CONSTRUCTION OF A POLYMERIC LIQUID-MEMBRANE ION-SELECTIVE ELECTRODE (ISE)AND ITS APPLICATION FOR DETERMINATION OF NITRATE IN TOMATOES

MARÍA DE LOS A. ARADA PÉREZ [A], ISEL CORTES NODARSE [B], MEHRDAD YAZDANI-PEDRAM [C]*

[a] Universidad de Oriente, Santiago de Cuba 90500,Cuba.
[b] Instituto de Materiales y Reactivos (IMRE-UH),Universidad de La Habana, la Habana 10400.
[c] Departamento de Química Orgánica y Fisicoquímica y Centro para la Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales (CIMAT), Universidad de Chile, Casilla 233, Santiago, Chile.
mayyazd@yahoo.es

ABSTRACT

A potentiometric all-solid-state type ion-selective electrode (ISE) for NO_3^- was constructed and characterized. It is based on a mixture of tetra-decyl-ammonium nitrate (TDAN) as ionophore, di-butyl phthalate (DBP) as plasticizer and poly (vinyl chloride) (PVC) as matrix. Nitrate concentrations in tomatoes samples, randomly collected from central market at Santiago de Cuba, were determined using the described ISE by standard addition potentiometry. Spectrophotometric determinations using Brucine were performed as comparative method. Accurate and precise results were obtained. Accordingly, an analytical procedure for NO_3^- determination in tomatoes using the constructed ISE could be formulated.

key words: ion-selective electrode (ISE), nitrate, tetra-decyl-ammonium nitrate, liquid membranes, plasticizer, poly(vinyl chloride).

INTRODUCTION

Nitrate ions are present in great variety of samples where it makes it necessary to determine it analytically. In this way, the nitrate ion is an essential part of the nutrients for marine

life. However, an excess of this ion can deteriorate the ecosystem by eutrofication process. The norm NC 93-02 (1985)[1] in Cuba establishes a maximum permissible concentration of 45 mg/L in waters for domestic washing purposes.

In soil, the nitrogen in the form of NO_3^- is essential for plants to grow. By considering the mobility of NO_3^- in soil, it results very important to study the nitrate in soil as well as in plants.

Vegetables and roots such as spinach and carrot constitute the principal source of nitrate in human diet. Drinking water is also an important source of the nitrate. The level of nitrate, in both cases, is influenced by indiscriminate use of nitrogenated fertilizers.

A large number of analytical methods for determination of NO_3^- in different types of samples have been described[2-8]. These include kinetic, chromatographic, potentiometric, amperometric, spectrophotometric and flow injection methods.

Potentiometric determination of nitrate by using an ion selective electrode (ISE)[9-10] constitutes an analytical variant that allows direct determination of this ion, minimizing previous treatment of the samples. This resulted to achieve a simple, fast and selective analysis. In this work the determinations of nitrate in tomatoes were carried out by using an ion-selective electrode of all-solid-state type with plasticized PVC as polymeric liquid membrane on a conducting solid support. This electrode was constructed in a similar manner as those previously constructed and characterized by Arada-Pérez and Pérez-Marin[11-13].

EXPERIMENTAL

Materials and Methods

All reagents used in this study 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 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 W. Buchi melting point apparatus.

The water used in this work was bi-distilled deionised water with a conductivity of less than 2 $\mu S/cm^{-1}$. The PVC liquid membrane was prepared in a similar way as employed by Arada-Pérez[13] for the characterization of ion selective electrodes for nitrate determination.

A Crison model (GLP22) digital pH meter with a precision of ± 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 and saturated AgCl solution from Russell (product reference number 70-00-22) was used as internal reference solution and a solution of 0.1 mol/dm^3 of K_2SO_4 was employed in the external electrode compartment.

The electromotive force (EMF) determinations were carried out by using an open cell at 25 ± 0.5°C .

The calibration parameters were obtained by applying the method of additions[14] and determining the activity of the principal ion by using the Debye-Hückel equation (equation 1).

$$\log f = 0.51 Z^2 I^{1/2} \Big/ 1 + I^{1/2}$$

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.

The calibration curves were used to calculate parameters such as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). This was done through data adjustment by linear regression method following the Nernst law.

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

All reagents were weighed by using a Sartorius model BP 61S analytical balance with a precision of ± 0.1mg.

The composition of the electrochemical cell was as follows:

Ag/AgCl|KCl 0.1mol/dm^3|K_2SO_4 0.1mol/dm^3||sample||PVC membranel conducting supportl $Cu_{(s)}$

The epoxy conducting resin was prepared by mixing Araldite M and Hardener H form Ciba-Geigy and graphite powder from Merck, as already described by Arada-Pérez[13] for nitrate sensors, obtaining a resistance of ≤ 2 KΩ.

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[15,16].

Sample preparation and treatments

Ripe tomatoes from a lot available in the central market of Santiago de Cuba were analyzed. Fifteen laboratory samples were randomly selected and were analyzed with triplicate replica.

5g of sample was cut into small pieces, smashed and passed through a 40 micron plastic sieve to obtain the juice. The residue left after filtration was then added to the juice and transferred to a 100 mL volumetric flask and completing to 100 mL with a 1% $KAl(SO_4)_2$ solution.

Standard addition

The potential E_1 (mV) of 10 mL of sample was measured. Then 1.4 mL of an standard nitrate solution with a concentration of 180 mg/L was added to the sample solution and its potential E_2 (mV) was measured. The concentration of nitrate in the samples was determined by using the following equations:

$$Cm = Cstd \cdot Q \quad (2)$$

$$Q = (Vstd / Vm + Vstd \cdot 10^{\Delta E/S} - Vm) \quad (3)$$

Where, Cm is the concentration of the sample, Cstd is the concentration of the standard, Vm is the volume of the sample, Vstd is the volume of added standard solution, S is the slope of the employed electrode and ΔE is the difference between the measured potentials.

A calibration curve was constructed by applying the Brucin UV spectroscopy method where transmittance values were plotted against concentration.

Once the color between a series of standards and sample was developed in the darkness for ten minutes, a witness was adjusted to 100% transmittance for a wavelength of 410 nm and the intensity was measured. The concentration of the sample was then determined by interpolation.

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 15 sample runs for three replicas were processed with by means of the Systar 5.0 software. No significant differences between the results for a given degree of confidence (α = 0.05) was found for compared determinations.

The rejection of anomalous values was realized by using the Dixon test[17] for a 5% false rejection. The method of Cochran[17] was employed in order to compare the dispersions (to compare data dispersions) and to find out if these were homogeneous.

RESULTS AND DISCUSSION

Characteristic parameters of the employed electrode

The constructed all-solid-state type liquid membrane selective electrode for nitrate was characterized. The characteristic parameters obtained during its characterization are presented in table 1.

Table 1. Characteristic parameters for the constructed ISE.

Slope (S, mV/dec^{-1})	-61.2 ± 0.2
LPD (mol/dm^3)	$9.59.10^{-6}$
LLLR (mol/dm^3)	$2.82.10^{-5}$
r	0.99934
Life-Time (Months)[13]	> 6 months
pH	3 – 11
Estimated cost of each electrode	8.00 – 10.00 USD
Sequence of interferences for a concentration of 0.01 mol/dm^3 of interfering anion[13]	ClO_3^->Cl^->Bz^->BrO_3^->Br^->CrO_4^{2-}>IO_3^- >HPO_4^{2-}>SO_4^{2-}>CO_3^{2-}>$C_2O_4^{2-}$

r: Correlation coefficient.

Membrane degradation

One of the factors that limits the life-time of the liquid membrane electrodes is the loss of the sensor (ionophore) by leaching from the membrane to the measuring solution[16,18]. The shortening of the life-time of the electrode is mainly due to the loss of the ionophore from polymeric membrane by migration to the surface of the membrane and thereafter to the measuring aqueous solution. The high dielectric constant of the water makes it a very polar medium. This causes strong interaction with the ionophore which is polar in nature. Therefore, its migration to the measuring solution will occur by leaching from the membrane during the use of the electrode. This phenomena is very usual in the case of polar ionophores[16,18].

FTIR spectroscopy was used in this work in order to follow the loss of the ionophore from the membrane by analyzing the corresponding nitrate absorption band. Infrared spectra in the frequency range of 4000 – 400 cm^{-1} were obtained by using a Mattson Genesis FTIR series instrument. Total attenuated reflectance ATR-FTIR technique was used.

Sample preparation for FTIR analysis

Polymeric membranes were separated from electrodes and were washed thoroughly with bidistilled water in order to eliminate visible solution from the surface of the membrane. The face of the membrane exposed to the measuring solution was carefully mounted on the surface of a highly reflexive ZnSe plaque taking care that no air bubbles was entrapped between sample and the ZnSe plaque surface. Infrared spectra of polymeric membrane containing only the plasticizer (control sample), unconditioned polymeric membrane with all its components and the conditioned membrane with a life-time of 4 month are shown in Figures 1a, 1b and 1c respectively.

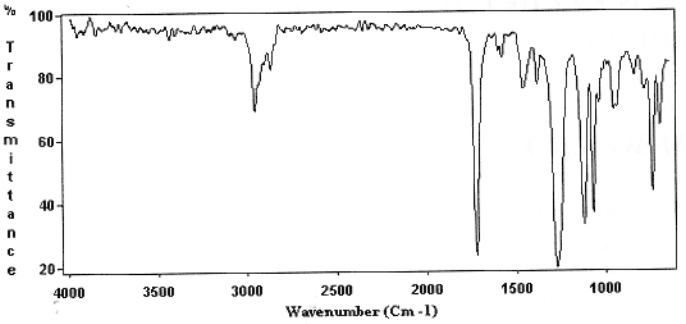

Fig.1a. Infrared spectrum of polymeric membrane (control sample)

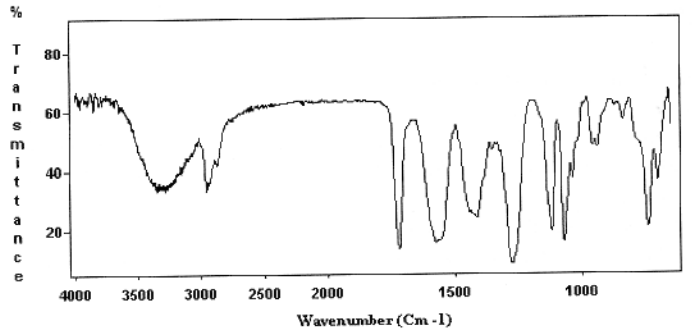

Fig. 1b. Infrared spectrum of unconditioned polymeric membrane.

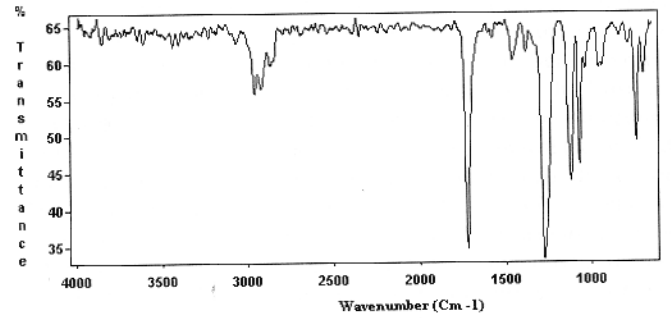

Fig. 1c. Infrared spectrum of conditioned membrane with a life-time of 4 month.

The absorption bands assignments for different components of the membrane are as follows:

DBP: ν^{as}_{CH2}(2963), ν^{s}_{CH2}(2872), $\nu_{C=O}$(1727), δ^{s}(1464 y 1384), ν_{C-O}(1282, 1257 y 1073), $\gamma_{CH(orto)}$(747); TDAN: ν^{as}_{CH2}(2920), ν^{s}_{CH2}(2850), δ^{s}(1383), ν_{C-N}(1339), ρCH_2(720); PVC ν^{as}_{CH2}(2925), ν^{s}_{CH2}(2852), δ^{s}_{C-H}(1429), ν_{C-Cl}(1253), ν_{C-Cl}(613).

The FTIR of a control sample consisting of a physical mixture of DBP and PVC was registered. This was done in order to corroborate that in the region where absorption bands corresponding to ν_{C-N} are encountered no absorption bands from polymeric matrix exist which could lead to erroneous assignments.

The spectrum of the unconditioned membrane with all of its components was also registered and the following band assignments were made: $\nu^{as}_{NO3^-}$ (1576 cm^{-1} and 1416 cm^{-1}), ν_{OH}(3300).

The spectra of conditioned membranes at different life-time of the electrode showed that the intensity of the nitrate absorption bands ($\nu^{as}_{NO3^-}$) diminishes with time of the use of the electrode. This is due to the partial loss of the ion-pair, used as ionophore, from the membrane by leaching. The lipophilicity[19] of both ionophore and that of the solvent mediator contribute to this negative effect. The FTIR spectra showed that neither the plasticizer or PVC was lost during the life-time of the electrode.

The diminishing of the area under the nitrate absorption band during the life-time of the electrode is shown in figure 2. Loss of the electrode response was observed as the active sites (ionophore) were lost by exudation from the membrane.

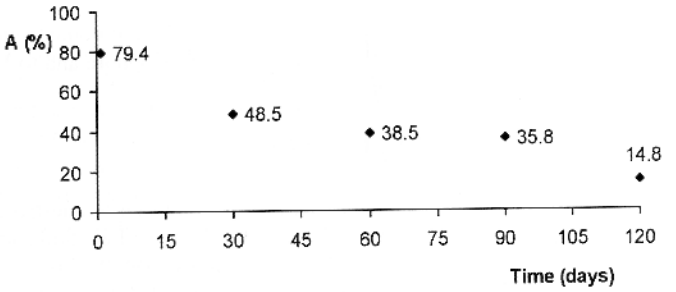

Fig. 2. Loss of the ionophore from polymeric liquid membrane as function of time.

It was confirmed by this study that the life-time of liquid membranes containing a charged mobile carrier is fundamentally limited by the loss of the ionophore.

Determination of NO_3^- in tomato samples

The concentration of NO_3^- in the analyzed lot by both potentiometric method with standard addition and by direct UV spectroscopy were compared. The measured concentration values corresponding to each method are presented in table 2 together with their interval of confidence and values of the variation coefficients expressed as percentages.

Table 2. Nitrate concentration in tomato lot by potentiometric and UV spectroscopy.

Method	Potentiometric (Addition of standard)	Spectrophotometric (U.V)
Concentration (mg/L)	18.30 ± 0.48	19.15 ± 0.53
VC (%)	6.7	6.7

VC: Variation coefficient.

The statistical comparison of the measurements for a level of significance of α=0.05 allowed us to confirm that no significant differences among the measurements exists.

In this way, it can be considered that the pontentiometric method reports exact results since the values obtained were compared with those obtained by UV spectroscopy which is a known analytical method with a different basis. Similarly, the values of variation coefficients obtained are less than 10% which can be considered indicative of an adequate

precision for the quality control for this type of the sample.

It is possible to confirm that the analyzed tomatoes lot complies with the requirements of the norm NC 93-02 (1985)[1].

CONCLUSIONS

An ion selective electrode of the all-solid-state type formed by a polymeric liquid membrane and by using TDAN as ionophore (7 wt.-%), DBP as solvent mediator (64 wt.-%) and PVC as matrix (29 wt.-%), sensible to nitrate ions with adequate characteristics for routine application is reported here. The results obtained permitted the utilization of the constructed ion-selective electrode for precise determination of nitrate in tomatoes.

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REFERENCES

1. NC 93-02 (1985). Agua potable: Requisitos sanitarios y muestreo.
2. I. Walonga, W. Van Vark, J. G. Houba, . J. J. Van Der Lee, Soil and plant analysis. Part 7 Plant Analysis Procedures, (1989), 126
3. M. S. Finch, D. J. Hydes, C. H. Clayson, B. Weigl, J. Dakin, P. G. Willian, Anal. Chim. Acta, 377(2-3), (1998),167-177
4. A. Bralthwalte, F. J. Smith, Chromatography Methods. (1996), 501-504
5. R. Pérez Olmos, A. Rios, J. R. Fernández, R. A. S. Lapa, J. L. F. C. Lima, Talanta,53(4), (2001),741-748
6. J. Davis, M. J. Mooreroft, S. J. Wilkins, R. G. Compton and M. F. Cardosi, Analyst, 125(4), (2000),737-742
7. T. Le Goff, J. Marsh, J. Braven, L. Ebdon, D. Scholefield, Green Chemistry, 4(5), (2002), 486-491
8. T. Le Goff, J. Braven, L. Ebdon, N. P. Chikottt, D. Scholefield and J. W. Wood, Analyst, 127(4), (2002),507-511
9. I. Isildak, A. Asan, Talanta, 48(4), (1999),967-978
10. M. Mitrakas, R. Tsitouridou, B. Kabasakalis, J. Georgiou, Toxicol. Environ. Chem., 22 , (1989),163 – 168
11. María de los A. Arada Pérez, J. Calvo, L. Pérez Marín, J. Alonso, J. E. Tacoronte, Revista Cubana de Química XI, (1999), 80 – 85
12. L. Pérez-Marin, María de los A. Arada Pérez, J. E. Tacoronte, Afinidad, LV 475, (1998),179-182,
13. María de los A. Arada Pérez, J. Calvo, M. Yazdani-Pedram, Sens. Actuat. B, 89 (2003), 262-268.
14. IUPAC Compendium of Analytical Nomenclature. Oxford, Pergamon Press, (1978), 168 – 173
15. E. Martinez, "Sensors potenciometric all- solid- state d' amoni i la seva conversio en biosensors d' urea construció, evaluació aplicació". Tesis Doctoral Universidad Autónoma de Barcelona, (1990)
16. T. Araki, H. Tsukube, Liquid Membrane. Chemical Applications. Ed. CRC Press, Inc. Boca Raton, (1990)
17. Estadística Aplicada. Oestle. Ed. Científico Técnica. C. Habana (1985)
18. O. Dinten, U. E. Spichger, N. Chaniotakis, P. Gehring, B. Rusterholz, W. E. Morf, W. Simon, Anal. Chem., 63, (1991), 596-603
P. I. Bailey, Analysis with Ion - Selective Electrodes, 2nd Ed., Heyden. Larden, (1980)