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Use of bismuth tungstate based solid membrane as lead(II)ion-selective electrode

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A new solid membrane electrode prepared using bismuth tungstate ion-exchanger and "Araldite", an inert binder, responds linearly to Pb^{2+} ion in the concentration range $1.0\text{-}1.0 \times 10^{-4} M$. The electrode has a *p*H range 2.0-6.0, static response time 20 s and a usable working life of two months. The selectivity coefficients for various monovalent, bivalent and trivalent cations have been evaluated.

The toxic effects of lead, which is usually present in various industrial products and by-products, on human life are well known. Therefore, lead has often been the subject of environmental monitoring, and a convenient direct method for the determination of lead is highly desirable. A few lead-ion-selective electrodes[1,2] have been developed and used to determine lead in solutions.

In the present note, we describe a new Pb^{2+} ion-selective solid membrane electrode which is based on bismuth tungstate inorganic ion-exchanger and "Araldite" (binder). The performance characteristics of the electrode have been thoroughly investigated.

Experimental

All the reagents used were of A R grade and used as such without further purification. All solutions were prepared in doubly distilled water.

Preparation of bismuth tungstate ion-exchanger

Bismuth tungstate was prepared by the method described by Rawat *et al.*[3]

Preparation of membrane electrodes

Homogeneous membranes of bismuth tungstate could not be prepared as these were too fragile. Heterogeneous membranes of the exchanger prepared in 30% "Araldite" by weight were found to be quite stable and gave satisfactory response. Finely powdered exchanger was thoroughly mixed up with "Araldite" in the ratio 7:3 by weight and then spread and pressed between two pieces of polythene sheets. After 2-3 days, the completely dried membranes were removed from the polythene sheets. Membranes of thickness $\simeq 0.5$ mm having smooth surface and no cracks were selected for the preparation of solid membrane electrodes. The membranes equilibrated in 0.1 *M* $Pb(NO_3)_2$ for 3-4 days were washed well and stuck to one end of a hollow glass tube (diam. $\simeq 1.0$ cm) with "Araldite".

Membrane potential measurements

The following cell was set up for potential measurements:

Saturated calomel electrode (SCE)	Test solution	Bismuth tungstate membrane	0.1 *M* $Pb(NO_3)_2$	Saturated calomel electrode (SCE)

All the potential measurements were made with a *p*H meter (ECIL, Hyderabad, India) at 25±1°C. When not in use, the electrode was placed in 0.1*M* $Pb(NO_3)_2$ solution.

Results and discussion

Potential response

The potentials were recorded by varying the concentration of $Pb(NO_3)_2$ in test solution from 1.0 M to 10^{-6}M. The plot of potential versus-log activity of Pb^{2+} ion is shown in Fig. 1. It is seen that the electrode responds linearly to Pb^{2+} in the range $1.0\text{-}1.0 \times 10^{-4} M$ with a slope of 31.9 mV $decade^{-1}$ of activity. The slope is slightly higher than the expected Nernstian

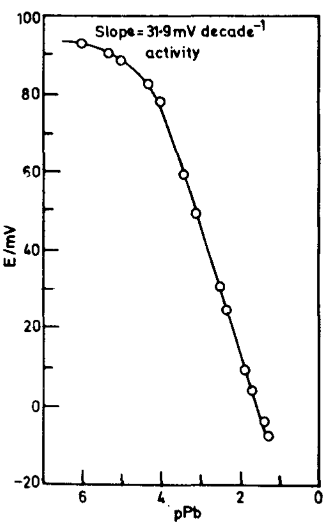

Fig. 1—Potential-response of bismuth tungstate based Pb^{2+}-selective electrode as a function of lead activity

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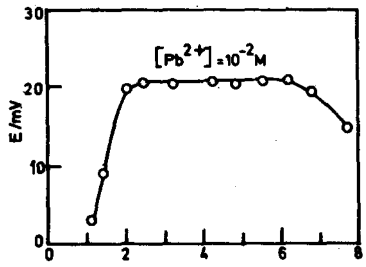

Fig. 2—Effect of pH on potential response of Pb^{2+}-selective electrode

value. It is not unusual to observe higher slopes with solid-state electrodes[4].

Response time and effect of pH

The static response time of the Pb^{2+}-selective electrode was found to vary from $\simeq$20s at higher concentrations ($>10^{-3}M$) to 1 min at lower concentrations ($\simeq 10^{-4}M$). The electrode was usable for about two months without any significant change of slope; however, an overall drift of ± 1 mV in potentials was observed.

The pH dependence of the electrode was investigated in the pH range 0.5 to 6.5 at $10^{-2}M$ concentration of Pb^{2+}. The pH of the solutions was adjusted by the addition of HCl/NaOH at a fixed ionic strength of 0.15 M maintained with $NaNO_3$. The results are depicted in Fig. 2. It is seen that the electrode has a working pH range of 2.0-6.0.

Response to other ions

The performance of the electrode was assessed in presence of various interfering ions by evaluating the selectivity coefficient data using separate solution method[5]. Monovalent, bivalent and trivalent interfering cations cause no significant interference if the selectivity coefficients for these ions are less than 100.0, 1.0 and 0.2, respectively (calculated by using Nikolskii equation for electrode potential). The selectivity coefficients for various monovalent, bivalent and trivalent cations have been summarized in Table 1. It is seen that most of the cations do not cause any significant interference. Only Co^{2+}, Ni^{2+} and Hg^{2+} cause some interference as the selectivity coefficients for these cations are slightly greater than 1.0. Therefore, the electrode is useful for the estimation of lead ions in presence of other cations provided they are present in lower concentrations than that of lead ions. However, the electrode cannot be used in presence of Co^{2+}, Ni^{2+} and Hg^{2+}.

Table 1—Selectivity coefficients ($K^{Pot}_{Pb^{2+},B}$) for Pb^{2+}-selective bismuth tungstate solid-membrane electrode [Interfering ion concentration = $10^{-2}M$]

Interfering ion (B)	($K^{Pot}_{Pb^{2+},B}$)	Interfering ion (B)	($K^{Pot}_{Pb^{2+},B}$)
Li^{+}	3.1	Co^{2+}	1.2
Na^{+}	2.1	Ni^{2+}	1.2
K^{+}	3.3	Mn^{2+}	0.4
Rb^{+}	2.1	Cu^{2+}	0.8
NH_4^{+}	9.7	Cd^{2+}	0.5
Ag^{+}	10.8	Zn^{2+}	0.5
Tl^{+}	11.9	Fe^{3+}	0.3
Mg^{2+}	0.3	Al^{3+}	0.2
Ca^{2+}	0.6	Cr^{3+}	0.1
Sr^{2+}	0.4	Hg^{2+}	1.3
Ba^{2+}	0.3		

The electrode reported in this communication is comparable to the existing electrodes[1,2] with respect to potential response range for lead, response time and pH range. However, the electrode is not very highly selective; nevertheless, it is useful for the direct potentiometric estimation of lead ions in solution.

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