

New Monolithic Ion-Exchange Media for Use in Ion Chromatography

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INTRODUCTION

In recent years, a number of researchers have focused on preparation of monolithic media. While silica-based monolithic media have been available for some time, the availability of polymer-based monolithic media has been limited to materials for use with macromolecules. A number of academic groups have explored the possibility of preparing polymeric monolithic media for ion chromatography, but so far none have prepared materials which are comparable to the performance of commercially available packed column formats. In this paper we will describe the first polymeric monolithic ion-exchange materials suitable for commercial applications. These new monolithic ion-exchange materials exhibit high permeability, characteristic of such materials, and in addition exhibit significantly higher chromatographic performance than has been reported to date. The improved performance was made possible by several new advancements in polymeric monolithic stationary phases including: a methodology for bonding the monolith to the wall of polymeric capillary tubing, optimization of the pore morphology, and improvements in stationary phase synthesis methodologies. Furthermore, this synthesis methodology has been adapted to 1-mm internal diameter column formats so that columns can be used at high linear velocity without the need for the excessively high flow rates characteristic of 4.6-mm internal diameter monolithic materials.

OVERCOMING MONOLITH SHRINKAGE

Synthesis is performed within column hardware using one of the following methods:

- Polymerization with subsequent swelling in eluent to achieve a seal against the tubing wall
- Post-polymerization axial compression to compensate for polymerization shrinkage
- Post-polymerization functionalization induced swelling to achieve a seal against the tubing wall
- Polymerization with covalent attachment to the tubing wall

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During post-polymerization compression, dynamic compression (water at high flow rates) and/or mechanical compression (insertion of piston-frits) is used to seal the monolith against the column wall.

Split peaks are observed when the analyte travels both *through* the monolith and *between* the monolith and the walls of the column housing.

When the monolith is sufficiently compressed, peak shape and efficiency are significantly improved.

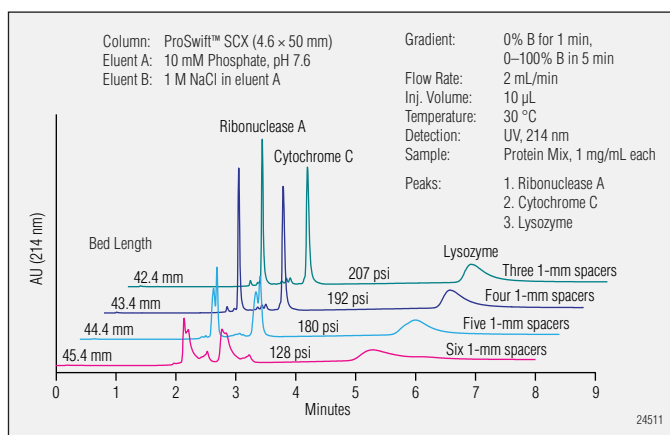


Figure 1. Optimization of axial compression on an SCX prototype monolith.

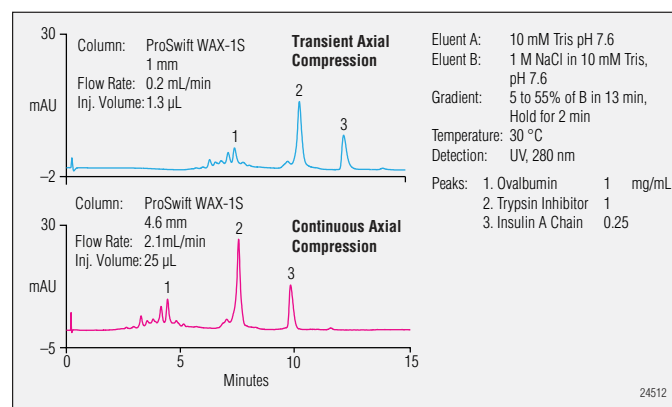


Figure 2. Comparison of axial compression methods.

COVALENT ATTACHMENT STRATEGIES

- Modification of the tubing surface to incorporate radical grafting sites (facilitates hydrogen abstraction or heteroatom abstraction)
- Attachment of monomers to the tubing surface
- Attachment of reactive polymers to the tubing surface
 - Direct attachment using covalent coupling (grafting onto)
 - Formation of polymer in the presence of the tubing under grafting conditions (grafting through)

MONOLITH PREPARATION

Activate a PEEK™ capillary to promote grafting.

Mix monolith components:

- Monomers (styrene, divinylbenzene)
- Porogens (Isooctane, Propionitrile, THF and/or Decanol)
- Initiator (AIBN)

Fill column, cap ends of capillary, and pressurize.

Polymerize at 70 °C overnight.

Rinse with 100% acetonitrile.

IC Separation Media Design Requirements

Optimal performance for IC separation media:

- PS-DVB polymeric media (compatible with extreme pH)
- Polymeric column hardware (compatible with extreme pH)
- Narrow bore column (enables continuous operation)
- Monolithic media (high permeability enables high flow)

Monolith must be bonded to polymeric column hardware.

Stationary phase attached as a surface film using either:

- Monolayer of colloidal ion-exchange nanoparticles (or)
- Electrostatically grafted, hyperbranched condensation polymer

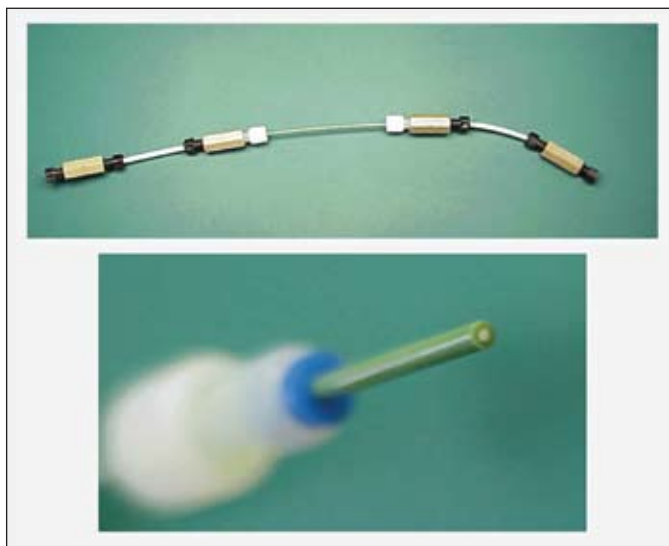


Figure 3. Monolith IC column development.

Acetonitrile-Water Pressure Test

The observed backpressure of the column is related to its permeability and the viscosity of the eluent. When the monolith is sufficiently bonded to the wall so that flow does not bypass the monolith pore structure, the backpressure is related only to the eluent viscosity. If channeling occurs when the monolith is in a shrunken state (in this case, when in water) the monolith will appear to be more permeable and the resulting backpressure will be much lower than expected. Using these principles, the backpressure ratio of water to acetonitrile (when no channeling occurs) should be 2.54. Using a lower ratio will result in insufficient wall adhesion.

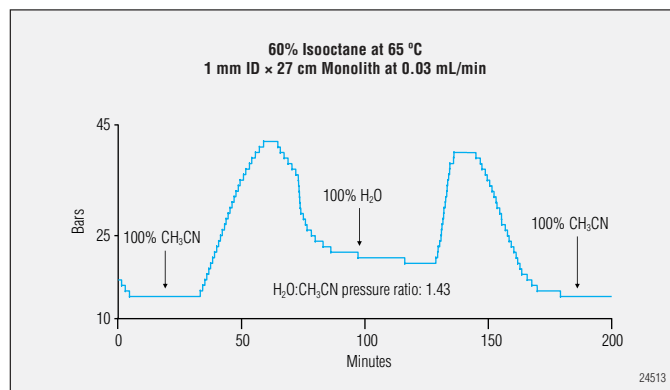


Figure 4. Acetonitrile-water pressure test.

The profile also reveals changes to the column as the column is cycled between swelling and shrinking solvents.

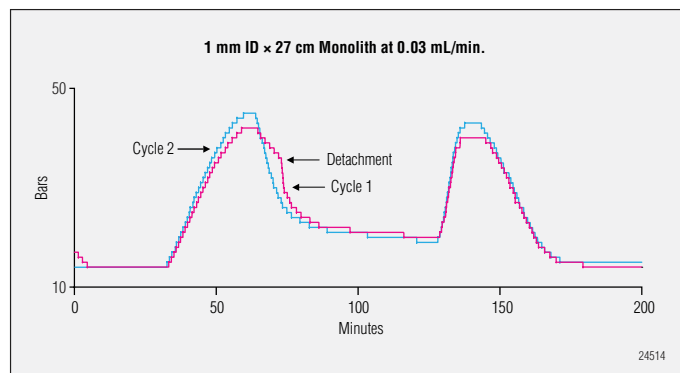


Figure 5. Detachment during testing.

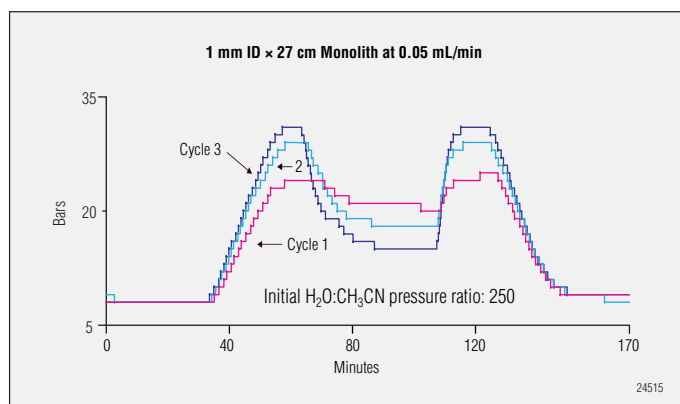


Figure 6. Progressive loss of adhesion during testing.

As wall adhesion improves, the water-acetonitrile pressure ratio increases towards the target.

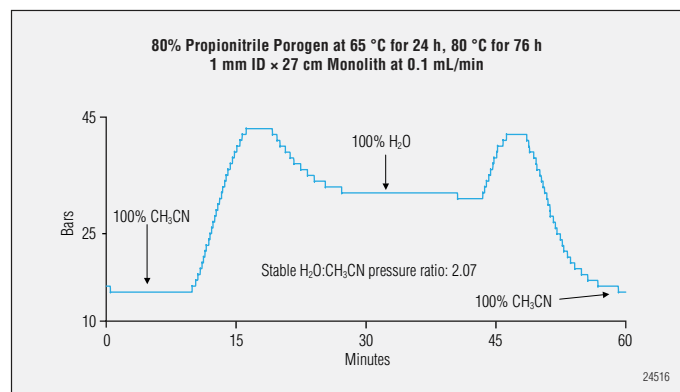


Figure 7. Acetonitrile-water pressure test.

A test probe is also used to monitor the path of an unretained analyte. The void volume can be calculated based on the known pore volume of the monolith. When an analyte elutes too early, this indicates that the flow path is *around* rather than *through* the porous structure of the monolith.

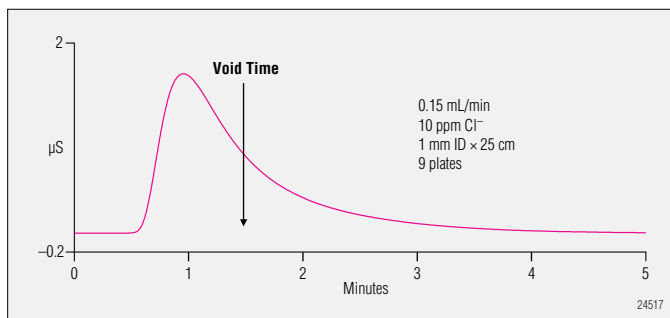


Figure 8. Dispersion test with an unretained test probe.

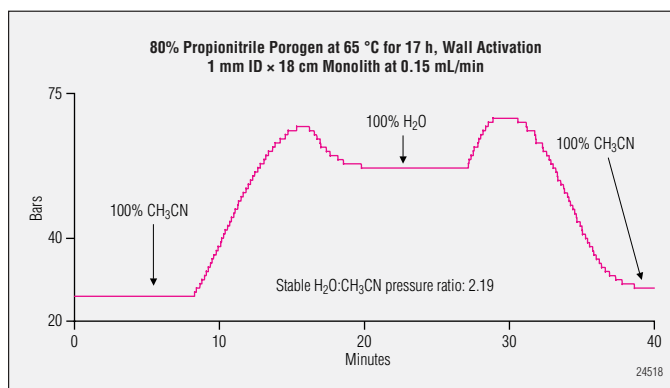


Figure 9. Acetonitrile-water pressure test.

When wall bonding is achieved and the analyte flows through the pores of the monolith, a gaussian peak elutes at a time equivalent to the pore volume of the column.

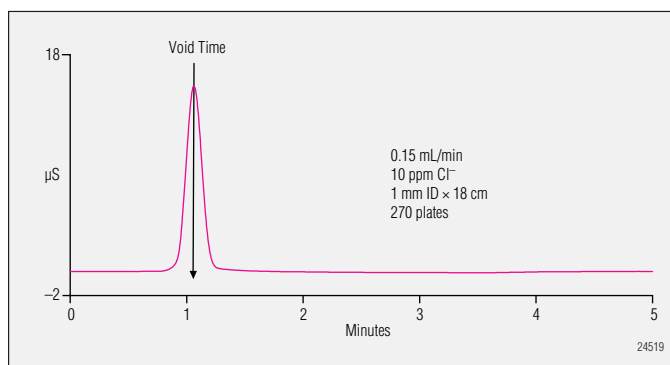


Figure 10. Dispersion test with an unretained test probe.

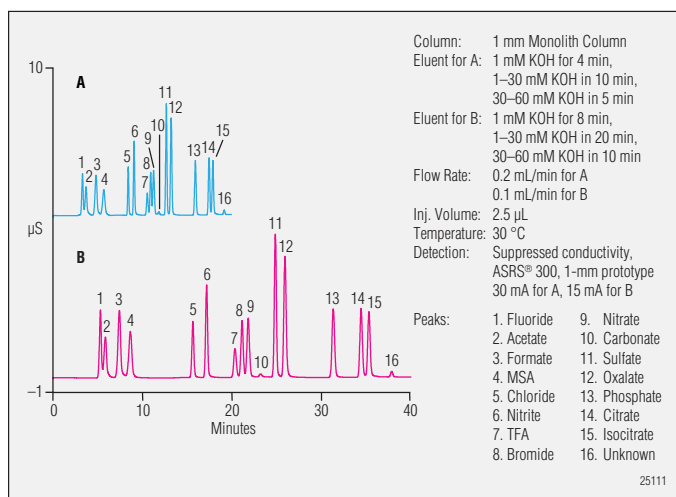


Figure 11. Effect of flow rate on resolution with monolithic media using AS11-HC latex.

Achieving wall bonding is essential to achieving small molecule analysis. Modification of the monolith with an ion-exchange latex allows successful separation of small ions (Figure 14).

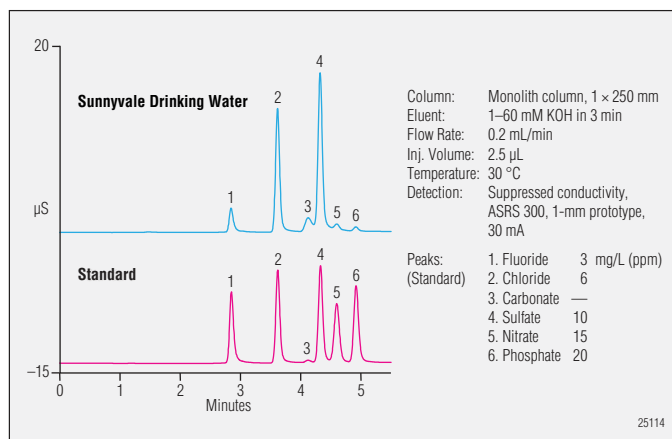


Figure 14. Fast gradient separation of common anions with monolithic media.

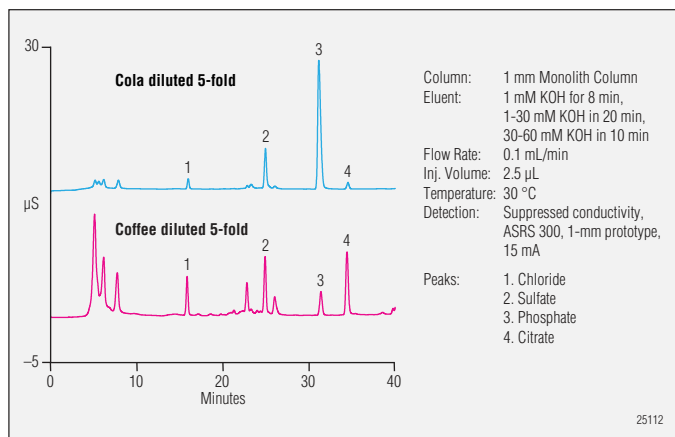


Figure 12. High resolution separation of organic acids and inorganic anions using monolithic media.

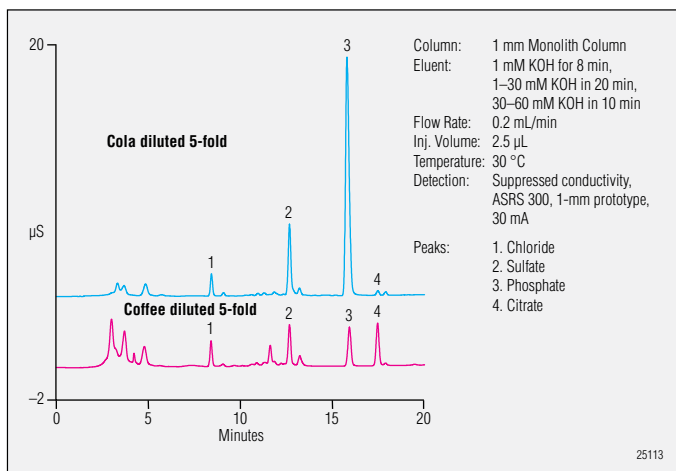


Figure 13. Resolution of organic acids and inorganic anions using monolithic media at high linear velocity.

CONCLUSIONS

- For larger-diameter polymer monoliths, continuous axial compression provides good chromatographic performance.
- For 1 mm polymer monoliths, wall effects which allow transient axial compression can provide equivalent performance.
- Chemical modification of PEEK capillaries enables covalent attachment of polymer monoliths and improved chromatography for small molecules.
- Monolith chromatographic performance is now adequate for commercially viable small molecule monoliths.

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