Sensors and Actuators B 147 (2010) 61–66

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A highly selective optical sensor for catalytic determination of ultra-trace amounts of nitrite in water and foods based on brilliant cresyl blue as a sensing reagent

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ARTICLE INFO

Article history:
Received 11 August 2009
Received in revised form 1 March 2010
Accepted 8 March 2010
Available online 15 March 2010

Keywords:
Optical sensor
Nitrite
Brilliant cresyl blue
Water and food samples
Spectrophotometry

ABSTRACT

A new optical sensor has been developed for nitrite determination based on the use of brilliant cresyl blue (BCB) immobilized on triacetyl cellulose membrane using absorption spectrophotometry. The sensor is based on the reaction of BCB with bromate as an oxidant in the presence of nitrite in acidic media to produce a colorless product. Nitrite has a strong catalytic effect on the reaction of BCB with bromate. The difference in the absorbance of the optode at 570 nm between uncatalyzed and catalyzed reactions (ΔA) was found to be directly proportional to the concentration of nitrite. A detection limit was found to be 1.76 nmol L^{-1} (0.08 ng mL^{-1}). The corresponding detection limit of 1.9 nmol L^{-1} is well below the maximum admissible concentration level of 2.2 μmol L^{-1} required by the European Community. The sensor response from different probes ($n = 8$) gave an RSD% of 2.4% at 2.17 μmol L^{-1} nitrite concentration. The proposed sensor was successfully applied for the determination of nitrite in water and food samples.

1. Introduction

The increasing concentration of nitrite in groundwater, rivers, and lakes has caused serious hazards to public health and the environment. Nitrites are largely used as preservatives and fertilizing agents. However, the continuous ingestion of these ions can have serious implications for animal and human health [1–4]. For instance, nitrites can react irreversibly with hemoglobin to produce methemoglobin, thereby reducing blood capacity to transport oxygen. Nitrite can also damage the nervous system, liver, spleen, and kidneys of small fish at concentrations as low as 0.25 part per million. Excessive amounts of nitrite typically used for food preservation has been proved to be carcinogenic as it serves as a precursor to the formation of *N*-nitrosamines [4–6]. The toxicity of nitrite is primarily due to its interaction with blood pigment to produce methemoglobinalmia. The reaction between nitrite and secondary or tertiary amines results in the formation of N-nitroso compounds, some of which are known to be carcinogenic, tetratogenic, or mutagenic [7–9]. Therefore, determination of nitrite is of great importance due to its harmful effects on human health Thus, sensitive, selective, and precise methods are required for the determination of nitrite.

A number of methods have been described in the literature for nitrite determination that are based on such analytical methods as titrimetric [10], catalytic-spectrophotometric [7–9,11] chromatographic [12,13], and electrochemical [14–17] techniques. However, most of these conventional approaches are expensive and time-consuming, which frequently generate considerable waste and require highly trained technicians. In addition, these methods are either not adequately sensitive or selective for ultra-trace determination of nitrite or are time-consuming. Moreover, they cannot be applied quickly for real-time and on-site measurement of nitrite. In this context, rapid detection and environmental monitoring as well as clinical and food diagnostics have paved the way for the elaboration of alternative analytical devices known as optical sensors. The catalytic method is one of procedures in terms of sensitivity [7–9], and the fact that no expensive or special equipment is required adds to its attractions.

Optical chemical sensors have been used for the determination of cations and anions, because of their advantages such as good sensitivity and selectivity, ease of fabrication, and low cost. Depending on simple instrumentation, they are easier and cheaper to employ than any other analytical method available. Development of optode has been mostly based on the immobilization of a reagent in/on the membranes by either physical [18,19] (adsorption, encapsulation, sol–gel, etc.) or chemical (covalent bond) methods [20]. Optodes are used based on different analytical techniques such as absorbance [21], fluorescence [22], or reflectance [18,19] measurements. To

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doi:10.1016/j.snb.2010.03.014

the best of the authors' knowledge, only a few studies have been reported on the determination of nitrite based on optical sensors [23–27] using spectrophotometric measurement [23–26] and the quenching effect on chemiluminescence of CdSe [27]. Despite their advantages, all the optodes, however, suffer from the interference of oxalate and Fe(III) and from their inability to measure nitrite at concentrations below 5 ng mL^{-1}.

This paper presents a sensitive and highly selective optode fabricated for catalytic determination of low levels of nitrite in acidic media, in which the sensing reagent is brilliant cresyl blue (BCB) immobilized on a triacetyl cellulose membrane. Our findings indicate that bromate could oxidize BCB in acidic media resulting in decoloration of the membrane. Nitrite has a strong catalytic effect on this reaction. The difference in the absorbance of the immobilized form of BCB at 570 nm between uncatalyzed and catalyzed reactions is directly proportional to the concentration of nitrite. The measurements are carried out at room temperature with good selectivity and precision. The proposed method is then applied for the determination of nitrite in food and water samples with satisfactory results.

2. Experimental

2.1. Reagents

All solutions were prepared using reagent grade chemicals and doubly distilled water was used throughout.

BCB solution, 0.020 g per 100 mL, was prepared daily by dissolving 0.020 g of the reagent (Merck) in 100 mL of water solution in a 100-mL standard flask.

Bromate solution 0.10 mol L^{-1} was prepared by dissolving 1.670 g of potassium bromate (Merck) in water and diluted in a 100-mL volumetric flask with water.

Nitrite stock solution, 1000 μg mL^{-1}, was prepared by dissolving 0.15 g (dried for 4 h at 105–110 °C) sodium nitrite (Merck) in water and diluting to 100 mL in a standard flask. A pellet of sodium hydroxide was added to prevent the liberation of nitrous acid and 0.5 mL of chloroform was added to inhibit bacterial growth. Working standard solutions were freshly prepared daily by diluting the stock solution with water.

2.2. Apparatus

UV–vis spectra were measured with a double beam spectrophotometer, Jasco Model V–750, using 1.0 cm quartz cells. The sensing membrane was placed and fixed in a disposable plastic cuvette and all measurements were performed in a batch mode.

A (plastic) homemade cell frame was used with a special frame 9 mm × 40 mm in size as shown in Fig. 1. The film was placed between the two stabilizers (in the slit) and the cell was directly mounted in the spectrophotometer.

Solution pH was measured using a pH-meter, Metrohm Model 827 pH Lab, equipped with a combined glass–Ag/AgCl electrode (Model 6.0228.010).

2.3. Membrane preparation

The immobilized indicator on a triacetyl cellulose membrane was prepared according to the following procedure: the transparent triacetyl cellulose membranes were produced from waste photographic film tapes that were previously treated with commercial sodium hypochlorite for several seconds in order to remove colored gelatinous layers. The films were treated with a solution of 5.4×10^{-6} mol L^{-1} BCB for 4 h at room temperature. Then, the membranes were washed with water in order to remove the loosely trapped indicator. The prepared sensor had a thickness (path length) of 0.14 mm. The prepared membranes were stable over several weeks of storage under dry conditions.

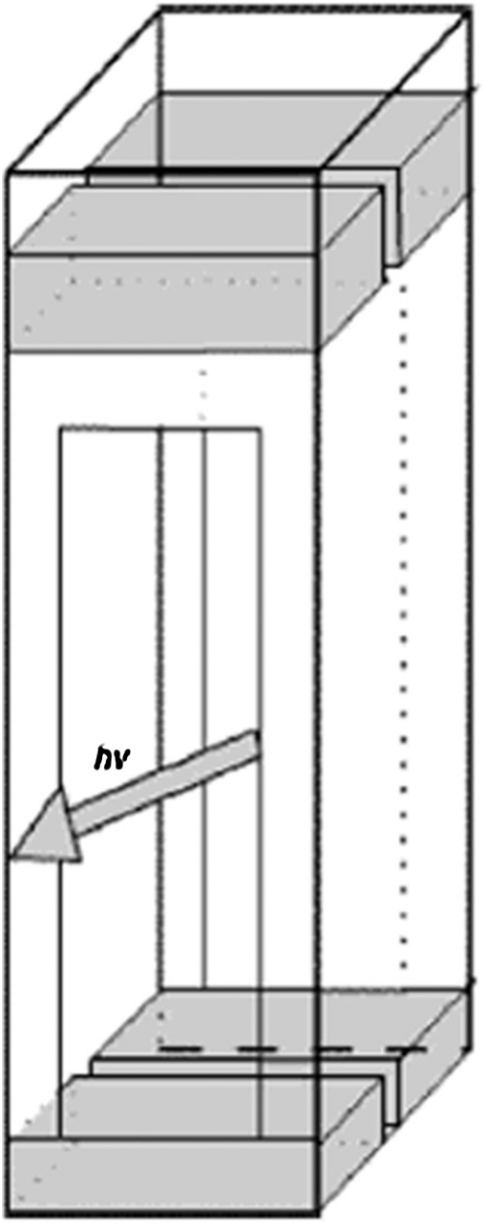

Fig. 1. A homemade cell frame.

2.4. Recommended procedure

The catalytic reaction was monitored spectrophotometrically by monitoring the change in the absorbance of the sensor at 570 nm at a fixed time of 0–2 min from initiation of the reaction using the optical sensor. The absorbance of the membrane sensor was measured before contacting it with the reaction solution (before the reaction initiation). Then, the prepared membrane was placed into 4.0 mL solution containing 0.070 mol L^{-1} sulphuric acid plus 0.02 mol L^{-1} bromate solution. Finally, 20.0 μL of nitrite containing (0.68–11,946.0 ng) to the solution was added with which the membrane was equilibrated for 2 min. The membrane sensor was washed with water and the absorbance of the membrane sensor was measured at 570 nm initially for the uncatalyzed (without nitrite) and for the catalyzed (with nitrite) reactions after 2 min. The difference in the absorbance from 0 to 2 min was assigned as