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Simultaneous ion-exclusion/cation-exchange chromatography of anions and cations in acid rain waters on a weakly acidic cation-exchange resin by elution with sulfosalicylic acid

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Abstract

A simple, selective, and sensitive method for the simultaneous determination of anions (sulfate, nitrate, and chloride) and cations (sodium, ammonium, potassium, magnesium, and calcium) in acid rain waters was developed using ion-exclusion/cation-exchange chromatography with conductimetric detection. A weakly acidic cation-exchange resin column (Tosho TSKgel OA-PAK-A) and a sulfosalicylic acid–methanol–water eluent was used. With a mobile phase comprising 1.25 mM sulfosalicylic acid in methanol–water (7.5:92.5) at 1.2 ml/min, simultaneous separation and detection of the above anions and cations was achieved in about 30 min. Linear calibration plots of peak area versus concentration were obtained over the concentration ranges 0–1.0 mM for anions ($R=0.9991$) and 0–0.5 mM for cations ($R=0.9994$). Detection limits calculated at $S/N=3$ ranged from 4.2 to 14.8 ppb for the anions and from 2.4 to 12.1 ppb for the cations. The reproducibility of retention times was 0.14–0.15% relative standard deviation (RSD) for anions and 0.18–0.31% for cations, and reproducibility of chromatographic peak areas was 1.22–1.75% RSD for anions and 1.81–2.10% for cations. The method was applied successfully to the simultaneous determination of anions and cations in aerosols transported from mainland China to central Japan, as determined by a meteorological satellite data analyzer. © 2000 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 the effects of acidification of the aquatic environment caused by acid rain, it is important to develop a suitable approach for automatically monitoring acid rain and related environmental 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, so

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their simultaneous determination provides and almost complete picture of the composition of most acid rain samples.

Ion chromatography (IC) has been recognized as a useful approach for the determination of anions and/or cations in many types of natural waters, including acid rain. In previous papers [2–5], 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 the anions and cations commonly found in acid rain. In these studies, a weak acid (tartaric acid) was used as the eluent and our previous results have suggested that the concentration of tartaric acid is a very important factor for both the ion-exclusion chromatographic separation of anions and the cation-exchange chromatographic separation of cations.

In the present study, a simple, selective, and highly sensitive method involving simultaneous ion-exclusion/cation-exchange chromatography has been accomplished by elution of the analyte ions with a strong acid (sulfosalicylic acid) having hydrophobic characteristics instead of the weak acid (tartaric acid) having hydrophilic characteristics which was used in the previous study [2–5]. The effectiveness of this method is demonstrated in the application to monitoring of acid aerosols transported from mainland China to central Japan by the jet stream.

2. Experimental

2.1. Instrumentation

Two portable IC analyzers equipped with a conductivity detector and a 0.1-ml loop injector were used. These instruments comprised a Shimadzu PIA-1000 (Kyoto, Japan) [5] and an Asahi Technion ARM-1 (Tokyo, Japan), both being operated at 1.2 ml/min. The chromatographic data was saved directly onto a floppy disk and then processed using Shimadzu CLASS-M10A (Ver.1.6) software on a NEC-9821 V13 personal computer or using Tohsu LC-8020 software on a Fujitsu FMV-Biblo notebook computer.

2.2. Reagents and procedures

Commercially available analytical-reagent grade chemicals were used for the preparation of standard solutions of the desired anions and cations. Analytical-reagent grade tartaric acid, sulfosalicylic acid and methanol were used. Deionized, distilled water was used for the preparation of standard solutions and eluent.

Simultaneous ion-exclusion/cation-exchange chromatographic separation of anions and cations was carried out using two 15 cm×7.8 mm I.D. TSK-gel OA-PAK-A (Tosoh, Tokyo, Japan) weakly acidic cation-exchange columns connected in series. These columns were packed with polymethacrylate-based weakly acidic cation-exchange resin in the H⁺-form (5- μ m particle size, 0.1 mequiv./ml) and were operated at 30°C. Eluents comprised tartaric acid–methanol–water and sulfosalicylic acid–methanol–water at the concentrations specified in the figure captions. The pH values of tartaric acid–methanol–water and sulfosalicylic acid–methanol–water eluents and rain samples were determined using a Toa Dempa 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- μ m membrane filter before chromatographic analysis. Satellite meteorological images (visible and infrared pictures) were obtained from the GMS-5 satellite situated on the equator near Indonesia and were processed by a NEC NESDUS-20W computer (Tokyo, Japan) using Windows 98 software at 1-h intervals. By using this method, the transportation route of rain clouds from mainland China to Japan was analyzed.

3. Results and discussion

3.1. Effect of sulfosalicylic acid concentration

In cation-exchange chromatography, acidic eluents may be used for the simultaneous separation of mono- and divalent cations on weakly acidic cation-exchange resins [6–8]. 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 [9–14]. 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 as diluted $[H^+]$ 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 cation-exchange chromatography with conductimetric detection on a weakly acidic cation-exchange column.

In previous studies [2–5], tartaric acid–methanol–water eluent has been found to be the most suitable for the simultaneous separation and detection of the anions and cations. We now investigate the use of eluents comprising strong acid having a hydrophobic nature, such as sulfosalicylic acid. The effect of the concentration of sulfosalicylic acid in the eluent on the retention volumes (V_R) of the anions and cations was investigated to optimize the simultaneous separation conditions. V_R values of the anions showed a slight increase with increasing concentration of sulfosalicylic acid in the eluent (Fig. 1) as expected from the ion-exclusion effect, and the resolution of the anions increased. On the other hand, the V_R values of the cations decreased significantly on increasing the concentration of sulfosalicylic acid, as expected from the ion-exchange effect. For comparison, V_R values obtained with 0–10 mM tartaric acid eluent are shown in Fig. 2, from which it can be seen that both eluents exhibited similar retention behaviour. 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. Whilst such an eluent dip for a strong acid like sulfosalicylic acid is expected to occur at the column void volume, the V_R of this peak with sulfosalicylic acid was larger than the column void volume because of hydrophobic interactions of the eluent species with the unfunctionalised portions of the stationary phase.

The background conductance of the eluent increased with increasing concentration of sulfosalicylic acid in the eluent (328 $\mu\text{S}/\text{cm}$ for a 0.5 mM eluent, 579 $\mu\text{S}/\text{cm}$ for a 1.0 mM eluent, and 804

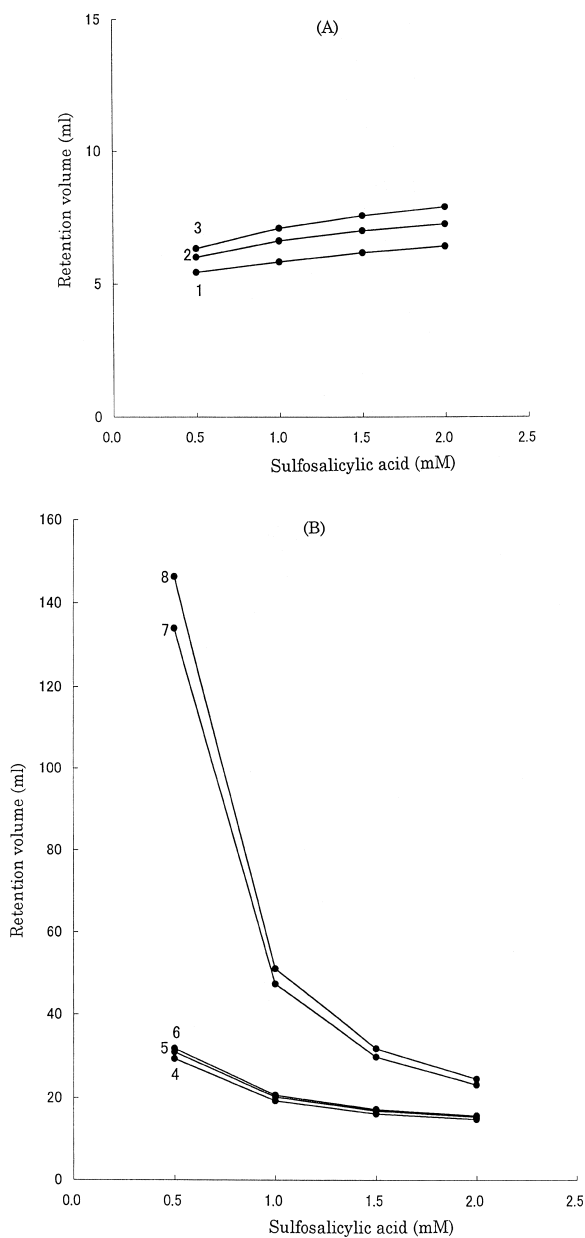


Fig. 1. Effect of sulfosalicylic acid concentration on retention volumes (V_R) of (A) anions and (B) cations. Eluent pH 2.9; sample: mixture of 0.5 mM Na_2SO_4 , NH_4NO_3 , KNO_3 , CaCl_2 , and MgSO_4 (0.1 ml). (1) SO_4^{2-} , (2) Cl^- , (3) NO_3^- , (4) Na^+ , (5) NH_4^+ , (6) K^+ , (7) Mg^{2+} , (8) Ca^{2+} .

$\mu\text{S}/\text{cm}$ for a 1.5 mM eluent). Since an increase in the eluent conductance also caused a decrease in the sensitivity of conductivity detection, it was con-

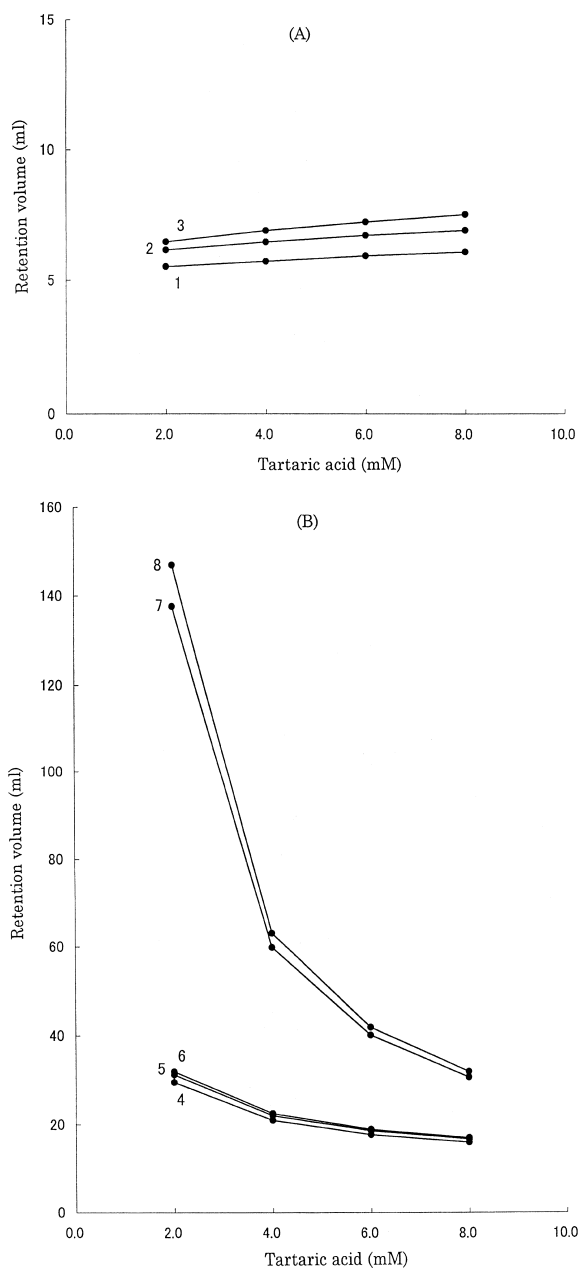


Fig. 2. Effect of tartaric acid concentration on V_R of (A) anions and (B) cations. Conditions and legend as for Fig. 1.

cluded that the lowest possible eluent concentration of sulfosalicylic acid should be used, commensurate with reasonable peak resolution and separation time. After consideration of these factors it was concluded the optimal concentration of sulfosalicylic acid for

the simultaneous ion-exchange/cation-exchange chromatographic separation of the anions and cations was in the range 1.0–1.5 mM. Fig. 3 shows the simultaneous separation of anions and cations obtained using a 1.5 mM sulfosalicylic acid eluent ($\text{pH} \approx 2.8$).

3.2. Effects of other mobile phase parameters

An increase in the concentration of sulfosalicylic and tartaric acids in the eluent is accompanied by an increase in hydronium concentration and the contribution of this effect to the elution properties of each eluent was studied by comparing V_R values for eluents having the same hydronium ion concentration. Fig. 4 shows the results obtained and indicates that the two eluent acids behaved similarly and that sulfosalicylic acid was slightly stronger than tartaric acid in the cation-exchange mode, presumably due to secondary interactions between sulfosalicylic acid and the stationary phase arising from hydrophobic effects.

In order to improve the resolution of both anions and cations by manipulating the degree of hydrophobic adsorption of the sulfosalicylic acid onto the stationary phase, the effect on the V_R values of the anions and cations caused by the addition of methanol to a 1.25 mM sulfosalicylic acid eluent ($\text{pH} \approx 2.9$) was investigated. The results are shown in Fig. 5, from which it can be seen that addition of methanol had a relatively small effect on the retention of the anions and the monovalent cations, but a significant decrease in retention of the divalent cations was evident at higher concentration of methanol. The most efficient separation of anions and cations was achieved in the range of 5–10% of methanol.

As shown in Fig. 6, a high-resolution ion-exclusion/cation-exchange chromatogram of the anions and cations was obtained in less than 30 min using 1.25 mM sulfosalicylic acid and methanol–water (7.5:92.5) as the mobile phase ($\text{pH} \approx 2.9$), operated at a flow-rate of 1.2 ml/min.

3.3. Analytical performance characteristics

The ion-exchange/cation-exchange chromatography system at the optimal elution conditions

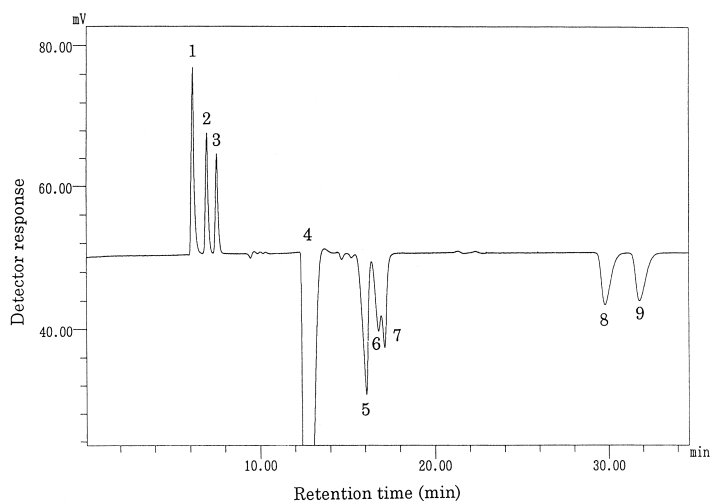


Fig. 3. Ion-exclusion/cation-exchange chromatogram of anions and cations by elution with 1.5 mM sulfosalicylic acid. Eluent pH: 2.8; Other chromatographic conditions are the same as for Fig. 1. (1) SO_4^{2-} , (2) Cl^- , (3) NO_3^- , (4) Eluent-dip, (5) Na^+ , (6) NH_4^+ , (7) K^+ , (8) Mg^{2+} , (9) Ca^{2+} Eluent conductivity: $\sim 600 \mu\text{S}/\text{cm}$.

exhibited linear calibration plots of peak area versus concentration for anions and cations over the concentration ranges 0–1.0 mM for anions ($R=0.9991$) and 0–0.5 mM for cations ($R=0.9994$). Detection limits calculated at $S/N=3$ ranged from 4.2 to 14.8

ppb for the anions and from 2.4 to 12.1 ppb for the cations. These values are suitable for the monitoring of acid rain. The reproducibility of retention times at the optimal elution conditions was 0.14–0.15% relative standard deviation for anions and 0.18–0.31% 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

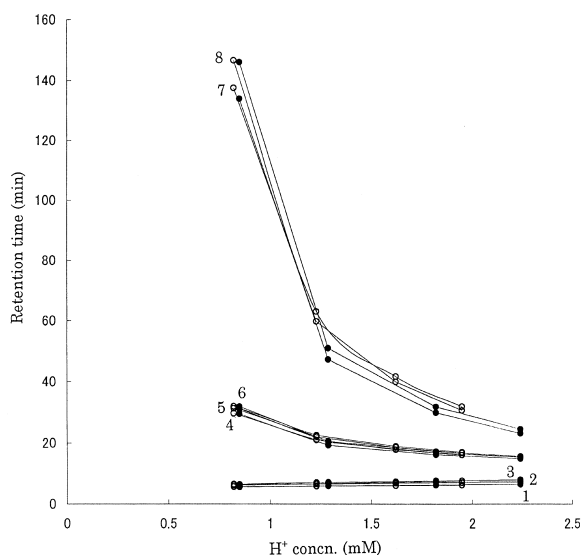


Fig. 4. Effect of hydrogen ion concentration of sulfosalicylic acid and tartaric acids eluents on V_R of anions and cations. \circ , Tartaric acid (2–8 mM); \bullet , sulfosalicylic acid (0.5–2.0 mM). Legend as for Fig. 1.

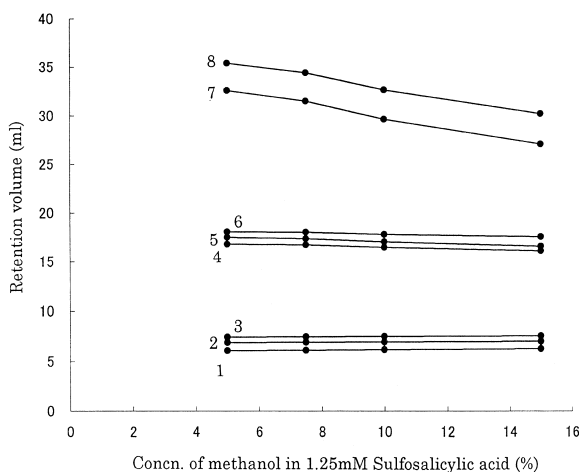


Fig. 5. Effect of volume percentage methanol in 1.25 mM sulfosalicylic acid eluent on V_R of anions and cations. Legend as for Fig. 1.

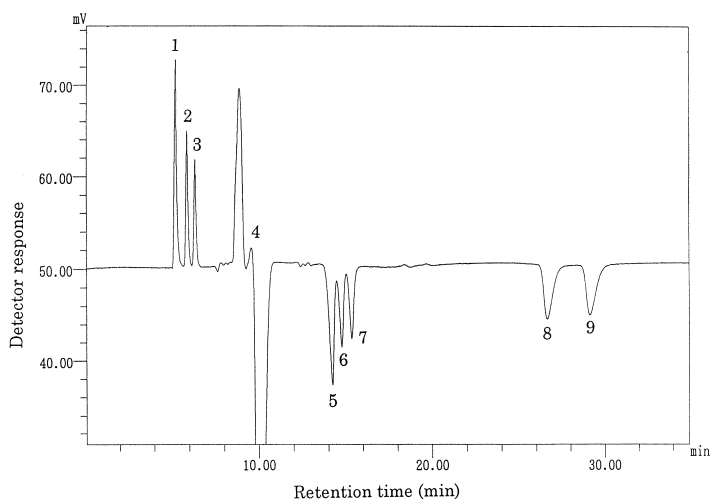


Fig. 6. Ion-exclusion/cation-exchange chromatogram of anions and cations by elution with 1.25 mM sulfosalicylic acid in methanol–water (7.5:92.5, v/v). Other chromatographic conditions are the same as in Fig. 1. Peak identities as for Fig. 4.

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.

3.4. Application to acid rain monitoring in East Asia

Frequent analyses of acid rain components in rain 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 acid aerosols over the East-Asia region. Therefore, an acid rain monitoring system consisting of a portable-type IC system coupled with meteorological satellite data analyses was applied to typical acid rain events containing aerosols originating from mainland China and moving to central Japan [4,5]. The developed ion-exchange/cation-exchange chromatography method was applied successfully. Meteorological data showed that transportation of aerosols by the atmospheric jet stream (with velocity of 30–100 m/s) required a period of about 20 h. Fig. 7 shows ion-exchange/cation-exchange chromatograms of acid rain water samples at pH 4.09 (Fig. 7a) and 5.04

(Fig. 7b), collected in the City of Nagoya. Separation of all anions and cations enabled the identification and quantification of three anions (SO_4^{2-} , NO_3^- and Cl^-) and five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) in these samples.

The presence of both SO_4^{2-} and NO_3^- indicates the long-range transportation of acidic species from mainland China. Deposition and biological nitrification of NH_4^+ under aerobic conditions results in acidification of aquatic environments due to the formation of nitric acid, so the monitoring of NH_4^+ in acid rain water is very important for the evaluation of acid rain effects. The origin of NH_4^+ is probably the result of biological reactions with microorganisms in the aquatic environment under aerobic conditions. On the other hand, the presence of Ca^{2+} 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 from mainland China. Finally, the presence of Na^+ , K^+ , Mg^{2+} 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.

4. Conclusions

An ion-exchange/cation-exchange chromatograph-

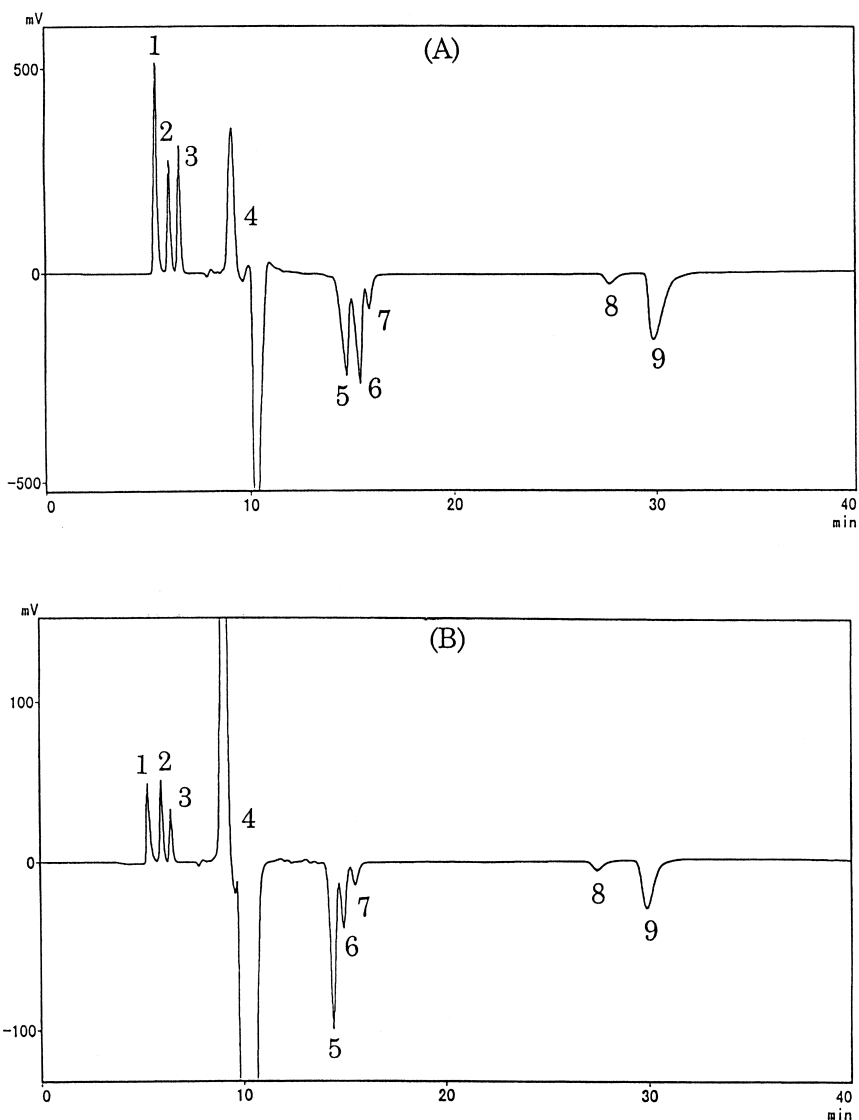


Fig. 7. Ion-exclusion/cation-exchange chromatograms of anions and cations in acid rain transported from mainland China to central Japan over 20 h by the jet stream. (A) Acid rain water at pH 4.09. (B) Acid rain water at pH 5.04. Instrument: Shimadzu PIA-1000 portable-IC. Detection sensitivity: $1V=100 \mu S/cm$. Other chromatographic conditions and peak identities as in Fig. 4.

ic 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–methanol–water was used as the eluent, together with a weakly acidic cation-exchange resin column. This method was applied successfully to the simultaneous determination of

anions and cations in several acid rain waters and has been used for evaluating the effects of acid rain on natural and urban environments in Japan. For the evaluation of ionic balance calculated from the concentrations of anions and cations in several acid rain waters determined by this method, a detailed study is required and this will be the subject of future work.

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