

High-speed simultaneous ion-exclusion/cation-exchange chromatography of anions and cations on a weakly acidic cation-exchange resin column

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Abstract

The simultaneous ion-exclusion/cation-exchange separation column packed with a polymethacrylate-based weakly acidic cation-exchange resin of 3 μm particle size was used to achieve the simultaneous high-speed separation of anions and cations (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , NH_4^+ , Ca^{2+} and Mg^{2+}) commonly found in environmental samples. The high-speed simultaneous separation is based on a combination of the ion-exclusion mechanism for the anions and the cation-exchange mechanism for cations. The complete separation of the anions and cations was achieved in 5 min by elution with 15 mM tartaric acid–2.5 mM 18-crown-6 at a flow-rate of 1.5 ml/min. Detection limits at $S/N=3$ ranged from 0.36 to 0.68 μM for anions and 0.63–0.99 μM for cations. This method has been applied to the simultaneous determination of anions and cations in several environmental waters with satisfactory results.

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1. Introduction

The measurement of common inorganic anions (SO_4^{2-} , Cl^- , and NO_3^-) and cations (Na^+ , K^+ , NH_4^+ ,

Mg^{2+} and Ca^{2+}) found in environmental waters is an important matter to evaluate water quality of some environmental waters including rain, lake, underground and river waters [1]. Therefore, the simultaneous determination of these ionic components is essential for monitoring of the environmental waters. Ion chromatography is a very effective method in order to determine both anions and cations in many types of natural water. Especially, simulta-

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neous ion-exclusion/cation-exchange chromatography using acidic eluent on a single separation column has been recognized to be an effective method to simultaneously determine anions and cations [1–8].

A weakly acidic cation-exchange resin packed with carboxyl functional groups as a separation column for the simultaneous ion-exclusion/cation-exchange chromatographic determination of the anions and cations has been often used [1–8]. While the carboxyl column has been available for the cation-exchange chromatographic separation of inorganic cations [9–11], it has been an effective also for the ion-exclusion chromatographic separation of inorganic and/or organic anions [12,13]. The advantage using the column is easy to control the dissociation of the carboxyl groups in the resin-surface and the penetration reaction of anions to the resin can be accelerated.

The results obtained suggested that the concentration of acid in the eluent was an important factor for ion-exclusion and cation-exchange chromatographic separation of anions and cations, respectively, on the weakly acidic cation-exchange resin. This method was applicable for the water quality monitoring of the environmental water samples. However the analysis times for the simultaneous ion-exclusion/cation-exchange chromatography of the anions and cations were comparatively long (ca. 15–30 min).

The purpose of this study is to demonstrate the usefulness of cation-exchange resin with small particle size in order to achieve high-speed simultaneous ion-exclusion/cation-exchange chromatographic separation of anions and cations. In general, the use of a separation column having small particle size is useful to increase the theoretical plate of analyte peak in liquid chromatographic separation.

In the present study, a simple, sensitive and high-speed ion-exclusion/cation-exchange chromatography method has been developed for the simultaneous determination of anions and cations by using the separation column packed with 3 μm particles and elution with a mixture of tartaric acid and crown ether. The effectiveness of this method is demonstrated in the practical application to the simultaneous determination of three anions and five cations in rain and river waters in 5 min.

2. Experimental

2.1. Apparatus

Ion separation was performed on a Tosoh Model IC-2001 equipped with the following devices: vacuum degasser, pump, column oven, auto-sampler, and conductivity detector (Tosoh, Tokyo, Japan). The separations were carried out using two types of polymethacrylate-based weakly acidic cation-exchange resin columns in the H^+ -form: TSKgel Super-IC-A/C (3 μm particle size, 0.2 mequiv./ml cationic exchange capacity, 150 \times 6.0 mm I.D.) and TSKgel OApak-A (5 μm particle size, 0.1 mequiv./ml cationic exchange capacity, 150 \times 6.0 mm I.D.), which are specially synthesized separation columns at Tosoh. The experimental conditions for ion chromatography (IC) were as follows: column temperature 40 $^{\circ}\text{C}$, eluent flow-rate 1.5 ml/min, and injection volume 30 μl .

2.2. Chemicals

Standard solutions, washing solvents and eluents were prepared with distilled and deionized water. All reagents used in this study were purchased from Wako (Osaka, Japan). Each stock solution of Na_2SO_4 , KNO_3 , NH_4NO_3 , MgSO_4 , and CaCl_2 was solved to 0.1 M and mixed with distilled and deionized water for calibration purpose. A tartaric acid as an eluent was used by considering the peak resolutions of anions and cations, separation times, detection sensitivity and eluent background conductivity, when using the weakly acidic cation-exchange resin columns.

3. Results and discussion

3.1. Choice of cation-exchange resin columns

In this study, the separation performance of TSKgel Super-IC-A/C packed with 3 μm particles and 0.2 mequiv./ml capacity (1) and TSKgel OApak-A packed with 5 μm particles and 0.1 mequiv./ml capacity (2) was compared in terms of the resolution of the anions and cations on 6 mM tartaric eluent (pH 2.67; eluent conductivity: 690

$\mu\text{S}/\text{cm}$). Although a simultaneous separation of the anions and cations was obtained in both separation columns, peak resolutions of both anions and cations using column 1 were significantly greater than those using column 2. For this reasons, TSKgel Super-IC-

A/C was judged to be the better separation column in this study.

3.2. Effect of tartaric acid concentration

The effect of tartaric acid concentration in eluent on the retention volumes (V_R) of analyte ions using TSKgel Super-IC-A/C was investigated. As shown in Fig. 1, the V_R values of the anions slightly increased by increasing the concentration of tartaric acid as expected from the ion-exclusion effect, and the resolutions of the anions were improved. This means that the penetration of anions to the resin-phase was increased by the neutralization of carboxyl groups in the resin with increasing concentration of hydrogen ion, in the tartaric acid eluent. Additionally, the difference of penetration between analyte anions with carboxyl groups on the surface of the column seems to be dependent on the nature of anion (e.g., hydrate energy, ion size, and polarizability) and side-effects such as hydrophobic interaction. On the other hand, the V_R values of the cations drastically decreased by increasing the concentration of tartaric acid as expected from the cation-exchange effect. This means that the degree of cation-exchange reaction of the cations, especially Mg^{2+} and Ca^{2+} , to the cation exchanger (i.e., carboxyl groups) was greatly decreased with increasing hydrogen ion concentration in the eluent. Therefore, the separation time of anions and cations was significantly shortened with increasing the concentration of tartaric acid in the eluent.

The background conductance of the eluent increased with increasing concentration of tartaric acid in the eluent (924 $\mu\text{S}/\text{cm}$ for a 10 mM eluent, 1127 $\mu\text{S}/\text{cm}$ for a 15 mM eluent, and 1387 $\mu\text{S}/\text{cm}$ for a 20 mM eluent). An increase of the concentration of the tartaric acid eluent caused a decrease in the conductivity response. Therefore, the lowest possible eluent concentration of tartaric acid was required in order to obtain a high sensitive detection with conductivity. Consequently, the optimum concentration of tartaric acid for the simultaneous ion-exclusion/cation-exchange chromatography of anions and cations with TSKgel Super-IC-A/C was in the range of 10–15 mM by considering these factors. Fig. 2 shows the simultaneous separation of anions and cations obtained using a 15 mM tartaric acid

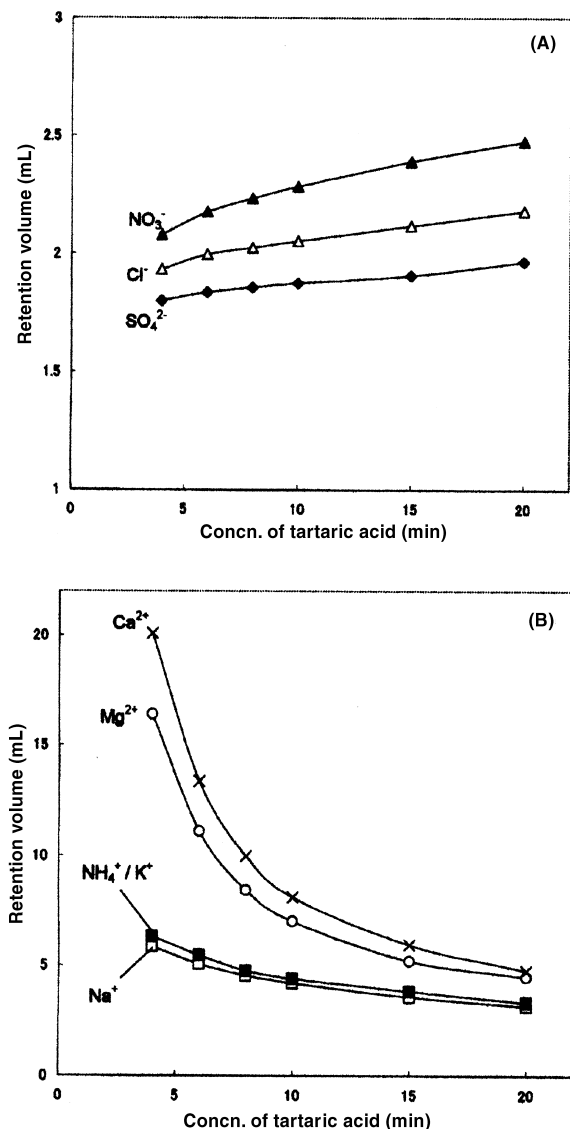


Fig. 1. Effect of tartaric acid concentration in the eluent on the retention volumes of anions and cations. Column: TSKgel Super-IC-A/C (15 cm \times 6 mm I.D.). Column temperature: 40 °C. Injection volume: 30 μl . Eluent flow-rate: 1.5 ml/min. Line identities: (A) \blacklozenge = SO_4^{2-} , \triangle = Cl^- , \blacktriangle = NO_3^- , (B) \square = Na^+ , \blacksquare = NH_4^+ and K^+ , \circ = Mg^{2+} , and \times = Ca^{2+} .

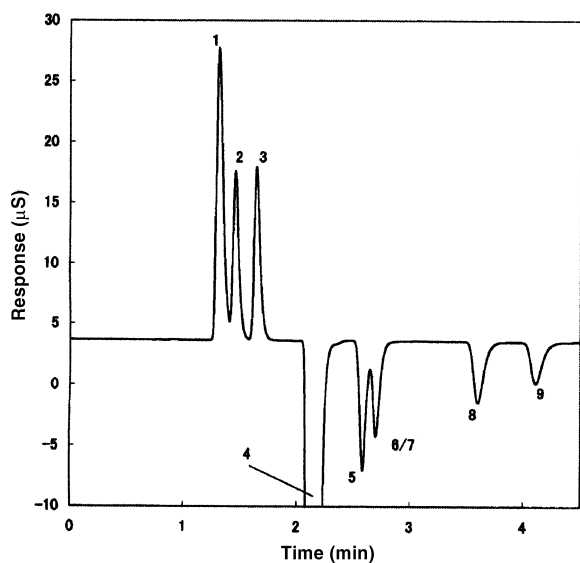


Fig. 2. Simultaneous ion-exclusion/cation-exchange chromatograms of anions and cations by elution with 15 mM tartaric acid (pH 2.44). Peak identities (mM): 1=SO₄²⁻ (0.2), 2=Cl⁻ (0.1), 3=NO₃⁻ (0.2), 4=elution dip, 5=Na⁺ (0.1), 6=NH₄⁺ (0.1), 7=K⁺ (0.1), 8=Mg²⁺ (0.1) and 9=Ca²⁺ (0.1). Other conditions as in Fig. 1.

eluent (pH 2.44). A good separation of anions and cations, except for the monovalent cations Na⁺, NH₄⁺, and K⁺, was obtained using this eluent.

3.3. Effect of 18-crown-6

The influences on the V_R values of the anions and cations by adding 18-crown-6 to the elution with 15 mM tartaric acid were investigated. Addition of 18-crown-6 to an eluent has been known to be very effective in improving peak resolution between monovalent cations [5,13,14]. This behavior can be explained by stability constant of complexation of the alkali metal ions with 18-crown-6 absorbed on the cation-exchange resin of separation column ($\log K_{Na}=0.80$, $\log K_{NH_4}=1.23$, and $\log K_K=2.03$) [15]. Especially, K⁺ can form a very stable metal-in-hole type complex with 18-crown-6, because the internal cavity size of 18-crown-6 is the same size as K⁺. The retention times of anions and divalent cations were unchanged with increasing concentration of 18-crown-6, in contrast to those of monovalent cations and the peak resolution between NH₄⁺ and

K⁺ dramatically improved. The complete separation among monovalent cations can be achieved with the addition of 2 mM 18-crown-6 to the eluent. Finally, an elution with 15 mM tartaric acid and 2.5 mM 18-crown-6 was adopted as an optimal condition for this high-speed simultaneous ion-exclusion/cation-exchange chromatography of the anions and the cations, and the whole retention time obtained was less than 5 min (Fig. 3).

3.4. Analytical performance characteristics

Calibration graphs were obtained by plotting peak area for the concentration of these anions and cations at the optimal elution condition. Linear calibration graphs were obtained in the concentration ranges 0–1.0 mM for anions ($r^2=0.9973$ for SO₄²⁻, 0.9991 for Cl⁻ and 0.9997 for NO₃⁻), 0–1.0 mM for cations ($r^2=0.9998$ for Na⁺, 0.9993 for K⁺, 0.9972 for Mg²⁺ and 0.9988 for Ca²⁺), and 5.0 µM–0.5 mM for NH₄⁺ ($r^2=0.9988$). Detection limits, calculated at $S/N=3$, ranged from 0.36 to 0.68 µM (13.1–34.7 µg/l) for anions and 0.63–0.99 µM (11.3–35.8 µg/l) for cations. Although these values are suitable for

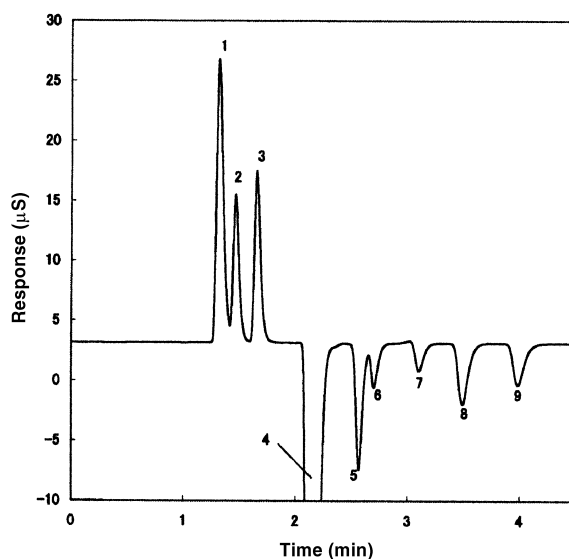


Fig. 3. Simultaneous ion-exclusion/cation-exchange chromatogram of the anions and cations by elution with 15 mM tartaric acid/2.5 mM 18-crown-6 (pH 2.44). Peak identities: 1=SO₄²⁻, 2=Cl⁻, 3=NO₃⁻, 4=elution dip, 5=Na⁺, 6=NH₄⁺, 7=K⁺, 8=Mg²⁺, and 9=Ca²⁺. Other conditions as in Fig. 1.

the monitoring of environmental samples, they are significantly poorer than those obtained using the tartaric acid–18-crown-6 eluent reported previously [5]. The poorer detection limits arise from an increase in the background noise due to the addition of high concentrations of tartaric acid. In the fifth continuous measurements, the reproducibility of

retention times of standard samples of 0.1 mM at the optimal elution condition was 0.17–0.51% relative standard deviation (RSD), and those of peak areas were 1.30–3.97% RSD. The reproducibility for cations was poorer than that of anions, because it arises from error involved in performing area integration on a negative peak.

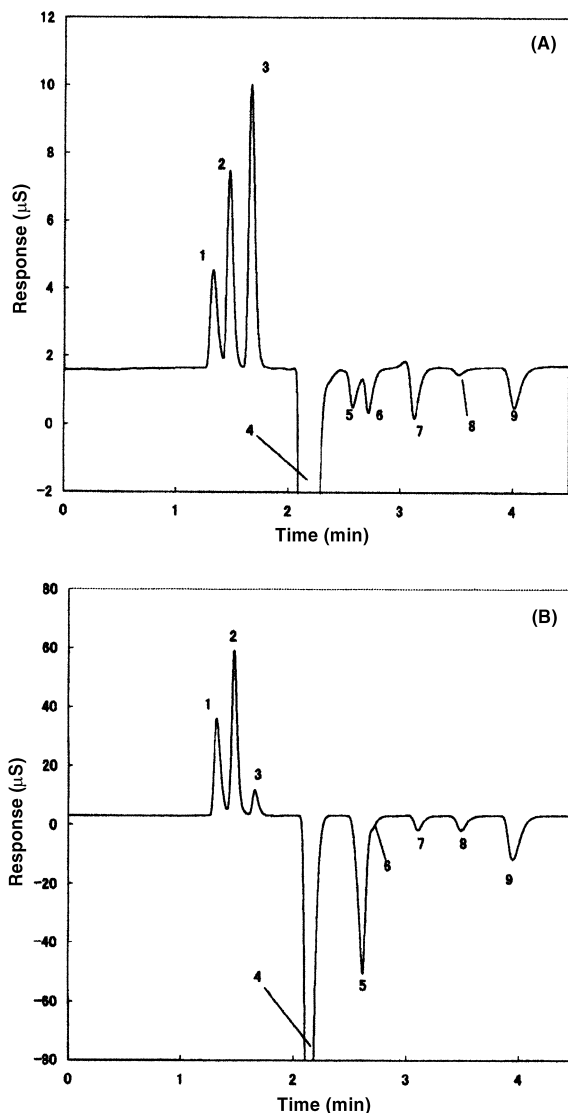


Fig. 4. Chromatograms of (A) rain water (pH 4.21) and (B) river water (pH 7.28) by elution with 15 mM tartaric acid/2.5 mM 18-crown-6 (pH 2.44). Peak identities: 1= SO_4^{2-} , 2= Cl^- , 3= NO_3^- , 4=elution dip, 5= Na^+ , 6= NH_4^+ , 7= K^+ , 8= Mg^{2+} and 9= Ca^{2+} . Other conditions as in Fig. 1.

3.5. Application to the analysis of rain and river waters

As result of application to real samples, major anions and cations (SO_4^{2-} , Cl^- , NO_3^- , Na^+ , K^+ , NH_4^+ , Mg^{2+} and Ca^{2+}) contained in some environmental waters, rain and river waters, were determined by using the proposed ion-exclusion/cation-exchange chromatography (Fig. 4). Each analyte sample was analyzed after filtration through a 0.45- μm membrane filter. The successful separation among all of environmental analytes could be achieved. Table 1 summarizes the determination in the environmental samples, compared with conventional anion-exchange chromatography for anions and cation-exchange chromatography for cations. The results demonstrated that the system developed here is a useful method for the accurate determination of these anions and cations. As a final point, the overall sample turn-around time (washing of syringe, injection of sample, and separation) in this method was less than 6 min, therefore 10 runs within 60 min were possible.

4. Conclusions

A high-speed ion-exclusion/cation-exchange chromatography method has been developed for the simultaneous determination of the anions and cations commonly found in environmental waters, based on the simultaneous mechanisms of ion-exclusion for anions and cation-exchange for cations. A combination of 15 mM tartaric acid–2.5 mM 18-crown-6 and a separation column packed with a weakly acidic cation-exchange resin of 3 μm particle size was found to be very effective for the determination of anions and cations in the environmental waters such as rain or river waters.

Table 1

Concentrations (μM) of anions and cations in rain and river waters obtained with the proposed ion-exclusion/cation-exchange chromatography ($n=5$)

Analyte	Proposed ion-exclusion/ cation-exchange chromatography		Suppressed anion-exchange chromatography ^a		Nonsuppressed cation-exchange chromatography ^b	
	Rain water (pH 4.21)	River water (pH 7.28)	Rain water (pH 4.21)	River water (pH 7.28)	Rain water (pH 4.21)	River water (pH 7.28)
SO ₄ ²⁻	24.3	138	26.0	130	–	–
Cl ⁻	52.8	475	54.6	482	–	–
NO ₃ ⁻	119	55.7	122	50.2	–	–
Na ⁺	11.3	600	–	–	12.7	588
NH ₄ ⁺	33.9	126	–	–	31.7	120
K ⁺	49.6	192	–	–	50.8	180
Mg ²⁺	4.30	95.2	–	–	4.07	98.4
Ca ²⁺	34.3	465	–	–	38.2	448

^a Suppressed anion-exchange chromatography of anions by elution with 1.7 mM NaHCO₃–1.8 mM Na₂CO₃ using strongly basic anion-exchange resin column. Column: TSKgel Super-IC-Anion (15 cm×4.6 mm I.D.). Other conditions as in Fig. 1.

^b Non suppressed cation-exchange chromatography of cations by elution with 2.5 mM HNO₃–0.5 mM histidine using weakly acidic cation-exchange resin column. Column: TSKgel Super-IC-Cation (15 cm×4.6 mm I.D.). Eluent flow-rate: 1.2 ml/min. Other conditions as in Fig. 1.

A separation column having the smaller cation-exchange capacity (<0.1 mequiv./ml resin) will be studied to achieve highly sensitive detection and high-speed separation for anions and cations with lower eluent background conductivity.

A further investigation must consider the problems for the practical application of ion-exclusion/cation-exchange chromatography to the simultaneous determination of anions and cations in real samples.

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