Optimization of a salinity-interference-free indophenol method for the determination of ammonium in natural waters using *o*-phenylphenol

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ABSTRACT

The indophenol blue (IPB) method based on Berthelot's reaction is one of the most widely used methods for the determination of ammonium in natural waters. This study comprehensively optimized the kinetics of the IPB reaction under different reagent concentrations, temperature and salinity. The normally used toxic and odorous phenol was replaced by the less toxic, stable flaky crystalline compound, *o*-phenylphenol. With the application of nitroprusside as the catalyst, the reaction can be finished within 20 min at room temperature and the formed color compound is stable for 24 h. Under the optimized conditions, the method shows high reproducibility (relative standard deviations of 0.64–1.71%, n = 11), highly linear calibration up to 100 μM (R^2 = 0.9995, n = 165, 17 days) and a low detection limit of 0.2 μM. This method was successfully applied to measure ammonium in estuarine and coastal surface water (n = 63). The results showed insignificant differences with the results obtained using both the standard AutoAnalyzer method and a fluorometric *o*-phthaldialdehyde method at the 95% confidence level. Compared with previous studies, this method shows the advantages of relatively fast reaction, low toxicity and easy reagent preparation. It is salinity-interference-free and robust (no temperature control is required, reagents can be stored up to 10 days), and suitable for routine analysis under harsh field conditions.

1. Introduction

Nitrogen, the most abundant chemical element in the atmosphere, is an essential building block in the structures of many key biomolecules (e.g., amino acids, nucleotides, amino sugars) [1]. In aquatic environments, inorganic nitrogen (present as nitrate, nitrite, and ammonium) is essential to fuel production by phytoplankton and macrophytes, but if driven to high levels by pollution can cause severe ecological and toxicological effects [2,3]. The chemical form of ammonium is important due to its toxicity in aquatic ecosystems, with ammonia (NH_3) and the relatively less toxic ionized ammonium ion (NH_4^+) both present, and the latter predominant in most natural waters (at pH lower than 8.75) [4]. The sum of NH_3 and NH_4^+ is hereafter referred to as "ammonium". The concentration of ammonium is accordingly an important water quality parameter to policy makers, regulatory bodies and the community [5], and its accurate determination is of great interest and challenging for both environmental scientists and oceanographers [1,6].

Multiple methods exist for ammonium measurement. Molins-Legua et al. [4] critically evaluated the main parameters involved in several methods for measuring ammonium in different water matrices and gave guidelines for selecting suitable methods. More recently, Šraj et al. [7] reviewed analytical challenges and advantages of using flow-based methodologies for ammonium determination in estuarine and marine waters. Further comparisons of different methods can also be found in part of some papers and book chapter [8–12]. Three methods are particularly common for the determination of ammonium in natural waters [7,9,10]: i) extraction of ammonium as NH_3 via gas diffusion, coupled with a variety of detection methods, ii) reaction with *o*-phthaldialdehyde (OPA) and fluorometric detection, iii) colorimetric detection of the complex organic products of the classic Berthelot reaction. The utilization of gas diffusion can minimize or eliminate the interferences such as ions and organic nitrogen compounds (e.g. amino acids) [5,13]. The OPA-based fluorometric method is very sensitive and suitable for nanomolar level ammonium measurement [14,15]. These methods have been applied for the laboratory or field analysis of different samples by researchers [7,9]. However, the indophenol blue (IPB) method based on Berthelot's reaction is still the most widely used method for the determination of ammonium in natural waters, which is also the standard methods in different documents [16–18].

Briefly, the IPB method consists of reacting ammonia and hypochlorite to form a monochloramine, which subsequently reacts with a

phenolic compound under alkaline conditions in the presence of catalytic quantities of nitroprusside. The absorbance of the formed IPB is linearly proportional to the concentration of ammonium [7,18]. The mechanism of the Berthelot reaction is very complicated. Searle [19] comprehensively reviewed (with 386 references) the IPB method for the determination of ammonium and other N-containing chemicals. The reaction conditions, such as reagent choices (phenols, hypochlorite sources, catalysts, complexing reagents), reagent concentrations, order of addition, pH, temperature and matrix (e.g. seawater) can all affect the sensitivity of the reaction [19–21]. Different researchers may get varied results even with the nominal same chemistry, which means the accurate measurement of ammonium is the most challenging among the nutrient analyses [4,7]. For instance, during the Fifth ICES Intercomparison Exercise for the determination of nutrients in seawater, there were large disparities in the ammonium results among the participants: standard deviations were 22–23% at the medium and high concentration levels, and 56% at the low level [22].

There have been a few comprehensive studies of the kinetic and mechanistic aspects of the IPB method, mostly in freshwater [23–25]. However, seawater is more complicated because of high ionic strength and buffering capacity [26]. For example, in applying the IPB method for seawater analysis, Pai et al. [27] found a "pH-shift" problem associated with the buffering capacity of Mg^{2+} and added citrate (used as complexing reagent), which was not a simple "salinity effect" from the difference of ionic strength. There are contradictory views with regard to the essential concentrations of different reagents for IPB method, as well as the temperature and time required for the formation of IPB [19,22].

These factors prompted a mechanistic study of the Berthelot reaction in some detail, particularly with the aim to improve the practicability and reproducibility of the method for routine analysis. Moreover, the commonly used reagent phenol is caustic, odorous, toxic, and difficult to handle because it exists in transition between solid and liquid phases at room temperature. Besides sodium salicylate [24], the reagent *o*-phenylphenol (OPP) can be another safer alternative of phenol for indophenol reaction because it is available as stable solid (tabular flaky crystals) and has no caustic odor, or the toxicity of phenol [28,29]. The OPP-based indophenolic compound is not significantly affected by amino acids or urea under relatively large salinity range [28]. However, there are no detailed reports about reaction kinetics, reagent storage requirements, or salinity interference effects, which are crucial and challenging for field application in estuarine and coastal areas [6,7]. Here we report comprehensive studies of these aspects of the IPB method using OPP, and the development of a simple, fast, and robust procedure for the determination of ammonium in natural waters. There is no need to correct for salinity effects, and thus it can be used for routine analysis of fresh and seawater samples, and offers great benefits to estuarine and coastal studies. Excellent precision and reproducibility, illustrate the superiority of the new method over previous procedures.

2. Experimental

2.1. Reagents and standards

All the chemicals used in this study were reagent grade or better and purchased from Sinopharm Chemical Reagent Co., China, unless stated otherwise. Ultra-pure water was freshly collected from a Millipore water purification system (www.merckmillipore.com). Aged surface oligotrophic seawater collected from the South China Sea was used as low nutrient seawater (LNSW) for study of matrix effects. It contained only nanomolar level ammonium, as measured before [15,30], which was negligible for the purposes of this study.

The ammonium stock solution was prepared by dissolving oven-dried (105 °C for 2 h) NH₄Cl (Fluka, USA) in pure water, and stored at 4 °C while not in use. Working standards were prepared by stepwise
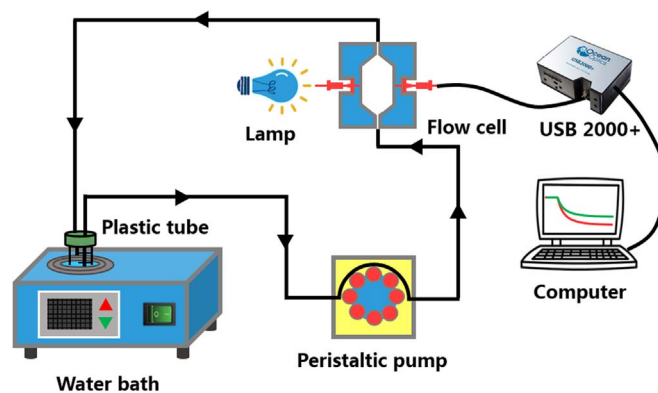

Fig. 1. Schematic diagram of continuous flow manifold configuration for dynamics study of the IPB method.

dilution. The recipe of IPB reagents used in the experiment was as follows: (1) citrate solution of 500 g/L was prepared by dissolving 50 g tri-sodium citrate in 100 mL water with ultrasonic assistance for dissolution; it is stable for months at 4 °C; (2) alkaline OPP solution of 20 g/L was prepared by dissolving 2 g of OPP and 1 g NaOH in 100 mL water; (3) alkaline sodium dichloroisocyanurate (NaDTT) solution of 10 g/L was prepared by dissolving 1 g of NaDTT (Sigma-Aldrich, USA) and 1 g NaOH in 100 mL water; (4) alkaline sodium nitroprusside (NP) solution of 5 g/L was prepared by dissolving 0.5 g NP (Merck-chemicals, Germany) and 6 g NaOH in 100 mL water. The reagent bottles were sealed in plastic bags to prevent atmospheric ammonia contamination. The OPP, NaDTT and NP solution are stable for at least 10 days kept in a refrigerator.

2.2. Experimental setup for reaction dynamics investigations

The experimental setup for studying the dynamics of the IPB method was similar to our previous study of urea analysis [31], as shown in Fig. 1. For 25 mL standard test solution, citrate, OPP, NaDTT, and sodium nitroprusside solutions of different concentrations were added sequentially into a plastic tube and mixed thoroughly. Then immediately the tube was put in the water bath (Jintan Shunhua Instrument, China). A peristaltic pump (BT100-1L, Baoding Longer Precision Pump, China) was used to circulate the liquid. The liquid flowed through a cross-shaped flow cell, which is bubble-interference free and has been described elsewhere [32,33]. A continuous optical measurement system (a tungsten halogen lamp (LS-11-LL) and a miniature USB 2000+ CCD spectrophotometer, both from Ocean Optics, USA) were used to detect absorbances at 700 nm (for signal) and 850 nm (for baseline correction).

The dynamics tests used LNSW standard solutions spiked with 20 μM ammonium. At the end of each dynamics experiment, a spectrum was taken to compare the final IPB product absorbance characteristics. The pH of the final reaction liquid was measured using a pH meter (Orion STAR A211, Thermo Scientific, USA), which had been calibrated using NBS standard reference buffer. All the experiments were conducted at 25 °C except for the temperature effect experiment. During the optimization experiments for OPP, NaDTT, and NP solutions, the NaOH concentrations in the final reaction mixture were kept the same. Because three reagents contain NaOH, the investigation of NaOH concentration effect was carried out only changing the NaOH in NP solution while keeping the recipe of OPP and NaDTT solutions the same as detailed in Section 2.1.

2.3. Procedure for routine analysis

For laboratory routine analysis, a 25 mL water sample (or standard solution) was added to a plastic tube, and 4 mL citrate solution, 1 mL

OPP solution, 1 mL NaDTT solution and 1 mL NP solution were added to the solution sequentially without delay and mixed thoroughly, which is essential to prevent decomposition of monochloramine [27]. The mixture was rested at room temperature for 20 min, after which the formed IPB was found to be stable for 24 h. The absorbance was measured at 700 nm using a simple spectrophotometer equipped with a 1 cm cuvette (V1100D, Mapada Instruments, China). Because the sensitivity of this method is identical in both freshwater and seawater (*discussed below*), pure water can be used to prepare calibration curves, and these applied to samples with varying salinity.

2.4. Sampling

Lake water was collected from Furong Lake in the Xiang'an campus of Xiamen University. River water was collected from Min and Jiulong River, Fujian, China. Seawater was collected from Xiamen Bay and South China Sea. These samples were filtered through a 0.45 µm syringe type polyether sulfone filter immediately after collection. The filtered samples were kept at 4 °C and analyzed within 24 h.

3. Results and discussion

3.1. Order of reagent addition

For IPB method, different orders of reagent addition have been evaluated and inversion of the order or inadequate mixing can cause erratic results [22,34]. In our preliminary research using phenol, we also found the order was of great importance (data not shown). Therefore, based on the previous publications [19,22,27,34] and the preliminary results, the order of reagent addition in this study was set as: citrate, OPP, NaDTT, and NP solution. Thorough mixing is needed after each addition. The possible reactions are shown in Fig. 2.

3.2. Effects of different reagents on reaction rates and endpoints

In addition to the main active ingredients listed in Section 3.1, citrate is used as a complexing reagent for seawater analysis, and needs to be present in excess. Pai et al. [27] found it was necessary to raise the citrate concentration by 20% to ensure it is in excess of $[Mg^{2+}]$. Here we chose to add 4 mL citrate solution (500 g/L) in 25 mL samples, according to previous study [28]. The effects of different reagents concentrations on the IPB formation are presented in Fig. 3.

OPP has been proved to be an effective alternative to phenol in the IPB reaction [28,29]. As shown in Fig. 3-A, at lower OPP concentrations (0.16 and 0.31 g/L), the reaction was unfinished after 15 min and the maximum absorption wavelengths exhibited small "blue-shifts" (Fig. 3-B). All the kinetic curves and spectra were identical when OPP concentration was higher than 0.63 g/L. Thus, the optimized final OPP concentration in the reaction mixture was chosen as 0.63 g/L.

NaDTT was used instead of hypochlorite owing to its stability and convenience of use [27]. As shown in Fig. 3-C/D, in the lower range of tested concentration (0.08–0.37 g/L) of NaDTT solution, the kinetic curves and spectra were almost identical; the reaction was faster with higher NaDTT concentration (0.47–0.78 g/L), but reaction mixture color was unusual, with tiny red "dots". Therefore, the final OPP concentration in the reaction mixture was optimized as 0.31 g/L.

NP is the most widely used catalyst of IPB reaction because of the increased reaction rate, sensitivity and stability of the indophenol produced [19,25]. As shown in Fig. 3-E/F, it is obvious the reaction was accelerated with increasing concentrations of NP. No difference in the kinetic curve and spectra was observed when the concentration was higher than 0.13 g/L. Therefore, the final NP concentration in the reaction mixture was optimized as 0.16 g/L.

In seawater analysis, the salinity content of the sample sometimes affects the color development of the indophenol reaction. This problem is actually associated with change of pH rather than salinity itself in the reaction solution, and extra alkali reagent should therefore be added to seawater samples [27,28]. As shown in Fig. 3-G, at lower NaOH concentration (0.94–1.56 g/L), the reaction did not finish within 15 min. At high NaOH concentration of 2.50 g/L, slight precipitation was observed. Therefore, the NaOH concentration in alkaline NP solution was chosen as 60 g/L to be consist with this optimization (final concentration in the mixture of sample and reagents was 1.88 g/L).

3.3. Effect of temperature

Under the optimized reagent conditions described above, the effect of temperature on the reaction was evaluated in the range 10–60 °C. As shown in Fig. 4, the formation of the product was temperature dependent, which is in accordance of previous study [35]. With increased temperature, the equilibration time decreased. At room temperature (20–30 °C), the reaction can be complete in less than 360 s. Although heating can increase the rate of color development, organic nitrogenous compounds might hydrolyze during heating under alkaline conditions
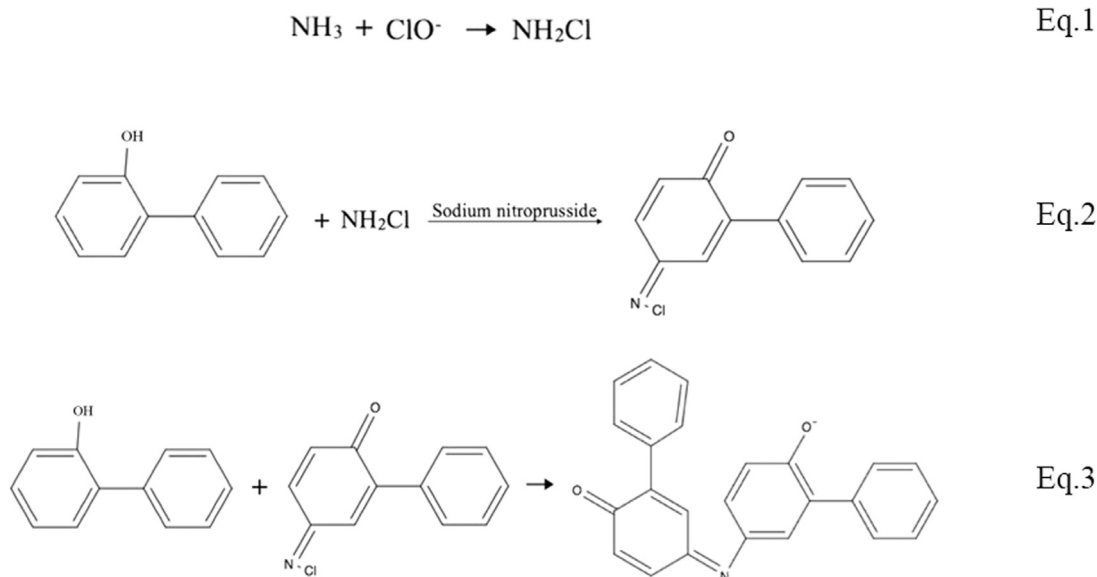
$$NH_3 + ClO^- \rightarrow NH_2Cl \qquad \text{Eq.1}$$

Eq.2

Eq.3

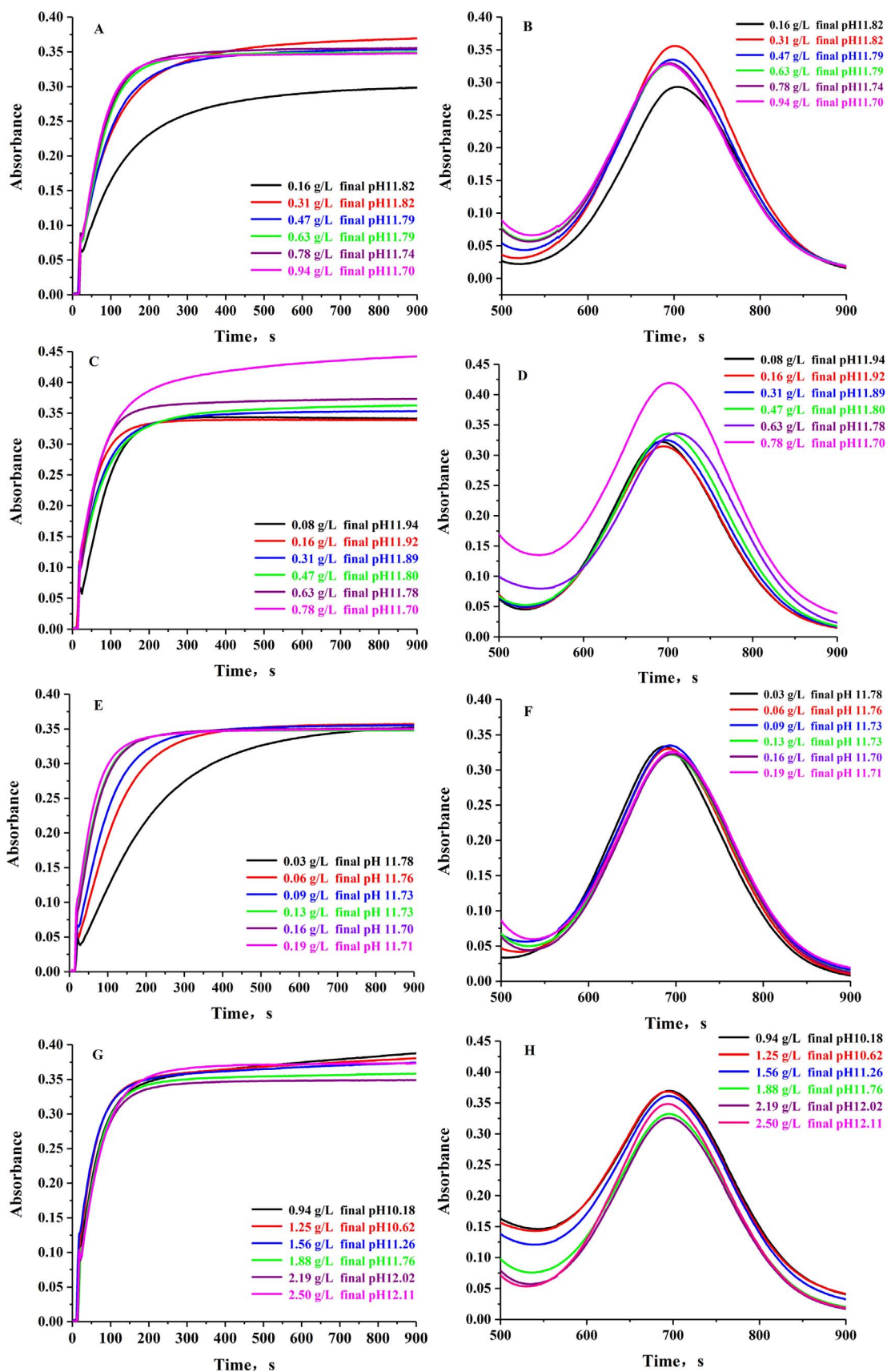**Fig. 2.** Mechanism of ammonium detection of OPP-based indophenol method.

Fig. 3. Effects of reagents concentrations (A/B: OPP; C/D: NaDTT; E/F: NP; G/H: NaOH) on the kinetics of the colorimetric IPB reaction and the final spectra of IPB compound. The values in the legends are the concentrations of different reagents and the pH value in the final reaction mixture.
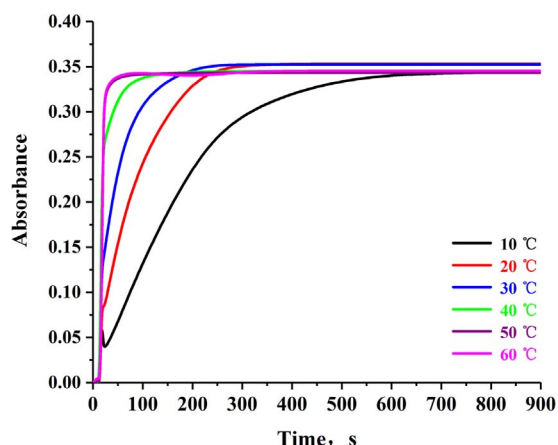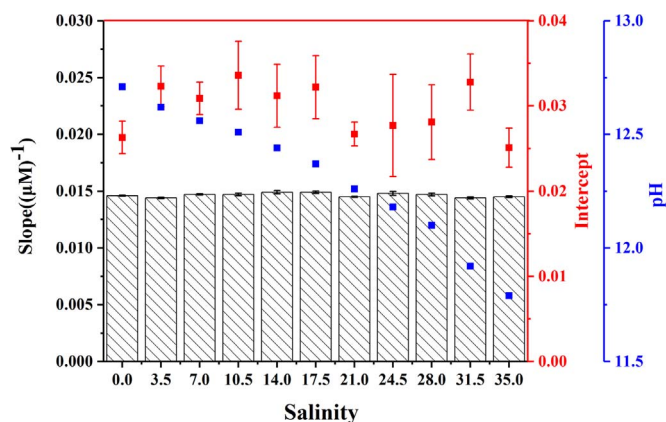
Fig. 4. Effect of temperature on reaction.

Fig. 5. Effect of salinity on reaction.

[21]. Therefore, room temperature is used in the further research, which also offers the advantage of simpler experimental equipment. For cold water analysis (e.g. polar area), temperature pre-adjustment or longer reaction time would be needed.

3.4. Effect of salinity

To study the effects of salinity, samples of varied ammonium concentrations (0, 10, 20, 30, 40, 50 and 60 µM) and different salinities were measured according to Section 2.3. The matrix were prepared by

mixing pure water and LNSW in different ratios. It was found that the reaction kinetics were salinity related. For example, the times for full reaction are 5 and 20 min for samples of salinity 35 and 0, respectively. As shown in Fig. 5, after reacting to achieve full colorization for ~ 30 min, the slopes and intercepts of the highly linear calibration curves ($R^2 > 0.999$) at different salinities were insignificantly different. The pH of the final reaction solution decreased with increased salinity, because the buffering capacity of Mg^{2+}-citrate increased at higher salinity [27]. In contrast to previous work, no extra NaOH solution is needed for saline samples. Therefore, this method can be considered a salinity-interference-free method and can be applied to various natural samples without salinity correction or the need to use varying reagent recipes. This advantage meant a wider and more convenient application, especially for highly challenging environments for chemical analysis such as estuarine and coastal areas [7].

3.5. Figures of merit

Under the optimized conditions described above, a calibration curve ranging from 0 to 100 µM ammonium was obtained with excellent linear regression ($R^2 = 0.9995$, n = 165, Fig. 6). It should be noted that these calibration curves were obtained on 17 different days with different matrix (pure water and saline water), showing high inter-day repeatability. The IPB molar absorptivity is around $1.9 \times 10^4\,M^{-1}\,cm^{-1}$, which is similar to studies using other reagents [19].

The relative standard deviations (RSDs) for the repetitive determination of samples at different concentrations (10, 30 and 50 µM) were 1.7%, 0.83% and 0.64% (n = 11), respectively, evidencing the good precision and high intra-day repeatability of the method. The detection limit was 0.2 µM based on the calculation of three times the standard deviation of the measured blanks (n = 11), which was low enough to meet the established guideline values for ammonium in marine waters [7 and references therein].

As shown in Table 1, the formed IPB color compound can be stable for at least 24 h at room temperature, which is useful when immediate analysis is not possible (e.g. on small fishing boat for natural water sampling).

3.6. Stability of reagent

Our long term goal is to combine the OPP based chemistry and automated flow analysis techniques for on-line ammonium monitoring in a river or shipboard/underway seawater analysis. Therefore, the evaluation of long-term stability of the reagent is essential for these applications in harsh conditions. As shown in Fig. 7, when stored in refrigerator, OPP, NaDTT and NP solution can be stable for at least 10
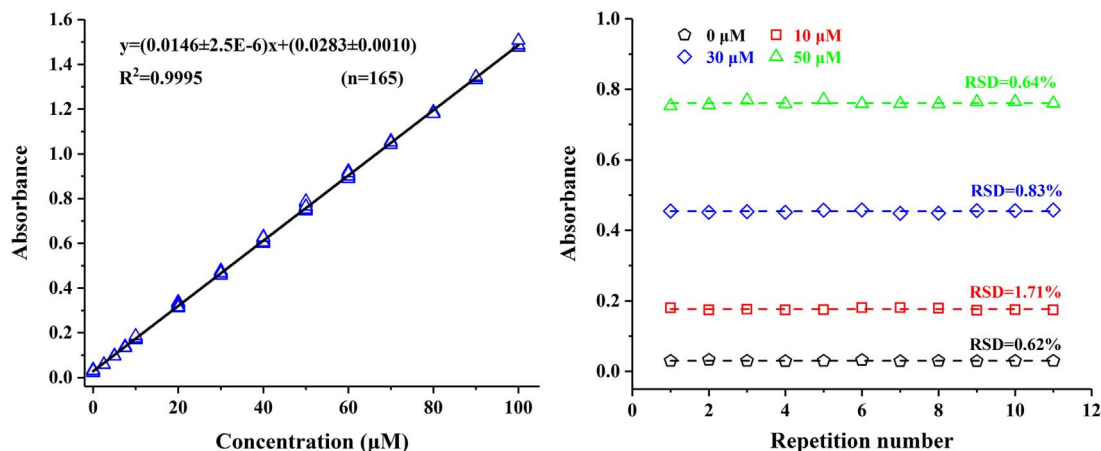

Fig. 6. Calibration curve (left) and repetitive determination data (right).

Table 1
Calibration curves at different reaction time.

Time after reaction, h	Calibration curve	R^2	pH
0.5	y = (0.0144 ± 6.3E−5)x + (0.0251 ± 0.0014)	0.9999	11.79
2.0	y = (0.0145 ± 6.0E−5)x + (0.0228 ± 0.0022)	0.9999	11.80
4.0	y = (0.0145 ± 6.1E−5)x + (0.0239 ± 0.0022)	0.9999	11.78
12.0	y = (0.0143 ± 7.0E−5)x + (0.0291 ± 0.0025)	0.9999	11.75
24.0	y = (0.0142 ± 6.6E−5)x + (0.0270 ± 0.0024)	0.9999	11.70

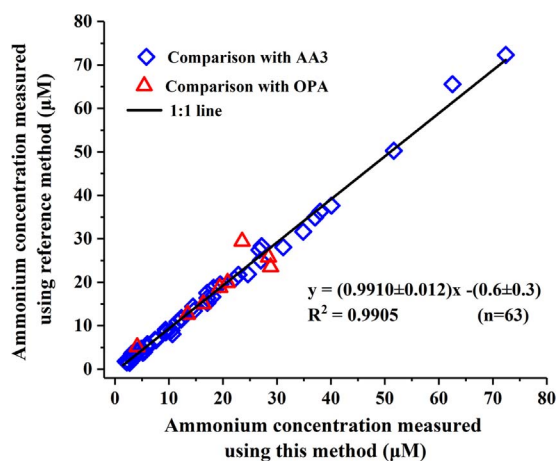**Fig. 7.** The absorbances of calibration curves using reagents stored for different durations.

Fig. 8. Comparison of analytical results obtained using this method and reference methods.

days. Afterwards, the absorbances increased slightly. Although the calibration curves are still linear ($R^2 > 0.999$) using aged reagents after 15 days (data not shown), it is recommended to re-check the efficiency and possible contamination of the reagents periodically. Longer storage time might be possible by using an inert gas to purge the water used to prepare the reagents and keeping then in opaque gas tight bags.

3.7. Validation of the method

Two separate approaches were conducted to validate the method:

(1) A total of 63 natural water samples were analyzed using this method and two other reference methods: an automated continuous flow (AutoAnalyzer III) method based spectrophotometric IPB chemistry using phenol [18] (n = 55) and a flow injection fluorometric method using OPA [36] (n = 8). The measured ammonium concentration ranged from 2 to 74 μM. As shown in Fig. 8, the values measured using this method and values obtained using the reference methods agreed very well, especially considering the OPA method was based on a totally different chemistry. There is no statistically significant difference between these two sets of data with the paired Student's *t*-test at the 95% confidence level.
(2) The recovery of ammonium spikes added to different real samples was tested, and found to vary between 97.1% and 108% (Table 2), indicating good accuracy and minimal matrix effects.

3.8. Application

In order to evaluate the wide applicability of this method, in additional to the samples collected for comparison and recovery evaluation, two more serious samples were analyzed using this method. As shown in Fig. 9, the ammonium concentration at different sites and a reservoir (Shuikou reservoir, Fujian, China) and estuary area (Jiulong river and Xiamen Bay, Fujian, China) were measured. These samples were also measured using a reference method [18], and the comparison data were shown in Fig. 8. The variation in ammonium concentrations could be attributed to the biological activities (e.g. ammonium removed by phytoplankton during photosynthesis) and river input (e.g. manure discharge from the animal husbandry industry) [37,38].

4. Conclusions

The accurate and reliable determination of ammonium is extremely important but also very challenging for marine and environmental scientists. The main reason is some fundamental mechanisms of the IPB method are indistinct. During this study, the parameters affecting the IPB reaction in saline waters have been comprehensively evaluated. The use of non-caustic-odor and easily prepared OPP reduced the inconvenience of using phenol. Compared with previous studies, this method shows the advantages of relatively fast reaction, low toxicity, and an easy reagent preparation recipe. It is salinity-interference-free, and
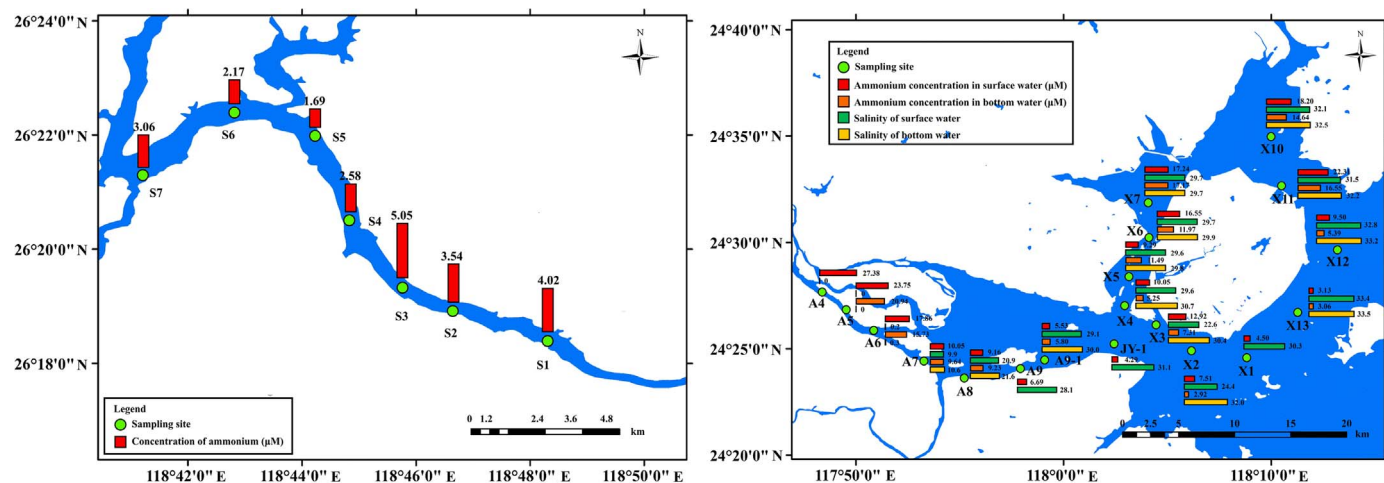
Table 2
Summary of ammonium concentration and recoveries in different aqueous samples.

Sample	Added, μM	Found, μM	Added, μM	Found, μM	Recovery, %
Tap water	0	0.90	5	5.90	100
Lake water	0	17.0	40	58.3	103
Mineral water	0	0.47	5	5.40	98.6
Seawater 1	0	0.46	5	5.80	107
Seawater 2	0	1.71	5	6.16	97.1
Seawater 3	0	ND[*]	5	5.39	108
River water 1	0	3.47	10	13.8	103
River water 2	0	5.32	20	26.5	106
River water 3	0	0.94	5	5.80	97.2

* ND, not detected.

Fig. 9. The spatial distribution of ammonium concentration in the surface water of Shuikou reservoir (left) and ammonium concentration and salinity in the surface and bottom water of Jiulong river and Xiamen Bay (right), Fujian, China.

offers procedural robustness (e.g. no temperature control, reagent storage up to 10 days, relatively insusceptible reaction conditions, etc.), making it highly suitable for routine analysis in the laboratory or under harsh field conditions. Future work will target the combination of this method with flow techniques [7,10] for more automated analysis of natural waters.

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