Improvement of the UV-induced Reduction Efficiency of Nitrate by Manganese (II) chloride based on Sequential Injection Analysis

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Abstract. The traditional method of reducing nitrate by ultraviolet radiation was improved in this study. Manganous (II) Chloride (MnCl₂) was added on the basis of original reagent to improve the efficiency of nitrate reduction by Ultraviolet radiation (UV), and the optimum reaction conditions of improved UV reduction method were discussed. It was found that the best UV-reduced reduction efficiency of nitrate obtained at the concentration of 1.0 g/L photoreduction DTPA, the concentration of Tris was 1.0 g/L with 8.0 of pH in the presence of 0.8g/L MnCl₂ with 2 min UV radiation. The reduction efficiency increased by about 25.00% compared with the traditional analysis method, reached to 88.24%. The linear relationship of the established method was good at the range of 0-500μg/L, and the detection limit was 2.17μg/L. The average concentration of nitrate in the coastal seawater was 8.89μg/L and the relative standard deviation was 0.23%. We added the standard solution of NO₃-N with the concentrations of 100μg/L and 300μg/L to the seawater samples, respectively, with the recovery of standard addition among 99.90%~100.34%. The established method improved the UV reduction efficiency of nitrate and got high reproducibility and good accuracy which can be used to monitor nitrate content by in-situ analyzer.

1. Introduction
The determination of nitrate content in the natural waters is essential, as the nitrate content relates directly to the excess of nutrients in surface and groundwaters. The most sensitive and widely used method for nitrate determination is the Griess reaction for nitrite quantification with prior reduction of nitrate to nitrite [1, 2]. Among the methods of nitrate reduction to nitrite, the ultraviolet reduction method has the advantages of simple operation, no maintenance [3, 4]. The traditional method of ultraviolet reduction is to reduce nitrate to nitrite by using photo-reductant DTPA and buffer solution Tris under ultraviolet irradiation. Compared with the cadmium column reduction method it also avoids the use of harmful reagents [5, 6], but it is worthwhile to improve the low efficiency and poor stability of ultraviolet reduction [7].

The research on nitrate reduction by transition metal ions at home and abroad mainly focused on the V³⁺ [8-15]. Qu et.al. found that the transition metal ions Mn²⁺ promoted ultraviolet reduction efficiency of nitrate [16]. To the best of our knowledge, there are only 2 articles about nitrate reduction using MnCl₂ as
catalyst which are all used for laboratory detection [16, 17], and automatic flow analysis of nitrate using Manganese (II) chloride (MnCl₂) has not been reported before.

In recent years, in-situ analytical instruments have emerged as the times require and attracted more and more attention. The present paper describes the new method using the sequential injection analysis (SIA) for nitrate determination employing MnCl₂ combined with UV reduction. Compared to the traditional UV reduction method, the newly proposed method allows more stable and sensitive detection of nitrate. In this paper, we built the sequential analysis system, and optimized the dosage of reagents as well as the reaction time of ultraviolet radiation. Then we applied this system to detect the sea water in Qingdao, and compared it with the traditional ultraviolet reduction method. The results indicate that the SIA method is relatively sensitive for nitrate determination, and it also appears well suited for in situ analysis.

2. Material and Methods

2.1 Reagents and solutions

All solutions were prepared with analytical grade chemicals and used without further purification.

The chromogenic reagent was prepared by dissolving 2.0g sulfonamide (SAM) into 140ml HCl (14%), and by mixing with 0.16g N-(1-naphtyl)-ethylenediamine dihydrochloride (NED), the final volume was completed to 200ml with pure water.

The photo-induced reagent consisted of 20g diethylene triamine pentaacetate acid, 0.8g manganese 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 nitrate stock standard solutions was prepared by dissolving 0.722g oven dried (100°C,1h) potassium nitrate in 1L pure water. The nitrite stock standard solutions was prepared by dissolving 0.493g oven dried (100°C,1h) sodium nitrite in 1L pure water.

2.2 Apparatus

The schematic diagram of sequential injection analysis for determination of nitrate with ultraviolet radiation photo-reduction method is presented in Fig.1. The system was consisted of integrated structure of 8-positioin selection valve and injection pump (Tecan Cavro), and the valve switching processes were operated with software programmed in LabVIEW (National Instruments, USA). The injection pump was used to deliver the samples and reagents.

The UV light source used was an 11 W low-pressure mercury lamp (UVCN, Aerospace Hongda, Beijing) with maximum emission at 254nm, and the shell of the lamp was made up of quartz. The emission at 254nm is strong and sharp. The ultraviolet reduction reactor was constructed of quartz tube (20mm i.d., 30mm external diameter) formed into an annular around the UV source, which has higher ultraviolet transmittance than the PTFE tube[18].

The optical detection module needs to measure the absorbance at 540 nm wavelength to determine the nitrate concentration, and also needs to take into account the design of miniaturization and micro-flow. The monochrome LED (Broadcom Kingbright) is used as light source and photodiode (Hamamatsu Texas Instruments) as light signal receiving device is a commonly used in absorbance detection.
2.3 Procedure and Sampling
Sequential injection-ultraviolet reduction-spectrophotometric determination by controlling injection pump and rotary valve. Two volumes of sample were drained by injection pump, one volume DTPA-Tris buffer solution and one volume of MnCl₂ solution were mixed in the syringe and injected into the ultraviolet reduction device. Turn on the ultraviolet light and irradiated for 2 minutes (no ultraviolet light was turned on when nitrite was detected). The nitrate in the water sample was converted into nitrite by ultraviolet photoreduction method. Then two volumes of the reduced solution were extracted and mixed with a volume of the color reagent. SAM reacts with nitrite, and the reaction product reacts with NED to form deep red azo dye, which is injected into an optical flow detection module to determine the absorbance at 540 nm wavelength and obtain the nitrate content of the sample.

According to the above processes, the nitrate/nitrite standard solutions and different seawater samples were detected.

3. Results and Discussion

3.1 Optimization of ultraviolet reduction
The efficiency of the UV reduction reaction is affected by various parameters, such as concentration of reduction reagent, pH and reaction time.

3.1.1 Optimization of reagent concentrations. Ultraviolet reduction essentially belongs to incomplete reduction method. Nitrite produced by reduction can be combined with oxygen atom and oxidized to nitrate\(^\text{[19]}\). The photo-reaction equation is as follows:

\[
\text{NO}_3^- \rightleftharpoons \text{NO}_2^- + \frac{1}{2}\text{O}_2 \text{[5]}
\]

In the presence of DTPA, the recombination reaction was appeared to be difficult, as the DTPA act as photo-reductant\(^\text{[18]}\).

To establish a suitable concentrate of DTPA, we discussed the effect of DTPA with different concentration on absorbance and the results are shown in Fig.2. When DTPA concentration was lower than 1.0 g/L, nitrite and oxygen atoms would recombine and the ultraviolet reduction efficiency would decrease. When DTPA concentration was higher than 1.0 g/L, it might precipitate in the acidic chromogenic reagent\(^\text{[17]}\), which affected the detection results. Therefore, the optimum concentration of DTPA is 1.0 g/L.
It was found that MnCl$_2$ was beneficial to the reduction of nitrate to nitrite, and improved the ultraviolet reduction efficiency of nitrate\cite{18}. In order to explore the optimum reaction concentration of MnCl$_2$, the effects of MnCl$_2$ on absorbance were analyzed experimentally at the concentration of 0-2.0 g/L (Fig.3). Taking 100 ug/L KNO$_3$-N as an example, it was found that the absorbance increased on increasing the MnCl$_2$ concentration in the range of 1.0 g/L, but decreased on increasing the MnCl$_2$ concentration higher than 1.0 g/L. However, compared with the experimental results of 0.8g/L and 1.0g/L of MnCl$_2$, when the concentration of MnCl$_2$ was 0.8g/L, experimental results had a lower relative standard deviation (n=3, RSD=0.44\%) and a higher repeatability than the concentration of MnCl$_2$ was 1.0g/L. Hence, the optimal concentration of MnCl$_2$ is 0.8g/L.

3.1.2 Optimization pH of ultraviolet reduction. Ultraviolet reduction has very low reduction efficiency under acidic conditions and the alkaline conditions is beneficial to the ultraviolet reaction\cite{19}. Therefore, the effect of pH in the range of 6.0-9.0 on the ultraviolet reduction was studied (Fig.4). When the pH value was 8.0, the absorbance value was the highest, and the experimental results had good repeatability (n=3, RSD=0.44\%). When the pH value of buffer solution is higher than 8.0, the precipitation in the solution mixed with acidic chromogenic agent can’t be completely dissolved, resulting in uneven mixing of samples and reagents, and the experimental results are unstable. Therefore, the optimal pH value of buffer solution is 8.0.

3.1.3 Optimization time of ultraviolet reduction. We determined the absorbance value of the same sample after reaction with chromogenic agent when the sample was irradiated by ultraviolet light for different time lengths (Fig. 6).
Fig.6 influence of ultraviolet reduction time on absorbance

It was found that the absorbance value increased on increasing the time length in the range of 1.0-1.5 min, but had no significant change were observed at time length longer than 2.0 min, and then the absorbance value decreased on increasing the time length in the range of 2.0-3.0 min. When the UV irradiation time was 1.5 min, the test results were unstable (n=3, RSD=2.79%). Therefore, the optimum time for ultraviolet radiation is 2 min (n = 3, RSD = 0.61%).

3.2 Optimizing of Chromogenic Agents

The different reagent concentrations were studied to achieve optimal chromogenic reaction and we designed a univariate experiment to achieve the goal, and the results were showed as Fig.7 and Fig.8. With the increase of NED concentration, the absorbance increases, and the optimum concentration of NED was 0.8 g/L. The SAM concentration for nitrite reaction was tested in the range of 0.4-15 g/L. It was obvious that the optimum concentration of SAM was 10.0 g/L.

3.3 Analytical figures of merit

With all the optimized conditions, the regression equation of nitrate and nitrite determination were $y=0.00297X+0.01357$ ($n=3$, $R^2=0.9998$) and $y=0.00337X+0.01767$ ($n=3$, $R^2=0.9998$), respectively. The reduction efficiency of NO$_3^-$ was 88.24% calculated by the slope ratio of the two working curves. The detection limit of the method was 2.17 µg/L by dividing the standard deviation of the three-fold blank by the slope of the standard curve.

Under the Traditional Ultraviolet Reduction Conditions, the reduction efficiency of NO$_3^-$ was 70.59% and the detection limit was 8.59 µg/L. In the presence of MnCl$_2$, the ultraviolet reduction efficiency of NO$_3^-$ increased about 25.00%.

3.4 Sample analysis

The proposed method was applied to analyze the nitrate in Qingdao Sculpture Garden. The average concentration of NO$_3^-$ in seawater samples was 8.89µg/L and the relative standard deviation was 0.23%. The result of ultraviolet reduction without MnCl$_2$ was 8.80µg /L and the relative standard deviation was 0.58%.

4. Conclusions

A sequential injection analysis method combined with spectrophotometric method for nitrate
determination was established. Based on the traditional method of ultraviolet reduction of nitrate, MnCl₂ reagent was added to improve the efficiency of ultraviolet reduction. This method is accurate, precise, simple and easy to operate. It solves the problem of low reduction efficiency of the traditional method of ultraviolet reduction. It can be used in situ analyzer to determine the content of NO₃⁻ in seawater.

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