

Screen-printed Potentiometric Selective Electrode Based on an Ammonium Quaternary Salt for Nitrate Detection

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Abstract

In this study, a screen-printed electrode for nitrate ions was evaluated with a selective membrane based on tetradecyl ammonium nitrate as the ionophore, o-nitrophenyl octyl ether as the plasticizer, and polyvinyl chloride as the polymeric matrix. The electrodes were printed on polyethylene terephthalate sheets using a screen-printing frame with the electrode template. Then, the selective membrane was deposited by drop casting. The principal analytical parameters were determined by the method of additions recommended by IUPAC. The membrane showed a good linear response range of 5.38×10^{-6} to 1×10^{-2} mol/L, being Nernstian according to the slope of -57.13 mV/dec (theoretical slope: -59.16 mV/dec), with a practical detection limit of 2.96×10^{-6} mol/L and a lower limit of linear response of 5.38×10^{-6} mol/L. The potentiometric selectivity coefficients for Cl^- , Br^- , I^- , SO_4^{2-} , and IO_3^- ions were determined using the mixed solutions method. The Br^- ion was found to be the most relevant interferent. The electrode showed a fast stable response (20 s), as well as the possibility of use in a wide pH range (3–12) without compromising the potentiometric response.

Keywords

polymeric liquid membrane, nitrate, screen-printed electrode, potentiometry, ammonium quaternary salt

1 Introduction

Over the years, many nitrate-selective sensors have been developed, with different membrane compositions, from solid to liquid membranes, and different composites; as well as different designs [1–4]. On the other hand, many ionophores have been used to detect this ion, with quaternary ammonium salts being particularly suitable for anion detection by ion exchange [1, 5].

In this context, screen printing has been a technique widely used in recent years to fabricate sensitive electrodes [6–9]. The most important feature is the construction of a new generation of miniaturized sensors that can meet the requirements of portable analytical devices, replacing conventional electrodes.

Domínguez Renedo et al. [10] present developments in the electrochemical application of screen-printed sensors, according to the types of materials used to modify the working

electrode. They describe unmodified screen-printed electrodes (SPEs), film-coated SPE, enzyme-modified SPE, and immunoassays based on SPE. The authors highlight the potential of these types of sensors for various applications and demonstrate the importance of research in these devices for modern electroanalysis.

Thus, the application for different analytes, from drugs to heavy metals, has been reported [11, 12]. For instance, Alberti et al. [13] presented a molecularly imprinted polymer-based, screen-printed, potentiometric cell for sensing atrazine. Atrazine is a widely used herbicide that is highly persistent and toxic. The sensor exhibited a linear response range from 5×10^{-7} to 5×10^{-6} mol/L, with a calibration slope of 40 mV/dec. The detection limit was 4×10^{-7} mol/L, lower than that of other potentiometric selective electrodes for this contaminant.

On the other hand, Ichimura et al. [14] presented a fully screen-printed potentiometric sensor for chloride ions that employs a hydrogel-based touchpad for simple, noninvasive daily electrolyte analysis in human sweat. This printed system exhibited a near-Nernstian slope of -55.1 mV/dec, with a detection limit of 0.11 mmol/L.

Hassan et al. [15] reported on a novel, screen-printed, potentiometric electrode based on a crown ether/nano-manganese oxide/Nafion composite that enables the determination of trace levels of copper ions in biological fluids. The electrode exhibited a response with a slope of 30.2 mV/dec over the linear concentration range from 5.2×10^{-9} to 6.2×10^{-3} mol/L, with a detection limit of 1.1×10^{-9} mol/L.

Nitrate ions are of environmental and human health importance. As nitrate is one of the species involved in the natural nitrogen cycle, it is often used as an indicator of contamination, since microbial activity produces it from other species, such as ammonium [16]. The most common anthropogenic sources of nitrates in water and soil are agriculture and some industrial activities such as mining [17, 18]. For this reason, rapid, sensitive, and reliable nitrate quantification is essential for environmental studies. Simple methods that allow portability and analytical decentralization, such as selective electrodes, have been investigated [3, 6].

Printed graphite-epoxy ion-selective electrodes (ISEs) are an example of the evolution achieved in the field of potentiometric analysis, since they integrate the indicator electrode and the reference electrode into a single piece, facilitating portability and automation. These devices are a feasible and superior alternative to methods commonly used in the laboratory for nitrates, such as UV-vis molecular absorption spectrophotometry.

Regarding the development of printed potentiometric sensors for nitrate ions, Jiang et al. [7] presented inkjet-printed, solid-state, nitrate-selective electrodes for agricultural applications. They achieved this by directly inkjet-printing a silver electrode using silver ink on a flexible substrate. The nitrate-responsive membrane, which had a PVC matrix, was made with tetra-*n*-octyl ammonium bromide, di-*n*-butyl phthalate, and tetrahydrofuran. The electrodes exhibited a response with a slope ranging from -52 to -50 mV/dec in the 10^{-4} to 10^{-1} mol/L nitrate concentration range. This printed electrode was applied to soil samples. On the other hand, Thuy et al. [19] presented a Co_3O_4 nanoparticle-modified SPE sensor for detecting nitrate ions in aquaponic systems. In this work, a layer of nanoparticles was deposited, followed by the nitrate-selective membrane

with a PVC matrix and the response based on tri-*n*-decyl-methyl ammonium nitrate. This sensor exhibited a Nernstian slope of -56.78 mV/dec within a nitrate ion concentration range of 10^{-7} to 10^{-2} mol/L. These studies show that, despite the existence of different technologies for constructing printed electrodes, quaternary ammonium salts remain essential for the selective recognition of nitrate ions in potentiometric sensors.

In the present work, the potentiometric response of a screen-printed ISE for nitrate ions based on an ammonium quaternary salt was investigated. The novelty lies in the simple fabrication of the screen-printed ISE based on a PVC membrane containing the ionophore tetradecyl ammonium nitrate (TDAN) on a graphite-epoxy substrate with polyethylene terephthalate as the supporting material. This system is an evolution to a screen-printed ISE of a previously investigated electrode with this membrane but with a traditional tubular structure. This printed electrode can serve as the basis for developing a sensor by incorporating a reference electrode into the device. Thus, it can function as a fast and reliable analytical tool for environmental, industrial, and clinical applications.

2 Materials and methods

2.1 Reagents and instruments

All reagents used in this work were of analytical quality (purity $> 95\%$) and were acquired from Sigma Aldrich. TDAN was synthesized in our laboratory following an ion exchange procedure using tetradecyl ammonium bromide and potassium nitrate, with separation steps to remove the bromide ion. Elemental analysis of the ammonium quaternary salt was carried out at the University of Rome La Sapienza, using a Carlo-Erba EA 1110 CHNS-O elemental analyzer. The melting point was determined using a BUCHI melting point apparatus. The water used in this work was double-distilled with a conductivity of less than 2 $\mu\text{S}/\text{cm}$. A Thermo Scientific Orion Star A214 instrument was used for potentiometric measurements.

2.2 Preparation of the membrane and the SPE

The prepared membrane contained 7 wt.% ionophore, 64 wt.% plasticizer and 29 wt.% PVC as polymeric matrix [5]. The home-made electrodes were printed on polyethylene terephthalate sheets using a screen-printing frame with the electrode template. The SPEs were then dried in an oven at 40 $^{\circ}\text{C}$ for 48 h to achieve curing of the electrodes. Then, the indicator electrode was modified by depositing a drop of the modifier suspension as shown in Fig. 1. After this, the

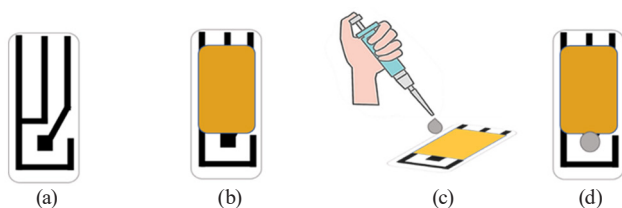


Fig. 1 Scheme of the deposition of the electrode membrane:
(a) printed electrode, (b) definition of the indicator electrode area, (c) drop-casting modification, (d) screen-printed ion-selective electrode

electrodes were allowed to stand for 24 h before use. The reference electrode was Ag/AgCl/KCl (0.1 mol/L) and it was not part of the printed electrode. It was connected to the working solution by a 0.1 mol/L K_2SO_4 salt bridge.

2.3 Measuring of the electromotive force (EMF)

Electromotive force (EMF) measurements were carried out using a cylindrical glass cell at room temperature. The calibration curves were used to calculate parameters such as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). Calibration curves were obtained by applying the method of additions [5], determining the activity of the main ion using the activity coefficient calculated by the simplified Debye-Hückel equation (Eq. (1)).

$$-\log f = \frac{0.51Z^2I^{1/2}}{1 + I^{1/2}}, \quad (1)$$

where f is the activity coefficient, Z is the charge of the ion, and I is the ionic strength (mol/L).

The selectivity coefficients (K_{AB}^{Pot}) were determined by using the method of mixed solutions [5] and calculated through Eq. (2).

$$K_{AB}^{Pot} = a_A / a_B^{Z_A/Z_B}, \quad (2)$$

where a_A is the activity of the primary ion (mol/L), a_B is the activity of the interfering ion (mol/L), Z_A is the charge of the primary ion, and Z_B is the charge of the interfering ion.

The influence of the pH on the printed electrode response was evaluated representing the variation of the potential as a function of the pH of the solution. The starting point was the potential difference for 150 mL of a 10^{-2} mol/L KNO_3 solution. Once the printed ISE was introduced into the solution, it was connected to a potentiometer along with the reference electrode to measure the potential difference due to the nitrate concentration, and the glass electrode was connected to another potentiometer for pH measurement during the potentiometric experiment. Sulfuric acid was added until a low pH was reached, and then sodium hydroxide solution (1 mol/L) was added carefully to obtain the pH of study, and the potential value was registered.

The response time of the printed electrode was determined using the direct method, starting with 25 mL of the primary ion at a concentration of 10^{-4} mol/L; the indicator electrode was introduced into the calibration cell, and the potential was measured every 5 s.

The calculation of the confidence interval of the slope was done for 95% confidence through Eq. (3):

$$\Delta X = \frac{t(\alpha, df) Sd}{\sqrt{N}}, \quad (3)$$

where ΔX is the confidence interval, α is the confidence level, df are the degrees of freedom, Sd is the standard deviation, and N is the number of determinations.

3 Results and discussion

Fig. 2 shows the calibration curves of the proposed SPE for nitrate for different periods ranging from 48 h to 35 days. Table 1 presents the calibration parameters obtained from the linear fit of each of the curves. It can be noted that a slope close to the Nernstian value for a monoelectronic transfer, i.e., -59.16 mV/dec, is obtained for different time periods. This indicates that the selective electrode allows a correct response for the analyte which is a monovalent anion. The PDL is lower at 48 h, then increases to values slightly above 3.0×10^{-6} mol/L when reaching fifteen days onwards. A similar behavior is obtained for LLLR, where values also increase after 15 days. These results indicate a slight loss of sensitivity with the passing of days, but this is not significant if considering that the difference is small between 48 h and 35 days. In all cases, the correlation coefficient indicates a strong linear relationship between the measured potential and the logarithm of nitrate ion activity in the linear response zone of the calibration curves.

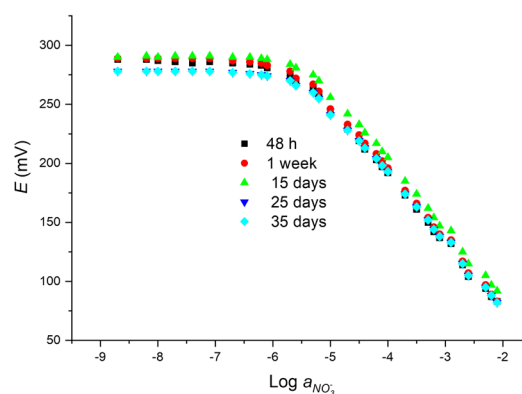


Fig. 2 Calibration curves for nitrate ions with the screen-printed potentiometric selective electrode using the addition method for different periods from 48 h to 35 days

Table 1 Calibration parameters for nitrate ions with the screen-printed potentiometric selective electrode using the addition method for different periods from 48 h to 35 days

Parameters	Period				
	48 h	1 week	15 days	25 days	35 days
S (mV/dec)	-56.82 ± 1.82	-57.67 ± 2.06	-58.33 ± 1.86	-56.55 ± 1.30	-56.30 ± 1.62
PDL (mol/L)	2.52×10^{-6}	2.77×10^{-6}	3.33×10^{-6}	3.18×10^{-6}	3.04×10^{-6}
LLLR (mol/L)	6.10×10^{-6}	6.10×10^{-6}	6.39×10^{-6}	6.39×10^{-6}	6.94×10^{-6}
R	-0.9990	-0.9988	-0.9991	-0.9995	-0.9991
N	19	19	18	16	16

S: Slope, PDL: Practical detection limit, LLLR: Lower limit of linear response, R: Correlation coefficient, and N: Number of determinations

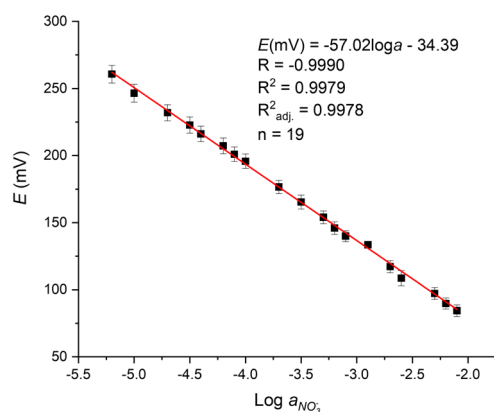
Fig. 3 shows the calibration curve in the potentiometric response region identified above. It can be observed a response with a slope very close to the Nernstian value and correlation and determination coefficients greater than 0.99, being acceptable. Table 2 presents the analysis of variance (ANOVA) of the calibration, where the p-value is less than 0.05, indicating that there is a statistically significant linear relationship for 95% confidence.

Table 3 shows the calibration parameters for a commercial ISE for nitrate ions. It can be observed that at 48 h, the calibration slope is greater in absolute value than that obtained for the SPE ($58.30 > 56.82$ mV/dec, respectively), but this changes with the progress of days, where a tendency of the slope to decrease its absolute value with respect to the SPE can be observed. In addition, the calibration slope of the commercial electrode shows higher

uncertainty, as can be noted from the confidence intervals. On the other hand, the PDL and LLLR values of the SPE are lower by one order of magnitude (10^{-6} mol/L) compared to those of the commercial electrode (10^{-5} mol/L). This indicates that the proposed electrode can detect and quantify lower concentrations of nitrate than those that can be achieved with the commercial ISE. All these results show that the screen-printed selective electrode is superior to the commercial ISE in terms of potentiometric performance and durability, demonstrating the competitiveness and superiority of the constructed device.

The effect of the pH of the test solution on the selective electrode response was studied at 1.0×10^{-2} mol/L nitrate. Fig. 4(a) shows that, from pH 3, the measured potential remains practically constant until the last value tested, which was pH 12. This pH range is wider than that reported for other nitrate selective electrodes. For example, Le Goff et al. [20] presented a nitrate electrode containing immobilized amino acid betaines as a sensitive element. In this case, the sensitive ability of the membranes was reported from pH 2 to 8. On the other hand, Li et al. [21] reported a solid-state ISE based on polyaniline for nitrate-nitrogen detection in a pH range from 3.5 to 10. Another sensor, reported by Pietrzak et al. [22], based on cobalt(II) complex with 4,7-diphenyl-1,10-phenanthroline, showed stable response from pH 5.4 to 10.6.

Fig. 4(b) shows the graph of the study of the response time of the printed electrode. It can be observed that the potential is constant after 20 s, which allows to affirm that this is the minimum response time of the proposed printed ISE. This response time is in the order commonly reported for nitrate sensors, which is usually within a few seconds [23, 24]. However, the response in this case is obtained in less time than the sensor system reported by Cho et al. [25] based on the reaction of nitrate ions with titanium trichloride and detection with an ammonium electrode. In that case, the response time was in the order of minutes. On the other hand,

**Fig. 3** Calibration curve for the screen-printed selective electrode for nitrate ions**Table 2** Analysis of variance for the calibration curve

Source	SS	DF	MS	F-ratio	p-value
Model	1	2006.84	2006.84	8255.42	0.0000
Error	17	4.13	0.24		
Total	18	2010.97			

SS: Sum of squares, DF: degrees of freedom, MS: mean square

Table 3 Calibration parameters for nitrate ions with a commercial potentiometric ISE using the addition method for different periods from 48 h to 35 days

Parameters	Period				
	48 h	1 week	15 days	25 days	35 days
S (mV/dec)	-58.30 ± 4.47	-55.70 ± 5.82	-54.64 ± 5.72	-59.26 ± 3.70	-54.64 ± 5.72
PDL (mol/L)	2.01×10^{-5}	1.22×10^{-5}	1.08×10^{-5}	1.53×10^{-5}	1.08×10^{-5}
LLLR (mol/L)	5.91×10^{-5}	2.95×10^{-5}	3.23×10^{-5}	5.93×10^{-5}	3.23×10^{-5}
R	-0.9703	-0.9890	-0.9879	-0.9944	-0.9879
N	17	18	17	15	17

Reference electrode: Ag/AgCl/KCl (0.1 mol/L)/K₂SO₄ (0.1 mol/L), S: Slope, PDL: Practical detection limit, LLLR: Lower limit of linear response, R: Correlation coefficient, and N: Number of determinations

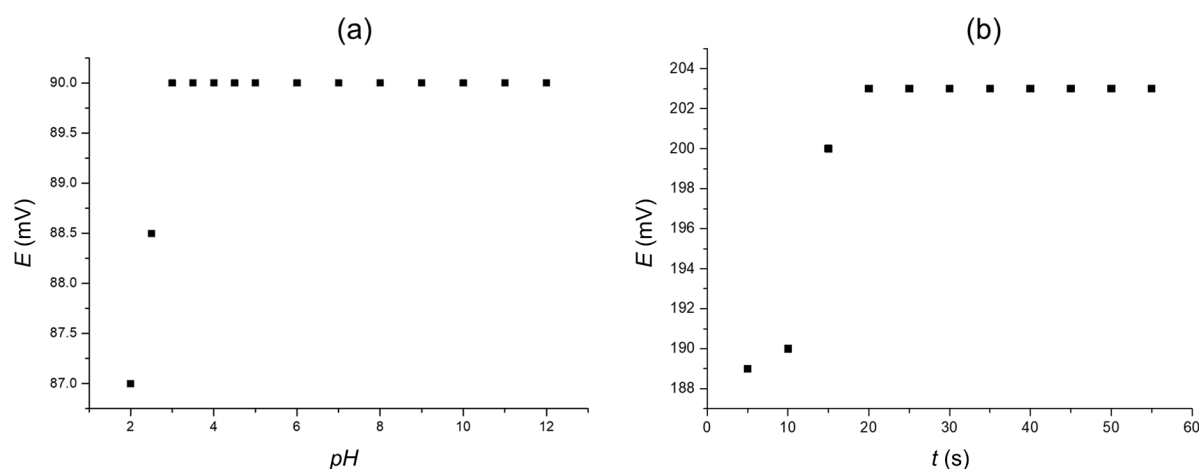


Fig. 4 (a) Effect of the pH of a 10^{-2} mol/L nitrate solution on the response of the screen-printed potentiometric electrode, (b) Potential as a function of time for a concentration of primary ions of 10^{-4} mol/L

Masadome et al. [26] presented a microfluidic polymer chip with an integrated ISE detector for the assay of nitrate in environmental samples. The ISE was based on tetradodecylammonium bromide as an anion exchanger and 2-nitrophenyl octyl ether as plasticizer. The ISE showed response time in the order of minutes (<2 min).

The selectivity of the printed ISE was studied by measuring the degree of the interference of different ions on the potentiometric response. As can be noted in Table 4, the electrode showed good selectivity for nitrate ions in the presence of SO₄²⁻ as interfering anion. The main interfering anions were Br⁻, IO₃⁻, Cl⁻, and I⁻. The values of K_{AB}^{Pot} obtained in this study are very similar in order to that obtained by Arada et al. [5].

4 Conclusions

A screen-printed nitrate-selective electrode based on the quaternary ammonium salt TDAN as ionophore, o-nitro phenyl octyl ether as plasticizer, and PVC as a matrix showed a fast and stable linear response to the primary ion,

Table 4 Values of the selectivity coefficients K_{AB}^{Pot} obtained for the printed selective electrode for a concentration of 10^{-2} mol/L of the interfering anions

Interfering ion	K_{AB}^{Pot}	Reported [5]
Cl ⁻	4.5×10^{-3}	8.69×10^{-3}
Br ⁻	7.4×10^{-2}	4.56×10^{-2}
I ⁻	3.2×10^{-3}	—
SO ₄ ²⁻	1.2×10^{-4}	1.48×10^{-4}
IO ₃ ⁻	2.2×10^{-3}	5.22×10^{-4}

with slope of -57.13 mV/dec, PDL of 2.96×10^{-6} mol/L, and LLLR of 5.38×10^{-6} mol/L. The Br⁻ anion showed a strong interfering effect, whereas IO₃⁻, Cl⁻ and I⁻ showed moderate effects. The printed ISE presents a rapid and stable response comparable with other devices, and even better than those obtained in some cases, including other ammonium salt-based electrodes. The potentiometric SPE for nitrate ions allows electrochemical measurements in a wide pH range from 3 to 12.

The screen-printed ISE with a selective membrane based on the TDAN ionophore provides a novel and reliable option for rapidly analyzing nitrate ions in environmental, industrial, and clinical samples. Once the reference electrode is incorporated into the printed device, it will serve as an analytical tool for on-site analysis, which is important in agriculture and in the chemical, mining, metallurgical, food, and other industries where nitrate ions may be involved. This highlights the contribution of this potentiometric device to technological and environmental control in industrial sectors. Additionally, the

proposed printed ISE can be easily fabricated from inexpensive materials, making it a cost-effective option for nitrate ion detection.

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