Characterization of Carbon-Modified Silicas for Use in Analytical Liquid Chromatography

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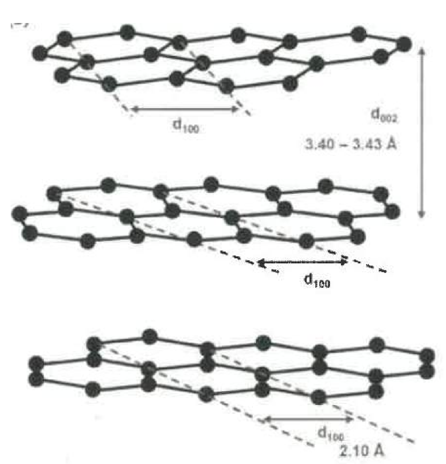
Abstract

We have recently developed a series of novel carbon-modified porous silica materials for use in analytical and preparative separations, and as solid-phase extraction media. The analytical materials exhibit unique characteristics compared to other commercially available carbon phases as they are substantially more stable at high pressures and exhibit acceptable mass transfer characteristics. Users of carbon-based phases are aware that some compounds are very difficult to elute from existing commercial carbon-based materials. The new materials described here significantly address this problem through both the ability to adjust the carbon loading on the underlying substrate, and the use of a relatively inert substrate. We will report on the basic characterization of a suite of materials that cover a wide range of carbon loading, including: retention of non-polar and polar compounds, and selectivity. We will also show the potential of these materials for use in two-dimensional separations.

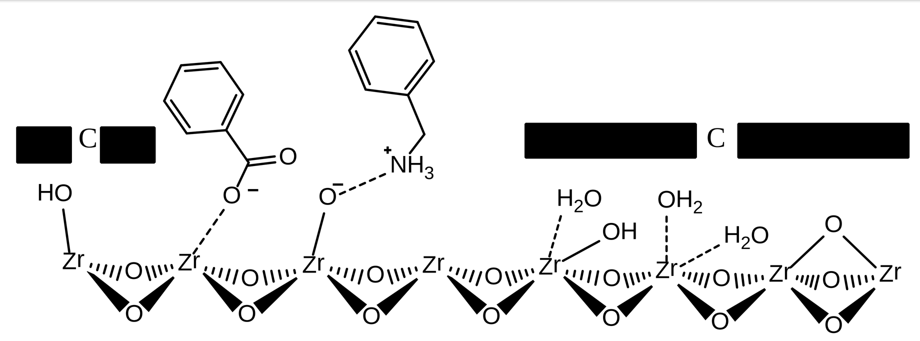
Commercially Available Carbon-Based Materials

Existing

Pure Carbon, also known as:
Porous Graphitic Carbon[1] (PGC, GCB), Hypercarb™

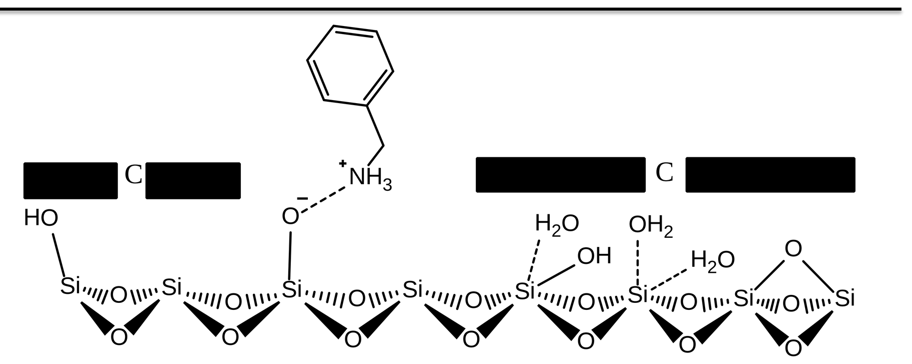


Carbon on Zirconia, also known as:
ZirChrom-CARB™



New

Carbon on Silica, referred to as COS



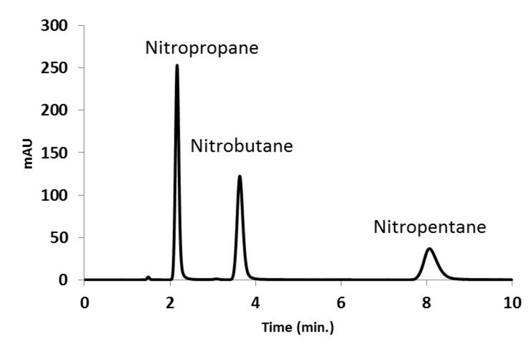
*We also note that Carr and coworkers have described the preparation of a material beginning with porous silica, followed by deposition of a thin layer of aluminum, and finally carbon modification by a CVD process[2].

Comparison of Materials for Analytical Separations

Carbon Features	Performance Consideration	Carbon on Silica	Carbon on Zirconia	Porous Graphitic Carbon
Any substrate particle architecture	Affects speed/performance optimization	+ + +	-	-
Manufacturing scalability	Product cost	+ + +	+ + +	-
High mechanical stability (packing, high operating pressure	Compatibility with UHPLC, fast LC	+ + +	+ + +	-
Tunable carbon load	Adjustable retention to aaccommodate large range in analyte properties	+ + +	+	-

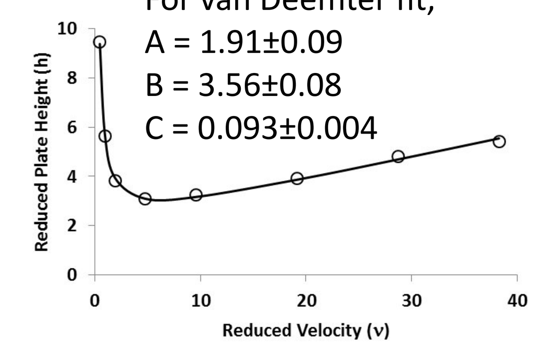
Analytical Materials – Basic RPLC Behavior (COS)

Peak Shape

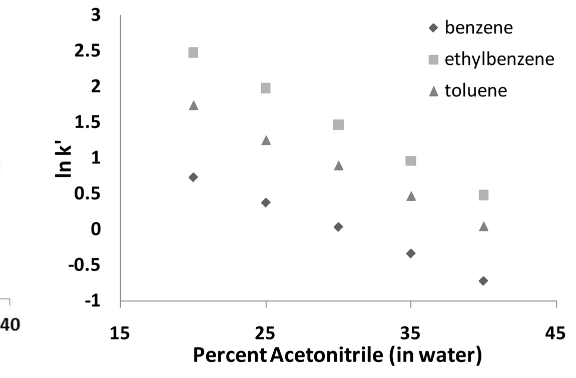


Dynamics

For van Deemter fit,
A = 1.91±0.09
B = 3.56±0.08
C = 0.093±0.004

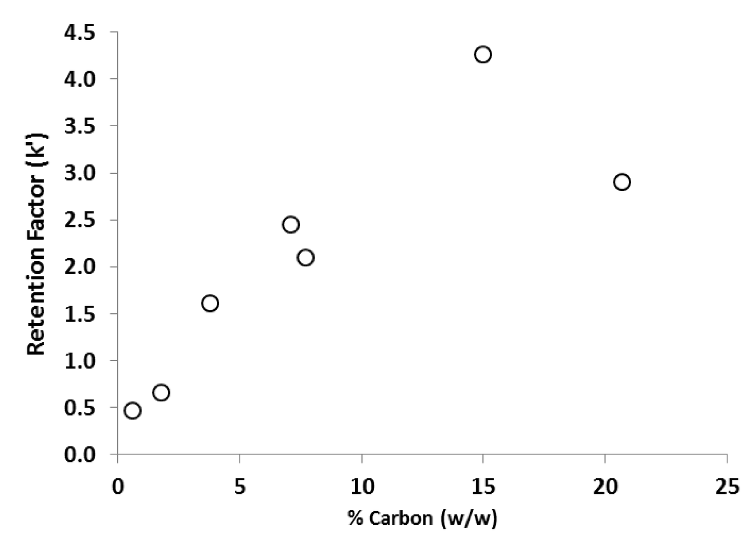


Reversed-Phase Retention



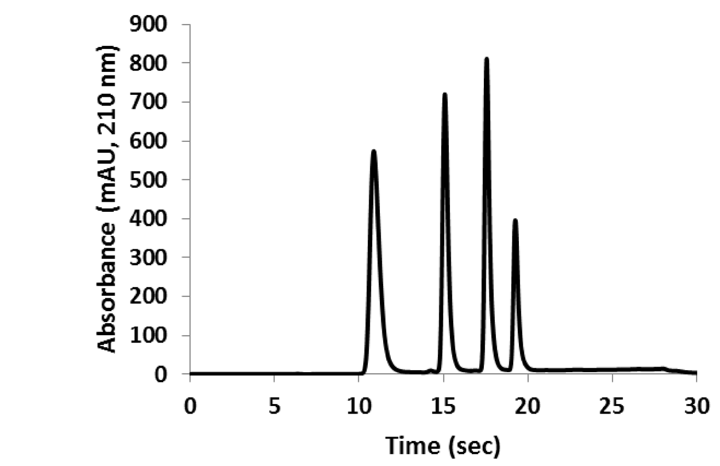
LC Conditions: 50 mm x 4.6 mm i.d. column (~17% carbon, w/w), 15/85 ACN/water (except LSST data); Temperature, 40 °C.

Tunable Retention



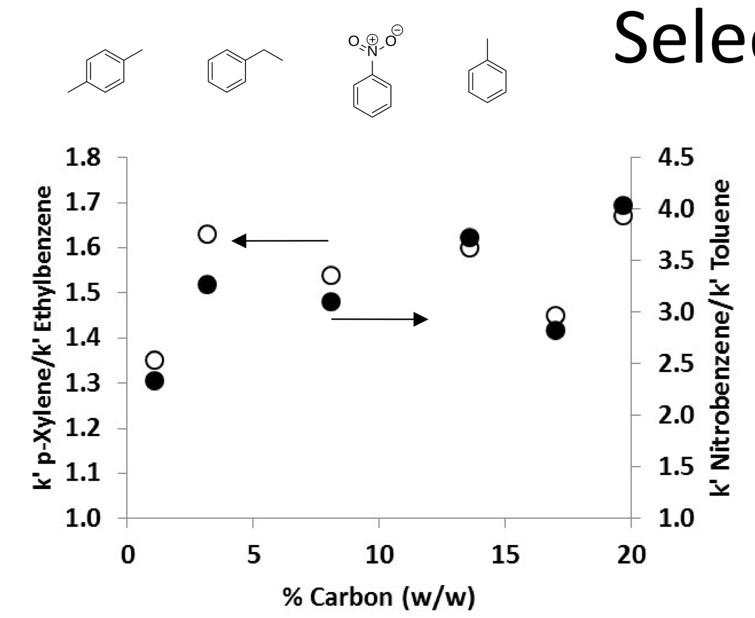
LC Conditions: Solute – Nitrobutane; 10/90 ACN/water; Temperature, 40 °C; Silica substrate, Agilent RxSil 80.

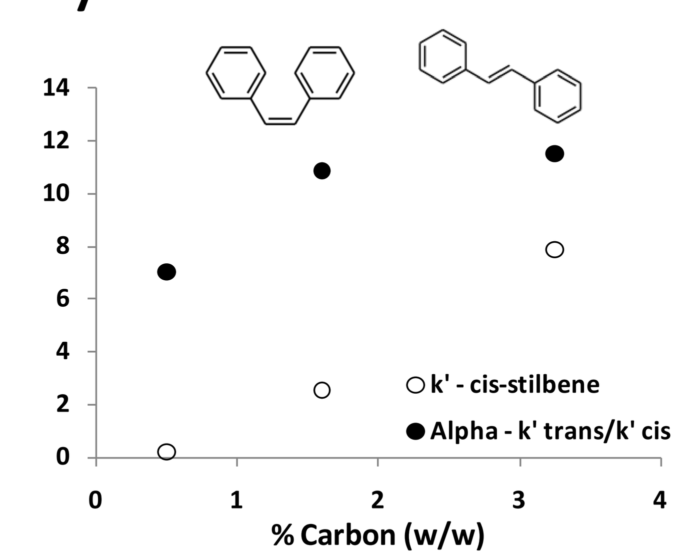
Fast Gradients on Superficially Porous Substrate



LC Conditions: Solutes – Nitropropane - Nitrohexane; Gradient elution from 5-100% ACN in 20 sec.; Temperature, 40 °C; 1.5 mL/min.; Silica substrate, Agilent Poroshell 120.

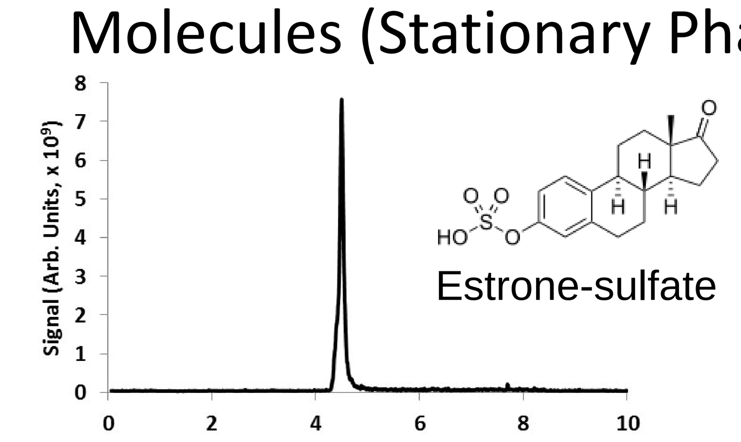
Selectivity





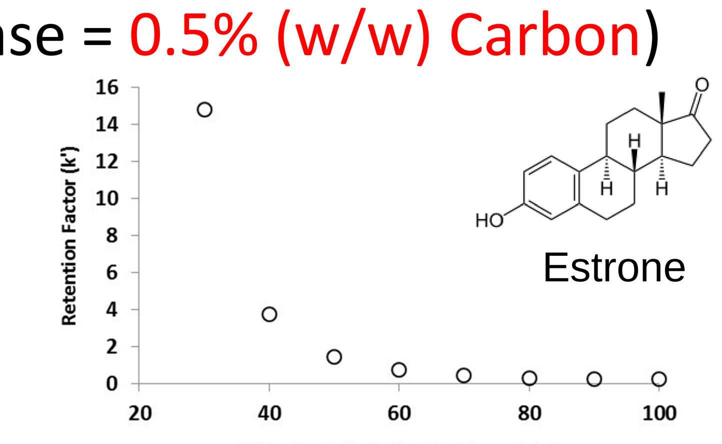
Carbon-like selectivities are exhibited over a very wide range of carbon load (~0.5-20% w/w)

LC/MS Compatibility and Retention of Highly Planar Molecules (Stationary Phase = 0.5% (w/w) Carbon)



Good peak shape for strong Lewis bases, even in formic acid buffer

LC Conditions: Gradient elution with solvent A – 0.1% formic acid, and B - ACN; Injection volume, 5 μL; Temperature, 40 °C; Detection in ESI negative mode.

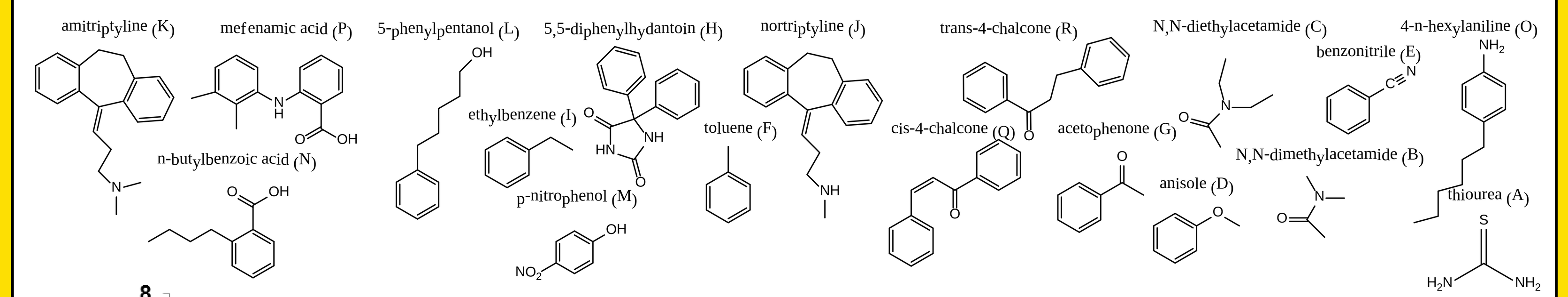


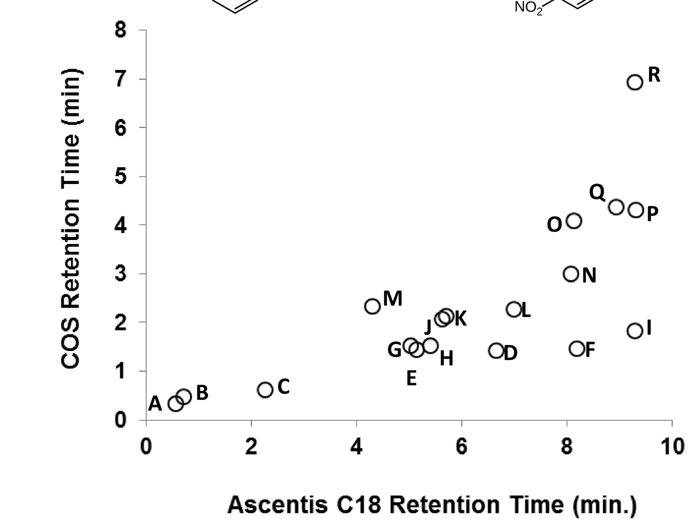
Reasonable retention for highly planar molecules, without exotic solvents

LC Conditions: Solvent A – 0.1% formic acid, and B - ACN; Injection volume, 5 μL; Temperature, 40 °C.

Chromatographic Selectivity for Ionizable Compounds

Snyder/Dolan Hydrophobic Subtraction Model Probes[3]



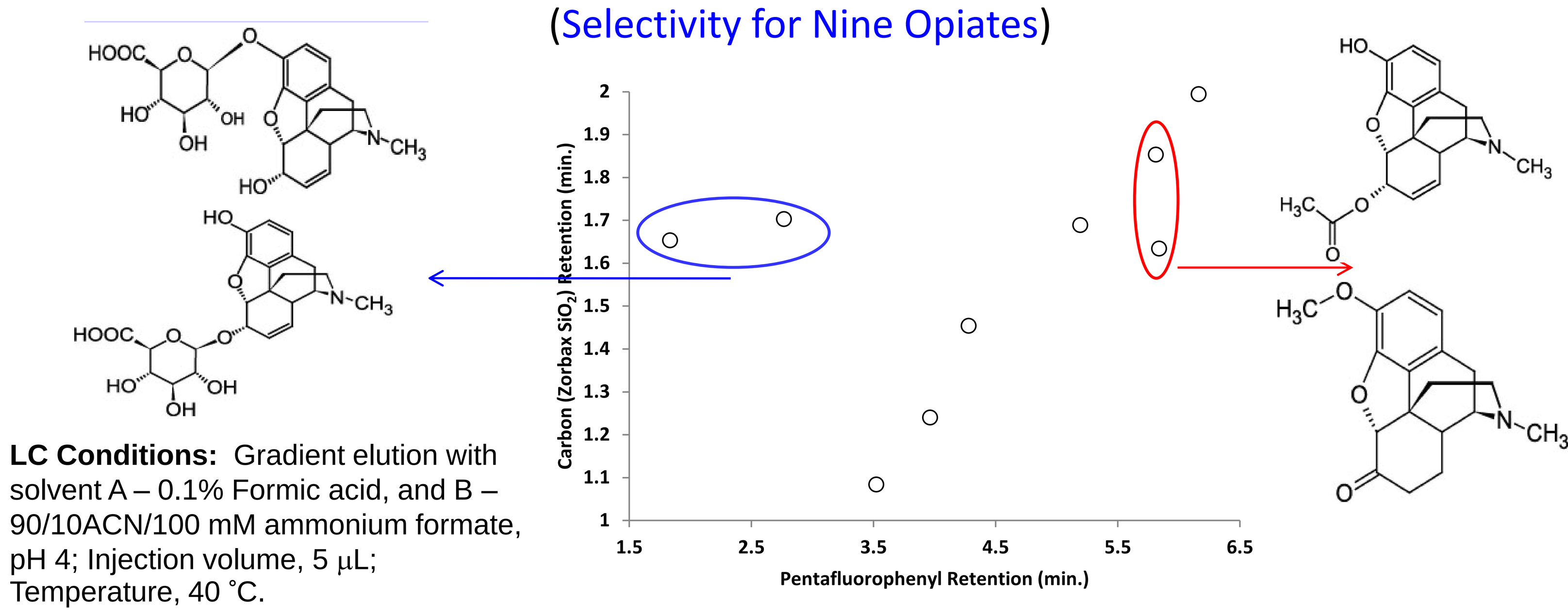


- Selectivity comparisons of carbon-based phases to bonded silica phases (e.g., C18) are well established[1,4].
- In this compound set, selectivity differences are difficult to interpret – further work is required.

LC Conditions: 50 or 100 mm x 4.6 mm i.d. columns (COS is 4% carbon, w/w); Gradient elution from 10 to 75% ACN with 60 mM potassium phosphate buffer at pH 2.8; Temperature, 40 °C.

Different RP Selectivity is Useful for 2DLC Separations

(Selectivity for Nine Opiates)



LC Conditions: Gradient elution with solvent A – 0.1% Formic acid, and B – 90/10ACN/100 mM ammonium formate, pH 4; Injection volume, 5 μL; Temperature, 40 °C.

Conclusions

- Carbon phases based on silica substrates (COS) show tremendous potential for analytical liquid chromatography applications.
- COS materials exhibit characteristic carbon selectivities over a very wide range of carbon load.
- The inertness of the silica substrate for the COS materials allows the analysis of strong Lewis bases, even under LC/MS-friendly conditions.
- COS phases exhibit selectivities for ionizable and polar compounds that are highly complementary to typical reversed-phase selectivities, and are useful in two-dimensional HPLC separations.

References

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2) Paek, C.; Huang, Y.; Filgueira, M. R.; McCormick, A. V.; Carr, P. W. *Journal of Chromatography, A.* 2012, 1229, 129–139.
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Acknowledgements

- Camille and Henry Dreyfus Foundation Faculty Start-Up Award (DS, $$$)
- Agilent Technologies (silica substrates)
- Howard Hughes Medical Institute (IGH, $$)
- Gustavus Adolphus College ($$$)
- Supelco (Pentafluorophenyl and C18 columns)