

Comparison of Different Synthesis Strategies for the Preparation of Polymeric Monoliths for Ion Chromatography

C. Pohl and C. Saini, Dionex Corporation, Sunnyvale, CA, USA

INTRODUCTION

In recent years, considerable effort has been focused on the development of monolithic materials for use in ion chromatography. Monolithic media offers the potential benefits of faster analysis or improved resolution with comparable analysis speed. However, most research in this area has utilized silica based media well known to be unacceptable for ion chromatography applications due to its pH limitations. In addition, virtually all polymeric media prepared in dimensions likely to be useful for ion chromatography has been prepared in fused silica capillaries. Unfortunately, fused silica capillaries are not suitable for use in ion chromatography under the alkaline conditions commonly employed in the analysis of anions. In this paper, we explore potential opportunities for the preparation of polymeric monolithic aggregates in polymeric column hardware.

MONOLITHIC MEDIA

Advantages of Monolithic Media in Ion Chromatography

- Improved separation efficiency and/or speed
- No frits or column end fittings required (simplifying low dead-volume plumbing)
- Small bore formats compatible with preparation of 0.5–2 meter columns
- Small bore formats suitable for use under continuous operating conditions (minimizing delays associated with system startup and shutdown)

Disadvantages of Conventional Monolith Preparation

- Shrinkage of the monolith during polymerization necessitates either:
 - Bonding to the capillary wall (difficult to achieve with polymeric capillaries)
 - Using a mobile phase swollen monolith structure (lower physical stability and poor mass transport)
- Each monolithic material requires laborious and difficult polymerization optimization
- Difficult to utilize existing stationary phases without extensive optimization work

IC Separation Media Design Considerations

- Suppressed conductivity detection necessitates extreme eluent pH (< 3 for cation separations and > 11 for anion separations)
- Sample pH values are frequently extreme
- Ion exchange retention provides greater focusing power than reversed phase, providing improved performance with high linear velocity gradient separations
- An all electrolytic IC instrument provides improved performance when operated continuously

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 columns (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 1 illustrates the use of a pressure profiling method as a means of determining the extent of adhesion of a monolith to the walls of a PEEK capillary. The theoretical pressure ratio of 100% water: 100% acetonitrile should be approximately 2.6:1 (based on the viscosity ratio of the two solvents at 25°C). In a non-bonded monolith in a PEEK capillary the ratio is actually less than one, because in acetonitrile the monolith swells to seal against the walls of the capillary, whereas in water the monolith shrinks and pulls away from the capillary wall, leaving a gap. Figure 2 demonstrates the pressure profile for a monolith that has been covalently bonded to the PEEK capillary. The next step will be to chemically modify the monolith and then evaluate the chromatographic properties of such covalently bonded monoliths.

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Monolith Sealing Techniques

- *In situ* preparation: synthesis within column hardware with one of the following “sealing” methods:
 - Polymerization with covalent attachment to the column hardware
 - Polymerization with subsequent swelling in eluent
 - Post-polymerization axial compression
 - Post-polymerization functionalization induced swelling
- Post-polymerization packaging: synthesis followed by insertion into column hardware
 - Preformed monolith can be inserted into heat shrink tubing which can then be glued or otherwise sealed into conventional column hardware

Conventional Monolith Preparation

- Modify the PEEK capillary to enable covalent attachment of the monolith
- Mix monolith components
 - Monomers (styrene, divinylbenzene)
 - Porogens (THF, Dioxane, Decanol, Dibutyl ether, etc.)
 - Initiator (AIBN)
- Fill capillary and cap ends of capillary
- Polymerize in a water bath overnight at the polymerization temperature
- Rinse with 100% acetonitrile

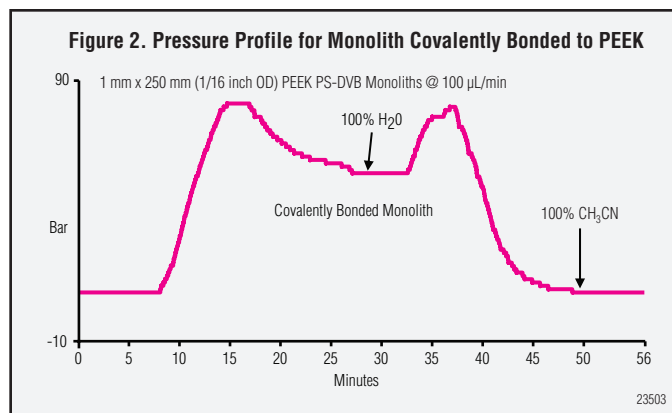
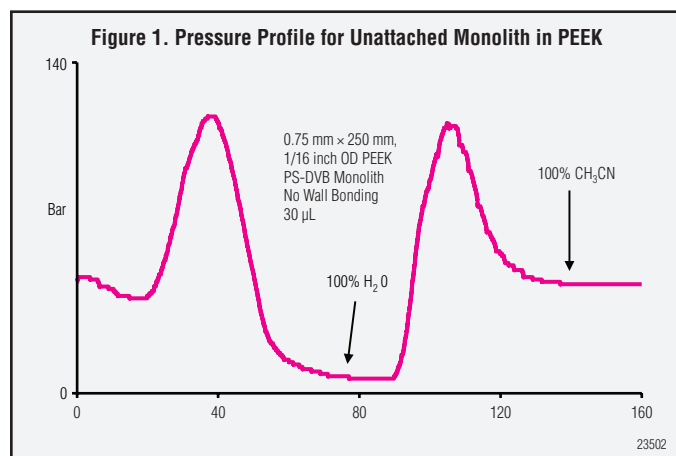


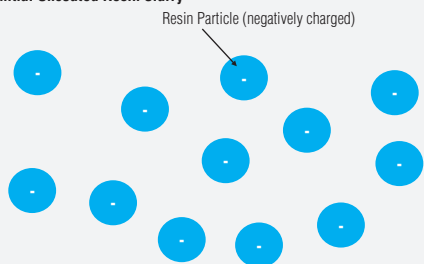
Figure 3 illustrates schematically the construction process for fabricating monolithic media based on particle aggregation. The first step in the process is to pack a column with particles which have been derivatized to yield a negatively charged surface (Figure 3A). Next, a solution containing an equimolar mixture of a primary amine and a diepoxide are passed through the column, producing a cationic condensation polymer in situ which binds to the resin surface (Figure 3B). The column is then unpacked, slurried in the packing solution and mixed with a fresh batch of particles with a negatively charged surface while stirring. The resulting mixture is then repacked into new column hardware. The resulting column exhibited significantly lower column pressure than expected for the particle size due to the formation of particle aggregates (Figure 3C). If desired, particles not already coated with cationic condensation polymer can be coated in situ with colloidal cationic particles (Figure 3D).

Advantages of Aggregated Particle Monoliths

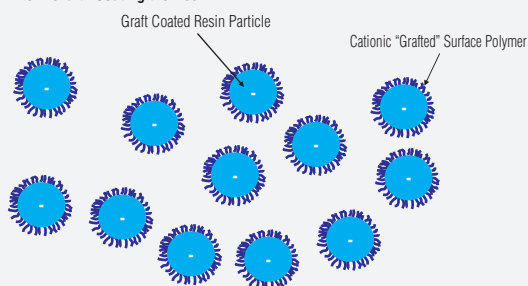
- Polymeric media already preformed, so no bed shrinkage
- No wall adhesion necessary since packing prevents wall gaps
- Compatible with a wide range of column hardware
- Can be used with a wide variety of chromatographic media
- Suitable for preparation of many different stationary phase combinations including:
 - Anion exchange (one or more modes)
 - Cation exchange (one or more modes)
 - Anion and cation exchange
 - Anion and/or cation exchange with reversed phase

Figure 3. New Approach to Monolith Synthesis

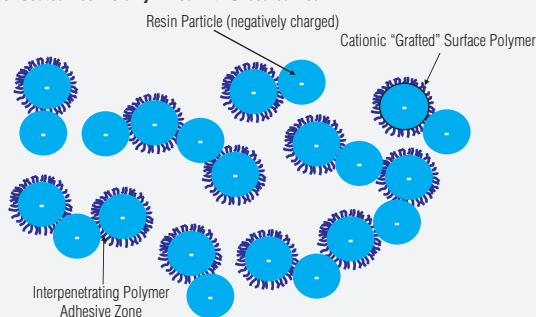
A. Initial Uncoated Resin Slurry



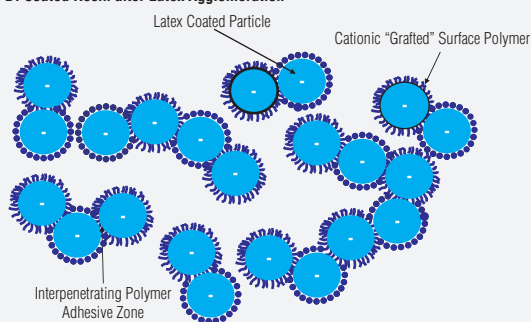
B. After "Graft" Coating the Resin



C. Coated Resin Slurry Mixed with Uncoated Resin



D. Coated Resin after Latex Agglomeration



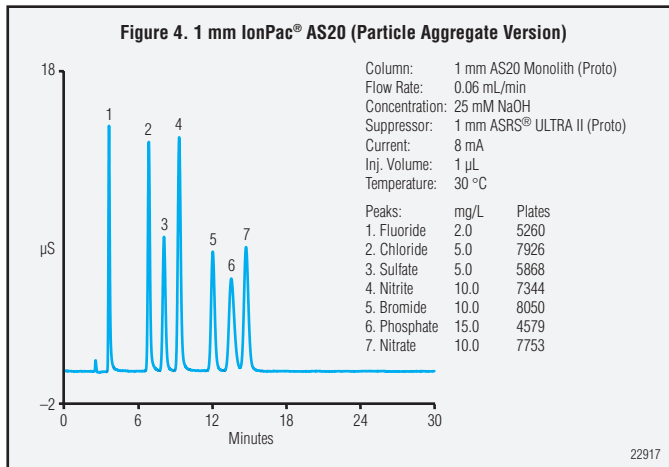
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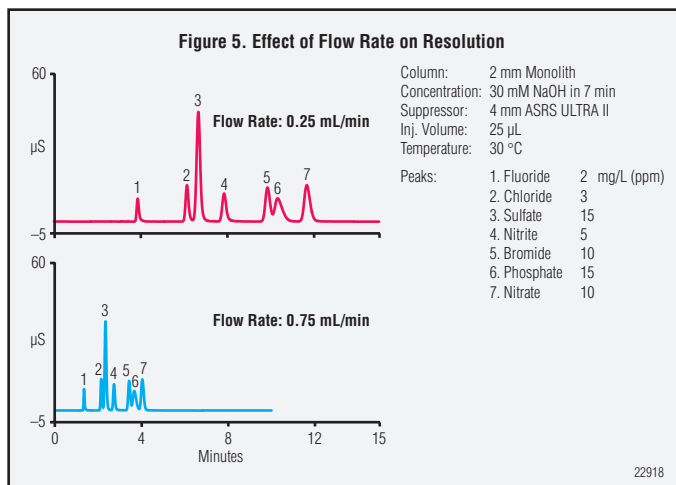
Preparation of Aggregated Particle Monoliths

- Application of the basement layer to resin in a packed column:
 - Pass diepoxide-amine solution mixture (1:1 mole ratio) through column at 65 °C for 120 min
- Application of a growth layer:
 - Pass diepoxide solution through column at 65 °C for 30 min
 - Pass amine solution through column at 65 °C for 30 min
- Unpack the column, redisperse the resin, mix with uncoated resin and pack
- Apply a second basement layer as above (optional)
- Apply additional growth layers as above
- Apply additional latex coating layer (optional)

RESULTS

Figures 4 and 5 illustrate the analytical utility of the aggregated particle monolith preparation method. Figure 4 shows preparation of a 1 mm monolith with excellent chromatographic performance for small molecules under isocratic conditions. Preparation of 1 mm monolithic columns with good chromatographic properties for small molecules is difficult to accomplish using conventional monolith synthesis methods. Figure 5 illustrates the minimal impact on resolution of flow rate with the particle aggregate monolith.





CONCLUSIONS

Covalent bonding of styrenic polymer monoliths to PEEK capillaries has been demonstrated. Chromatographic optimization is underway. A new particle aggregate monolith synthesis method provides an improved means of preparing monolithic media compatible with stationary phase synthesis techniques developed for particulate media. The new technique is compatible with polymeric column hardware and avoids the requirement for covalent bonding of the monolith to the column hardware. The use of pre-polymerized particles circumvents issues associated with shrinkage problems characteristic of conventional monolith synthesis while providing excellent efficiency for small molecules, even under isocratic conditions. High permeability media can be prepared by adjusting the extent of aggregation. An entirely new type of material utilizing both colloidal ion exchange coatings and condensation ion exchange coatings has been prepared with excellent results.

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Dionex Corporation

1228 Titan Way
 P.O. Box 3603
 Sunnyvale, CA
 94088-3603
 (408) 737-0700

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