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Sensitive Electrochemical Detection of the Nitrite Ion Using an ISEM-3 Graphite Electrode and Comparison with Other Carbon-Containing Materials †

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Abstract

The need for an accurate, rapid and affordable method for the determination of nitrite ions is due to its toxic effects on humans at elevated levels in wastewater and drinking water. The electrochemical determination is faster, cheaper and less labor intensive. It is based on the study of the electrochemical oxidation NO_2^- ion at different carbon electrodes. In this work, it was established by the cyclic voltammograms for the ISEM-3 graphite electrode has excellent limit of detection to nitrite ions: 5×10^{-6} M at pH 3, which makes it possible to determine the NO_2^- content below the maximum permissible concentration (6.5×10^{-5} M) in water.

Keywords: electrochemical determination of nitrites; graphite sensor; electrocatalysis

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1. Introduction

Nitrite, an important intermediate in the nitrogen cycle in ecosystems, performs many functions in various industries: it is used in agriculture as fertilizers, is often used in various food products as a preservative in the production and processing of pickled meat and fish products, and is found in tap water and biological samples [1,2] Too much nitrite content harms the environment and has a negative impact on human health [1]. As a result of the interaction of nitrites with amine compounds in the human body, the content of carcinogenic nitrosamines increases, which cause serious health problems, including cancer of the stomach and esophagus, and congenital defects of the central nervous system [2]. NO_2^- ions also promotes the conversion of hemoglobin into methemoglobin, which can lead to a serious illness [3].

Therefore, in recent decades, the determination of nitrites by quantitative analysis has been of considerable interest. The World Health Organization has established that the limit value of the concentration of nitrites in drinking water is only 3.0 mg L^{-1}, and for fisheries reservoirs the norm is 0.08 mg L^{-1} [1]. However, most of the determination methods have limitations, such as the use of hazardous reagents, the need for a time-

consuming sample preparation procedure that requires technical personnel and expensive equipment [3]. Electrochemical methods (cyclic voltammetry, amperometry, coulometry, potentiometry), in comparison with traditional analytical methods, have significant advantages such as cost-effectiveness, speed, and ease of operation [2,4]. The electrochemical sensors show high selectivity to NO_2^- in presence the interference of some common ions (e.g., NO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, Ca^{2+} and Mg^{2+}) and oxidizable compound including sodium sulfite and ascorbic acid [5]

In the electrochemical detection of nitrite ions, the most sensitive mechanism is based on the direct electrocatalytic oxidation of the nitrite ion on the electrode surface, resulting in the formation of nitrate [2]. The rate of the oxidation reaction and the oxidation potential depend on the kinetics of electron transfer and the electroactive ability of the electrode materials [6]. The oxidation of nitrite ions is shown by the following reaction in acidic and alkaline environments:

$$HNO_2 + H_2O - 2e^- = NO_3^- + 3H^+ \qquad E_0 = 0.94 \text{ V } vs. \text{ RHE} \tag{1}$$

$$NO_2^- + 2OH^- - 2e^- = NO_3^- + H_2O \qquad E_0 = 0.01 \text{ V } vs. \text{ RHE} \tag{2}$$

The recent developments for electrochemical detection of nitrate, nitrite and ammonium are discussed and the critical examination of current nitrate, nitrite and ammonium studies as realistic monitoring processes is presented in the short modern review [7].

Due to the use of various functional nanomaterials in electrochemical sensors, the sensitivity and accuracy of electrochemical measurements are significantly increased, which is of great importance for the field of analytical chemistry [6,8,9]. Carbon materials as a nitrite ion sensor have a number of advantages: good electronic conductivity, cheapness, ease of use, wear resistance, and stability in various environmental conditions. Various carbon-based electrodes for the determination of nitrite ions have been extensively studied in recent years: glassy carbon [10], glassy carbon modified with polyvinylimidazole [11], multi-walled carbon nanotubes [12].

In most studies, the nitrite ion determination reaction was carried out on glassy carbon-based materials, but the oxidation of nitrite on a bare graphite electrode has been less studied. In addition, there is little data on a full-fledged study of graphite in a wide range of changes in the concentration of nitrite ions and the pH of electrolytes.

Thus, the aim of this work is the electrochemical determination of nitrite ions on a graphite electrode, and the tasks included: screening of carbon electrodes (graphite and glassy carbon and graphite modified with Ag particles) using cyclic voltammetry to determine nitrite ions; determination of the detection limit of nitrite ions in solutions; determination of the area of linear dependence of current-concentration at concentrations of nitrite ions in the maximum concentration range.

2. Materials and Methods

The ISEM-3 graphite was used as the main working electrode. The oxidation of nitrite ion was studied by cyclic voltammetry. The synthesis of an additional graphite electrode with electrodeposited Ag particles was carried out at constant potential and the electrode was characterized by SEM. All reagents ($AgNO_3$, $NaNO_2$) used were of analytical grade, unless otherwise indicated. Distilled water was used to prepare all reagents and solutions.

The Autolab 302N potentiostat-galvanostat equipped with Nova 2.1.7 (Metrohm, Netherlands-Switzerland) software was used for all electrochemical experiments. The silver chloride electrode (Ag/AgCl) served as a reference electrode, the auxiliary electrode was a platinum plate ($S = 2$ cm^2). A three-electrode standard electrochemical cell was filled with a volume of 50 mL of electrolyte and degassed with Ar (99.999%) for 30 min. The

polarization curves were recorded by cyclic voltammetry (CV) with a scanning rates specified in the following sections. Cyclic voltammograms were measured without mixing.

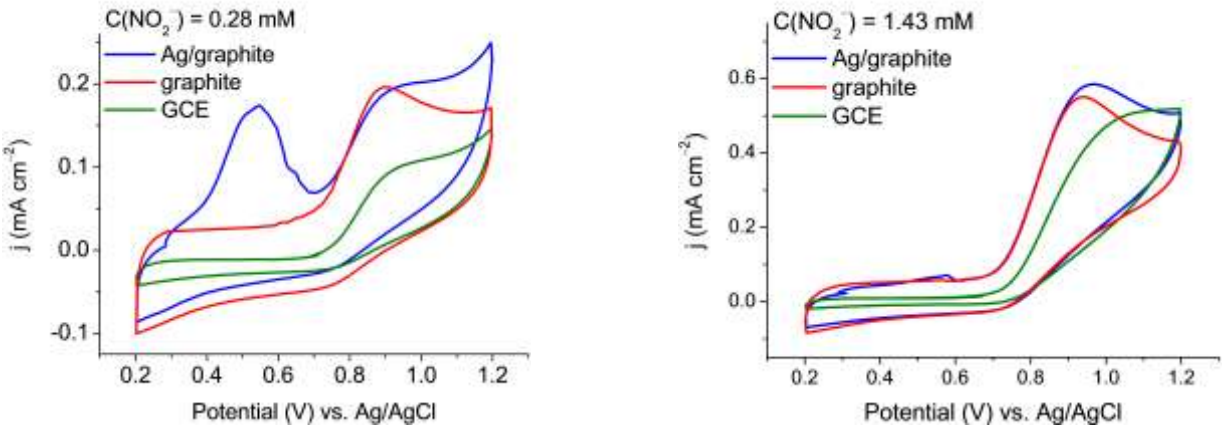
The carbon-containing materials under study were the working electrode. The geometric surface area (in the form of a disk) was as follows: 0.198 cm^2 (ISEM-3 graphite), 0.097 cm^2 (glassy carbon), 0.18 cm^2 (graphite coated with electrodeposited Ag-particles). ISEM-3 graphite and glassy carbon electrodes were used as is, and graphite coated with electrodeposited Ag-particles was prepared according to the original technique: were deposited in a potentiostatic mode (−0.6 V vs. Ag/AgCl) from a solution containing 5 mM $AgNO_3$ in 0.1 M KNO_3 for 300 s.

3. Results and Discussion

3.1. Determination of Nitrite Ions on Various Type of Carbon Electrodes

This study demonstrates that a graphite electrode is well suited for the determination of nitrite ion in aqueous solutions using cyclic voltammetry at different pH of electrolytes and the limit of detection (LOD) was 5 μM. The oxidation of nitrite ion is compared with the electrodes: glassy carbon (GC), ISEM-3 graphite, graphite coated with electrodeposited Ag-particles. The studies showed that the graphite electrode exhibited high sensitivity over a wide range of solution pH (1−11.5). The best results and the minimum NO_2^- detection concentration were achieved at pH 3.

Figure 1 shows the voltammograms for the determination of nitrite ions for three electrode samples at the boundary concentrations of the tests. For both high and low concentrations of nitrite ions, the ISEM-3 graphite sample shows the most pronounced peak. The graphite coated with electrodeposited Ag-particles sample shows the highest sensitivity at high concentrations, but is inferior at low concentrations. For the GC sample, the peaks are not clearly pronounced at all concentrations studied.

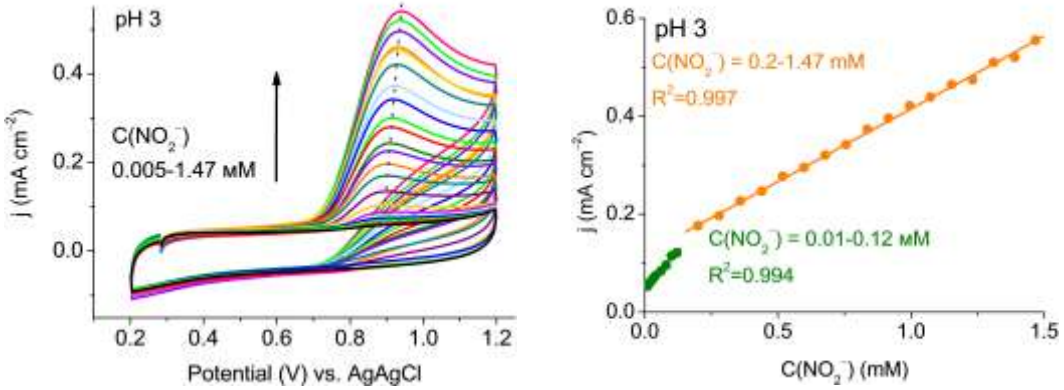


(**a**) (**b**)

Figure 1. (**a**) Cyclic voltammograms of graphite, modified Ag, ISEM-3 graphite and glassy-carbon electrode (GCE) in the presence of 0.28 mM and 1.43 mM nitrite (buffer system at pH 3 with 50 mV s^{-1} scan rate).

3.2. Determination of Nitrite Ions on ISEM-3 Graphite Electrode Sensor

An excellent pronounced peak of nitrite ion oxidation when using ISEM-3 graphite electrode is shown in Figure 2a. With increasing concentrations, only a slight potential shift occurs, and the clearly linear dependence of the peak current density on an increase in nitrite ion concentrations, which is illustrated in Figure 2b.

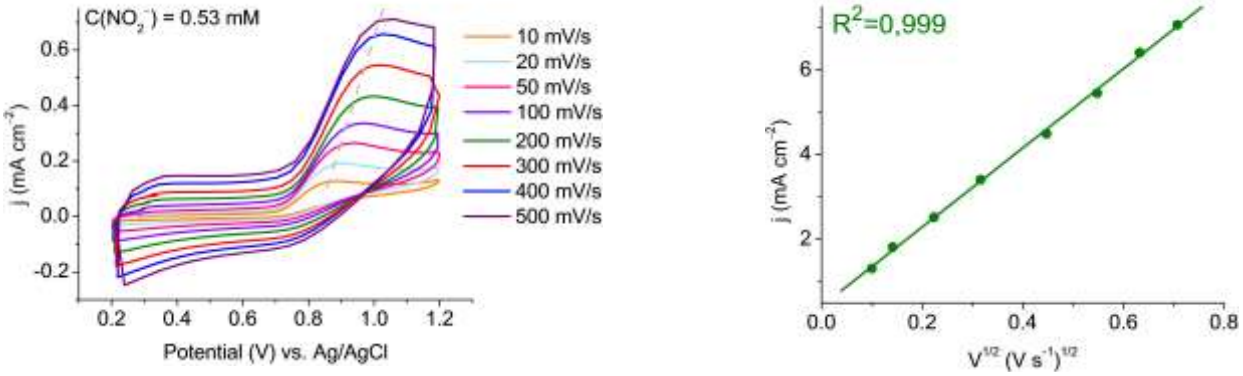


(**a**) (**b**)

Figure 2. (**a**) Cyclic voltammograms of ISEM-3 graphite electrode sensor at different concentrations of nitrite at 50 mV s^{-1} scan rate in buffer system at pH 3; (**b**) Corresponding fitting curves for the oxidation peak current vs concentration of nitrite ions.

3.3. Scan Rate Study

In the final part of our study, cyclic voltammograms measurements were carried out over a wide range of potential scanning rates (Figure 3a). The linear dependence of the peak current density on the square root of the potential scanning rate is a proof of a diffusion-controlled process (Figure 3a).



(**a**) (**b**)

Figure 3. (**a**) Cyclic voltammograms of ISEM-3 graphite electrode sensor at different scan rates in the presence of 0.53 mM concentration of nitrite in buffer system at pH 3; (**b**) corresponding fitting curve for the oxidation peak current vs square root of scan rate.

The interference of potentially interfering ions in real water are NO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-. Based on the study of the electrooxidation of nitrite in solutions with different pH it can be concluded that 100-fold Ca^{2+}, SO_4^{2-}, K^+, PO_4^{3-}, CO_3^{2-}, NO_3^-, Cl^- and plenty of Ac^- and Na^+ does not affect the accuracy of nitrite ion determination. An application to a water sample in this work was not carried out.

4. Conclusions

By using the CV method, it was found that the ISEM-3 graphite electrode has the excellent sensitivity to nitrite ions in aqua solution and its use for the determination of nitrite ions in solutions is possible in a wide range of pH values (1–10), the best of which was pH 3. The LOD on a graphite electrode is 5×10^{-6} M at pH 3, which makes it possible

to determine the NO_2^- content below the maximum permissible concentration (6.5×10^{-5} M) in water.

As a perspective for our future work, it can be assumed that graphite- and glassy-carbon-based electrodes can be optimized by modifying with carbon nanotubes, which, according to literature data and preliminary experiments, can further enhance sensitivity to nitrite ions.

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