



Development of electrochemical sensors based on silver nanoparticles electrodeposited on gold screen-printed electrodes: application to nitrate trace analysis in water

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Abstract. A simple, reusable and sensitive electrochemical sensor based on a gold screen-printed electrode modified with silver nanoparticles has been developed for the detection of nitrate in water. Scanning electron microscopy, square wave voltammetry and electrochemical impedance spectroscopy were used to characterize the modification of the electrode surface. The modified electrode with different silver nanoparticle loadings was also tested, as well as the influence of scan rate on the reduction of nitrate. The sensor exhibited a wide linear response to nitrate from 100 to 1500 μM and a detection limit of 7.7 μM , which is significantly less than the maximum contaminant level admitted in drinking water (800 μM). The reproducibility, repeatability and selectivity of the sensor have also been examined. The suitability of the proposed sensor for real sample detection was successfully demonstrated via recovery studies performed in spiked tap water samples. The proposed approach was used to determine nitrate in freshwater, and the results were in good agreement with those obtained from a commercial nitrate sensor. These advantages make the developed sensor a promising alternative approach for integration into an online monitoring system for water monitoring.

1 Introduction

Nitrogen species play an important role in determining freshwater ecosystem health and ecological status. Nitrate (NO_3^-) can be found naturally in soil, water, vegetables and foods. Moreover, these ions are widely used as food preservatives and fertilizers; thus, wastewater from anthropogenic activities such as agriculture and industry results in significant hazards to environmental waters (Wakida and Lerner, 2005). High levels of nitrate can cause unnatural blooms of aquatic plants and algae, resulting in “red tides” and the death of fish (Camargo et al., 2005; Lee, 2006). In addition, when nitrate enters the food chain through groundwater or surface water, it can have negative effects on human health. In infants, for example, nitrate is the main cause of blue baby disease or methemoglobinemia, through drinking water containing high concentrations of nitrate (Knobeloch et al., 2000). Thus, concern has been expressed regarding high nitrate ion levels in water. For this reason, the maximum contaminant level of nitrate in drinking water should not exceed 800 μM accord-

ing to recommendations of the World Health Organization (WHO; World Health Organization, 2006). Therefore, developing sensors for detecting nitrate at trace concentrations has become a very important subject of research. Several analytical methods have been reported and used for the determination of nitrate in different matrices including ion chromatography (Lopez-Moreno et al., 2016), high-performance liquid chromatography (HPLC) (Kodamatani et al., 2009), ultra-performance liquid chromatography (UPLC) (Siddiqui et al., 2015), UV spectrometry (Alahi and Mukhopadhyay, 2018) and mass spectroscopy (Li et al., 2011). However, these methods require dedicated equipment, large bench space, long analysis times and highly qualified technicians which makes them expensive and inconvenient for faster detection of nitrate. Currently, much interest is given to developing rapid, accurate and portable methods for the determination of nitrate in the field, and electrochemical sensors are one of the most promising approaches. In the scenario of electroanalytical methods dedicated to automated determination of large numbers of samples, an excited and intelligent strategy is the

coupling of a flow injection analysis (FIA) system with an electrochemical sensors for the detection of nitrate (Gamboa et al., 2009b; Badea et al., 2001; Bui et al., 2016). FIA offers interesting advantages such as versatility, accuracy, low cost, speed and automation, among others. Modification of the surfaces of such electrochemical sensors with nanomaterials can enhance these advantages due to their high surface area, high electrical conductivity, high catalytic activity and strong adsorption capability, which have made them very valuable (Ahmad et al., 2017; Ben Messaoud et al., 2018, 2017b; Ben Jaballah et al., 2022, 2021; Gaur et al., 2021; Paulraj et al., 2021, 2020; Lokesh et al., 2016; Thanigai Arul et al., 2016; Saasa et al., 2015). Some of the nanomaterials which have been used as catalysts for the electro-reduction of nitrate are platinum (Dima et al., 2003), copper (Motaghedifard et al., 2021), carbon (Wang et al., 2018), gold (Zhao et al., 2019) and silver (Wang et al., 2021a). Because of their excellent electrocatalytic activity and large surface-to-volume ratio, silver nanoparticles (AgNPs) have also been used for the modification of electrodes. However, the preparation and modification of electrochemical sensors based on AgNPs for nitrate in reported studies seem to be complex and time-consuming, such as the following composites containing AgNPs: AgNPs–chitosan–polyvinylpyrrolidone (Wang et al., 2021b), AgNPs–polypyrrole (Atmeh and Alcock-Earley, 2011; Ghanbari, 2013) and AgNPs–polymethacrylic acid (Bonyani et al., 2016). Although the reported levels of nitrate are low, it is still a challenge to determine nitrate directly in water samples without the need for pH adjustment (Patella et al., 2021; Hanane et al., 2020).

In the present work, a simple, reusable and easy-to-prepare electrochemical sensor based on a gold screen-printed electrode (AuSPE) modified with AgNPs was developed. In order to obtain the highest sensing performance, the optimal electrodeposition time of AgNPs, as well as the best deposition technique, was evaluated. Furthermore, a NaCl solution, at neutral pH, was used as electrolyte, providing the opportunity to directly measure nitrate content in real water samples without the need to change the electrolyte pH, condition which is often required for the detection of nitrate as reported in the literature (Liang et al., 2016; Li et al., 2012; Tsai et al., 2010). The surface modification was characterized by scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV) as well as the analytical performance of the modified electrodes. The sensitivity, reproducibility, selectivity, repeatability and stability of the sensor have been determined. The developed analytical approach was applied successfully for the determination of nitrate in real environmental freshwater samples without the need for pH adjustment, and equivalent results were obtained and compared to commercial nitrate sensors. Moreover, the developed nitrate electrochemical sensor was applied to real environmental freshwater samples without spiking with standard solutions.

The features of the proposed sensor, including simplicity and celerity of the fabrication and analysis, as well as the good performance and stability in time at room temperature, make this sensing technology a promising alternative approach for its integration into portable sensing platforms for nitrate detection in water.

2 Experimental

2.1 Reagents and materials

Potassium nitrate (KNO_3), silver nitrate (AgNO_3), sodium chloride (NaCl), potassium ferricyanide [$\text{K}_3\text{Fe}(\text{CN})_6$], potassium ferrocyanide [$\text{K}_4\text{Fe}(\text{CN})_6$], interfering substances (calcium dichloride (CaCl_2), potassium chloride (KCl), sodium nitrite (NaNO_2), sodium bicarbonate (NaHCO_3), sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$), magnesium sulfate (MgSO_4)), and a phosphate-buffered saline (PBS) tablet were purchased from Sigma-Aldrich. Gold screen-printed electrodes (AuSPEs) (ref. C223AT) and the respective connector (ref. DSC) were purchased from DropSens, Spain. The AuSPE consists of a ceramic substrate with a three-electrode system where the gold and counter electrodes are made of gold, and the reference electrode is made of silver. The diameter of the working electrode was 1.6 mm, resulting in a geometric area of 2.01 mm^2 .

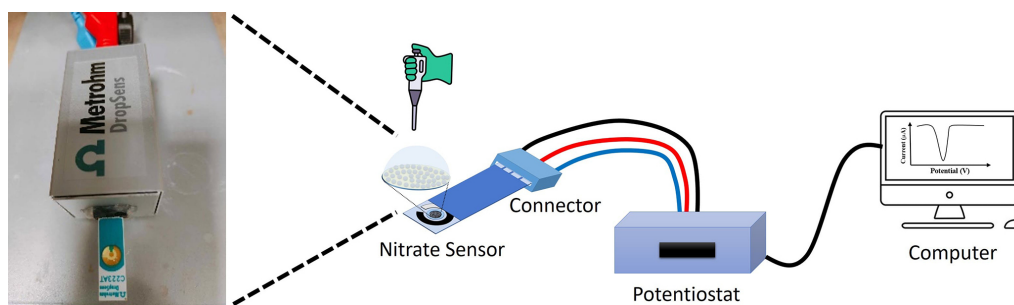
2.2 Solutions

A stock solution of nitrate and of the interferents were dissolved in NaCl solution (0.6 M). A 10 mM sulfuric acid solution (H_2SO_4) was used to clean the electrode surface before the modification. A 3.5 mM AgNO_3 solution dissolved in KNO_3 was used as electrolyte solution (at a concentration of 100 mM). A 5 mM [$\text{Fe}(\text{CN})_6$] $^{3-}$ / $^{4-}$ solution was prepared in 10 mM PBS solution ($\text{pH} = 7.4$) using $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$. Freshwater samples were filtered through a $0.2 \mu\text{m}$ sterile polyethersulfone filter and tested with the developed electrochemical sensors as well as with a commercial nitrate potentiometric electrode (perfectionTM, ref. 51344727, from Mettler Toledo).

2.3 Instrumentation and electrochemical measurements

The electrochemical measurements were performed using a potentiostat/galvanostat (PGSTAT302N/FRA32M) monitored by NOVA 2.1 software from Metrohm Autolab, the Netherlands. The sensors were connected to the potentiostat using a connector to read out the SPEs (ref. DSC, DropSens, Spain). The scheme of the experimental setup is presented in Scheme 1.

For electrodeposition of the AgNPs onto the gold electrodes surface, chronoamperometry was used, applying a -0.2 V potential step for 7 s.



Scheme 1. Electrochemical measurement setup.

Cyclic voltammetry (CV) measurements were recorded over a potential range from 0 to +1.5 V in 0.01 M H₂SO₄ at a scan rate 100 mV s⁻¹ for the pretreatment of the AuSPE and from -1.4 to 0 V for the study of the electrochemical behavior of the nitrate sensor using different scan rates between 10 and 100 mV s⁻¹ and 5 mV as potential step.

To confirm the electrode surface modification, EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz and with a root mean square (rms) perturbation voltage of 5 mV in a 5 mM of [Fe(CN)₆]^{3-/4-} solution.

To characterize the electrode modification and test the nitrate sensor, SWV measurements were carried out at a pulse amplitude of 60 mV with a frequency of 100 Hz. The potential varied from 0.0 to -1.4 V.

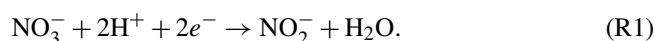
For the testing of the analytical performance of the sensors, different concentrations of nitrate were tested (from 50 to 10 000 µM).

Potentiometric measurements of real samples were performed at room temperature using a commercial nitrate ion-selective electrode (ISE) of inner filling solution (perfectION™, ref. 51344727) connected to a pH/ion meter S220 (SevenCompact™, ref. 30019028) from Mettler Toledo.

2.4 Electrode modification

The AuSPE was rinsed with isopropanol and Milli-Q water and dried with N₂. Secondly, The AuSPE was conditioned in sulfuric acid solution (H₂SO₄, 0.01 M) by cyclic voltammetry between $E_1 = 0$ V and $E_2 = 1.5$ V at 100 mV s⁻¹ until reproducible cycles were obtained (20 cycles). The electrodeposition process of the AgNPs onto the gold electrode surface was previously reported (Ivanišević, 2023; Zahran et al., 2021) for electrochemical sensors development. Briefly, the electrodeposition of the AgNPs onto the gold electrodes was performed by casting a drop (75 µL) of KNO₃ solution containing 3.5 mM of AgNO₃ on the surface of the AuSPE, followed by the application of a voltage ($E = -0.2$ V), using a chronoamperometry method for 7 s. Thereafter, the modified electrode was washed with Milli-Q water and dried with N₂.

Figure 1 shows the fabrication process of the proposed reusable and easy-to-fabricate nitrate sensor. According to the references (Huang et al., 2012; Dhanya et al., 2013), the most probable mechanism is that a AgNP film catalytically reduces H⁺ to form nascent hydrogen. This produced nascent hydrogen will then react with nitrate, which will further react with the electrode surface to form nitrite. Therefore, AgNP layers should lead to the formation of a catalyst that can be used for the selective electrochemical reduction of NO₃⁻ to NO₂⁻ according to the following reaction:



3 Results

3.1 SEM characterization

The electrode surfaces before and after modification were investigated by SEM (Fig. 2). Figure 2a shows the SEM image of the bare AuSPE. After electrode surface modification, the SEM image (Fig. 2b) clearly shows the presence of AgNPs. To confirm that, energy-dispersive X-ray mapping (Fig. 2c) reported the presence and the homogeneous distribution of AgNPs (blue color) on the electrode surface.

3.2 Optimization of the modified electrode preparation

In order to control the exact quantity of silver nanoparticles deposited on the gold surface, the electrodeposition realized to form AuSPE/AgNPs electrodes was controlled by time. Therefore, the effect of electrodeposition time was studied by varying the time range from 5 to 15 s. As shown in Fig. 3, the highest current response of the proposed sensor for nitrate detection was achieved with an electrodeposition of 7 s. Thus, the electrodeposition time of 7 s was selected and used for further studies to maximize the sensitivity of the sensor for the determination of nitrate.

3.3 Electrochemical properties of the modified electrode

Unmodified and modified electrodes were characterized by SWV in the presence of nitrate. Figure 4 shows SWV in NaCl solution (0.6 M) containing 10mM nitrate at bare AuSPE and

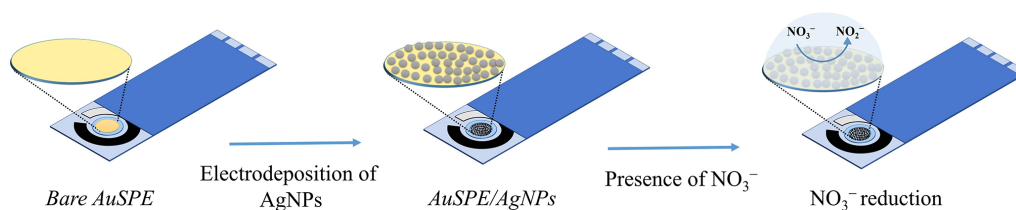


Figure 1. Schematic illustration of the electrode modification process of the proposed nitrate sensor.

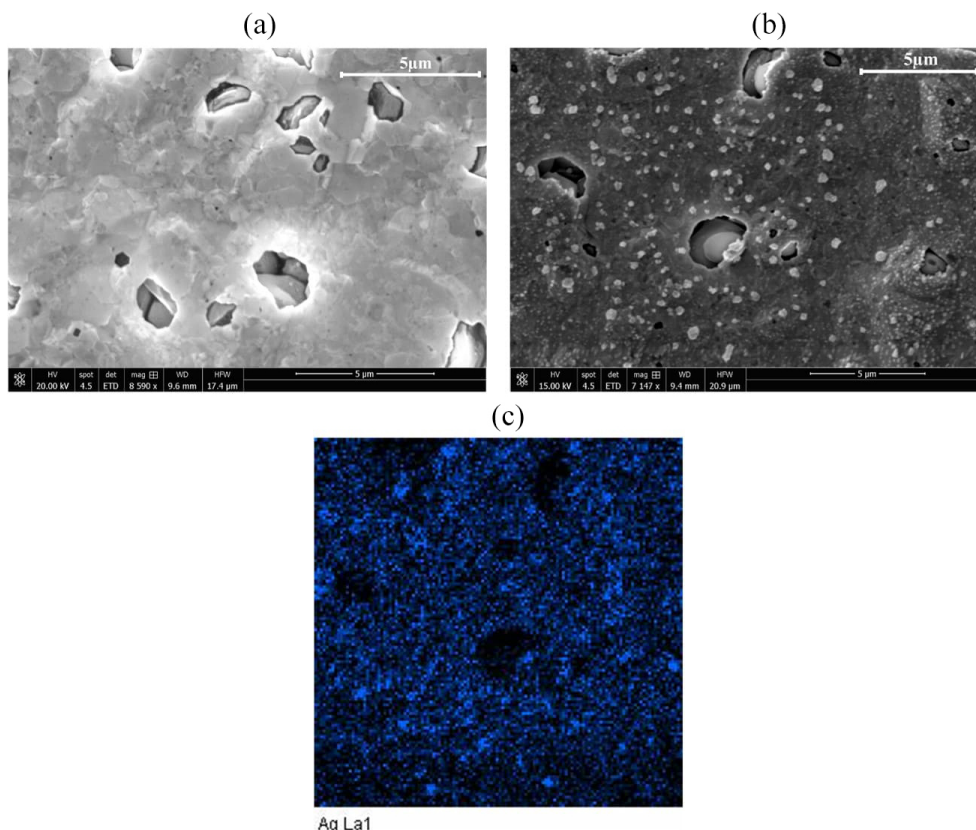


Figure 2. SEM micrographs of bare AuSPE (a) and after AgNP deposition (b). Mapping analysis of the AgNPs on the AuSPE surface (c).

AuSPE/AgNPs. After modifying the electrode with AgNPs, a reduction peak of nitrate was observed at -1.05 V, indicating that their presence on the surface of AuSPE catalyzes the reduction of nitrate. This result could be attributed to the unique physicochemical and catalytic properties of AgNPs, as well as their superior electrical conductivity (Paul et al., 2021; Zahran et al., 2021).

The EIS method was used to investigate the electron transfer on the interface of the bare and modified AuSPEs. This technique has been widely employed for the electrochemical behavior investigation of the reaction dynamics and the membrane/solution structure (Ben Messaoud et al., 2016, 2017a, 2023, 2022). Figure 5 presents Nyquist plots of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at different electrodes. The Nyquist spectra of bare AuSPE and AuSPE/AgNPs were fitted using an appropriate equivalent circuit shown in the inset of Fig. 5. The

circuit comprises the solution resistance (R_s) in series with a parallel combination of a charge transfer resistance (R_{ct}) and Warburg impedance (W); both are in parallel with constant phase element (CPE). A decrease of R_{ct} was observed when the AuSPE was modified with AgNPs from 335.6 to 290.1Ω , indicating that AgNPs enhance the conductivity and facilitate electron transfer compared with the bare AuSPE.

3.4 Electrochemical behavior of nitrate at the modified electrode

Useful information involving electrochemical mechanisms generally can be acquired from the relationship between current density and scan rate. Therefore, the influence of scan rate on the reduction of 10 mM nitrate at AuSPE/AgNPs was studied by CV and is illustrated in Fig. 6a. It can be seen that

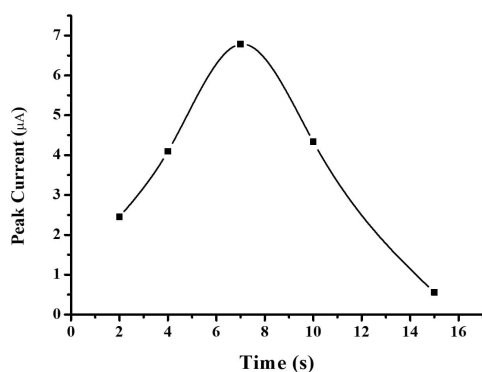


Figure 3. Influence of electrodeposition time of AgNPs in the reduction of peak current for the detection of $500 \mu\text{M NO}_3^-$ using the SWV method.

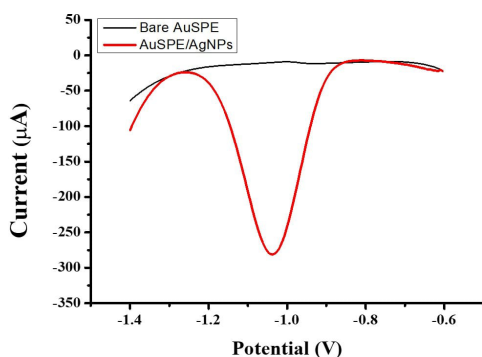


Figure 4. SWV of bare AuSPE and AuSPE/AgNPs in NaCl solution (0.6 M, pH = 7) containing 10 mM nitrate.

peak current density increases linearly with the square root of scan rate in the range from 10 to 100 mV s^{-1} (Fig. 6b), indicating that the reduction of nitrate was controlled by diffusion processes in the range of scan rate studied, which is coherent well with AgNPs-based sensors for nitrate reported in the literature (Wang et al., 2021b; Bonyani et al., 2016; Ghanbari, 2013).

3.5 Determination of nitrate

3.5.1 Analytical performance

The analytical performance of the sensor was studied and optimized in order to find a stable relation between the variation of NO_3^- concentration and the measured current. The determination of nitrate using the optimized configuration, AuSPE/AgNPs, was performed by SWV for different nitrate concentrations and is shown in Fig. 7a. With the increase in nitrate concentration, more nitrate ions will be available on the electrode surface for reduction, and there is a proportional increase in the measured peak current. The calibration plot constructed from the SWV response, illustrated in Fig. 7b, shows a linear range from 100 to $1500 \mu\text{M}$. The detection

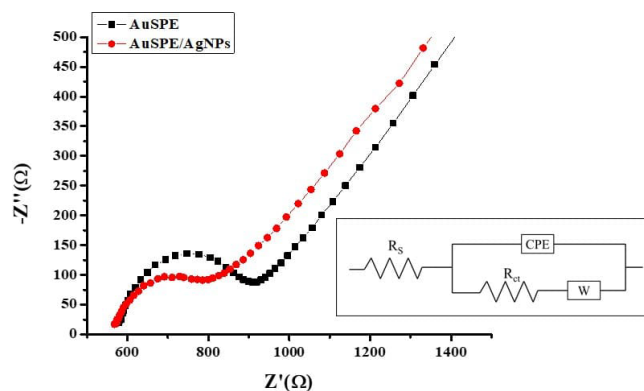


Figure 5. Nyquist plots of bare AuSPE and AuSPE/AgNPs in the solution of $5 \text{ mM } [\text{Fe}(\text{CN})_6]^{3-/4-}$; the inset is the equivalent electrical circuit used to fit both Nyquist spectra.

limit was determined to be $7.7 \mu\text{M}$ ($N = 4$), which was calculated as $(3 \times \text{SD}_{\text{blank}}) / \text{slope}$ (Shrivastava and Gupta, 2011).

The performance obtained by the proposed sensor is important as it is clear from the comparison with previous reports on modified electrode sensors with nanomaterials, shown in Table 1. Also, remarkable advantages such as simplicity and fast preparation time (of only 7 s) were achieved compared to other reported architectures from the literature, as shown in Table 1. Another major merit of the current approach is that the developed sensor can be used around neutral pH, which is a necessary condition for direct nitrate analysis in real environmental samples. Most nitrate sensors based on other modified materials can only be used effectively in acidic or basic aqueous conditions (Liang et al., 2016; Li et al., 2012; Tsai et al., 2010), which does not allow them to directly monitor nitrate levels in water that has a pH close to neutral in nature.

3.5.2 Reproducibility, repeatability and stability at AuSPE/AgNPs

Reproducibility, repeatability and stability are key elements of the sensor performance. Reproducibility is the ability of a sensor to yield identical results regardless of the number of times the sensor fabrication is repeated. The reproducibility of the fabricated sensor towards nitrate detection was calculated by taking the response of four separately fabricated sensors ($N = 4$). For that, the relative standard deviation (RSD) value of the current values measured from each fabricated sensor was calculated. RSD less than 10 % is desirable. The RSD for measuring $2000 \mu\text{M}$ nitrate by SWV at four different electrodes prepared in the same way was 1.7 %. This shows that the AuSPE/AgNPs modification has a good reproducibility, and it is better than that achieved by some reports (Can et al., 2012; Manea et al., 2010; Li et al., 2019; Andreoli et al., 2011; Zhou et al., 2013; Tsai et al., 2010). Since there is no significant difference between the prepared electrodes,

Table 1. Comparison of the analytical performance of the proposed sensor for nitrate detection with literature reports.

Electrode configuration	Electrode deposition time	Method	pH	Linear range (μM)	LOD (μM)	Reproducibility RSD (%)	Stability with time	Real samples tested	Reference
Cu/PPM	Cu (16 s)	CV	3	12.5–300	NA	NA	NA	NA	Li et al. (2010)
Graphene/PDDA/PSS/CuNP/AuE	PDDA (20 min) PSS (10 min) Graphene (20 min) CuNP (NA)	DPV	NA	10–90	7.9	NA	NA	Lake water	Wang et al. (2018)
CNT/PPy/NRBE	NA	Amperometry	7.5	440–1450	170	5.4	70% after 10 d	Spiked water	Can et al. (2012)
AgZEGE	NA	CV/ Amperometry	7	1000–10 000	100 (CV) 600 (CA)	4.1 (CV) 3.8 (CA)	NA	Spiked tap water	Manea et al. (2010)
μCuE array	NA	SWV	2	10–1070	1.8	NA	NA	Mineral water	Iranaldo S da Silva et al. (2013)
CuMSs/PANI/MNE	PANI (≈ 8 min) CuMSs (12 s)	DPV	2	20–6000	8	NA	At least 7 d	River water	Li et al. (2019)
Ag/CUME and Ag/AgUME	Ag (100 s)	CV	7	4–1000	3.2–5.1	NA	NA	Spiked synthetic aquifer	Zhad and Lai (2015)
Ag/ITO	NA	SWV	14	20–5000	NA	3.3	NA	NA	Tsai et al. (2010)
AgNPs/PPy/GC	PPy (300 s) AgNPs (10.1 s)	DPV	7	2–100	2	1.1	80% after 60 d	Sausages, cheese and mineral water	Ghanbari (2013)
Cu nanowire	NA	LSV	1	10–400	1.7–3	NA	NA	Mineral water	Stortini et al. (2015)
Cu sheet by electroplating	NA	Amperometry	2	100–2500	4.2	NA	NA	Soft drinks, mineral water	Gamboa et al. (2009a)
Graphene/Cu	NA	Amperometry	13	9–940	10	NA	NA	NA	Özgülter et al. (2013)
AgNPs/AuSPE	AgNPs (7 s)	SWV	7	100–1500	7.7	1.7	85.36% after 43 d	Spiked tap water, freshwater	This work

LOD: limit of detection; CV: cyclic voltammetry; DPV: differential pulse voltammetry; Cu: copper; PPy: plated platinum microelectrode; CuNP: copper nanoparticles; AuE: gold electrode; PDDA: poly(diallyldimethylamine chloride); PSS: poly(sodium 4-styrene sulfonate); CNT: carbon nanotube; PPy: polypyrrole; NRBE: nitrate reductase biofilm electrode; AgZEGE: Ag-doped zeolite-expanded graphite-epoxy composite electrode; μCuE : copper microelectrodes; CuMSs: copper microspheres; PANI: polyaniline; MNE: micro-needle electrode; GC: glassy carbon; Ag: silver; CUME: carbon ultramicroelectrode; AgUME: silver ultramicroelectrode; ITO: indium tin oxide; AgNPs: silver nanoparticles; LSV: linear sweep voltammetry; NA: not available.

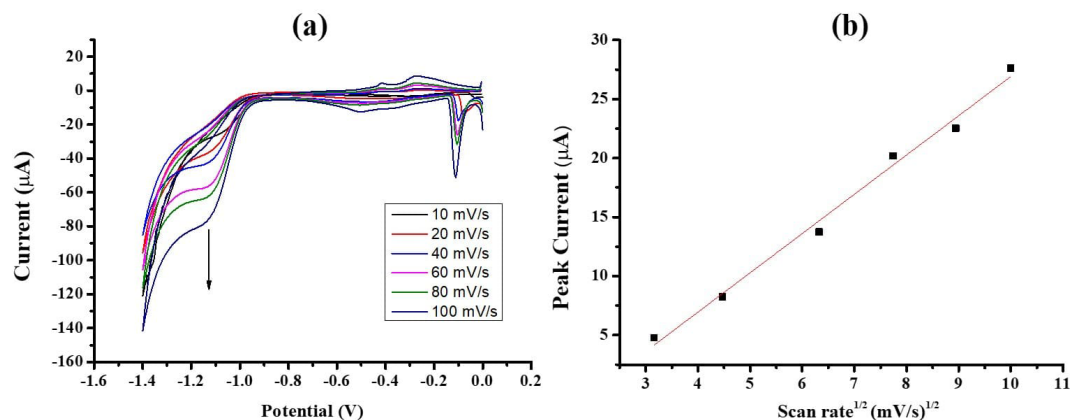


Figure 6. (a) Cyclic voltammograms at AuSPE/AgNPs in NaCl (0.6 M, pH=7) containing 10 mM nitrate at 10, 20, 40, 60, 80 and 100 mV s⁻¹. (b) Plot of reduction peak current density vs. square root of scan rate.

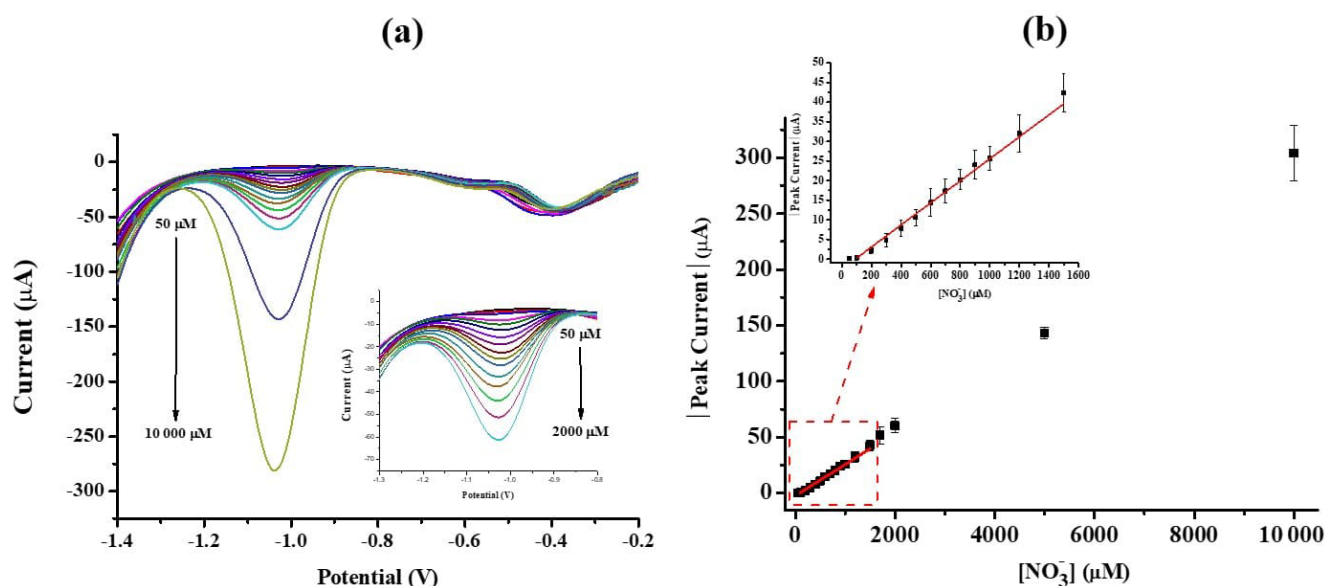


Figure 7. (a) SWV of different concentrations of nitrate from 50 to 10000 μM at AuSPE/AgNPs in NaCl (0.6 M, pH=7); the inset is the magnified SWV plot at low concentration. (b) Corresponding calibration curve ($N = 4$).

the same calibration curve could be applied to all the sensors. The repeatability of the single AuSPE/AgNP-modified sensor toward 2 mM nitrate was studied by observing the current response over 11 independent SWV measurements under the same experimental conditions. Between measurements, the electrodes were rinsed with Milli-Q water and dried with N₂. An RSD of 2 % (Fig. 8) was achieved for the repeatability tests, which is superior to other reported sensors (Ahmad et al., 2017; Zhou et al., 2013; Alagha et al., 2020). The stability of the proposed sensor was also investigated by measuring the electrode response with 1 mM nitrate on different days. Between measurements, the electrodes were stored dry and at room temperature, since it was envisioned that the application of these sensors is in a real scenario where sensors can only be kept at room temperature. The current response

decreased to 91.3 % after 6 d, while the current response retained 85.3 % of the initial response after 43 d, which indicates the good storage capability of the present sensor. The stability obtained by the present sensor is better compared to that obtained in Zhou et al. (2013) (92 % in 30 d) and Can et al. (2012) (70 % in 10 d), but in those studies the electrode was kept at 4 °C. These studies suggest that storage at lower temperature could increase the stability of the sensor for longer periods of time (> 45 d). Therefore, other conditions must be tested in the future to increase the stability of our developed sensor.

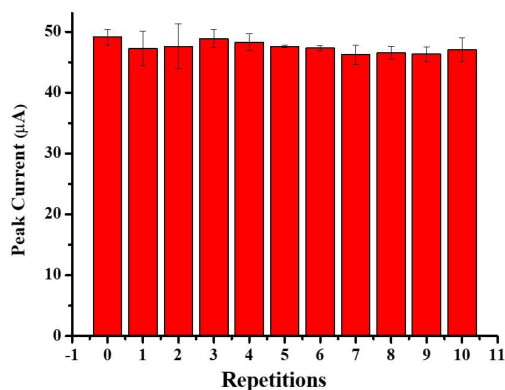


Figure 8. Response of AuSPE/AgNPs repeated 10 times using the same modified electrode.

Table 2. Influence of interferents, at a concentration of 10 mM, on the response to 1 mM nitrate.

Interferent	Peak current change (%)
Ca^{2+}	-1.0
K^{+}	-0.5
NO_2^{-}	-2.7
HCO_3^{-}	+1.3
$\text{CH}_3\text{COO}^{-}$	-0.1
Mg^{2+}	-1.9
CO_3^{-}	+2.8

3.5.3 Interferences and practical application

The selectivity of the electrochemical sensor towards nitrate was investigated in the presence of some possible interfering substances at concentrations 10-fold higher than nitrate. The interferents tested included Ca^{2+} , K^{+} , NO_2^{-} , HCO_3^{-} , $\text{CH}_3\text{COO}^{-}$, Mg^{2+} and CO_3^{-} . As can be seen in Table 2, none of them exhibited a significant change in the nitrate response; the signal change was less than 3 % for all interferents. The proposed sensor thus demonstrated a good selectivity for the determination of nitrate.

In order to evaluate the performance of AuSPE/AgNPs in practical analytical applications, the sensor performance for the determination of nitrate in real water samples was carried out. To keep the same conditions performed for the calibration curve, a solution with the same ionic-strength properties was used for the measurement, by mixing equal parts of water sample and a 1.2 M NaCl solution. The doped samples were then spiked with different amounts of nitrate (500, 1000 and 5000 μM). Accuracy was determined through recovery experiments. The recovery percentage (%) was calculated by the following equation according to IUPAC Recommenda-

Table 3. Nitrate detection using the AuSPE/AgNPs sensor and standard nitrate sensor in three freshwater samples.

Samples	Results from commercial sensor (μM)	Results from AuSPE/AgNPs (μM)
Freshwater 1	576.6	667.3
Freshwater 2	1283.3	1331.6
Freshwater 3	1700.0	1501.1

tions 2002 (Burns et al., 2002).

$$\text{Recovery (\%)} = \frac{[\text{NO}_3^{-}]_{\text{found}} - [\text{NO}_3^{-}]_{\text{sample}}}{[\text{NO}_3^{-}]_{\text{added}}} \times 100, \quad (1)$$

where $[\text{NO}_3^{-}]_{\text{found}}$ is the concentration of nitrate measured from the spiked sample, $[\text{NO}_3^{-}]_{\text{added}}$ is the concentration of nitrate added (spike value) and $[\text{NO}_3^{-}]_{\text{sample}}$ is the concentration of nitrate from the original sample which in this case is equal to zero because nitrate was not found in the tap water samples. Recovery values close to 100 % indicate higher trueness of the method (Taverniers et al., 2004). The recoveries achieved were 101.9 %, 103.2 %, and 101.0 %, respectively, indicating that the sensor is adequate for application in water samples.

To validate the potential application of the developed sensor in natural water samples, three freshwater samples were tested by using the proposed sensor and comparing with a commercial potentiometric ion-selective nitrate sensor (Table 3). Comparable results were obtained using both sensors, with an RSD between 2.6 % and 10.3 % for three samples tested, indicating the trustful analytical performances of the developed sensor.

4 Conclusions

A simple, reusable and sensitive electrochemical sensor based on a AuSPE modified with AgNPs has been developed for nitrate detection. Different amounts of AgNPs were tested, and the best experimental condition for higher sensitivity was obtained with a electrodeposition time of 7 s. The proposed AgNP-based sensor shows important features such as a low detection limit of 7.7 μM and wide linear detection range from 100 to 1500 μM . Moreover, the sensor showed a good repeatability and stability, a short time of analysis, and a high selectivity towards nitrate compared to other possible interferent species (Ca^{2+} , K^{+} , NO_2^{-} , HCO_3^{-} , $\text{CH}_3\text{COO}^{-}$, Mg^{2+} and CO_3^{-}). The practical application in spiked tap water samples was successfully carried out, achieving good recoveries (between 101.0 % and 103.2 %). Moreover, the developed sensor was efficaciously applied for the determination of nitrate in freshwater samples with comparable results to commercial nitrate sensors.

The unique advantages of the proposed sensor, such as small footprint, cost-effectiveness, simplicity, fast analysis, low sample volumes (typically in the microliter range) required and good performance provide a promising alternative approach for the integration of the developed sensor into a portable or automated sensing platform for nitrate detection in water. In this way, the sensing system may be helpful for screening of nitrate in water bodies, speeding up decision-making at different levels.

Data availability. No data sets were used in this article.

Author contributions. NBM: investigation, methodology, formal analysis, validation, writing (original draft and review and editing). MBdS: conceptualization, investigation, methodology, formal analysis, writing (original draft and review and editing). BE: conceptualization, supervision, writing (review and editing), funding acquisition, project management. RBQ: conceptualization, investigation, methodology, formal analysis, funding acquisition, project management, supervision, writing (original draft and review and editing).

Competing interests. The contact author has declared that none of the authors has any competing interests.

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