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Determination of trace nitrite by anodic stripping voltammetry

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A sensitive anodic stripping procedure for trace nitrite in the presence of added cetyltrimethylammonium bromide (CTMAB) is described. The method is based on the electrodeposition and subsequent oxidation of CTMAB–nitrite complex on a glassy carbon electrode in a supporting solution, consisting of Britten–Robinson buffer solution, pH range 3.6–4.0, and CTMAB. The peak height is proportional to the concentration of nitrite over the range 0.01–0.25 $\mu g\,ml^{-1}$, and the relative standard deviation is less than 3.3%. This method has been used for the determination of trace nitrite in water and meat products with 90–110% recovery. © 1997 Elsevier Science Ltd

INTRODUCTION

The potential hazard of nitrite to human health has been well documented (Concon, 1988; Hill, 1991; Shibamoto & Bjeldanes, 1993). Many analytical methods for the determination of nitrite have been developed. Various spectrophotometric methods based on the diazotization reaction of nitrite with some aromatic amines and formation of azo dyes have been intensively investigated (Rand *et al.*, 1976; Flamerz & Bashir, 1985). Fluorimetric methods for nitrite determination have been developed (Damiani & Burini, 1986; Ohta *et al.*, 1986) and both sensitivity and selectivity improved. Various electrochemical techniques have also been proposed for the determination of nitrite, such as polarography (Chang *et al.*, 1977; Gao *et al.*, 1990; Markusova & Fedurco, 1991; Lu, 1992, 1994) and ion chromatography (Bosch *et al.*, 1995). In recent years, more emphasis has been placed on the use of solid electrodes for such applications. Reduction of nitrite at gold, platinum and carbon electrodes has been reported (Mengoli & Musiani, 1989). However, reductive techniques are limited by the negative potentials that are required for detection, where interference from metal cations, hydrogen peroxide and oxygen may be problematic.

A large number of methods have been developed for the voltammetric determination of nitrite by oxidation at solid electrodes. Nitrite oxidation at a bare glassy carbon electrode was reported (Newberg & Lopez de Haddad, 1985), but this method suffered interference from both ascorbate and chloride ions. The determination of nitrite following oxidation at both electrochemically pretreated (Chamsi & Fogg, 1988) and polymer-modified (Cox & Kulkarni, 1986; Barisci *et al.*, 1989) glassy carbon electrodes at lower operational potentials has therefore been investigated. With the ruthenium polymer modified electrodes reported by Barisci *et al.* (1989), the major problem associated with the electrodes was their long-term stability.

A novel method for the determination of trace nitrite using a glassy carbon electrode by anodic stripping voltammetry is described in this article. The method is based on the adsorptive accumulation of cetyltrimethylammonium bromide (CTMAB)–nitrite complex. The procedure is easy and convenient to operate, and it results in high sensitivity and selectivity. The detection limit is 0.01 $\mu g\,ml^{-1}$ and most common anions and cations do not interfere.

EXPERIMENTAL

Apparatus and reagents

A Model MF-1A voltammetric analyser (Jiangsu Electroanalysis Instrumental Factory, China) coupled with a Model 103-X-Y recorder (Shanghai Dahua Instrumental Factory, China) was used. The working electrode was a glassy carbon electrode. A saturated calomel electrode (SCE) and a platinum wire served as reference and counter electrode, respectively. A Model GSP-79-03 magnetic stirrer (Jiangsu Electronic

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Instrumental Factory, China) with a 1.5-cm stirrer bar was used in the preconcentration and electrode renewal steps. A Model TY accurate acidimeter (Xiamen Second Analytical Instrumental Factory, China) was used for pH determination. A Model 721 spectrophotometer (Shanghai Sicond Analytical Instrumental Factory, China) was used for a comparison nitrite determination. The voltammetric cell was a 50-ml beaker.

Unless otherwise specified, all reagents were of analytical reagent grade; all solutions were prepared from triple-distilled water.

A 1000 $\mu g\,ml^{-1}$ stock solution of nitrite was prepared by direct dissolution of sodium nitrite in water and stored in the dark. The working solutions of nitrite were prepared from the stock solution by appropriate dilution with pure water just before use.

A 0.01 mol $litre^{-1}$ CTMAB solution used as ion surface-active reagent was obtained by dissolving CTMAB in water. Britton–Robinson (BR) buffer solution (contains phosphoric acid, acetic acid and boric acid) was prepared by adjusting the pH value with acetic acid or sodium hydroxide solution. Aluminium oxide (α-Al_2O_3) of analytical reagent grade (99.99%) was used for electrode polishing.

All experiments were performed at room temperature (22–25°C). All potentials given in this article are referred to the SCE. It was not necessary to remove the dissolved oxygen from the solution for quantitative analysis.

Sample preparation

For the determination of nitrite in lake water, a 100-ml sample was first filtered through fine filter paper; the filtrate was taken as the test solution. For nitrite determination in foods, 5.0 g of meat product slurry were taken into a 50 ml beaker, then 12.5 ml of saturated sodium borate solution were added. The sample solutions were washed into a 500-ml volumetric flask with 300 ml of hot water (70°C), heated in a boiling water-bath for 15 min, then placed in cold water to cool to room temperature. Then 5 ml of potassium ferrocyanide solution were added dropwise to the sample solutions, and 5 ml of zinc acetate added to precipitate the protein. The solution was made up to the mark with water and allowed to stand for about 30 min. The solutions were filtered through paper and the filtrates analysed for nitrite.

Procedure

To the standard or sample solution (0.01–0.25 $\mu g\,ml^{-1}$ nitrite), 0.6 ml of 0.01 mol $litre^{-1}$ CTMAB solution was added; the solution was then diluted to 50 ml with BR buffer solution (pH 3.6–4.0) and transferred to a 50-ml voltammetric cell. The glassy carbon electrode was polished with very fine paper and aluminium oxide (α-Al_2O_3) for about 1 min before use. The accumulation potential (+0.8 V) was applied to the electrode for 90 s while the solution was gently stirred. The stirring was stopped and, after 15 s, the voltammetric curve (Fig. 1) was recorded by applying an anodic linear scan from +0.8 V to +1.4 V using the differential pulse stripping method. The presence of nitrite was identified by the stripping potential at approx. +1.05 V and quantified by the corresponding oxidation peak current. After each determination, the electrode needs tidying up; it also needs polishing after every four determinations.

RESULTS AND DISCUSSION

A comparison of tetradecane pyridinium bromide, tetrabutylammonium bromide, CTMAB and Triton surface-active reagents showed that the current wave of nitrite was defined best and its peak height was the highest and most constant when CTMAB was in the solution, although all four reagents had an enhancing effect.

For a solution containing 0.2 $\mu g\,ml^{-1}$ nitrite ion, no peak was found when there was no CTMAB. It can be seen from Fig. 2 that the peak height increases with the addition of 0.01 mol $litre^{-1}$ CTMAB up to 0.6 ml, above which it starts to decline. Therefore, 0.6 ml of 0.01 mol $litre^{-1}$ CTMAB was selected as the optimum surface-active reagent addition (final volume 50 ml), which corresponded to a CTMAB concentration of 1.2×10^{-4} mol $litre^{-1}$.

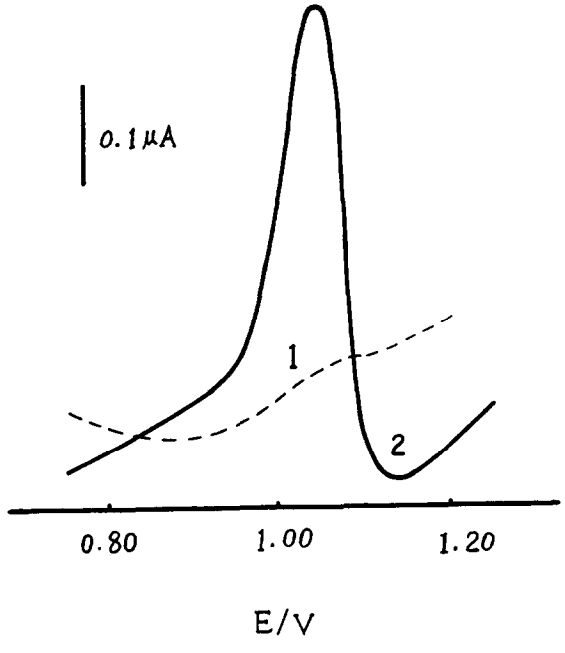

Fig. 1. Linear-sweep anodic stripping voltammograms of nitrite (NO_2^-) after stirring for 90 s at +0.8 V. The solution contains 1.2×10^{-4} mol $litre^{-1}$ CTMAB and pH 3.9 BR buffer solution. Scan rate, 100 mV s^{-1}. Scan 1, no NO_2^-; scan 2, 0.20 $\mu g\,ml^{-1}$ NO_2^- added.

The pH of the solution has a great effect on the anodic stripping peak current. From Fig. 3 it can be seen that the largest peak current was obtained in the pH range 3.6–4.0. Therefore, this pH range was chosen as optimum.

The effect of the accumulation potential on the anodic stripping peak current was examined in the potential range 0.2–1.0 V under the above optimum conditions. From Fig. 4 it can be seen that the largest peak current was obtained at an accumulation potential of +0.8 V and then decreased rapidly with increasing potential. Therefore, +0.8 V was selected as the accumulation potential in the procedure.

The dependence of the maximum stripping peak current on the accumulation time was also examined. Under the other optimum conditions, there was a linear relationship between the stripping peak current and accumulation time in the range of 0–75 s, above which it became constant (Fig. 5). In these experiments, 90 s was selected as the accumulation time.

The effect of scan rate on the stripping peak current was examined over the 50–200 mV s^{-1} range. It was found that the peak increases linearly with increasing scan rate. However, the higher the scan rate, the higher

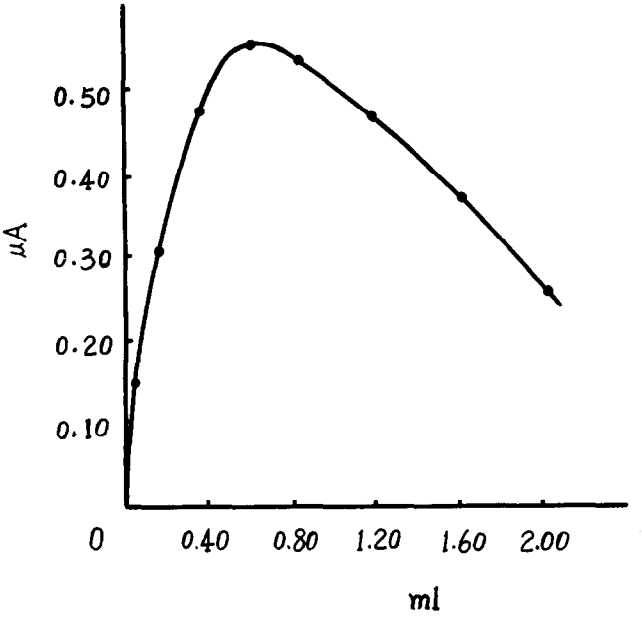

Fig. 2. Dependence of the anodic stripping peak current of nitrite (NO_2^-) on the amount of 0.01 mol $litre^{-1}$ CTMAB. The solution and other conditions are the same as those in Fig. 1.

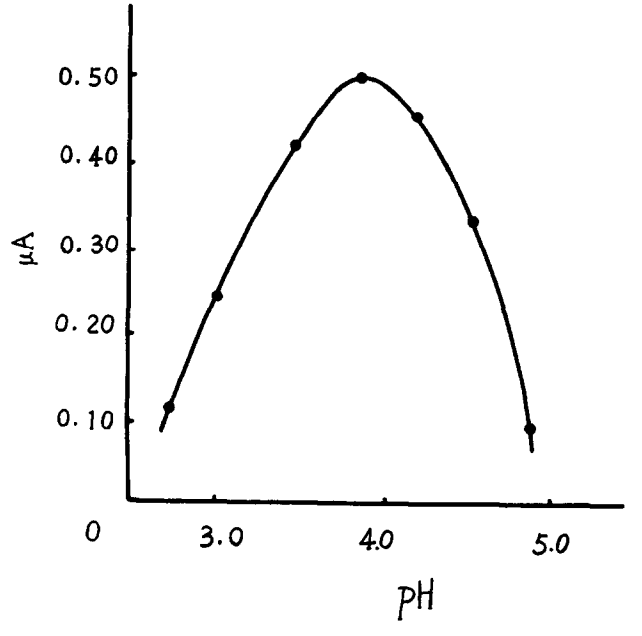

Fig. 3. Dependence of the anodic stripping peak current of nitrite (NO_2^-) on the pH value. The solution and other conditions are the same as those in Fig. 1.

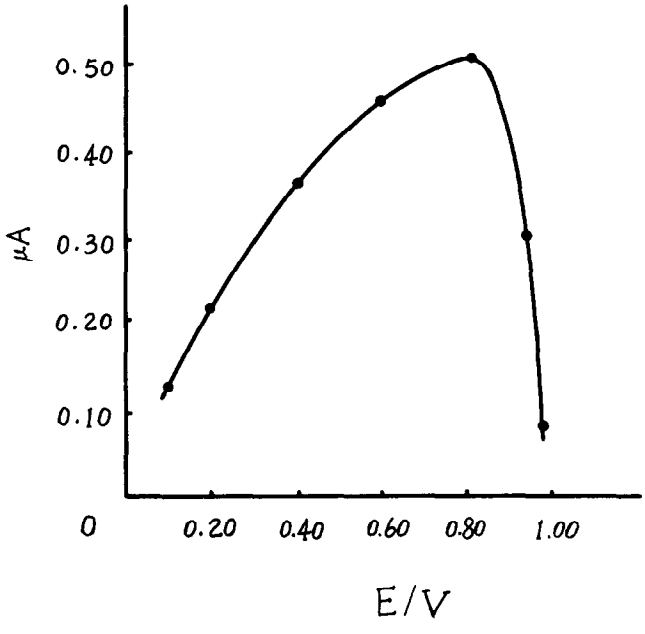

Fig. 4. Dependence of the anodic stripping peak current of nitrite (NO_2^-) on the accumulation potential. The solution and other conditions are the same as those in Fig. 1.

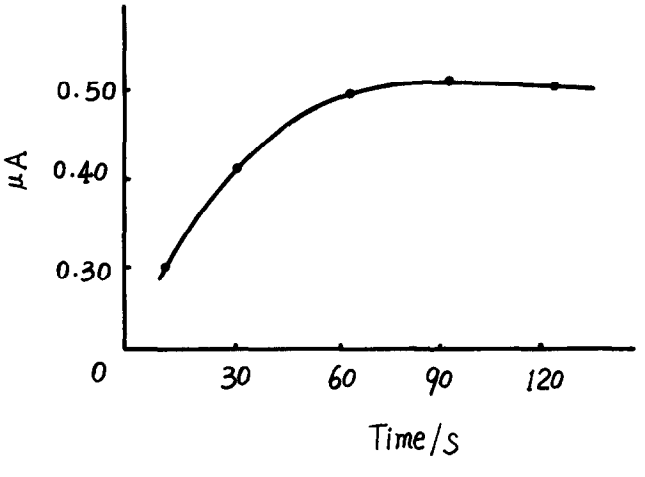

Fig. 5. Dependence of the anodic stripping peak current of nitrite (NO_2^-) on the accumulation time. The solution and other conditions are the same as those in Fig. 1.

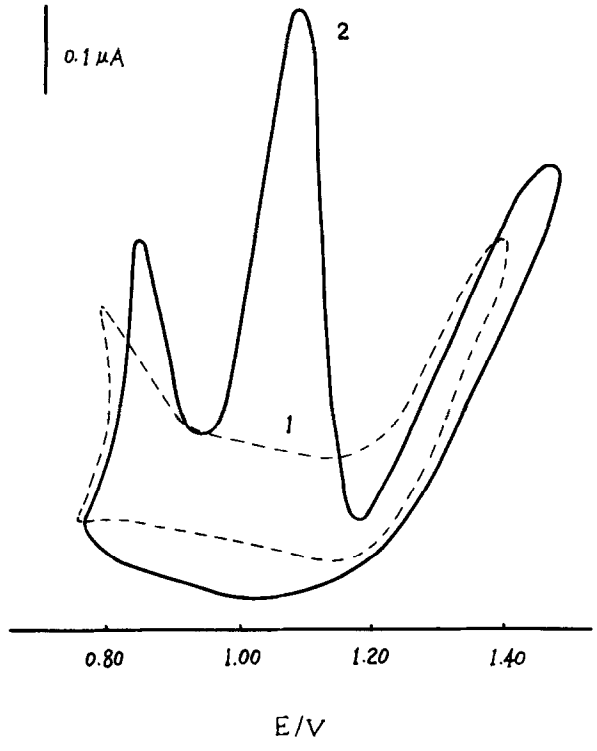

Fig. 6. Cyclic voltammograms of nitrite (NO_2^-). The solution and other conditions are the same as those in Fig. 1.

the charge current produced, which caused difficulties in recording. Thus, in practice, 100 mV s^{-1} was used as the scan rate.

The selectivity of the method was tested by studying the effects of common ions on the determination of 0.20 μg ml^{-1} nitrite. The results showed that most of the ions, such as K^+, Na^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}, do not interfere with the determination. The tolerance for various ions was studied. The results showed that at least 100-fold amounts of Br^-, 50-fold amounts of $S_2O_3^{2-}$, and 10-fold amounts of Al^{3+} have little effect on the determination, but concentrations above those stated start to cause some interference.

Figure 6 shows cyclic voltamperograms obtained with 1.2×10^{-4} mol litre^{-1} CTMAB and pH 3.9 buffer solution in the presence and absence of nitrite ion. When nitrite ion was absent, there was a stable residual current over a wide potential scan range (+0.8 V to +1.4 V), and no distinct redox wave was observed. When 0.20 μg ml^{-1} nitrite ion was present in that solution, an anodic peak was observed (at about +1.05 V) during the scan in the positive direction. Scanning in the reverse direction did not produce a cathodic peak, indicating the irreversibility of the oxidation process. According to the former study, the anodic response increased with the accumulation time, indicating interfacial adsorption of the CTMAB–nitrite complex, which caused a corresponding oxidation peak current at about +1.05 V for measurement.

Table 1. Results for determination of nitrite in the samples

Samples	This method (μg ml^{-1})	Spectrophotometric method (μg ml^{-1})
Lake water 1	0.063 ± 0.002	0.064 ± 0.001
Lake water 2	0.176 ± 0.004	0.178 ± 0.002
Sausage 1	0.047 ± 0.001	0.048 ± 0.001
Sausage 2	0.141 ± 0.005	0.142 ± 0.001

Values are expressed as mean ± standard deviation ($n = 3$).

Under the optimum condition, a linear relationship was obtained between the peak current and the nitrite ion concentration in the range 0.01–0.25 μg ml^{-1} (correlation coefficient 0.998). In this range, nitrite can be determined quantitatively in natural water, waste water or human foods.

In this practical analysis, the method was applied to the determination of nitrite in two different lake water samples and two sausage samples. The results are summarized in Table 1. The results obtained by this method are in accordance with those obtained by a spectrophotometric method (Method for determination of nitrite and nitrate in foods, 1987). In order to evaluate the validity of the proposed method, recovery studies were carried out on samples to which known amounts of nitrite had been added. The recoveries were 90–110%.

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