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Simultaneous ion-exclusion chromatography–cation-exchange chromatography with conductimetric detection of anions and cations in acid rain waters

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Abstract

A simple, selective and sensitive method was investigated for simultaneously determining anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) in acid rain and related environmental waters in central Japan. The method involves simultaneous ion-exclusion–cation-exchange chromatography with conductimetric detection on a polyacrylate weakly acidic cation-exchange resin column with a weak-acid eluent. With the weak-acid eluent (tartaric acid) both anions and cations were separated simultaneously, based on ion-exclusion and cation-exchange mechanism. Owing to the presence of H^+ ions in the tartaric acid eluent, the detector response was positive for the anions and negative for the cations. Using a 5 m*M* tartaric acid–7.5% methanol–water eluent, good simultaneous separation and detection were achieved in about 30 min. The results indicated an ionic balance of about 100% between the anions (including HCO_3^-) and the cations (including H^+).

1. Introduction

The acid rain caused by SO_2 and NO_x in air is a major environmental pollution problem, not only in Europe and North America but also in Japan. Frequent analyses of acid rain waters is essential to establish the effect of acidification of the aquatic environment caused by air pollution. Therefore, it is very important to develop effective methods for automatically monitoring acid rain and related environmental waters.

The major ionic components of acid rain are H^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} as cationic components and Cl^-, NO_3^- and SO_4^{2-} as anionic components [1]. The ionic balance between these nine ionic components is almost 100%, and their simultaneous determination is therefore very important.

There are several different ion chromatographic (IC) strategies for the simultaneous determination of anions and cations. The cations can be converted into anions by using a complexing agent such as EDTA and then all species are separated and detected as anions [2]. In another approach, a mixed-bed ion-exchange column containing both cation and anion exchangers was

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used for the simultaneous separation of mono- and divalent anions and cations using a single sample injection [3]. IC using anion- and cation-exchange columns in series, followed by UV or conductivity detection, has also been reported [4,5].

The purpose of this study was to develop a simple, selective, efficient and highly sensitive IC method for the simultaneous determination of anions and cations, and to apply simultaneous ion-exclusion–cation-exchange chromatography (CEC) with conductimetric detection to acid rain and related environmental waters. A polyacrylate-based weakly acidic cation-exchange resin column and a weak-acid eluent were used for the simultaneous separation of anions by ion exclusion and cations by cation exchange. Based on selectivity, sensitivity, stability and utility, a conductometric detector was chosen for the simultaneous detection of both anions and cations.

2. Experimental

2.1. Chromatographic system

The IC system used was a Tosoh CCPD non-suppressor ion chromatograph with a non-metallic eluent delivery pump operating at 1–1.2 ml/min. A Tosoh CM-8000 conductimetric detector was used. A Tosoh SC-8010 chromatographic data system was used for instrument control and for data collection and processing.

2.2. Eluents

Eluents consisting of water, strong acid–water, weak acid–water and methanol–water were compared for the simultaneous separation of both anions and cations. All eluents were continuously degassed with a Tosoh SD-8022 on-line degasser.

2.3. Columns

The ion-exclusion–CEC separation of both anions and cations was carried out on a Tosoh TSKgel OA-PAK weakly acidic cation-exchange resin column (H^+ form) with polyacrylate copolymer (particle size 5 μm) (300 mm × 7.8 mm I.D.). The ion-exclusion chromatographic separation of HCO_3^- with ion-exchange enhancement of conductivity detection [6] was carried out on a Tosoh TSKgel-SCX strongly acidic cation-exchange resin columns (H^+ form and Na^+ form, in series) with polystyrene–divinylbenzene copolymer (particle size 5 μm) (each 100 mm × 7.8 mm I.D.).

2.4. pH measurement

The pH values of samples were measured with a Toa Denpa IM-40S ion meter with a glass electrode.

2.5. Chemicals

All chemicals were of analytical-reagent grade. Deionized, distilled water was used for the preparation of standard solutions and eluents.

Stock standard solutions of anions and cations were prepared by dissolving appropriate amounts of acids, alkalis and alkaline earth metal salts in water.

2.6. Sample pretreatment

Samples were collected in or near the city of Nagoya, which is located in central Japan. For the forest soil extraction water samples, the samples were subjected to IC analysis after extraction by ultrasonication with acid rain water for 15 min. The soil, which is a typical brown forest soil in Japan, was collected in Kumamoto, located in western Japan. All samples were subjected to IC analysis after filtration with a 0.45-μm membrane filter.

3. Results and discussion

3.1. Selection of eluent

The cation-exchange resin column used is commercially available under trade-name

TSKgel OA-PAK. The column is packed with a weakly acidic cation-exchange resin and is usually used for the ion-exclusion chromatographic separation of weakly ionized organic acids by using strong-acid (sulphuric acid) or weak-acid (phosphoric acid) eluents. The effectiveness of weak-acid eluents such as succinic and benzoic acid with $pK \approx 4$ in the ion-exclusion chromatography of various organic weak acids on a strongly acidic cation-exchange resin has been reported by Tanaka and Fritz [7].

On the other hand, it is well known that such weakly acidic cation-exchange resins are capable of separating rapidly and efficiently mono- and divalent cations under isocratic conditions by elution with a strong-acid eluent. Accordingly, it was expected that such acidic eluents would be applicable as the common eluent for the simultaneous separation of anions and cations by ion exclusion and cation exchange. In order to accomplish the simultaneous separation of anions by the ion-exclusion mechanism and cations by the cation-exchange mechanism, several kinds of eluents with different acidity were tested.

Fig. 1 shows the separation of strong acid anions (Cl^-, NO_3^-, SO_4^{2-}), weak-acid anions (PO_4^{3-}, $HCOO^-$, CH_3COO^-, HCO_3^-) and mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) by elution with water, a strong acid and weak acids.

When water was used as the eluent, it was possible to separate the weak acid anions alone, except for PO_4^{3-}, from the strong acids by ion exclusion, as shown in Fig. 1A. The separation of the cations is impossible because all of them are fixed on the resin. When a strong acid (sulphuric acid) was used as the eluent, it was possible to separate the cations alone by cation exchange, as shown in Fig. 1B. The separation of the anions is impossible because all of the anions are incompletely ion excluded from the resin. When weak acids (tartaric and citric acid and EDTA) with $pK_1 \approx 2$–3 were used as the eluent, it was possible to separate simultaneously the anions and cations by ion exclusion and cation exchange, respectively, as shown in Fig. 1C–E.

As can be seen from Fig. 1C–E, although all of anions except HCO_3^- were detected conductimetrically, the detector responses were much lower with weak-acid anions such as $HCOO^-$ and CH_3COO^- than with strong-acid anions such as SO_4^{2-}, Cl^-, and NO_3^-. HCO_3^-, which is a very weakly acidic anion, was not detected. This means that the ionization of the weak-acid anions is suppressed, depending on the acidity and concentration of the acidic eluent.

The detector response was positive for the anions and negative for the cations. The detector response for the cations is negative because this method is based on indirect conductimetric detection.

Considering the resolution of both anions and cations, separation time, detection sensitivity, and eluent background conductivity, it was concluded that the best choice for the eluent is tartaric acid.

3.2. *Effect of tartaric acid concentration*

In order to optimize the simultaneous separation and detection of cations and anions, the effect of tartaric acid concentration in the eluent on the retention volumes (V_R) of the anions and cations was investigated.

In the ion-exclusion chromatographic separation of the anions, the V_R values of the anions increased with increasing concentration of tartaric acid in the eluent. The peak resolution also increased, as shown in Fig. 2A. In the CEC separation of the cations, the V_R values of the cations decreased drastically on increasing the concentration of tartaric acid in the eluent. The peak resolution was also increased, as shown in Fig. 2B.

The eluent background conductivity increased on increasing the tartaric acid concentration in the eluent (694 $\mu S\ cm^{-1}$ at 6 m*M*). Because an increase in the eluent conductivity caused a decrease in the sensitivity of conductivity detection, it was concluded that a much lower eluent concentration of tartaric acid should be used to obtain a reasonable peak resolution and separation speed. From the above results, it was concluded that the optimum concentration of tartaric acid for the simultaneous ion-exclusion–CEC separation of the cations and anions is *ca.* 3–5 m*M*.

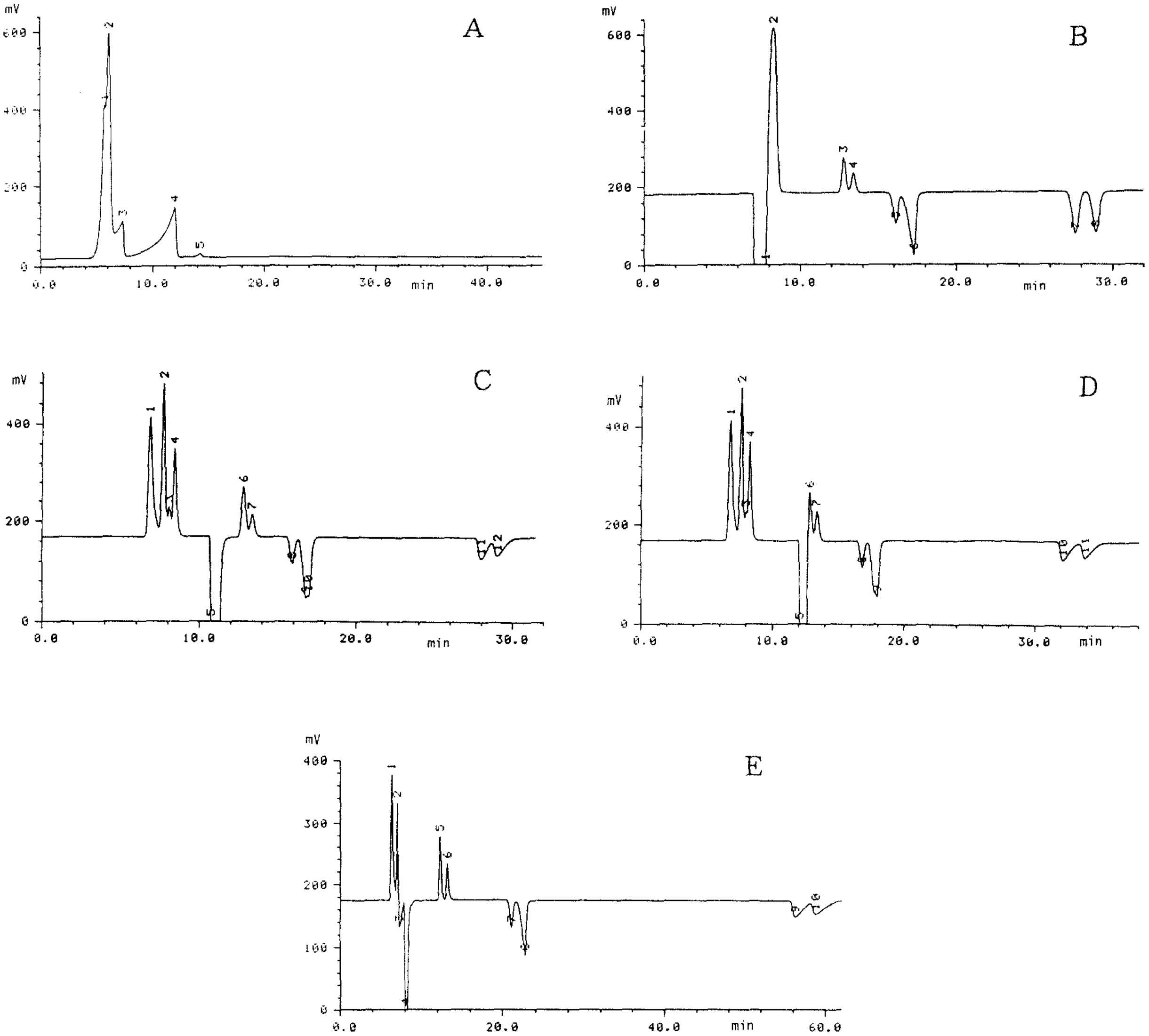

Fig. 1. Typical simultaneous ion-exclusion–CEC of anions and cations obtained by elution with (A) water, (B) strong acid and (C–E) weak acids. Column, Tosoh TSKgel OA-PAK polyacrylate-based weakly acidic cation-exchange resin; column temperature, room temperature (26°C); detector sensitivity, 1000 mV = 100 μS cm^{-1}; eluent flow-rate, 1 ml/min; injection volume, 0.1 ml; sample, mixture of 0.1 m*M* HNO_3, KCl, NH_4NO_3, $(NH_4)_2SO_4$, $NaHCO_3$, $CaCl_2$, $MgCl_2$, KH_2PO_4, 1 m*M* HCOOH and 5 m*M* CH_3COOH. Eluents (conductivity): (A) water (0 μS cm^{-1}); (B) 1 m*M* sulphuric acid (693 μS cm^{-1}); (C) 6 m*M* tartaric acid (694 μS cm^{-1}); (D) 6 m*M* citric acid (636 μS cm^{-1}); (E) 1 m*M* EDTA (409 μS cm^{-1}). Peaks: (A) 1 = SO_4^{2-}; 2 = Cl^-; NO_3^-; PO_4^{3-}; 3 = $HCOO^-$; 4 = CH_3COO^-; 5 = HCO_3^-; (B) 1 = eluent dip; 2 = SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-}; 3 = $HCOO^-$; 4 = CH_3COO^-; 5 = Na^+; 6 = NH_4^+, K^+; 7 = Mg^{2+}; 8 = Ca^{2+}; (C) 1 = SO_4^{2-}; 2 = Cl^-; 3 = PO_4^{3-}; 4 = NO_3^-; 5 = eluent dip; 6 = $HCOO^-$; 7 = CH_3COO^-; 8 = Na^+; 9 = NH_4^+; 10 = K^+; 11 = Mg^{2+}; 12 = Ca^{2+}; (D) 1 = SO_4^{2-}; 2 = Cl^-; 3 = PO_4^{3-}; 4 = NO_3^-; 5 = eluent dip; 6 = $HCOO^-$; 7 = CH_3COO^-; 8 = Na^+; 9 = NH_4^+, K^+; 10 = Mg^{2+}; 11 = Ca^{2+}; (E) 1 = SO_4^{2-}; 2 = Cl^-; 3 = PO_4^{3-}, NO_3^-; 4 = eluent dip; 5 = $HCOO^-$; 6 = CH_3COO^-; 7 = Na^+; 8 = NH_4^+, K^+; 9 = Mg^{2+}; 10 = Ca^{2+}.

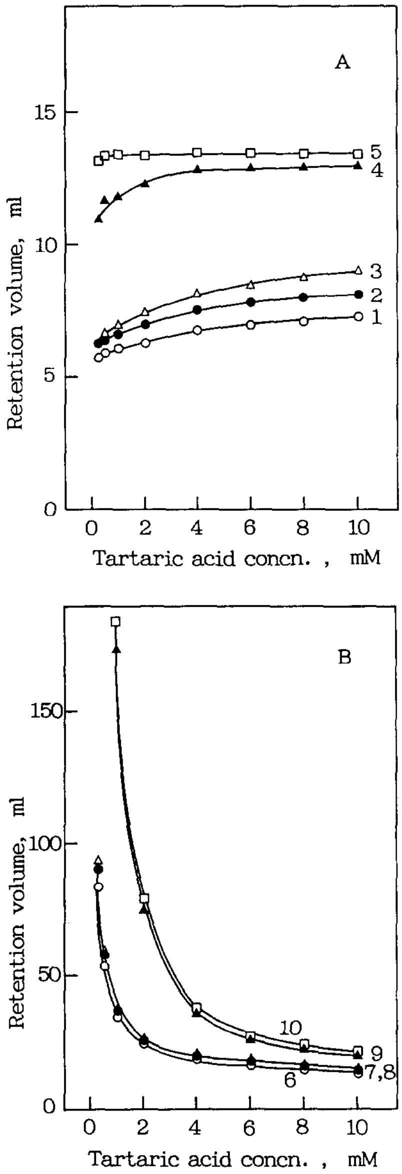

Fig. 2. Effect of tartaric acid concentration in the eluent on retention volumes (V_R) of (A) anions and (B) cations. Lines: 1 = SO_4^{2-}; 2 = Cl^-; 3 = NO_3^-; 4 = $HCOO^-$; 5 = CH_3COO^-; 6 = Na^+; 7 = NH_4^+; 8 = K^+; 9 = Mg^{2+}; 10 = Ca^{2+}. Chromatographic conditions as in Fig. 1.

3.3. Effect of methanol concentration

In order to accomplish a reasonable resolution of both anions and cations, the effect of methanol concentration in 4 m*M* tartaric acid eluent on the V_R values of the anions and cations was investigated.

The V_R values of the anions were almost unchanged, except that of acetate ion, as shown in Fig. 3A. Those of the cations increased gradually for monovalent cations and decreased gradually for divalent cations, as shown in Fig. 3B. From these results, the best concentration of

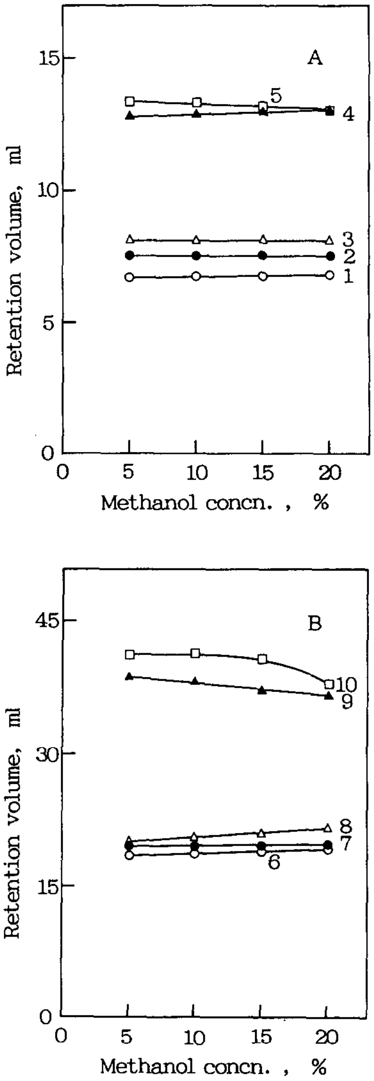

Fig. 3. Effect of methanol concentration in 4 m*M* tartaric acid eluent on retention volumes (V_R) of (A) anions and (B) cations. Lines: 1 = SO_4^{2-}; 2 = Cl^-; 3 = NO_3^-; 4 = $HCOO^-$; 5 = CH_3COO^-; 6 = Na^+; 7 = NH_4^+; 8 = K^+; 9 = Mg^{2+}; 10 = Ca^{2+}. Chromatographic conditions as in Fig. 1.

methanol in the eluent was concluded to be *ca.* 7.5%.

Although the simultaneous separation of the anions and cations was accomplished by ion-exclusion–CEC with elution with 3 m*M* tartaric acid–7.5% methanol–water (Fig. 4A), the separation time was long. Therefore, the tartaric acid concentration in the eluent was increased from 3 to 5 m*M* and the flow-rate was increased from 1.0 to 1.2 ml/min. Fig. 4B shows the ion-exclusion–CEC of the anions and cations with elution with 5 m*M* tartaric acid–7.5% methanol–water. A high-resolution chromatogram was obtained under these elution conditions.

As the conductimetric detector response was positive for anions and negative for cations, the polarity of the signal from the detector was changed automatically from negative to positive, in order to measure easily the CEC peak areas of the cations, after the ion-exclusion chromatographic separation of the anions.

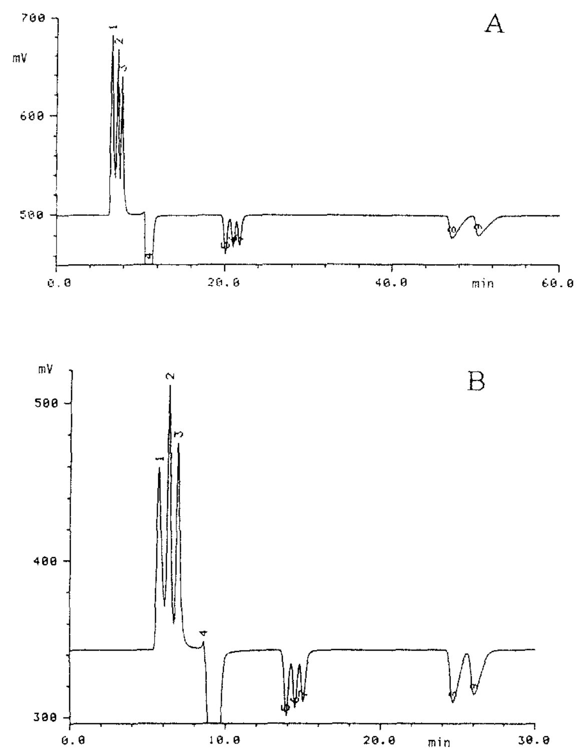

Fig. 4. Simultaneous ion-exclusion–CEC separation of anions and cations by elution with (A) 3 m*M* tartaric acid–7.5% methanol–water at 1 ml/min and (B) 5 m*M* tartaric acid–7.5% methanol–water at 1.2 ml/min. Eluent conductivity: (A) = 389 μS cm^{-1}; (B) = 536 μS cm^{-1}. Peaks: 1 = SO_4^{2-}; 2 = Cl^-; 3 = NO_3^-; 4 = eluent dip; 5 = Na^+; 6 = NH_4^+; 7 = K^+; 8 = Mg^{2+}; 9 = Ca^{2+}. Other chromatographic conditions as in Fig. 1.

3.4. Retention volumes of common anions and cations

Table 1 gives the V_R values of common anions and cations obtained by elution with 3 m*M* tartaric acid–7.5% methanol–water.

For the retention of monovalent weak-acid anions such as NO_2^-, F^-, $HCOO^-$ and CH_3COO^-, the V_R values depended on their pK_1 ($NO_2^- < F^- < HCOO^- < CH_3COO^-$). The V_R of PO_4^{3-}, which is a weak-acid anion (pK_1 = 2.1), was smaller than that of NO_3^- (strong-acid anion), because the charge of PO_4^{3-} is −2 (HPO_4^{2-}) and that of NO_3^- is −1 in the acidic eluent.

For the retention of mono- and divalent strong-acid anions such as SO_4^{2-}, $S_2O_3^{2-}$ and Cl^-, the V_R values depended on their charge ($Cl^- < SO_4^{2-} = S_2O_3^{2-}$) rather than their p$K_1$ values (complete dissociation).

For the retention of monovalent strong-acid halide anions such as Cl^-, Br^- and I^-, which are ionized completely, the V_R values appear to be

Table 1
Retention volumes of common anions and cations on elution with 3 m*M* tartaric acid–7.5% methanol–water

Ion[a]	V_R (ml)	Ion	V_R (ml)
SO_4^{2-} (S)	6.77	Li^+	20.76
$S_2O_3^{2-}$ (S)	6.80	Na^+	21.12
Cl^- (S)	7.43	NH_4^+	22.07
PO_4^{3-} (W)	7.62	K^+	22.43
Br^- (S)	7.75	Rb^+	22.23
NO_3^- (S)	7.98	Cs^+	22.37
I^- (W)	9.12	Mg^{2+}	44.40
NO_2^- (W)	11.02	Ca^{2+}	47.47
F^- (W)	11.26	Sr^{2+}	48.20
$HCOO^-$ (W)	12.67	Ba^{2+}	67.80
CH_3COO^- (W)	13.26		

[a] S = Strong-acid anion; W = weak-acid anion.

dependent on their ionic radii rather than their pK_1 values (complete dissociation). Although the reason is not clear, another effect such as the hydrophobic adsorption effect based on the difference in their ionic radii might be predominant in this separation. The hydrophobic adsorption effect is well known as a side-effect in the separation of common inorganic anions by ion-exchange chromatography with a polymeric resin.

Therefore, in ion-exclusion chromatography using a weakly acidic cation-exchange resin and a weak-acid eluent, it was found that the V_R values of the anions were strongly related to their pK_1 values and the charge as the main effect in the ion-exclusion chromatography and their hydrophobicity as a side-effect. As has been reported by Tanaka *et al.* [8], the V_R values of common strong- and weak-acid anions on a strongly acidic cation-exchange resin column by elution with water are increased in proportion to the increase in their pK_1 values and the hydrophobicities.

For the CEC separation of cations by the cation-exchange mechanism, the V_R values of the cations were strongly related to their cation-exchange affinities (their ionic radii and charge). The elution order of mono- and divalent cations was almost identical with that in conventional CEC.

3.5. Calibration

Calibration graphs were obtained by plotting peak areas against the concentrations of anions and cations. Linear calibration graphs were obtained in at least the concentration ranges 0–0.8 mM for the anions and 0–0.4 mM for the cations.

3.6. Detection limits

The detection limits of the anions and cations at a signal-to-noise ratio of 3 are given in Table 2. Although the eluent background conductivity is relatively high (536 μS cm^{-1}) because of the use of tartaric acid as the eluent, these values were reasonable for application to various acid rains and related environmental waters.

Table 2

Detection limits of major anions and cations related to acid rain water determined by elution with 3 mM tartaric acid–7.5% methanol–water

Ion	Detection limit[a]	
	μM	ppb
SO_4^{2-}	0.16	15
Cl^-	0.10	3.6
NO_3^-	0.14	9
Na^+	0.20	4.6
NH_4^+	0.30	5.4
K^+	0.32	12.5
Mg^{2+}	0.28	6.8
Ca^{2+}	0.28	11.2

[a] Signal-to-noise ratio = 3.

3.7. Reproducibility

The reproducibility of the ion-exclusion–CEC chromatographic peak areas of anions and cations with elution with 3 mM tartaric acid–7.5% methanol–water was 0.02–0.2% ($n = 6$). Reproducible chromatograms were obtained during repeated chromatographic runs.

3.8. Application of ion-exclusion–CEC to acid rain waters

In order to evaluate the effect of acid rain on the aquatic environment, it is essential to demonstrate the effectiveness of the present method when applied to various environmental waters including acid rain waters and forest soil waters of different pH.

First, the ion-exclusion–CEC method was applied to the simultaneous determination of anions and cations in several rain waters of different pH. Fig. 5 shows the ion-exclusion–CEC of anions and cations in a typical acid rain water at pH 4.81 taken near Nagoya. A good simultaneous separation of the anions and the cations was obtained and it was found that this acid rain water sample contains SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}.

Table 3 gives the results for the anions and the cations, including H^+, in the above rain water

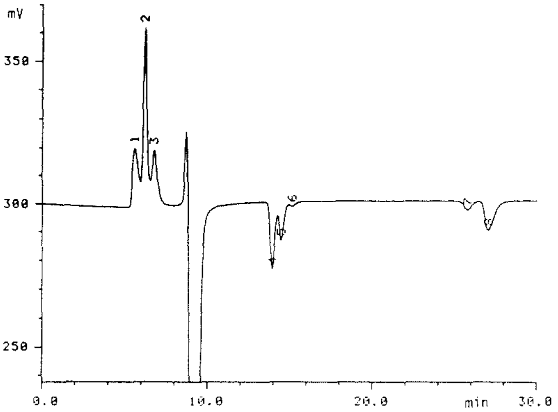

Fig. 5. Simultaneous ion-exclusion–CEC of anions and cations in rain water of pH 4.81 taken near Nagoya. Peaks: 1 = SO_4^{2-}; 2 = Cl^-; 3 = NO_3^-; 4 = Na^+; 5 = NH_4^+; 6 = K^+; 7 = Mg^{2+}; 8 = Ca^{2+}. Chromatographic conditions as in Fig. 4.

samples. The pH values of these samples were in the range 4.21–5.49. The results showed that this method is very useful for the simultaneous determination of the anions and cations in acid rain water because the ion balance (anions/cations) ranged from 0.98 to 1.07, except for the rain water sample at pH 5.49, which had an ion balance of 0.80. This might be due to the presence of HCO_3^- and the lack of detection of HCO_3^- by ion-exclusion–CEC. Therefore, the ion-exclusion chromatography of HCO_3^- with conductimetric detection using a conductivity enhancement column [6] was carried out to determine the ion balance of environmental waters of neutral pH.

3.9. Application of ion-exclusion–CEC and ion-exclusion chromatography to environmental waters related to acid rain

Figs. 6 and 7 show (A) a typical ion-exclusion–CEC of anions and cations and (B) ion-exclusion chromatogram of HCO_3^- in forest soil water (pH 7.20) and in brown forest soil extraction water (pH 4.95), sonicated with acid rain water (pH 4.72), respectively, taken in or near Nagoya.

Good ion-exclusion–CEC separation of the anions and the cations and ion-exclusion chromatographic separation of HCO_3^- were accomplished for the forest soil water of neutral pH. The results obtained showed that this environmental water contains SO_4^{2-}, NO_3^-, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, in addition to HCO_3^-, as shown in Fig. 6A and B.

On the other hand, ion-exclusion–CEC of the brown forest soil extraction water showed the presence of the cations and anions and ion-exclusion chromatography showed the presence of unidentified weak acids and no HCO_3^-, as shown in Fig. 7A and B. This unidentified peak might be due to organic weak acids because the sample was taken from the surface layer of the forest brown soil containing humic substances from biodegraded plants and bacteria. The peak identification of this organic weak acid will be the subject of future research.

Table 4 gives the results for anions including HCO_3^- and cations including H^+, together with the ion balance (anions/cations), for various acid rains and related environmental waters obtained

Table 3
Determination of major anions and cations in rain waters by ion-exclusion–CEC

Rain water	Concentration (mequiv./l)									Ion balance (anions/cations)
	SO_4^{2-}	Cl^-	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	H^+ (pH)	
A	0.051	0.034	0.035	0.018	0.054	0.005	0.004	0.018	4.34	1.03
B	0.035	0.015	0.034	0.005	0.044	0.002	0.001	0.002	4.21	1.00
C	0.007	0.008	0.007	0.005	0.009	0.0005	0.0005	0.0005	4.87	0.98
D	0.016	0.006	0.010	0.001	0.024	0.001	ND[a]	0.001	4.80	1.07
E	0.006	0.016	0.003	0.016	0.005	0.001	0.003	0.003	5.49	0.80

[a] Not detected.

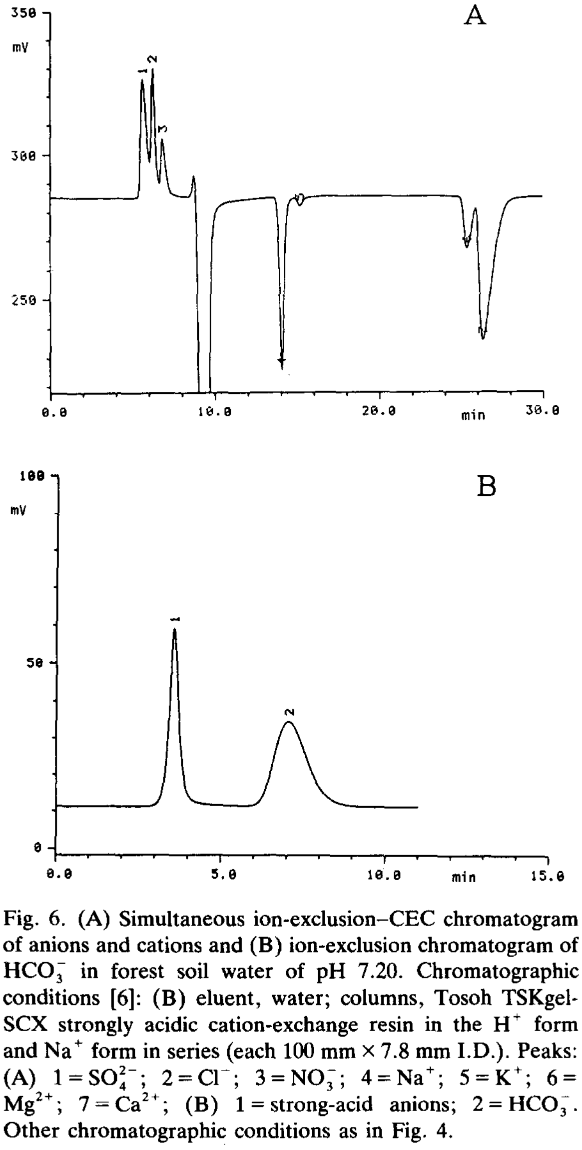

Fig. 6. (A) Simultaneous ion-exclusion–CEC chromatogram of anions and cations and (B) ion-exclusion chromatogram of HCO_3^- in forest soil water of pH 7.20. Chromatographic conditions [6]: (B) eluent, water; columns, Tosoh TSKgel-SCX strongly acidic cation-exchange resin in the H^+ form and Na^+ form in series (each 100 mm × 7.8 mm I.D.). Peaks: (A) $1 = SO_4^{2-}$; $2 = Cl^-$; $3 = NO_3^-$; $4 = Na^+$; $5 = K^+$; $6 = Mg^{2+}$; $7 = Ca^{2+}$; (B) 1 = strong-acid anions; $2 = HCO_3^-$. Other chromatographic conditions as in Fig. 4.

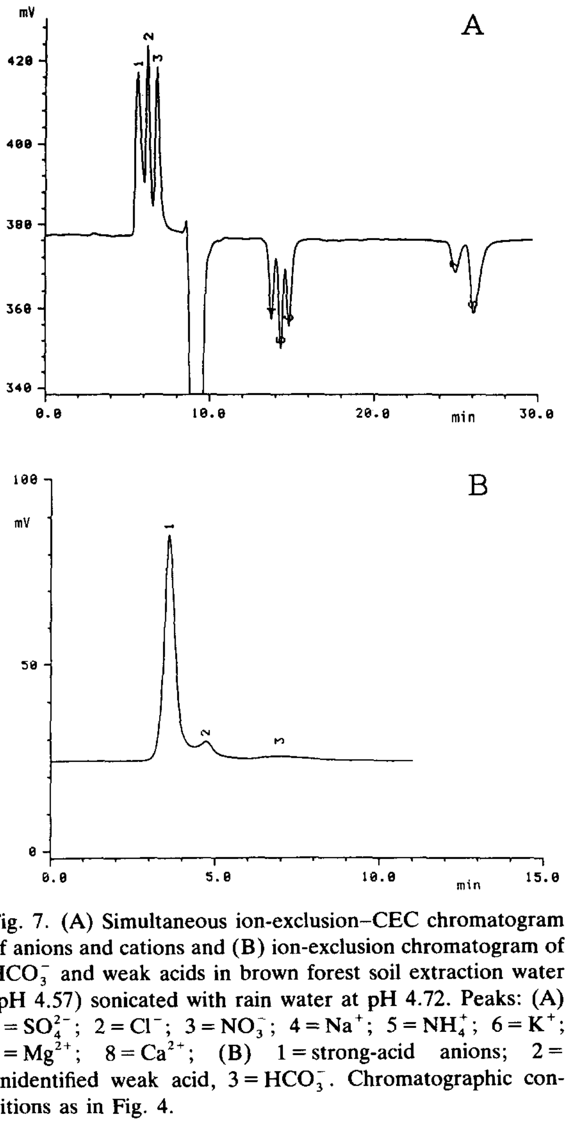

Fig. 7. (A) Simultaneous ion-exclusion–CEC chromatogram of anions and cations and (B) ion-exclusion chromatogram of HCO_3^- and weak acids in brown forest soil extraction water (pH 4.57) sonicated with rain water at pH 4.72. Peaks: (A) $1 = SO_4^{2-}$; $2 = Cl^-$; $3 = NO_3^-$; $4 = Na^+$; $5 = NH_4^+$; $6 = K^+$; $7 = Mg^{2+}$; $8 = Ca^{2+}$; (B) 1 = strong-acid anions; 2 = unidentified weak acid, $3 = HCO_3^-$. Chromatographic conditions as in Fig. 4.

by ion-exclusion–CEC and ion-exclusion chromatography. The results show that the ion balances for all the environmental water samples except the forest soil extraction water samples are reasonable. For the forest soil extraction water, despite the absence of HCO_3^-, the ion balance was below 1.0 (0.65 and 0.85). This might be due to the presence of other organic weak acids in the forest soil.

4. Conclusions

A method for the simultaneous determination of anions and cations, based on the simultaneous separation of the anions and cations by both ion-exclusion and cation-exchange mechanisms, with conductimetric detection has been developed. The separation and detection are selective for the anions and cations. The method was

Table 4
Determination of major anions and cations in acid rain and related environmental waters by ion-exclusion–CEC and ion-exclusion chromatography

Sample	Concentration (mequiv./l)										Ion balance (anions/cations)
	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	H^+ (pH)	
Rain water (A)	ND[a]	0.061	0.077	0.039	0.057	0.037	0.002	0.013	0.065	4.81	0.94
Rain water (B)	ND	0.042	0.014	0.036	0.005	0.037	ND	0.002	0.012	4.45	1.01
Forest soil water (A)	0.490	0.120	0.057	0.038	0.170	ND	0.015	0.087	0.459	7.20	0.98
Forest soil water (B)	0.270	0.160	0.100	0.020	0.190	ND	0.027	0.170	0.210	6.97	0.92
Forest soil extraction water (A)[b]	ND	0.110	0.058	0.071	0.061	0.080	0.070	0.038	0.110	4.95	0.65
Forest soil extraction water (B)[b]	ND	0.080	0.045	0.053	0.030	0.046	0.019	0.022	0.062	4.57	0.86
Snow water	ND	0.013	0.029	0.008	0.024	0.003	0.001	0.004	0.013	5.09	0.94
River water (A)	0.350	0.240	0.170	0.036	0.350	ND	0.026	0.072	0.390	7.03	0.95
River water (B)	0.960	0.930	0.540	0.150	1.500	ND	0.130	0.150	0.680	7.19	1.05
Lake water (A)	0.170	0.290	0.190	0.019	0.180	ND	0.040	0.130	0.370	6.78	0.93
Lake water (B)	0.550	0.290	0.180	0.063	0.220	ND	0.065	0.10	0.660	6.97	1.04

[a] ND = Not detected.
[b] Sonicated with acid rain water at pH 4.72.

successfully applied to the simultaneous determination of anions and cations in several acid rains and related environmental waters, which is very important for evaluating the effect of acid rain on the aquatic environment.

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