PVC based membrane of Ti(IV) iodovanadate for Pb(II) determination

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ABSTRACT

Ti(IV) iodovanadate has been synthesized by mixing a mixture of aqueous solutions of 0.1 M sodium vanadate and 0.1 M potassium iodate with 0.1 M solution of Ti(IV) chloride at pH 1.0. Distribution coefficients (K_d) of various metal ions were determined on the column of Ti(IV) iodovanadate which showed the selectivity of Pb(II) ions by this cation exchange material. So Ti(IV) iodovanadate has been used as an electoactive material for the construction of Pb(II) selective electrode. The main purpose of this study is to develop an inexpensive, simple and reliable ion-selective electrode for Pb(II) determination. The sensor exhibit Nernstian response for Pb(II) ions over a wide concentration range of 1×10^{-7} M to 1×10^{-1} M with a slope of 30 ± 0.4 mV per decade of activity. The electrode is suitable for use in aqueous solution in a pH range of 2-7.2 with a response time of 10 second. The membrane electrode can be used at least for 4 months without any divergence in potential. The selectivity coefficients were determined by the mixed solution method and revealed that the electrode was selective for Pb(II) ions in the presence of interfering cations. The sensor could be used as an indicator electrode in the potentiometric titration of Pb(II) ions with EDTA. The practical applicability of the proposed sensor has been reported for Pb(II) determination in a standard rock sample and water sample. The results are found to be in good agreement with those obtained by using conventional methods.   © 2008 Trade Science Inc. - INDIA

1. INTRODUCTION

Over recent years, the need of controlling the level of environmental pollutants in natural waterways, portable water and soils has generated increasing interest in the development of novel sensors for the detection of heavy metals. Among the heavy metals, lead is the most commonly encountered toxic pollutant in the environment as a result of its use in batteries, gasoline, solder, pipes and paints. It is a serious poison and tends to accumulate in the bone structure when ingested in levels exceeding the natural elimination rate of about 300 µg Pb/day[1]. Lead can damage to the nervous system and the kidneys. To monitor this type of metals in large number of environment samples, potentiometric detectors based on ion-selective electrodes are suited because they offer advantages such as high selectivity, sensitivity, fast response, good precision, simplicity and low cost[2,3]. These methods make possible direct monitoring of activities of selected species without pretreatment. The use of ion-selective electrodes (ISEs) for the detection and determination of lead has received much interest and many ligands have been investigated as sensing agents in electrodes[4]. Dicyclohexano-18-crown-

6, dibenzo-18-crown-6, benzo-18-crown-6, 15-crown-5 and their alkoxy, alkyl and methyl ester derivatives have also been successfully used as electroactive materials to develop selective sensors for Pb(II) ions[5-10]. Piroxicam, tetrabenzyl pyrophosphate, pyridinecarboximide derivatives, porphyrins, calixarenes, etc., have also been used as electroactive materials in Pb(II) selective electrodes[11-22] which show narrow working concentration range, high response time and suffer interference from some metal ions. A literature survey revealed that a limited number of membrane sensors using inorganic ion exchangers have been developed and most of these suffer from poor selectivity[23]. In the present study, we have used Ti(IV) iodovanadate inorganic cation exchanger as a sensing material for the construction of Pb(II) ion-selective electrode. The present sensor offers the advantages of thermal stability, simplicity, sensitivity, low cost, reliability, fast response and long life. In addition, the proposed sensor has been used for the determination of Pb(II) in a standard rock sample and water sample.

2. EXPERIMENTAL

2.1. Reagents

Titanium chloride (99%, Riedael-de Haen, Germany), potassium iodate (Otto Chemie, Bombay, India), sodium vanadate (Otto Chemie, Bombay, India). All other chemicals and reagents used were of analytical reagent grade.

2.2. Instrumentation

A single electrode pH meter (Toshniwal, India), a UV-Vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker and a digital potentiometer (Equiptronics EQ 609, India) with silver-silver chloride electrode as reference electrode were used.

2.3. Synthesis of Ti(IV) iodovanadate

Ti(IV) iodovanadate was synthesized by mixing a mixture of aqueous solutions of 0.1 M sodium vanadate and 0.1 M potassium iodate with 0.1 M solution of Ti(IV) chloride at pH 1.0. The gelatinous precipitates, so formed were allowed to stand for 24 hrs in the mother liquor. The supernatant liquid was removed and the precipitates were washed with demineralized water

several times to remove excess reagents. The products were dried at 40 ± 2^0C in an oven. The dried products were then kept in demineralized water for cracking and to obtain the particle of the size range ~125 μm. These were converted to H+ form by placing them in 1.0 M HNO_3 solution and washed with demineralized water to remove excess acid and finally dried at 40 ± 2^0C.

2.4. Sorption studies

In order to get an idea of partition behavior of the exchanger towards the separation of metal ions of analytical interest, distribution coefficients (K_d) were determined in deminaralized water, di-methyl formamide and formamide mediums (TABLE 1). A, 0.4 g exchanger in H+ form was treated with 40 ml solution of metal ions in required solvent medium in a 100 ml Erlenmeyer flask. The mixture was shaken for 6 hrs at 25 ± 2^0C in a temperature controlled incubator shaker. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M disodium salt of EDTA. The K_d values may be expressed as follows-

$$K_d = \frac{\text{milli equivalent of metal ions / gm of ion - exchanger}}{\text{milli equivalent of metal ions / mL of solution}}$$

$$Kd = \frac{I-F}{F} \times \frac{V}{M} \text{ ml g}^{-1} \tag{1}$$

where I is the initial amount of the metal ion in the solution phase, F is final amount of metal ion in the solution phase after treatment with the exchanger, V is the volume of the solution (ml) and M, the amount of ion exchanger taken (g).

2.5. Membrane preparation

The membranes were prepared as suggested by Coetzee and Benson[24]. The electroactive material Ti(IV) iodovanadate cation exchanger was grinded to fine powder and different amounts of this was mixed thoroughly with a fixed amount of PVC and dissolved in 10 ml of tetrahydrofuran (THF). The mixtures were vigorously shaken and when the solution got viscous, it was poured in a dust free Pyrex glass circles and solutions were allowed to evaporate at room temperature. The mixing ratio of the ion exchanger was varied in order to obtain a composition, which gave the best performance. In this way three sheets of different thickness were prepared.

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2.6. Conditioning and characterization of membrane

The physicochemical properties of the membrane viz- water content, porosity, thickness and swelling etc. were determined as described elsewhere[25,26] after conditioning the membrane.

For conditioning, the membranes were equilibrated with 1 M NaCl and a few ml of CH_3COONa to adjust the pH in the range 5-6.5 (to maintain acid present in the film).

To find out the water content, the conditioned membranes were first dipped in water to elute diffusible salts and blotted with whatmann filter paper to remove surface moisture and weighed the water content was calculated as-

% Total weight $= (W_w - W_d)/ W_w \times 100$ **(2)**

where W_w is the weight of the wet membrane and W_d if the weight of dry membrane.

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\varepsilon = \frac{Ww - Wd}{AL\rho w} \quad (3)$$

where A is the area of the membrane, L is the thickness of the membrane and ρw is the density of water.

Membrane thickness was measured by taking the average thickness of the membrane by using screw gauze and the swelling was measured as the difference between the average thicknesses of the membrane before and after equilibration with 1M NaCl for 24 hrs. Composition of best performed membrane is listed in TABLE 2 along with their response characteristics.

2.7. Electrode Preparation

A transparent membrane of 5 mm. diameters was cut from master membrane and glued to one end of a Pyrex glass tube with the help of araldite. The glass tube was filled with a 0.1 M $Pb(NO_3)_2$ solution. Silver/silver chloride electrodes were used as internal and external reference electrodes. All the potential measurements using the following cell were made at 25±0.5°C. The whole arrangement can be shown as-

Internal reference electrode (Ag/AgCl)|3.0 M KCl Internal electrolyte, 0.1 M Pb^{2+}|Membrane|Sample solution|3.0 M KCl | External reference electrode (AgCl/Ag)

The performance of the electrode was investigated by measuring the e.m.f. of Pb(II) ion solution over the pH range of 1×10^{-1} to 1×10^{-10} M. The membrane electrode was conditioned by soaking in a 0.1 M $Pb(NO_3)_2$ solution for 2 days and atleast 1 hr before use. After performing the experiment, membrane electrode was removed from the test solution and kept in o.1 M Pb $(NO_3)_2$. Potential measurement of the membrane electrode were plotted against the selected concentration of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

3. RESULTS AND DISCUSSION

Ti(IV) iodovanadate was synthesized by mixing a mixture of aqueous solutions of 0.1 M sodium vanadate and 0.1 M potassium iodate with 0.1 M solution of Ti(IV) chloride at pH 1.0. In order to explore the potentiality of this new inorganic cation exchange material in the separation of metal ions, distribution studies of various metal ions have been performed in demenaralized water, di-methyl formamide and formamide mediums (TABLE 1). The distribution studies of various metal ions showed the selectivity of Pb(II) ions by this cation exchange material. So Ti(IV) iodovanadate has been used as an electroactive material for the preparation of Pb(II) ion-selective membrane electrode. Three samples of Ti(IV) iodovanadate membrane were prepared using different mixing ratios of electroactive Ti(IV) iodovanadate with a fixed amount

TABLE 1: Distribution coefficient (K_d) of metal ions on Ti(IV) iodovanadate in different solvent systems

Metal ions	Deminralized water	Di-methyl formamide	Formamide
Mg^{2+}	208	240	220
Ca^{2+}	186	214	196
Sr^{2+}	168	196	196
Ba^{2+}	168	179	170
Cr^{3+}	410	520	493
Fe^{3+}	280	418	387
Co^{2+}	168	630	520
Ni^{2+}	162	680	610
Zn^{2+}	178	597	436
Cd^{2+}	192	423	382
Hg^{2+}	187	287	218
Pb^{2+}	2418	2612	2319
Al^{3+}	204	521	476
Ce^{3+}	180	423	382

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TABLE 2: Characterization of ion-exchanger membrane

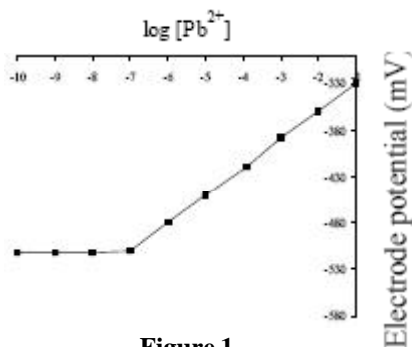| S. no.	Membrane composition		Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % wt of wet membrane	Working conc. range (Molar)	Slope (±0.4mV/decade of activity)	Response time (sec.)
	TIV (mg)	PVC (mg)							
S-1	150	200	0.41	2.4	0.082	0.12	1.0×10^{-7} to 1.0×10^{-1}	30	10
S-2	250	200	0.68	10.5	0.384	0.15	1×10^{-6} to 1.0×10^{-1}	34	18
S-3	300	200	0.84	14.7	0.412	0.20	5.6×10^{-6} to 1.0×10^{-1}	33	26

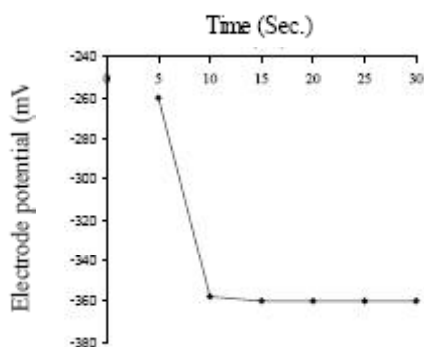**TIV-Ti(IV) iodovanadate**

Figure 1

Figure 2

of PVC. These three membranes were characterized to find out the membrane of good electrochemical performance for the purpose of preparation of an ion-selective membrane electrode. It is clear from TABLE 2 that, as the amount of Ti(IV) iodovanadate increased the thickness, porosity, swelling and water content increased. Generally an ideal membrane should have less thickness, moderate swelling and water content capacity. Membrane S-1 which has minimum amount of Ti(IV) iodovanadate has low order of water content, swelling porosity, thickness and shows wide working concentration range and quick response. So membrane S-1 was selected for the preparation of ion selective electrode for detail studies.

3.1. Working concentration range and slope

The electrode prepared from membrane sample S-

1 shows response for the Pb(II) ions in the concentration range of 1×10^{-7} M to 1×10^{-1} M with an average slope of 30 ± 0.4 mV (figure 1). Thus the working concentration range was found to be 1×10^{-7} M to 1×10^{-1} M for Pb(II) ions. A calibration curve was made by measuring the electrode response to standard solution prepared by serial dilution method without the addition of extra indifferent salts.

3.2. Response time and lifetime of the membrane electrode

The response time of a membrane sensor is an important factor. The average time required for the electrode to reach a potential response was found 10 second as shown in figure 2. The membrane electrode could be used for at least 4 months without any measurable divergence in its response for Pb(II) ions. It is very important that the performance of any ion-selective electrode should be checked every time before using it for any analytical purpose. However the sensor was stored in 0.1 M Pb(II) solution during non-usage. Repeated monitoring of the potential on the same portion of the sample (1×10^{-3}M) gave a standard deviation of ± 1 mV and there was no significant change in the slope.

3.3. Effect of pH on the test solution

In order to determine the useful pH range over which the electrode can be used without any pH interference, the potential of the electrode was determined over a pH range of 1.0-8.0 (Figure 3). pH was adjusted by drop wise addition of a 0.1 M solution of HNO_3 or NaOH and the e.m.f. of the electrode was measured at each pH value. It is clear from the figure that the potential remained constant in the pH range 2-7.2 which can be taken as the working pH range of the proposed sensor. Sharp change in potential values above pH 7.2 and below pH 2.0 may be due to the hydrolysis of Pb^{2+} ions and H^+ ions interference, respectively[1].
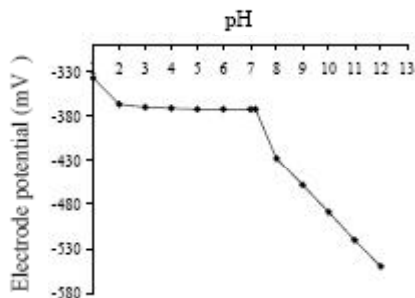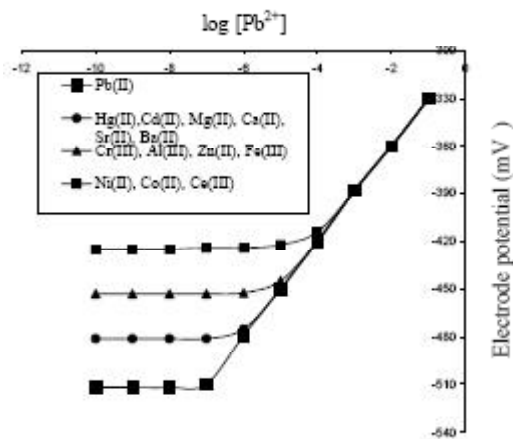
Figure 3

Figure 4

TABLE 3: Selectivity coefficients($K_{Pb,M}^{POT}$) of various interfering ions for Pb²⁺ ion-selective electrode

Interfering ion (M^{n+})	Selectivity coefficients ($K_{Pb,M}^{POT}$)
Hg^{2+}	1×10^{-6}
Cr^{3+}	1×10^{-6}
Fe^{3+}	1×10^{-6}
Ni^{2+}	1×10^{-5}
Co^{2+}	1×10^{-5}
Zn^{2+}	1×10^{-5}
Ce^{3+}	1×10^{-5}
Cd^{2+}	1×10^{-4}
Al^{3+}	1×10^{-4}

3.4. Selectivity coefficients

One of the important characteristics of any ion-selective electrode is its relative response to the primary ions over other ions present in the solution, which is termed as selectivity coefficient $K_{A,B}^{POT}$. These were determined by the mixed solution method as discussed elsewhere[27]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} to 1×10^{-10}M) of the primary ion. Now, the potential measurements were made by using the membrane electrode assembly and the results are summarized in TABLE 3. It is shown from the figure 4 that Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+} and Cd^{2+} ions do not interfere with the determination of Pb^{2+} ions and the interference due to Cr^{3+}, Al^{3+}, Fe^{3+} and Zn^{2+} is negligible. Ce^{3+}, Co^{2+} and Ni^{2+} register slight interference. Thus the results indicating that these interfering cations would not significantly disturb the functioning of Pb^{2+} ion-selective electrode and electrode is selective in the presence of these cations.

A comparison of the present Pb^{2+}-ISEs with those already reported in the literature is given in TABLE 4. From TABLE 4, it is clear that the performance of the proposed Pb(II) ion-selective membrane electrode is comparable and better in many respects, such as the slope, response time, linear concentration range, life time, pH range and selectivity.

4. Analytical applications

4.1. Determination of Pb(II) in rock sample

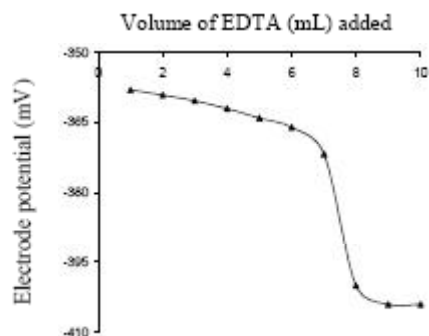In order to test the analytical validity of this approach, the electrode has been used for the determina

TABLE 4: Comparison of figure of merit of the present work with other studies

S. no.	Working concentration range (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Detection Limit (M)	Interference	Reference
1	5×10^{-5} to 1×10^{-2}	28.3	NR	10	2.8×10^{-5}	Zn^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, K^+, Ag^+, Mn^{2+}, Tl^+, Li^+, NH_4^+, Sr^{2+}	15
2	4×10^{-6} to 1×10^{-2}	26-33.1	4.5-7	10	0.4-3.7 µg/L	Ag^+, Cd^{2+}, Ca^{2+}, Hg^{2+}	16
3	1×10^{-5} to 1×10^{-1}	30	4-8	45	$>4 \times 10^{-6}$	Ag^+, Cu^{2+}	20
4	2×10^{-6} to 1×10^{-2}	29.3	3.5-6.3	45	$>1.2 \times 10^{-6}$	NR	21
5	1×10^{-5} to 1×10^{-1}	30	3-9	60	$>1 \times 10^{-5}$	K^+, Hg^{2+}	28
6	1×10^{-5} to 1×10^{-1}	28	3-6	300	$>1 \times 10^{-6}$	K^+	29
7	1×10^{-6} to 8×10^{-3}	29	3-6	40	$>8 \times 10^{-7}$	Hg^{2+}	30
8	1×10^{-7} to 1×10^{-1}	31	2-6.0	25	1×10^{-7}	Cd^{2+}, Al^{3+}	Proposed sensor

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Figure 5

TABLE 5: Determination of Pb(II) in real samples using AAS, spectrophotometer and proposed sensor

Sample	Adjusted pH	AAS ($\mu g \times 10^{-4}$)	Spectro-photometer ($\mu g \times 10^{-4}$)	Proposed sensor ($\mu g \times 10^{-4}$)
Rock sample	5.0	3 ±0.02	2.4±0.05	2.6±0.04
Water sample	5.0	6±0.03	6.3±0.07	5.7±0.06

tion of lead in a standard rock sample (Mica shist (SDC-1), United states geological rock sample) and water sample. Two other techniques namely AAS, Uv-Vis spectrophotometer were also used for this purpose. The results obtained are presented in TABLE 5 and compared with those obtained by using AAS and Uv-Vis spectrophotometer. The sensor is found to be in satisfactory agreement with that obtained from atomic absorption spectrometer (AAS) and Uv-Vis spectrophotometer. These observations and results have been confirmed that present electrode can be used for practical analysis.

4.2. Potentiometric titration

The analytical utility of this membrane electrode has been established by using it as an indicator electrode in the potentiometric titration of Pb^{2+} ions with an EDTA solution as a titrant (figure 5). A 10 ml of 1×10^{-3} solution of Pb^{2+} was titrated against 0.01 M EDTA solution at working pH of this electrode (5.0). The addition of EDTA causes a decrease in potential as a result of the decrease in free Pb^{2+} ion concentration due to the formation of Pb^{2+}- EDTA complex which give the idea of end point and therefore the proposed sensor can be used as an indicator electrode for the potentiometric determination of Pb^{2+} ions.

CONCLUSION

In the present work, Ti(IV) iodovanadate has been used as an electroactive material for the preparation of Pb(II)-selective electrode. The membrane electrode has good operating characteristics such as sensitivity, stability and response time etc. The electrode could be used for Pb(II) determination in the concentration range of 1×10^{-7} M to 110^{-7} M at the functional pH range of 2-7.2. The sensor shows either comparable or better performance to the existing electrode already reported by many researchers for Pb(II) determination regarding response characteristics (TABLE 4). The electrode could successfully be employed as indicator electrode in the potentiometric titration of Pb(II) against EDTA as well as to determine Pb(II) ions quantitatively in a standard rock sample.

ACKNOWLEDGMENT

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