

## Electrochemical determination of nitrate from water sample using Ag-doped zeolite-modified expanded graphite composite electrode

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**Abstract** Ag-doped zeolite modified expanded graphite composite electrode (AgZEGE) was prepared and applied for the electrochemical determination of nitrate anion from aqueous solution. The electrochemical behaviour of nitrate anions on the electrode was investigated by cyclic voltammetry in 0.1 M NaOH supporting electrolyte. The AgZEGE exhibited the electrocatalytic activity towards the cathodic reduction of nitrate anions, which was also influenced by applied electrochemical technique. The electroanalytical performance for the electrochemical detection of nitrate was determined using cyclic voltammetry (CV), chronoamperometry (CA) and differential pulse voltammetry (DPV). An enhancement of electroanalytical parameters for the determination of nitrate at the EG-Z-Ag-Epoxy electrode was reached by applying a preconcentration step by adsorption on electrode surface prior to voltammetric quantification. Under this condition, the lowest limit of detection of 0.1 mM illustrates the analytical versatility of this electrode.

**Keywords:** Ag-doped zeolite, modified expanded graphite composite electrode, nitrate

### 1. Introduction

Water quality has received increased attention due to the serious surface and groundwater contamination and the European Community has been taking measures concerned with nitrogen pollution in waters for over twenty years [1]. Nitrate constitutes a well-known water contaminant due to its use as fertilizer in agriculture and it represents the end product of oxidation process of nitrogen species from water [2]. The high nitrate concentration exhibits a significant impact on water environment, e.g., eutrophication and deterioration of water quality [3]. Also, the correlation between high cancer level and nitrate concentration requires the qualitative and quantitative determination of nitrate anion for the environmental control. Several methods for the determination of nitrate anion, based on spectrophotometry, chromatography and electrochemistry were reported [4-8]. The electrochemical determination of nitrate anion can be classified as potentiometric (ion-selective electrodes) or voltammetric/ampereometric methods.

This last electrochemical technique is based on the electrochemical reduction of nitrate anions at the electrode surface, and different electrode materials were used [5-10]. The difficulty of direct determination of nitrate on bare unmodified electrode is based on slow kinetics of the charge transfer and surface passivation effect [5].

Modified electrodes with a suitable catalyst and easy surface regeneration abilities represent a more suitable choice in the voltammetric determination of pollutants, because of their efficiency, sensitivity, and the selectivity that can be obtained by varying the modifier.

Zeolites constitute promising candidates as electrode material envisaging their use in the electroanalysis of organic and inorganic compounds despite the requirement of increasing their electrical conductivity [11-14]. Zeolite-modified electrodes have been developed for the determination of various compounds, e.g., sugars, herbicides, surfactants, neurotransmitters, pharmaceuticals, alkali metal and ammonium ions [15, 16]. The use of a mixture of a zeolite and graphite in various forms has been

proposed [17]. Zeolite-supported electrocatalysts can be exploited to improve the performance of electroanalytical detection [16]. In general, zeolite-modified electrodes exhibit an ion-exchange capacity and a molecular selectivity subjected to size, shape and charge. An electrochemical scheme using doped zeolite modified electrode that relies on analyte preconcentration or catalyst-assisted reactivity, can be used [15, 18].

The purpose of this work is to evaluate the electroanalytical performance of Ag doped zeolite modified expanded graphite composite electrode (AgZEGE) for the determination of nitrate anion. The electrocatalytic activity and enhancement factor of the current signal of the AgZEGE composite electrode with respect to the preconcentration/voltammetric response of nitrate anion has also been explored. Ag- doped Romanian zeolite, which contains clinoptilolite as major mineral component (68%, wt.) and low weight percents of quartz, albit and illite [19] was used to prepare the AgZEGE electrode.

## 2. Experimental

Ag-doped zeolite modified expanded graphite composite electrode (AgZEGE) was obtained by film casting from two-component epoxy resin (LY5052, Araldite) mixed with conductive expanded graphite (EG) filler powder (Conductograph, SGL Carbon) and silver-doped zeolite (clinoptilolite) [19]. The ratio between the components was chosen to reach 20 weight percent (w/w) content of expanded graphite, 20 weight percent (w/w) content of silver-doped zeolite. It was not possible to add the full amount of EG and Z-Ag to the matrix resin directly, due to the high surface area of the graphite flakes. Therefore, the mixing was performed in a roll-mill at room temperature. The two parts of the epoxy were mixed together and the full amount of EG was added in steps forming a thick paste. Then the epoxy was cured in a hot press at 50 °C for 60 minutes. Simultaneously, the material was shaped in a plate of 1 mm thickness. The plate was cooled down for about 12 h to room temperature. The prepared carbon-based composites showed good mechanical strength and low electrical resistance.

Prior to use, the working electrode disc with a surface area of 19.63 mm<sup>2</sup> 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 minutes and rinsing with distilled water.

The electrochemical performance of the electrode was studied by cyclic voltammetry (CV), chronoamperometry (CA) and differential pulse voltammetry (DPV). DPV is a pulse technique, dependent on applied parameters, *i.e.*, a scan rate of 50 mV·s<sup>-1</sup>, a pulse modification of 50 mV in amplitude and 50 ms in duration at intervals of 200 ms.

An electrochemical pre-treatment by three repetitive cyclings between -0.5 V to 1.25 V versus saturated calomel electrodes (SCE) in 0.1 M NaOH 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.

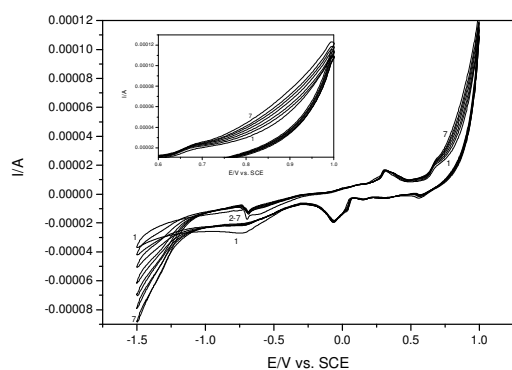
Accumulation was performed at open circuit potential (OCP) in the analyte solution, the electrode was then removed and rinsed with distilled water, and immersed in the detection cell for recording the voltammetric curve. Electrode regeneration was achieved by mechanical polishing and above-mentioned electrochemical pre-treatment.

The reagents of sodium nitrate and sodium sulphate were analytical grade from Merck, freshly prepared with double-distilled water.

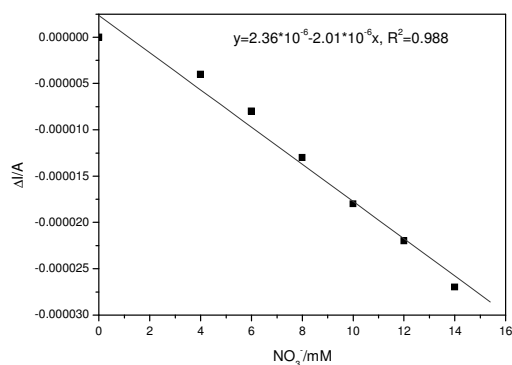
## 3. Results and Discussions

Figure 1 shows the cyclic voltammograms obtained for the Ag composite electrode in 0.1 M NaOH in the presence of different concentrations of sodium nitrate. In the presence of nitrate anions, the cyclic voltammogram is modified on the cathodic range starting with -1.0V vs. SCE, when nitrate reduction occurred. After cathodic scanning, in the anodic potential range of Ag(II) oxide involving [20], the anodic peak increased with nitrate concentration, due to the electrooxidation of nitrite formed by the electrochemical reduction of

nitrate. The cathodic peak registered at -1.35 V vs. SCE increased linearly with nitrate concentration (Fig. 2). It can be underlined that the anodic current of Ag (II) oxide is increased with nitrate concentration, but with a lower sensitivity (see inset Fig. 1).



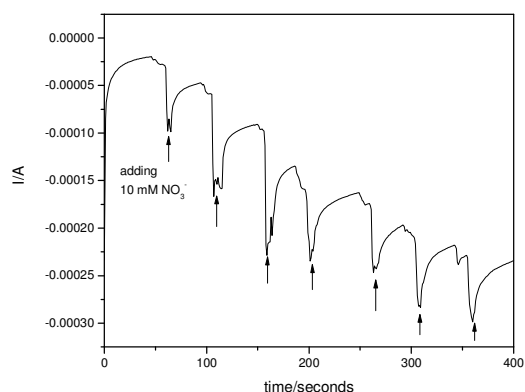
**Fig. 1.** 3rd scan of cyclic voltammograms of AgZEGE in 0.1 M NaOH (curve 1) in the presence of different nitrate concentrations: 2-2.5 mM; 3-4 mM; 4-6 mM; 5-8 mM; 6-10 mM; 7-12 mM.



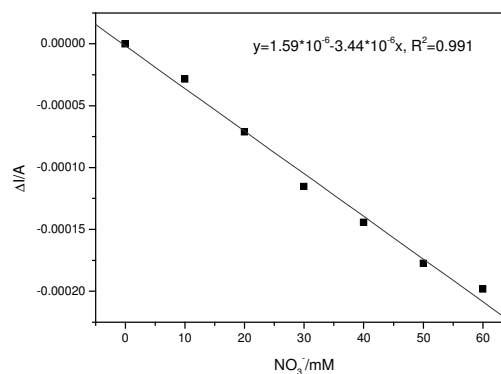
**Fig.2.** The calibration plots of cathodic current from backward branches of CVs recorded at -1.35 V/SCE vs. nitrate concentration

By using chronoamperometry, the direct detection of nitrate anion occurred at the potential value corresponding to the nitrate reduction (-1.35 V/SCE, Fig. 3). The useful net current signals recorded at -1.35 V /SCE (after about 50 seconds) are linearly dependent on the nitrate concentration in the explored concentration range between 10 mM

and 60 mM (Fig. 4). The electroanalytical parameters obtained under these conditions are gathered in Table 1.



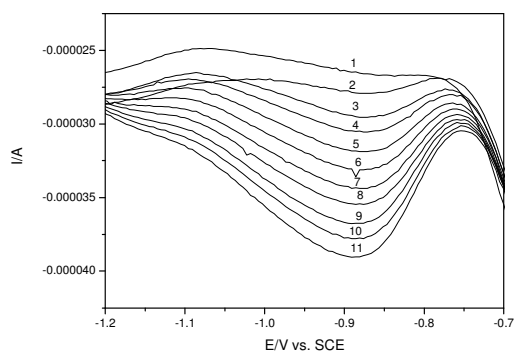
**Fig 3.** Chronoamperometric records obtained at AgZEGE for successive additions of 5 mM nitrate in 0.1 M NaOH supporting electrolyte; working potential: -1.35V/SCE.



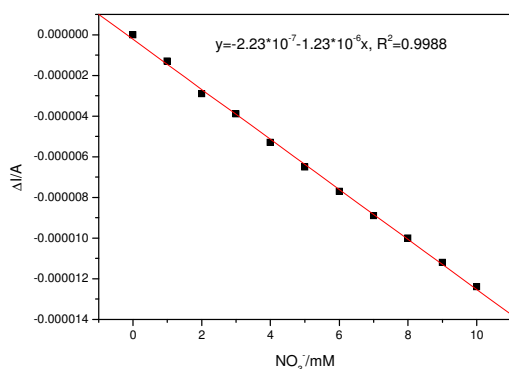
**Fig.4.** The calibration plots of cathodic current recorded after 50 seconds vs. nitrate concentration.

In Fig. 5 is shown the differential pulse voltammograms of AgZEGE electrode in 0.1 M NaOH and in the presence of different nitrate concentrations. Under these conditions of potential range, this technique led to the appearance of the peak of cathodic nitrate reduction much less negative (-0.9 V vs. -1.35 V/SCE at CV or CA application). The correlation between voltammetric

response recorded at -0.88 V /SCE versus nitrate concentration is shown in Fig. 6.



**Fig 5.** Differential pulse voltammograms recorded on AgZEGE electrode with a potential scan rate  $0.05 \text{ V}\cdot\text{s}^{-1}$  between -0.7 V and -1.2 V vs. SCE in 0.1 M NaOH supporting electrolyte (1) and in the presence of different nitrate concentrations: 2-11: 1-10 mM.

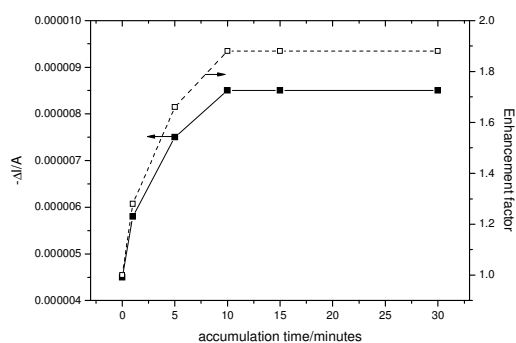


**Fig. 6.** The dependence of differential pulsed voltammetric signal recorded at -0.9 V/SCE vs. nitrate concentration

For using the EG-Z-Ag-Epoxy electrode in preconcentration-voltammetric detection scheme the accumulation time is very important, because it could influence the degree of adsorption on the electrode surface. An important role that may be played by the zeolite is its availability to concentrate species within its porous structure.

To determine the enhancement factor as the ratio of peak current after and before sorption process, the effect of accumulation time on anodic peak current densities were investigated by DPV [Sensorsurea]. Figure 7 shows the dependence of the

useful signal corresponding to the cathodic peak current corresponding to nitrate determination and enhancement factor on the accumulation time for 2 mM nitrate. By increasing accumulation time up to 10 minutes the amount of nitrate at electrode surface increased leading to the enhancement of useful signal. The enhancement factor of about 1.88 revealed an effective concentration effect of nitrate anion on AgZEGE electrode. The better electroanalytical performance obtained by using preconcentration- differential pulsed voltammetric detection scheme is gathered also in table 1.



**Fig. 7.** Peak current responses and enhancement factor for 2 mM nitrate reduction on AgZEGE, as a function of the accumulation time, with background current density subtraction. Detection was performed in 0.1 M NaOH supporting electrolyte by DPVs recorded at -0.88 V/SCE.

The electroanalytical performances for nitrate detection using AgZEGE, with corresponding characteristic parameters, working conditions and techniques applied in various situations are gathered in Table 1. Good sensitivities, correlation coefficients higher than 0.98, and relative standard deviation (RSD) lesser than 5, calculated for three replicates, were associated with the suitable electroanalytical conditions.

The LOD was determined using the equation [20]:

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

**Table 1.** Electroanalytical performance of AgZEGE electrode for the detection of nitrate

Peak potential	Technique used	Concentration range(mM)	Sensitivity (mA·mM <sup>-1</sup> )	LOD*
-1.35	CV	4-14	2,0·10 <sup>-3</sup>	1.0
-1.35	CA	5-35	3,4·10 <sup>-3</sup>	0.9
-0.9	DPV	1-10	1,2·10 <sup>-3</sup>	0.5
-0.9	Preconc/ DPV	0.5-5	2,1·10 <sup>-3</sup>	0.1

#### 4. Conclusions

The Ag-doped zeolite modified expanded graphite composite electrode exhibited the electrocatalytic activity towards the cathodic reduction of nitrate anions. Increasing anodic current due to the oxidation of nitrite resulted from nitrate reduction, informed about the possibility of indirect amperometric/voltammetric detection of nitrate anion.

The cathodic working potential for nitrate reduction was influenced by the type of electrochemical technique. Also, the electrochemical technique, e.g., CV, CA, DPV and preconcentration -DPV influenced the performance of the electroanalytical detection of nitrate.

Even the CA allowed the best sensitivity for the nitrate detection, applying DPV exhibited a better the lowest limit of detection at a cathodic potential less negative.

By applying a chemical preconcentration step prior to voltammetric/amperometric quantification a moderate enhancement of electroanalytical sensitivity and the lowest limit of detection (LOD) for the determination of nitrate at AgZEGE was reached.

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#### 6. References

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