

# Anodic Stripping Voltammetric Determination of Nitrite Using Carbon Paste Electrode Modified with Chitosan

Ibrahim H. I. Habib

Microanalytical Chemistry Lab, Applied Organic Chemistry Department, National Research Centre, Cairo, Egypt  
E-mail: ihihabib@yahoo.com

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## Abstract

A simple method for anodic stripping voltammetric determination of nitrite using carbon paste electrode modified with biomolecular chitosan, is described. In this method, the electrode is activated electrochemically by scanning 5 replicates over the potential range from +500 to +1400 mV immersing in 0.5 M HCl solution. Following this step, the nitrite sample containing 0.1 M KCl is pre-concentrated on the activated electrode at +500 mV for 30 s. The deposited anions are then oxidized by different modes of sweep in the oxidation direction. Chemical and electrical parameters affecting the voltammetric measurements are optimized. The peak current is linear proportional to the  $\text{NO}_2^-$  concentration within the range 0.41 - 4.1  $\mu\text{g/ml}$ , with detection limit 0.187  $\mu\text{g/ml}$  using differential pulse mode. The relative standard deviation is 0.285 % for 2.46  $\mu\text{g/ml}$  (five replicates). No interference is observed due to oxygen dissolved in the sample so that nitrogen purging is not needed in this case. The result obtained by the modified electrode is more accurate and selective than the unmodified electrode.

**Keywords:** Chitosan, Carbon Paste Electrode, Nitrite, Anodic Stripping Voltammetry

## 1. Introduction

Nitrite is one of the pollutants widely found in natural waters, wastes from fertilizers or intentional additions of nitrites for corrosion control or protection of meat products. Nitrite ions can interact with amines to form nitrosamines which are known as carcinogenic substances. They also may react with hemoglobin and reduce the oxygen carrying capacity of it [1,2]. Thus, its concentration in various types of samples has to be controlled by sensitive methods.

The most commonly used method for nitrite determination ranging from trace to ultra trace levels is the electrochemical techniques. This includes polarography [3-7], amperimetry [8,9] and voltammetry [10-14]. The sensitivity can be further enhanced if the surface of bare electrodes is modified chemically with active thin film offering significant advantageous for design and development of electrochemical sensors. According to the literature survey, all electrodes modified by complexes of iron [15,16], palladium [17], iridium [18], cobalt [19], copper [20], mercury [21], cetyltrimethylammonium bromide [10], phosphomolybdic [22,23] or silicotungstic acids

[24,25] have been used successfully for electrochemical oxidation of nitrite. Boron-doped diamond electrode [26] has also been applied for monitoring nitrite, but it needs special instruments not ever available elsewhere.

Chitosan, on the other hand, is natural product extracted from the shell of shrimps, crabs and insects [27]. Because of its ability to bind strongly with many metals [28], chitosan and its derivatives have been applied for electrochemical determination of silver [29,30], platinum [30], palladium [30], gold [30,31], lead [32,33] and iron [34]. In the present work, carbon paste electrode modified with natural chitosan represents the simplest and reproducible analytical tool to determine nitrite in samples.

## 2. Experimental

### 2.1. Apparatus and Reagents

A Metrohm model 693 VA processor and 694 VA stand equipped with a Ag/AgCl-3 M KCl and a platinum counter electrode are employed. The modified carbon paste electrode is used as the working electrode and prepared as described below.

## 2.2. Preparation of the Modified Carbon Paste Electrode

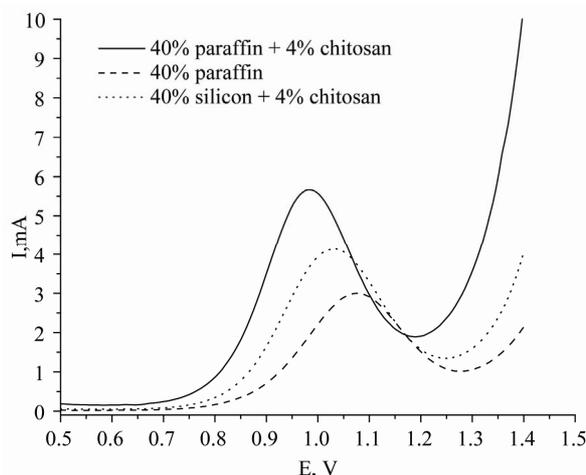
The carbon paste is prepared by mixing 175 mg paraffin oil (Fluka), 250 mg synthetic carbon powder 1 - 2 micron (Aldrich) and 48 mg low-viscous Chitosan (Fluka) in agate mortar. The electrode is consisted of stainless steel tube with i.d. 2.5 mm and 30 mm deep, moving through it an inner screwed stainless steel connector. The tube is coated externally with Teflon. The tube is packed with the modified carbon paste, compressed with inner screw and smoothed on a wetted Whatman filter paper.

## 2.3. Procedure

The fresh surface electrode is first immersed in 0.5 M HCl solution and electrically activated by direct current sweep five replicates from +500 to +1400 mV with scan rate 50 mV/s. The solution is then exchanged by 10 ml of 0.1 M KCl solution containing 0.41 - 4.1  $\mu\text{g}$  of nitrite and pre-concentrated for 30 s at +500 mV with stirring at 2000 rpm. After resting for 10 s, one of electrical modes (direct current fast DC, differential pulse DP, square wave SW or first-harmonic alternating current AC1) is ramped from +500 to +1400 mV with scan rate 50 mV/s, pulse amplitude 50 mV, pulse duration 20 ms, measurement time 10 ms, frequency 30 Hz for SW and AC1. The experiment is triplicated without electrode re-generation and two standard solutions of nitrite are added sequentially. Average of current peaks due to the sample and standard solutions are taken. For new electrode, the experiment is repeated with new activation of electrode as described before.

## 3. Results and Discussion

Preliminary experiments are carried out to optimize the sensor composition. The height of peak current obtained for nitrite is used to compare the performance of the different chemical and physical parameters. Each parameter is analyzed triplicate with the same sensor and the corresponding average value of peak height is plotted. The working electrode containing 40% (w/w) water-immiscible organic binders (pasting liquids), *viz.* paraffin or silicon oils, with/without 4% chitosan are prepared and examined under identical conditions, *i.e.* immersing in 0.5 M HCl prior accumulation and differential pulse stripping voltammetric measurements of nitrite in 0.1 M KCl solution. It is obvious from **Figure 1**, the 40% paraffin oil with 4% chitosan accumulates afforded highest stripping peak at potential of about +900 mV. Thus, the modifier enhances the sensitivity of the electrode twice more than using paraffinic bare CPE. This enhancement

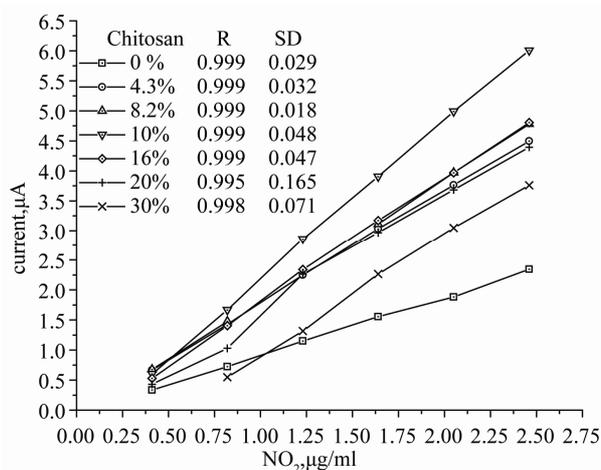


**Figure 1.** Differential pulse DP cathodic stripping voltammograms for determining nitrite in absence and presence of chitosan with scan rate 60 mV/s, pulse amplitude 50 mV in 0.3 M KCl.

could be explained by the fact that the  $-\text{NH}_2$  group is converted into  $-\text{NH}_3^+$  making it easy to increase the electrostatic attraction of negatively charged nitrite ions on its surface in a similar manner for determining negatively charged palladium, platinum<sup>30</sup> and lead<sup>32</sup> chloride complexes

The sensitivity and linear responses towards the nitrite concentrations can also be enhanced by increasing the proportion of chitosan up to 10% (w/w) chitosan. Beyond this proportion a depression in the sensitivity is observed as shown in **Figure 2**.

On the other hand, the influence of HCl and KCl, separately or in mixture solutions, revealed that in acidic solutions (pH < 3.3) nitrite is escaped as NO gas and lost



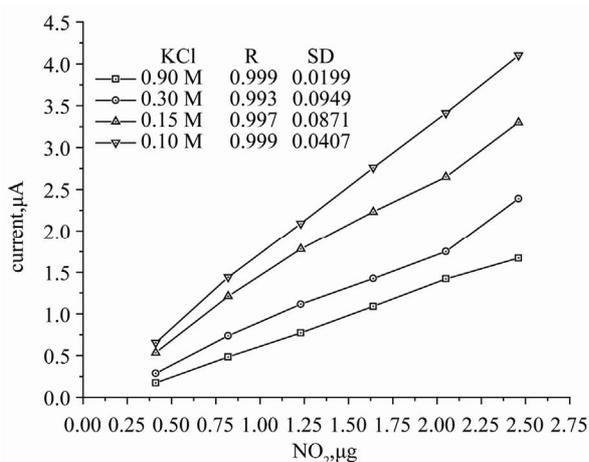
**Figure 2.** Effect of chitosan (% w/w) on the stripping current at different concentrations of nitrite (0.41 - 2.46  $\mu\text{g}/\text{mol}$   $\text{NO}_2$ ) using DP mode with scan rate 60 mV/s, pulse amplitude 50 mV in 0.3 M KCl.

more when nitrogen gas is bubbled giving up weak peak current. In a neutral medium,  $\text{pH} > 3.3$ , nitrite anion is predominated promoting to strong peak current. Thus, in order to avoid  $\text{NO}$  gas formation, two separating solutions on two sequential steps are achieved, 0.5 M HCl solution for the protonation of chitosan followed by 0.1 M KCl solution for applying as a neutral supporting electrolyte medium. The latter effect is as depicted in **Figure 3** where the concentration of 0.1 M KCl gives the highest peak current and best linear relation.

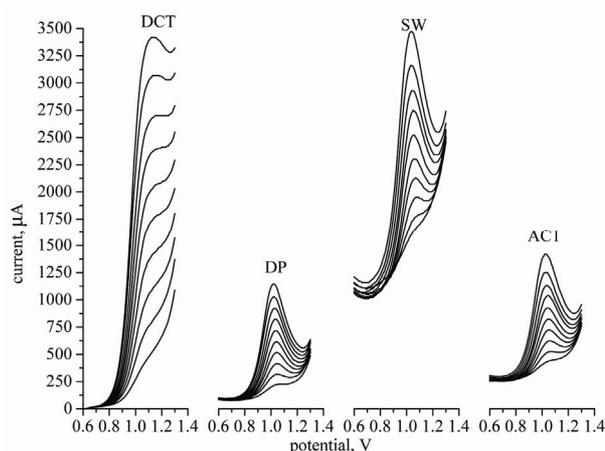
The variation of scan rate from 10 to 120 mV/s revealed that the diffusion current is related linearly with square root of scan rate, but the oxidation reaction proceeded irreversibly as the peak potential shifted linearly to more positive potential with increasing the scan rate. No reduction peak is observed on the reverse scan within the studied potential range indicating that the overall process is chemically irreversible in agreement with the previous reports for nitrite oxidation at different types of electrodes [35,36].

Modulating the direct current fast ramp DCT with various wave forms by using superimposed differential pulse DP, square-wave SW or first harmonic a.c. modulation AC also studied to explore which one of modes will enhance the sensitivity.

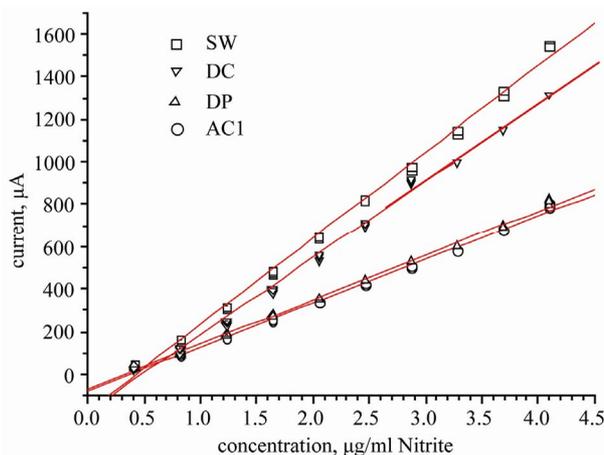
As shown in **Figures 4** and **5**, variation of current with concentration of nitrite ions showed a linear behavior between 0.41 and 4.1  $\mu\text{g}/\text{mol}$  of nitrite with correlation coefficients 0.994, 0.999, 0.998 and 0.998 for different modes of sweep DC, DP, SW and AC1, respectively. The detection limit based on "three standard deviations of the blank  $3s_B$  method [37] is found to be in turn, 0.281, 0.187, 0.207 and 0.241  $\mu\text{g}/\text{ml}$  nitrite. The analytical parameters for nitrite determination are reported in **Table 1**.



**Figure 3.** Effect of KCl on the stripping current at different concentrations of nitrite (0.41 - 2.46  $\mu\text{g}/\text{ml}$   $\text{NO}_2$ ) using 10% chitosan carbon paste electrode and DP mode with scan rate 60 mV/s and pulse amplitude 50 mV.



**Figure 4.** Different modes of sweeps, DCT, DP, SW and AC1, at different concentrations of nitrite (0.41 - 2.46  $\mu\text{g}/\text{ml}$   $\text{NO}_2$ ) using 10% chitosan carbon paste electrode with scan rate 60 mV/s, pulse amplitude 50 mV in 0.1 M KCl.



**Figure 5.** Regression lines for determining nitrite using different modes of sweep.

**Table 1.** Analytical parameters for nitrite determination at chitosan modified CP electrode.

Mode	R	Slope, nA/ $\mu\text{g}$	Intercept, nA/ $\mu\text{g}$	LOD $\mu\text{g}$	Repeatability RSD, %
AC1	0.998	204.78	-74.76	0.241	0.668
DP	0.999	208.35	-66.17	0.187	0.285
DC	0.994	360.86	-173.00	0.281	1.018
SW	0.998	404.86	-169.084	0.206	0.437

An extremely attractive feature of the chitosan modified carbon paste electrode is its highly stable response toward nitrite oxidation. Repeatability "RSD" using different mode is found to be 1.018%, 0.285%, 0.437% and 0.668%, respectively, for five successive determination of 2.46  $\mu\text{g}/\text{ml}$  nitrite. For the same modified chitosan

electrode, reproducibility, without and with successive cut off/polishing five times, is found to be 0.285% and 0.347%, respectively, for 2.46 µg/ml nitrite and using DP mode.

It is concluded that the new and simple carbon paste electrode modified with chitosan has been shown to offer comparable performance to the more expensive glassy carbon or diamond electrodes for the practical use to analysis NO<sub>2</sub><sup>-</sup> ions at trace concentrations in real samples by anodic stripping voltammetry with high sensitivity and selectivity.

#### 4. Acknowledgements

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