ZirChrom®

New Thermally and Chemically Stable HPLC Stationary Phases based on Zirconia

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ZirChrom®

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... For Peak Performance

Specialists in High Efficiency, Ultra-Stable Phases for HPLC

Outline

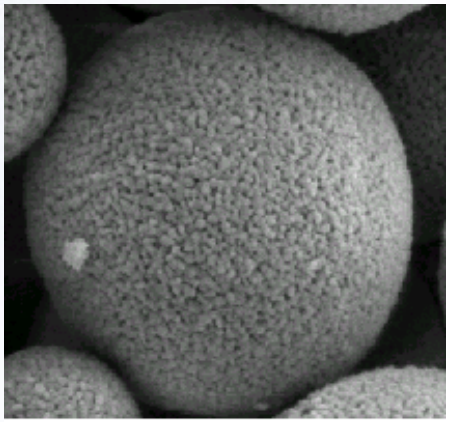
- **Development of Ultra-Stable Stationary Phases**
  - **Properties of Zirconia**
  - **Synthesis Strategy for Zirconia-based HPLC Columns (Z-phases)**
  - **Practical Benefits of High Temperature HPLC**
  - **Examples of Ultra-Fast High Temperature Separations**
- **Conclusion: Polymer and Carbon coated zirconia-based HPLC Stationary phases are stable at temperature >> 100°C.**

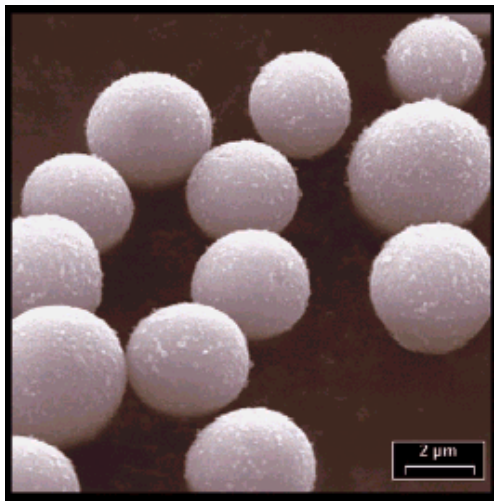
ZirChrom® Particle Properties

ZirChrom®-PBD and -PS particles are prepared by coating with a layer of highly crosslinked polymer

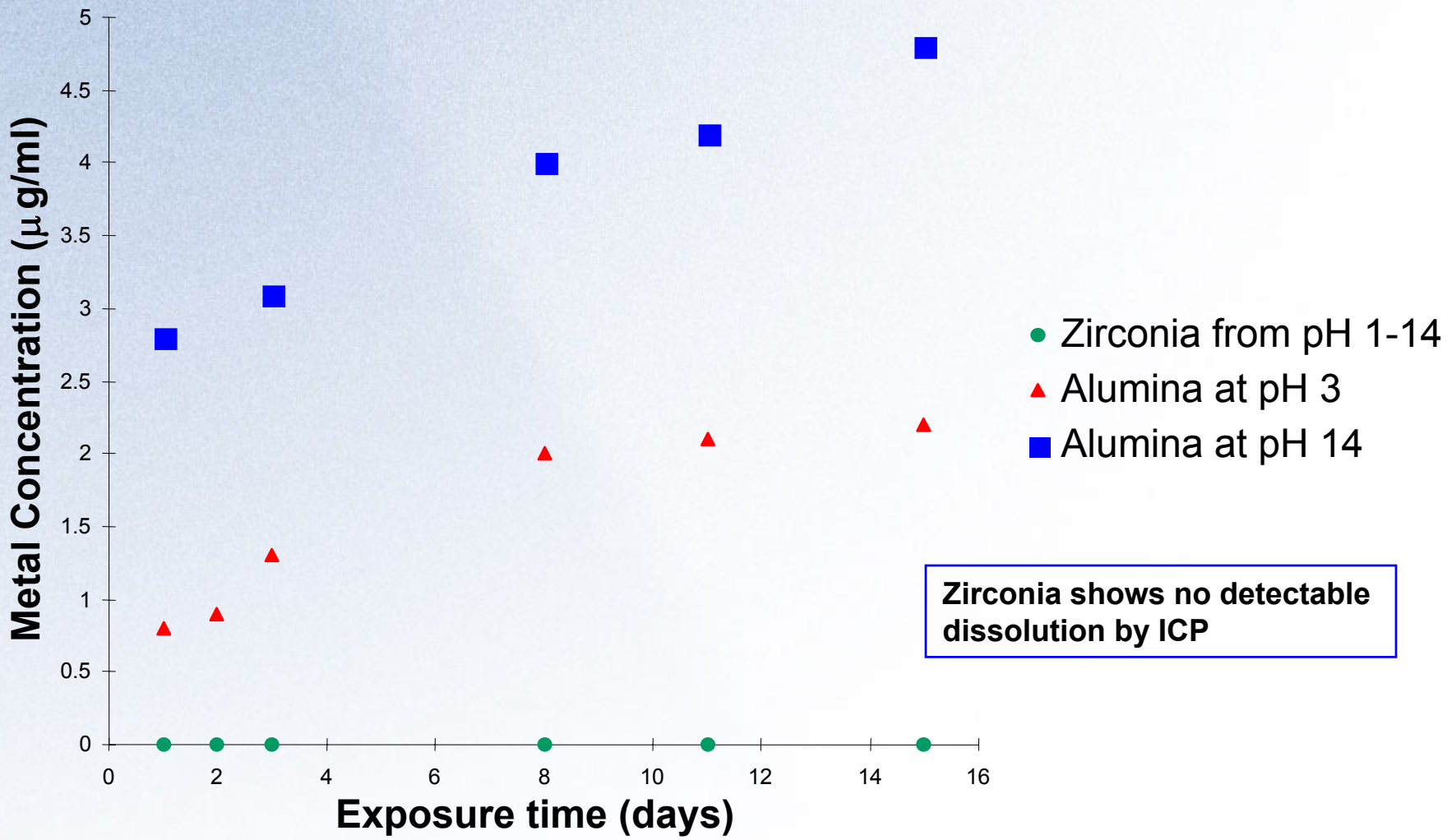
ZirChrom®-Carb and DiamondBond® -C18 particles are prepared by coating base particles with a thin layer of carbon using a chemical vapor deposition process

Characteristic	Property
Surface Area (m^2/g)	22
Pore Volume (cc/g)	0.13
Pore Diameter (Å)	250-300
Porosity	0.45
Density (g/cc)	5.8 (2.5x silica)
Particle Diameters (µ)	3.0, 5.0, 10, 25





Chemical Stability of Zirconia



Retention and Selectivity Variables

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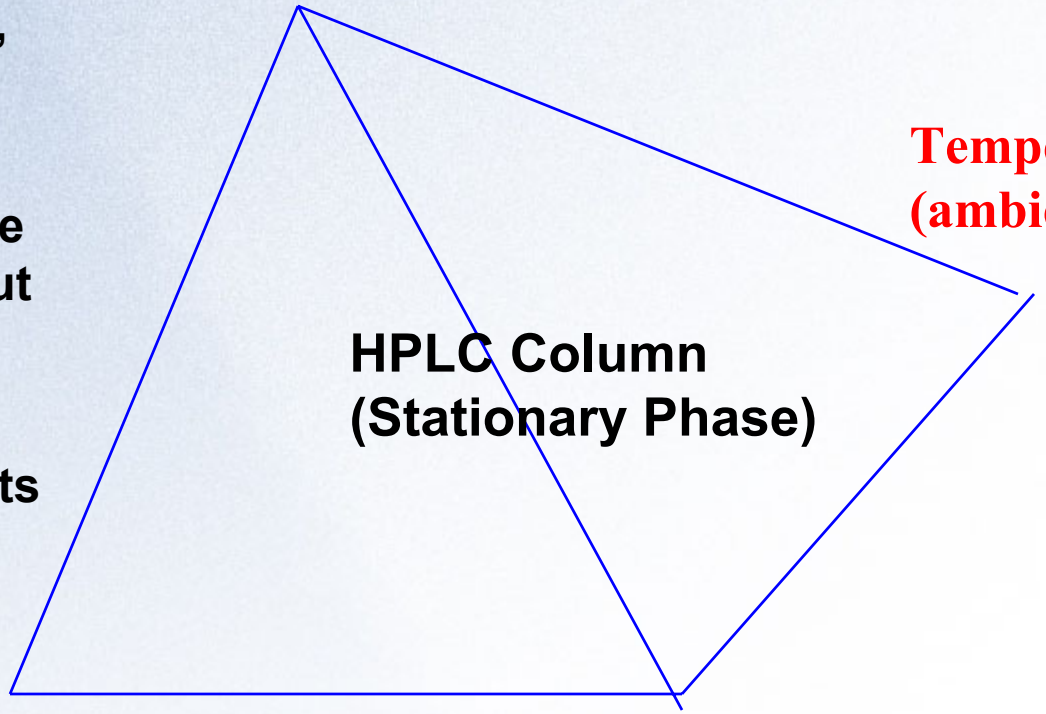
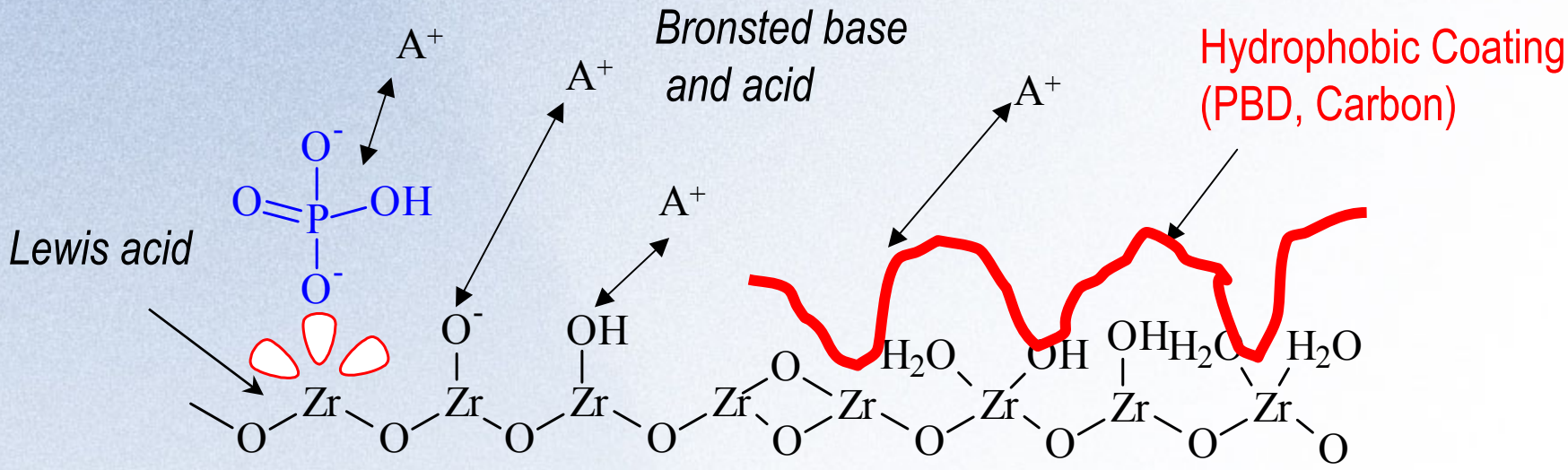
- Once an HPLC column is selected, there are four main variables to adjust.
- Temperature is the least often used, but may be the most convenient to try.
- Temperature affects both retention and selectivity.

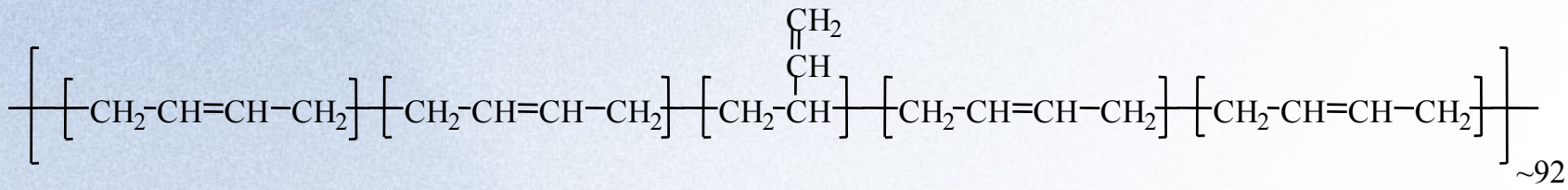


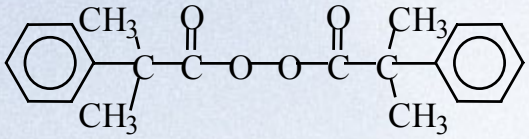
Zirconia Has Unique Surface Chemistry



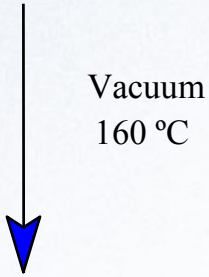
- **Zirconia by itself has very rich surface chemistry**
- **Coated zirconia phases (Carbon and PBD) have mixed surface properties**
- **The retention of various basic and acidic analytes can be fine tuned by changing pH, buffer and salt concentration, in addition to mobile phase modifier concentration and type**

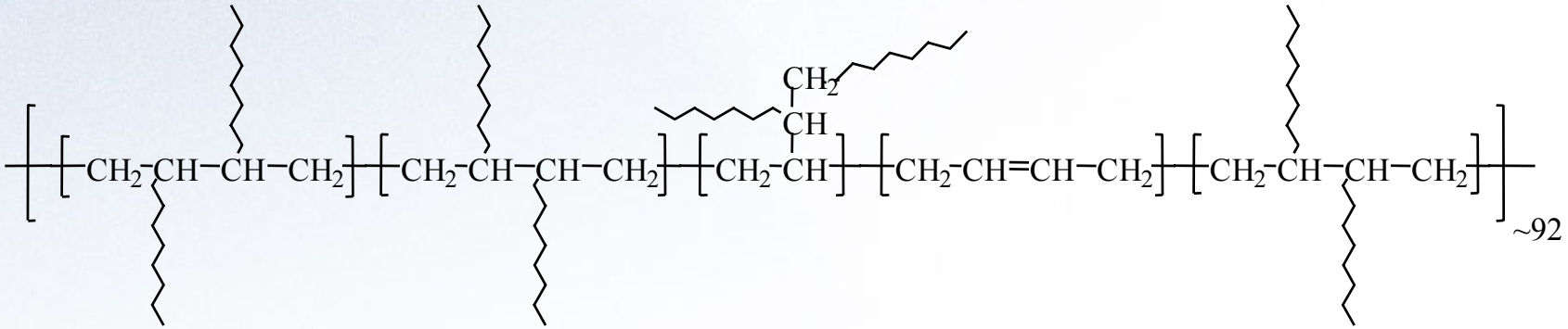
ZirChrom®-PBD
Polybutadiene coated zirconia





Dicumyl Peroxide

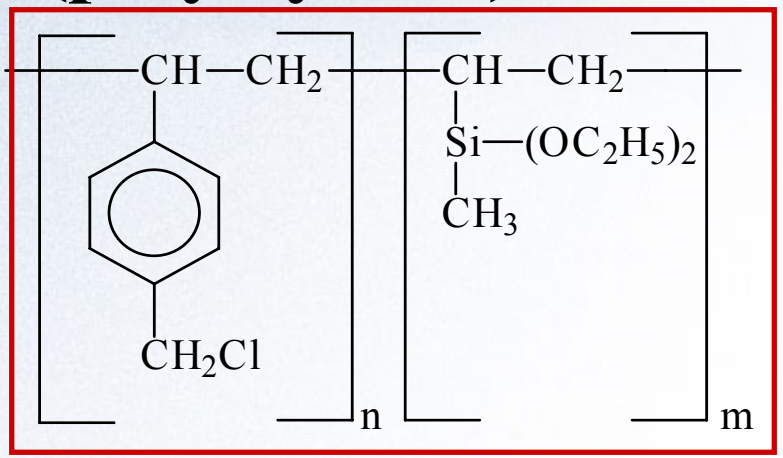




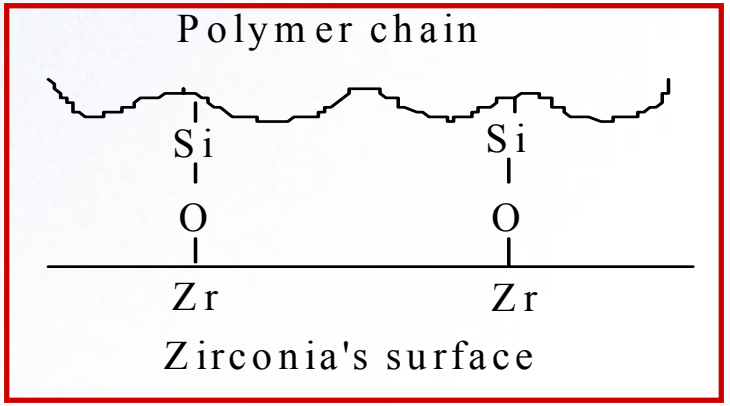
Synthetic Strategy for ZirChrom®-PS (polystyrene)

ZirChrom®

Step 1. Synthesis of Copolymer (CMS/DEMVS) with DCP



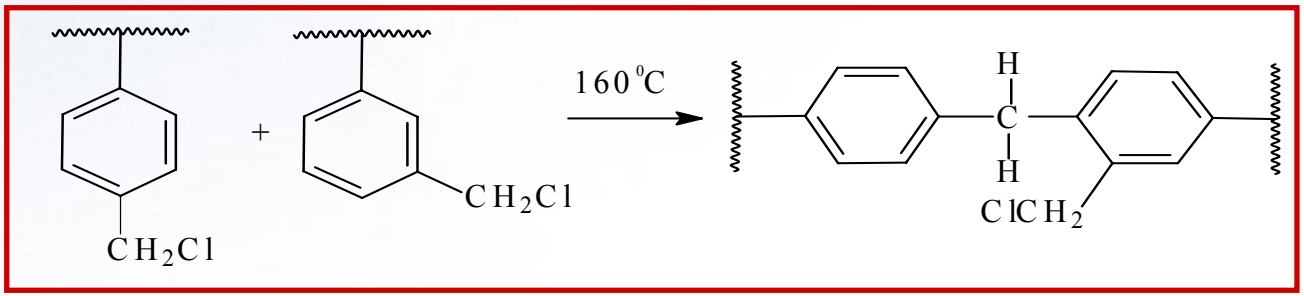
Step 2. Adsorption of Copolymer



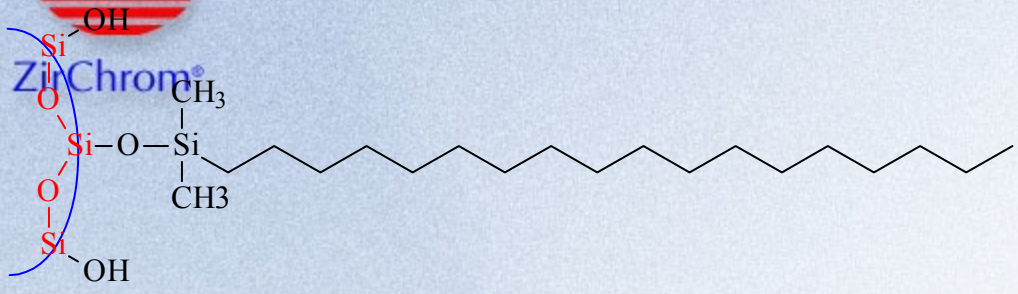
Step 3. Thermal Crosslinking

CMS/VMS-ZrO_2

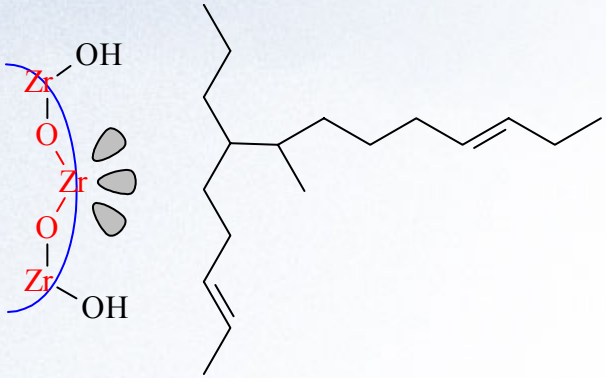
PS-ZrO_2



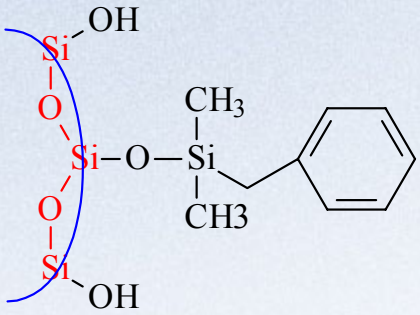
Structure of Stationary Phases



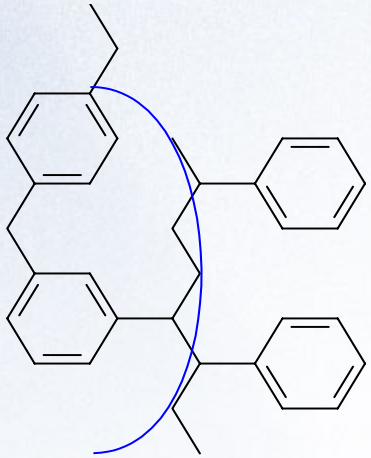
C18-SiO_2



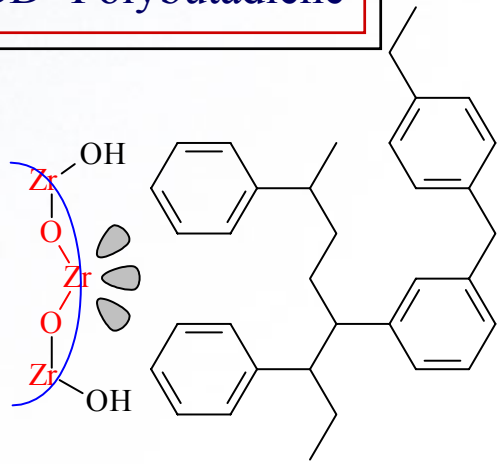
PBD-ZrO_2
PBD=Polybutadiene



Phenyl-SiO_2

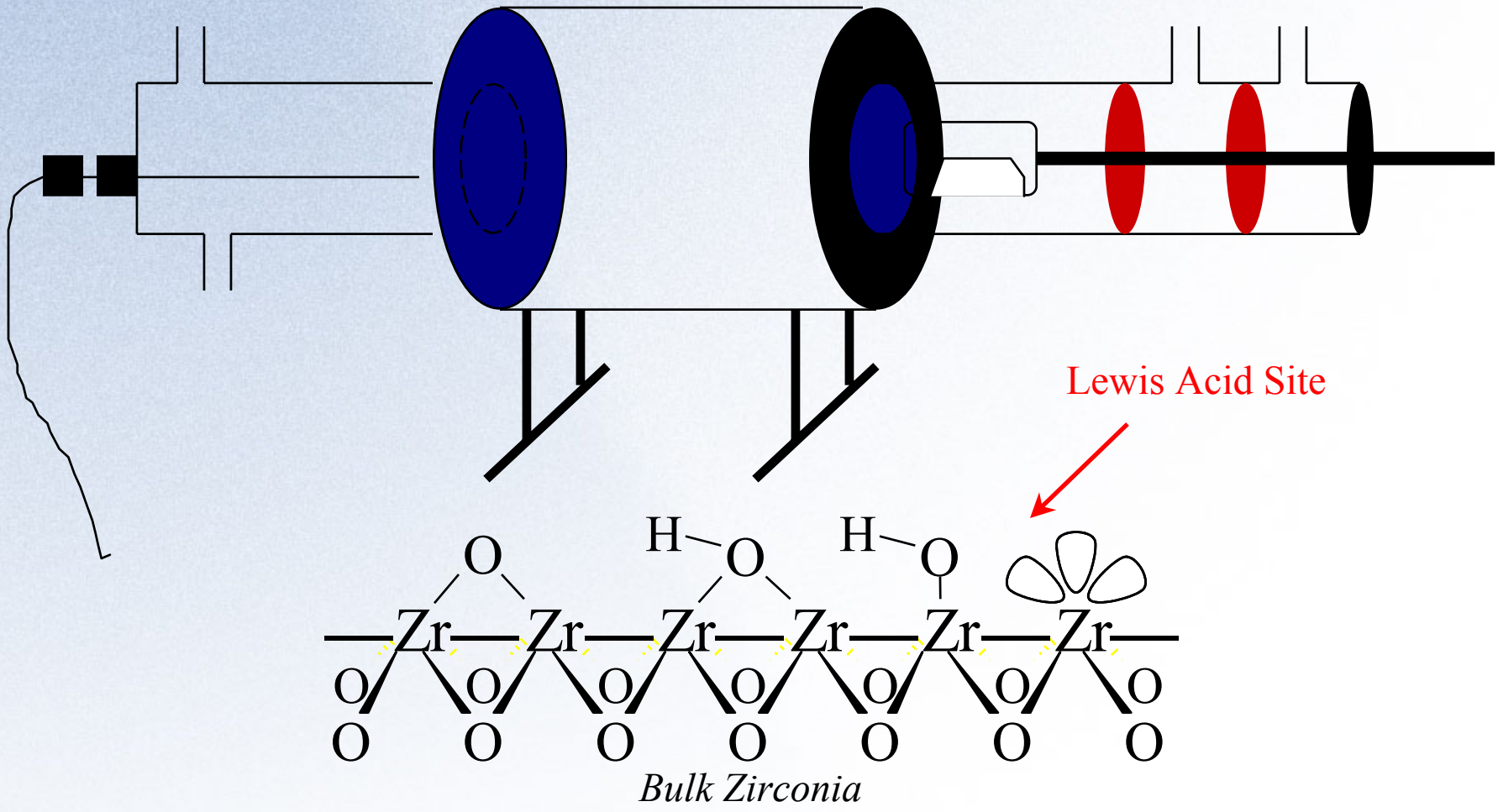


PRP-1
PRP=Polystyrene-Divinylbenzene



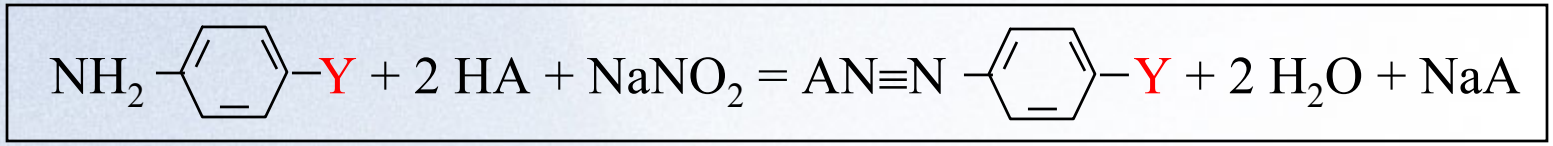
PS-ZrO_2
PS=Polystyrene

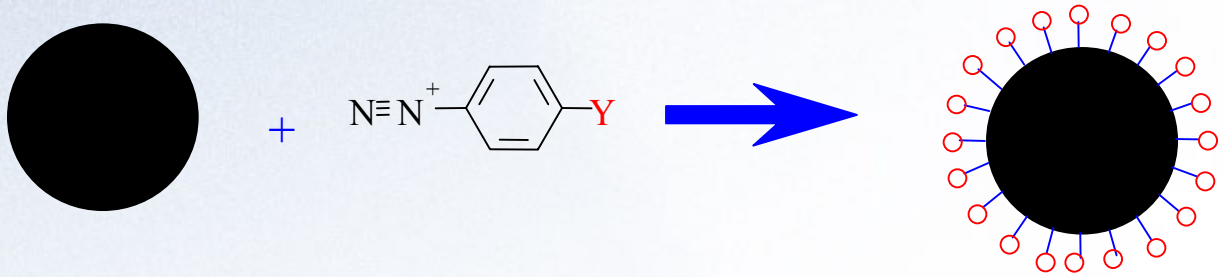
Synthesis of ZirChrom®-CARB - Carbon Clad Zirconia



DiamondBond: A New Class of Stationary Phase Media

- General approach - Cabot Corporation (Billerica, MA):
  - functionalizing agent X-R-Y
  - X reacts with surface
  - Y = functional group
- X is typically a diazonium salt





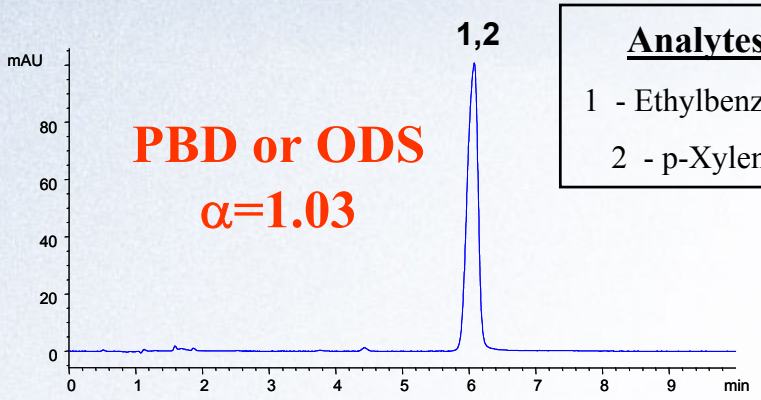
Carbon Clad Zirconia Diazonium Salt Modified Carbon Clad Zirconia

Carbon Has Unique Selectivity

LC Conditions

Column: ZirChrom®-PBD, 100 x 4.6 mm

Mobile phase: 35/65 A/B	Flow rate: 1.0 mL/min.
	Temperature: 30 °C
A: ACN	Injection volume: 5 µL
B: Water	Detection: 254 nm



Analytes

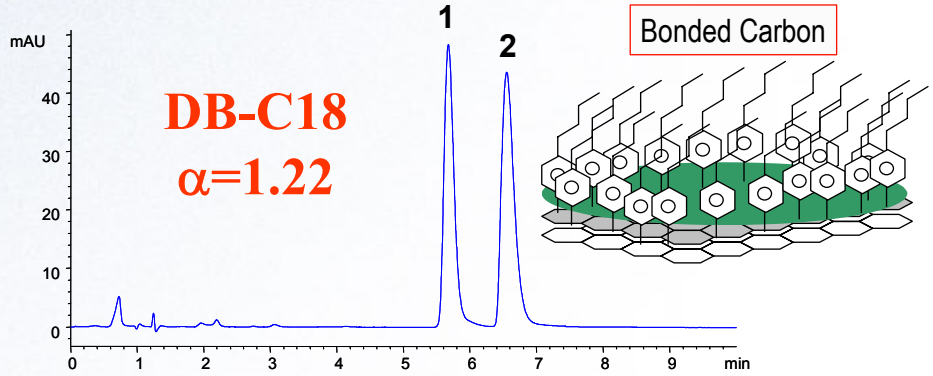
1 - Ethylbenzene

2 - p-Xylene

LC Conditions

Column: DiamondBond-C18, 100 x 4.6 mm

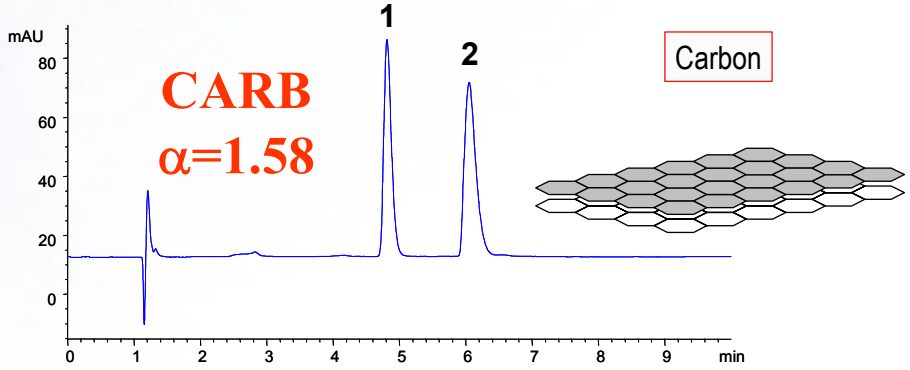
Mobile phase: 37.5/5/57.5 A/B/C	Flow rate: 1.0 mL/min.
	Temperature: 60 °C
A: ACN	Injection volume: 5 µL
B: THF	Detection: 254 nm
C: Water	



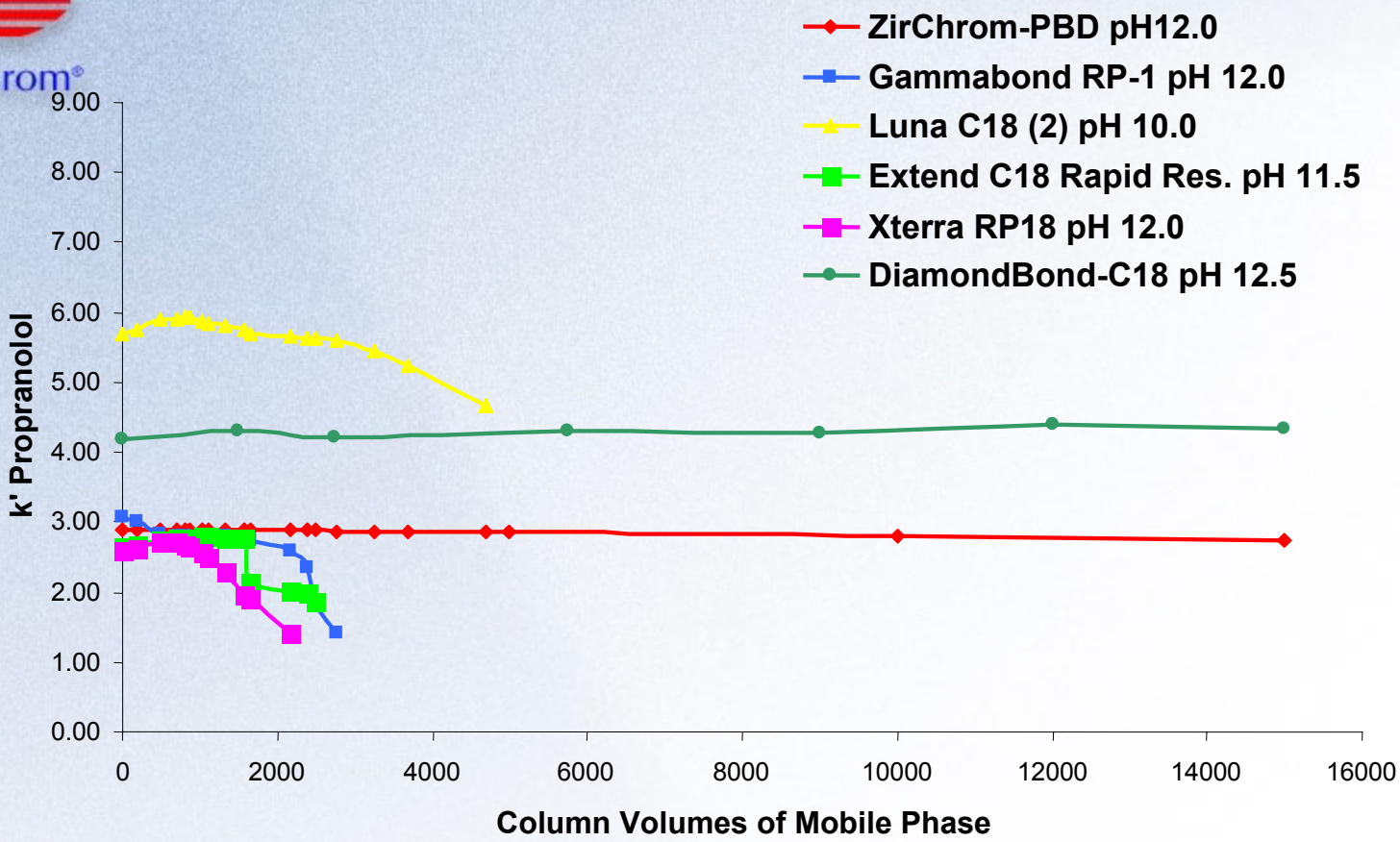
LC Conditions

Column: ZirChrom®-CARB, 100 x 4.6 mm

Mobile phase: 32.5/67.5 A/B	Flow rate: 1.0 mL/min.
	Temperature: 60 °C
A: ACN	Injection volume: 5 µL
B: Water	Detection: 254 nm



High pH Stability Comparison*



Exposure Conditions: Mobile phase, ACN/50mM Potassium phosphate buffer at indicated pH; Temperature, 30 °C.

LC Conditions: Mobile phase, ACN (or THF)/50mM Potassium phosphate buffer at indicated pH; Flow Rate, 1.0 mL/min.; Temperature, 30 °C; Injection Volume, 5 uL; Detection, 254nm.

* Column names are the trademarks of their respective manufacturers.

Increasing Separation Speed

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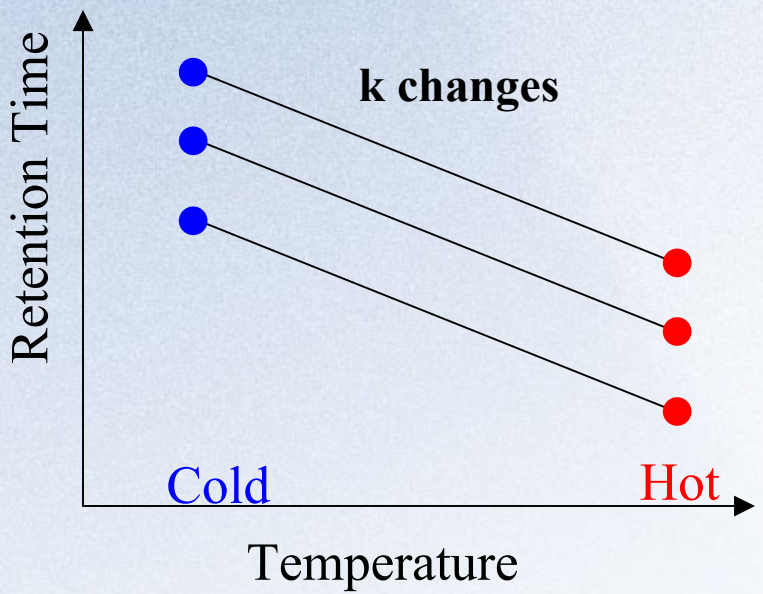
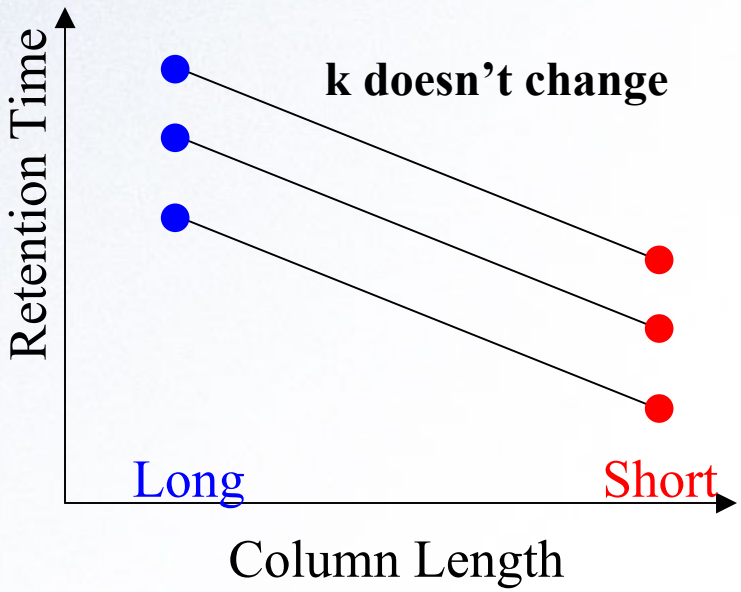
Column Temperature vs. Column Length vs. Flow Rate

T increases 50 °C ⇨ *k*' decreases 3-fold

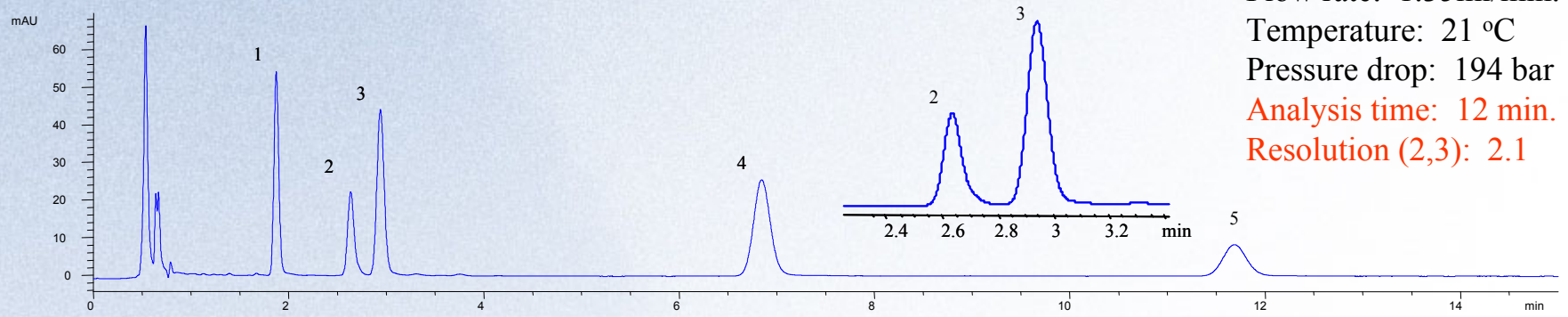




Increasing only flow rate to reduce retention time is the least desirable option because pressure increases and performance drops. Increasing temperature and decreasing column length are better ways to decrease retention time and speed up analysis; however, decreasing length reduces efficiency and resolution, while increasing temperature doesn't.

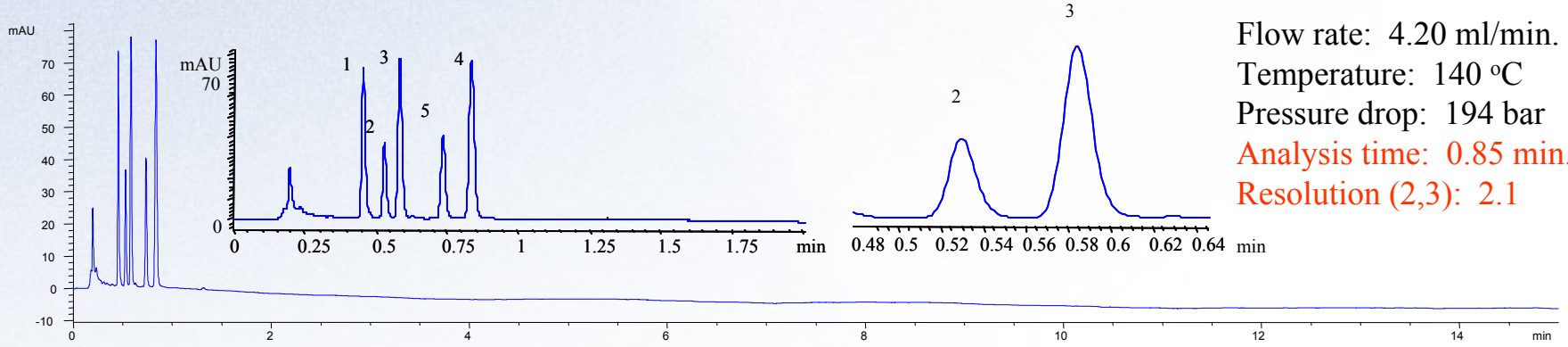
Decrease Analysis Time without Losing Resolution

LC Conditions Mobile Phase, 29/71 ACN/50mM Tetramethylammonium hydroxide, pH 12.2; Flow Rate, 1.35 mL/min; injection, Volume 0.5 microliters, Pressure drop = 195 bar; Solutes: 1=Doxylamine, 2=Methapyrilene, 3=Chlorpheniramine 4=Triprolidine, 5= Meclizine, Column dimension, 100 x 4.6 mm id ZirChrom-PBD, 254 nm detection.



Flow rate: 1.35ml/min.
Temperature: 21 °C
Pressure drop: 194 bar
Analysis time: 12 min.
Resolution (2,3): 2.1

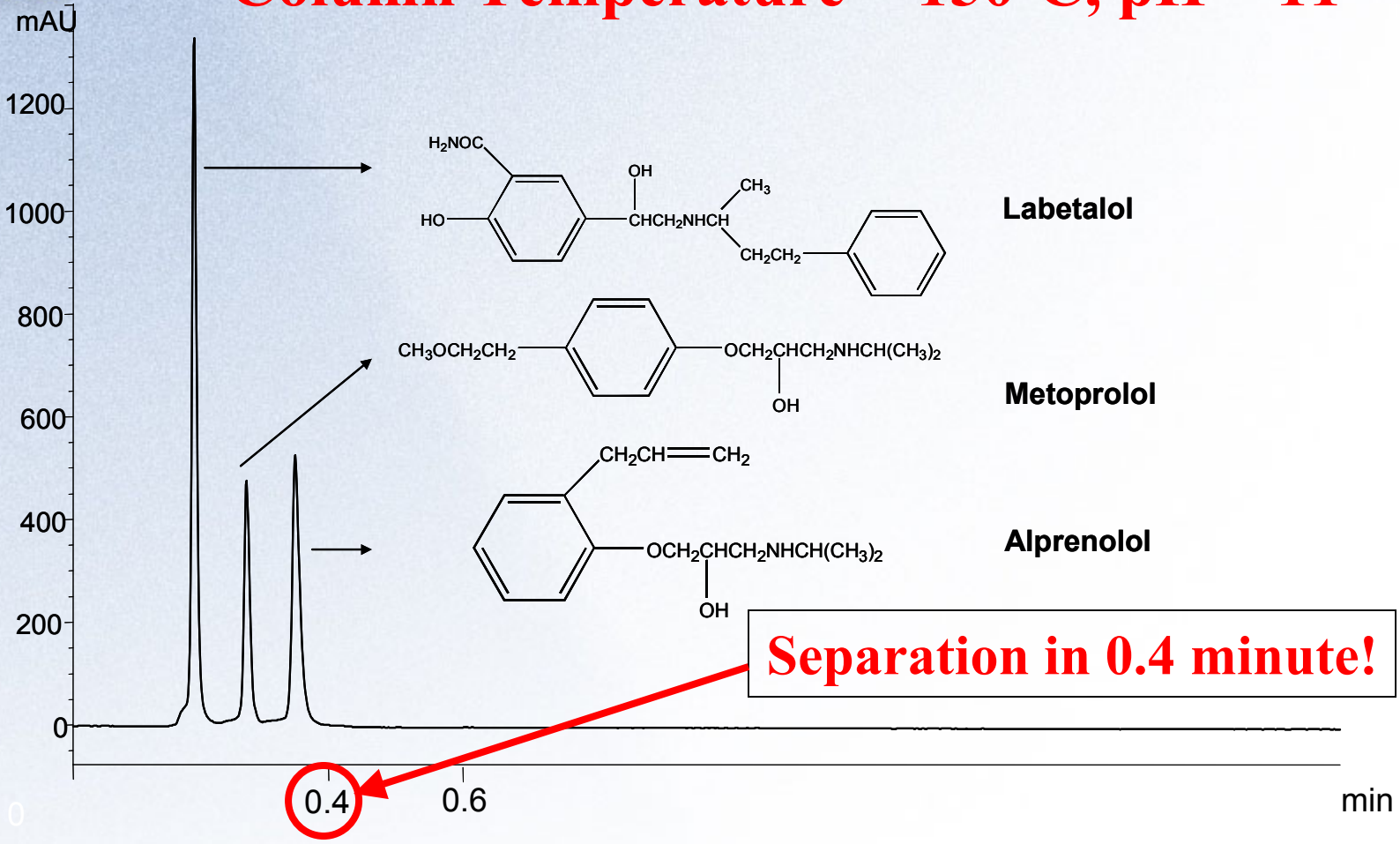
LC Conditions Mobile Phase, 20.5/79.5 ACN/50mM Tetramethylammonium hydroxide, pH 12.2; all other conditions the same as above.



Flow rate: 4.20 ml/min.
Temperature: 140 °C
Pressure drop: 194 bar
Analysis time: 0.85 min.
Resolution (2,3): 2.1

Fast β-Blockers Separation

Column Temperature = 150°C, pH = 11



LC Conditions: Column, 50 x 4.6 Discovery Zr-CarbonC18 , OD0121601A; Mobile phase, 45/55 ACN/20mM Ammonium Phosphate pH11.0; Flow rate, 3.0 ml/min; Temperature, 150 °C; Injection volume, 1.0 ul; Detection at 210 nm; Solutes, 1=Labetalol, 2=Metoprolol, 3=Alprenolol

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