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# Simple flow-injection system for the simultaneous determination of nitrite and nitrate in water samples☆

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## Abstract

A novel spectrophotometric reaction system was developed for the determination of nitrite as well as nitrate in water samples, and was applied to a flow-injection analysis (FIA). The spectrophotometric flow-injection system coupled with a copperised cadmium reductor column was proposed. The detection was based on the nitrosation reaction between nitrite ion and phloroglucinol (1,3,5-trihydroxybenzene), a commercially available phenolic compound. Sample injected into a carrier stream was split into two streams at the Y-shaped connector. One of the streams merged directly and reacted with the reagent stream: nitrite ion in the samples was detected. The other stream was passed through the copperised cadmium reductor column, where the reduction of nitrate to nitrite occurred, and the sample zone was then mixed with the reagent stream and passed through the detector: the sum of nitrate and nitrite was detected. The optimised conditions allow a linear calibration range of 0.03–0.30 $\mu$g $NO_2^-$-N $ml^{-1}$ and 0.10–1.00 $\mu$g $NO_3^-$-N $ml^{-1}$. The detection limits for nitrite and nitrate, defined as three times the standard deviation of measured blanks are 2.9 ng $NO_2^-$-N $ml^{-1}$ and 2.3 ng $NO_3^-$-N $ml^{-1}$, respectively. Up to 20 samples can be analyzed per hour with a relative standard deviation of less than 1.5%. The proposed method could be applied successfully to the simultaneous determination of nitrite and nitrate in water samples.

*Keywords:* Flow-injection analysis; Phloroglucinol; Nitrite; Nitrate; Simultaneous determination

## 1. Introduction

The determination of nitrite and nitrate is of general importance because of their harmful impact on human health. The toxicity of nitrite is primarily due to the fact that it can react with secondary or tertiary amines present in human body to form nitrosamines, which are known to be carcinogens, and nitrite can react with iron(III) of haemoglobin to produce methaemoglobinaemia disease. Moreover, nitrite can be used as an important indicator for the organic pollution of water, since it could be formed during the biodegradation of nitrogenous organic matter. Nitrate can enter the environment as a result of leaching from the soils containing nitrogenous fertiliser. Elevated concentrations of nitrate in water sources lead to a potential risk to human health because nitrate is also reduced to nitrite in environment.

Numerous analytical techniques have been proposed for the determination of nitrite and nitrate. Simultaneous determination of both ions is usually accomplished by several methods such as ion chromatography [1,2], gas chromatography–mass spectrometry [3] and capillary electrophoresis [4,5]. However, their instrumentation is expensive, needs the separation step and is not suitable for their use for analysis of large number of samples.

A flow-injection analysis (FIA) is therefore preferably used for the simultaneous determination of nitrite and nitrate after their conversion into measurable species. Several reactions and detection methods have been developed [6–12]. Some of those are time-consuming, need heating for acceleration of the detection reaction, sometime solvent extraction is necessary for analyte separation and procedures are rather complicated. Motomizu et al. developed a simple detection reaction for nitrite ion: the reaction was based on the nitrosation of *N*,*N*-bis(2-hydroxypropyl)aniline in acidic medium at

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80 °C [13,14]. During the nitrosation reaction under heating at 80 °C, the red-coloured intermediate appears and shows the absorption at 500 nm of the absorption maximum, which is gradually decreased: the final product of the nitrosation reaction is 4-nitroso-*N*,*N*-bis(2-hydroxypropyl)aniline ($\lambda_{max} = 400$ nm). Therefore, the reaction was favourably applied to FIA for the determination of nitrite and nitrate. A widely used method for the simultaneous determination of nitrite and nitrate is based on the reduction of nitrate to nitrite and subsequent spectrophotometric determination via the diazotization reaction of sulfanilamide and the successive coupling reaction with *N*-(1-naphtyl)ethylenediamine (NED) [15,16]. However, there are some problems for the diazotization-coupling reaction, such as the toxicity of the reagents used and the necessity of great care controlling the acidity for each step of analysis.

A variety of reducing agents have been investigated to facilitate the conversion of nitrate to nitrite including zinc [17], hydrazine [18,19], amalgamated cadmium [20] and copperised cadmium [21–23]. Photo-induced reduction of nitrite to nitrate was also applied to the conversion of nitrate to nitrite [24]: the conversion efficiency was 70–84%. Nitrate is reduced to nitrite mostly by using copperised cadmium column, which is essentially preferred when using flow-injection system.

In this work, a FIA system was developed for the simultaneous determination of nitrite and nitrate. The detection principle is based on the single-step nitrosation of a commercially available phenolic compound. The production of nitroso compound formed by the reaction of nitrous acid with phenolic species is easily performed under moderate conditions and lead to the result in the incorporation of nitroso functional group onto aromatic ring of the phenolic compound. Phloroglucinol, containing three hydroxyl groups, can react quickly with nitrite ion in acidic medium, as shown in Fig. 1. Nitrate was reduced to nitrite by using the copperised cadmium reductor column. Nitrite and nitrate can be determined simultaneously by the proposed FIA system.

## 2. Experimental

### 2.1. Chemicals and reagents

All of the reagents used were analytical reagent grade. Water purified with Milli-Q system (Elix 3/Milli-Q Ele-

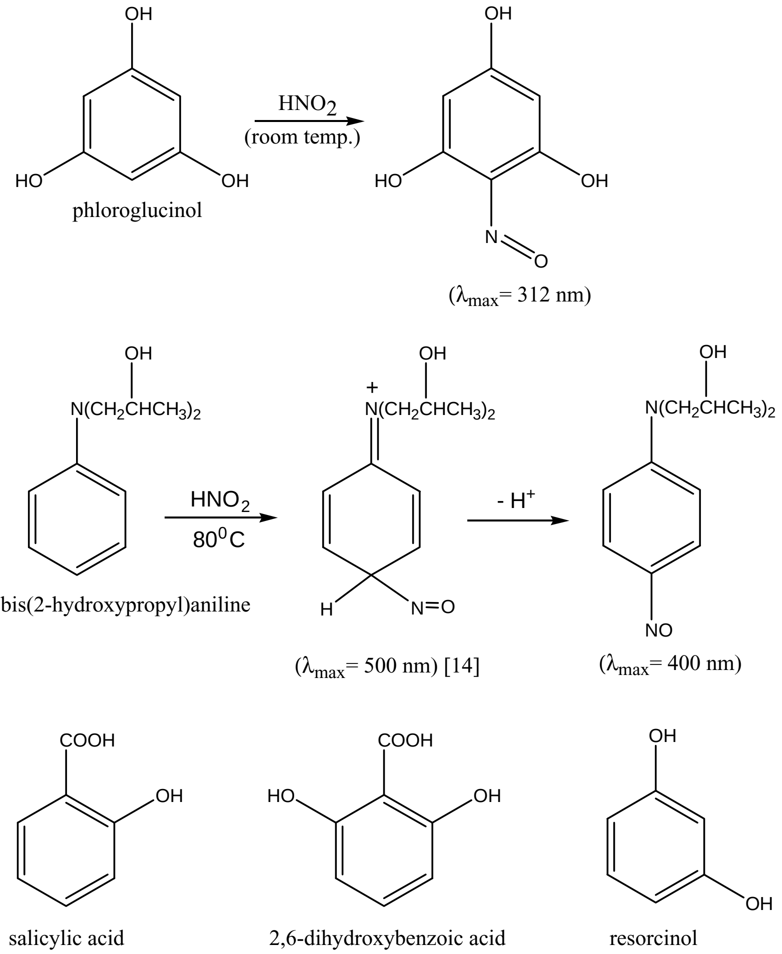

Fig. 1. Scheme of nitrosation reaction.

ment, Nihon Millipore) was used throughout the experiments. Stock standard solutions of 1000 μg $NO_2^-$-N $ml^{-1}$ and 1000 μg $NO_3^-$-N $ml^{-1}$ were prepared by dissolving sodium nitrite and sodium nitrate in water, respectively. Working standard solutions were freshly prepared by diluting the stock standard solutions to the desired concentrations with water.

A carrier solution was prepared according to Higuchi and Motomizu [25] by dissolving 1.50 g ammonium chloride and 0.35 g EDTA (disodium salt, dihydrate) in water, the pH was adjusted to 8.2 with NaOH and the solution was diluted to 500 ml with water.

### 2.2. Apparatus

Spectrophotometric measurements were obtained using a UV-2400PC UV-Vis recording spectrophotometer (Shimadzu, Japan).

The FI system used is schematically depicted in Fig. 2. The manifold was equipped with a double plunger pump (FI-710L SNK, Japan), six-port injection valve, a copperised cadmium reductor column (2 mm i.d. × 15 cm) [25], a spectrophotometer (UV-8010, Tosoh, Japan) and a signal recording FIA monitor/data processing apparatus (F.I.A. Instruments, Japan).

The carrier and the reagent solutions were pumped via the double plunger pumping system and the standards or samples were injected into the $NH_4Cl$/EDTA carrier stream by using the six-port injection valve. The injected sample was split into two streams at the Y-shaped connector. One of the streams merged directly and reacted with the reagent stream; $NO_2^-$ in the samples was detected (first peak). The other stream was passed through the copperised cadmium reductor column, where the reduction of $NO_3^-$ to $NO_2^-$ occurred. The sample zone was passed through the delay coil to obtain a separate peak and then mixed with the reagent stream and passed through the detector; the sum of $NO_3^-$ and $NO_2^-$ was detected (second peak). Thus, the $NO_3^-$ concentration was determined by the difference.

## 3. Results and discussion

### 3.1. Selection of the reagent suitable for rapid nitrosation reaction

Several kinds of reagents for the nitrosation with nitrite ion were examined with respect to rapid and reproducible reaction in moderate experimental conditions. The reagents examined are shown in Fig. 1. As reported in the previous studies [13,14], the final product of *N*,*N*-bis(2-hydroxypropyl)aniline with $NO_2^-$ is less sensitive than phloroglucinol. Other phenol and naphthol derivatives gave small amounts of nitroso compounds and were less sensitive than phloroglucinol. Of these reagents, phloroglucinol could react with $NO_2^-$ to form its nitroso compound very quickly. As a result, phloroglucinol was selected as the detection reagent. Under the milder conditions employed for the reaction together with less critical in pH control, the reagents and the product, all involve less toxicity comparing to those found by using the commonly used reagent, *N*-(1-naphtyl)ethylenediamine (NED), which provides advantages in practical analysis.

### 3.2. Absorption spectra

Fig. 3 shows the absorption spectra of phloroglucinol in 0.3 mol $l^{-1}$ HCl, before and after the reaction with nitrite and nitrate ions. As can be seen, the absorption increased greatly in the presence of nitrite. The maximum absorption was obtained at 312 nm. On the other hand, this reagent does not react with nitrate ion. Therefore, nitrate was determined after its reduction to nitrite by the copperised cadmium column.

### 3.3. Optimisation of the flow-injection system

In order to obtain a well separation between two peaks, corresponding to $NO_2^-$ and $NO_2^-$ plus $NO_3^-$, the length of the delay coil was optimised. The results obtained showed that a good separation between two peaks was made by using the delay coil length of 30 cm.

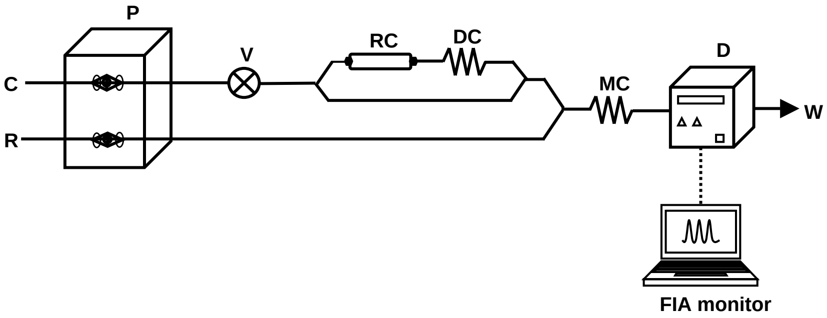

Fig. 2. Flow-injection system used for the simultaneous determination of nitrite and nitrate: C, carrier solution; R, reagent solution; P, double plunger micro pump; V, six-port injection valve; RC, reductor column; DC, delay coil; MC, mixing coil; D, detector; W, waste.

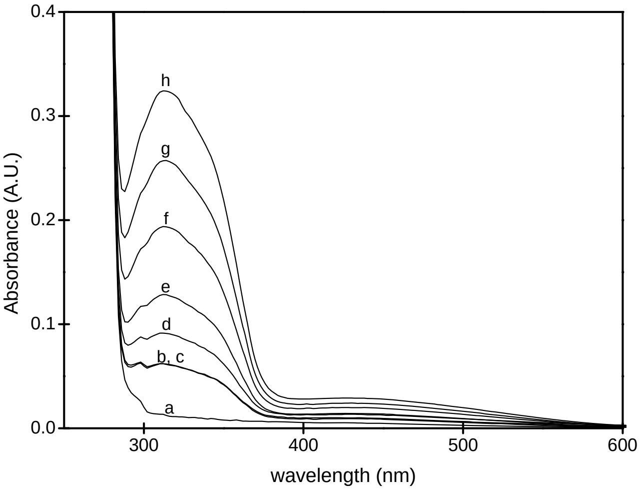

Fig. 3. The absorption spectra of phloroglucinol and its derivative with nitrite and nitrate: (a) 5.0 mmol l$^{-1}$ phloroglucinol; (b) a + 0.3 mol l$^{-1}$ HCl; (c) b + 1.00 μg ml$^{-1}$ $NO_3^-$; (d) b + 0.10 μg ml$^{-1}$ $NO_2^-$; (e) b + 0.20 μg ml$^{-1}$ $NO_2^-$; (f) b + 0.50 μg ml$^{-1}$ $NO_2^-$; (g) b + 0.75 μg ml$^{-1}$ $NO_2^-$; (h) b + 1.00 μg ml$^{-1}$ $NO_2^-$.

The flow rate of the carrier and the reagent solutions was very important with respect of the reduction efficiency with the copperised cadmium reductor column, the residence time necessary for the nitrosation reaction and the separation of two peaks. The effect of total flow rate of the double plunger pump was examined over the range of 1.0–1.8 ml min$^{-1}$. The results are shown in Fig. 4(a) and (b). The sensitivity of nitrite and nitrate changed very little by varying the flow rate in the range studied. By using the copperised cadmium reductor column of 15 cm, the reduction rate is very fast enough for the concentration range of 0.10–1.00 μg $NO_3^-$-N ml$^{-1}$. Moreover, the nitrosation reaction between nitrite ion and phloroglucinol is very fast.

The length of a reaction coil was also examined. Longer reaction coils gave longer residence time, whereas too long reaction coil could lead to broaden peak and poor reproducibility. Therefore, the reaction coil length of 50 cm was selected for this work.

### 3.4. Optimisation of reagent concentration

According to the nitrosation reaction, the formation of nitroso derivative could be taken place in an acidic medium. Therefore, the effect of concentrations of HCl was studied in the range of 0.1–1.0 mol l$^{-1}$. Fig. 4(c) and (d) shows the effect of HCl concentrations on the sensitivity of nitrite and nitrate determinations, respectively. The peak height, obtained by using the FIA system in Fig. 2, slightly increased with increasing the concentrations of HCl. However, a higher noise level was obtained by using high concentrations of HCl. Therefore, 0.4 mol l$^{-1}$ HCl in the reagent solution was chosen for this experiment.

The effect of the concentration of reagent, phloroglucinol, was studied in the range of 1–10 mmol l$^{-1}$, as shown in Fig. 4(e) and (f). The sensitivity, peak height, increased with increasing the reagent concentration and reached the constant at 5 mmol l$^{-1}$. Therefore, the concentration of phloroglucinol of 7.5 mmol l$^{-1}$ was adopted.

Table 1
Selected conditions for the simultaneous determination of nitrite and nitrate by the proposed FI system

| | |
|---|---|
| Carrier | 0.05 mol l$^{-1}$ $NH_4Cl$ + 1.8 × 10$^{-3}$ mol l$^{-1}$ EDTA (pH 8.2) |
| Reagent solution | 7.5 × 10$^{-3}$ mol l$^{-1}$ phloroglucinol + 0.4 mol l$^{-1}$ HCl |
| Reductor column | Copperised cadmium column (2 mm i.d. × 15 cm) |
| Delay coil length (cm) | 30 |
| Mixing coil length (cm) | 50 |
| Injection volume (μl) | 200 |
| Total flow rate (ml min$^{-1}$) | 1.50 (0.75 ml min$^{-1}$ each) |
| Detection (nm) | 312 (10 mm path length) |

### 3.5. Analytical characteristics

Under the selected experimental conditions summarised in Table 1, the analytical characteristics of the proposed method were evaluated by examining linear range, precision, detection limit and sampling frequency. The results are summarised in Table 2. The detection limit defined as the concentration of analyte giving signals equivalent to three times of the standard deviation of the blank signal. In order to evaluate the precision of the method, 11 injections of the standard solutions containing 0.15 and 0.4 μg $NO_3^-$-N ml$^{-1}$ were performed. The R.S.Ds. less than 1.5% were obtained. The flow signals corresponding to the nitrite and nitrate solutions at the concentration range of 0.03–0.30 μg $NO_2^-$-N ml$^{-1}$ and 0.10–1.00 μg $NO_3^-$-N ml$^{-1}$, respectively, are shown in Fig. 5.

### 3.6. Effect of foreign ions

The influence of common ions normally found in water samples was examined under the selected conditions. For this study, at a time, foreign ion of a known concentration was added to a solution containing fixed concentrations of 3.52 × 10$^{-5}$ mol l$^{-1}$ nitrite or 0.15 μg $NO_2^-$-N ml$^{-1}$ and 1.26 × 10$^{-4}$ mol l$^{-1}$ nitrate or 0.40 μg $NO_3^-$-N ml$^{-1}$. Sig-

Table 2
Analytical characteristics of the FI system for the simultaneous determination of nitrite and nitrate

| Parameters | Nitrite | Nitrate |
|---|---|---|
| Linear ranges | 0.03–0.30 μg $NO_2^-$-N/ml$^{-1}$ | 0.10–1.00 μg $NO_3^-$-N/ml$^{-1}$ |
| Limit of detection (3$\sigma$) | 2.9 ng $NO_2^-$-N/ml$^{-1}$ | 2.3 ng $NO_3^-$-N/ml$^{-1}$ |
| Precision ($n$ = 11, R.S.D.%) | 1.5 (0.15 μg $NO_2^-$-N/ml$^{-1}$) | 1.0 (0.4 μg $NO_3^-$-N/ml$^{-1}$) |
| Sample throughput (h$^{-1}$) | 20 | |

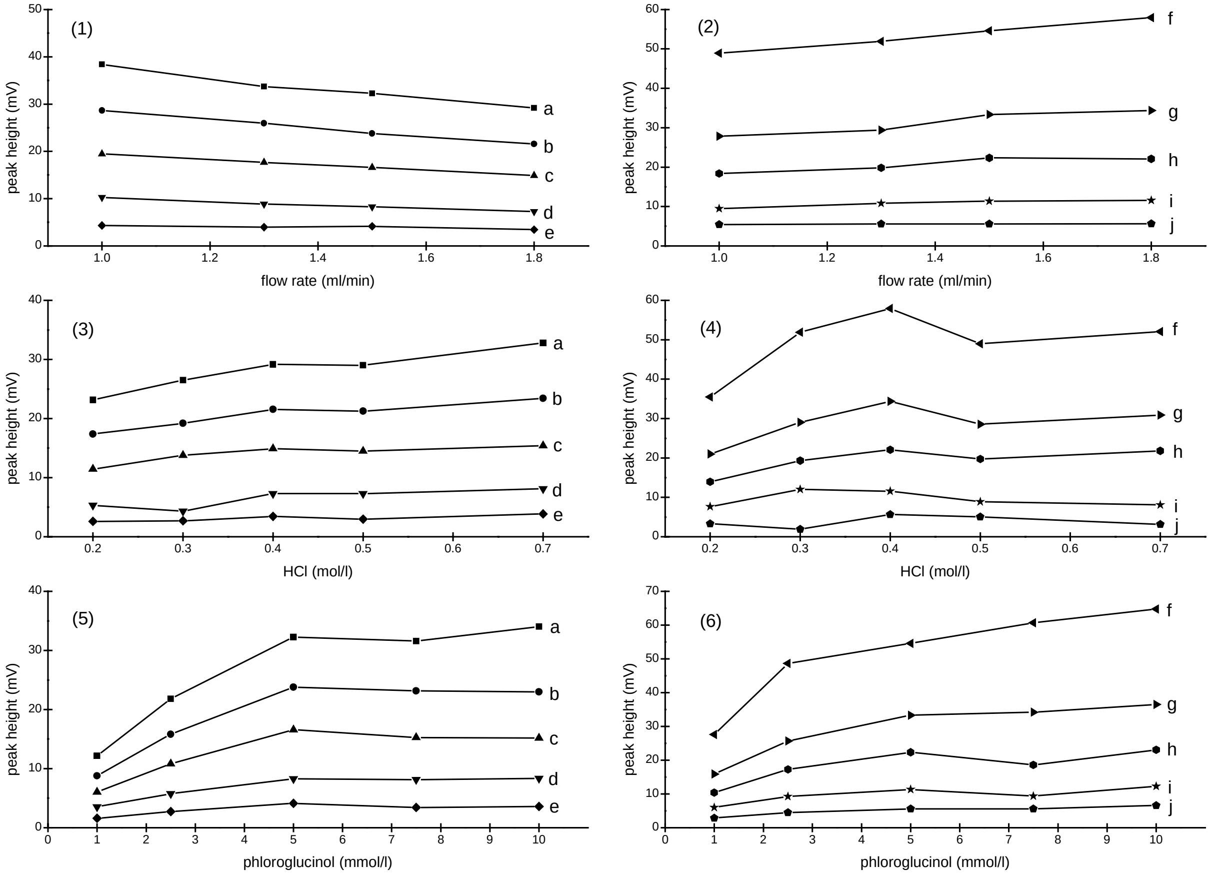

Fig. 4. Effect of some experimental parameters on the determination of nitrite and nitrate by the proposed method: (1) effect of flow rate on the nitrite determination; (2) effect of flow rate on the nitrate determination; (3) effect of HCl concentration on the nitrite determination; (4) effect of HCl concentration on the nitrate determination; (5) effect of reagent concentration on the nitrite determination; (6) effect of reagent concentration on the nitrate determination. Concentration of nitrite: (a) 0.30 μg $NO_2^-$-N ml$^{-1}$; (b) 0.20 μg $NO_2^-$-N ml$^{-1}$; (c) 0.15 μg $NO_2^-$-N ml$^{-1}$; (d) 0.07 μg $NO_2^-$-N ml$^{-1}$; (e) 0.03 μg $NO_2^-$-N ml$^{-1}$; concentration of nitrate: (f) 1.00 μg $NO_3^-$-N ml; (g) 0.60 μg $NO_3^-$-N ml$^{-1}$; (h) 0.40 μg $NO_3^-$-N ml$^{-1}$; (i) 0.20 μg $NO_3^-$-N ml$^{-1}$; (j) 0.10 μg $NO_3^-$-N ml$^{-1}$.

nals were observed and the recoveries were calculated by comparing the signals with those obtained using the standard solution without foreign ion. The tolerance limit was defined as the maximum concentration of a foreign ion causing a deviation of less than ±5%. The results are summarised in Table 3. It can be seen from Table 3 that the ions normally presenting in common water samples do not interfere with the determination of nitrite and nitrate in the proposed procedure.

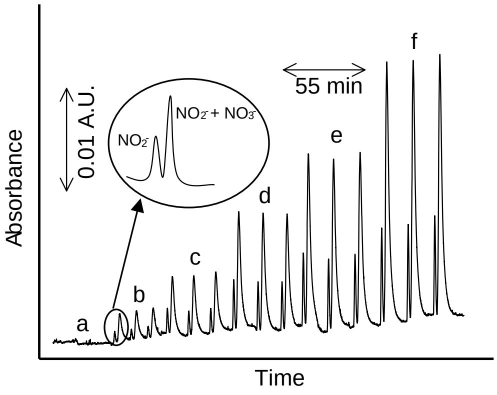

Fig. 5. Flow signals for nitrite and nitrate standard solutions: (a) blank; (b) 0.03 μg $NO_2^-$-N ml$^{-1}$ + 0.10 μg $NO_3^-$-N ml$^{-1}$; (c) 0.07 μg $NO_2^-$-N ml$^{-1}$ + 0.20 μg $NO_3^-$-N ml$^{-1}$; (d) 0.15 μg $NO_2^-$-N ml$^{-1}$ + 0.40 μg $NO_3^-$-N ml$^{-1}$; (e) 0.25 μg $NO_2^-$-N ml$^{-1}$ + 0.60 μg $NO_3^-$-N ml$^{-1}$; (f) 0.30 μg $NO_2^-$-N ml$^{-1}$ + 1.00 μg $NO_3^-$-N ml$^{-1}$.

### 3.7. *Application to samples*

In order to investigate the applicability of the proposed method to the analysis of real samples, some natural water sample such as tap waters, river waters and some locally available mineral drinking waters were analysed for nitrite and nitrate. The water samples were collected and analysed within 24 h without any preservation. Before injecting the samples into the FIA system, the water samples were filtered through a 0.45 μm membrane filter attached to the sample injection syringe. Table 4 shows the analytical results of nitrite and nitrate in water samples, as well as the results of the recovery test at different nitrite and nitrate concentration levels. Quantitative recoveries were obtained. Table 5 shows the comparison of the proposed method with the standard method [16]. The evaluation by *t*-test at 95%

Table 3
Tolerance limit of foreign ions in the simultaneous determination of nitrite and nitrate

| Ion | Added as | Tolerance concentration (mol l$^{-1}$)[a,b] of a foreign ion to the determination of | |
|---|---|---|---|
| | | Nitrite[c] | Nitrate[d] |
| $Cl^-$ | NaCl | $2.8 \times 10^{-3}$ | $2.8 \times 10^{-4}$ |
| $F^-$ | NaF | $2.6 \times 10^{-3}$ | $5.2 \times 10^{-4}$ |
| $SO_4{}^{2-}$ | $Na_2SO_4$ | $3.1 \times 10^{-4}$ | $2.0 \times 10^{-4}$ |
| $CO_3{}^-$ | $Na_2CO_3$ | $1.6 \times 10^{-3}$ | $1.6 \times 10^{-3}$ |
| $PO_4{}^{3-}$ | $KH_2PO_4$ | $1.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ |
| $Na^+$ | NaCl | $4.3 \times 10^{-3}$ | $4.3 \times 10^{-3}$ |
| $K^+$ | KCl | $2.6 \times 10^{-3}$ | $1.2 \times 10^{-3}$ |
| $NH_4{}^+$ | $NH_4Cl$ | $5.5 \times 10^{-3}$ | $8.3 \times 10^{-4}$ |
| $Ca^{2+}$ | $CaCl_2$ | $2.4 \times 10^{-3}$ | $5.0 \times 10^{-4}$ |
| $Mg^{2+}$ | $MgSO_4$ | $4.1 \times 10^{-3}$ | $8.2 \times 10^{-4}$ |

[a] Maximum concentration studied.

[b] Tolerance limit definition given in the text.

[c] A solution containing nitrite of $3.52 \times 10^{-5}$ mol l$^{-1}$ (or 0.15 μg $NO_2{}^-$-N ml$^{-1}$).

[d] Nitrate of $1.26 \times 10^{-4}$ mol l$^{-1}$ (or 0.40 μg $NO_3{}^-$-N ml$^{-1}$).

Table 5
Results of nitrite and nitrate determinations using the proposed and the standard methods

| Sample | Nitrite found (μg $NO_2{}^-$-N ml$^{-1}$) | | Nitrate found (μg $NO_3{}^-$-N ml$^{-1}$) | |
|---|---|---|---|---|
| | Proposed method | Standard method [16] | Proposed method | Standard method [16] |
| A1 | n.d. | n.d. | n.d. | n.d. |
| A2 | n.d. | n.d. | 2.09 | 2.29 |
| A3 | n.d. | n.d. | 1.03 | 1.11 |
| B | n.d. | n.d. | 1.03 | 1.06 |

A: mineral drinking water; B: tap water; n.d.: not detected.

confidence level indicates that the results obtained by the proposed method agreed well with those obtained by the standard method. It should be noticed that nitrite was not detected in the sample. In general, river water samples in Japan, which are not contaminated with industrial and domestic wastes, contain nitrite and nitrate at concentrations of $10^{-6}$ and $10^{-5}$ mol l$^{-1}$, respectively. Nitrite possibly can be oxidised to nitrate by oxygen, sunlight and some micro organisms. For tap waters, chlorine is added, and therefore, nitrite cannot be present. Also, drinking waters are pre-treated before bottling. For the analysis of sea water, further optimisation and the pre-treatment step may be necessary.

## 4. Conclusion

A FI simultaneous determination of nitrite and nitrate using a new reagent, phloroglucinol is proposed. The FI procedure is quite simple, rapid and does not need careful pH and temperature controls. The method is reproducible and covers an analytically valuable detection range which is suitable for natural water samples. The copperised cadmium reductor column is automatically regenerated by the carrier solution containing $NH_4Cl$/EDTA and it can be continuously used for a relatively long period. Application to some clean water samples was demonstrated.

Table 4
Determination of nitrite and nitrate in different water samples using the proposed method

| Sample | Nitrite | | | | Nitrate | | | |
|---|---|---|---|---|---|---|---|---|
| | Added (μg ml$^{-1}$) | Found (μg ml$^{-1}$) | Recovery (%) | Found in sample (μg ml$^{-1}$) | Added (μg ml$^{-1}$) | Found (μg ml$^{-1}$) | Recovery (%) | Found in sample (μg ml$^{-1}$) |
| A1 | 0 | 0 | – | n.d. | 0 | 0.29 | – | 0.37 |
| | 0.075 | 0.070 | 95 | | 0.20 | 0.49 | 96 | |
| | 0.150 | 0.150 | 101 | | 0.40 | 0.71 | 104 | |
| A2 | 0 | 0 | – | n.d. | 0 | 0.32 | – | 0.40 |
| | 0.075 | 0.075 | 95 | | 0.20 | 0.53 | 106 | |
| | 0.150 | 0.150 | 101 | | 0.40 | 0.74 | 104 | |
| B1 | 0 | 0.020 | 0 | 0.040 | 0 | 0.23 | – | 0.46 |
| | 0.075 | 0.090 | 93 | | 0.20 | 0.44 | 104 | |
| | 0.150 | 0.150 | 99 | | 0.40 | 0.66 | 106 | |
| B2 | 0 | 0 | – | n.d. | 0 | 0.21 | – | 0.43 |
| | 0.075 | 0.08 | 106 | | 0.20 | 0.40 | 92 | |
| | 0.150 | 0.16 | 106 | | 0.40 | 0.58 | 91 | |
| C1 | 0 | 0 | – | n.d. | 0 | 0.34 | – | 0.86 |
| | 0.075 | 0.070 | 95 | | 0.20 | 0.55 | 103 | |
| | 0.150 | 0.140 | 95 | | 0.40 | 0.77 | 106 | |
| C2 | 0 | 0 | – | n.d. | 0 | 0.12 | – | 0.14 |
| | 0.075 | 0.07 | 100 | | 0.20 | 0.31 | 95 | |
| | 0.150 | 0.16 | 107 | | 0.40 | 0.48 | 91 | |
| C3 | 0 | 0 | – | n.d. | 0 | 0.65 | – | 1.30 |
| | 0.075 | 0.08 | 104 | | 0.10 | 0.75 | 99 | |
| | 0.150 | 0.16 | 104 | | 0.20 | 0.83 | 91 | |

A: tap water; B: river water; C: mineral drinking water; n.d.: not detected.

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