Lead-Selective Poly(vinyl chloride) Membrane Electrode Based on 1-Phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone

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A PVC membrane electrode for lead ion based on 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) as ionophore was demonstrated. The optimum composition of the membrane was 30 wt% poly(vinyl chloride), 60 wt% dibutyl phthalate as a plasticizer, 4 wt% ionophore and 6 wt% sodium tetraphenylborate as additive. The electrode exhibits a Nernstian response (28.7 mV decade^{-1}) for Pb^{2+} over a wide concentration range (1.0×10^{-1} to 1×10^{-6} M) with a detection limit of 6.0×10^{-7} M. This sensor has a short response time and can be used for at least 2 months without any divergence in potentials. The proposed electrode could be used in a pH range of 3.0-6.0 and revealed good selectivities for Pb^{2+} over a wide variety of other metal ions. It was successfully applied as an indicator electrode for the potentiometric titration of lead ion with potassium chromate and for the direct determination of lead in mine.

Key Words : Lead ion-selective electrode, PVC membrane, Potentiometry Pb^{2+} analysis, Neutral ionophore

Introduction

Over recent years, the importance 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. Potentiometric detectors based on ion-selective electrodes are suited, because they offer advantages such as high selectivity, sensitivity, good precision, simplicity and low cost.[1,2] These methods make possible direct monitoring of activities or concentrations of selected species without any sample pre-treatment. During the last two decades, a large number of neutral ionophores with high selectives for specific metal ions have been developed and have found widespread applications in potentiometric and optical sensors for the determination of the respective metal ions in a variety of real samples.[3,4] Because of the increased industrial use of lead and its serious hazardous effect to human health,[5] the electrochemical properties and preparation of the lead ion selective membrane electrodes have been extensively studied by using different ligands as sensing agents in electrodes based on ionophore-doped poly(vinyl chloride) (PVC) membrane.[6-17] We have recently prepared a lead-selective membrane electrode based on cryptand (222) neutral carrier.[18] Also, we have used neutral ionophores, in the construction of PVC-membrane electrodes for Hg^{2+},[19] Ni^{2+},[20] and Ag^{+}.[21] In this work, we report the use of 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) as an excellent neutral carrier in construction of a lead-PVC membrane electrode.

Experimental Section

Reagents and apparatus. Reagent grade dibutyl phthalate (DBP), bis(2-ethylhexyl) phthalate (BEHP), sodium tetraphenylborate (NaTPB), oleic acid (OA), potassium chromate, tetrahydrofuran (THF) and the nitrate salts of all cations (all from Merck) were used as received. Poly(vinyl chloride) (PVC) of high relative molecular weight was purchased from Fluka. All other chemicals were of analytical reagent grade from either Merck or Fluka. pH adjustments were made with dilute nitric acid or sodium hydroxide. All solutions were prepared with doubly distilled deionized water. For preparation of real samples, 1.0 g of lead mineral was dissolved in nitric acid and the resulting solution appropriately diluted.

All emf measurements were carried out with the following cell assembly:

Ag/AgCl/3.0 M KCl/internal solution, 1.0×10^{-2} M $Pb(NO_3)_2$/PVC membrane/test solution/3.0 M KCl/AgCl/Ag

A Metrohm ion analyzer pH/mV meter (model 691) was used for potential measurements at room temperature. The atomic absorption measurements were performed by the aid of a Buck Scientific Spectrometer (model VGP 210).

Synthesis of ionophore. 1-Phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) used as the ionophore was prepared as follows. An amount (0.860 g, 5 mmol) of 4-bromoaniline was dissolved in 15 mL 3.0 M hydrochloric acid in the presence of sodium nitrite. Then, a solution of 1-phenyl-2-quinolidene-2-yl-ethane-1-one (1.235 g, 5 mmol) in absolute ethanol (25 mL) was added and the mixture was stirred magnetically in 15 °C for 30 minutes. The resulting precipitate was filtered and recrystallized from absolute ethanol. After vacuum drying, the pure product of 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) (Fig. 1) was obtained as a yellow solid, yield 89%; m.p = 142 °C; IR (KBr, cm^{-1}): 1595 (s), 1660 (m), 1616 (s); ^{1}H NMR ($CDCl_3$, ppm): 7-8.7 (m, 10H, $C_9H_6N+C_6H_4$), 16.52 (S, 1H, NH); MS, m/z 430.298 (M^{+}); Elemental Analysis, Calculated for $C_{23}H_{16}N_3OBr$: C

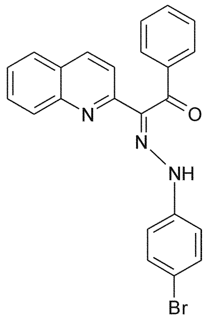

Figure 1. Structure of 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP).

64.20, H 3.74, N 9.76 and Br 18.57%; Found: C 64.35, H 3.61, N 9.60 and Br 18.69%.

Electrode preparation. The general procedure for the preparation of the polymeric membrane was as follows. The amounts of membrane ingredients under optimal compositions (*i.e.* 4 mg ionophore PQDBP, 60 mg plasticizer DBP, 30 mg PVC and 6 mg additive NaTPB) were mixed and dissolved in THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until on oily concentrated mixture was obtained. A pyrex tube (3-5 mm i.d.) was dipped into the mixture for about 10 s so that a nontransparent membrane was formed. The tube was pulled out from the mixture and kept at room temperature for about 1 h. The tube was then filled with internal filling solution (1.0×10^{-2} M lead nitrate). The electrode was finally conditioned for 4 h by soaking in 1.0×10^{-2} M lead nitrate. A silver/silver chloride electrode was used as an internal reference electrode. The ratio of various ingredients, concentration of equilibrating solutions and time of contact were optimized to provide membranes which result in reproducible, stable potentials, with relatively little noise.

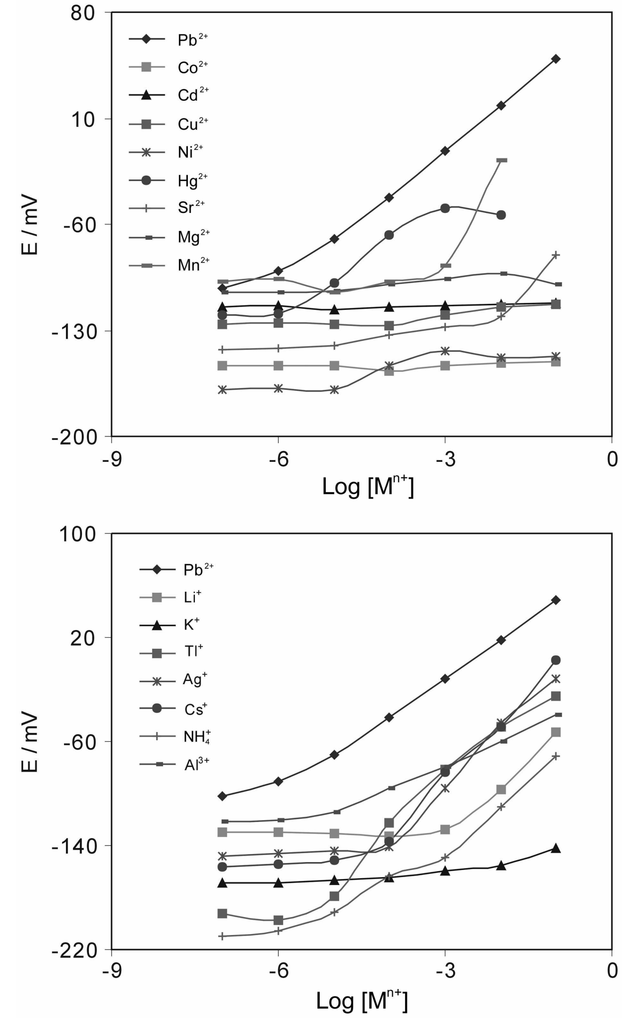

Figure 2. Potential responses of several ion selective electrodes based on PQDBP to various metal ions.

Results and Discussion

Optimization of membrane components. The structure of PQDBP is suitable to form metal chelate complexes. In preliminary experiments, the ionophore PQDBP was used as a neutral carrier to prepare PVC membrane ion-selective electrodes for a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions. It should be noted that the each electrode was conditioned in a 1.0×10^{-2} M solution of the corresponding cation for 12 h. The potential responses of the present ion-selective electrode to various ions are shown in Figure 2. As seen, while the slopes of the linear parts of the emf responses of the electrodes for all other cations are shown much lower than those expected by the Nernst equation, the resulting lead selective electrode exhibits a Nernstian behavior over a wide concentration range. The UV-Vis spectra of PQDBP in the presence and absence of the lead ion in ethanol solution was nicely in support of this fact (Fig. 3). The substantial increase in the absorbance at 400 and 330 nm and also shift of the peak of PQDBP to lower wavelength after the contact of the ionophore solution with a lead-containing phase, improved the specific interaction of Pb^{2+} with the PQDBP. The PQDBP is a compound with N-group donors. Interaction of PQDBP with Pb^{2+} is may be due to the fact that the position of the three nitrogen atoms is matched with size of lead ions. Also, it should be noted that the nitrogen atoms can be participate in complex formation with heavy metal ions.[14] Therefore, we studied in detail the properties of the electrode for lead ion. It is well known that, not only the nature of ionophore, but also the membrane composition and the properties of the plasticizer and additive affect on the sensitivity and selectivity of ISE.[22-25] The performance characteristics of several membranes having ingredients of different proportions are listed in Table 1. It is seen that the membrane number 11 with the PVC : DBP : PQDBP : NaTPB percent ratio of 30 : 60 : 4 : 6 resulted in the Nernstian behavior of the membrane electrode with a slope of 28.7 mV decade^{-1} over a concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. As seen, with no PQDBP (No. 1) the calibration slope of electrode was very small (*ca.* 8.5 mV decade^{-1}). Moreover, the amount of PQDBP was affecting

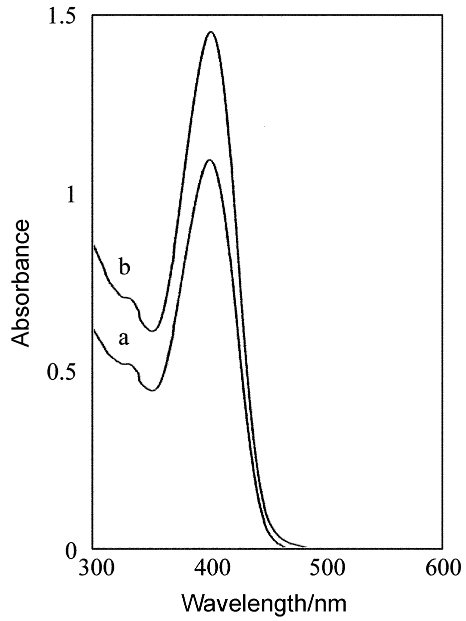

Figure 3. UV-Vis absorption spectra of ethanol solution of 1.0 × 10^{-4} M PQDBP (a) and 1.0 × 10^{-4} PQDBP treated with 1.0 × 10^{-4} $Pb(NO_3)_2$ (b).

the sensitivity of the membrane electrodes. However, 4 wt% PQDBP was chosen as the optimum amount of ionophore in the membrane, since the higher or lower amount of ionophore resulted in reduced slope of the electrode or wide of concentration linear range. Also, among two different plasticizers employed, the use of DBP resulted in the best response characteristics (Compare Nos. 7 and 14, also 11 and 13). It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex.[22] The plasticizer: PVC ratio of about 2 is the most frequently used value in ISE for suitable application (No. 11). The lipophilic anionic sites in the PVC-membrane are used to lower the membrane resistance and improve the response behavior. It is well known that the presence of lipophilic additives in ISEs not only diminishes the ohmic resistance[26,27] and enhances the response behavior and selectivity [28,29] but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes.[30,31] As it seen from Table 1, in the absence of an anionic additive (No. 2), the slope of the PVC membrane is lower than Nernstian response. However, the presence of the lipophilic anionic additive improves response sensitivity.[31] This phenomenon is probably due to interfacial kinetic limitations in the transfer of ions from the sample solution to the membrane phase and vice versa. Lipophilic anionic components can efficiently catalyze this cation transfer.[30] The data given in Table 1 show that, NaTPB is a more effective anionic additive than OA in preparing the Pb^{2+}-ISE (Compare Nos. 7 and 17 also, 11 and 16). Calibration slopes of electrode with different amounts of NaTPB showed that an electrode with membrane containing 6% NaTPB has the closest to Nernstian slope (28.7 mV per decade). Increasing the amount of NaTPB from this optimum caused an increase in the slope (No. 12).

Response and characteristic of electrode. The practical limit of detection, taken as the concentration of Pb^{2+} at the point of intersection of two extrapolated linear segments of the calibration graph, was about 6.0 × 10^{-7} M. The concentration of the internal solution $Pb(NO_3)_2$ in the electrode was changed from 1.0 × 10^{-3} to 1.0 × 10^{-1} M and the potential response of the Pb^{2+} ion-selective was measured. It was

Table 1. Optimization of membrane ingredients

Membrane No.	Composition (%)				Slope (mV decade^{-1})	Linear range (M)
	PQDBP	PVC	Additive	Plasticizer		
1	–	30	6(NaTPB)	64(DBP)	8.5	10^{-6}-10^{-1}
2	4	32	–	64(DBP)	14.4	10^{-5}-10^{-2}
3	9	30	1(NaTPB)	60(DBP)	20.1	10^{-6}-10^{-2}
4	7	30	3(NaTPB)	60(DBP)	22.5	10^{-5}-10^{-1}
5	6	40	4(NaTPB)	50(DBP)	21.0	10^{-4}-10^{-2}
6	6	35	4(NaTPB)	55(DBP)	18.9	10^{-4}-10^{-1}
7	6	30	4(NaTPB)	60(DBP)	17.7	10^{-5}-10^{-2}
8	6	25	4(NaTPB)	65(DBP)	21.5	10^{-4}-10^{-2}
9	6	20	4(NaTPB)	70(DBP)	22.5	10^{-4}-10^{-2}
10	5	30	5(NaTPB)	60(DBP)	20.2	10^{-5}-10^{-1}
11	4	30	6(NaTPB)	60(DBP)	28.7	10^{-6}-10^{-1}
12	3	30	7(NaTPB)	60(DBP)	30.8	10^{-5}-10^{-1}
13	4	30	6(NaTPB)	60(BEHP)	15.1	10^{-6}-10^{-1}
14	6	30	4(NaTPB)	60(BEHP)	14.8	10^{-5}-10^{-2}
15	6	30	4(OA)	60(BEHP)	17.6	10^{-6}-10^{-2}
16	4	30	6(OA)	60(DBP)	25.5	10^{-5}-10^{-1}
17	6	30	4(OA)	60(DBP)	13.5	10^{-5}-10^{-2}
18	4	30	6(OA)	60(BEHP)	10.0	10^{-6}-10^{-2}

found that the variation of the concentration of the internal solution does not cause any significant effect on the corresponding potential response. However, a solution of 1.0 × 10^{-2} M $Pb(NO_3)_2$ was used as internal solution since it had a better slope. The time of contact and concentration of equilibrating solution were optimized so that the electrode generates stable and reproducible potentials at relatively short response times. The optimum equilibration time in a 1.0 × 10^{-2} M $Pb(NO_3)_2$ was 4 h. For analytical applications, the response time of a membrane sensor is an important factor. The average time required for the electrode to reach a potential response within ± 1 mV of the final equilibrium value after successive immersion in a series of Pb^{2+} solutions, each having a tenfold difference in concentrations, was ≈14 s for concentrations 1.0 × 10^{-6} to 1.0 × 10^{-2} M. This is most probably due to the fast exchange kinetics of the complexation-decomplexation of lead ion at the test solution-membrane interface. The standard deviation of fourteen identical potential measurements at 1.0 × 10^{-3} M of Pb^{2+} ion was ± 0.5 mV. This membrane electrode could be used for at least 2 months without any measurable divergence in its response for Pb^{2+} ion. The sensor long lifetime is due to that, the ionophore is well soluble in the membrane matrix and has a sufficient lipophilicity to prevent leaching from the membrane into the sample solution.[22]

The pH dependence of the potentials of the proposed electrode for 1.0 × 10^{-3} M $Pb(NO_3)_2$ was tested in the pH range 2.0-7.0 using HNO_3 or NaOH solution, and the results are illustrated in Figure 4. As can be seen, the potential response remains almost constant over the pH rang 3.0 to 6.0, beyond which the potential changes considerably. The increasing potential at lower pH (< 3), means that the electrode responses to hydrogen ions and the decreasing potential at higher pH values (> 6) could be due to formation of some hydroxy complexes of Pb^{2+} ion in solution.[14] The properties of Pb^{2+}-ISE such as response slope, working concentration range, detection limit, pH dependence, response time and lifetime of the electrode were summarized in Table 2.

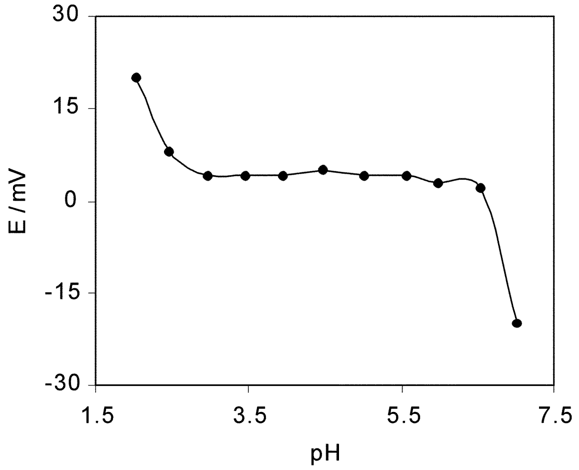

Figure 4. Effect of 1.0 × 10^{-3} M Pb^{2+} solution pH on the potential response of the lead ion selective electrode.

Table 2. Specifications of lead ISE based on PQDBP.

Properties	Values/range
Slope	28.7 mV $decade^{-1}$
Linear range	1.0 × 10^{-6} to 1.0 × 10^{-1} M Pb^{2+}
pH range	3.0-6.0
Detection limit	6.0 × 10^{-7} M Pb^{2+}
Response time	≈14 s (for 1.0 × 10^{-6} to 1.0 × 10^{-2} M Pb^{2+})
Optimized membrane composition	PVC (30%). DBP (60%). PQDBP (4%). NaTPB (6%)
Standard deviation	± 0.5 mV for 1.0 × 10^{-3} M Pb^{2+} (n = 14)
Lifetime of the electrode	At least 2 months

Interference study. The most important characteristic of an ion-selective membrane electrode is its responses for the primary ion in the presence of the other cations present in solution which usually described in terms of selectivity coefficient. The potentiometric selectivity coefficients ($K^{pot}_{Pb,M}$) were evaluated graphically by the mixed solution method[32,33] from potential measurement on solutions containing a fixed amount of Pb^{2+} (1.0 × 10^{-3} M) and varying amounts of the interfering ions (M^{n+}) according to the

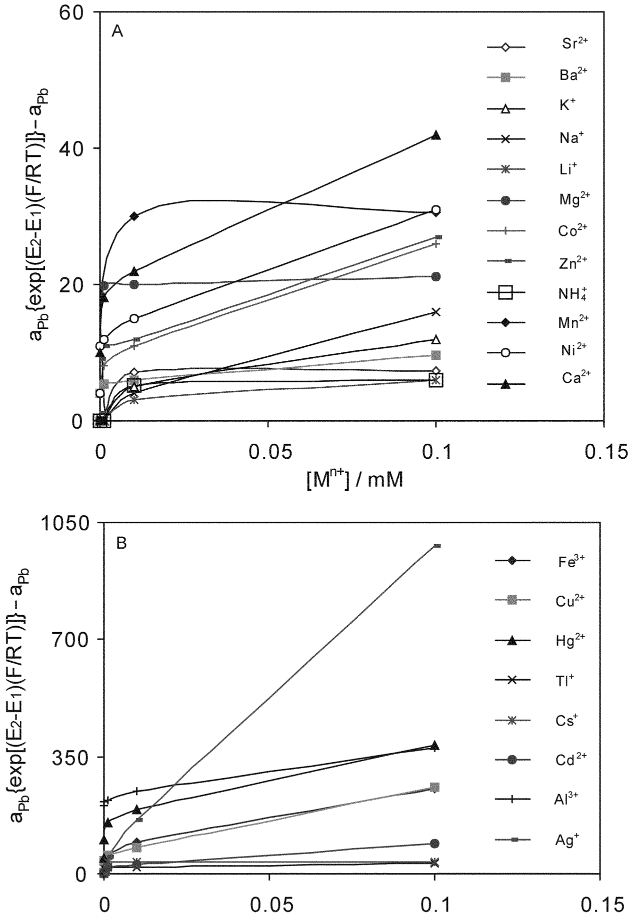

Figure 5. Variation of $a_{Pb}\{exp[(E_2-E_1)(F/RT)]\}-a_{Pb}$ versus $[M^{n+}]$ for the lead ion selective electrode based on PQDBP. In all cases the lead ion concentration was 10^{-3} M.

Table 3. Selectivity coefficient ($K^{Pot}_{Pb,M}$) of various interfering ions for lead ion-selective electrode based on PQDBP

Interfering ion	$K^{Pot}_{Pb,M}$	Interfering ion	$K^{Pot}_{Pb,M}$
Na^+	1.3×10^{-3}	Ca^{2+}	2.7×10^{-3}
K^+	7.1×10^{-4}	Cu^{2+}	2.0×10^{-1}
Ag^+	9.4×10^{-2}	Zn^{2+}	1.7×10^{-3}
Li^+	3.1×10^{-4}	Cd^{2+}	7.0×10^{-3}
Tl^+	1.2×10^{-3}	Hg^{2+}	2.2×10^{-1}
Cs^+	1.2×10^{-4}	Sr^{2+}	2.2×10^{-5}
NH_4^+	1.0×10^{-4}	Mg^{2+}	1.4×10^{-1}
Ni^{2+}	1.9×10^{-3}	Ba^{2+}	4.3×10^{-1}
Mn^{2+}	7.3×10^{-5}	Al^{3+}	7.8×10^{-3}
Co^{2+}	1.8×10^{-3}	Fe^{3+}	1.0×10^{-2}

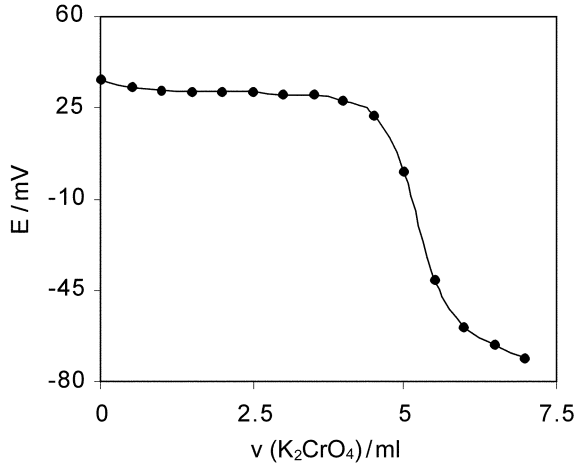

Figure 6. Potentiometric titration curve of 50.0 mL of 1.0×10^{-3} M Pb^{2+} with 1.0×10^{-2} M of potassium chromate.

equation:

$$K^{pot}_{Pb,M} \cdot a_M^{2/n} = a_{Pb}\{\exp(E_2 - E_1)(F/RT)\} - a_{Pb} \qquad (1)$$

where E_1 and E_2 are the electrode potentials for a solution of Pb^{2+} ion alone and for a solution containing interfering ions (M^{n+}) and lead ions, respectively. According to equation (1), the $K^{pot}_{Pb,M}$ values for diverse ions can be evaluated from the slope of linear range of variation of $a_{Pb}\{\exp(E_2 - E_1)(F/RT)\} - a_{Pb}$ versus $a_M^{2/n}$. Figure 5 shows plots of $a_{Pb}\{\exp(E_2 - E_1)(F/RT)\} - a_{Pb}$ versus a_M for different interference ions. It is worth noting that the plots are not linear at the whole range of concentration. Therefore, the linear part of plot has been only used for determination of selectivity coefficient. The resulting values are summarized in Table 3. As can be seen, with the exception of Ag^+, Cu^{2+}, Hg^{2+} and Fe^{3+}, for all diverse ions used, the selectivity coefficients of cations tested are in the order of 7.0×10^{-3} or smaller, which seems to indicate that these metal ions exert negligible disturbances on the functioning of the Pb^{2+} membrane sensor. However, Ag^+, Cu^{2+}, Hg^{2+} and Fe^{3+} with the selectivity coefficients in order of 0.2 or smaller, reveal some reversible interfering effect in the Pb^{2+} selective electrode functioning. The relatively high interfering effect of these ions may originate from the high stability of their complexes with PQDBP. It should be noted that an even more server interference effect from these cations on the functioning of other Pb^{2+} selective electrodes has been reported.[10-12,16,17,20,24,34-36] In Table 4, the detection limit, response time, pH range and major interfering ions (> 7.0×10^{-3}) of the proposed membrane electrode are compared with the corresponding values previously reported for some PVC-membrane Pb^{2+} selective electrodes. As seen, the proposed electrode shows somewhat similar (or worse), in some case, or superior, in most cases, to the previously reported lead membrane electrodes, especially for interference such as Co^{2+}, Mn^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, alkali and alkaline earth metal ions.

Analytical applications. The lead-selective membrane electrode introduced not only be used for direct determination of Pb^{2+} ions, but also it can be useful as an indicator electrode in titration of Pb^{2+} with CrO_4^{2-}. The results of the titration 50.0 mL of 1.0×10^{-3} M solution of Pb^{2+} ion with a 1.0×10^{-2} M potassium chromate solution are shown in Figure 6. The potential of the electrode was decreased upon addition of the chromate precipitation agent. It is clear that the concentration of lead ion in solution can be accurately determined from the resulting neat titration curve providing a sharp end point. The proposed electrode was also successfully applied to the determination of lead in the residue of Kushk lead and zinc mine (Bafgh, Yazd, Iran). An amount of 1.0 g of lead mineral sample was dissolved in 5.0 mL of concentrated nitric acid by heating and the pH of solution

Table 4. Comparison of characteristics of different lead ion-selective electrodes

References	Major interfering ions	Detection limit (μM)	Response time (s)	pH range
[11]	Cu^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Hg^{2+}, Li^+, Na^+, K^+	1.9	–	4.0 – 5.5
[12]	Hg^{2+}, Ag^+, Na^+, K^+	2	20	4.2 – 6.0
[14]	Al^{3+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Mg^{2+}, Ba^{2+}, Zn^{2+}, Ag^+, Na^+	4.0	45	4.0 – 8.0
[15]	Fe^{3+}, Cu^{2+}, Hg^{2+}, NH_4^+, Ag^+, Na^+	0.5	–	5.0 – 10.0
[17]	Hg^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ag^+	1.5	70	2.0 – 7.0
[18]	Al^{3+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Ca^{2+}, Zn^{2+}, Mg^{2+}, Ba^{2+}, Ag^+, Na^+, K^+	5.0	30	2.5 – 7.5
[36]	Hg^{2+}, Cd^{2+}, Tl^+, Ag^+	0.8	40	2.0 – 6.0
This work	Fe^{3+}, Cu^{2+}, Hg^{2+}, Ag^+	0.6	14	3.0 – 6.0

was adjusted to the optimum electrode pH-range (3.0-6.0). The solution was filtered through a filter paper. The filtrated solution was diluted to 100 mL with distilled water in a calibrated flask. The lead content in sample was determined by direct potentiometric (by using the standard addition method). The results obtained from three replicate measurements $(3.38 \pm 0.20) \times 10^{-4}$ M were found to be in satisfactory agreement with that obtained atomic absorption spectrometry. AAS. $(3.56 \pm 0.06) \times 10^{-4}$ M. Thus, it can be concluded that, the membrane electrode may have applications in the environmental monitoring of Pb^{2-} ions.

Conclusions

We have prepared PVC-based membrane electrodes selective to lead ion. containing a neutral ionophore 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone (PQDBP). The membrane selective electrodes prepared under optimal PVC-membrane ingredients. revealed near theoretical sensitivity (28.7 mV decade^{-1}). very fast response (≈14 s). good linear range (1.0×10^{-6}-1.0×10^{-1} M). long lifetime (at least 2 months) and selectivity over a large number of metal ions. Although, some metal ions. such as Ag^+, Hg^{2+}, Cu^{2+} and Fe^{3-} reveal some reversible interfering effect in Pb^{2+} selective electrode functioning. In general the electrochemical properties were comparable to those of the previously recorded for lead ion-selective electrodes.[6.14.16-18] The proposed Pb^{2-}-membrane electrode was applied to the titration of Pb^{2-} solution with potassium chromate as well as the determination of lead in mineral samples.

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