Revista Cubana de Química
ISSN: 0258-5995
revcubanaquimica@cnt.uo.edu.cu
Universidad de Oriente
Cuba

Arada, María de los Ángeles; Vicente Luis, Santiago; Altava, Belén; Galindo, Francisco
Construction and evaluation of chloride ion-selective electrodes
Revista Cubana de Química, vol. 27, núm. 2, mayo-agosto, 2015, pp. 119-130
Universidad de Oriente
Santiago de Cuba, Cuba

Rev. Cubana Quím.
Vol. 27, no. 2, mayo-agosto, 2015, págs. 119-130, e-ISSN: 2224-5421

Construcción y evaluación de electrodos selectivos de iones cloruro

Construction and evaluation of chloride ion-selective electrodes

***Dra. C. María de los Ángeles Arada*[I], *Dr. C. Santiago Vicente Luis*[II],**
***Dra. C. Belén Altava*[II], *Dr. C. Francisco Galindo*[II]**

may@cnt.uo.edu.cu, luiss@uji.es

[I]*Department of Analytical Chemistry, Universidad de Oriente, Santiago of Cuba, Cuba;* [II]*Department of Inorganic and Organic Chemistry, Jaume I University, Castellón, Spain*

Recibido: 3 octubre de 2014 Aprobado: 3 diciembre de 2014

Resumen

En este artículo se presenta una membrana de PVC selectiva de iones cloruro, utilizando bis (2-etilhexilo) (DOS) como plastificante y 2-(5-(4-nitrofenil)furil)-4,5-difenil imidazol como ionóforo. Los electrodos construidos mostraron una rápida respuesta potenciométrica al ion cloruro en el rango de concentración de 10^{-6} a 10^{-2} mol · dm^3 con pendiente nernstiana. En el caso de los electrodos preparados, que contienen el 1 % y el 3 % del peso del ionóforo, el tiempo de vida del sensor fue estimado de 6 a 7 días. El tiempo de vida del sensor que contiene el 7 % del peso del ionóforo fue de 15 a 18 días. El electrodo que contiene el 7 % del peso del ionóforo fue aplicado como electrodo indicador en la valoración potenciométrica de iones de plata con NaCl.

Palabras clave: membrana de PVC selectiva de iones cloruro, electrodo selectivo de iones (ESI), 2-(5-(4-nitrofenil)furil)-4,5-difenil imidazol, sensor químico.

Abstract

In this paper we report a chloride ion-selective PVC membrane, using bis (2-ethylhexyl) sebacate (DOS) as plasticizer and 2-(5-(4-nitrophenyl)furyl)-4,5-diphenyl imidazole (FFDFIN) as ionosphere. The constructed electrodes showed a fast potentiometric response to chloride in the concentration range from 10^{-6} to 10^{-2} mol · dm^{-3} with Nernstian slopes. In the case of electrodes prepared containing 1 and 3 wt % of the ionosphere, the lifetime of the sensor was estimated to be about 6-7 days. The lifetime of the sensor containing 7 wt % of ionosphere was about 15-18 days. The electrode containing 7 wt % of ionosphere was applied as an indicator electrode in the potentiometric titration of silver ions with NaCl.

Keywords: chloride ion-selective PVC membrane, ion-selective electrode (ISE), 2-(5-(4-nitrofenyl) furyl)-4,5-difenyl imidazole, chemical sensor.

Introduction

The accurate determination of low levels of the chloride ion is essential, according to its important biological relevance [1]. As an example, chloride is an essential component of the human diet, being the minimal request for adults of 750 mg day. Besides, this ion plays an important role in the regulation of extra-cellular fluids and variations in its concentration in biological fluids are often associated to different abnormal metabolic processes and diseases [1].

Different methodologies have been reported for the determination of the chloride ion. These include chromatographic, spectrophotometric, voltmetric, turbid metric and volumetric methods such as the classical Volhard titration [2-5]. Although several methodologies have become standard in the field for chloride determination, many of them suffer from important disadvantages, in particular due to the need of large analysis times and tedious sample pre-treatments.

The use of selective electrodes represents an alternative method for the potentiometric determination of different species; allows reducing some of the drawbacks associated with the chloride ion analysis by other methodologies [6-17]. In the last few years, the construction of robust electrochemical sensors, sensitive and precise, capable of detecting and quantifying the concentration of different substances in a variety of solutions including biological fluids and direct samples from ecosystems has been a subject of much interest.

Ion-selective electrodes (ISE) are very appropriate for this purpose because they are easy to build, the results are obtained quickly, they show good selectivity for inorganic ions, they are of relatively low cost and they are portable and easily handled so they can be used in the places of interest.

Here we report the use of 2-(5-(4-nitrophenyl)furyl)-4, 5-diphenyl imidazole, a highly selective carrier for the building of ISE devices for the detection of the chloride ion using a PVC membrane with bis(2-ethylhexyl) sebacate (DOS) as the plasticizer.

Experimental

A pH/mV meter Crison digital pH meter with a precision of ± 0,1 mV was used for measuring the potential difference between reference and indicator electrodes. A microprocessor-based Hanna pH meter model 213 was used for all pH measurements using an Oaklon model WD–35881–00 combined electrode with epoxy body and an IKA hot plate-magnetic stirrer.

All the reagents used in this study were of analytical grade. Polyvinylchloride (PVC) from Aldrich was directly used as received as the polymeric matrix, employing Araldite Ceys (mixing of A and B components) for the grafting. The plasticizer bis (2-ethylhexyl) sebacate (DOS) from Sigma-Aldrich was employed as supplied as the solvent mediator of the PVC liquid membrane.

Tetrahydrofurane (THF) and NaCl were of analytical grade and obtained from Scharlau. Bidistilled water with conductivity less than 2 $\mu S/cm^{-1}$ was used for all experiments. All reagents were weighed by using an analytical balance with a precision of ± 0, 1 mg.

The pH adjustments were made with dilute H_2SO_4 or NaOH solutions as required. The ionophore was synthesized in the Polymer Laboratory of the Faculty of Chemical and Pharmaceutical Sciences, University of Chile, Santiago, Chile. Its characterization was carried out in the same department and in the Department of Inorganic and Organic Chemistry of the Jaume I University, Castellón, Spain.

The elemental analyses were carried out using a Carlo-Erba Ea 1110 Elemental Analyzer and melting points were determined with a Buchi melting point apparatus. FT-IR spectra were obtained on Bruker IFS28.

The composition of the prepared membranes was as follows: 1, 3 or 7 wt % of the ionophore, 33 wt % of PVC and 66, 64 or 60 wt % of the plasticizer. The mixture was dissolved in 3 mL of dry THF. The resulting membrane cocktail was then deposited on a previously formed 1:1 epoxy-graphite composite solid contact and the solvent was evaporated to obtain the final membrane.

The electrodes were conditioned in $1 \cdot 10^{-2}$ mol · dm^{-3} solution containing their primary ions for 24 h before use. The reference electrode was a double-junction Ag-AgCl containing 0, 1 mol · dm^{-3} K_2SO_4 solutions in the outer compartment. The electrochemical cell used was: Ag/AgCl| 0,1 mol · dm^{-3} KCl |0,1 mol · dm^{-3} K_2SO_4||test solution||PVC memb.|cond.supp. $|Cu_{(s)}$.

Determination of the electromotive force (EMF)

The electromotive force (EMF) determinations were carried out by using an open cell to ambient temperature. 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 a linear regression method.

The calibration parameters were obtained by applying the method of additions [18], determining the activity of the principal ion by using the Debye-Hückel equation (1).

$$-\log f = \frac{0{,}51 Z^2 I^{1/2}}{1 + I^{1/2}} \qquad (1)$$

The selectivity coefficients (K_{AB}^{Pot}) were determined in the presence of various foreign ions by using the method of mixed solutions [18] (2).

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

Synthesis of 2-(5-(4-nitrophenyl) furyl)-4, 5-diphenyl imidazole

The synthesis of 2-(5-(4-nitrophenyl) furyl)-4, 5-diphenyl imidazole (FFDFIN) was carried out from 5-(4-nitrophenyl) furfural and benzyl in the presence of ammonium acetate and glacial acetic acid.

The reaction between benzyl (I) and 5-(4-nitrophenyl)furfural (II) was carried out by adding 1,94 g (0,009 2 mol) of (I) to 2 g (0,009 2 mol) of (II) and in the presence of 14 g (0,2 mol) of ammonium acetate. Glacial acetic acid (40 mL) was used as solvent. The reaction mixture was heated for 5 h at reflux temperature and then 25 mL of distilled water was added.

The crude product was then filtered and washed with water followed by dissolution in 250 mL of water. After cooling, the precipitate was filtered and the product was recrystallized from butyl acetate to yield the pure product in 64, 2 %.

The different analyses carried out on this compound were in good agreement with the formation of the expected structure. Thus, the FT-IR spectrum showed the presence of the N-H absorption bands at 3 500 cm^{-1} along with absorption bands at 1 500-1 600 cm^{-1} region corresponding to the aromatic fragments.

The presence of the nitro group was confirmed by existing of the absorption bands at 1 370 and 1 517 cm^{-1}. The spectrum also showed the complete absence of absorption bands in the C=O stretching region.

The ^{1}H NMR of FFDFIN showed the presence of the expected signals at 7,1-7,6 ppm for the phenyl groups at C4 and C5 of the imidazole group, at 8,0-8,4 ppm for the 4-nitrophenyl group located at C2 of the imidazole and at 6,0-6,5 ppm for the imidazole

N-H and for the hydrogen atoms at the furan ring. The elemental analysis of the salt gave: C 72,77 %, H 8,74 % and N 10,17 %.

Results and discussion

Electrode preparation and characterization

Different membranes were prepared through the combination of FFDFIN and PVC in different ratios. After optimization of the conditions of use, experimental data revealed that this kind of electrodes were highly selective to the chloride ion relative to several other ions (figure 1).

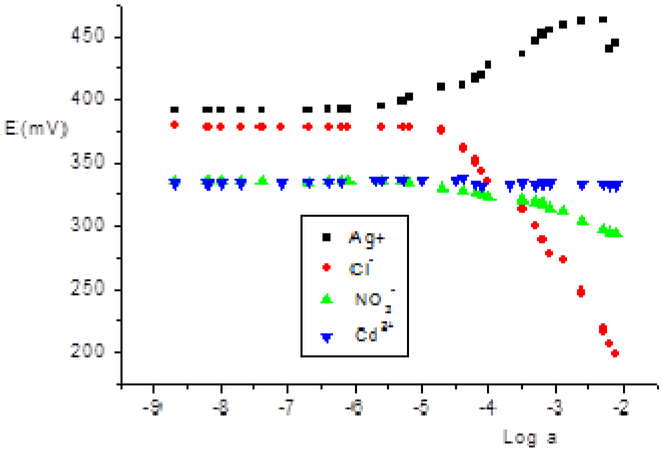

Figure 1. Potential responses obtained for different ions using the selective electrodes based on FFDFIN and 7 wt % of the ionophore

In general, the characteristics and properties of an ion-selective electrode, i.e., sensitivity, lifetime, selectivity and other properties are dependent on the amount and type of plasticizer, polymer matrix and the nature of the carrier employed [19]. In this regard, we studied the influence of the different compositions assayed for the membranes on their properties. The characteristic parameters of the optimized membranes are summarized in table 1.

TABLE 1. OPTIMIZATION OF THE SELECTIVE MEMBRANES

Membrane No	Plasticizer (%)	PVC (%)	Ionophore (%)	Slope (mV/decade)
1	66	33	1	-65,52
2	66	33	1	-65,52
3	66	33	1	-66,03
4	64	33	3	-66,13
5	64	33	3	-65,68
6	64	33	3	-65,29
7	60	33	7	-62,75
8	60	33	7	-62,58
9	60	33	7	-64,17

The response of the electrodes prepared with different amounts of plasticizers and ionophores was studied providing some clear trends. In all cases studied, the electrodes showed Nernstian slope per decade for chloride activity in wide range of the activity studied, showing detection limits in the order of 10^{-6}-10^{-2} mol · dm^{-3}.

The detection limit decreases considerably with the lifetime. The electrodes with 1 % of the ionophore shows short lifetime. Results obtained by 1, 3 or 7 wt % of the ionophore are statistically compared demonstrating that there are no significant differences between slope (mV/dec) results obtained with the ISEs.

The statistical comparison of the slope measurements for the different membranes provided a level of significance of $\alpha = 0,05$, which is an acceptable value and confirms the lack of significant differences in this regard.

In order to achieve a detailed study of the response of the electrodes to the chloride anion, the corresponding calibration curves were obtained (figure 2). These calibration curves were used to calculate the essential parameters such as slope (S), practical detection limit (PDL) and lower limit of linear response (LLLR). This was done through data fitting using a linear regression method following the Nernst law.

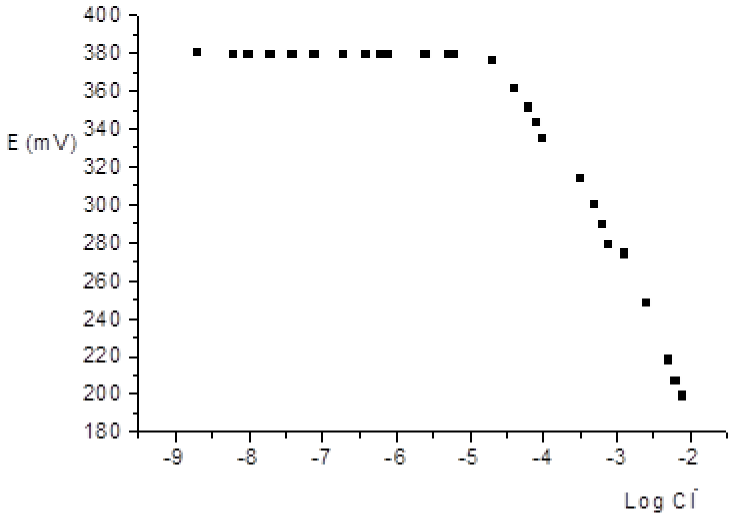

Figure 2. Calibration curve for chloride ion-selective electrode prepared by using 7,0 wt % of the ionophore

The results obtained for the ISEs containing 1, 3 or 7 wt % of ionophore have been gathered in table 2.

TABLE 2. CHARACTERISTIC CALIBRATION PARAMETERS FOR THE SENSORS CONTAINING 1, 3 OR 7 wt % OF THE IONOPHORE

Ionophore	ESI	Calibration parameters
2-(5-(4-nitrophenyl)furyl)-4,5-diphenyl imidazole	Cl^- 1 wt %	S(mV/dec) -65,69 ± 0,8 Correlation coefficient: 0,999 2 LPD mol · dm^{-3} 7,122 · 10^{-6} LIRL mol · dm^{-3} 2,408 · 10^{-5}
	Cl^- 3 wt %	S(mV/dec) -65,70 ± 0,8 Correlation coefficient: 0,999 2 LPD mol · dm^{-3} 7,020 x 10^{-6} LIRL mol · dm^{-3} 2,102 x 10^{-5}
	Cl^- 7 wt %	S(mV/dec) -63,16 ± 0,8 Correlation coefficient: 0,999 2 LPD mol · dm^{-3} 7,221 · 10^{-6} LIRL mol · dm^{-3} 2,428 · 10^{-5}
	Ag^+ 7 wt %	S(mV/dec) 15,57
	NO^-_3 7 wt %	S(mV/dec) -21,81

The effect of the pH of the test solutions on the response of the sensor was studied using different solutions being $1 \cdot 10^{-1}$ mol · dm^{-3} in NaCl. In order to carry out properly this study, it is important avoiding simple combined pH electrodes. These contain an Ag/AgCl reference electrode immersed in a chloride ion solution (usually 3 mol · dm^{-3}) and the potential diffusion of the chloride ion from this solution to the working solution could induce significant interferences in the measurements.

A second aspect to be considered is the variation in the potential at the liquid union between the reference and the working solution. This variation can occur, in particular, at low pH because of the high mobility of the hydronium ion and can be minimized if the nature of the ionic species present in solution does not experiment significant variations.

According to this, H_2SO_4 was selected for the acidification of the medium taking into consideration that the sulphate anion is present in the reference electrode, while NaOH was selected as the base for the basification of the medium. In this way, the variation in the liquid union potential can be essentially attributed to the differences in concentrations, but not to the existence of different species in the solution.

The responses in the values for the potential indicated that no significant changes take place within the pH range 2-6.

In order to determine the true potential for the analytical application of this ISE, the possible interference by different anions was studied by using the method of mixed solutions [18]. Some results are gathered in table 3, displaying the values for the corresponding selectivity coefficients in terms of K_{AB}^{Pot} and Log K_{AB}^{Pot} , using 7 wt % of the ionophore.

As can be seen in table 3, the selectivity coefficients range at about 10^{-2}, indicating they most significantly disturb the functioning of the chloride selective membrane. The lifetime of the sensor is also an important parameter to assess its practical applicability. In the case of electrodes prepared containing 1 and 3 wt % of the ionophore, the lifetime of the sensor was estimated to be about 6 days.

The lifetime of the sensor containing 7 wt % of the ionophore was about 15-18 days. After these periods of time, the electrochemical behaviors of the sensors gradually deteriorate.

TABLE 3. POTENTIOMETRIC SELECTIVITY COEFFICIENTS FOR VARIOUS INTERFERING IONS

Ion	K_{AB}^{Pot}	Log K_{AB}^{Pot}
NO^-_3	$5{,}424 \cdot 10^{-2}$	-1,265 6
Br^-	$5{,}575 \cdot 10^{-2}$	-1,253 7
I^-	$6{,}665 \cdot 10^{-2}$	-1,176 1
BrO^-_3	$7{,}525 \cdot 10^{-2}$	-1,123 7
IO^-_3	$8{,}75 \cdot 10^{-2}$	-1,057 9

The response stability of the sensor as function of time was studied for an electrode constructed by using 7 wt % of ionophore (figure 3). The static response time obtained was less than 30 seconds.

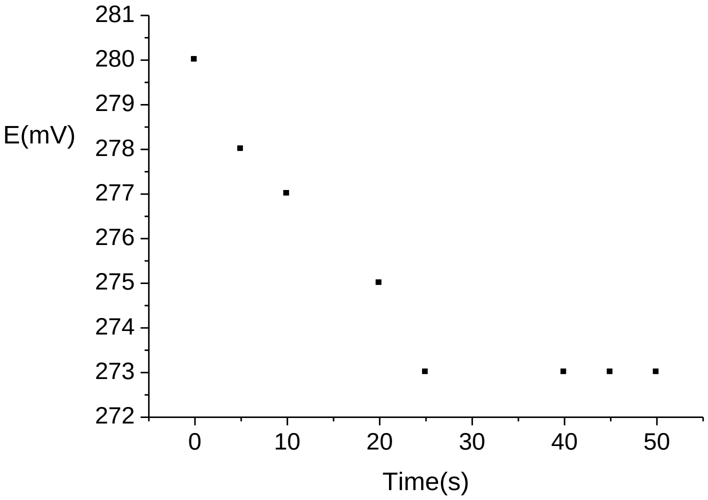

Figure 3. Stability of the response time of the sensor constructed by using a 7 wt % of the ionophore

Preliminary analytical application of the sensor

The utility of the sensor for chloride ion determination was evaluated through its use as an indicator electrode in the titration of silver ions with NaCl (the sensor containing 7 wt % the ionophore). An example of the resulting titration curves is shown in figure 4. As can be seen, the amount of silver ions in solution could be determined with the electrode.

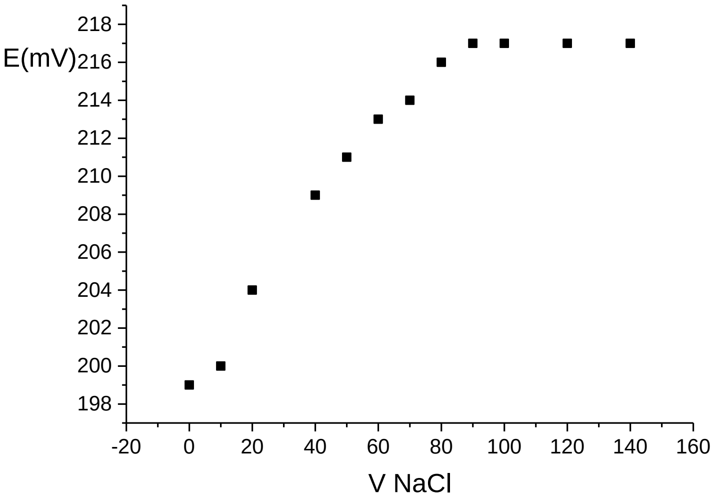

Figure 4. Potentiometric titration curve of 100 µL $AgNO_3$ with NaCl $1 \cdot 10^{-3}$ mol · dm^{-3} by using the sensor containing 7 wt % of ionophore as an indicator electrode

Conclusion

A new ion-selective electrode formed by a polymeric liquid membrane and by using 2-(5-(4-nitrophenyl)furyl)-4,5-diphenyl imidazole (FFDFIN) as ionophore, DOS as plasticizer and PVC as matrix, sensible to chloride ion can be considered highly reproducible. The ISEs showed Nernstian slope with a practical detection limit (PDL) in order of 10^{-6} mol · dm^{-3} and short response time. The results obtained permitted the utilization of the constructed ion-selective electrode for precise determination of chloride.

References

1. MINETTI, M. L.; ZANNIER, M. S.; SBODIO, O. A.; TERCERO, E. J., "Determinación de Cloruro de sodio en quesos argentinos", *Revista FAVE-Ciencias Veterinarias,* 2002, 1(1), 43-48.
2. XIAO, J. B., "Determination of nine components in bayer liquors by high performance ion chromatography with conductivity detector", *J. Chil. Chem. Soc.* 2006, 51(3), 964-967.
3. JUÁREZ, M.; MARTIN-HERNÁNDEZ, M. C., "Contenido de elementos minerales en quesos del mercado español, determinados por espectrofotometría de absorción atómica", *Revista Agroquímica de Tecnología de Alimentos,* 1983, 23, 417-422.

4. ARAI, K.; KUSU, F.; NOGUCHI, N.; TAKAMURA, K.; OSAWA, H., “Selective determination of chloride and bromide ions in serum by cyclelic voltammeter”, *Anal. Biochem***.** 1996, 15, 240(1), 109-113.
5. HARRIS, D. C., *Quantitative Chemical Analysis*, 6th ed., New York, W. H. Freeman & Company, 2003.
6. ROTHMAIER, M.; SIMON, W., “Chloride-Selective Electrodes Based on Mercury Organic Compounds as Neutral Carriers”, *Anal. Chim. Act*, 1993, 271, 135-141.
7. XIAO, K. P.; BUHLMANN, P.; NISHIZAWA, S.; AMEMIYA S.; UMEZAWA, Y., “A Chloride Ion-Selective Solvent Polymeric Membrane Electrode Based on a Hydrogen Bond Forming Ionophore”, *Anal. Chem*., 1997, 69, 1038-1043.
8. MAHAJAN, R. K., *et al*., “Anion Receptor Functions of Lanthanide Tris(diketonate) Complexes”, *Chem. Comm*., 2003, 22, 2238-2241.
9. BABU, J. N.; BHALLA, V.; KUMAR, M.; MAHAJAN, R. K.; PURI, R. K., “A Chloride Selective Sensor Based on a Calixarene Possessing a Urea Moiety”, *Tetrahedron Lett*., 2008, 49, 2772-2775.
10. BABU, J. N.; BHALLA, V.; KUMAR, M.; PURI, R. K.; MAHAJAN, R. K., “Chloride Ion Recognition Using Thiourea/Urea Based Receptors Incorporated into 1,3-disubstituted Calixarenesw”, *New J. Chem*., 2009, 33, 675-681.
11. COMISIÓN VENEZOLANA DE NORMAS INDUSTRIALES, *Carbón: determinación del contenido de cloro: método del electrodo selectivo de ion*, Norma Venezolana Covenin 2600-89, Caracas, FONDONORMA, 1989, 7 p., ISBN: 9800604219.
12. GARRIDO FERNÁNDEZ, A.; GARCÍA GARCÍA, P., “Estudio comparativo de métodos para la determinación de NaCI en las salmueras de aceitunas”, *Grasas y Aceites*, 1985, 36, 134-137.
13. RODRÍGUEZ, Z.; HERNÁNDEZ, B.; PERALTA, G.; GAYTÁN, E.; MOYA, R. “Determinación de halogenuros en residuales del Laboratorio de Producción del Centro de Bioactivos Químicos con electrodos selectivos”, *Revista Cubana de Química*, 1998, 10(1-2), 80-87.
14. ÁLVAREZ ROMERO, G. A.; RAMÍREZ SILVA, M. T.; GALÁN VIDAL, C. A.; PÁEZ HERNÁNDEZ, M. E., “Uso de un compuesto de grafito-resina epóxica-polipirrol para el desarrollo de un electrodo potenciométrico selectivo a iones cloruro”, en XXV Congreso de la Sociedad Mexicana de electroquímica, 3rd Meeting of the Mexican Section of the Electrochemical Society (31 may.-4 jun., 2010), Zacatecas, 2010.

15. García García, P.; Brenes Balbuena, M.; Garrido Fernández, A., "Métodos instrumentales para la determinación de NaCl en las salmueras de aceitunas", *Grasas y Aceites,* 1991, 42(4), 261-266.
16. Garrido Fernández, A.; García García, P., "Estudio comparativo de métodos para la determinación de NaCI en las salmueras de aceitunas", *Grasas y Aceites,* 1985, 36, 134-137.
17. Hooker, K.; Alvarado, Ana Lorena; "Validación de la determinación de cloruros y humedad, para la evaluación de combustibles alternos para hornos de cementeras", *Tecnología en Marcha,* 2010, 23(3), 24-32.
18. International Union of Pure and Applied Chemistry, "Recommendations for nomenclature of ion-selective electrodes", *Pure & Appl. Chem.*, 48, 127-132, Great Britain, Pergamon Press, 1976.
19. Arada Pérez, M. de los Á.; Pérez Marín, L.; Calvo Quintana, J.; Yazdani Pedram, M., "Influence of different plasticizer on the response of chemical sensors based on polymeric membrane for nitrate ion determination", *Sens. Actuat. B-Chem*., 2003, 89, 262-268.