Polymer Coated Titania for Analytical and Preparative Reversed-Phase Chromatography

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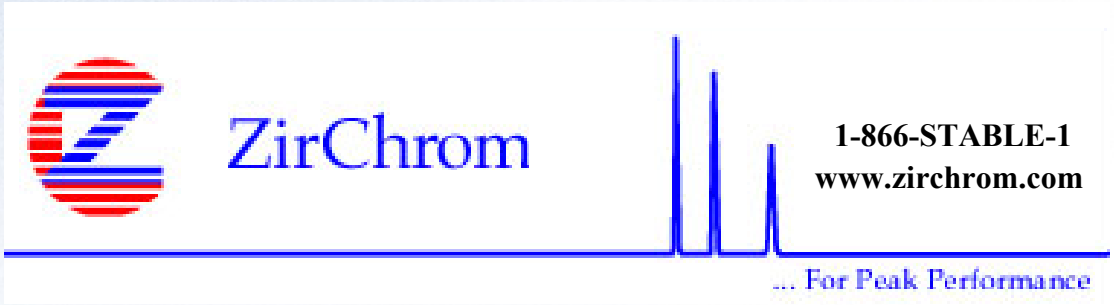


Outline

- Properties of Titania
- RP Phase Stationary Phase
- Chromatographic Data
  - Selectivity Comparison of Sachtopore-RP, Silica C18, ZirChrom-CARB, and ZirChrom-PBD
  - Effect of Lewis Base Mobile Phase Additive on Elution of Basic Compounds
- Chemical and Thermal Stability Testing

Conclusion - The Sachtopore®-RP shows very similar selectivity to ZirChrom®-PBD and has excellent stability from pH 1-12 and up to 100 °C.

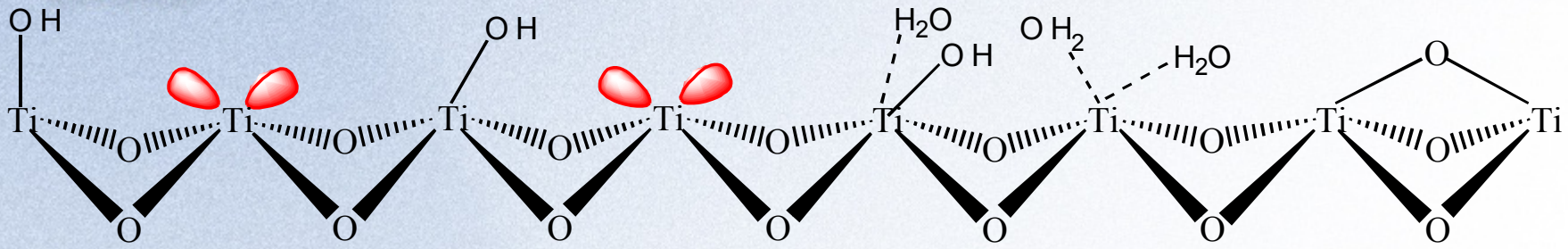
Element Electronic Structures

- Silicon (element 14; 2.3 g/cc; Si^{4+} ionic radius 0.400 Å)
  - $Ne3s^23p^2$
- Titanium (element 22; 4.5 g/cc; Ti^{4+} ionic radius 0.605 Å)
  - $Ar3d^24s^2$
- Zirconium (element 40; 6.5 g/cc; Zr^{4+} ionic radius 0.720 Å)
  - $Kr4d^25s^2$

All have four valence electrons so some chemistry is similar, but presence of d orbitals and very electropositive nature allow Ti and Zr (metals) to form strong electron donor-acceptor complexes (coordination chemistry).

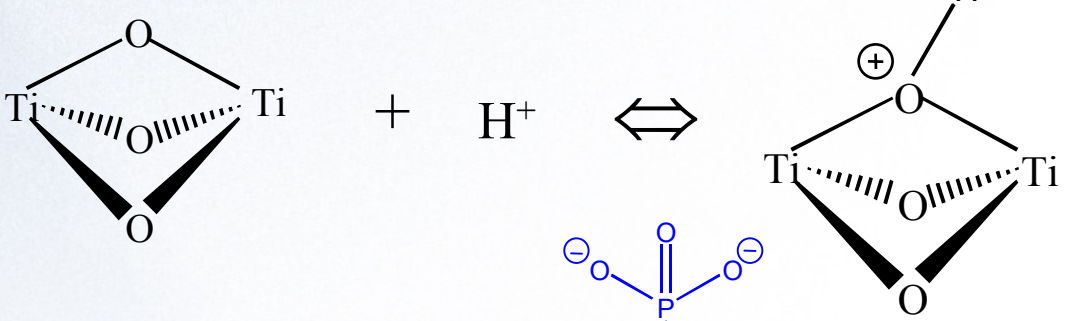
Surface Chemistry of Titania-Based Supports for HPLC

ZirChrom®

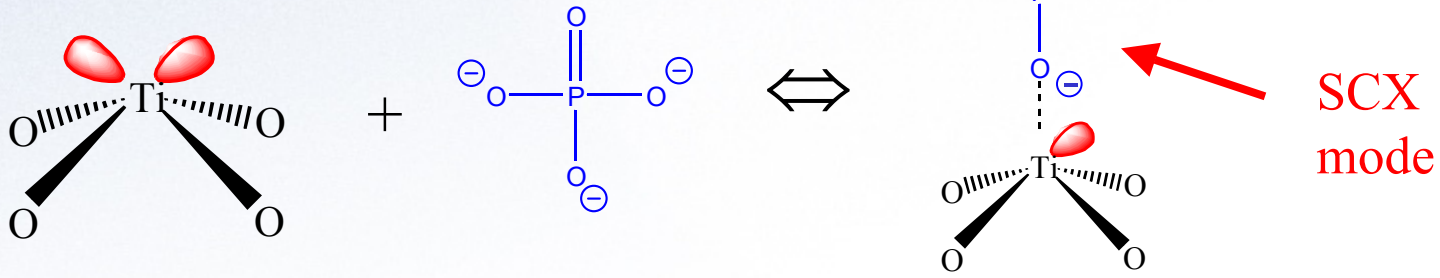


Weak Brönsted Acid: $TiOH + OH^- \Leftrightarrow TiO^- + H_2O$

Weak Brönsted Base:



Strong Lewis Acid:



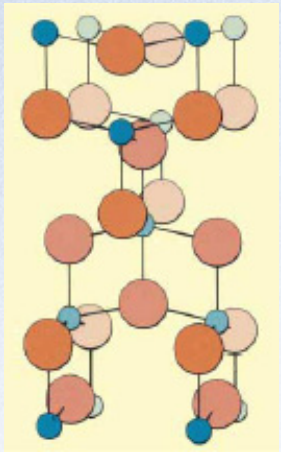
Titania Crystal Forms

ZirChrom®

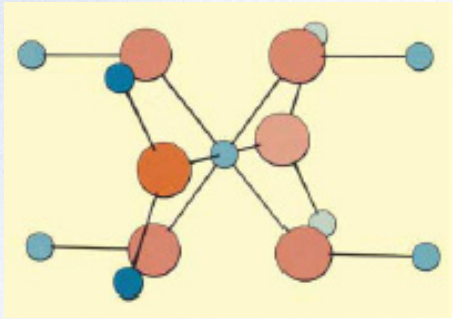
Anatase (tetragonal), 300 °C
Rutile (tetragonal), 600 °C
Brookite (orthorhombic), 850 °C.

Crystallographic data and pI values of sorbents

	SiO_2	TiO_2	Al_2O_3	ZrO_2
Ionisation potential (V)	45.14 (Si^{4+})	43.27 (Ti^{4+})	28.45 (Al^{3+})	34.34 (Zr^{4+})
Coordination number	4	6	6	7
Ion radius (A)	0.41 (Si^{4+})	0.68 (Ti^{4+})	0.5 (Al^{3+})	0.8 (Zr^{4+})
Ionisation potential/coordination number (V)	11.29	7.33	4.74	4.83
pI of sorbent (pH)	2.2	6.6	8.1	6
Porosities of test columns (%)	73	74	79	69



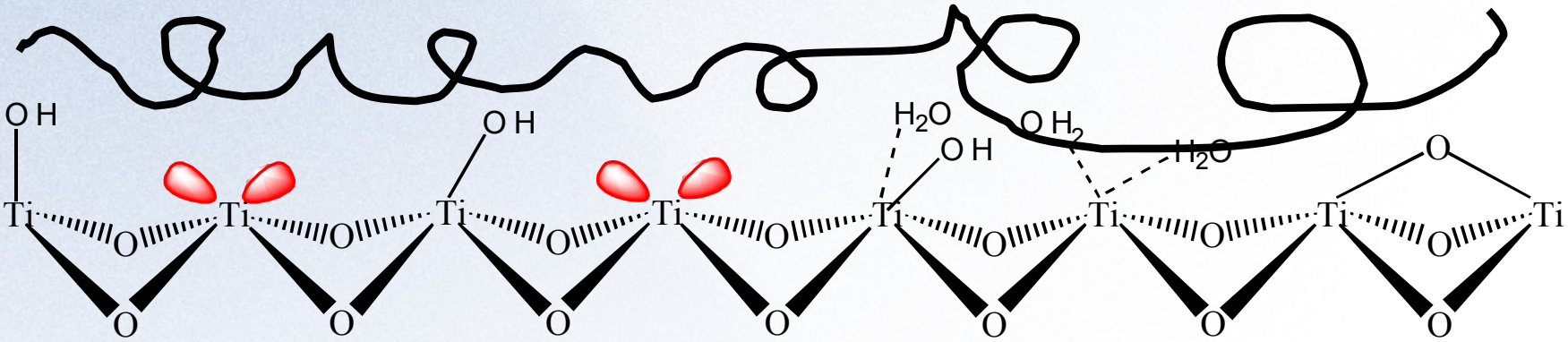
Anatase



Rutile

Polyethylene Coated Titania

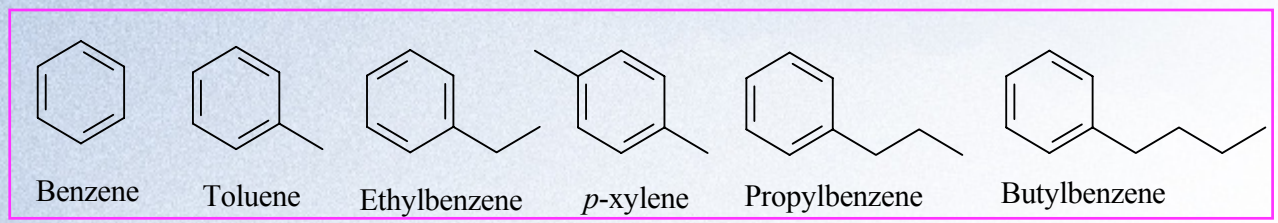
$$-\left[CH_2\text{-}CH_2\right]_n-$$ Polyethylene



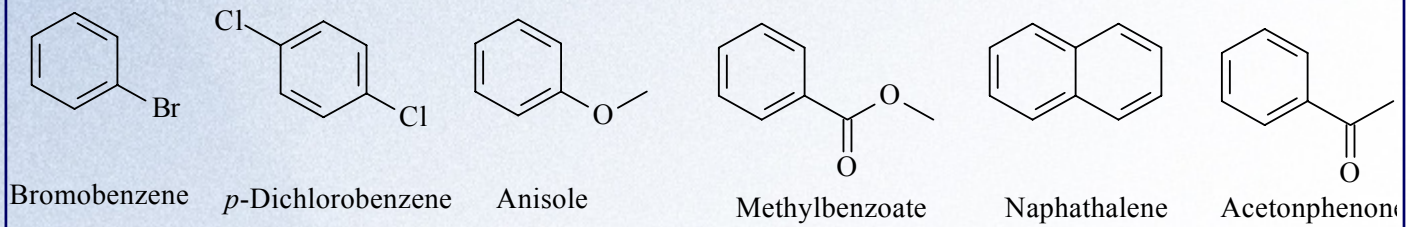
22 Non-electrolyte Solutes

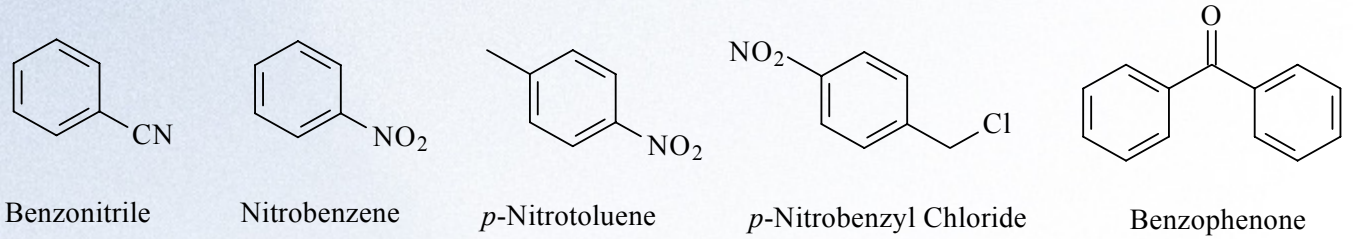
ZirChrom®

Nonpolar

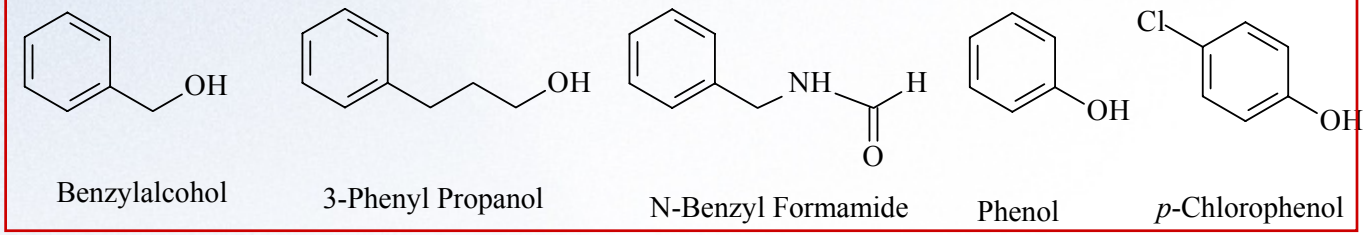


Polar

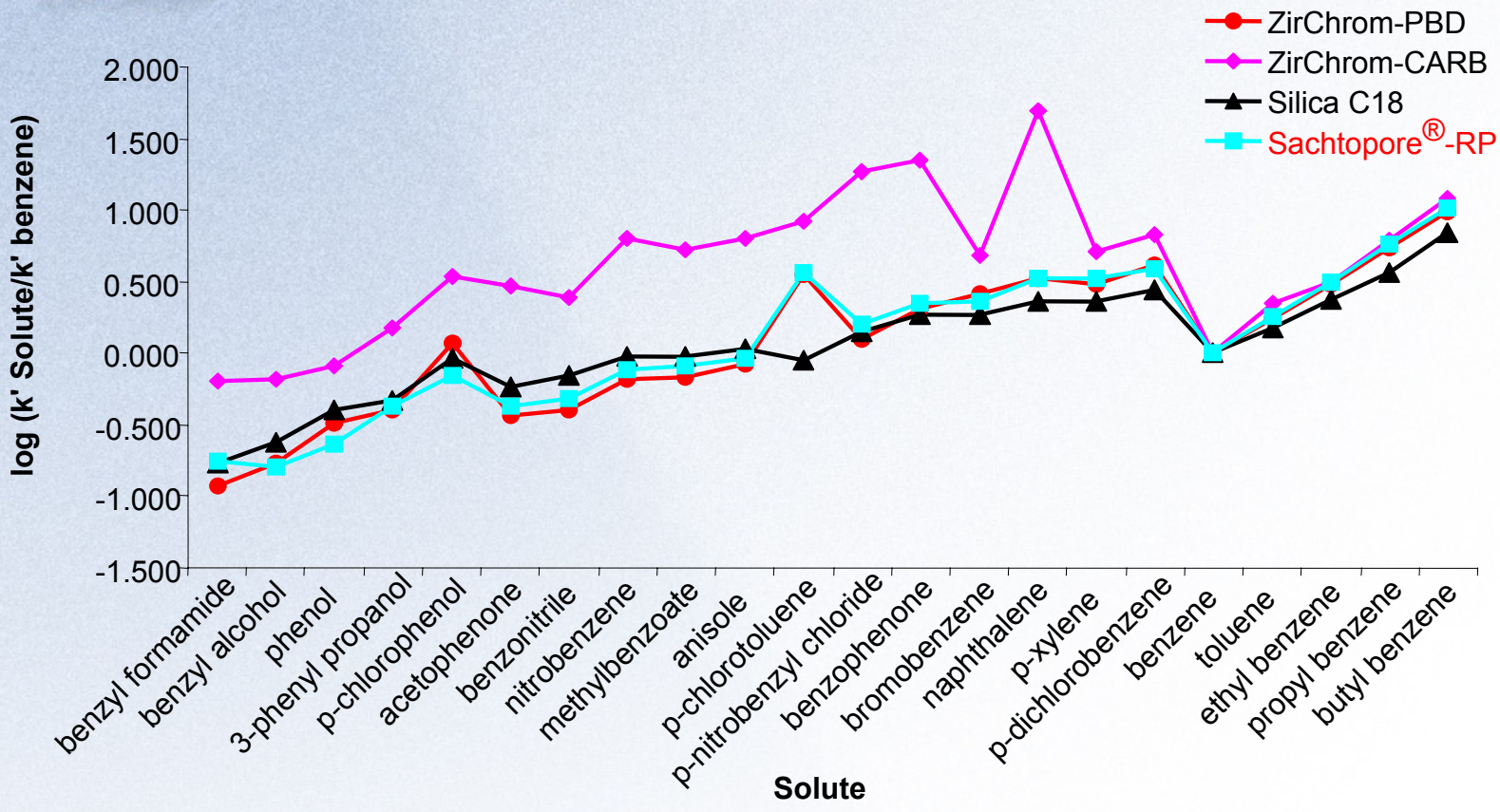




HB Donor

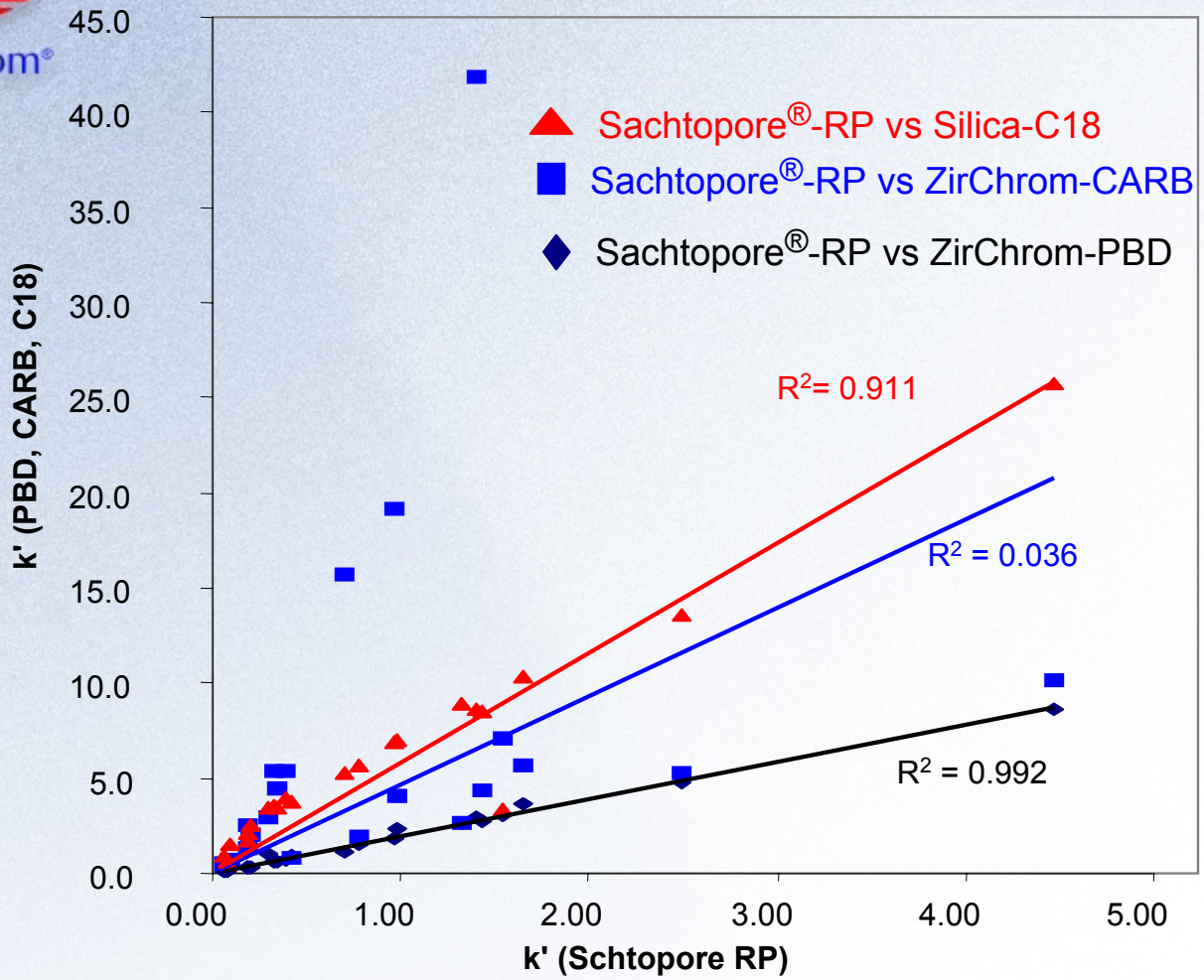


Selectivity Comparison



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

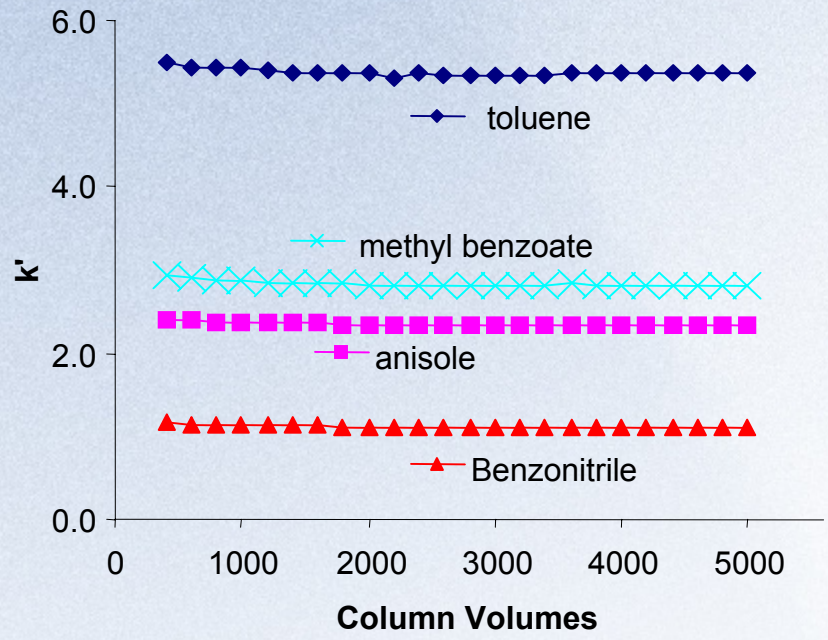


LC Conditions: Mobile phase, 40/60 ACN/Water; Flow rate, 1.0 ml/min.; Temperature, 30 °C; Injection volume, 5ul; Detection at 254nm.

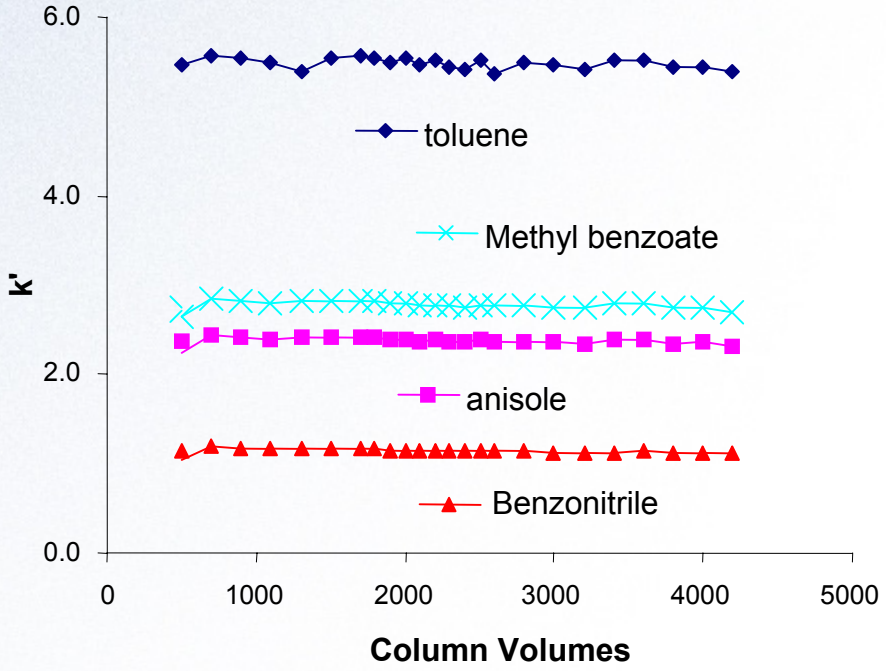
Reference: Melander, W.; Stoveken, J.; Horvath, C. *J. Chromatogr.* **1980**, *199*, 35-56.

Chemical Stability

pH 1.0

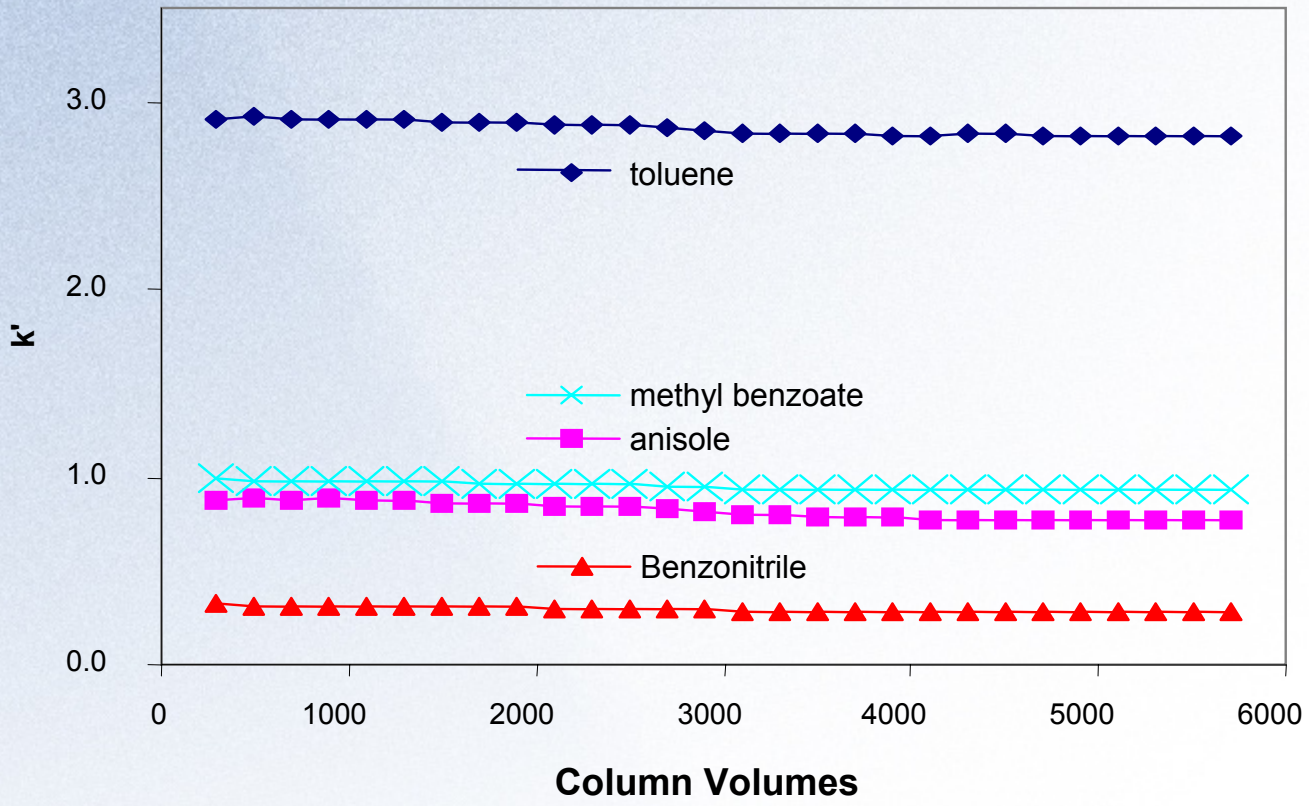


pH 12.0



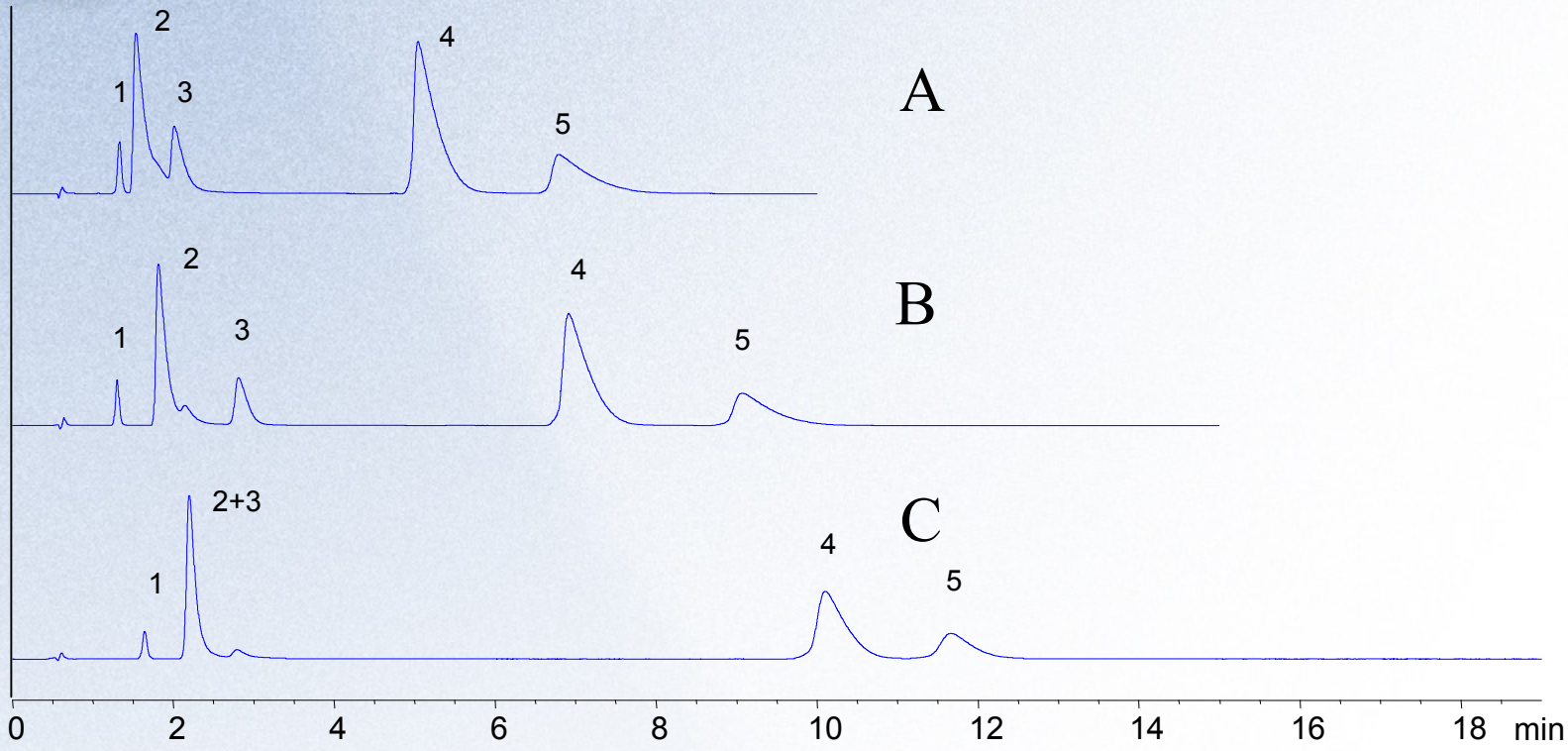
Exposure and Evaluation Conditions: Mobile phase, 15/85 ACN/0.1M Nitric acid, pH 1.0, or 0.01M Tetramethylammoniumhydroxide, pH 12.0; Flow rate, 1.0 ml/min.; Temperature, 30 °C; Injection volume, 5 µl; Detection at 254 nm; Column, 50 mm x 4.6 mm i.d. Sachtopore®-RP .

Temperature Stability at 100 °C



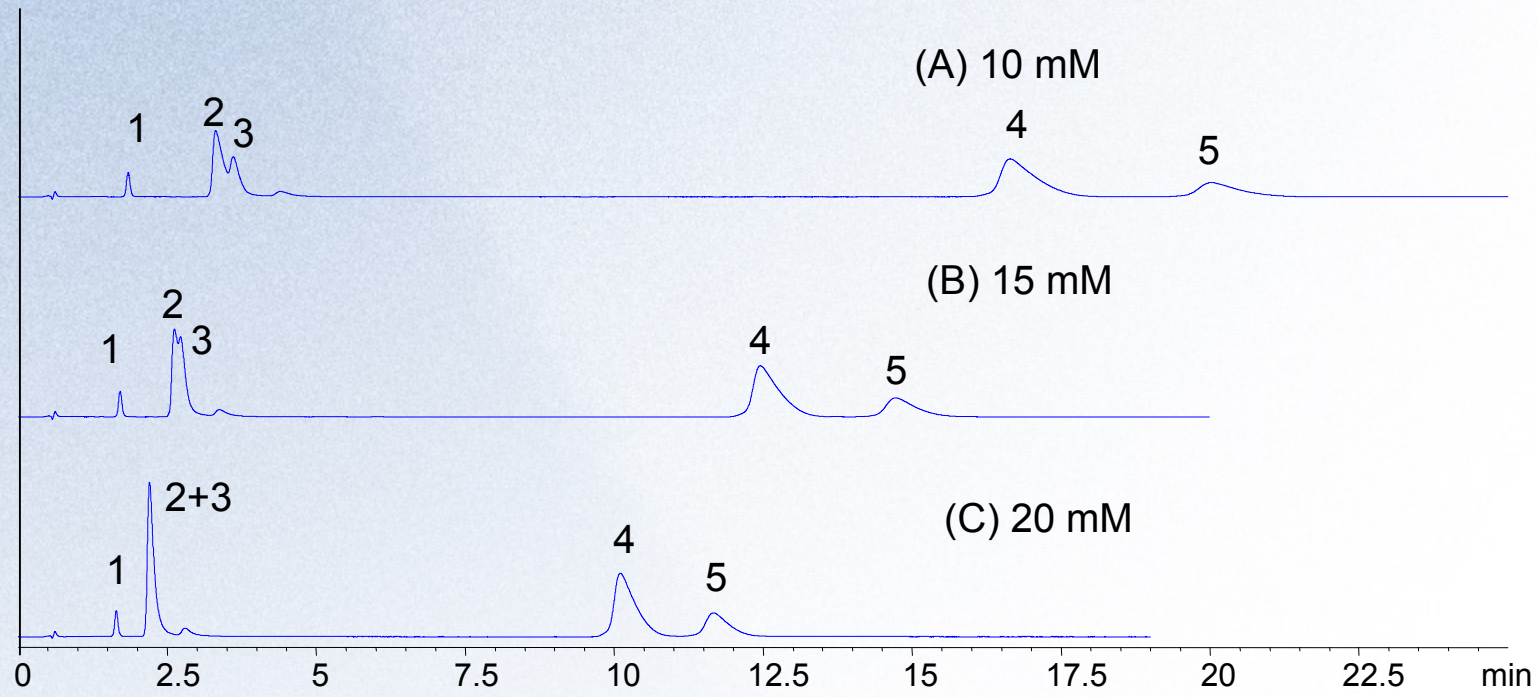
Exposure and Evaluation Conditions: Mobile phase, 15/85 ACN/water; Flow rate, 1.0 ml/min.; Temperature, 100 °C with Metalox heater; Injection volume, 5 ml; Detection at 254 nm; Column, 50 mm x 4.6 mm i.d., Sachtopore®-RP .

Effect of Lewis Base Additive on Separation of Basic Drugs



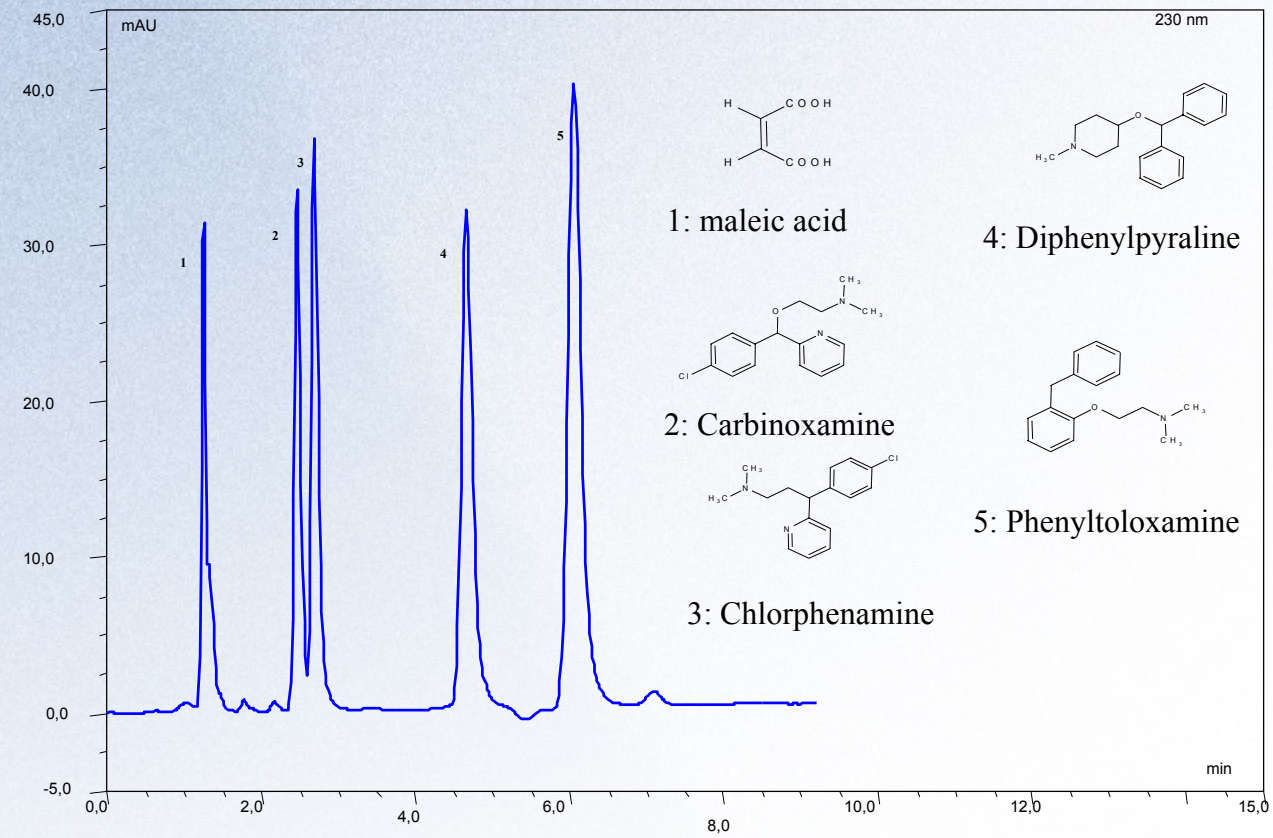
Chromatographic Conditions: Column 50X4.6 mm Sachtopore®-RP, Mobile phase: 30/70 ACN/20 mM buffer (pH=7). (A) ammonium acetate, (B) ammonium fluoride, (C) ammonium phosphate. flow rate: 1ml/min, temperature: 40 °C. Wavelength: 254 nm. Solutes: (1) lidocaine, (2) quinidine, (3) tryptamine, (4) amitriptyline, and (5) nortriptyline.

Effect of Ionic Strength on Separation of Basic Drugs



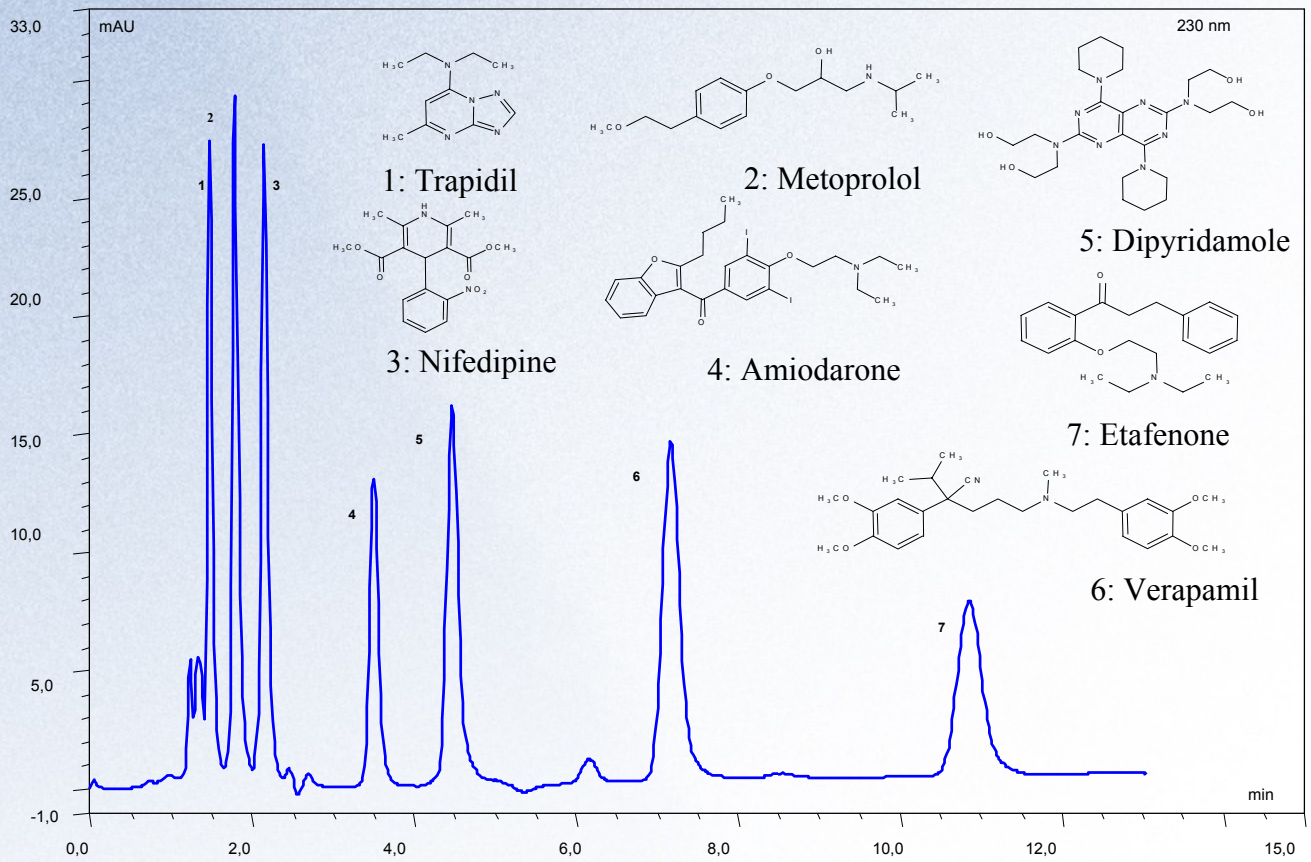
Chromatographic Conditions: Column 50X4.6 mm Sachtopore®-RP , Mobile phase: 30/70 ACN/phosphate buffer (pH=7). (A) 10 mM, (B) 15 mM, (C) 15 mM. flow rate: 1ml/min, temperature: 40 °C. Wavelength: 254 nm. Solutes: (1) lidocaine, (2) quinidine, (3) tryptamine, (4) amitriptyline, and (5) nortriptyline.

Antihistimines Separation at pH 10



LC Cconditions: Mobile phase, 74% (50 mM H_3PO_4 + 5 mM KH_2PO_4), 26% ACN, pH 10; Flow rate, 1.0 ml/min.; Temperature, Ambient; Injection volume, 20 µl; Detection at 220 nm; Column, Sachtopore®-RP (300 Å, 3 µm, 150x4 mm).

Separation of Basic Cardiac Drugs at pH 10



LC Cconditions: Mobile phase, 70% (10 mM Borax + 10 mM Soda), 30% ACN, pH 10; Flow rate, 1.0 ml/min.; Temperature, Ambient; Injection volume, 20 µl; Detection at 230 nm; Column, Sachtopore®-RP (300 Å, 3 µm, 150x4 mm).

Semi-Prep Separation of Pentifylline (vasodilator)

ZirChrom®

Particle Sizes:

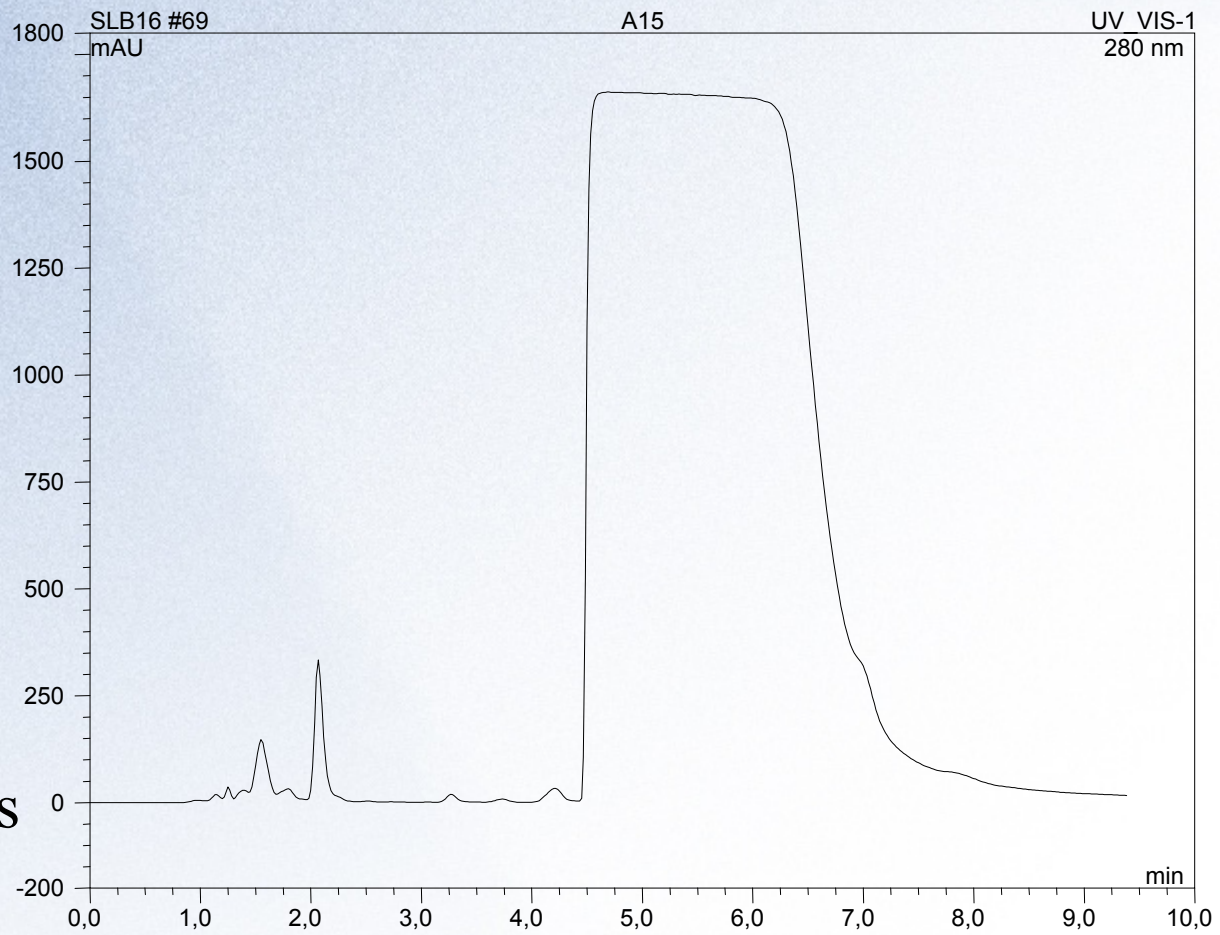
3,5,10,20,40,80

100 micron

1 mm

Pores sizes:

60, 100, 300, 500, 1000, 2000 Angstroms



LC Cconditions: Mobile phase, (+ 10 mM $Na_2B_4O_7$ + 1 mM H_3BO_3), pH 8.8; Flow rate, 1.0 ml/min.; Temperature, Ambient; Injection volume, 20 µl; Detection at 254 nm; Column, Sachtopore®-RP (300 Å, 3 µm, 150 x 4 mm).

Conclusions

- The Sachtopore®-RP shows *similar selectivity* to ZirChrom®-PBD (ODS-like for neutrals).
- The Sachtopore®-RP has *excellent stability* from pH 1-12 and up to 100 °C.
- The type of Lewis base buffer has a profound effect on *selectivity* for Sachtopore®-RP.
- Basic (amine) analytes generally undergo *RP/CEX mixed-mode retention mechanism* on Sachtopore®-RP.

Acknowledgments

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Dr. Bingwen Yan - ZirChrom

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For more information and web access to the free **Buffer Wizard:** www.zirchrom.com