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

Pittcon 2005

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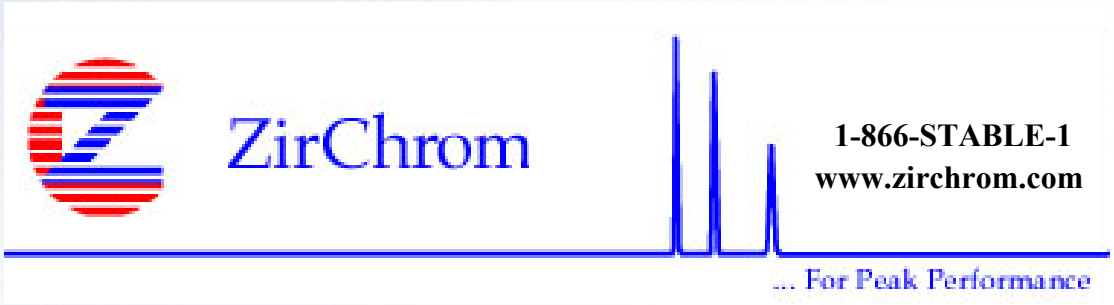

Outline

- Project Goal
- Phase Synthesis
- Chromatographic Data
  - Comparison of ZirChrom -Select, ZirChrom-CARB, and ZirChrom-PBD
  - Separation of benzoic acids without a Lewis base mobile phase additive
- Selectivity Comparison to Polybutadiene (PBD) and Carbon coated zirconia
- Chemical and Thermal Stability Testing

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

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 (1.0% 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.

22 Non-electrolyte Solutes

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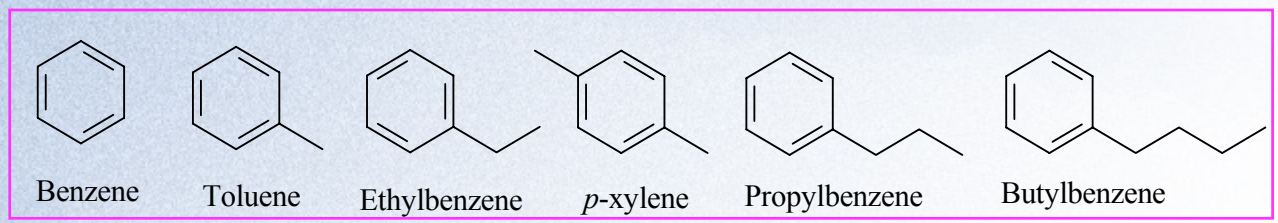
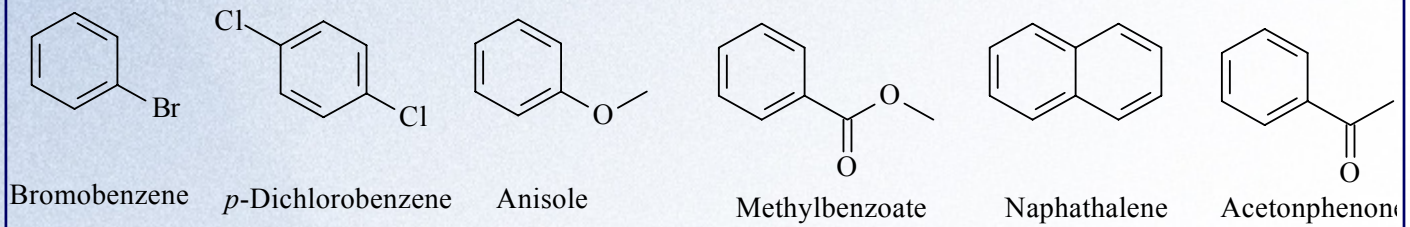
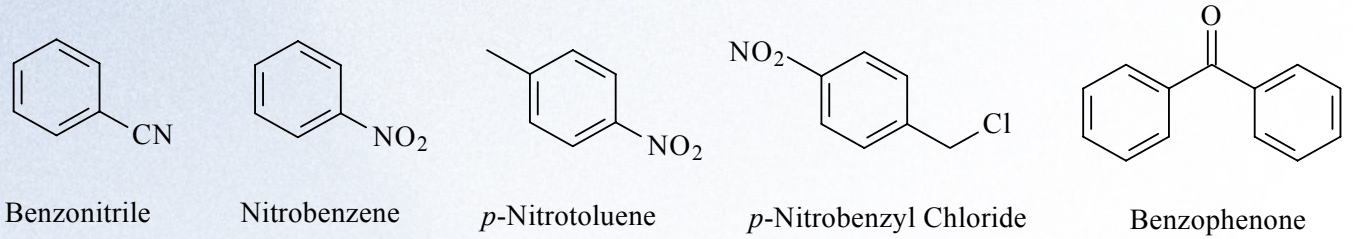
Nonpolar

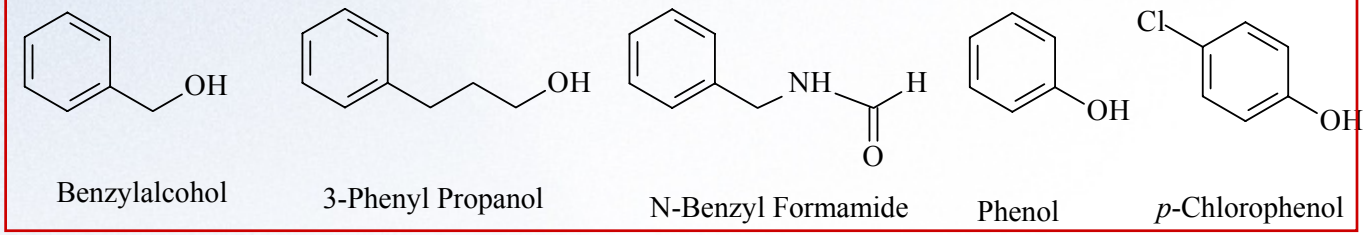


Polar

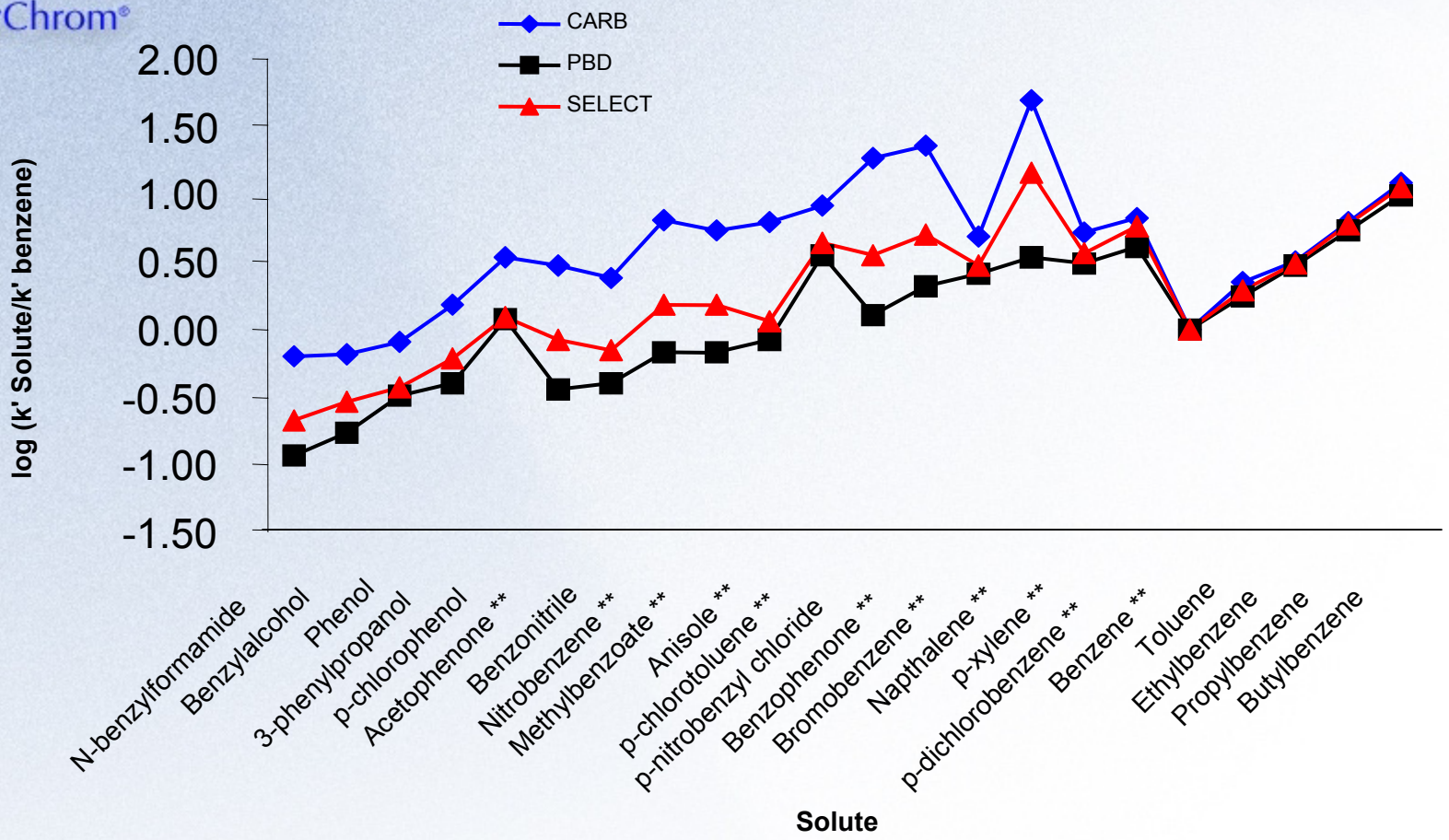




HB Donor

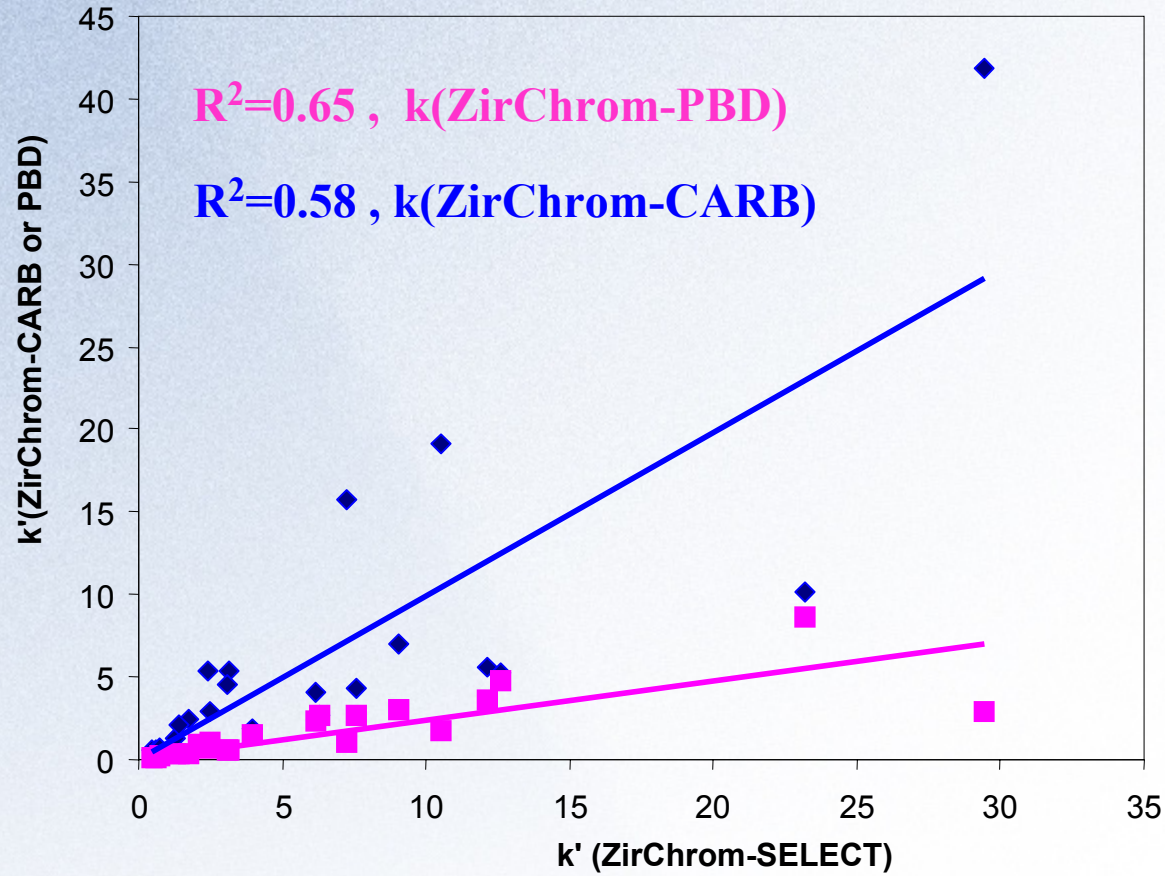


Selectivity Comparison



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

κ-κ Comparison

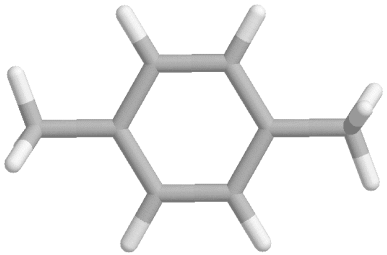


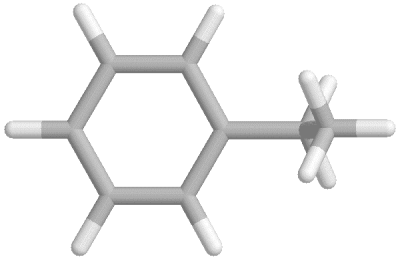
LC Conditions: Mobile phase, 40/60 ACN/Water; Flow rate, 1.0 ml/min.; Temperature, 30 °C; Injection volume, 5ul; Detection at 254nm.

Reference: Melander, W.; Stoveken, J.; Horvath, C. *J. Chromatogr.* **1980**, *199*, 35-56.

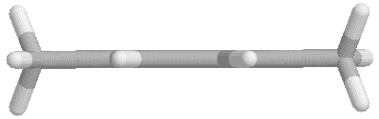
p-xylene

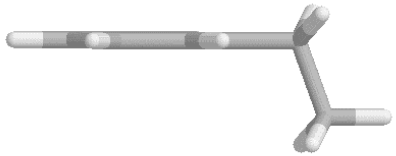
ethylbenzene

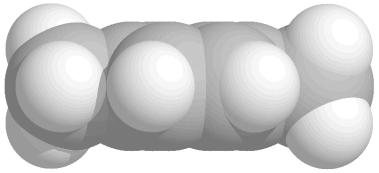


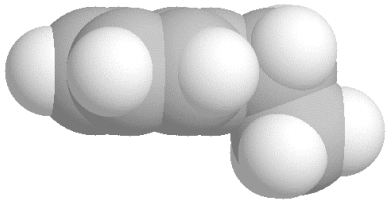


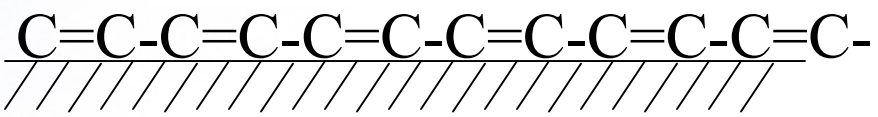
Shape Selectivity











Shape Selectivity: ZirChrom-SELECT and ZirChrom-CARB

LC Conditions

Column: 50 x 4.6 mm

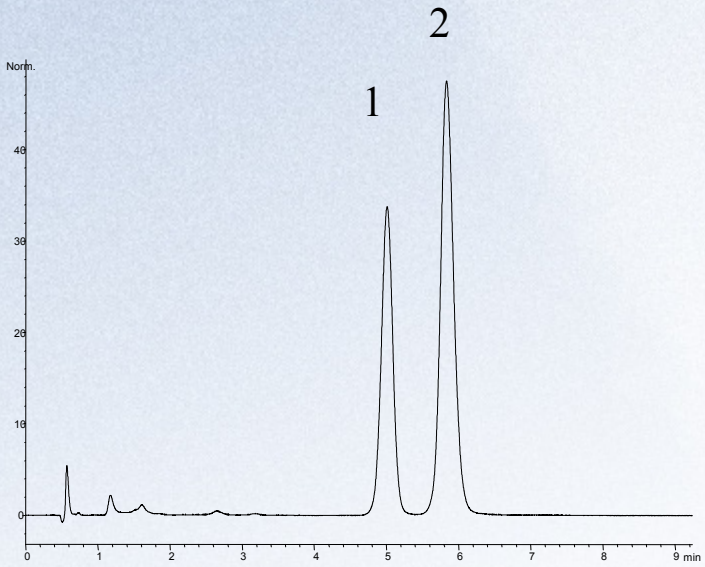
Mobile phase: 32.5/67.5 A/B
A: ACN
B: Water

Flow rate: 1.0 mL/min.
Temperature: 60 °C
Injection volume: 5 µL
Detection: 254 nm

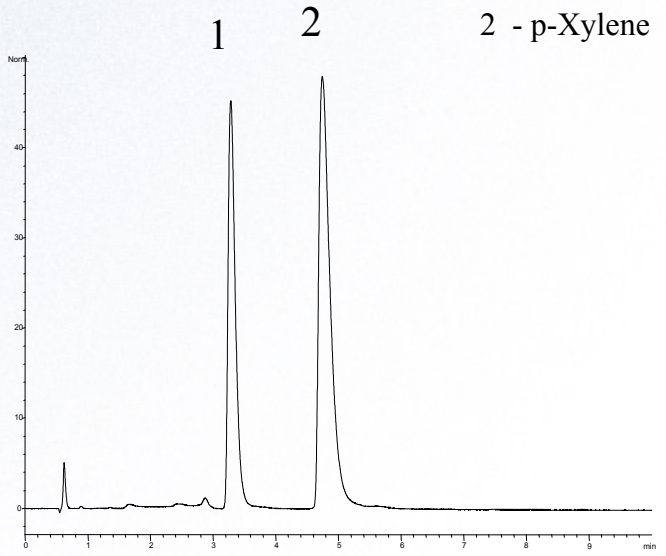
Analytes

1 - Ethylbenzene

2 - p-Xylene



ZirChrom-SELECT



ZirChrom-CARB

Shape Selectivity: ZirChrom-SELECT and ZirChrom-PBD

LC Conditions

Column: 50 x 4.6 mm

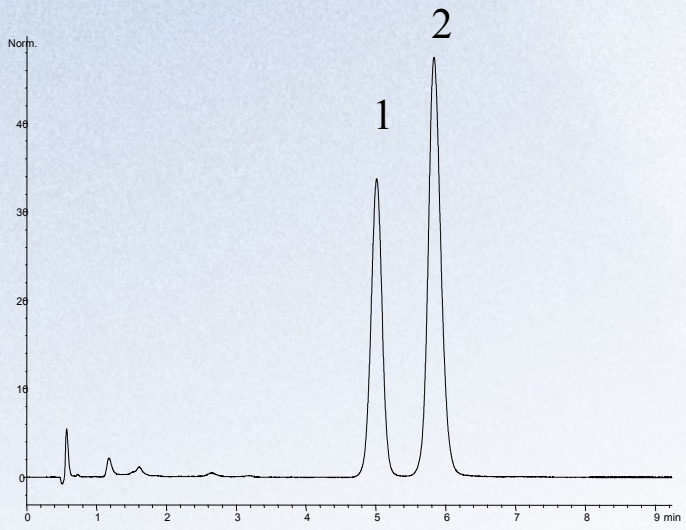
Mobile phase: 35/65 A/B
A: ACN
B: Water

Flow rate: 1.0 mL/min.
Temperature: 30 °C
Injection volume: 5 µL
Detection: 254 nm

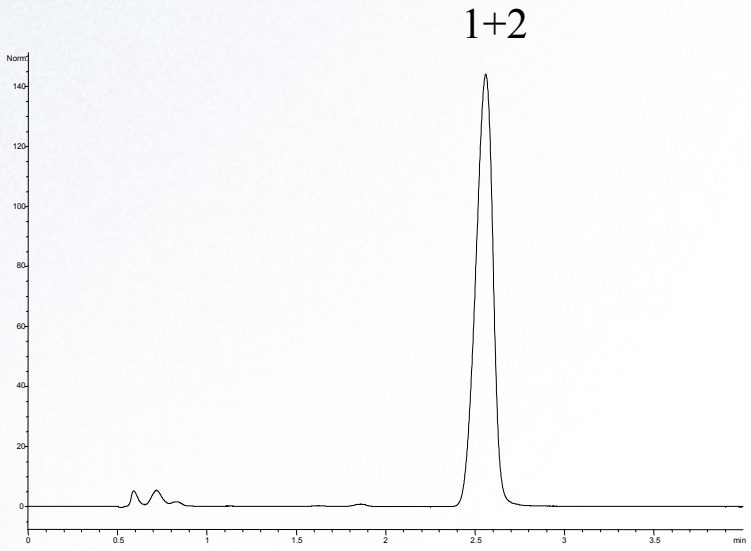
Analytes

1 - Ethylbenzene

2 - p-Xylene

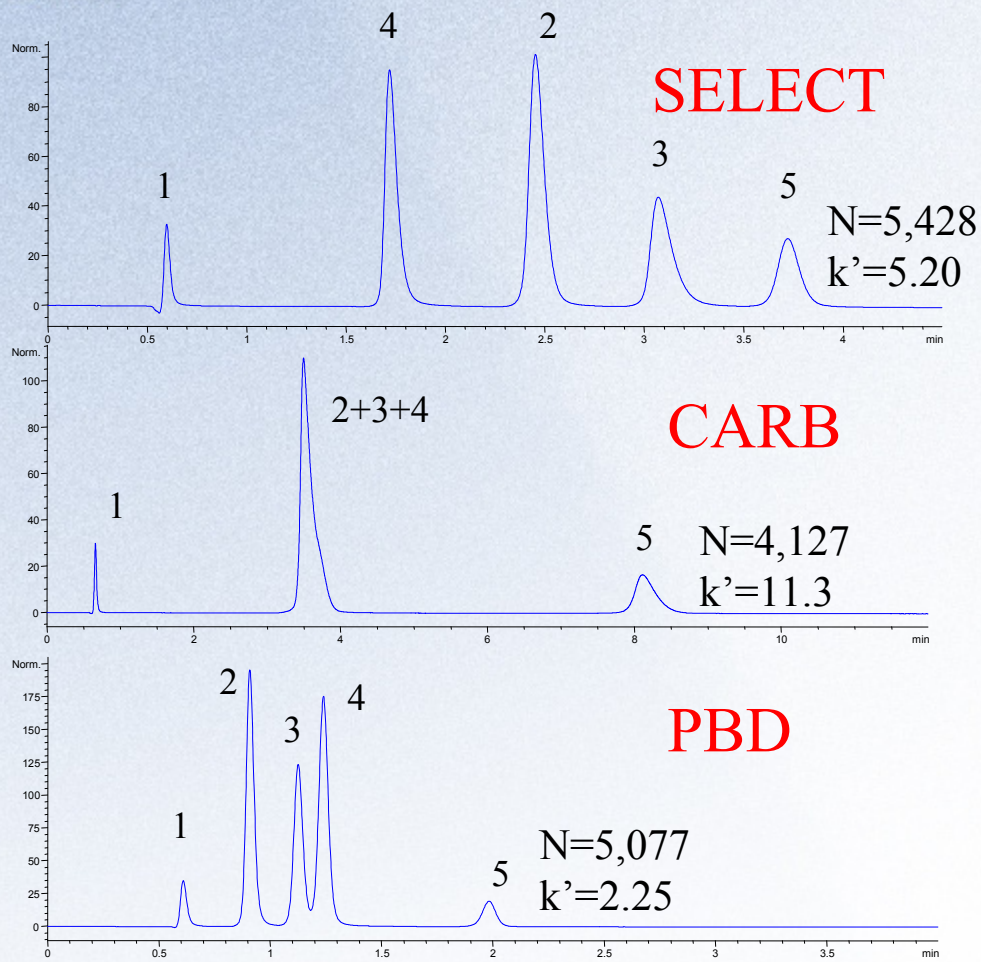


ZirChrom-SELECT



ZirChrom-PBD

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



Mobile Phase:
35/65 ACN/water.

Flow rate: 1 ml/min.

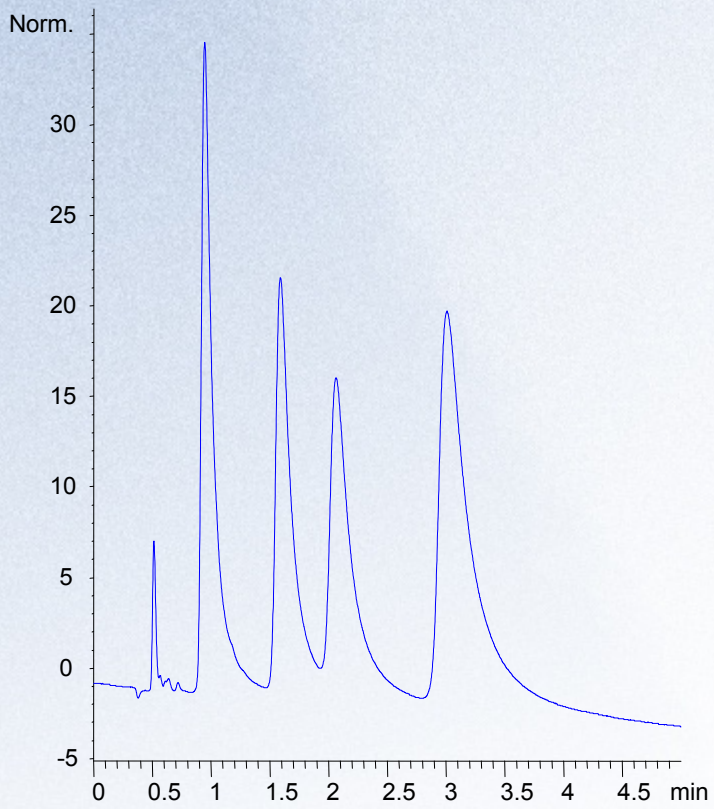
Temperature: 30 °C.

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.

Separation of alkoxylbenzoic acids without Lewis base in the Mobile Phase



Mobile Phase:
50/50 ACN/water.

Flow rate: 1 ml/min.

Temperature: 60 °C.

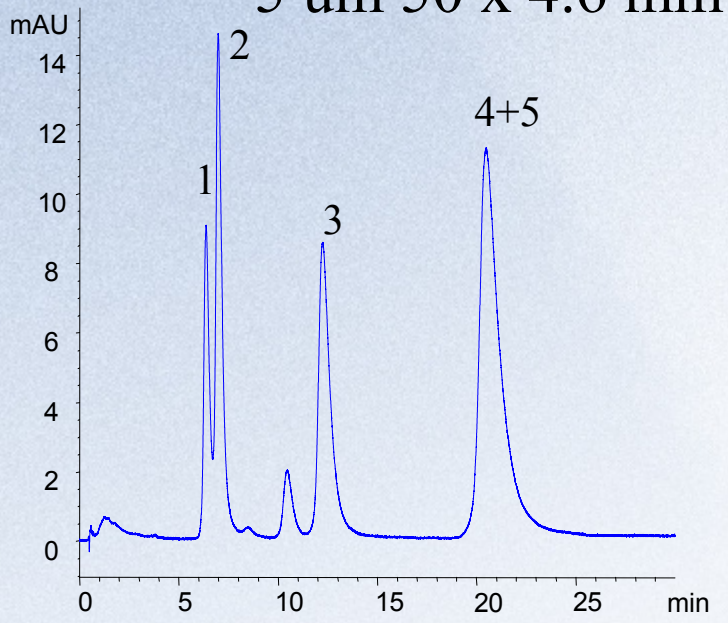
UV Detection: 254 nm

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

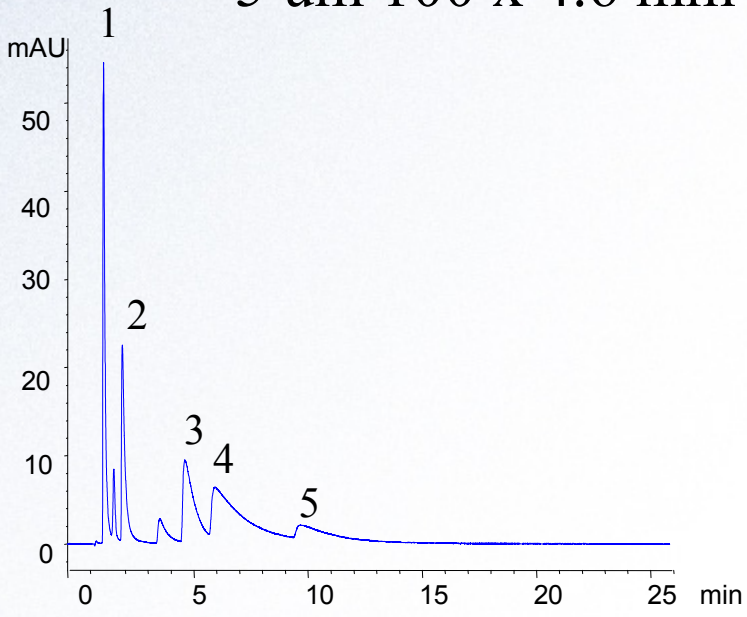
Column: 5cm x 4.6 mm ID, 5 micron, 300 Angstrom.

Drugs Separation on HyperCarb and ZirChrom-Select

ZirChrom-SELECT
5 um 50 x 4.6 mm



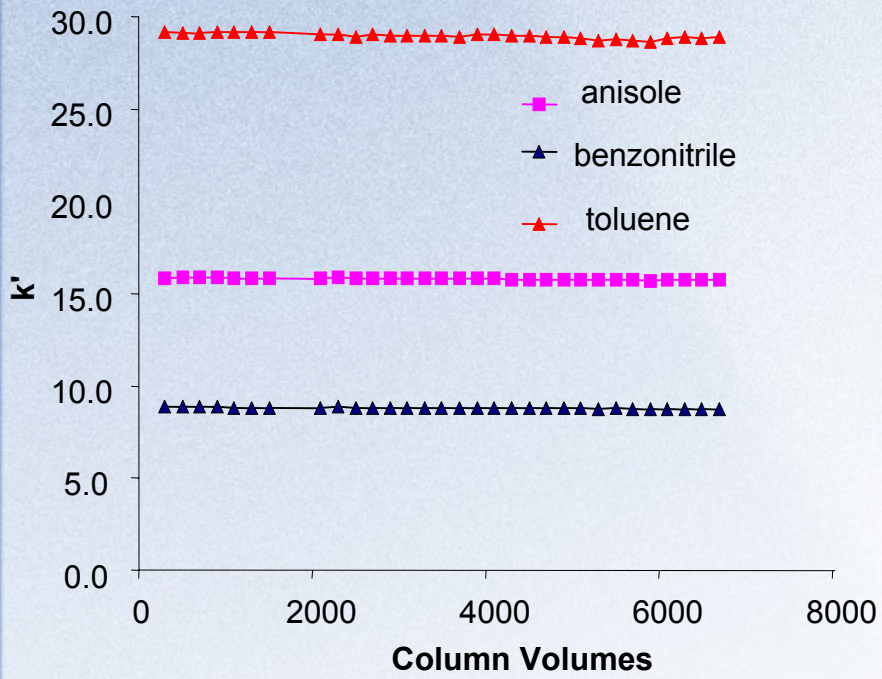
HyperCarb
5 um 100 x 4.6 mm



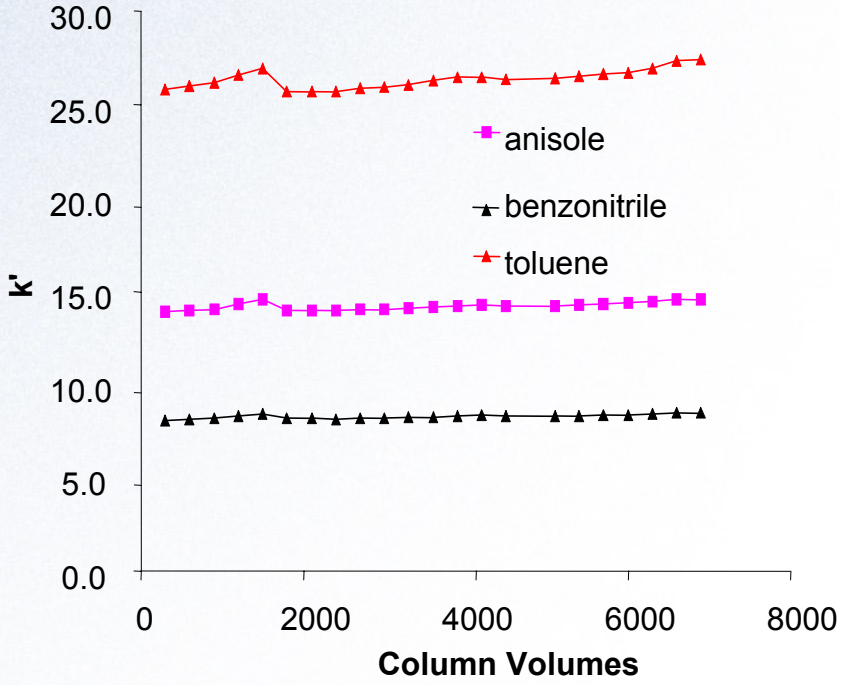
Chromatographic Conditions: Mobile phase: 65/35 ACN/(20 mM acetic acid, 5 mM octylamine pH=5 adjusted with ammonium hydroxide; Flow rate:1 ml/min; Temperature: 35 ^{o}C; Solutes: (1) Methapyrilene, (2) Brompheniramine, (3) Doxepin, (4) Amitriptyline, and (5) Nortryptyline. Detection: 254 nm.

Chemical Stability

pH 1.0

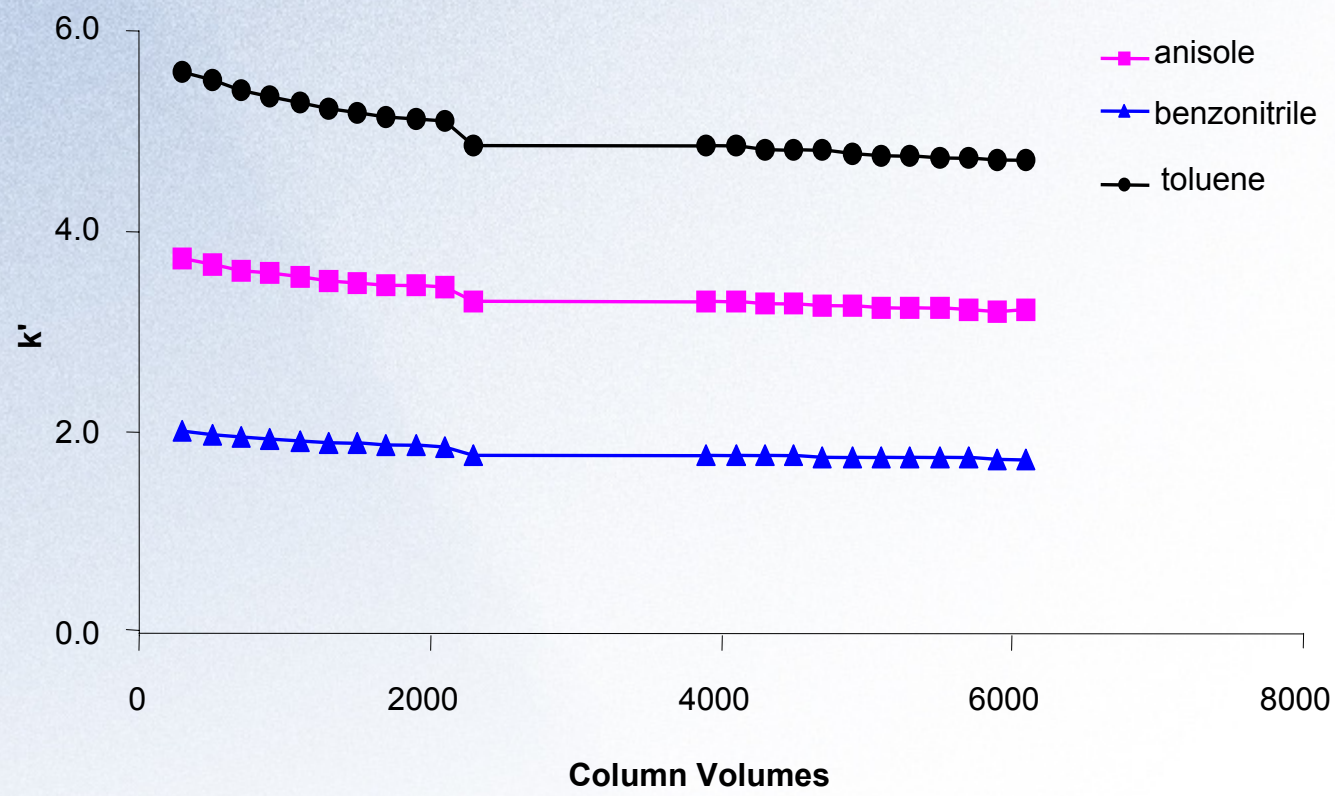


pH 10.0



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 µl; Detection at 254 nm; Column, 50 mm x 4.6 mm i.d. ZirChrom-SELECT.

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., ZirChrom-SELECT.

Conclusions

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

ZirChrom®

Thanks *very much* for listening!

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