

Preparation and Application of Polymeric Monolithic Media in Ion Chromatography

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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 benefit 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

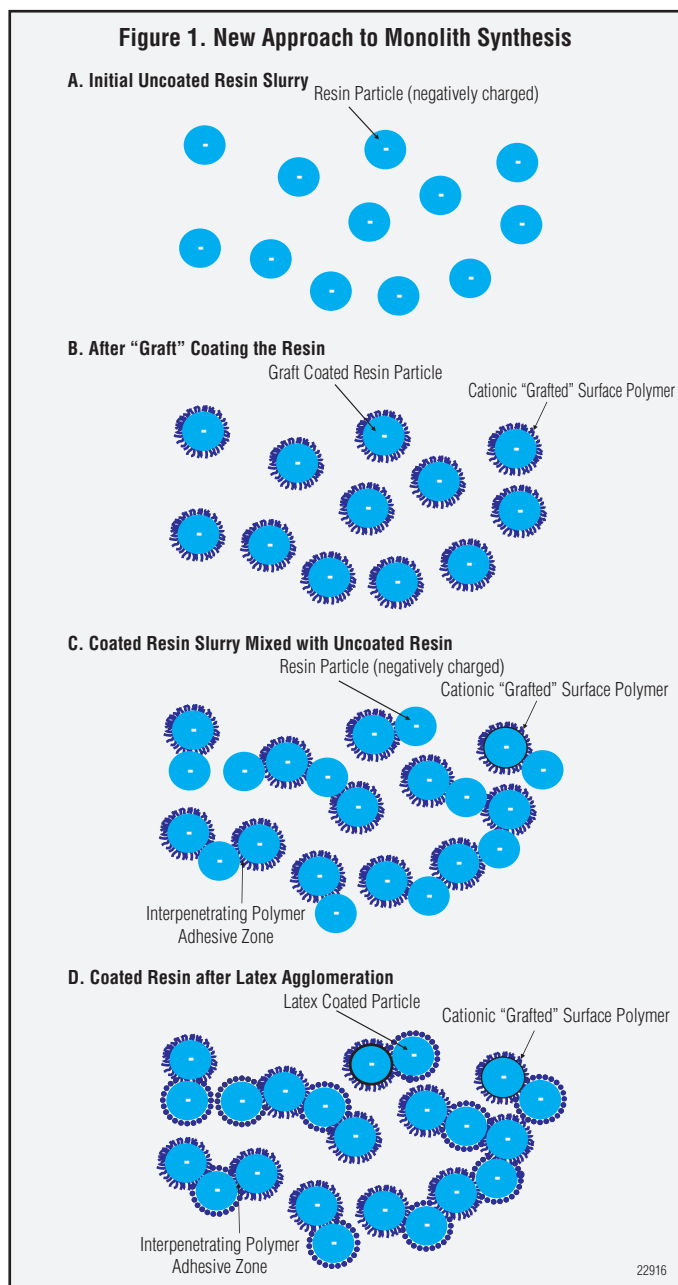
IC Separation Media Design Requirements

- 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 1A. UltiMate™ 3000 Capillary/Nano LC System with fractionation option and dual-gradient pump.

Figure 1 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 1A). 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 1B). 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 1C). If desired, particles not already coated with cationic condensation polymer can be coated in situ with colloidal cationic particles (Figure 1D).



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

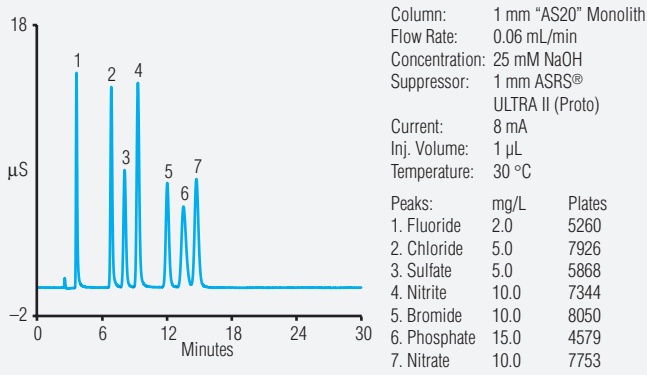
Preparation of Aggregated Particle Monoliths

- 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 consisting of:
 - 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

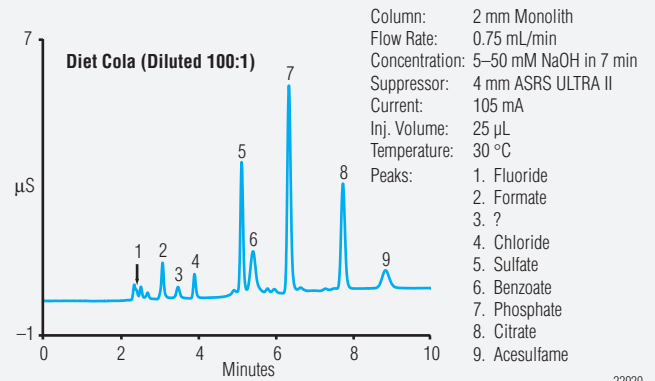
Figures 2–7 illustrate the analytical utility of the new monolith preparation method. Figure 2 shows preparation of a 1 mm monolith with excellent chromatographic performance for small molecules under isocratic conditions. Preparation of 1 mm monolithic columns with good chromatographic properties for small molecules is difficult to accomplish using conventional monolith synthesis methods. Figure 3 illustrates the minimal impact on resolution of flow rate with the particle aggregate monolith. Figures 4 and 5 illustrate excellent chromatographic performance under gradient conditions, even with small molecules. Figure 6 illustrates the impact of latex coating on monolith selectivity while Figure 7 shows an improved separation achievable only with a combination of condensation polymer coating and latex coating.

Figure 2. 1 mm IonPac AS20 (Particle Aggregate Version)



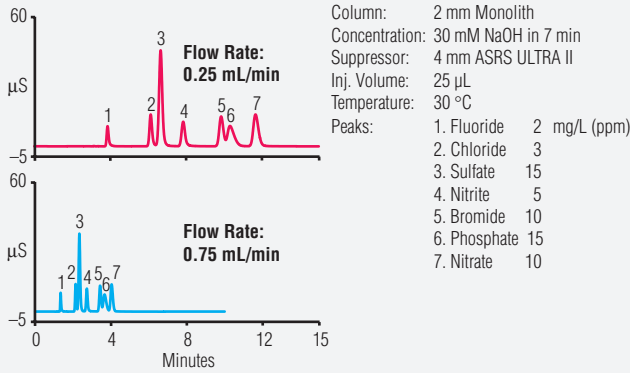
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Figure 5. Fast Analysis of a Cola Beverage with a Monolithic Column



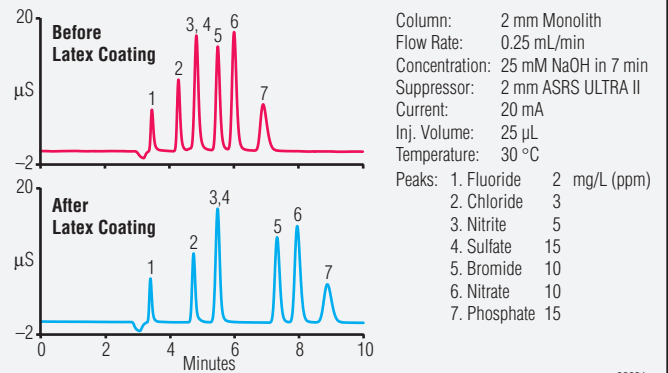
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Figure 3. Effect of Flow Rate on Resolution



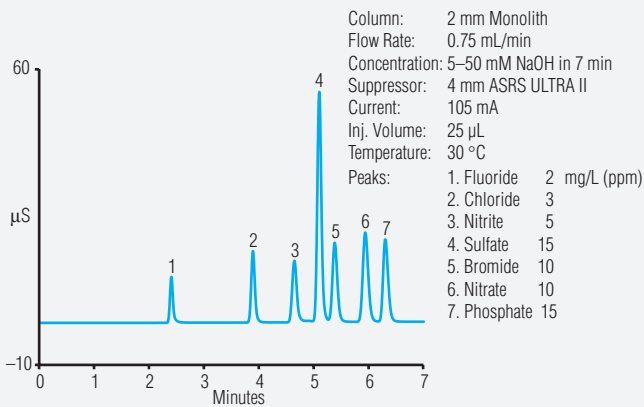
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Figure 6. Effect of Latex Coating on Monolith Selectivity



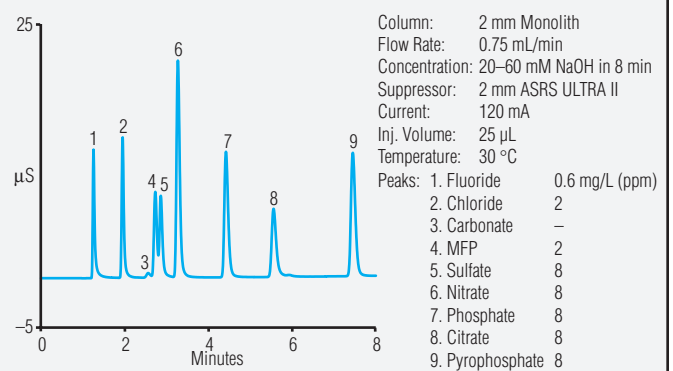
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Figure 4. Aggregated Particle Monolithic Column in Gradient Mode



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Figure 7. Improved Separation Using Aggregated Particle Monolithic Column with Latex Coating



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CONCLUSIONS

The 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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