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Selective determination method for measurement of nitrite and nitrate in water samples using high-performance liquid chromatography with post-column photochemical reaction and chemiluminescence detection

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ABSTRACT

A simple, sensitive and selective method for the simultaneous determination of nitrite and nitrate in water samples has been developed. The method is based on ion-exchange separation, online photochemical reaction, and luminol chemiluminescence detection. The separation of nitrite and nitrate was achieved using an anion-exchange column with a 20 mM borate buffer (pH 10.0). After the separation, these ions were converted to peroxynitrite by online UV irradiation using a low-pressure mercury lamp and then mixed with a luminol solution prepared with carbonate buffer (pH 10.0). The calibration graphs of the nitrite and nitrate were linear in the range from 2.0×10^{-9} to 2.5×10^{-6} M and 2.0×10^{-8} to 2.5×10^{-5} M, respectively. Since the sensitivity of nitrite was about 10 times higher than that of nitrate, the simultaneous determination of nitrite and nitrate in the water samples could be efficiently achieved. This method was successfully applied to various water samples – river water, pond water, rain water, commercial mineral water, and tap water – with only filtration and dilution steps.

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1. Introduction

The concentration of nitrite and nitrate in water environments are important indicators of water quality, because large amounts of these species may be toxic and induce eutrophication. Therefore, many analytical methods for the determination of nitrite and nitrate have been reported, including systems employing ion chromatography [1,2], capillary electrophoresis [3,4], and micro-total analysis system [5] coupled with UV or conductivity detector. However, these methods do not have enough sensitivity and suffer from interfering compounds. Therefore, various sensitive and selective detection methods that use the reactivity of nitrite have been applied. The most famous method for the selective determination of nitrite is Griess method and modifications of this method [6]. This method is based on the diazotization reaction with aromatic amino group followed by coupling with the formation of azo dye. Further, colorimetric methods [7,8], fluorimetric methods [9], electrochemical methods [10,11], and chemiluminescent methods have also been reported. These determination methods are described in recent reviews [12–14].

Among all these methods, various chemiluminescent methods have been reported since these methods can be sensitive and selective [15–19,23,24]. Gas-phase chemiluminescent method based on the reduction of nitrite to nitric oxide (NO), which reacts with ozone to produce chemiluminescence, is one of the most effective methods for the determination of nitrite [16,17]. However, this method necessitates special and expensive instruments. Other methods mainly involve luminol chemiluminescence reaction. Nitrite is oxidized by H_2O_2 in a sulphuric acid medium into peroxynitrous acid that can be detected as a peroxynitrite by the chemiluminescent reaction with an alkaline solution of luminol. This reaction was applied to the determination of nitrite in environmental water samples using the flow injection analysis (FIA) system [18]. Ferricyanide is generated from the reaction of ferrocyanide with nitrite in an acidic medium, which then reacts with an alkaline luminol solution to emit chemiluminescence. This reaction has been applied to the determination of nitrite in food using micro-FIA system [19].

In order to apply the determination of nitrate to the above-mentioned detection method, the reduction of nitrate to nitrite is involved. In general, the reduction of nitrate to nitrite was carried out by passing the sample solution through a copperized cadmium column. However, this procedure has many problems. On the other hand, the photoreduction method that uses a low-pressure mercury lamp is a convenient way for the reduction of nitrate to nitrite [20].

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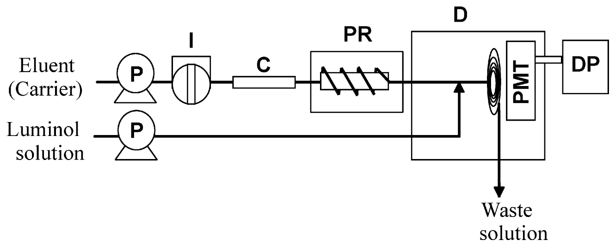

Fig. 1. Schematic diagram of the HPLC-CL system. P, pump; I, injector (100 μL); C, anion-exchange column; PR, photochemical reactor; D, chemiluminescence detector; PMT, photomultiplier tube; DP, data processor.

This is because light is used as a reagent instead of a copperized cadmium column, thereby eliminating the production of harmful effluents and renewal handling. Therefore, the photoreduction was combined with the above nitrite detection methods [21–24]. However, the development of simpler, faster, and more sensitive methods is still desirable for the simultaneous determination of nitrite and nitrate.

The authors recently showed that UV-irradiated *N*-nitrosamines under the basic aqueous condition would yield chemiluminescence upon mixing with a luminol solution, which was prepared using a carbonate buffer without the addition of oxidants such as hydrogen peroxide [25]. This chemiluminescent reaction scheme probably proceeds as follows. NO is generated from the cleavage of the N–NO bond of *N*-nitrosamines by UV irradiation. At the same time, a superoxide anion radical is generated from water or dissolved oxygen by UV irradiation in the basic aqueous solution. NO reacts with the superoxide radical and generates peroxynitrite. Peroxynitrite reacts with luminol through a peroxynitrite–bicarbonate intermediate and induces strong chemiluminescence. As mentioned above, nitrate in the aqueous solution is reduced to nitrite by UV irradiation. Furthermore, it is well known that nitrite undergo photolysis to form NO [20]. Therefore, the online photochemical reaction and subsequent luminol chemiluminescence detection system can be expected to applicable for determining nitrite and nitrate.

In this study, we report a new selective determination method of nitrite and nitrate in water samples such as river water, pond water, rain water, commercial mineral water, and tap water using high-performance liquid chromatography (HPLC) with post-column photochemical reaction and subsequent chemiluminescent detection based on luminol chemiluminescence. The reduction of nitrite and nitrate to NO and the generation of peroxynitrite could be completed only by UV irradiation, which dramatically simplified the detection system. Although this method needs the HPLC separation, it is simpler and the most sensitive one when considering the simultaneous determination of nitrite and nitrate among all the previously reported techniques.

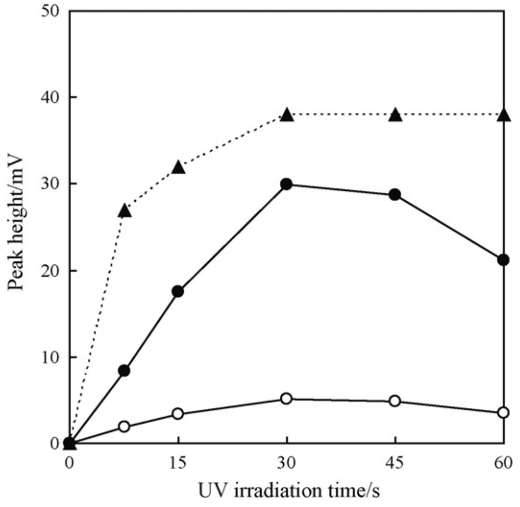

Fig. 2. Effect of UV irradiation time on the chemiluminescence intensity. Sample: nitrite (●), 1.0 μM; nitrate (○), 1.0 μM. Background level (▲). Conditions: carrier, 20 mM borate buffer–methanol (98:2, v/v, pH 10.0); carrier flow rate, 1.0 mL/min.

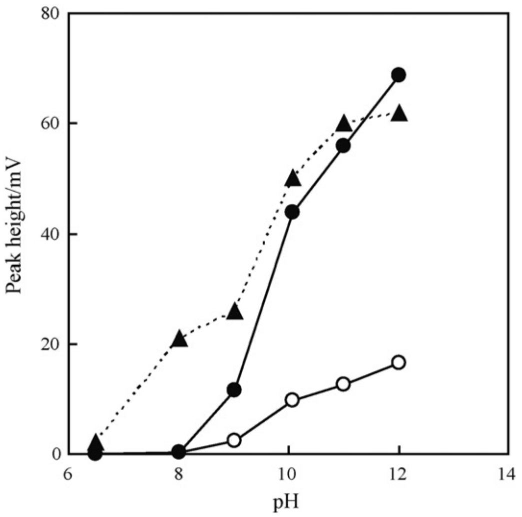

Fig. 3. Effect of pH on the chemiluminescence intensity. Sample: nitrite (●), 1.0 μM; nitrate (○), 1.0 μM. Background level (▲). Conditions: carrier, 10 mM borate buffer–methanol (98:2, v/v); carrier flow rate, 1.0 mL/min.

2. Experimental

2.1. Reagents and solutions

The stock solutions of standard nitrite and nitrate were prepared by dissolving an appropriate amount of sodium nitrate and sodium nitrite (Wako, Osaka, Japan) in water, respectively. Luminol (5-amino-2,3-dihydrophtalazine-1,4-dione) stock solution (20.0 mM) was prepared by dissolving 70.9 mg of luminol (5-amino-2,3-dihydro-1,4-phthalazinedion, Wako) in 20 mL of carbonate buffer (0.5 M, pH 10.0). These stock solutions were stored at 4 °C. All the other chemicals were of reagent grade or a better grade. Water for all the solutions was purified using a Yamato Auto Still WA-200 (Yamato Scientific, Tokyo, Japan) and Milli-Q Gradient A10 water purification system (Millipore, Tokyo, Japan).

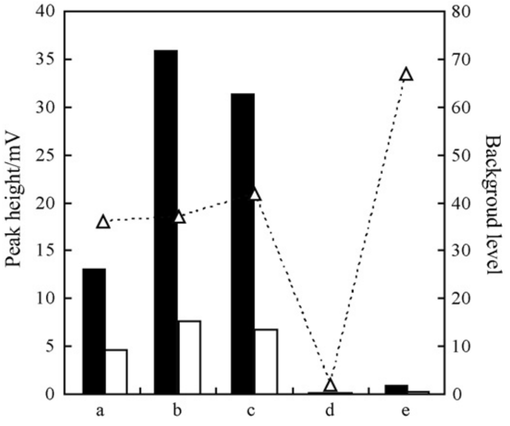

Fig. 4. Effect of organic modifier on the chemiluminescence intensity. Conditions: carrier, 10 mM borate buffer (pH 10.0)–organic solvent; carrier flow rate, 1.0 mL/min. Sample: nitrite (■), 1.0 μM; nitrate (□), 1.0 μM. Background level (▲). (a) Buffer; (b) 2% methanol; (c) 10% methanol; (d) 2% acetone; (e) 2% acetonitrile.

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