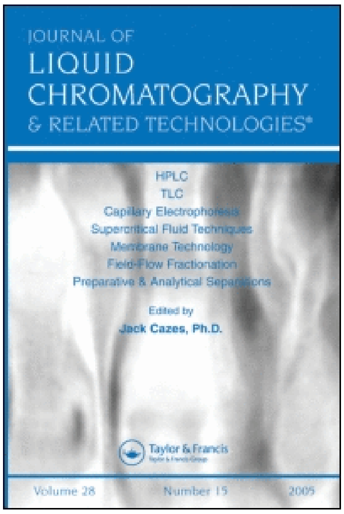

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SIMULTANEOUS DETERMINATION OF ANIONS AND CATIONS IN ENVIRONMENTAL SAMPLES BY USING A WEAKLY ACIDIC CATION-EXCHANGE COLUMN WITH 2,6-PYRIDINEDICARBOXYLIC ACID, SULFOSALICYLIC ACID, AND 18-CROWN-6 AS ELUENT

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ABSTRACT

Weakly acidic cation exchange resin can be used for simultaneous separation of anions and cations when acidic eluents were employed. On the weakly acidic cation exchange resin, anions

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were retained by ion exclusion mechanism, while cations by cation exchange mechanism. The selection of eluent is very important for the separation of interesting analytes. In this study, a mixture of 0.6 mmol/L 2,6-pyridinedicarboxylic acid (PDCA), 0.75 mmol/L sulfosalicylic acid (SSA), and 6.0 mmol/L 18-crown-6 was employed as eluent 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+}).

A good separation of these anions and cations on the weakly acidic cation exchange column (Tosoh TSKgel OApak-A) was achieved in 16 min. The linear range of peak area calibration curves for all analytes were up to two orders of magnitude. The conductivity detection limits calculated at S/N=3 were from 0.2 to 1.6 µmol/L for anions and cations. The method developed in this work was successfully applied to the simultaneous determination of major inorganic anions and cations in several environmental water samples.

INTRODUCTION

It is very important to determine the common inorganic anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) in environmental samples, such as acid rain, river water, snow water, and drinking water. The most useful ion chromatographic method for the simultaneous analysis of these anions and cations, is the ion exclusion chromatography/cation exchange chromatography (IEC/CEC) method using a single weakly acidic cation exchange column, which was developed by Tanaka and coworkers.(1-6) In these methods, for the simultaneous separation of these anions and cations, a longer column (TSKgel OApak-A, 7.8 mm i.d. x 300 mm), or two shorter columns (TSKgel OApak-A, 7.8 mm i.d. x 150 mm) contacted in series, and a carboxylic acid eluent (tartaric acid or sulfosalicylic acid) were employed. Inorganic anions, mono-, and divalent cations were eluted by three groups, respectively, and the elution time for one run was over 30 min on the weakly acidic cation exchange column. The separation of the ions in the same group was difficult, while very large resolutions between different groups were obtained.

The separation of anions could be improved by increasing the concentration of acidic eluents, but increasing eluent concentration was limited by the resolution of mono- and divalent cations. In order to short the analytical time, Tanaka et al.(7) developed a rapid method using a single shorter column (TSKgel Oapak-A, 7.8 mm i.d. x 150 mm) and a sulfosalicylic acid eluent. In order to improve the separation of monovalent cations, 18-crown-6 is usually added to the acidic eluent,(6,7) because 18-crown-6 could form stable complexes with monovalent cations, especially K^+ and NH_4^+.

2,6-Pyridinedicarboxylic acid (PDCA), as a good complexing agent for divalent cations, especially Ca^{2+} and Mg^{2+}, was used as eluent for simultaneous elution of mono- and divalent cation in cation exchange chromatography.(8,9) In this work, a mixture of SSA and PDCA was used as eluent in which PDCA could improve the separation of Ca^{2+} and Mg^{2+}. As a result, Ca^{2+} peak enters into the monovalent cation group, and a good simultaneous separation of these anions and cations was achieved in 16min. The simultaneous IEC/CEC method developed in this work was successfully applied to the simultaneous determination of inorganic anions and cations in rainwater, tap water, and snow samples.

EXPERIMENTAL

Reagents and Procedures

All reagents used were of analytical reagent grade unless specified. The eluent, standards, and all dilutions were prepared using distilled deionized water. 2,6-Pyridinedicarboxylic acid (PDCA) was purchased from Aldrich (Milwaukee, WI,USA), sulfosalicylic acid (SSA) was purchased from Kishida (Osaka,Japan), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) was from Wako (Osaka, Japan). The standard mixture of anions and cations was prepared from 0.1 mol/L each of Na_2SO_4, NH_4NO_3, KNO_3, $CaCl_2$, and $MgSO_4$.

Instrumentation

Ion chromatographic analyses were conducted on a Tosoh Model 8020 ion chromatograph (Tokyo, Japan), which consisted of two Model DP-8020 pumps, A CM-8020 conductivity detector, a UV-8020 UV-Vis detector, a CO-8020 column oven, a SD-8022 on-line vacuum degasser, and a SA-8020 auto-sampling module. A Tosoh chromatographic workstation (LC-8020) was utilized to control the instrument and for data processing.

Simultaneous ion-exclusion chromatography/cation exchange chromatography separation of inorganic anions and cations was carried out using a Tosoh (Tokyo, Japan) TSKgel OApak-A column (7.8mm i.d. x 150 mm), packed with polymethacrylate-based weakly acidic cation exchange resin in the H^+-form (particle size: 5 μm, exchange capicity:0.1mequiv./mL). The selected chromatographic conditions were as follows: eluent, a mixture of 0.75 mmol/L SSA, 0.6 mmol/L PDCA. and 6.0 mmol/L 18-Crown-6; flow rate, 1.2 mL/min.; column temperature, 35°C; sample size, 20μL.

Sample Preparation

Two rain waters (rain 1999 and rain 2000) were collected in the City of Nagoya in central Japan, rain 1999 was collected on November 11~12, 1999 and in 2000 on January 12~13, 2000. Tap water was obtained from National Industrial Research Institute of Nagoya and snow samples were collected in the City of Nagoya from February 8~9, 2000. All samples were filtered with 0.45 μm membrane filters before analysis. The tap water was diluted 5-fold and the other samples were injected directly.

RESULTS AND DISCUSSION

Simultaneous Separation of Inorganic Anions and Cations

Acidic eluents, especially carboxylic acids might be used in ion exclusion chromatography on weakly acidic cation exchangers for the simultaneous separation of anions and cations. SSA is a rather suitable eluent for simultaneous separation of inorganic anions and cations in IEC/CEC. As shown in Fig. 1 (A), only SSA as eluent could not separate NH_4^+ and K^+. The resolution of monovalent cations could be improved by adding crown ethers, such as 18-crown-6 to the eluent. As shown in Fig. 1 (B), a good separation was obtained when 6.0mmol/L 18-crown-6 was added to the eluent. In non-suppressed ion chromatography, requiring simultaneous conductivity detection of anions and cations, the dip peak caused from carboxylic acid eluents could usually be observed. A dip peak is not desired for real applications because it interferes with the separation and determination of analytes in many situations. On the weakly acidic cation exchange column used in this work, the dip peak caused from eluents was eluted generally between the anion group and monovalent cation group. The dip peak of SSA eluent was separated from both the anion group and monovalent cation group.

On the cation exchange resins (including the weakly acidic cation exchange resin used in ion exclusion chromatography), Ca^{2+} was eluted after Mg^{2+} when the common carboxylic acids, such as tartaric acid, citric acid, peromellitic acid, and sulfosalicylic acid were used as eluent, while Ca^{2+} was eluted faster than Mg^{2+}, and entered to the monovalent cation group when the PDCA was used as eluent. A sharper peak for Ca^{2+} and a great resolution between Ca^{2+} and Mg^{2+} were obtained compared with other eluents. The chromatograms with and without 6.0 mmol/L 18-crown-6 in 1.5 mmol/L PDCA eluent were shown in Fig. 2. The separation of anions could be improved by increasing the PDCA concentration, but the peak group including monovalent cations and Ca^{2+} and PDCA dip could not be separated when the concentration of PDCA eluent was over 1.8 mmol/L.

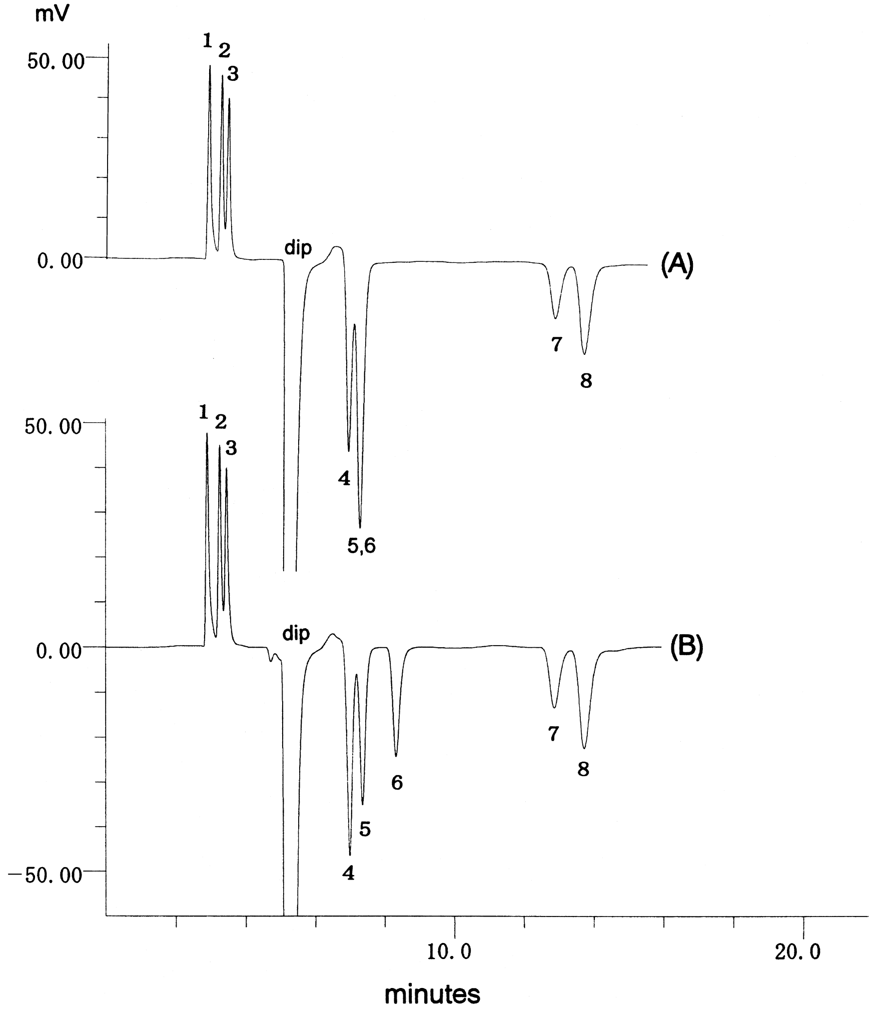

Figure 1. Simultaneous separation of anions and cations using SSA as eluent. Column: TSK gel OApak-A (7.8 mm i.d. x 150 mm); Eluent: (A) 1.25 mmol/L SSA, (B) 1.25 mmol/L SSA + 6.0 mmol/L 18-crown-6; Flow rate: 1.2 mL/min; Column oven: 35°C; Sample size: 20 μL; Peaks: 1, SO_4^{2-}; 2, Cl^-; 3, NO_3^-; 4, Na^+; 5, NH_4^+; 6, K^+; 7, Mg^{2+}; 8, Ca^{2+}.

Combining the strong eluting ability of SSA for both mono- and divalent cations with the special eluting selectivity of PDCA for Ca^{2+}, more potential simultaneous separation of anions and cations was achieved. As shown in Fig. 3, the resolution between cations, especially Ca^{2+} and Mg^{2+}, was improved when the mixture of 0.75 mmol/L SSA and 0.6 mmol/L PDCA and 6.0 mmol/L 18-crown-

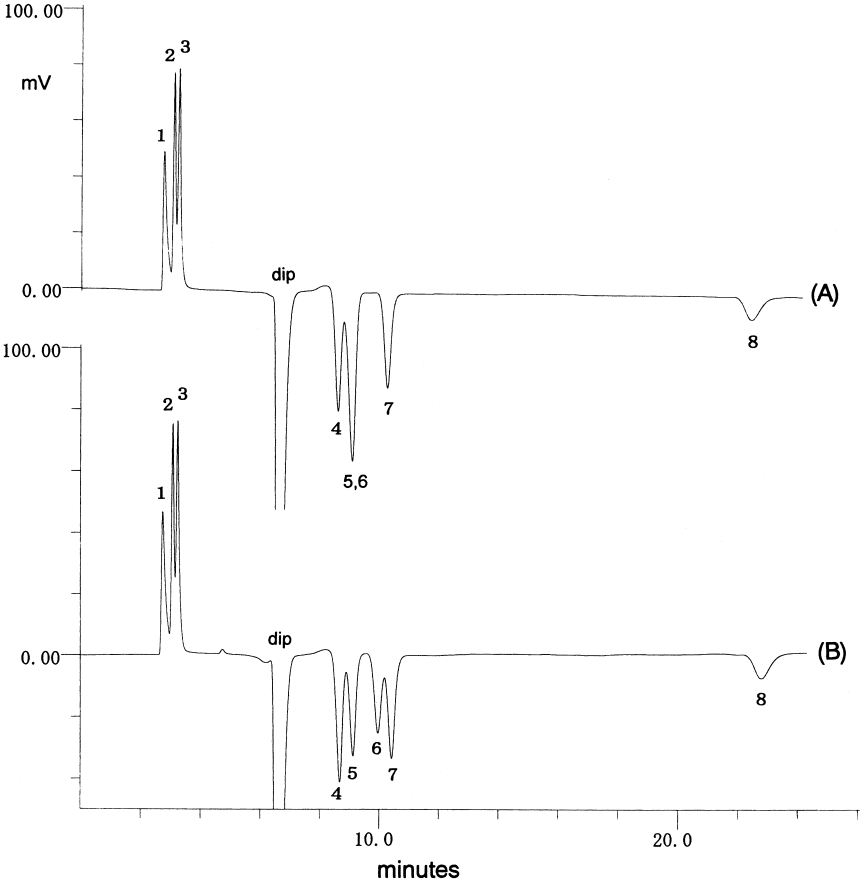

Figure 2. Simultaneous separation of anions and cations using PDCA as eluent. Eluent: (A) 1.5 mmol/L PDCA, (B) 1.5 mmol/L PDCA + 3.0 mmol/L 18-crown-6. Other conditions were same as in Fig. 1. Peaks: 1, SO_4^{2-}; 2, Cl^-; 3, NO_3^-; 4, Na^+; 5, NH_4^+; 6, K^+; 7, Ca^{2+}; 8, Mg^{2+}.

6 was used as eluent. There were two dip peaks (dip1 caused from SSA and dip2 from PDCA) on the chromatogram, but they did not influence the separation of anions and cations.

Effect of Eluent Concentration

The effect of SSA concentration in the mobile phase containing 0.6 mmol/L PDCA and 6.0 mmol/L 18-crown-6 on the retention times of anions and

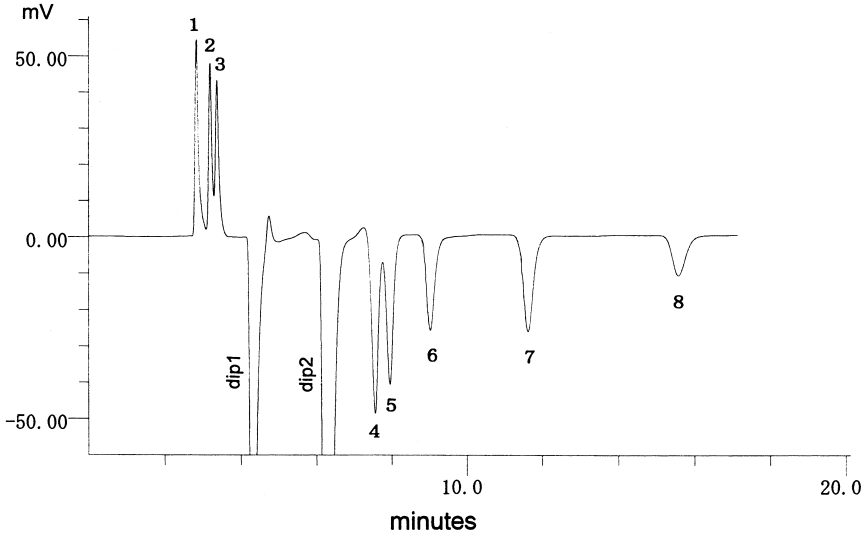

Figure 3. Simultaneous separation of anions and cations using a mixture of 0.75 mmol/L SSA, 0.6 mmol/L PDCA and 6.0 mmol/L 18-crown-6 as eluent. Other conditions were same as in Fig. 1. Peaks: 1, SO_4^{2-}; 2, Cl^-; 3, NO_3^-; 4, Na^+; 5, NH_4^+; 6, K^+; 7, Ca^{2+}; 8, Mg^{2+}.

cations was shown in Fig. 4. Only a little increase in the retention times was observed for three inorganic anions, while an obvious decrease in retention times was observed for cations, especially divalent cations, as SSA concentration increased. For this reason, the simultaneous separation of mono- and divalent cations could be achieved within a shorter time using SSA as eluent, rather than other carboxylic acid eluents. The retention times of the dip peaks of both SSA and PDCA were obviously increased when SSA concentration was increased, and the peaks of Na^+ and NH_4^+ were overlapped with the peak of PDCA when the concentration of SSA was over 1.0 mmol/L. Therefore, 0.75 mmol/L SSA was added to the mobile phase in this work.

The effect of PDCA concentration in the mobile phase containing 0.75 mmol/L SSA and 6.0 mmol/L 18-crown-6 on the retention times of anions and cations was shown in Fig. 5. Only a little increase in the retention times of three inorganic anions was observed, but better resolution for the three anions was obtained as PDCA concentration was increased. An obvious decrease in the retention times for two divalent cations, especially Ca^{2+}, was observed compared with three monovalent cations as PDCA concentration increased. The retention time of the dip pea (dip1) caused from SSA eluent was relatively unchanged, while the dip peak (dip2) from PDCA eluent was obviously

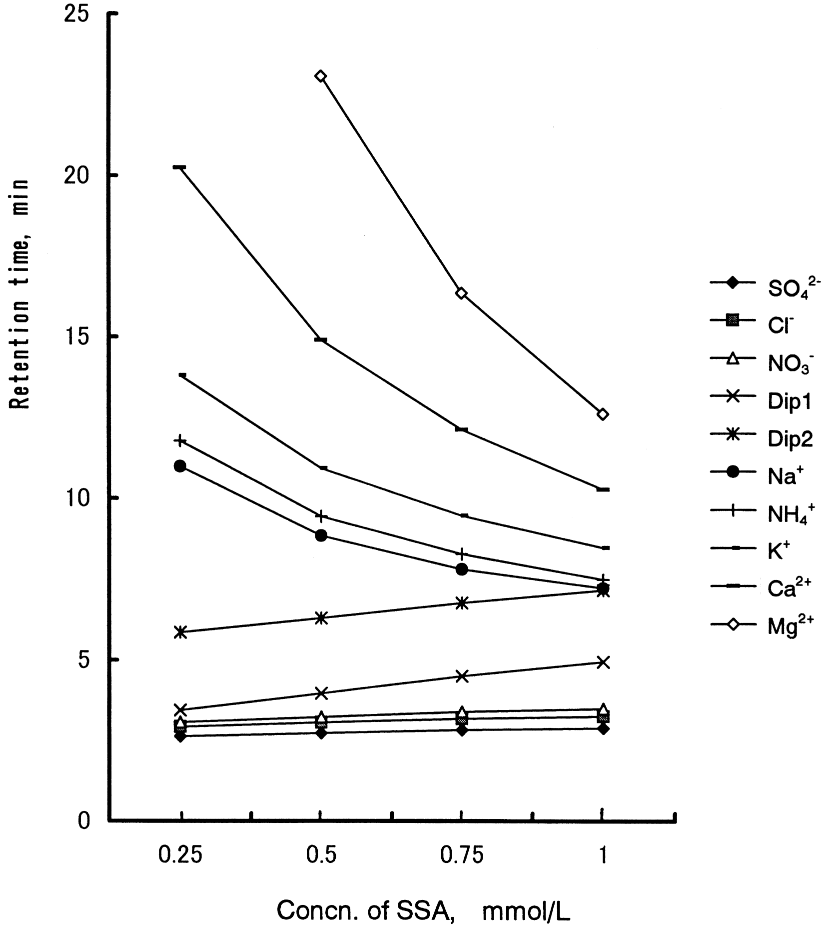

Figure 4. Effect of SSA concentration in mobile phase containing 0.6 mmol/L PDCA and 6.0 mmol/L 18-crown-6 on the retention of anions and cations.

increased when the PDCA concentration was increased, and the peaks of Na^+ and NH_4^+ were overlapped with the dip peak of PDCA when the concentration of PDCA was over 0.8 mmol/L. In this work, 0.6 mmol/L PDCA was added to the mobile phase.

On the weakly acidic cation exchange resin, a satisfactory separation for Na^+, NH_4^+, and K^+, especially for NH_4^+ and K^+, was difficult if only carboxylic acid was used as eluent. Crown ethers were well known to form stable com-

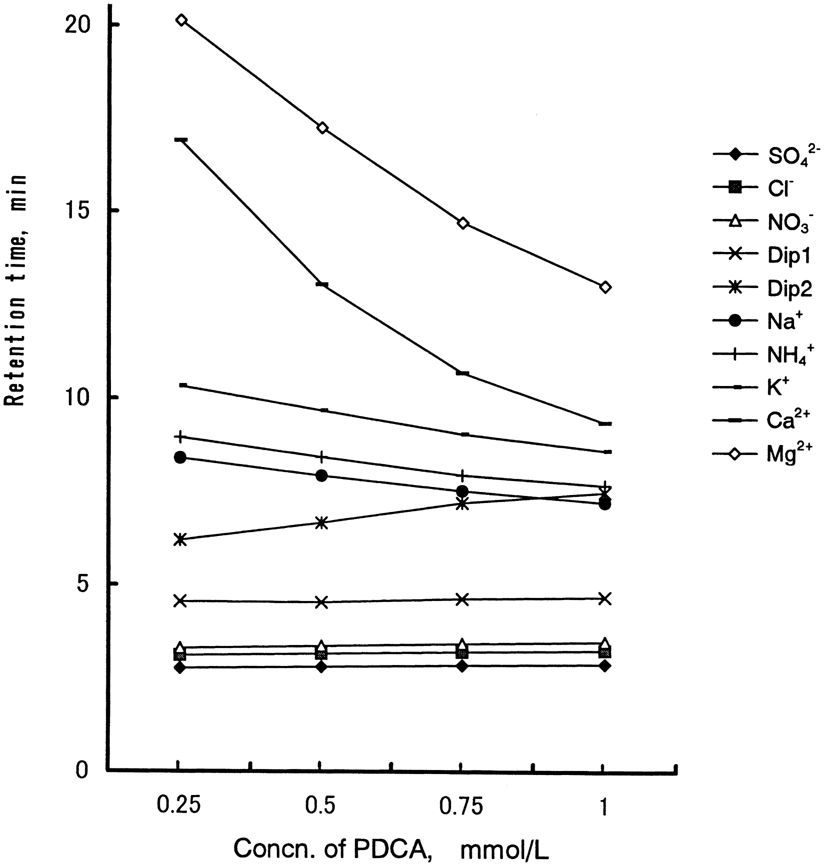

Figure 5. Effect of PDCA concentration in mobile phase containing 0.75 mmol/L SSA and 6.0 mmol/L 18-crown-6 on the retention of anions and cations.

plexes with cations, especially monovalent cations. On the basis of these stabilities, 18-crown-6 was added to acidic eluents to improve the separation of monovalent cations. The effect of concentration of 18-crown-6 in the mobile phase containing 0.75 mmol/L SSA and 0.6 mmol/L PDCA on the retention times of anions and cations was shown in Fig. 6. The retention time of K^+ was obviously increased, while those of other cations and inorganic anions and dip peaks were almost same.

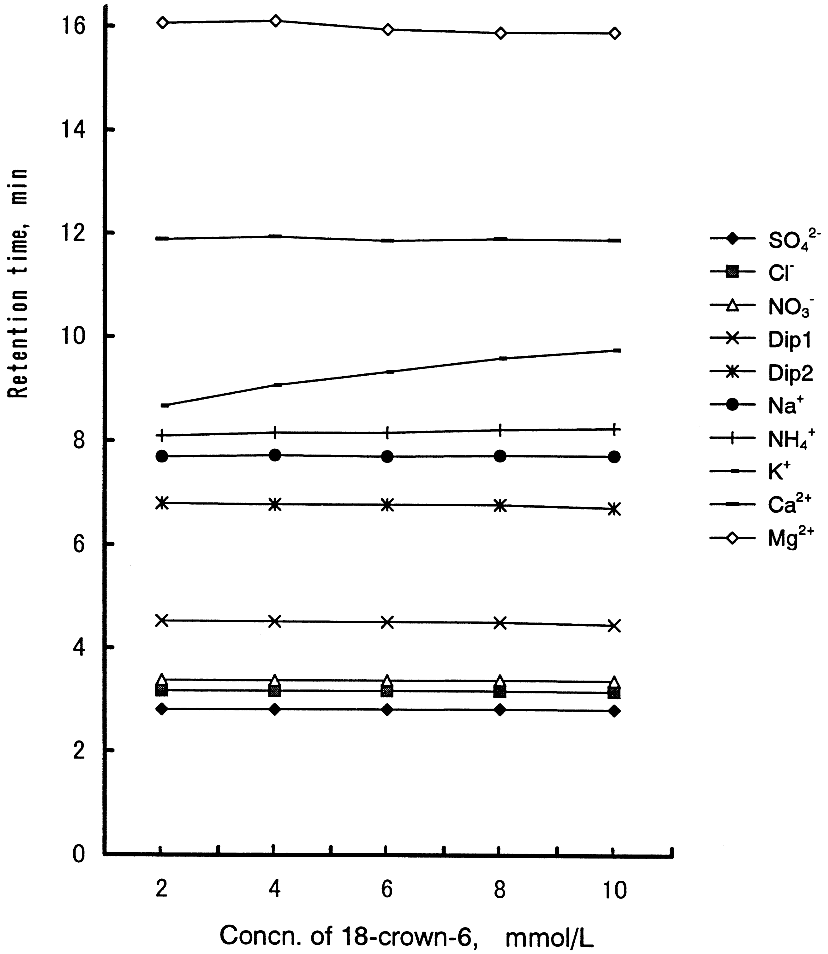

Figure 6. Effect of 18-crown-6 concentration in mobile phase containing 0.75 mmol/L SSA and 0.6 mmol/L PDCA on the retention of anions and cations.

Analytical Performance Parameters

The calibration curves of all anions and cations were obtained by plotting the peak areas against the concentrations of these ions. The detection limits of all anions and cations were determined at a signal-to-noise ratio of three. The linear range of peak area calibration curves and the detection limits of all anions and cations were listed in Table 1. The linear range of calibration curves were up to

Table 1. Linear Range of Peak Area Calibration Curves and the Detection Limits

Ions	Linear Range (μ mol/L)	Detection Limits (μ mol/L)
SO_4^{2-}	2~250	0.3
Cl^-	2~500	1.0
NO_3^-	2~500	1.2
Na^+	2~250	0.2
NH_4^+	2~250	0.9
Ca^{2+}	5~250	1.3
K^+	2~250	0.8
Mg^{2+}	5~125	1.6

two orders of magnitude and the detection limits calculated at S/N=3 ranges from 0.2 to 1.6 μmol/L for anions and cations.

Application to the Environmental Samples

The IEC/CEC method developed in this work was applied to the simultaneous determination of major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in rain water (Rain 1999 and Rain 2000), tap water, and snow samples. As examples, the chromatograms of rainwater (Rain2000), tap water, and snow water were shown in Fig. 7, and the determination results of these samples were shown in Table 2. Obvious difference in the contents for all ion species was detected, especially SO_4^{2-} and NH_4^+ was observed in the rainwater samples at different times. This can be explained by the effect of temporal atmosphere, environment, and weather. The content of sodium chloride (Na^+ and Cl^-) in snow was very high. It could be considered that sodium chloride was carried to the center of Japan together with snow from the sea.

CONCLUSION

In ion exclusion chromatography/cation exchange chromatography (IEC/CEC) using single weakly acidic cation exchange resin, anions were retained by ion exclusion mechanism, while cations by cation exchange mechanism. The IEC/CEC method is very useful for the simultaneous separation of inorganic anions and cations in environmental samples. In this study, a mixture of 0.6 mmol/L 2,6-pyridinedicarboxylic acid (PDCA), 0.75 mmol/L sulfosalicylic acid (SSA), and 6.0 mmol/L 18-crown-6 was employed as eluent. More potential simultaneous separation of anions and cations was achieved, because

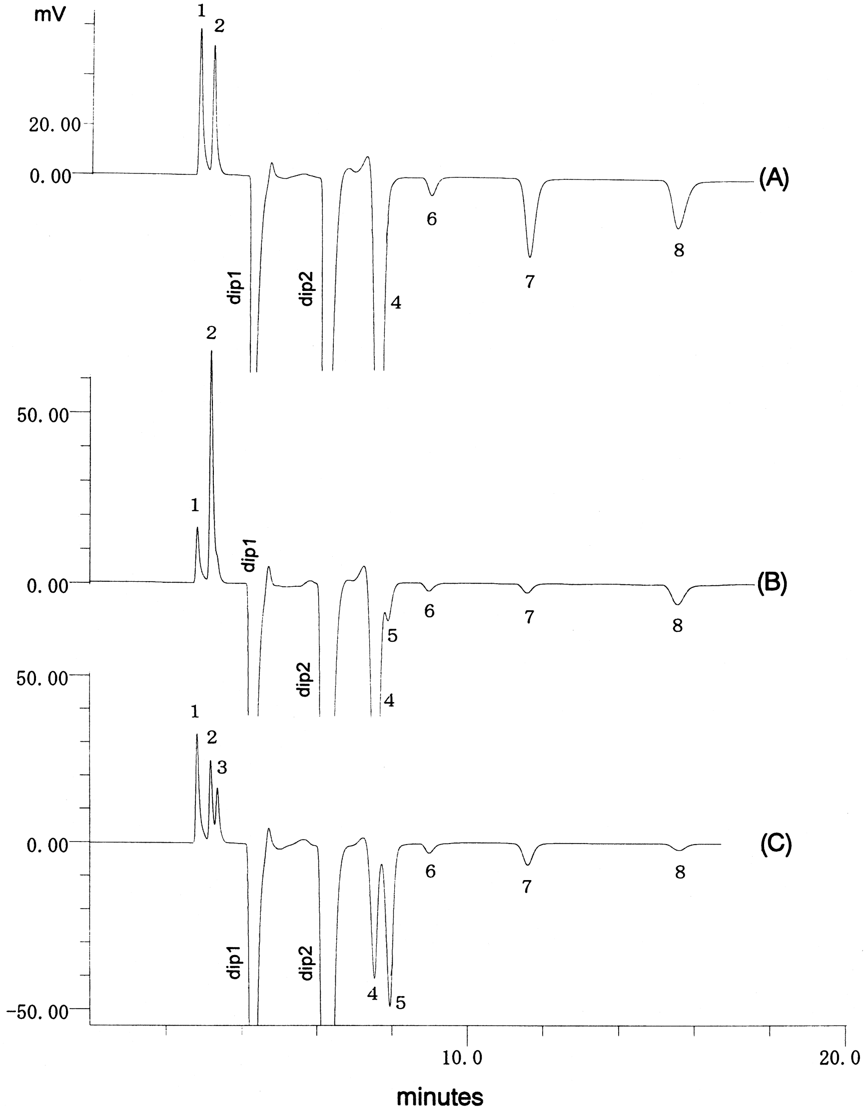

Figure 7. Chromatograms of (A) tap water with 5-folds dilution and (B) snow and (C) rain water (Rain 2000). Conditions and peak numbers were same as in Fig. 3.

Table 2. Determination Results (μ mol/L) of Anions and Cations in Environmental Water Samples (n=5)

	Rain 1999		Rain 2000		Tap Water		Snow Water	
Ions	Mean	RSD/%	Mean	RSD/%	Mean	RSD/%	Mean	RSD/%
SO_4^{2-}	12.40	3.35	28.08	2.24	51.85	1.52	14.03	2.67
Cl^-	33.75	2.51	46.07	1.87	105.9	1.39	154.6	1.83
NO_3^-	30.78	2.89	33.95	1.61	N.D.*		N.D.*	
Na^+	23.61	3.16	31.49	1.07	209.3	1.60	110.6	0.68
NH_4^+	7.74	3.31	56.92	1.26	N.D.*		10.45	2.81
K^+	2.79	3.30	5.02	2.71	10.86	4.28	4.47	4.35
Ca^{2+}	14.57	2.15	8.25	3.30	53.60	1.58	3.16	3.78
Mg^{2+}	5.06	3.32	7.00	2.76	39.23	1.01	12.02	4.22

*Not determined.

the eluent used in this work has combined the strong eluting ability of SSA for both mono- and divalent cations with the special eluting selectivity of PDCA for Ca^{2+}.

REFERENCES

1. Tanaka, K.; Ohta, K.; Fritz, J.S.; Matsushita, S.; Miyanaga, A. J. Chromatogr. A **1994**, *671*, 239.
2. Tanaka, K.; Fritz, J.S. Am. Environ. Lab. **1995**, *7*, 30.
3. Tanaka, K.; Haddad, P.R. Trends Anal. Chem. **1996**, *15*, 266.
4. Tanaka, K.; Ohta, K.; Haddad, P.R.; Fritz, J.S.; Lee, K.-P.; Hasebe, K.; Ieuji, A.; Miyanaga, A. J. Chromatogr. A **1999**, *850*, 311.
5. Tanaka, K.; Ohta, K.; Haddad, P.R.; Fritz, J.S.; Miyanaga, A.; Hu, W.; Hasebe, K. J. Chromatogr. A **2000**, *884*, 167.
6. Kwon, S.M.; Lee, K.P.; Tanaka, K.; Ohta, K. J. Chromatogr. A **1999**, *884*, 79.
7. Tanaka, K.; Ohta, K.; Hu, W..; Hasebe, K.; Miyanaga, A.; Hattori, T.; Lee, K.P.; Dasgupta, P.K.; Haddad, P.R.; Fritz, J.S. Industrial Water (Japanese) **2000**, *505*, 1.
8. Ding, M.Y.; Suzuki, Y.; Koizumi, H. Bunseki Kagaku(Japanese) **1993**, *42*, 49.
9. Ding, M.Y.; Suzuki, Y.; Koizumi, H. Chromatographia **1995**, *40*, 539.

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