

Applications of an alternative stationary phase for the separation of anions by chemically suppressed ion chromatography

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ABSTRACT

A hydroxymethyl methacrylate-based anion exchanger with quaternary amine functional groups is shown to have a proper selectivity for the separation of common inorganic anions on chemically suppressed ion chromatography systems. Its performance is comparable to the agglomerated pellicular-based anion exchangers commonly used for this purpose. The applications of this new anion exchanger as an alternative stationary phase for chemically suppressed ion chromatography are featured with separations of some simple inorganic and organic anions using both isocratic and gradient elution techniques.

INTRODUCTION

In chemically suppressed ion chromatography (IC), high conductivity eluents such as carbonate–hydrogencarbonate or hydroxide are used for the separation of anions. Since the pH values of these eluents are considerably high, the stationary phases used for this purpose must be stable within the eluent pH range and have the proper selectivity to separate the anions of interest. A variety of anion exchangers are commercially available for IC analysis of anions [1,2], however, not all are suitable for chemically suppressed IC. Agglomerated pellicular-based anion exchangers are the most common stationary phases used for this purpose [3,4]. The outstanding chromatographic performance of these anion exchangers is well known. Agglomerated ion-exchange resins contain an internal core particle, to which a monolayer of small diameter particles that carry the functional groups is attached. These resins exhibit excellent chromatographic performance due

to the very short diffusion paths available to solute ions during the ion exchange process. This material has been used to separate a wide variety of anions using both carbonate–hydrogencarbonate and hydroxide eluents.

This paper describes an alternative stationary phase which is based on hydroxyethyl methacrylate (HEMA). HEMA is a macroporous copolymer of 2-hydroxyethyl methacrylate and ethylene dimethacrylate. The theoretical aspects, the chemical and physical properties of this material, and the use of HEMA-based anion exchangers for the separation of a wide variety of anions using single-column IC methods have been discussed previously [5]. It has been recently shown that this material also can be used for the separation of anions in chemically suppressed IC [6]. In this work, the performance characteristics of HEMA-based anion exchangers are compared to the agglomerated pellicular-based anion exchangers. The application of this material as an alternative stationary phase is shown with the

separation of simple inorganic and organic anions using both isocratic and gradient elution techniques.

EXPERIMENTAL

The ion chromatograph used was a Dionex (Sunnyvale, CA, USA) BioLC system. It consists of a gradient program module (Model GPM-1) and a conductivity detector (Model CDM-2). The sample introduction was done with a Rheodyne (Reno, NV, USA) Model 9125 injector. The eluent suppression was achieved using the anion micromembrane suppressor (Model AMMS1) and the regenerant was supplied to the suppressor through an AutoRegen accessory. All data were recorded with a Spectra-Physics (Santa Clara, CA, USA) Model SP 4400 Chromjet integrator.

Separations were carried out on the Alltech (Deerfield, IL, USA) Universal Anion Column (150 mm \times 4.6 mm I.D.) packed with 10- μ m particles of HEMA-based anion exchanger with trimethylamine functional groups. The estimated ion-exchange capacity of the anion exchanger is 0.1 mmol/g. For comparison study, a Dionex HPIC AS4A column was used.

All eluents and standards were prepared from reagent-grade chemicals (Aldrich, Milwaukee, WI, USA). HPLC-grade water was used to prepare all eluents, standards and samples. The appropriate eluent compositions as well as the gradient programs used are given as a part of the legends to all figures.

RESULTS AND DISCUSSION

The characteristics of the HEMA-based anion exchanger as an alternative stationary phase for the separation of anions by chemically suppressed IC is evaluated and compared to the pellicular polystyrene-divinylbenzene-based ion exchangers. The most popular pellicular column, AS4A, made by Dionex is used for this purpose.

One of the most common eluents used for the isocratic separation of anions on the AS4A column is 1.7 mM NaHCO₃ and 1.8 mM Na₂CO₃. This eluent was chosen to separate the seven common inorganic anions on both columns. Fig. 1A shows the chromatogram obtained on the pellicular-based

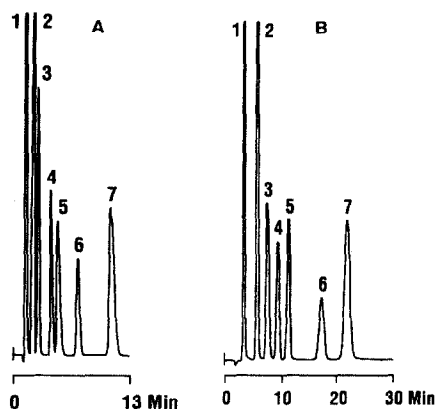


Fig. 1. Separation of the seven common inorganic anions on (A) pellicular-based column (250 mm \times 4.0 mm I.D.) and (B) HEMA-based column (150 mm \times 4.6 mm I.D.) using 1.7 mM NaHCO₃-1.8 mM Na₂CO₃ eluent. Flow-rate: 1.0 ml/min; detector: suppressed conductivity, 10 μ S full scale; injection volume: 100 μ l. Peaks: 1 = fluoride (10 ppm); 2 = chloride (20 ppm); 3 = nitrite (20 ppm); 4 = bromide (20 ppm); 5 = nitrate (20 ppm); 6 = phosphate (30 ppm); 7 = sulfate (30 ppm).

column. An excellent separation is obtained for all the anions. Fig. 1B shows the separation of anions on the HEMA-based column. A nice separation is also obtained for all the anions. The selectivity toward the anions for both columns are in the similar order, beginning with fluoride, followed by chloride, nitrite, bromide, nitrate, phosphate and sulfate.

The efficiency reported as number of theoretical plates (N) calculated by the half-height method [$N = 5.54 \cdot (t_R/W_{1/2})^2$] for both columns are shown in Table I. Since N values are meaningful only if they are calculated for peaks with moderately large values of capacity factors ($k' > 5$) [7], only nitrate, phosphate and sulfate peaks were used. Same eluent composition (1.7 mM NaHCO₃-1.8 mM Na₂CO₃) and chromatographic conditions were used for both columns. The results show that the efficiency per column for both columns are comparable. Comparable efficiencies of the shorter (150 mm \times 4.6 mm I.D.) HEMA-based column and the longer (250 mm \times 4.0 mm I.D.) AS4A column indicate that HEMA-based column has a better resolving power.

However, the total run time is approximately 44% longer on the HEMA-based column. This is

TABLE I

THE EFFICIENCY (NUMBER OF THEORETICAL PLATES PER COLUMN) OF PELLICULAR-BASED AND HEMA-BASED COLUMNS

The efficiency was calculated using half-height method.

| Anion | Efficiency (<i>N</i>) | |
|-----------|---|---|
| | Pellicular-based column (250 mm × 4.0 mm I.D.) | HEMA-based column (150 mm × 4.6 mm I.D.) |
| Nitrate | 2880 | 4780 |
| Phosphate | 3716 | 3184 |
| Sulfate | 4070 | 4092 |

not surprising considering the higher anion-exchange capacity factors, k' , as listed in Table II. Early-eluting anions exhibit 2–3-fold increase in k' , while the late-eluting anions exhibit 1.5-fold increase. The trifold increase in the k' value for fluoride ion results in longer retention time, thus providing better resolution from the column void volume. In Fig. 1A and as reported elsewhere [8], the fluoride retention time appears at the column void volume using the agglomerated pellicular-based column.

The HEMA-based column is useful for applications which demand the use of columns with higher ion-exchange capacities. Fig. 2 shows the separation of nine anions on both columns. Fluoride and formate peaks are well resolved on the HEMA-based column (Fig. 2A), while on the AS4A column, they are coeluted (Fig. 2B). Since the AS4A column was designed for faster analysis, the eluent

TABLE II

ANION-EXCHANGE CAPACITY FACTORS (k') OF ANIONS ON THE PELLICULAR- AND HEMA-BASED COLUMNS

| Anion | Pellicular-based column | HEMA-based column | $k'_{\text{HEMA}}/k'_{\text{pellicular}}$ |
|-----------|-------------------------|-------------------|---|
| Fluoride | 0.31 | 1.08 | 3.48 |
| Chloride | 1.23 | 2.46 | 1.95 |
| Nitrite | 1.72 | 3.48 | 2.02 |
| Bromide | 3.08 | 4.58 | 1.49 |
| Nitrate | 3.75 | 5.67 | 1.51 |
| Phosphate | 6.03 | 9.05 | 1.50 |
| Sulfate | 9.54 | 11.64 | 1.22 |

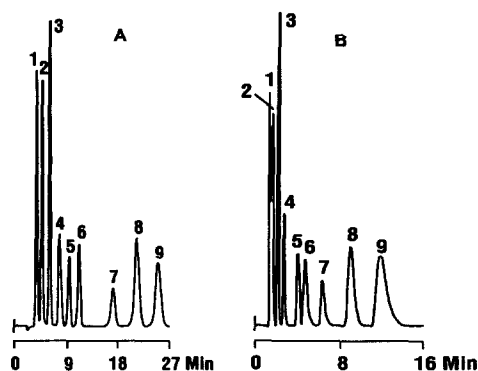


Fig. 2. Separation of nine inorganic and organic anions on (A) HEMA-based column (150 mm × 4.6 mm I.D.) and (B) pellicular-based column (250 mm × 4.0 mm I.D.). Peaks: 1 = fluoride (6 ppm); 2 = formate (25 ppm); 3 = chloride (12 ppm); 4 = nitrite (12 ppm); 5 = bromide (12 ppm); 6 = nitrate (12 ppm); 7 = phosphate (18 ppm); 8 = sulfate (18 ppm); 9 = oxalate (40 ppm). Chromatographic conditions as in Fig. 1.

concentration was diluted to give more comparable run times to the HEMA-based column. By reducing the eluent concentration to 0.8 mM NaHCO₃–0.9 mM Na₂CO₃, the sulfate retention time on the AS4A increases to 31 min, which is approximately 10 min longer than on the HEMA-based column. Under this new conditions, the fluoride and formate peaks are still coeluting. This results show that the HEMA-based column has comparatively better resolving power especially with respect to weakly retained anions such as fluoride and formate.

The isocratic separation of several actual analytical samples are shown in Fig. 3. An eluent composition of 2.8 mM NaHCO₃–2.2 mM Na₂CO₃ was used for these separations to decrease the overall analysis time by approximately 20%. Under this condition, resolution of all the seven common inorganic anions is still achieved. The coal sample was obtained by oxygen bomb combustion of 1 g of coal in a Parr bomb after pre-purge to remove atmospheric nitrogen. Water was used as the collector solution. The solution was filtered and diluted before injection. The sodium fluoride dental gel and the toothpaste were mixed with deionized water (0.1 g/10 ml), sonicated for 10 min to release the fluoride, filtered and diluted before injection. Resolution of fluoride from the column void volume is achieved in all samples.

HEMA-based anion exchangers can be success-

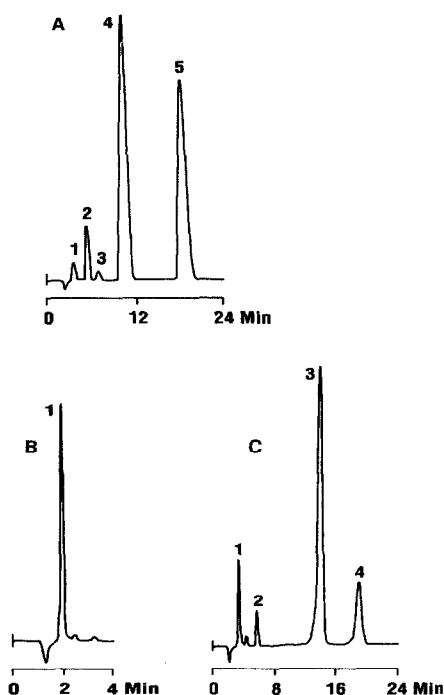


Fig. 3. Separation of anions in actual analytical samples. (A) Coal, peaks: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = nitrate; 5 = sulfate. (B) Sodium fluoride dental gel; peak 1 = fluoride. (C) Toothpaste; peaks: 1 = fluoride; 2 = chloride; 3 = phosphate; 4 = monofluorophosphate. Column: HEMA-based (150 mm \times 4.6 mm I.D.); eluent: 2.8 mM NaHCO_3 -2.2 mM Na_2CO_3 ; flow-rate: 1.0 ml/min; detector: suppressed conductivity, 10 μS full scale; injection volume: 100 μl .

fully employed in gradient elution techniques because of their inherent high capacity and high efficiency. This is demonstrated by the examples shown in Fig. 4. Fig. 4A shows the gradient separation of some inorganic and organic anions with varying charges (-1 to -3). Fig. 4B and C shows the chromatograms obtained for fruit juices. The fruit juices were diluted and filtered through 0.5 μm syringe filters prior to injection. No attempt was made to optimize the gradient program and no special precautions were taken in eluent preparation and storage for these analysis. Although this chromatogram does not show much resolving power of the gradient elution technique, the spacings between the peaks do indicate that it is possible to resolve more anions using HEMA-based column. The observed baseline drifts in these examples are not unusual in

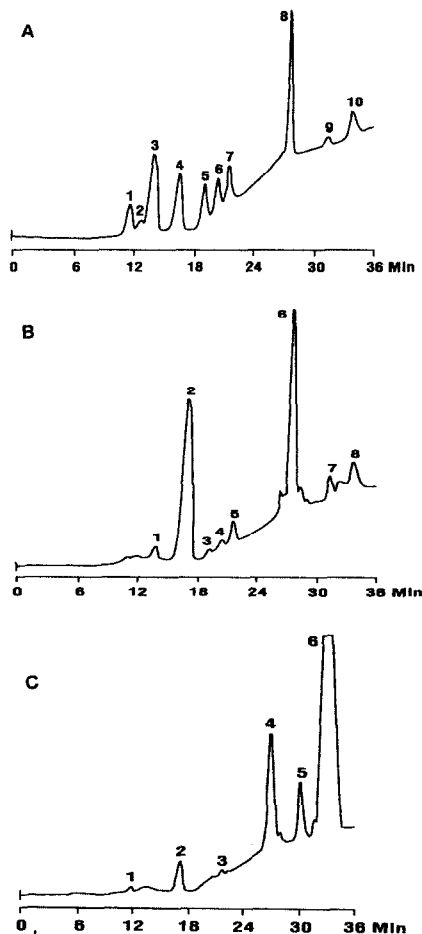


Fig. 4. Gradient elution of inorganic and organic anions. (A) Standard; peaks: 1 = fluoride (0.5 ppm); 2 = acetate (1 ppm); 3 = formate (2 ppm); 4 = chloride (1 ppm); 5 = nitrite (1 ppm); 6 = bromide (1 ppm); 7 = nitrate (1 ppm); 8 = sulfate (1.5 ppm); 9 = phosphate (1.5 ppm); 10 = citrate (10 ppm). (B) Tomato juice; peaks: 1 = formate; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = sulfate; 7 = phosphate; 8 = citrate. (C) Lime juice, peaks: 1 = fluoride; 2 = chloride; 3 = nitrate; 4 = sulfate; 5 = phosphate; 6 = citrate. Eluents: eluent A, deionized water; eluent B, 30 mM sodium hydroxide. Gradient program: A-B (95:5) at 0 min, (90:10) at 15 min, (50:50) at 25 min, (40:60) at 35 min, (95:5) at 38 min. Flow-rate: 1.0 ml/min; detector: suppressed conductivity, 10 μS full scale; injection volume: 50 μl .

gradient IC runs. The drifts have been attributed to the problem of contaminants in the eluents which change during the gradient run [8]. When using NaOH as the eluent, contamination by carbonate produced from the absorption of carbon dioxide from the atmosphere can cause a drift in the con-

ductance. NaOH gradients are successful only when special precautions are taken in eluent preparation and storage. The baseline drift can also be eliminated by subtracting the baseline of a blank run using a computer-aided data acquisition.

The HEMA-based anion exchanger has been shown to be a useful alternative to the conventional agglomerated pellicular anion exchangers for the separation of anions by chemically suppressed IC. The HEMA-based columns exhibit higher capacities for all anions and especially for weakly retained anions such as fluoride and formate. It is useful for applications which require the use of columns with higher ion-exchange capacities. It can be used for both isocratic and gradient elution techniques.

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