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Highly sensitive and selective spectrofluorimetric determination of nitrite in food products with a novel fluorogenic probe

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ABSTRACT

A simple, sensitive, selective and convenient spectrofluorimetric method for detection of nitrite has been successfully developed. This method is based on the highly efficient and specific reaction of nitric oxide with a dihydropyridine derivative to form a highly fluorescent pyridine derivative, in aqueous solution. Under optimum conditions, excellent detection linear range was achieved from 0.2 to 4.5 μmol L^{-1} with a detection limit of 0.02 μmol L^{-1} (S/N = 3), lower than or comparable to most of other spectrofluorimetric methods. The relative standard deviation for ten determinations of 2.0 μmol L^{-1} nitrite was 1.0%. The proposed method has been applied to determine nitrite levels in food products with recoveries of 93.3%–103.5%.

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1. Introduction

Nitrite has been used as preservatives in the food industry for a long time (Li, Yu, Jiang, Zhou, & Liu, 2003b). It has been realized that excessive amount of nitrite in food would pose a serious threat to public health. Nitrite can lead to the production of carcinogenic *N*-nitrosamine when it reacts with secondary amines and amides in the stomach (Seike et al. 2004). Furthermore, nitrite in the blood stream converts hemoglobin to methemoglobin, thereby interfering with the oxygen transport system in the body (Burden, 1961). Due to these toxic effects, a sensitive and specific method for the determination of nitrite in food products is of great importance.

Various methods for nitrite detection have been developed, among them the most commonly used is spectrophotometry which is based on the Griess reaction (Bratton & Marshall, 1939; Griess, 1879; Helaleh & Korenaga, 2001; Sun, Zhang, Broderick, & Fein, 2003; Tsikas, 2007). However, this method suffers from poor sensitivity and interference from other matrices and anions. Other methods such as chemiluminescence (Cox, 1980; He, Zhang, Huang, & Hu, 2007; Pelletier et al. 2006; Zhang, Zhang, Lu, Zhao, & Zheng, 2012), chromatography (Butt, Riaz, & Iqbal, 2001; Niedzielski, Kurzyca, & Siepak, 2006; Sarudi & Nagy, 1995), capillary electrophoresis (Della Betta, Vitali, Fett, & Costa, 2014; Miyado et al. 2004; Öztekin, Nutku, & Erim, 2002), electrochemistry (Afkhami, Soltani-Felehgari, Madrakian, & Ghaedi, 2014; Canbay, Şahin, Kıran, & Akyilmaz, 2015; Zhou, Wang, Gai, Li, & Li, 2013) and spectrofluorimetry (Biswas, Chowdhury, & Ray, 2004; Chen, Tong, & Zhou, 2007; Dombrowski & Pratt, 1972; Li, Wang, Zhang, & Zhang, 2003; Liu, Yang, Abdel-Halim, & Zhu, 2013; Liu et al. 2009; Wang, Adams, & Van Schepdael, 2012; Wiersma, 1970; Zhang, Fan, & Jin, 2010) have also been reported. But not all the methods are suitable for routine trace determinations, because some of them are always expensive and time-consuming, thus, the wide utilization of these methods is largely limited. In comparison to other methods, spectrofluorimetric methods gained much more attention due to its simplicity, convenience, high sensitivity and selectivity, low limits of detection and low-cost. Thus, highly desirable sensitive and selective fluorescent probes play a pivotal role in the development of spectrofluorimetric methods for the detection of nitrite.

A number of fluorescent probes for the determination of nitrite have been reported. Among them, the most frequently reported were aromatic vicinal diamines such as 2,3-diaminonaphthalene

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(DAN) (Wiersma, 1970). The reaction of aromatic vicinal diamines with nitrite in acidic conditions leads to the formation of triazole compounds. However, there are several disadvantages of using these reagents. The electron-rich aromatic vicinal diamines are intrinsically susceptible to self-oxidation. Most of them were synthesized in lab scale and market unavailable. In our previous work, a new spectrofluorimetric method has been proposed to determine trace amount of nitrite in food products using the market available DAF-FM DA as a fluorescent probe (Kojima et al. 1999). But the instability and high-cost of the probe may prevent it from routine monitoring use. In spite of the progress made so far, developing highly sensitive and specific fluorescent probes for nitrite is still a major challenge in this field.

It is reported that Hantzsch ester, a dihydropyridine derivative, is able to quantitatively react with nitric oxide (*NO*) to give the corresponding pyridine (Itoh, Nagata, Matsuya, Miyazaki, & Ohsawa, 1997; Itoh, Nagata, Okada, & Ohsawa, 1995). In our laboratory, a new class of highly sensitive and selective fluorogenic probes which consist of the Hantzsch ester and an excellent fluorophore, 7-methoxycoumarin, was developed via rational design and successfully applied to the detection of *NO* in living cells (Ma et al. 2014). These probes are nearly non-fluorescent, but they can react with *NO* to yield highly stable and fluorescent pyridine compounds. Considering the fact that *NO* could be generated from nitrite in acidic conditions, we speculated that these reagents could also react with nitrite in acidic conditions to form the corresponding pyridine compounds. In this paper, the feasibility of this speculation was confirmed. A series of dihydropyridine-based fluorogenic probes developed in our laboratory was evaluated for detection of trace amount of nitrite in acidic solution.

It was found that in acidic solution, fluorescence (FL) emission of one of fluorogenic probes, Probe 1, was dramatically enhanced in the presence of nitrite ions. Similar enhancement of FL intensity was also found when it reacted with *NO* to form the pyridine derivative, Compound 2. Such FL enhancement led us to set up a new method for nitrite determination. In this paper, Probe 1 was proposed as a new fluorogenic probe for nitrite determination and the determination conditions were optimized. This fluorogenic probe-based spectrofluorimetric method was successfully applied to the determination of nitrite in food samples with good precision and accuracy. The probe showed several advantages over other fluorogenic probes for determination of nitrite such as high sensitivity and selectivity, high fluorescence quantum efficiency, excellent photo-stability and low-toxicity, indicating that this probe is quite suitable for the determination of nitrite in food products.

2. Experimental

2.1. Apparatus

All fluorometric measurements were performed with a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, America) equipped with a 1 cm × 1 cm quartz cell. The slit widths in terms of wavelength were 5 nm for excitation and emission, respectively. A FEP20-FiveEasy Plus pH meter (Mettler-Toledo Instruments Co., LTD. Shanghai, China) was used. A thermostat bath model WB-2000 (Changchengkegongmao Co., Zhengzhou, China) maintained at the desired temperature was used for the experiments. All solutions were prepared in ultrapure water (R = 18.2 MΩ) purified by a Milli-Q Gradient system (Millipore, Molsheim, France).

2.2. Reagents and solutions

All chemicals were of analytical grade from Beijing Chemical Reagent Co. (Beijing, China) and used without further purification. Aqueous solutions were prepared with Milli-Q water at room temperature. All fluorescence intensity measurements were made at room temperature.

Probe 1 (synthesized in our lab) solution (3.0×10^{-4} mol L^{-1}) was prepared in DMSO and could remain stable for over a month. A standard stock solution of sodium nitrite (10^{-3} mol L^{-1}) was prepared by dissolving sodium nitrite (dried at 110 °C for 4h) in Milli-Q water, A pellet of sodium hydroxide (about 5.0 mg) was added to prevent the decomposition of nitrite to nitrous acid. Twenty drops of chloroform (0.3 mL) were added to inhibit the bacterial growth and thus make the nitrite solution stable (Lew, 1977). This standard stock solution was prepared weekly and kept in a refrigerator at 4 °C. Working solution was prepared freshly from the stock solution by appropriate dilution. Hydrochloric acid (0.10 mol L^{-1}) was prepared from concentrated hydrochloric acid. Phosphate buffer solution (0.05 mol L^{-1}, pH 7.4) was prepared by mixing 0.05 mol L^{-1} solutions of NaH_2PO_4 and Na_2HPO_4 in 19:81 (v/v) ratio. Solutions of inorganic ions were prepared from their water soluble salts (or the oxides and carbonates in acids).

2.3. General procedure

To a 10 mL colorimetric tube containing a certain volume of standard nitrite solution, 1.0 mL of Probe 1 solution (3.0×10^{-4} mol L^{-1}) and 1.0 mL of 0.10 mol L^{-1} HCl were added. The mixture was diluted to the volume of 5 mL with Milli-Q water and mixed well. Then the mixture was incubated for 30 min in a hot water bath at 60 °C, cooled to room temperature. Dilute the whole solution to the volume of 10 mL with phosphate buffer solution (0.05 mol L^{-1}, pH 7.4). The final pH of the solution was 7.0. The FL intensity was measured at 458 nm against a corresponding nitrite blank, keeping the excitation wavelength at 390 nm.

2.4. Sample analysis

All food samples were purchased from local supermarket in Beijing and triturated.

Meat products (10.0 g) were weighed in a beaker, then 25 mL of borax solution (5%) and 350 mL of hot water were added. The mixture was incubated in a boiled water bath for 15 min. Then 10 mL of potassium ferrocyanide aqueous solution and 10 mL of zinc acetate aqueous solution were added to precipitate the protein. Dilute the volume to 500 mL with Milli-Q water, followed by filtration through filter paper. Each time 1.0 mL of the filtrate was determined with the method described in Section 2.3.

Pickled vegetables were cleaned and dried, then 10.0 g of which were weighed in a beaker. 25 mL of borax solution (5%) and 350 mL of hot water were added. The mixture was incubated in a boiled water bath for 15 min. Cooled to room temperature and the volume was diluted to 500 mL. After being filtered, 1 mL of the solution was transferred into a 10 mL colorimetric tube and determined with the method described in Section 2.3.

3. Results and discussion

3.1. Photophysical properties and proposed mechanism

The feasibility and efficiency of Probe 1 based spectrofluorimetric method for detection of nitrite was first evaluated with sodium nitrite. As shown in Scheme 1, Probe 1 which was nearly non-fluorescent ($\Phi = 0.01$) interacted with sodium nitrite in acidic solution to quantitatively generate a highly fluorescent species, Compound 2 ($\Phi = 0.87$) which is separated and fully characterized. The data of ^{1}H NMR, ^{13}C NMR and MS spectra were listed in

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