

## Design of a In-situ Ammonia Nitrogen Analyzer in Seawater

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**Abstract.** A in-situ ammonia nitrogen analyzer in seawater was designed based on wet chemical reaction principle, combined the fluorospectrophotometry method with flow injection analysis. The analyzer was controlled by peristaltic pump and tree-way valve, which has the advantages of high sensitivity, low-reagent consumption and can measure the concentration of ammonia nitrogen in seawater in-situ. The detection range was 10~500 $\mu\text{g/L}$ , while the detection limit was 1.80 $\mu\text{g/L}$  and the relative standard deviation (RSD) was less than 2%. The on-site comparison tests between the ammonia nitrogen analyzer and the national standard methods were finished, and the results indicated that the analyzer was entirely feasible and could reflect the content and changes of the ammonia nitrogen in the seawater.

### 1. Introduction

Nutrients in seawater is an important parameter for marine ecological environment monitoring, while ammonia nitrogen is an important index in seawater nutrients monitoring project, the content of ammonia nitrogen in seawater is also an important indication of the quality of seawater, the degree of water pollution and the self-purification status <sup>[1,2]</sup>. At present, the detection of ammonia nitrogen in seawater is mainly used the way of laboratory measurement by sampling in the field of the sea. But this kind of method has the shortcoming of real time effectiveness, the sample is easy to be polluted, waste manpower and material force etc <sup>[3]</sup>. Therefore, it is very important to convert the laboratory method to in-situ online measurement <sup>[4]</sup>. Indophenol blue spectrophotometric and sodium hypobromide oxidation are the main methods to measure ammonia nitrogen in seawater <sup>[5]</sup>. In addition, there are other many methods suitable for ammonia nitrogen detection in sea water, such as nessler's colorimetric method, fluorescence spectra method, flow injection method, ammonia gas sensitive electrode method, instrument method, gas phase molecular absorption spectrum method, etc <sup>[6]</sup>. Among these methods, fluorescence spectra method has attracted wide attention for its advantages of high sensitivity, single mixed reagent, simple operation, non-toxic reagent, good stability, etc. This method is not only suitable for the determination of ammonia nitrogen in fresh water, but also suitable for the analysis of ammonium in high salinity seawater and estuarine environment <sup>[7,8]</sup>.

In this article, we designed a in-situ ammonia nitrogen analyzer for seawater based on wet chemical reaction principle, combined the fluorospectrophotometry method with flow injection analysis technology, controlled the process through pumping seawater samples and chemical reagent into a micro flow path automatically to complete the optical detection and obtain the data, so the laboratory



analysis method was taken to the measurement site to establish a underwater micro-laboratory. This in-situ online ammonia nitrogen analyzer has the advantages of low energy consumption, more stable data, faster measurement and low reagent consumption. This ammonia nitrogen analyzer was applied to the surface seawater of Qingdao and the results were satisfactory.

## 2. Experimental

### 2.1. Test principle

The ammonia nitrogen in the water can react with phthalaldehyde (OPA) in the alkaline medium when heated to 45°C and then to generate a kind of heterindole derivatives which can emit fluorescence at 400-480nm wavelength range under excitation at 365nm wavelength. The concentration of ammonia nitrogen is directly proportional to the fluorescence intensity. In this constructed ammonia nitrogen analysis instrument, the sea water is sampled by peristaltic pump, and then OPA working solution is pumped under the control of peristaltic pump and electromagnetic valve. The reaction solution will be mixed and heated adequately in the home-made mixing and heating device and then the reaction product goes to flow cell to finish the optical detection and then discharge the waste liquid. We test the fluorescence intensity of a series of standard solutions with this ammonia nitrogen analyzer to establish the standard working curve, and then the ammonia nitrogen content of seawater samples can be tested according to the standard working curve.

### 2.2. Reagents and chemicals

All reagents and solvents used were of guaranteed reagent and were purchased from commercial sources. The water used was Milli-Q ultra-pure deionized (DI) water. The ammonium nitrogen standard solution and the reagents used in the comparison test were prepared according to the national standard. Phthalaldehyde (OPA) working solution was prepared according to the following methods:

- (a) Borate buffer solution: dissolve 5g sodium borate in 250mL water;
- (b) Sodium sulfite solution: dissolve 0.4g of sodium sulfite in 50mL water;
- (c) OPA solution: dissolve 1g of OPA in 25mL water ethanol.

Add 250ml (a), 2.5ml (b) and 25ml (c) in a beaker and mix them adequately to prepare the OPA working solution.

### 2.3. Design of the detecting system

The flow chart for detecting system is shown in figure 1. The system is mainly composed of high precision micro peristaltic pump (Longer Pump), quartz material "U" type fluorescence flow cell (customization, 10 mm optical path), the electromagnetic valve (SMC) and teflon tube (IDEX, diameter 1.0 mm).

The system uses the peristaltic pump to control the flow rate of the fluid (0~25ml/min), and the fluid conveying volume can be controlled by adjusting time. The solenoid valve is two position and three-way which can control the selective delivery of OPA working reagent. In order to ensure that ammonia nitrogen and OPA can react with each other completely, a mixing and heating device was installed before the flow cell by winding the polytetrafluoroethylene tube on an electric heating rod. The entire measurement process can complete in 3mins, and the analytical process descriptions are listed in table 1.

The LED lamp with short response time, light intensity stability and low power consumption is selected as the light source. The filtered LED light transmits through a plastic optical fiber, and then the emitted light is detected by a silicon photodiode. The self-made optical fiber coupling device adopts a double-optical path structure, one path is for detection and another path is for reference to eliminate the influence of LED emission intensity with working voltage and temperature. Figure 2 shows the change of light intensity over time in the detection process.

The core processor of the control system is the ARM cortex-m4 architecture, which is embedded in the real-time operating system of the  $\mu$ C-OSII. The system is controlled by the ITAE quadratic

optimal control system, and the system control process is simulated by using the system centralized parameter modeling. According to the simulation results, the parameters of the controller are adjusted to achieve the accuracy of the control process.

Signal processing system includes signal acquisition module and data processing module. The signal acquisition module collects optical signals through photomultiplier, and uses the front signal processing circuit module to perform multi-stage amplification and low-pass filtering, and at the same time, the wavelet transform algorithm is adopted to improve the signal-to-noise ratio and the expected characteristic of the signal. In the data processing module, we use linear regression to calculate the content of ammonia nitrogen in the seawater.

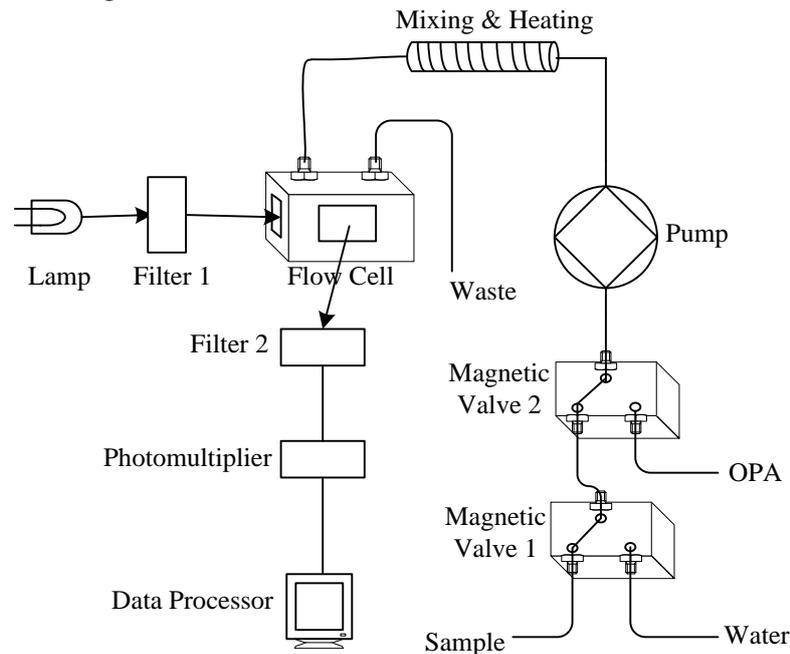


Figure 1. Flow chart for detecting system

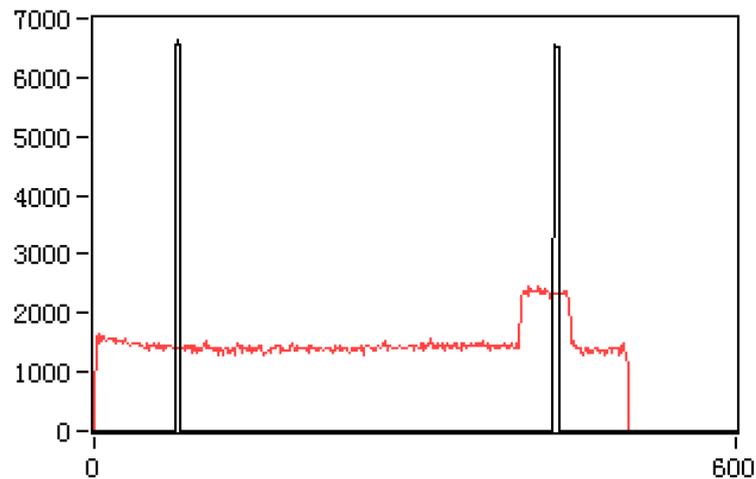


Figure 2. The light intensity varies with time during the detection process (The horizontal coordinate is for time, the vertical coordinate is for light intensity; black line shows reference light intensity, the red line shows the detection light intensity)

Table 1. Analytical process description

Step s	Procedures	Waiting time/S	Introductions
1	Open valve 2, open pump	0.5	Start filling OPA
2	Close valve 2	20	Finish filling OPA
3	Open lamp, open heating	0.5	Sampling and reading blank value
4	Open valve 2	10	Start adding OPA
5	Close valve 2	3	Finish adding OPA
6	Close pump	40	Reacting and reading detection value
7	Close lamp, close heating	0.5	Finish the detection
8	Open valve 1, open pump	0.5	Start flushing the pipe
9	Close valve 1, close pump	20	Finish the whole process

### 3. Results and discussion

#### 3.1. Calibration and limit of detection

The standard concentration series of ammonium were prepared according to national standard (GB17378.4-2007) and the standard curve fluorescence intensity against ammonium concentration was obtained as shown in figure 3, with the best linear measurement range 10-500 µg/L and having a regression equation  $I=0.0057C+0.0307$  ( $R^2=0.9985$ ), showing a good linear relationship.

The detection limit (DL) was obtained by parallel measurement 11 times used deionized water as blank solution. Then the standard deviation (SD) was calculated and the DL was calculated according to the formula  $DL = 3.3 SD$ , and the result was 1.80 µg/L, showed a satisfactory sensitivity.

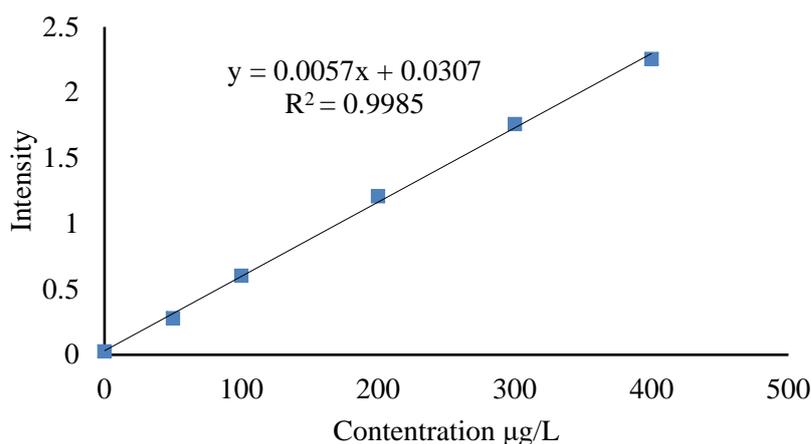


Figure 3. Standard work curve for the analyzer

#### 3.2. Accuracy and precision

3 times parallel detection were done for 3 samples of known concentration respectively and calculated the average values of the results. Then calculated the relative error which indicated the degree of accuracy and calculated the relative standard deviation (RSD) which indicated the degree of precision,

the results were listed in the table 2. The results show that the relative error is less than  $\pm 2\%$  and the relative standard deviation is also less than 2%. The accuracy and precision meet the requirements of seawater sample analysis. The ammonia nitrogen analyzer for seawater can also be used for rapid measurement in laboratory.

Table 2. Data list for accuracy and precision

Standard values ( $\mu\text{g/L}$ )	Detection values ( $\mu\text{g/L}$ )				Relative error (%)	RSD (%)
	1	2	3	Average value		
20	20.45	20.63	19.98	20.35	1.77	1.65
100	98.37	97.65	98.01	98.01	-1.99	0.38
200	197.63	201.35	203.31	200.76	0.38	1.44

### 3.3. Contrastive test

In August 2016, the in-situ ammonia nitrogen analyzer were placed in the ocean shore test station (coordinate:  $36^{\circ}06'N$ ,  $120^{\circ}31'E$ ) to detect the concentration change of ammonia nitrogen online at 10:00 every day for two weeks. And at the same time the sea water was sampled and tested in the lab according to national method of bromate oxidation by ultraviolet-visible spectrophotometer (agilent Cary 100). The results of the contrastive test between instrument method and national method are shown in the figure 4, which indicate that both data are basically consistent, and the in situ ammonia nitrogen analyzer can reflect the change trend of ammonia nitrogen content in seawater, which is suitable for in-situ online monitoring.

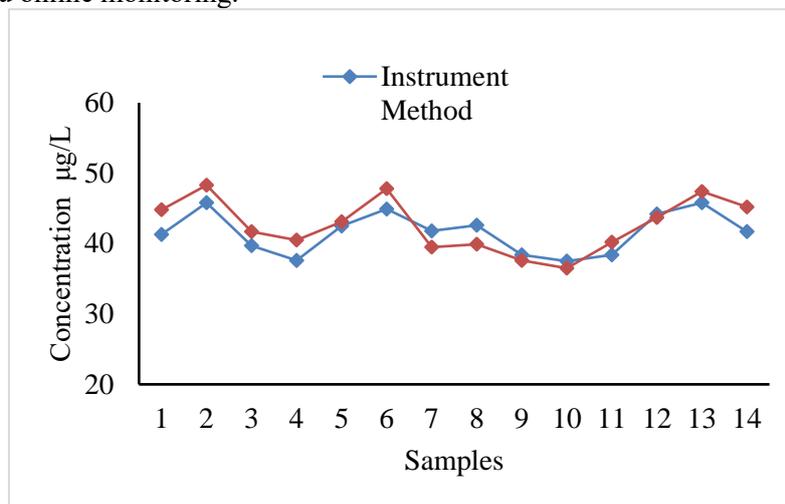


Figure 4. Comparison data between instrument method and national standard

## 4. Conclusions

A in-situ ammonia nitrogen analyzer in sea water was designed based on wet chemical reaction principle, and combined highly sensitive fluorescence spectrophotometry method with flow injection technology. This analyzer is proved to be simple and rapid, low consumption, sensitive, precision and accuracy is higher. The comparison test with national standard method also shows a high consistency, and so the analyzer is very suitable for in-situ rapid detection.

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