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Simultaneous electrochemical determination of nitrate and nitrite in aqueous solution using Ag-doped zeolite-expanded graphite-epoxy electrode

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ABSTRACT

In this work a new electrochemical sensor based on an Ag-doped zeolite-expanded graphite-epoxy composite electrode (AgZEGE) was evaluated as a novel alternative for the simultaneous quantitative determination of nitrate and nitrite in aqueous solutions. Cyclic voltammetry was used to characterize the electrochemical behavior of the electrode in the presence of individual or mixtures of nitrate and nitrite anions in 0.1 M Na_2SO_4 supporting electrolyte. Linear dependences of current versus nitrate and nitrite concentrations were obtained for the concentration ranges of 1–10 mM for nitrate and 0.1–1 mM for nitrite using cyclic voltammetry (CV), chronoamperometry (CA), and multiple-pulsed amperometry (MPA) procedures. The comparative assessment of the electrochemical behavior of the individual anions and mixtures of anions on this modified electrode allowed determining the working conditions for the simultaneous detection of the nitrite and nitrate anions. Applying MPA allowed enhancement of the sensitivity for direct and indirect nitrate detection and also for nitrite detection. The proposed sensor was applied in tap water samples spiked with known nitrate and nitrite concentrations and the results were in agreement with those obtained by a comparative spectrophotometric method. This work demonstrates that using multiple-pulse amperometry with the Ag-doped zeolite-expanded graphite-epoxy composite electrode provides a real opportunity for the simultaneous detection of nitrite and nitrate in aqueous solutions.

1. Introduction

Nitrites and nitrates can serve as indicators for environmental pollution and for food control. The increasing contamination of water resources for human consumption by nitrates and nitrites due to the anthropogenic activities as agriculture and wastewaters is receiving worldwide attention.

The presence of nitrite in drinking water could cause serious human diseases like methemoglobinemia and stomach cancer by the production of N-nitrosamines. Also, nitrate presence can produce the same effect based on its reduction to nitrite in the digestive system.

The maximum limits in drinking water of 50 mg l^{-1} for nitrate and 3 mg l^{-1} for nitrite respectively, are recommended by the World Health Organization [1].

Many methods have been developed to detect individual nitrate and nitrite, most of them based on spectrophotometry [2,3], ion-chromatography [4,5], flow-injection analysis [6], and capillary electrophoresis [7]. In addition to these methods, which are laborious to perform or require chemical reagents, the electrochemical approaches are favorable owing to the rapid response and simple operation [6,8–12]. However, the determination of individual nitrate and nitrite on a bare solid electrode is limited because the electrode activity may decrease very fast during the direct reduction of nitrate and nitrite [9], and a better choice for the nitrite determination is based on its direct oxidation on solid electrode surfaces [8].

Therefore, chemically modified electrodes have been developed for the determination of nitrite [13–20] and nitrate [6,9,21]. Several types of composite electrodes based on silver and graphite have been proposed for the voltammetric determination of nitrate [9,22]. Also, their properties and practical applications in the electroanalytical field have been reviewed [23–27].

The advantages and disadvantages of various techniques and strategies for the detection of nitrite and/or nitrate have been presented in a review by Moorcroft et al. [28].

Zeolite-modified electrodes have been developed for the determination of various compounds and the use of a mixture of a

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Table 1
The electroanalytical parameters for nitrite and nitrate determination using CV.

Aqueous matrix and concentration range	Cathodic sensitivity (recorded at −1.35 V/SCE)/mA mM^{-1}	Anodic sensitivity (recorded at +0.9 V/SCE)/mA mM^{-1}	LOD	RSD
0.1–1 mM nitrite	–	0.0542	0.005	2.8
1–10 mM nitrate	0.007	0.002	0.1	4.1
0.1–1 mM nitrite and 1–10 mM nitrate	0.007	0.0735[a]	–	4.0

[a] This sensitivity represents in fact a useful signal due to the sum of nitrite contribution that was added to the system and of nitrite resulted from nitrate reduction during the scanning.

Table 2
The electroanalytical parameters for nitrite and nitrate determination using CA.

Aqueous matrix and concentration range	Cathodic sensitivity (recorded at −1.35 V/SCE)/mA mM^{-1}	Anodic sensitivity (recorded at +0.9 V/SCE)/mA mM^{-1}	LOD	RSD
0.1–1 mM nitrite	–	0.0165	0.01	2.9
1–10 mM nitrate	0.0034	0.00055	0.6	3.8
0.1–1 mM nitrite and 1–10 mM nitrate	0.0034	0.022[a]	–	3.9

[a] This sensitivity represents in fact a useful signal due to the sum of nitrite contribution that was added to the system and of nitrite resulting from nitrate reduction during the scanning.

zeolite and graphite in various forms has been proposed [29]. Zeolite-supported electrocatalysts can be exploited to improve the performance of the electrocatalytic responses with reduced overpotentials and increased voltammetric/amperometric signals allowing low detection limits and high sensitivities [30].

Also, certain electrochemical techniques exhibit specific peculiarities to enhance the performance of electroanalytical detection. Multiple-pulsed amperometric (MPA) detection coupled with flow-injection analysis systems can be an alternative technique to prevent contamination of the electrode and allows simultaneous determination of electroactive compounds. The most optimal use of this detection method, reported in the literature, is related with the quantification of a single analyte [31]. However, the development of the technique for multicomponent analysis would be very useful for the determination of different components in many types of samples [32].

The simultaneous determination of nitrate and nitrite is of great importance. Most of the simultaneous determinations of nitrite and nitrate are based on the reduction of nitrate to nitrite, followed by the determination of nitrite using chromatographic [33,34] and spectrophotometric techniques [35,36]. An electrochemical method for the determination of nitrate and nitrite reductase activities of *Rhizobium japonicum* envisaging the fabrication of biosensors for nitrate and nitrite has been reported [37].

In this work, the electrochemical methodologies for direct simultaneous determination of nitrate and nitrite in aqueous solutions using an Ag-doped zeolite-expanded graphite-epoxy composite electrode (AgZEGE), cyclic voltammetry (CV), chronoamperometry (CA), and multiple-pulsed amperometry (MPA) are described. Using all these techniques, the electroanalytical parameters for the determination of individual and direct simultaneous nitrate in the concentration range of 1–10 mM and 0.1–1 mM for nitrite are determined. In addition, a strategy based on a specific MPA operation for direct detection of nitrate with better sensitivity (10 fold) is presented.

2. Experimental

The composite electrode was obtained by film casting of a two-component epoxy resin (LY5052, Araldite) mixed with a conductive expanded graphite (EG) filler powder (Conductograph, SGL Carbon) and silver-doped zeolite (clinoptilolite).

The ratio of the components was selected to obtain 20 wt% (w/w) content of expanded graphite, 20 wt% (w/w) content of silver-doped zeolite. The prepared zeolite-modified electrode showed good mechanical strength and low electrical resistance [38]. Prior to use, the working electrode disc with a surface area of 19.63 mm^2 was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.3 μm alumina powder (Metrohm, Switzerland) in distilled water for 5 min and rinsing with distilled water. The electrochemical performances of this electrode for the detection of nitrate and nitrite were studied using CV, CA, and MPA. Subsequently, an electrochemical pretreatment by three repetitive cyclings between −1.5 V and 1 V versus SCE in 0.1 M Na_2SO_4 supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode, and the AgZEGE working electrode.

All chemicals were analytical reagent grade from Merck and all solutions were prepared with doubly distilled and deionised water.

3. Results and discussion

Preliminary studies were carried out employing cyclic voltammetry with the AgZEGE electrode in 0.1 M NaOH and 0.1 M Na_2SO_4 as supporting electrolytes in the presence of different concentrations of nitrate and nitrite. Better results related to the sensitivities were obtained in 0.1 M Na_2SO_4, which was chosen for further experiments. Fig. 1a–c shows a series of typical cyclic voltammetric

Table 3
The electroanalytical parameters for nitrite and nitrate determination using MPA.

Aqueous matrix and concentration range	Cathodic sensitivity (recorded at −1.35 V/SCE)/mA mM^{-1}	Anodic sensitivity (recorded at +0.9 V/SCE)/mA mM^{-1}	LOD	RSD
0.1–1 mM nitrite	–	0.057	0.004	2.9
1–10 mM nitrate	0.025	0.0166	0.08	3.5
0.1–1 mM nitrite and 1–10 mM nitrate	0.025	0.22[a]	–	3.6

[a] This sensitivity represents in fact a useful signal due to the sum of the nitrite contribution that was added into the system and of nitrite resulted from nitrate reduction during the scanning.

curves in 0.1 M Na_2SO_4 and with the addition of different concentrations, ranged between 1–10 mM nitrite (a), 1–10 mM nitrate (b), and mixtures of 0.1–1 mM nitrite and 1– 10 mM nitrate (c). As expected, the AgZEGE electrode exhibited the oxidative/reductive peak corresponding to redox peaks of the Ag/Ag(I) couple. Under these working conditions, nitrite exhibited a well-defined oxidation peak around +0.9 V versus SCE reference electrode. This peak could be ascribed to the oxidation process of nitrite to nitrate. Also, during cathodic direction, even no cathodic peak appeared, the cathodic current increasing was noticed starting at around −1 V/SCE electrode, which would correspond to the nitrate reduction to nitrite.

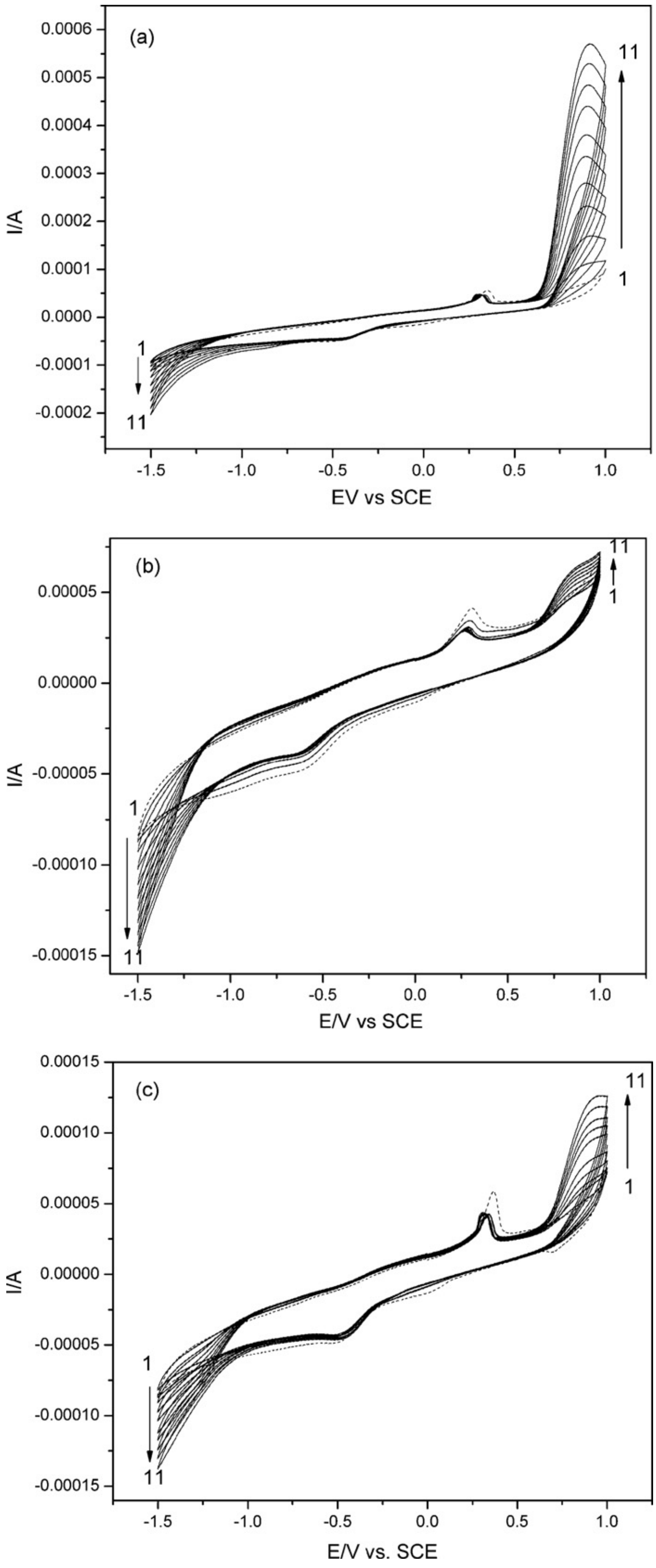

Fig. 1. Cyclic voltammograms of the AgZEGE electrode recorded in 0.1 M Na_2SO_4 supporting electrolyte with addition of: 1–10 mM nitrite (a), 1–10 mM nitrate (b), mixture of 0.1–1 mM nitrite and 1–10 mM nitrate (c). Scan rate: 50 mV s^{-1}.

Based on obtained CVs, the best linear dependence of currents versus the nitrate concentration was achieved at the potential value of −1.35 V/SCE, with a correlation coefficient better than 0.99, and this potential value was selected for further detection experiments. Also, the calibration curve of the anodic peak currents recorded at +0.9 V/SCE versus nitrite concentrations exhibited a linear range with a good correlation coefficient (0.998). The electroanalytical parameters for the detection of nitrate and nitrite using CV were determined for three replicates and the results are gathered in Table 1. Based on these results, a better limit of detection and sensitivity of about ten times for nitrite versus nitrate detection is noticed. Also, for this nitrate concentration range an indirect determination of nitrate can be achieved at the same potential value of nitrite oxidation with a lower sensitivity. This phenomenon can be attributed to the faster rate of the oxidation process of nitrite in comparison with the rate of nitrate reduction.

Series of CV recordings using the AgZEGE electrode in 0.1 M Na_2SO_4 supporting electrolyte and the mixture of 0.1–1 mM nitrite and 1–10 mM nitrate led to linear dependences of both anodic and cathodic currents versus concentrations. These dependencies provide the basis for an amperometric electroanalytical method for the simultaneous determination of nitrate and nitrite by voltammetry and chronoamperometry. The concentration range for nitrite was chosen in order to avoid a significant contribution to the cathodic branch. As can be noticed from the results presented in Table 1 within these concentration ranges the sensitivity for nitrate detection was not affected by the presence of nitrite. The useful anodic current recorded at +0.9 V/SCE represents the sum of nitrite added to the system and the nitrite resulted during the cathodic reduction of nitrate.

The following methodology can be applied to determine simultaneously and quantitatively each anion, expressed in mM, in their aqueous solution mixture:

- based on the linear regression equation for nitrate analysis:

$$I_{\text{mixture}}(\text{mA}) = 0.032 - 0.07C_{\text{Nitrate}}$$

- based on the linear regression equation for nitrite analysis:

$$I_{\text{mixture,}\ \ \text{anodic}} - (0.0264 - 10 \times 0.002C_{\text{Nitrate}}) = -0.036 + 0.0542C_{\text{Nitrite}}$$

However, for practical working applications the optimum analytical procedure should involve the recording of the chronoamperogram, based on the existing well-established essential point of reference provided by the voltammograms. In order to reach the simultaneous detection of nitrate and nitrite anions during recording a single chronoamperogram, two levels of constant potential were applied in concordance with the CV, one corresponding to nitrate reduction to nitrite (−1.35 V/SCE) and the other corresponding to nitrite oxidation (+0.9 V/SCE). Fig. 2a–c presents the series of the chronoamperograms recorded at both

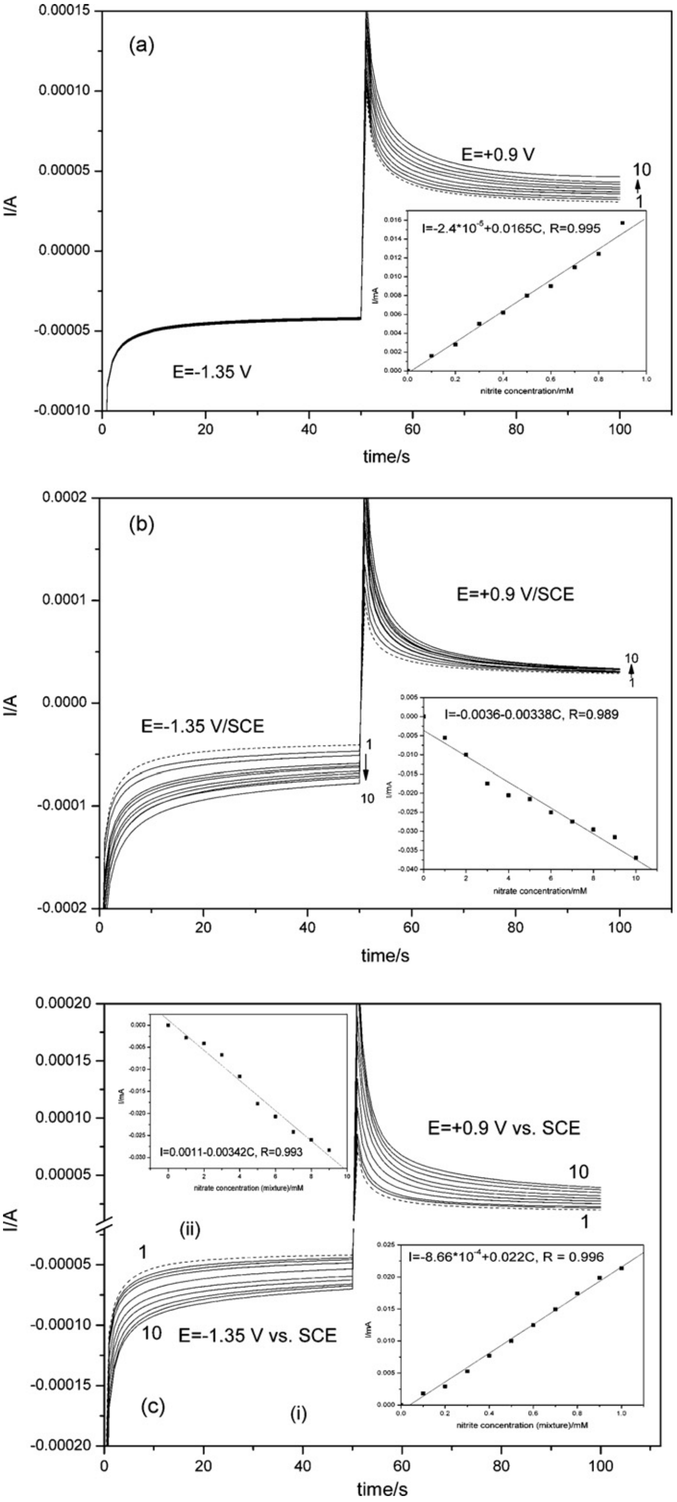

Fig. 2. Chronoamperograms (CAs) of the AgZEGE electrode at two potential levels, i.e., −1.35 V and +0.9 V versus SCE; quiescent solution, batch system, recorded in 0.1 M Na_2SO_4 supporting electrolyte with the addition of: 1–10 mM nitrite (a), 1–10 mM nitrate (b), mixture of 0.1–1 mM nitrite and 1–10 mM nitrate. Insets: Calibration plots corresponding to current readings from CAs at 50 s for nitrite (a), nitrate (b) and nitrate from mixture (c).

constant potentials in the presence of different concentrations ranging between 0.1–0.9 mM nitrite (a), 1–9 mM nitrate (b), and mixtures of 0.1–0.9 mM nitrite and 1–9 mM nitrate (c). Linear regression analysis resulted in the equations with good overall correlation coefficients, above 0.98 (see insets of Fig. 2a–c).

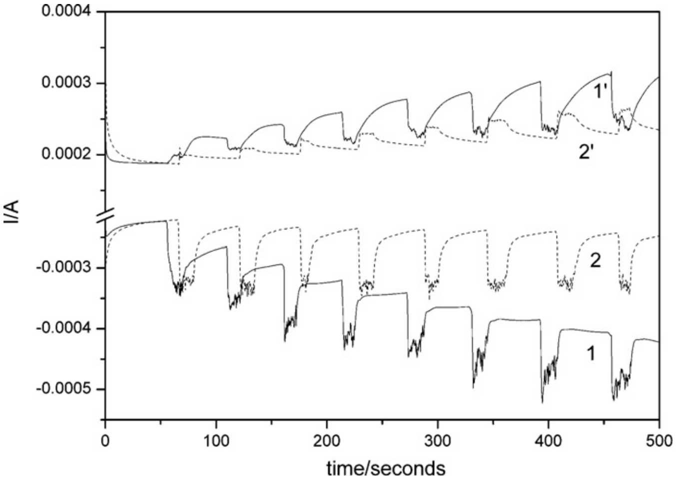

Fig. 3. Multiple-pulsed amperograms (MPAs) recorded at the AgZEGE electrode in a 0.1 M Na_2SO_4 supporting electrolyte and adding 1 mM nitrate concentrations (curves 1 and 1′), or adding 0.1 mM nitrite concentrations (curves 2 and 2′); $E_{\text{reduction}}$ was −1.35 V/SCE (curves 1 and 2) and $E_{\text{oxidation}}$ was +0.9 V/SCE (curves 1′ and 2′); $t_{\text{oxidation}}$ and $t_{\text{reduction}}$ were 150 ms.

Under conditions of constant potential and quiescent solutions, the lowest detection limit (LOD) based on a 3-sigma method (calculated as three times the standard deviation of the blank over the sensitivity) [39], was estimated to be 0.01 mM for nitrite and 0.6 mM for nitrate. The consistency of the chronoamperometry measured for three replicates shows the reproducibility characteristics of the electrode for the detection of nitrate and nitrite by chronoamperometry.

The electroanalytical parameters determined under these working conditions are gathered in Table 2.

The above-described methodology applied for CV to determine simultaneously and quantitatively each anion, expressed in mM, in the mixture can be used also for this CA technique in relation with the calibration plots determined:

- based on the linear regression equation for nitrate analysis:

$$I_{\text{mixture}}(\text{mA}) = 0.0036 - 0.0034C_{\text{Nitrate}}$$

- based on the linear regression equation for nitrite analysis:

$$I_{\text{mixture, anodic}} - (0.0011 - 10 \times 0.00055C_{\text{Nitrate}}) = -0.00024 + 0.0165C_{\text{Nitrite}}$$

However, when constant-potential amperometry is used as the detection method, the sensitivity obtained was poor compared to CV, probably due to electrode fouling. An alternative to the amperometric detection for the simultaneous detection of these species and proposed in this work is the use of MPA based on switching only between the two potential pulses, whose values were similarly with CA ones under continuous agitation. The pulses were applied continuously using the following scheme:

(a) −1.35 V/SCE for a duration of 150 ms, where nitrate is reduced to nitrite
(b) +0.9 V/SCE for a duration of 150 ms, where nitrite is oxidized to nitrate

These working conditions for applying MPA were chosen for comparison with CA results and were applied both for individual and simultaneous detection of nitrate and nitrite in the 0.1 M

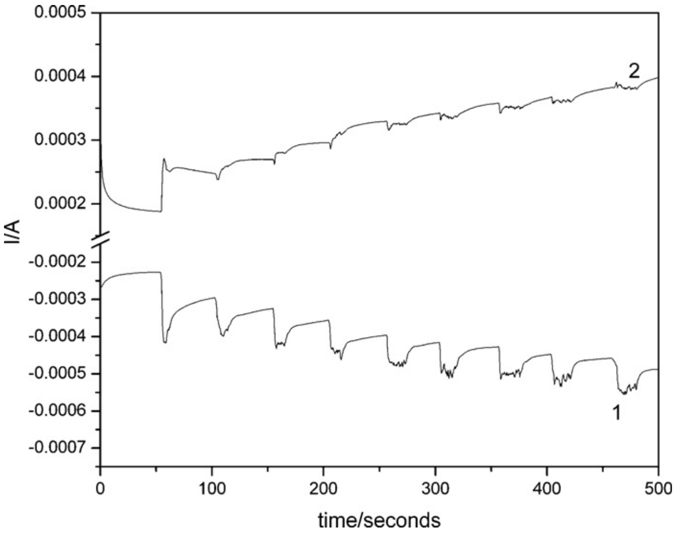

Fig. 4. Multiple-pulsed amperograms (MPAs) recorded at the AgZEGE electrode in 0.1 M Na_2SO_4 supporting electrolyte and adding mixture of 1 mM nitrate and 0.1 mM nitrate concentrations; $E_{reduction}$ was −1.35 V/SCE (curve 1) and $E_{oxidation}$ was +0.9 V/SCE (curve 2); $t_{oxidation}$ and $t_{reduction}$ were 150 ms.

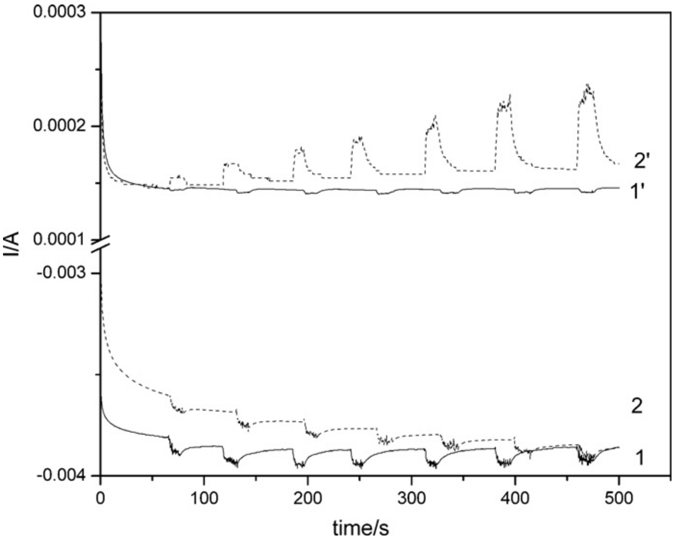

Fig. 5. Multiple-pulsed amperograms (MPA) recorded at AgZEGE electrode in 0.1 M Na_2SO_4 supporting electrolyte and successive adding 0.1 to 0.7 mM nitrate (curves 1–1′) or in the presence of 0.7 mM nitrate and successive adding 0.1 to 0.7 mM nitrite (curves 2–2′); $E_{reduction}$ was −1.35 V/SCE (curves 1–2) and $E_{oxidation}$ was +0.9 V/SCE (curves 1′–2′); $t_{reduction}$ was 50 ms and $t_{oxidation}$ was 250 ms.

Na_2SO_4 supporting electrolyte. Fig. 3 presents the pulsed amperograms recorded at both potential values for the individual detection of nitrite and nitrate, the concentration of nitrate being ten times higher than the nitrite one. As can be seen, applying MPA for nitrate detection (curves 1) led to both cathodic and anodic amperometric responses, the sensitivities for direct cathodic detection and indirect anodic detection are presented in Table 3. The sensitivity for nitrite detection by MPA is much better than that by CA and better than by CV. Also, for nitrate detection both sensitivities for direct cathodic and indirect anodic detection were improved in comparison with the above-presented techniques CV and CA. This aspect could be own probably a electrochemical in situ preconcentration of nitrate species at the electrode–electrolyte interface during the oxidation step as electrochemical product generated from nitrite oxidation. The same explanation could be valuable for indirect anodic detection of nitrate due to alternating the two reduction and oxidation processes by potential pulsing between −1.35 V and +0.9 V versus SCE. Fig. 4 shows the multiple-pulsed amperogram recorded in 0.1 M Na_2SO_4 and mixtures of different concentrations of nitrate (1–9 mM) and nitrite (0.1–0.9 mM). As it was shown for the applied techniques, CV and CA, by applying MPA the useful signal recorded at the anodic potential value represents a cumulative effect of the amperometric signal corresponding to nitrite added and formed during the reduction process at −1.35 V/SCE (see Table 4). Also, it has been highlighted that under this ratio of 10 to 1 between nitrate and nitrite, the amperogram recorded at −1.35 V/SCE corresponded only to added nitrate into the system without interfering of nitrite.

Table 4
The optimization of nitrate determination using MPA.

MPA parameters	Cathodic useful signal/mA)	Anodic useful signal/mA)
$E_{reduction}$ = −1.35 V; $t_{reduction}$ = 150 ms $E_{oxidation}$ = +0.9 V; $t_{oxidation}$ = 50 ms	[a]	0.03
$E_{reduction}$ = −1.35 V; $t_{reduction}$ = 50 ms $E_{oxidation}$ = +0.9 V; $t_{oxidation}$ = 150 ms	0.011	0.0013
$E_{reduction}$ = −1.35 V; $t_{reduction}$ = 50 ms $E_{oxidation}$ = +0.9 V; $t_{oxidation}$ = 250 ms	0.25	–
$E_{reduction}$ = −1.35 V; $t_{reduction}$ = 150 ms $E_{oxidation}$ = +0.9 V; $t_{oxidation}$ = 150 ms	0.025	0.0166

[a] No reproducible results were obtained.

The above-proposed methodology for both techniques, i.e., CV and CA, can be used for applying MPA in relation with linear regression calculated for these working conditions, such as:

- based on the linear regression equation for nitrate analysis:

$$I_{\text{mixture, cathodic}}(\text{mA}) = -0.014 - 0.025C_{\text{Nitrate}}$$

- based on the linear regression equation for nitrite analysis:

$$\begin{aligned} I_{\text{mixture, anodic}} - (0.037 - 10 \times 0.0166C_{\text{Nitrate}}) \\ = 0.0016 + 0.057C_{\text{Nitrite}} \end{aligned}$$

To investigate the optimal conditions for the batch injection analysis performance, times of oxidation and reduction processes were varied using a 1 mM nitrate solution. Because the nitrate reduction process occurred with slow rate, the conditions corresponding to enhancing sensitivity for nitrate detection were followed. In Table 4 the parameters for applying MPA are shown. A very good sensitivity for nitrate detection with very low contribution in the anodic part was obtained under MPA conditions of $E_{reduction}$ = −1.35 V/SCE for 50 ms and $E_{oxidation}$ = +0.9 V/SCE for 250 ms. An example of application of this strategy is shown in Fig. 5. Under these conditions, it was possible to detect nitrate by successive and continuous adding 0.1 mM nitrate, and no significant contributions to anodic current was noticed, a desired aspect in relation with direct simultaneous detection of both anions at cathodic and anodic potentials for the same sample and at the same time without mutual interferences. However, the sensitivity for the nitrite detection is worse and this strategy is limited only to the use of moderate concentrations of nitrite.

A recovery test was performed by analyzing three parallel tap water samples, which contained 1 mM nitrate and 0.1 mM nitrite. This test was run in 0.1 M Na_2SO_4 as supporting electrolyte and a recovery of 95% with a RSD of 3.8% was found for nitrate and a recovery of 98% with a RSD of 3.2% was found for nitrite using MPA applying at two potentials, the first at −1.35 V/SCE for a time duration of 150 ms, and the second at +0.9 V/SCE for a time duration of 150 ms. Finally, the results obtained by this method were compared with that obtained by means of a conventional spectrophotometrical method [40]. Based on the results obtained, it can be concluded that the two methods lead to very close results and that the accuracy of the proposed MPA method is good.

4. Conclusions

This work presented a new method for simultaneous determination of nitrate and nitrite in aqueous solutions using batch injection analysis with cyclic voltammetry, chronoamperometry, and multiple-pulsed amperometry.

An Ag-doped zeolite-modified expanded graphite composite electrode exhibited useful features for the voltammetric and amperometric individual and simultaneous determination of nitrite and nitrate in aqueous solutions.

The application of each electrochemical technique allowed the direct and simultaneous detection of 1–10 mM nitrate and 0.1–1 mM nitrite in the same sample. Applying MPA improved the sensitivity both for nitrate and nitrite detection and under working conditions of two potentials levels, the first at −1.35 V/SCE for a time duration of 150 ms and the second at +0.9 V/SCE for a time duration of 150 ms. Under these working conditions, nitrate influenced significantly the electrochemical signal corresponding to nitrite detection.

A strategy for direct simultaneous detection of nitrate at a cathodic potential with enhanced sensitivity (10 fold) and of nitrite at an anodic potential was established under MPA conditions of applying $E_{\text{reduction}} = -1.35$ V/SCE for 50 ms and $E_{\text{oxidation}} = +0.9$ V/SCE for 250 ms.

The proposed methodologies based on applying MPA of simultaneous determination of nitrite and nitrate either as direct and selective nitrate detection and indirect anodic simultaneous nitrate and nitrite detection or direct selective and simultaneous detection of nitrite and nitrate are simple, fast, cheap, and do not require any sample preparation. This method has a good potential to be applied as routine analysis and to substitute laborious spectrophotometric methods.

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