

# Construction and Characterization of a Lead(II) Ion Selective Electrode with 1-furoil-3,3-diethylthiourea as Neutral Carrier

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*Construcción y caracterización de un electrodo selectivo a ion plomo(II) usando 1-furoil-3,3-dietiltiourea como portador neutro*

*Construcció i caracterització d'un elèctrode selectiu a ió plom(II) emprant 1-furoil-3,3-dietiltiourea com a portador neutre*

## RESUMEN

Se construyeron electrodos selectivos a ion plomo(II), ESI, basados en membranas de PVC plastificado y usando 1-furoil-3,3-dietiltiourea como ionoforo y tributilfosfato como plastificante. La membrana se aplicó sobre un soporte de resina epoxy conductor. Algunos parámetros de evaluación del electrodo son presentados en este trabajo. El ESI posee una respuesta lineal en el intervalo de concentración entre  $10^{-6}$ – $10^{-3}$  mol/dm<sup>3</sup>, con un pendiente de 29.61 mV/década. El tiempo de respuesta estable obtenido es menor que 20 segundos. El tiempo de vida útil del ESI es de un mes. Se calculó el coeficiente de selectividad ( $K_{AB}^{Pot}$ ) para iones de Cu<sup>2+</sup>, Cd<sup>2+</sup> y Ca<sup>2+</sup> empleando el método de soluciones mixtas y se analizó la dependencia del potencial del electrodo en función del pH. La morfología de las membranas se analizó mediante microscopia electrónica de barrido (MEB) a diferentes tiempos de uso de la membrana del ESI. Las imágenes MEB mostraron cambios morfológicos de las superficies de las membranas, probablemente debido a la reacción de Pb<sup>2+</sup> con el ionoforo y/o la pérdida de los componentes de la membrana por exudación.

**Palabras claves:** Electrodo selectivo a iones (ESI). Electrodo selectivo para plomo(II). 1-furoil-3,3-dietiltiourea. Portador neutro. Microscopia electrónica de barrido.

## SUMMARY

Lead(II) ion selective electrode, ISE, based on plasticized PVC membranes with 1-furoyl 3,3 diethyl thiourea as ionophore and tributylphosphate as plasticizer have been developed. The membrane was applied on a conducting epoxy resin support. Some parameters of evaluation of the electrode are presented in this work. The ISE have linear response in the concentration range of the  $10^{-6}$ – $10^{-3}$  mol/dm<sup>3</sup>, with slope of 29.61 mV/decade. The static response time obtained was less than 20 seconds. The ISE is useful for more than one month. The selectivity coefficients ( $K_{AB}^{Pot}$ ) for Cu<sup>2+</sup>, Cd<sup>2+</sup> and Ca<sup>2+</sup> ions were calculated by employing the mixed solutions method and the pH dependence of the potential was analyzed. Scanning electron microscopy (SEM) of the membranes was registered at different time of the use of the ISE. The SEM images showed morphological changes of the membrane surface probably due to both the reaction between the Pb<sup>2+</sup> and the ionophore and/or loss of the membrane components by exudation.

**Key words:** Ion selective electrode (ISE). Lead(II) selective electrode. 1-furoil-3,3-diethylthiourea. Neutral carrier. Scanning electron microscopy.

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## RESUM

Es construeixen elèctrodes selectius a ió plom(II), ESI, basats en membranes de PVC plastificat i emprant 1-furoil-3,3-dietiltiurea com a ionòfor i tributilfosfat com a plastificant. La membrana s'aplica sobre un suport de reïna epoxy conductor. Es presenten en aquest treball alguns paràmetres d'avaluació de l'elèctrode. L'ESI posseeix una resposta lineal en l'interval de concentració entre  $10^{-6}$ – $10^{-3}$  mol/dm<sup>3</sup>, amb una pendent de 29.61 mV/dècada. El temps de resposta estable obtingut és menor que 20 segons. El temps de vida útil de l'ESI és d'un mes. Es calcula el coeficient de selectivitat ( $K_{AB}^{Pot}$ ) per a ions de Cu<sup>2+</sup>, Cd<sup>2+</sup> i Ca<sup>2+</sup>, emprant el mètode de solucions mixtes, i s'analitza la dependència del potencial de l'elèctrode en funció del pH. La morfologia de las membranes s'analitza mitjançant microscòpia electrònica d'escombratge (MEB) a diferents temps d'ús de la membrana de l'ESI. Les imatges MEB mostraren canvis morfològics de les superfícies de les membranes, probablement com a resultat de la reacció de Pb<sup>2+</sup> amb el ionòfor i/o la pèrdua dels components de la membrana per exudació.

**Mots clau:** Elèctrode selectiu a ions (ESI). Elèctrode selectiu per a plom(II). 1-furoil-3,3-dietiltiurea. Portador neutre. Microscòpia electrònica d'escombratge.

## 1. INTRODUCTION

The construction of sensitive and precise devices based on electrochemical sensors, capable of detecting and quantifying the concentration of polluting substances in different ecosystems, has been the subject of growing interest in recent years<sup>(1-4)</sup>. Ion selective electrodes (ISE) are very appropriate for this purpose because they show good selectivity for inorganic ions, they are easy to build, the results are obtained quickly, they are relatively of low cost and they can be taken and used in the places of interest.

The ISEs based on polymeric liquid membranes doped with a neutral carrier (ionophore) belong to the solid state type potentiometric sensors. The inclusion of an ionophore in the liquid membrane allows the chemical recognition by different mechanisms. One of these mechanisms is that of complex formation with the ion of interest, where the complexation reaction must be fast and reversible.

Although compounds with a wide variety of structures, coming from different families, such as crown ethers<sup>(6-7)</sup> and large number of cyclic carboxylic acid derivatives<sup>(8,9)</sup> have been used as ionophores or neutral carriers, only few thiourea derivatives have been employed<sup>(10-13)</sup>.

In this work we report for the first time the use of 1-furoil-3,3-diethylthiourea as neutral carrier in a solid state potentiometric ISE based on PVC liquid membrane sensible to Pb (II) cation. The aim of this work was to construct the aforementioned ISE and to determine the different parameters that characterize this type of devices.

## 2. EXPERIMENTAL

The experimental work was carried out in the organic materials laboratory of the institute for materials and reactive (IMRE) of the University of Havana. 1-Furoil-3,3-diethylthiourea (F3DET) was synthesized and characterized in the organic materials laboratory and its structure is shown in figure 1.

All reagents used in this study were of analytical grade from Aldrich. A Sartorius analytical balance model BP 61S with the precision of 0.1 mg was used and bidistilled water was

obtained from an Aquatron model A4D apparatus. Tributylphosphate was used as plasticizer (solvent mediator) since is the only that dissolves the ionophore. Tetrahydrofuran of analytical grade from Merck was used to dissolve the PVC and to homogenize the membranes component. 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 and Pérez-Marín for nitrate sensors<sup>(4)</sup> obtaining a resistance of  $\leq 2$  K $\Omega$ .

The construction of the electrode was realized by employing the method reported by Lima and Machado in 1986<sup>(15)</sup>. The composition of the liquid membrane was 5% of ionophore, 33% of PVC and 62% of tributyl phosphate as solvent mediator.

Potentiometric measurements were performed by using a Crison model G-LP22 potentiometer with a precision of  $\pm 0.1$  mV. The electrical resistance of the epoxy resin-graphite contact was measured by using a digital YFE multimeter model YF-2100.

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 mol/dm<sup>3</sup> of K<sub>2</sub>SO<sub>4</sub> was employed in the external electrode compartment. The Reilys diagrams were determined by using a TGL model 11640 pH electrode.

The composition of the electrochemical cell was as follows: Ag/AgCl|KCl 0.1 mol/dm<sup>3</sup>|K<sub>2</sub>SO<sub>4</sub> 0.1 mol/dm<sup>3</sup>||sample solution|PVC membranel conducting support. Cu<sub>(s)</sub>. Calibrations were carried out in an open cell of 40 cm<sup>3</sup> capacity and with constant stirring. All experiments were performed at 25.0  $\pm$  0.5 °C.

A Tesla scanning electron microscope model SB-343A was used to register the microphotographs of the membranes. SEM images were obtained at a potential energy acceleration of 20 kV with a 60  $\mu$ A current.

## 3. RESULTS AND DISCUSSION

### 3.1 Determination of the calibration parameters

The calibration parameters were obtained by applying the method of additions<sup>(16)</sup> recommended by the IUPAC.

With the aim of determining if the way of storing the electrode affects its response and characteristics, the constructed ESI were divided in two groups. Group A were stored in a  $10^{-2}$  mol/dm<sup>3</sup> solution of Pb(NO<sub>3</sub>)<sub>2</sub> after each calibration and group B were stored in dry state.

The E against a curve for each calibration was established and the slope (S) was determined by using a linear regression of the data in the nerstian zone of the curve. The "lack of fit test" containing Statgraphics Plus 3.1 program package was employed in this work in order to check if the linear method was adequate for all calibrations performed instead of considering the magnitude of the correlation coefficient. The practical detection limit (PDL) and the lower limit of detection (LLD) were calculated by using the Origin 6.1 package software.

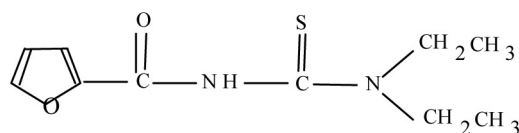


Figure 1. Structure of 1-furoil-3,3-diethylthiourea.

**TABLE I**  
**Values of slopes [mV/decade] obtained for each calibration of ISE for Pb<sup>2+</sup> cation.**

	ESI	D 1	D 3	D 7	D 9	D 13	D 16	D 18	D 21	D 24	D 28	D 31	
<b>A</b>	1	27.5	29.8	29.8	29.51	29.5	29.66	29.7	29.8	29.70	29.50	29.5	
	2	31.5	29.5	30.5	29.82	29.8	29.84	29.8	29.8	29.84	29.56	29.8	
	3	27.8	29.4	29.5	29.36	29.4	29.86	29.0	29.5	30.04	29.50	29.4	
	4	31.5	28.8	30.5	29.18	28.8	29.45	29.1	29.6	29.14	29.45	29.1	
	5	27.8	29.5	29.8	29.56	29.5	29.72	29.7	29.0	29.76	29.76	29.5	
	6	27.8	29.6	29.8	29.79	29.6	29.84	29.7	29.8	29.84	29.84	30.3	
		D 2	D 6	D 8	D 11	D 14	D 17	D 20	D 23	D 25	D 27	D 30	D 34
<b>B</b>	7	27.9	29.4	29.8	29.8	29.8	29.8	29.8	29.8	29.2	29.8	29.3	29.9
	8	29.4	29.4	29.8	29.4	29.9	29.3	29.3	29.9	29.4	29.4	29.3	29.4
	9	28.7	29.8	29.6	29.1	29.7	29.8	29.7	29.0	29.5	29.5	29.5	29.5
	10	27.9	29.4	29.8	30.0	29.8	29.8	29.8	29.1	29.8	29.8	30.2	29.8
	11	28.0	29.1	29.8	29.8	29.9	29.9	29.9	29.8	29.9	29.9	29.4	29.0
	12	29.5	29.4	29.8	29.5	29.8	29.5	29.7	29.7	29.5	29.1	29.4	29.5

**A:** Electrodes conserved in a 10<sup>-2</sup> mol/dm<sup>3</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution, **B:** Electrodes kept in dry state, **D:** day.

The values of slopes obtained from calibration curves of both groups of electrodes are shown in table I. It is seen from this table that all constructed electrodes responded adequately to Pb<sup>2+</sup>, however, the values of the slopes corresponding to the first day statistically differ from the rest of the values. For this reason, they were not considered for the analysis of the data reported in table II. This difference is attributed to the fact that the electrodes needed at least 24 hours of conditioning. The homogeneity of the variances after 48 hours was corroborated by the Cochran criterion.

Analysis of the variance for a classification variable is shown in table II. Since  $p > 0.05$  in both cases, the averages of the S are the same in the period that is analyzed. The mayor differences encountered among the electrodes is due to the manual procedure used for their construction which was shown to be reproducible.

An average value of 29.61 mV/decade was calculated for both conservation procedures of the electrodes. The only difference detected between these electrodes is that the electrodes conserved in solution had a life-time of 31 days while those kept in dry state had a life-time of 34 days. This could be due to the loss of the plasticizer or to the degradation of the ionophore as already reported in the literature for this type of ISE<sup>(17, 18)</sup>.

It was determined experimentally that the constructed electrodes sensible to Pb<sup>2+</sup> ions had a response time of less than 20 sec., where they can be classified as fast responding<sup>(19)</sup> (see figure 2). The ISEs showed a PDL of 2·10<sup>-6</sup> mol/dm<sup>3</sup> and an LLLR of 3.1 · 10<sup>-6</sup> mol/dm<sup>3</sup>.

**TABLE II**  
**Analysis of the variance of a classification variable of ISE for Pb<sup>2+</sup> cation.**

	Variations	Sum of Squares	Df	Mean Square	p-value
<b>A</b>	Between days	1.6	9	0.2	0.1
	Inside units	5.2	50	0.1	
	Total	6.7	59		
<b>B</b>	Between days	1.0	10	0.10	0.28
	Inside units	4.3	55	0.08	
	Total	5.3	65		

**A:** Electrodes conserved in a 10<sup>-2</sup> mol/dm<sup>3</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution.  
**B:** Electrodes kept in dry state.

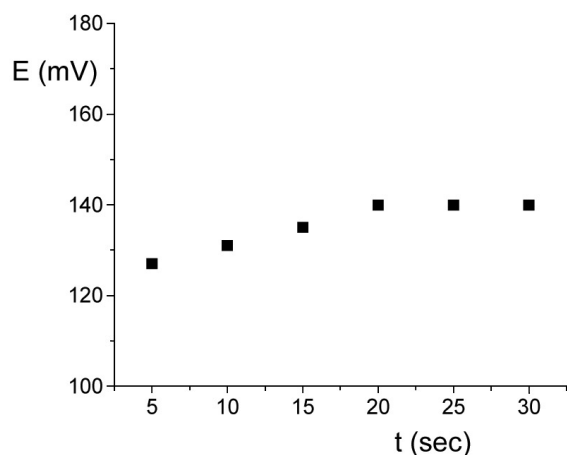


Figure 2. Potential stability as function of time for  $Pb^{2+}$  ISEs.

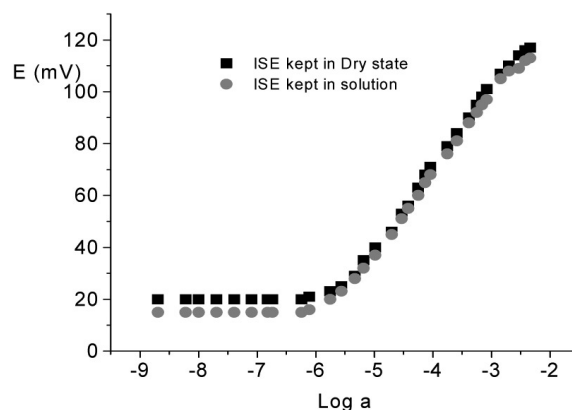


Figure 3. Calibration curves for  $Pb^{2+}$  ISEs.

Figure 3 shows the calibration curves obtained for both group of electrodes. It is seen from this figure that they have a wide response range between  $10^{-6}$  to  $10^{-3}$  mol/dm<sup>3</sup>.

### 3.2. Influence of pH

A  $Pb(II)$  solution with a concentration of  $10^{-2}$  mol/dm<sup>3</sup> was used for this study. The experimental results showed that the variation of pH affected notably the electrode potential. It is seen from figure 4 that the electrode potential remains constant in two small pH intervals of 2.75 to 3.25 and 5.3 to 5.8. The increase observed in the first pH zone is attributed to the response of the membrane to  $H_3O^+$  cations through anionic impurities contained in PVC<sup>(9, 17)</sup>. Above pH 5.8, the potential is not stable and finally it decays as consequence of the precipitation of hydrated  $Pb(II)$  oxide.

### 3.3. Determination of the interference of $Ca^{2+}$ , $Cd^{2+}$ and $Cu^{2+}$ ions.

The influence of ionic species:  $Ca^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  was evaluated by determining the corresponding potentiometric selectivity coefficients ( $K_{AB}^{Pot}$ ) by using both the fixed solutions as well as the mixed solution methods<sup>(20)</sup>. The values obtained are shown in table III.

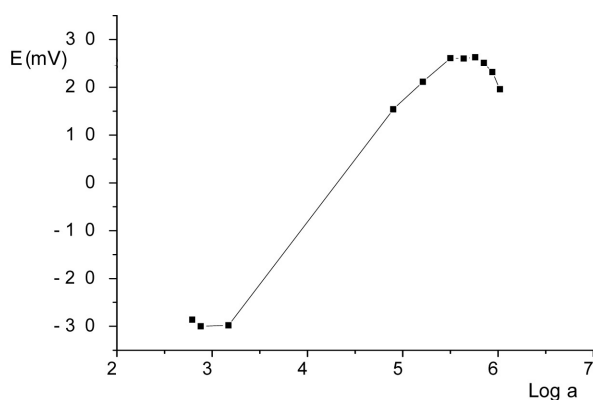


Figure 4. Reilley's diagram, variation of potential as function of pH.

The order of interference observed in this work coincides with those reported for other  $Pb^{2+}$  ion selective electrodes containing similar type of ionophores<sup>(21-23)</sup>. A similar order is obtained if one organize them in accordance with their hardness-softness nature reported by Pearson<sup>(24)</sup>, that is  $Cu^{2+}$  (intermediate acid),  $Cd^{2+}$  (soft acid) and  $Ca^{2+}$  (hard acid). In this case,  $Cu^{2+}$  behaves in a similar manner as  $Pb^{2+}$  since both cations are intermediate acid that justify the mayor interference of this ion compared to others. A similar order of interference was also observed when they were organized in accordance with their charge density, i.e. charge/ionic radius ( $\text{\AA}$ ) relation<sup>(25)</sup>, that is to say  $Cu^{2+}$  (2.597) >  $Cd^{2+}$  (2.062) >  $Ca^{2+}$  (2.02). The reactivity of ionophore toward these cations is explained through different possibilities of coordination shown by tiourea (figure 1). In this case no intramolecular hydrogen bonding is formed, as has been reported for other tioureas<sup>(13)</sup>. The presence of two ethyl groups allows the enrichment of the electronic density of the nitrogen atom, which favors its participation in the formation of a complex with metallic cation together with oxygen and sulfur atoms.

### 3.4. Scanning electron microscopy (SEM) of ISE membranes.

SEM micrographs of  $Pb^{2+}$  ISE membranes at different stage of its operation are shown in figure 5. Figure 5 (a) corresponds to the surface of the membrane without activation, where flat layers with irregular shapes is observed. Figure 5 (b) shows the SEM image of the activated membrane responding to  $Pb^{2+}$ , where the surface of the membrane shows pores of different sizes together with white aggregates attributed to the formation of complex between the metal and

TABLE III  
Values of selectivity coefficients ( $K_{AB}^{Pot}$ ) of ISEs for  $Pb^{2+}$  ion.

Interfering ion	Log ( $K_{AB}^{Pot}$ )	( $K_{AB}^{Pot}$ )
$Ca^{2+}$	-1.76	$1.71 \cdot 10^{-2}$
$Cd^{2+}$	-0.82	$1.49 \cdot 10^{-1}$
$Cu^{2+}$	0.47	2.95

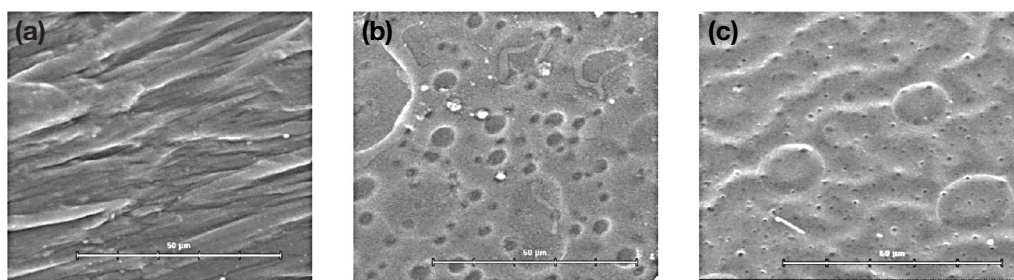


Figure 5. SEM micrographs of  $\text{Pb}^{2+}$  ISE membrane in its different stages of operation, (a) unactivated, (b) activated membrane responding to  $\text{Pb}^{2+}$ , (c) membrane with loss of response to  $\text{Pb}^{2+}$ .

ionophore. Figure 5 (c) corresponds to the SEM of deactivated membrane, where the pores are much smaller than those of activated membrane and without the presence of white aggregates. The morphological changes observed could be the consequence of both the reaction between the  $\text{Pb}^{2+}$  and the ionophore and/or loss of the membrane components by exudation. The loss of components from ISE membranes with the consequence of their loss of response is already reported in the literature<sup>(17,18)</sup>.

#### 4. CONCLUSIONS

The activation process of ISE for  $\text{Pb}^{2+}$ , with 1-Furoil-3,3-diethyl thiourea (F3DET) as neutral carrier, needs 48 hours. This ISE has a slope of 29.61 mV/decade, responds adequately to  $\text{Pb}^{2+}$  and has a life-time of 31-34 days depending on the conditions used for its storage. The constructed ISEs showed a PDL of  $2 \cdot 10^{-6}$  mol/dm<sup>3</sup> and an LLLR of  $3.1 \cdot 10^{-6}$  mol/dm<sup>3</sup>. The static response time obtained was less than 20 seconds. It can be used in the pH intervals of 2.75 to 3.25 and 5.3 to 5.8. Some divalent cations such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  showed interferences. The loss of response of the electrodes was attributed to the loss of the components of the liquid membrane resulting in the deterioration of their properties.

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