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DOI

[10.1016/j.psep.2016.05.006](https://doi.org/10.1016/j.psep.2016.05.006)

Publication date

2017

Document Version

Final published version

Published in

Process Safety and Environmental Protection

Citation (APA)

Baciu, A., Manea, F., Pop, A., Pode, R., & Schoonman, J. (2017). Simultaneous voltammetric detection of ammonium and nitrite from groundwater at silver-electrodecorated carbon nanotube electrode. *Process Safety and Environmental Protection*, 108, 18-25. <https://doi.org/10.1016/j.psep.2016.05.006>

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Simultaneous voltammetric detection of ammonium and nitrite from groundwater at silver-electrodecorated carbon nanotube electrode

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ARTICLE INFO

Article history:

Received 5 January 2016

Received in revised form 14 March 2016

Accepted 5 May 2016

Available online 12 May 2016

Keywords:

Ammonium

Nitrite

Simultaneous voltammetric detection

Silver-electrodecorated carbon nanotubes-epoxy composite electrode

Electrochemical techniques

Groundwater

ABSTRACT

Ammonium and nitrite are listed by Water Framework Directive as core parameters that should be monitored for the groundwater as drinking water source. This work describes the sensitive protocols for the simultaneous detection of ammonium and nitrite in water at a new silver-electrodecorated carbon nanotubes-epoxy composite electrode (Ag-CNT) using advanced voltammetric technique. A carbon nanotubes-epoxy composite electrode obtained by two-roll mill procedure was decorated electrochemically with silver nanoparticles. This new electrode displays excellent electrocatalytic activity towards the direct oxidation of ammonium and nitrite at well separated less potential values (+0.15 V/SCE for ammonium and +0.7 V/SCE for nitrite). Very good detection sensitivities (0.613 mA mM⁻¹ for ammonium and 0.980 mA mM⁻¹ for nitrite) and the lowest limits of detection (1 μM for ammonium and 0.7 μM for nitrite) were achieved by differential-pulsed voltammetry (DPV) under optimum operating conditions of 0.05 V step potential, 0.2 V modulation amplitude and the scan rate of 0.05 V s⁻¹. This detection protocol was successfully applied to the simultaneous determination of ammonium and nitrite in groundwater samples, and the results were found to be consistent with the values obtained by the standardized spectrophotometry methods.

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1. Introduction

Nitrogen compounds are ubiquitous in nature. They exist naturally as nitrogen cycle in the environment in several forms as gaseous nitrogen, ammonia nitrogen, nitrates, nitrites and organic nitrogen. For water there are the regulations for the maximum allowance concentrations for the nitrogen-based compounds in the direct relation with the water type, e.g., groundwater, surface and wastewater.

Groundwater and surface water are very important sources for drinking water and the maximum allowance concentrations are set by Drinking Water Directive (ECC) as 0.5 mgL⁻¹ for each ammonium and nitrite compound. Also, in the framework of the protection and conservation of all water bodies to achieve “good” quality status that is known as the main objective of the Water Framework Directive, the ammonium and nitrite are listed as core parameters that should be monitored for the groundwater as drinking water source

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<http://dx.doi.org/10.1016/j.psep.2016.05.006>

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(2000/60/EC, WFD), Nitrites presence in water occurs by both natural and anthropogenic processes. The natural processes consist of the oxidation of ammonia or reduction of nitrate by microorganisms in plants, soil and water, being intermediate species in the nitrogen cycle. From the point of the anthropogenic process, nitrite presence in water can be a result of excessive use of fertilizer, as a result of defective management practice in farming activity, inappropriate treatment of the wastewater related to the biological step based on nitrification-denitrification processes, or discharges from industrial and mining processes (Baciu et al., 2015; Yilong et al., 2015). Also, it is well-known the negative effect of the nitrite on the human health to produce diseases like stomach cancer or methemoglobinemia (Santos et al., 2009; Sahraoui et al., 2013).

Ammonium is formed naturally in groundwater as a result of the reaction of biochemical decomposition of organic nitrogen compounds and reduction of nitrites and nitrates (Hussaian et al., 2015). It is also, commonly found in groundwater due to anthropogenic activities, mainly due to leaching from fertilizers, municipal waste disposal, leaking from animal farm waste. Ammonium concentrations exceeding the imposed limit indicates a sanitary water pollution (Bohlke et al., 2006), and contributes to the eutrophication process of surface water.

There are a lots of methods for the determination of individual nitrite and ammonium, based on spectrometry (Garcia-Robledo et al., 2014; Krom, 1980), ion-chromatography (Michalski and Kurzyca, 2006), flow-injection analysis (Kazemzadeh and Ensafi, 2001; Nobrega et al., 1995). Also, HPLC have been developed that are faster, more accurate and more sensitive than spectrophotometric methods. However, the most methods are often laborious to perform and require chemical reagents (Chou et al., 2003; Mesequer-Lloret et al., 2005).

Several electrochemical methods have been reported for the quantitative assessment of individual ammonium and nitrite, most of them are based on the potentiometric principles using ion-selective sensors (Molins-Legua et al., 2006; Yilong et al., 2015), and other are based on voltammetric/amperometric techniques (Najafi and Darabi, 2014; Badae et al., 2009). The electrochemical methods have been developed as reliable and inexpensive sensing methods with low limit of detection and high sensitivity that are in direct relation with the electrode material and the electrochemical techniques (Baciu et al., 2015; Manea et al., 2010). On the strength of this matter, many efforts have been directed to the enhancement of the performance of the voltammetric techniques. Differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) are very operative for electroanalysis application due to their high sensitivity based mainly on background current minimization (Molina et al., 2011). There are reported papers related to the applications of voltammetric techniques to detect and monitor the nitrite and ammonium at a bare solid electrode, e.g., copper electrode (Davis et al., 2000; Dutt and Davis, 2002), palladium electrode (Milhano and Pletcher, 2008), platinum electrode (Wu et al., 2004), gold electrode (Silva and Mazob, 1998), glassy carbon electrode (Kozub et al., 2010). However, the determination of nitrite and ammonium on a bare solid electrode is difficult due to slow electron transfer rate and surface passivation effect (Yilong et al., 2015). To overcome these disadvantages, the modifications of the electrode surface with a suitable catalyst have been proposed. Several types of carbon have

been used as a substrate for various catalysts to detect nitrite and ammonium, e.g., copper-graphite electrode (Kaminskaya et al., 2004), gold nanoparticle composite coated glassy carbon electrode (Huang et al., 2008), carbon black modified electrode (Malha et al., 2013), potassium doped graphene electrode (Li et al., 2012), iridium modified carbon fibre (De et al., 2000), lead oxide graphite composite electrode (Sljukic et al., 2007).

In addition, nanoparticles-type catalysts exhibit specific peculiarities to enhance the electroanalytical performance related to the sensitivity and the lowest limit of detection by the larger electroactive surface area and higher electrocatalytic effect towards the reduction or oxidation process responsible for the electroanalytical response (Inngam et al., 2012; Wang et al., 2012; Qu et al., 2015).

To our knowledge, there are no reports about the simultaneous electrochemical detection of ammonium and nitrite in aqueous matrices. The aim of our study was to develop electroanalytical strategies based on certain advanced voltammetric techniques for the simultaneous and sensitive detection of ammonium and nitrite anions in aqueous solution using a specific silver-electrodecorated carbon nanotubes-epoxy composite electrode (Ag-CNT). Direct oxidation of both ammonium and nitrite on this specific electrode and as consequence, their determination were investigated by cyclic voltammetry (CV). Square-wave (SWV) voltammetry and differential-pulsed voltammetry (DPV) techniques-based procedures were tested, developed and optimized for selective and simultaneous detection of ammonium and nitrite.

2. Experimental

2.1. Materials

The epoxy resin used in the study was Araldite[®]LY5052/Aradur[®]5052 purchased from Huntsman Advanced Materials, Switzerland. Carbon nanotubes synthesized by catalytic carbon vapor deposition were produced by Nanocyl[™], Belgium. Their main characteristics consisted of 90% carbon purity, 90% CNT content, average diameter of 9.5 nm, average length of 1.5 μm , and surface area of 250–300 m^2/g .

2.2. Preparation of CNT-based composite electrodes

The dispersion of CNT in tetrahydrofuran were achieved by ultrasonication about 10 min prior to mixing with the polymer resin. After the sonication process, the solutions of CNT-THF were sonicated again with epoxy resin to obtain a more homogeneous mixture. An effective two roll mill method was used to prepare the electrodes in order to achieve high levels of dispersion and distribution. The details of the preparation methods have been already published elsewhere (Manea et al., 2012). The ratio between the components was chosen to reach 20%, wt. CNT and respective, 20%, wt. epoxy resin. The mixture was then poured into PVC tubes and cured in a vacuum oven at 80 °C for 24 h, followed by cooling down at room temperature, and the composite electrode with disc surface area of 19.63 mm^2 was obtained. The electrical contacts of the electrodes were assured using copper wire. Then, the surface of the obtained electrode was decorated with silver by electrodeposition at a constant potential of -0.4 V vs. SCE for 10 s in the presence of 0.1 M AgNO_3 solution.

2.3. Morphological, electrical and electrochemical measurements

The electrical conductivity of each composite material was determined by a four-point resistance measurement (Mironov et al., 2007). A Scanning Electron Microscope (Philips CM30T) was used to examine morphologically the working electrode surface.

All electrochemical 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 (SCE) as reference electrode, a platinum counter electrode and Ag-CNT working electrode. The electrochemical behaviour of the electrode envisaging nitrite and ammonium detection was studied by cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and square-wave voltammetry (SWV). Before each electrochemical experiment, three repetitive cyclings between -0.5 V and $+1.5$ V vs. SCE in 0.1 M Na_2SO_4 supporting electrolyte was performed as an electrochemical pre-treatment. The limit of detection (LOD) and the quantification limit (QL) for target analytes under these experimental conditions were determined with Eqs. (1) and (2) (Baciu et al., 2010):

$$\text{LOD} = \frac{3S_B}{b} \quad (1)$$

$$\text{LQ} = \frac{10S_B}{b} \quad (2)$$

where S_B is the standard deviation of the mean value for three replicates of the blank and b is the slope in the analytical curve.

To validate the electrochemical detection method, the standardized spectrophotometric methods for nitrite and ammonium determination was used for comparison (Eaton et al., 2005).

3. Results and discussion

3.1. Morphological and electrical characterization

The qualitative information about the distribution of multi-walled carbon nanotubes in epoxy matrix for composite electrode has been provided by SEM imaging. Fig. 1 shows SEM image of Ag-CNT composite electrode that reveals a well distribution of the multi-walled carbon nanotubes within the epoxy matrix. The electrochemical deposition of silver

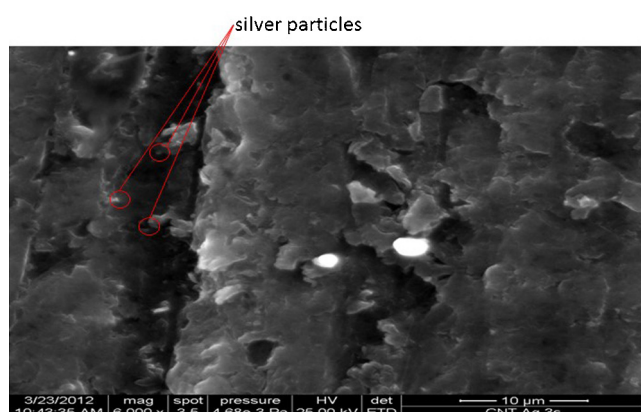


Fig. 1 – SEM images of the cross-section of the Ag-CNT electrode surface.

nanoparticles on CNT performed by maintaining the potential value at -0.4 V/SCE is a diffusion-controlled process and, hence, spontaneous formation of silver nanoparticles on CNT surface occurs, which are deposited in aggregated form. The Ag particles were distributed randomly on the electrode surface and characterized by various sizes. The four-points probe method has been provided the electrical conductivity for electrode of 0.713 S cm^{-1} , which is appropriate for the electro-analytical applications.

3.2. Cyclic voltammetric measurements

The electrochemical characterization of ammonium and nitrite envisaging their oxidation processes on Ag-CNT electrode was studied by the cyclic voltammetry in the presence of 0.1 M Na_2SO_4 as supporting electrolyte (Fig. 2a). 0.2 mM NH_4^+ concentrations were added continuously and corresponding CV was recorded until NH_4^+ concentration reached 1 mM, after each the same concentrations of NO_2^- were added and their mixture resulted. The electrochemical behaviour of Ag-CNT electrode in the presence of NH_4^+ showed the presence of

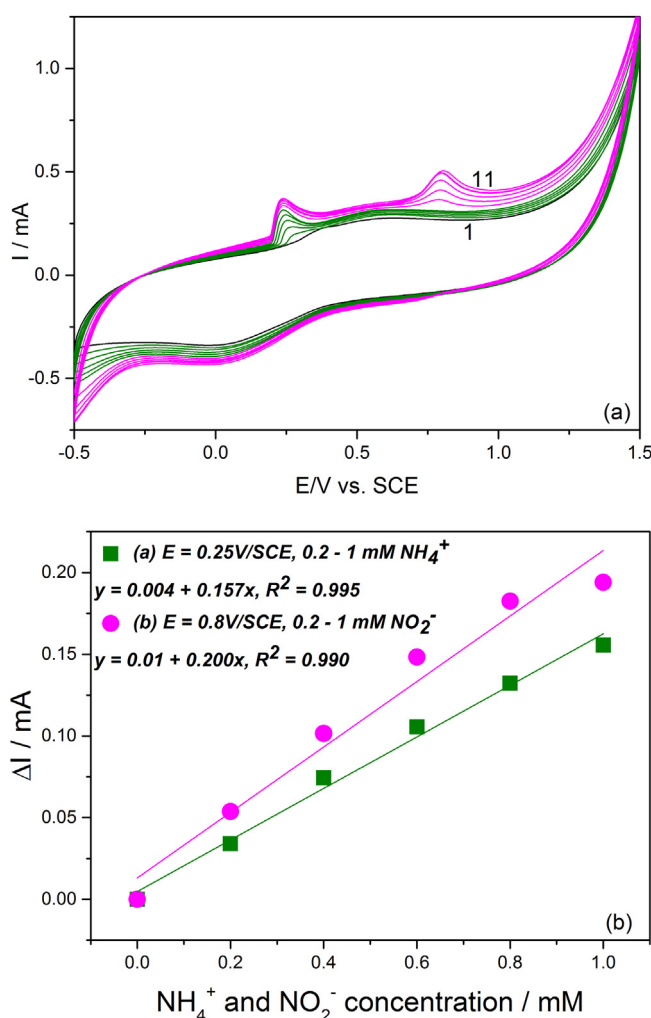


Fig. 2 – (a) Cyclic voltammograms recorded on a Ag-CNT electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 0.2 – 1 mM ammonium (curves 2–6) followed by consecutive adding of 0.2 mM nitrite (curves 7–11), a potential scan rate of 0.05 V s^{-1} , a potential range of -0.5 to $+1.5$ V/SCE; (b) calibration plots of the current recorded at: $E = +0.25$ V/SCE vs. ammonium concentration and $E = +0.8$ V/SCE vs. nitrite concentration.

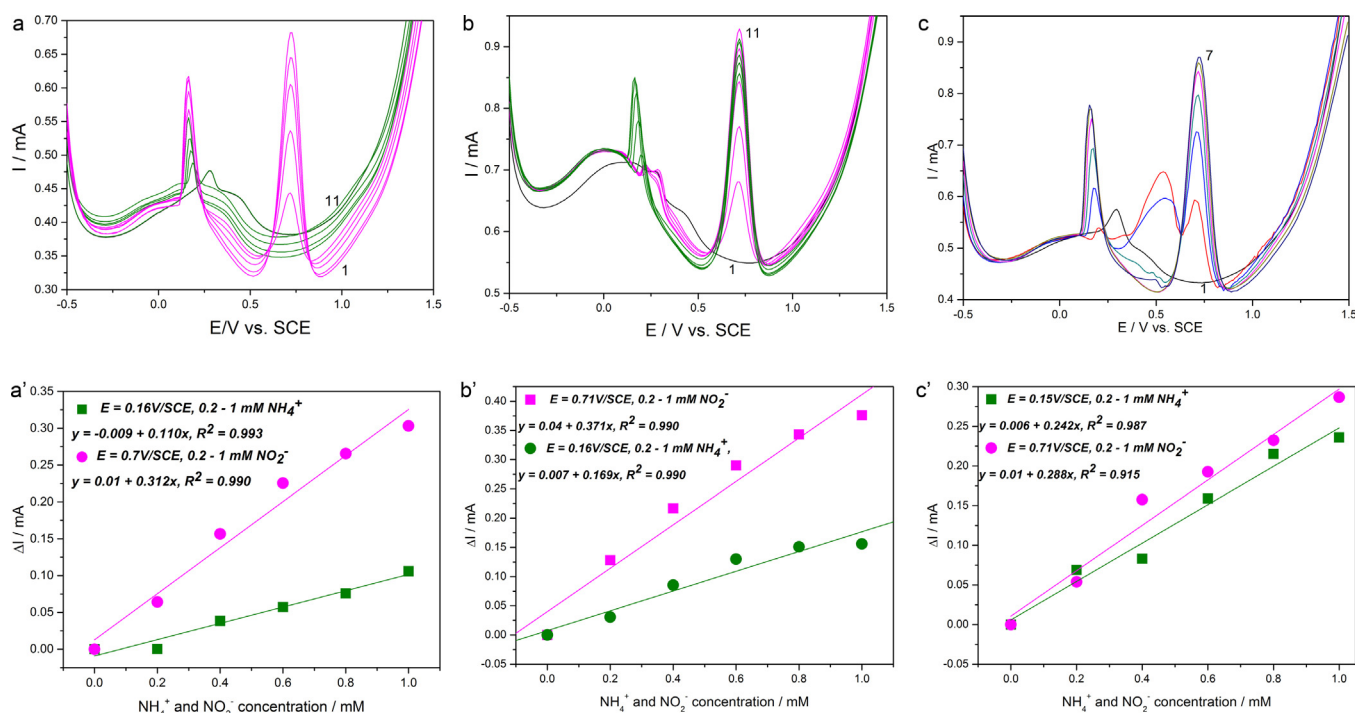


Fig. 3 – (a) Differential-pulsed voltammograms recorded on Ag-CNT electrode under 0.01 V step potential and 0.1 V modulation amplitude, scan rate 0.05 V s^{-1} , between -0.5 and $+1.5 \text{ V vs. SCE}$ in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte (curve 1) and in the presence of $0.2\text{--}1 \text{ mM}$ ammonium concentrations (curves 2–6) followed by successive adding 0.2 mM curve 2–11; (a') calibration plots of the current recorded at: $E = 0.2 \text{ V/SCE vs. ammonium concentrations}$ and $E = 0.8 \text{ V/SCE vs. nitrite concentrations}$. (b) Differential-pulsed voltammograms recorded on a Ag-CNT electrode under 0.01 V step potential and 0.1 V modulation amplitude, scan rate 0.05 V s^{-1} , between -0.5 and $+1.5 \text{ V vs. SCE}$ in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte (curve 1) and in the presence of $0.2\text{--}1 \text{ mM}$ of nitrite concentrations and mixture of ammonium concentrations ($0.2\text{--}1 \text{ mM}$, curve 2–11); (b') calibration plots of the current recorded at: $E = 0.7 \text{ V/SCE vs. nitrite concentrations}$ and $E = 0.15 \text{ V/SCE vs. ammonium concentrations}$. (c) Differential-pulsed voltammograms recorded on a Ag-CNT electrode under 0.01 V step potential and 0.1 V modulation amplitude, scan rate 0.05 V s^{-1} , between -0.5 and $+1.5 \text{ V vs. SCE}$ in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte (curve 1) and in the presence of $0.2\text{--}1 \text{ mM}$ of mixture of ammonium and nitrite concentrations ($0.2\text{--}1 \text{ mM}$, curve 2–7); (c') calibration plots of the current recorded at: $E = 0.15 \text{ V/SCE vs. ammonium concentrations}$ and $E = 0.7 \text{ V/SCE vs. nitrite concentrations}$.

an anodic peak at the potential value of $+0.25 \text{ V/SCE}$ corresponding to the formation of a soluble complex of diamine silver ($\text{Ag}(\text{NH}_3)_2^+$) (Manea et al., 2008). NO_2^- presence led to the appearance of an anodic peak at the potential value of $+0.8 \text{ V/SCE}$ corresponding to NO_2^- oxidation to NO_3^- (Manea et al., 2010). Linear dependences of the anodic current recorded at $+0.25 \text{ V/SCE vs. NH}_4^+$ concentration and of the anodic current recorded at $+0.8 \text{ V/SCE vs. NO}_2^-$ concentration were determined (Fig. 2b). A small deviation was noticed at higher concentration of nitrite, which should be due to a possible effect of the electrode surface. It must be noticed that on the reverse cathodic scanning, in the presence of both ammonium and nitrite, the cathodic current increased with the concentration of nitrogen species, which should be due to the reduction of the oxidized nitrogen species. A more influence can be observed in the presence of nitrite. Also, the presence of NO_2^- strengthens the anodic peak corresponding to diamine complex formation, and this peak did not appear in the absence of ammonium (the results are not shown here).

The difference between the detection potential values for each species at least of 250 mV is appropriate for the investigation of the possibility of their simultaneous detection. For these ammonium and nitrite species the detection potential values is about 550 mV using Ag-CNT electrode, which is very promising for their simultaneous detection.

Based on the CV results as the reference basis, further experiments were conducted to improve the sensitivity for

the simultaneous detection of each nitrogen compound. Thus, the advanced voltammetric techniques of differential pulsed and square-wave voltammetry were applied for the simultaneous detection of ammonium and nitrite. The first advanced voltammetric technique applied was the differential-pulsed voltammetry (DPV).

3.3. Differential-pulsed voltammetry results

Taking into consideration that simultaneous presence of nitrite and ammonium can interfere each other to their detection, the three detection protocols using differential pulsed voltammetry technique operated under 0.01 V step potential, 0.1 V modulation amplitude and the scan rate of 0.05 V s^{-1} were proposed as follows:

- The detection of NO_2^- in the presence of NH_4^+ , which means recording DPVs in the presence of various concentration of NH_4^+ (0.2 mM to 1 mM) followed by adding continuously the same concentration of NO_2^- ;
- The detection of NH_4^+ in the presence of NO_2^- , where in the first stage DPV were recording in the presence of 0.2 mM to 1 mM NO_2^- followed by adding the same concentration of NH_4^+ ;
- The simultaneous detection of NH_4^+ and NO_2^- by adding continuously and successively the mixture of 0.2 mM

$\text{NO}_2^- + 0.2 \text{ mM NH}_4^+$ to reach the mixture characterized by the final concentration of 1 mM NO_2^- and 1 mM NH_4^+ .

The DPV results obtained for all detection protocols are presented in Fig. 3a–c and the calibration plots in Fig. 3a'–c'. The sensitivity reached for each species is gathered in Table 1.

Fig. 3 a and a' shows the results obtained for the above-presented protocol (a). As it was found by CV, the presence of nitrite, the peak corresponding to the formation of the diamine-silver complex is more pronounced, which confirm the influence of nitrite on the ammonium detection. Fig. 3 b and b' presents the results determined for the detection protocol (b). Also, it can be noticed that ammonium presence affected slightly the nitrite detection in a different way. A smaller sensitivity is noticed in the presence of ammonium. These findings are confirmed by the last detection protocol (c), of which results are shown in Fig. 3 c and c', and a simultaneous calibration is imposed for the simultaneous detection of these nitrogen species. Another aspect very important for the detection in general is represented by the detection potential values, for which a low value is desired. DPV use allowed a shifting the detection potential value from +0.25 V to +0.15 V vs. SCE for ammonium and from +0.8 to +0.7 V vs. SCE for nitrite.

Since the DPV method offers an improved sensitivity in electrochemical signals and detection limits in relation with the operating conditions, the optimum response of simultaneous determination of ammonium and nitrite was further investigated by DPV. The peak current achieved in DPV is influenced by the operation parameters such as potential scan rate, step potential, modulation amplitude. In order to establish the optimum operating condition in the simultaneous detection of the target species, the influence of step potential on the peak current response was investigated. Thus, the differential pulse voltammogram was recorded at Ag-CNT electrode in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte, in the presence of ammonium and nitrite concentration ranged between 0.2 to 1 mM , with modulation amplitude of 0.2 V/SCE , a potential scan rate of 0.05 V s^{-1} , and different step potential 0.01 V , 0.02 V and 0.05 V . Based on these results, it can be concluded that the optimum step potential was obtained for the value of 0.05 V in direct relation with the sensitivity and correlation coefficient, Fig. 4a and b shows the results under optimum operation condition of 0.2 V modulation amplitude, 0.05 V s^{-1} scan rate, and 0.05 V step potential. Under these conditions, the best values of sensitivity were achieved, 0.613 mA mM^{-1} for ammonium and 0.980 mA mM^{-1} for nitrite.

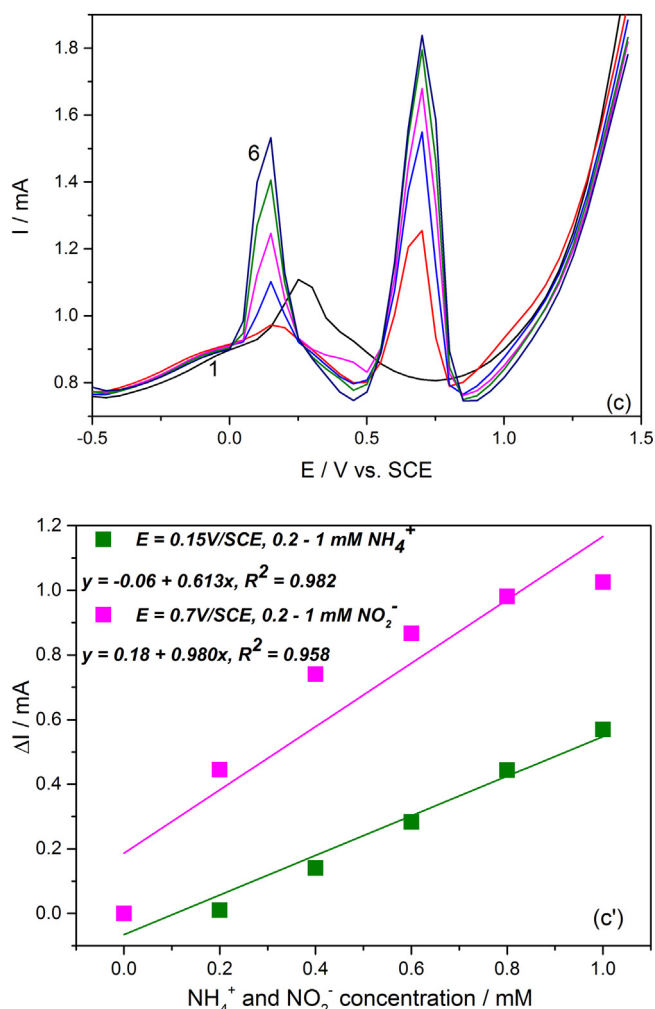


Fig. 4 – (a) Differential-pulsed voltammograms recorded on a Ag-CNT electrode under 0.05 V step potential and 0.2 V modulation amplitude, scan rate 0.05 V s^{-1} , between -0.5 and $+1.5 \text{ V}$ vs. SCE in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte (curve 1) and in the presence of 0.2 – 1 mM of mixture of ammonium and nitrite concentrations (0.2 – 1 mM , curves 2–7); (b) Calibration plots of the current recorded at: $E = 0.15 \text{ V/SCE}$ vs. ammonium concentrations and $E = 0.7 \text{ V/SCE}$ vs. nitrite concentrations.

Further experiments were conducted to achieve good response of simultaneous voltammetric detection of ammonium and nitrite by exploiting the square-wave voltammetry (SWV) method. Also, various operating schemes to determine

Table 1 – Sensitivities determined for ammonium and nitrite detection by DPV operated at step potential of 0.01 V and modulation amplitude of 0.1 V for each detection protocol.

Detection protocol	E/V vs. SCE		Sensitivity, mA mM^{-1}	
	NH_4^+	NO_2^-	NH_4^+	NO_2^-
(a)				
NH_4^+ individual				
NO_2^- in the presence of NH_4^+	0.15	0.7	0.110	0.312
(b)				
NO_2^- individual				
NH_4^+ in the presence of NO_2^-	0.15	0.7	0.169	0.371
(c)				
Simultaneous NH_4^+ and NO_2^-				
Mixture of NH_4^+ and NO_2^-	0.15	0.7	0.242	0.288

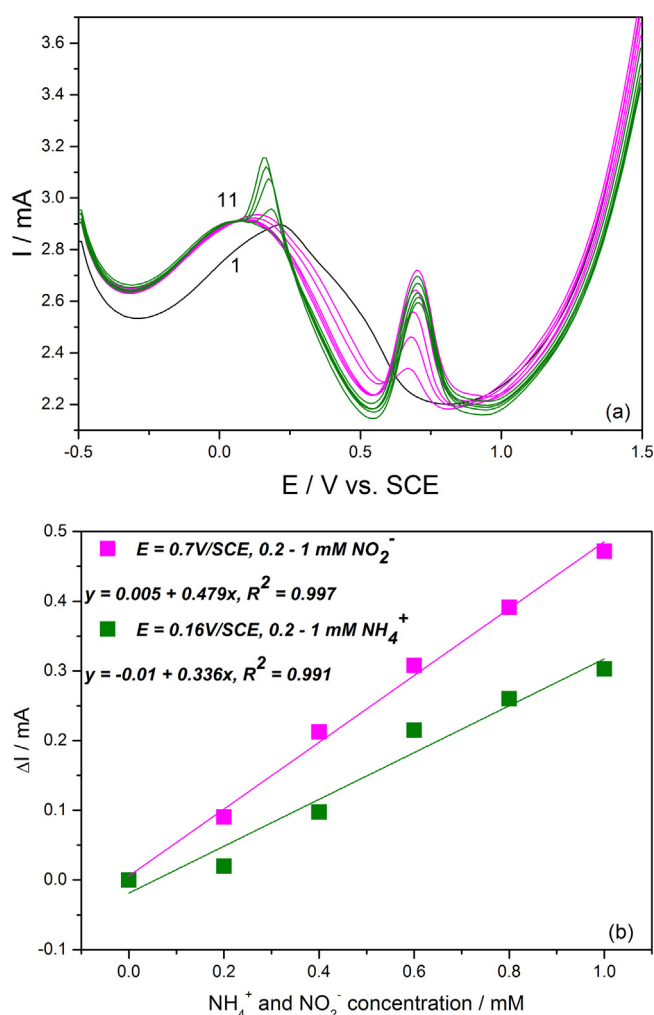


Fig. 5 – (a) Square-wave voltammograms recorded on a Ag-CNT electrode under 0.01 V step potential and 0.2 V modulation amplitude, frequency of 10 Hz, scan rate 0.1 V s^{-1} , between -0.5 and $+1.5 \text{ V vs. SCE}$ in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte (curve 1) and in the presence of $0.2\text{--}1 \text{ mM}$ of nitrite concentrations and of ammonium mixture concentrations ($0.2\text{--}1 \text{ mM}$, curves 2–11); (b) calibration plots of the current recorded at: $E = +0.15 \text{ V/SCE}$ vs. nitrite concentrations and $E = +0.7 \text{ V/SCE}$ vs. ammonium concentrations.

the optimum condition were tested using this technique to achieve the best electroanalytical parameters for ammonium and nitrite detection. The best results that allowed reaching a good sensitivity for both species are obtained under the operation condition of 0.01 V step potential, 0.2 V modulation amplitude and a frequency of 10 Hz .

Fig. 5a shows square-wave voltammogram recorded at Ag-CNT electrode in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte under 0.01 V step potential, 0.2 V modulation amplitude and a frequency of 10 Hz , in the presence of ammonium and nitrite mixture concentration ranged between 0.2 mM to 1 mM . Fig. 5b shows the calibration plots of the peak current recorded at 0.15 V for ammonium concentration and for the nitrite concentration at peak potential of 0.7 V , and it can be noticed that both sensitivities and the lowest limits of detection are worse in comparison with the results reached by operating DPV under optimum conditions.

The optimum operation condition regarding reaching the best electroanalytical parameters for the simultaneous

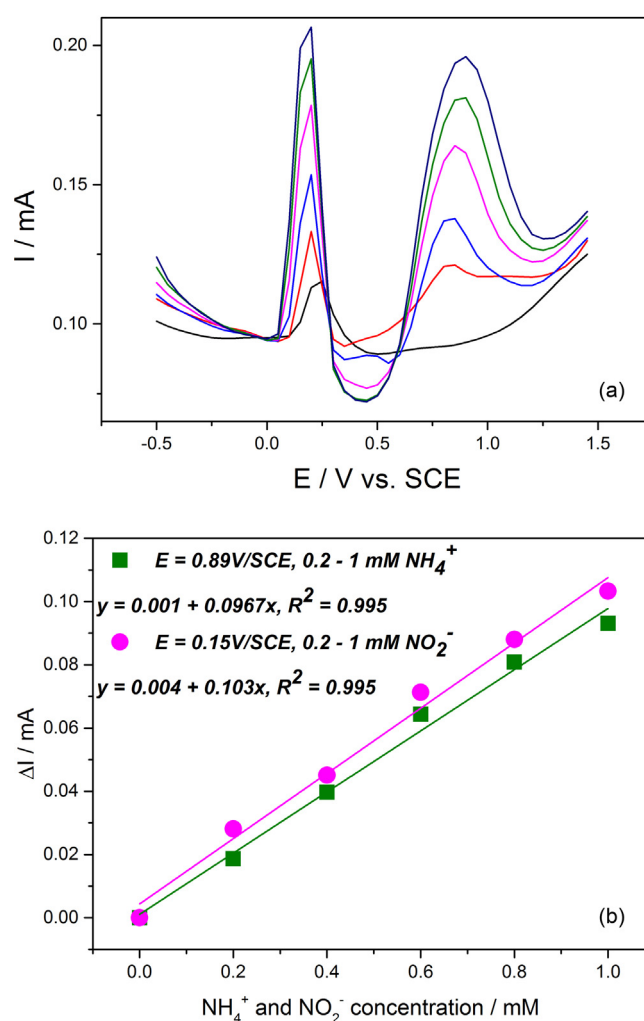


Fig. 6 – (a) Differential-pulsed voltammograms recorded on a Ag-CNT electrode under 0.05 V step potential and 0.2 V modulation amplitude, scan rate 0.05 V s^{-1} , between -0.5 and $+1.5 \text{ V vs. SCE}$ in water without supporting electrolyte (curve 1) and in the presence of mixture of $0.2\text{--}1 \text{ mM}$ ammonium and nitrite concentrations (curves 2–7); (b) calibration plots of the current recorded at: $E = +0.15 \text{ V/SCE}$ vs. ammonium concentrations and $E = +0.7 \text{ V/SCE}$ vs. nitrite concentrations.

detection of ammonium and nitrite assumed operating DPV technique, under 0.05 V step potential, 0.2 V modulation amplitude and 0.05 V s^{-1} scan rate. Thus, this protocol was applied for real groundwater, and the results of calibration procedure are presented in Fig. 6a and b. In general, it must be mentioned that the macroelectrode cannot be applied directly in real water without a deliberately adding supporting electrolyte. This special electrode by its morphology and structure posed the special features similar to microarray due to the presence of carbon nanotubes and silver nanoparticles as composite. The sensitivities reached under these real water samples are lower in comparison with those reached in $0.1 \text{ M Na}_2\text{SO}_4$ supporting electrolyte and the detection potential values are higher, but similar values for the lowest of detection limits are achieved (see Table 2). These results are very promising for the simultaneous detection of ammonium and nitrate in real water.

A recovery test was performed by analyzing three parallel tap-water samples, which contained 0.6 mM ammonium and 0.6 mM nitrite. This test was run in $0.1 \text{ M Na}_2\text{SO}_4$ supporting

Table 2 – The electroanalytical parameters determined for simultaneous detection of ammonium and nitrite at Ag-CNT electrode using DPV and SWV techniques.

Technique	Conditions, Step potential, V/Modulation amplitude, V/Frequency, Hz	E/V vs. SCE		Sensitivity, mA mM ⁻¹		R ²		LOD, mM		LQ, mM	
		NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻	NH ₄ ⁺	NO ₂ ⁻
DPV	0.01/0.1	0.15	0.7	0.242	0.288	0.981	0.915	0.004	0.0026	0.0133	0.0088
DPV	0.05/0.2	0.15	0.7	0.613	0.980	0.982	0.957	0.001	0.0007	0.0033	0.0035
SWV	0.01/0.2/10	0.15	0.7	0.336	0.479	0.991	0.996	0.0016	0.0009	0.0053	0.0084
DPV	0.05/0.2	0.2	0.85	0.0967	0.103	0.995	0.995	0.003	0.006	0.019	0.020

electrolyte and a recovery of 95% with a relative standard deviation of 3.8% was found for ammonium and a recovery of 96% with a relative standard deviation of 2.8% was found for nitrite using the DPV under operating condition of 0.05 V step potential, 0.2 V modulation amplitude and the scan rate of 0.05 V s⁻¹. Finally, the results obtained by this method were compared with those obtained by means of the standardized spectrophotometric methods for nitrite and ammonium determination (Eaton et al., 2005). 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 DPV method is good. The interference effect of various anion and cation species that are common water matrix components was investigated in the presence of 1 mM ammonium and 1 mM NaNO₂. These species were added at the concentrations 100 times higher. No interference effect was noticed in the presence of Mg²⁺, Ca²⁺, Mn²⁺, Fe³⁺, SO₄²⁻, NO₃⁻, CO₃²⁻, I⁻, Cl⁻, F⁻.

All electroanalytical parameters established for the simultaneous detection of ammonium and nitrite under the optimum operating conditions for each voltammetric technique used are gathered in Table 2. It can be noticed that the best electroanalytical parameters for the simultaneous voltammetric detection were achieved by the DPV technique.

4. Conclusions

New protocols for the simultaneous detection of ammonium and nitrite in aqueous solutions and real groundwater using cyclic voltammetry, differential-pulsed voltammetry, and square-wave voltammetry techniques using a new silver electrodecorated carbon nanotube-epoxy composite electrode have been demonstrated for the first time. The best electroanalytical parameters for the simultaneous detection of nitrite and ammonium were achieved using differential pulse voltammetry operated under the optimized operating conditions consisting of a 0.05 V step potential, 0.2 V modulation amplitude and 0.05 V s⁻¹ scan rate. Very good sensitivities of 0.613 mA mM⁻¹ for ammonium and 0.980 mA mM⁻¹ for nitrite, and the lowest limits of detection of 1 μM for ammonium and 0.7 μM for nitrite were achieved. Moreover, this new electrode exhibited useful features for the simultaneous voltammetric detection of ammonium and nitrite in real groundwater without necessity to add the supporting electrolyte, making this electrode suitable for the *in-field* detection and monitoring applications.

Based on the results regarding the detection performance in relation with the sensitivity, the lowest limit of detection, the accuracy and the interference effect, the elaborated

protocol that involve Ag-CNT electrode exhibited a great potential for the practical applications.

Acknowledgements

Funding for this study was provided by the Romanian National Research Programs–PN II WATUSER no. 60/2012, PN II Ideas no. 165/2011 and PN II RU-TE no. 123/2015.

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