Short communication

Acid-rain monitoring in East Asia with a portable-type ion-exclusion–cation-exchange chromatographic analyzer

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Abstract

A monitoring system consisting of a portable-type conductimetric ion-exclusion–cation-exchange chromatographic (CEC) analyzer and a meteorological satellite data analyzer has been investigated for the evaluation of the effects of acid precipitation on natural and urban environments in East Asia. The portable ion-exclusion–CEC analyzer uses a polymethacrylate-based weakly acidic cation-exchange resin column in the H^+-form and a weak-acid eluent (tartaric acid–methanol–water) and is applied for the simultaneous determination of anions (SO_4^{2-}, NO_3^-, and Cl^-) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in precipitation transported from mainland China to central Japan, as mapped by the meteorological satellite data analyzer. Linear calibration graphs of peak area versus concentration for anions and cations were observed in the concentration range 0–1.0 mM for the anions and 0–0.5 mM for the cations. Detection limits at a signal-to-noise ratio of 3 were in the range 5.18–12.1 ppb for the anions and 6.58–16.5 ppb for the cations. The practical utility of this monitoring system is presented.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Acid rain is a widespread environmental pollution problem, not only in Europe and North America but also in East Asia, including Korea and Japan. In order to analyze and evaluate the effects of acid precipitation on natural and artificial (urban) environments caused by acid rain, it is necessary to monitor the ionic components of rain. The major ionic components of acid rain water consist of the cations

H^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}, and the anions Cl^-, NO_3^-, and SO_4^{2-} [1]. It has been shown that the ionic balance (i.e. Σ anions minus Σ cations) between these nine components is close to zero, demonstrating that other ionic components make an insignificant contribution.

The development of a simple, convenient and highly sensitive method for the simultaneous determination of these ionic acid-rain components is very important for estimating and evaluating acid-rain effects. Additionally, since the water quality of acid rain is related strongly to meteorology and

topography, the correlation of chemical data with meteorological data for acid rain water is a very significant factor. Ion chromatography (IC) has been recognized to be very useful approach for the determination of anions and/or cations in several kinds of environmental waters, including acid rain water [2–4]. As has been reported by Tanaka and coworkers [5–7], simultaneous ion-exclusion–cation-exchange chromatography (CEC) performed on a cation-exchange resin column with single sample injection is a very effective approach for the simultaneous separation and detection of both anions and cations. In previous papers, we have reported that a monitoring system consisting of a conventional CEC analyzer and a meteorological satellite data analyzer is very useful to analyze and evaluate acid-rain effects on natural and urban environments caused by acid rain in East-Asia. In previous studies, a large-scale instrument was used and the methodology required samples to be collected from the desired location and transported to the laboratory for analysis.

In this paper, the simultaneous CEC approach with conductimetric detection has been developed further using a portable-type IC analyzer applicable to on-site analysis. The effectiveness of this approach is demonstrated by its application to several acid rain waters in Japan.

2. Experimental

2.1. Instrumentation and reagents

The portable-type IC analyzer (Shimadzu PIA-1000, Kyoto, Japan) was equipped with a conductivity detector and a 0.1 ml-loop injector and was fitted with a non-metallic eluent delivery pump operated at 1.2 ml/min. The chromatographic data were saved directly onto a floppy disk and then processed using Shimadzu Class-M10A (Ver.1.6) software performed on a NEC-9821 V13 personal computer.

The simultaneous ion-exclusion–CEC separation of anions and cations commonly found in acid rain water was carried out on a cation-exchange column (Tosoh TSKgel OA-PAK-A, Tokyo, Japan) packed with polymethacrylate-based weakly acidic cation-exchange resin in the H^+-form (5 μm particle size, 15 cm$\times$7.8 mm I.D.$\times$2) at 30°C. The eluent used was 6 mM tartaric acid–7.5% methanol–water.

Commercially available analytical-reagent grade chemicals and deionized, distilled water were used for the preparation of standard solutions of anions and cations, and for the preparation of eluents.

2.2. Sampling of precipitation

Precipitation was collected in the city of Nagoya in central Japan and the nearby mountainous area using a Rain-Go-Round rain sampler for 1-mm increments of rainfall or a 10-l polyvinylchloride bucket for bulk rain sampling. The rain water samples were passed through a 0.45-μm membrane filter before chromatographic analysis. The analysis of meteorological data (visible and infrared pictures) obtained directly from a satellite (GMS-5) situated on the equator near Indonesia was carried out by a NEC NESDUS-20W (Tokyo, Japan) on Windows 95 software for 1-h intervals using the NEC Value Star NX personal computer. By using this satellite picture analyzer, the pathway of rain clouds from mainland China to Japan was determined.

3. Results and discussion

3.1. Simultaneous ion-exclusion chromatography–CEC separation and detection of anions and cations

Before describing the concept of the portable-type ion-exclusion chromatography–CEC analyzer, the separation and detection mechanism employed in the system will be discussed briefly. In CEC, acidic eluents may be used for the simultaneous separation of mono- and divalent cations on weakly acidic cation-exchange resins [8,9]. The same eluents are also used frequently in IEC for the simultaneous separation of strong and weak acids on weakly acidic cation-exchangers [5–13]. Additionally, a conductimetric detector can be used for the detection of both anions and cations. Accordingly, it should be possible to determine simultaneously both anions and cations by a combination of IEC and CEC with

conductimetric detection on a weakly acidic cation-exchange column.

A 6 mM tartaric acid in methanol–water (7.5:92.5) eluent was found to be most suitable for the simultaneous separation and detection of the desired anions and cations in standard solution with this eluent, as shown in Fig. 1. The analysis of an acid rain water sample at pH 4.80 using this system is shown in Fig. 2. The results shown were obtained by operating the IC instrument in the field using a car battery as the power source. A very minor baseline drift, observed under these conditions, was presumably due to eluent temperature fluctuations caused by lack of temperature control of the eluent reservoir. However, there was no problem for the peak area measurement for both anions and cations. The good separation of all the desired species was accomplished in less than 30 min. The detector

response was positive for the anions and negative for the cations because the latter species were detected by an indirect detection mechanism [5].

3.2. Analytical performance of a portable-type IC analyzer

The ion-exclusion chromatography–CEC system, when operated at the laboratory, used a.c. 100 V as the power source and exhibited linear calibration graphs of peak area versus concentration for anions and cations in the concentration range 0–1.0 mM for the anions and 0–0.5 mM for the cations. Detection limits at a signal-to-noise ratio of 3 were in the range 5.18–12.1 ppb for the anions and 6.58–16.5 ppb for the cations. These values are appropriate for application of the method to acid-rain monitoring. Similar results for calibration graphs and detection limits
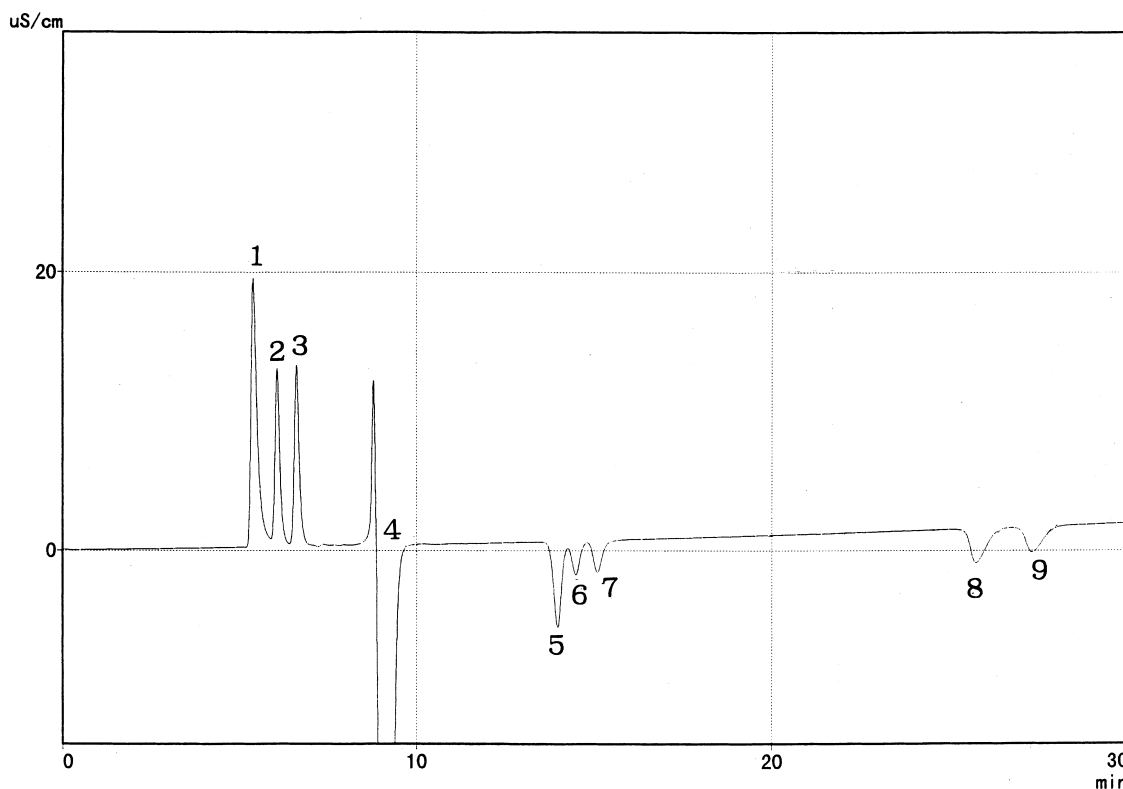

Fig. 1. Simultaneous separation of anions and cations in standard solution using a portable-type IC analyzer, operated at the field. Eluent: 6 mM tartaric acid in methanol–water (7.5:92.5), 1.2 ml/min flow-rate; Column: TSKgel OA-PAK-A (15 cm×7.8 mm I.D.×2); Sample: mixture of 0.5 mM Na_2SO_4, NH_4NO_3, KNO_3, $CaCl_2$, and $MgSO_4$; 0.1 ml sample loop. (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+}.
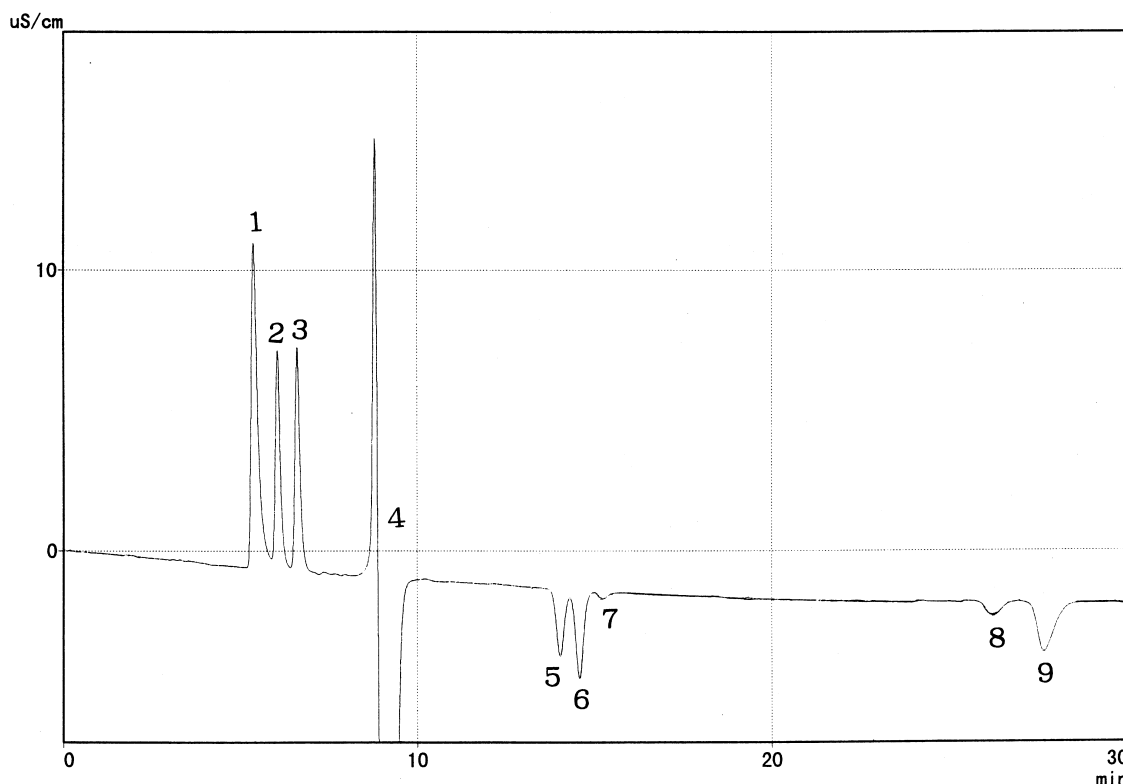
Fig. 2. Simultaneous separation of anions and cations in acid rain at pH 4.80 using a portable-type IC analyzer, operated at the field. Chromatographic conditions and peak identities are the same as in Fig. 1.

were also obtained in the application of ion-exclusion chromatography CEC at the field.

The reproducibility of chromatographic peak areas was 0.79–0.85% relative standard deviation (RSD) for anions and 1.23–2.16% RSD for cations using six replicate chromatographic runs operated at the laboratory. The somewhat poorer reproducibility for cations is due to the error generated by the reversal of negative peak signals to positive ones, so that peak integration could be performed by the chromatographic data system. Similar results for reproducibility were also obtained in the application of ion-exclusion chromatography–CEC at the field.

3.3. Application of a portable-type IC and meteorological satellite data analyzers to acid-rain monitoring in East Asia

Frequent analyses of acid-rain components in rain originating from mainland China and falling in Japan are essential to estimate and evaluate the effects on the 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 rain over the East Asia region. Therefore, an acid-rain monitoring system consisting of the portable-type IC analyzer and a meteorological satellite data analyzer was investigated for typical acid rains transported from mainland China to central Japan by the effect of jet stream (ca. 30–100 m/s).

The portable-type IC analyzer operated at the laboratory could be applied successfully to the simultaneous determination of anions and cations in acid rain transported from mainland China including an effect of local washout. Fig. 3 shows a typical ion-exclusion chromatography– CEC chromatogram of anions and cations in the acid rain at pH 4.09 for a 1-mm precipitation taken in the city of Nagoya in October, 1997. The simultaneous separation permits
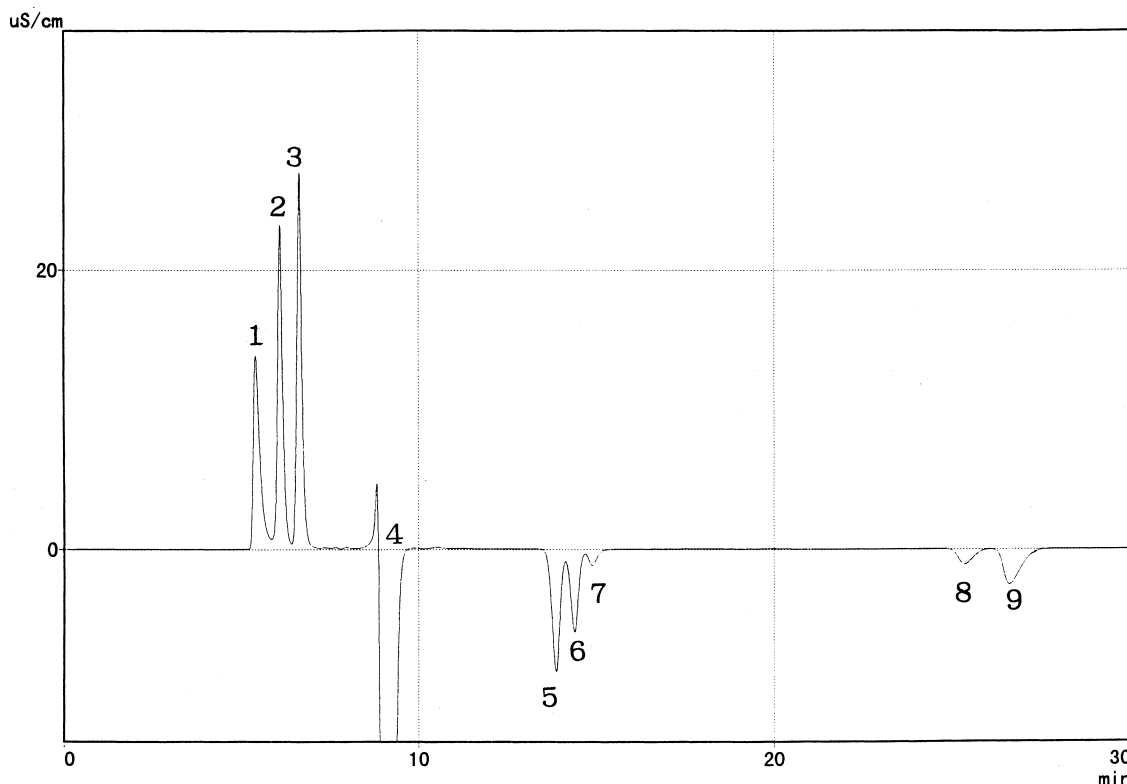
Fig. 3. Simultaneous ion-exclusion chromatography–CEC chromatogram of anions and cations in acid rain water at pH 4.09 after 1 mm of precipitation, operated at the laboratory. Chromatographic conditions and peak identities are the same as in Fig. 1.

the identification and quantification of three anions and five cations. The chromatographic analysis shows that acidic components (such as SO_4^{2-} and NO_3^-) and basic components (such as NH_4^+, Mg^{2+}, and Ca^{2+}) were transported from central China to central Japan via the Korean peninsula over a period of 15 h, as obtained by the meteorological satellite data analysis. The presence of Mg^{2+} and Ca^{2+} arises from small clay particles of so-called "yellow sand" in the Yellow river valley in central China. These have the effect of decreasing the acidity of the acid rain from mainland China. The presence of Na^+, K^+, and Cl^- is predominantly the result of saltation of sea water (warm current) in the east part of the East China Sea and the Sea of Japan.

3.4. Variability of ion concentrations during rain events by application of IC

In general, it is well known that the concentrations

of ionic components in acid rain are influenced by the amount of precipitation. Therefore, the effect of precipitation on the concentrations of anions and cations (including H^+ in rain water) was investigated for every 1 mm of precipitation in a particular rain event by using a Rain-Go-Round rain sampler.

Fig. 4 shows the relationship between the precipitation (mm) and the concentrations of anions and cations for each millimeter of precipitation (up to a total of 7 mm) and for the remaining precipitation (8–13.4 mm) collected into the final point in the figure. With the exception of NH_4^+, the concentrations of anions and cations decreased generally with increasing precipitation. The pH mirrored the behavior of NH_4^+ because this is the basic component. NH_4^+ in rain water has a significant ecological effect and its biological nitrification under aerobic conditions results in acidification of the aquatic environment. Therefore, monitoring of NH_4^+ in acid rain water is very important for the evaluation
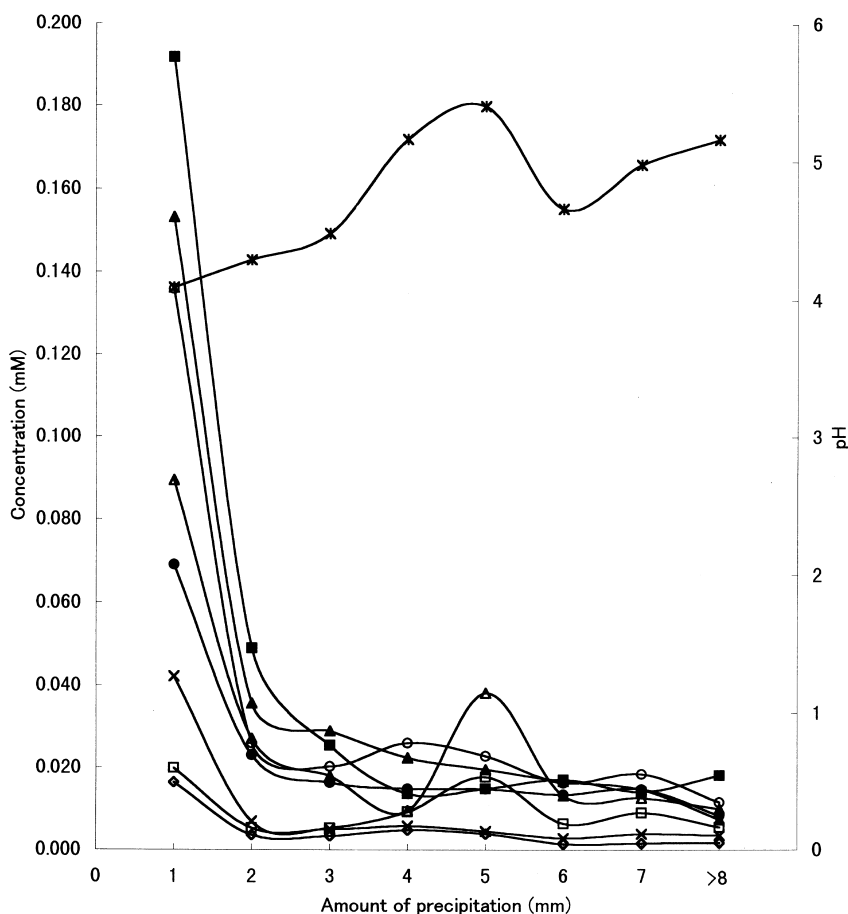
Fig. 4. Variability of ion concentrations during a rain event. Concentrations are given for 1 mm precipitation increments. Total precipitation is 13.4 mm. ●=SO_4^{2-}, ▲=Cl^-, ■=NO_3^-, ○=Na^+, △=NH_4^+, □=K^+, ◇=Mg^{2+}, ×=Ca^{2+}, *=pH.

of the effects of acid rain in the environment. The increased concentration of NH_4^+ observed after about 5 mm of rainfall is presumably due to a significant change in weather conditions at that time.

4. Conclusions

A new monitoring system for on-site analysis of acid rain consisting of a combination of a portable-type IC analyzer for the simultaneous determination of anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) commonly found in acid rain waters and a meteorological satellite data analyzer has been described. This monitoring system was very useful to analyze and evaluate acid-rain

effects on natural and urban environments in East Asia. The major analytical problems remaining to be solved in the field of acid-rain monitoring by ion-exclusion chromatography–CEC is the determination of H^+ and HCO_3^- (index of buffer capacity to acid rain).

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