The Development of ZrO_2 Based HPLC: From Colloid to Column

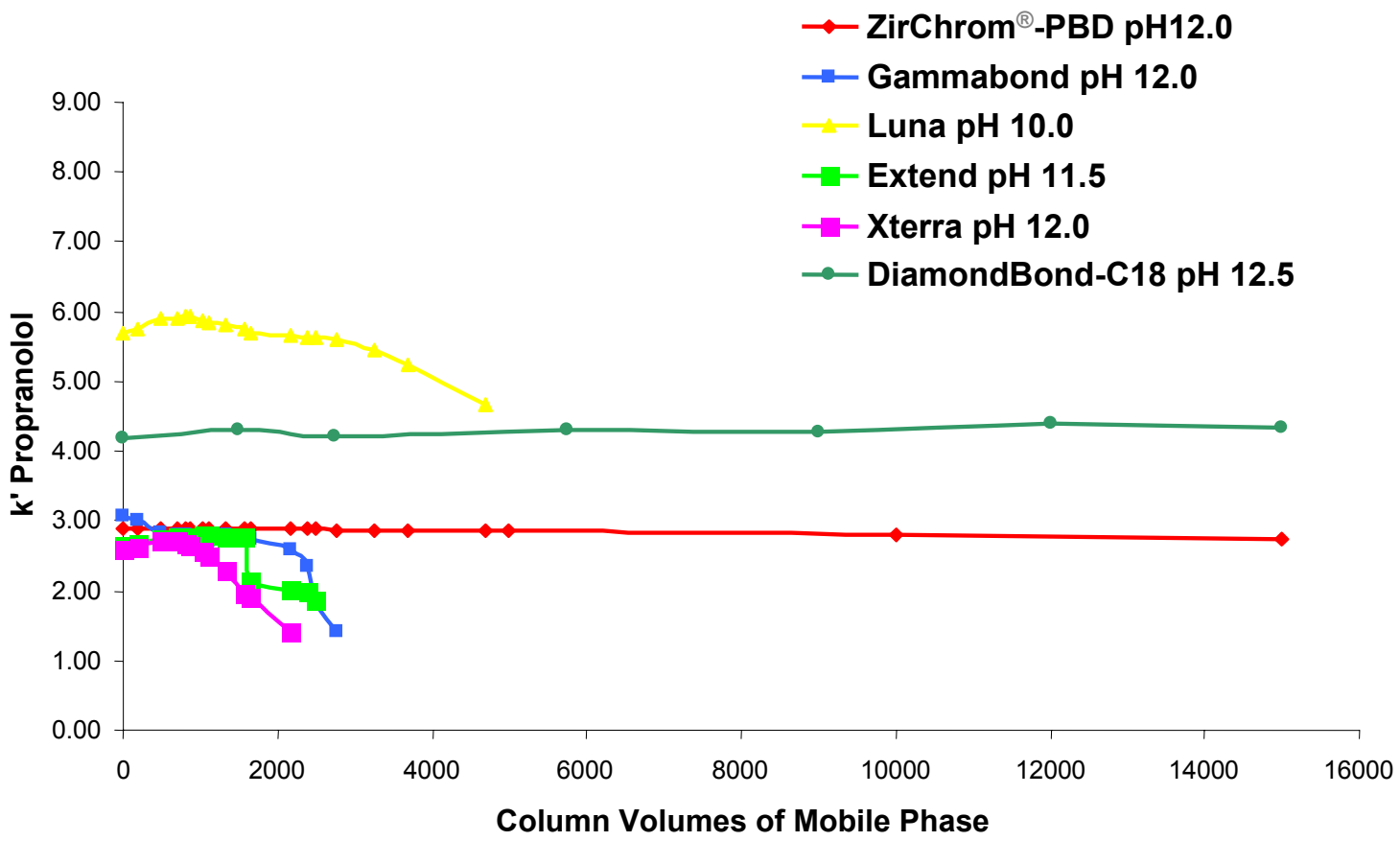
Department of Chemistry

University of Minnesota

Outline

- **Colloid to particle.**
- **Stationary phase synthesis.**
  - Polybutadiene-ZrO_2
  - Polystyrene -ZrO_2
  - P-EDTA/PBD -ZrO_2
  - Carbon Clad -ZrO_2
- **Phase Properties.**
  - Stability
  - Selectivity
- **Network Polymer Silica Phases.**
  - Acid stability

High pH Stability Comparison

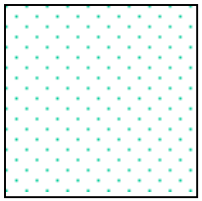


Exposure Conditions: Mobile phase, ACN/50mM Potassium phosphate buffer at indicated pH; Temperature, 30 °C.

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.

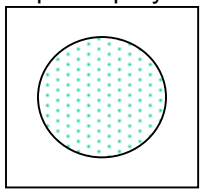
Methods of Making Spherical Particles from Colloids

Aqueous suspension of ceramic colloid

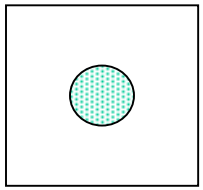


Spray drying

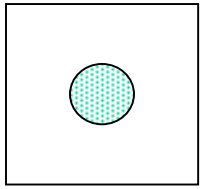
Droplets sprayed in air



Dried

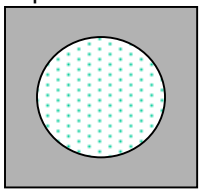


Sintered

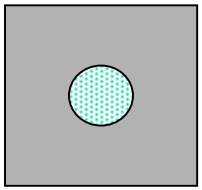


Oil emulsion

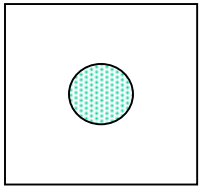
Droplets emulsified in oil



Water extracted into oil, dried

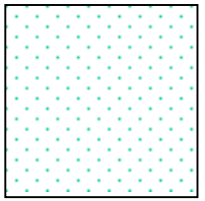


Washed, sintered

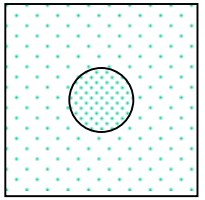


Polymerization

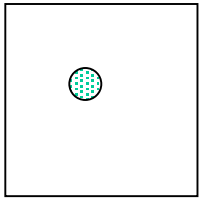
Water-soluble monomers added



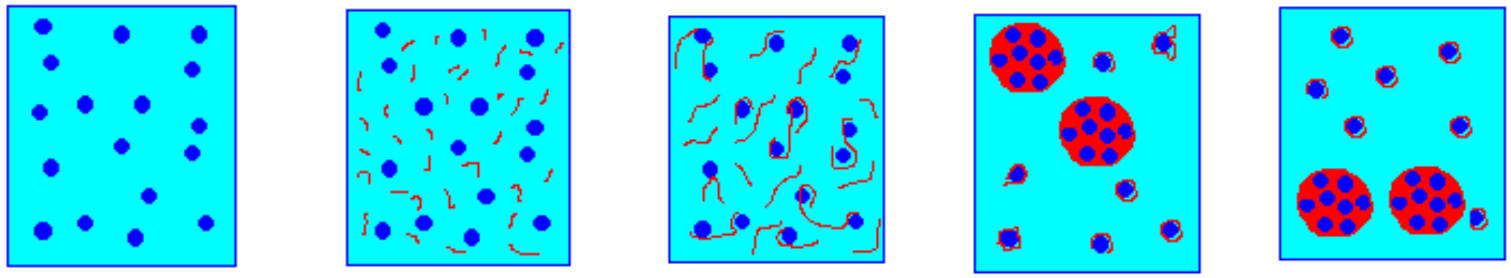
Polymer precipitated (collecting colloid)



Washed, polymer burned, remaining ceramic sintered



Polymerization-Induced Colloid Aggregation of Zirconia (PICA)

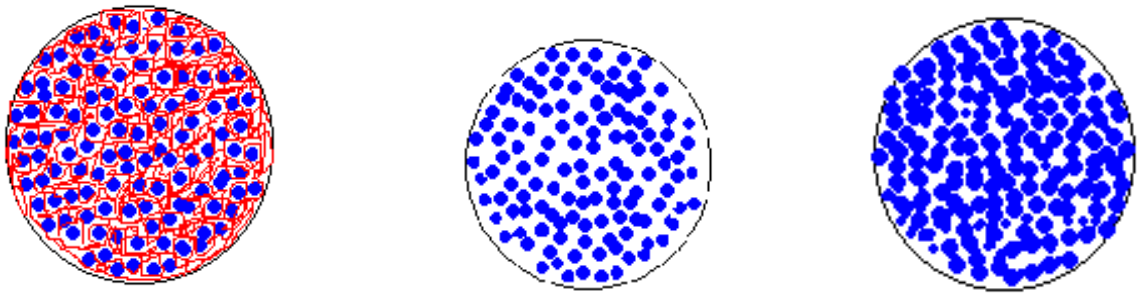


1000A sol
pH 1.5-1.8
20 wt% solids

urea (7.5 g/l sol)
formaldehyde
8:1 vol ratio
sol:formaldehyde

15-30 min.

Dilute and
collect
by filtration

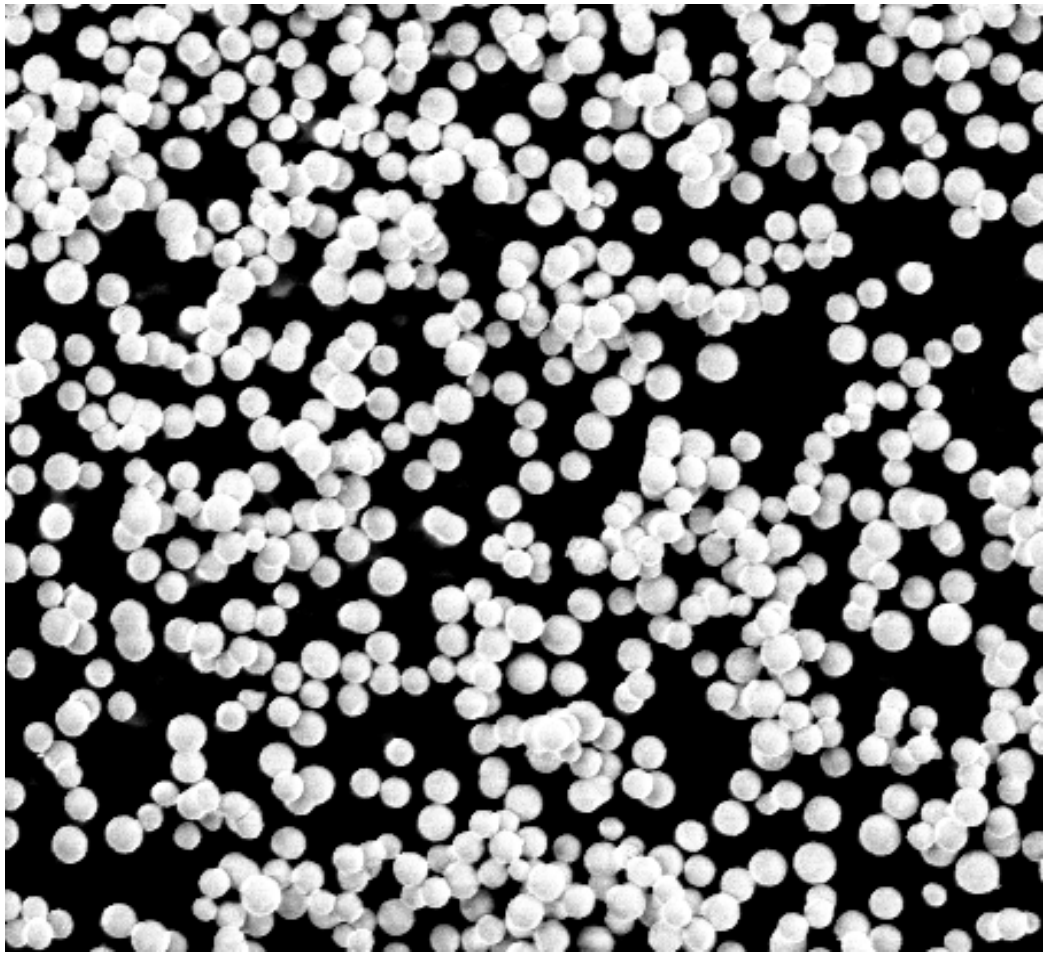


175°C, 3 days,
vacuum drying

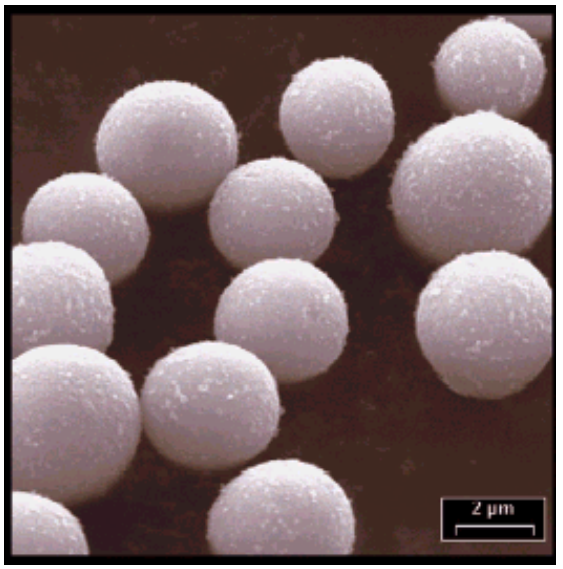
375°C, 2h,
air burn

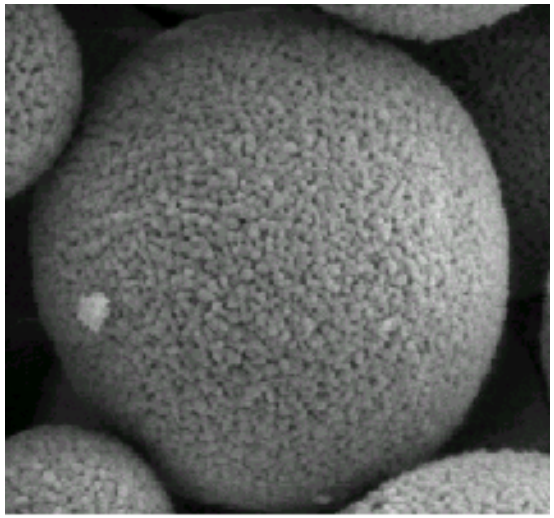
Sinter and harden
750°C, 3h
900°C, 6h

SEM of Porous Zirconia



3.0 μ





1μm 25000X

Particles are **monodisperse and spherical as formed!**

Properties of PICA 7

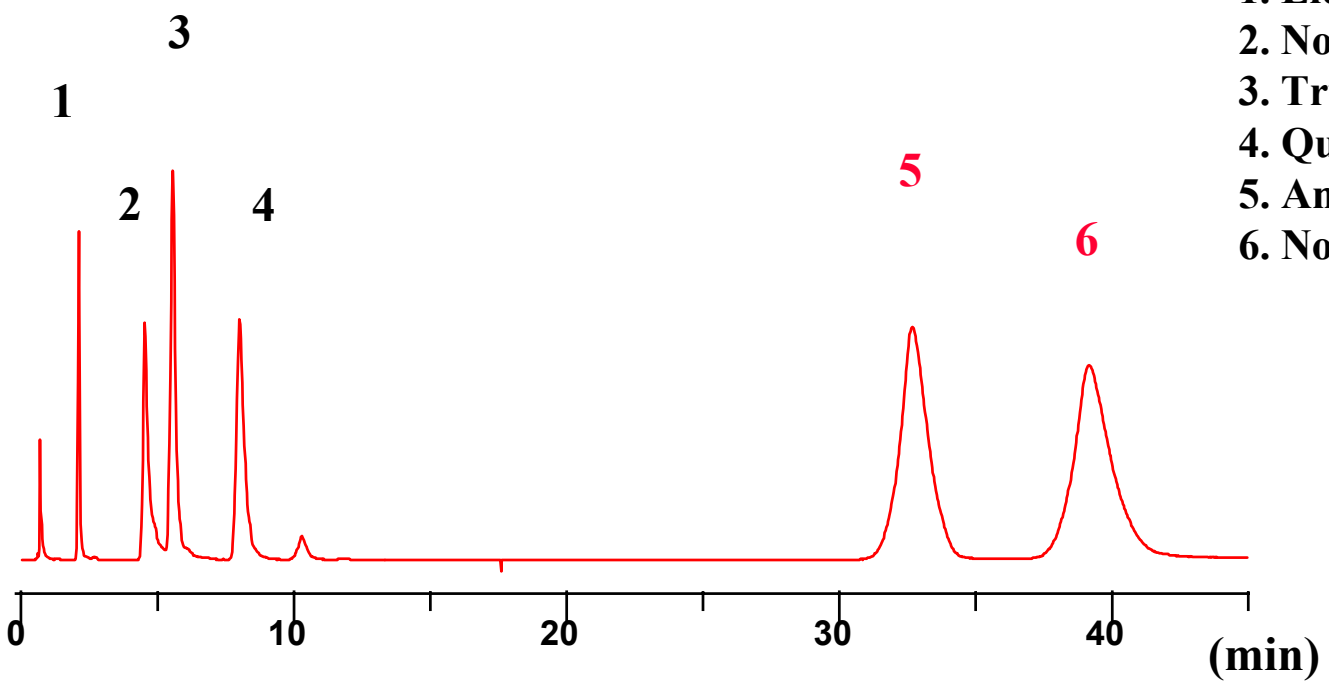
Characteristic	Property
Surface area(m^2/g)	30
Pore volume (cc/g)	0.5
Pore diameter (A)	250-300
Porosity	0.5
Density (gm/cc)	5.8
Particle diameter (μ)	2.5

Deposition of Polybutadiene (PBD)

- Suspend zirconia particles in hexane solution containing PBD and dicumyl peroxide.
- Sonicate the slurry with vacuum for 5 minutes.
- Rotate the slurry at 20 rpm for 2 hours.
- Remove hexane by vacuum at 36 ºC.
- Cross-link PBD in vacuum oven at 160 ºC for 4 hours.
- Extract particles with toluene for 12 hours.

Performance

Separation on PBD-Zirconia

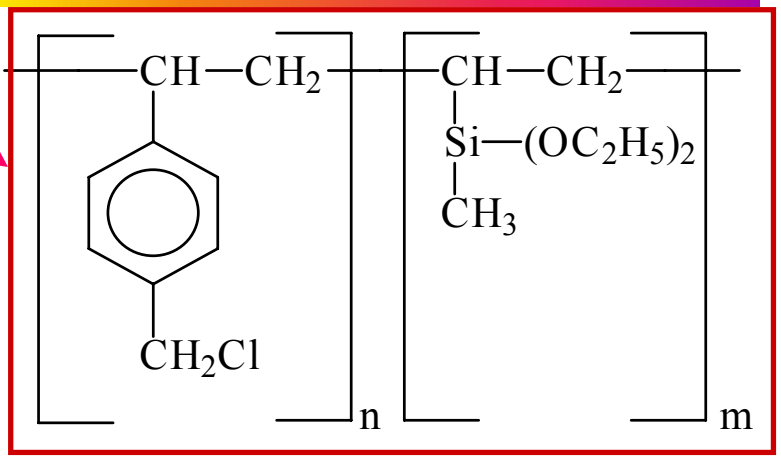


1. Lidocaine
2. Norpseudoephedrine
3. Tryptamine
4. Quinidine
5. Amitriptyline
6. Nortriptyline

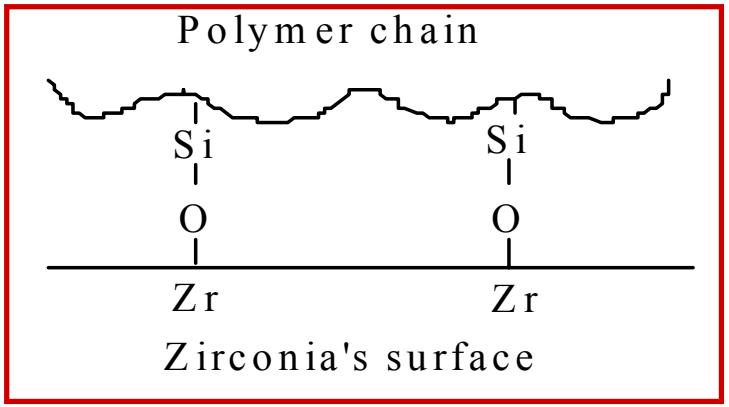
20% ACN, 20 mM ammonium phosphate, pH 7.5; 0.8 mL/min; 30 °C

Polystyrene-ZrO_2 Synthetic Strategy

Step 1. Synthesis of Copolymer (CMS/VMS)



Step 2. Adsorption of Copolymer

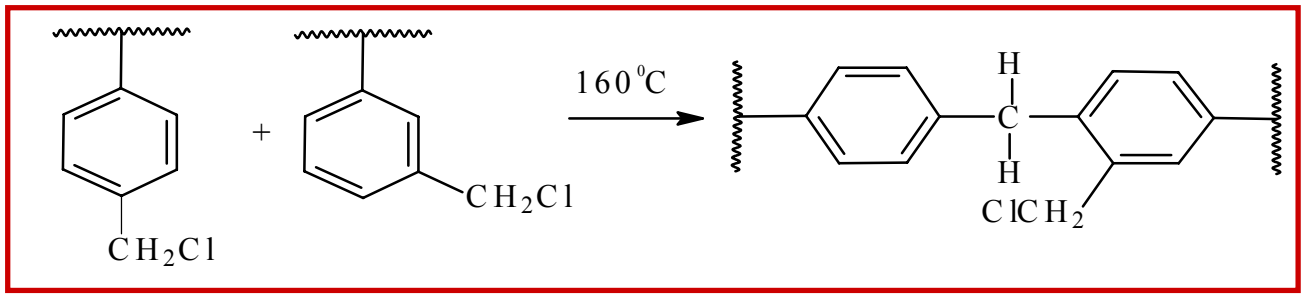


Step 3. Thermal Crosslinking

$CMS/VMS-ZrO_2$

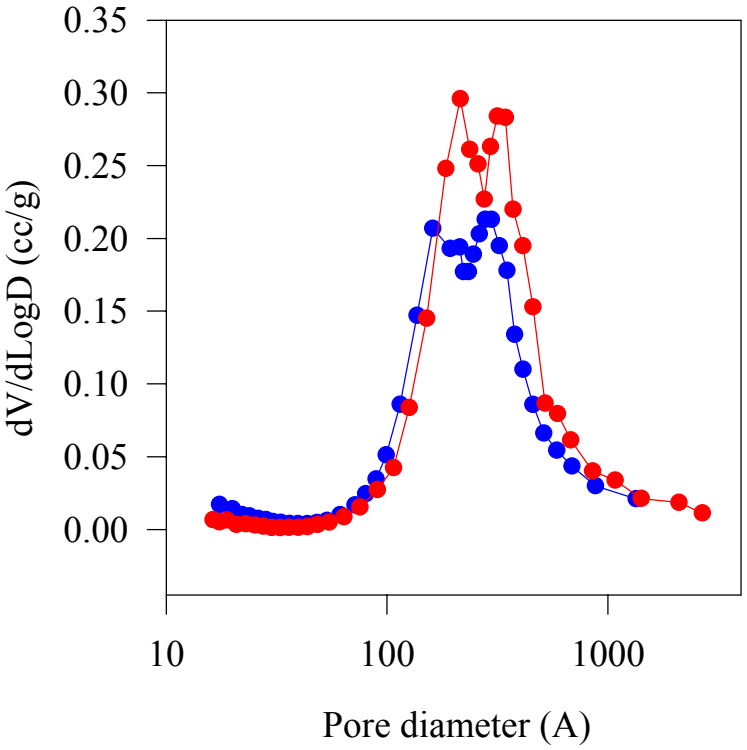
‖

$PS-ZrO_2$

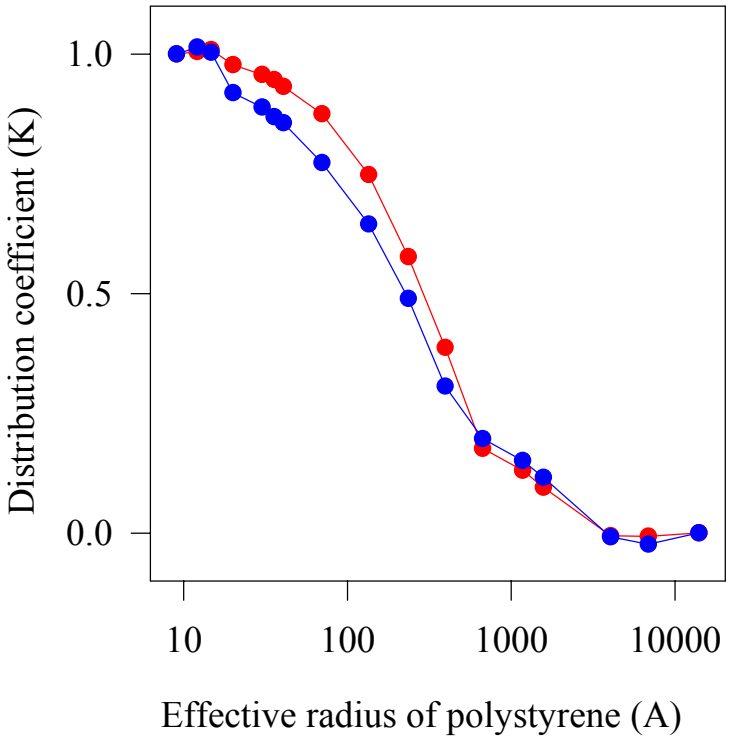


Pore Size Distribution

Nitrogen Porosimetry



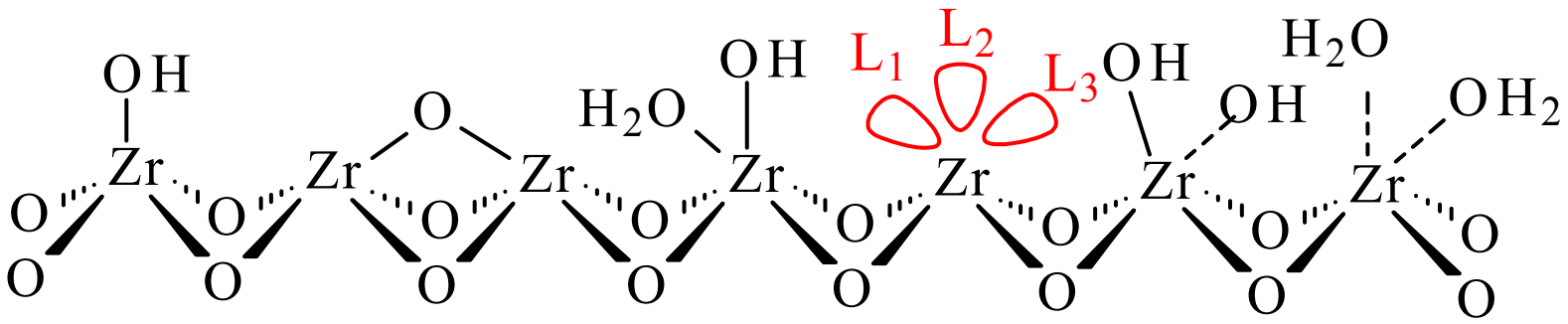
Size Exclusion Chromatography



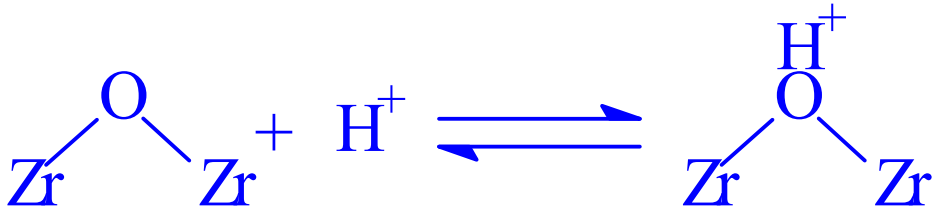
- Bare Zirconia
- PS-ZrO_2

- **no significant change in pore size distribution.**

Nature of Zirconia's Surface

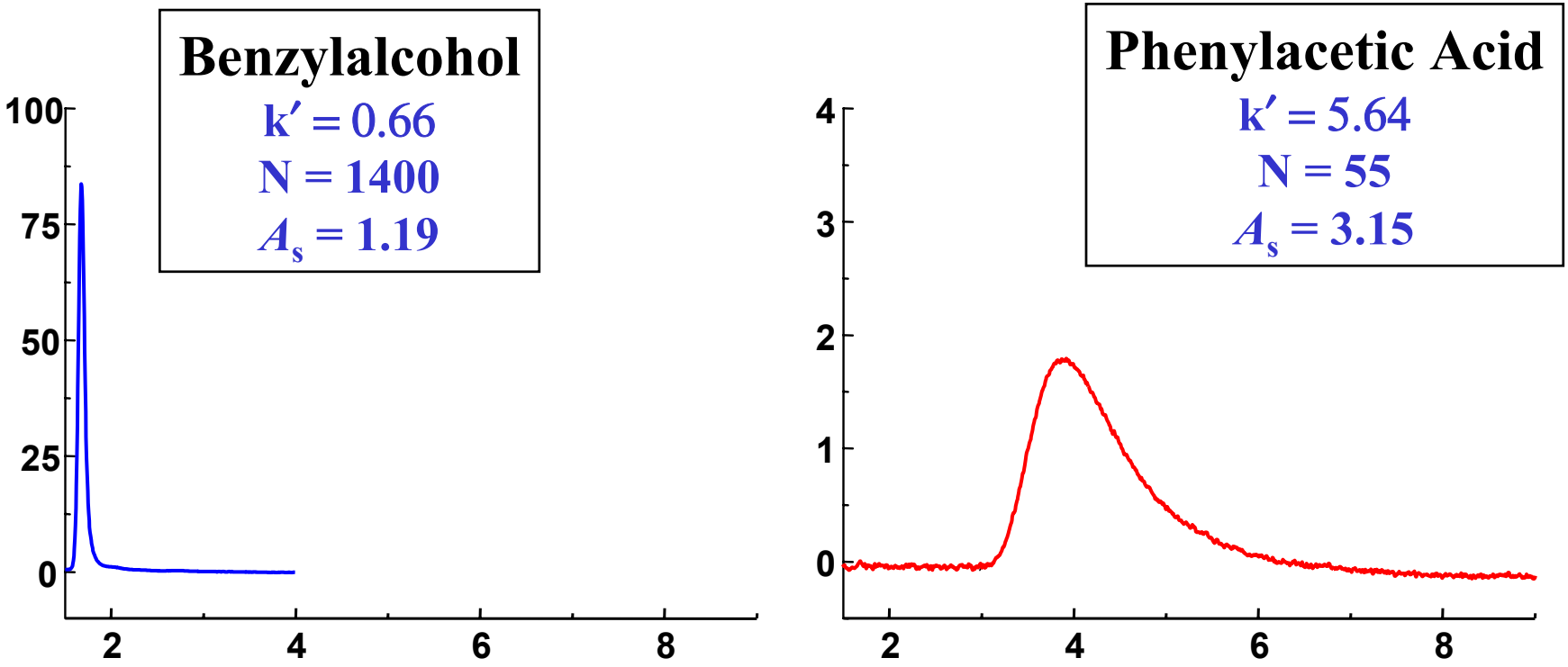


Brönsted Acid: $ZrOH + OH^- \rightleftharpoons ZrO^- + H_2O$

Brönsted Base: 

Lewis Acid: $Zr(OH_2) + {}^-OOC-R \rightleftharpoons ZrOOC-R + H_2O$

Acidic Analytes on PBD-ZrO_2

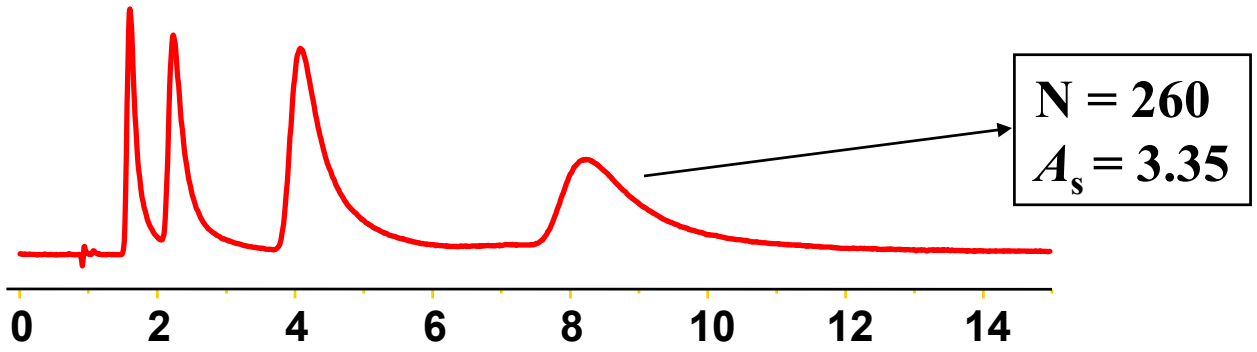


Acidic Analytes: Long Retention and Low Efficiency

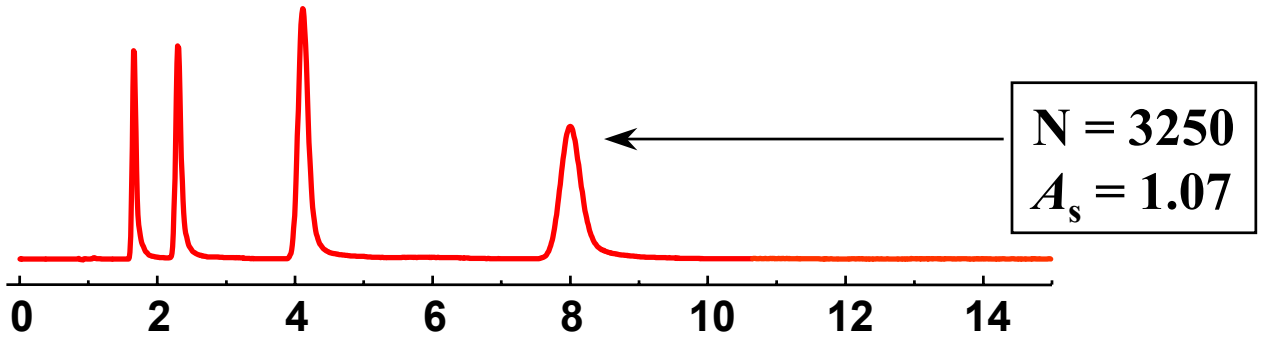
10% ACN, 0.3 M acetic acid, pH 2.4; 30 °C; 1 mL/min.

Effect of Eluent on Alkoxybenzoic Acids

40 mM Acetate pH 4

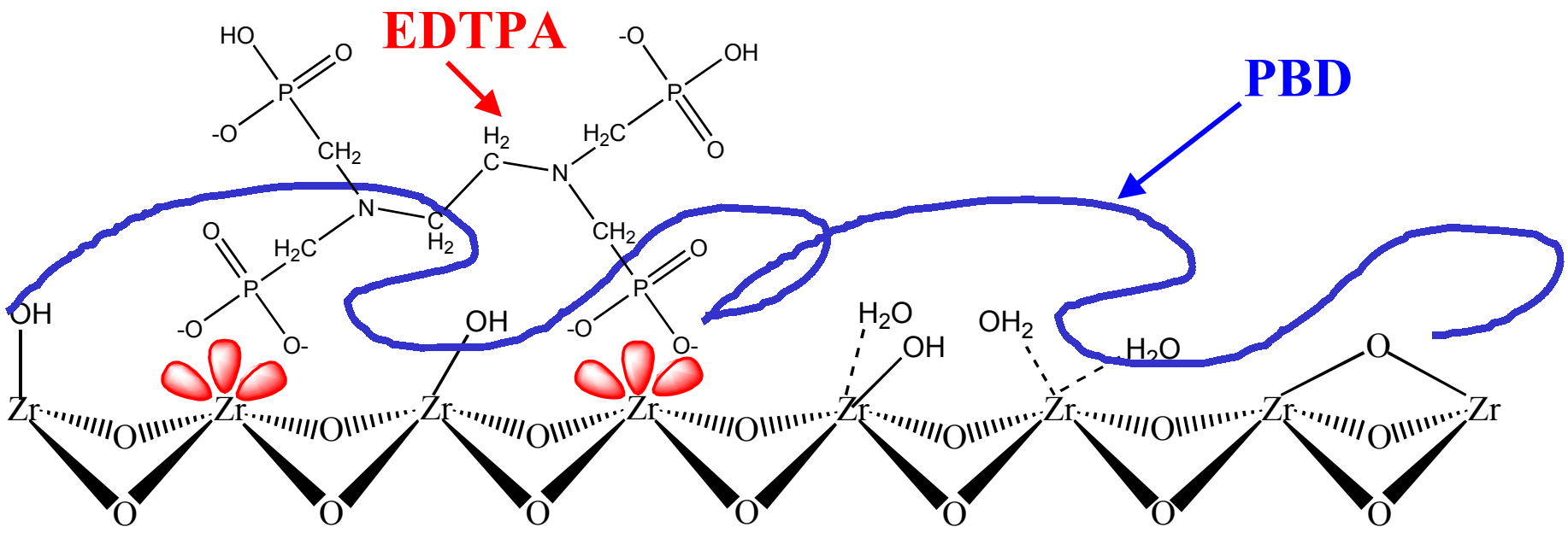


40 mM Phosphate pH 2.15



25% ACN, 40 mM above additive, 5 mM NH_4F; 0.6 mL/min; 30 °C; 254 nm.

Lewis Acid Sequestered Phase Synthesis



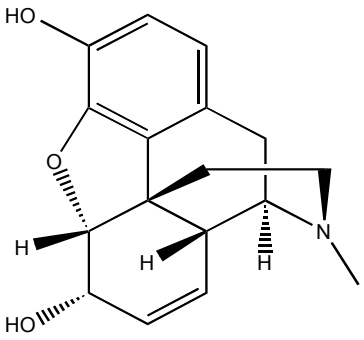
1. Coat bare zirconia with polybutadiene (PBD).
2. PBD Crosslinking using dicumyl peroxide as initiator.

3. Reflux PBD-ZrO_2 in Ethylenediamine N,N,N',N' tetra(methylenephosphonic) acid (EDTPA) solution.

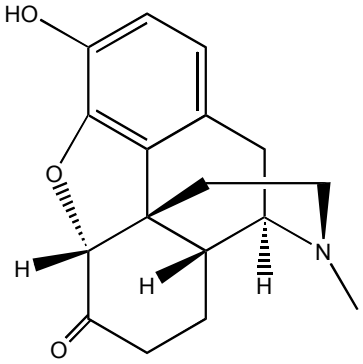
4. Wash to remove residual EDTPA.

Courtesy ZirChrom

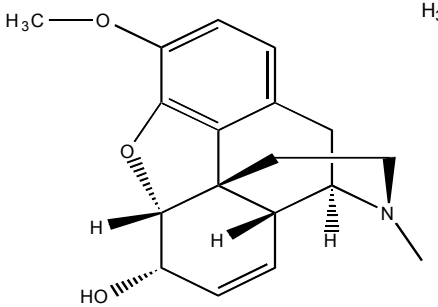
LC-MS Compatible Phase for Bases



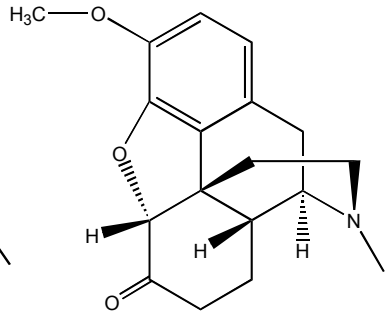
Morphine
M.W. 285.33



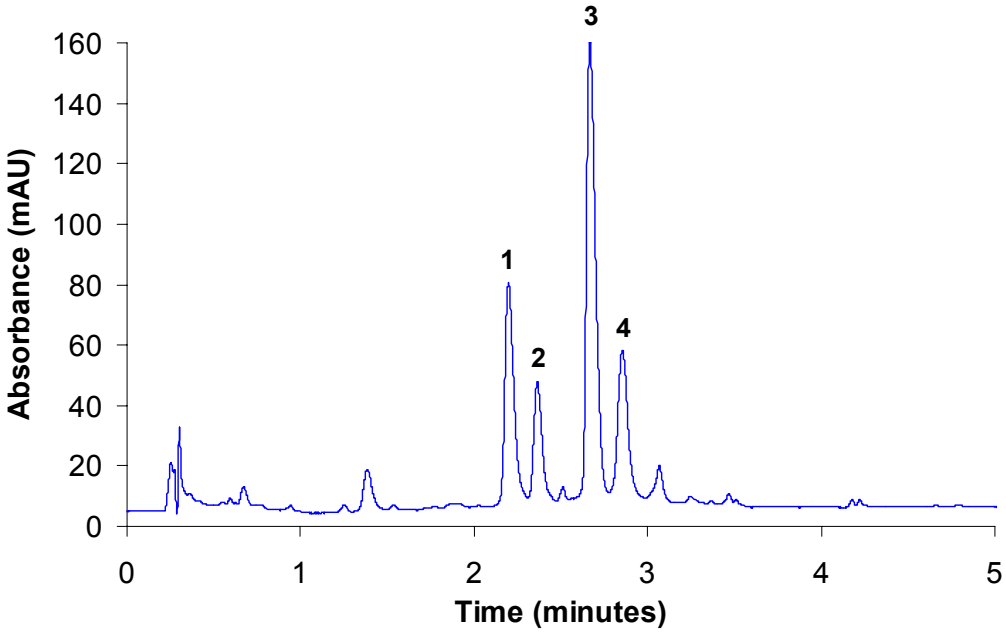
Hydromorphone
M.W. 285.33



Codeine
M.W. 299.36



Hydrocodone
M.W. 299.36

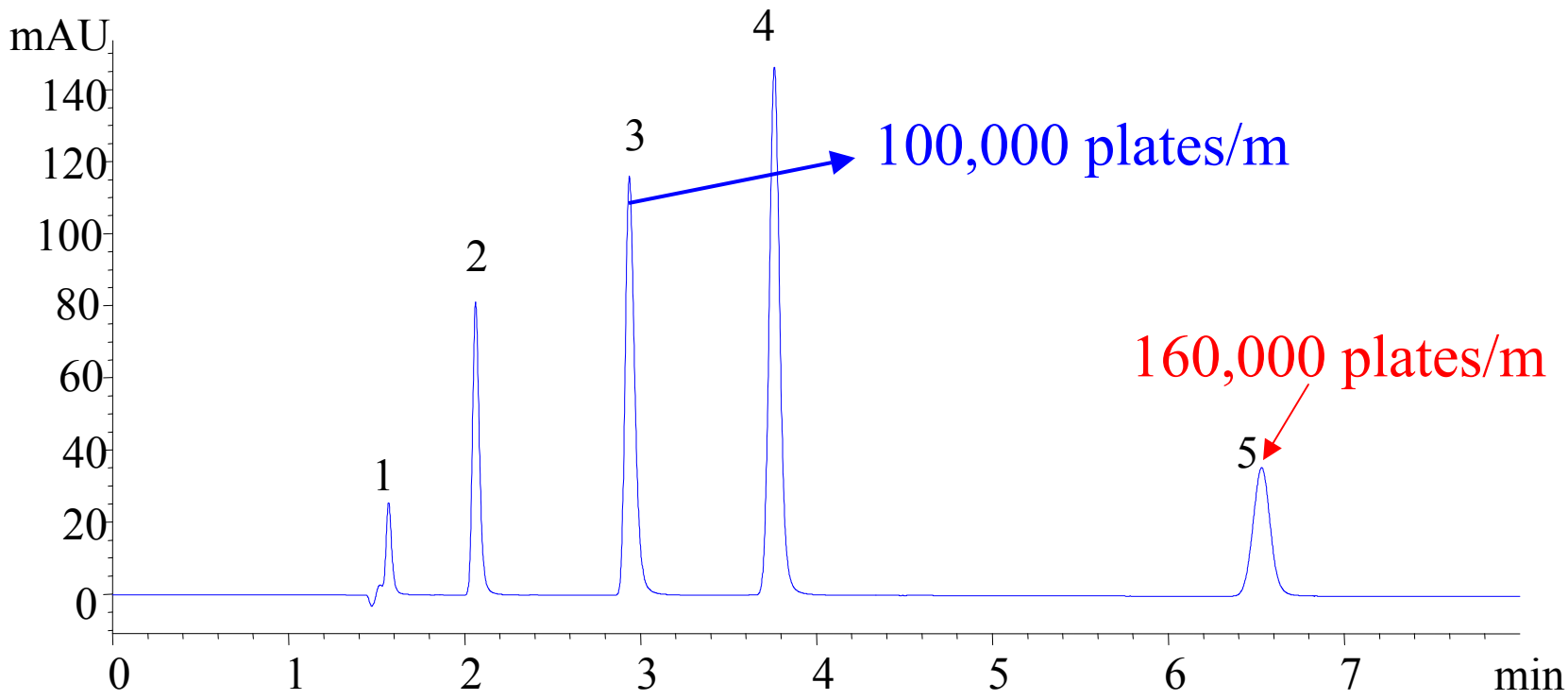


Time (min.)	%A	%B
0	90	10
5	10	90

LC Conditions: Column, 50 mm x 4.6 mm i.d. **ZirChrom-EZ**; Mobile phase, A = 20mM ammonium acetate, pH 6.0, B = ACN; Flow rate, 2.00 ml/min.; Temperature, 35 °C; Injection volume, 10 µl; Detection at 254 nm.; Solutes: 1=Morphine, 2=Hydromorphone, 3=Codeine, 4=Hydrocodone

Courtesy ZirChrom

Column Efficiency



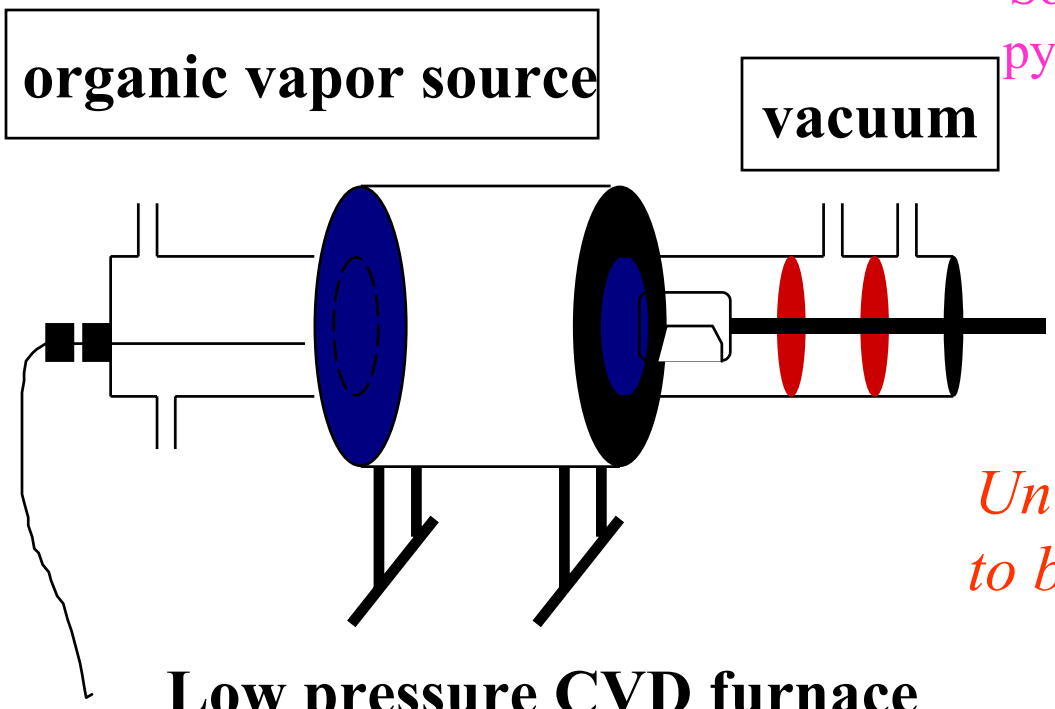
LC Conditions: Column, 150 mm x 4.6 mm i.d. **ZirChrom-EZ**; Mobile phase, 35/65 ACN/Water, Temperature, 30 °C; Injection volume, 5 µl; Detection at 254 nm.; Solutes: 1=Acetone, 2=Phenol, 3=4-Chlorophenol, 4=Anisol, 5=Toluene

Courtesy ZirChrom

Carbon Coating of ZrO_2 by CVD

Phase Synthesis

- Place zirconia particles in reactor tube
- Heat reactor to 700°C
- Flow organic vapor over hot zirconia particles
- Soxhlet extract phase to remove soluble pyrolysis products

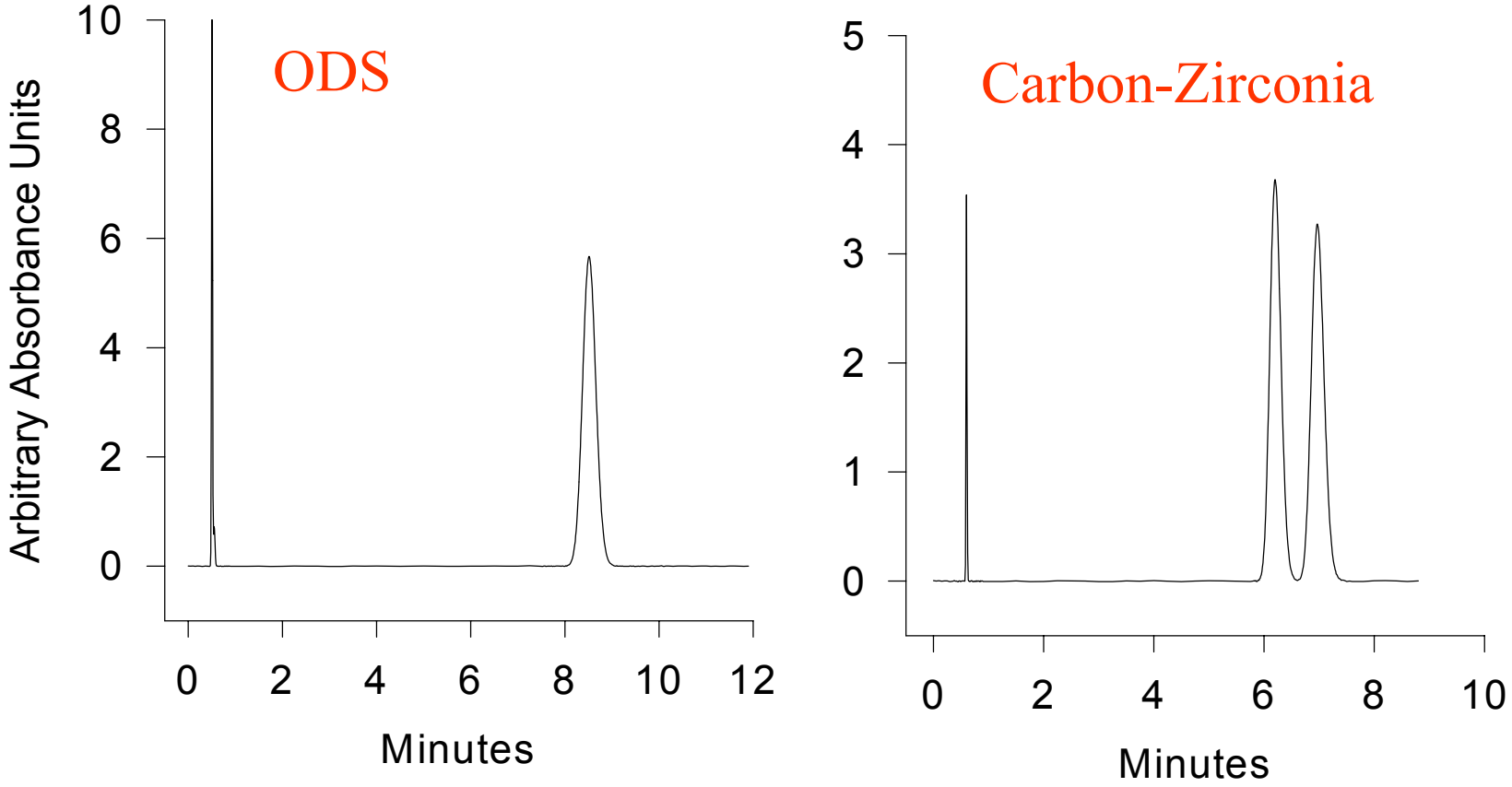


Low pressure CVD furnace

Unique selectivity compared to bonded or polymer-coated phases

Stereoisomer Selectivity: Carbon vs. Alkanes

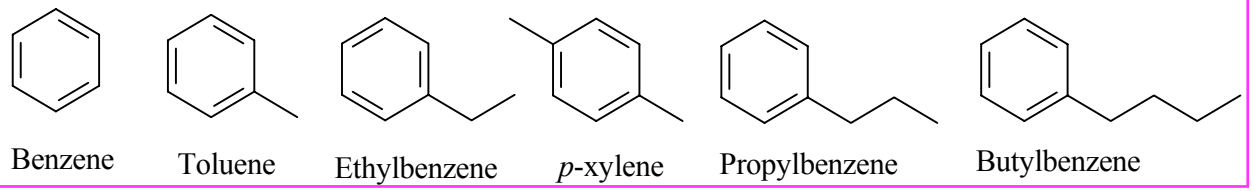
Stereoisomer Separation on Carbon-Zirconia



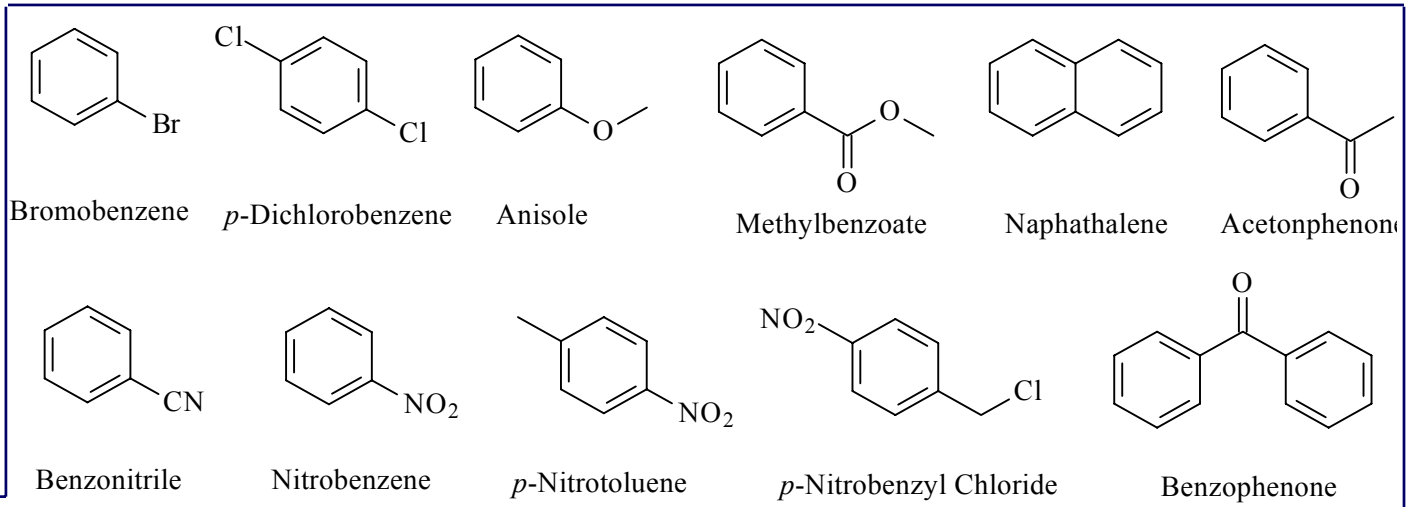
(±)-Warfarin-(R)-MTPA ester

Non-electrolyte Probes

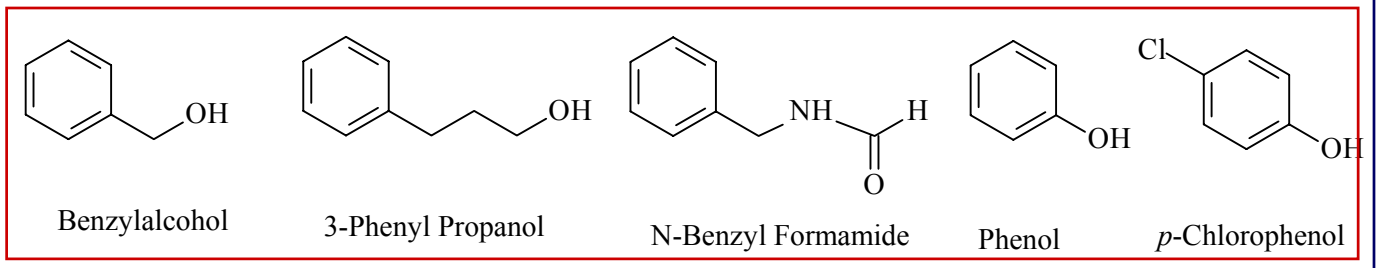
Nonpolar



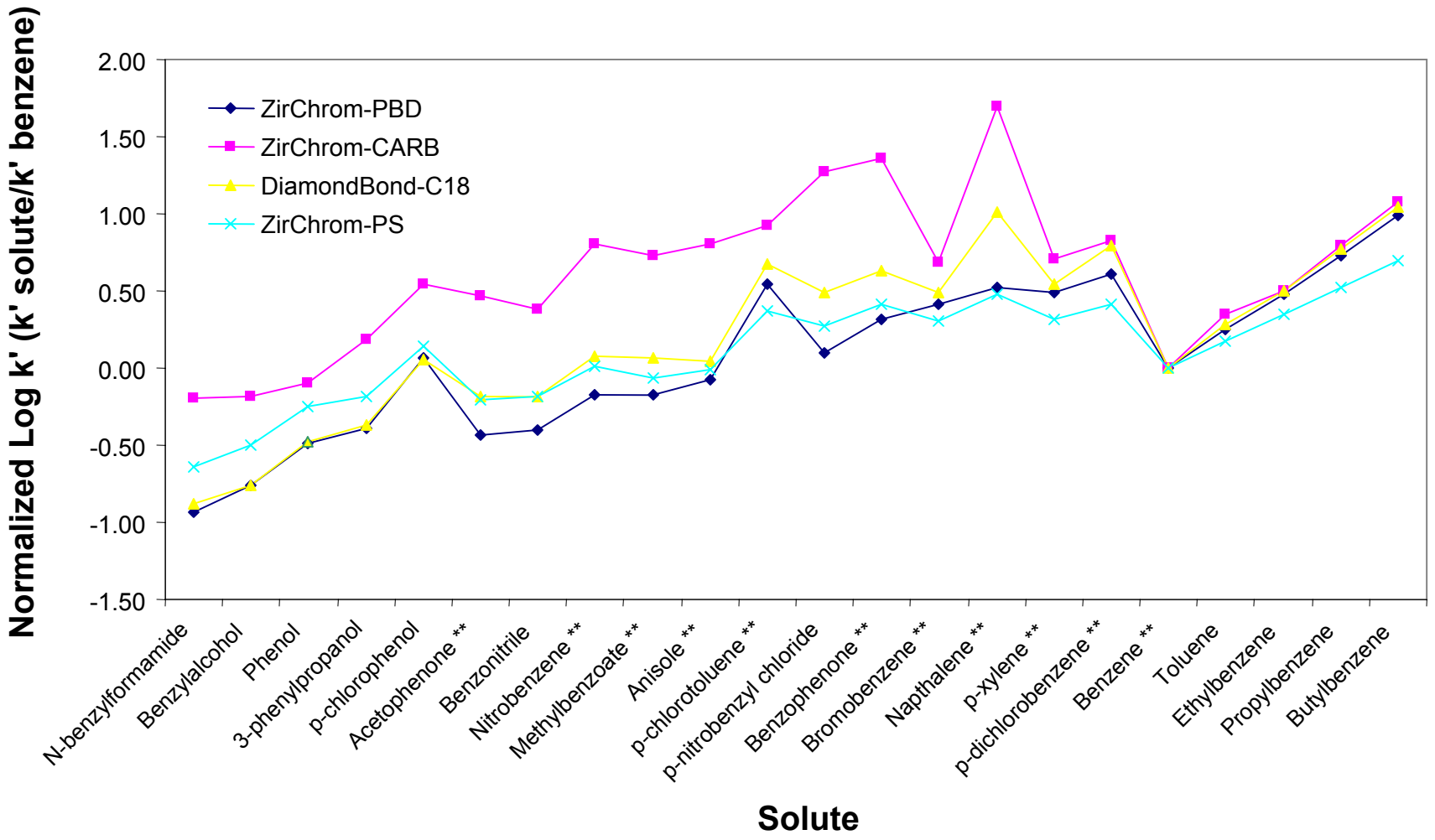
Polar



HB Donor



Selectivity Comparison



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