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Ion-exchange chromatography of mono- and divalent cations in natural waters on a weak-acid anion-exclusion column

Kazuhiko Tanaka^{a,*}, Kazutoku Ohta^a, Paul R. Haddad^b, James S. Fritz^c

^aNational Industrial Research Institute of Nagoya, 1-1, Hirate-cho, Kita-ku, Nagoya 462-8510, Japan

^bUniversity of Tasmania, GPO Box 252-75, Hobart, Tasmania 7001, Australia

^cAmes Laboratory and Iowa State University, Ames, IA 50011-3020, USA

Abstract

Ion-exchange chromatography with indirect conductimetric detection for the simultaneous determination of mono- and divalent cations is investigated using an anion-exclusion chromatographic column packed with polymethacrylate-based weakly acidic cation-exchange resin in the H⁺ form (Tosoh TSKgel OA-PAK-A, 300 mm×7.8 mm I.D.). An eluent comprising a strong acid, a weak organic acid, methanol and water is used. Using 0.75 mM sulfuric acid, 2 mM tartaric acid, 7.5% (v/v) methanol in water as eluent, the monovalent cations (Na⁺, NH₄⁺, and K⁺) and divalent cations (Mg²⁺ and Ca²⁺) were separated simultaneously by a cation-exchange mechanism in about 25 min. The application of this method to the analysis of several natural waters including rain, river, lake, underground and forest soil waters for estimating acid rain effects on the natural and urban environments is presented. © 1998 Elsevier Science B.V.

Keywords: Mobile phase composition; Water analysis; Environmental analysis; Inorganic cations

1. Introduction

The frequent analyses of ionic components in acid rain waters is important to estimate the effect of acidification to the natural and urban environments caused by acid rain. Ion chromatography (IC) has been widely recognized as a useful and powerful technique for the analyses of anionic and cationic components in various natural waters related to acid rain [1,2]. The major ionic components of acid rain consist of H⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ as cationic components and Cl⁻, NO₃⁻ and SO₄²⁻ as anionic components. The ionic balance between these nine ionic components is almost unity [3–7].

The acidic components (such as H⁺, SO₄²⁻ and NO₃⁻) provide an estimate of the acidity of acid rain water, whilst the basic components (such as Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) provide an estimate of the neutralization capacity of the water [8].

In general, specialty IC instrumentation and cation-exchange resins are needed for the simultaneous determination of the mono- and divalent cations. The need therefore exists for a simple, convenient and economical IC method for this analysis which uses conventional IC or high-performance liquid chromatography (HPLC) equipment and a readily available cation-exchange column. Tanaka et al. [4] have shown that it was possible to determine simultaneously the weakly ionized aliphatic carboxylic acids and mono- and divalent cations by a simultaneous ion-exclusion–cation-exchange mechanism when an anion-exclusion column packed with poly-

*Corresponding author.

methacrylate-based weakly acidic cation-exchange resin in the H^+ form (TSKgel OA-PAK) was used with a strong acid (e.g., H_2SO_4) eluent. The effectiveness of the TSKgel OA-PAK in ion-exclusion chromatography has been reported for the separation of some weakly ionized organic acids [9].

The purpose of the present study was to evaluate the applicability of the above anion-exclusion column in non-suppressed IC of mono- and divalent cations and to establish a simple and economical method for the simultaneous determination of common mono- and divalent cations in acid rain and related natural waters, including rain, river, underground, lake and forest soil waters.

2. Experimental

The IC system used in this study was a Tosoh (Tokyo, Japan) CCPD non-suppressed ion chromatograph with non-metal eluent delivery pump operated at a flow-rate of 1.0 ml/min. The detector was a Tosoh CM-8000 conductimetric detector. A chromatographic data system (Tosoh SC-8000) was used for instrument control and for data collection and processing. The separation of mono- and divalent cations by cation-exchange was carried out on an anion-exclusion column (Tosoh TSKgel OA-PAK-A) packed with a polymethacrylate-based weakly acidic cation-exchange resin in the H^+ form (5 μm particle size, 300 mm \times 7.8 mm I.D.).

The eluents consisted of water, strong acid–water, strong acid–weak acids–water and their methanol–water mixed eluents and were used to compare the performance for simultaneous separation of mono- and divalent cations. All eluents were continuously degassed by a Tosoh SD-8022 on-line degasser.

All chemicals used were of analytical reagent grade. Deionized, distilled water was used for the preparation of standard solutions and eluents. Standard stock solutions of mono- and divalent cations were prepared by dissolving appropriate amounts of Cl^- , SO_4^{2-} and NO_3^- salts in water.

Samples of acid rain and other waters were collected in or near the City of Nagoya in central Japan. All samples were passed through a 0.45- μm membrane filter before chromatographic analysis.

3. Results and discussion

3.1. Separation of mono- and divalent cations by elution with water or sulfuric acid

As has been reported previously [4,9], the TSKgel OA-PAK-A is designed for use in the ion-exclusion chromatographic separation of weakly ionized organic acids by using water or a strong acid (e.g., H_2SO_4) as the eluent. This column is generally used together with a pre-column (TSKgel OA-PAK-P) packed with a strongly acidic cation-exchange resin in the H^+ form in order to trap all cations present in the eluent or the sample, except H^+ ion. In the present study, the pre-column was removed to enable the cation-exchange chromatographic separation of the mono- and divalent cations.

Fig. 1 shows the ion-exclusion chromatogram of a mixture of strong acid anions, weak acid anions, aliphatic carboxylic acids and mono- and divalent cations on the TSKgel-OA-PAK-A after elution with water (Fig. 1A) or 1 mM H_2SO_4 (Fig. 1B). When water is used as the eluent, it is possible to achieve partial separation of the strong acid anions, weak acid anions and aliphatic carboxylic acids by the ion-exclusion mechanism, but separation of the cations was hindered because they are irreversibly on the resin. On the other hand, when 1 mM sulfuric acid is used as the eluent, an improved separation of the anionic species is obtained, as well as simultaneous separation of most of the monovalent cations and divalent cations by a cation-exchange mechanism. The values of retention volume (V_R) for the divalent cations are larger than those of the monovalent cations due to the greater affinity for the resin of the divalent species.

From the above results, it is concluded that the anion-exclusion column used in this study could be effective for the cation-exchange separation of mono- and divalent cations. Therefore, further studies were undertaken to investigate the utility of this approach.

3.2. Selection of optimal eluent composition

The effects of a number of factors on the retention volumes of the mono- and divalent cations are investigated to identify conditions where resolution

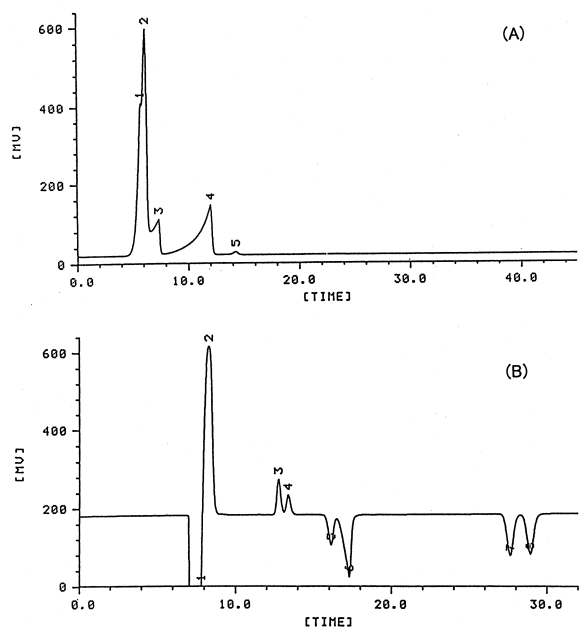


Fig. 1. Ion-exclusion chromatographic separation by elution with water (A) and cation-exchange chromatographic separation by elution with 1 mM H_2SO_4 (B) for strong acid anions, weak acid anions and mono- and divalent cations. Chromatographic conditions: column: Tosoh TSKgel OA-PAK-A polymethacrylate-based weakly acidic cation-exchange resin in the H^+ -form (300 mm \times 7.8 mm I.D.); eluent flow-rate: 1.0 ml/min; column temperature: 25°C; detector sensitivity: 1000 mV=100 $\mu\text{S}/\text{cm}$; unit of retention time: min; injection volume: 0.1 ml; sample: mixture of 0.1 mM HNO_3 , KCl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaHCO_3 , CaCl_2 , MgCl_2 , KH_2PO_4 , 1 mM HCOOH and 5 mM CH_3COOH . Peak identities: (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+} .

of these species could be accomplished within a reasonable elution period. These factors include the concentrations of H_2SO_4 and methanol in the eluent, the column temperature and the type and concentration of complexing agents in the eluent.

Fig. 2 shows that the retention volumes decreased rapidly with increasing concentration of sulfuric acid and as expected for a cation-exchange system, the rate of decrease in retention volumes is greatest for the divalent species. Ideally, a plot of the log capacity factor (k') versus the log (eluent) gives a straight line with different slopes depending on the valency of the ions and assuming a constant ion-exchange capacity. Generally, the slopes are 1.0 and

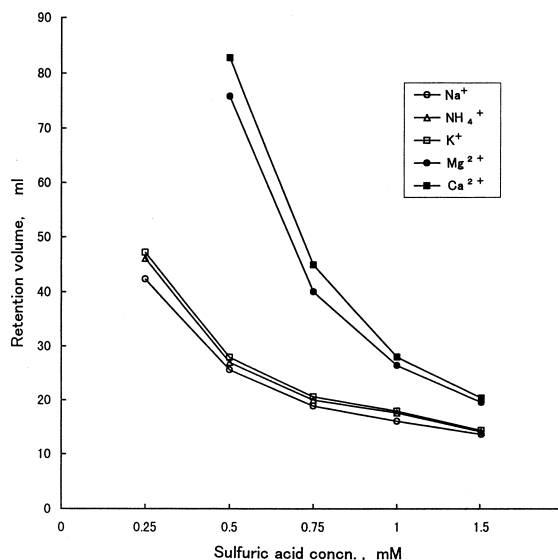


Fig. 2. Effect of H_2SO_4 concentration in the eluent on retention volumes (V_R) of mono- and divalent cations. Other chromatographic conditions as in Fig. 1.

2.0 for monovalent cations and divalent cations, respectively if the cation-exchange is the predominant mechanism for this separation. When plotting data obtained as $\log(k')$ versus $\log(\text{H}_2\text{SO}_4)$, straight lines are obtained for both mono- and divalent cations. The slopes obtained were 1.0 and 1.6 for monovalent cations and divalent cations, respectively. The reason for this small value (<2) for divalent cations might be due to the decrease in the cation-exchange capacity of the weakly acidic cation-exchange resin under the acidic elution conditions.

The background conductance of the eluent increased linearly with increasing H_2SO_4 concentration in the eluent (1040 $\mu\text{S}/\text{cm}$ at 1.5 mM) and the detection sensitivity is decreased at higher background conductances. The above results suggested a low eluent concentration of H_2SO_4 is necessary to obtain reasonable separation, perhaps at the expense of increased elution time. After consideration of these factors the optimal concentration of H_2SO_4 in the eluent was judged to be in the range 0.5–1.0 mM.

The effect of methanol concentration in a 0.75 mM H_2SO_4 eluent on retention volumes of the mono- and divalent cations is investigated below. The results are shown in Fig. 3, from which it can be

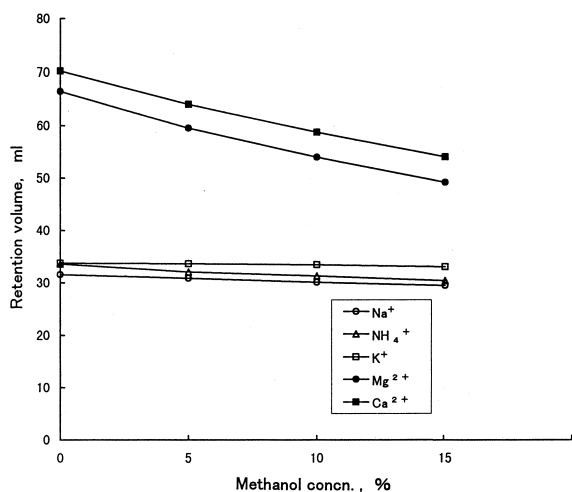


Fig. 3. Effect of methanol concentration in a 0.75 mM H_2SO_4 eluent on retention volumes of mono- and divalent cations. Other chromatographic conditions as in Fig. 1.

seen that addition of methanol (Fig. 3) had a relatively small effect on the retention of the monovalent cations, but a significant decrease in retention of the divalent cations was evident at higher concentrations of methanol. The most efficient separation of cations was achieved in the range 5–10% of methanol.

The influence of column temperature on the separation of the mono- and divalent cations is investigated over the range 10–40°C. Temperature effects are relatively minor except in the case of K^+ for which retention decreased markedly above 25°C, to the temperature at which NH_4^+ and K^+ were co-eluted (35°C, Fig. 4). The ambient temperature in the laboratory was 20°C. Hence, a higher temperature would be required if adequate temperature control was necessary, therefore the optimal column temperature was judged to be 25°C.

When the separation is performed using the optimal conditions determined above, namely 0.75 mM H_2SO_4 and 5% methanol in water at 25°C, the separation time is too long for routine analysis because of the slow elution of the divalent cations. Therefore, the effects on retention of complexing agents such as tartaric acid, citric acid and EDTA were studied since these species have often been used as complexing agents in the cation-exchange separation of divalent cations in IC, to reduce

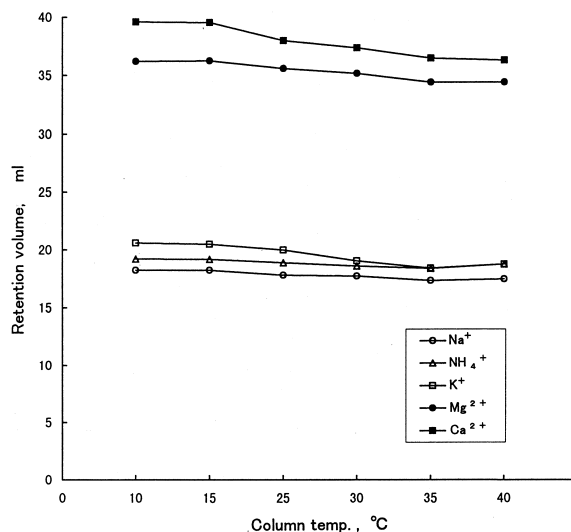


Fig. 4. Effect of column temperature on retention volumes of mono- and divalent cations. Eluent: 0.75 mM H_2SO_4 –5% aqueous methanol. Other chromatographic conditions as in Fig. 1.

retention by partial complexation with the analytes. Fig. 5 shows the effect of the addition of tartaric acid at different concentrations to an eluent comprising 0.75 mM H_2SO_4 and 5% methanol in water. Retention volumes of the monovalent cations decreases slightly due to the increased eluent pH, whilst the retention volumes of the divalent cations decreases with increasing the concentration of tartaric acid due to the increased complexation of the analytes. Similar chromatographic behavior is obtained using citric acid and EDTA which acted as the complexing ligands upon addition to the eluent.

The optimal range of eluent compositions for the cation-exchange separation of mono- and divalent cations is found to be 1–2 mM tartaric acid in 0.5–1.0 mM H_2SO_4 and 5–10% methanol. Fig. 6 shows the separation obtained using an eluent of 0.75 mM H_2SO_4 –2 mM tartaric acid–7.5% aqueous methanol. A reasonable separation and indirect conductimetric detection is achieved in 25 min.

3.3. Analytical performance parameters

Calibration graphs of peak area versus concentration are linear over the concentration range 0.02–0.4 mM for both the mono- and divalent cations. The detection limits at $S/N=3$ are ca. 0.1 μM for

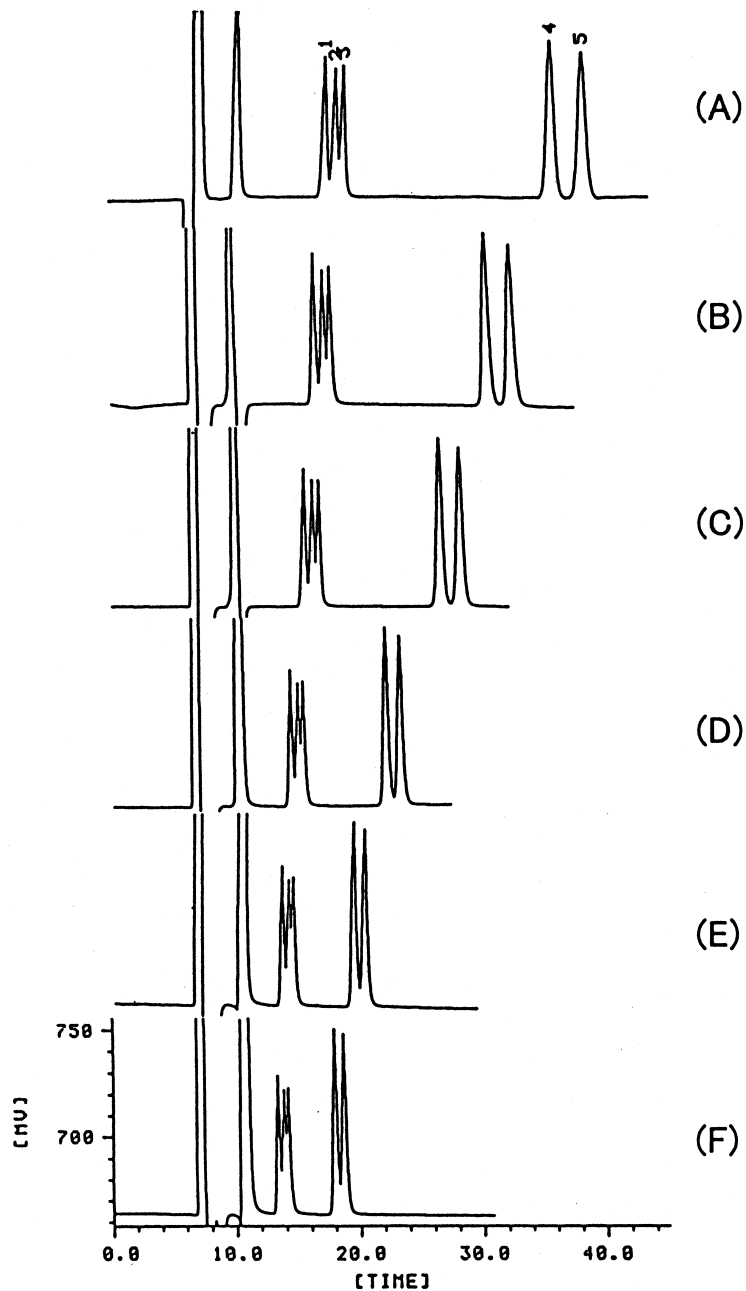


Fig. 5. Effect of tartaric acid in the eluent on retention volumes of mono- and divalent cations. Eluent: 0.75 mM H_2SO_4 -5% aqueous methanol-(0–4 mM) tartaric acid. Column temperature: 25°C. Tartaric acid concentration: A=0 mM, B=0.5 mM, C=1 mM, D=2 mM, E=3 mM, F=4 mM; 1= Na^+ , 2= NH_4^+ , 3= K^+ , 4= Mg^{2+} , 5= Ca^{2+} . Other chromatographic conditions as in Fig. 1.

monovalent cations and ca. 0.05 μM for divalent cations. Although the eluent background conductivity is relatively high (ca. 692 $\mu\text{S}/\text{cm}$) because of

the use of an acidic eluent, these detection limits are suitable for application to various acid rain and related natural waters. The reproducibility of the

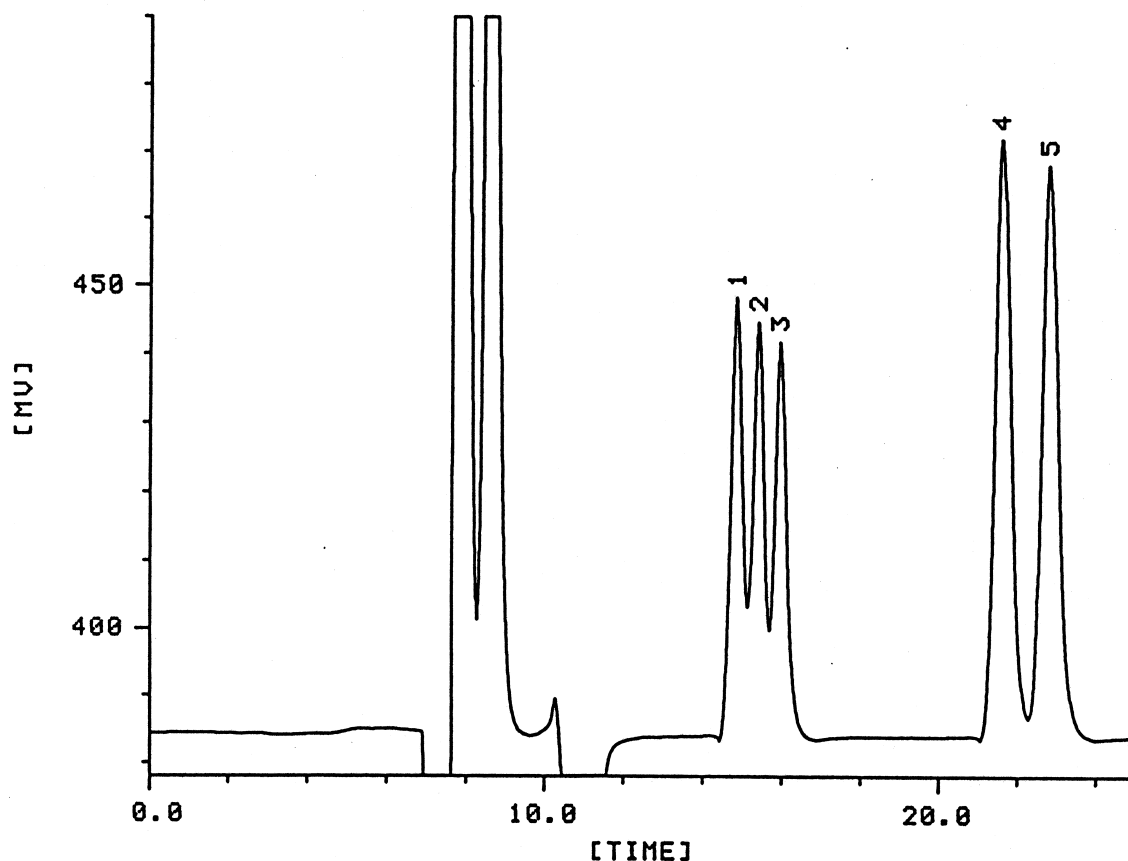


Fig. 6. Simultaneous cation-exchange chromatographic separation of mono- and divalent cations by elution with a 0.75 mM H_2SO_4 , 2 mM tartaric acid and 7.5% aqueous methanol on an anion-exclusion column. 1= Na^+ , 2= NH_4^+ , 3= K^+ , 4= Mg^{2+} , 5= Ca^{2+} . Other chromatographic conditions as in Fig. 1.

method is 0.05–0.11% relative standard deviation (R.S.D.) for the retention volume and 0.35 to 0.54% R.S.D. for the peak area ($n=6$).

3.4. Application to acid rain and related natural waters

The previously discussed method is applied to the simultaneous determination of mono- and divalent cations in a range of natural water samples of differing pH values. Fig. 7A shows the separation of the cations in an acid rain water (pH 4.7) from rain cloud transported from central China to central Japan by the jet stream, whilst Fig. 7B shows the analysis of a brown forest soil water of pH 4.9 (5 g soil/100

ml rain water). A satisfactory simultaneous separation of mono- and divalent cations is achieved and it was found that both samples contained all five cations.

Next, this method is applied to the simultaneous determination of the mono- and divalent cations in several natural waters with neutral pH (pH 6.9–7.2). These samples include mountain forest soil water, river water, lake water and underground water collected in or near the city of Nagoya in central Japan. The chromatograms obtained showed satisfactory separations for all natural water samples tested, and a typical example (in this case, for lake water) is shown in Fig. 8.

The cation-exchange elution behavior of Fe^{3+} ,

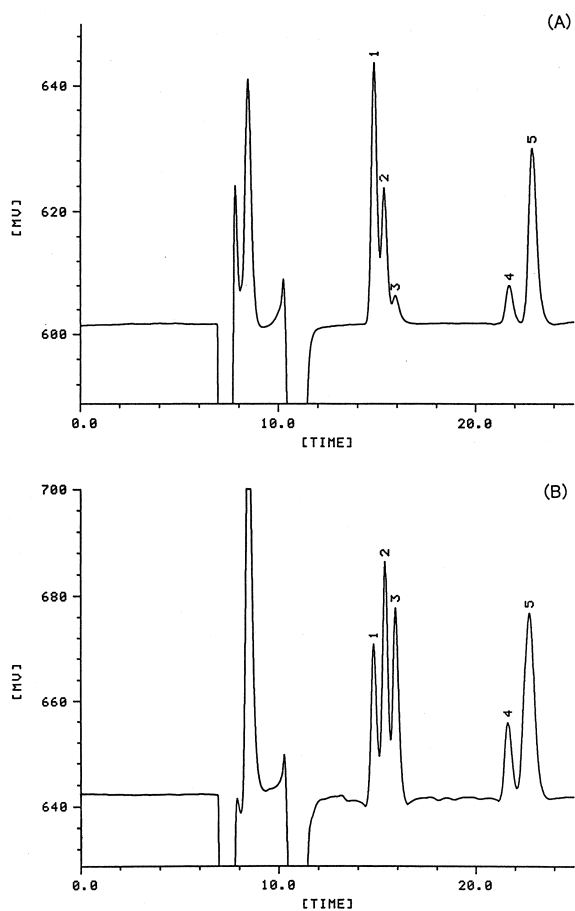


Fig. 7. Simultaneous cation-exchange separation of mono- and divalent cations in (A) acid rain water of pH 4.7 and in (B) brown forest soil water of pH 4.9. 1=Na⁺, 2=NH₄⁺, 3=K⁺, 4=Mg²⁺, 5=Ca²⁺. Other chromatographic conditions as in Fig. 6.

Al³⁺, Mn²⁺ in the soil water extracted by acid rain water at elevated concentrations will be the subject of future work.

4. Conclusions

A simple, convenient and economical non-suppressed IC method for the simultaneous determination of mono- and divalent cations is presented which uses a sulfuric acid–tartaric acid–aqueous methanol eluent. The method uses a cation-exchange mechanism on a commercially available anion-exclu-

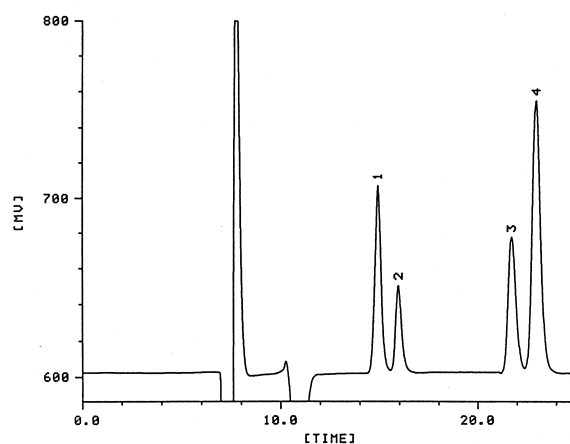


Fig. 8. Simultaneous cation-exchange separation of mono- and divalent cations in lake water at neutral pH. 1=Na⁺, 2=K⁺, 3=Mg²⁺, 4=Ca²⁺. Other chromatographic conditions as in Fig. 6.

sion column packed with polymethacrylate-based weakly acidic cation-exchange resin in the H⁺ form and indirect conductimetric detection. The method is successfully applied to the simultaneous determination of mono- and divalent cations in acid rain water and some related natural waters.

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