Anal. Bioanal. Electrochem., Vol. 13, No. 3, 2021, 383-392

Analytical & Bioanalytical Electrochemistry

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Full Paper

Preparation and Characterization of Pb(II) Ion Selective Electrode based on Dithizone as Chemical Sensor

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Received: 10 September 2020 / Received in revised form: 3 December 2021 /
Accepted: 5 December 2021 / Published online: 31 December 2021

Abstract- The research on the preparation and characterization of Pb^{2+} Ion Selective Electrode (ISE) using dithizone (DTZ) as ion carrier has been done. Membrane of ISE was made with the optimum composition with ratio of DTZ : PVC : DOP was 6 : 3 : 1. The membrane was doped using 1M Pb^{2+} solution within 7 days, and characterized using FT-IR to determine the shift of wave number from the spectrum of the group from membrane before and after doped. The results of characterization of FT-IR spectra of membrane after doped, shows that there is a shift of wave number from absorption spectra of secondary amine (N-H) group and absorption spectra of thiol (S-H) group didn't appear. The result of characterization of Pb^{2+} ISE shows that ISE worked well with range concentration of 1×10^{-4}-1×10^{-1} M, with Nernst slope was 29.5 mV/decade and the limit of detection was 1.5×10^{-4} M. The electrode worked optimally at pH 5, the response time was 9-48 seconds and can be used within 6 weeks. The presence of interfere ions, such as Ag^+, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cl^- and SO_4^{2-} didn't affect to the determination of Pb^{2+} ions in the samples.

Keywords- Ion selective electrode; PVC Membrane; Dithizone; Pb^{2+}; Nernstian slope

1. INTRODUCTION

Heavy metal lead (Pb) contamination in various types on the sample water is a health hazard. Infants and young children are particularly vulnerable to the adverse health effects of lead. Exposure to lead impairs children's physical and mental development, and even low levels of lead in the blood of children can cause a reduced intelligence quotient (IQ) and attention span, learning disabilities, and behavioral problems, among others. High lead levels may cause severe neurological problems such as coma, convulsions, and damage to kidneys [1]. Hence the determination of trace amounts of lead is important for environmental monitoring and this demands sensitive and accurate determination of lead.

Determination of Pb at level traces has increased the research attentiveness due to its harmful effects and accumulation in the biological system and environment. Some spectrophotometric methods such as electro thermal atomization-atomic absorption spectroscopy (ETA-AAS) [2,3], inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-optical emission spectroscopy (ICP-OES) or the inductively coupled plasma-mass spectroscopy (ICP-MS) [4], chromatography [5] and photometry [6-8] are used for the low level determination of lead ions in solution. But these methods generally require sample pre-treatment and infrastructure back up and hence are not convenient for routine analysis.

Potentiometric detectors based on ion-selective electrodes (ISE) are efficiently suitable for accurate, reproducible and selective determination of various metal ions [9]. The widespread use of ISE is inseparable from the benefits offered by ISE as it is capable of measuring in a wide range, unaffected by sample color or turbidity, does not require large samples, can be made portable, offers rapid process of the measurement, easy to operate and has lower cost of measurement compared to other methods [10]. In ISE the ion selective membrane is placed between the sample solution and the internal reference solution and interfacial potentials are developed on both sides of the membrane [11]. ISE have been attractive for detecting heavy metal traces because of their very low detection limits, good selectivity, wide dynamic range, low cost, and portability for in-situ measurements [12]. Several neutral compounds with oxygen, nitrogen and sulphur donor atoms have been used as ionophores as lead(II) selective sensors [13,14], such as; fabrication of Pb^{2+} ISE on 1-((3-((2-Hydroxynaphthalen-1-yl) Methyleneamino)-2,2-Dimethylpropylimino) Methyl) Naphthalen-2-ol as New Neutral Ionophore [9], sensitive lead (II) solid-contact potentiometric sensor based on naphthalene-sulfonamide derivative [15], polyaniline TiO_2 solid contact [16] and Ion-selective potentiometric determination of Pb(II) ions using PVC-based carboxymethyl cellulose Sn(IV) phosphate composite membrane electrode [17].

Dithizone (DTZ) is one of the organic chelating agents that used to analyze metal ions. Dithizone has been widely used and developed for several analytical methods. Dithizone can react with several metal ions and form certain complex compounds in the form of metal dithizoneate. Dithizone as ionophore can be made into a membrane using PVC matrix as reinforcement and adding a certain amount of plasticizer DOP [18]. The conductivity of membrane contained Dithizone can be improved by adding a certain amount of metals into the membrane. Metals added are referred to as a dopant metal [19]. Dithizone has a high selectivity and sensitivity in Pb ion detection [20].

In this study, Pb^{2+} ISE has been developed from membranes of DTZ by adding dopants Pb^{2+} into the membrane contained DTZ at matrix PVC through immersion, then characterized the membrane contained DTZ using FT-IR spectroscopy and Pb^{2+} ISE includes: detection limits, Nernstian slope, life time, response time, pH and the effect of interfere ions (selectivity).

2. EXPERIMENTAL SECTION

2.1. Materials

The materials used in this research are dithizone, polyvinylchloride, dioctylphtalate (DOP), tetrahydrofuran (THF), $Zn(CH_3COO)_2$, KNO_3, HNO_3, NaOH, $Pb(NO_3)_2$, $Pb(Cl)_2$, $Cd(CH_3COO)_2$, $Cu(NO_3)_2$; all reagents were of analytical-reagent grade (E. Merck), glue and aquabidest.

2.2. Instrumentation

The equipment used in this research are electrode, multimeter digital (Royalux YX-360 TRn), magnetic stirrer, analytical balance, pH meter (Orion 420A) and FT-IR Spectroscopy (Shimadzu). Other equipment such as laboratory standard glassware, analytical balance, oven, and hot plate with stirrer was used for all measurement.

2.3. Procedure

2.3.1. Membrane Contained DTZ Preparation

PVC (0.3 g) was weighed quantitatively and dissolved in 20 mL of THF and stirred using a magnetic stirrer. While stirring, added 0.1 g of DOP as a plasticizer and 0.6 g of DTZ gradually to the mixture and stirred homogenously for 4 hours at room temperature. After that, the mixture was poured into a petri dish and left until all the solvents evaporate.

2.3.2. Membrane Doped

The membrane was cut into several rectangular sections with a side length of 1.5 cm. Membranes dipped in a solution of $Pb(NO_3)_2$ 1M for 7 days. After that, membranes were removed and dried at room temperature.

2.3.3. Characterization of Membrane

The purpose of this method is to observe the binding of Pb^{2+} dopant in the membrane contained DTZ and the shift of wave number from the spectrum of the group from membrane before and after doped with Pb^{2+}. Membranes before and after doped were characterized by FT-IR Spectroscopy.

2.3.4. Working Electrode Assembly

The membrane contained DTZ-Pb^{2+} was affixed with glue to the electrode and the electrode filled with $Pb(Cl)_2$ 1 M which had been added with KNO_3 1 M as a ion strength adjusted buffer solution with ratio 1: 2 ($Pb(Cl)_2$: KNO_3) [15].

2.3.5. Characterization of Pb^{2+} ISE

Pb^{2+} ISE characterization consists of the Nernst Slope, detection limit, effect pH, response time, life time and the effect of disturbing ions (selectivity). Stock solution (Pb^{2+}1 M) was diluted with variations concentration (1×10^{-1} - 1×10^{-7} M). Internal solution was made from the mixing 1M Pb^{2+} and 1M KNO_3 (1 : 2) and measured the potential using Pb^{2+} ISE as the working electrode using a pH meter while stirring with a magnetic stirrer. The measurement results obtained graph the relationship between potential (mV) and log [Pb^{2+}]. The Nernstian slope was determined from the slope of the linear concentration range, while the detection limit was determined from the extrapolation point of the curve between log [Pb^{2+}] to potential (mV). With the same procedure, it could determine the effect of pH, response time, life time and the effect of interference ions: Ag^{+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cl^{-} and SO_4^{2-}.

3. RESULTS AND DISCUSSION

3.1. Characterization of Membrane

The characterization of the membrane contained DTZ (Fig. 1) shows a peak at 684.44 cm^{-1} indicating the absorption of C-Cl derived from PVC. Wave numbers at 2924.09 and 2826.36 cm^{-1} is the absorption of aliphatic C-H stretch which is supported from bending region at 1381.03 cm^{-1}. At wave number 3062.96 cm^{-1} shows the absorption of C-H aromatic groups. The carbonyl group (C=O) stretch of the ester compound is shown at wavenumber 1712.79 cm^{-1} which is supported by the absorption of C-O at wave number 1118.71 cm^{-1} derived from plasticizer of DOP. Membrane contained DTZ has typical absorptions of azo groups (N=N), thiols (S-H) and secondary amines (N-H) which are shown at 1604.77; 2422.59 and 3448.72 cm^{-1} respectively. In addition, there is absorption at wave number 1288.45 cm^{-1} which indicates absorption of C-N groups. It can be concluded that the membrane contained dithizone.

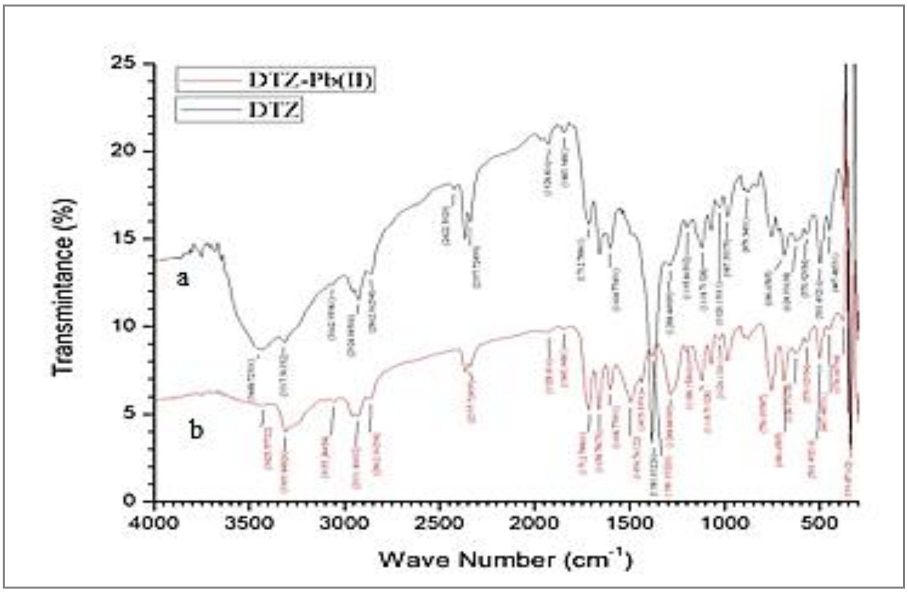

Fig. 1. FT-IR Spectra membrane contained DTZ (a) before and (b) after Doped with Pb^{2+}

While membrane contained DTZ that has been doped with Pb^{2+}, there is a shift of the wave number from the absorption of the N-H group to 3425.58 cm^{-1} with decreased intensity and the presence of the S-H group at the wave number 2422.59 cm^{-1} does not appear. It shows that the Pb^{2+} ion is bound to the membrane, where Pb^{2+} interacts with thiol (S-H) and amine (N-H) groups in the dithizone, where S and N atoms in the dithizone have a free electron pair that will be donated to Pb^{2+} and forming covalent coordination bonds so that complex compounds can be formed [20]. The reaction of complex formation of DTZ with Pb^{2+} is shown in Fig 2.

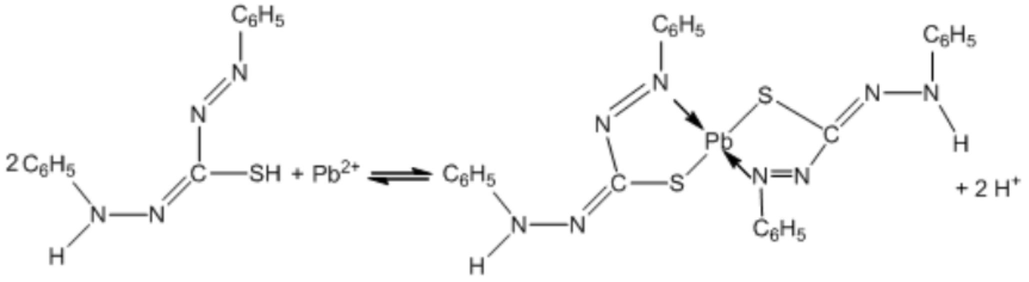

Fig. 2. Reaction of complex formation of dithizone with Pb^{2+}

3.2. Nernstian Slope and Detection Limit

Nernstian slope is an important parameter for determining the feasibility of electrode for use in analysis. ISE is considered feasible if the Nernstian slope close to the theoretical value, a low detection limit and has a wide linear concentration range. The Nernstian slope value is obtained from the slope curve between log Pb^{2+} concentration and potential (mV) in the linear region.

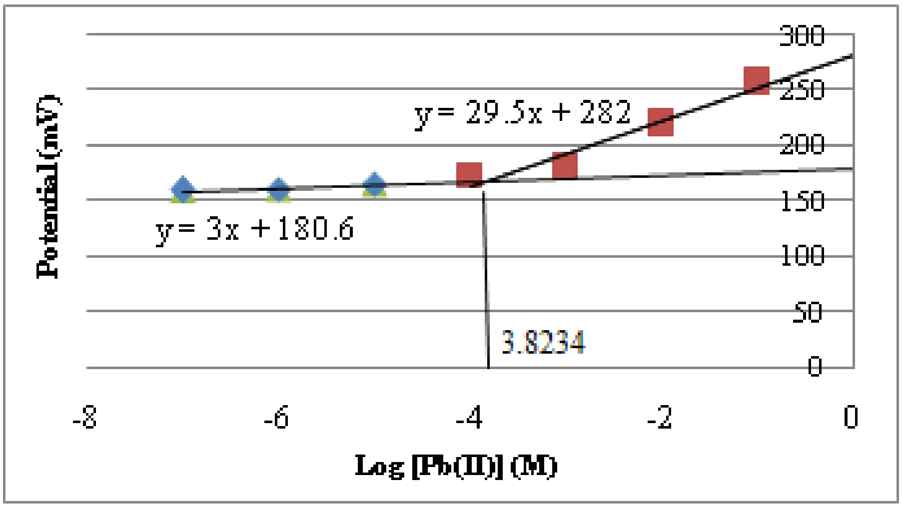

Fig. 3. Determination of Nernstian Slope and Detection Limit

Based on Fig 3, it shows that the Nernstian slope obtained from Pb^{2+} ESI using dithizone as an ionophore is 29.5 mV/decade with a linear concentration range between 1×10^{4} - 1×10^{-1} M, so it can be concluded that the Pb^{2+} ISE are feasible to use in analysis because it close to theoretical Nernstian value, where for divalent cations is 29.6±5 mV/decade [21]. Detection limits is an extrapolation of the curve between log concentration (M) and potential. From the curve extrapolated point value is -3.8234 equal to 1.5×10^{-4} M or 0.3105 mg/L.

3.3. Effect of pH

The effect of pH on the potential was carried out by adjusting the concentration of standard solution Pb^{2+} (1×10^{-3} M) in the pH range 2-9 using HNO_3 and NaOH. The measurement results are shown in Fig 4.

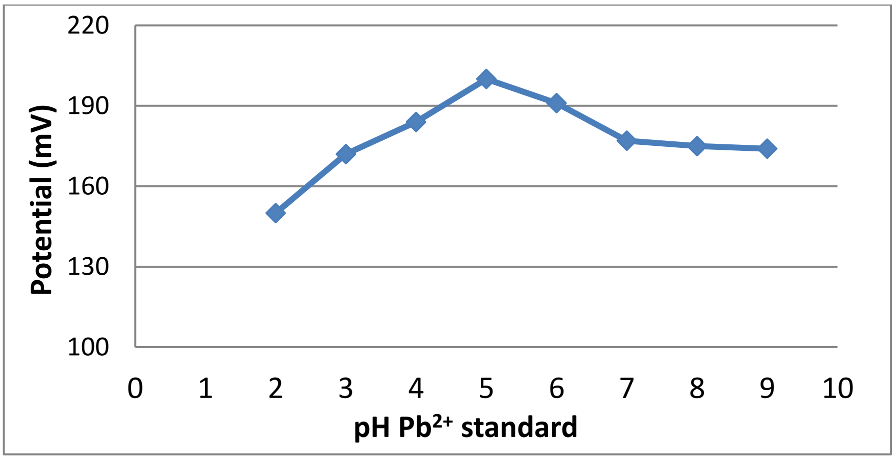

Fig. 4. Effect of pH Measurement Pb^{2+} with 10^{-3} M Pb^{2+}

In Fig 4, it shows that at pH 5 is the optimum pH which has a high potential (200 mV). It indicates that the formation of complex compounds between Pb^{2+} with dithizone is stable. Below pH 5, the reaction between Pb^{2+} with dithizone is unstable due to the protonation of nitrogen (N) and sulfur (S) atoms which can reduce interactions between dithizone and Pb^{2+}, whereas above pH 5 Pb^{2+} ions will form hydroxyl complexes and precipitate [20].

3.4. Response Time

Response time is the time required by ISE to provide a stable potential due to equilibrium at the interface of the solution with the electrode surface [22]. There is an exchange of Pb^{2+} ions in a standard solution with Pb^{2+} ions which are on the surface of the electrode until they reach equilibrium which is indicated by the potential value generated constant.

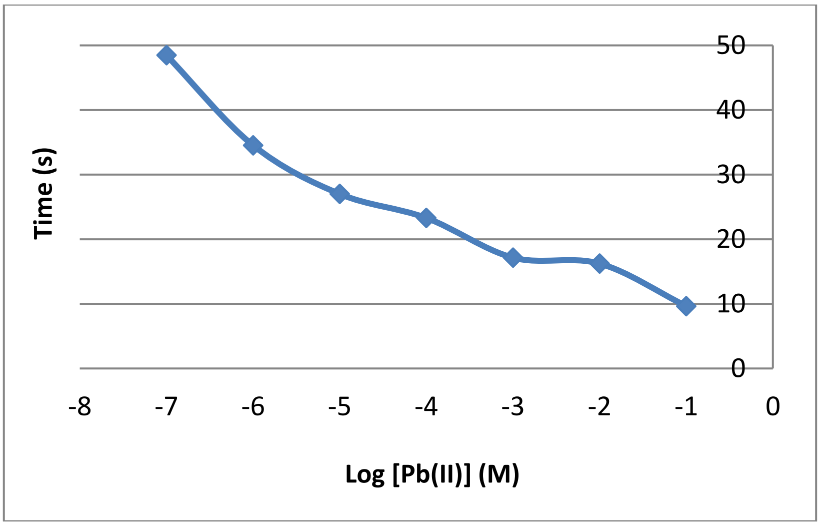

Fig. 5. Effect of Concentration Against Response Time

Based on Fig 5, the response time is around 9-48 seconds, where the higher the concentration of the test solution, the faster the response time. This is due to the high concentration of solution containing more Pb^{2+} ions. As a result, the mobility of ions in the solution also increases compared to solutions with low concentrations so that the time needed for the membrane to reach equilibrium become faster.

3.5. Life Time

Life time is a time that shows how long the ISE is still feasible to use by looking at the value of the Nernstian slope measured within a certain time interval whether it is still close to the theoretical value or not.

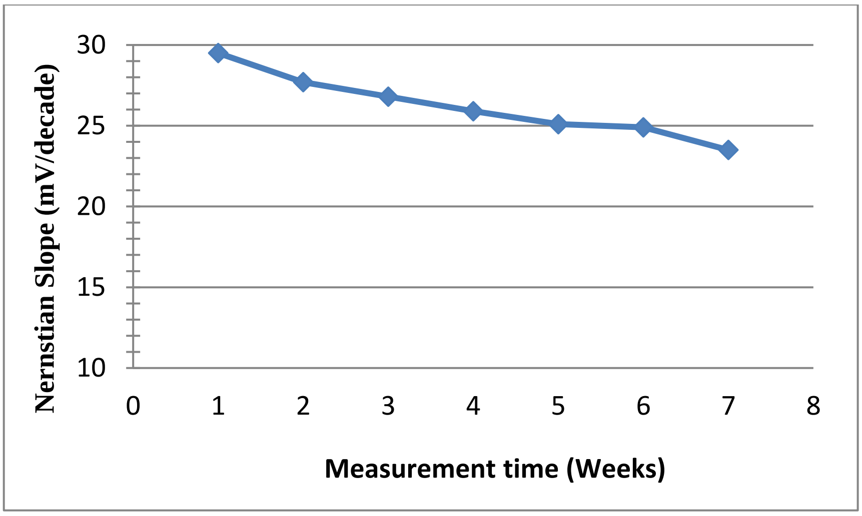

Fig. 6. Nernstian Slope Measurement for every week

Based on the Fig. 6, the Nernstian slope value obtained on the 7th week decreased to 23.5 mV/decade, which indicates that the Pb^{2+} ISE is not feasible to use for analysis because it deviates from the theoretical Nernstian slope, where for divalent is 29.6 ± 5 mV/decade or equivalent to 24.6 - 33.6 mV/decade [23]. It shows that the sensitivity of Pb^{2+} ISE decrease due to the longer membrane contact with water so that the swelling process of the membrane occurs. In this condition it is very possible to lose the plasticizing properties, the carrier ion or the target ion can enter from the membrane surface into the solution so that it affects the measurement results and Nernstian slope [24].

3.6. Effect of Interference Ion

The selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ion over other ions present in solution, are important characteristics of an ISE. In this study, the effect of interference ions on the Pb^{2+} ISE were investigated through MPM (Match Potential Method) [1,25], where the potential measurements were carried out on the main ion solution (a_i) with various concentrations (1×10^{-7}-1×10^{-1} M), contain foreign ions with a fixed concentration (a_j) was 10^{-3} M. To determine the selectivity (K_{ij}^{pot}) is done by calculating the coefficient selectivity:

$$K_{Pb^{2+},B}^{pot} = \frac{aPb^{2+}}{a_j} \qquad 1)$$

The measurement results of selectivity coefficient value of Pb^{2+} ISE for interfere ions can be seen in Table 1. Based on Table 1, the selectivity coefficient for interfere ion Zn^{2+} is 0.0511. It indicates that Pb^{2+} ISE is 5.11 times more selective with Pb^{2+} ions than Zn^{2+} ions. In table 1, all K_{ij}^{pot} value for all interfere ions is less than 1 ($K_{ij}^{pot}<1$). It can be concluded that the interfere ions (Ag^+, Zn^{2+}, Cd^{2+} Cd^{2+}, Cl^- and SO_4^{2-}) at 10^{-3} M did not interfere with the performance of Pb^{2+} ISE in the measurement of Pb^{2+} ions in the sample.

Table 1. Selectivity coefficient value of ISE Pb^{2+} for interfere ions

Interference Ion (10^{-3} M)	K_{ij}^{pot}
Ag^+	0.1642
Zn^{2+}	0.0511
Cu^{2+}	0.0644
Cd^{2+}	0.0898
Cl^-	0.1102
SO_4^{2-}	0.0964

4. CONCLUSION

FT-IR spectra results indicate a change of wave number of thiol (S-H) group and amine (N-H) group of DTZ, show that it is possible the binding of Pb^{2+}. The measurement of the several parameters Pb^{2+} ISE characteristics are very good, shown by the Nernstian slope value was 29.5 mV/decade, with a detection limit was 1.5×10^{-4} M with response time 9-48 seconds. The electrode works well at pH 5, can be used for 6 weeks and has a good selectivity towards interfere ions such as Ag^+, Zn^{2+}, Cu^{2+}, Cd^{2+}, Cl^- and SO_4^{2-}.

Acknowledgement

The authors would like to thank the Head and staff of Laboratorium of Analytical Chemistry, Faculty of Sciences Mulawarman University Samarinda, East Kalimantan for the laboratory facilities and equipment support provider of this research.

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