CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 45, Issue 2, February 2017
Online English edition of the Chinese language journal

Cite this article as: Chin J Anal Chem, 2017, 45(2), 151–156.

RESEARCH PAPER

Determination of Nitrate in Seawater with Valve-Free Continuous Flow Analysis

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Abstract: A valve-free continuous flow method and its corresponding instrument were established, with only two multi-channel pump for delivering the sample and reagent, without any injection or solenoid valves and sample loop for selecting and adding the sample or reagent. Nitrate was reduced to nitrite with Cu-Cd reductant column, and then detected with spectrophotometric detector. The proposed method was suitable for determination of nitrate at normal level in most of estuary and coastal seawaters. With the optimum parameters, the linear range and detection limit were 5–180 μM and 0.27 μM, respectively. The nitrate samples (10 and 80 μM) were continually measured for 11 times, and the relative standard deviations were 1.4% and 1.3%, respectively. The recovery of real samples at different salinity was ranged from 99.4% to 106.1%. There were no significant differences in the analytical results between the proposed method and a reference method, i.e., flow injection analysis. In comparison with flow injection analysis, the method and instrument were less cost and easy to operate, and was suitable to be applied in general laboratories and field for continuous monitoring. The method was successfully applied to measure nitrate of seawater samples in Xiamen western harbor and underway monitor nitrate in the Jiulongjiang estuary.

Key Words: Valve-free; Continuous flow analysis; Seawater; Nitrate

1 Introduction

Nitrate (NO_3^-), as a macronutrient, exists widely in natural waters. It will cause eutrophication when an excess of NO_3^- is discharged into aquatic ecosystems[1]. Therefore, the monitoring of NO_3^- concentration is necessary. As described in National Standard Method of China[2], NO_3^- is reduced to nitrite (NO_2^-) with Cu-Cd reductant column and reacted with reagent based on Criess reaction, and then the pink color azo dye is detected with a spectrophotometer. The standard method has a higher NO_3^- reduction rate, but usually suffers from the problems of bothersome process and high labor consumption. Therefore, it is not suitable for the analysis of a large number of samples neither for field application. Some commercial instruments are available for nutrient analysis, such as BRAN+LUEBBE AutoAnalyzer3 and SKALAR[3,4]. Those instruments are based on the principle of segmented continuous flow analysis (SCFA) with high automation and sample throughput, however, their instruments are generally expensive for budget-limited laboratories. Nowadays, flow injection analysis (FIA) technique was extensively developed and applied in seawater analysis. Some NO_3^- analysis systems based on FIA were invented[5–7]. To improve the accuracy and replicability of analysis, those systems usually used injection valve or solenoid valve for selecting and adding the sample or reagent. On the other hand, the valves increased the cost of the analytical system, and the valve control was also complex. Those systems were not suitable to be applied in general laboratories. Once some simple devices can replace the valves, it will reduce the instrumental cost and simplify the control program to a certain extent. Currently, some researchers[8] reported a method of quantitative injection of reagents into samples by using syringe pumps, and realized simultaneously detection of four metal ions, but only one chromogenic

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Received 28 October 2016; accepted 12 November 2016

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This work is sponsored by the National Natural Science Foundation of China (No. 41306090), and the Fund (2017) for Equipment and Infrastructure Construction of MEL from Ministry of Finance, China.

DOI: 10.1016/S1872-2040(16)60991-X

reagent was needed for the chemical reaction. In practice, for nitrate determination with Cu-Cd reductant column method, single chromogenic reagent could not satisfy the requirements of the analysis. To inject more than one reagent for NO_3^- determination, the valves were indispensable[9,10].

A valve-free continuous flow analysis system[11] was established previously by our research group. The continuous flow analysis technique was adopted in the present study to mix the reagent with sample. Without any valves, lots of air bubbles were introduced into the stream when changing the samples. With a well-designed flow cell, the bubbles did not interfere with the optical detection. The system was successfully applied to determine nitrite, phosphate, and silicate in various water samples. However, in the determination of NO_3^- by this system with Cu-Cd reductant column, the copper on the surface of cadmium could be oxidized by the bubbles, and the NO_3^- reduction rate would be greatly affected. Therefore, the previous system was needed to be improved. In this study, a debubbler device was introduced in front of column to effectively avoid the air bubbles. This improved system was successfully applied to measure NO_3^- in seawater samples of Xiamen western harbor and underway monitor NO_3^- in the Jiulongjiang estuary.

2 Experimental

2.1 Instruments and reagents

USB 2000+ spectrophotometer and LS-1-LL tungsten halogen lamp (Ocean Optics Inc., USA) were used as detector and light source. BT100-1L 6-channel peristaltic pump (Baoding Longer Precision Pump Co., China) was used to deliver the sample and reagent, and silicon tubings (Baoding Longer Precision Pump Co., China) of 0.5 mm i.d. and 2.0 mm i.d. were used as the pump tubings. All other tubings for connecting different parts of the manifold were polytetrafluoroethylene tubings (Valco Instruments Co., USA) of 0.75 mm i.d. HH-1 thermostatic water bath (Shanghai Meixiang Instrument Co., China) was used to control the reaction temperature. The software programmed in LabVIEW 8.2 (National Instruments, USA) was used for data acquisition. A laboratory-made flow cell with 1.2-cm light path was used.

All solutions were prepared with freshly made ultrapure water (resistivity ≥ 18.2 MΩ cm) obtained through Millipore purification system (Millipore Co., USA). All chemicals used here were analytical grade and purchased from Sinopharm Chemical Reagent, China, unless otherwise indicated. NO_3^- stock solution (100 mM) was prepared from solid KNO_3, which was dried at 110 °C for 2 h before used. Working standard solutions were obtained from appropriate dilution of the stock solutions with ultrapure water. Approximately 2.5 g of sulfonamide (SAM) and 0.25 g of *N*-(1-Naphthyl) ethylenediamine dihydrochloride (NED) were dissolved in 500 mL of HCl (5%, *V*/*V*, guarantee reagent) as a mixed reagent for color development. The stock solution and mixed reagent were stored at 4 ºC until being used. The artificial seawater with salinity of 35 was prepared by dissolving 31 g of NaCl and 10 g of $MgSO_4$ into 1.0 L of ultrapure water and stored in a plastic bottle at room temperature. The pH value of NH_4Cl-NaOH buffer solution (2.5%, *m*/*V*) was adjusted to 8.3 with NaOH solution (5 M).

2.2 Operational procedure

The schematic diagram of valve-free continuous flow analysis system is presented in Fig.1. Sample was delivered to a debubbler at a relative high flow rate with peristaltic pump 1 (P1), then the sampling tubing was switched to ultrapure water for washing after the sampling completed. The sampling tubing was switched from one sample to another without stopping P1, and a large number of bubbles was introduced into the stream, and removed with the debubbler. The sample

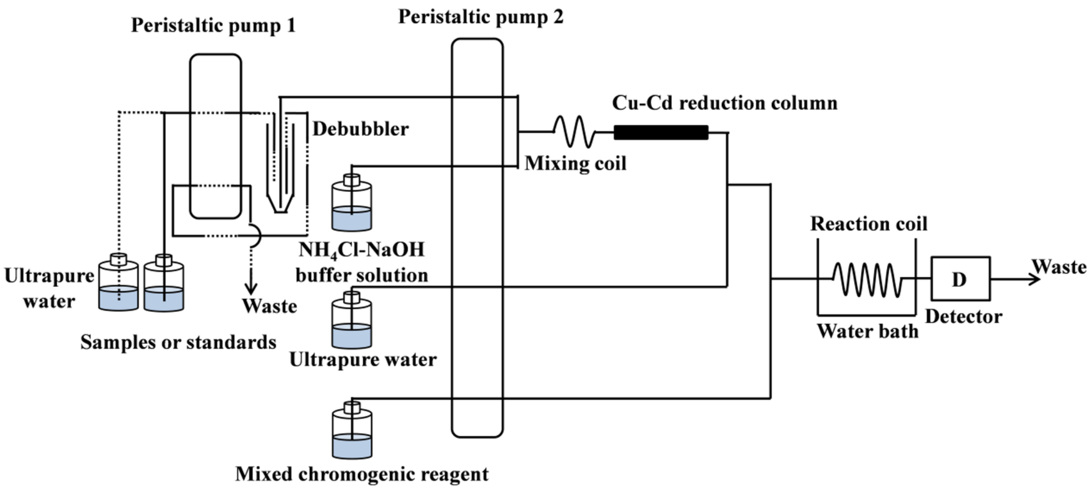

Fig.1 Manifold configuration of valve-free continuous flow system for nitrate determination