

Full Paper

Coated Wire Lead Ion Selective Electrode Based on Dithizone

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Abstract- PVC based membrane of 1,5-diphenylthiocarbazone (dithizone) reveals a Nernstain potentiometric response with the slope of 29 ± 2 mV per decade for Pb^{2+} over a concentration range (5.0×10^{-6} - 1.0×10^{-2} M). The used electrode was suitable in aqueous solutions in a pH range of 8 to 10. The response time of the electrode is about 15 s and was used for a period of 45 days. The proposed electrode was used in two different applications such as the determination of lead concentration in a part of lead water pipe and as an indicator electrode for potentiometric titration of Pb^{2+} ions.

Keywords- Lead Ion Selective Electrode, Potentiometric Titration, Indicator Electrode

1. INTRODUCTION

The need for the determination of lead and other heavy metals increased during the last few years because of growing environmental problems. The electrochemical properties and preparation of lead ion selective membrane electrodes have been studied by using active materials, including solid-state membranes made of sulfide, oxide, selenide and other salts of lead together with silver sulfide [1-5] and also liquid ion-exchange membranes [6-8].

Recently, much interest has been paid to the use of ionophore ligands as sensing materials for selective electrodes due to their unique properties. The use of complexing agents offers the possibility of designing ligands with a wide range of functional groups and, consequently, different abilities to form complexes. Several neutral compounds with oxygen, nitrogen and sulphur donor atoms have been examined as ionophores for lead selective electrodes [9-11].

In this paper, the coated wire lead ion selective electrode based on 1,5-diphenylthiocarbazone (dithizone) exhibits significantly high sensitivity, stability, and selectivity for Pb^{2+} over many common metal ions and was successfully applied to the direct determination of lead in a real sample. Also, it was used for the potentiometric determination.

2. EXPERIMENTAL

2.1. Reagents

The chemicals used are of analytical grade and were used without any further purification. Deionized distilled water was used for preparing all aqueous solutions. High molecular weight polyvinyl chloride powder (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP) and *o*-nitrophenyloctylether (NPOE) from Aldrich were obtained. Tetrahydrofuran (THF), 1,5-diphenylthiocarbazone (dithizone) and salts of metal nitrate or chloride from Fluka were obtained.

2.2. Apparatus and EMF measurements

Potentials were measured with a digital Hanna pH / mV meter (model 8417) made in Romania. All potential measurements were carried out at 25°C. Double junction Ag/AgCl electrode from Hanna made in Italy was used as reference electrode. The electrode cell assembly of the following type was used:

Ag | AgCl | KCl (3.5 M) | test solution | PVC membrane | copper wire

2.3. Electrode preparation

The terminal of copper wire was coated by a mixture contains 30.5% PVC, 66.7% NPOE and 2.8% dithizone. The copper wire was dipped into the mixture several times till a layer of proper thickness is formed covering its terminal. The layer thickness was about 0.5 mm [12]. This layer was allowed to dry in air for 24 h, and conditioned in a solution containing a mixture of 10^{-2} M Pb^{2+} and 0.15 M sodium citrate at pH of 10 for 12 h [13]. The electrode was stored in the same solution when not in use.

3. RESULTS AND DISCUSSION

3.1. Effect of membrane composition

Several membranes of different compositions were prepared. The ratios of PVC, ionophore and plasticizers were varied [14]. Some of the results of this study are summarized in Table 1. It is clear from these results that the composition of the membrane highly affects the response and performance of the electrode. The ratios of all constituents should be optimized for best performance of the sensor.

The membrane composition which is suitable with regard to Nernstian's slope was found to contain 30.5% PVC, 2.8% dithizone as ionophore and 66.7% NPOE as plasticizer.

Table 1. Optimization of membrane ingredients

No.	Composition (wt. %)				Slope, mV/decade of activity	Linear range (mol L ⁻¹)
	Ligand (Dithizone)	PVC	Plasticizer			
			DBP	DOP		
1	15.0	85.0			7.5±1.0	5.0×10 ⁻⁴ -1.0×10 ⁻¹
2	3.0	35.0		62	20.0±1.5	1.0×10 ⁻⁴ -5.0×10 ⁻¹
3	4.0	40.0	56		18.0±1.0	5.0×10 ⁻⁵ -1.0×10 ⁻²
4	2.8	30.5		66.7	29.0±2.0	5.0×10⁻⁶-1.0×10⁻²

3.2. Effect of pH

The effect of pH on the potentiometric response of the coated copper wire electrode was tested for solutions of 1.0×10⁻³ and 1.0×10⁻⁴ M Pb²⁺ ions. To achieve the required pH of the test solution, HNO₃ and NaOH were used. As shown in Fig. 1, the potential records were constant at pH ranged from 8 to 10.

The decrease in the observed potential at pH values higher than 10 may be due to the formation of lead hydroxide in solution. On the other hand, its decrease at pH values lower than 8 may be due to the liberation of protons from dithizone in the basic medium which helps on the reaction between lead ions and dithizone [15]. Accordingly, it was decided to perform all measurements at pH of 10 (using Reynold's Lead Citrate Stain).

3.3. Calibration curve and statistical data

The developed coated copper wire electrode provides a linear response to the concentrations of lead ion in the range of 5.0×10⁻⁶ to 1.0×10⁻² M with a cationic slope of 29±2 mV/dec., which is very close to the Nernstian slope value [16] as shown in Fig. 2. The limit of detection was 3.4×10⁻⁶ M. The prepared electrode could be used for at least 45 days without any measurable divergence, and when not in use was stored in 1.0×10⁻² M lead ion solution.

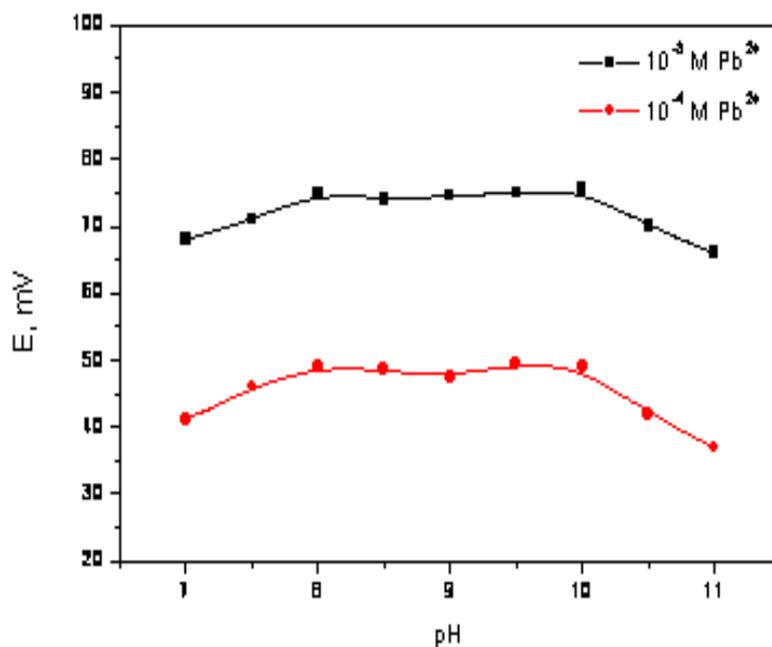


Fig. 1. Effect of the pH of the test solution on the potential response of coated wire lead ion selective electrode

3.4. Response time

The response time of the electrode was evaluated by potential reading for the electrode dipped alternatively into two stirred solutions of lead ions 1.0×10^{-5} and 1.0×10^{-3} M [17], respectively. The actual potential vs. time is shown in Fig. 3. As can be seen, the electrode reaches its equilibrium response in about 15 s.

3.5. Selectivity

The selectivity coefficients of the developed electrode were determined against a number of interfering ions using the separate solution method (SSM). The selectivity coefficients $K_{Pb^{2+},B}$ were calculated using the equation [18]:

$$\text{Log } K_{Pb^{2+},B} = [(E_B - E_{Pb^{2+}}) / S] + [1 - (Z_{Pb^{2+}}/Z_B)] \text{Log } a_{Pb^{2+}}$$

Where $E_{Pb^{2+}}$ and E_B are the observed potentials (mV) for the same concentration of Pb^{2+} and interfering ions, respectively, S is the slope, $a_{Pb^{2+}}$ is the activity of Pb^{2+} , $Z_{Pb^{2+}}$ and Z_B are the charge number of lead and interfering ion B, respectively. The obtained data as shown in Table 2 indicate that the developed electrode exhibits a good selectivity for Pb^{2+} among most of the tested metal ions.

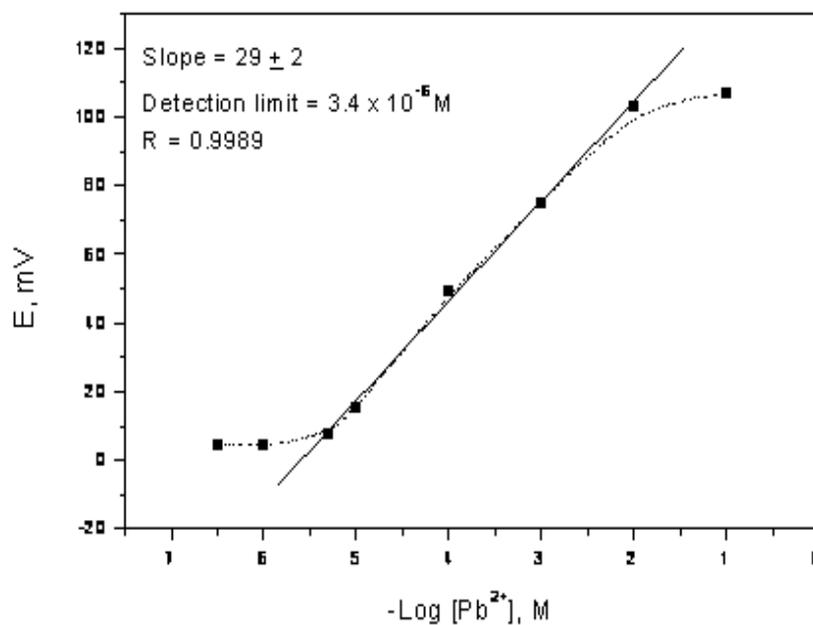


Fig. 2. Calibration graph for coated wire lead ion selective electrode uses me membrane contain 30.5% PVC, 2.8% dithizone and 66.7% NPOE (No.4 see Table 1)

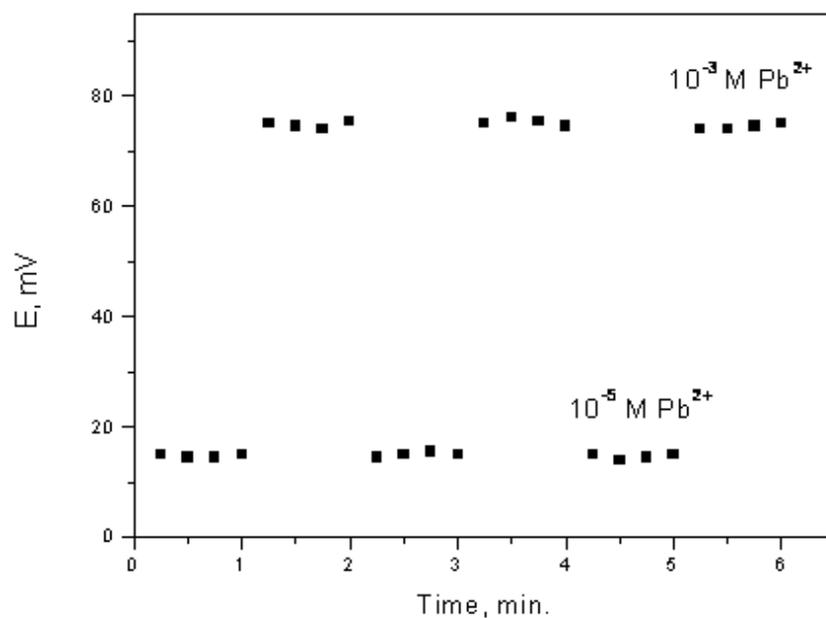


Fig. 3. Dynamic response time of the electrode membrane for two concentrations (from low to high and vice versa)

Table 2. Selectivity Coefficients of Electrode

Interfering cations (10^{-2} M)	Selectivity coefficients ($K_{Pb^{2+},B}$)
Na ⁺	2.6×10^{-4}
K ⁺	4.3×10^{-4}
Li ⁺	2.3×10^{-4}
Co ²⁺	3.1×10^{-3}
Ni ²⁺	3.6×10^{-3}
Cd ²⁺	6.3×10^{-4}
Zn ²⁺	4.7×10^{-4}
Cu ²⁺ , Fe ²⁺ , Hg ²⁺ , Ag ⁺	precipitate

3.6 .The analytical applications of the developed electrode

3.6.1. Potentiometric titration

The coated copper wire lead ion selective electrode was used for monitoring direct titration of 10 ml of 5.0×10^{-3} M Pb²⁺ with 1.0×10^{-2} M of NaCl. The obtained results are presented in Fig. 4. As can be seen, the electrode works well under laboratory conditions.

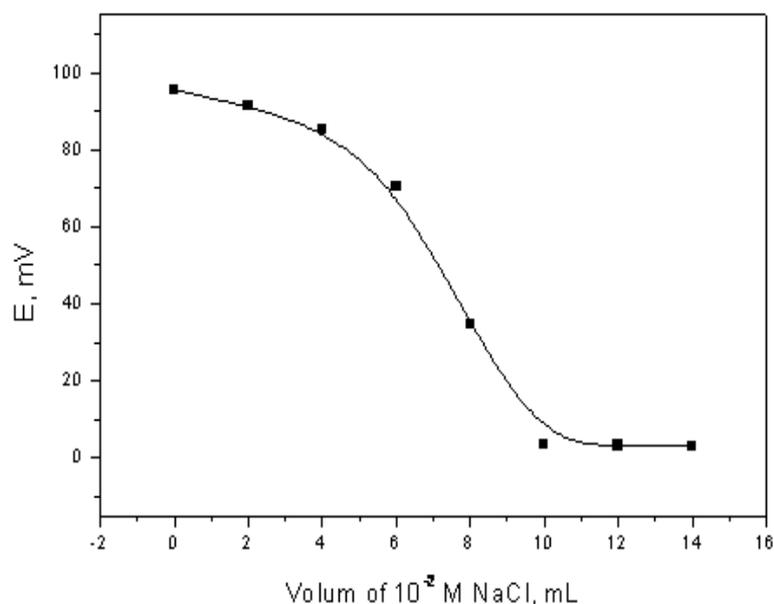


Fig. 4. Titration of 10 ml of 5×10^{-3} M Pb²⁺ ion with 10^{-2} M NaCl by the use of the proposed lead ion selective electrode (No. 4) as an indicator electrode

3.6.2. Determination of Pb^{2+} ion concentration in lead water pipe

The developed electrode was used to determine the lead ion concentration in a part of water pipe which was made from lead. A sample of 0.1 g was put in a beaker which contains 30 ml of 6 M HNO_3 . It was heated at 90 °C with stirring for 1 h [19]. After filtration, the filtrate was completed to 50 ml by distilled water after addition of 1.75 g from sodium citrate and its pH was reached to 10.

The lead ion concentration was determined potentiometrically and its concentration was 9.1×10^{-3} M, also by atomic absorption spectrometry (AAS), as a reference method and the concentration of lead ion was 9.5×10^{-3} M. The results show a good agreement between the two methods.

4. CONCLUSIONS

According to the obtained results in the present work, the proposed electrode is easy to be prepared and used. It has good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range). This electrode can be used for determination of lead ion concentration in potentiometric titrations and real samples.

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