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

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Abstract

A postcolumn fluorometric derivatization method for the determination of trace amounts of ammonium ion (μg/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 × 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.

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,

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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 ammomia 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*-phthaldialdehyde (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-NH_3 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 μg/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 NH_4^+ was 12.8 μg/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 NH_4^+ 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*-phthaldialdehyde (>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.

The standard solutions of ammonium ion were diluted to proper concentrations (each 0.1, 0.2, 0.5, 1, 2, 3, 4 and 5 μM). Extreme care is necessary to make low-level standards, freshly deionized water must be used and exposure to ambient air avoided. Such standards must be used immediately after preparation. Doubly deionized water prepared with a Milli-Q system (Millipore, Bedford, MA, USA) or doubly deionized-distilled water was used exclusively for all solutions (≥18.2 MΩ-cm resistivity). Solution pH was measured with a Radiometer analytical Ioncheck 45 meter and combination glass electrode (Mettler Toledo Inlab 439/120). The pH of sample solutions was adjusted by adding aliquots of 1 M or 0.1 M NaOH to the desired pH. The pH of the buffer was checked periodically and readjusted when necessary.

Photochemical redox reactions of copper(II)/amino-acid complexes were studied. Real samples were from photochemical redox reactions of Cu(II)/alanine complex. They were analyzed once illuminated at 313 nm for 10 min and without any previous treatments or filtration. The method was also evaluated by using seawater samples collected from the south-western coast of Taiwan on 24 August, 2004. The samples were stored at 4 °C in plastic bottles.

2.2. Apparatus

The ion chromatographic system consisted of the following components connected in series: a microvolume double-plunger pump (LC-10AD, Shimatzu, Tokyo, Japan), a Rheodyne (Cotati, CA, USA) Model 7125 injector, a guard column and a cation-exchange analytical column, a postcolumn reactor (described in the next paragraph), and a variable-wavelength fluorometric detector equipped with a xenon lamp (RF-10AxL, Shimatzu, Tokyo, Japan). The flow diagram of the IC-FL system is shown in Fig. 1.

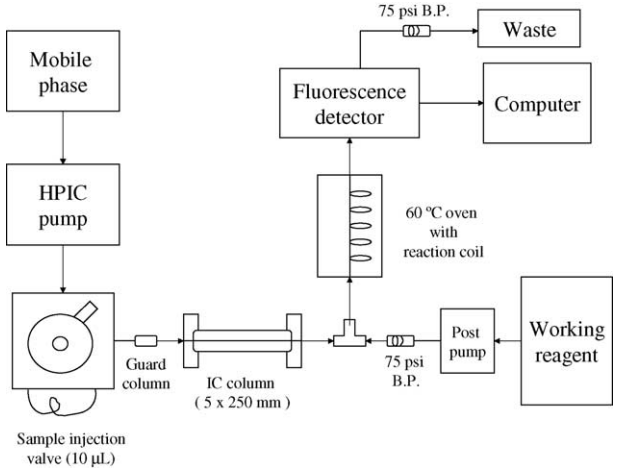

Fig. 1. Schematic diagram of IC-FL system for ammonium ion analysis. Optimal operation condition: mobile phase, 30 mM Methanesulfonic acid (MSA) solution at 1.0 mL/min; working reagent, 50 mM OPA, 3.2 mM sodium sulfite, 0.32 M borate buffer solution (pH 12.0) at 0.25 mL/min.

For continuous postcolumn derivatization in liquid chromatography, the CRX 400 postcolumn reactor (Pickering Laboratories, CA, USA) was constructed with a reaction coil composed of 0.5 mm I.D. × 15.28 m (1.6 mm O.D.) knitted PTFE tubing with reaction volume 3.0 mL. The reaction coil was made of precision-bore, heavy wall PTFE tubing embedded in a heated silicone rubber block and wound on an aluminum spool, with the heater in the center. The coil was wrapped with aluminum foil to restrict oxygen permeation through the PTFE tubing. UV–vis absorbance measurements were made with a double-beam scanning spectrophotometer (Shimadzu UV-1601, Tokyo, Japan) and a custom-built constant-temperature (25 °C, Fisher 910 recirculator) variable-pathlength aluminum cuvette holder (black-anodized). Varian Cary Eclipse fluorescence spectrophotometer (Victoria, Australia) was used for measuring ammonium concentrations in batch experiments.

2.3. Analytical methods

Two columns were tested in this study: Alltech Universal cation column (100 mm × 4.6 mm I.D., 7 μm particle size) and Dionex IonPac CS16 analytical column (250 mm × 5 mm I.D., <6 μm particle size). We adopted the latter one as it gave better reproducibility of ammonium peak area and faster equilibration in high-salinity water samples (such as 0.10 M NaCl). The high-capacity cation-exchange Dionex IonPac CS16 analytical column (250 mm × 5 mm) and a CG16 guard column (50 mm × 5 mm) were operated at 25 °C with an isocratic 30 mM methanesulfonic acid (MSA) eluent at flow-rate 1.0 mL/min, corresponding to 150 s of postcolumn derivatization at 60 °C. For the optimum reaction conditions after mixing, the postcolumn derivatization reagent was selected to be 0.32 M sodium borate buffer (pH 12.0) containing 50 mM OPA and 3.2 mM sodium sulfite at flow-rate 0.25 mL/min. The injection volume was 10 μL.

3. Results and discussion

3.1. Spectral characteristics of the reaction product and detection sensitivity

The excitation and emission spectra of the OPA-NH_3-sulfite reaction product are shown in Fig. 2. The reaction product of ammonia with OPA reagent has the optimum excitation wavelength (λ_{ex}) at 364 nm and the optimum emission wavelength (λ_{em}) at 425 nm, showing similar spectral characteristics as shown by Genfa and Dasgupta [18]. In addition to sulfite, it is well known that OPA also reacts with organic thiols such as 2-mercaptoethanol and 3-mercaptopropionic acid to form intensely fluorescent isoindole derivatives in the ternary reaction of OPA with ammonia or primary amines [36]. The reducing agent can also be the analytical target if it is the limiting reagent. For example, a method for the determination of cyanide ion by reaction with sufficient

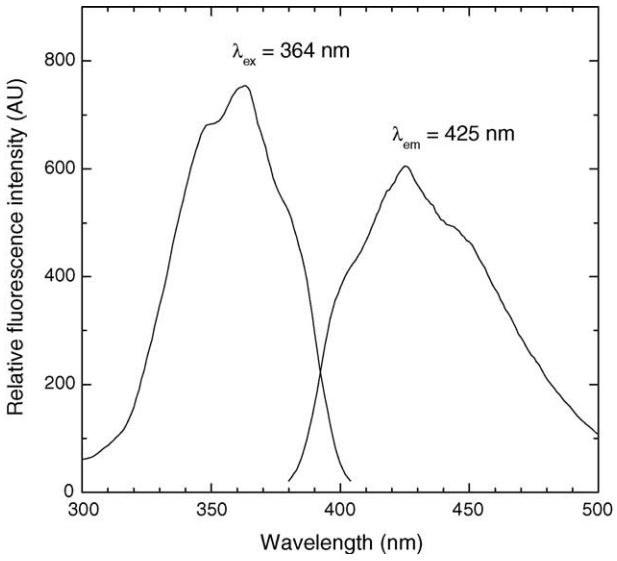

Fig. 2. Excitation (ex) and emission (em) spectra of products of OPA-NH_3-sulfite (pH 10.0). See text for details.

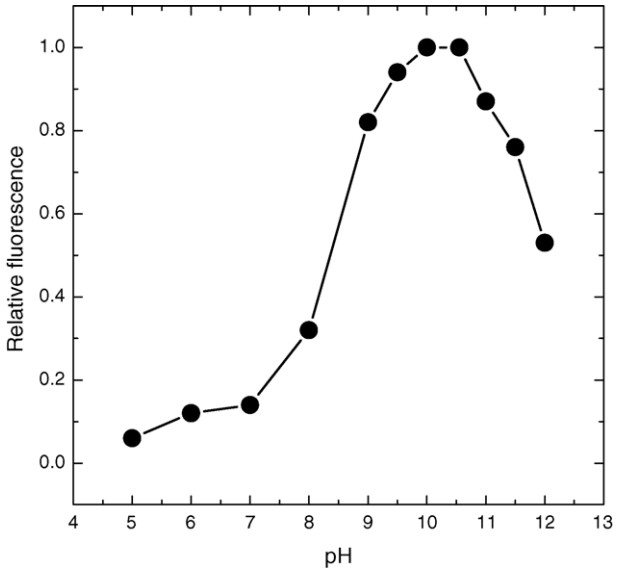

Fig. 3. Effect of reaction pH on the fluorescence of OPA-NH_3-sulfite product. The test ammonium concentration was 5 μM in 10 mM OPA, 0.16 mM sulfite, and 0.16 M borate buffer at 60 °C.

ammonium ion and OPA has been developed [37]. In this study, two other reducing agents, 2-mercaptoethanol and 3-mercaptopropionic acid, were tested and compared with sulfite for the determination of ammonia by reaction with OPA. The final solution for the three cases contained the same concentration of ammonia (5 μM) and OPA (10 mM). The excitation and emission spectra of the OPA-2-mercaptoethanol-NH_3 and OPA-3-mercaptopropionic acid-NH_3 reaction products are essentially the same and similar to those shown in Fig. 2 but with maximum excitation and emission wavelengths at 336 and 459 nm, respectively. Results obtained in each case at the optimal excitation and emission wavelengths show that the fluorescence intensity follows in order: sulfite, 2-mercaptoethanol, and 3-mercaptopropionic acid, with the ratio of 6.1:1.7:1. Therefore, it is clearly that the sulfite reaction product is superior to organic thiols for the determination of ammonia by reaction with OPA.

In the following investigation, the pH, the reaction temperature and time, the buffer composition, and reagent concentration were studied in a batch system and were optimized. The final solution for all these cases contained the same concentration of ammonium (5.0 μM).

3.2. Reaction kinetics: effect of pH, temperature, reaction time, and reagent concentration

The effect of reaction pH on the fluorescence of OPA-NH_3-sulfite product was investigated. As shown in Fig. 3, the intensity increased with increasing pH from 5 up to 10. The formation of the fluorescent isoindole is complex and may involve steps which could be pH dependent [38]. Ammonia exists in aqueous systems as both NH_3 and NH_4^+. The increase in the concentration of NH_3 is probably the reason for the increase in fluorescence intensity with pH. When the pH was higher than 11, the fluorescence peak decreased. The maximum intensity was achieved at pH 10–10.5, similar to previous studies [15,18].

The effect of reaction temperature on the fluorescence intensity was studied. As shown in Fig. 4, the intensity increased with increasing temperature from 40 to 60 °C. When the reaction temperature was above 60 °C, the fluorescence peak decreased probably because of the decomposition of NH_3-OPA fluorescing derivative. Sulfite is a weaker nucleophile than organic thiols and as such the reaction is expected to be slower for sulfite. The effect of reaction time on the fluorescence intensity is shown in

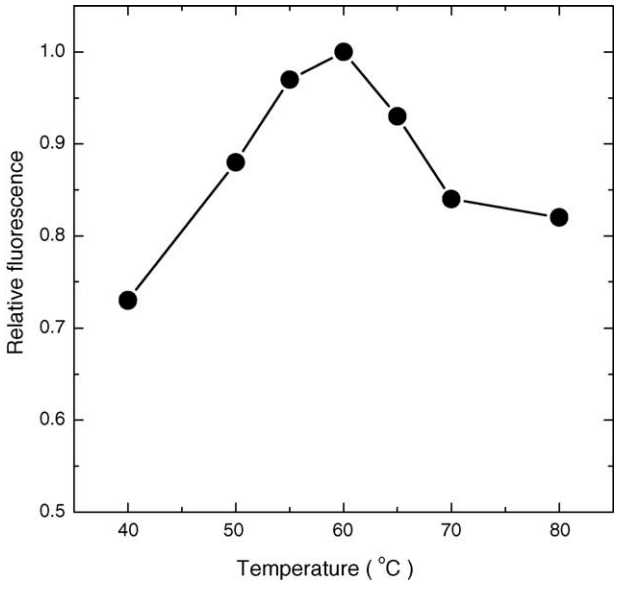

Fig. 4. Effect of reaction temperature on the fluorescence of OPA-NH_3-sulfite product. The test ammonium concentration was 5 μM in 10 mM OPA, 0.16 mM sulfite, and 0.16 M borate buffer at pH 10.

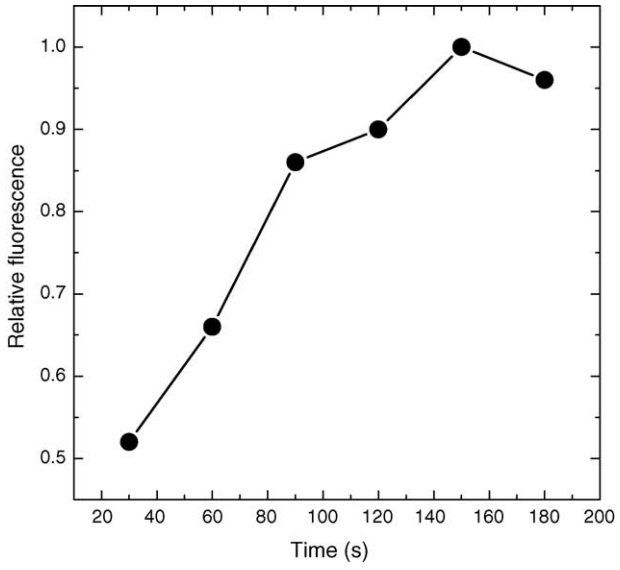

Fig. 5. Effect of reaction time on the fluorescence of OPA-NH_3-sulfite product. The test ammonium concentration was 5 μM in 10 mM OP A, 0.16 mM sulfite, and 0.16 M borate buffer at pH 10 and reaction temperature 60 °C.

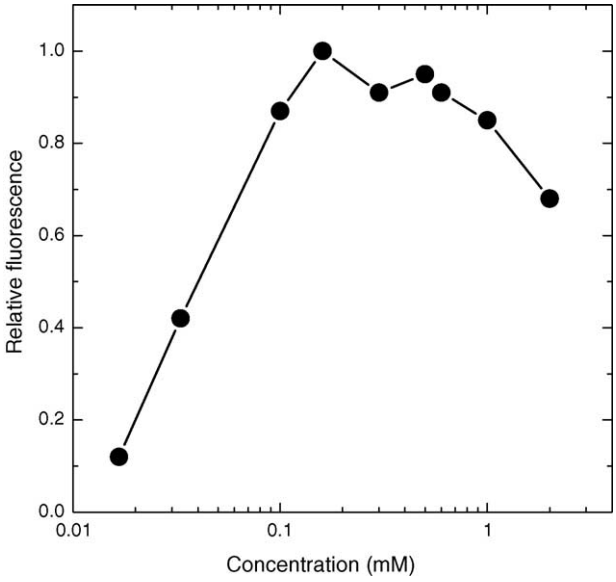

Fig. 6. Effect of sodium sulfite concentration on the fluorescence of OPA-NH_3-sulfite product. The test ammonium concentration was 5 μM in 10 mM OPA and 0.16 M borate buffer at pH 10. The reaction temperature was at 60 °C.

Fig. 5. The intensity gradually increased with increasing time. When the reaction time was longer than 150 s, the reaction was complete and the fluorescence peak remained stable and high. In the present method the optimum reaction temperature was determined to be 60 °C, a temperature 25 °C lower than in the flow injection system from Genfa and Dasgupta [18]. This may be attributed to the longer reaction time, 150 s compared to 40 s in the flow injection system. Consequently, the postcolumn reactor was operated at 60 °C and the residence time of sample in the reactor was 150 s.

The effect of reagent concentrations on the fluorescence of OPA-NH_3-sulfite product was examined. The fluorescence intensity increased as the OPA concentration of the reagent increased up to 10 mM. Further increase in the OPA concentration caused a slight decrease in fluorescence. A similar trend was also observed and the optimum concentration of OPA at 10 mM is not markedly different from those for the thiol reaction system [16,18]. The fluorescence intensity was more sensitive to the concentration of sulfite than that of OPA reagent. As shown in Fig. 6, the maximum fluorescence intensity was obtained for sulfite concentration between 0.16 and 0.6 mM in the reaction medium. On the basis of these results, a 0.16 mM concentration of sulfite was chosen. It should be noted that the optimum sulfite concentration is four times lower than in the postcolumn reactor. The concentration of borate was varied from 0.025 to 0.2 M for the fluorescence of OPA-NH_3-sulfite product reaction. No effects of borate concentration on the fluorescence intensity could be observed. The concentration of borate was set at 0.16 M.

3.3. System performance

The precision (expressed in terms of relative standard deviation, RSD) of the IC-FL method for the ammonium determination was fairly good for the peak area (RSD < 4%). The RSD for the retention times was typically less than 1%. Calibration graph was constructed with ammonium standards ranging from 0.05 to 5.0 μM in the condition of 100 μM Cu(II), 2.0 mM alanine, and 0.20 M NaCl at pH 6.0. The data points from the calibration curve were subjected to the least-squares regression analysis and the linearity of the present method was good as suggested by the square of correlation coefficients being better than 0.997. The method detection limits (MDLs) were calculated as three times the standard deviation of seven replicate measurements at 0.1 μM, close to blank concentration [39,40]. The MDL for the determination of ammonia was at the μg/L level, corresponding to picomole of ammonia in the injected sample.

3.4. Interferences

Interferences to ammonium determination were observed with amino acids, cupric, and sodium, which exist in typical samples for this study. It was especially important to check interferences from amino acids, since OPA is used as a specific reagent for these compounds in certain analytical conditions. Genfa and Dasgupta reported that the responses of the similar reaction system described to 11 common amino acids were measured relative to ammonium at a concentration level of 10 μM [18]. Their results showed that the OPA-sulfite reaction system is obviously more selective for NH_3 than for amino acids. Among 11 amino acids, the highest relative response is 6.02% for alanine relative to ammonium. Table 1 lists levels of interference with 2 μM ammonium from different concentrations of alanine. The results show that alanine gave a diminished recovery under batch conditions. Negative interferences

Table 1
Interference of various concentrations of alanine on the recoveries of ammonium by (A) batch systems and (B) a postcolumn derivatization system[a]

(A) Batch systems		(B) Postcolumn derivatization	
Alanine (mM)	Recovery (%)[b]	Alanine (mM)	Recovery (%)[b]
0.01	100	0.20	97
0.02	95	0.50	94
0.05	89	1.00	109
0.10	86	1.50	95
0.16	73	2.00	104
0.21	61		

[a] The test ammonium concentration was 2 μM in 10 mM OPA, 0.64 mM sulfite, and 0.16 M borate buffer at pH 10 and 60 °C.
[b] Recoveries shown are relative to the response of the experimental system without alanine.

were to be expected because alanine may compete with ammonium for OPA-sulfite reaction. In contrast, alanine did not interfere at the concentration level 1000 times higher than that of ammonium by the postcolumn derivatization method. Therefore, if ammonium is not first separated from amino acids, measurements are subject to inevitable interferences from primary amines. The method showed considerable selectivity for ammonia over alanine by a factor of 12 000.

Copper(II) interference was checked for in the range of 20–250 μM and no effect was detected. Copper(II) concentrations in natural waters do not reach interference levels. As an alternative strategy, EDTA was used to effectively mask the interferences by copper(II), which is known to be a quencher of fluorescence. Because the CS 16 is a high-capacity cation-exchange column, samples with a wide range of ionic strength up to 0.20 M NaCl can be analyzed without interference from the matrix. Baseline instability occurred when ionic strength was beyond 0.20 M. Nevertheless, it should be noted that no effects of salt (or ionic strength) up to 0.54 M NaCl were observed on the fluorescence of OPA-NH_3-sulfite product reaction.

3.5. Application

One of the major advantages of the present method is its high sensitivity and selectivity compared with other techniques for ammonium ion. The method is particularly well suited for the determination of ammonium ion in matrices with high concentrations of amino acids and sodium ion. A standard and two real samples from seawater and photolyzed solution were analyzed to test the utility of the proposed IC-FL method, as depicted in Fig. 7. The seawater sample collected from the south-western coast of Taiwan was analyzed and 0.41 μM of ammonium was measured, as shown in Fig. 7(A). The value is close to that observed in Woods Hole seawater [20].

It has been shown that the structure of organic Cu(II) complexes has a strong impact on the quantum yield of photolysis of Cu(II)/dicarboxylate complexes [41,42]. To elucidate the effects of ligand structure on the photochemical redox reactions of Cu(II) complexes, photoproduction of ammonia in the system must be determined. A given Cu(II)/alanine solution was studied at 25 °C, containing 50 μM Cu(II), 2.0 mM alanine, 100 μM phosphate, and 0.10 M NaCl at pH 6.0. After illuminated at 313 nm for 8 min, the photolyzed solution was analyzed. As shown in Fig. 7(B), the alanine peak eluted at 10.6 min. 1.62 μM of ammonium was measured at 15.2 min, followed by an unknown peak occurring at 17.8 min. The unknown peak may probably represent a new photoproduct, which requires further elaborate investigations to clarify the mechanism of photolysis of Cu(II)/amino acid complexes.

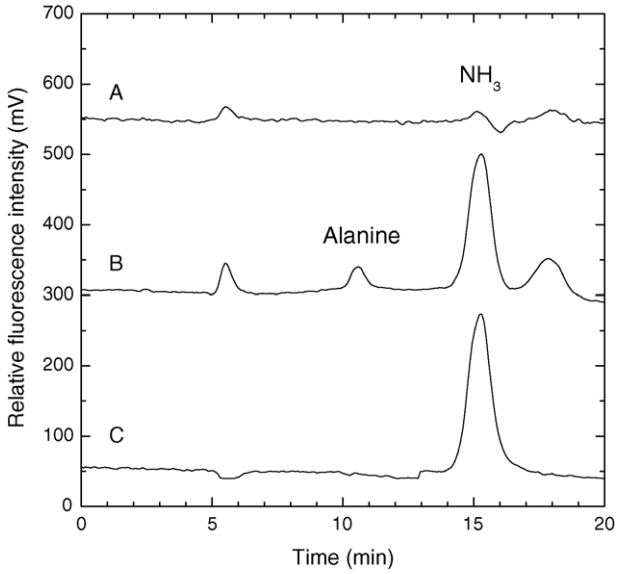

Fig. 7. Chromatograms of (A) diluted seawater (10 × dilution), (B) real sample from photolysis of Cu(II)/alanine complex system at 313 nm for 8 min, and (C) standard solution containing 2.0 μM ammonium ion. Other conditions as in Section 2.3.

4. Conclusion

A highly sensitive, reproducible and selective determination of ammonium ion was performed using ion chromatography employing postcolumn derivatization with OPA and sulfite. The IC-FL method has been successfully applied to the analysis of trace amounts of ammonium ion in copper(II)/alanine complex systems and seawater matrices. The new method described is simple and highly effective in the presence of interferences including amino acids and salts.

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