

Fluorometric determination of ammonium ion by ion chromatography using postcolumn derivatization with *o*-phthaldialdehyde

Chun-Ting Kuo, Po-Yen Wang, Chien-Hou Wu*

*Environmental Chemistry Laboratory, Department of Atomic Science, National Tsing Hua University,
101, Sec. 2, Kuang Fu Road, Hsinchu 30013, Taiwan*

Available online 9 June 2005

Abstract

A postcolumn fluorometric derivatization method for the determination of trace amounts of ammonium ion ($\mu\text{g/L}$ level) under matrices with high concentrations of sodium and amino acids has been developed. In this method, ammonium ion was determined by ion chromatography combined with fluorometric detection (IC-FL) in less than 16 min. IC was performed in a high-capacity cation-exchange Dionex IonPac CS16 analytical column (250 mm \times 5 mm) under isocratic conditions with 30 mM methanesulfonic acid (MSA) as mobile phase at flow-rate 1.0 mL/min. To remove amino acid interference, the postcolumn derivatization based on the reaction of ammonia with *o*-phthaldialdehyde (OPA) and sulfite was applied. The excitation and emission wavelengths were 364 and 425 nm, respectively. The effects of pH, reaction temperature and time, OPA-reagent composition and concentration, and sample matrix were studied. The linear range and detection limit of this method were similar to the standard method. The IC-FL method with a postcolumn fluorometric derivatization allows the routine determination of ammonium ion in extreme matrices where the ratios of sodium and amino acids to ammonium are up to 2 800 000:1 and 28 000:1, respectively.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ammonium ion; Ion chromatography; Fluorometric detection; Postcolumn derivatization; *o*-Phthaldialdehyde

1. Introduction

Ammonium ion is an important micronutrient and intermediate of the nitrogen cycle in aquatic ecosystem [1]. Typical concentrations found in seawater vary from 0 to 25 μM in coastal waters to less than 0.5 μM in surface oceanic waters [2]. Ammonium is also a common alkaline pollutant in freshwater. Ammonium is routinely measured in the USA for wastewater discharge compliance monitoring and the European Union and Japan in drinking water [3]. Therefore, the development of a sensitive and selective analytical method for ammonium is significant in the environmental evaluation of water pollution and fundamental to the understanding of nitrogen cycling in aquatic ecosystems.

Various detection methods and techniques have been developed for the analysis of ammonium ion, such as spectrophotometry, voltammetry, fluorometry, and ion

chromatography. Typically, the spectrophotometric method based on the Berthelot reaction is the most widely used for quantitative determination of ammonia and the standard method for examination of water in the US Environmental Protection Agency (EPA) [4–8]. The Berthelot method involves the formation of the deep blue color of indophenol from hypochlorite-phenol solution and ammonia under alkaline conditions [5,9]. However, the oxidation step takes as long as 3–4 h at room temperature even with catalyst such as sodium nitroprusside. Although a recent modification has hastened the process studied at different temperatures (37–80 °C), interference from ammonia or amines generated by thermal decomposition or hydrolysis of nitrogen containing organics is still serious [6]. Moreover, the Berthelot method is more difficult to apply in seawater than in freshwater due to the pH and buffering capacity problems. The pH shift in seawater analysis has been demonstrated and the shift to a lower pH may result in a lower sensitivity and a slower reaction rate [10]. In addition, the method is subjected to interferences from copper, zinc, iron, sulfides, thiols,

* Corresponding author. Tel.: +886 3 5715131x5856; fax: +886 3 5718649.
E-mail address: chwu@mx.nthu.edu.tw (C.-H. Wu).

ascorbic acid, and dissolved organic nitrogen compounds such as amino acids, urea, and nucleic acids [4,11]. Two other disadvantages are insufficient sensitivity and precipitation of magnesium as hydroxide in the alkaline conditions. Existing electroanalytical methods for ammonia analysis include catalytic cathodic stripping voltammetry and potentiometry with ammonia selective electrodes [2,12]. However, these methods are susceptible to interferences by amines and the direct analysis may require long equilibration time. Flow injection chemiluminescence analysis has also been used for the determination of ammonium concentration in rainwater samples [13,14]. However, a limitation to widespread application of this technique is its low sensitivity.

Fluorometry is attractive for its high sensitivity, especially for the method involving the reaction of ammonia with *o*-phthalaldehyde (OPA) [15–23]. It is well-known that OPA reacts with ammonia or primary amines to afford highly fluorescent isoindole derivatives. This method can be utilized in precolumn or postcolumn derivatization mode. Precolumn derivatization is a simple and commonly used procedure; however, this procedure has some limitations. For example, OPA-labeled ammonia decomposes over time with the rate of decomposition being ammonia-dependent. Additionally, this procedure must contend with impurities and product stability. Finally, variations in reaction times and the time between derivatization and analysis will impact the quantitative results. Postcolumn derivatization provides a reproducible labeling procedure. Goyal et al. attempted the optimization of all pertinent parameters of the OPA-NH₃ reaction in the presence of 2-mercaptoethanol [16]. However, the method had a strong matrix effect in the sample medium. Genfa and Dasgupta modified the reaction conditions, replacing 2-mercaptoethanol by sulfite [18]. The reaction showed considerable selectivity for ammonia over amino acids by a factor of 17–590 for 11 common amino acids and no ionic strength effect. The improved method has been successfully used for the determination of ammonium in coastal, estuarine, and fresh waters [19,20,23].

Ion chromatography (IC) is particularly useful for the separation, identification, and quantification of ammonium ion at the $\mu\text{g/L}$ level [17,24–29]. Rey et al. developed a column-switching system to change the order of carboxylated (the IonPac CS12A, Dionex) and sulfonated (the IonPac CS10, Dionex) stationary phase columns followed by suppressed conductivity detection for the determination of trace ammonium (or sodium) ion in the presence of large concentration of sodium (or ammonium) ion [30]. The system allows quantitative analysis of sodium-to-ammonium ion concentration ratios in the order of up to 20 000:1. Huang et al. developed a system which combines column switching and concentration for the determination of ammonia in seawater [31]. The method of detection limit for NH₄⁺ was 12.8 $\mu\text{g/L}$ in the presence of sodium at 1000 mg/L. However, when the concentration of sodium is higher than 2000 mg/L, the small ammonium peak could not be detected because of the huge tail of the sodium peak. On the other hand, a

new column containing carboxylic acid, phosphonate and 18-crown-6 ether groups (IonPac CS15, Dionex) and a very high-capacity column containing carboxylic acid groups only (IonPac CS16, Dionex) were developed to address this limitation [3,32–34]. Introducing 18-crown-6 ether groups into the stationary phase results in higher selectivity for NH₄⁺ and K⁺ [35]. Due to its high cation exchange capacity, the IonPac CS16 column allows a simple acidic isocratic eluent for the determination of up to 1:10000 concentration ratios of ammonium to sodium [3]. However, analyzing samples of much higher concentration ratios of sodium-to-ammonium, such as in seawater, still poses a challenge.

One goal of our research is to investigate the photochemical reactions of copper(II)/amino acid complexes in aquatic systems. Photochemical processes have been shown to cleave small moieties from recalcitrant dissolved organic matter [1]. To date, our preliminary results indicate that photoproduction of ammonia from the Cu(II)/amino-acid complex systems (with 2–50 mM amino acids and ionic strength 0.10 M) occurs under monochromatic radiation at 313 nm. To be able to assess the photoreactivity of Cu(II)/amino-acid systems and characterize such photoreactions, the photoformation of ammonia must be determined under different conditions.

We reconsidered the version of Gardner and John so that ammonium ion could be separated by ion chromatography and determined with fluorometric detection [17]. This work was aimed at establishing a simple and sensitive fluorometric method for determining ammonium ion. Specifically, ammonium ion was separated from related compounds, such as amino acids, on a cation-exchange column and was then derivatized with two reagents, OPA and sodium sulfite in the postcolumn reactor.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical or reagent grade, or the highest purity available from several suppliers and were used as received. Ammonium chloride (>99.5%), sodium chloride (>99.8%), and potassium chloride (>99.5%) were obtained from Riedel-de Haën (Seelze, Germany). Sodium sulfite, 2-mercaptoethanol, 3-mercaptopropionic acid, *o*-phthalaldehyde (>99%), cupric chloride dihydrate (>99.0%), boric acid (>99.8%), and methanesulfonic acid (>98%) were purchased from Merck (Darmstadt, Germany). Sodium hydroxide, hydrogen chloride, and acetonitrile were from J.T. Baker. Other reagents used were L-alanine (>99.0%, Fluka), 2-nitrobenzaldehyde (>98%, Aldrich), and sodium tetraborate (>99%, Sigma-Aldrich). A standard solution of ammonium (0.10 M) was prepared by dissolving ammonium chloride into doubly deionized water. The concentration of the standard solution was also compared with those (100 and 1000 mg/L) obtained from AccuStandard (New Haven, USA) and Merck, respectively.

Download English Version:

<https://daneshyari.com/en/article/10547956>

Download Persian Version:

<https://daneshyari.com/article/10547956>

[Daneshyari.com](https://daneshyari.com)