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Simultaneous determination of the three main inorganic forms of nitrogen by ion chromatography

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ABSTRACT

An ion chromatographic method for the determination of nitrite, nitrate and ammonium simultaneously is described. An appropriate eluent–column–detector combination for separating and detecting these ions is discussed. On a bifunctional ion-exchange column, nitrite and nitrate anions were separated by anion exchange and ammonium cation by cation exchange. Nitrite and nitrate were detected by UV spectrometry and ammonium using a chemically suppressed conductivity detector. The detection limits for the three ions were all below 0.02 ppm (w/w) and the relative standard deviations for the three ions were all less than 0.5%. Several samples such as water, soil and acid rain were analysed with this method and the recoveries of the three ions were all within 100 ± 5%. The results agreed well with those obtained by a standard method.

INTRODUCTION

The simultaneous determination of cations and anions in one sample injection has the potential to increase the efficiency of a laboratory engaged in ion chromatographic analyses. As the selection of the eluent–column–detector combination is crucial to the success of the simultaneous determination of anions and cations, few methods have been reported in this field. One of these methods used a cation-exchange column, an anion-exchange column and a switching valve, and ions were detected with a conductivity detector [1]. Other methods used a bifunctional column, ions being detected by conductimetric detection [2–4], by indirect photometric detection [5,6] or using a UV and a fluorescence detector in series [7]. However, the sensitivity and selectivity of these methods were not very good.

This paper reports a system consisting of dilute hydrochloric acid–glycine as eluent, a bifunctional ion-exchange column and a UV spectrophotometric–conductivity detector that can simultaneously determine nitrite, nitrate and ammonium ions. The methods is very sensitive and selective, and few species interfere.

EXPERIMENTAL

Apparatus and reagents

All chromatography was performed on a Dionex Model 2000i ion chromatograph equipped with a UV–Vis detector and a CDM-I conductivity detector. Output data were recorded on a Dionex dual-pen recorder. A Dionex HPIC-GC5 guard column, a Dionex HPIC-CS5 separation column and a Dionex CMMS suppressor were used. The sample loop volume was 50 μl. The eluent was a mixture of 5 m*M* hydrochloric acid and 8 m*M* glycine solution. The regenerant was 10 m*M* potassium hydroxide solution. Glycine was of biochemical reagent grade and other chemicals were of analytical-reagent grade.

Analytical procedure

The samples which were eluted from the separation column first flowed into a UV spectrophotometric cell where nitrite and nitrate were detected,

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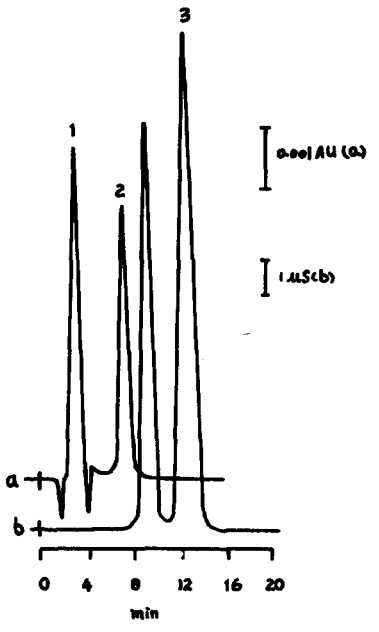

Fig. 1. Simultaneous separationof the nitrite, nitrate and ammonium ions. (a) UV detection; (b) conductivity detection. Peaks: 1 = NO_2^- (10 ppm, w/w); 2 = NO_3^- (5 ppm); 3 = NH_4^+ (5 ppm).

then through the cation suppressor and conductivity detector cell where ammonium was detected. The eluent flow-rate was 2.0 ml/min and the regenerant flow-rate 1.0 ml/min. The recorder chart paper speed was 0.25 cm/min. The UV–Vis detector was set at 215 nm. The samples were injected directly after the baseline was stable. The peak-height methods was used for quantative analysis. Fig. 1 shows the separation of nitrite, nitrate and ammonium.

RESULTS AND DISCUSSION

Selection of instrumentation

UV and conductivity detectors were chosen for two reasons. First, nitrite and nitrate absorbed well at 215 nm whereas other common anions and cations did not, and the conductivity detector was sensitive to ammonium ions without a postcolumn derivatization reaction. Second, these detectors are the most commonly used type and are available in many laboratories. The UV and conductivity detectors were connected is series.

To separate nitrite, nitrate and ammonium ions simultaneously without chemical pretreatment, an appropriate column would contain two kinds of ion-exchange function. The HPIC-CS5 separation column has a resin core of polystyrene cross-linked with divinylbenzene which is surface sulphonated for cations exchange and aminated latex with quaternary ammonium groups for anion exchange, *i.e.*, it is a bifunctional column. The experiments showed that it could separate anions and cations simultaneously, so it was chosen as the separation column in this work.

Selection of eluent

There were several important factors for consideration in the selection of the eluent for the simultaneous determination of anions and cations. (a) The eluent should be capable of separating and eluting the analyte ions effectively, and contain both efficient cation- and anion-eluting ions for separating anions and cations simultaneously on one column. (b) The eluent must not produce a high response to the detector. When a UV detector is used, the eluents should be chosen to be non-absorptive or slightly absorptive at the UV wavelength used. When a chemically suppressed conductivity detector is used, the conductivity of the eluent should be suppressed easily. (c) A highly acidic eluent could cause partial protonation of weakly acidic nitrite anions. As a result, the effective ionic concentration and hence the sensitivity would decrease. It is clear that the concentration of hydrogen ions in the eluent should be low.

Based on the above considerations, a mixture of dilute hydrochloric acid and glycine (NH_2CH_2COOH) was chosen as eluent. The hydrogen ions in dilute hydrochloric acid could elute cations, whereas the chloride ion elute anions without oxidation or reduction reaction with nitrite or nitrate. Glycine is the simplest amino acid, its pK_{a_1} = 2.34 (K_{a_1} = 0.00457), pK_{a_2} = 9.60 and the pH of the isoelectric point is 5.97. If the concentration of hydrogen ions is above 4.6 m*M*, glycine exists mainly in the form of the protonated ion $HGly^+$. As the pH is increased, glycine passes through being a neutral molecular at its isoelectric point and finally becomes a monovalent anion at basic pH. Protonated ion $HGly^+$ is much more powerful for eluting cations than an eluent containing only hydrogen ions,

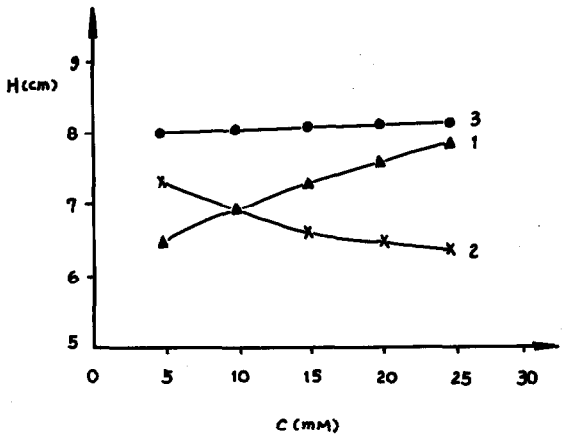

Fig. 2. Effect of HCl concentration on the peak heights of the three ions. 1 = NH_4^+; 2 = NO_2^-; 3 = NO_3^-.

so the elution of ammonia was accelerated. In addition to being powerful, eluents containing glycine have very low background conductivity after suppression [8], because glucine is either removed from the dynamic suppressor through the anion-exchange membrane into the regenerant stream, or is eluted from the suppressor as a neutral molecule as its isoelectric point is close to the effluent pH of the suppressor. This behaviour of glycine increased the sensitivity of ammonium detection.The presence of $HGly^+$ decreased the concentration of free hydrogen ions, hence the protonation of nitrite was decreased and the sensitivity of nitrite detection was increased.

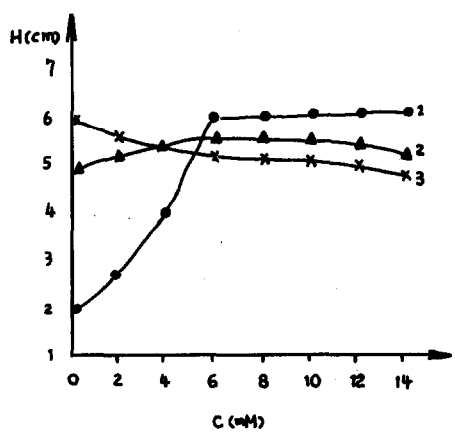

Fig. 3. Effect of glycine concentration on the peak heights of the three ions. 1 = NH_4^+; 2 = NO_2^-; 3 = NO_3^-.

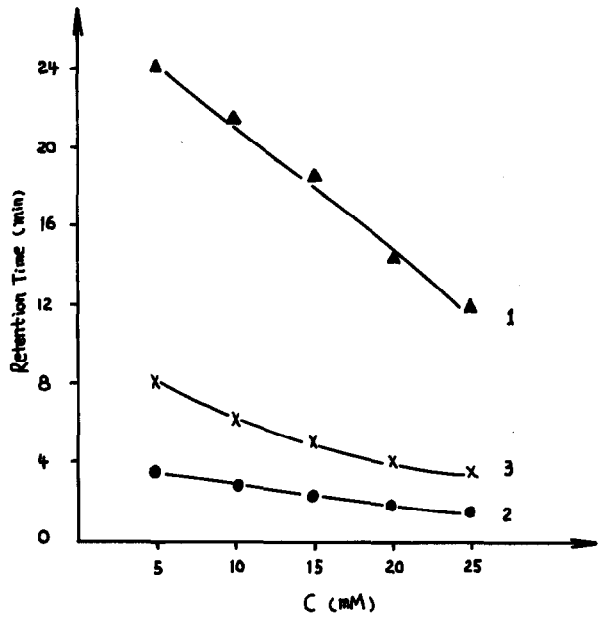

Fig. 4. Effect of the HCl concentration on the retention times of the three ions. 1 = NH_4^+; 2 = NO_2^-; 3 = NO_3^-.

The effect of the eluent concentration on the peak height and retention time is shown in Figs. 2–5. It was found that the concentration of glycine exerted

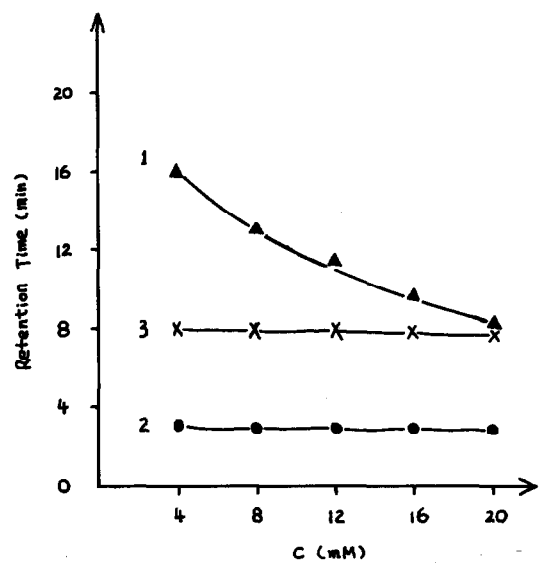

Fig. 5. Effect of the concentration of glycine on the retention times of the three ions at a constant concentration of 5 m*M* HCl. 1 = NH_4^+; 2 = NO_2^-; 3 = NO_3^-.

TABLE I

EFFECT OF FLOW-RATE ON PEAK HEIGHT, RETENTION TIME AND SYSTEM PRESSURE

Parameter	Ion	Flow-rate (ml/min)					
		3.3	3.0	2.5	2.0	1.5	1.0
Peak height (cm)	NO_2^-	7.6	7.5	7.2	7.0	6.5	5.8
	NH_4^+	8.9	8.7	8.5	8.2	7.8	6.5
	NO_3^-	6.8	6.6	6.4	6.1	5.8	5.0
Retention time (min)	NO_2^-	1.3	1.8	2.0	2.5	3.0	4.0
	NH_4^+	8.0	9.0	10.5	12.0	14.5	16.5
	NO_3^-	5.4	6.0	6.8	7.5	8.2	10.0
System pressure (p.s.i.)[a]		1700	1580	1420	1200	860	680

[a] 1 ps.i. = 6894.76 Pa.

TABLE II

LINEARITY, RELATIVE STANDARD DEVIATIONS (R.S.D.) AND DETECTION LIMITS FOR NITRITE, NITRATE AND AMMONIUM IONS

Ions	Linearity correlation coefficient	R.S.D. (%) (n = 9)	Detection limit (μg/l)
NH_4^+	0.9999 (0–20 ppm)	0.27	8
NO_2^-	0.9999 (0–40 ppm)	0.36	10
NO_3^-	0.9991 (0–20 ppm)	0.38	20

TABLE III

RECOVERIES OF NITRITE, NITRATE AND AMMONIUM IN REAL SAMPLES

Sample	Ion	Result (ppm)	Added	Recovery (%)
Acid rain	NH_4^+	2.7	2.50	101.48
	NO_3^-	3.55	2.50	102.40
	NO_2^-	0.05	5.00	99.00
Tap water	NH_4^+	0.36	2.50	103.60
	NO_3^-	13.73	2.50	104.60
	NO_2^-	0.0	5.00	98.43
Soil extraction solution	NH_4^+	0.42	2.50	99.60
	NO_3^-	7.85	2.50	101.72
	NO_2^-	1.36	5.00	97.45

a much greater influence on the peak height and retention time of ammonium than on those of nitrite and nitrate ions, as glycine was a powerful eluting cation for ammonium. When the hydrochloric acid concentration increased, the retention times of the three ions decreased; however, the peak height of nitrite became lower. In view of all the factors discussed, including the low pH of the eluent, large peak height, short retention time and good separation of the three ions, the optimum eluent composition selected was a mixture of 5 mM hydrochloric acid and 8 mM glycine.

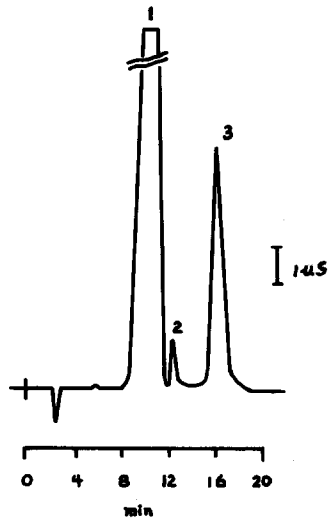

Fig. 6. Determination of ammonium ions in drinking water. Peaks: 1 = Na^+; 2 = NH_4^+; 3 = K^+.

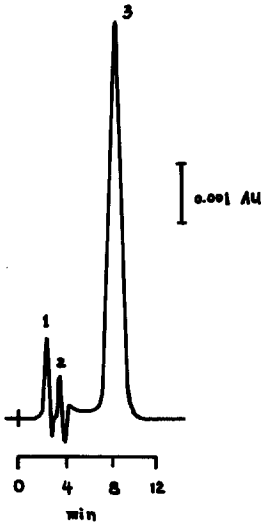

Fig. 7. Determination of nitrite and nitrate in soil. Peaks: 1 = Cl^-; 2 = NO_2^-; 3 = NO_3^-.

Table I shows the effect of the eluent flow-rate on peak height, retention time and system pressure. Considering the resolution and the pressure that the whole analytical system could withstand, 2.0 ml/min was chosen as the optimum eluent flow-rate.

Selectivity and detection limit

Although the method presented here has a high sensitivity towards alkali metals, there was no interference in the determination of ammonium when the concentrations of sodium and potassium ions were 100 times higher than that of ammonium ions. Divalent cations are very strongly retained on the HPIC-CS5 column and cannot be eluted by the eluent. They occupied the cation-exchange functional sites and shortened the retention time of ammonium ions. When the retention time of ammonium ions has halved, the divalent cations should be removed from the column with 0.2 *M* hydrochloric acid.

Because of the good resolution and non-absorption at 215 nm, common anions did not interfere with the detection of nitrite and nitrate.

In order to detect nitrite at low concentrations (<0.05 ppm), the UV–Vis detector was set at a high sensitivity. Because glycine had a weak absorption at 215 nm, the water dip was large and interfered with the detection of nitrite at a high sensitivity setting. The watere dip, which elutes near the nitrite peak and interferes with this peak, can be eliminated by the addition of the equivalent of 0.1 ml of concentrated (100-fold) eluent to 10 ml of each standard and sample.

TABLE IV

COMPARISON OF THE RESULTS OBTAINED BY THE PROPOSED METHOD AND THE EPA METHOD [9]

Analyte	Concentration in synthetic sample (ppm)	Concentration found (ppm)	
		This method	EPA method
NH_4^+	5.00	5.15	5.10
NO_3^-	2.50	2.45	2.30
NO_2	2.00	2.00	2.10

Sample analysis

Table II shows the linearity, relative standard deviations and detection limits for the determination of the three ions. The results and recoveries for the analyses of water, acid rain and soil are given in Table III. Two typical chromatograms for sample analyses are shows in Figs. 6 and 7. A synthetic sample was analysed by the proposed method and an EPA standard method [9] and the results agreed well (Table IV).

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