



ZirChrom®

Synthesis of a New Thermally and Chemically Stable Lewis-Acid Deactivated Carbon-based Zirconia Stationary Phase for RPLC

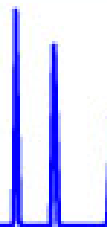
Eastern Analytical Symposium 2004

CLAYTON V. MCNEFF¹, BINGWEN YAN¹,

¹ZirChrom Separations, Inc., 617 Pierce Street, Anoka, MN 55303



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... For Peak Performance



Outline

- Project Goal
- Phase Synthesis
- Chromatographic Data
 - Comparison of Zr-Select, ZirChrom-CARB, and ZirChrom-PBD
 - Separation of benzoic acids without a Lewis base mobile phase additive
- Selectivity Comparison
- Chemical and Thermal Stability Testing

Conclusion - The Zr-SELECT phase shows *intermediate selectivity* to ZirChrom-PBD and the ZirChrom-CARB, has good efficiency and is Lewis acid site deactivated.



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Goal -

Produce an efficient novel carbon-based stationary phase that has very different selectivity than traditional bonded phases for orthogonal (2D) method development.



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Phase Synthesis

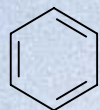
1. Start with carbon clad zirconia (1.2% carbon by weight).
2. Lewis acid site deactivate with a metal chelator that can be cross-linked into a hydrophobic polymer.
3. Evaporatively coat with a hydrophobic polymer such as polybutadiene.
4. Cross-link the Lewis acid site deactivator and polymer together and extract extensively.



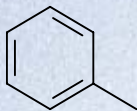
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22 Non-electrolyte Solutes

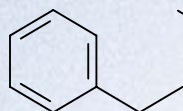
Nonpolar



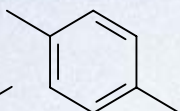
Benzene



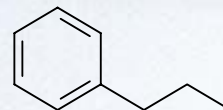
Toluene



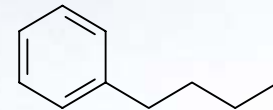
Ethylbenzene



p-xylene

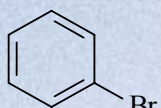


Propylbenzene

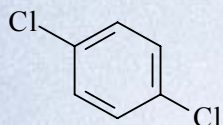


Butylbenzene

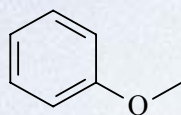
Polar



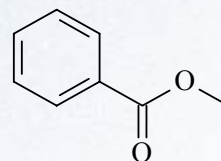
Bromobenzene



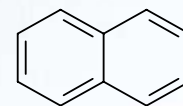
p-Dichlorobenzene



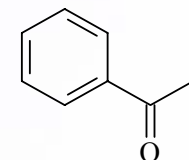
Anisole



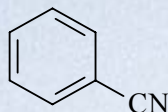
Methylbenzoate



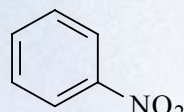
Naphthalene



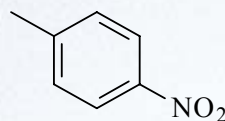
Acetophenone



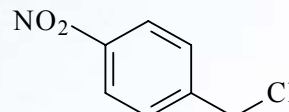
Benzonitrile



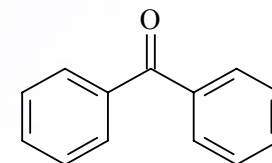
Nitrobenzene



p-Nitrotoluene

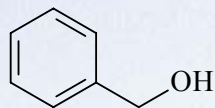


p-Nitrobenzyl Chloride

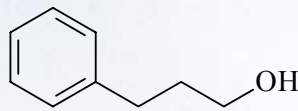


Benzophenone

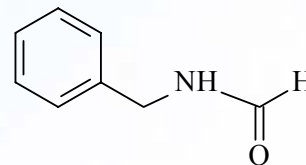
HB Donor



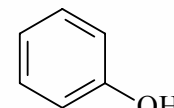
Benzylalcohol



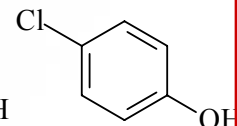
3-Phenyl Propanol



N-Benzyl Formamide



Phenol

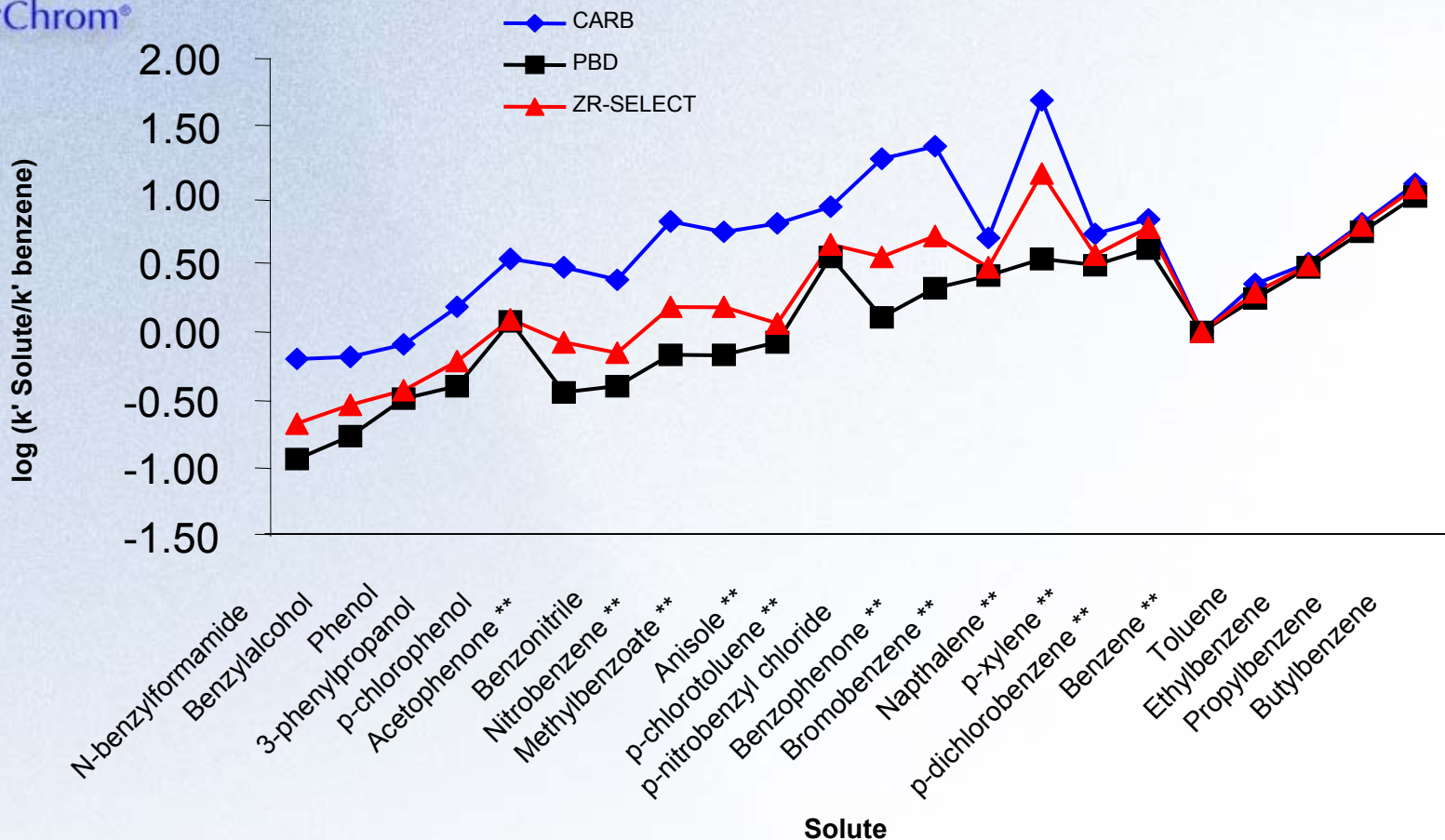


p-Chlorophenol



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Selectivity Comparison

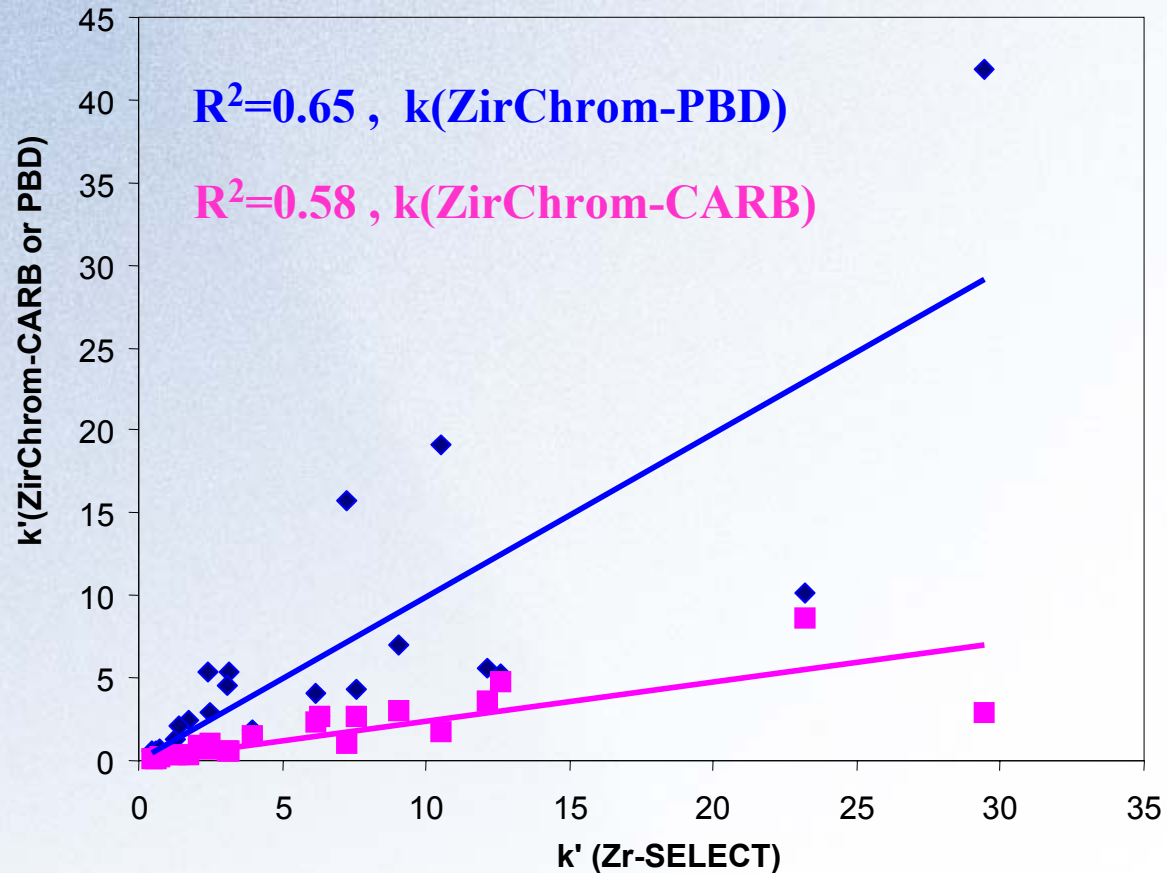


LC Conditions: Mobile phase, 40/60 ACN/Water; Flow rate, 1.0 ml/min.;
Temperature, 30 °C; Injection volume, 5ul; Detection at 254nm.



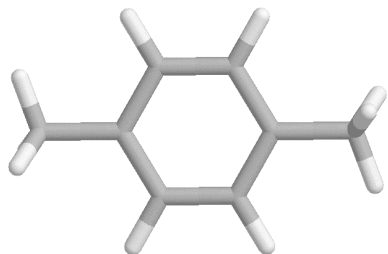
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K-K Comparison

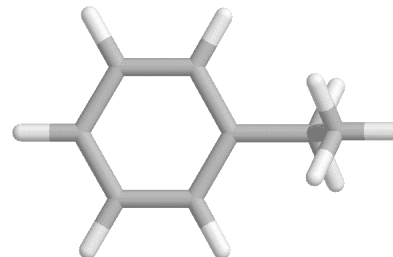


LC Conditions: Mobile phase, 40/60 ACN/Water; Flow rate, 1.0 ml/min.; Temperature, 30 °C; Injection volume, 5ul; Detection at 254nm.

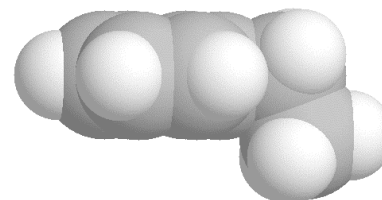
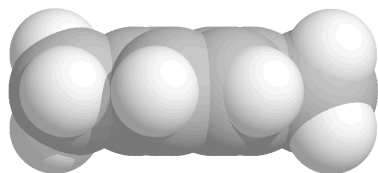
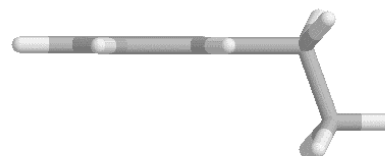
p-xylene



ethylbenzene



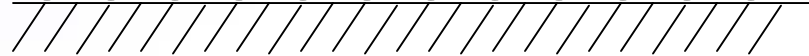
Shape Selectivity



C-C-C-C-C-C-C-C-C-C-C-C



C-C-C-C-C-C-C-C-C-C-C-C





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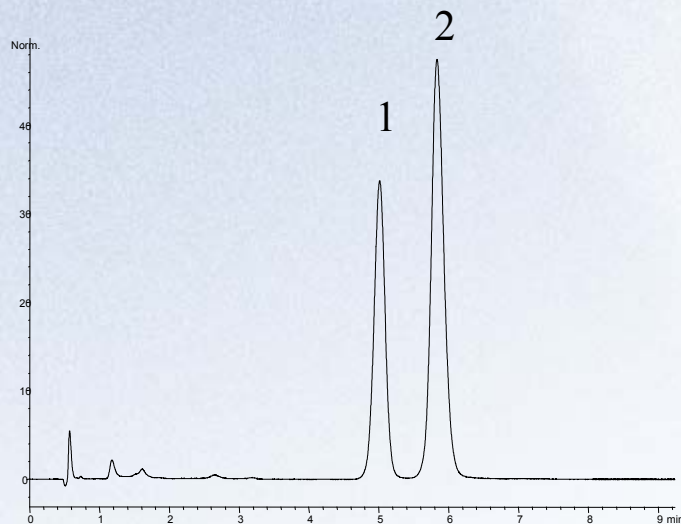
Shape Selectivity: Zr-SELECT and PBD

LC Conditions

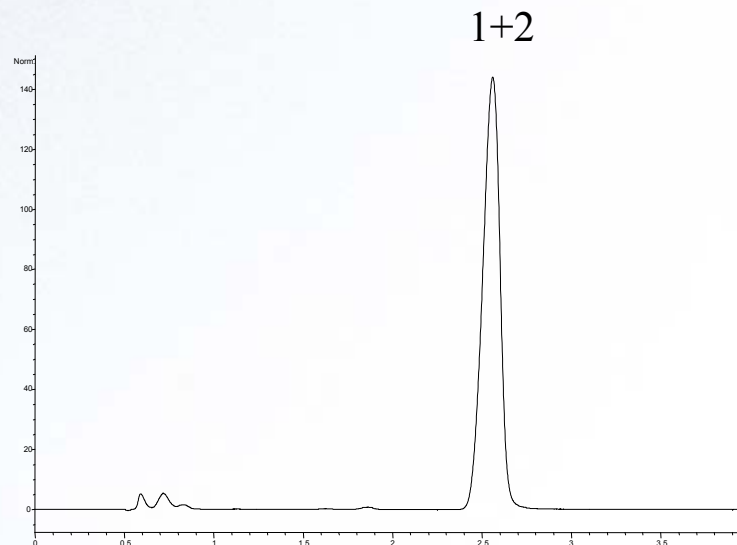
Column: 50 x 4.6 mm
Mobile phase: 35/65 A/B
A: ACN
B: Water
Flow rate: 1.0 mL/min.
Temperature: 30 °C
Injection volume: 5 µL
Detection: 254 nm

Analytes

- 1 - Ethylbenzene
- 2 - p-Xylene



Zr-SELECT



ZirChrom-PBD



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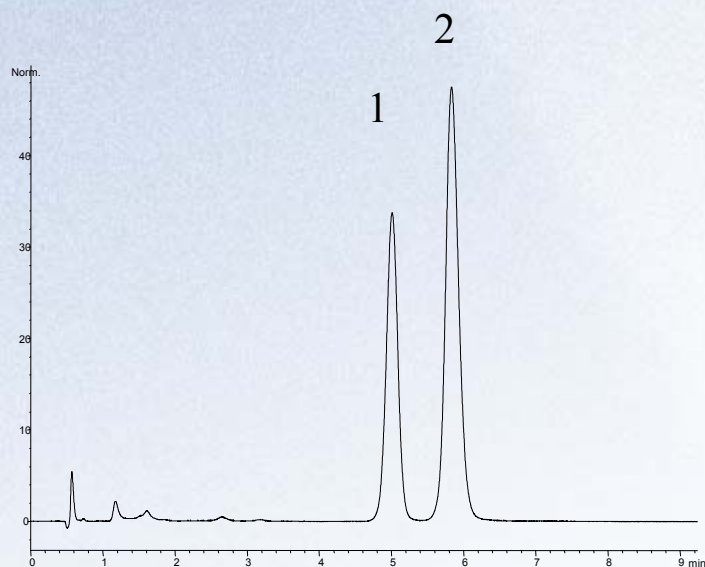
Shape Selectivity: Zr-SELECT and CARB

LC Conditions

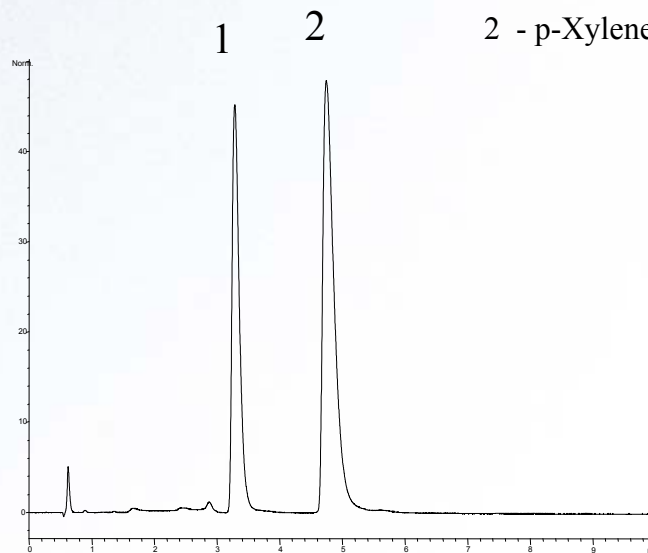
Column:	50 x 4.6 mm
Mobile phase:	Flow rate: 1.0 mL/min.
32.5/67.5 A/B	Temperature: 60 °C
A: ACN	Injection volume: 5 µL
B: Water	Detection: 254 nm

Analytes

- 1 - Ethylbenzene
- 2 - p-Xylene



Zr-SELECT

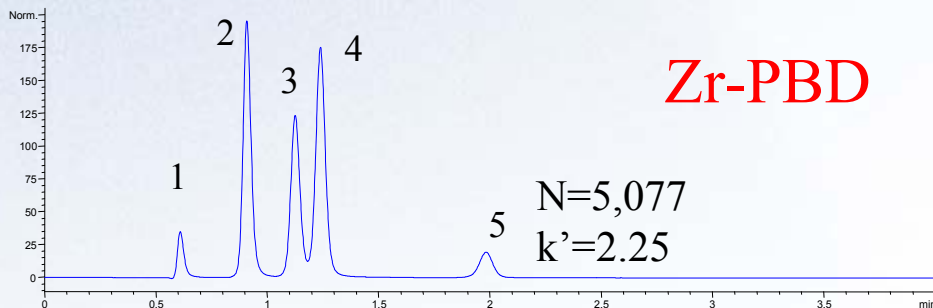
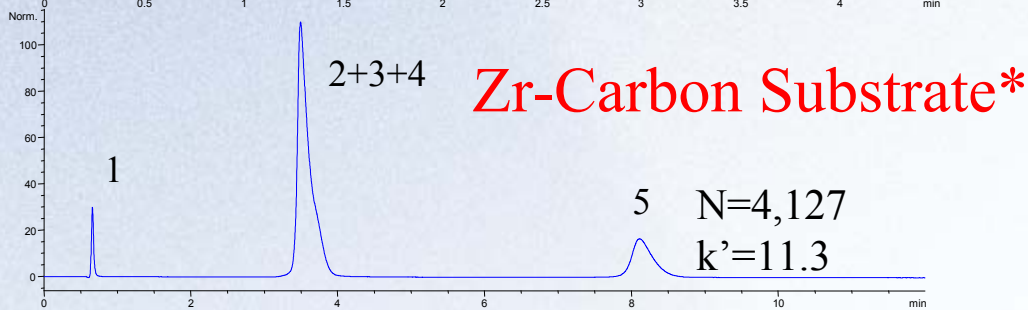
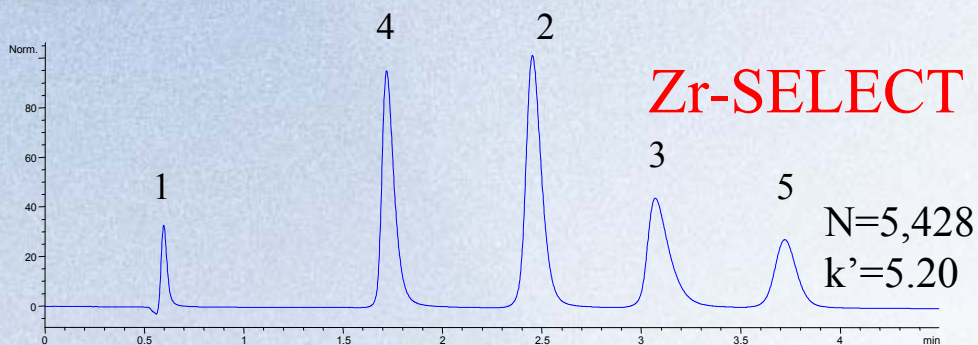


ZirChrom-Carb



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Zr-SELECT, ZirChrom-CARB, and ZirChrom-PBD



Mobile Phase:

35/65 ACN/water.

Flow rate: 1 ml/min.

Temperature: 30 °C.

UV Detection: 254 nm

Solutes:

1. acetone
2. benzonitrile
3. methyl benzoate
4. anisol
5. toluene

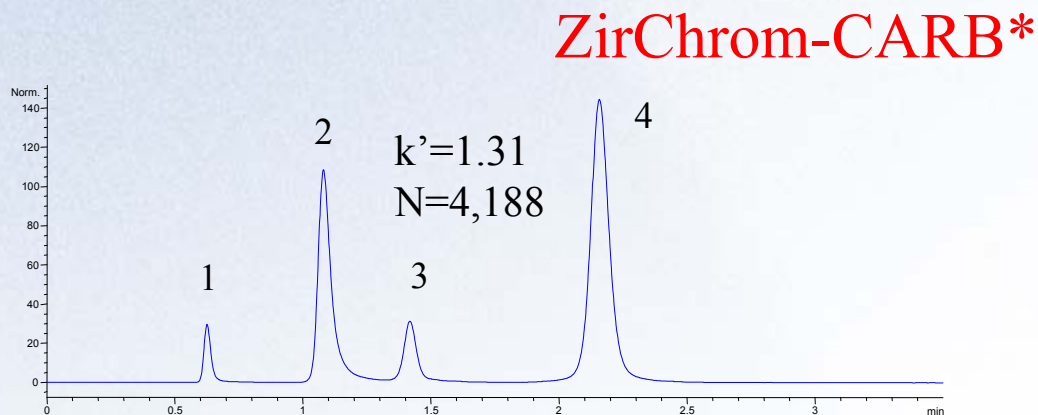
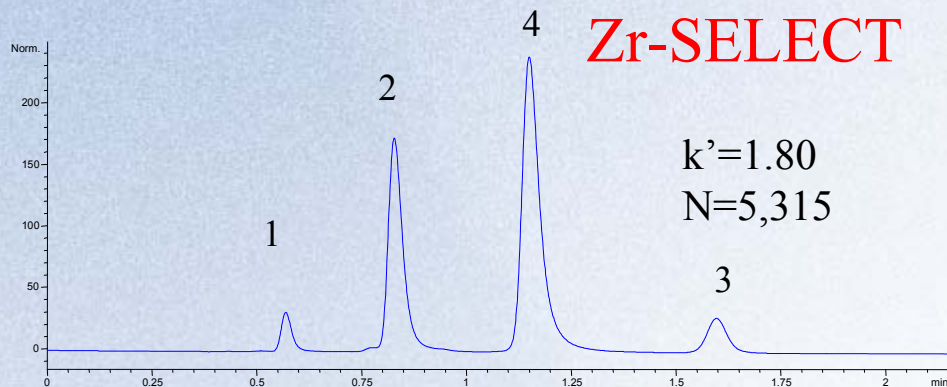
Column: 5cm x 4.6 mm ID, 5 micron.

*Note that CARB Substrate = DB substrate



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Zr-SELECT and ZirChrom-CARB



Mobile Phase:
50/50 ACN/water.

Flow rate: 1 ml/min.

Temperature: 60 °C.

UV Detection: 254 nm

Solutes:

1. acetone
2. p-cresol
3. ethylbenzene
4. nitrobenzene

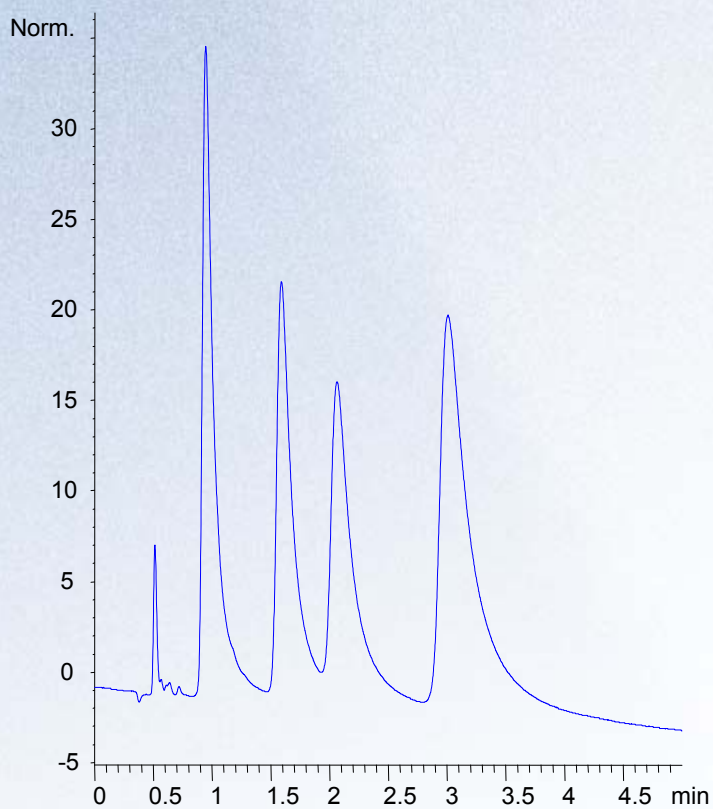
Column: 5cm x 4.6 mm ID, 5 micron.

*Note that CARB Substrate = DB
substrate

*Slightly higher carbon loading than commercial ZirChrom-CARB.



Separation of alkoxybenzoic acids without Lewis base in the Mobile Phase



Mobile Phase:
50/50 ACN/water.

Flow rate: 1 ml/min.

Temperature: 60 °C.

UV Detection: 254 nm

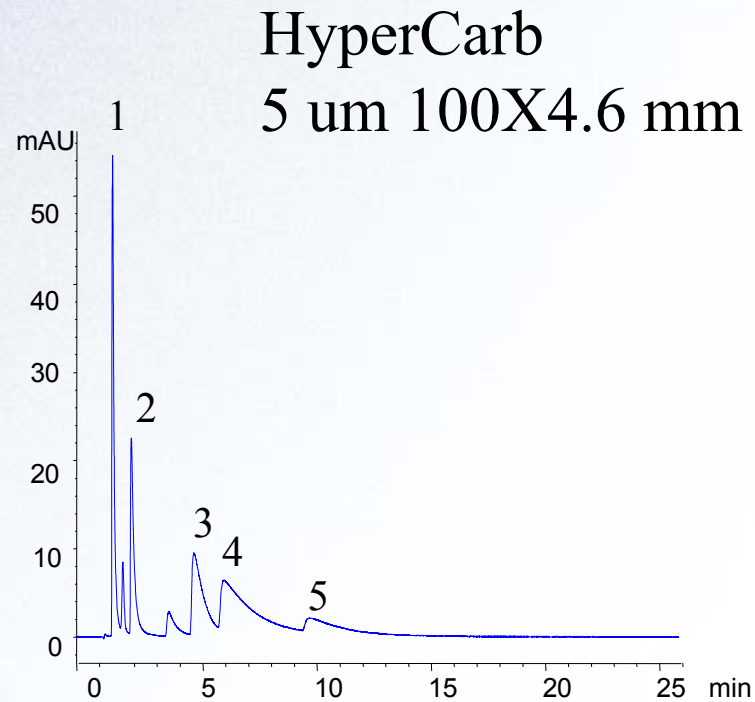
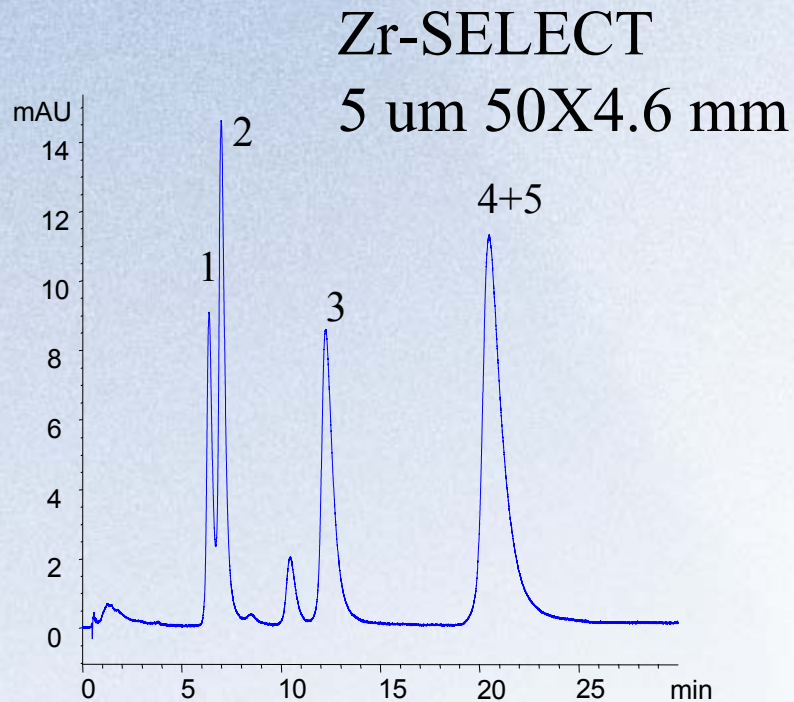
Solutes:

1. 4-hydroxybenzoic acid
2. 4-ethoxybenzoic acid
3. 4-propoxybenzoic acid
4. 4-butoxybenzoic acid

Column: 5cm x 4.6 mm ID, 5 micron.



Drugs Separation on HyperCarb and ZR-SELECT



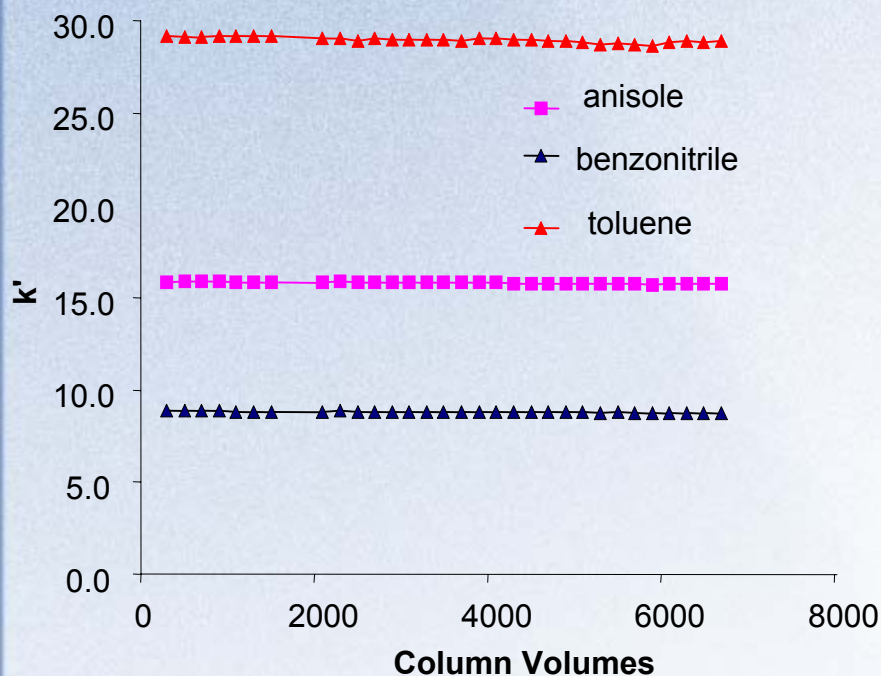
Chromatographic Conditions: Mobile phase: 65/35 ACN/(20 mM acetic acid, 5 mM octylamine pH=5 adjusted with ammonium hydroxide; Flow rate:1 ml/min; Temperature: 35 °C;
Solutes: (1) Methapyrilene, (2) Brompheniramine, (3) Doxepin, (4) Amitriptyline, and (5) Nortriptyline. Detection: 254 nm.



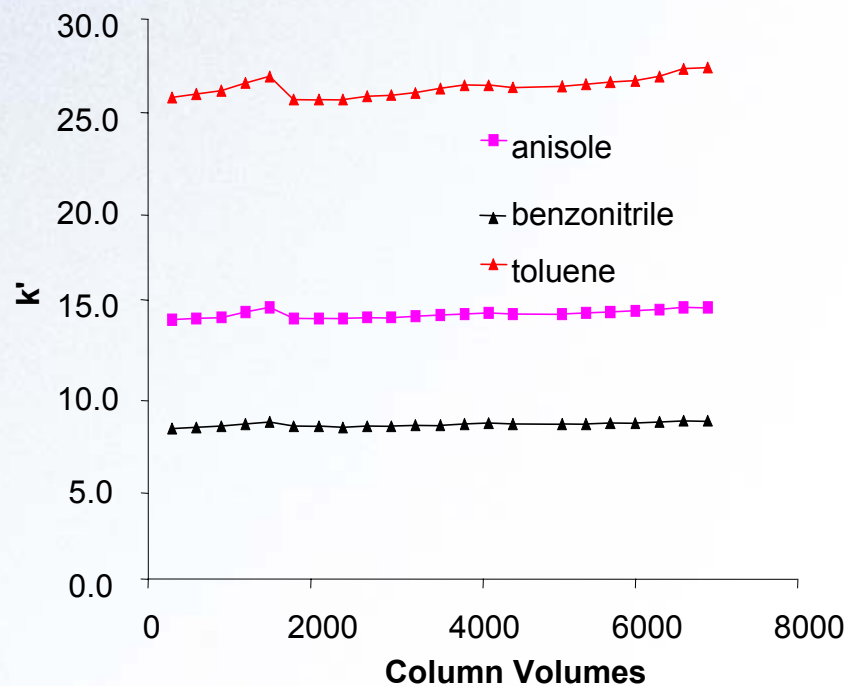
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Chemical Stability

pH 1.0



pH 10.0

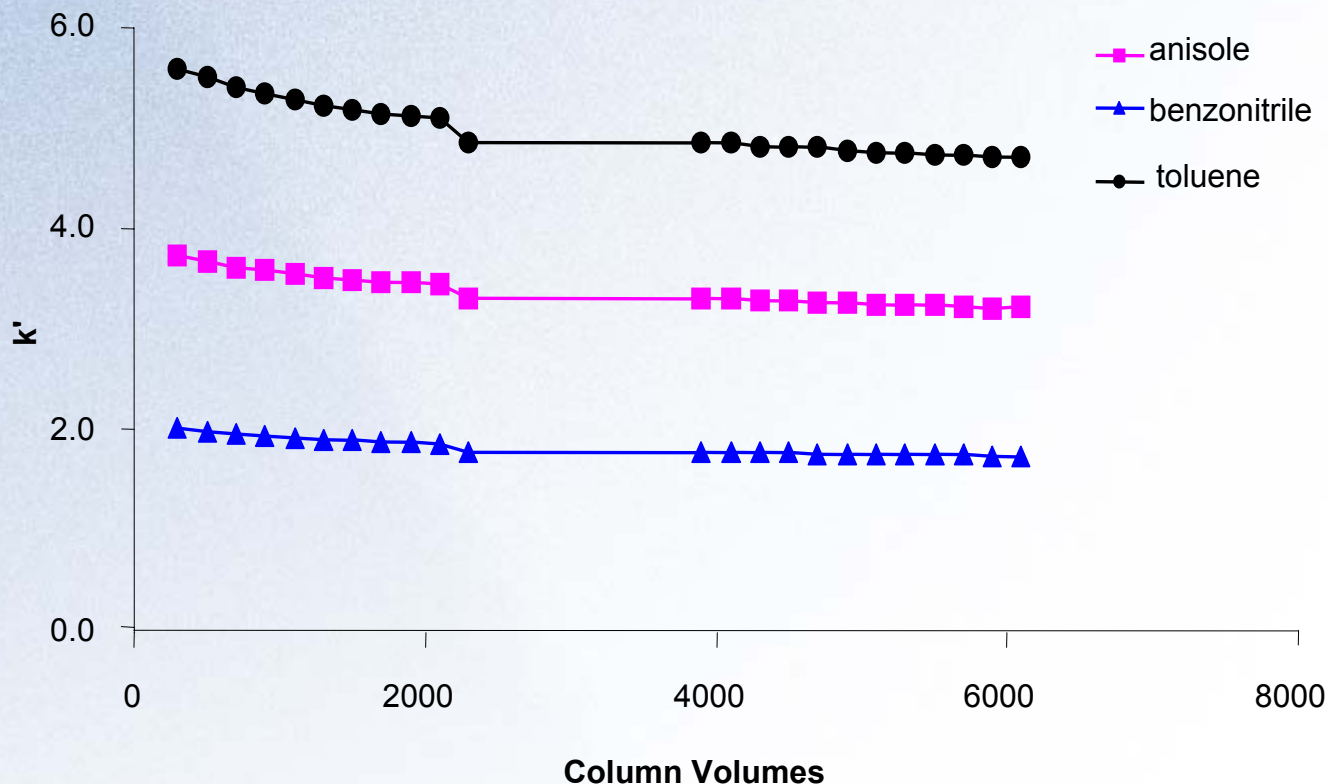


Exposure and Evaluation Conditions: Mobile phase, 15/85 ACN/0.1M Nitric acid, pH 1.0, or 0.1mM Ammonium hydroxide, pH 10.0; Flow rate, 1.0 ml/min.; Temperature, 30 °C; Injection volume, 5 μ l; Detection at 254 nm; Column, 50 mm x 4.6 mm i.d. Zr-SELECT.



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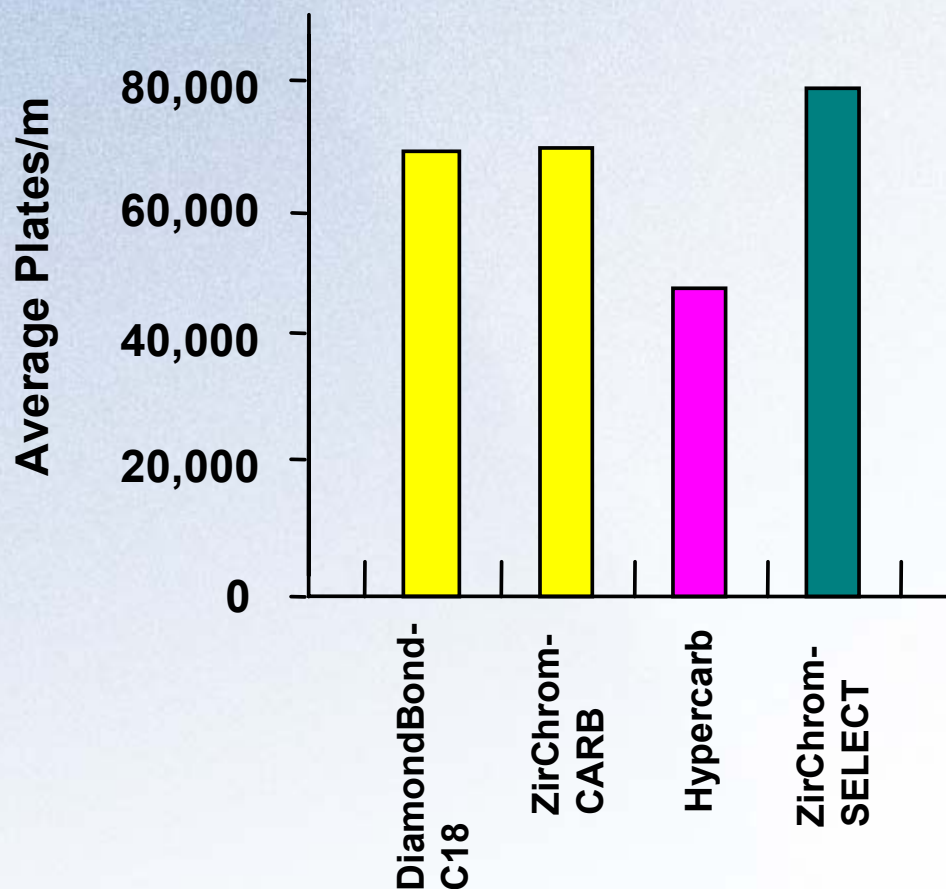
Temperature Stability at 100 °C



Exposure and Evaluation Conditions: Mobile phase, 15/85 ACN/20mM Ammonium acetate, pH 4.5; Flow rate, 1.0 ml/min.; Temperature, 100 °C with Metalox heater; Injection volume, 5 ml; Detection at 254 nm; Column, 50 mm x 4.6 mm I.d., Zr-SELECT.



Efficiency Comparison of Carbon-Based Columns*



LC Conditions: Mobile Phase, 45/5/50 Acetonitrile/THF/50mM Potassium phosphate buffer, pH 7.0; Flow Rate, 1.0 mL/min.; Injection volume, 1 ul; 254 nm detection; Column Temperature: 30°C. Solutes: uracil, phenol, pyridine, 4-butylbenzoic acid, N,N – dimethylaniline, toluene.

* Column names are the trademarks of their respective manufacturers.



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Conclusions

- The Zr-SELECT phase shows *intermediate selectivity* to ZirChrom-PBD (ODS-like for neutrals) and the ZirChrom-CARB.
- The Zr-SELECT phase is *Lewis acid site deactivated*.
- The Zr-SELECT Phase has *excellent stability* from pH 1-10 and up to 100°C.
- The amount of “*carbon-character*” *can easily be modified* by the proportion of carbon layer and polymer coating.
- The Zr-SELECT phase has *good column efficiency* compared to other commercial carbon-based columns.



Thanks *very much*
for listening!

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