r-FI Method for Successive Determination of Nitrite and Nitrate in Water with Glass-tube Separator and Gas-phase Chemiluminescent Detector

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Abstract

A reverse flow injection (r-FI) determination of nitrite and nitrate is presented. Nitrite and nitrate were converted into nitric oxide (NO) in acidic media using iodide and titanium(III) as reducing agents, respectively, which were injected into sample stream. NO was transferred into air in a glass-tube separator, and then was reacted with ozone and the resulting chemiluminescence was detected. The peak heights are proportional to the concentration ranges of 1×10^{-8} to 2×10^{-5} M of nitrite and of 5×10^{-7} to 2×10^{-4} M of nitrate. The total time for the analysis of nitrite and nitrate in one sample was less than 2 min.

Key words: nitrite, nitrate, nitric oxide, gas-phase chemiluminescence

Introduction

Nitrate and nitrite play important roles in nutrient cycles in aquatic environments [1,2]. In sewage water treatment, the elucidation of these components is important for water quality control of effluents [3,4]. The simultaneous determination of these components is desirable from the standpoint of saving time and making decisions concerning water quality control.

Conventionally, the concentrations of nitrite and nitrate were determined individually using colorimetric methods, such as the naphthyl ethylene-diamine method for nitrite [5] and the naphthylethylene-diamine method upon reduction to nitrite for nitrate [6]. More recently, ion exchange chromatography has come to be used for the determination of nitrite and nitrate [7]. However, these methods require much time to determine the concentrations of these inorganic nitrogenous species in sample water.

Aoki [8] previously reported a method for continuous determination of nitrite. In this method, nitric oxide (NO) was stripped from aqueous phase through a gas-permeable membrane and the gas-phase chemiluminescence (CL) resulting from the reaction of NO with ozone was detected. Recently, Durham et al.[9] reported a method for the determination of nitrite similar to our method. Later, Aoki and Wakabayashi[10] reported a method for successive determination of nitrite and nitrate by reduction to NO with the gas-permeable membrane and detection of the gas-phase CL described above. In long run of experiments, the surface of the membrane was clogged by titanium dioxide which was the reaction product and insoluble solid. In the present paper, we present a reverse FI (r-FI)

method for the successive determination of nitrite and nitrate in water using a glass-tube separator instead of the membrane separator. In this system, a reagent-injection was used to minimize reagent consumption.

Experimental Section

Apparatus and Procedure

A schematic diagram of the present r-FI system is shown in Fig.1. Water sample (S), such as river or lake water, was fed at a rate of 8.5 ml/min into the system with a peristaltic pump (P;Cole Parmer ,Model 7553-80). Each Reagent was loaded via a loop injector (volume of 500 μl; Rheodyne ,Model 5020)(I). A 19% w/w titanium (III) chloride in 0.5M sulfuric acid (Ti(III) reagent) was injected as a reducing agent to determine the total amount of nitrate and nitrite in the sample, while a 19% w/w potassium iodide in 0.5M sulfuric acid (iodide reagent) was injected instead of Ti(III) reagent to determine nitrite in the sample. In the reaction coil (RC)(PTFE tubing;i.d.1mm,o.d.2mm;length 1600mm), clean air (A)(passed through an activated carbon column (C1) and a silica gel column(C2)) was bubbled through the carrier sample containing the reagent in order to enhance the stripping of the reaction product in a glass-tube separator (GS). The flow rate of the clean air was 8.5 ml/ min. The separator had a length of 400mm, an outer diameter of 12mm , and an inner diameter of 10mm and was inclined downward at angle of 30 degrees with respect to a level surface. In the separator, the sample solution flowed down along a wall and the clean air flowed over this liquid film on the wall at a flow rate of 171.5 ml/min. The reaction

product was transferred into the stream of clean air. The air carrier
was passed to an NO analyzer (D)(Kimoto Co.Japan) at a flow rate of 180
ml/min by an air pump provided in this analyzer. Since the water vapor
in the air carrier interferes with the detection of nitric oxide (NO) by
the CL reaction, it was removed by means of a Nafion permeation tube
system [11] in the NO analyzer. The CL,resulting from the reaction between
NO in the dried air and ozone supplied from an ozone generator, was
detected with the NO analyzer and the CL intensity was recorded (R).

　　　The CL signals in injection of the iodide reagent and the Ti(III)
reagent correspond to nitrite and the total amount of nitrate and
nitrite, respectively, The difference between the CL signals corresponds
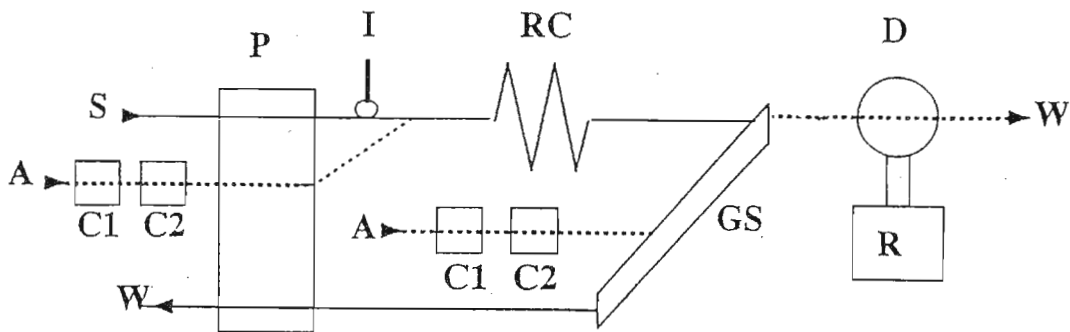to nitrate in the sample.

Fig.1 Schematic diagram of present method.
S:sample, P:peristaltic pump, I:reagent injection loop, A:air,
C1:activated carbon column, C2:silica gel column, RC:reaction coil,
GS:glass-tube separator, D:NO analyzer, R:recorder, W:waste.

Reagents

Unless otherwise mentioned, reagents were of analytical reagent grade. Deionized water was used in the preparation of all solutions.

Stock solutions of nitrite and nitrate were prepared from potassium nitrite, and potassium nitrate, respectively. Working standard solutions were prepared by serial dilution of the stock solutions just before use.

Ti(III) reagent was prepared by adding 1ml of concentrated sulfuric acid to 35ml of 20 %(w/w) titanium (III) chloride solution (Wako Pure Chemical,LTD.Japan). The final concentrations of Ti(III) chloride and sulfuric acid in the Ti(III) reagent were therefore 15% w/w and 0.5M, respectively. Iodide reagent was prepared by adding 1ml of concentrated sulfuric acid to 35ml of 20%(w/w) potassium iodide solution. The final concentrations of potassium iodide and sulfuric acid in the iodide reagent were therefore 19% w/w and 0.5M, respectively.

Results and Discussion

The optimum conditions of reagent concentrations for the determination of nitrite and nitrate with the membrane-separator have already been described in detail elsewhere[8,10]. The conditions were the same as those in the glass-tube separator system. Therefore, the following sections shall mainly concern the optimum conditions for the determination of nitrite and nitrate with the tube-separator. In this system, the length of the separator was fixed at 40 cm. The iodide reagent and the Ti(III) reagent were used as the reducing agents for nitrite and/or

nitrate,respectively.

Optimization of Flow Rate

Figure 2 shows the effect
of flow rate of sample con-
taining nitrite or nitrate on
the CL intensity. In the case
of nitrite, the CL intensity
increased with the increase
in flow rate of sample. In
the case of nitrate,however,
the CL intensity had peak at
around 4 ml/min.

Air-stripping can be
used to enable much of NO
to transfer into the stream
of clean air. Figure 3 shows
the effect of flow rate of
air on the CL intensity. The
CL intensity increased as the
flow rate of air increased.

Consequently, the flow
rates of sample and air were
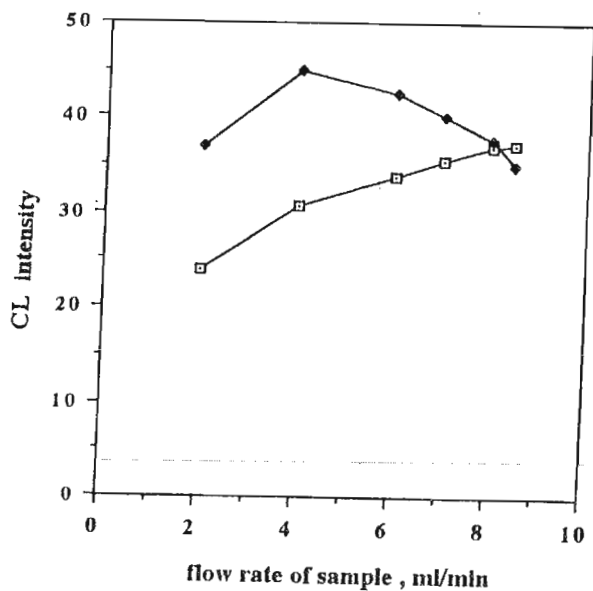selected to be 8.5 ml/min.

Fig. 2   Effect of flow rate of sample on
CL   intensity.

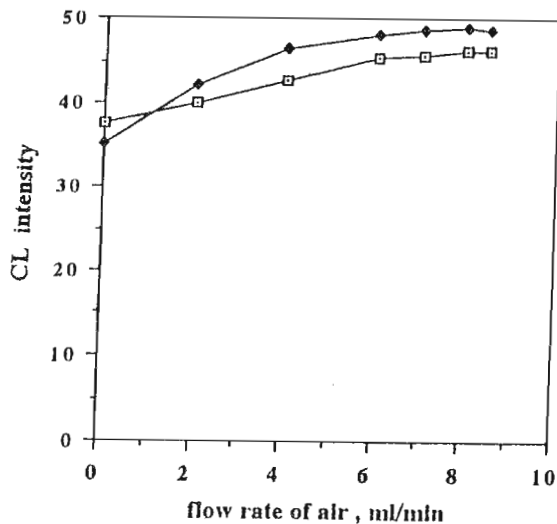—□— : 10^{-6} M nitrite,   —♦— : 10^{-5} M nitrate

Fig.3   Effect of flow rate of air on
CL   intensity.

—□— : 10^{-6} M nitrite,   —♦— : 10^{-5} M nitrate

Analytical Performance

Figure 4 shows the representative r-FI signals for nitrite and nitrate by the present method.

The conversion rate of the above nitrogeneous compounds to NO was examined using a new type of NO-releasing compounds[13], which spontaneously decompose in solution to generate NO. Among them, NOC7 (Dojindo Laboratories,Japan) was selected for this purpose. NOC7 rapidly decomposes in acidic solution to release 2 moles of NO per mole. A 0.5M sulfuric acid was passed through as the sample (S) in the present r-FI system shown in Fig.1 and a 1×10^{-5}M solution of NOC7 was loaded with a loop injector.The peak heights obtained with NOC7 were compared to those obtained with the nitrogeneous compounds. The conversions of nitrite and nitrate at a concentration of 1×10^{-5}M to NO were thus estimated to be 16.0% and 1.6%, respectively.
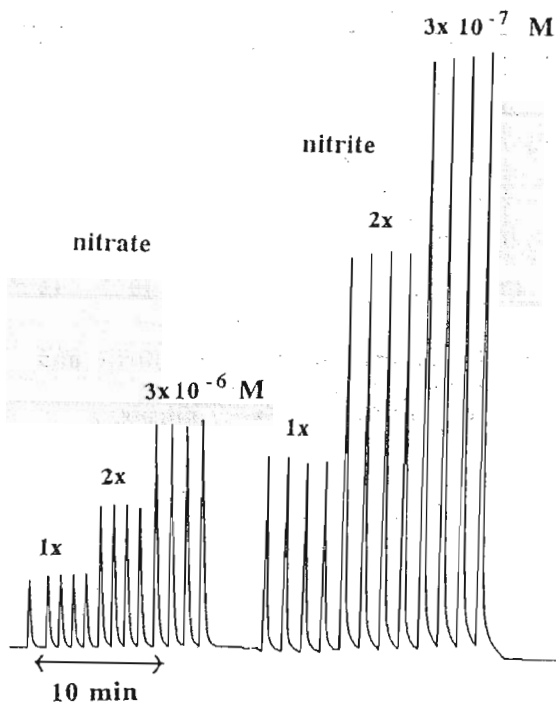

Fig. 4   Representative FIA signals by present method.

Figure 5 shows calibration curves for nitrite and nitrate by the present r-FI method. The peak heights are proportional to the concentration ranges of 1×10^{-8} to 2×10^{-5} M of nitrite and of 5×10^{-7} to 2×10^{-4} M of nitrate. The relative standard deviations (n=5) at 1×10^{-8} M were 0.6% for nitrite and 6.7% for nitrate, respectively. Since it takes about 1 minute from the injection of the reagent for the peak to settle back down to the baseline in the case of nitrite and nitrate, successive analysis of the two compounds can be performed within 2 min.
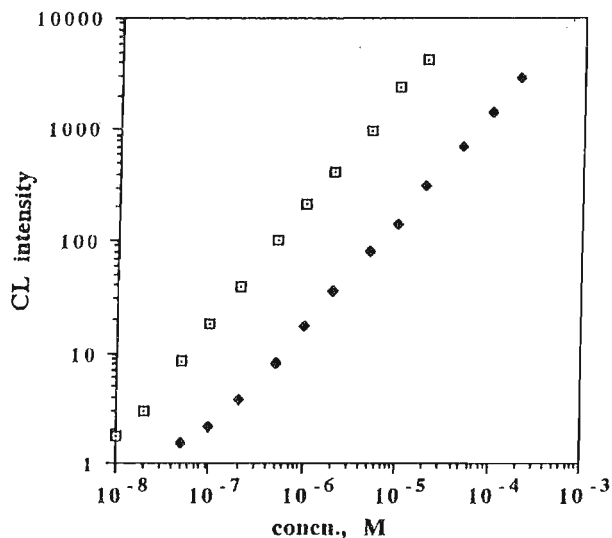

Fig. 5   Calibration curves of nitrite and nitrate by present method.
—□— : nitrite,   —◆— : nitrate .

Conclusion

The present r-FI method enables successive determination of nitrite and nitrate in water. This method allows rapid and sensitive measurement of these compouns in aquatic environments and has particularly advantageous for water quality control in sewage water plants and water purification plants, etc.

References

(1) Ehrlich,L.H. Geomicrobiology,2nd ed.;Marcel Dekker;New York,1990; Chapter 11.

(2) Schlesinger,H.W. Biogeochemistry ;Academic Press;San Diego,1991; Chapter 12.

(3) Tchobanoglous,G;Burton,L.F. Wastewater Engineering -Treatment, Disposal, and Reuse,3rd ed.;McGraw-Hill;New York,1991;pp.429-434.

(4) Horan,J.N. Biological Wastewater Treatment Systems - Theory and Operation;John Willey & Sons;Chichester,1990;pp.217-230.

(5) Jacobs,M.B.;Hockheiser,S. Anal.Chem.1958,30,426-428.

(6) Wood,D.E.;Armstrong,A.F.Jr.;Richards,A.F. J.Mar.Biol.Ass.U.K.,1967,

47,23-31.

(7) Small,H.;Miller,E.T.Jr. Anal.Chem.1982,54,462-469.

(8)Aoki,T. Biomed.Chromatogr.1990,4,128-130.

(9)Durham,J.A.;Barkley,M.R.;Sievers,E.R. Anal.Chem.1995,67,220-224.

(10)Aoki,T.;Wakabayashi,M. Anal.Chim.Acta,1995,308,308-312.

(11)Ho,H.M.;Gilbault,G.G.;Rietz,B. Anal.Chem.1983,55,1830-1836.

(12)Aoki,T. Environ.Sci.& Technol.1989,23,46-50.

(13)Hrabie,A.J.;Klose,R.J.;Wink,A.D.;Keefer,K.L. J.Org.Chem.1993,58,
     1472-1476.