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Application of SiO_2 Nanoparticles/Ionic Liquid Composite in Modified Carbon Paste Electrode for the Determination of the Lead (II) in Real Samples

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ABSTRACT

The aim of this study was the determination of lead ion concentration by carbon paste ion selective electrode. The electrode response characteristics have been investigated. The Carbon Paste Electrode (CPE) contains graphite powder, nanoparticles, ionophore and ionic liquid. The potential measurements were carried out with a potentiometer. The selectivity of the electrode towards different cationic species was evaluated by Separate Solution Method (SSM). Among the different compositions studied, the carbon paste incorporating 60% Graphite powder, 29% ionic liquid, 5% ionophore and 6% nanoparticles exhibit the best response characteristics. The electrode exhibits a linear response to Pb (II) over a concentration range ($1.0 \times 10^{-6} – 1.0 \times 10^{-2}$) with a Nernstian slope of 29.8 mV per decade. It has a short response time (about 5 s). The detection limit of this electrode was 5.49×10^{-7} M. The potential remained unchanged in the range of pH between 7-11. The suggested electrode was successfully used as an indicator for potentiometric determination of Pb (II) in water samples. It was defined by good analytical parameters: low detection limit, high sensitivity, wide measuring range, wide pH range. All selected cations would not affect the selectivity of the present lead electrode.

Keywords: Ion selective electrode, Carbon paste, Ionic liquid, Ionophore, Potentiometer

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INTRODUCTION

Ion-selective electrode and the determination of lead ion

In order to detect and measure the various substances and ions, the fabrication of different sensors is very important. Ion-Selective Electrode (ISE) is one of the most successful kinds of chemical sensors. It used to determine the concentration of ions by relatively simple measurements of electrical potentials with a voltmeter. ISE respond to ions with changes in the measured electrical potential. This potential achieved by extremely similar the Nernst equation. The main development of ionophore-based ISEs, was carried out by an experimental setup strongly resembling the glass electrode, e.g., Micro electrodes [1]. It was followed the introduction of several related techniques. For many years ago, the researchers needed to manufacture a new specific ISE with high selectivity and sensitivity, long lifetime, wide linear concentration range, good reproducibility and low cost [2]. Selectivity is not only a main feature of an ISE, but also it can be used to determine the stoichiometries and stabilities of ionophore complexes. As well as it used to optimize the selectivity in view of specific applications [1]. Ion selective electrodes based on ionophore have some advantages such as the speed and ease of ISE procedures. In addition, ISEs have wide dynamic ranges and relatively low cost. They are well established for alkali and alkaline-earth metal cations [2]. Many primary researchers on ISEs for heavy metal cations (Pb^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) were inspired by ionophores that were already easily available from other research [1].

Because it’s a very toxic element, the lead is an important ion in chemistry. Lead is used in various industrial products; as a result, it causes water and atmospheric pollution. It is generally present in the environment as inorganic Pb^{2+} which can be easily detected and determined by lead ion-selective electrode [3]. Several methods have been developed for determination of lead ion in aquatic environments [4-7]. Some reports on determination of Pb (II)ion using a carbon paste electrodes have been reported. Recently a review article was reported paracetamol as an ionophore with MWCNTs can be satisfied applied in order to modify the CPE for determination of low concentration of lead (M. Bagheri Jun 2015) [8].

Carbon Paste Electrodes (CPEs)

Carbon Paste Electrodes, one of the Ion Selective Electrodes, have attracted a lot of attention. It has advantages over membrane electrodes e.g. chemical inertness, renewability, robustness, stable response, low ohmic resistance, no need for internal solution and suitability for different kinds of sensing and detection applications [9]. CPEs belong to nontoxic and environmentally friendly electrodes. Also problems with passivation are simply eliminated by a simple and fast renewal of their surface [10]. Over the past five decades, carbon paste contains a mixture of carbon (graphite) powder and a binder (pasting liquid). It has become one of the most popular electrode materials used for the laboratory preparation of various sensors, electrodes, and detectors. At first, non-conductive reagents, such as paraffin oil or mineral oil were used as binders, but their electrochemical capability was poor because of their low conductivity [11]. In this research work, ionic liquid has replaced the paraffin as pasting liquid, so the performance of the electrode was better.

In this study, we report a carbon paste electrode prepared from graphite powder, ionophore, ionic liquid and Nanoparticles, which is used as a potentiometric Pb^{2+}-selective electrode.

MATERIALS AND METHODS

Reagents and solutions

All reagents used were analytically pure grade. The distilled water was used for preparing all aqueous solutions. The Graphite powder (Merck, Germany) along with the Ion liquid 1-Ethyl-3-Methylimidazolium was used for the preparation of the carbon pastes. Chloride and nitrate salts of cations (Na^+, Mn^{2+}, Cu^{2+}, Mg^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Li^+, Fe^{3+}, Zn^{2+} and Ag^+) used were of the highest purity available (all from Merck). The modifier N, N', N"-Tricyclohexil Phosphoric Triamid, was used as Ionophore. Al_2O_3 powder was used to polish and smooth the surface electrode. The Silicon Oxide (SiO_2) Nanoparticles were purchased from Merck Company.

Apparatus

A Metrohm potentiometer (PH meter model of 780) was used for potentiometric measurements. The reference electrode was a Saturated Calomel Electrode (SCE). The Carbon paste electrode was used as a working electrode. Digital scales four zeros (model of Sartorious TE 145) was used.

Preparation of carbon paste electrode

A carbon paste electrode was prepared by mixing 0.06 g of graphite powder and 0.029 g of ionic liquid and 0.005 g of ionophore and 0.006 g of nanoparticles in a mortar. The mixture was packed at the end of the tube. Then the carbon paste electrode was polished on a glossy paper with Al_2O_3 powder and well rinsed with water. The electrode puts in a solution of lead nitrate (1.0×10^{-3} M) for 24 h.

Procedure

The solutions ($1.0 \times 10^{-8} - 1.0 \times 10^{-1}$ M) of lead cation were prepared. The carbon paste electrode was connected to the potentiometer and the calomel reference electrode was connected to the reference terminal of the meter. The two electrodes were dipped in a 50 ml beaker containing prepared solutions. The solution was stirred using a magnetic stirrer. The potential of the electrode was recorded. The performance of the electrode toward Pb(II) was investigated by measuring Electro Motive Force (EMF). It was plotted as a function of the logarithm of the Pb^{2+} concentration. According to the plotted graph, the electrode response to Pb(II) with a good Nernstian slope was determined. To have a good slope and high selectivity, we've optimized composition of the components used in the electrode. At first, we changed the amounts of ionophore while the composition of the other components was fixed. Then the other components, e.g. ionic liquid, nanoparticles, and plasticizer were optimized. In all cases, we changed amounts of the desired compound in proportion to graphite powder while the other components were fixed. In order to investigate the effect of pH, some of the solutions Pb (II) ions with known concentrations was poured into the beaker. Then it was located on a stirring. The electrodes Carbon paste, calomel and pH were placed in to the solutions. The pH of this solution was adjusted to pH=1 by the addition of concentrated HNO_3. The solution stirred until the response of the potentiometer became stable and the potential was measured. Then NaCl was gradually added to the solution until pH=13. The potential was recorded after adding each drop. Finally the pH graph in term of potential was drawn. The response time of this electrode was measured by the series of lead solution. In the each of them the Pb (II) concentration was increased tenfold. When potential remained constant was examined for concentration range.

The selectivity coefficients were determined by the Separate Solution Method (SSM). In the SSM, the potential of a cell, including a working electrode and a reference electrode is measured in two separate solutions. One containing the lead ions, E_1 and the other containing the interfering ions (J), E_2. These values were used to calculate the selectivity coefficient from the following equation [6]:

$$\text{——} + \log [Ag] - \log [J^{z+}]^{1/z} \qquad (1)$$

Where, S is the slope of the calibration graph).

To evaluate the lifetime of the carbon paste electrode, five the same electrodes were prepared. They were tested for a period of 10 weeks. After 8 week the test was repeated by the same electrode. The carbon paste electrode was used as an indicator electrode in titration of 20 ml 1.0×10^{-4} M Pb^{2+} solution with 0.01 M Ethylenediaminetetraacetic Acid (EDTA). At the start of titration, the potential changes were recorded as a result of changes in the volume of titer. The end point of the titration was determined using the graph.

RESULTS

Optimization of the amount of modifier in the electrode

To achieve a perfect selectivity, we've optimized composition of the components used in the electrode. The results are summarized in Table 1.

Table 1: Optimization of the carbon paste ingredients

NO.	Composition of carbon paste (wt. %)					Slope (mV/decade)	Dynamic range
	Ion liquid	Ionophore	Graphite powder	MWCNT/fe_3o_4 sio_2	Plasticizer		
1	0.025	0.003	0.002	0.055	0.015	21.48	$1.0 \times 10^{-2} \sim 1.0 \times 10^{-6}$
2	0.002	0.032	0.06	0.006	-	26.45	$1.0 \times 10^{-2} \sim 1.0 \times 10^{-6}$
3	0.028	0.006	0.06	0.006	-	28.16	$1.0 \times 10^{-2} \sim 1.0 \times 10^{-6}$
4	0.029	0.005	0.06	0.006	-	29.8	$1.0 \times 10^{-2} \sim 1.0 \times 10^{-6}$
5	0.032	0.002	0.06	0.006	-	31.05	$1.0 \times 10^{-2} \sim 1.0 \times 10^{-6}$

Calibration graphs

Using the optimized composition and conditions described above, the potentiometric response of the electrode was studied based on the Pb^{+2} concentration in the range of $1.0 \times 10^{-6} - 1.0 \times 10^{-2}$ M (Figure 1).

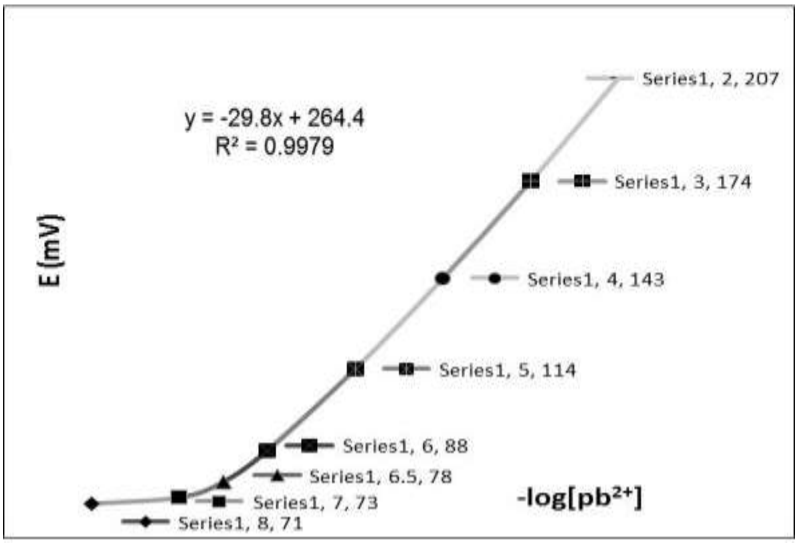

Figure 1: Calibration graph of Pb electrode

Effect of pH

The behavior of the lead electrode in relation to the variation of pH (1-14) was studied (Figure 2).

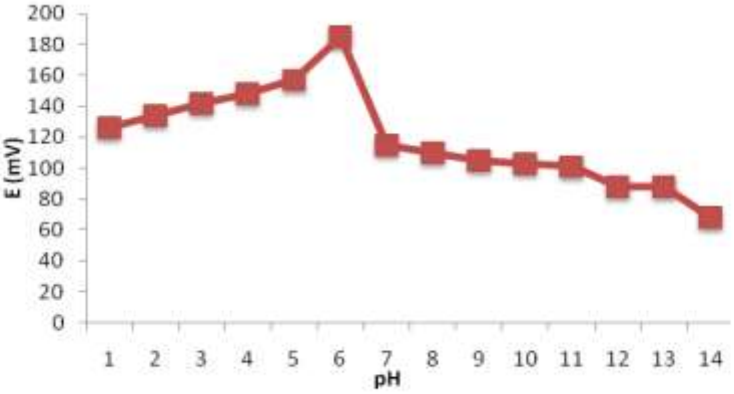

Figure 2: Effect of the pH on the response of the electrode

Response time of electrode

The response time in variation of concentration from 1×10^{-8} to 1×10^{-1} M Pb^{+2} is shown in Figure 3, the measured response time was about 5 s.

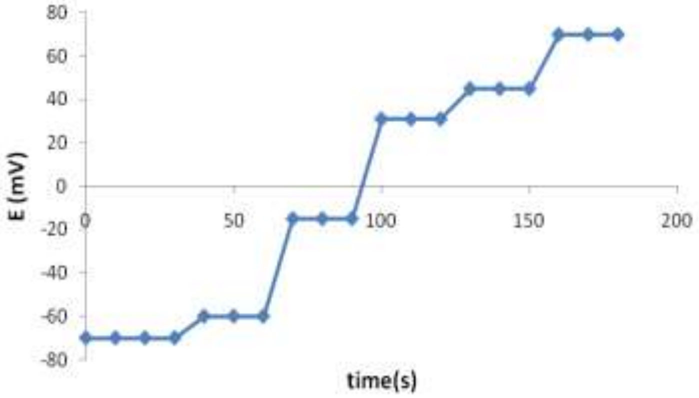

Figure 3: Response time of electrode

Selectivity of electrode

The influence of some inorganic cations such as of Li^+, Na^+, K^+, Ca^{2+}, Zn^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, NH^{4+}, Pb^{2+}, Co^{2+}, Fe^{3+}, Al^{3+} and Cr^{+3} on the electrode response were investigated. The selectivity of the electrode was measured by Separate Solution Method (SSM). The results are categorized in the Table 2.

Table 2: Selectivity coefficients for the responsive electrode

Interfering ions		Interfering ions	
Mg^{2+}	6.3×10^{-2}	Fe^{3+}	1.9×10^{-3}
Cd^{2+}	2.0×10^{-2}	Na^+	7.6×10^{-1}
Hg^{2+}	3.9×10^{-2}	Co^{2+}	5.8×10^{-2}
Ni^{2+}	5.7×10^{-3}	Ag^+	1.4×10^{-1}
Cu^{2+}	2.1×10^{-2}	Zn^{2+}	4.4×10^{-3}
Li^+	3.8×10^{-2}	Mn^{2+}	3.5×10^{-3}

-Selectivity coefficient

Lifetime

The obtained results showed a slight gradual decrease in the slopes after two weeks (from 30.036-28.62 mV decade^{-1}). After eight weeks decrease in the slopes (to 27.70 mV decade^{-1}) was observed (Figure 4).

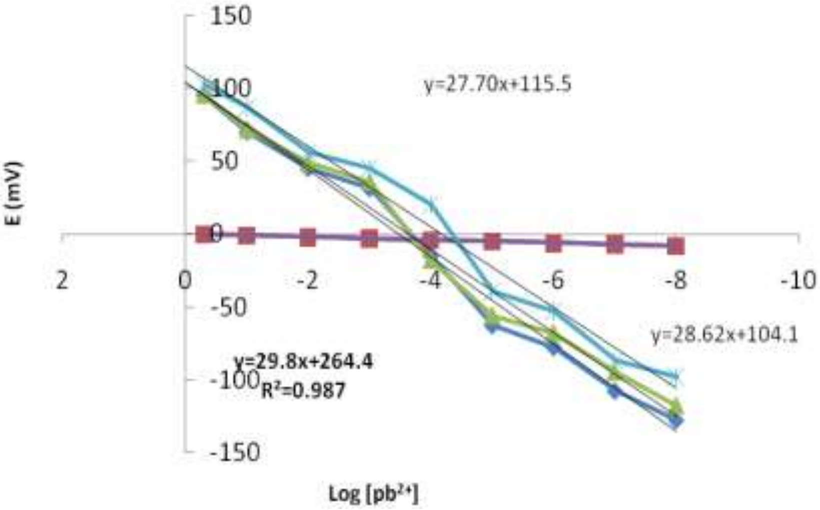

Figure 4: Lifetime of electrode

Potentiometric titration

The obtained potentiometric titration curve is shown in Figure 5.

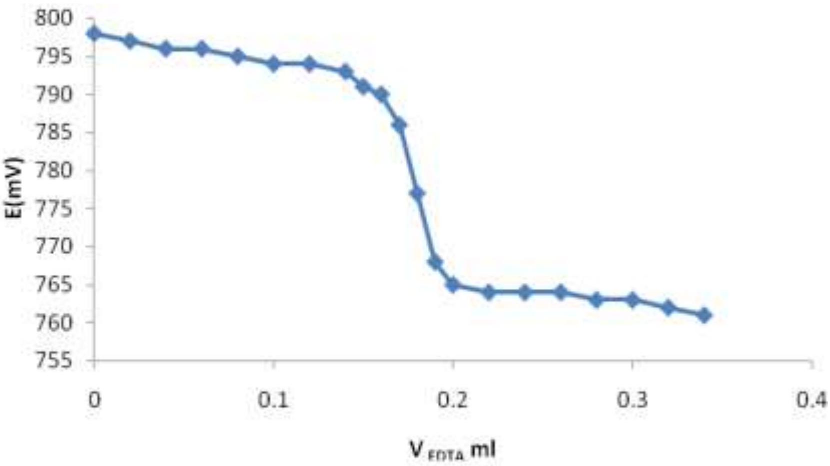

Figure 5: Potentiometric titration curve of 1.0×10^{-4} M solution Pb^{+2} with EDTA

DISCUSSION

The proposed electrode based on ionophore as the ion selective electrode can be used for the determination of lead concentrations in pure solutions, and water samples. Among the different composition studied, the electrode 4 (Table 1) incorporating 29% ion liquid, 5% ionophore, 60% graphite powder and 6% nanoparticle shows the best sensitivity and response. So this composition was used to study others operation parameters of the electrode.

CONCLUSION

The electrode showed a Nernstian slope of 29.8 ± 0.15 mV decade^{-1} and a wide concentration range from 1.0×10^{-6} to 1.0×10^{-2} M. The detection limit of this electrode was low (5.49×10^{-7} M). The response time of this electrode over the different concentrations range of lead was shown in Figure 3 (short response time about 5 s). The potential remained almost unchanged over a pH range of 7-11. The observed changes in the high range related to the production hydroxy complex of lead ions. In acidic areas ionophore can be protonated, so the selectivity of electrode was decreased. Table 2 shows that all twelve cations would not high affect the selectivity of the present lead electrode, and compare to previously report the presence of other ions have no effects on the electrode performance (M. Bagheri, A. Talaiekhozani, F. Ahmadv and Jun 2015). The obtained results showed a slight gradual decrease in the slope after two weeks (Figure 5). For the present electrode the decrease of slope may be attributed to surface contamination or the compounds decay after a long period. It causes loss of the useful lifetime and the accuracy of the electrode. The simplicity, sensitivity and selectivity of the method are comparable to, or even better than those reported sooner. This method can be studied for more samples in the future.

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