

# Eclética Química

*Print version ISSN 0100-4670 On-line version ISSN 1678-4618*

**Eclet. Quím. vol.22 São Paulo 1997**

**<http://dx.doi.org/10.1590/S0100-46701997000100017>**

**Uses of nitrate ion sensitive electrodes**

Rubén DEL TÓRO DÉNIS\*

Ana María PEÓN ESPINOSA\*

Hubert DANDIE MARSHALLECK\*

Andres BROCAR ESTEVEZ\*

**ABSTRACT:** Some models of ion-selective electrodes (ISE) and other methods have been elaborated, to quantify nitrate levels in environmental samples (water, fruits, vegetables and others), using direct potentiometry

**KEYWORDS:** Ion-selective electrodes; direct potentiometry; nitrate concentration.

## **Introduction**

The world wide specialized literature has reported in the last few years a human's life injure due to nitrate contamination.<sup>1,6</sup>

Such dangerous effect has been revealed in different environmental samples, such as fruits, vegetables and other food.<sup>3</sup>

It's kown for example, that water well is quite often one of the more contaminated source in the field, causing serious health problems mainly in the infant population.<sup>2,5,8</sup>

Our Department has been assigned the task of determining the ion nitrate concentration by using Ion-Selective Electrodes (ISE).

To this end, we have elaborated some models of Ion-Selective Electrodes and other methods in order to quantify nitrate level in environmental samples.

## **Experimental**

For the determination of nitrate contents in various environmental samples (waters, fruits, vegetables, and other), it has been developed a nitrate sensitive electrode with a plastificated membrane (PVC-Membrane): Direct Contact, electrodes with internal reference solution and other different electrode variants and their methodologies.<sup>4,7,9,10</sup>

It has been used as electrode active substance a high weight molecular quaternary ammonium nitrate immobilized in PVC-Matrix with adequate plastificant.

The measurements system used is formed by an ion selective indicator electrode and the Ag/AgCl reference electrode linked to a millivolt-meter, pH-meter, ionometer (digital or analogical one), reflecting the dependence of  $pNO_3$  vs  $E(mv)$  in correspondence with the Nernst Equation. In the practical use of the electrode, it's necessary the use of a buffer solution for the ionic strength regulation. It could be shown as the most notable interference the  $HCO_3^-$ , Cl, Br, anions of organic acids; I,  $MnO_4^-$  and other.

## Results and discussions

These electrodes show a lineal dependence between  $0.1$  and  $1 \cdot 10^{-5} \text{ mol L}^{-1}$  with a slope of  $56 \pm 3 \text{ mV}$  next to the teoric value at  $298 \pm 1 \text{ K}$  being the electrode response practically instant. The minimum limit of detection is approximately  $8 \cdot 10^{-6} \text{ mol L}^{-1}$ . The probable interference was studied and the value of the potentiometric selectibility coefficient respect to  $Cl^-$ ,  $HCO_3^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $ClO_4^-$ , is quite similar to the values reported by foreign firms.

The error in the determination of nitrates by direct potentiometry was compared with Brucine Method and UV ([Table 1](#), [2](#)). The interference effect of the  $Cl^-$  and  $HCO_3^-$  ions present frequently in water was deeply studied, showing how in the practical fulfillment of the analysis, it should have been avoided first by the elimination of the hydrogen carbonate at pH 3, and the subsequent increment by the addition on nitrate to the sample ([Figure 1](#)).

Table 1 - Determination of the % relative error in the nitrate analysis by direct potentiometry and Brucine Method ( $p = 95\%$ ,  $n = 5$ )

Concentration of nitrate standard solution (mol/L)	Average concentration found by potentiometry	% error	Concentration of nitrate standard solution (mg/L)	Average concentration found by Brucine Method	% error
$1.0 \cdot 10^{-4}$	$0.93 \cdot 10^{-4}$	7,00	6,16	6,40	3,85
$1.5 \cdot 10^{-4}$	$1.58 \cdot 10^{-4}$	5,33	9,15	10,39	13,55
$2.0 \cdot 10^{-4}$	$1.89 \cdot 10^{-4}$	5,50	12,20	13,37	9,62
$3.0 \cdot 10^{-4}$	$2.84 \cdot 10^{-4}$	5,30	15,25	15,53	2,52
$3.5 \cdot 10^{-4}$	$3.32 \cdot 10^{-4}$	5,14	18,30	15,74	13,98
$4.0 \cdot 10^{-4}$	$3.79 \cdot 10^{-4}$	5,25	21,35	23,32	9,24
$4.5 \cdot 10^{-4}$	$4.26 \cdot 10^{-4}$	5,33	24,40	30,11	23,41
$5.0 \cdot 10^{-4}$	$4.75 \cdot 10^{-4}$	5,00	27,45	27,99	1,98
			30,50	30,71	0,68

Table 2 - Comparison of the results obtained in the nitrate standard solutions by ISE and U V ( $n = 5$ )

Exp	Values introduced	Determined by ISE	Determined by UV	% Relative error	
	(mg/L)	(mg/L)	(mg/L)	ISE	U V
1	5	4.9	5.4	2.0	8.0
2	10	10.8	10.7	8.0	1.0
3	20	20.6	22.0	3.0	7.0
4	30	30.1	32.1	0.3	6.6
5	50	50.3	54.7	0.6	9.4

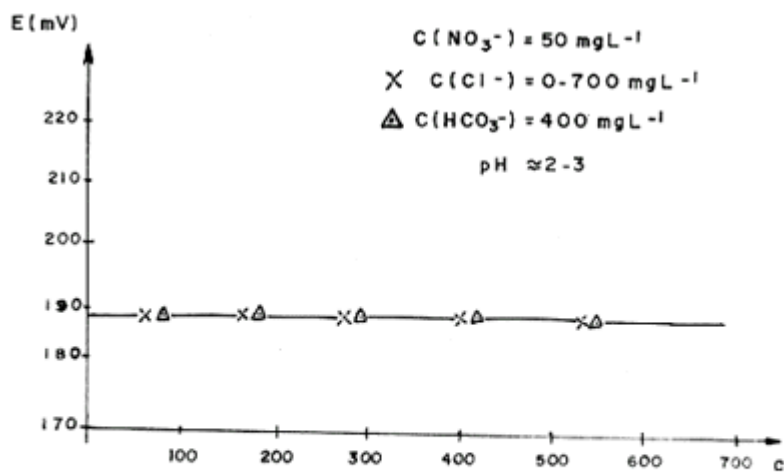
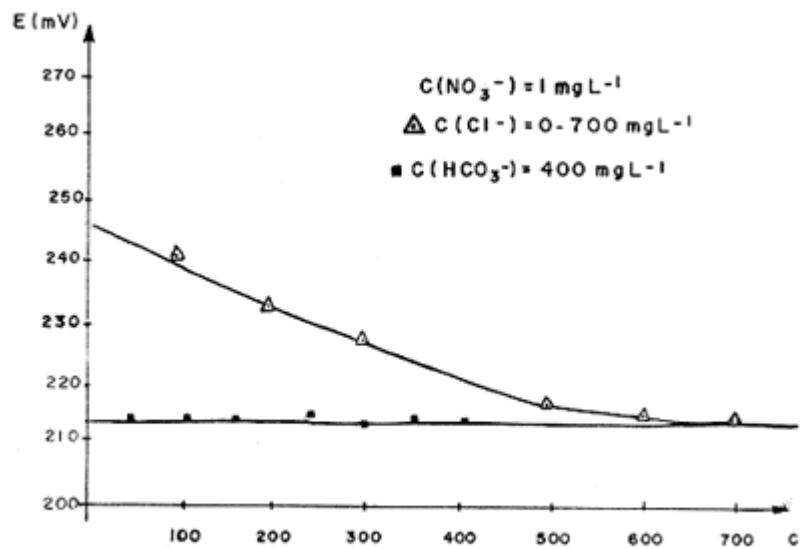


FIGURE 1 - Influence of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  concentration in the electrode potential of nitrate selective electrode.

Electrodes made at the Chemistry Department in the University of Camagüey have been employed in the determination of nitrates in potatoes, onions, carrots and green tomatoes. The statistical analysis was carried out. Test of Hypothesis between two media sample with unknown ( $p = 95\%$ ) using different methodologies has been done ([Table 3](#)).

Table 3 - Results obtained by using plastificated electrode and direct contact electrode (without internal solution) (mg NO<sub>3</sub>/kg weigh)

Methodology Type of sample	Plastificated electrode	Direct contact electrode	T/ Calculate	T/ Tabulate	Confidence interval	Significative diference
Calibrate curve Sample: potatoes	205,0± 11,0	199,0± 4,0	0,9076	1,860	± 1,860	NO
Limit solution Sample: potatoes extract	270,0± 16,0	275,0± 8,0	0,3682	2,132	± 2,132	NO
Sample addition Sample: potatoes	193,5± 5,0	194,3± 6,0	0,1656	2,132	± 2,132	NO
Sample addition Sample: onion	265,6± 8,0	262,7± 5,0	- 0,426	2,132	± 2,132	NO
Sample addition Sample: carrot	32,0± 3,0	30,8± 2,0	- 0,741	2,132	± 2,132	NO
Sample addition Sample: green tomatoes	48,0± 4,0	45,0± 3,0	- 1,179	2,132	± 2,132	NO

## Conclusions

We have elaborated electrodes of different variants for determination of nitrate concentration by direct potentiometry. The effectivity of these dispositives is demonstrated in the control of content of nitrates in diverse surrounding samples, which allows its diffusion in different branches of economy public health and high education.

DEL TÓRO DÉNIZ, R., PEÓN ESPINOSA, A. M., DANDIE MARSHALLECK, H., BROCAR ESTEVEZ, A. Usos de eletrodos sensíveis a íons nitrato. *Ecl. Quím. (São Paulo)*, v.22, p.205-210, 1997.

**RESUMO:** Alguns modelos de eletrodos de íon seletivo e outros métodos foram elaborados para determinar os níveis de nitrato em amostras de água, frutas, vegetais e outros, usando potenciometria direta.

**PALAVRAS-CHAVE:** Eletrodos de íon seletivo; potenciometria direta; concentração de nitrato.

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Recebido em 10.6.1996.

Aceito em 25.9.1996.

\* Department of Chemistry - University of Camagüey - Apdo 5372 - Zona Postal 3 - Camagüey - Cuba.