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Simultaneous determination of nanomolar nitrite and nitrate in seawater using reverse flow injection analysis coupled with a long path length liquid waveguide capillary cell



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ABSTRACT

A reverse flow injection analysis (rFIA) method coupled with 1 m liquid waveguide capillary cell and spectrophotometric detection for simultaneous determination of nanomolar nitrite and nitrate in seawater was developed. The design of two analytical channels sharing the same detection system in the proposed method allowed the analysis of both nitrite and nitrate with single sample injection. Different strategies of reagent injection were investigated to obtain a higher sensitivity and a better peak shape. A dual-wavelength detection mode was chosen to eliminate the light source shifting and sample matrix interference. Experimental parameters were optimized based on a univariate experimental design and the matrix effect from seawater was preliminarily investigated. The proposed method had high sensitivity with detection limit of 0.6 nmol L^{-1} for both nitrite and nitrate. The linearity was $2\text{--}500 \text{ nmol L}^{-1}$ for both analytes, and the upper limit could be extended by choosing a lower sensitivity detection wavelength. The analytical results of 26 surface seawater samples obtained with the proposed method showed good agreement with those using a reference method operated using an automated segmented flow analyzer. The proposed method could greatly minimize the trouble introduced by bubbles in the segmented flow analyzer. It also had the advantages of high precision and high sample throughput (nitrite and nitrate detected in triplicate; 5 h^{-1}). Compared to normal flow injection analysis, the rFIA method is superior due to its lower reagent consumption, less dispersion of sample, as well as higher sensitivity.

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1. Introduction

Nitrogen is an essential element for marine phytoplankton growth and plays a crucial role in many biogeochemical cycles [1,2]. Dissolved inorganic nitrogen (DIN) species including nitrite, nitrate and ammonium, as the fixed nitrogen, can be used by many microbes and often limit primary productivity [3]. Nitrite, which is at the intermediate redox position between ammonium and nitrate, concentrates to exceed 50 nmol L^{-1} only within a narrow layer in the ocean, known as the primary nitrite maximum [4]. The distribution of nitrate, which is the principal form of DIN, typically spans up to 5 orders of magnitude in the open ocean, from several nanomolar in surface waters increasing to micromolar with the increase of depth [5]. Accurate quantification of nanomolar nitrite and nitrate is essential for understanding the marine nitrogen cycle and the dynamics of marine ecosystems.

However, the conventional spectrophotometric analytical techniques [6,7] which have a detection limit of 100 nmol L^{-1} , are not sensitive enough to detect the variations of nitrite in most open ocean samples and of nitrate in surface water samples.

Much effort has been devoted to the development of new methods for the analysis of nitrite and nitrate at trace level, including chemiluminescence [8–11], fluorescence [12,13] and ion chromatography [14]. However, the methods and instruments in these studies require skilled operators and are mainly lacking in field testing and application, especially compared to the spectrophotometric method. Since it is a challenge to find a new chromogenic agent that has higher selectivity and larger molar absorptivity for nitrite and nitrate [15], the sensitivity-enhanced colorimetric approaches based on the classic Griess assay are still the most popular for the determination of nitrite and nitrate at nanomolar level in seawater. The Griess assay typically relies on the diazotisation of a suitable aromatic amine by reaction of nitrite with sulfanilamide (SAM) and N-1-naphthylethylenediamine dihydrochloride (NED) and the formation of a pink-colored azo dye. Nitrate in the samples is usually reduced to the more-reactive

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nitrite using a copper-coated cadmium column, and then determined through the Griess assay [16].

There are mainly two approaches to enhance the sensitivity of conventional spectrophotometry, one involves enrichment of the azo compound using a solid phase extraction cartridge [17–21] and the other increases the optical path length for the measurement cells by means of liquid waveguide capillary cell (LWCC) devices [15,22–28]. The enrichment method concentrates the chromophore, as well as the reagents, resulting in an increased blank. Therefore this method is sensitive to atmospheric contamination where contaminants gradually dissolve in the reagent, such as in the case of nitrite and nitrate detection. Furthermore, the enrichment method is time consuming and requires large sample volume. According to the Lambert–Beer law, the sensitivity of spectrophotometric methods can be enhanced by extension of the optical path length. The LWCC provides a long optical path length by constraining light propagation within a liquid medium (water) that has a higher refractive index (1.33) than the surrounding solid tubing (1.29) made of a flexible fluoropolymer material (Teflon AF, DuPont) [29]. The LWCC coupled with standard spectrophotometric analysis can simply achieve a very low detection limit and has been widely used for trace element analysis [29,30].

In order to obtain a high sample throughput, high precision and minimum contamination, LWCC is usually combined with automated analytical systems, such as flow injection analysis (FIA), sequential injection analysis (SIA) and segmented continuous flow analysis (SCFA). FIA systems, which have the advantages of higher sample throughput and precision over SIA and can avoid the bubbles introduced in SCFA, have proved to be simple, robust, low-cost and appropriate in nutrient analysis [31]. FIA systems are basically classified into normal FIA (nFIA) and reverse FIA (rFIA). In rFIA, the reagent is injected into a continuously flowing stream of the sample rather than injecting the sample into a continuously flowing carrier solution in nFIA. Based on this, in rFIA the sample dispersion is lessened, analytical sensitivity improved, the matrix effect overcome and consumption of reagent minimized [32]. There is unavoidable contamination from impure reagents or/and carrier solution, which may also have absorbance at the detection wavelength. This interference is sometimes not big enough to be detected in conventional spectrophotometric systems; however in a high sensitive LWCC system, it can cause high background, high noise, and limited linear range. In our experience, if the flow analysis system continually sends the mixture of all reagents and the carrier/sample through the LWCC, the formed compound was absorbed onto the inner wall of the LWCC, leading to attenuation of transmission light. This problem can be

eliminated by using rFIA, in which the formed compound only exists in the injected reagent zone, and the sample carrier can behave as a wash solution to keep the LWCC clean. Moreover, since the baseline of the peak obtained in rFIA is the absorbance of the sample solution, the potential interferences from salt effect and colorful compounds in the sample can be corrected using sample absorbance as a background signal.

Recently, simple rFIA systems combined with an LWCC and a spectrophotometric detector have been successfully used for the determination of nanomolar soluble reactive phosphorus and iron in seawater [33,34]. Also, a sensor combined rFIA system and a fluorescence detector has been successfully used for the simultaneous determination of nanomolar concentrations of nitrite, nitrate, and ammonia in seawater [13]. Using the rFIA manifold, the background fluorescence released from dissolved organic matter is corrected for.

There is no reported work relating to the use of an rFIA with an LWCC for simultaneous determination of nanomolar nitrite and nitrate in seawater. In this study, a simple rFIA system coupled with an LWCC was developed for this purpose. Experimental parameters including flow rate, reagent loop, reagent concentration, and length of the mixing coils were investigated to achieve satisfactory sensitivity and precision. The matrix effect was also preliminarily studied.

2. Experimental

2.1. Reagents and solutions

All the chemicals used were of analytical grade, and supplied by Sinopharm Chemical Reagent Co., China (<http://www.reagent.com.cn>), unless stated otherwise. All solutions were prepared with fresh Milli-Q water (18.20 M Ω cm), obtained from a Millipore Purification Water System (Millipore Co., MA, USA, <http://www.millipore.com>). All bottles and vials used were soaked in 20% (v/v) HCl for at least 12 h, and rinsed with the Milli-Q water thoroughly.

Nitrite and nitrate stock solution (each 100 mmol L⁻¹) were prepared from solid NaNO₂ and KNO₃, which were dried at 105 °C for 1 h. The standard stock solutions were stored at 4 °C in a refrigerator. Working standards were obtained by appropriate dilution of the stock solutions with Milli-Q water daily.

The SAM solution was prepared by dissolving 0.3 g SAM in 200 mL 4% (v/v) HCl (guaranteed grade, Merck, <http://www.merck-china.com>) solution, and the NED solution was prepared by dissolving 0.03 g NED in 200 mL Milli-Q water. The SAM and NED solutions were prepared daily.

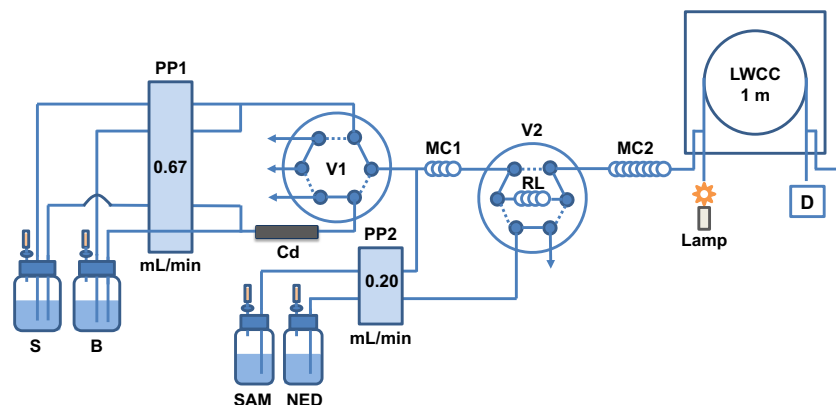


Fig. 1. The rFIA manifold configuration coupled with an LWCC for the determination of nanomolar nitrite and nitrate in seawater. S, sample; B, NH₄Cl buffer solution; PP1 and PP2, peristaltic pumps; V1 and V2, 6-port, 2-position injection valves; Cd, copper-coated cadmium reduction column; MC1 and MC2, mixing coils; RL, reagent loop; D, detector; the solid line of V1 and V2 represents the valve at position A, and the dashed line represents position B.

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