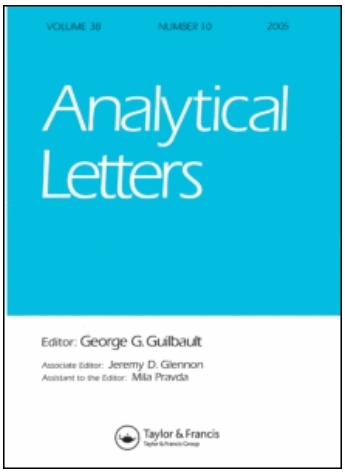

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Barium(II)-PVC Membrane Sensor Based on 4-4'-Methylenediantipyrine as a Neutral Carrier

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SENSORS

Barium(II)-PVC Membrane Sensor Based on 4-4′-Methylenediantipyrine as a Neutral Carrier

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Abstract: A highly selective and sensitive poly(vinyl chloride) membrane electrode, using 4-4′-Methylenediantipyrine as an ionophore, has been prepared and examined as a Ba^{2+}-selective electrode. The influence of the anion excluder (sodium tetraphenyl borate, NaTPB) and the effect of the plasticizers dibutyl phthalate (DBP), nitrobenzene (NB), and benzyl acetate (BA) were studied. The best performance was obtained with the sensor having a membrane composition (w/w) of (MAP, 2.0%), (PVC, 30%), (NB, 66%), (NaTPB, 2.0%) with a wide working concentration range of 1.0×10^{-6} to 1.0×10^{-2} M between the pH values of 3.4 and 10.6. Furthermore, a Nernstian slope of 29.7 ± 0.3 mV/decade of activity was demonstrated with a response time of 15 s. The sensor could be used over a period of 2 months with no potential divergence, revealing a good selectivity for a broad variety of cations including alkali, alkaline earth, heavy and transition metals. Regarding the practical applicability of this sensing device, it was successfully applied for the Ba^{2+} ions detection in a lithophone pigment and as an indicator electrode in the potentiometric titration of the under study cations.

Keywords: 4-4′-methylenediantipyrine, ion-selective electrode, potentiometry, PVC membrane, sensors

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INTRODUCTION

The utility of ion selective electrodes (ISE) is being increasingly appreciated by analytical chemists, in view of the rapid, world-wide growth of industry and technology, because they represent rapid, accurate, and low cost procedures for trace metal analysis. In general, a liquid membrane sensor is a device comprised of a nonpolar solvent supported by a highly porous polymeric layer. The liquid membrane allows only the selective permeation of certain ionic species through itself, due to of the incorporation of special ingredients called "ionophores," or, in other words, "ion carrier." A consequence of this selective permeation is a potential difference formation at the two membrane surfaces, measured by the two reference electrodes at both sides of the membrane (Ganjali et al. 2007).

According to the literature survey, a series of novel membrane sensors based on polyethers (Moody and Thomas 1986; Khmelnitskaya and Kolokolov 1995), organophosphine (Saleh 2000) as neutral carrier, and dimethyl-4,4-dimethoxy-5,6,5,6-dimethylene dioxy biphenyl-2,2-dicarboxylate liver drug (Hassan et al. 2003), and dimethyl 1-acetyl-8-oxo-2,8-dihydro-1H-pyra-zolo[5,1-a]isoindole-2,3-dicarboxylate (Zamani et al. 2006a) as an ionophore in plasticized PVC matrix have been prepared and successfully used for the analysis of the developed sensor. These showed good sensitivity, stability, and significant selectivity for the analysis of the barium(II) ions.

Recently, several selective and sensitive polyvinyl chloride (PVC)-membrane ISEs for various metal ions have been reported (Zamani et al. 2007a; Liu et al. 2006; Zamani et al. 2007b; Luo et al. 2007; Zamani et al. 2006b; Zamani et al. 2006c; Zhang 2007; Zamani et al. 2007c; Zamani et al. 2007d; Zamani et al. 2007e; Zamani et al. 2007f; Behmadi et al. 2007; Zamani et al. 2007g; Pooyamanesh et al. 2007). However, the purpose of this work was the construction of a highly selective and sensitive barium(II)–PVC membrane electrode, based on 4-4′-Methylenediantipyrine (MAP) (Fig. 1) as a suitable carrier, for the potentiometric determination of Ba^{2+} ions.

EXPERIMENTAL

Reagents

The nitrate and chloride salts of all cations, along with the reagent grades of dibutyl phthalate (DBP), benzyl acetate (BA), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC were supplied from the Merck Chemical and the Aldrich Co. The ligand 4-4′-Methylenediantipyrine (MAP) was

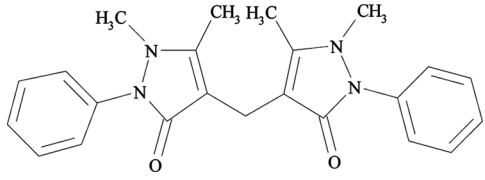

Figure 1. Structure of MAP.

purchased from Fluka. The nitrate and chloride salts of all the used cations were of the highest available purity and used without any further purification, except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout the experimental measurements. All reagents were used without any modification.

Electrode Preparation

First, 30 mg of the powdered PVC and 66 mg of the NB plasticizer were completely blended in 5 mL of THF. Then, 2 mg of NaTPB and 2 mg of the MAP ionophore were added to this mixture. The solution, after being mixed well, was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d.) was dipped into the mixture for about 10 s, in order to attain the transparent membrane formation of about 0.3 mm in thickness (Behmadi et al. 2007; Pooyamanesh et al. 2007; Ganjali et al. 2006a; Ganjali et al. 2003; Shokrollahi et al. 2007; Ganjali et al. 2006b; Zamani et al. 2005a; Zamani et al. 2005b; Zamani et al. 2008a; Zamani et al. 2006d; Abedi et al. 2007; Zamani et al. 2007f; Saleh et al. 2006a; Ganjali et al. 2006c; Ganjali et al. 2007; Saleh et al. 2006b; Ganjali et al. 2005a; Ganjali et al. 2005b; Zamani et al. 2008b). In the end, the tube was removed from the solution, kept at room temperature for 12 h, and filled with an internal filling solution (1.0×10^{-3} M $Ba(NO_3)_2$). The electrode was conditioned for 36 h by soaking in a 1.0×10^{-2} M $Ba(NO_3)_2$ solution. As an internal reference electrode, a silver/silver chloride coated wire was used.

EMF Measurements

The potential measurements were performed by a Corning ion analyzer (250 pH/mV meter) at room temperature with the aid of the cell assembly of:

Ag–AgCl | 1.0×10^{-3} M $Ba(NO_3)_2$ | PVC membrane: test solution | $Hg-Hg_2Cl_2$, KCl (satd).

The activities were calculated in line with the Debye–Huckel procedure (Kamata et al. 1998).

RESULTS AND DISCUSSION

MAP-based Electrode Response Towards the Ba(II) Ions

In preliminary investigations MAP was used as an ionophore in the PVC membrane for a number of alkali, alkaline earth, transition and heavy metal ions, including sodium, potassium, zinc, copper, nickel, cobalt, cadmium, lead, lanthanum, cerium, iron, magnesium, calcium, strontium, and barium. The potential responses of the most sensitive ion-selective MAP based membrane electrodes are listed in Fig. 2 (a,b). As it is evident, among the different tested cations, Ba^{2+} with the most sensitive response seems to be suitably determined with the MAP-based PVC membrane. Therefore, this ionophore was selected as the suitable sensor material for the Ba^{2+}-selective sensor fabrication.

The Membrane Composition Effect on the Potential Response of the Ba(II) MAP-based Sensor

Taking into consideration that the sensitivity and selectivity of a given ionophore depend radically on the membrane ingredients as well as the nature of the solvent mediator and the nature of the used additives (Rosatzin et al. 1993; Zamani et al. 2006e; Zamani et al. 2006f; Zamani et al. 2006g; Ammann et al. 1985), the membrane composition influence on the potential responses of the Ba(II) sensor was assessed. The results are summarized in Table 1. It is noticed that the membrane [No. 4] with the optimized compositions of 2% ionophore and 66% NB in the presence of 30% PVC and 2% NaTPB lead to the best sensitivity with the Nernstian slopes of 29.7 ± 0.3 mV/decade across a very wide dynamic range. As it is obvious from Table 1, the presence of 2% NaTPB offered the electrode nice Nernstian potential responses. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives (like NaTPB) improves the potentiometric behavior of certain selective electrodes. This improvement can be achieved not only by reducing the ohmic resistance and improving the response behavior and selectivity, but also (in cases where the extraction capability of the ionophore is poor) by enhancing the sensitivity of the membrane electrodes (Ammann et al. 1985; Huster et al. 1990; Zamani et al. 2006h; Zamani et al. 2006i; Zamani et al. 2007h; Bakker et al. 1997). Among the three tested solvent mediators, we found that in the construction of the barium membrane

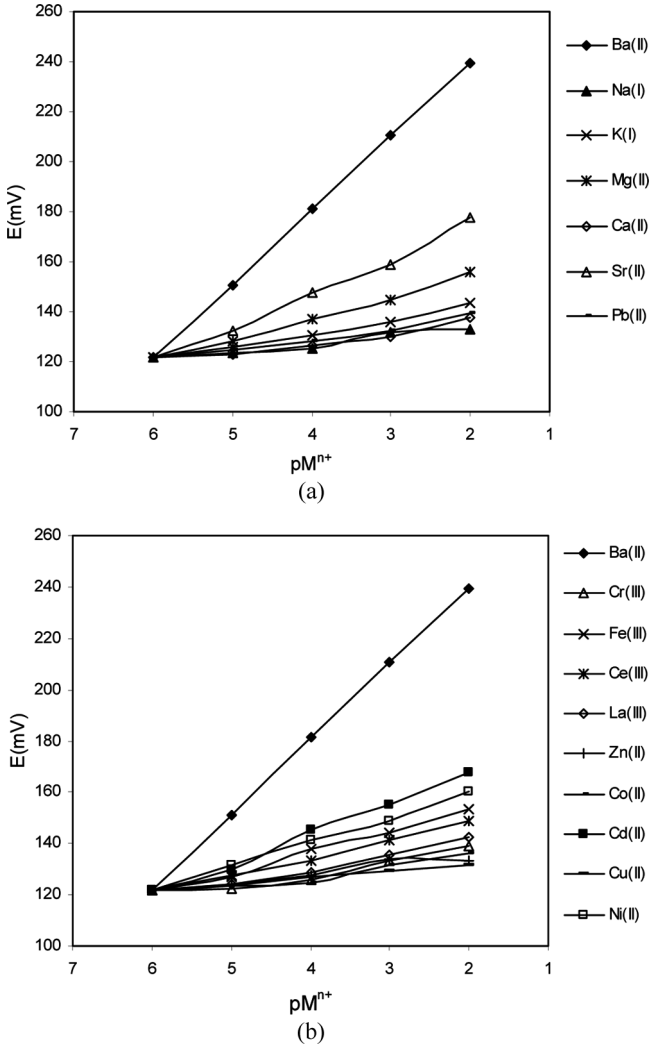

Figure 2. Potential responses of various ion-selective electrodes based on MAP.

sensor, NB, exhibited a superior performance with respect to that of DBP and BA.

Calibration Graph and Lifetime of the Ba(II) Sensor

The optimum equilibrium time for the membrane electrode, in the presence of 1.0×10^{-2} M $Ba(NO_3)_2$, was 12 h, after which it would generate

Table 1. Optimization of the membrane ingredients

Sensor no.	Composition of the membrane (wt,%)				Slope (mV/decade)	Dynamic Linear range (M)
	PVC	Plasticizer	MAP	NaTPB		
1	30	NB, 68	1	1	16.4 ± 0.2	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$
2	30	NB, 67	2	1	23.8 ± 0.4	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
3	30	NB, 66	3	1	22.5 ± 0.6	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
4	30	NB, 66	2	2	29.7 ± 0.3	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
5	30	NB, 65	2	3	27.3 ± 0.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
6	30	BA, 66	2	2	27.5 ± 0.2	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$
7	30	DBP, 66	2	2	26.6 ± 0.7	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$

stable potentials in contact with the barium solutions. The electrode displayed a linear response to the activity of Ba^{2+} ions in the range of 1.0×10^{-6} to 1.0×10^{-2} M (Fig. 3). The slope of the calibration graph was 29.7 ± 0.3 mV per decade. The limit of detection was 5.2×10^{-7} M, as determined from the intersection of the two extrapolated segments of the calibration graph.

The proposed PVC-based membrane sensor could be used for at least 2 months (usage of 1 h daily and, then, washed and dried). After this period, the electrode slope reduced (from 29.7 to 27.8 mV per decade).

pH effect

The pH influence of the test solution (containing 1.0×10^{-3} and 1.0×10^{-2} M of Ba^{2+} ions) on the potential responses of the three membrane sensors was tested in the pH range of 2.0–12.0. The corresponding results are presented in Fig. 4 (a and b). Apparently, the potential remained constant from the pH value of 3.4 to 10.6, beyond which some drifts in the potentials were observed. The observed drift at higher pH values could be attributed to the formation of some Ba^{2+} hydroxyl complexes in the solution. At lower pH values the potentials increased, indicating that the membrane sensor responded to the protonium ions, as a result of the extent protonation of the ionophore nitrogen atoms. The H_3O^+ ions started to contribute to the charge transport process of the membrane, thereby causing interference.

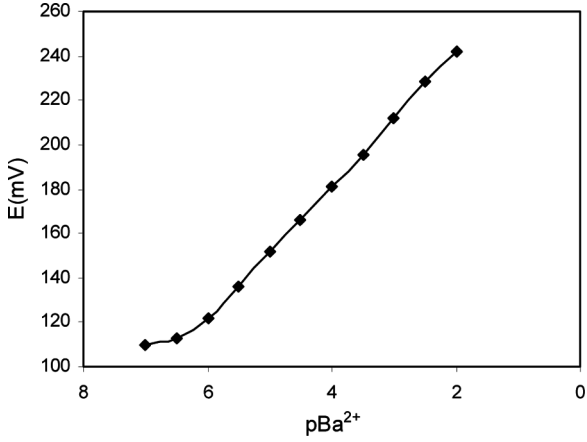

Figure 3. Calibration curve of the barium electrode based on MAP.

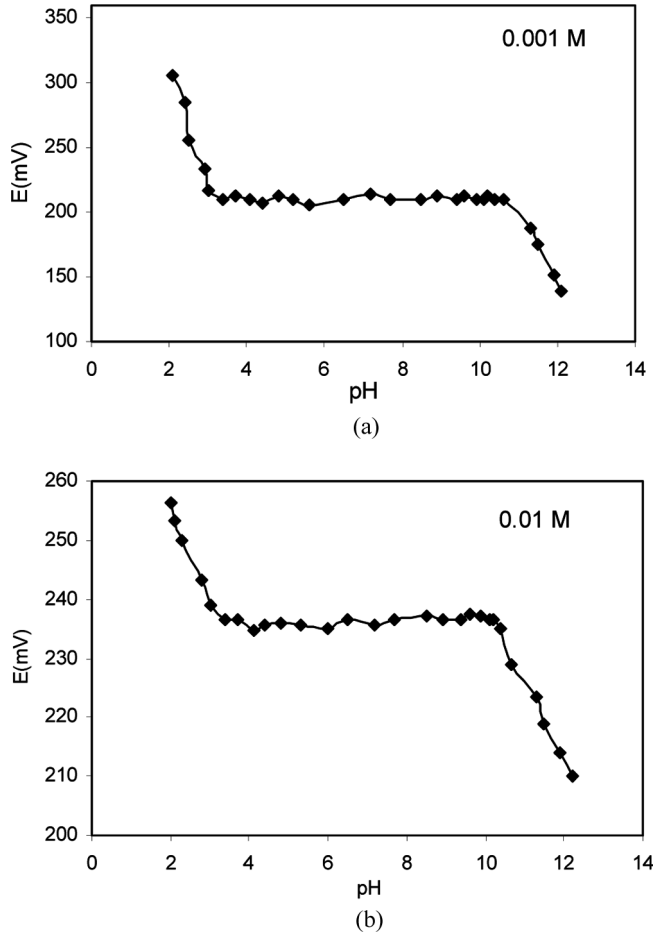

Figure 4. The pH effect of the test solutions (1.0×10^{-2} and 1.0×10^{-3}M) on the potential response of the barium sensor.

Dynamic Response Time

For any ion-selective, response time is one of the most important factors. As response time, we define the average time required for the Ba(II) sensor to reach a potential within ± 1 mV of the final equilibrium value, after successive immersions of a series of Ba(II) ion solutions, each having a 10-fold concentration difference. In this study, this parameter was measured and the related results were plotted against the potential (Fig. 5). As can be observed, the plasticized membrane electrode reaches

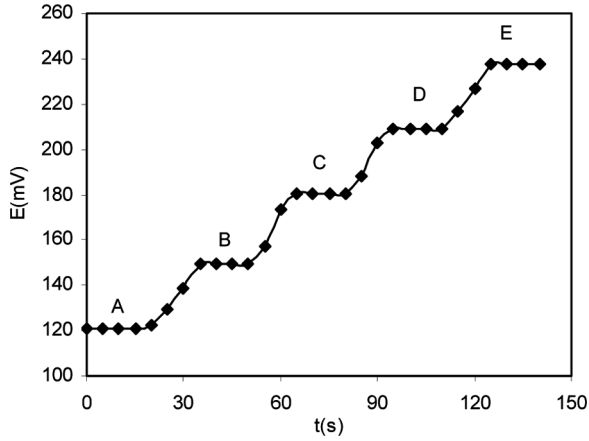

Figure 5. Dynamic response time of the barium electrode for step changes in the Ba^{2+} concentration: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

its equilibrium responses in a very short time ($\sim$15 s) over the entire concentration range.

The Ba(II) Electrode Selectivity

The influence of the interfering ions on the response behavior of any ion-selective sensor is usually described in terms of selectivity coefficients, K_{sel}. In this work the selectivity coefficients were determined with the aid of the matched potential method (MPM) (Umezawa et al. 1985; Zamani et al. 2007i; Zamani et al. 2007j; Abedi et al. 2008). According to this method, the specified activity (concentration) of the primary ions ($A = 1 \times 10^{-5}$ M) is added to a reference solution (5.0×10^{-6} M of $Ba(NO_3)_2$), and the potential is measured. In a separate experiment, the interfering ions ($B = 1 \times 10^{-5}$ to 1.0×0^{-1} M) are successively added to an identical reference solution, until the measured potential matches that obtained before the addition of the primary ions. The MPM selectivity coefficients are then given by the resulting primary ion activity to the interfering ion activity ratio, $K^{MPM} = a_A/a_B$.

A comparison is exhibited in Table 2 between the selectivity coefficients of the developed Ba(II) sensor with those of the best previously reported Ba(II) electrodes (Gupta et al. 1999; Othman et al. 2006; Jaber et al. 1976). As is immediately obvious, the selectivity coefficients of the electrode for all the diverse ions are in the order of 9.2×10^{-3} or smaller, indicating they would not significantly disturb the function of the Ba(II)

Table 2. Comparison of the selectivity coefficients, response time, detection limit, and concentration range of different Ba(II) electrodes

	Gupta et al. 1999	Othman et al. 2006	Jaber et al. 1976	This work
Selectivity coefficients	FIM	SSM	MSM	MPM
Na^{+}	−1.34	−3.27	−1.64	−3.45
K^{+}	−1.20	−2.03	−1.69	−3.14
Pb^{2+}	−1.74	−1.60	–	−3.25
La^{3+}	–	–	–	−3.09
Ce^{3+}	−1.92	−3.72	–	−3.00
Cr^{3+}	−1.92	–	–	−3.30
Fe^{3+}	−1.79	–	–	−2.79
Mg^{2+}	−1.74	−2.72	−3.09	−3.00
Ca^{2+}	−1.12	−2.24	−3.09	−3.32
Sr^{2+}	−1.11	−2.09	−1.19	−2.04
Cu^{2+}	–	−2.45	−3.00	−3.60
Ni^{2+}	–	−3.73	−3.09	−2.33
Co^{2+}	−1.92	−3.92	–	−3.30
Cd^{2+}	−1.51	−4.57	–	−2.27
Zn^{2+}	–	−4.55	–	−3.38
Response time (sec)	15	20	<60	15
Linearity range (M)	1.4×10^{-5} – 1.0×10^{-1}	5.0×10^{-5} – 1.0×10^{-1}	5.0×10^{-5} – 1.0×10^{-1}	1.0×10^{-6} – 1.0×10^{-2}
Limit of detection (M)	–	2.5×10^{-6}	–	5.2×10^{-7}

selective membrane sensor. Furthermore, it is clear that the concentration range, the response time, the detection limit of the recommended electrode, and the selectivity coefficients are superior to those stated by other researchers.

ANALYTICAL APPLICATION

Analysis of Barium(II) in Lithophone Pigment

An accurate weight (0.5 ± 0.01 g) of the lithophone pigment CIS was dissolved in 10 mL of hot concentrated nitric acid (Othman et al. 2006). The solution was then heated for 30 min and filtered. The filtrate and the washing solutions were adjusted to pH 6 and transferred to a 50.0 mL

Table 3. Analysis of barium(II) in lithophone pigment

	Ba(II) Concentration (ppm)	
Sample	Ba-ISE	AAS
1	57.5 ± 0.3	56.2 ± 0.3
2	26.3 ± 0.3	23.4 ± 0.4
3	97.5 ± 0.4	91.2 ± 0.2

calibrated flask and completed to the mark with double distilled water. The potential of the test solution was then measured and the barium(II) content was determined with the aid of the standard curve prepared under the same experimental conditions (Table 3). Alternatively, the standard addition method was also employed for barium(II) determination in lithophone pigment.

Titration with EDTA

The suggested barium cation-selective electrode was found to work well under the laboratory conditions. The selective barium membrane sensor was used as an indicator electrode in the titration of a 1.0×10^{-4} M barium ion solution with a standard solution of 1.0×10^{-2} M EDTA. The resulting titration curve is shown in Fig. 6. According to this figure, the sensor is capable of monitoring the amount of barium ions effectively.

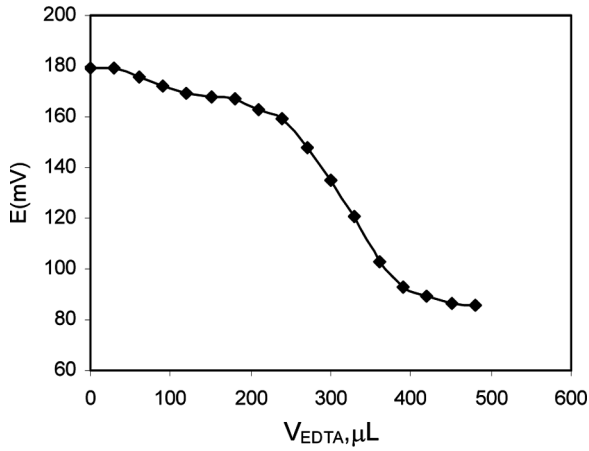

Figure 6. The potentiometric titration curve of 30.0 mL from the 1.0×10^{-4} M Ba^{2+} solution with 1.0×10^{-2} M of EDTA.

CONCLUSION

The PVC-based membrane electrode of the 4-4′-Methylenediantipyrine ligand with the composition 2% ionophore, 2% NaTPB, 30% PVC, and 66% NB exhibited the best performance characteristics. This electrode illustrated a Nernstian response, a detection limit of 5.2×10^{-7} M, and a fast response time of 15 s in the presence of barium with the pH range 3.4–10.6. The fabricated membrane sensor revealed a satisfactory selectivity for Ba(II) cations across a broad variety of metal ions. The sensor was used as indicator electrode in the potentiometric titration of barium with EDTA and could be used for the Ba^{2+} determination in lithophone pigment.

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