A highly selective and sensitive disposable carbon composite PVC-based membrane for determination of lead ion in environmental samples

A. Abbaspour*, E. Mirahmadi, A. Khalafi-nejad, S. Babamohammadi

Chemistry Department, college of sciences, Shiraz University, Adabiat Crossroads, Shiraz 7145685464, Iran

ABSTRACT

A Pt wire coated with phenyl hydrazone derivative–carbon composite in a poly(vinyl chloride) membrane was used for detection of lead. The sensor had a Nernstian slope of 29.46 ± 0.41 mV/decade over a wide linear concentration range of 7.7×10^{-7} to 1.0×10^{-1} mol L^{-1} for Pb(NO$_3$)$_2$. The detection limit was 3.2×10^{-7} mol L^{-1} and the electrode was applicable in the pH range of 3.7–6.3. It had a short response time of approximately 6 s and was used at least for 70 days. The electrode has exhibited good selectivity for Pb(II) relative to 19 other metal ions. The functionality of the proposed sensor was also investigated in binary water–alcohol mixture and it concluded that 23% water–methanol and 20% water–ethanol content could not bring out any changes in its potential. The practical analytical utility of the electrode was demonstrated by measurement of Pb(II) in mineral rock and potentiometric titration of sulfate anion.

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1. Introduction

The need for the determination of lead and other heavy metals increased during the last few years because of growing environmental problems [1]. Lead, a toxic chemical pose a vast range of dangers to human's health. In addition to renal disease, cardiovascular effects, and reproductive toxicity, lead may cause irreversible neuralgic damage. The increased industrial use of lead and its serious effect on human health have resulted in the extensive study of the electrochemical properties and preparation of lead sensors [2].

Common analytical methods for lead determination are furnace AAS and polarography. In spite of good sensitivities of these methods, they are very expensive and time consuming in practice. Furthermore, we need chemical sensors for monitoring purposes. Besides the necessity of very low detection limits, the other main problem is to reach good selectivity properties. Especially good selectivity over alkali and alkaline–earth metals has to be obtained, as for example the natural concentration of calcium in drinking water is about 10^{-3} M [3].

Ion-selective electrodes (ISEs) are established tools that are capable of directly determining the activities of many analytes [4,5]. A variety of ion-selective electrodes have been reported for determination of lead. In these electrodes different compounds in a PVC-based membrane are used for detection of Pb^{2+} [6–11]. Most of these electrodes have classical arrangement, i.e. internal solution ion-selective electrodes (IS-ISEs). There are only a few solid-contact lead-selective electrodes have fabricated [12–15].

The development of miniaturized and micro-sized ISE probes continues to be an active topic of research, because most commercial ISEs, with tip diameters of the order of 3–15 mm, are regarded as macro in size. Such large sensors are not suitable for measurements in small volumes of sample or for the desired in vivo applications of ISEs that biomedical researchers have long awaited. This quest for miniaturization has resulted in the development of coated wire electrodes (CWEs) [16]. Although long-term stability may be a problem, CWEs have been found to be quite useful for many direct determinations if the electrodes are calibrated often. The first report on CWEs was published by Cattrall and Freiser [17]; since then a variety have been reported [18,19].

In recent years, the electrodes and detectors of most interest have been composites of insulating organic polymers filled with electrical conductors, for example carbon powders, ligands, and additives [20,21]. Different forms of carbon or graphite with different polymers as binders have been reported; glassy carbon electrodes [22–24], a carbon film electrode [25], and carbon–poly(vinyl chloride) (PVC) have been used for analytical detection [19,20,26].

Although conductor polymer composites are being increasingly used in electrochemistry, carbon–PVC composites are rarely used, because of the difficulty of electrode preparation [27].

In this study we have shown that carbon composite electrodes can be prepared easily as coatings on wire electrodes. Carbon-based

* Corresponding author. Tel.: +98 7112284822/0926.
E-mail address: Abbaspour@chem.susc.ac.ir (A. Abbaspour).

materials have been used because of their many advantages, for example low background, low cost, high stability, and resistance to passivation [28].

We previously reported, for the first time, use of a PVC–carbon composite on platinum wire as a CWE for analysis of Ag(I) and Pb(II). In comparison with most commercially available electrodes, these electrodes were readily prepared and had high selectivities with a low detection limits [12,29]. The object of this work is to demonstrate use of a new carbon–PVC–hydrazone composite electrode on platinum wire for rapid and selective determination of lead over a wide concentration range (7.7×10^{-7} to 1.0×10^{-1} mol L^{-1}). The significance of this membrane composition is twofold, use of carbon for increasing sensitivity and use of ionophore which is an important aspect of increasing the selectivity of this composition. In addition this sensor was also applicable in water-miscible organic solvents such as methanol and ethanol. Although complex and expensive methods are used to detect lead with low detection limits, as already mentioned, our method has many advantages, for example low cost, easy preparation, requirement of simple and inexpensive potentiometric instrument. The results obtained demonstrate that this electrode is in most cases is superior to previously reported lead-selective electrodes.

2. Experimental

2.1. Reagents and chemicals

Analytical-reagent grade dibutyl phthalate (DBP), dibutyl sebacate (DBS), diethyl sebacate (DES), and o-nitrophenyl octyl ether (o-NPOE) were obtained from Fluka. Poly(vinylchloride) (PVC), carbon powder and tetrahydrofuran (THF) were purchased from Merck. Chloride and nitrate salts of metals were provided from Merck or Fluka and were used without any purification. All solutions were prepared from analytical reagents with triply distilled water.

2.2. Ionophore preparation

Ionophores which were used are, benzyl 2-(3-(phenylhydrazono)-2-oxoindolin-1-yl) acetate (ionophore I), 1-cyclopentyl-3-(2-phenylhydrazono) indolin-2-one (ionophore II) and butyl-3-(2-phenylhydrazono) indolin-2-one (ionophore III) (Fig. 1).

Typical procedure for synthesis of ionophores (ionophore III) is in the literature [30]. In a double-neck round bottomed flask (100 mL) a mixture of 1-buthylindoline-2,3-dione (2.03 g, 0.01 mol), phenyl hydrazine (1.62 g, 0.015 mol) and catalytic amount of acetic acid (two to three drops) was dissolved in ethanol (15 mL). The solution was refluxed for 10 h. After this time the reaction was completed as it was indicated by TLC and then the reaction mixture was kept at refrigerator overnight. Filtration of reaction mixture followed by washing with cool ethanol and recrystallization from MeOH/H$_2$O gave pure yellow crystalline of corresponding phenylhydrazone. The characteristics of products are as follow:

Ionophore I: R_f (EtOAc/n-hexane, 1:3) 0.50; mp 198–199 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 12.64 (s, 1H, NH), 6.71–7.95 (complex, 14H, aryl, isatin), 5.20 (s, 2H, COOCH$_2$), 4.58 (s, 2H, N-CH); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 40.82, 67.52, 108.42, 114.43, 119.11, 121.35, 122.99, 123.40, 126.27, 127.98, 128.35, 128.57, 128.65, 129.43, 139.62, 142.37, 142.44, 160.31, 167.45; IR (KBr) ν_{max} 3285.6, 2916, 2856.9, 1765.3, 1604.1, 1356.2 cm^{-1}.

Ionophore II: R_f (EtOAc/n-hexane, 1:8) 0.56; mp 47–48 °C; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 12.98 (s, 1H, NH), 7.93–6.84 (complex, 9H, aryl, isatin), 3.73 (t, 2H, N-CH2, J = 7.0 Hz), 1.63–1.75 (m, 2H, C(2)butyl), 1.32–1.47 (m, 2H, C(3)butyl), 0.96 (t, 3H, CH3, J = 7.5 Hz);
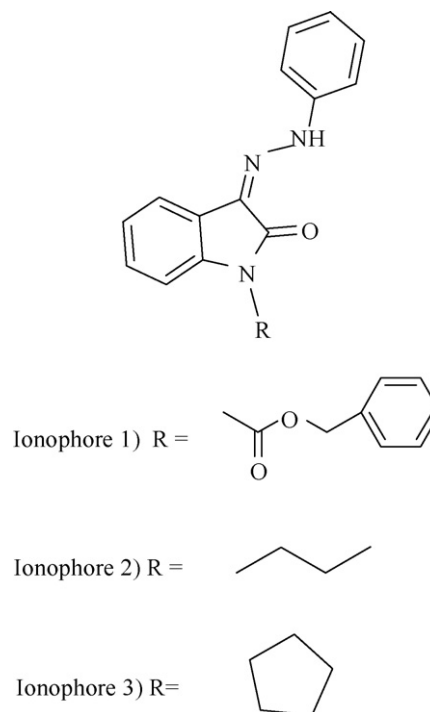

Fig. 1. Chemical structure of ionophores.

^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 13.77, 20.27, 29.94, 39.25, 108.67, 114.28, 118.94, 121.38, 122.36, 1213.09, 126.98, 127.89, 129.40, 140.38, 142.65, 162.65, 162.20; IR (KBr) ν_{max} 3201.6, 3093.6, 2962.5, 1731.3, 1596.5 cm^{-1}.

Ionophore III: R_f (EtOAc/n-hexane, 1:3) 0.87; ^{1}H NMR (250 MHz, CDCl$_3$): δ = 12.97 (s, 1H, NH), 7.87–6.85 (complex, 9H, aryl, isatin), 4.58–4.71 (m, 1H, N-CH), 1.83–1.93 (m, 4H, C(2)cyclopentyl), 1.45–1.64 (m, 4H, C(3) cyclopentyl); ^{13}C NMR (62.5 MHz, CDCl$_3$): δ = 25.21, 27.92, 52.04, 109.94, 113.60, 118.99, 121.74, 122.15, 122.81, 127.65, 131.32, 139.45, 142.70, 162.28; IR (KBr) ν_{max} 3226.2, 3002.2, 1736.2, 1690.5, 1604.1, 1395.2 cm^{-1}.

2.3. Membrane preparation

The schematic setup and general protocol for preparation of this sensing electrode used in this work was similar to our previous studies [31–34] except that this electrode was a carbon composite PVC coated wire electrode with a lead-selective ionophore. This cocktail mixture was prepared by mixing ionophore (2%); carbon powder (4%); o-NPOE (62.7%); PVC (31.3%). A total weight of 150 mg of the mixture was dissolved in 1.5 cm^3 of dry freshly distilled THF and the mixture was homogenized by using ultrasound. Coating process of this carbon composite coated platinum wire electrode was performed by dipping Pt wire five times into this homogenized mixture. After coating process, the membrane was air-dried for 12 h until a thin film was formed by using the technique as our previous work [29]. The electrode was finally conditioned for 3 h in a 10^{-1} M of Pb(NO$_3$)$_2$ solution.

2.4. Apparatus and emf measurements

All measurements of emf were made at 25 °C by using a Metrohm pH meter (Model 654) with the following cell assembly:

Ag/AgCl, KCl (sat'd.)//Pb^{2+} solution/membrane/Pt wire

Activities were calculated in accordance with the Debye–Huckel procedure [35].

The performance of the electrode was investigated by measuring the emf values for the metal ion solution over a concentration range of 4.6×10^{-8} to 0.1 M by adding successive aliquots of known concentrations of metal ion to 30 cm^3 of water.

3. Results and discussion

3.1. Electrode response characteristics

Before any optimization the potential responses of platinum coated wire electrodes for solutions containing each cation separately were obtained and the results are shown in Fig. 2. As this figure exhibits this sensor has a better response characteristic to the lead ion than to the other cations. Accordingly at the rest of experiment, membrane components were optimized to give Nernstian response to lead ion. The Pt coated wire electrode with optimum composition was showed a linear Nernstian response with a slope of 29.46 ± 0.41 mV/decade over the range of 7.7×10^{-7} to 1.0×10^{-1} M and a correlation coefficient of 0.999 ($n = 7$).

3.2. Optimization of membrane composition

Studies on the response characteristics of lead ion-selective electrodes based on ionophores 1–3, were shown that ionophore number 3 has the best behavior than the others with a good Nernstian response over a wide linear range (8×10^{-7} to 3.2×10^{-2}). The results are given in Table 1 (electrodes 1–3). So we have used ionophore No. 3 to fabricate lead-selective electrode.

Several solvent mediators (o-NPOE, DES, DBS, DBP) were tested. The lead ion-selective electrode based on o-NPOE exhibited a better Nernstian slope (29.46 ± 0.41 mV/decade) than DES, DBS and DBP (with slopes of 15.55, 18.96 and 14.97 mV/decade, respectively) as they are given in Table 2 in a wide concentration range 7.7×10^{-7} to 1.0×10^{-1} M of Pb(NO$_3$)$_2$. Therefore, o-NPOE was chosen as plasticizer in the rest of experiments.
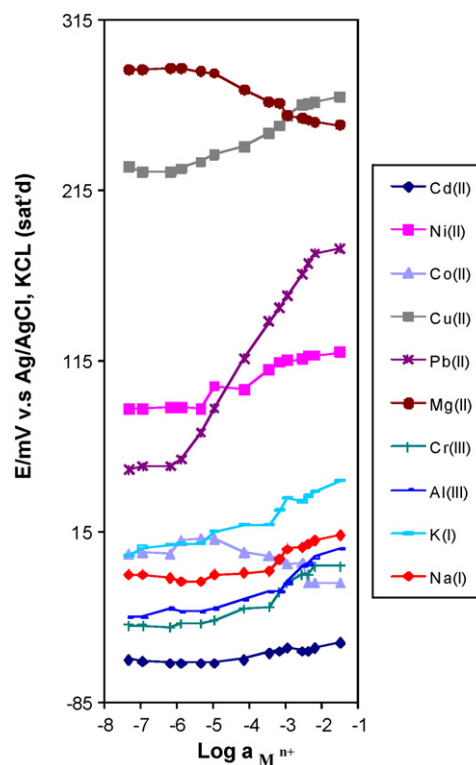

Fig. 2. The potential response of various cations on CWE.

The performance of membranes of different composition was investigated; the results are given in Table 2. It is apparent from the table that the response of the electrode coated with the composite containing no ligand (No. 14) has a super-Nernstian slope of 36.53 mV/decade over a short range of concentration. The electrode which is coated with the composite containing 0.0% carbon powder (No. 13) has a near Nernstian slope of 22.76 mV/decade in the concentration range of 4.0×10^{-6} to 1.2×10^{-2} mol L^{-1} whereas

Table 1
Effect of ionophore on the electrode response.

| No. | Coating composition (%) | | | | Slope (mV/decade) | r^2 | Concentration range (M) |
	Plastisizer (o-NPOE)	PVC	C[a]	Ionophore			
1	62.6	31.3	4	2 (I$_1$)	26.61	0.991	7.2×10^{-5} to 1.0×10^{-2}
2	62.6	31.3	4	2 (I$_2$)	24.10	0.989	4.6×10^{-6} to 1.0×10^{-1}
3	62.6	31.3	4	2 (I$_3$)	30.64	0.998	8.0×10^{-7} to 1.0×10^{-1}

I$_1$, ionophore number 1; I$_2$, ionophore number 2; I$_3$, ionophore number 3.
[a] Carbon powder.

Table 2
Various membrane composition Pt electrode for Pb(II) detecting (using ionophore number 3).

| No. | Coating composition (%) | | | | | | | Slope (mV/decade) | r^2 | Concentration range (M) |
	DES	o-NPOE	DBP	DBS	PVC	C[a]	Ionophore No. 3			
4	62.7	–	–	–	31.3	4.0	2.0	15.55	0.995	4.0×10^{-6} to 1.2×10^{-2}
5	–	–	62.7	–	31.3	4.0	2.0	14.97	0.974	7.7×10^{-5} to 7.0×10^{-3}
6	–	–	–	62.7	31.3	4.0	2.0	18.96	0.996	1.3×10^{-5} to 1.0×10^{-1}
7	–	62.7	–	–	31.3	4.0	2.0	29.74	0.999	7.7×10^{-7} to 1.0×10^{-1}
8	–	62.3	–	–	31.2	4.0	2.5	31.14	0.997	4.0×10^{-6} to 1.0×10^{-1}
9	–	61.0	–	–	30.5	4.0	4.5	23.65	0.994	4.0×10^{-6} to 1.0×10^{-1}
10	–	63.3	–	–	31.7	4.0	1.0	30.97	0.999	1.0×10^{-5} to 1.2×10^{-2}
11	–	63.7	–	–	31.8	2.5	2.0	25.97	0.997	4.0×10^{-6} to 1.0×10^{-1}
12	–	61.7	–	–	30.8	5.5	2.0	31.05	0.997	4.0×10^{-6} to 4.2×10^{-3}
13	–	65.3	–	–	32.7	–	2.0	22.76	0.996	4.0×10^{-6} to 1.2×10^{-2}
14	–	64.0	–	–	32.0	4.0	–	36.53	0.996	4.0×10^{-6} to 4.2×10^{-3}

[a] Carbon powder.
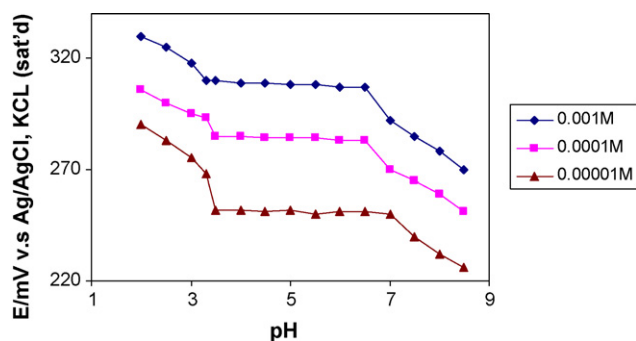
Fig. 3. pH effect on proposed composite electrode in three different concentration of chromium ion in the pH range of 2.0–8.0.

Table 3
Performance of the electrode in binary water–alcohol system.

Percentage of alcohol (%)	Potential (mV vs. Ag/AgCl, KCl(sat'd))	
	Methanol	Ethanol
0	355	351
3	355	351
6	355	351
9	355	351
12	355	351
15	355	351
18	355	351
21	355	352
24	356	358
27	360	362
28	365	368

at the optimum composition of ionophore (2.0%), carbon powder (4.0%), o-NPOE (62.7%), and PVC (31.3%) the obtained slope was 29.46 mV/decade in the concentration range of 7.7×10^{-7} to 1.0×10^{-1} mol L^{-1} (No. 7).

The performance of the carbon powder for increasing the sensitivity of the electrode was demonstrated by comparing the slope of electrodes No. 11 and 12 in Table 2. As this table shows an electrode with the optimum amount of ionophore but with less carbon than its optimum value (No. 11) has a sub-Nernstan slope. Changing the composition of the electrode by increasing the amount of carbon to more than its optimum value (No.12) was resulted in a supper-Nernstian response.

It is also clear from Table 2 that the detection limit and dynamic range for this CWE not only influenced by carbon, but also depend on the amount of the ionophore. The results obtained in this study indicated that the electrodes based on both the butyl-3-(2-phenylhydrazono) indolin-2-one and the carbon powder show a high selectivity and sensitivity for lead ions.

3.3. Effect of pH and water-miscible solvent on electrode potential

The pH dependence of the potentials of the proposed electrode for 1.0×10^{-3}, 1.0×10^{-4}, and 1.0×10^{-5} mol L^{-1} lead solutions were investigated over the pH range of 2.0–8.0 (HNO$_3$ or NaOH solutions were used to adjust the pH) and the results are depicted in Fig. 3. The potential responses remained constant over the pH ranges of 3.5–6.0, 3.7–6.0, and 3.7–6.3 at concentration ranges of 1.0×10^{-3}, 1.0×10^{-4}, and 1.0×10^{-5} mol L^{-1} of Pb(NO$_3$)$_2$, respectively. Drift was observed at low pH values could be due to the response of the electrode to H$^+$ ions whereas at higher pH values the formation of hydroxy complexes of Pb^{2+} ions may cause a decrease in potential value.

The electrode response was also investigated taking water-miscible organic solvents such as methanol and ethanol. The potential of the electrode was found to be virtually constant for 1.0×10^{-3} mol L^{-1} lead solutions up to 23% content of the methanol and 20% of ethanol which clearly suggested that the electrode can be applied to estimate the lead ions in presence of the water-miscible organic solvents without any interference. The results are given in Table 3. This feature is important in the cases that analytical sample is not completely soluble in water but it could be solved by water–alcohol mixture.

3.4. Detection limit, reproducibility, repeatability response time and lifetime of the chromium electrode

The limit of detection, which is evaluated according to IUPAC recommendations [36] was 3.2×10^{-7} M of Pb(NO$_3$)$_2$. The reproducibility was investigated by preparing seven similar electrodes at optimum membrane composition then the slope of each electrode

was determined and the average slope with standard deviation was 29.78 ± 0.58 mV/decade (RSD = 1.95%).

For the repeatability study, the calibration curves of one electrode in five times were obtained during 10 days, the calibration curves had been taken every other day. The average slope with standard deviation was 29.46 ± 0.41 mV/decade (RSD = 1.39%).

The response time of the electrode was evaluated (according to IUPAC definition) by measuring the time required to achieve a 90% value of steady potential for a lead solution. A response time of 6 s was obtained for this carbon–PVC membrane.

To investigate the lifetime of the electrode the calibration curves of lead electrode at its optimized composition were periodically obtained for 70 days.

3.5. Selectivity coefficients of lead-selective electrode

The potentiometric selectivity coefficients, which reflected the relative response of the membrane sensor for the primary ion over other ions, present in solution, is perhaps the most important characteristics of an ion-selective sensor. The selectivity coefficients to nineteen common cations were investigated by the matched potential method (MPM) [36,37]. This method gets rid of the limitations of the corresponding methods based on Nicolsky–Eisenmen equation for determining the potentiometric selectivity coefficient (including the fixed interference and the mixed solution methods) [38]. These limitations include non-Nernstian behavior of interfering ions and an inequality of the charges of the primary and interfering ions. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the inter-

Table 4
Selectivity coefficients calculated by MPM.

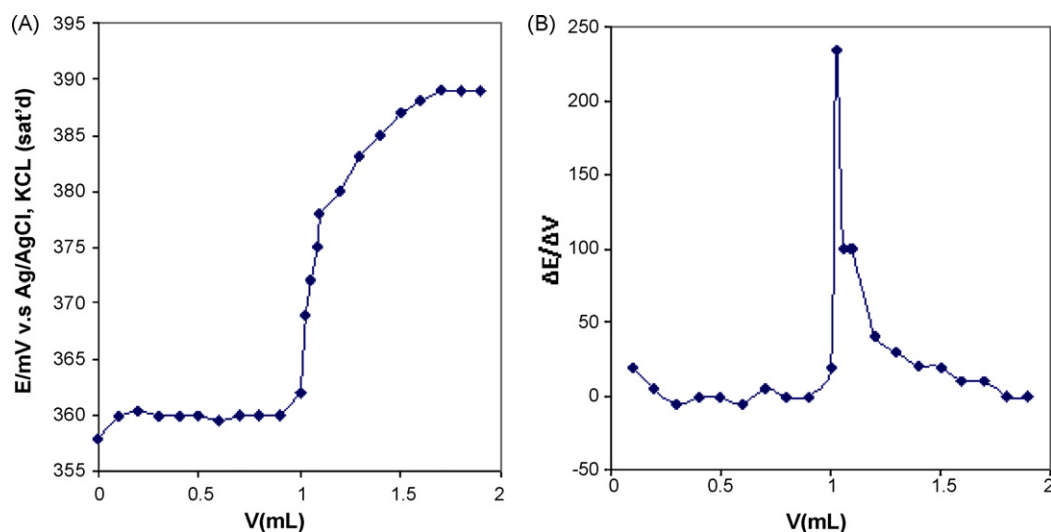| Interfering ion	$K_{A,B}^{pot}$
Li$^+$	4.8×10^{-4}
Cd^{2+}	3.8×10^{-4}
Ca^{2+}	6.3×10^{-3}
Ba^{2+}	3.2×10^{-3}
Co^{2+}	8.1×10^{-4}
Ni^{2+}	5.4×10^{-3}
Cu^{2+}	1.7×10^{-3}
Mg^{2+}	8.7×10^{-5}
Hg^{2+}	1.2×10^{-2}
Na$^+$	7.8×10^{-3}
Ag$^+$	4.1×10^{-2}
Al^{3+}	3.4×10^{-3}
Zn^{2+}	7.1×10^{-4}
Cs$^+$	6.7×10^{-3}
NH$_4^+$	5.9×10^{-3}
La^{3+}	7.1×10^{-3}
Fe^{2+}	2.4×10^{-2}
Cr^{3+}	2.9×10^{-3}
K$^+$	3.4×10^{-3}

Fig. 4. (A) Potentiometric titration curve and (B) first-derivative curve of 20.0 mL 1×10^{-3} M of sulfate ion solution by 0.02 M Pb^{2+} solution.

Table 5
Comparison of proposed electrode with other solid-contact lead-selective electrodes.

pH range	Concentration range (M)	Slope (mV/decade)	Detection limit (M)	Lifetime (days)	Response time (s)	Reference
3.0–6.7	1.0×10^{-7} to 1.0×10^{-3}	29.42 ± 0.5	5.0×10^{-8}	105	10	[14]
1.7–6.0	5×10^{-6} to 1×10^{-1}	29.4 ± 1	2×10^{-6}	90	15	[16]
1.5–6.0	1×10^{-6} to 1×10^{-1}	30 ± 1	6×10^{-7}	150	30	[40]
3.5–5.5	5×10^{-6} to 1×10^{-2}	28.0	3.2×10^{-6}	–	6	[41]
2.0–4.0	5×10^{-5} to 1×10^{-1}	25.8	5×10^{-6}	–	5–10	[42]
3.5–5.0	1×10^{-5} to 1×10^{-2}	28.0 ± 0.2	1.4×10^{-6}	56	17	[43]
2.0–5.0	1×10^{-5} to 1×10^{-1}	29.4 ± 0.5	5×10^{-6}	60	10–20	[44]
5.0–7.0	1×10^{-6} to 1×10^{-2}	27.8 ± 0.2	4×10^{-7}	–	20	[45]
3.6–6.0	7.7×10^{-7} to 1.0×10^{-1}	29.46 ± 0.41	3.2×10^{-7}	70	6	This work

fering ion (B) that gives the same potential change in a reference solution. Thus, first the change in potential upon changing the primary ion activity is measured, and then the interfering ion would be added to an identical reference solution until the same potential change is obtained.

The selectivity coefficient, $K_{A \cdot B}^{\text{pot}}$, is determined as:

$$K_{A \cdot B}^{\text{pot}} = \frac{\Delta A}{a_B}$$

where $\Delta A = a'_A - a_A$, a_A is initial primary ion activity and a'_A the activity of A in the presence of interfering ion, a_B. It should be noted that the concentration of Pb^{2+} used as primary ion in this study was 5.0×10^{-6} M. The resulting selectivity coefficient values thus obtained for the proposed Pb^{2+} sensor are given in Table 4. As this tables shows all cations would not affect the selectivity of the present lead electrode.

3.6. Potentiometric titration

The proposed Pb(II) membrane sensor was found to work well under laboratory conditions. It was successfully applied to the titration of a sulfate ion solution with Pb(II) ion solution, and the resulting titration curve and the corresponding derivative curve are shown in Fig. 4. As shown, the amount of sulfate ions can be accurately determined with this electrode.

3.7. Determination of lead in mineral rock

Lead enters the environment via different ways such as volcanism and plant metabolism. Another way in which lead has found its way into environment is weathering of rocks and soil that contain

lead component [39]. Therefore, determination of lead is not only important in industrial wastewater samples, but it is also essential to determine the amount of lead in the soil and rocks that undergo weathering. The sensor was used for the determination of lead in mineral rock after it dissolved in nitric acid solution using standard addition method. 43.5 ± 0.5 µg g^{-1} of lead was obtained by proposed sensor which is comparable with the amount determined by atomic absorption spectroscopy (43.8 ± 0.3 µg g^{-1}).

3.8. Comparison of the proposed electrode with other lead electrodes

The characteristic responses of this and other solid-contact lead-selective electrodes are listed in Table 5. When the data are compared it is apparent that this electrode is superior to previously reported electrodes in most cases. Although this sensor has reasonable detection limit and pH range compare to our previous study, this electrode is with the advantages of having the capability of being used in wider concentration range (which is more suitable for industrial samples). In addition the response time of this electrode is shorter than our previous work which makes it more applicable for flow injection analysis methods.

4. Conclusions

We have shown that electrode prepared from a composite of carbon, and poly(vinyl chloride) can be used for analytical applications. This composite electrode is sufficiently stable and has a long lifetime. The proposed electrode also has many other advantages; it is, for example, economical, easy to prepare, and requires simple and inexpensive potentiometric equipment. The results obtained indi-

cate that this electrode is usually superior to previously reported lead-selective electrodes. Finally this electrode not only can be used in aqueous media, but also is applicable for determination of lead ion in binary water–alcohol system.

Acknowledgement

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