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ION-EXCLUSION CHROMATOGRAPHY OF THE AMMONIUM ION ON AN ANION-EXCHANGE RESIN

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SUMMARY

Ion-exclusion chromatography of NH_4^+ has been investigated on an anion-exchange resin (OH^-). NH_4^+ was chromatographed by ion exclusion as NH_4OH formed by anion exchange, and monitored with a flow coulometric detector for the detection of OH^- , and/or with a conductometric detector.

The chromatographic conditions for the separation of NH_4^+ from diverse cations, the separation mechanism and each detector response are discussed. This method has been applied to the determination of NH_4^+ in sewage and river water. The results obtained agree well with those obtained by the phenate method.

INTRODUCTION

The ammonium ion is a pollutant causing eutrophication of the aqueous environment. The determination of NH_4^+ in environmental water is usually carried out by colorimetric methods, such as nesslerization and phenate methods¹. However, these methods suffer from several chemical interferences and a distillation step is necessary. Recently, ion chromatography developed by Small *et al.*² has been recognized as a suitable method for the determination of NH_4^+ in environmental samples³. However, for a weak base such as ammonia, this method gives a non-linear detector response due to incomplete protonation or dissociation⁴, and often requires the regeneration procedure of a stripper column [anion-exchange resin (OH^-)] with an alkaline solution.

On the other hand, ion-exclusion chromatography (IEC) developed by Wheaton and Bauman⁵ is a convenient method for the separation of non-ionic species from ionic species. In IEC on a cation-exchange resin (H^+), various anions have been separated as the corresponding acids formed by cation exchange^{6,7}.

Therefore, it is expected that NH_4^+ can be separated by ion exclusion from alkali and alkaline earth metal ions contained in environmental water as NH_4OH formed on an anion-exchange resin (OH^-).

This paper discusses the chromatographic conditions for the separation of NH_4^+ from alkali and alkaline earth metal ions, the separation mechanism, analytical graph and detection limit. The method was applied to the determination of NH_4^+ in sewage and river water.

EXPERIMENTAL

Apparatus

A Spectra-Physics 3500B liquid chromatograph equipped with a Hitachi 030 flow coulometric detector (FC) and a Yanagimoto C-202 conductometric detector (COND) was used for isocratic elution of NH_4^+ and diverse ions with water and water-organic solvents (acetone or dioxane). For FC, details of the electrochemical reaction for NH_4^+ detection have been given elsewhere⁸. A glass-jacketted column (535×9 mm I.D.) packed with a Hitachi 2632 anion-exchange resin (OH^-) (particle size, 18 ± 2 μm ; degree of cross-linking, 8%) was used. The column was thermostated at 20–60°. This column was stable at temperatures up to 60° as reported previously⁸. The eluent flow-rate was 1 ml/min. Sample solution (0.1–1 ml) was injected into the column with a variable-loop injector.

Chromatograms obtained with FC and COND were recorded with a two-pen strip chart recorder (National VP-6541A). The retention times and peak areas were recorded with a computing integrator (Auto Lab, System I) and a digital integrator (Takeda-riken, TR-2213).

A Hitachi 323 recording spectrophotometer was used for the determination of NH_4^+ in practical samples by the phenate method¹.

Reagents

All stock solutions of the NH_4^+ and cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+}) used were prepared by dissolving the corresponding reagent grade chlorides in deionized water. Organic solvents and the other chemicals were of reagent grade.

Preparation of actual samples

Each sample was filtered with a 0.45- μm Millipore filter-paper in a Swinny holder, and the filtrates were injected into the chromatograph.

RESULTS AND DISCUSSION

Retention volumes of cations

NH_4^+ and the diverse cations were chromatographed as the corresponding hydroxides with water as eluent. Table I shows the retention volumes of the cations obtained with FC. The retention volumes of the alkali metal ions showed almost the same values. Those of the alkaline earth metal ions, except Be^{2+} , were slightly higher than these. The ions Be^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} and Co^{2+} were not detected with FC and COND. These results may be explained by the extremely weak basicities and

TABLE I

RETENTION VOLUMES OF NH_4^+ AND DIVERSE CATIONS DETERMINED WITH FC
 ND = Not detected. Injection volume, 0.1 ml of 100 mg/l cations.

<i>Cation</i>	<i>Retention volume (ml)</i>
Li^+	13.01
Na^+	13.05
NH_4^+	17.22
K^+	13.15
Rb^+	13.23
Cs^+	13.32
Be^{2+}	ND
Mg^{2+}	14.72
Ca^{2+}	13.31
Sr^{2+}	13.71
Ba^{2+}	14.50
Cu^{2+}	ND
Ni^{2+}	ND
Co^{2+}	ND
Fe^{3+}	ND

low solubilities. The retention volume of NH_4^+ was higher than those of other cations.

From the above results, it was found that the retention volumes of the cations can be correlated with their basicities. This means that the ion exclusion effect based on the Donnan membrane equilibrium between OH^- of the solute and OH^- of the anion-exchange resin is predominant for the separation of the cations, *i.e.* the alkali ions are completely ion-excluded by the OH^- of the resin, because the alkali metal hydroxides are ionized completely in the eluent. NH_4^+ is incompletely ion-excluded by the OH^- of the resin, because NH_4OH is ionized incompletely ($\text{p}K_b = 4.7$). Alternatively, this indicates that NH_4^+ diffuses into the resin. Therefore, the NH_4^+ could be selectively separated from the mixture of alkali and alkaline earth metal ions as shown in Fig. 1.

Effect of column temperature

The effect of column temperature on the column efficiency (HETP) and peak resolution (R_s) with the mixture of Na^+ and NH_4^+ was investigated in the temperature range of 20–60°. The HETP values found were 0.35–0.38 mm for Na^+ and 0.21–0.22 mm for NH_4^+ , and the R_s values between Na^+ and NH_4^+ were 2.93–2.94. Therefore, the HETP and R_s were hardly affected by column temperature. No variation of the retention volumes of Na^+ and NH_4^+ was observed.

Effect of organic solvents in eluent

The $\text{p}K_b$ value of a weak base such as NH_4OH is higher in a water–organic solvent than in water. We have reported elsewhere that in IEC of acids on a cation exchange resin (H^+) the retention volumes are dependent on the $\text{p}K_a$ values^{6,7}. Therefore, it is expected that in IEC of NH_4^+ on an anion-exchange resin (OH^-) an increase of the $\text{p}K_b$ of NH_4OH results in an increase of retention volume. The effect of acetone or dioxane on the retention volumes of Na^+ and NH_4^+ was

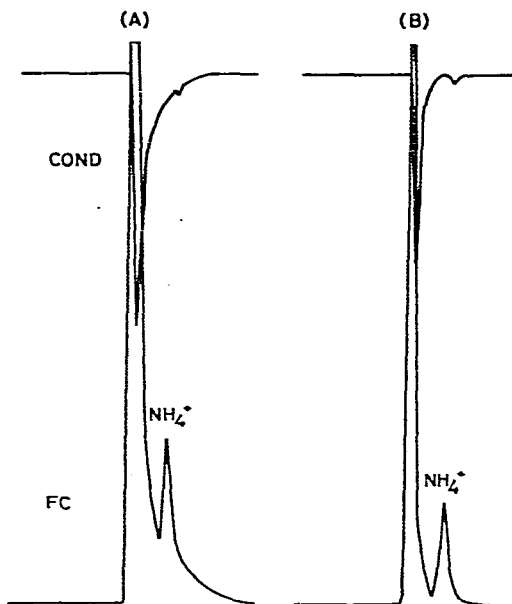


Fig. 1. Typical chromatograms of NH_4^+ in authentic mixtures of alkali metal ions (B) or alkali and alkaline earth metal ions (A). Concentration of cations (mg/l): Li^+ , 10; Na^+ , 30; NH_4^+ , 20; K^+ , 50; Rb^+ , 100; Cs^+ , 100; Mg^{2+} , 30; Ca^{2+} , 50; Sr^{2+} , 100; Ba^{2+} , 100. Injection volume: 0.1 ml.

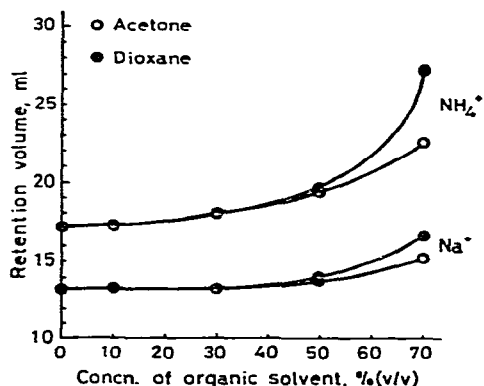


Fig. 2. Effect of concentration of organic solvents on retention volumes of Na^+ and NH_4^+ .

investigated in the concentration range of 0–70%. The results are shown in Fig. 2. The retention volume of NH_4^+ increased gradually with an increase in acetone or dioxane concentration, whereas that of Na^+ slightly increased with an increase in acetone or dioxane concentration. The effect of organic solvents on the retention volume of NH_4^+ was larger in water–dioxane than in water–acetone. The $\text{p}K_b$ of NH_4OH depends on the dielectric constant of the eluent. Thus, since the dielectric constant of dioxane (2.1) is lower than that of acetone (21.7), the $\text{p}K_b$ of NH_4OH is higher in water–dioxane than in water–acetone. Therefore, the dielectric constant is an important factor for the IEC separation of NH_4^+ . A similar behaviour has been observed in IEC of phosphoric acid on a cation exchange resin (H^+)⁶. By using water–organic solvents as the eluent, NH_4^+ can be successfully separated from large amounts of alkali and alkaline earth metal ions.

The volume of the anion-exchange resin bed in the column gradually decreased with an increase in acetone or dioxane concentration in the eluent. When 70% dioxane was used as the eluent, a shrinkage of *ca.* 5% was observed. However, the column could be repeatedly used without re-packing.

Effect of sample volume

The effect of sample volume on the HETP and R_s of Na^+ and NH_4^+ was investigated in the sample volume range of 0.1–1 ml. Each sample contained 10 μg each of Na^+ and NH_4^+ . The results are shown in Table II. The HETPs of Na^+ and NH_4^+ increased with an increase in sample volume, but the R_s between these ions

TABLE II

EFFECT OF SAMPLE VOLUME ON HETP AND R_s OF Na^+ AND NH_4^+ DETERMINED WITH FC

Sample volume (ml)	Sample concn. (mg/l)	HETP (mm)		R_s ($\text{Na}^+ - \text{NH}_4^+$)
		Na^+	NH_4^+	
0.1	100	0.39	0.20	2.96
0.25	40	0.42	0.21	2.81
0.5	20	0.52	0.28	2.42
1.0	10	0.83	0.56	1.88

decreased with an increase in sample volume. However, even with a 1-ml injection, a good R_s value was obtained.

Reproducibility of NH_4^+ measurement

The reproducibilities of the chromatograms of NH_4^+ obtained with FC and COND were determined under the conditions of 0.1-ml injections of 20 mg/l NH_4^+ and a column temperature of 50°. The coefficients of variation obtained by the peak area method were 2.6% for FC and 2.7% for COND. Reproducible chromatograms were obtained with both detectors throughout repeated chromatographic runs.

Detector response of Na^+ and NH_4^+

The detector responses of Na^+ and NH_4^+ were determined from the chromatograms obtained with FC and COND. The results are shown in Table III. In COND, the ratio of the peak areas ($\text{NH}_4^+/\text{Na}^+$) per micromole was 0.2. This value is due to the difference between the equivalent conductances of NaOH and NH_4OH , i.e. the equivalent conductance of NaOH is higher than that of NH_4OH . In contrast, in FC, this ratio was 1.0. This result indicates that the electrochemical reaction of OH^- from NH_4OH and hydroquinone proceeds stoichiometrically in the same manner as that of OH^- from NaOH and hydroquinone.

TABLE III

DETECTOR RESPONSES OF Na^+ AND NH_4^+

Detector	Relative peak area per micromole		Ratio ($\text{NH}_4^+/\text{Na}^+$)
	Na^+	NH_4^+	
FC	100	102.3	1.02
COND	100	20.09	0.20

Calibration graph

The calibration graphs for NH_4^+ were constructed for the concentration range of 10–100 mg/l. The relationships between the concentration of NH_4^+ and the peak area or peak height obtained with FC and COND are shown in Fig. 3. A good linear relationship was obtained with FC, but not with COND. This difference is caused by the incomplete dissociation of NH_4OH .

From the above results, FC is a more powerful detector than COND for the IEC determination of NH_4^+ .

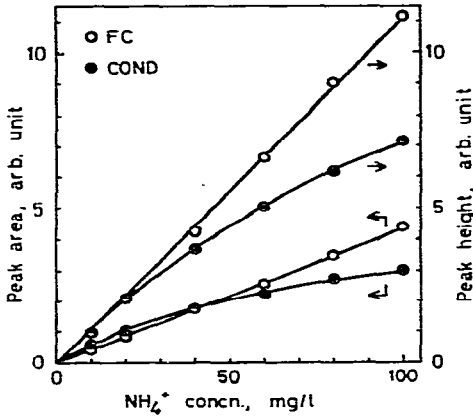


Fig. 3. Calibration curves for NH_4^+ obtained with FC and COND.

TABLE IV
DETECTION LIMITS OF NH_4^+

Detector	Detection limit (ng)
FC	3.3
COND	2.2

Detection limit

The detection limit of NH_4^+ was determined with water as eluent, 0.1-ml injections of 1 mg/l NH_4^+ and a column temperature of 50° . The detection limit is defined as that concentration which gives a signal twice as strong as that produced by the background noise ($S/N = 2$). Table IV shows the detection limits of NH_4^+

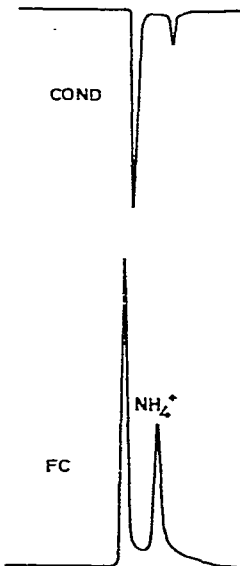


Fig. 4. Chromatograms of NH_4^+ in activated sludge process water obtained with FC and COND.

obtained with FC and COND. Nanogram levels of NH_4^+ were detectable with both methods.

Determination of NH_4^+ in some actual analyses

The determination of NH_4^+ in sewage and river water was carried out by the IEC and phenate methods. Fig. 4 shows a chromatogram of a sewage sample treated by the activated sludge process. As shown in Table V, the agreement between the values obtained by both methods was good.

TABLE V
ANALYTICAL RESULTS FOR ACTUAL SAMPLES
ND = Not detected.

Sample	NH_4^+ concn. (mg/l)	
	Present method*	Phenate method
Activated sludge process water (influent water)	35.3	37.2
Activated sludge process water (treated water)	17.7	15.4
River water (Kiso river)	ND	ND
River water (Syonai river)	1.35	1.23

* Determined with FC.

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