# Comparative study on cadmium column reduction and UV-induced reduction for online determination of nitrate in seawater

**C L Guo[1], S W Zhang[1], Y Q Cheng[1,3], R Ma[1,2] and X Cao[1]**

[1]Institute of Oceanographic Instrumentation, Qilu University of Technology (Shandong Academy of Sciences); Shandong Key Laboratory of Ocean Environmental Monitoring Technology, Qingdao City, Shandong Province, 266001, China
[2]Engineering College, Ocean University of China, Qingdao City, Shandong Province, 266100, China

E-mail: guocuilian@163.com

**Abstract.** An online detection system for nitrate in seawater was designed and set up based on flow injection analysis and spectrophotometry. We used this system to compare and study the two reduction methods for nitrate in seawater: cadmium column reduction method and UV light-induced reduction method. The cadmium column could reach the optimal reduction condition in 300 s while the UV light could reach the optimal reduction condition in 480 s. The two methods both had good linear relationship in the range of 5-500 μg/L. The reduction efficiency for Cd-column and UV light were 95% and 80% respectively under the same conditions. The detection limit was 2.5 μg/L for Cd-column reduction method and was 3.4 μg/L for UV-induced reduction method. The relative standard deviation (RSD) for the two methods were both less than 3%. The recovery rate for Cd-column reduction method and UV-induced reduction method were 98.22% and 100.83% respectively.

## 1. Introduction

Nitrate is widely found in marine water and it is one of the most important parameters for marine ecological monitoring [1,2]. The traditional determination of nitrate in seawater is carried out in the laboratory after field sampling by research ship, using the reduction of nitrate to nitrite by Zn-Cd reduction method or Cu-Cd reduction method by spectrophotometry according to the national standard (GB 17378.4-2007) [3]. This traditional method has the disadvantages of poor real-time performance, complex operation and large pollution [4,5]. In recent years, online measurement devices and methods for seawater nitrate determination based on flow injection technology and spectrophotometry have become one of the research hotspots in the ocean field [6-8]. In the online determination of nitrate in seawater, the reduction of nitrate to nitrite is mainly by Cd-column reduction method [9,10]. In addition, the reduction of nitrate to nitrite by UV light-induced reduction method has recently attracted a big attention in the word [11,12]. In this paper, an online detection system for nitrate in seawater was designed and set up based on flow injection analysis and spectrophotometry, and a comparative research was carried out between Cd-column reduction method and UV light-induced reduction method.

## 2. Experimental

*2.1. Method descriptions*

In the two methods, the seawater and the reagents are automatically sampled by the control of peristaltic pump and electromagnetic valves. In Cd-column reduction method, the sea water is added with imidazole buffer solution and then the mixture is passed through a cadmium coil to reduce the $NO_3^-$ into $NO_2^-$. In UV-induced reduction method, the sea water is added with diethylene triamine pentaacetic acid (DTPA) and tris-(hydroxymethyl) aminomethane (TRIS) mixture solution and then the liquid is passed in a teflon coil wrapped around a UV lamp to reduce the $NO_3^-$ into $NO_2^-$. Then the nitrite solution react with sulfanilamide (SAA) and n-(1-naphtyl) ethylendiamine (NED) in a self-made teflon mixed loop to form a pink colored product measurable at 540 nm and then discharge the waste water. Before the sample detection, the blank value should be tested with pure water instead of seawater sample. After the sample detection, the whole system needs to be washed with pure water. The content of nitrate in seawater can be obtained by establishing the standard working curve. In the actual detection of nitrate in seawater, it is necessary to detect the content of nitrite contained in seawater for later deduction.

*2.2. Reagents and chemicals*

All reagents and solvents used were of reagent quality and the water used in the experiment was ultra-pure deionized water. The nitrate and nitrite standard solutions were prepared according to the national standard (GB 17378.4-2007). Other regents were prepared according to table 1.

**Table 1.** List of the reagents for the nitrate analysis in seawater.

| Reagents | Preparations |
|---|---|
| Imidazole buffer solution (BUF) | Imidazole 3.4g/L , sulfate $1\times10^{-4}$ mol/L (adjust pH to 7.5 with HCl) |
| Diethylene triamine pentaacetic acid and tris-(hydroxymethyl) aminomethane mixture solution (DTPA+TRIS) | DTPA 47.5g/L, TRIS 237.8/L (adjust pH to 7.7 with HCl) |
| Sulfanilamide solution (SAA) | SAA 20g/L, HCl 1.8 mol/L |
| Ethylendiamine solution (NED) | NED 3g/L |

*2.3. Experiment conditions*

As shown in figure 1, the detecting system is mainly composed of peristaltic pump (Longer Pump, set rotate speed 2 ml/min), customized quartz material "U" type flow cell (path length 2 cm), electromagnetic valves (SMC, two positions and three ways), cadmium coil (Green Eyes, 7 circles), teflon tube (IDEX, diameter 1.0 mm), teflon coil (winding length, 90 cm ) wrapped around a UV lamp (Philips, 4 W) and a self-made teflon mixed loop (winding length, 80 cm ). The pumping time for BUF reagent or DTPA+TRIS mixture reagent was 5 s, and the pumping time for SAA and NED were both 3 s. There are two differences between Cd-column reduction method and UV-induced reduction method, as shown in the two red dotted line boxes of figure 1. One difference is the added reagent before the reduction reaction and the other difference is the reduction method.

The LED lamp (540 nm) emits light to the tested liquid in the flow cell through the fiber and then the remaining light after absorption is detected by a photodiode and the data will be recorded and processed by the computer. The software for system control and data processing are written by LABVIEW (NI Company).

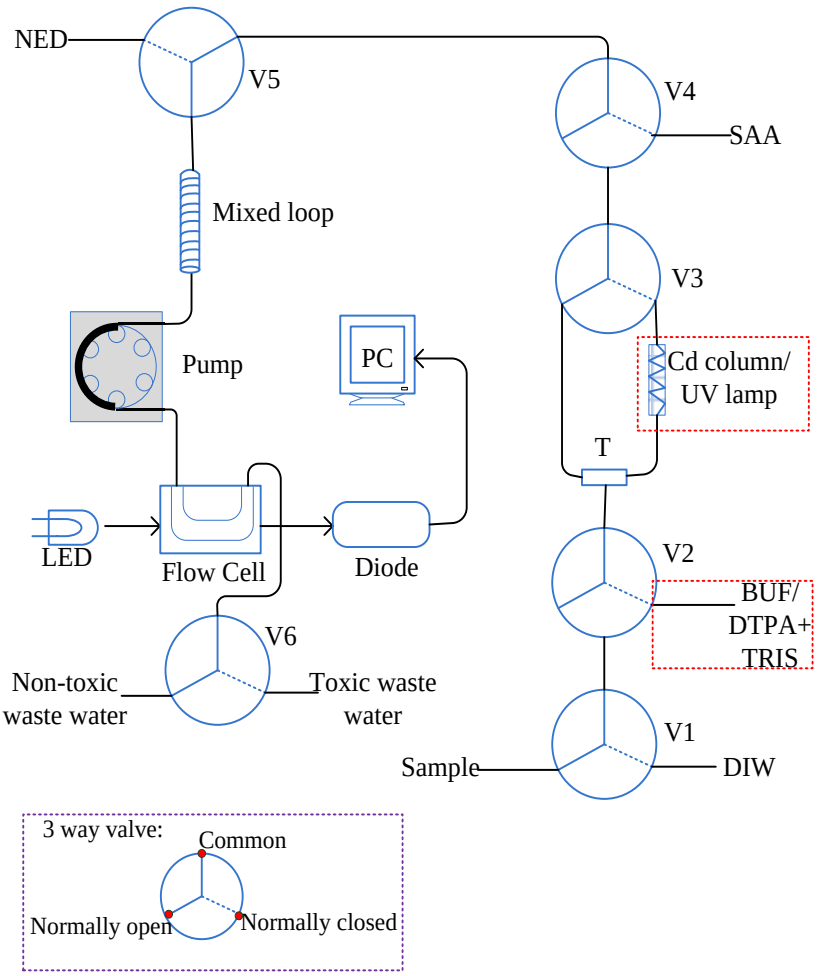


**Figure 1.** Flow chart for detecting system.

## 3. Results and discussions

### *3.1. Time for the reduction reaction*

Under the above experiment conditions, the nitrate solution with known concentration of 150 μg/L was used as sample to test the relationship between the reduction stay time and the product absorbance. At the beginning, the absorbance of both the methods increased with the increase of reduction stay time. But the absorbance didn't change anymore when the reduction stay time increased to some certain extent. According to the experiment, the optimal reduction stay time for the Cd-column reduction method was 300 s, and the optimal duration of the UV reduction method was 480 s.

### *3.2. Calibration and limit of detection*

Under the optimal experimental conditions, the standard working curves were obtained by the two methods as shown in figure 2. The regression equation for Cd-column reduction method is $A=0.0041C+0.0003$ ($R^2=0.9995$), and the regression equation of UV reduction method is $A=0.0034C+0.0061$ ($R^2= 0.9997$), both shows a good linear relationship in the range of 5-500 μg /L for nitrate. The correlation coefficient meets the requirement of more than 0.98 in national standard (GB17378.4-2007). The standard working curve for nitrite was also obtained by the same system. By comparing the slope of the curve, the reduction efficiency of the Cd-column reduction method was about 95% and the reduction efficiency of UV-induced reduction method was about 80%.

The blank water solution was measured 11 times continuously to get the standard deviation and the

detection limit was 3 times the standard deviation. The detection limit of Cd-column reduction method was 2.5 μg/L and the detection limit of UV-induced reduction method was 3.4 μg/L, both showed satisfactory sensitivities.

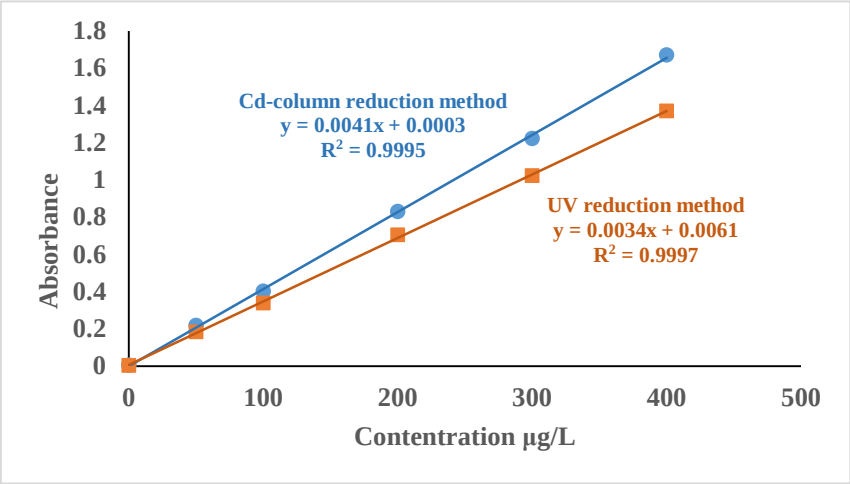


**Figure 2.** Standard work curves for Cd-column reduction and UV reduction.

*3.3. Accuracy and precision*

The concentrations of three known standard solutions were measured three times in parallel to get the average values and the results are listed in the table 2, in which Cd means Cd-column reduction method and UV means UV-induced reduction method. The results show that the relative error is less than ±1% for Cd-column reduction method and the relative error is less than ±3% for UV-induced reduction method. The relative standard deviations are both less than 3% for the two methods. The accuracy and precision meet the requirements of nitrate analysis in seawater.

**Table 2.** Data for accuracy and precision.

| Standard values (μg/L) | Average values (μg/L) | | Relative error (%) | | RSD (%) | |
|---|---|---|---|---|---|---|
| | Cd | UV | Cd | UV | Cd | UV |
| 20 | 20.06 | 19.89 | 0.30 | -0.53 | 1.73 | 2.69 |
| 100 | 99.27 | 97.57 | -0.73 | -2.42 | 2.27 | 0.96 |
| 300 | 300.76 | 288.62 | 0.25 | -3.79 | 0.96 | 1.01 |

*3.4. Sample analysis*

Sampled the seawater from ZhanQiao of Qingdao as representative water sample, filtered the sample with 0.45 μm microporous filter membrane before the measurement. The sample was measured 10 times in parallel by every method. The average concentration was 72.34 μg/L by Cd-column reduction method, RSD was 1.46%.The average concentration was 71.82 μg/L by UV-induced reduction method, RSD was 1.84%. Then standard solution of 100 μg/L was added to the seawater sample from ZhanQiao, and the recovery rate were 98.22% and 100.83% for Cd-column and UV-induced reduction method.

## 4. Conclusions

Through the study in this paper, it is found that the reduction efficiency of the cadmium column is still higher than that of the UV-induced reduction, but UV-induced reduction has the disadvantages of more stable reduction efficiency, does not need to be activated and does not produce toxic substances. So UV-induced reduction method is also a very suitable choice for online detection device of nitrate in seawater.

**Acknowledgments**
This work was supported by the National Key R & D Plan (No. 2016YFC1400800), the National Natural Science Foundation of China (No. 21207080), The Natural Science Foundation of Shandong Province, China (No. ZR2016DM17 and ZR2014YL006) and the Special Funds for Scientific Research of Marine Public Welfare Industry (No. 201505007-2).

**References**
[1] Yang Y, Cheng X S and Liu P X 2011 *PTCA (PART B: CHEM ANAL)* **47** 514-6
[2] Lin K N, Ma J, Yuan D X, Huang Y M, Feng S C and Wu Q L 2017 *Chinese Journal of Analytical Chemistry* **45** 151-6
[3] General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China 2007 *The Specification for Marine Monitoring- Part 4: Seawater Analysis (GB17378.4-2007)* (Beijing: Standards Press of China) pp 115-7
[4] Li D, Feng W W, Chen L X and Zhang J 2016 *Spectroscopy and Spectral Analysis* **36** 442-44
[5] Wang L L, Liu X H, Mi M, Zhang Q F, Zong Y P and Zhang Y F 2014 *Transducer and Microsystem Technologies* **33** 75-7
[6] Burakham R, Oshima M, Grudpan K and Motomizu S J 2004 *Talanta* **64** 1259-65
[7] Zhang M, Yuan D X, Feng S C and Huang Y M 2011 *Chinese Journal of Analytical Chemistry* **39** 943-4
[8] Guo C L, Zhang S W, Cheng Y Q, Ma R, Chu D Z and Zhang L 2018 *Shandong Science* **31** 1-8
[9] Petsul P H, Greenway G M and Haswell S J 2001 *Analytica Chimica Acta* **428** 155-61
[10] Wei F X, Fu X W and Ma X Z 2011 *Chinese Journal of Analysis Laboratory* **30** 10-3
[11] Zhang M, Zhang Z,Yuan D X, Feng S C and Liu B M 2011 *Talanta* **84** 443-50
[12] Motomizu S J and Sanada M 1995 *Analytica Chimica Acta* **308** 406-12