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Journal of Chromatography A, 997 (2003) 191–197

JOURNAL OF
CHROMATOGRAPHY A

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Selective determination of ammonium ions by high-speed ion-exclusion chromatography on a weakly basic anion-exchange resin column

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Abstract

This paper describes an ion-exclusion chromatographic system for the rapid and selective determination of ammonium ion. The optimized ion-exclusion chromatographic system was established with a polymethacrylate-based weakly basic anion-exchange resin column (TSKgel DEAE-5PW) as the separation column, an aqueous solution containing 0.05 mM tetramethylammonium hydroxide (pH 9.10) as eluent with conductimetric detection for the analyte determination. Under the optimum chromatographic conditions, ammonium ion was determined within 2.3 min with a detection limit ($S/N=3$) better than 0.125 μM . Ammonium ion in rain and river waters was precisely determined using this ion-exclusion chromatographic system.

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Keywords: Water analysis; Environmental analysis; Ammonium ions; Inorganic cations; Tetrabutylammonium hydroxide

1. Introduction

Ammonium ion (NH_4^+) is the most serious pollutant causing eutrophication of aqueous environments. Its determination is usually carried out by colorimetric methods, such as nesslerization and phenate methods [1]. However, these methods suffer from several chemical interferences and require distillation step. Ion chromatography (IC) established by Small et al. [2] has been regarded as one of the most

suitable methods for determining NH_4^+ ions in environmental waters, and a lot of reports have been published on this topic [3–6].

As one of the important parts in IC, ion-exclusion chromatography has already been used for the separation of inorganic and organic weak basic compounds, i.e., NH_4^+ ion, aliphatic, aromatic and ethanolamines [7–10]. The polystyrene–divinylbenzene-based with high-capacity strongly basic anion-exchange resin in the OH^- form was usually used in ion-exclusion chromatography to separate cations, and Haddad et al. discussed the factors affecting retention of basic solutes on this kind of stationary phase using dilute sodium hydroxide as eluent [9].

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Tanaka et al. [8] reported an ion-exclusion chromatography method for separating NH_4^+ ion from other cations on an anion-exchange resin in the OH^- form using only water as an eluent, demonstrating that NH_4^+ ion was separated by ion-exclusion as NH_4OH formed by anion-exchange and monitored with a flow coulometric detector for the OH^- detection and/or with a conductimetric detector.

The aim of this study is to establish an efficient ion-exclusion chromatography method for the determination of NH_4^+ ion selectivity and rapidly. We found that the dissociation on the resin phase was easy to control on a weakly basic anion-exchange resin column (Tosoh TSKgel DEAE-5PW) when eluting with organic solvent or basic compounds. Therefore, this column demonstrated the effectiveness for improving the peak resolution of NH_4^+ ion.

The proposed ion-exclusion chromatography method is simple, sensitive and rapid to determine NH_4^+ ion from alkali and alkaline earth metal ions with conductimetric detection. This method was applied to the determination of NH_4^+ ion in rain and river water samples with satisfactory results.

2. Experimental

2.1. Apparatus

The ion chromatograph (Tosoh, Tokyo, Japan) consisted of a Tosoh LC-8020-Model II chromatographic data processor, a DP-8020 dual pump operated at flow-rate of 1 ml/min, an SD-8022 on-line degasser, a CO-8020 column oven operated at 40 °C and a CM-8020 conductimetric detector. The injection volume was 100 μl .

2.2. Separation column

Two kinds of separation columns were used in this study. One was a polymethacrylate-based weakly basic anion-exchange resin in the OH^- form, TSKgel DEAE-5PW packed with 10 μm particles (75 \times 7.5 mm I.D.), and the other was a polystyrene-divinylbenzene-based strongly basic anion-exchange resin in the OH^- form, TSKgel SAX packed with 5 μm particles (75 \times 7.5 mm I.D.). The specially ordered separation columns were packed by Tosoh.

The columns were equilibrated thoroughly with the eluent before chromatographic runs (ca. 30 min).

2.3. Reagents

All reagents were of analytical-reagent grade, purchased from Wako (Osaka, Japan) and were dissolved in distilled and deionized water for the preparation of standard solutions and eluents. The stock solutions of alkali metal and alkaline earth metal ions, ammonium ion, and aliphatic amines used in this study were purchased from Wako and prepared by dissolving 0.1 M with distilled and deionized water. Appropriate amounts of LiOH, NaOH, KOH, NH_4OH , $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ at a concentration of 0.1 M each were diluted with water as necessary. Aliphatic amines (methylamine, ethylamine, propylamine, butylamine, pentylamine, triethanolamine and triethylamine) were dissolved to 0.1–0.2 mM in water.

3. Results and discussion

3.1. Choice of separation column

In this study, the separation performance of a strongly basic anion-exchange resin (TSKgel SAX) and of a weakly basic anion-exchange resin (TSKgel DEAE-5PW) was compared in terms of the peak resolution of NH_4^+ ion separated from alkali and alkaline earth metal ions on ion-exclusion chromatography. As shown in Fig. 1, the ion-exclusion chromatographic separation of NH_4^+ ion was obtained by elution with pure water at 1.0 ml/min. Although a reasonable ion-exclusion chromatographic separation of NH_4^+ ion from alkali and alkaline earth metal ions was achieved on both separation columns, the peak resolution of NH_4^+ ion using a weakly basic anion-exchange resin column (Fig. 1B) was much better than that using a strongly basic anion-exchange resin column (Fig. 1A).

A weakly basic anion exchanger (tertiary amine functional group) on the resin surface is partially protonation or dissociation by hydroxide ion in water eluent. Therefore, weak bases such as NH_4^+ ion are easily permeated/penetrated the resin surface of a weakly basic anion-exchange column rather than in a

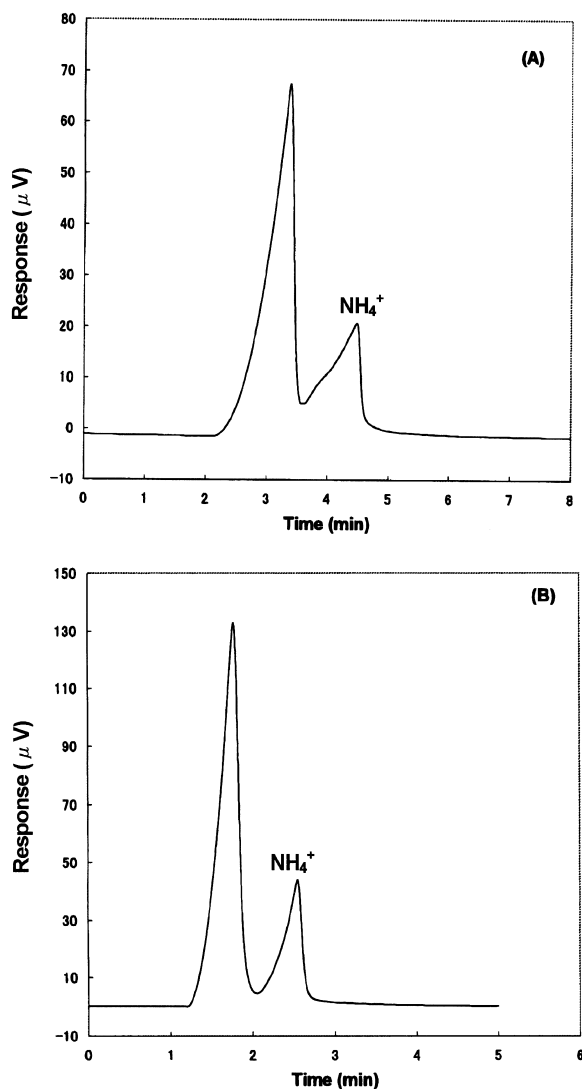


Fig. 1. Typical chromatograms of NH_4^+ ion in standard mixtures of alkali and alkaline earth metal ions by elution with water using strongly and weakly basic anion-exchange resin columns. Columns: (A) TSKgel SAX (75×7.5 mm I.D.) and (B) TSKgel DEAE-5PW (75×7.5 mm I.D.). Column temperature: 40°C . Eluent flow-rate: 1.0 ml/min. Peak identities: (first peak) Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} (0.05 mM for each solute), (second peak) NH_4^+ (0.1 mM).

strongly basic anion-exchange column which is ionized in the wide pH range. Consequently, a weakly basic anion-exchange resin TSKgel DEAE-5PW was judged to be the better separation column for the selective separation of NH_4^+ ion.

3.2. Retention volumes and distribution coefficients for basic compounds

Retention behaviors of several basic compounds eluting with water using a weakly basic anion-exchange resin are listed in Table 1, together with their $\text{p}K_{\text{b}1}$ values. The retention volumes (V_{R}) of alkali metal ions (Na^+ and K^+) were closely related to the column void volume (1.75 ml) since electrostatic repulsion from the positively charged amine functional groups in the separation column. The V_{R} values of alkaline earth metal ions (Ca^{2+} and Mg^{2+}) were slightly higher than those of alkali metal ions. These results can be explained by the extremely weak basicity and low solubility. The V_{R} of NH_4^+ ion and weak bases were higher than those of inorganic cations.

The distribution coefficient (K_{d}) values were calculated according to the following equation, which was given in previous reports [9,11,12]:

$$V_{\text{R}} = V_0 + K_{\text{d}}V_{\text{i}}$$

where V_{R} is retention volume, V_0 the column void volume and V_{i} the volume of liquid inside the resin in the column.

As summarized in Table 1, the K_{d} values of the cations tend to increase with increasing $\text{p}K_{\text{b}1}$ and/or hydrophobicity. Most of the K_{d} values of analyte

Table 1
Retention behavior of some basic compounds

Solute	$\text{p}K_{\text{b}1}$ ^a	V_{R} (ml) ^b	K_{d} ^b
KOH	-10.00	1.77	0.01
NaOH	-5.00	1.77	0.01
$\text{Ca}(\text{OH})_2$	2.43	1.84	0.04
$\text{Mg}(\text{OH})_2$	2.60	1.84	0.04
NH_4OH	4.75	2.63	0.40
Methylamine	3.34	2.63	0.40
Ethylamine	3.30	2.63	0.40
Propylamine	3.40	3.86	0.95
Butylamine	3.37	4.18	1.09
Pentylamine	3.37	5.52	1.70
Triethanolamine	6.24	3.78	0.91
Triethylamine	3.00	4.39	1.19
MeOH	15.00	3.97	1.00

^a Ref. [9].

^b K_{d} = Distribution coefficient. $V_{\text{R}} = V_0 + V_{\text{i}}K_{\text{d}}$; $V_0 = 1.75$ ml (LiOH), $V_0 + V_{\text{i}} = 3.97$ ml (MeOH), and $V_{\text{i}} = 2.22$ ml.

cations were between 0 and 1, but those of butylamine, pentylamine and triethylamine were higher than 1. This means that adsorption by the resin matrix is a side-effect due to the greater hydrophobic nature.

3.3. Effect of organic solvent

The pK_{b1} values of weak bases such as NH_4^+ ion or aliphatic amines are higher in water–organic solvent than in water [8]. In ion-exclusion chromatography of acids on a cation-exchange resin in the H^+ form, the V_R values are dependent on the pK_{a1} values [11,12]. Therefore, in ion-exclusion chromatography of NH_4^+ ion on an anion-exchange resin in the OH^- form, an increase of the pK_{b1} value of NH_4^+ ion can be expected to result in an increase of the V_R value.

Here, the effect of acetonitrile (MeCN) on the retention volumes of Na^+ and NH_4^+ ions and some aliphatic amines was investigated in the concentration range 0–40%. As can be seen in Fig. 2B, the retention volumes of aliphatic amines decreased with increase of MeCN concentration in the eluent. This tendency showed the same results even in the use of organic solvents as the eluent (e.g., methanol, propanol and butanol). The behaviors of aliphatic amines show a reduction in adsorption effect on the resin phase in the column because the solubilities of the amines are increased with increasing concentration of organic solvents. On the other hand, the retention volume of the NH_4^+ ion increased with increasing MeCN concentration, though that of the Na^+ ion was almost not affected (Fig. 2A). The behavior of the NH_4^+ ion shows an increase in penetration effect on the resin phase.

Although the peak resolution of the NH_4^+ ion in a water–organic solvent eluent was better than that in the water eluent, the peak shape of other cations including alkali and alkaline earth metal cations was significantly broadened (data not shown).

3.4. Effect of basic eluent

The use of a basic compound as an eluent can suppress the ionization of both NH_4^+ ion and the inner surface of the weakly basic anion exchanger (e.g., tertiary amine functional groups) due to an

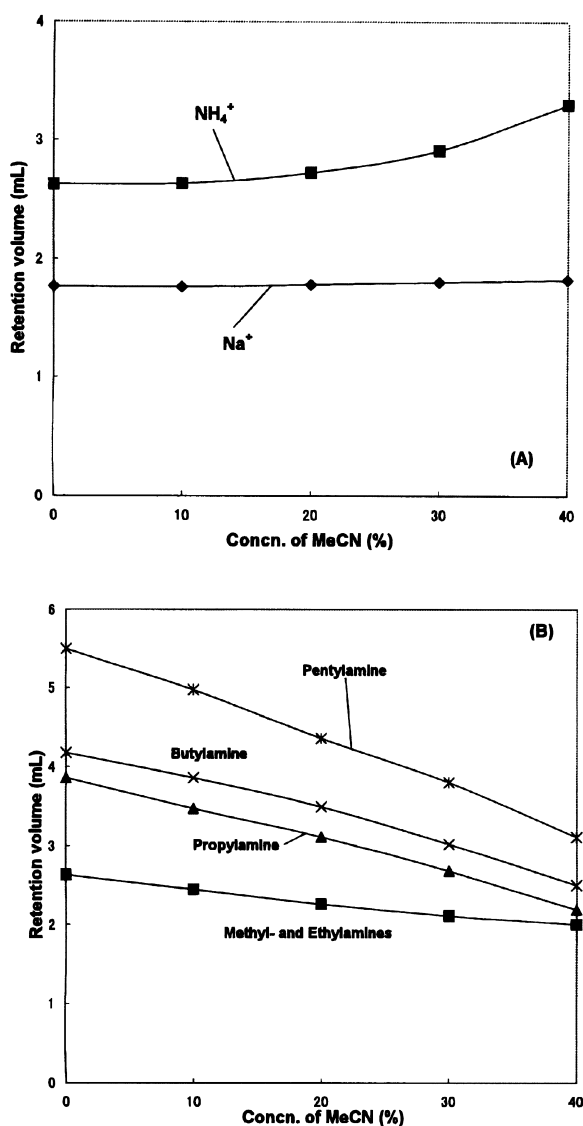


Fig. 2. Effect of concentration of acetonitrile (MeCN) on the retentions of some basic compounds. Column: TSKgel DEAE-5PW. Line identities: (A) $\diamond = Na^+$ and $\blacksquare = NH_4^+$, (B) $\blacksquare =$ methyl- and ethylamines, $\blacktriangle =$ propylamine, $\times =$ butylamine and $*$ = pentylamine. Other conditions as in Fig. 1.

increase of concentration of OH^- in the eluent. This means that the penetration effect of NH_4^+ ion on the resin phase of the separation column is accelerated on the basis of the effect of the Donnan membrane equilibrium. The effect of several of basic eluents (e.g., sodium hydroxide, tetrabutylammonium hy-

droxide, ethylenediamine, triethylamine) was thus investigated for the further improvement for the separation behavior on the ion-exclusion chromatographic separation of the NH_4^+ ion. As a result, the elution with tetrabutylammonium hydroxide (TBA-OH) for the separation found to be the most effective in terms of the peak resolution between the NH_4^+ ion and other inorganic cations, separation times, detection sensitivity and eluent background conductivity, when using the weakly basic anion-exchange resin.

The effect of TBA-OH concentration in the eluent on the retention volumes (V_R) of Na^+ and NH_4^+ ions using a weakly basic anion-exchange resin was investigated. As shown in Fig. 3, the V_R values of Na^+ ion slightly increased with increasing the concentration of TBA-OH as expected from the ion-exclusion effect, in contrast, that of the NH_4^+ ion largely increased. Moreover, the peak shapes of both NH_4^+ ion and other cations were dramatically sharpened.

The background conducting level of the eluent was increased with increasing concentration of TBA-OH in the eluent (4 $\mu\text{S}/\text{cm}$ for a 0.01 mM eluent, 17 $\mu\text{S}/\text{cm}$ for a 0.05 mM eluent and 38 $\mu\text{S}/\text{cm}$ for a

0.1 mM eluent), causing a decrease in the sensitivity of conductimetric detection. Therefore, the lowest possible eluent concentration of TBA-OH should be used in order to obtain reasonable peak resolution and retention time. As a result, the optimum concentration of TBA-OH for the ion-exclusion chromatographic separation of NH_4^+ was 0.05 mM considering these factors. Fig. 4 shows the excellent separation of NH_4^+ from other cations obtained using a 0.05 mM TBA-OH eluent (pH 9.10) at 1.2 ml/min.

3.5. Analytical performance characteristics

Calibration graphs were obtained by plotting peak area for the concentration of NH_4^+ ion under the optimal elution conditions. A linear calibration graph was obtained in the range of the concentration of 0–0.5 mM for NH_4^+ ion ($r^2=0.9982$), and a non-linear graph was obtained at concentrations higher than 0.5 mM. The detection limit of NH_4^+ ion was calculated at $S/N=3$ was 0.495 μM (8.91 $\mu\text{g}/\text{l}$). The reproducibility of retention times of NH_4^+ ion at 0.1 mM at the optimal elution condition was 0.082%

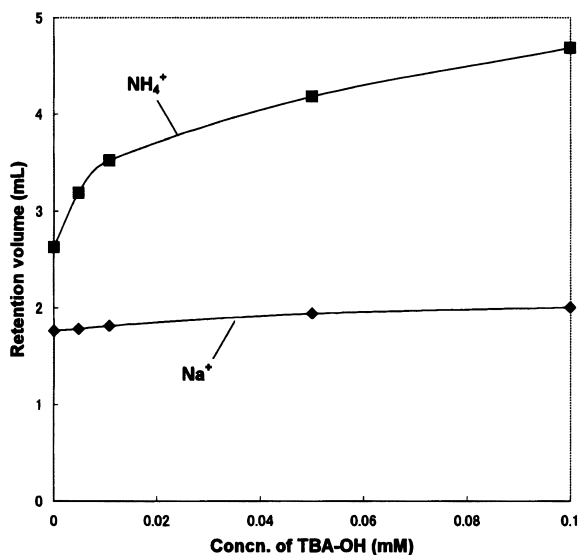


Fig. 3. Effect of tetrabutylammonium hydroxide (TBA-OH) concentration on the retentions of Na^+ and NH_4^+ ions. Line identities: $\blacklozenge = \text{Na}^+$ and $\blacksquare = \text{NH}_4^+$. Other conditions as in Fig. 2.

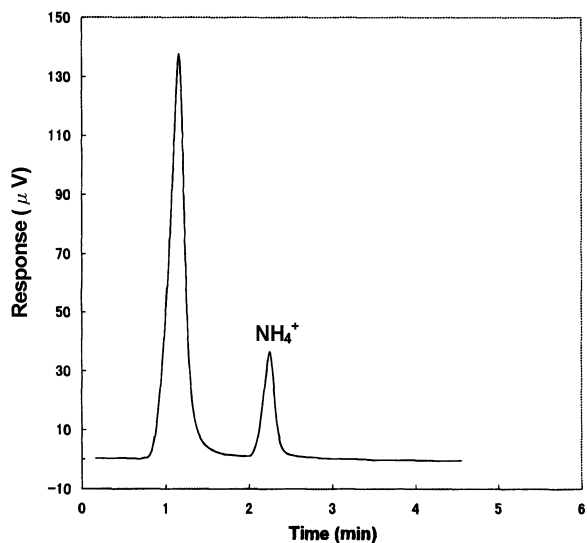


Fig. 4. Ion-exclusion chromatogram of NH_4^+ ion in standard mixtures of alkali and alkaline earth metal ions by elution with 0.05 mM tetrabutylammonium hydroxide (TBA-OH). Flow-rate: 1.2 ml/min. Other conditions as in Fig. 2.

relative standard deviation (RSD), and that of peak area was 0.489% RSD in repeated chromatographic runs ($n=11$). The reproducibility for inter-day (for 1 week) retention time was 0.101% and that of peak area was 0.513%.

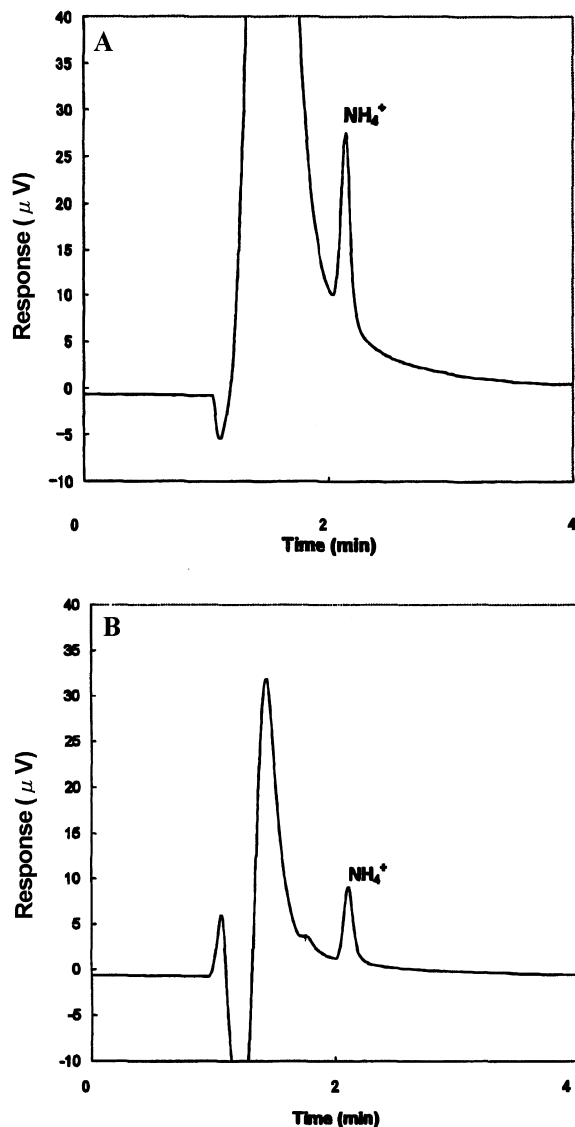


Fig. 5. Chromatograms of (A) river water (pH 7.77) and (B) rain water (pH 4.58) by elution with 0.05 mM TBA-OH at a 1.2 ml/min. The concentrations of NH_4^+ ion determined were 118 μM in river and 44.9 μM in rainwater. Other conditions as in Fig. 2.

3.6. Application to environmental water samples

As practical application to the real samples, NH_4^+ ion in rain and river waters were determined by using the proposed ion-exclusion chromatography (Fig. 5). Each analyte sample was analyzed after filtration through a 0.45 μm membrane filter. The determination of NH_4^+ ion included in environmental samples could be successfully achieved in 3 min. The results demonstrated to be the simple, selective and rapid method for the determination of NH_4^+ ion.

4. Conclusions

The ion-exclusion chromatographic separation of NH_4^+ ion on a weakly basic anion-exchange resin column provided a simple, selective and rapid analytical method, in which the separation was achieved by using aqueous eluent. The ion-exclusion chromatographic separation of aliphatic amines was mainly based on adsorption effect to the resin surface of the column. In contrast the ion-exclusion chromatographic separation of NH_4^+ ion was based on penetration effect. The selective determination of NH_4^+ ion in the environmental waters such as rain or river waters was easily achieved using diluted TBA-OH as the eluent.

A further investigation will be carried out to solve the problems related to the practical application of ion-exclusion chromatography to simultaneously separate alkali metal, alkaline earth metal and NH_4^+ ions in several environmental samples.

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