Lead Ion Selective Electrode Based on 1, 5-diphenylthiocarbazone

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Abstract

PVC based membrane of 1,5-diphenylthiocarbazone (dithizone) reveals a Nernstian potentiometric response with the slope of 29 ± 2 mV per decade for Pb²⁺ over a wide concentration range (5.0×10⁻⁶-1.0×10⁻² M). The electrode is suitable for use 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 showed successful applications to the direct determination of lead in a sample of lead water pipe and also as indicator electrode for potentiometric titration of lead ions with NaCl solution.

Key words: Lead ion selective electrode, dithizone, potentiometry, PVC based membrane.

Introduction

The need for the determination of heavy metals increased during the last years because of growing environmental problems1-3. Lead is one of the heavy elements, which is almost present in the different industrial waste effluents. Many industries such as lead glasses4 and optical sensors5 use lead salts as main components. It is also considered as one of the radionuclides that present in the radioactive waste solution. Accurate determination of lead ions is of great interest since it is sometimes present in very minute concentrations in such matrices. This work is decided to introduce an ion selective electrode (ISE) for accurate and precise quantitative analysis of lead ions.

Much interest has been paid to the use of ionophore ligands as sensing materials for selective electrodes due to their unique properties6-12. 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 electrodes13-15.

In this paper, the coated wire lead ion selective electrode based on 1,5-diphenylthiocarbazone (dithizone) exhibits significantly high sensitivity, stability, and selectivity for Pb²⁺ over many common metal ions and was successfully applied to the direct determination of lead in real samples. Also, it was used for the potentiometric determination of lead ions in solutions.

Material and Methods

Reagents: The chemicals used are of analytical grade and used without any further purification. Doubly 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) were obtained from Aldrich. Tetrahydrofuran (THF), 1,5-diphenylthiocarbazone (dithizone) and salts of metal nitrate or chloride were obtained from Fluka.

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

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 terminal16. This layer was allowed to dry in air for 24 h. The coated wire was then conditioned in a solution containing a mixture of 10⁻² M Pb²⁺ and 0.15 M sodium citrate at pH of 10 for 12 h 17. The electrode was stored in the same solution when not in use.

Results and Discussion

Effect of Membrane Composition: Several membranes of different compositions were prepared. The ratios of PVC, ionophore and plasticizers were varied18. 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.

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 1.0×10⁻² M Pb²⁺ ions. To achieve the required pH of the test solution, HNO₃ and NaOH were used. As shown in figure 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. Accordingly, it was decided to perform all measurements at pH of 10.

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 5.0×10⁻⁴ to 1.0×10⁻² M with a cationic slope of 29 ± 2 mV/dec., which is very close to the Nernstian slope value as shown in figure 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 1.0×10⁻⁵ M lead ion solution.

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 1.0×10⁻³ and 1.0×10⁻³ M, respectively. The actual potential versus time is shown in figure 3. As can be seen, the electrode reaches its equilibrium response in about 15 s.

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_{Pb²⁺,B} were calculated using the following equation:

$$\log K_{Pb²⁺,B} = [(E_B - E_{Pb²⁺}) / S] + [1 - (Z_{Pb²⁺}/Z_B)] \log a_{Pb²⁺}$$

Where E_{Pb²⁺} and E_B are the observed potentials (mV) for the same concentration of Pb²⁺ and interfering ions, respectively, S is the slope, a_{Pb²⁺} is the activity of Pb²⁺, Z_{Pb²⁺} 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 Pb²⁺ among most of the tested metal ions.

Analytical applications: 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 figure 4. As can be seen, the electrode works well under laboratory conditions.

Determination of Pb²⁺ 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 from the pipe was put in a beaker contains 30 ml of 6 M HNO₃. It was heated at 90°C with stirring for 1 hour. 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 using the proposed electrode. The concentration was found to be 9.1×10⁻³ M. Atomic absorption spectrometry (AAS), as a reference method was used and the concentration of lead ion was found to be 9.5×10⁻³ M. The results show a good agreement between the two methods.

Conclusion

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.

References


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**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition (wt. %)</th>
<th>Slope, mV/decade of activity</th>
<th>Linear range (M)</th>
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<tbody>
<tr>
<td></td>
<td>Ligand (Dithizone)</td>
<td>PVC</td>
<td>Plasticizer</td>
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<td></td>
<td></td>
<td></td>
<td>DBP</td>
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<td>4</td>
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<td>85.0</td>
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Table-2
Selectivity coefficients of electrode

<table>
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<th>Interfering cations (10^{-2} M)</th>
<th>Selectivity coefficients (K_{Pb^{2+}_{B}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na^+</td>
<td>2.6×10^{-4}</td>
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<tr>
<td>K^+</td>
<td>4.3×10^{-4}</td>
</tr>
<tr>
<td>Li^+</td>
<td>2.3×10^{-4}</td>
</tr>
<tr>
<td>Co^{2+}</td>
<td>3.1×10^{-3}</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>3.6×10^{-3}</td>
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<tr>
<td>Cd^{2+}</td>
<td>6.3×10^{-4}</td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>4.7×10^{-4}</td>
</tr>
<tr>
<td>Cu^{2+}, Fe^{2+}, Hg^{2+}, Ag^{+}</td>
<td>precipitate</td>
</tr>
</tbody>
</table>

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

Figure-2
Calibration graph for coated wire lead ion selective electrode using membrane contains 30.5% PVC, 2.8% dithizone and 66.7% NPOE
**Figure-3**
Dynamic response time of the electrode membrane for two concentrations (from low to high and vice versa)

**Figure-4**
Titration of 10 ml of $5 \times 10^{-3}$ M Pb$^{2+}$ ion with $10^{-2}$ M NaCl by using the proposed lead ion selective electrode (No. 1) as an indicator electrode