



ELSEVIER

Journal of Chromatography A, 850 (1999) 79–84

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Simultaneous determination of anions and cations by ion-exclusion chromatography–cation-exchange chromatography with tartaric acid/18-crown-6 as eluent

Se-Mog Kwon^a, Kwang-Pill Lee^{b,*}, Kazuhiko Tanaka^c, Kazutoku Ohta^c

^aTaegu City Health and Environmental Research Institute, Taegu 706-090, South Korea

^bKyungpook National University, Taegu 702-701, South Korea

^cNational Industrial Research Institute of Nagoya, Nagoya 462-8510, Japan

Abstract

Ion-exclusion chromatography–cation-exchange chromatography was developed for the simultaneous separation of common inorganic anions and cations (Cl^- , NO_3^- and SO_4^{2-} ; Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) on a weakly acidic cation-exchange column by elution with weak acid. Generally, the resolution among these monovalent cations was only moderate, thereby hindering the determination of these analytes in natural-water samples. Therefore, 18-crown-6 was added to the eluent to improve the resolution. A good separation of these anions and cations on a weakly acidic cation-exchange column was achieved in 30 min by elution with 5 mM tartaric acid/6 mM 18-crown-6/methanol–water (7.5:92.5). The ion-exclusion chromatography–cation-exchange chromatography method developed here was successfully applied to the separation of major anions and cations in an environmental water sample. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Mobile phase composition; Water analysis; Environmental analysis; Inorganic anions; Inorganic cations; Crown ethers; Tartaric acid

1. Introduction

Ion-exclusion chromatography–cation-exchange chromatography (CEC) is very useful for the simultaneous separation of common inorganic anions (Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) in natural-water samples. The technique uses conductivity detection on a weakly acidic cation-exchange column (TSKgel OA-Pak A), using a weak-acid eluent developed by Tanaka et al. [1]. In ion-exclusion chromatography–CEC, anions

are separated by an ion-exclusion process and are detected by direct conductivity. In contrast, cations are separated by a cation-exchange process and are detected by indirect conductivity. However, the peak resolution among monovalent cations is often moderate. Improvement of peak resolution is required for the achievement of accurate determination of these species.

Crown ethers are well known to form stable complexes with cations, especially monovalent cations [2]. On the basis of these stabilities, 18-crown-6 was added to acidic eluents to improve peak resolution of mono- and divalent cations on a weakly acidic cation-exchange column [3,4].

The aim of this study was to improve of peak

*Corresponding author. Tel.: +82-53-950-5901; fax: +82-53-952-8104.

E-mail address: kplee@kyungpook.ac.kr (K.-P. Lee)

resolution among monovalent cations in ion-exclusion chromatography–CEC. Therefore, the addition of 18-crown-6 to 5 mM tartaric acid/methanol–water (7.5:92.5) as eluent was carried out. As a result, when using 5 mM tartaric acid/6 mM 18-crown-6/methanol–water (7.5:92.5) as eluent, good simultaneous separation of these anions and cations was achieved in 30 min. The ion-exclusion chromatography–CEC method developed here was successfully applied to analysis of anions and cations in rain- and river-water samples.

2. Experimental

2.1. Instruments

The ion chromatograph consisted of a Waters (Milford, MA, USA) Model 600 programmable

pump operated at a flow-rate of 1.2 ml/min, a Waters column oven operated at 25°C, a Waters Model 431 conductimetric detector and a Rheodyne (Cotati, CA, USA) Model 7725I sample injector equipped with a 100- μ l sample loop. An Autochro Win (Younglin, South Korea) Data Module was employed for instrument control, and for data collection and processing.

A Tosoh TSKgel OA-Pak A column (300 \times 7.8 mm I.D.) packed with a carboxylated polyacrylate resin (particle size: 5 μ m) in the H⁺ form was used for the simultaneous separation of anions and cations in ion-exclusion chromatography/CEC.

An Orion (Boston, MA, USA) Model 545 pH meter was used for the measurement of pH of environmental water samples.

2.2. Reagents

All reagents (except for methanol) were analytical-

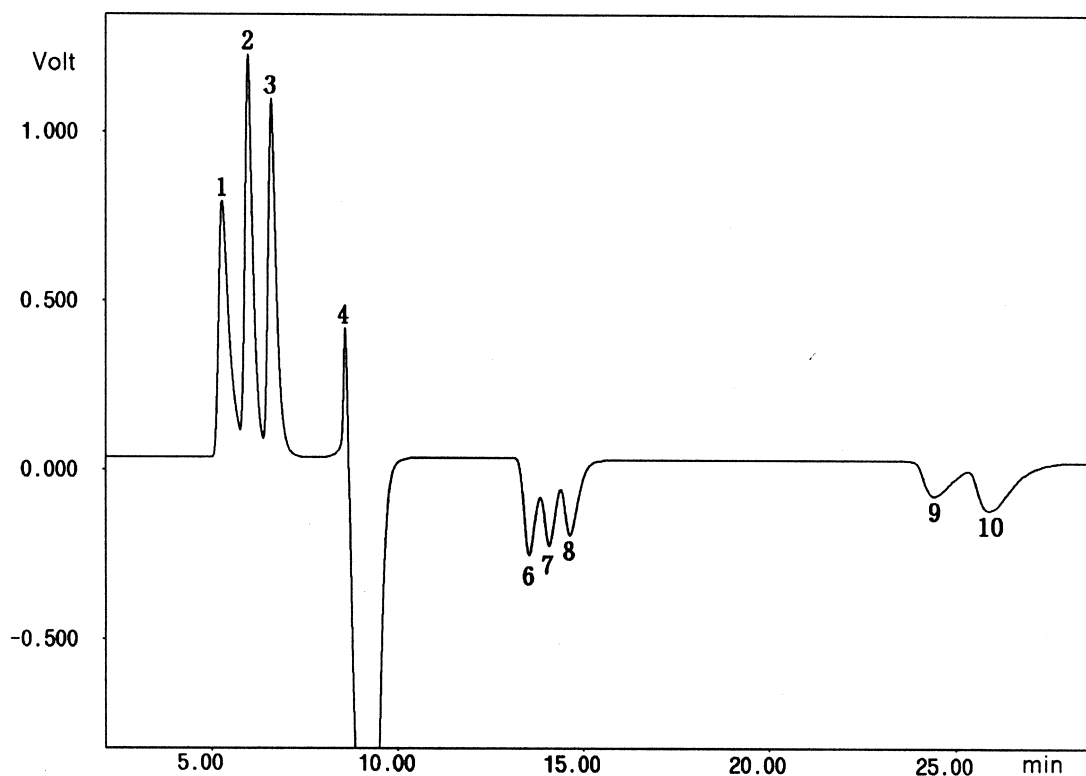


Fig. 1. Chromatogram of common inorganic anions and cations by elution with 5 mM tartaric acid/methanol–water (7.5:92.5). Conditions: flow-rate: 1.2 ml min⁻¹; column: TSKgel OA-Pak A, 300 \times 7.8 mm I.D.; column temperature: 25°C; detection: conductivity; injection volume: 100 μ l; sample: mixture of 0.1 mM KNO₃, NH₄NO₃, CaCl₂ and 0.05 mM Na₂SO₄ and Mg SO₄. Peaks: 1=SO₄²⁻, 2=Cl⁻, 3=NO₃⁻, 4=eluent dip, 5=unknown, 6=Na⁺, 7=NH₄⁺, 8=K⁺, 9=Mg²⁺, 10=Ca²⁺.

reagent grade; methanol was HPLC grade. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was purchased from Aldrich (Milwaukee, WI, USA) and other reagents were purchased from Merck (Rahway, NJ, USA).

Distilled deionized water was used for the preparation of eluents and standard solutions.

3. Results and discussion

3.1. Effect of 18-crown-6 in 5 mM tartaric acid/methanol–water (7.5:92.5) eluent

As shown in Fig. 1, when using 5 mM tartaric acid/methanol–water (7.5:92.5) as eluent, the separation of common inorganic anions and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) on the TSKgel OA-Pak A column was moderate. Especially, the separation of monovalent cations was not satisfactory. Further investigation was required for improvement of peak resolution among monovalent cations.

Since other researchers [3,4] had demonstrated the ability of 18-crown-6 to improve cation separation, various concentrations of the crown ether were added to the 5 mM tartaric acid/methanol–water (7.5:92.5) eluent.

As shown in Fig. 2, with increase of the concentration of 18-crown-6 in the eluent, the retention volume of NH_4^+ and K^+ increased and those of other cations were almost same. The retention volume of inorganic anions were not validated due to no interaction between anions and 18-crown-6. Since the order of the increase of the retention volumes for the monovalent cations was $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+$, the peak resolution among these monovalent cations was improved. Additionally, since the order was in agreement with that predicted from stability constants ($\log K_{\text{Na}^+} = 0.8$, $\log K_{\text{NH}_4^+} = 1.23$ and $\log K_{\text{K}^+} = 2.03$) [5], it is suggested that 18-crown-6 in the eluent was adsorbed on the cation-exchange stationary phase and then acted as a selective cation exchanger.

As shown in Fig. 3, when using 5 mM tartaric acid/6 mM 18-crown-6/methanol–water (7.5:92.5)

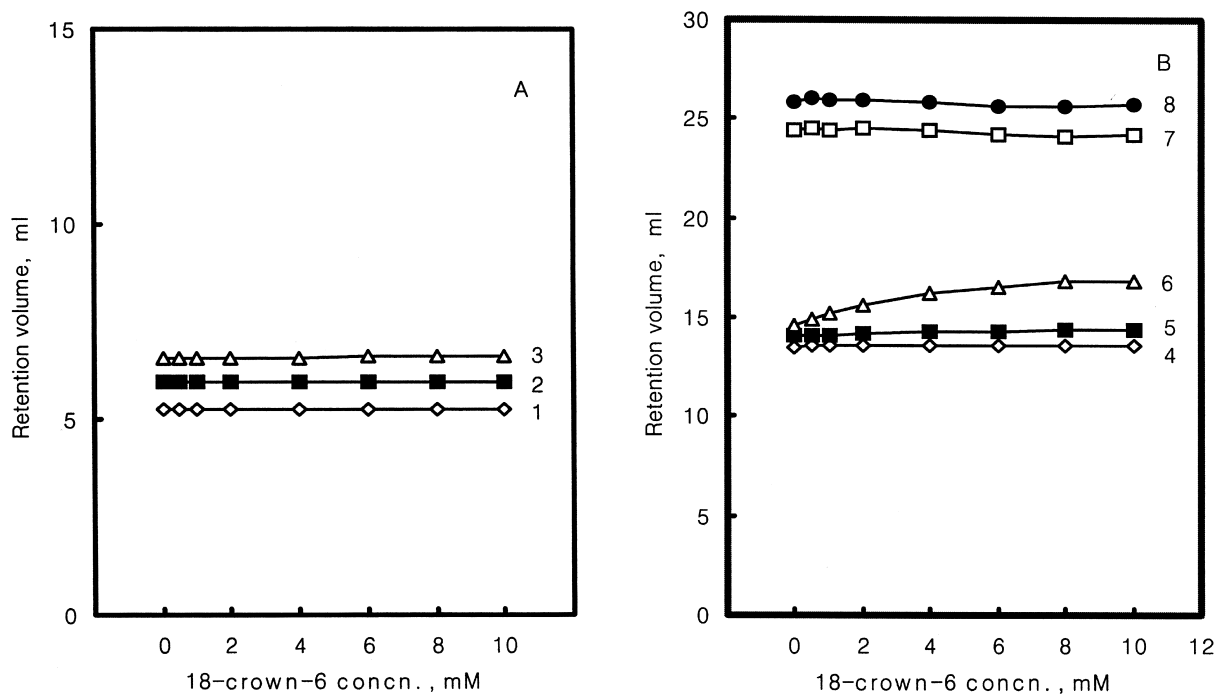


Fig. 2. Effect of concentration of 18-crown-6 in 5 mM tartaric acid/methanol–water (7.5:92.5) eluent on retention volumes of common inorganic anions and cations. Eluent: 0–10 mM 18-crown-6 in 5 mM tartaric acid/methanol–water (7.5:92.5). Symbols: $\diamond = \text{SO}_4^{2-}$, $\blacksquare = \text{Cl}^-$, $\triangle = \text{NO}_3^-$, $\diamond = \text{Na}^+$, $\blacksquare = \text{NH}_4^+$, $\triangle = \text{K}^+$, $\square = \text{Mg}^{2+}$, $\bullet = \text{Ca}^{2+}$. Other chromatographic conditions as in Fig. 1.

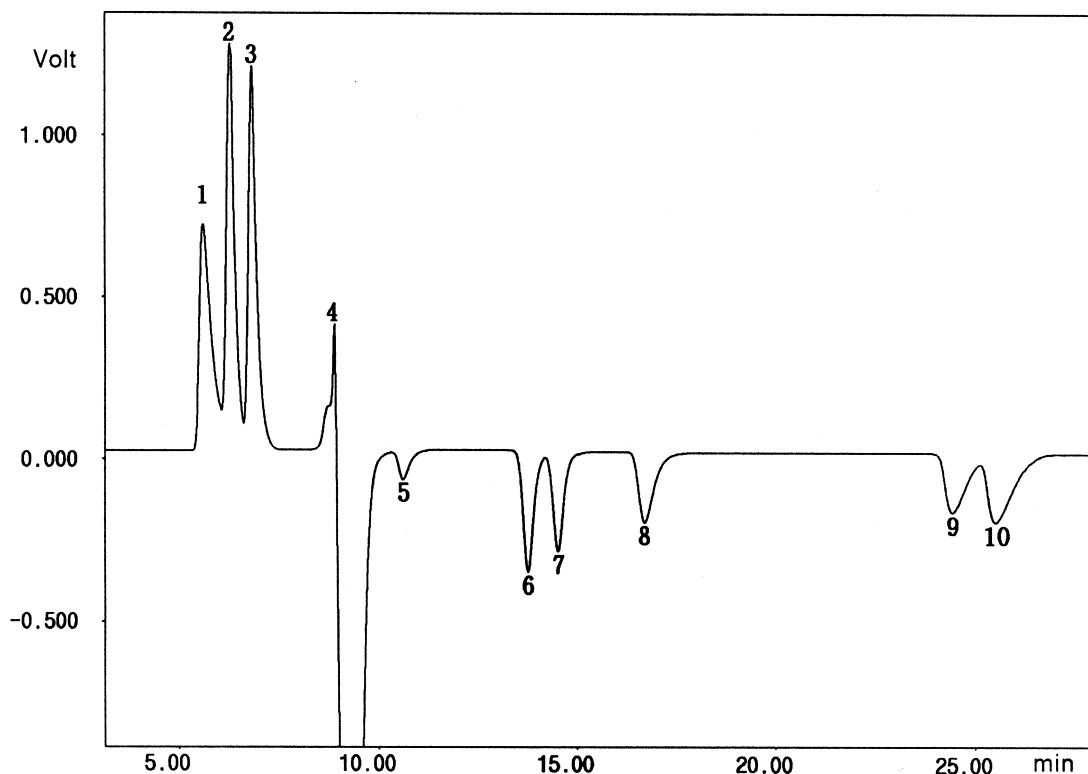


Fig. 3. Chromatogram of common inorganic anions and cations by elution with 5 mM tartaric acid/6 mM 18-crown-6/methanol–water (7.5:92.5). Other chromatographic conditions as in Fig. 1.

as eluent, good simultaneous separation of these anions and cations was achieved in 30 min.

3.2. Analytical performance parameters

Calibration graphs were obtained by plotting peak area against the concentration of these anions and cations. Linear calibration graphs ($r^2 > 0.99$) were obtained in the concentration ranges 0–0.8 mM for anions and 0–0.4 mM for the cations. This calculation was the same in a previous paper [1].

The detection limits determined at a signal-to-noise ratio of three were 0.25 μM (24 ppb) for SO_4^{2-} , 0.19 μM (6.7 ppb) for Cl^- , 0.30 μM (19 ppb) for NO_3^- , 0.36 μM (8.3 ppb) for Na^+ , 0.47 μM (8.5 ppb) for NH_4^+ , 0.69 μM (27 ppb) for K^+ , 0.35 μM (8.5 ppb) for Mg^{2+} and 0.46 μM (18 ppb) for Ca^{2+} . These detection limits were reasonable for the de-

termination of these anions and cations in environmental water.

3.3. Application to the analysis of rain and river water

The ion-exclusion chromatography–CEC method developed here was applied to the simultaneous separation of major anions and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) in rain- and river-water samples. The sample was analyzed after filtration through a 0.45- μm membrane filter.

As shown in Fig. 4, the peak resolution among analyte anions and cations was quite satisfactory. This result indicated that the ion-exclusion chromatography–CEC method developed here was very useful for the accurate determination of these anions and cations in rain and river water.

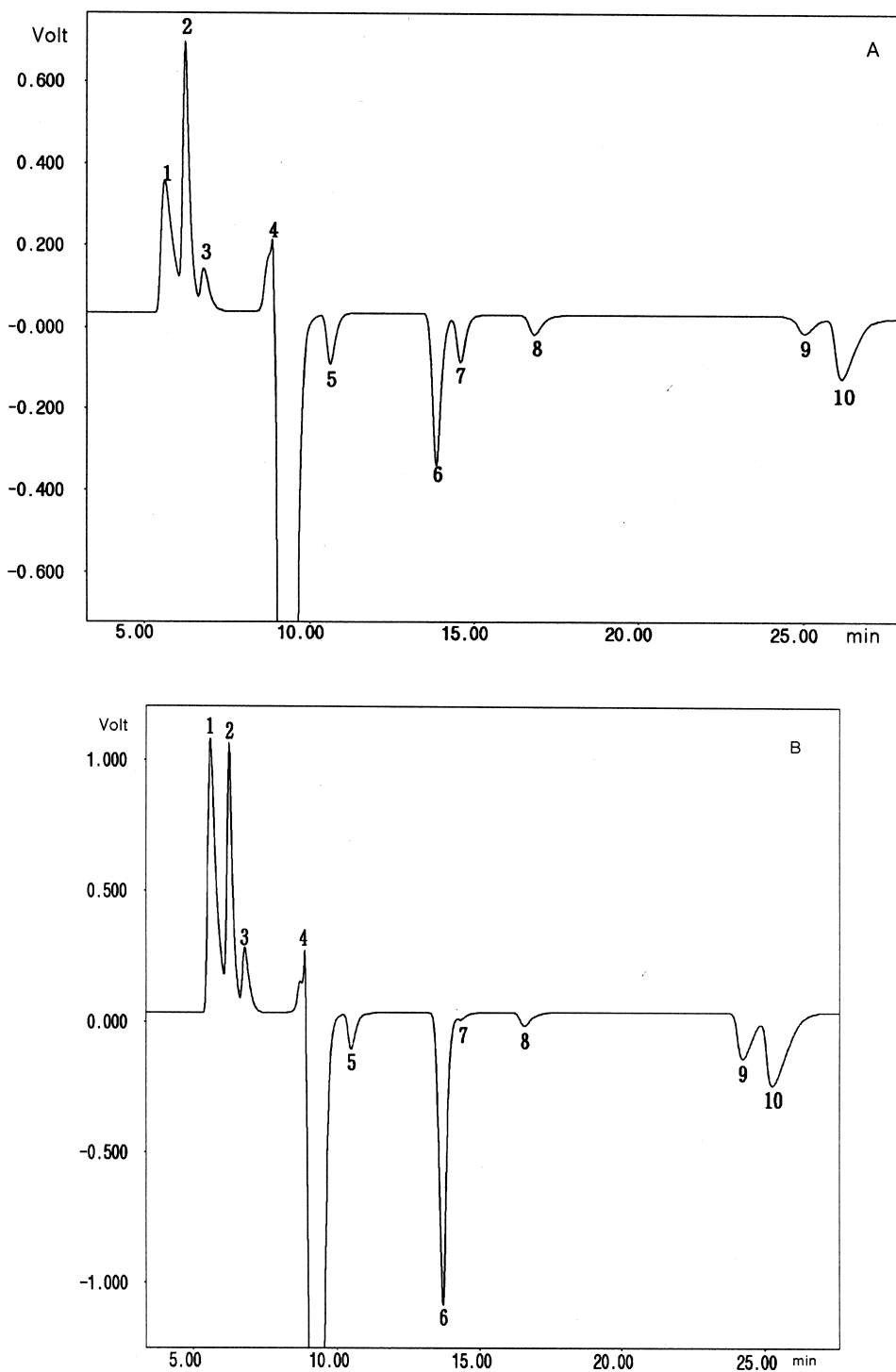


Fig. 4. Chromatogram of (A) rain water (pH 6.33), (B) river water (pH 7.60) by elution with 5 mM tartaric acid/6 mM 18-crown-6/methanol–water (7.5:92.5). (A) Peaks (concentration, mM): 1=SO₄²⁻ (0.052), 2=Cl⁻ (0.101), 3=NO₃⁻ (0.020), 4=eluent dip, 5=unknown, 6=Na⁺ (0.094), 7=NH₄⁺ (0.036), 8=K⁺ (0.020), 9=Mg²⁺ (0.008), 10=Ca²⁺ (0.061). (B) Peaks (concentration, mM): 1=SO₄²⁻ (0.718), 2=Cl⁻ (0.787), 3=NO₃⁻ (0.245), 4=eluent dip, 5=unknown, 6=Na⁺ (1.490), 7=NH₄⁺ (0.039), 8=K⁺ (0.115), 9=Mg²⁺ (0.248), 10=Ca²⁺ (0.703). Chromatographic conditions as in Fig. 1.

There is no contamination problem from the membrane filter used in this study.

References

- [1] K. Tanaka, K. Ohta, J.S. Fritz, S. Matsushita, A. Miyanaga, *J. Chromatogr. A* 671 (1994) 239.
- [2] C.J. Perderson, *J. Am. Chem. Soc.* 89 (1967) 7017.
- [3] M.W. Luabi, B. Kampus, *J. Chromatogr. A* 706 (1995) 103.
- [4] M. Ono, H. Kumagai, T. Sakai, Y. Date, Y. Inoue, *Ind. Water* 469 (1997) 25.
- [5] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.H. Lamb, J.J. Christensen, *Chem. Rev.* 85 (1985) 271.