

A new membrane electrode that is fast, selective and sensitive to low amounts of nitrate

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Research Article

Keywords: Ion selective electrode, Nitrate, Membrane, Potentiometry

Posted Date: September 16th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10908152/v1>

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Abstract

A fast and selective electrode sensitive to low amounts of nitrate was developed. Chemical variables were used to optimize the potentiometric response of the electrodes and maximize nitrate selectivity over potential interferences. The electrode sensitivity was measured as -57 ± 2 mV in accordance with the Nernst equation at a 10-fold change in the concentration of 0.1 mol/L nitrate from 1.0×10^{-6} . Its ability to operate in a wide pH range and its short response time provided advantages over other nitrate electrodes. Another advantage of the electrode was that it was not sensitive to other anions and cations. The amount of nitrate in sausage and drinking water was measured with an electrode. The results were determined to be consistent by the visible spectroscopy method.

Introduction

Nitrate is naturally found in high amounts in water and vegetables. It has been used as a mineral to give characteristic color and flavor to foods. The importance of nitrate for human health is that after nitrate is broken down or reduced to nitrite, it turns into nitroso compounds that have cancerous properties [1–2].

The presence of inorganic forms of nitrogen, such as nitrates or ammonium, is crucial, but unfortunately, in excess, it can do more harm than good. Above-average levels of these compounds in surface water (rivers, lakes, seas) cause excessive growth of algae and cyanobacteria, leading to water eutrophication, reducing oxygen levels in the water, and consequently causing the death of aquatic animals [3–5]. Nitrates can also contaminate groundwater, thereby reducing the quality of drinking water. According to the World Health Organization (WHO), the nitrate content in water should not exceed 50 mg/L. Nitrate pollution in water is mainly caused by the runoff of NO_3 -fertilizers from fields into water bodies, leaky septic tanks, and pollutants' emissions from industrial areas [6–7].

Some analytical methods were applied in different matrices for nitrate determination. These are ultra violet spectroscopy [8–9], ion chromatography [10–11], atomic absorption spectroscopy [12–13] and electroanalytic methods [14–16]. These methods provide good results, but they have numerous limitations. They are quite expensive, and the analysis is not cost-effective, not only due to the price of the equipment used, but also because of other factors such as sample preparation time—which is often lengthy and requires sample purification—the duration of the measurement itself, and the use of expensive reagents that are frequently toxic and environmentally unfriendly. In addition, when using these methods, we cannot perform in-situ measurements. Therefore, an alternative solution is being sought, and here the problem of costly, time-consuming, and environmentally unfriendly analyses can be solved by using potentiometric sensors, namely ion-selective electrodes (ISE).

In recent years, nitrate-sensitive ion-selective electrodes have been prepared for nitrate analysis. Some of them contained a membrane matrix and some a solid-state matrix. These electrodes measured the amount of nitrate in water [17–20], plants [21–22], soil [23–24]. It has been determined that these analyses are easier, faster and less costly.

In this study, an electrode that is easy to prepare, fast to analyze, and highly selective is sensitive to nitrate. Chemical factors were examined to increase electrode sensitivity and appropriate parameters were determined. Nitrate in sausage and drinking water samples were analyzed with the electrode. The results were compared by measuring with visible spectroscopy.

Materials and methods

Chemicals

In the preparation of the electrode, methyltridodecyl methyl ammonium nitrate (IE) (Aldrich) was used as ion exchanger, poly(vinylchloride) (PVC) as filler, and dibutyl phthalate (DBF) (Merck) as plasticizer. These three components were dissolved in tetrahydrofuran (Merck) for the formation of the membrane. KNO_3 (Merck) and other salts were of analytical grade.

Methods

Potential measurements were made with a Jenway 3040 ion meter. All potential values reported, are taken with respect to an 924036 Double Junction Ag/AgCl saturated reference electrode which was hold in a Luggin-Haber capillary. Reagent grade chemicals were used without further purification. All solutions were prepared with triple distilled water.

Preparation of Electrode

The membrane was prepared with the composition containing 10.0% IE, 50.0% PVC and 40% DBF. These components were dissolved in THF in petri dishes with a diameter of 7 cm to obtain membranes [25]. The obtained selective membrane was glued to a 1 cm diameter silicone tube with a special adhesive. After drying, the excess membrane was cut. Silver wire and 1.0 mol/L KNO_3 and 0.01 mol/L KCl solution were added to this electrode. The electrode was kept in 1.0×10^{-4} mol/L KNO_3 solution for 1 day for conditioning.

Preparation of sausage and water sample

A sausage sample of approximately 50 g was taken, mixed with 100 mL of ultrapure water in a blender. It was filtered through cotton gauze. As (III) solution of unknown concentration was added. The nitrite in the sausage was oxidized to nitrate [26]. Ankara drinking water sample was taken directly from the tap.

Result and discussion

Potentiometric Measurements

A nitrate electrode and an Ag/AgCl electrode were placed in our cell, where standard NO_3^- solutions were prepared from LiNO_3 salt. The potential of 1×10^{-6} M nitrate solution was read. Standard solutions were added to increase the concentration in the cell by 10 times and the potential values were recorded. The calibration graph was created by plotting the potential values against nitrate concentration and given in Fig. 1. The electrode sensitivity was calculated from the slope of this line.

Electrode Composition

The potential values of nitrate electrodes prepared with different compositions having the same membrane mass against concentration were measured and the calculated slope values are given in Table 1. According to the results obtained, it was seen that the electrode consisting of 10% ID, 50% PVC and 40% plasticizer had the highest sensitivity. The LOD value of the electrode was calculated as 2×10^{-7} mol /L.

Table 1
Sensitivity of electrodes of different composition to nitrate ion
(1×10^{-6} -0.1 mol/L)

Electrode composition	Slope: mV	LOD: mol/L	R ²
5%ID, 60% PVC, 35% DBF	-27.3 ± 0.7	6×10^{-6}	0.9845
10%ID, 50% PVC, 40% DBF	-56.5 ± 0.4	2×10^{-7}	0.9999
15%ID, 50% PVC, 35% DBF	-35.2 ± 1.1	1×10^{-6}	0.9936
15%ID, 60% PVC, 25% DBF	-29.3 ± 0.9	5×10^{-6}	0.9879

Effect of pH

While there was 1×10^{-5} mol/L nitrate solution in our cell, additions were made from 0.1 mol/L HCl and NaOH solutions. The change in potential values was measured by changing the pH value of the solution and the values are given in Fig. 2. According to the measured results, it was seen that the electrode potential was not affected in the pH range of 1–8.

Response Time

The electrode composition also affects the response time. A short response time of the electrode indicates high sensitivity. The cell was added to increase the nitrate concentration by 10 times and the times when the electrode potential value was constant were recorded. The measured values are given in Fig. 3. According to these values, the electrode response time was determined as 20 s.

Interference

The sensitivity of the electrode to nitrate ion as well as other anions and cations was measured using the mixed solution method. This sensitivity is defined as the selectivity coefficient [27]. The selectivity coefficients of the electrode are given in Table 2. It was found that the electrode was not sensitive to other anions and cations. This feature made the electrode more important.

Table 2
Selectivity coefficients of the electrode

$${}^{pot}K_{A,B}$$

Ions	${}^{pot}K_{A,B}$	Ions	${}^{pot}K_{A,B}$
Cl ⁻	1x10 ⁻³	Na ⁺	4x10 ⁻⁴
F ⁻	2x10 ⁻⁴	K ⁺	1x10 ⁻³
SO ₄ ²⁻	1x10 ⁻⁵	Cu ²⁺	2x10 ⁻⁵
CO ₃ ²⁻	3x10 ⁻⁵	Fe ³⁺	2x10 ⁻⁵

Nitrate analysis in sausage and drinking water samples

The sausage sample that was made soluble and oxidized to nitrite and nitrate was analyzed with the water sample electrode for the amount of nitrate in it [28]. The same samples were also analyzed with a Hanna brand visible spectrophotometer device. The results are given in Table 3 as the average of 4 measurements and 95% confidence level. The t and F tests were applied to the results obtained from both methods. It was seen that the results were compatible.

Table 3
Comparative analysis of nitrate (mg/L) in sausage and water

Sample	Nitrate Electrode	Spectrophotometer	t Test (t _{critical} = 3.16)	F Test (F _{critical} = 9.60)
Sausage	0.36 ± 0.03	0.35 ± 0.04	1.78	3.21
Water	1.52 ± 0.14	1.53 ± 0.19	2.34	4.08

Conclusion

A new nitrate selective membrane electrode was developed. The variables affecting the sensitivity of this electrode were examined. It was determined that the sensitivity was high at 10% ID, 50% PVC and 40%

DBF composition. It was observed that the sensitivity of this electrode had a slope of approximately – 57 mV. The response time of the electrode was 20 s and it was accepted as an important feature that it could work in the pH range of 1–8. In addition, the fact that the electrode was not sensitive to other anions and cations is accepted as an important advantage.

Nitrate electrode with fast, easy analysis and high selectivity was prepared. The determination of important features of the developed nitrate selective electrode showed that it is suitable for analysis in real samples. The LOD value is 2×10^{-7} mol/L, there is no interference effect and it works in wide pH values are important features. It is easy to prepare and has a short analysis time compared to other methods.

Declarations

Conflict of interest

The authors have no relevant financial or non-financial interests to disclose.

Funding

Authors state no funding involved.

Acknowledgement

The preparation of the samples in this study and nitrate analysis by potentiometric methods were carried out in Gazi University Chemical Technology Laboratory.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Figures

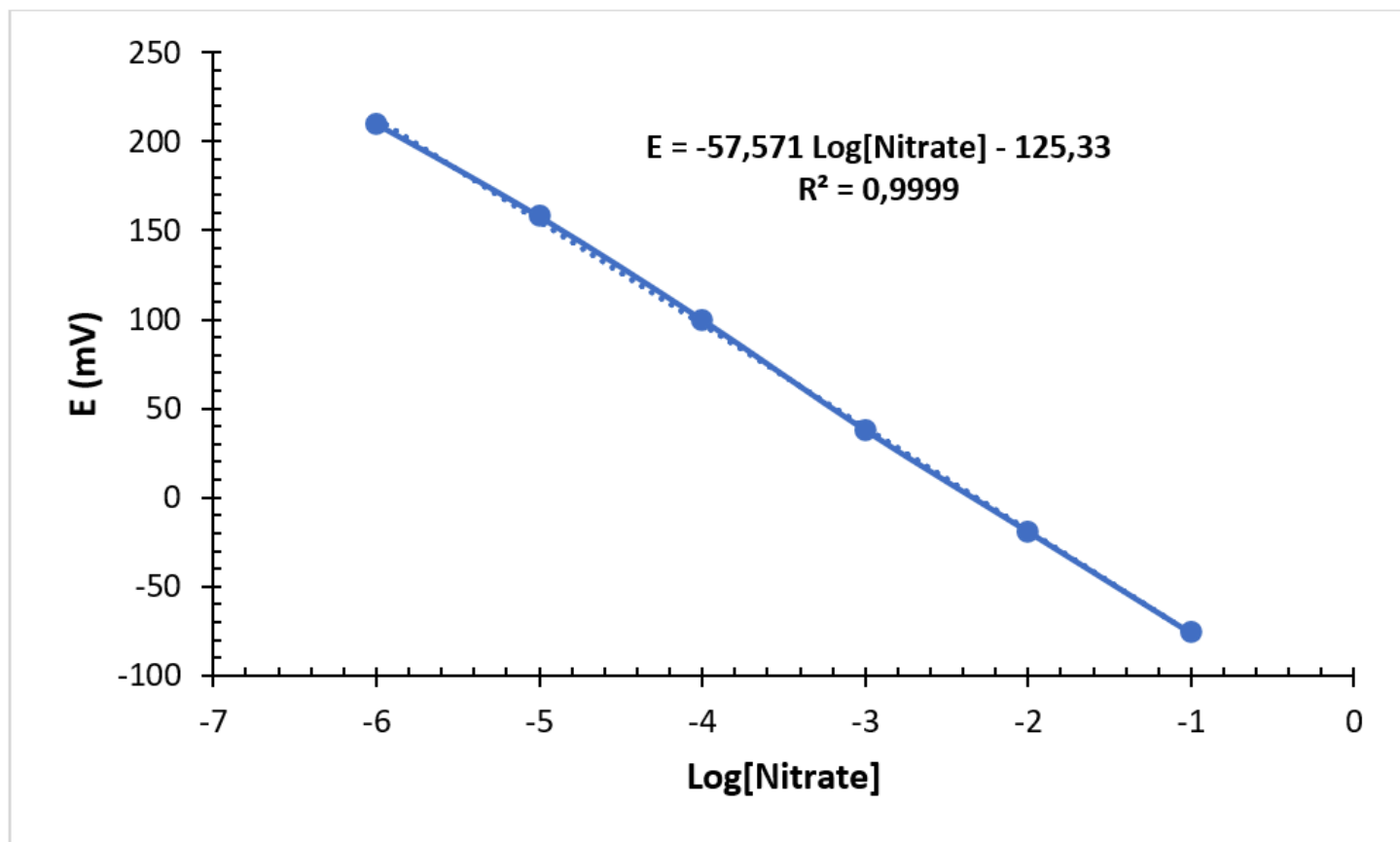


Figure 1

Calibration graph of electrode against nitrate concentration.

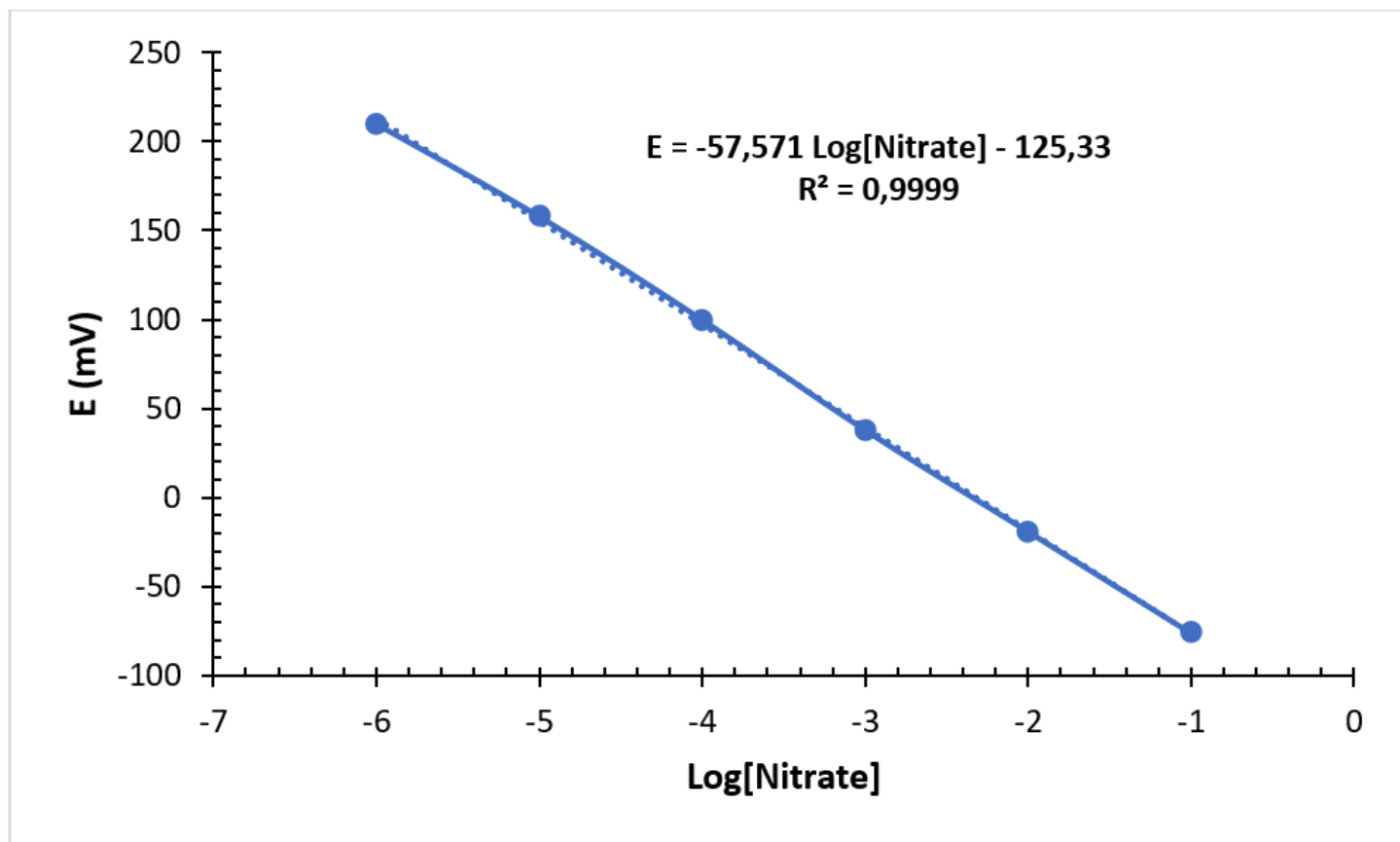


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Calibration graph of electrode against nitrate concentration.

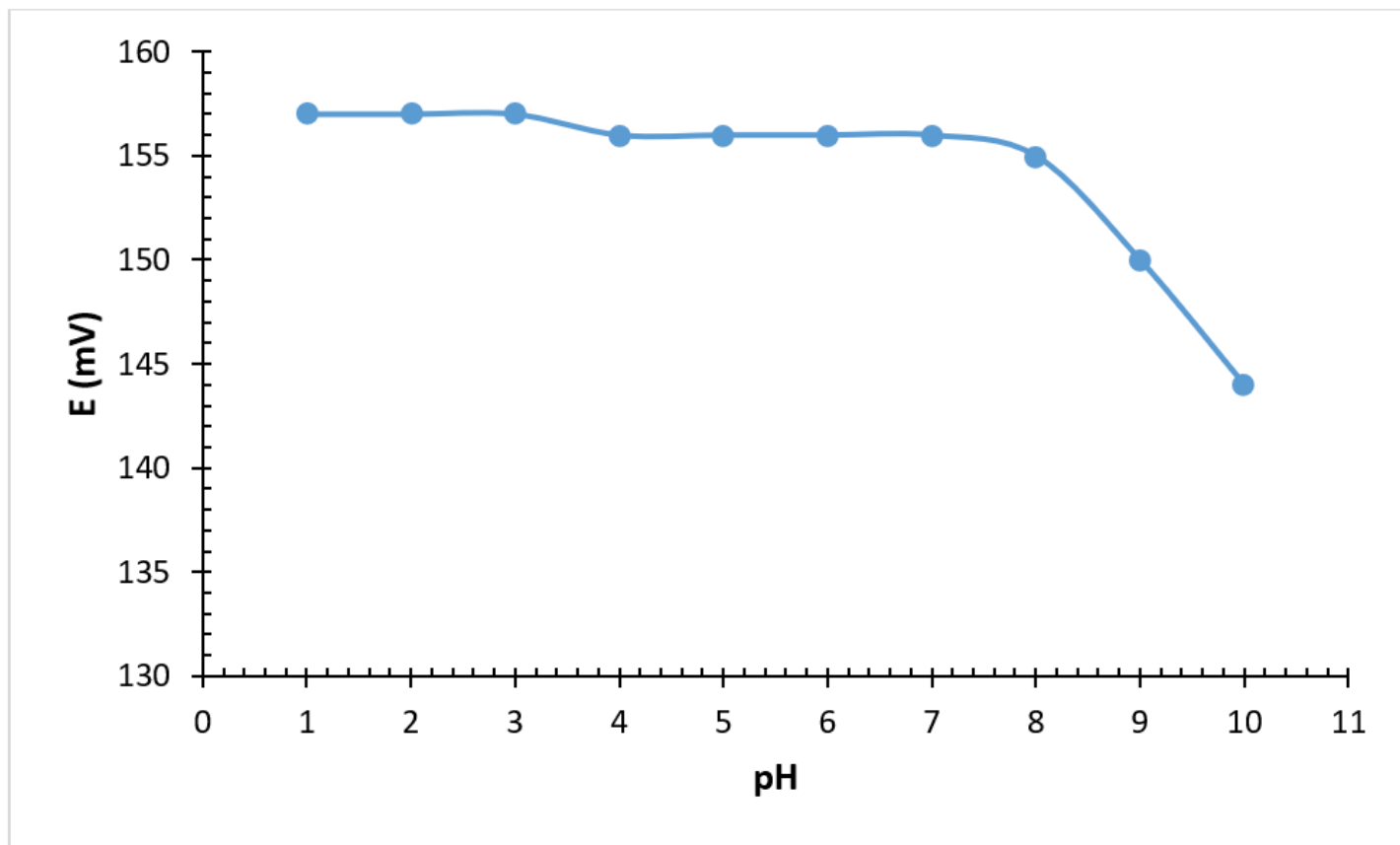


Figure 2

Change in electrode potential value with pH

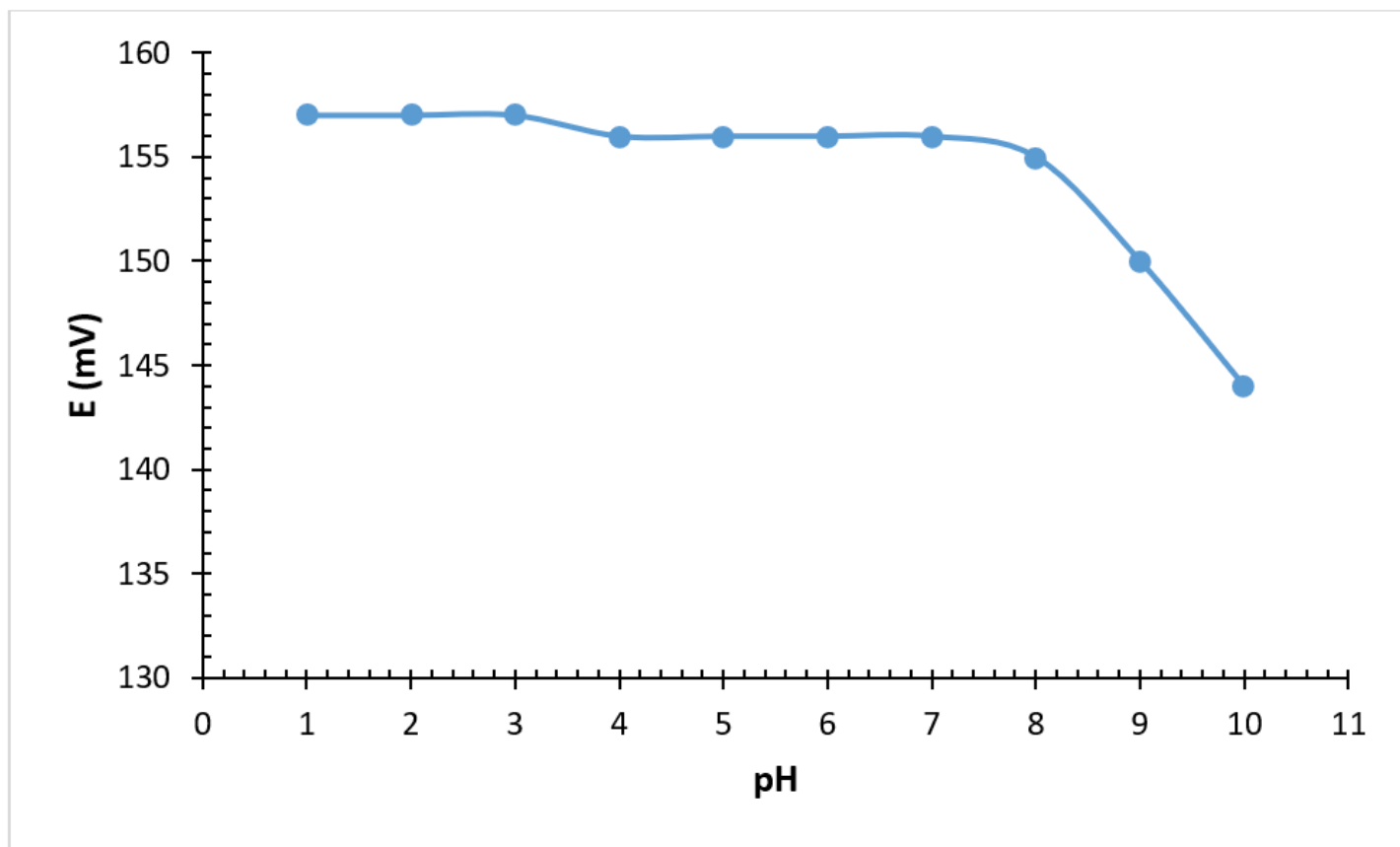


Figure 2

Change in electrode potential value with pH

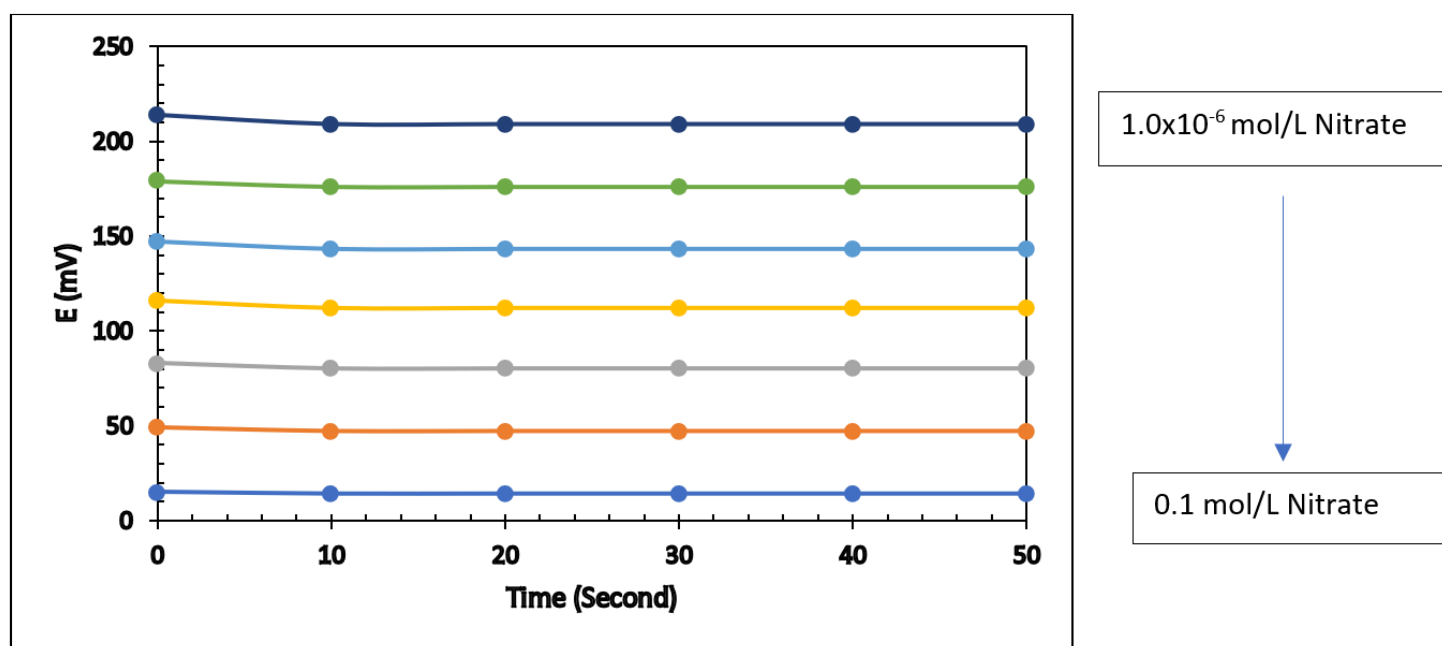


Figure 3

Electrode response time.

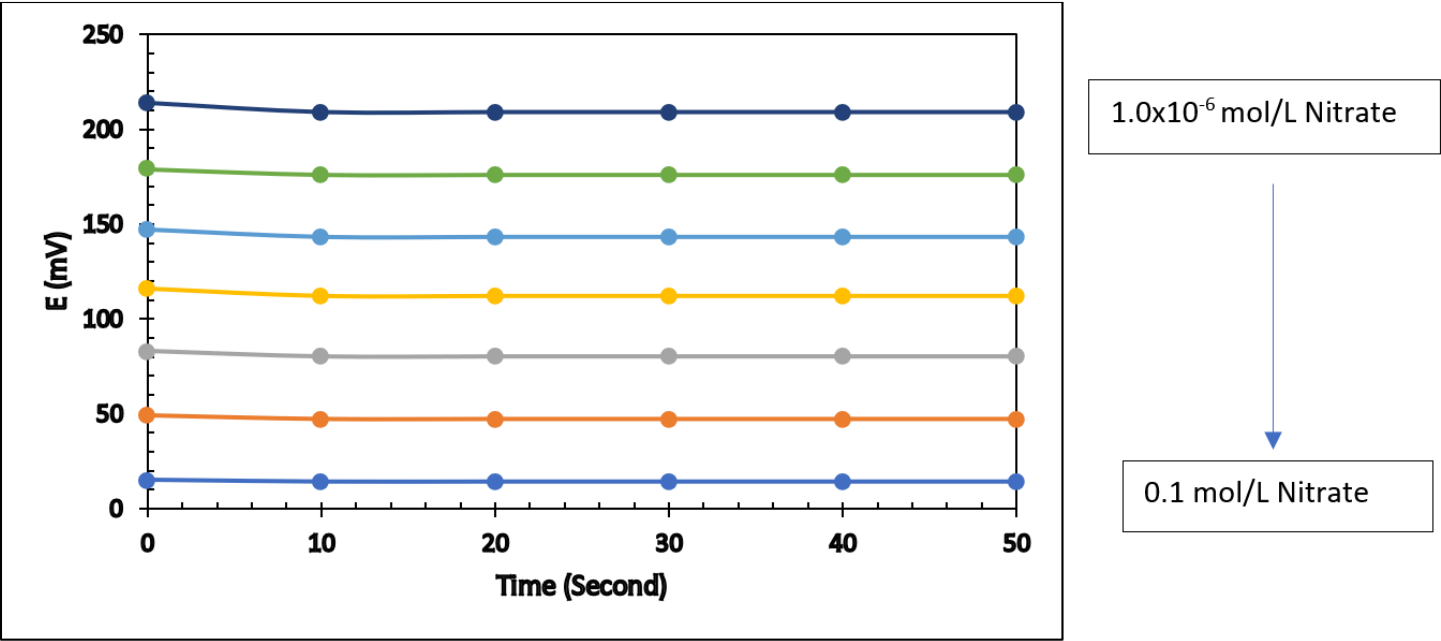


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Electrode response time.