



# A renewable copper electrode as an amperometric flow detector for nitrate determination in mineral water and soft drink samples

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## ABSTRACT

A novel approach was developed for nitrate analysis in a FIA configuration with amperometric detection ( $E = -0.48$  V). Sensitive and reproducible current measurements were achieved by using a copper electrode activated with a controlled potential protocol. The response of the FIA amperometric method was linear over the range from 0.1 to 2.5 mmol L<sup>-1</sup> nitrate with a detection limit of 4.2 μmol L<sup>-1</sup> (S/N = 3). The repeatability of measurements was determined as 4.7% ( $n = 9$ ) at the best conditions (flow rate: 3.0 mL min<sup>-1</sup>, sample volume: 150 μL and nitrate concentration: 0.5 mmol L<sup>-1</sup>) with a sampling rate of 60 samples h<sup>-1</sup>. The method was employed for the determination of nitrate in mineral water and soft drink samples and the results were in agreement with those obtained by using a recommended procedure. Studies towards a selective monitoring of nitrite were also performed in samples containing nitrate by carrying out measurements at a less negative potential ( $-0.20$  V).

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## 1. Introduction

Nitrate can be found naturally in soil, water, vegetables and foods. In soil, the presence of nitrate is essential for the conversion of nitrogen unused by plants and its concentration is controlled by some processes like reduction by bacteria (denitrification), uptake by plants and decay of organic matter [1–3]. Anthropogenic sources of nitrate in soil are correlated to the intensive cultivation of lands and application of nitrogen fertilizers [1–3]. As a result of the high solubility of nitrate in water, this chemical species is easily leached down into groundwater, leading to a contamination of water supplies.

In the last years, concern has been expressed about the increasing levels of nitrate ion in drinking water, due to the toxicological problems associated with the formation of *N*-nitrous compounds [1–4]. Accordingly, these compounds are classified as carcinogenic hazard to humans and animals. Moreover, high levels of nitrate in water could result in disequilibrium of the freshwater ecosystem, due to a fast eutrophication process. The intake of large amounts of nitrate for infants could result in the “blue-baby syndrome”, as a consequence of nitrate reduction in the organism to nitrite and further reaction of this metabolite with haemoglobin. Hence, the absorption and transfer of oxygen to cells is compro-

mised. For this reason, nitrate levels (as N-NO<sub>3</sub><sup>-</sup>) in potable water should not exceed 11 mg L<sup>-1</sup> (or 0.8 mmol L<sup>-1</sup>) and 10 mg L<sup>-1</sup> (or 0.7 mmol L<sup>-1</sup>), according to recommendations of the World Health Organization (WHO) [5] and the US Environmental Protection Agency (EPA) [6], respectively. Taking into account these aspects, it is clear that the development of fast and sensitive methods for quantification of nitrate in natural water samples is a pertinent topic in Analytical Chemistry.

Several procedures have been reported in the literature to quantify nitrate in different matrices and they were reviewed by Compton et al. [7]. Different techniques have been used such as UV/vis, chemiluminescence, fluorimetry, infrared, Raman and molecular cavity emission, chromatography, capillary electrophoresis and electrochemistry. In the case of electrochemical methods, copper [8–15], nickel [16], copper–nickel alloys [17], copper–cadmium alloys [18], copper–palladium alloys [1], platinum [19,20], lead [21], silver [22], rhodium [23], boron-doped diamond [24], gold [25] and polypyrrole nanowires [26] have been employed as substrate materials. The use of bare unmodified electrodes for the direct determination of nitrate is difficult owing to the slow kinetics of the charge transfer step. Hence, methods based on the direct reduction of nitrate are characterised by low sensitivity and irreproducibility and associated with surface passivation effects [27]. Nonetheless, procedures to increase the sensitivity in direct electroanalytical determinations of nitrate are generally associated with activation of the electrodic surface, especially when copper cathodes [13] are used. The indirect determination of nitrate

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has been proposed after a derivatisation procedure [28], as also reported in a method for nitrite analysis [29].

The use of a copper surface as amperometric detector in a flow-through configuration has been already explored by our group in the determination of sulphite in alkaline conditions [30]. As fresh copper surfaces are more effective for cathodic reactions, we have also proposed the development of a renewable process for the activation of copper electrodes without the necessity to introduce copper ions into the sample [13]. However, as the majority of other published works involving the electroanalytical determination of nitrate, measurements were obtained in a batch mode with low analytical frequency. In the present work, we describe our efforts to associate the renewable copper surface with a mechanised process (flow injection analysis). The analytical applicability of this high-throughput proposed method was examined by measuring the nitrate content in mineral water and soft drink samples.

## 2. Experimental

### 2.1. Chemicals, materials and samples

All solid reagents were of analytical grade and were used without further purification. Sulphuric acid, sodium sulphate, potassium nitrite and potassium nitrate were obtained from Merck (Darmstadt, Germany). The supporting electrolyte for flow injection experiments was a  $0.1 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_4$  solution, pH 2.0 (adjusted with  $\text{H}_2\text{SO}_4$ ). In almost all cases the solutions were prepared by dissolving the reagents in deionised water processed through a water purification system (Nanopure Infinity, Barnstead). Samples of mineral water and soft drink were acquired from a local market. Carbon dioxide was removed from soft drink samples by thorough bubbling with argon. Nitrite solutions were standardised as reported in the literature [31].

### 2.2. Electrodes and instrumentation

An Autolab PGSTAT 30 (Eco Chemie) bipotentiostat with data acquisition software made available by the manufacturer (GPES 4.8 version) was used for electrochemical measurements. Experiments were done in a conventional electrochemical cell, a Ag/AgCl (saturated KCl) electrode and a stainless-steel tube being used as reference and counter electrodes, respectively. A copper sheet (Pertech® of Brazil) fabricated by copper electroplating in a substrate composed of paper and phenolic resin was used as working electrode (area =  $56 \text{ mm}^2$ ). This copper sheet is used for fabrication of printed circuit boards. The flow injection apparatus consisted of an aquarium air pump (to propel the solution by pressurization), a homemade rotatory injection valve and an acrylic cell mounted in a thin layer configuration [32,33].

### 2.3. Activation of the electrode surface in FIA experiments

The working electrode surface is activated by two potential steps prior current measurements, Fig. 1. To drive copper dissolution, the working electrode is polarised at +0.50 V (step a). Then, the redeposition is carried out at -0.25 V (step b). Both steps are performed in absence of flow, otherwise, copper ions would escape from the diffusion layer after the anodic dissolution. These two steps (copper dissolution and redeposition) are required to produce a fresh copper layer with an active role concerning the cathodic reduction of nitrate, as previously demonstrated [13]. The optimisation of both time parameters involved in the pre-treatment potential program (steps a and b) was investigated as an attempt of enhancing the sensitivity of nitrate determinations. After the activation process, the electrode was polarised at the potential required for nitrate reduction. Three samples were injected after each activation step.

### 2.4. Spectrophotometric analysis

An evaluation of the accuracy of the proposed method for quantitative determinations of nitrate in mineral water samples was performed by UV-spectrophotometry without derivatisation at 220 nm in a Hitachi U-3000 spectrophotometer using a 1.00 cm optical pathlength quartz cuvette. As soft drink samples are more complex and contain large amounts of organic compounds (glucose), comparative measurements were obtained with the UV-spectrophotometry Griess assay. The reduction of nitrate to nitrite was accomplished by using a copperised cadmium reactor column prior to spectrophotometric measurements with the Griess method at 543 nm.

## 3. Results and discussion

Previous reports on the literature [8,12,13] have demonstrated that the reduction of nitrate can be promoted on a fresh copper surface, in accordance with Eq. (1):



Taking into account the necessity of a fresh copper layer, a protocol involving the dissolution of the outer copper layer for further redeposition of copper ions is required. A schematic representation of the pre-treatment procedure used in the FIA system is shown in Fig. 1. At the activated detector surface, FIA experiments were carried out to investigate the best applied potential for nitrate reduction. From the results obtained in hydrodynamic voltammetric experiments (not shown), the working potential value -0.48 V was selected as the most appropriate to ensure complete analyte reduction at the copper sensor.

The optimisation of both parameters (dissolution and redeposition time) was also investigated. Data in Fig. 2, curve A, shows that no faradaic signal is obtained at a non pre-treated surface (i.e. bare copper electrode), a different situation being observed as the amount of copper ions redeposited during the cathodic process increases (for a constant dissolution time). In a similar way, the signal for nitrate reduction increases with the increase in the dissolution time (for a constant redeposition time) (Fig. 2, curve B). Optimal conditions were achieved by using 30 s, respectively, for the dissolution and redeposition steps, and this procedure was employed for all analytical determinations.

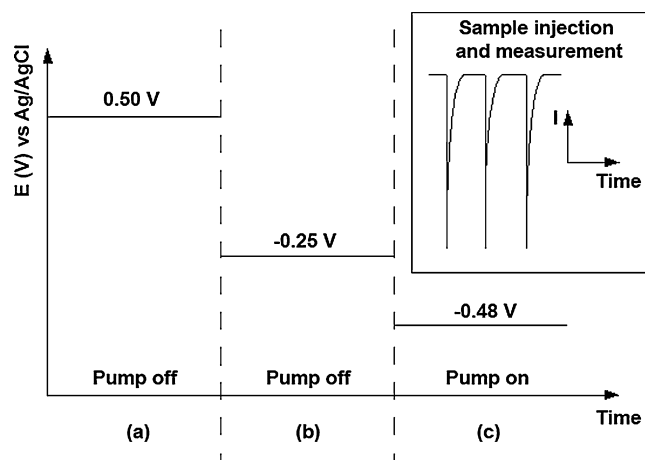


Fig. 1. Schematic representation of the copper surface activation protocol in the FIA system: copper dissolution (a); copper redeposition (b) and nitrate electroreduction (c). The inset shows the amperometric signal recorder after 3 injections of a nitrate solution in the FIA apparatus.

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