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High-performance ion-exclusion/cation-exchange chromatography of anions and cations in acid rain waters on a weakly acidic cation-exchange resin

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Abstract

A new method for the simultaneous determination of anions (sulfate, nitrate, and chloride) and cations (sodium, ammonium, potassium, magnesium, and calcium) in acid rain waters was investigated using high-performance ion-exclusion/cation-exchange chromatography with conductimetric detection on a separation column packed with a polymethacrylate-based weakly acidic cation-exchange resin in the hydrogen-form and an eluent comprising 1.5 mM sulfosalicylic acid–6 mM 18-crown-6 at pH 2.6, operated at 1.5 ml/min. Effective separation and highly sensitive conductimetric detection for the anions and the cations was achieved in about 14 min. Since the ionic balance (equivalents of anions/equivalents of cations) of acid rain waters of different pH (4.40–4.67) ranged from 0.97 to 0.94, evaluation of the water quality of acid rain was possible. This method was successfully applied to the simultaneous determination of the anions and the cations in acid rain transported from mainland China and North Korea to central Japan monitored by a meteorological satellite data analyzer. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acid rain is a widespread environmental pollution problem, occurring not only in Europe and North America, but also in East Asia including Japan. In order to evaluate and estimate the effects of acidifi-

cation of the aquatic environment caused by acid rain, it is important to develop a suitable approach for monitoring acid rain waters. The major ionic components of acid rain consist of H^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} as the cationic components and Cl^- , NO_3^- , and SO_4^{2-} as the anionic components [1]. The ion balance between these nine components is almost unity. Therefore, the simultaneous determination of these ionic components is necessary for the complete analysis of acid rain waters.

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In previous papers [2–8], we have reported that simultaneous ion-exclusion/cation-exchange chromatography can be performed on a weakly acidic cation-exchange resin column using a single sample injection, resulting in the simultaneous determination of anions and cations commonly found in acid rain. In these studies, a weak acid (tartaric acid) or a strong acid (sulfosalicylic acid) was used as the eluent and our previous results have suggested that the pH of the eluent is the most important factor for both the ion-exclusion chromatographic separation of anions and the cation-exchange chromatographic (CEX) separation of cations.

In the present study, a simple and selective method involving high-performance simultaneous ion-exclusion/CEX of the anions and the cations has been accomplished by elution with a mixture of sulfosalicylic acid (having hydrophobic characteristics) and a crown ether (having chelating ability for alkali metal cations such as Na^+ , NH_4^+ , and K^+). The effectiveness of this method is demonstrated by the monitoring of acid rains transported from central mainland China and North Korea to central Japan.

2. Experimental

2.1. Instrumentation

A portable-type ion chromatograph (Asahi Technion IC-2001, Tokyo, Japan) equipped with a conductivity detector and a 0.1-ml loop injector was used. The chromatographic data were collected with a Fujitsu FMV-Biblo notebook computer directly interfaced with the ion chromatograph by a RS-232C cable and then processed using Tosoh LC-8020 software.

2.2. Reagents and procedures

All reagents were of analytical-reagent grade and were purchased from Wako (Osaka, Japan). Deionized, distilled water was used for the preparation of standard solutions and eluents.

Simultaneous ion-exclusion/CEX separation of anions and cations was carried out using two separation columns (15 cm \times 7.8 mm I.D.) connected in tandem or a single separating column used alone.

These columns were packed with TSKgel OA-PAK-A polymethacrylate-based weakly acidic cation-exchange resin in the H^+ -form, 5 μm particle size, cation-exchange capacity 0.1 mequiv./ml (Tosoh, Tokyo, Japan) and operated at 30°C. Eluents comprised tartaric acid–water and sulfosalicylic acid–crown ether–water at the concentrations specified in the figure captions. The pH values of the eluents and acid rain waters were determined using a Toa Denpa HM-14P portable ion meter fitted with a glass electrode.

Bulk samples of acid rain were collected in the City of Nagoya in central Japan and passed through a 0.45- μm PTFE membrane filter before chromatographic analysis. Satellite meteorological images (visible and infrared pictures) at 1-h intervals were obtained from the GMS-5 satellite situated on the equator near Indonesia and were processed by an NEC NESDUS-20W computer (Tokyo, Japan) using Windows 98 software. By using this method, the transportation route of rain clouds from mainland China or North Korea to central Japan was determined.

3. Results and discussion

3.1. Selection of eluent

In CEX, acidic eluents may be used for the simultaneous separation of mono- and divalent cations on weakly acidic cation-exchange resins [9,10]. These same eluents are also used frequently in ion-exclusion chromatography for the simultaneous separation of strongly and weakly acidic anions on weakly acidic cation exchangers [11–17]. Additionally, a conductimetric detector can be used as a universal detector for the detection of both anions and cations. Anions will be detected directly and will appear as increases in conductance compared to the background, whereas cations will be detected indirectly and will appear as decreases in conductance compared to the background. Accordingly, it should be possible to determine simultaneously both anions and cations by a combination of ion-exclusion chromatography and CEX with conductimetric detection on a weakly acidic cation-exchange column.

In previous studies, eluents comprising tartaric

acid–methanol–water [2–6] and sulfosalicylic acid–methanol eluent [7] were found to be suitable for the simultaneous separation and conductimetric detection of the anions (Cl^- , NO_3^- , and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). In this study, the performance of tartaric acid and sulfosalicylic acid eluents was compared in terms of the resolution of the anions and cations. Fig. 1 shows the ion-exclusion/CEX chromatograms obtained during elution with 8 mM tartaric acid ($\text{pH}\approx 2.5$; eluent conductivity: 871 $\mu\text{S}/\text{cm}$) and after elution with 1.5 mM

sulfosalicylic acid ($\text{pH}\approx 2.6$; eluent conductivity: 803 $\mu\text{S}/\text{cm}$) on the two separation columns connected in tandem. Although a reasonable simultaneous separation of the anions and cations was obtained in both eluents, significant peak broadening for the divalent cations Mg^{2+} and Ca^{2+} was obtained with the tartaric acid eluent. For this reason, sulfosalicylic acid was judged to be the better eluent.

3.2. Effect of sulfosalicylic acid concentration

The effect of the concentration of sulfosalicylic acid in the eluent on the retention volumes (V_R) of the anions and cations using a single separation column was investigated. As shown in Fig. 2, the V_R values of the anions showed a slight increase with increasing concentration of sulfosalicylic acid in the eluent, as expected from the ion-exclusion effect, and the resolution of the anions increased. On the other

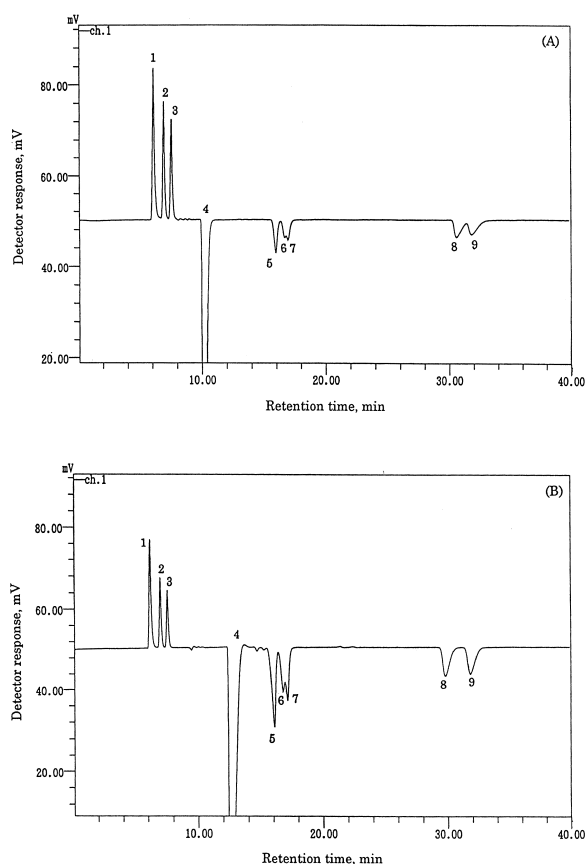


Fig. 1. Simultaneous ion-exclusion/cation-exchange chromatograms of anions and cations by elution with 8 mM tartaric acid (A) or 1.5 mM sulfosalicylic acid (B) on two separation columns connected in tandem. Eluent flow-rate: 1.2 ml/min; sample concentration: 0.15–0.2 mM for anions and 0.1 mM for cations. 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+} .

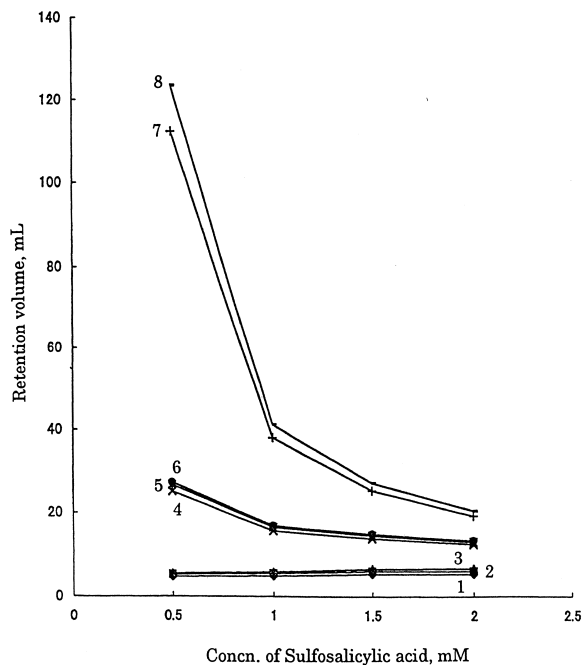


Fig. 2. Effect of sulfosalicylic acid concentration in the eluent on the retention volumes of anions and cations on a single separation column. Lines: 1= SO_4^{2-} , 2= Cl^- , 3= NO_3^- , 4= Na^+ , 5= NH_4^+ , 6= K^+ , 7= Mg^{2+} , 8= Ca^{2+} . Other chromatographic conditions as for Fig. 1.

hand, the V_R values of the cations decreased significantly on increasing the concentration of sulfosalicylic acid, as expected from the cation-exchange effect. A negative eluent dip was observed for sulfosalicylic acid, with this dip appearing between the peaks of the anions and the peaks of the cations. This is due to the hydrophobic interaction of sulfosalicylic acid with the unfunctionalised portions of the stationary phase.

An increase in the eluent conductance accompanied an increase in the concentration of sulfosalicylic acid in the eluent and this caused a decrease in the sensitivity of conductivity detection. It was therefore concluded that the lowest possible concentration of sulfosalicylic acid in the eluent should be used, commensurate with reasonable peak resolution and separation time. After consideration of these factors the optimal concentration of sulfosalicylic acid for the simultaneous ion-exclusion/CEX separation of the anions and cations was determined to be 1.5 mM (pH 2.6; 803 $\mu\text{S}/\text{cm}$). As shown in Fig. 3, a good simultaneous separation of the anions and the cations, except for the monovalent cations Na^+ , NH_4^+ , and K^+ , was obtained using this eluent.

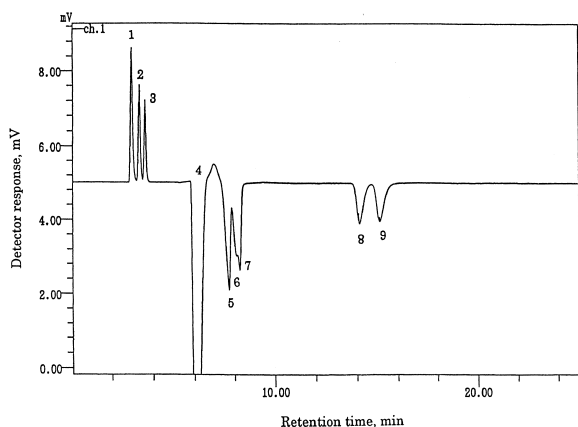


Fig. 3. Simultaneous ion-exclusion/cation-exchange chromatogram of anions and cations using elution with 1.5 mM sulfosalicylic acid on a single separation column. Eluent flow-rate: 1.5 ml/min. Peaks: 1= SO_4^{2-} , 2= Cl^- , 3= NO_3^- , 4=eluent dip, 5= Na^+ , 6= NH_4^+ , 7= K^+ , 8= Mg^{2+} , 9= Ca^{2+} . Other chromatographic conditions as for Fig. 1.

3.3. Effect of crown ether

The effect on the V_R values of the anions and cations caused by the addition of crown ether (18-crown-6) to a 1.5 mM sulfosalicylic acid eluent was investigated. It is well known that the addition of crown ethers in acidic eluents is very effective to improve peak resolution between mono- and divalent cations [5]. Fig. 4 shows that the V_R values of the anions and divalent cations were almost unchanged, whereas those for monovalent cations, especially K^+ , showed an increase. This behavior can be explained by the stability constants for complexation of the alkali metal ions with 18-crown-6 ($\log K_{\text{Na}} = 0.8$, $\log K_{\text{NH}_4} = 1.23$, $\log K_{\text{K}} = 2.03$). From Fig. 4 a suitable concentration of crown ether in the sulfosalicylic acid eluent was determined to be 6 mM. As shown in Fig. 5, a high-performance ion-exclusion/CEX chromatogram of the anions and the

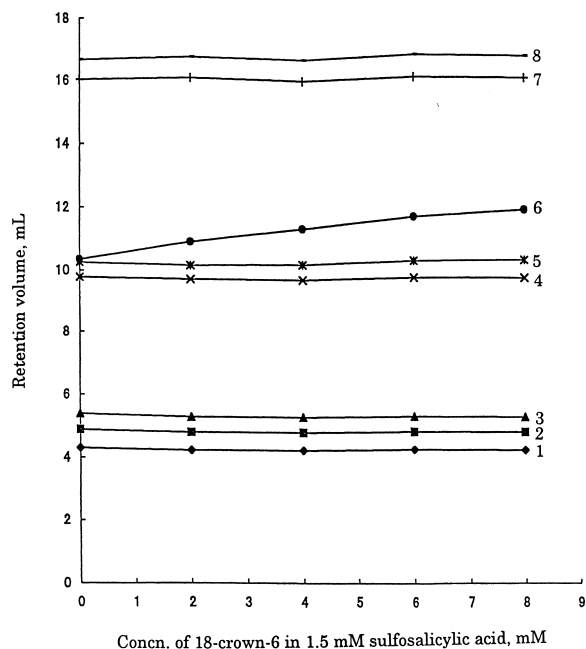


Fig. 4. Effect of crown ether concentration in 1.5 mM sulfosalicylic acid on the retention volumes of anions and cations on a single separation column. Lines: 1= SO_4^{2-} , 2= Cl^- , 3= NO_3^- , 4= Na^+ , 5= NH_4^+ , 6= K^+ , 7= Mg^{2+} , 8= Ca^{2+} . Other chromatographic conditions as for Fig. 3.

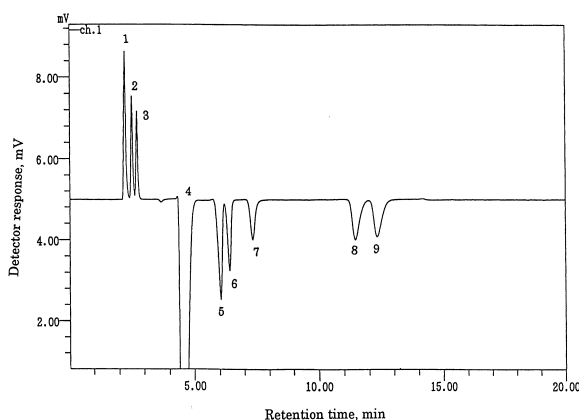


Fig. 5. Simultaneous ion-exclusion/cation-exchange chromatogram of anions and cations using elution with 1.5 mM sulfosalicylic–6 mM crown ether on a single separation column. Peaks: 1=SO₄²⁻, 2=Cl⁻, 3=NO₃⁻, 4=eluent dip, 5=Na⁺, 6=NH₄⁺, 7=K⁺, 8=Mg²⁺, 9=Ca²⁺. Other chromatographic conditions as for Fig. 4.

cations was obtained in less than 14 min using 1.5 mM sulfosalicylic acid and 6 mM 18-crown-6 as the mobile phase (pH 2.6), operated at a flow-rate of 1.5 ml/min.

3.4. Analytical performance characteristics

The ion-exclusion/CEX system operated at the optimal eluent conditions exhibited linear calibration plots of peak area versus concentration for anions and cations over the concentration ranges 0–0.5 mM for anions ($R=0.9995$ –1.000) and 0–0.5 mM for cations ($R=0.9977$ –1.000). Detection limits calculated at $S/N=3$ ranged from 45.7 to 92.5 ppb for the anions and from 14.6 to 66.4 ppb for the cations. Although these values are suitable for the monitoring of acid rain, they are significantly poorer than those obtained using the tartaric acid–methanol eluent and the Shimadzu PIA-1000 portable ion chromatograph reported previously [7]. The poorer detection limits arise from increased background noise due to temperature variations of the eluent reservoir and column oven. The reproducibility of retention times at the optimal elution conditions was 0.19–0.22% relative standard deviation for anions and 0.17–0.91% for cations, as determined from six complete

chromatographic runs on the same sample. Reproducibility of chromatographic peak areas was 1.22–1.75% relative standard deviation for anions and 1.81–2.10% for cations, again for six chromatographic runs. The poorer reproducibility for cations arises from error involved in performing area integration on negative peaks.

3.5. Application to acid rain monitoring in East Asia

Frequent analyses of acid rain components in rain from cloud moving from mainland China to Japan are essential to evaluate the effects of acid rain on natural and urban environments in Japan. In the context of acid rain monitoring in Japan, it is also important to analyze meteorological data to investigate the long-range transportation of rain cloud over the East Asia region. Therefore, an acid rain monitoring system consisting of a portable-type ion chromatograph coupled with meteorological satellite data analyses was implemented to monitor typical acid rain samples originating from rain cloud transported from mainland China and moving to central Japan [4,6,7].

Fig. 6A shows an ion-exclusion/CEX chromatogram on the anions and cations in acid rain water at pH 4.67 collected from rain out of clouds transported from mainland China to central Japan (City of Nagoya) over a 15-h period. The identification and quantification of three anions (SO₄²⁻, NO₃⁻, and Cl⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) in this sample was possible. The presence of both SO₄²⁻ and NO₃⁻ indicates the long-range transportation of acidic species from central mainland China. The biological nitrification of NH₄⁺ under aerobic conditions results in acidification of aquatic environments due to the formation of nitric acid, so the monitoring of NH₄⁺ in acid rain water is very important for the evaluation of acid rain effects. The origin of NH₄⁺ was most probably the result of biological reactions with microorganisms in the aquatic environment under aerobic conditions. On the other hand, the presence of Ca²⁺ results from small clay particles of the so-called “yellow sand” in the Yellow River valley in central China. These have the effect of decreasing the acidity of acid rain

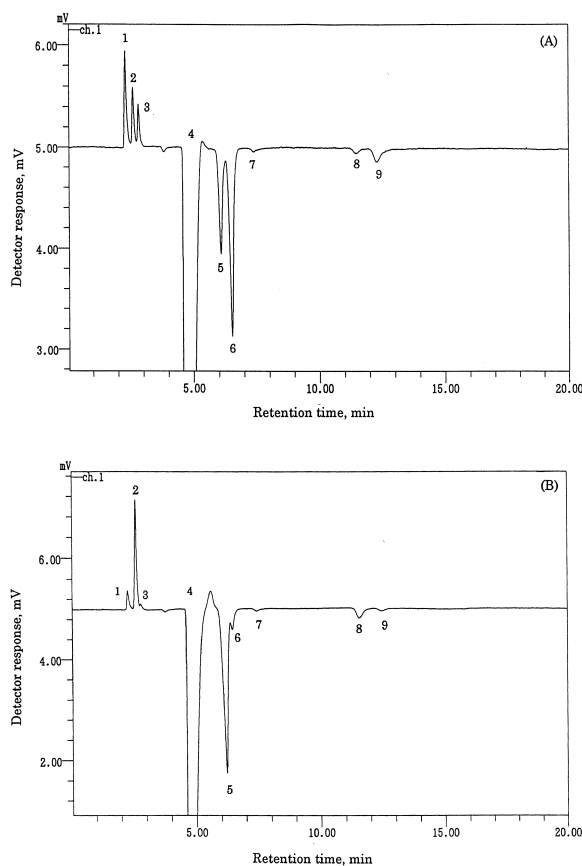


Fig. 6. Typical high-performance simultaneous ion-exclusion/cation-exchange chromatograms of anions and cations in acid rain transported from mainland China (A) and North Korea (B) to central Japan on a single separation column. Peaks: 1=SO₄²⁻, 2=Cl⁻, 3=NO₃⁻, 4=eluent dip, 5=Na⁺, 6=NH₄⁺, 7=K⁺, 8=Mg²⁺, 9=Ca²⁺. Chromatographic conditions as for Fig. 5.

from mainland China. Finally, the presence of Na⁺, Mg²⁺, K⁺, and Cl⁻ is predominantly the result of salt from sea water in the east part of the East-China Sea and the Sea of Japan.

A further example, shown in Fig. 6B, is of an acid rain water at pH 4.57 collected from rain out of clouds transported from North Korea to central Japan (City of Nagoya) over a 15-h period. Again, the identification and quantification of three anions and five cations in this sample was possible. The ion-exclusion/CEX chromatogram shows a lower concentration of acidic components and suggests that the extent of formation of acidic substances in the North Korea region is less than that in the central mainland China.

The above examples show that the ion-exclusion/CEX method is very effective for the monitoring of acid rain in East Asia.

3.6. Ion balance of acid rain waters

Table 1 lists the analytical results of several rain waters of the types illustrated in Fig. 6, with values for [H⁺] (determined by a pH glass electrode method) also included. The ion balance (anions/cations) ranged from 0.94 to 0.97, except for the samples at pH 5.39 and 5.28 which gave ion balances of 0.76 and 0.68, respectively. These decreased values in ion balance are most probably due to the presence of HCO₃⁻, which was not quantified in the ion-exclusion/CEX system [2]. This suggests that the present system should be augmented by the determination of HCO₃⁻ using ion-exclusion chroma-

Table 1
Analytical results of acid rains transported from mainland China and North Korea to central Japan

Sample	Rainfall (mm)	pH	Concentration (mequiv./l)								Ion balance (anions/cations)
			SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	
A	15.6	5.39	0.0221	0.0130	0.0206	0.0120	0.0285	0.0022	0.0110	0.0152	0.76
B	5.0	4.67	0.1070	0.0572	0.0496	0.0520	0.1100	0.0032	0.0101	0.0292	0.94
C	4.4	4.40	0.0906	0.0644	0.0534	0.0625	0.0742	0.0028	0.0115	0.0250	0.97
D	14.4	5.28	0.0236	0.0149	0.0086	0.0136	0.0218	0.0012	0.0025	0.0245	0.69
E	4.0	4.57	0.0418	0.2150	0.0138	0.1650	0.0259	0.0066	0.0418	0.0156	0.94

tography on a strongly acidic cation-exchange resin column, coupled with conductimetric detection [2,18].

4. Conclusions

A high-performance ion-exclusion/CEX method has been developed for the simultaneous determination of anions and cations commonly found in acid rain water, based on the simultaneous mechanisms of ion exclusion and cation exchange. Dilute sulfosalicylic acid–crown ether–water at pH 2.6 has been used as the eluent, together with a weakly acidic cation-exchange resin column. This method was applied successfully to the analysis of several acid rain waters and has been used for evaluating the effects of acid rain on natural and urban environments in Japan.

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