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## ACCEPTED MANUSCRIPT

#### AQUEOUS SIZE-EXCLUSION CHROMATOGRAPHY OF POLYELECTROLYTES ON REVERSED-PHASE AND HYDROPHILIC INTERACTION CHROMATOGRAPHY COLUMNS

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#### **Highlights:**

- Reversed-phase and HILIC columns are suitable for aqueous SEC
- The best performance is seen with medium polarity and polar stationary phases
- An electrolyte and organic modifier in the mobile phase minimize non-SEC effects
- Higher column temperatures reduce non-SEC interactions
- Low molar mass oligomers are more susceptible to non-SEC interactions

#### Abstract

The size-exclusion separation of a water-soluble polyelectrolyte polymer, sodium polystyrene sulfonate (NaPSS), was demonstrated on common reversed-phase (C<sub>18</sub>, C<sub>4</sub>, phenyl, and cyano) and hydrophilic interaction chromatography (HILIC) columns. The effect of common solvents - acetonitrile (ACN), tetrahydrofuran (THF), and methanol (MeOH), used as mobile phase modifiers - on the elution of NaPSS and the effect of column temperature (within a relatively narrow range corresponding to typical chromatographic conditions, *i.e.*, 10 °C to 60 °C) on the partition coefficient,  $K_{SEC}$ , were also investigated. Non-size-exclusion chromatography (non-SEC) effects can be minimized by the addition of an electrolyte and an organic modifier to the mobile phase, and by increasing the column temperature (*e.g.*, to 50 °C or 60 °C). Strong solvents such as THF and ACN are more successful in the reduction of such effects than is the weaker solvent MeOH. The best performance is seen on medium polarity and polar stationary

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