



Field measurement of nitrate in marine and estuarine waters with a flow analysis system utilizing on-line zinc reduction

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ABSTRACT

A sensitive reagent-injection flow analysis method for the spectrophotometric determination of nitrate in marine, estuarine and fresh water samples is described. The method is based on the reduction of nitrate in a micro column containing zinc granules at pH 6.5. The nitrite formed is reacted with sulfanilamide and *N*-(1-naphthyl)ethylene diamine (Griess reagent), and the resulting azo compound is quantified spectrophotometrically at 520 nm. Water samples in the range of 3–700 $\mu\text{g L}^{-1}$ $\text{NO}_3^- - \text{N}$ can be processed with a throughput of up to 40 samples per hour, a detection limit of 1.3 $\mu\text{g L}^{-1}$ and reproducibility of 1.2% RSD (50 $\mu\text{g L}^{-1}$ $\text{NO}_3^- - \text{N}$, $n = 10$). The proposed method was successfully applied for the determination of nitrate in estuarine waters and the reliability was assessed by the analyses of certified reference materials and recovery experiments. The method is suitable for waters with a wide range of salinities, and was successfully used for more than 3200 underway nitrate measurements aboard *SV Pelican1* in the “Two Bays” cruise in January 2010.

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1. Introduction

Nitrate is one of the principal nutrients that stimulates the growth of macrophytes and phytoplankton causing so-called eutrophication of aquatic systems [1,2], and it is frequently the limiting nutrient in marine systems. Increases in nitrate concentrations in coastal and inland waters are mainly due to anthropogenic sources such as agriculture, and domestic and industrial wastewater discharges. In aquatic environments, the most common ionic forms of inorganic nitrogen are ammonium, nitrite, and nitrate. Ammonium tends to oxidize to nitrate in a two step process ($\text{NH}_4^+ \rightarrow \text{NO}^+ \rightarrow \text{NO}_3^-$) which is mediated by aerobic chemoautotrophic bacteria (*Nitrosomonas* and *Nitrobacter*), even if levels of dissolved oxygen decline to value as low as 1.0 $\text{mg O}_2 \text{ L}^{-1}$ [3]. Therefore, the concentration of nitrate in well-oxygenated surface waters is generally much higher than that of ammonium and nitrite.

Effective management, preservation and restoration of fresh, estuarine and marine waters relies on the ability to measure the spatial and temporal variations of nutrient species in a manner that provides a clear picture of the sources, transport and transformation of nutrient species in aquatic ecosystems. Analytical methods that are portable and which enable rapid, sensitive and robust mea-

surements of nutrients in the field are therefore highly desirable as a means of collecting spatial and temporal data.

Many analytical methods have been proposed for determination of nitrate in waters, including ion chromatography [4], gas chromatography–mass spectrometry [5], capillary electrophoresis [6], potentiometry [7], polarography [8], and spectrophotometry [9–11]. Of these, some cannot cope with the high ionic strengths of marine and estuarine water samples, while others involve instrumentation that is either bulky, or delicate, and therefore generally unsuitable for field application. Some may require the use of a separation step or the use of large volumes of reagents, be capable of only low sample throughput, or suffer from poor sensitivity and precision. These considerations, and the increasing demand for rapid and sensitive environmental analytical methods have led to the development of flow-based analytical methods for nutrient determinations in various samples [12–17].

Most flow injection analysis methods for the determination of nitrate determination are based on either homogeneous or heterogeneous reduction of nitrate to nitrite and subsequent colorimetric determination of the nitrite by Griess reaction, in which diazotization with sulfanilamide is followed by coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride (NED) to form a pink azo dye [18]. Titanium (III) and hydrazine have been used as soluble reductants for nitrate reduction (c.f. Table 1). Both approaches have limitations: the hydrazine method requires lengthy reaction times for reduction and color development in order to achieve adequate sensitivity [19], while titanium (III) chloride solution is violet and

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Table 1

Comparison of the analytical performance of the proposed method with other reported spectrophotometric flow analysis methods that utilize the Griess reagent for determination of nitrate in water samples.

Matrix	Reduction agent	Type of flow analysis system	Dynamic range ($\mu\text{g L}^{-1} \text{NO}_3^- \text{-N}$)	LOD ($\mu\text{g L}^{-1} \text{NO}_3^- \text{-N}$)	RSD (%)	Sample throughput (h^{-1})	Reference
Water samples	Zinc column	FIA	10–600	1.3	1.2	40	<i>This work</i>
Rain water samples	Hydrazine	FIA	226–2259		<3	40	[19]
Potable waters	Titanium (III) chloride	FIA	20–5000	20		30	[20]
Natural waters	Copperized cadmium column	FIA	14–9800	1.4	1	30	[21]
Water and soil samples	Copperized cadmium column	FIA	226–1129		1.5	90	[22]
River water samples	Copperized cadmium column	FIA	0–12000	24	1.4		[23]
Dairy samples	Copperized cadmium column	SIA	113–903	34	3.4	21	[24]
Soil samples	Copperized cadmium column	FIA	50–7000	44	1.02	35–40	[25]
Waste water samples	Copperized cadmium column	SIA	11–3390	2.2	<0.7	24	[26]
Water samples	Copperized cadmium–silver alloy	FIA	25–3000	13	0.1–6.7	100	[27]
Natural waters	Copperized cadmium column	FIA	0–7900	113	0.9	22	[28]
Water samples	Copperized cadmium column	FIA	0–5000		1.96	72	[29]
Water samples	Photo-induced conversion	FIA	0–1400	0.7	3	10	[30]
Biological samples	Cadmium column	FIA	0.35–280	0.35			[31]

FIA, flow injection analysis; SIA, sequential injection analysis.

absorbs light in the same range as the pink azo dye [20]. A photo-reduction method has also been reported for nitrate determination in flow injection analysis systems (c.f. Table 1).

However, long irradiation times are required to achieve total nitrate reduction, and the conversion rate has also been found to increase with pH in the range 5–7, with a conversion efficiency of 50% achieved at pH 7 [30]. At this pH there is the potential for UV photo-oxidation of ammonium, urea, and other N compounds to occur in the presence of dissolved oxygen [32].

The most widely used segmented continuous flow [33] and flow injection analysis methods for nitrate determination [21–25], utilize heterogeneous reduction of nitrate to nitrite with a column of copperized cadmium granules or a Cd tubular reductor. Use of the cadmium column is often unreliable because of over-reduction to hydroxylamine and ammonia [34], or because of the loss of reduction efficiency that occurs due to poisoning of the column during the course of an analytical run. Use of cadmium is also undesirable because of the potential occupational health issues and the production of toxic waste [30,35,36]. Therefore, the use of an environmentally friendly reductant is highly desirable. Cardoso de Faria and Pasquini reported a flow injection method that utilised a copperized zinc column instead of Cd reduction [37]. This method was effectively applied to the determination of nitrate in tap and mineral waters using similar reduction conditions to that employed in the Cd reduction method, and it is surprising that this modification has not been more widely adopted. Another alternative approach using an environmentally innocuous reagent involves the quantitative conversion of nitrate to nitrite with corn leaf nitrate reductase. However, even under optimal conditions, the reaction kinetics are slow, and sample throughput using a segmented continuous flow analyser is limited to 5–12 samples h^{-1} [35,38].

Nitrate can be converted to ammonia in an alkaline medium using zinc or Devarda's alloy reductant [39] and this approach has been reported for determination of nitrate with a gas-sensing probe [40] and a bulk acoustic impedance detector [41]. Zinc has also been used as a heterogeneous reducing agent for conversion of nitrate to nitrite in batch mode [42,43] which is optimal under neutral or slightly acidic conditions [44].

In this work, a simple hybrid reagent-injection flow analysis method that utilizes on-line zinc reduction in the spectrophotometric determination of nitrate is described. The consumption of Griess reagent is minimized by the use of reagent-injection, and the use of zinc entirely eliminates the use of cadmium and its associated toxic waste. The method, which involves reduction under weakly acidic conditions, has been shown to be suitable for on-line measurement of nitrate in marine, estuarine and fresh waters, and has been deployed in extended field trials aboard the *SV Pelican 1*.

2. Experimental

2.1. Reagents

All chemicals were of analytical-reagent grade, and ultra-pure water (Millipore Milli-Q water system) was used to prepare all solutions. A nitrate stock solution ($100.0 \text{ mg L}^{-1} \text{NO}_3^- \text{-N}$) was prepared by dissolving 0.1517 g of sodium nitrate (BDH, Pool, England), dried at 110°C for 3 h, in water and diluting to 250.00 mL. The solution was stored at 4°C . Working standards were prepared daily by serial dilution of the stock solution.

The color forming reagent was prepared daily by dissolving 1.000 g of sulfanilamide (E. Merck, Darmstadt, Germany) and 0.025 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride (Sigma–Aldrich, Steinheim, Germany) and 7.35 mL of concentrated hydrochloric acid and diluting to 50.0 mL with ultra-pure water.

The 0.1 mol L^{-1} citrate buffer solution (pH = 6.5) was prepared by dissolving 7.35 g trisodium citrate dihydrate (Sigma–Aldrich, Steinheim, Germany) in 150 mL of water, and the pH adjusted to 6.5 with 0.1 mol L^{-1} hydrochloric acid before dilution to 250 mL with ultra-pure water.

2.2. Preparation of the zinc reduction column

The column was made of a length of Tygon[®] tubing ($8 \text{ cm} \times 2.3 \text{ mm}$ i.d.) filled with metallic zinc granules (0.15–0.40 mm), which were retained by disks of $25 \mu\text{m}$ nylon mesh (Swiss Screens (Aust) Pty Ltd., Huntingwood, NSW, Australia). Before use, the column was activated by flushing it with 0.1 mol L^{-1} hydrochloric acid at 2 mL min^{-1} for 3 min followed by $0.4 \text{ mg L}^{-1} \text{NO}_3^- \text{-N}$ for 3 min at the same flow rate.

2.3. Instrumentation

The proposed method was developed and tested in the laboratory using a reagent-injection flow analysis system similar to that previously described for phosphate determination [17] and shown in Fig. 1. The sampling system consisted of a 12 V DC peristaltic pump (SP) (7518-00, Masterflex, Cole-Parmer Instrument Co, Vernon Hills, IL 60061, USA). This was used to collect sample from a water intake in the hull one metre below the surface and pump it through a coarse filter ($25 \mu\text{m}$ mesh nylon screen (Swiss Screens (Aust) Pty Ltd., Huntingwood, NSW, Australia), held in a membrane filter assembly (Swinnex[®] 47, Millipore Corp, Billerica, MA 01821, USA) before passing through a $0.2 \mu\text{m}$ pore-size tangential flow filtration (TFF) unit (Vivaflow[®] 50, Gelman, Pall Life Sciences, Ann Arbor, MI 48103, USA) at a flow rate of ca. 100 mL min^{-1} . A sin-

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