

# Determination of Nitrate in Drinking Water by Ion-Selective Electrode

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## ● Abstract

Nitrate concentration in drinking water was directly determined by employing an ion selective liquid membrane electrode (ISE). This was constructed with poly(vinyl chloride) as matrix on a solid conducting support. Tetra-decyl ammonium nitrate (TDAN) was used as ionophore and dibutyl phthalate as plasticizer and solvent-mediator. The constructed ISE showed Nernstian slope with value of  $-61,2 \pm 0,2$  mV/dec<sup>-1</sup>, practical detection limit (PDL) of  $9,59 \cdot 10^{-6}$  mol/dm<sup>3</sup>, lower limit of linear response (LLLR) of  $2,82 \cdot 10^{-5}$  mol/dm<sup>3</sup>, pH range of 5,0-11,5, life-time of >6 months without any divergence and with stable response of 15 seconds. Determination of nitrate ion concentration in drinking water was performed by direct potentiometric method. Reliability of the electrode was evaluated by measuring the nitrate concentration by ion chromatography as a comparative method. The results showed good agreement between the values obtained by both methods, indicating the applicability of the proposed electrode for accurate determination of nitrate concentration in drinking water, where the measured values were less than 10 mg/L.

Key words: ion-selective electrode, nitrate ion, tetra-decyl-ammonium nitrate, liquid membrane, poly (vinyl chloride).

## ● Resumen

La concentración de nitrato en agua de tomar fue directamente determinada empleando un electrodo de membrana líquida selectiva (ISE). Éste fue construido con cloruro de polivinilo como matriz sobre un soporte sólido conductor. Nitrato de tetradecilamonio (NTDA) fue usado como ionóforo, dibutilofalato como plastificante y solvente mediador. El ISE construido mostró pendiente nernstiana con un valor de  $-61,2 \pm 0,2$  mV/déc<sup>-1</sup>, con un límite práctico de detección (DPL) de  $9,59 \cdot 10^{-6}$  mol/dm<sup>3</sup>, y un límite inferior de respuesta lineal (LLLR) de  $2,82 \cdot 10^{-5}$  mol/dm<sup>3</sup>. El rango de pH fue de 5,0-11,5 con un tiempo de vida >6 meses. El mismo presentó estabilidad de su respuesta a los 15 seg. La determinación de la concentración del ion nitrato en agua potable fue realizada por el método potenciométrico directo. La fiabilidad del electrodo fue evaluado por la medida de la concentración de nitrato por el método de cromatografía iónica como método de comparación. Los resultados mostraron buenas concordancias entre los valores obtenidos por ambos métodos, indicando la aplicabilidad del electrodo propuesto para la determinación precisa de nitrato en agua potable. Los valores obtenidos fueron menores que 10 mg/L.

Palabras clave: electrodo ion selectivo, ion nitrato, nitrato de tetradecilamonio, membrana líquida, cloruro de polivinilo (PVC).

## ● Introduction

The environmental pollution constitutes a global problem, present specially in industrialized countries as well as developing countries. The world rushes to the atmosphere, in a continuous manner, highly toxic substances, constituting a danger for human health. These substances reaches different regions still far from the place where it was originated by various means. Thus these toxic substances fall on the surface of the earth in the form of acid rains, which cause multitude of noxious effects, so much on the ecosystem as well as on the materials /1/.

The nitrogen oxides, mainly the dioxides, are an example of pollutants that can contaminate the waters seriously, not only superficial, but also the underground waters, harming the human health /2/.

The presence of nitrogen can acidify the terrestrial ecosystem. As a result, waters from rivers, lakes, etc. are acidified and the pH of these fall. This causes the dissolution of the insoluble aluminum, which is present in very high concentrations in the rocks, the ground and the sediments, causing the death of fishes and crustaceans. This destroys the global food chain and causes ecological imbalances. Leaching of fertilizers to rivers and underground waters is another source of natural water contamination with nitrate.

The growing nitrate concentrations in the sources of drinkable water can cause illnesses such as the methahemoglobinemia, which hinders the transport of the oxygen in the blood and in occasions it can cause death in children, the so called baby's blue syndrome.

Water is the Earth's most valuable resource and many research groups are involved in producing analytical equipment and methods to guarantee the quality of drinking water, ensure that contaminants don't get into semiconductor manufacturing processes, or monitor industry effluents to prevent or minimize environmental pollution. It is therefore important to establish a methodology not only to determine the nitrate concentration in water but also in foods such as vegetables, meats, etc.

Although some of the existing analytical methods such as polarography, chromatography and spectroscopy allow us to determine this ion, they

suffer from being very slow and expensive /3, 4/. The use of ion selective electrodes allows to obtain reliable and similar results very quickly, taking every day more peak with the new electrodes that allow the determination of this ion /5-14/.

The aim of this work was to determine the concentration of nitrate in drinking water by using a new ion selective electrode constructed in our laboratory. This electrode was constructed in the same way as previously those built and characterized by Arada and Pérez /15/ without an internal reference solution, in which the liquid membrane was deposited on a solid conducting support. The reason that motivated us to use this electrode for determining nitrate in drinking water is the advantages of this electrode over the commercially available electrodes. These include its low cost, robustness, fast response, long life-time and can be used in a wide interval of pH (5,0-11,5).

## ● Experimental

### *Materials*

All reagents used in this study, either for the preparation of the polymeric liquid membrane or for sample evaluation, were of analytical grade. Poly(vinyl chloride) (PVC) from Fluka was used as polymeric matrix. The plasticizer used was di-butyl phthalate (DBP) from Riedel - de Haën and was employed as solvent mediator of the PVC liquid membrane. Tetrahydrofurane (THF) was analytical grade from Merck.

The quaternary ammonium salt, tetra-decyl ammonium nitrate (TDAN), used as ionophore, was synthesized in the laboratory of natural products of the university of Havana. The purity of TDAN salt was 98% as checked by elemental analysis. The elemental analysis of the TDAN salt was carried out at the university of Roma, La Sapienza, using a Carlo-Erba Elemental Analyzer model Ea + 1110. Its melting point was determined in the department of organic chemistry of the university of Roma using a melting point apparatus W. Buchi.

The water used in this work was bi-distilled deionised water with a conductivity of less than 2 S/cm<sup>-1</sup>.

A Crison model (GLP22) digital pH meter with a precision of  $\pm 0,1$  mV was used for measuring the potential difference between reference and indicator electrodes. The reference electrode used in this study was a Russell 90-00-29 Ag/AgCl double junction electrode. Saturated AgCl solution from Russell (ref. 70-00-22) was used as internal reference solution and a solution of  $0,1 \text{ mol/dm}^3$  of  $\text{K}_2\text{SO}_4$  was employed in the external electrode compartment.

The composition of the electrochemical cell was as follows:

$\text{Ag/AgCl} | \text{KCl } 0,1 \text{ mol/dm}^3 | \text{K}_2\text{SO}_4 \text{ } 0,1 \text{ mol/dm}^3 || \text{sample} || \text{PVC memb.} | \text{conducting support.} | \text{Cu(s)}$

The epoxy conducting resin was prepared by mixing Araldite M and Hardener H from Ciba-Geigy and graphite powder from Merck as already described by Arada and Pérez for nitrate sensors /15/ obtaining a resistance of  $2 \text{ k} \Omega$ .

The preparation of the electrode body and the application of the membrane was carried out in a similar manner as the method used for the construction of the all-solid-state ion selective electrodes reported in the literature /16/.

The PVC liquid membrane was prepared in a similar way as employed by Arada and Pérez /15/ for the characterization of ion selective electrodes for nitrate determination.

The Silver ISA controls the interferences and also it maintains the ionic force of the medium constant. This is composed of  $0,01 \text{ mol/dm}^3$  of  $\text{Al}_2(\text{SO}_4)_3$ ,  $0,01 \text{ mol/dm}^3$  of  $\text{Ag}_2\text{SO}_4$ ,  $0,02 \text{ mol/dm}^3$  of  $\text{H}_3\text{BO}_3$  and  $0,02 \text{ mol/dm}^3$  of  $\text{NH}_2\text{SO}_4\text{H}$ ; adjusted to pH 3.

## Methods

### Determination of the electromotive force

The electromotive force (EMF) determinations were carried out by using a double-walled cell thermostated at  $25 \pm 0,5$  °C by means of water circulation. The calibration curves were used to calculate such parameters as slope (S), practical detection limit (PDL) and Lower Limit of Linear response (LLLR). This was done following the Nernst law through data adjustment by linear regression method

The calibration parameters were obtained by applying the method of additions /17/ determining the activity of the principal ion by using the Debye-Hückel equation (equation 1).

$$\log f = \frac{0,51Z^2 I^{\frac{1}{2}}}{1 I^{\frac{1}{2}}} \quad (1)$$

Where,  $f$  is the activity coefficient of the ion to be determined,  $Z$  is its charge and  $I$  is the ionic force of the solution.

### Construction of the calibration curve

Starting from an standard solution of  $1 \text{ mol/dm}^3$  of nitrate, successive solutions in the concentration range from  $10^{-6}$  to  $10^{-1} \text{ mol/dm}^3$  were prepared. 10 mL of ISA-Ag was added to each standard solution and the potential generated,  $E$  (mV), was registered. A calibration curve was constructed by plotting  $E$  (mV) against concentration of nitrate in  $\text{mol/dm}^3$ . The resulting calibration curve is shown in fig. 1.

### Direct potentiometry

10 mL of ISA-Ag solution was added to a 10 mL of sample solution by constant stirring using a magnetic stirrer. The generated potential was registered for each sample and the concentration of nitrate was determined from the calibration curve by interpolation.

### Nitrate ion determination by ion chromatography

A Dionex ion chromatograph was used to determine the nitrate ion concentration. A conductivity detector in the range of 10-30 mS and a Spectra Physics integrator model 4290 was used. The volume of the injection loop was 50  $\mu\text{L}$  and a AG4A/SC column and a conductivity suppressor (AFS) with a anionic protector (AG4A/SC) was employed.

A mixture of 1.8 nM  $\text{Na}_2\text{CO}_3$  and 1.7 nM  $\text{Na}_2\text{HCO}_3$  was used as eluent at a rate of 2 mL/min and a regenerator of 25 nM  $\text{H}_2\text{SO}_4$  was used at a rate of 23 mL/min.

Water samples were taken from the water supply station of the province of Guantánamo, which provides drinking water to 70 000 habitants.

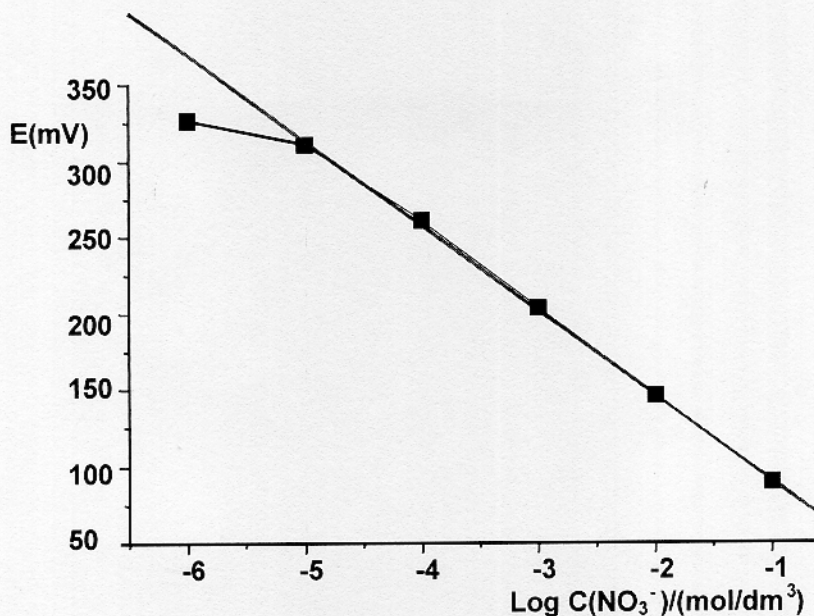


Fig. 1: Calibration curve for nitrate with ISE and ISA-Ag.

Standards as well as sample solutions with  $\text{NO}_3^-$  concentration in the range of 4-15 ppm were prepared by using distilled deionised water

The ionic conductivity of water samples were less than 3 mS/cm, which indicates that these contains low salt concentrations. In this way, the concentration of  $\text{HCO}_3^-$  was in the range of 212-220 mg/L and that of chlorine in the range of 8-214 mg/L.

Concentration of nitrate was determined by establishing a standard curve of known concentrations. This was done by analyzing standard solutions with known nitrate ion concentrations. The calibration curve was established by plotting peak area in the chromatogram against concentration of nitrate ion.

The experimental results were processed by a simple linear regression method and variance analysis. For the application of the lineal regression analysis, the values of three sample runs were processed with three replicas by means of the Systar 5.0 software. No significant differences between the results for a given degree of confidence ( $\alpha = 0,005$ ) was found for compared determinations.

The rejection of anomalous values was realized by using the Dixon test<sup>18</sup> for a 5 % false rejection. The method of Cochran was employed in order to compare the dispersions (to compare data dispersions) and to find out if these were homogeneous.

The intervals of confidence, either for the slope as well as the determined concentrations of nitrate in real samples, were determined for a degree of reliability of  $\alpha = 0,05$  by means of the following equation (2):

$$X = \frac{t(\alpha, gi)V}{\sqrt{N}} \quad (2)$$

Where, N is the number of determinations, V is the standard deviation,  $\alpha$  the degree of reliability, X is the interval of confidence and gi is the degree of freedom.

## ● Results and discussion

As can be seen from Table1, the value for the slope (S)  $-61,2 \pm 0,2 \text{ mV/dec}^{-1}$ , correspond to those expected by Nernst for a monovalent anion. The

membrane exhibited a working concentration range of the  $9,59 \cdot 10^{-6} \text{ mol/dm}^3$  -  $8,69 \cdot 10^{-2} \text{ mol/dm}^3$  with stable potential in 15 seconds.

The values obtained from the ordinates in origin, standards potential ( $E^\circ$ ) are not reported here since this is not recommended due to the fact that the values of  $E^\circ$  can suffer important changes with small variations of the slope. Moreover, this parameter corresponds to a concentration value of  $1 \text{ mol/dm}^3$ , which is much higher than those normally used.

**TABLE 1. CALIBRATION PARAMETERS FOR CONSTRUCTED ELECTRODE**

Parameter	Slope(S) (mV.dec. <sup>-1</sup> )	r	LPD (mol/dm <sup>3</sup> )	LLR (mol/dm <sup>3</sup> )	Sd(S)	Life-Time (Months)
Plasticizer (DBP)	-61,2 0,2	0,99934	$9,59 \cdot 10^{-6}$	$2,82 \cdot 10^{-5}$	1,24	> 6,0

**Sd(S): Standard deviation of the slope (S); r: Correlation coefficient.**

The concentration of nitrate in drinking water from the province of Guantánamo, Cuba was determined by direct potentiometry using an ion selective electrode constructed in our laboratory.

The ISE was calibrated by using the method of mixed solutions. The calibration curve obtained by applying direct potentiometry method is shown in fig. 1. It is seen from this figure that the slope obtained from the calibration curve is  $-61,2 \text{ mV} \cdot \text{dec}^{-1}$ , as is expected from Nernst equation for a monovalent anion, with a correlation coefficient (r) of 0,99934. The concentration of nitrate in real water samples as well as standard solutions were determined from the calibration curve by direct interpolation.

**TABLE 2. NITRATE ION CONCENTRATION(mg/L) IN DRINKING WATER SAMPLES BY USING ISE (TDAN-DBP-PVC) AND ION CHROMATOGRAPHY**

Sample	Directpotentiometry VC (%)	Ion chromatography VC(%)
1	9,93 0,01	1,54
2	8,30 0,05	1,20
3	5,90 0,05	1,70

**VC: Variation coefficient estimated for three replicates.**

Ion chromatography was used as comparative method for determination of nitrate ion concentration in real water samples. The results are shown in tables 2 and 3.

TABLE 3. ANALYSIS OF ADDED AND RECOVERED

Sample	Added	Found	% Recovered
1	1 mg/L	1,07 mg/L	107
	10 mg/L	10,07 mg/L	100,7
2	1 mg/L	0,8 mg/L	80
	10 mg/L	9,9 mg/L	99
3	1 mg/L	1,1 mg/L	110
	10 mg/L	10,1 mg/L	101

Comparison of results from direct potentiometry by using ISE for nitrate and those obtained from ion chromatography were carried out by applying the criterion  $t$  of Students showed that no significant differences between the two methods exists ( $\alpha = 0,05$ ).

As it is seen from tables 2 and 3, the amount of  $\text{NO}_3^-$  in real water samples were not greater than 10 mg/L. This indicated that the concentration of nitrate in water is less than critical value established by the norm NC 93-20 (1985)/19/. The maximum permissible concentration of nitrate in drinking water has been established as 45 mg/L.



## Conclusions

*The constructed ISE for nitrate in this work allows the determination of nitrate concentration in real samples of drinking water. This electrode was successfully employed for the direct determination of nitrate ion concentration in drinking water. Ion chromatography was also used as comparative method to determine the nitrate concentration in drinking water. The results showed good agreement between the values obtained by both method, indicating the applicability of the proposed electrode for accurate determination of nitrate concentration in drinking water.*



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