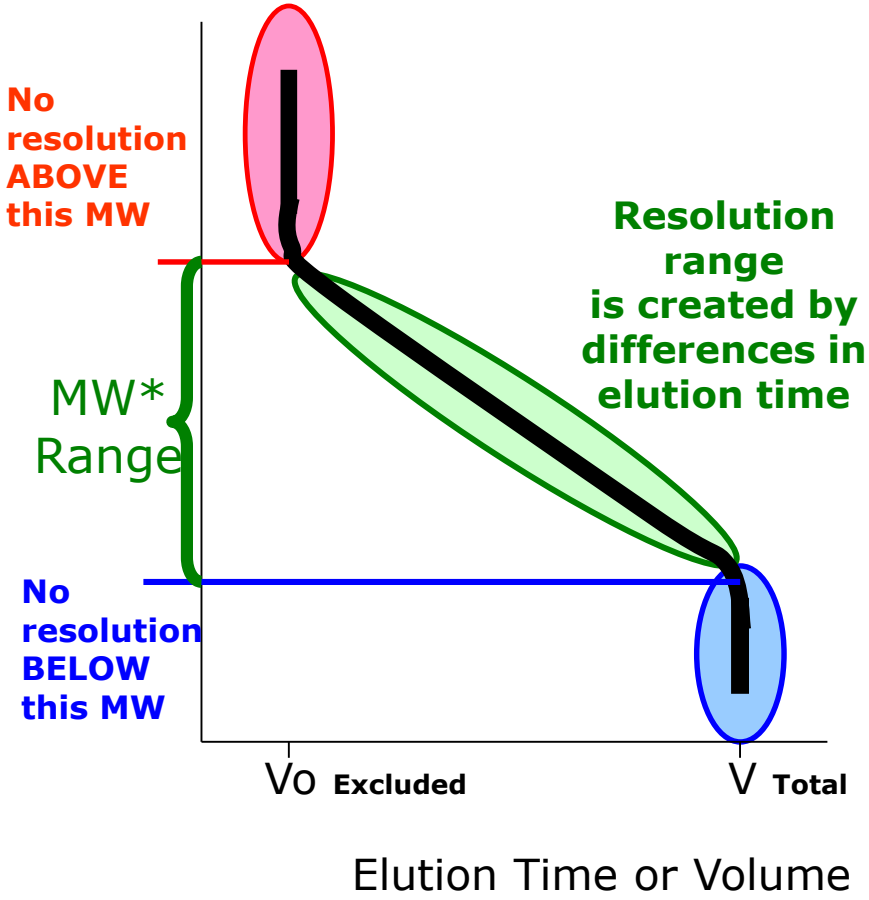
A calibration curve is built with low dispersity (narrow) standards with known molecular weight; (ideal if same structure as unknown polymer)(PS, PMMA...).

This calibration curve may be used to quantitate a polymer of different nature (PC, PMMA...). Then results are expressed in PS or PMMA equivalents, (or relative to PS or PMMA – incorrect for the polymer sample of interest).

The chromatographic process is based on hydrodynamic volume (H)
(size in solution), and not molecular weight.

Two different polymers with the same MW will elute at different retention volumes.



*MW is Log scale

Creating Column "Banks"
Same "Pore Size" Columns

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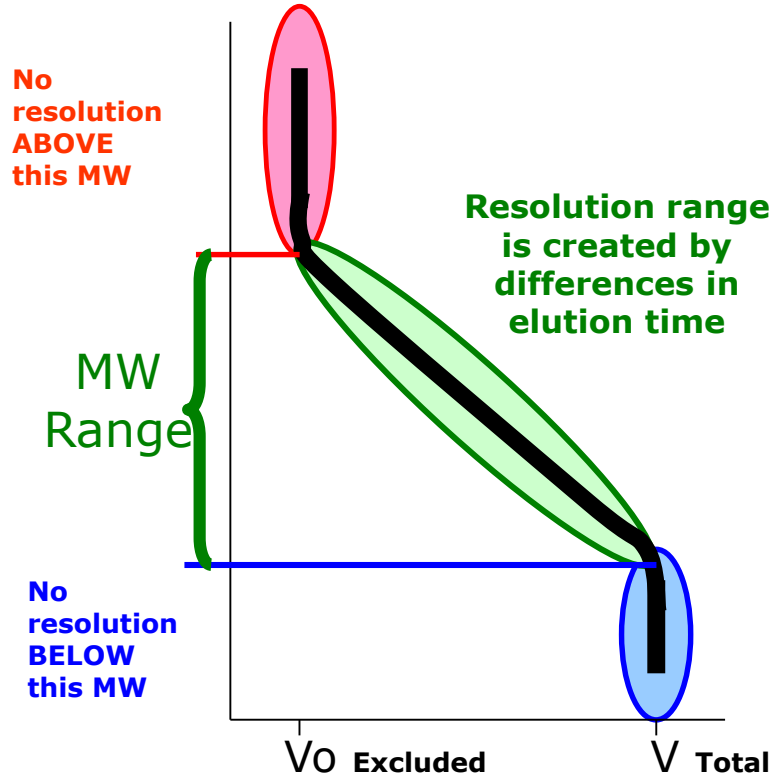

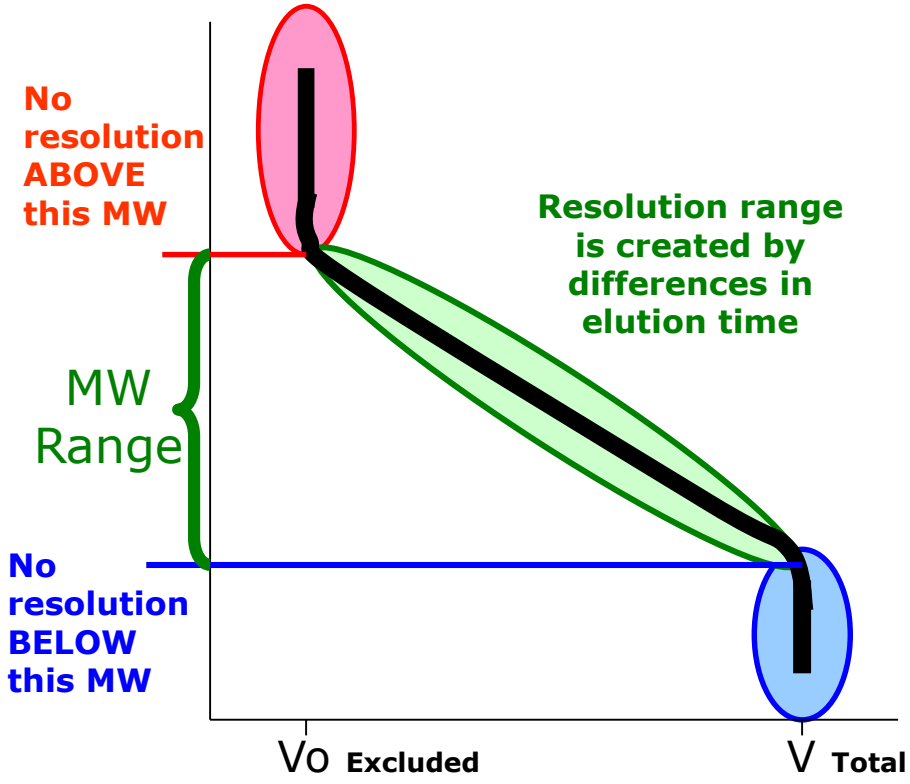

2 Columns of the SAME Type
- SAME MW Range
- More Resolution

Creating Column "Banks"
Different "Pore Size" Columns

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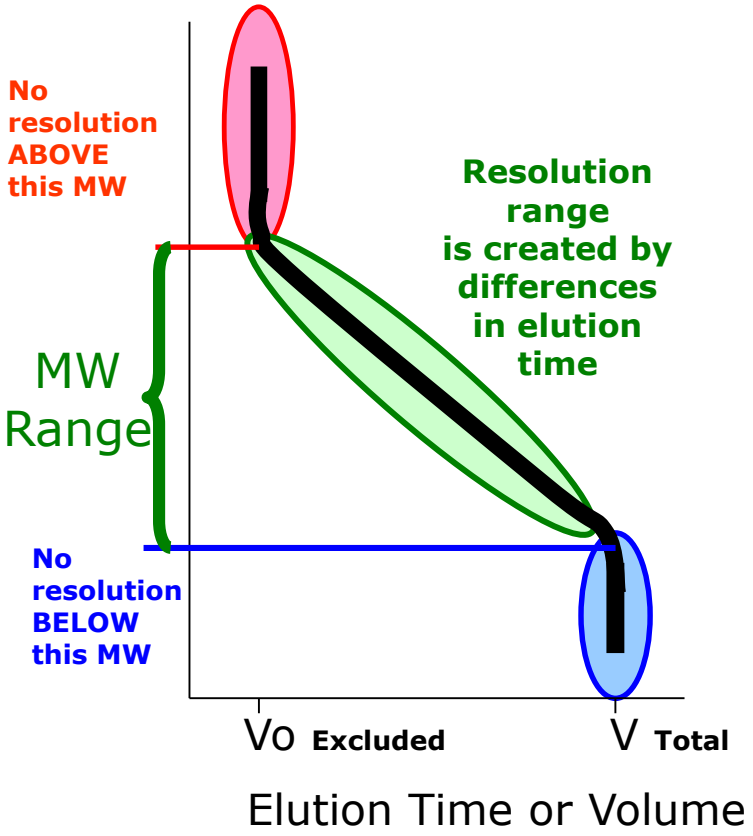

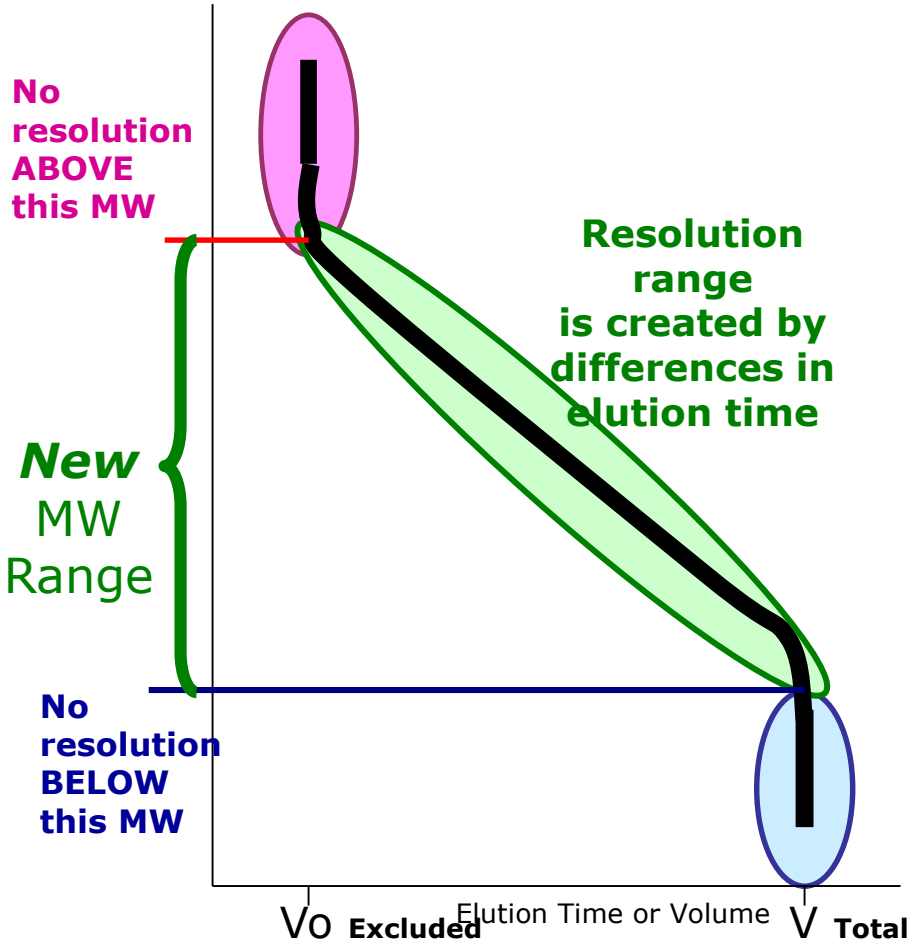

2 Columns of the Different Type
- EXPANDED MW Range
- More Resolution

Actual Calibration Curves for the Different Pore Size HT Columns

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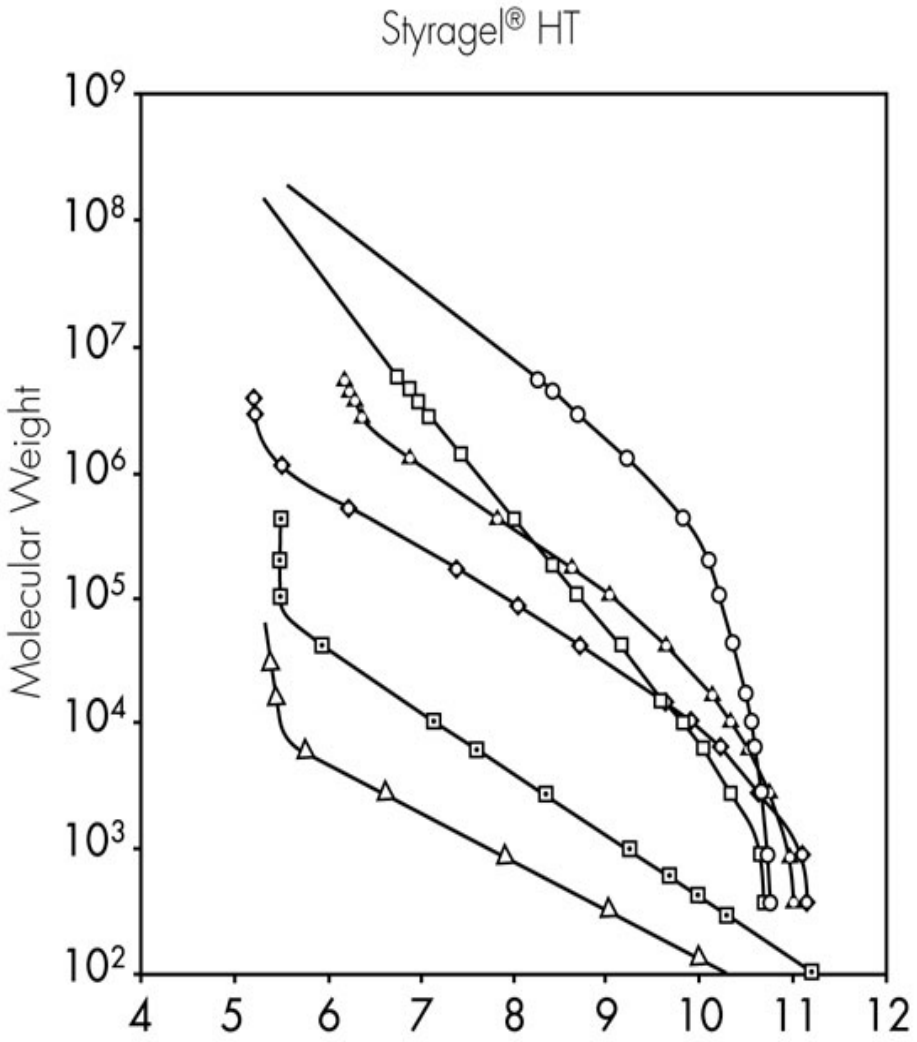
High Temperature



Conditions:
Sample: Polystyrene
Mobile Phase: THF
Flow Rate: 1 mL/min

Elution Volume (mL)

- Styragel® HT 2
- Styragel® HT 3
- Styragel® HT 4
- Styragel® HT 5
- Styragel® HT 6
- Styragel® HT 6E

HT 2 for Low MW
HT 6 for High MW
HT 6E for Blended

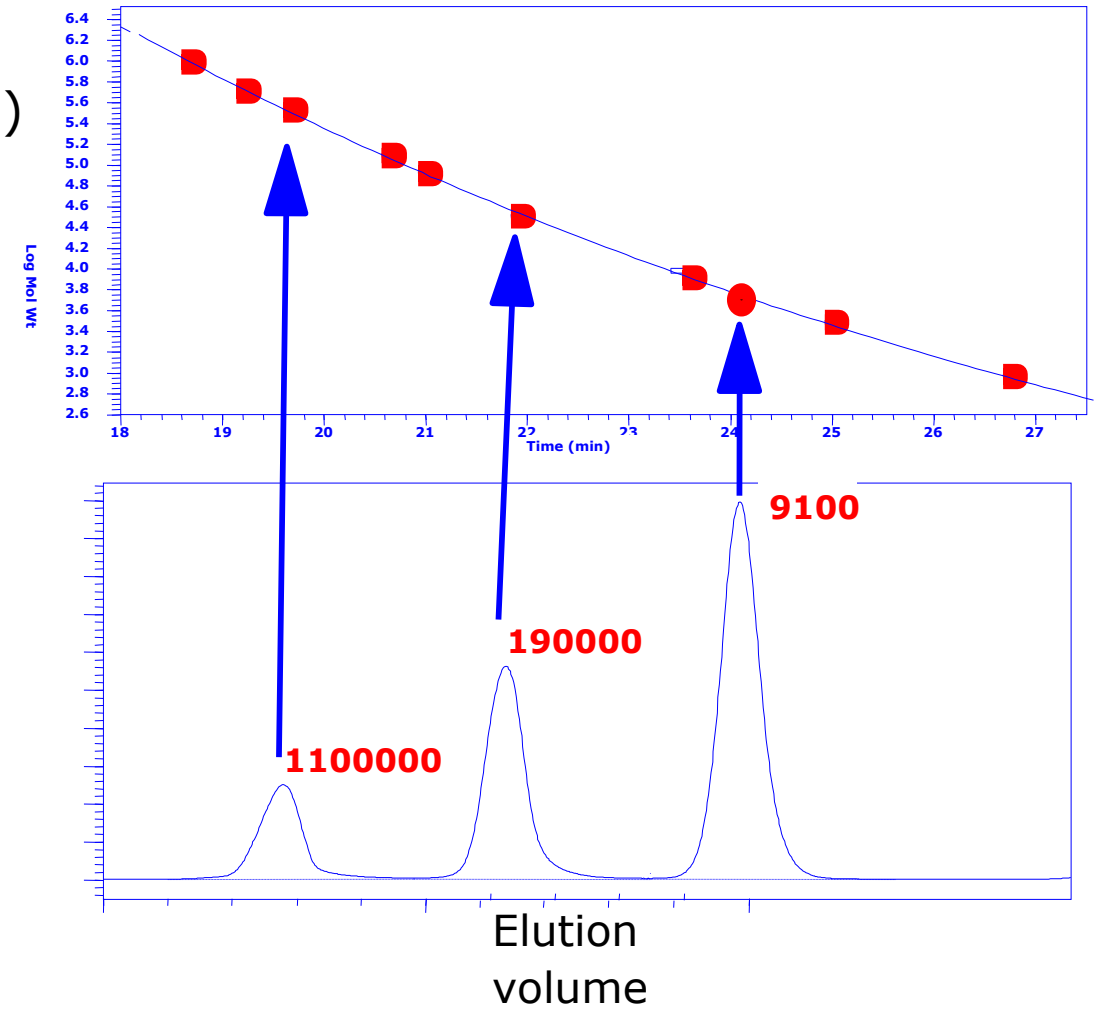
GPC Calibration 1 – Narrow Standards

To build a calibration curve:

- Narrow dispersity standards (PD<1.1)
- Elution volume at peak height
- Curve : Log(M) = f(Ve)

Calibration:

1. Usually >10 standards used bracketing MW range
2. Standards may be injected as a mixture
3. Mixtures should be 1 order of magnitude different (1000, 10000,100000)



GPC Calibration – Narrow Standards

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Organic Polymers	Aqueous Polymers
Polystyrene	Poly(ethylene oxides)
Polybutadienes	Poly(ethylene glycols)
Poly(methylmethacrylates)	Pullulans
Polyisoprenes	

Narrow Standards - Preparation Considerations

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- Narrow standards may be mixed together to develop a relative calibration curve
  - No more than 3 in one "cocktail" – be careful of concentrations
  - MW's should be one decade apart
- Narrow standards should only be swirled gently
- No need to filter narrow standards
- Add antioxidant if high temperature application

Sample Preparation Considerations

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- Sample may be mixed to facilitate dissolution
  - Be careful of shear for high MW (>1M) samples
- In some cases, sample solution should be filtered
  - Presence of microgels, fillers, any other insolubles
- Allow enough time for complete dissolution
- For certain crystalline polymers, high temperature may be needed
  - Example: Isotactic polypropylene requires 2 hours at 170C in an external oven
  - The PP may then be run at 145C

Sample Concentration Guide

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- The more dilute the polymer solution, the better
  - This will prevent viscosity effects and non-reproducible retention
  - A dilute solution will allow the polymer to open up into its most relaxed conformation
    - No chain entanglement
    - No microgel formation
- Injection volume no more than 100 µL per column
- For very high MW polymers, flow rate may have to be lowered
  - HMW columns may be needed as well to prevent shear

Sample Concentration Guide

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MW < 1,000	0.20 – 0.30%
MW 1,000 – 10,000	0.15 – 0.20%
MW 10,000 – 100,000	0.10 – 0.15%
MW 100,000 – 500,000	0.05 – 0.10%
MW 500,000 – 1M	0.01 – 0.05%
MW >1M	0.005 – 0.01%

Above concentrations assume
no more than
100 µL injection per column

GPC Column Operation Techniques

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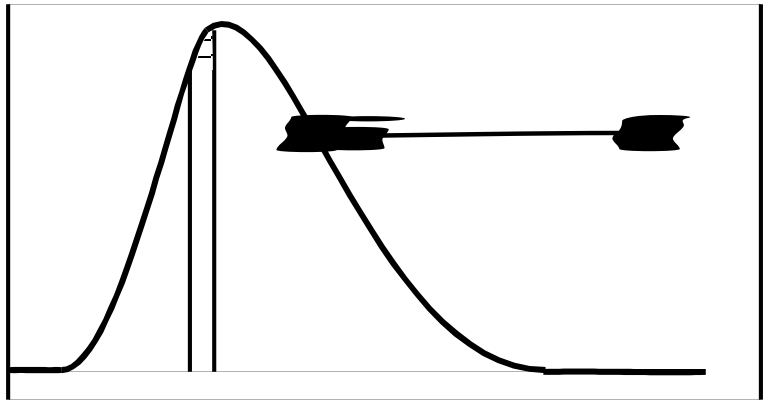
- Switch solvents by flushing to the column at 0.1ml/min overnight in the new solvent
- Increase flow rates at 0.1 ml/minute/minute to the columns specified flow rates
- Recommended to keep the flow through the columns at low flow, 50 ~ 100 μl/minute when idling
- For TCB at 140 - 150 C - purge the toluene out of the columns at 0.1 mL/min. overnight at ~80C and then ramp up to temperature over 300 min after 3 column volumes of TCB have passed through
- Detection
  - RI
  - Viscometry
  - UV

Polymer Distributions

- A polymer is a mixture of different size chain lengths of the same monomer. To measure this distribution of sizes we use molecular weight averages.
- Slices are made to the chromatogram, where the height of each slice (H_i), represents the population of molecules at that chain length or MW.



Polymer Distributions

Mv : Viscosity average molecular weight

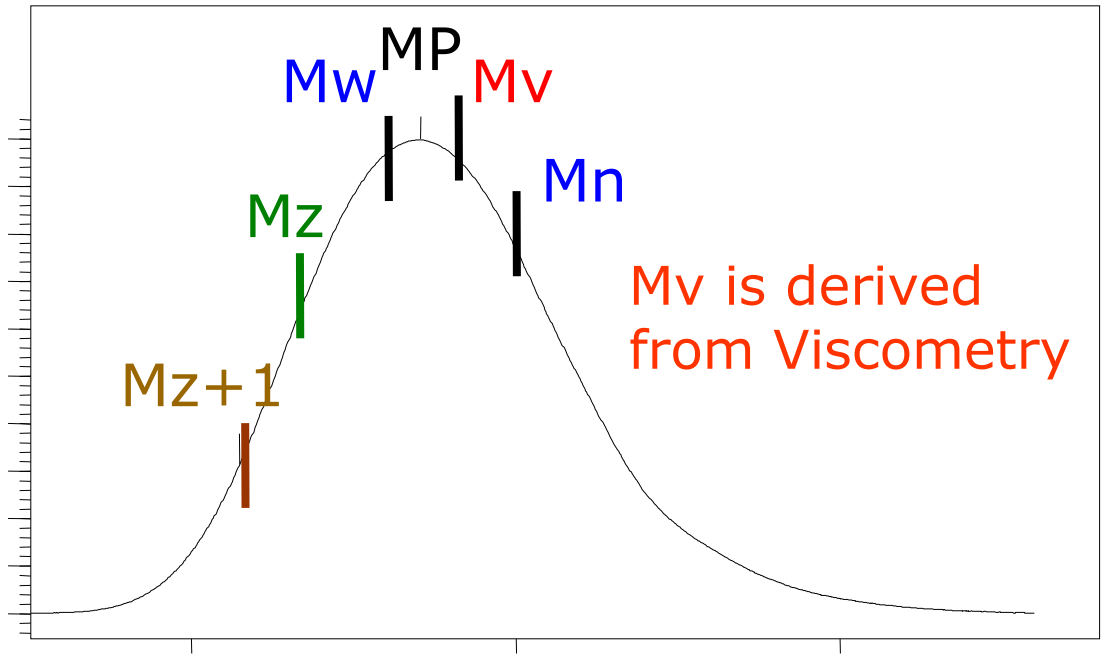
$[n] = K^*M_v^{\alpha}$ $0.5 < \alpha < 1$

where [n] = intrinsic viscosity

K & α: Mark Houwink factors

(Empirical, specific to each polymer)

Mn<Mv<Mw



GPC and Flow Rate Precision

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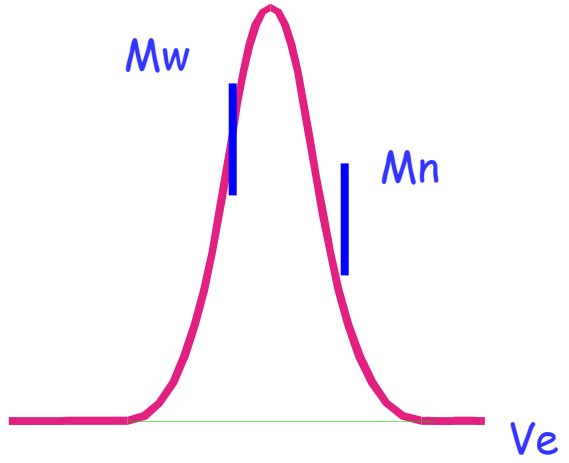
LC Peak Identification (Narrow Standard)

- Based on retention time

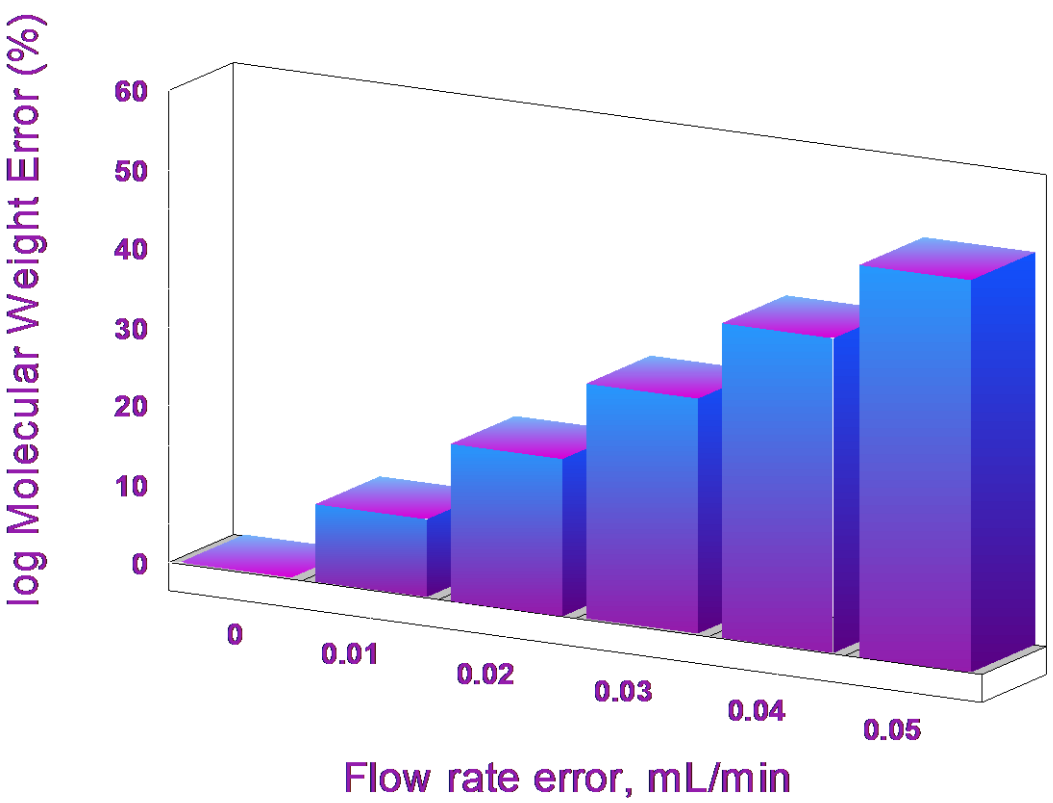
Molecular Weight Determination

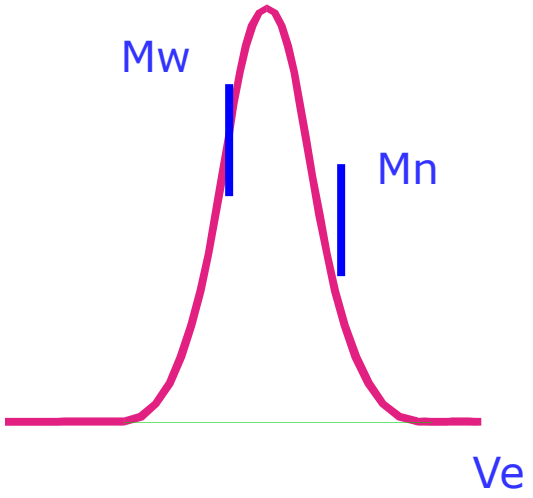
- Gel permeation chromatography (GPC)
- Based on volume of solvent flowing through the column
- Essential for the flow rate to be absolutely constant
- To calibrate, plot Log MW of standards vs volume (time)
- **Any flow variability will result in large MW errors**



GPC and Flow Rate Precision

Precise solvent flow is essential for precise GPC…





Practical use – Fingerprinting the Polymer

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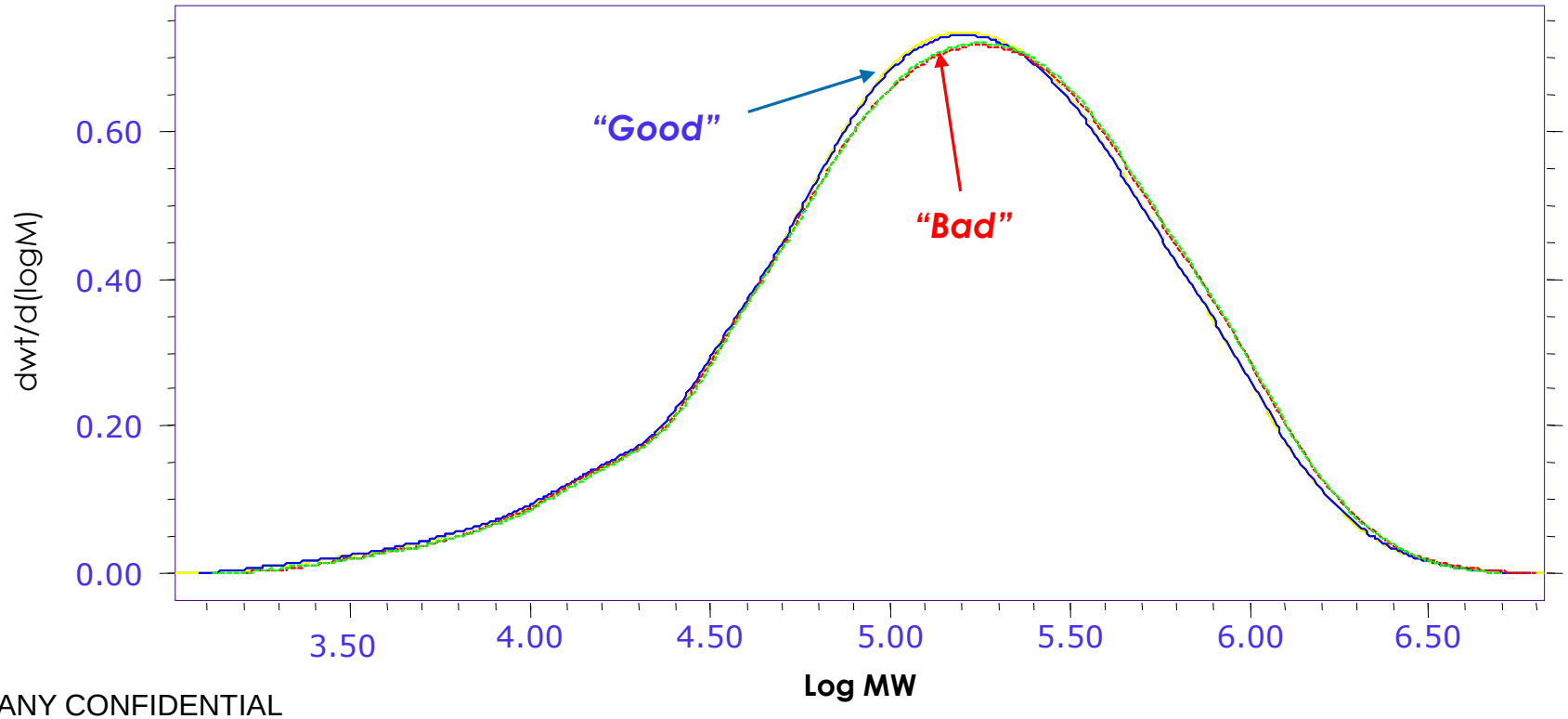
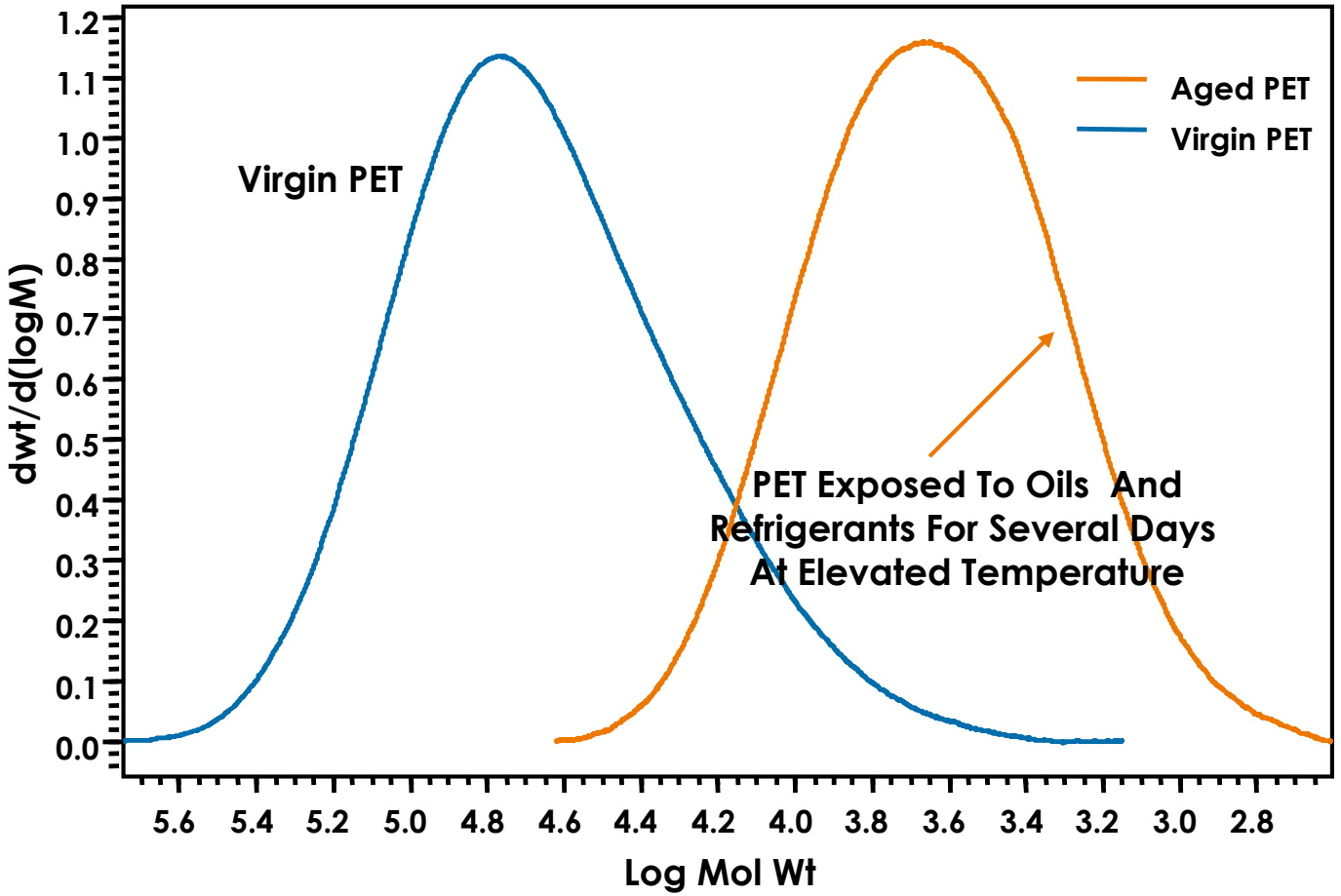
- **Comparisons of Molecular Weight Distributions of different samples can highlight even small *MW shift* information (good vs. bad PP's below)**

- **Determine "good from bad" - e.g. QC of resin batches… these are typical formulators – use Mw, Mn, Mz and polydispersity**



Degradation of Polyethylene Terephthalate – HFIP



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Outline

- What is GPC?
- GAP of Additives
- What's New?

Gradient Analysis of Polymers (GAP)

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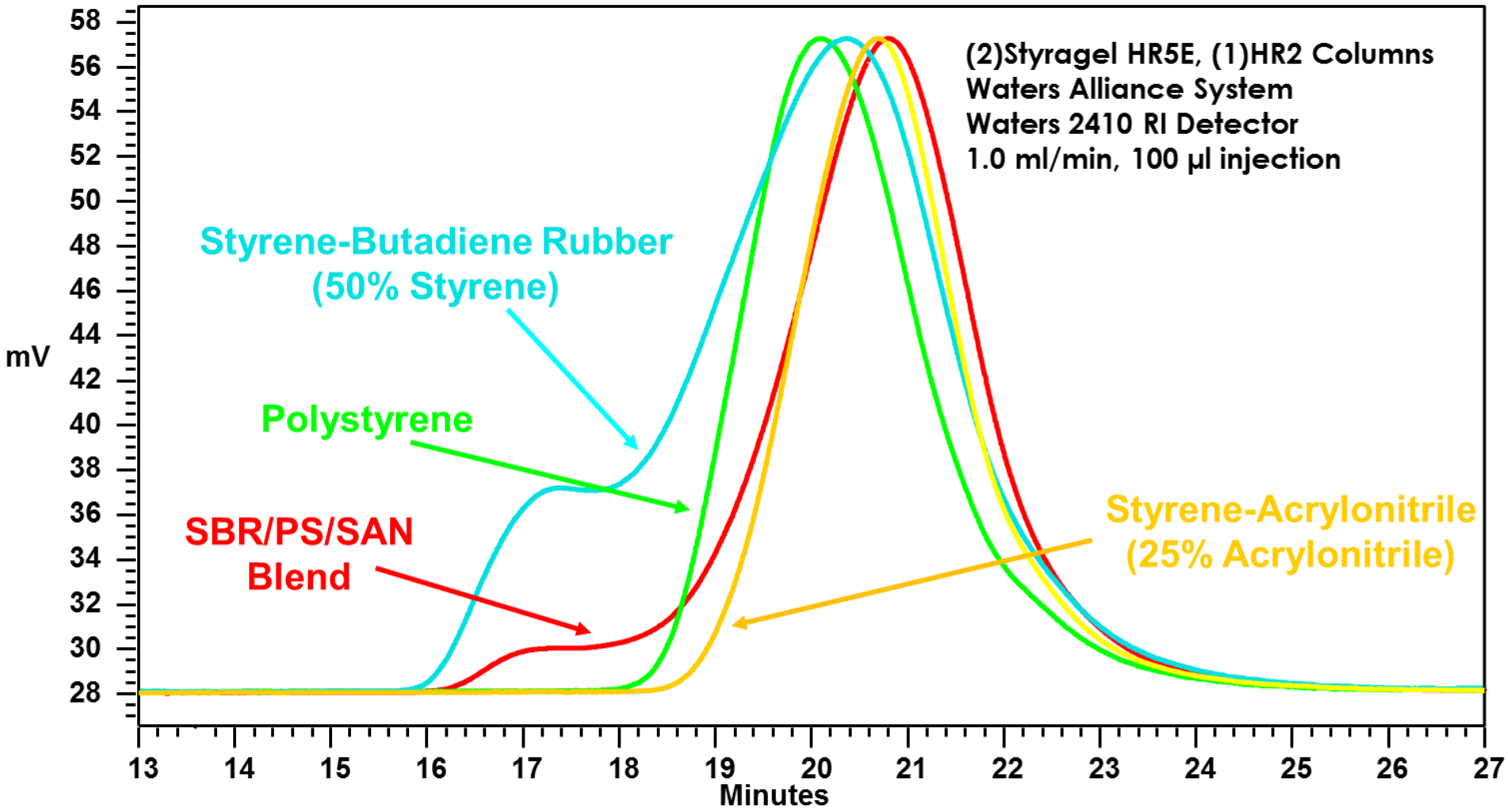
In recent years there has been increased interest in using gradient HPLC techniques, such as Gradient Polymer Elution Chromatography (GPEC), with polymers for determining the compositional drift of copolymers, the composition of polymer blends, or for the analysis of polymer additives. Depending upon the gradient conditions and columns selected for analysis, separations may be obtained dependent on molecular weight or based upon precipitation, or adsorption mechanisms. The use of an Evaporative Light Scattering Detector (ELSD) allows one to perform solvent gradients with a universal mass detector and observe both UV absorbing and non-UV absorbing polymer samples without baseline disturbances from the solvent gradient. The addition of a Photodiode Array Detector (PDA) allows for compositional analysis across the molecular weight distribution of many copolymers, can be useful for the identification of components in a polymer blend, and also is invaluable for the quantitation of polymer additives and other small molecules in traditional reverse phase separations.

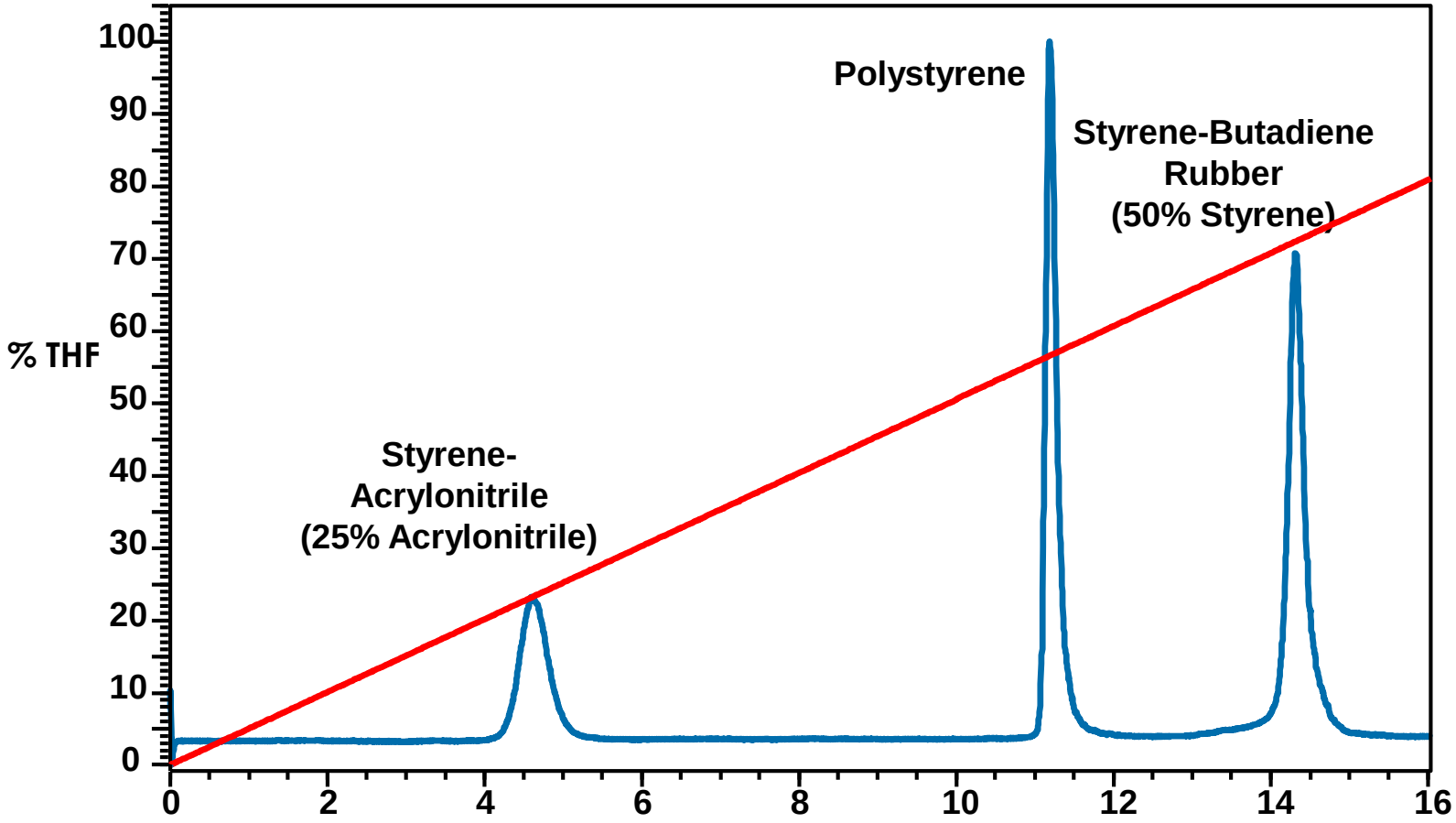
Experimental Conditions

System:	Waters Alliance 2690 Separations Module with column heater at 30 ºC
Detector 1:	Waters 996 Photodiode Array Detector
Detector 2:	Alltech Model 500 ELSD with LTA Adapter (Drift Tube at 40º C, 1.75 Liters/min Nitrogen)
Data System:	Waters Millennium 32 Chromatography Manager
Column:	As listed in Figures, 30 ºC
Flow Rate:	1mL/min
Samples:	10 - 25 µl injections of 0.2 - 0.5% samples
Gradient:	Linear gradient, conditions and mobile phases as listed in Figures.

GPC Analysis of a Polymer Blend

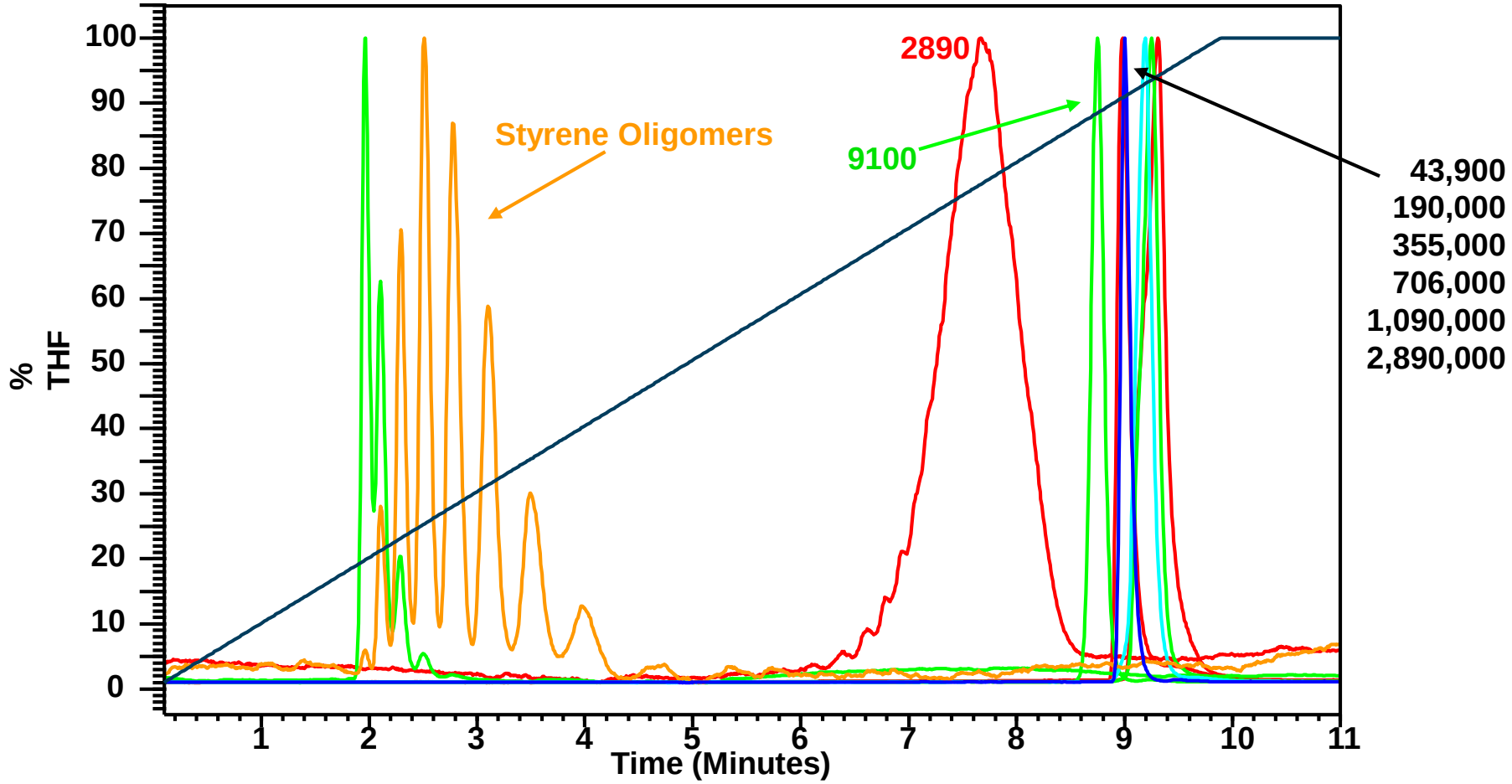


Gradient Analysis of a Polymer Blend



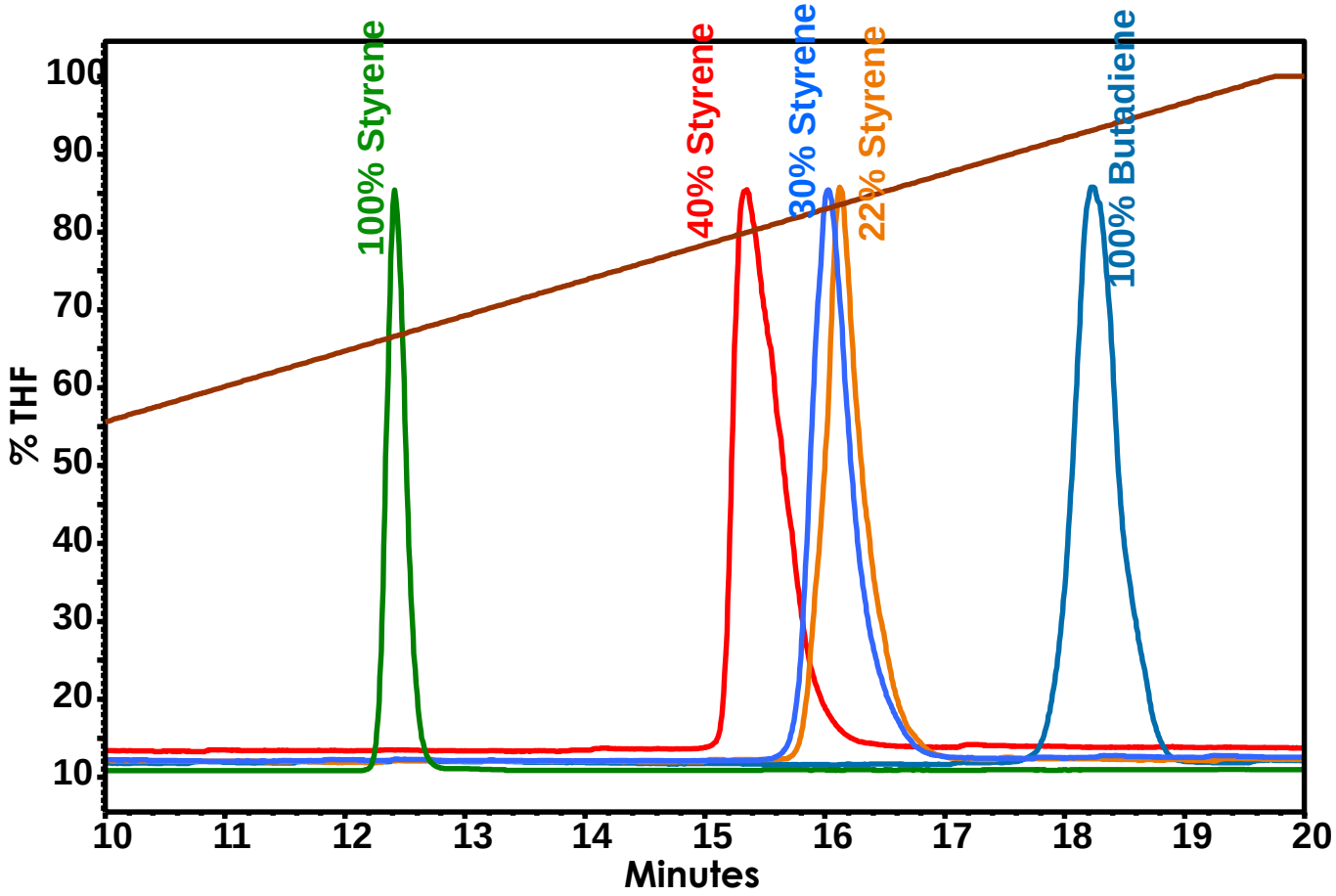
Symmetry Shield™ C8 Column (3.9x150mm)
100% ACN to 100% THF over 20 minutes ELSD Detection

Gradient Analysis of Narrow PS Standards



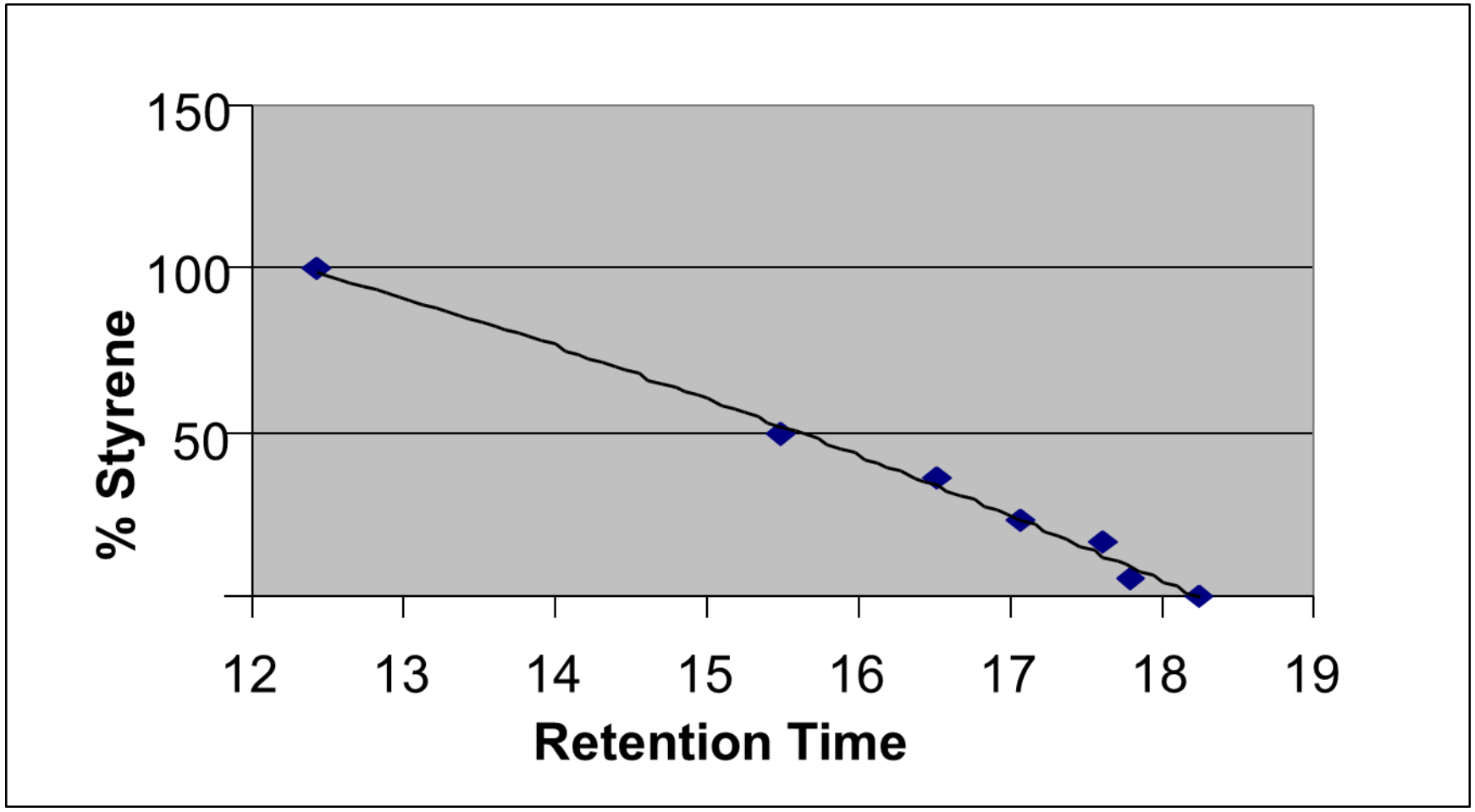
Symmetry Shield C8 (3.9x150mm)
100% ACN to 100% THF over 10 minutes ELSD Detection

Analysis of Styrene-Butadiene-Styrene Block



Prototype DVB/Vinylpyrolidone Column (3.9x150mm)
100% ACN to 100% THF over 20 minutes ELSD Detection

Calibration of %Styrene in SBR's



Gradient Analysis of Low Molecular Weight Waxes

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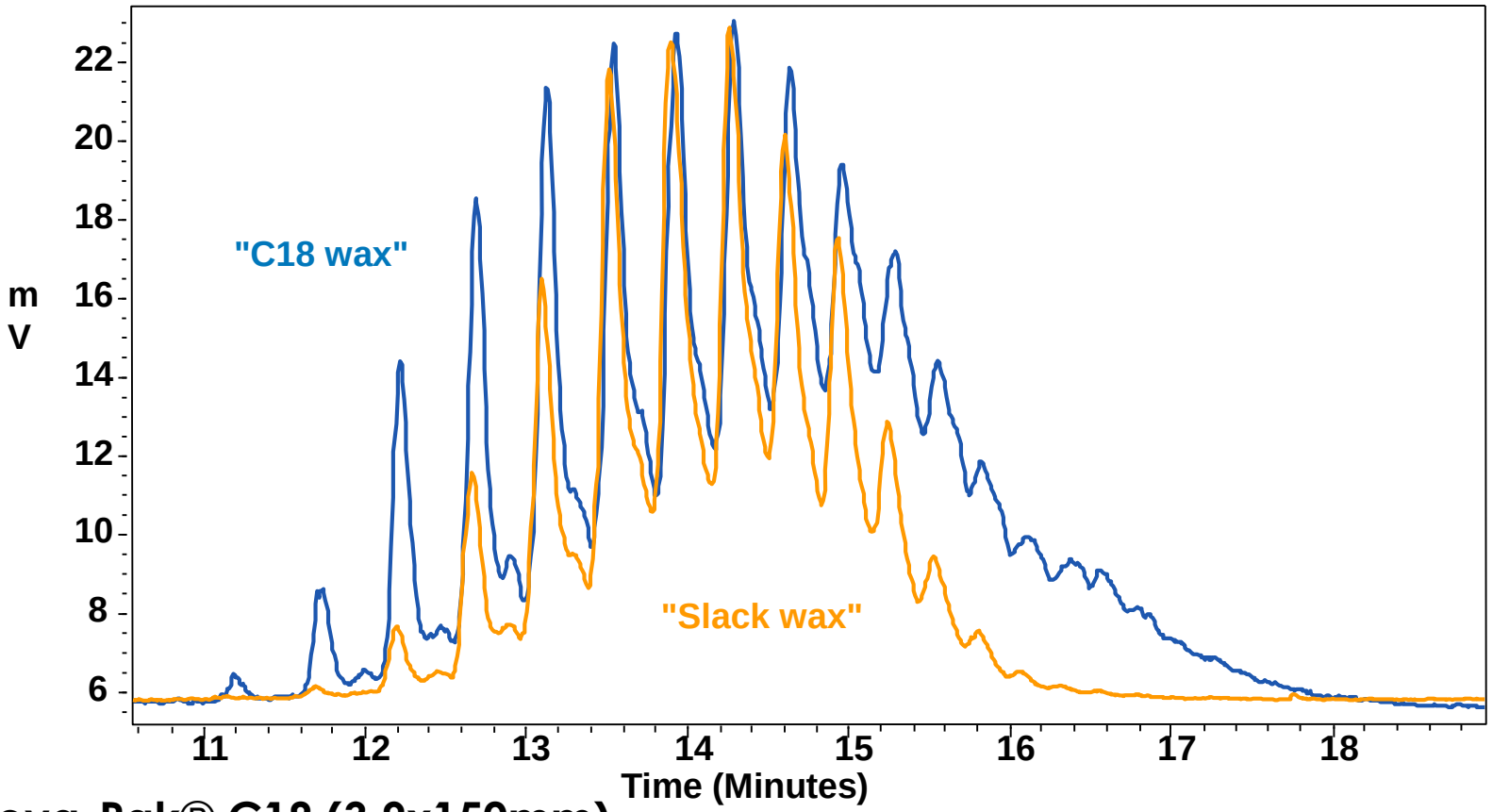
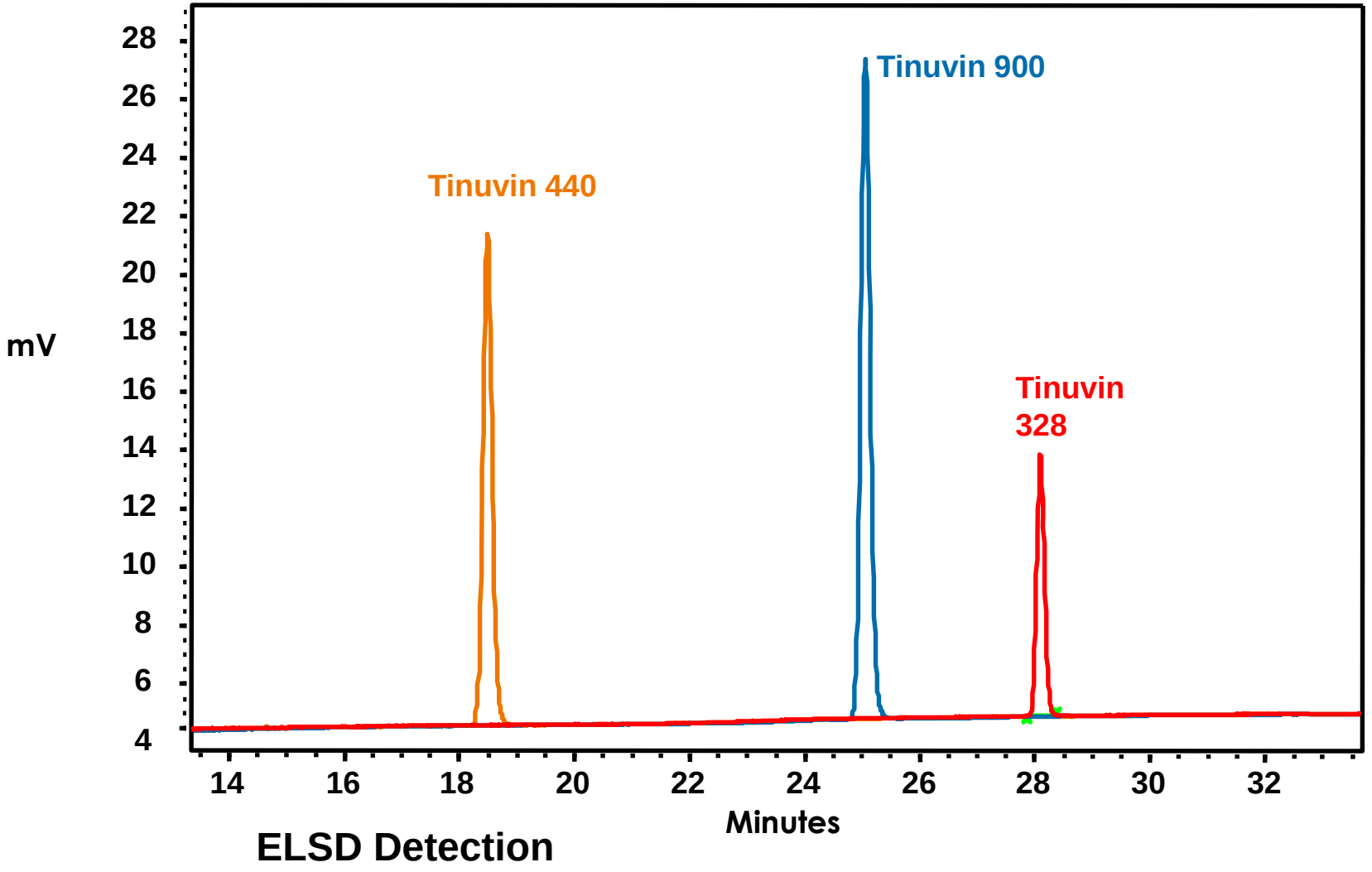
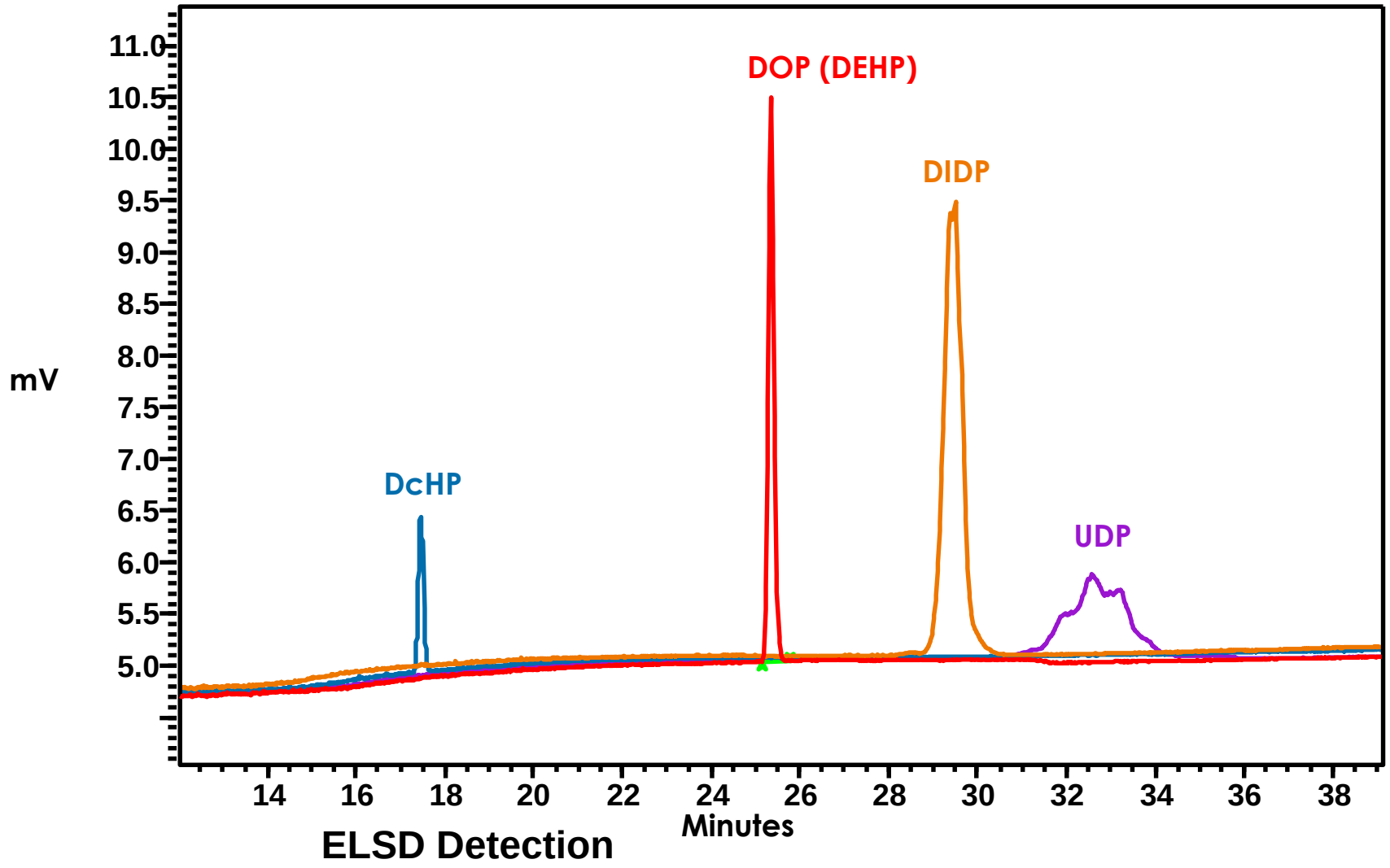


Nova-Pak® C18 (3.9x150mm)
100% ACN to 100% THF over 30 minutes ELSD Detection

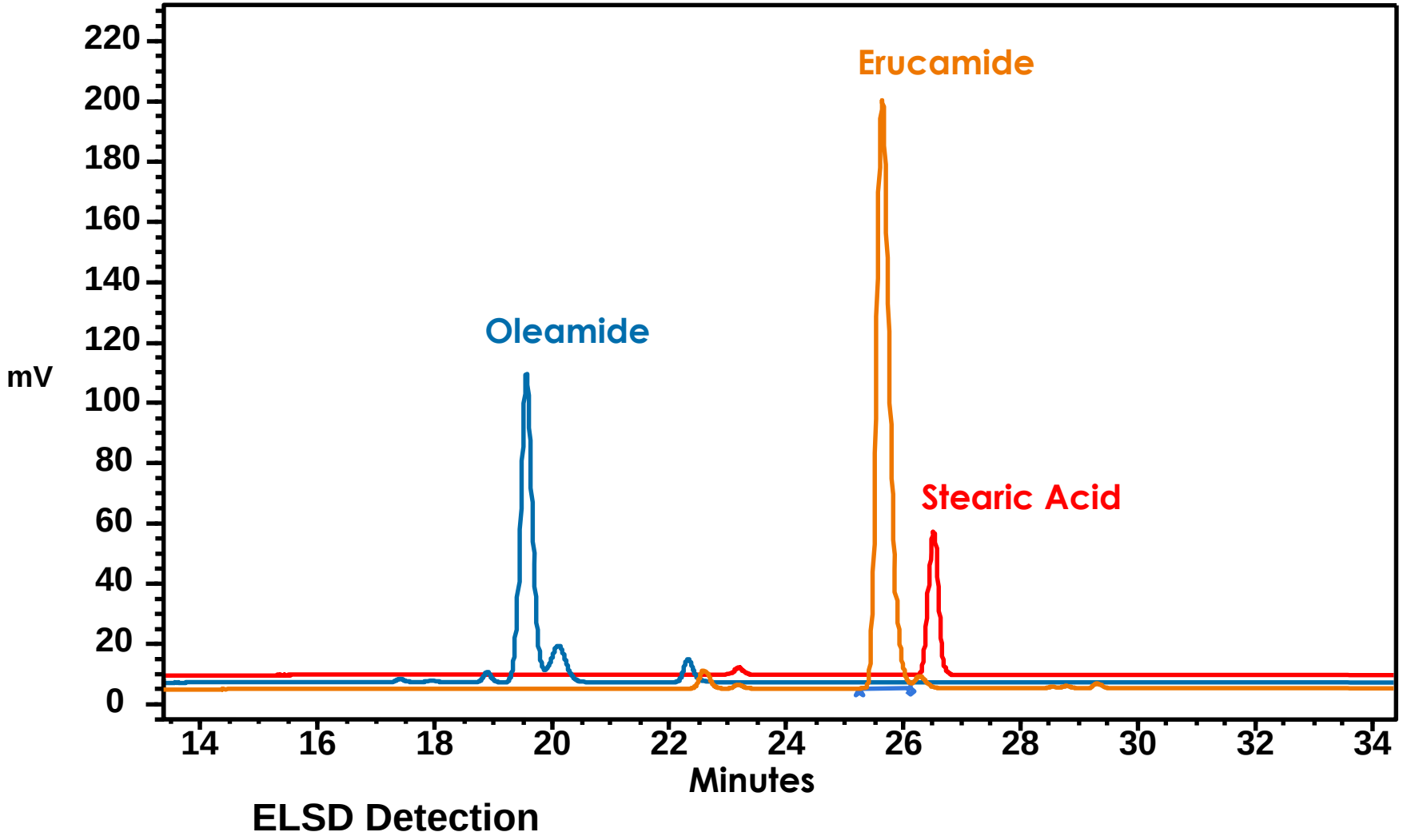
Polymer Additives – Tinuvins, (UV Stabilizers)



Polymer Additives – Phthalate Plasticizers



Polymer Additives - Slips and Antistats



Polymer Additives - Antioxidants
Overlay of 12 injections of Antioxidant Standard

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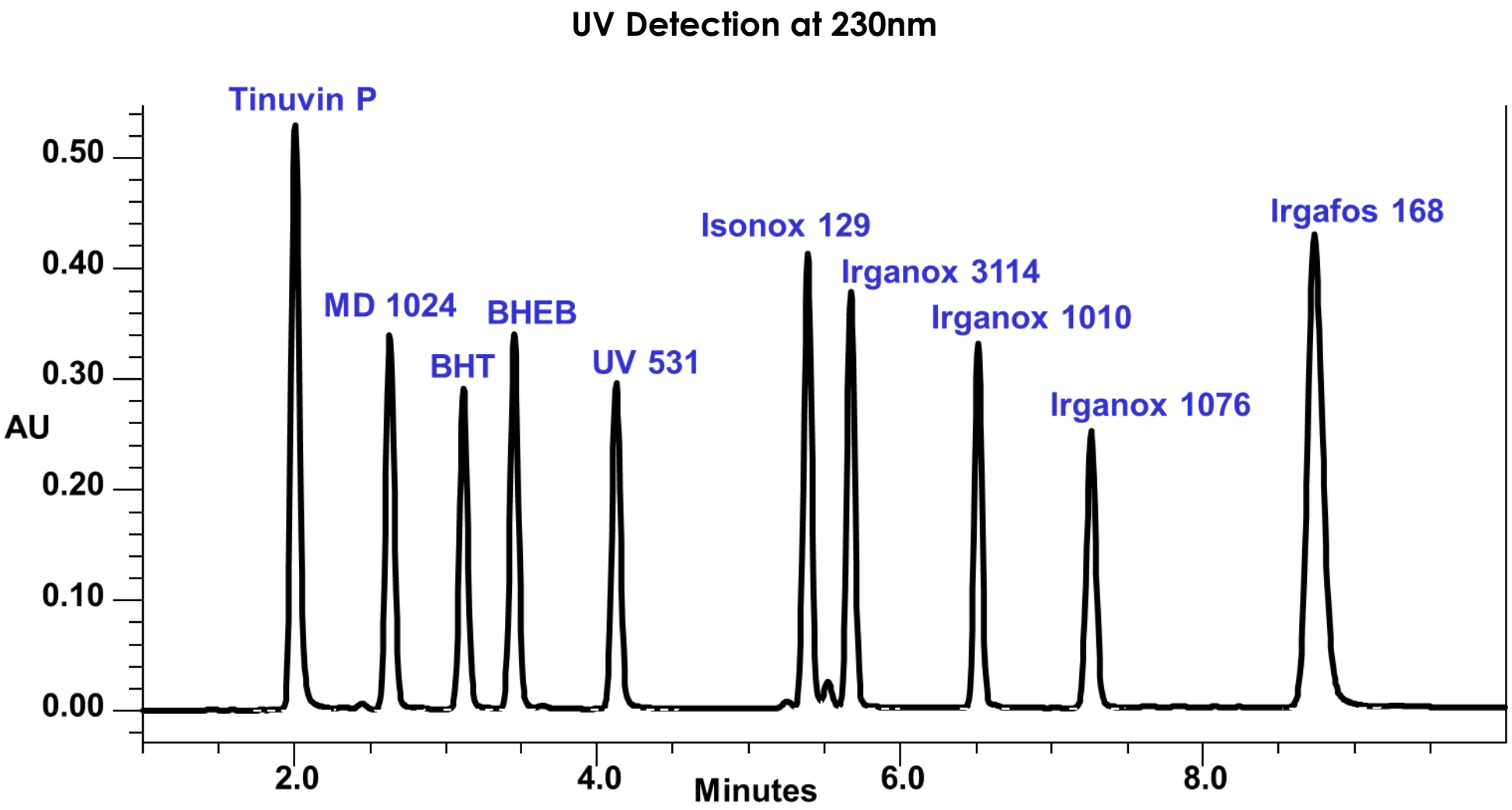

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Outline

- What is GPC?
- GAP of Additives
- What's New?

Birth of Polymer Chromatography
Dow/Waters Collaborations in GPC

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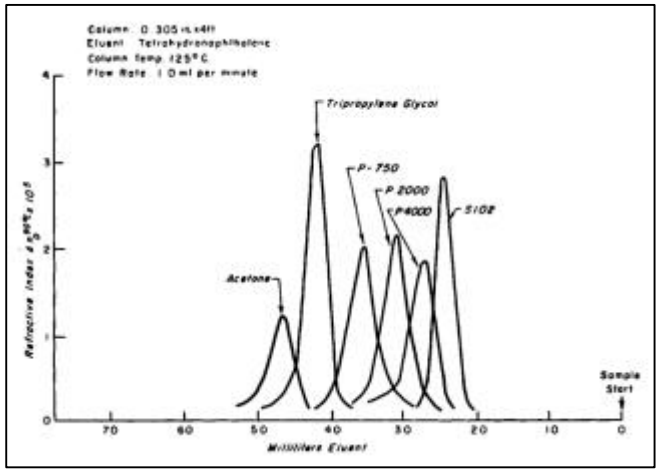
- 1962 - Jim Waters builds prototype low volume, high temperature refractometer for John C. Moore, Dow Chemicals
- 1963 – Waters exclusive license of US 3,326,875, " Separation of Large Polymer Molecules in Solution" from Dow Chemicals
- 1964 – Key paper by Moore
  - Reduces analysis from days to hours
  - Coins term "GPC"



GPC:1964 to today

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- Little change in column technology
- Primarily polymer-based resins
  - Styrene-DVB
  - Methacrylates
- Low resolution technique
  - Particle size reduction ~75 micron to ~5 micron
    - Minimal resolution improvement
  - Limitations in minimizing instrument dispersion
- “Universal columns” and fast GPC columns
  - Compromise speed for resolution
  - GPC/SEC remained a slow technique

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A Novel, Practical Approach to SEC/GPC Analysis

ACQUITY®

Advanced Polymer Chromatography™ (APC™) System

What's is the APC System?

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- ACQUITY APC System
  - Introduced at Pittcon 2013(Philadelphia)
- GPC/SEC polymer characterization with
  - sub-2µm /sub-3µm rigid hybrid particles
    - BEH chemistry introduced in 2004
- Complete solution
  - New higher efficiency columns
    - aqueous and organic
  - New chromatographic system
    - Designed for high efficiency columns
    - Low dispersion, precise flow rate

Recent Trends Polymer Development

Modern Chemistry

- Functional polymers
  - End-groups
  - Pendant groups
- Better control
  - Polymerization reactions
  - Molecular weight averages & polydispersity
- Next gen catalysts
  - New, innovative polymer structures

Green Chemistry

- Decrease organic solvents in processes
- Increase water based processes
- Bio-sourced polymers
- Biodegradable polymers

Key: Lower average molecular weight polymers

Analytical Challenges

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Speed of Analysis

Current approaches to size based separations compromise

- Peak resolution
- Characterization
- Data quality

Gel Based Columns

Typical materials include

- Styrene-DVB
- Methacrylates

Relatively fragile

Solvent to solvent conversion not easy

Poorly Resolved Low Molecular Weight Polymer & Oligomers

Traditional GPC is a low resolution technique

Low resolution limits characterization information

Innovative polymers and building blocks need high resolution

ACQUITY APC™ System

Limitations of High Speed Gel Permeation Chromatography

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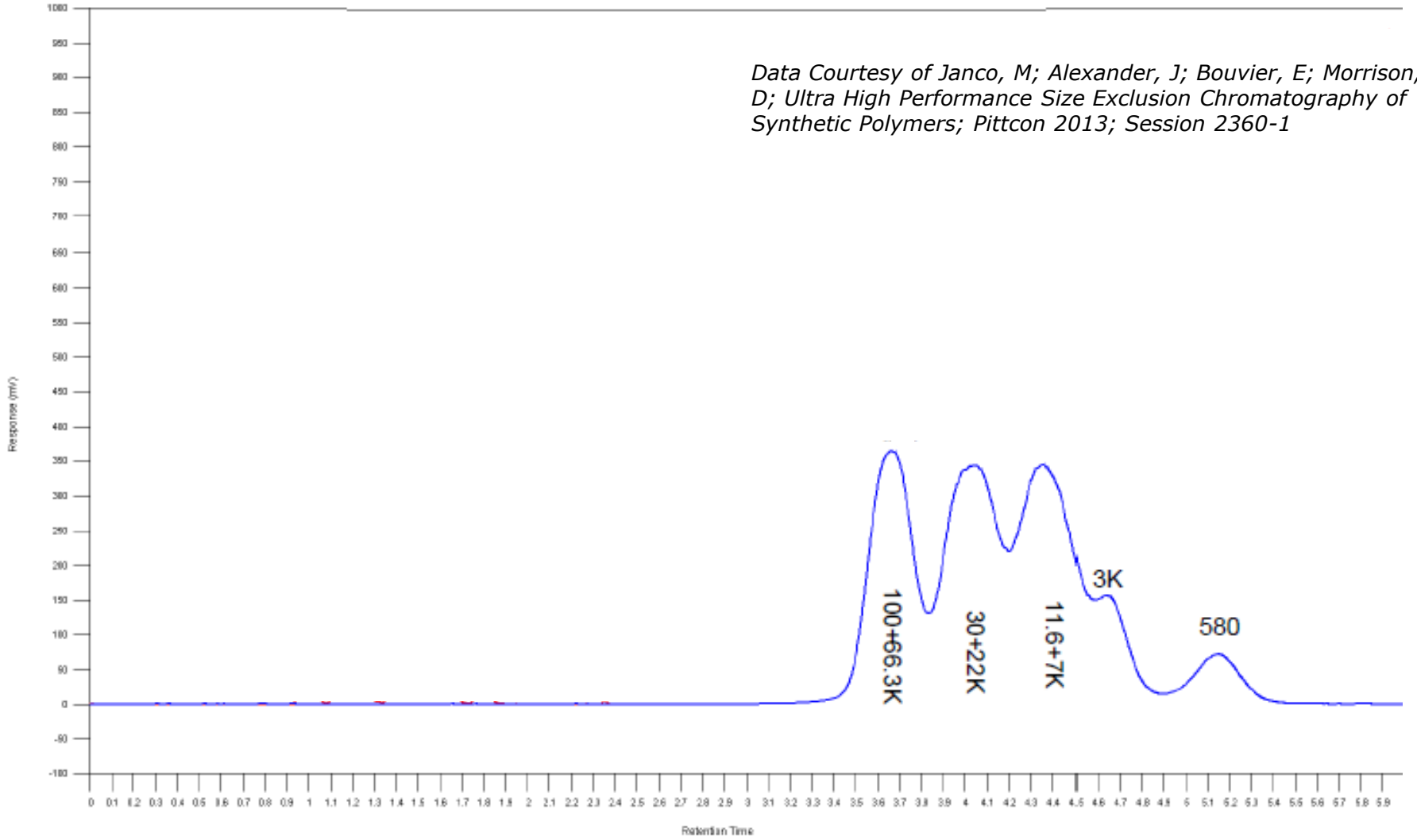

Data Courtesy of Janco, M; Alexander, J; Bouvier, E; Morrison, D; Ultra High Performance Size Exclusion Chromatography of Synthetic Polymers; Pittcon 2013; Session 2360-1

Advanced Polymer Chromatography versus High Speed Gel Permeation Chromatography

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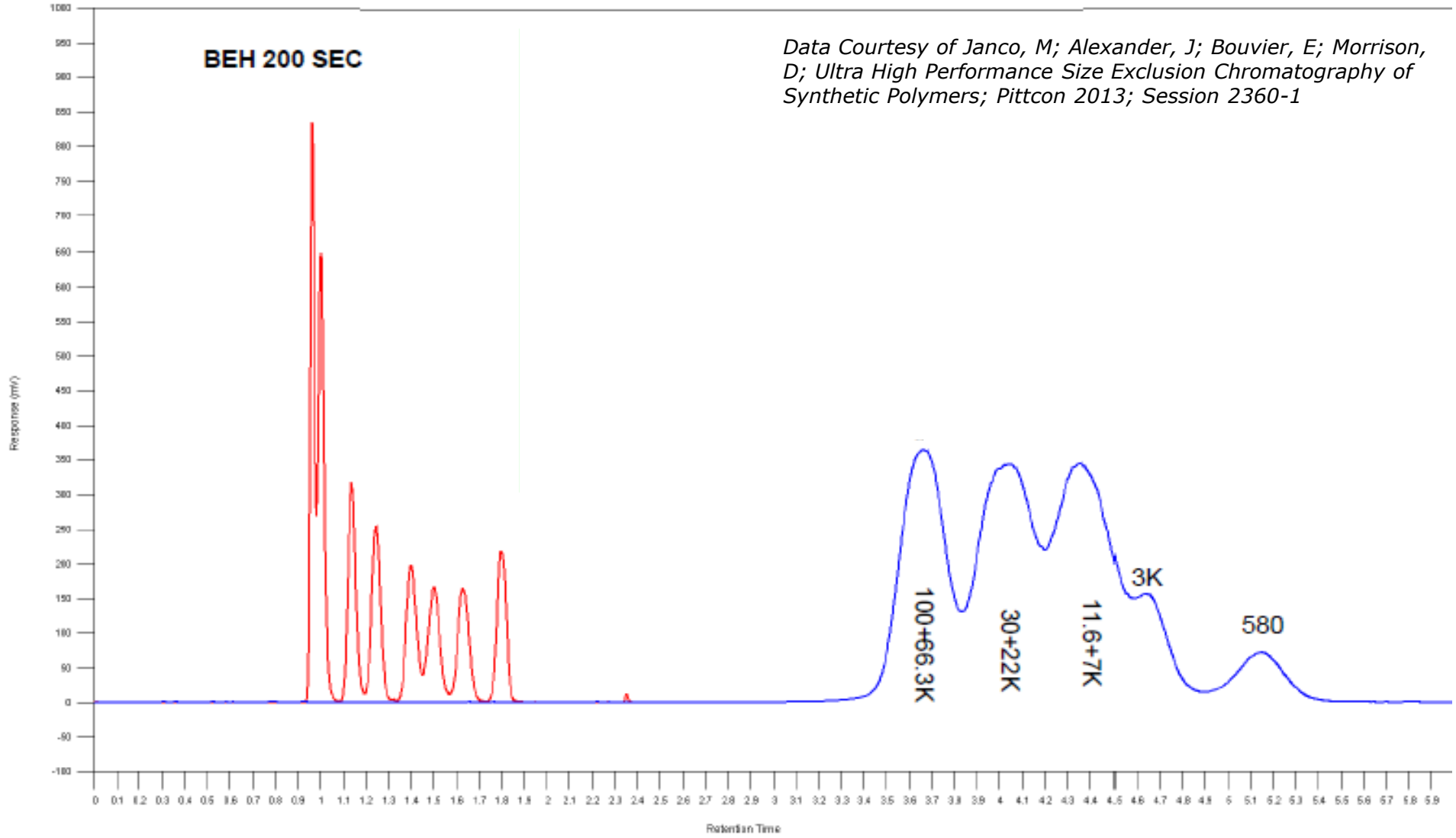
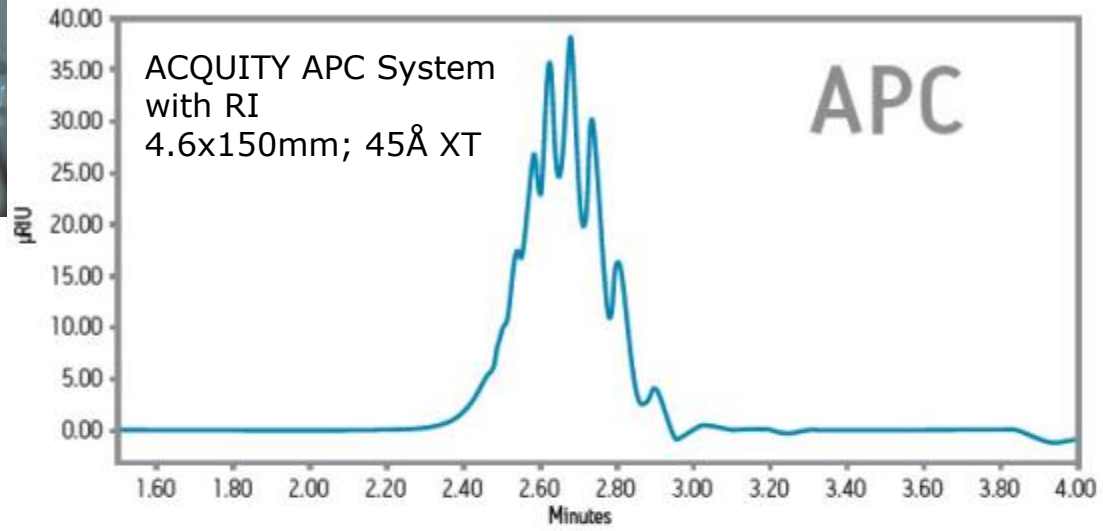
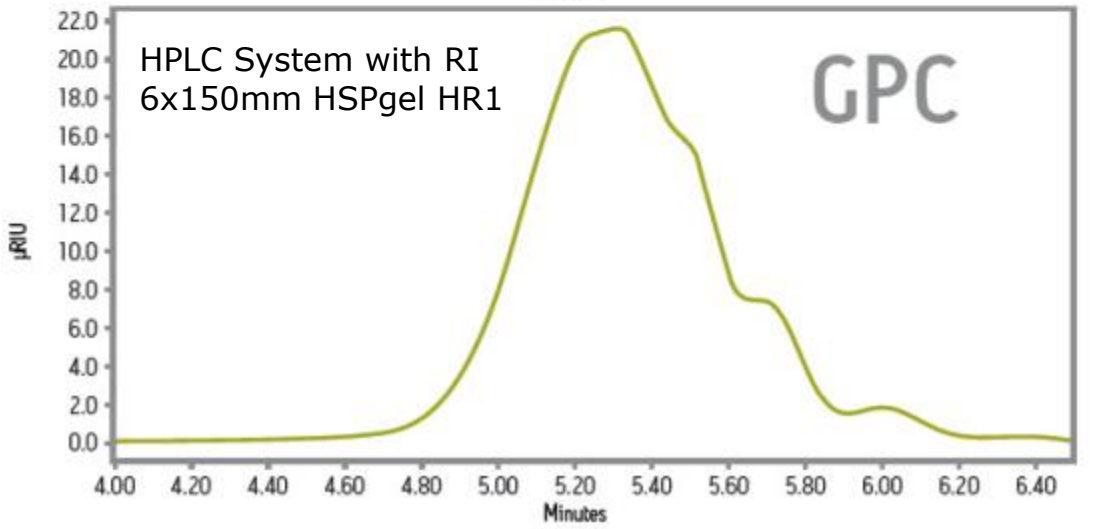


Data Courtesy of Janco, M; Alexander, J; Bouvier, E; Morrison, D; Ultra High Performance Size Exclusion Chromatography of Synthetic Polymers; Pittcon 2013; Session 2360-1

Low MW Polymer: Resolution Realized

Polystyrene Standard 510 Mp

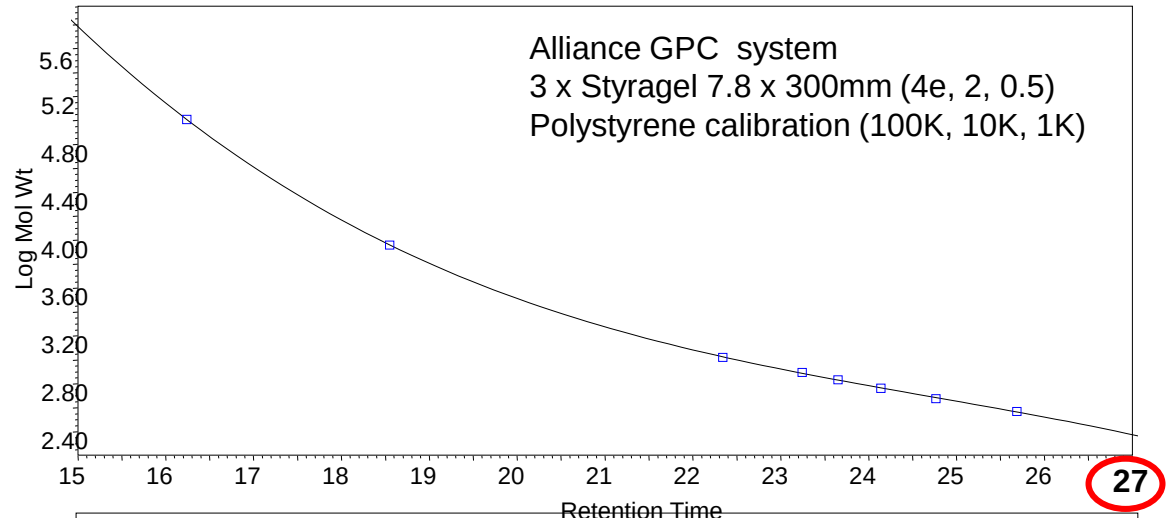


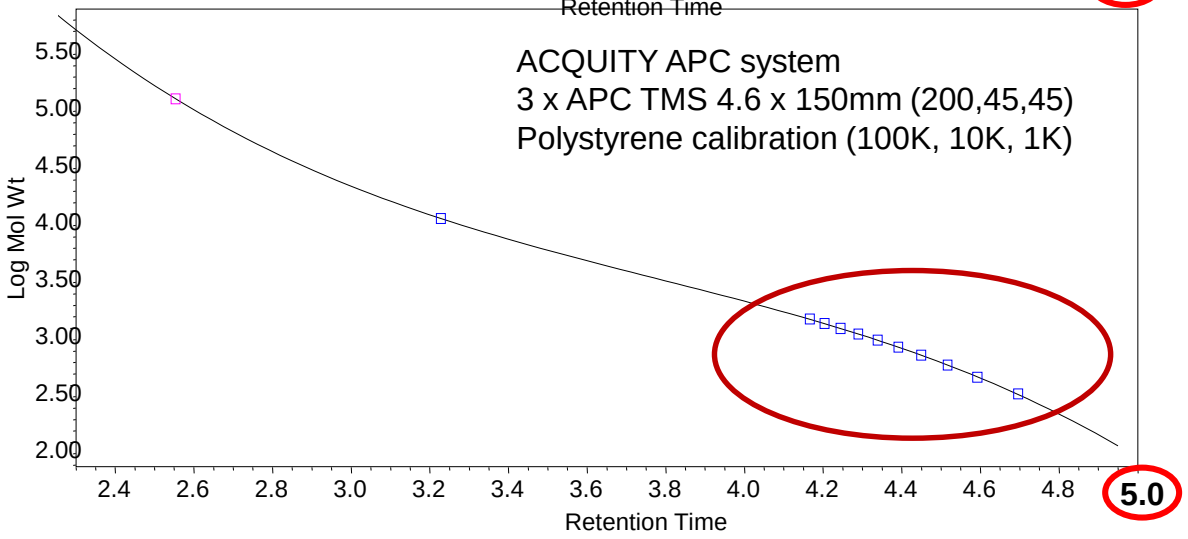


Speed of Analysis & Better Characterization

More resolution = more points for low molecular weight calibration

Better calibration = more accurate data





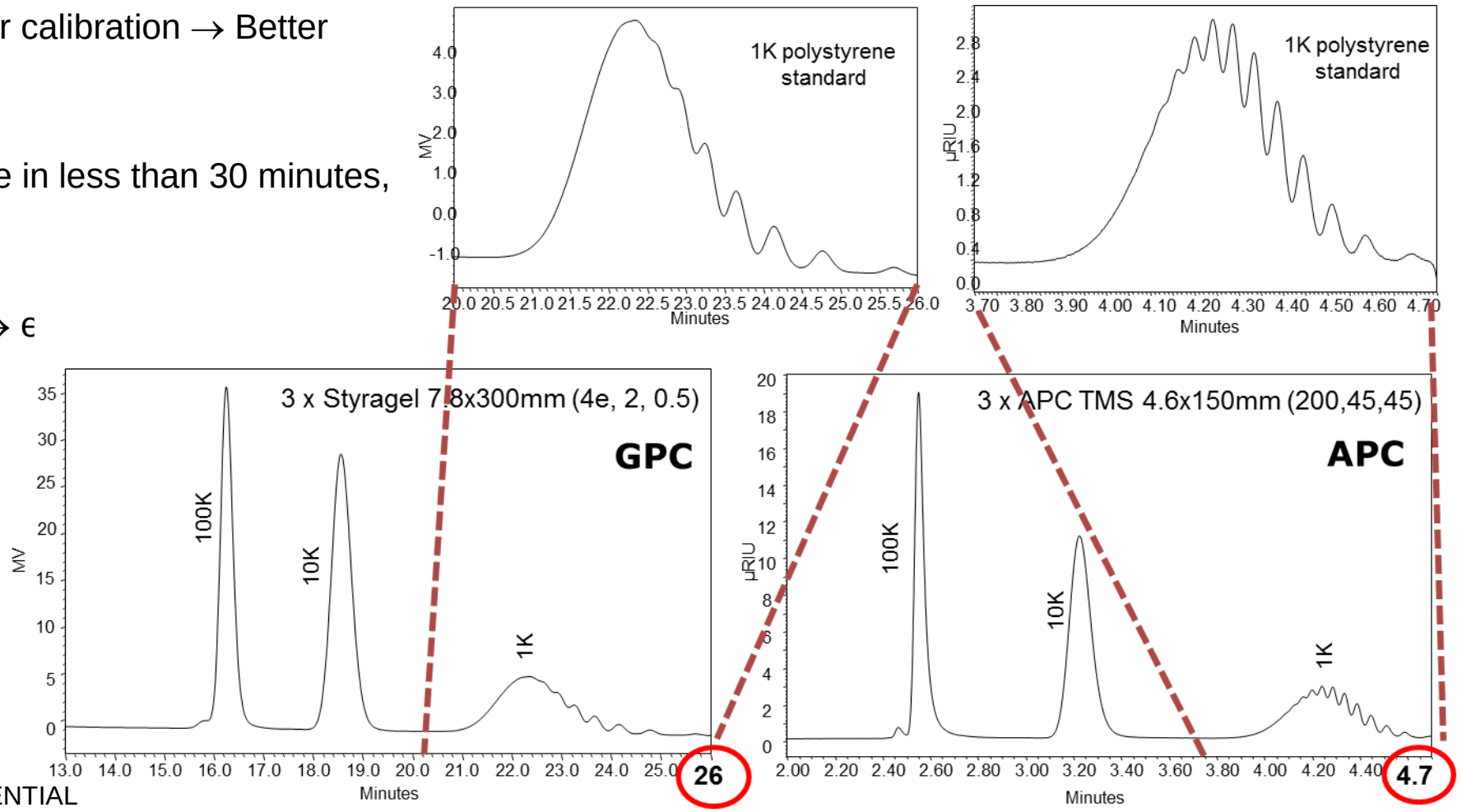
Speed of Analysis & Better Characterization

- Higher resolution & speed of APC
  - Easier to run more calibration standards, faster

- More calibration points → Better calibration → Better characterization

- FASTER calibration → Calibrate in less than 30 minutes, not hours

- DAILY calibration, not weekly → ϵ consistency and quality



Gel Based Columns versus Rigid Hybrid Particles

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THF

DMF

Toluene

One System.

One Bank of Columns.

Solvent Flexibility.

Rigid Hybrid Columns Solvent Flexibility

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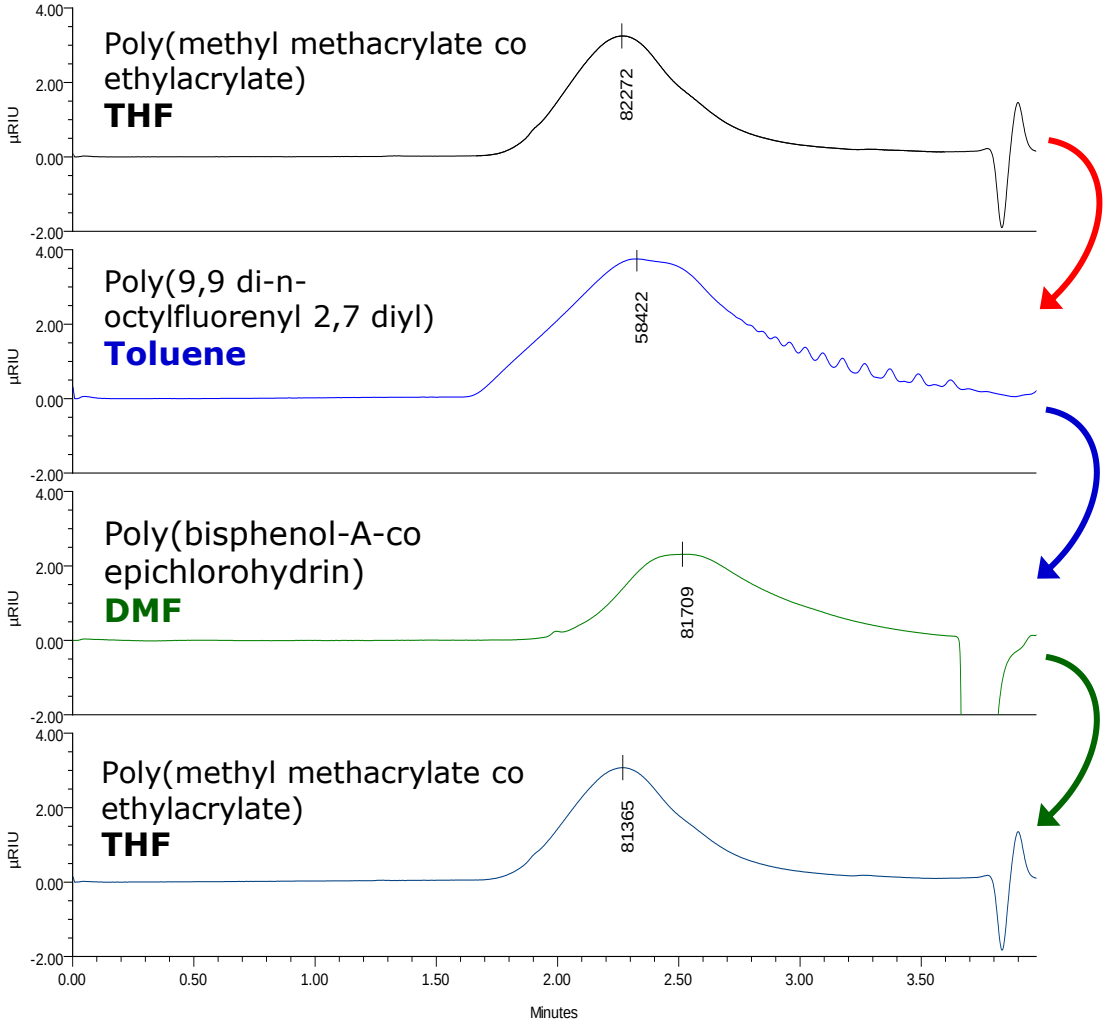
poly(methyl methacrylate co ethyl acrylate) in THF			
	before	after	% change
Mp	82272	81365	0.4
Mw	78650	78953	1.5
Mn	49383	50110	0.6
PDI	1.59	1.58	1.1



Ethylene-Bridged Hybrid (BEH) Particle Process

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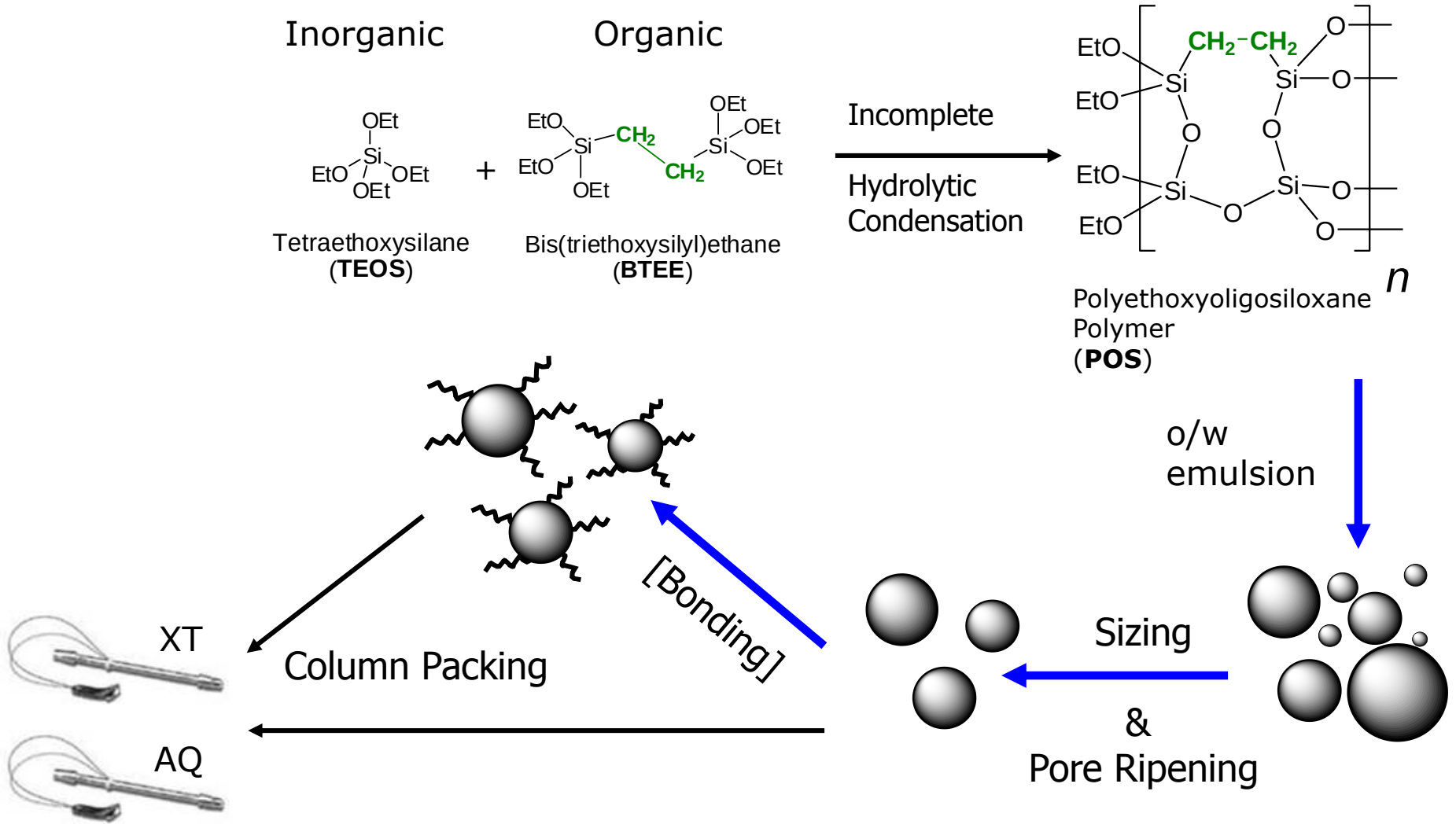
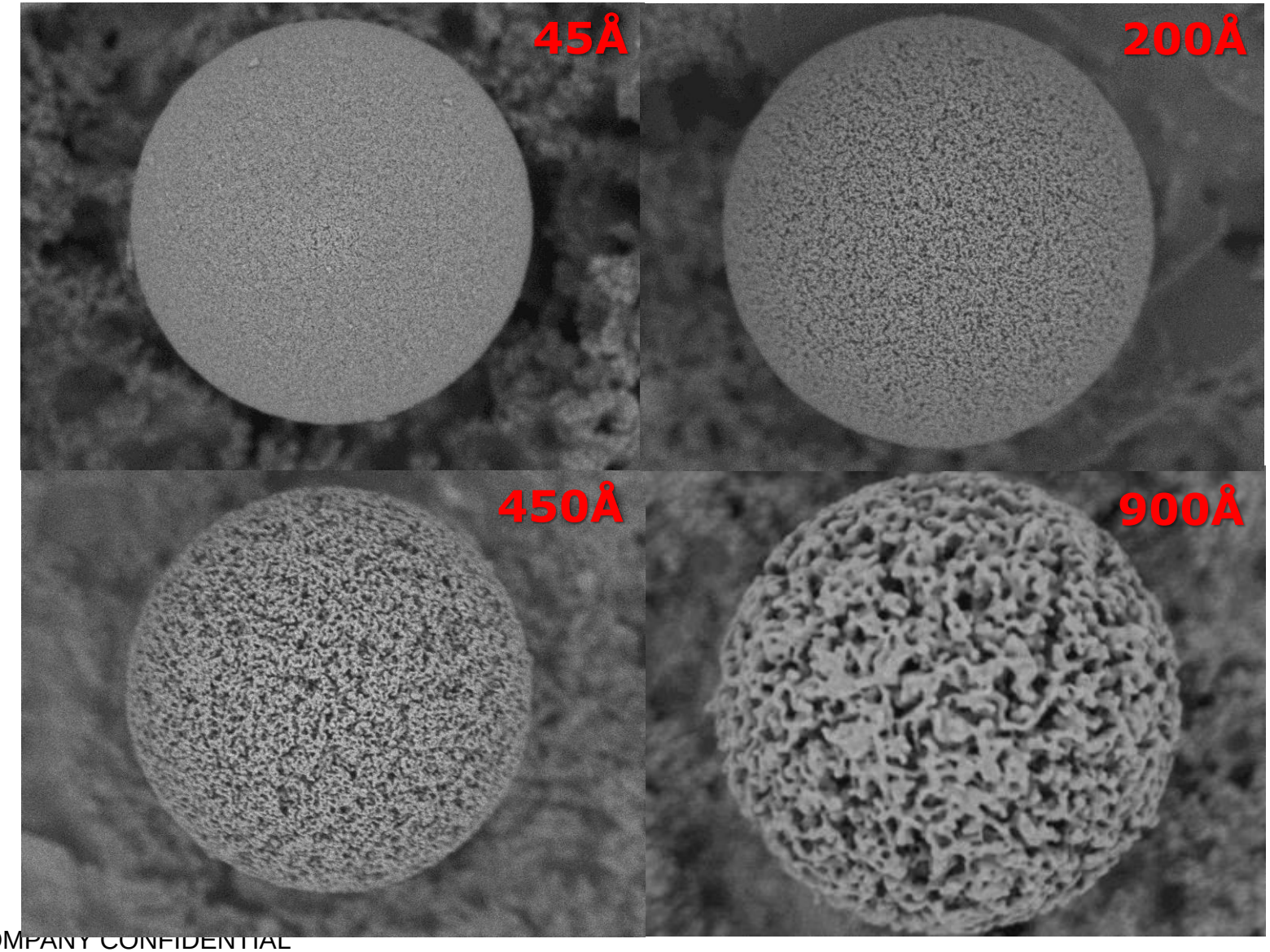


Wide Pore Bridged Ethyl Hybrid: SEM Images



ACQUITY APC Columns:
Built on Bridged Ethylene Hybrid (BEH)

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- More than 10 years experience
  - sub-2µm particles submitted to extreme conditions
    - pH, temperature, back pressure, flow rates, …

- BEH particles combine advantages of silica & polymeric material
  - Rigid, pressure resistant
  - Particle size & pore diameter well-controlled
  - Inert, resistant to temperature changes

- E-cord device
  - Traces usage history
    - QC certificate, injection count, temperature, back pressure)

ACQUITY APC Column Options

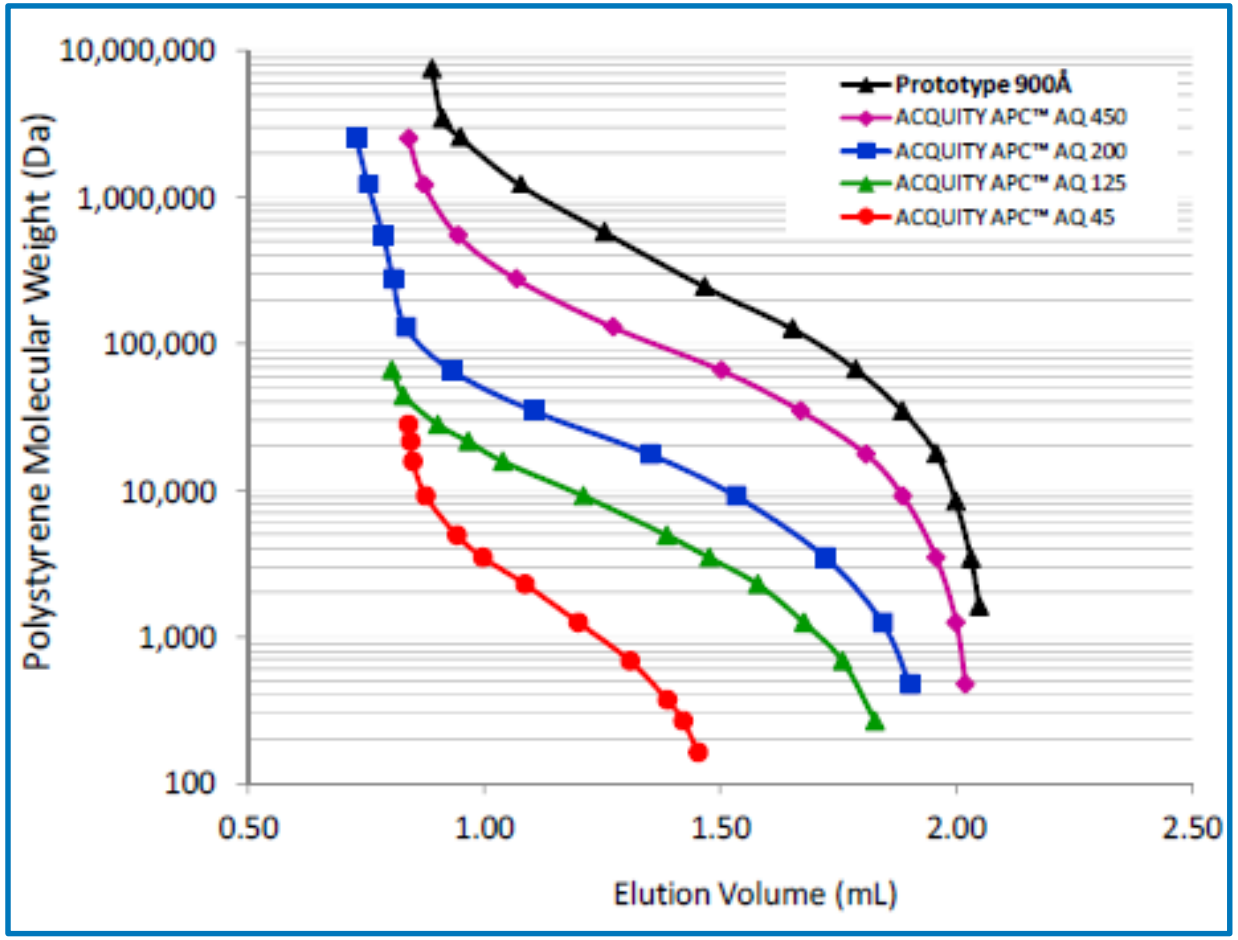
- Particles based on BEH chemistry

- Five pore sizes
  - 45 Å (200 – 5,000) 1.7µm
  - 125 Å (1,000 – 30k) 2.5µm
  - 200 Å (3,000 – 70k) 2.5µm
  - 450 Å (20k – 400k) 2.5µm
  - 900 Å (300k – 2M) 2.5µm

- Two surface chemistries
  - Organic solvent- XT
  - Aqueous buffers – AQ

- Three column lengths
  - 30 mm
  - 75 mm
  - 150 mm

- Internal diameter: 4.6 mm



ACQUITY Refractive Index Detector
Counter Current Heat Exchanger

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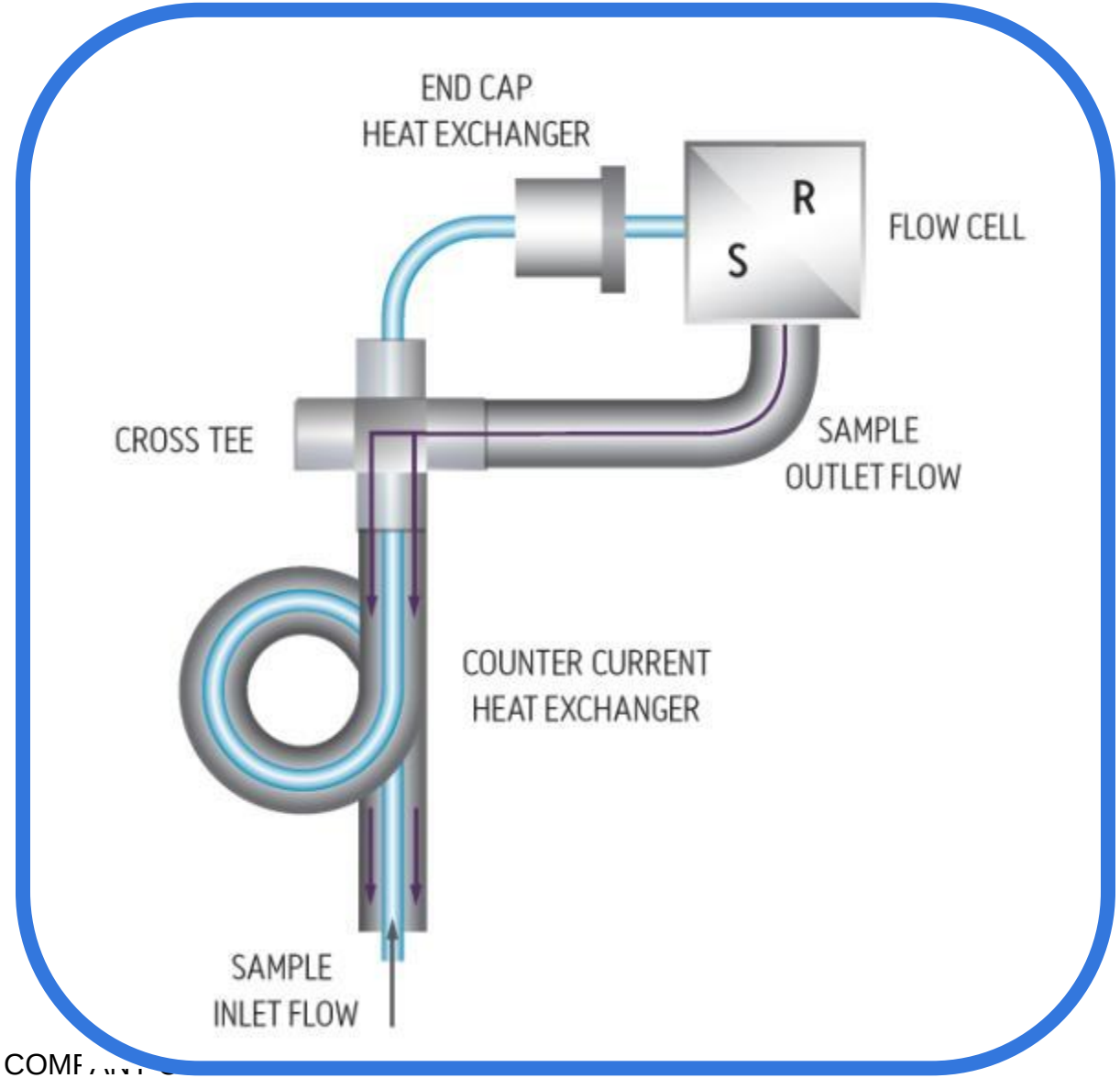

HPLC RI ~ 150µL

ACQ-RI < 15µL

ACQUITY Refractive Index Detector Results

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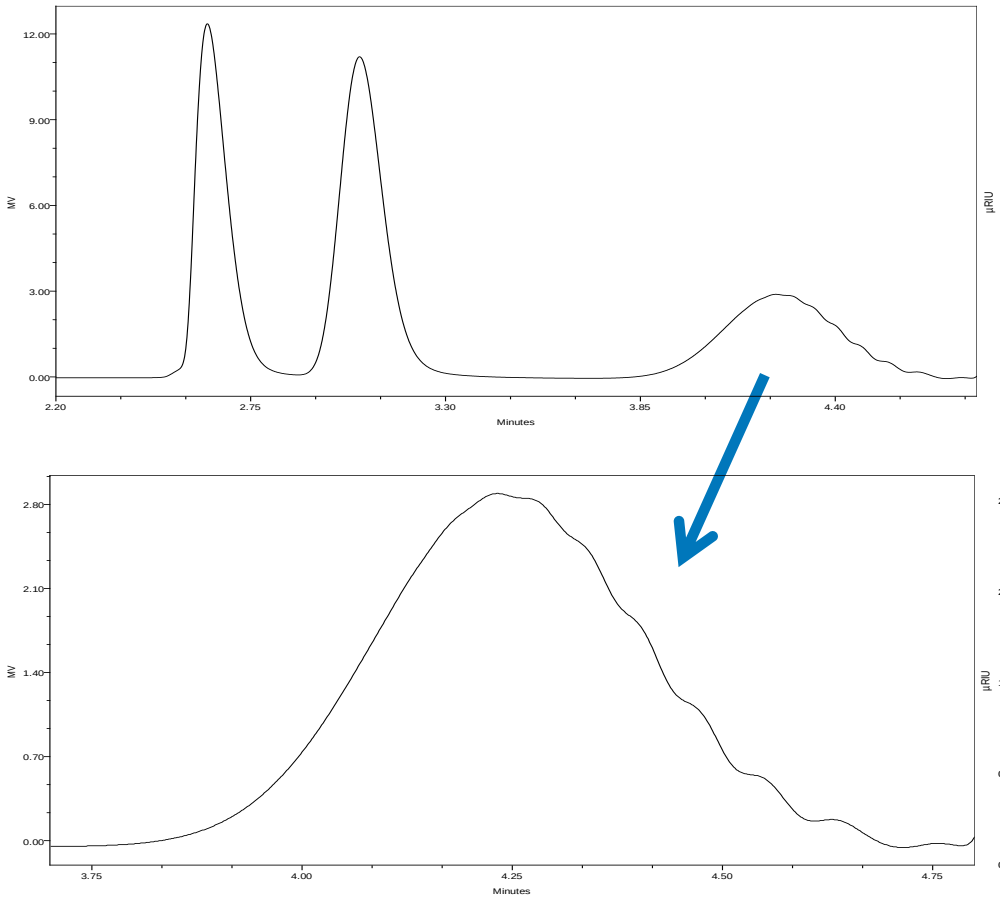
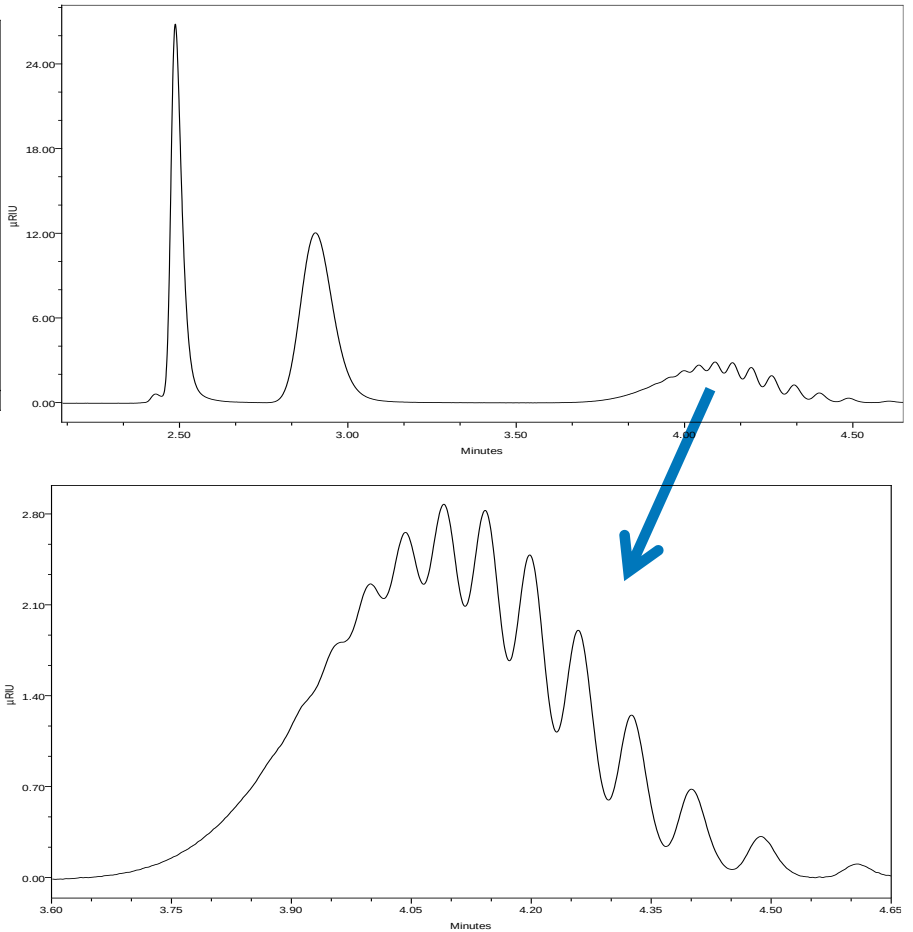
ACQUITY APC System with ACQUITY APC XT 4.6 x 150mm (45Å + 45Å + 200Å)

HPLC RI Detector



ACQUITY RI Detector



ACQUITY APC ISM Precision:
100 injections of Epoxy Resin Overlaid

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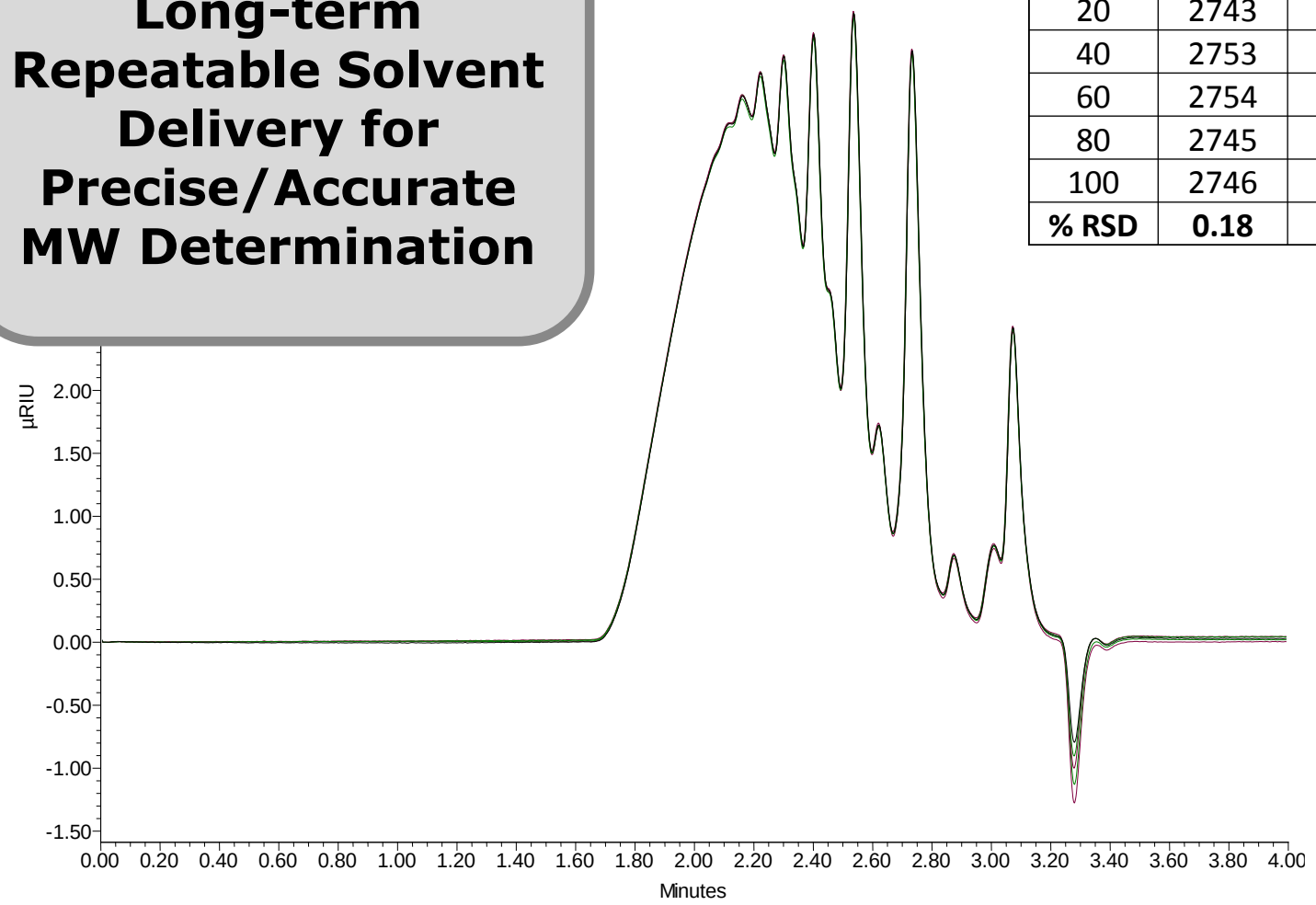
Long-term Repeatable Solvent Delivery for Precise/Accurate MW Determination

Injection	Mp	Mw	Mn	PDI
20	2743	6143	3870	1.587
40	2753	6160	3884	1.586
60	2754	6156	3884	1.585
80	2745	6146	3870	1.588
100	2746	6151	3878	1.586
% RSD	**0.18**	**0.11**	**0.18**	**0.08**



ACQUITY APC XT 4.6x150mm; 1 x 125Å (1,000-30,000) and 1 X 45Å (200-5,000)

Performance of Legacy Methods on ACQUITY APC System

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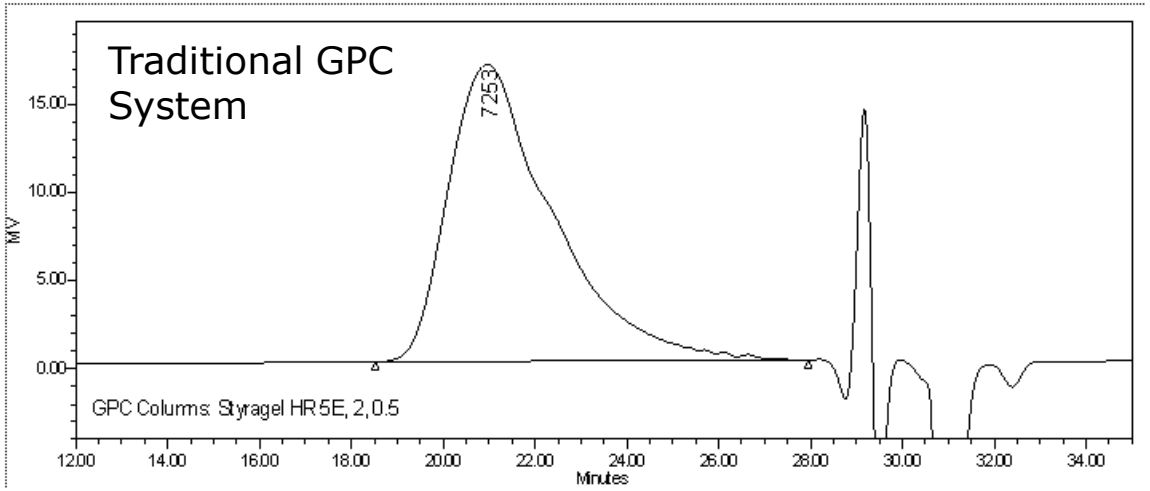

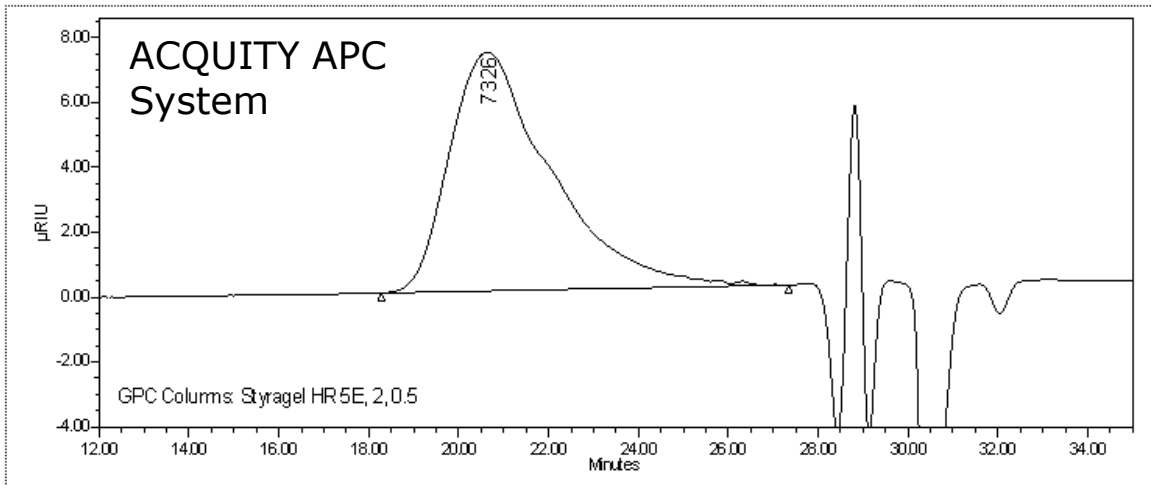

	GPC System	APC System	% Diff
M_w	7113	7105	0.1%
M_p	7253	7326	1.0%
M_n	3337	3325	0.4%
M_z	12267	12306	0.3%
PDI	2.131	2.137	0.3%

Want To Know More?

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- Visit the APC system mini web-site
  - www.waters.com/apc
  - Detailed information
  - System & column brochure
  - Information on components
  - Application notes

Want To Know More?

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J. Sep. Sci. 2013, 00, 1–10

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Research Article

Ultra-high performance size-exclusion chromatography of synthetic polymers

Demonstration of capability

Ultra-high performance size-exclusion chromatography (UHP SEC) is a newly developed disruptive technology that allows the high-resolution separation of synthetic polymers in as little as 2 min. The capability of UHP SEC for the characterization of synthetic polymers in organic solvents has been demonstrated. Using the Waters ACQUITY UPLC®[1] H-Class system and ethylene-bridged hybrid size-exclusion chromatography (SEC) columns packed with 1.7 to 2.5-μm particles with pore sizes ranging from 45 to 900 Å, size-based separations of polystyrene and poly(methyl methacrylate) standards in tetrahydrofuran and poly(ethylene oxide) standards in 20 mM ammonium acetate in methanol are achieved within 2–4 min. The speed of analysis is about ten times faster than conventional SEC separations, and greater resolution is achieved. Average molecular weights of selected commercial polymers have been determined using ultra-high performance and conventional SEC. Average *M* data of analyzed samples are in good agreement using the two approaches. An inherent limitation of SEC in UHP mode is the characterization of very high *M* polymers (above ca. 2 million Da) due to the deformation and/or mechanical shearing of large molecules at high flow rates.

Keywords: Polystyrene / Poly(methyl methacrylate) / Poly(ethylene oxide) / Ultra-high performance size-exclusion chromatography / UHP SEC
DOI 10.1002/jssc.201300444

Summary

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- Size Exclusion and Interactive polymer Chromatography are complimentary techniques for polymer characterization
  - SEC measures MWD of polymers
  - IPC measures CCD of copolymers and blends
  - Gradient HPLC can be used for polymer additive analysis (deformulation)

- New ACQUITY APC System
  - Brings all the advantages of sub-2µm & sub-3µm particles to polymer characterization (GPC/SEC)
  - Analysis time reduction by 5x (at minimum)
  - Daily calibration is easy
  - New columns compatible with any solvent
  - Rigid, BEH particles
  - Use one column set for different solvents
  - Achieve better results faster
  - Higher resolution, especially in low MW area