Short communication

Suppressed electrostatic ion chromatography with tetraborate as eluent and its application to the determination of inorganic anions in snow and rainwater

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Abstract

Tetraborate is investigated as the eluent ion for suppressed electrostatic ion chromatography (EIC) using a zwitterionic stationary phase. Good separation of a range of inorganic anions (SO_4^{2-}, Cl^-, NO_2^-, Br^-, NO_3^-, ClO_3^-, and I^-) was obtained, with detection limits for highly conducting ions (SO_4^{2-}, Cl^-, NO_2^-, Br^-, and NO_3^-) being less than $8 \cdot 10^{-8}$ M, and for weakly conducting anions (ClO_3^- and I^-) being $2.7 \cdot 10^{-7}$ and $5.8 \cdot 10^{-7}$ M, respectively. Calibration curves were linear up to 1.8 mM of each analyte. Retention times were found to increase with increasing eluent concentration and a linear relationship was observed between $\log k'$ and $\log[Na_2B_4O_7]$ for all analytes. This behaviour is attributed to the progressive formation of a binary electrical double layer at the surface of the zwitterionic stationary phase. Retention times of analytes could be manipulated by varying the concentration of the eluent. This new suppressed-EIC system was applied to the determination of inorganic anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, and Br^-) in snow and rainwater samples. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Tetraborate has found relatively limited use as an eluent ion in suppressed ion chromatography (IC) of anions, despite the very low conductance of its suppressed product (boric acid) in comparison to the more commonly used carbonate–bicarbonate eluents [1,2]. A major factor hindering the widespread application of the tetraborate eluent is that it shows

weak elution ability for most analyte ions, even those with low ion-exchange selectivity coefficients. Although an increase in the concentration of tetraborate in the mobile phase can improve the elution strength, the background conductance also increases and detection limits may be compromised. Tetraborate, therefore, has serious limitations as an eluent when conventional ion exchange is the mechanism of separation.

Previous studies in our laboratories have involved chromatographic separation of ions using zwitterionic stationary phases formed by coating an octadecylsilane reversed-phase column with a hydro-

phobic zwitterionic surfactant [3–5]. Separation of analyte ions (such as inorganic anions) was found to be possible using either water or very dilute electrolytes as eluents, showing that competition for the charged sites on the stationary phase between the analyte ions and the eluent ion was not required. In other words, the separation was based on a mechanism which differed from conventional ion exchange. This new type of ion chromatography has been termed 'electrostatic ion chromatography (EIC)' [3], and can be operated in either the non-suppressed [3–5] or the suppressed modes [6,7], depending on the type of eluent ion used. In the suppressed mode, carbonate and bicarbonate eluents gave excellent separation of the analyte anions, but the relatively high background conductance of the suppressed eluent (typically 45–48 μS cm^{-1}) restricted the detection limits for most anions to the low-μM range [6]. Furthermore, changes in the concentration of carbonate in the eluent did not cause any significant change in analyte retention. Use of a hydroxide eluent was found to be suitable for enhancing the detection sensitivity of suppressed EIC and analyte retention could be manipulated by varying the concentration of the eluent [7]. However, the high alkalinity of hydroxide eluents caused deterioration of the silica-based reversed-phase column in a relatively short period (after about 3 months of column usage).

In order to develop a suppressed-EIC system which showed the desirable attributes of high sensitivity, good separation, and the ability to manipulate retention by varying eluent concentration, tetraborate was investigated as the eluent ion. Some fundamental aspects of retention behaviour were examined and the new EIC system was applied to the determination of inorganic anions in rainwater and snow samples.

2. Experimental

2.1. Apparatus

The HPLC system used throughout this study was a Shimadzu LC-10A system, which consisted of a Shimadzu (Kyoto, Japan) LC-10AT pump, a manual sample injector (Rheodyne, Cotati, CA, USA) with a 100 μL injection loop, a CTO-10A column oven and a CR-6A Chromatopac data system (Shimadzu). A SPD-10A (Shimadzu) UV–visible detector (which was used to identify the UV-absorbing anions NO_2^-, Br^-, NO_3^-, and I^-) and a CDD-6A (Shimadzu) conductivity detector were used in tandem for the detection of the analyte ions. An anion self-regenerating suppressor (Model ASRS, Dionex, Sunnyvale, CA, USA) was inserted between the UV–visible detector and the conductivity detector for reducing the background conductance of the mobile phase. The ODS-packed column (250×4.6 mm I.D.) used for preparing the zwitterionic stationary phase was obtained from Chemical Inspection and Testing Institute (Tokyo, Japan).

2.2. Reagents

The zwitterionic surfactant used as the stationary phase was 3-(N,N-dimethylmyristylammonio)-1-propanesulfonate (Zwittergent-3-14), obtained from Fluka (Buchs, Switzerland). Analytical-reagent grade inorganic salts used for preparing analyte solutions were obtained from Wako (Osaka, Japan) and were used without further purification. Sodium tetraborate (analytical-reagent grade) used to prepare the eluents was also obtained from Wako. Water used throughout this study was prepared in the laboratory using a Millipore (Bedford, MA, USA) Milli-Q water purification system.

2.3. Column preparation

The separation column used throughout this study was obtained by modification of the ODS-packed column with Zwittergent-3-14. The surfactant was dissolved in 10 mM sodium tetraborate to give a 30 mM Zwittergent-3-14 solution. The ODS-packed column was then conditioned with this surfactant solution for about 40 min at a flow-rate of 1.0 mL/min. The column was then rinsed thoroughly with 10 mM sodium tetraborate solution and was then used for the separation of the anions.

3. Results and discussion

3.1. Relationship between k' and [Na₂B₄O₇]

Sodium tetraborate aqueous solutions of varying

concentration were used as eluents for the separation of a sample of inorganic anions containing 10 μM each of SO_4^{2-}, Cl^-, NO_2^-, Br^-, NO_3^-, ClO_3^-, and I^- (with Na^+ as the counterion). Plots of log k' versus log[$Na_2B_4O_7$] were prepared for each analyte ion and the results are shown in Fig. 1. For all analytes log k' increased linearly with an increase of log[$Na_2B_4O_7$] (correlation coefficient for all analytes except SO_4^{2-} exceeded 0.999). This relationship between log k' and log[$Na_2B_4O_7$] was the opposite of that expected from conventional ion exchange and gave clear evidence for the unique separation mechanism of EIC. A binary electrical double layer (EDL) retention model has been suggested by the present authors [8] and this hypothesis has been used to satisfactorily explain the retention process in EIC.

When applied to the eluent system used in the present study, the model proposes that the sodium tetraborate eluent establishes a binary EDL at the surface of the s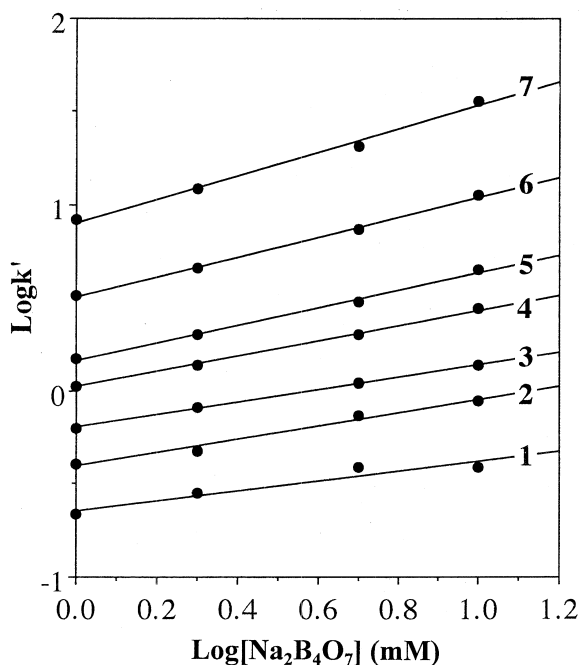tationary phase, comprising sodium ions bound to the anionic sites of the surfactant and tetraborate ions bound to the cationic sites of the surfactant. Since tetraborate has a very low affinity toward the quaternary ammonium sites on the zwitterionic stationary phase, the tetraborate EDL does not become saturated even when a relatively high concentration (10 mM) of tetraborate is used in the eluent. It therefore follows that the thickness of the tetraborate EDL increases progressively with increasing concentration of the eluent and since the counterion EDL (sodium ions adsorbed at the anionic site of the zwitterion) is of equal concentration to the tetraborate EDL, the thickness of the resultant binary EDL varies according to the concentration of the eluent. The model further proposes that the retention of analyte ions results from a combination of electrostatic attraction and repulsion from the binary EDL, with strongest retention occurring with a saturated binary EDL. Retention therefore increases with increasing eluent concentration until the binary EDL becomes saturated. This behaviour is accessible in a practical sense only for eluent ions which have very low ion-exchange selectivity coefficients (such as hydroxide and tetraborate), since more strongly adsorbed eluent ions (such as carbonate) form a saturated binary EDL at very low concentrations. Use of an eluent ion such as tetraborate therefore offers a means of adjusting the retention time, or even the separation selectivity, for the analyte ions and also offers the possibility of gradient elution in EIC.

Fig. 1. Relationship between log k' and log[$Na_2B_4O_7$] for the model analyte ions. Separations were achieved using an ODS column (250×4.6 mm I.D.) coated with Zwittergent-3-14; eluents were aqueous solutions of sodium tetraborate; eluent flow-rate was 1.0 mL/min; and suppressed conductivity detection was used. Identities for the plots: $1=SO_4^{2-}$, $2=Cl^-$, $3=NO_2^-$, $4=Br^-$, $5=NO_3^-$, $6=ClO_3^-$, and $7=I^-$.

3.2. Analytical performance characteristics

The sensitivity of the tetraborate EIC system was found to be superior to that using bicarbonate and/or carbonate as the eluent ions. Detection limits ($S/N=$ 3) for highly conducting anions (SO_4^{2-}, Cl^-, NO_2^-, Br^-, and NO_3^-) were less than $8\cdot10^{-8}$ M, and for weakly conducting anions (ClO_3^- and I^-) detection limits were $2.7\cdot10^{-7}$ and $5.8\cdot10^{-7}$ M, respectively. These detection limits are comparable to those obtained using suppressed EIC with hydroxide as eluent and background conductances for both eluents were similar (3.2 μS cm^{-1} for a 10 mM tetraborate eluent and 1.7 μS cm^{-1} for 10 mM hydroxide eluent).

Calibration curves were linear up to 1.8 mM for

all of the tested analyte ions. The RSD (relative standard deviation) of the retention time and peak heights for a standard sample containing 1.0 μM of each of the analytes was $<1.2\%$ for all species. Longevity studies with the method showed that the tetraborate eluent could be used for extended periods (in excess of 4 weeks) without noticeable deterioration of the ODS stationary phase. However, extended use of the hydroxide eluent is not recommended.

3.3. Applications

The suppressed-EIC system using tetraborate as eluent was applied to the analysis of inorganic anions in rainwater and snow samples (Figs. 2 and 3). Five anions (SO_4^{2-}, Cl^-, NO_2^-, Br^-, and NO_3^-) were found in both of these samples at concentrations of 42.1, 78.3, 0.81, 0.36, and 10.2 μM in snow, and 20.1, 38.7, 0.41, 0.17, and 5.2 μM in rainwater, respectively. It should be noted here that the IC
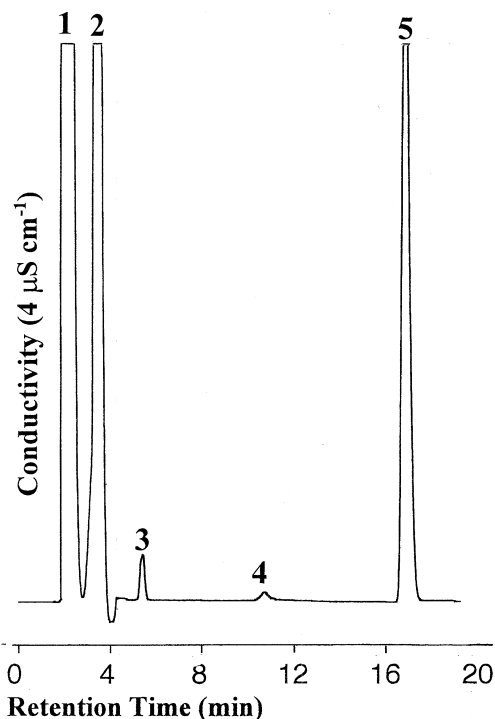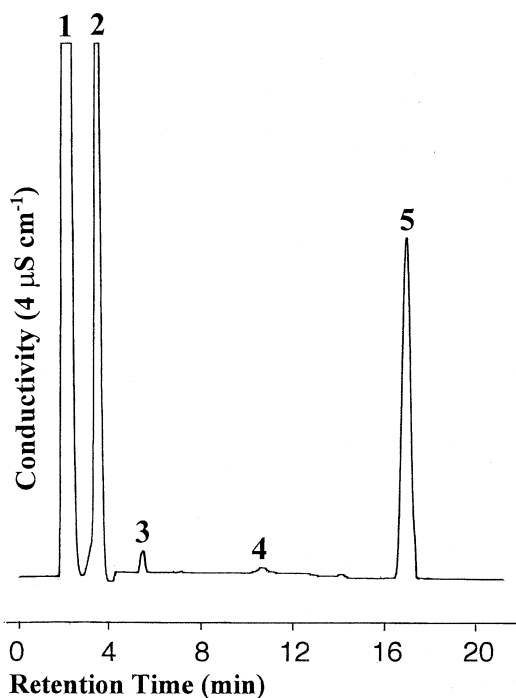

Fig. 3. Determination of inorganic anions in rainwater using suppressed EIC. Conditions and peak identities as for Fig. 2.

system proposed in this paper was unable to separate HPO_4^{2-} and F^- from SO_4^{2-}, with all three species being eluted near the void time. However, for the samples (rainwater and snow) examined in this study, HPO_4^{2-} and F^- were found to be absent using analysis by conventional anion-exchange IC. For this reason the first peak in the chromatogram is considered to correspond to SO_4^{2-}. Separation of HPO_4^{2-}, F^- and SO_4^{2-} will be a major target of our future research.

4. Conclusion

A zwitterionic surfactant stationary phase used in conjunction with a sodium tetraborate eluent provides a suppressed-EIC system for the sensitive detection of inorganic anions. Moreover, the weak retention of tetraborate on the quaternary ammonium group of the surfactant permits the establishment of a binary EDL having a thickness determined by the eluent concentration. This, in turn, permits the

Fig. 2. Determination of inorganic anions in snow using suppressed EIC with a 10 mM $Na_2B_4O_7$ solution as eluent. Other conditions as for Fig. 1. Peak identities: 1=SO_4^{2-}, 2=Cl^-, 3=NO_2^-, 4=Br^-, and 5=NO_3^-.

retention times of analytes to be varied by changing the eluent concentration and opens up the possibility of gradient elution in EIC. The approach used in this report will be extended using other weakly retained eluent ions, especially low-molecular-mass carboxylic acids.

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