Journal of Chromatography, 640 (1993) 351–353
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2769

Highly selective ion chromatographic determination of ammonium ions in waters with a suppressor as postcolumn reactor

A. M. Dolgonosov* and A. N. Krachak

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Kosygin str. 19, 117975 Moscow (Russian Federation)

ABSTRACT

A highly selective ion chromatographic method for the determination of ammonium ions using an anion-exchange separation column with a bipolar ion exchanger was developed. The method is based on the reaction in a suppressor column between ammonium ions and nitrous acid formed from the eluent components followed by the negative conductimetric signal. The determination of more than 0.1 ppm of NH_4^+ in water is possible in the presence of 100-fold amounts of alkali metals and inorganic anions.

INTRODUCTION

Ammonium ion is one of the components that need to be monitored in natural and waste waters. For this purpose a number of methods have been applied, including ion chromatographic methods in the cation-exchange separation mode [1–3]. To increase the selectivity and sensitivity of the determination of ammonium ions we have developed an ion chromatographic method with conductivity detection based on the highly selective reaction of ammonium ions with nitrous acid in the suppressor column.

PRINCIPLE OF IC DETERMINATION OF AMMONIUM IONS

In an acidic medium, the reaction between ammonium ions and nitrous acid occurs as follows:

$$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O \qquad (1)$$

Hence the reaction results in the formation of neutral molecules from the electroconductive starting compounds, which is reflected in conductimetric measurements in a large decrease in the conductivity signal. This is an essential prerequisite for increasing the sensitivity of the determination of ammonium ions.

As nitrous acid is very unstable, it is impossible to use it as an eluent, so sodium nitrite solution is used. To obtain the nitrous acid necessary for reaction 1, we have used a suppressor column with a cation exchanger in the H^+ form. To avoid the retention of ammonium ions in the part of the suppressor column present in the Na^+ form, an alkaline eluent was used, which converts ammonium ions into ammonia molecules according to the reaction

$$NH_4^+ + OH^- \leftrightharpoons NH_3 + H_2O \qquad (2)$$

The pressure in the chromatographic system is always sufficient for the complete dissolution of ammonia in the eluent (several bar). The suppressor column can exchange all the eluent cations with H^+ ions, hence these cations (with the exception of amides participating in a reaction similar to reaction 2) do not influence the determination of ammonium ions.

The separation column should possess an anion-exchange capacity in order to separate ammonium

---

* Corresponding author.

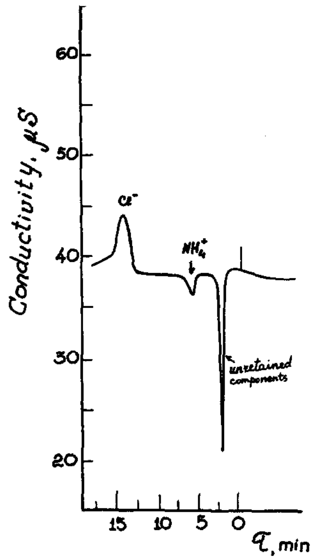

Fig. 1. Typical chromatogram for the IC determination of ammonium ions. For chromatographic conditions, see text. Concentration of ammonium ions, 0.2 mmol/l.

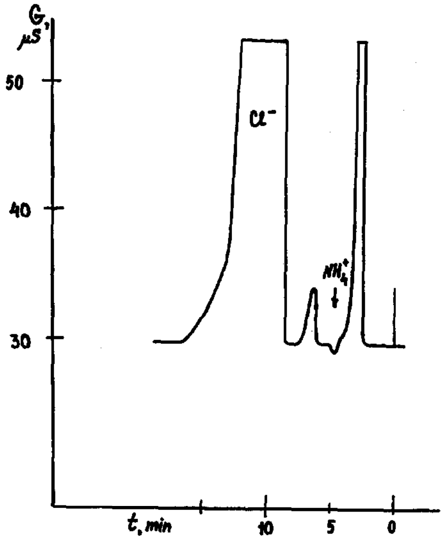

Fig. 2. IC analysis of sea water. For chromatographic conditions and sample preparation, see text.

ions from anions. On the other hand, the ammonium ion zone should move more slowly than the liquid phase in order to avoid superposition of the ammonium ion peak and peaks of unretained substances (*e.g.*, water). The anion exchanger is capable of retaining ammonia according to the ion-exclusion mechanism, but this effect is not sufficient for separating the ammonium ion peak from the water peak. To increase the ammonia retention, the stationary phase should act as a bipolar ion exchanger having both anion- and cation-exchange active sites.

By varying the eluent pH and the ratio between the cation- and anion-exchange capacities one can achieve a low concentration of ammonium ions (several percent), being in equilibrium with ammonia and, thereby, providing complete separation of ammonium ions from anions and unretained components.

EXPERIMENTAL

A ZVET-3006 ion chromatograph (DOKBA, Dzerzhinsk, Russian Federation) with a BIE-03 conductimeter (DOKBA) was used. A separation column (100 × 3 mm I.D.) was filled with KanK-BP bipolar central-localized sorbent (15 μm) [4] (GEOHI, Moscow, Russian Federation). Both the anion- and cation-exchange capacities of the packing were 0.2 mequiv./ml. A suppressor column (120 × 5 mm I.D.) was filled with Dowex-50X8 (50 μm) in the H^+ form. A 30-μl sampling loop was used. The eluent flow-rate was 1.7 ml/min.

The eluent and all solutions were prepared by dissolution of analytical-reagent grade chemicals (Reakhim, Moscow, Russian Federation) in doubly distilled water. An aqueous solution of sodium nitrite (0.5 mmol/l) and sodium hydroxide (3.0 mmol/l) was used as the eluent. An artificial sea-water sample was prepared by mixing sodium chloride (0.5 mol/l), sodium sulphate (0.02 mol/l) and potassium bromide (0.8 mmol/l), and 1.0 mmol/l ammonium chloride was added.

RESULTS AND DISCUSSION

Fig. 1 shows a typical chromatogram for the IC determination of ammonium ions. The height of the negative peak corresponding to ammonium ions is proportional to the amount of ammonium ions in the sample, as established by the correlation between the amounts of ammonium ions in various mixtures and the detector response at the position of the ammonium ion peak. This correlation can be expressed by the equation

$$\Delta G = -A[\mathrm{NH}_4^+]$$

where $A = 13.20 \pm 0.39$. The retention time of ammonium ions is 370 ± 10 s. The determination of ammonium ions is possible down to a concentration of 5 μmol/l (90 ng/ml; detection limit). Under the above conditions 100-fold molar excesses of alkali metal ions (Na^+, K^+) and inorganic anions (Cl^-, Br^-, SO_4^{2-}, etc.) do not interfere.

The proposed method can be applied to the determination of ammonium ions in natural waters, as shown in Fig. 2. The determination of ammonium ions in sea water is possible down to the level of a few parts per million.

REFERENCES

1 H. Small, T. S. Stevens and W. S. Bauman, *Anal. Chem.*, 47 (1975) 1801.

2 C. A. Pohl and E. L. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 442.

3 S. Bouyoucos, *Anal. Chem.*, 49 (1977) 401.

4 A. M. Dolgonosov, *React. Polym.*, 17 (1992) 95.