Highly Stable Polycarbosilane Bonded Phase Silica Columns for Elevated Temperature HPLC

Jody Clark

Dale Felix, Brian Jones

Stephanie Marin

Selerity Technologies, Inc.

Salt Lake City, UT

www.selerity.com

Introduction

High temperature liquid chromatography (HTLC) has become increasingly popular over the last several years because of the added benefits that it brings to the chromatographer. New instrumentation has been introduced into the market place that makes it possible to perform high temperature analysis efficiently and easily in laboratories. Along with the instrumentation, column development has progressed rapidly and columns that are stable at high temperatures and reversed phase conditions have been made available for high temperature separations. In this work, we will discuss a highly stable polycarbosilane bonded silica column that has proven to be stable up to 150°C.

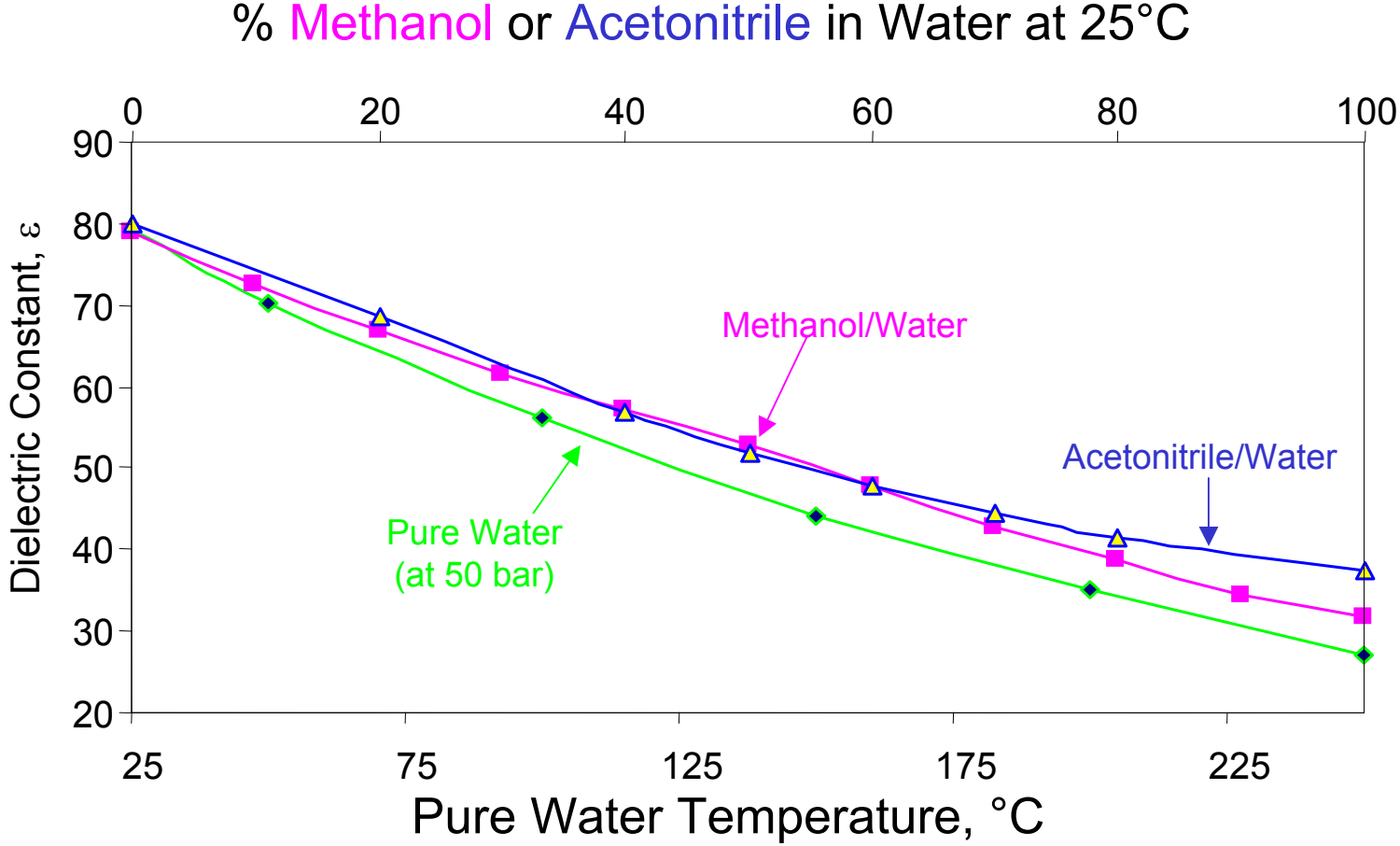
Benefits of Increasing Temperature

- Speed
- Efficiency
- Lower viscosity and back pressure permits higher flow rates with smaller particle size packings

What Kinds of Enhancement can be Expected?

- Peak focusing similar to programmed elution in GC
- New selectivity options
- Isocratic elution of a wide range of analytes
- Simultaneous use of compositional gradients or flow programming for additional flexibility

Solvent Polarity as a Function of Temperature



Data from Y. Yang et al. *J. Chromatogr. A* **810** (1998) 149.

Selectivity and Temperature in HPLC

- Hydrogen bonding decrease-supports, mobile phases and solutes
- Improved selectivity with amines
- pH influence on retention more pronounced
- Ionizable analyte retention is strongly affected
- General retention decrease with temperature under reversed phase conditions

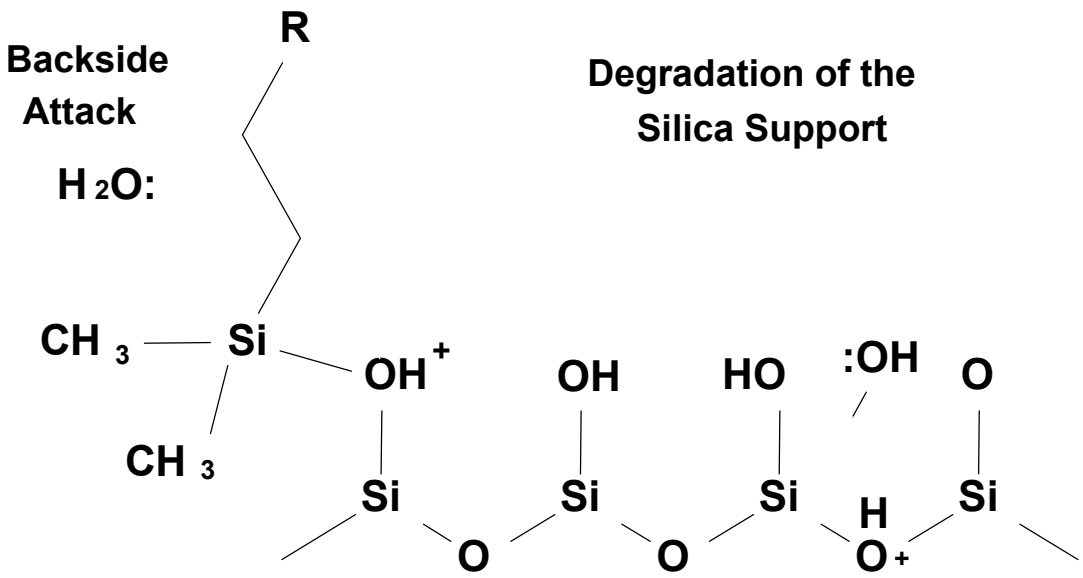
Stable Columns for Elevated Temperature HPLC

- Base material
  - Zirconia, Titania, Silica (+Hybrids), Polymeric
- Stationary phase
  - Bonded phases tend to be more stable
  - A high degree of crosslinking favors stability

- Traditional silica columns will break down at temperatures as low as 60°C

Hydrolytic Breakdown is Accelerated at Higher Temperatures

Water attacks the siloxane bond or behind point of phase attachment

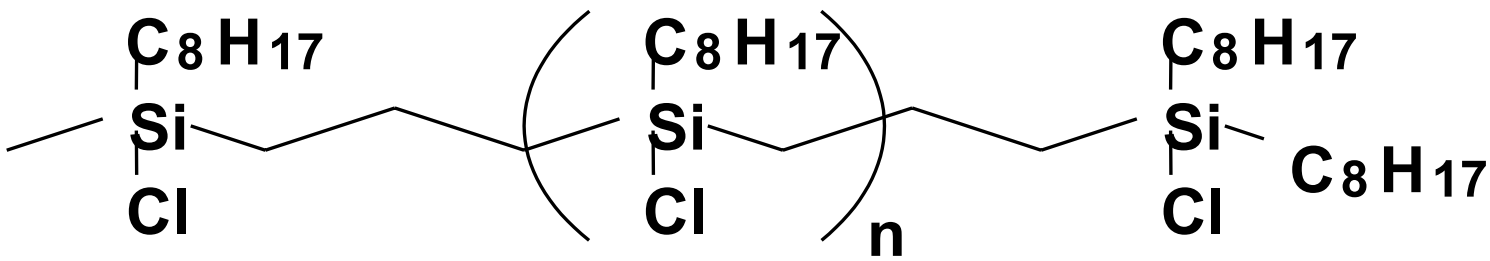


Polydentate Bonded Phase

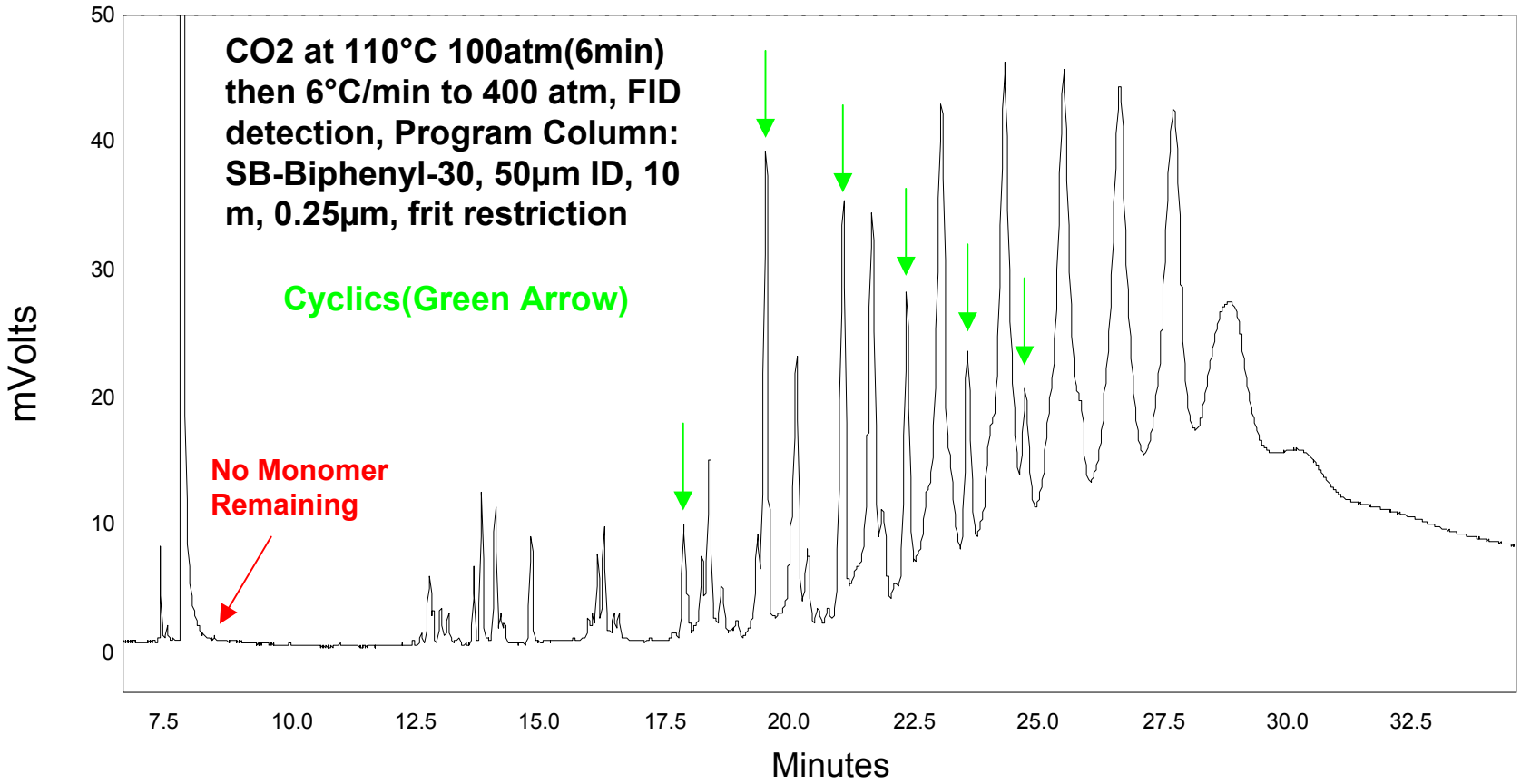
- Multiple attachment points to the particle surface
- Multiple crosslinking points to adjacent polymer chains
- Thermal and hydrolytically stable backbone
- Bonded to silica and zirconia

Functionalized Monomers are Prepared Using Grignard Chemistry

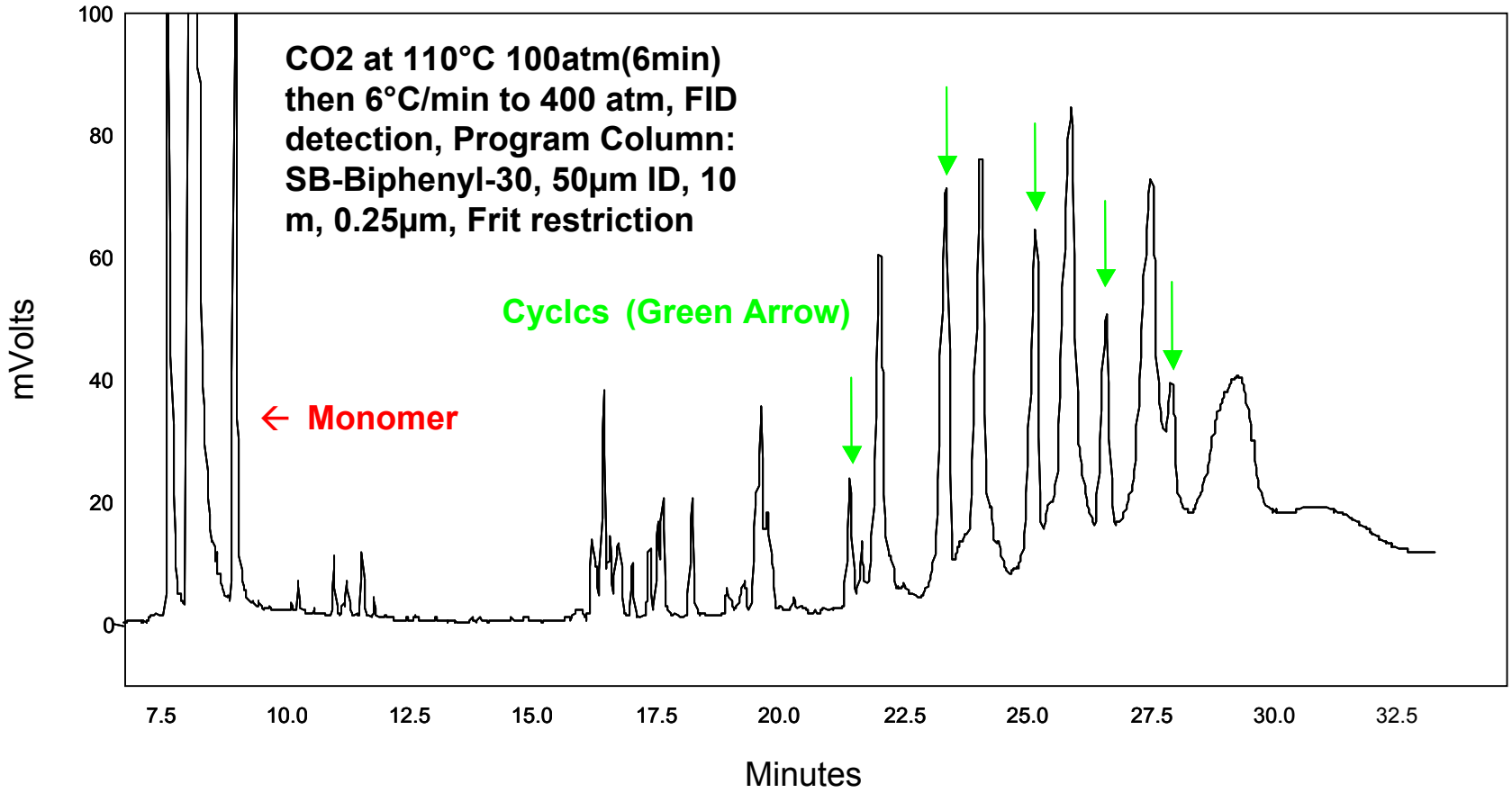
Polycarbosilane Bonded Phase Precursor



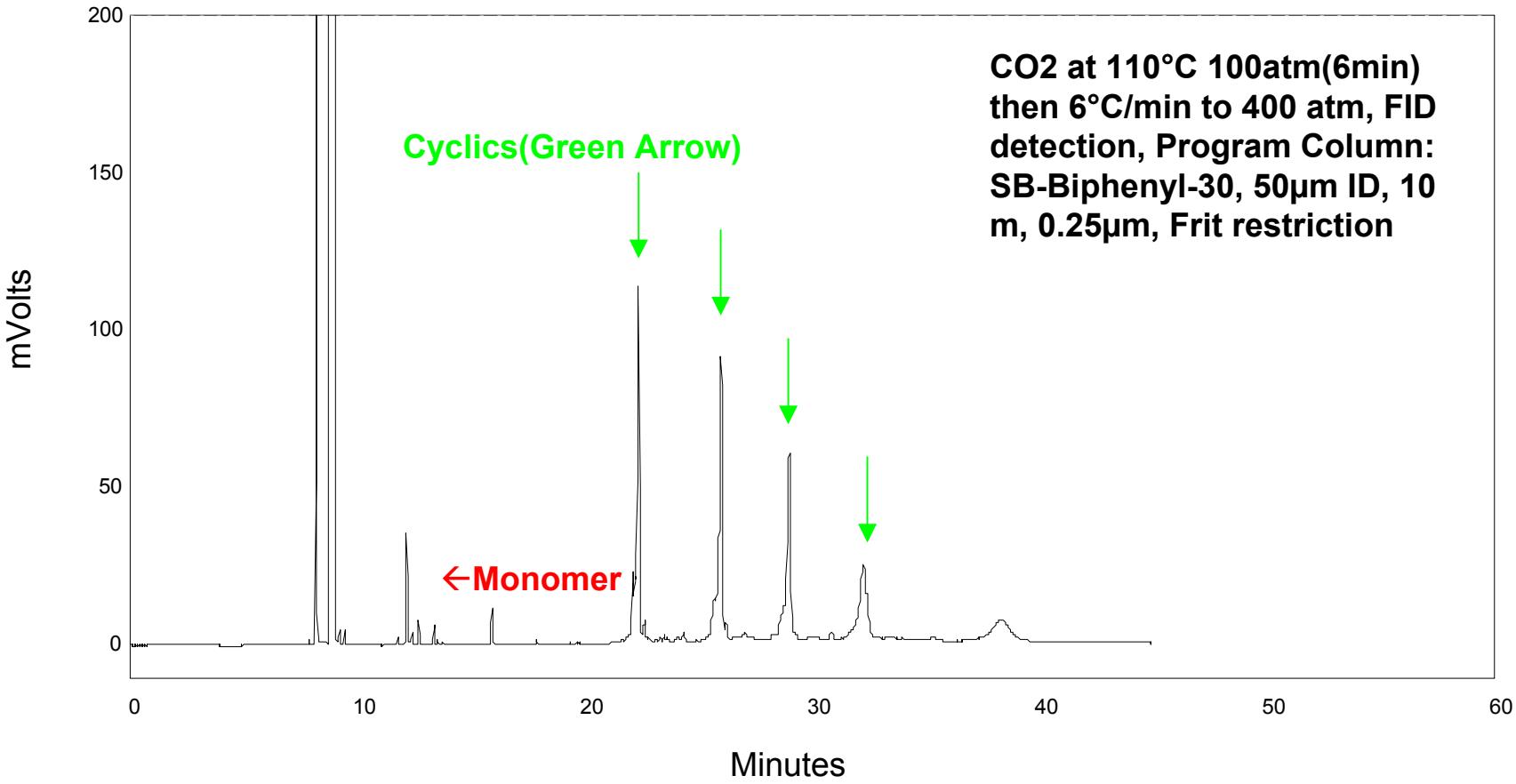
C_4 Polydentate Monomer Polymerization



C_8 Polydentate Monomer Polymerization 50 hrs

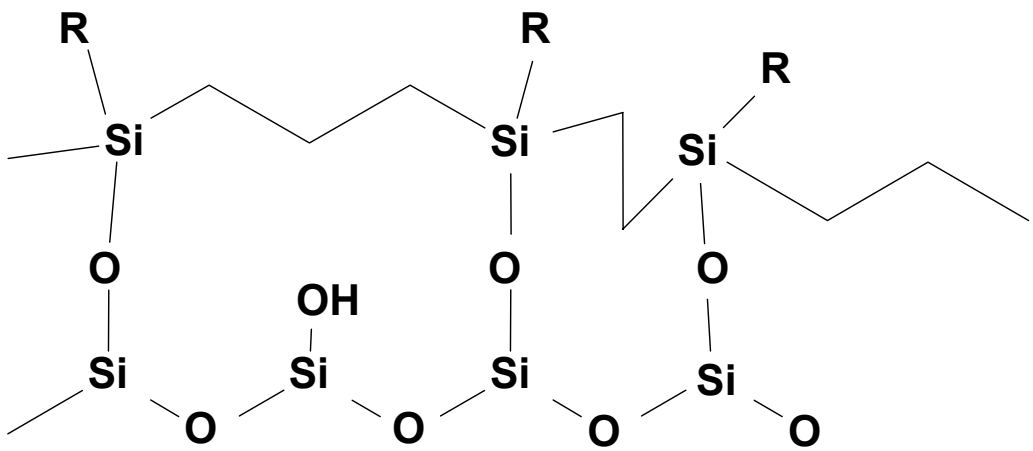


Phenyl Polydentate Monomer Polymerization

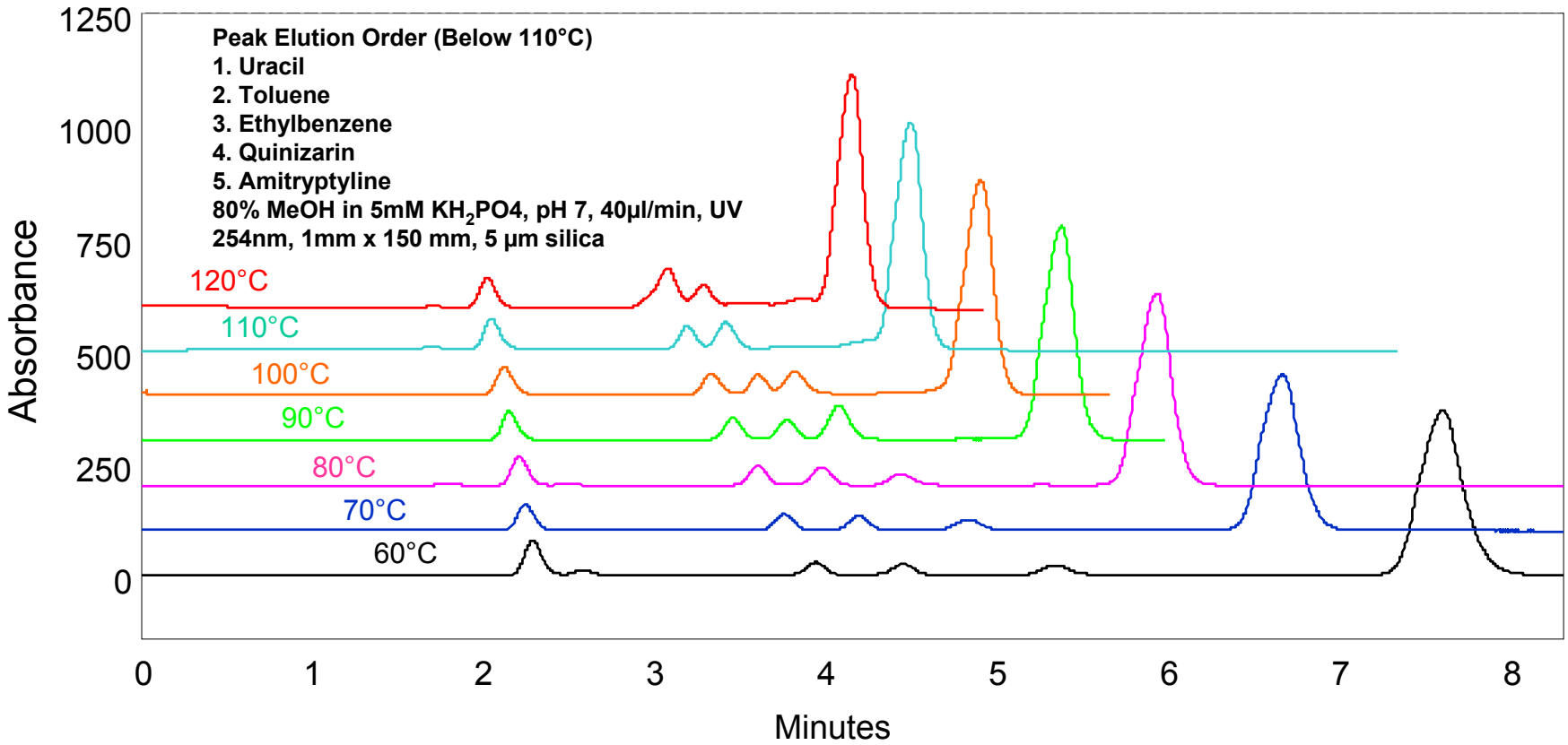


Polycarbosilane Bonding Structure

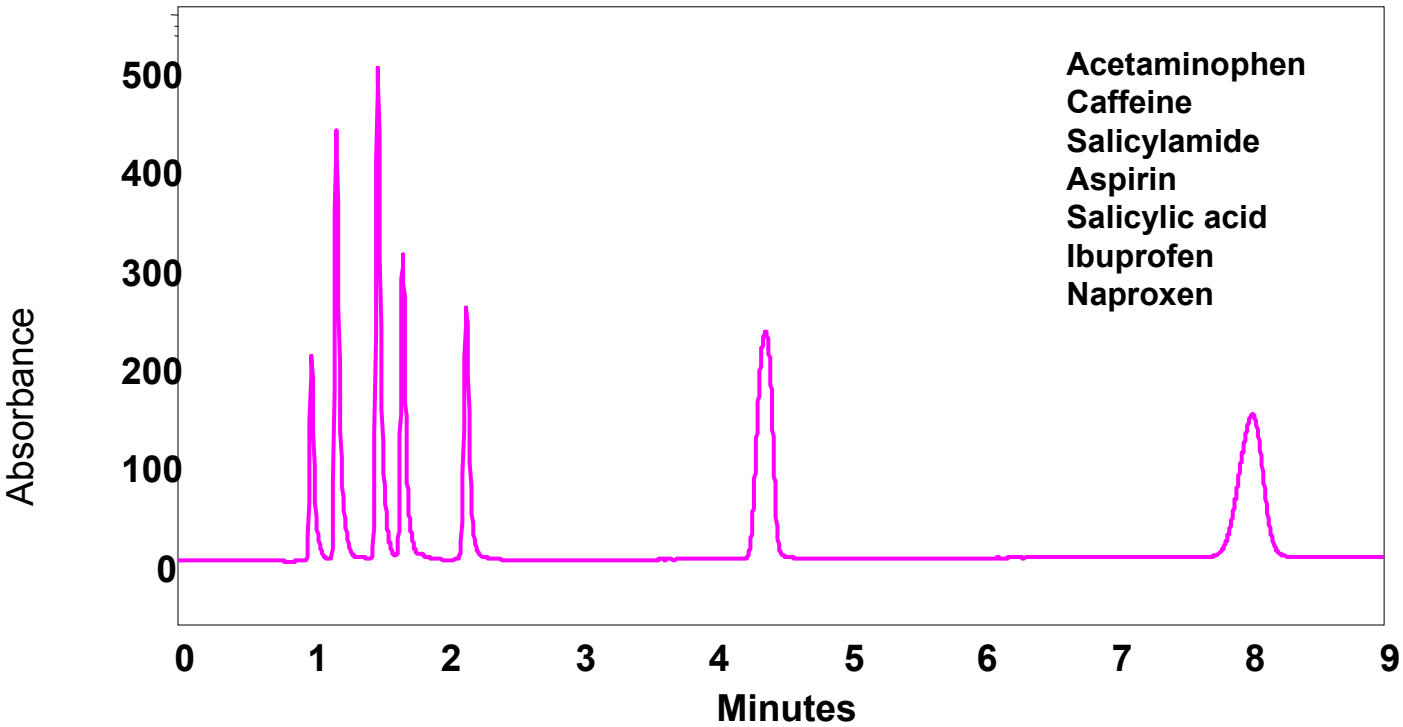
- Polymer chain protects surface silanol groups
- Attaches to surface at multiple points



C_4 Polydentate Column
NIST 870 Test Mixture

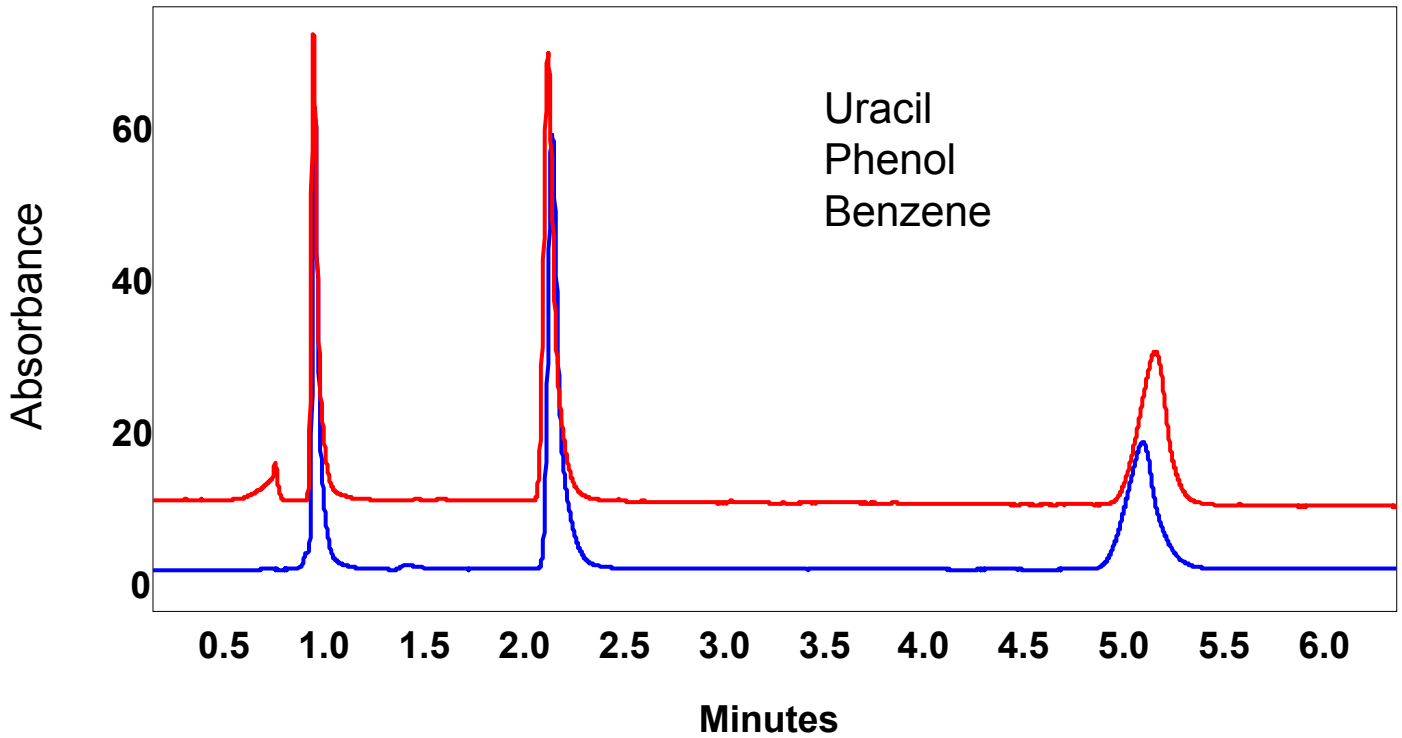


Separation of Analgesics Using a Thermal Gradient



Column: Selerity Blaze C8, 3 µm, 100 x 4.6 mm
Mobile Phase: 40:60 acetonitrile:water with 0.1%TFA
Flow Rate: 1.5 mL/min
Detection: UV 220 nm
Temperature Program: hold at 50°C for one minute, ramp to 100°C at 30°C/min, hold six min.

Performance Check After Multiple Thermal Gradient Runs to 150°C



Column: Selerity Blaze C8, 3 µm, 100 x 4.6 mm
Mobile Phase: 35:65 acetonitrile:water 50°C Isothermal
Flow Rate: 1 mL/min
Detection: UV 254 nm

Conclusions

- Temperature programming can be used successfully with columns up to 4.6 mm
- Polycarbosilane stationary phases with multiple bonding points can be used successfully at temperatures as high as 150°C

Future Work

- Expand chemistry to include polar functionality
- Surface coat silica tubing and particles for CE applications

Turn up the Heat

Selerity Technologies Inc.
2484 W. Custer Rd.
Salt Lake City, UT 84121
801-978-2295
www.selerity.com

Patent applications have been filed relative to the new technologies presented in this work.