

Ion chromatographic separation of hydrogen ion and other common mono- and divalent cations

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Abstract

We introduced an approach to the ion chromatographic determination of common mono- and divalent cations including hydrogen ion and demonstrated the ability of a C₃₀ column dynamically coated first with dodecylsulfate and then with 18-crown-6 ether to separate the cations by ion-exchange mechanism. Using an ethylenediamine solution containing a small concentration of 18-crown-6 ether and lithium dodecylsulfate at pH 6.2 as eluent, the cations were eluted in the order Li⁺ < Na⁺ < NH₄⁺ < H⁺ < K⁺ < Mg²⁺ < Ca²⁺ with symmetrical peaks. The conductivity vs. concentration plots were linear about three orders of magnitude, from millimolar to micromolar; and the detection limits were all <0.6 μM. Rainwater was analyzed directly using this ion chromatographic system with satisfactory results.

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1. Introduction

Ion chromatography (IC) can provide a convenient means to separate cations, and there have been a number of papers showing the usefulness of IC on the simultaneous determination of lithium (Li⁺), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), magnesium (Mg²⁺) and calcium (Ca²⁺) ions [1–8]. Recently, some studies [9–14] have been carried out in the field of ion chromatographic determination of hydrogen ion (H⁺), the ordinary but very important cation, to be as a supplemental means for the two most frequently used detection methods, acid–base titration and potentiometry [15–17]. Dasgupta and co-workers [9] demonstrated the ability of sulfonated polystyrenedivinylbenzene-based stationary phases to separate H⁺ and other monovalent cations (Li⁺, Na⁺, NH₄⁺ and K⁺) using a neutral salt solution containing a small concentration of the corresponding acid, e.g. sodium ethanesulfonate, as eluent based on cation exchange with high sensitivity to small changes in H⁺ concentration down to low mM-levels. Hu et al. employed

octadecylsilyl-silica (ODS) stationary phases coated with dodecylsulfate using acidified LiCl [10] and EDTA-2K [11] solutions as eluents, respectively, to separate monovalent cations, H⁺, Li⁺, Na⁺, NH₄⁺ and K⁺, with detection limits of H⁺ down to μM-levels. The same authors reported an IC method for separating H⁺ together with divalent cations, Mg²⁺, Ca²⁺ and Ba²⁺, on an ODS stationary phase coated with a phosphor-betaine type zwitter ionic surfactant, n-hexadecylphosphocholine, using pure water as eluent [12].

The aim of this study was to establish an effective IC method to complete the separation of H⁺ together with other mono- and divalent cations. Since first introduced by Sander and Wise [18] in 1987, C₃₀ column has been widely used in the determinations of carotenoids, retinoids, tocopherols, phosphatidylserine molecular species and inorganic anions by liquid chromatography (LC) based on its better sensitivity and selectivity [19–22]. Our interest was its application to the analysis of the mono- and divalent cations including H⁺. We modified a C₃₀ column by saturating it with lithium dodecylsulfate (Li-DS) and 18-crown-6 ether solutions, on which the simultaneous separation of Li⁺, Na⁺, NH₄⁺, H⁺, K⁺, Mg²⁺ and Ca²⁺ seven cations was achieved readily using a weak acidified ethylenediamine solution containing small concentration of Li-DS and 18-crown-6 as eluent.

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2. Experimental

2.1. Chemicals

All reagents were of analytical-reagent grade, purchased from Wako (Osaka, Japan) and were dissolved in house-distilled water ($\geq 18 \text{ M}\Omega \text{ cm}$) deionized through an Aquarius GS-500 system (Advantec Toyo Kaisha, Ltd., Japan). Stock standard solutions of the cations were prepared by dissolving appropriate amounts of hydrochloric acid, lithium chloride, potassium chloride, sodium nitrate, ammonium chloride, calcium chloride and magnesium sulfate at a concentration of 0.10 M. These were diluted as necessary (using boiled deionized water stored in a closed container to prepare the standard solutions with different pH values). Lithium dodecylsulfate (Li-DS) and 18-crown-6 ether were used for coating the columns and as the components of eluents. The reason for adding a low concentration of 18-crown-6 ether and dodecylsulfate to the eluent was to replenish some that are lost due to poor binding stability on the C_{30} surface. Ethylenediamine, ethylenediaminetetraacetic acid-dilithium salt dihydrate (EDTA-2Li) and lithium chloride were used for preparing the eluents. Hydrochloric acid was used for adjusting the pH value of eluent.

2.2. Instrumentation

Experiments were carried out on a Tosoh HPLC System (Tokyo, Japan) consisting of a data processing system, a DP-8020 eluent delivery pump, a CM-8020 conductimetric detector, a CO-8020 column oven, an SD-8022 degasser and an SIL-6B injector equipped with a 100 μl sample loop. A HM-14P pH meter (TOA Electronics, Tokyo, Japan) was for determining pH values of solutions used in the experiments and rainwater samples.

2.3. Preparation of stationary phases

The column used in this study was a Develosil C_{30} -UG-5 column (15 cm \times 4.6 mm i.d., Nomura Chemical Co., Seto, Japan). Two types of stationary phases coated with dodecylsulfate (DS) and 18-crown-6 ether were prepared. The first was a DS-(18)crown(6)-coated C_{30} stationary phase prepared by first passing about 100 ml of 40 mM Li-DS solution through the column, and then passing about 100 ml of 10 mM 18-crown-6 ether solution; the second was DS-coated C_{30} stationary phase prepared by only passing only about 100 ml of 40 mM Li-DS solution. In the preparation, the flow-rate was 0.50 ml/min and the column temperature was maintained at 25 $^{\circ}\text{C}$.

2.4. Rainwater analysis

Quality control procedures [23] were employed in the collection of rainwater samples. Three replicate samples were

collected with the volume of 20 ml, and a pH meter was used to measure their pH values directly. The collected rainwater samples were filtered through 0.30 μm nylon-66 membranes prior to direct analysis. They were analyzed under the optimized chromatographic conditions: the eluent was an aqueous solution containing 4.0 mM ethylenediamine, 0.1 mM 18-crown-6 ether and 0.05 mM Li-DS, and its pH value was adjusted to 6.2 by using HCl solution; the gain of the conductimetric detector was 0.1 $\mu\text{S}/\text{cm}$ and the response was STD (response time 1 s); the flow-rate was 1.0 ml/min; the baseline drift was minimized by keeping the column temperature at 30 $^{\circ}\text{C}$, and the instrument was equilibrated for about 30 min prior to use.

3. Results and discussion

3.1. Principles of separation and determination

Dynamic coating a reverse-phase ODS with ionic surfactant, e.g. dodecylsulfate, is a well-established and convenient way to create stationary phases with sulfonated groups for separating cations. An acidified ethylenediamine solution was chosen as eluent to separate Li^+ , Na^+ , NH_4^+ , K^+ , H^+ , Mg^{2+} and Ca^{2+} because it could supply divalent eluent cations with stronger elution ability. When the eluent was passing by the column, the ionized ethylenediamine ions became bound to the sulfonated groups on the stationary phase and an electric double-layer (EDL) was formed. As a sample was injected into the column, the cations in the sample displaced a corresponding number of the ionized ethylenediamine ions from the EDL, that was to say, they were retained by the stationary phase. The retained cations were then eluted by further ionized ethylenediamine ions supplied by the eluents. To verify the separation of H^+ on the DS-coated C_{30} stationary phase, a series of distilled water samples with different pH values adjusted using HCl solution were injected. As shown in Fig. 1, the height and area of peak 1 increased when the pH values of the injected samples decreased, which demonstrated that peak 1 was the response of H^+ . Fig. 2A was a chromatogram of the cations separated in the order $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ = \text{K}^+ < \text{H}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$ on the DS-coated C_{30} stationary phase using only an acidified ethylenediamine solution as eluent. The dodecylsulfate was partly protonated by H^+ ions and therefore a stronger retention of H^+ ion could be obtained, which could result in the separation of H^+ from other monovalent cations [10]. NH_4^+ was eluted together with K^+ because of their similar ionic radius [24].

To separate NH_4^+ and K^+ , DS-(18)crown(6)-coated C_{30} stationary phase was employed based on that 18-crown-6 ether could react with K^+ to form complex cation because of its selective complexation of potassium [25], which could result in the good resolution between K^+ and NH_4^+ . As shown in Fig. 2B, K^+ was eluted after NH_4^+ and H^+ .

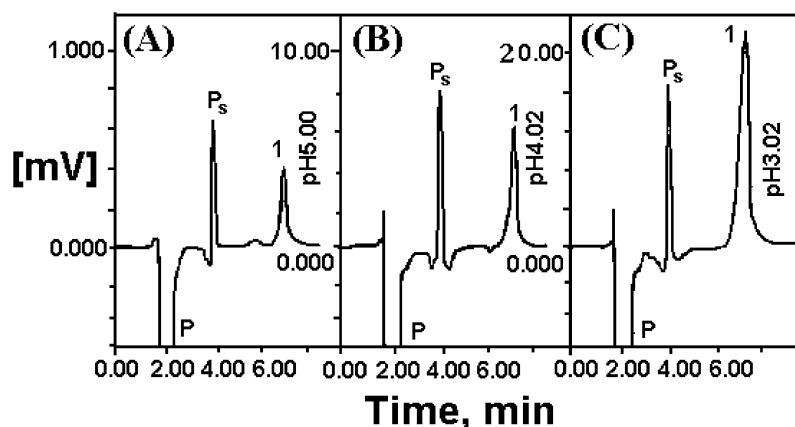


Fig. 1. Chromatograms of distilled water samples with different pH values on the DS-coated C_{30} stationary phase using only a 2.0 mM ethylenediamine solution (pH 6.2) as eluent. (A) pH 5.00; (B) pH 4.02; (C) pH 3.02. Peaks: p1, eluent dips; ps, vacancy peak; and 1, H^+ peak. Column, a Develosil C_{30} -UG-5 column; column temperature, $30^\circ C$; flow-rate, 1.0 ml/min; injection volume: 100 μ l.

The limiting molar ionic conductivities (λ° , $cm^2/\Omega mol$, $25^\circ C$) of the interested analytes are as follows [26,27]: Li^+ , 38.7; Na^+ , 50.1; NH_4^+ , 73.5; K^+ , 73.5; H^+ , 350; Mg^{2+} , 53.3; Ca^{2+} , 59.8. In conductivity detection of ion chro-

matography, the peak direction (polarity) of analytes is related to the λ° value of eluent, and it is irrespective of their concentration. As could be seen in Fig. 2, the chromatographic peaks of Li^+ , Na^+ , Mg^{2+} and Ca^{2+} were negative and that of NH_4^+ , K^+ and H^+ were positive, which demonstrated the λ° value of ethylenediamine (En) was between 59.8 and 73.5 (as references, $\lambda^\circ_{CH_3NH_3^+} = 58.7$ and $\lambda^\circ_{(CH_3)_2NH_2^+} = 51.9$). The significant difference between $\lambda^\circ_{H^+}$ and λ°_{En} should result in the response (peak areas) of H^+ to be much larger in the chromatograms than that of other cations when equal molar amounts were injected; however, we did not observe this. This could be explained by the ionization equilibria between the target H^+ and the weak acidified ethylenediamine solution used as eluent, $En + H^+ \leftrightarrow EnH^+$ and $EnH^+ + H^+ \leftrightarrow EnH_2^{2+}$; The peak detected by conductivity or shown in chromatograms did not represent the total H^+ ions.

A positive vacancy peak (p_s) with the same retention time as Li^+ (negative peak) could be observed and verified by the experiments when injecting some samples containing only cations of Li^+ or Na^+ with different concentration and a deionized water sample without adding any reagent, respectively, under the same chromatographic conditions (Fig. 3). Because it was superimposed upon the analytical peak for lithium, and because its magnitude was dependent upon the cation composition of the sample, quantitative analysis of lithium in such a system was affected. Its effect on the determination of Li^+ will be discussed in the following section of analysis performance.

3.2. Selection of eluent and column

Some different salts in the acidified eluent have been used to separate Li^+ , Na^+ , NH_4^+ , K^+ , H^+ , Mg^{2+} and Ca^{2+} ions. When using $LiNO_3$, $NaNO_3$ and KNO_3 solutions ($\approx pH 4.1$) as eluents, Mg^{2+} and Ca^{2+} could not be eluted because of the weak elution ability of Li^+ , Na^+ and K^+ ions and strong retention of Ca^{2+} and Mg^{2+} ions.

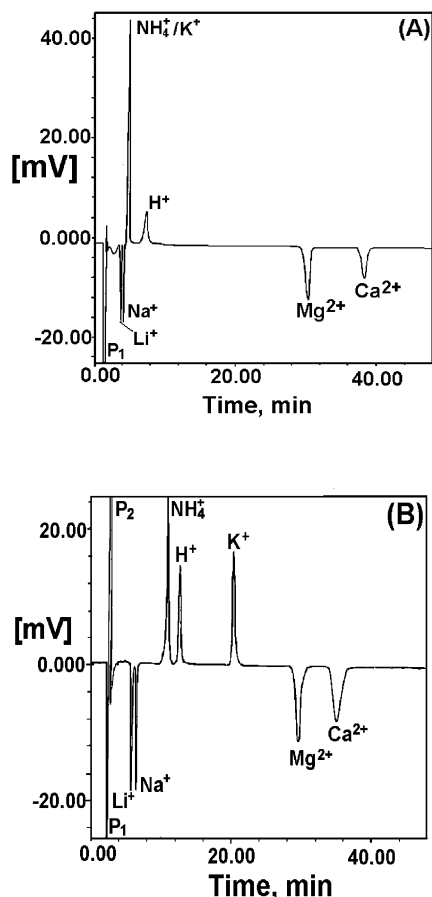


Fig. 2. Chromatograms of the ions on (A) the DS-coated C_{30} stationary phase and (B) the DS-(8)crown(6)-coated C_{30} stationary phase using only a 2.0 mM ethylenediamine solution (pH 6.2) as eluent. Peaks: p1 and p2, eluent dips; sample, a standard solution mixture of 0.25 mM the 7 cations. Others as in Fig. 1.

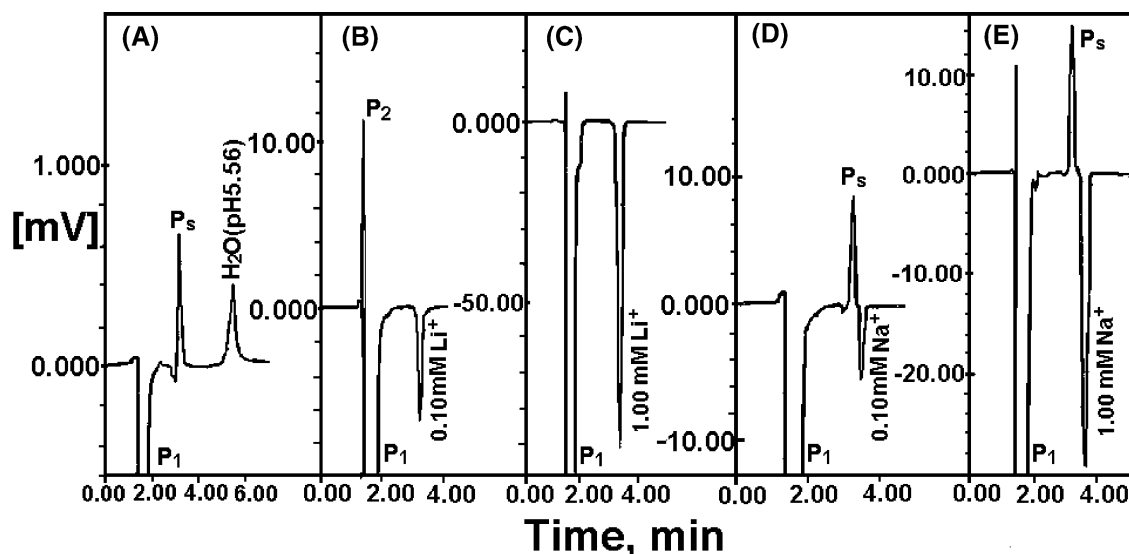


Fig. 3. Chromatograms of (A) H₂O; (B) 0.10 mM Li⁺; (C) 1.00 mM Li⁺; (D) 0.10 mM Na⁺; and (E) 1.00 mM Na⁺ on the DS-(8)crown(6)-coated C₃₀ stationary phase using a 4.0 mM ethylenediamine solution containing 0.05 mM Li-DS and 0.1 mM 18-crown-6 ether (pH 6.2) as eluent. Peaks: p₁ and p₂, eluent dips; and p_s, vacancy peak. Others as in Fig. 1.

When using an EDTA-2Li solution (\approx pH 4.8) as eluent, six cations were eluted in the order of H⁺ < Na⁺ < NH₄⁺ < K⁺ < Ca²⁺ < Mg²⁺. The special order (H⁺ was first eluted, and Ca²⁺ was eluted before Mg²⁺) was attributed to the presence of EDTA (H₂Y²⁻) in the eluent, which could accelerate the elution of H⁺ as the anionic form (H₃Y⁻) based on the reaction, H₂Y²⁻ + H⁺ \leftrightarrow H₃Y⁻, and form a more stable complex with Ca²⁺ [28]. However, both Ca²⁺ and Mg²⁺ gave asymmetrical peaks, which demonstrated that this eluent was not optimal. In this work, an acidified ethylenediamine solution was chosen as the eluent in order to elute divalent cations within a reasonable amount of time.

When using an acidified ethylenediamine eluent the alkali metal ions and ammonium ion however co-eluted due to their weak retention on some stationary phases, i.e. using DS-coated monolithic silica ODS columns. To increase the retention of the alkali metal ions and ammonium ion C₃₀ columns were used in this work. Under the specified conditions the seven cations were separated with symmetrical peak shapes as shown in Fig. 2B.

3.3. Roles of 18-crown-6 and Li-DS

Addition of 18-crown-6 ether to the eluent could result in a significant improvement in the resolution between potassium and ammonium. However, Fig. 4A showed that when using an acidified ethylenediamine solution containing mM-grade of 18-crown-6 ether as eluent, although NH₄⁺ and K⁺ were separated well on the DS-coated C₃₀ stationary phase, the shape of H⁺ peak was poor, possibly from the stationary phase not being in equilibrium with the eluent under the operating conditions.

In order to get a satisfactory H⁺ peak, we tried the separation on the DS-(18)crown(6)-coated stationary phase using only an acidified ethylenediamine solution as eluent. As shown in Fig. 4B, the separation of NH₄⁺ and K⁺ was improved, moreover, the shape of H⁺ peak was sharp and symmetric. The reason could be attributed to the weak interaction between hydrogen ion (analyte) and 18-crown-6 ether with low concentration on the stationary phase. Additionally, the unknown peak, p₃, in Fig. 4A disappeared when using DS-(18)crown(6)-coated C₃₀ stationary phase. However, as shown in Fig. 5, the retention time of K⁺ decreased over time, which meant some 18-crown-6 ether on the stationary phase had been lost from the column. Therefore, it was necessary to maintain a certain concentration of 18-crown-6 ether in the eluent to replace any 18-crown-6 ether lost from the column. Experiments on the effect of concentration of 18-crown-6 ether in the eluent, on retention time of K⁺ and responses (peak height) of H⁺ showed that, when the concentration was more than 0.05 mM, the relative change of retention time of K⁺ was small; when the concentration was <0.25 mM the peak height response of H⁺ was stable. Hence 0.1 mM 18-crown-6 ether was used in this work.

A certain concentration of DS was maintained in the eluent to replace any -DS lost from the column. Choosing Li-DS was because of the low ion-exchange ability of Li⁺. It was only as a supplement to the stationary phase. The effects of its concentration on the response (peak area) of the cations were estimated, and the results showed that these peak areas remained almost unchanged when the Li-DS concentration was between 0.02 and 0.2 mM. Consequently, 0.05 mM Li-DS was selected as an optimum concentration in this study.

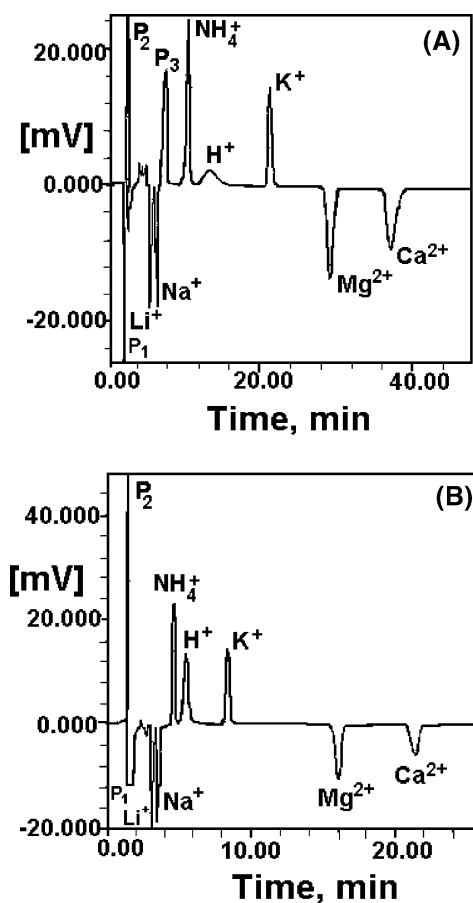


Fig. 4. Chromatograms of the separation of the cations on (A) DS-coated C₃₀ stationary phase using a 2.0 mM ethylenediamine solution containing 1.0 mM 18-crown-6 ether (pH 6.2) as eluent; and (B) DS-(8)crown(6)-coated C₃₀ stationary phase using a 4.0 mM ethylenediamine solution (pH 6.2) as eluent. Peaks: p₁ and p₂, eluent dips; p₃, unknown peak; sample, a standard solution mixture of 0.25 mM the seven cations. Others as in Fig. 1.

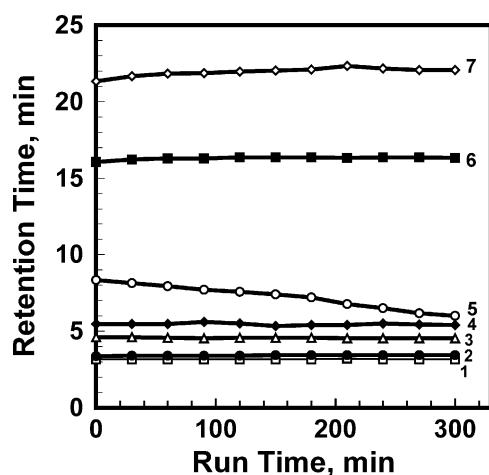


Fig. 5. Changes in retention time of the cations with the run time going on the DS-(8)crown(6)-coated C₃₀ stationary phase using a 4.0 mM ethylenediamine solution (pH 6.2) as eluent. Serial number: (1) Li⁺, (2) Na⁺, (3) NH₄⁺, (4) H⁺, (5) K⁺, (6) Mg²⁺ and (7) Ca²⁺. Others as in Fig. 1.

3.4. Effects of ethylenediamine concentration, eluent pH value, flow-rate and column temperature

With increasing the concentration of ethylenediamine in the eluent, the retention time of H⁺, Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ ions all decreased and background conductivity of the eluent increased. When the concentration exceeded 4.5 mM, the resolution between peaks of H⁺ and NH₄⁺ became declined, and higher background conductivity of eluent decreased the detection sensitivity. Therefore, 4.0 mM ethylenediamine was chosen as optimal, based on a compromise between the resolution, run time and detection sensitivity.

The effect of eluent pH value on the determination was investigated. The detection responses for a series of these cations as analytes when the eluent pH value was varied over the range 4.0–6.8. For the detector response of H⁺, it increased slightly from pH 5.3 and up to pH 6.5 with a maximum between 6.2 and 6.5, after which a decrease in response was observed; for the detector responses of divalent cations Mg²⁺ and Ca²⁺, they decreased from pH 4.0 and remained small changes between 5.6 and 6.2, after which they decreased again; for the detector responses of monovalent cations Li⁺, Na⁺, NH₄⁺ and K⁺, they were relatively constant over the eluent pH range of 4.0–6.8. An eluent pH of 6.2 was selected, at which satisfactory responses of these mono- and divalent cations were obtained.

Compared to other types of liquid chromatographic separations, ion-exchange separations often exhibit unique dependence on separation efficiency on eluent flow-rate since the ion exchange process often exhibits slow kinetics. Although increasing the flow-rate could shorten the run time, experiments showed that peak tailing became larger when flow rate was increased and the separation efficiency was therefore decreased. Here, a flow-rate 1.0 ml/min was chosen, at which all of the target ions could be separated efficiently with sharp and symmetric peak shape.

Since exchange kinetics improves with temperature, the retention time of cations decreased when column temperature increased. However, the DS-(18)crown(6)-coated C₃₀ stationary phase was unstable at a relative high column temperature. Column temperature was therefore kept at 30 °C.

3.5. Analysis performance

Analyses were carried out under the optimized chromatographic conditions and reproducibility was estimated by making replicate injections ($n = 7$) of a mixture of rain-water sample and a standard solution containing H⁺, Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ ions. The relative standard deviation (R.S.D.) of peak area of these cations were all <1.2%. The column-to-column reproducibility of the DS-(18)crown(6)-coated C₃₀ stationary phase was estimated by coating the column three times and injecting a mixture of the seven cations five times. The R.S.D. of peak area of these cations were all <1.3%. The DS-(18)crown(6)-coated

Table 1
Linearity and detection limits of the cations with conductimetric detection^a

Cation	Correlation coefficient (r^2)	Linear range (μM)	Detection limit ^b (μM)
Li ⁺	0.9998	60–4000	0.2
Na ⁺	0.9995	30–4000	0.5
NH ₄ ⁺	0.9979	5.0–4000	0.1
H ⁺	0.9963	10–2000	0.2
K ⁺	0.9978	5.0–4000	0.1
Mg ²⁺	0.9997	5.0–5000	0.1
Ca ²⁺	0.9960	5.0–5000	0.1

^a Chromatographic conditions as in Fig. 6.

^b Calculated using 5σ (σ represents the standard deviation of a blank solution, $n = 7$).

stationary phase was found to be stable during at least 1-month (operated daily for about 8 h), with R.S.D. for peak area and peak height all being <3.3%.

Calibration linearity for conductivity detection of H⁺, Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ ions was found to extend over about three orders of magnitude, from millimolar to micromolar; the correlation coefficient was better than 0.9960 for each plot; and the detection limits calculated by using 5σ were all <0.9 μM (σ represents the standard deviation of a blank solution, $n = 7$). The details were shown in Table 1. The relatively high detection limits and narrow linear relationship ranges of Li⁺ and Na⁺ were caused by the effects of the vacancy peak, p_s; however, its existing did not affect the determination of others cations.

3.6. Applications

Fig. 6 shows chromatograms of a spiked rainwater sample. The recoveries obtained with this method were tested by the analysis of a spiked rainwater sample and replicate injections ($n = 7$); and they were between 96 and 103%. Table 2 compares the data obtained by this method with those obtained using a potentiometric pH meter and the traditional IC method [1]. Good agreement was obtained between the methods.

Table 2
Content of the cations ions in rainwater (mean values of seven determinations)

Sample	Detection by this method		Detection by other methods	
	Detected (μM)	R.S.D. (%)	Mean (μM)	R.S.D. (%)
Li ⁺	0.00	2.4	^a 0.00	2.5
Na ⁺	97.0	2.5	^a 100	2.7
NH ₄ ⁺	123	2.1	^a 121	1.9
H ⁺	113	2.4	^b 110	4.1
K ⁺	18.6	2.4	^a 190	2.7
Mg ²⁺	15.4	2.3	^a 15.6	2.1
Ca ²⁺	19.0	2.5	^a 18.7	2.9

^a Determined by a traditional cation-exchange IC.

^b Determined by a potentiometric pH meter.

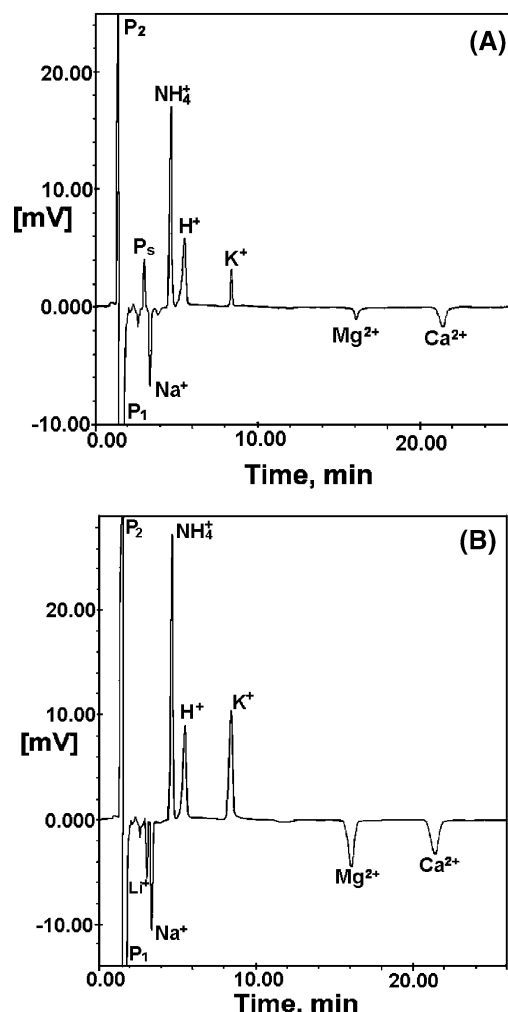


Fig. 6. Chromatograms of (A) rainwater sample and (B) rainwater sample + standard solution (mixture of 0.10 mM the seven cations) on the DS-(8)crown(6)-coated C₃₀ stationary phase using a 4.0 mM ethylenediamine solution containing 0.05 mM Li-DS and 0.1 mM 18-crown-6 ether (pH 6.2) as eluent. Peaks p₁ and p₂, eluent dips; p_s, vacancy peak. Others as in Fig. 1.

4. Conclusions

This work described an IC system for determining H⁺, Li⁺, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺ ions simultaneously and sensitively on the DS-(8)crown(6)-coated C₃₀ stationary phase using a 4.0 mM ethylenediamine solution with pH 6.2 containing 0.1 mM 18-crown-6 ether and 0.05 mM Li-DS as eluent. The approach resulted in a separation of the seven cations in real water samples within 22 min with μM -levels of detection.

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