Determination of monovalent inorganic anions in high-ionic-strength samples by electrostatic ion chromatography with suppressed conductometric detection

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Abstract

A new ion chromatographic (IC) system has been established by using micelles of 3-(N,N-dimethylmyristylammonio)propanesulfonate (Zwittergent 3–14) loaded onto a reversed-phase packed column as the separation column with an electronic rotary switching valve packed-bed suppressor for conductometric detection of inorganic anions. An aqueous H_3BO_3–$Na_2B_4O_7$ solution has been demonstrated to be the most desirable eluent for this IC system. The relationship between retention time and the concentration of the borate eluent was determined for a series of model anionic analytes and this relationship was found to be opposite to that exhibited in a conventional anion-exchange IC system. The rapid elution and complete separation of monovalent inorganic anions were obtained by initially using a high-concentration borate solution as the eluent for a short-period, and then switching to a lower-concentration borate eluent to complete the separation. Detection limits for nitrite, bromide, nitrate, and chlorate were 0.85, 0.88, 0.95 and 4.8 μM, respectively, when a 7.0 mM $Na_2B_4O_7$ eluent was used. Moreover, the ability to directly detect these monovalent anions in samples containing high concentrations of sulfate and/or chloride ions provided a major advantage of this approach.
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1. Introduction

The development of efficient suppressors has been an important factor in the advancement of ion chromatography (IC) as an analytical technique. Ion-exchange columns in the H^+ or OH^- form were used as the first suppressors [1] and these have been followed in turn by hollow-fiber membrane suppressors [2–4], micro-membrane suppressors [5,6], and the electric membrane-based self-regenerating suppressors [7–10]. Reduction of the background conductance of the eluent and enhancement of the conductance of the analyte are the essential functions of a suppressor. However, from the practical application point of view, the suppressor must also offer reliability and ease of

operation [11]. The early packed-bed suppressor satisfied these criteria but had the major disadvantage that off-line regeneration was required. Recent modifications to the packed-bed suppressor have overcome this limitation by using a fresh ion-exchange resin bed for each sample analysis, deployed by using an electronic rotary switching valve system. This system, devised by Sato et al. [12] is commercially available from Tosoh and forms an essential part of the Tosoh IC2001 system. This newly introduced packed-column suppressor has been demonstrated to provide minimal band broadening and exhibits similar chromatographic efficiency to the electric membrane-based self-regenerating suppressed IC system [12].

The aim of this study is to evaluate the applicability of this newly established packed-bed suppressor to eluent containing zwitterionic surfactants. Use of an IC stationary

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phase formed by the adsorption of zwitterionic surfactant onto a C_{18} substrate is a relatively new technique initially introduced by Hu et al. [13] and has been termed electrostatic ion chromatography (EIC). The eluent used in EIC has contained a small amount of the zwitterionic surfactant in order to stabilize the adsorbed layer of zwitterionic micelles comprising the stationary phase [14,15]. This approach has proved particularly suitable for direct spectrophotometric detection of inorganic anions in a range of samples [16–20]. Although suppressed conductometric detection has been applied successfully in EIC [21,22], the inclusion of the surfactant in the eluent has been detrimental to the membrane material of the electric membrane-based self-regenerating suppressor, leading to poor suppression performance and limited lifetime of the suppressor.

It the present study, the membrane suppressor has been replaced by the recently developed electronic rotary valve packed-bed suppressor in an effort to improve the efficiency and longevity of the suppressor in EIC of inorganic anions. The resultant experimental data have shown that the electronic rotary valve packed-bed suppressor is the most desirable suppressor for EIC and this newly established suppressed EIC system is highly applicable to samples containing high concentrations of chloride and sulfate ions.

2. Experimental

2.1. Instrumentation

The IC system used throughout this study was a Tosoh (Tokyo, Japan) model IC-2001 and consisted of a vacuum degasser, a pump, a column oven, an auto-sampler with a fixed sample injection volume of $30\,\mu l$, a conductivity detector, an electronic rotary switching valve packed-bed suppressor [12], and an IC-WS system controller for controlling the IC system and for the chromatographic data processing.

2.2. Columns and reagents

A C_{18} reversed-phase column (TSKgel, ODS-100S, $250\,mm \times 4.6\,mm$ i.d., Tosoh, Tokyo, Japan) modified by saturation with micelles of 3-(N,N-dimethylmyristylammonio) propanesulfonate (Zwittergent 3–14) was used as the separation column. The method used for preparing the Zwittergent 3–14-modified column was as described previously [14]. A conventional anion-exchange column (TSKgel Super IC-Anion, $150\,mm \times 4.6\,mm$ i.d., Tosoh, Tokyo, Japan) was also used to compare the retention behavior of the tested analyte anions.

The Zwittergent 3–14 reagent was obtained from Fluka (Buchs, Switzerland). Analytical-reagent grade inorganic salts used to prepare the samples and eluent were obtained from Wako (Osaka, Japan). Water used throughout this study was prepared in the laboratory using a Millipore (Bedford, MA, USA) Milli-Q water purification system.

3. Results and discussion

3.1. The newly established suppressed EIC system

Fig. 1 shows a typical chromatogram of separation of sulfate, fluoride, chloride, nitrite, bromide, nitrate, and chlorate (as their sodium salts), obtained using EIC with this newly established suppressor. The eluent used was an aqueous solution containing 1.0 mM Zwittergent 3–14, 7.0 mM $Na_2B_2O_7$, and 2.0 mM H_3BO_3 (pH 8.91). Note the more commonly used carbonate–hydrogencarbonate eluent was also applicable to this IC system, but the tetraborate eluent has the lower conductance to the suppressed conductometric detection. As can be seen from Fig. 1, this suppressed EIC system provided minimal band broadening and high chromatographic efficiency for separation of these model analyte anions. The separation selectivity was such that sulfate showed very little retention. The same sample was also analyzed using a conventional anion-exchange IC system under identical chromatographic conditions and Fig. 2 shows the resultant chromatogram. While sulfate was retained more strongly than in Fig. 1, it was still eluted earlier than occurs typically for strong-base anion exchangers, due probably to
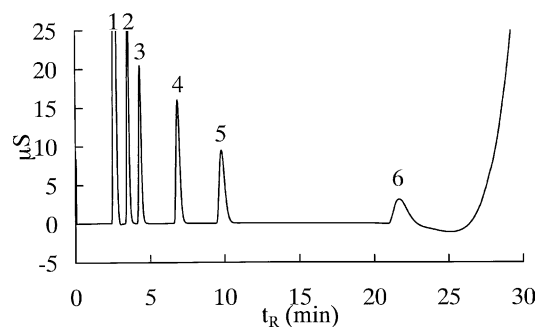

Fig. 1. Chromatogram of inorganic anions obtained using suppressed EIC. Column: C_{18} (250 mm × 4.6 mm i.d.) coated with Zwittergent 3–14 micelles. Eluent: 1.0 mM Zwittergent 3–14, 7.0 mM $Na_2B_2O_7$, and 2.0 mM H_3BO_3. Flow rate: 1.0 ml/min. Concentrations of each analyte ion in sample: 0.10 mM. Peak identities: (1) sulfate and fluoride; (2) chloride; (3) nitrite; (4) bromide; (5) nitrate; (6) chlorate.
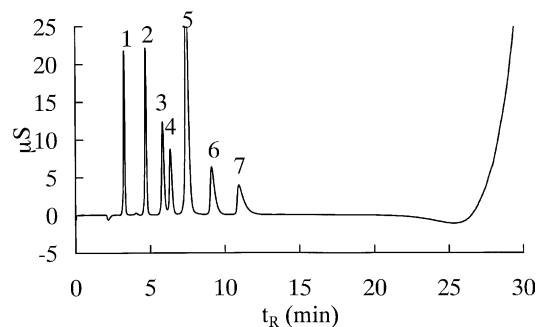

Fig. 2. Chromatogram of the same sample (as Fig. 1) obtained using a conventional anion-exchange column. Column: TSKgel Super IC-Anion (150 mm × 4.6 mm i.d.). Other conditions as in Fig. 1. Peak identities: (1) fluoride; (2) chloride; (3) nitrite; (4) bromide; (5) sulfate; (6) nitrate; (7) chlorate.
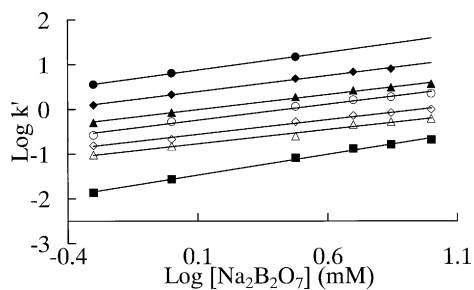
Fig. 3. Plots of $\log k'$ vs. $\log[Na_2B_4O_7]$. Conditions as for Fig. 1. 2.0 mM H_3BO_3 was present in each eluent. Plots: (●) iodide; (◆) chlorate; (▲) nitrate; (○) bromide; (◇) nitrite; (△) chloride; (■) sulfate.

the fact that the eluent contained Zwittergent 3–14 micelles [17,22]. The ion separation was dominated by conventional anion exchange.

Note the baselines in Figs. 1 and 2 undergo a sharp rise around 25 min which was indicative of the ion-exchange capacity of the packed-bed suppressor. The fresh ion-exchange resin bed was provided automatically for each sample analysis deployed by using an electronic rotary switching valve system.

3.2. Effects of eluent concentration in suppressed EIC

The concentration of $Na_2B_4O_7$ in eluents containing a fixed amount (2.0 mM) of H_3BO_3 was varied over the concentration range 0.5–10.0 mM and the retention times for sulfate, chloride, nitrite, bromide, nitrate, chlorate, and iodide obtained for each concentration were used to produce plots of logarithm of retention factor ($\log k'$) versus $\log[Na_2B_4O_7]$. The resultant plots (Fig. 3) show that $\log k'$ increased linearly with $\log[Na_2B_4O_7]$ for the analyte anions tested. The slopes of the plots for each of the monovalent anions were identical (0.79), while the slope for sulfate was 0.93. This behavior is the opposite to that which occurs in conventional anion-exchange, where plots of $\log k'$ versus $\log[eluent]$ are linear but have negative slopes. These experimental data can be explained by a fact that a mobile phase of high salt concentration can promote transfer of the analyte anions to the organic phase, i.e., the Zwittergent 3–14 micellar stationary phase. A serial study on effects of salt concentrations in mobile phase on retention behavior of inorganic anions have demonstrated further that ions in mobile phase are capable of modifying the net potential of the zwitterionic stationary phase [23–25]. Because of this reason, this IC approach had been termed electrostatic ion chromatography (EIC).

Variation of $[H_3BO_3]$ over the range 0–10 mM in eluents having a fixed concentration of $Na_2B_4O_7$ was undertaken and it was found that the $[H_3BO_3]$ exerted no influence on retention times. However, a fixed $[H_3BO_3]$ of 2.0 mM was maintained in all eluents to stabilize the pH.

Analyte ions having a high affinity for the Zwittergent 3–14 micelle stationary phase, such as chlorate and iodide ions, were eluted with reasonably short retention times using
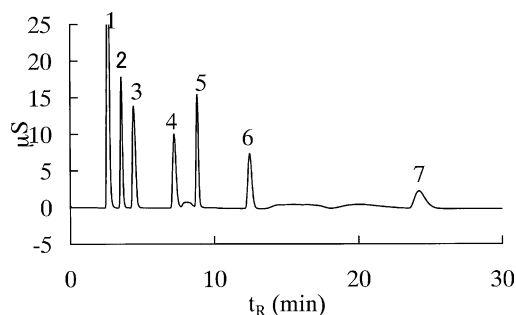

Fig. 4. Chromatogram obtained by initially conditioning the column with an eluent containing 7.0 mM $Na_2B_4O_7$ and then switching to an eluent containing 1.0 mM $Na_2B_4O_7$ at the point of injection. Other separation and detection conditions were as for Fig. 1. Peak identities: (1) sulfate/fluoride; (2) chloride; (3) nitrite; (4) bromide; (5) nitrate; (6) chlorate; (7) iodide.

eluents having a moderately low concentration of $Na_2B_4O_7$. For example, when the separation was performed with an eluent containing 1.0 mM $Na_2B_4O_7$, iodide and chlorate were eluted at retention times of 20.31 min and 8.23 min, respectively. Under these conditions, nitrate and bromide were baseline separated (retention times of 4.61 min and 3.71 min, respectively) but the other analytes in the test mixture were not separated. Complete separation of all analytes except fluoride and sulfate could be achieved using a reverse concentration gradient consisting of an initial eluent concentration of 7.0 mM $Na_2B_4O_7$ being used to equilibrate the column, with switching to 1.0 mM $Na_2B_4O_7$ when the sample was injected. The resultant chromatogram is shown in Fig. 4.

3.3. Direct determination of small amounts of inorganic anions in samples containing high concentrations of sulfate and chloride ions

The EIC method offered the ability to directly determine small amounts of nitrite, bromide, nitrate, chlorate, and iodide in samples containing high levels of sulfate and/or chloride ions. The determination of bromide, nitrate, chlorate, and iodide was found to be unaffected by the presence of sulfate and chloride up to 1.2 M (higher levels were not investigated), but interference in the determination of nitrite occurred for chloride levels exceeding 0.25 M and sulfate levels exceeding 0.92 M. Fig. 5 shows the analysis of an artificial seawater sample containing 18.0 μM each of nitrite, bromide, nitrate, and chlorate in a matrix comprising 0.482 M chloride and 0.029 M sulfate, using the same eluent conditions as for Fig. 1. Bromide, nitrate, and chlorate could be quantified but the nitrite peak was subject to interference. The separation of iodide in the seawater matrix was also possible using an eluent comprising 0.5 M $Na_2B_4O_7$, 2.0 mM H_3BO_3, and 1.0 mM Zwittergent 3–14 (chromatogram not shown). The sample used for Fig. 5 was also analyzed using a conventional anion-exchange column. The resultant chromatogram showed poor separation efficiency and the poor detectability of the analyte anions.
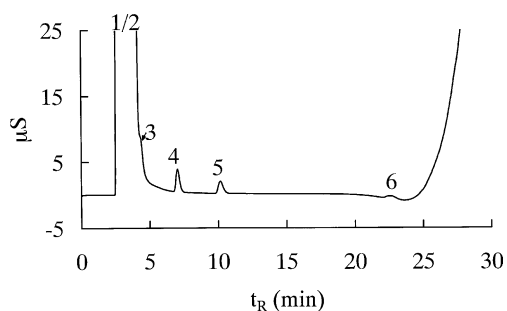
Fig. 5. Chromatogram of $18.0\,\mu M$ each of nitrite, bromide, nitrate, and chlorate in sample containing 0.482 M chloride and 0.029 M sulfate. Conditions were as for Fig. 1. Peak identities: (1) sulfate; (2) chloride; (3) nitrite; (4) bromide; (5) nitrate; (6) chlorate.

Table 1
Determination of bromide and nitrate in human urine using the proposed EIC system

Analyte	Concentration (μM) ($n = 5$)	Recovery (%)
Bromide	35.8 ± 0.6	99.5–100.6
Nitrate	386.6 ± 0.8	99.6–100.7

3.4. Detection limits of suppressed EIC for separation of the monovalent inorganic anions

The detection limits for the analyte anions were dependent on $[Na_2B_4O_7]$ in the eluent, with higher concentrations leading to longer retention times and hence poorer detection limits. For example, the detection limit for chlorate was $1.13\,\mu M$ with a 1.0 mM $Na_2B_4O_7$ eluent and $4.8\,\mu M$ with a 7.0 mM $Na_2B_4O_7$ eluent. However, detection limits for nitrite, bromide, and nitrate were 0.85, 0.88, and $0.95\,\mu M$, respectively, for a 7.0 mM $Na_2B_4O_7$ eluent.

3.5. Direct detection of bromide and nitrate in urine samples

Human urine samples were chosen as a sample matrix containing high levels of chloride ions. The analytical data obtained for bromide and nitrate after direct injection of urine are summarized in Table 1, together with the results of recovery experiments. Recovery values were close to quantitative.

4. Conclusion

A suppressed electrostatic ion chromatographic system has been established for the direct detection of monova-lent inorganic anions in samples containing high levels of sulfate and/or chloride ions. The stationary phase comprised zwitterionic micelles adsorbed to a C_{18} substrate and the mobile phase also contained the zwitterionic surfactant as a means of stabilizing the stationary phase. The suppressor used in this IC system was an electronic rotary switching valve packed-bed suppressor which was found to be highly tolerant to the surfactant contained in the eluent. This EIC system should also be applicable for the direct detection of inorganic ions in protein-containing samples.

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