Determination of total dissolved nitrogen in seawater based on Sequential Injection Analysis

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Abstract In this paper, we established a sequential injection method to monitoring the concentration of total dissolved nitrogen (TDN) in seawater, which combined with an UV-thermal digestion. The sequential injection method consumes less reagents and less time, mixes more evenly than the flow injection method. TDN detection process mainly includes three parts: the digestion process of conversion organic nitrogen to nitrate, the reduction process of nitrate to nitrite, and the process of reaction between nitrite and chromogenic agent. The UV-thermal digestion that transforms dissolved organic nitrogen (DON) into nitrate has the highest digestion efficiency. The nitrate reduction process with a UV lamp is considered a greener choice which avoids the toxic substance and complicated operation of cadmium column reduction. We analyzed the optimal concentrations of all the reagents used in the experiment with the univariate experimental design. The reaction conditions were optimized by using three kinds of DON, which were C₂H₅NO₂, CH₄N₂S and C₁₀H₁₄N₂Na₂O₈. Under the optimal reaction conditions, we tested the seawater in the Qingdao Sculpture Garden and the recovery rate of adding standard. In May, the TDN concentration of seawater in Qingdao Sculpture Garden was 122.94μg/L, the relative standard deviation was 0.34%. The recovery rate was as high as 99.94% to 100.39%. The outcomes indicate that the proposed method can apply to the potential in-situ monitor.

1. Introduction
Nitrogen is an essential nutrient in seawater and plays an important role in the primary productivity[1]. Total nitrogen (TN) includes inorganic nitrogen and organic nitrogen. In practice, TN is an important variable to keep track of the nitrogen budget, it’s commonly used for monitoring the state of the environment in aquatic environments[2] (such as lakes, waste streams and sea ).

Total dissolved nitrogen (TDN) includes dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON). DON in seawater, mainly released by microalgae, is an important nitrogen source for microorganisms[3], which is mainly released by microalgae. The measurement of DON in seawater was an important task for environmental engineers, and the key challenge was how to apply the technologies to in-situ detection and monitoring. Many methods have been developed to determine the concentration of DON, such as gaseous molecule absorption spectrum method, oxidation with potassium persulfate-UV spectrophotometric method and persulfate method[4]. however, our former
experiments have shown that these methods were too unstable to be used in in-situ instrumental monitoring in seawater.

The in-situ monitoring instruments for seawater determination have emerged as the times require and attracted more and more attention[5]. The most basic requirement of in-situ analytical instruments is automatic detection system, and in all automatic systems, the flow injection analysis (FIA) is one of the most common choices[6]. But compared with the sequential injection analysis (SIA), the FIA has a limitation in terms of sample volume[7]. In this paper, we describe a new analysis method with the SIA for TDN determination.

2. Material and Methods

2.1 Reagents preparation

All chemicals used in this experiment were of analytical grade or better, and all solutions were prepared with ultrapure water (resistivity≥18.2MΩ cm) using a Millipore water purification system (Millipore Co., USA).

The oxidation reagent of alkaline persulfate solution (OR) was prepared by dissolving 8.0 g sodium hydroxide in 300mL pure water, natural cooling the sodium hydroxide solution to room temperature, add 20.0 g potassium persulfate and stir until dissolved, then completed the final volume to 400mL with pure water.

The photo-induced reagent consists of 20g diethylene triamine pentaacetic acid, 0.8g manganous chloride and 100g Tris (hydroxymethyl) aminomethane in 800mL pure water, adjusted the pH of the solution with sodium hydroxide solution to 7.70, then completed the final volume to 1L with pure water.

The chromogenic reagent was prepared by mixed the sulfonamide (SAM) and N-(1-naphtyl)-ethylenediamine dihydrochloride (NED) at a volume ratio of 2:1; the SAM was prepared by dissolving 2.0g sulfonamide (SAM) into 140mL HCl (14%), then completed the final volume to 200mL with pure water; the NED was prepared by dissolving 0.48g NED in 150 mL pure water and the final volume was completed to 200mL with pure water.

The artificial seawater was prepared by dissolving 31g sodium chloride, 10g magnesium sulphate and 0.05g sodium bicarbonate in 1L pure water.

The selected for the study included potassium nitrate, ammonium chloride and urea, which are frequently occurring components in natural waters.

The nitrogen compounds used in this study included potassium nitrate (KNO3), glycine (C2H5NO2), sulfourea (CH4N2S), disodium ethylenediamine tetraacetate (C10H14N2Na2O8), and the stock solution was prepared with nitrogen content of 1g/L in artificial seawater.

2.2 Apparatus

The SIA flow chat is shown in Fig.1. The digestion tube made in quartz is used to heat oxidized samples at 130 °C. The upper and lower ends of the digestion tube are connected with solenoid valves. During the thermal digestion process, the solenoid valves are closed to ensure the closure of the digestion tube and prevent liquid splashing.

The UV reduction part and the optical detection part refer to our previous work[5, 8].

2.3 Technological process and Sampling

The sample mixed with oxidation reagent is delivered into the thermal digester, then close the solenoid valves at both ends, turn on the UV lamp and start heating. After the digester gets the target temperature, remains for 30 minutes. The digested liquid cold down to 70°C naturally, and mixed with the reduction reagent and delivered the mixed solution into the ultraviolet reduction reactor for irradiation. Then close the two solenoid valves, turn off the UV lamp. During the UV reduction process, the mixed solution keeps ultraviolet irradiation for 3 minutes. Thesolution was carried out and reacts with the chromogenic agent for 2 minutes, then pushed to detect which was detected at 540nm.
3. Experimental Result

3.1 Optimizing of digestion methods

Various parameters affect the efficiency of thermal digestion, for example pH, concentration and digestion time on digestion efficiency. The nitrogen compounds used in the experiments included glycine (C₂H₅NO₂), sulfourea (CH₄N₂S) and disodium ethylenediamine tetraacetate (C₁₀H₁₄N₂Na₂O₈).

3.1.1 Optimizing of the pH for digestion reagent

The digestion efficient of nitrogen has a higher value under the alkaline condition than acid condition \(^9\). In this paper, we compared the effect of adding boric acid to the original digestion reagent on the digestion efficiency. The results get in our experiments are shown in Fig.2.

![Fig.2 the effect of H₃BO₃](image)

![Fig.3 Digestion models](image)
After the digestion progress, the solutions with H$_3$BO$_3$ have higher pH values than the solutions without H$_3$BO$_3$, that the pH values are roughly around 7.00. However, the effectivity of digestion of dissolved organic nitrogen reduced with the addition of H$_3$BO$_3$. We got a high conversion rate (>90%) obtained with UV-thermal digestion, except for CH$_4$N$_2$S which was a more refractory compound when digested with H$_3$BO$_3$. It can be seen from the table that the digestion reagent without H$_3$BO$_3$ is more conducive to nitrogen release. Because of the obtained results, we selected the digestion reagent without H$_3$BO$_3$ in the subsequent experiments.

3.1.2 the difference between two models of digestion
It proved that the persulfate oxidation (PO) method was more suitable than the UV method for the recovery of standard chemicals[10, 11]. Based on that, we compared the efficiency of the two different digestion models which were mentioned above. The conversion rates of nitrogen compound to nitrate form was calculated with respect to the signal generated using standards of potassium nitrate at an equivalent nitrogen concentration. The conversion rates of the two kinds of digestion are shown in fig3.

As we can see in the fig.2, except for CH$_4$N$_2$S (the effectivity of UV digestion), the conversion rates of other substances were ranged from 87.3% to 95.7%. The conversion rates with UV & thermal digestion of all substances are higher than the individual UV digestion. So we choose the combined UV-thermal digestion model as the appropriate method.

3.1.3 the optimizing of digestion time
According to the <<Specification for Oceanographic Survey-Part 4: Survey of Chemical Parameters in Seawater>>, the digestion time of total nitrogen is 30 minutes. However, to the in-situ sensor, it’s too long. Based on this, the digestion time was optimized, taking C$_2$H$_5$NO$_2$ and CH$_4$N$_2$S as examples, we set up the digestion time for 15, 20, 25 and 30 minutes, and the experimental results show that the digestion efficiency is the highest in 30 minutes. However, compared to the digestion of the 20 minutes, the efficiency of improvement is not obvious. Considering the time and efficiency of digestion, 20 minutes digestion time is the best choice.

3.2 Optimization of ultraviolet reduction
The optimization of ultraviolet reduction conditions is explored with the reference article reported by Evgeny V. Dafner[12]. In this article, we mixed the reducing agents according to the volume ratio of previous studies[5].

4. Sample analysis
The relationship between nitrogen concentration and absorbance was y=4.099X+0.0618 (n=3, R$^2$=0.9968), with the detection limit 60.30 μg/L. And then we applied this method to determine the seawater in Qingdao Sculpture Garden. Then we knew that the average concentration of TDN in seawater was 122.94 μg/L with the relative standard deviation (RSD) 0.34%. In order to verify the accuracy and reliability of this method, 100 and 300 μg/L C$_2$H$_5$NO$_2$ standard solutions were added to the samples respectively. The recoveries of the improved ultraviolet reduction method ranged from 99.94% to 100.39% (Table 1).

| NO. | Determination concentration (μg/L) | Additive concentration (μg/L) | Total concentration (μg/L) | RSD % | Recovery rate % |
|-----|----------------------------------|-------------------------------|---------------------------|-------|-----------------|
| 1   | 122.94                           | 0                             | 123.36                    | 0.34  | 100.34          |
| 2   | 122.94                           | 100                           | 223.82                    | 0.39  | 100.39          |
| 3   | 122.94                           | 300                           | 422.70                    | 0.06  | 99.94           |
5. Conclusions
In this paper, we proposed the SIA analysis method to monitoring the concentration of TDN in seawater. In our experiments, we investigated the conversion rates of different nitrogen compounds by different digestion models, then ascertained the potassium persulfate ultraviolet co-digestion as the best digestion method. And we got a satisfactory linear ranges and recovery rate.

The proposed method was applied to analyze the TDN of seawater, and got a high utilization for routine analysis in in-situ determination.

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