

Research Article

Mg(II) Selective PVC Membrane Electrode Based on Methyl Phenyl Semicarbazone as an Ionophore

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A PVC-membrane-based Mg(II) selective electrode was constructed using methyl phenyl semicarbazone (MPS) as a neutral carrier. The sensor exhibits a Nernstian response for Mg(II) ion over a wide concentration range 1.0×10^{-8} to 1.0×10^{-1} M with the slope of 28.4 mV/decade having detection limit 1.7×10^{-9} M. It was relatively a fast response time (< 10 s for concentration $\geq 1.0 \times 10^{-3}$ and < 15 s for concentration of $\geq 1.0 \times 10^{-6}$ M) and can be used for 8 months without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity and high sensitivity for Mg(II) over a mono-, di-, and trivalent cation and can be used in a pH range of 1.0–9.5. It was also successfully used as an indicator electrode in potentiometer titration and in the analysis of concentration of magnesium in various real samples.

1. Introduction

Analytical methods for determining the alkaline earth metal ion have been studied extensively due to their importance in biological process [1, 2]. Polymeric membrane ion-selective electrode (ISE) provides one of the most powerful sensing methods because it is possible to select various sensory elements according to the charge and size of the target ion in clinical and environmental assays [3–10]. The ISEs dynamic response is generated by selective complexation of the target ion by ionophores dispersed in a polyvinyl chloride (PVC) matrix. The quick determination of minute quantities of ionic species by simple method has great importance in analytical chemistry. Potentiometric detection based on ion-selective electrode (ISE) is the simplest method; it has an advantage such as simple design and operation, reasonable selectivity, fast response applicability to colored, and turbid solution. Schiff's base with N and O donor atoms is well known [11, 12] to form strong complexes with alkaline earth metal ion. Some of the Schiff bases were reported which forms strong complexes with a specific ion due to geometric factor. Schiff base complexes have attracted much attention in solvent extraction [13, 14] as ion exchanger [15] as catalyst

[16]. Magnesium is found in dairy products, fish meat, and seafood. Besides this an adult human normally has 20 mg magnesium of which half is found in bones and the other half within cells. It has been observed that the activity of Mg^{2+} in blood serum decreases during liver transplantation due to accumulation of citrate and concomitant chelation of Mg^{2+} . Low Mg^{2+} activities were also found for certain suffering of acute migraine and headaches and in patient with cardiac diseases. The availability of ISEs with sufficient selectivity for Mg^{2+} has recently initiated a number of clinical investigations [17, 18]. Zhang et al. [19] reported magnesium-selective electrodes based on ETH 5504 as well as bis and tris (malondiamides) derivatives [20]. A review by Maj-Zurawaska [21] presented the ion magnesium-selective electrodes and their applications in analytical chemistry. However, most of the developed electrodes suffer from narrow working concentration range and severe interference from calcium. O'Donnell et al. [22] developed electrodes using various octaethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyl octyl ether as solvent mediator. Saleh [23] reported a PVC-based electrode using phenylenebis(ditolyl) phosphine oxide as ionophore.

The electrode gives an excellent discrimination of Ca^{2+} in the concentration range 6×10^{-5} to 1.0×10^{-1} M.

Preliminary studies show that methyl phenyl semicarbazone (MPS) tends to show affinity for magnesium. Taking into consideration all the above facts that methyl phenyl semicarbazone (MPS) has been studied as an electroactive phase in PVC matrix for the fabrication of Mg^{2+} -selective electrode, and the results are presented in this paper. The present electrode shows good selectivity for Mg^{2+} as compared to other cations.

2. Experimental

2.1. Chemicals. Reagent grade high molecular weight PVC, tetrahydrofuran (THF), acetophenone, semicarbazidehydrochloride, (Aldrich, Delhi) were used as received. Tris(2-ethylhexyl) phosphate (TEP), dioctylphthalate (DOP), n-benzylacetate (NBA), Tri-n-butylphthalate (TNBP), nitrobenzene (NB), Dibutylphthalate (DBP), and sodium tetraphenyl borate (NaTPB) and nitrate of all metal used (Merck) were of highest purity available and used without any further purification. Throughout double distilled deionized water was used.

2.2. Physical Measurement. The C, H, and N were analyzed on a carlo-Erba 1106 elemental analysis. Electron impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrophotometer; ^1H NMR spectra were recorded on a Hitachi FT-NMR, Model R-600 spectrophotometer using CDCl_3 as solvent. Chemical shift is given in ppm relative to tetra methylsilane. IR spectra (CsI) were recorded on a Bruker FT-IR spectrophotometer Model no. TEN 50R-27 spectrophotometer.

2.3. Synthesis of Ionophore. In (Figure 1) the hot ethanolic solutions (20 mL) of acetophenone (1.12 mL 0.01 m mol), semicarbazide hydrochloride (1.12 g 0.01 mol), and sodium acetate (0.82 g, 0.01 mol) were mixed with constant stirring [24]. On cooling a yellowish coloured compound has separated out. It was filtered, washed several times with cold EtOH, and dried in vacuum over P_4O_{10} .

2.4. Methylphenylsemicarbazone. Yield (85.0%), M.P: 165°C , Anal calc. for (%) = $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$: C, 61.02; H, 6.21; N, 23.72; Found: (%) : 61.36; H, 6.25; N, 23.86; Mass. (m/z): 176(M^-) FT-IR(CsI): $\nu(\text{NH}_2)$ 3479 (b), $\nu(\text{NH})$ 3148 (b), $\nu(\text{C}=\text{N})$ 1584, $\nu(\text{C}=\text{O})$ 1742; ^1H NMR (CDCl_3 300 MHz): δ ppm = 3.36 (2H, s, $-\text{NH}_2$); 6.48–7.79 (Ar-H); 2.43–2.5 (3H, CH_3).

2.5. Potential Measurements. All the membrane electrode potential measurements were performed at constant temperature ($25 \pm 0.05^\circ\text{C}$) using digital pH meter, potentiometer (ELICO LI-10, India) in conjugation with saturated calomel electrodes as reference electrodes. The representation of electrochemical cell for the EMF measurements is as follows.

3. External Reference Electrode (SCE) | Internal Solution 1.0×10^{-2} M $\text{Mg}(\text{NO}_3)_2$ | PVC Membrane | Test Solution | Internal (SCE) Reference Solution

The membranes were prepared using the basic method given by Craggs et al. [25], with certain variations in composition of PVC, ionophore, and plasticizers/solvent mediators like DBP, NB, DOP, and TNBP. The PVC membrane solution was prepared by mixing of ionophore (5%wt.), TNBP as plasticizer (60%wt.), PVC (30%wt.), and NaTBP (5%wt.) dissolved in THF. The resulting mixture was poured into a petri dish. The THF was allowed to evaporate at room temperature. A flexible membrane with a thickness of 0.2–0.4 mm was obtained. The discs of 6 mm diameter were cut and pasted to a Pyrex glass-tube with the help of Araldite. After getting dried, this tube was filled with 1.0×10^{-2} M internal solution of magnesium and immersed in the 1.0×10^{-2} M magnesium nitrate solution, at least for 2-3 days prior to use. It is known [26] that the sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of the plasticizer used. Thus, the ratio of membrane ingredients, time of contact, and concentration of equilibrating solution were optimized after a good deal of experimentation. Membranes, which generate reproducibility and stable potentials, have been studied. The blank membrane having only PVC as membrane ingredients was also prepared and studied. While membrane having PVC with plasticizer generated small potential with slope of ~ 5 mV/decade.

4. Results and Discussion

4.1. Response of the Cations. The plasticized PVC-based membrane electrode contains (MPS) as the neutral ion-carrier generated stable potential responses in solutions containing magnesium. Therefore, we studied in detail the performance of the membrane electrodes based on this carrier (MPS) for magnesium(II) ion in aqueous solutions. In preliminary experiment, membranes with and without carriers were constructed. The membranes with no carrier displayed insignificant selectivity toward magnesium(II) ion, and its response was not reliable, whereas, in the presence of the proposed carrier, the optimized membranes demonstrated Nernstian response and remarkable selectivity for magnesium(II) ion over a wide variety of metal ions, including alkali (Li^+ , Na^+ , K^+ , Cs^+), alkaline-earth (Ca^{2+} , Ba^{2+}), and transition and heavy metal ions (Co^{2+} , Ni^{2+} , Ag^+ , Hg^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Pb^{2+}). Some of them gave zero potential. The potentiometric response curves obtained for individual ions with ionophore (MPS) under identical conditions are given in Figure 2. Among these ions, except for Mg(II) ion, for all other ions the slope of the corresponding potential versus $\log [\text{Mn}^+]$ plots is much lower than the expected Nernstian slopes of 59.0, 29.5 mV per decade for the univalent and divalent cations, respectively, with very narrow linear ranges of concentration. This is likely due to the high selectivity of the ionophore for magnesium ions

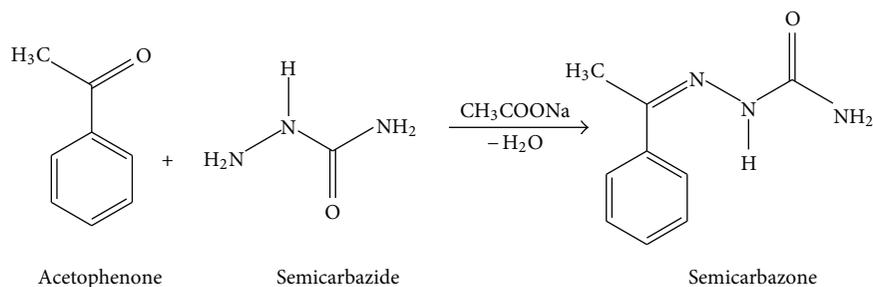


FIGURE 1: Syntheses of ionophore.

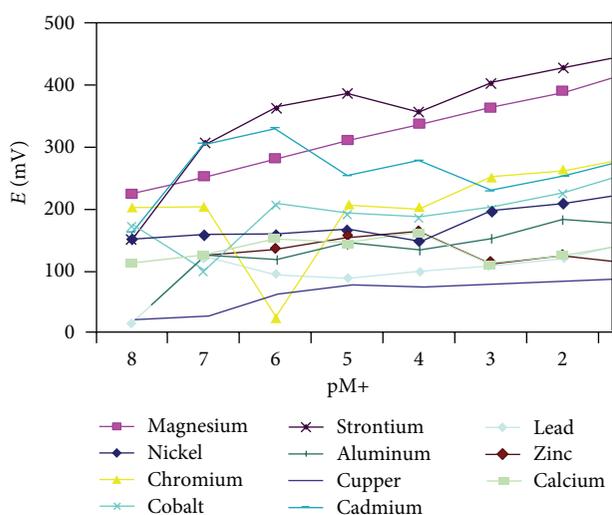
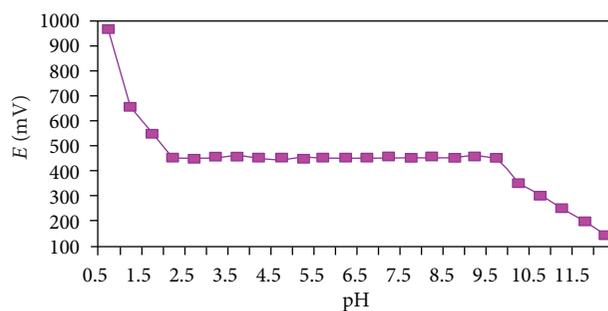


FIGURE 2: Potential response of various ion Selective electrodes based on MPS.

over other ions and rapid exchange kinetics of the resulting Mg(II)-ionophore (MPS) complex. It has been observed that the membrane performs best with Mg^{2+} as the response is linear over a wide concentration (1.0×10^{-8} to 1.0×10^{-1} M). Thus, membranes are used as Mg^{2+} sensor.

4.2. Working Concentration Range and Slope of Mg^{2+} Sensor. Before starting any experimentation, the membranes were equilibrated with 1.0×10^{-2} M Mg^{2+} solution. The experiments have shown that 2 days equilibration time is required for generating reproducible and stable potential. The working concentration range and slope have been evaluated from these plots and summarized in Table 1. It is seen from Figure 2 that the membrane without plasticizer (sensor no. 1) has composition (5 : 30 : 5-MPS : PVC : NaTPB) (w/w%); the concentration range is 1.0×10^{-5} to 1.0×10^{-1} M with a slope of 35.5 mV/decade of activity. Since the nature of plasticizer influences the dielectric constant of the membrane phase, the mobility of the ionophore molecular and state of compound [26], it were expected to play a key role in determining the ion-selective characteristics. So various plasticizers viz. DBP, NB, and TNBP were added in varying amounts to the membranes, and ion-selective characteristics

FIGURE 3: The effect of pH of test solution on the response of the Mg^{2+} ion selective electrode.

were studied. Also, the optimization of permselectivity of the membrane sensor is known to be highly dependent on the incorporation of additional membrane components [26, 27], therefore, NaTPB has also been added to the membranes with aim to improve the performance of the electrode. As shown in Table 1, the addition of NB plasticizer (sensor no. 3) reduces the slope to 22.0 mV/decade of activity, whereas the performance of the membrane with DPB plasticizer (sensor no. 2) is almost the same as that of membrane without plasticizer (sensor no. 1). The best performance is obtained with TNBP plasticizer with membrane (sensor no. 4) having composition 5 : 30 : 5 : 60 (MPS : PVC : NaTPB : NTBP) (w/w; mg). This sensor exhibits linear response to Mg^{2+} for wide working concentration range of 1.0×10^{-8} to 1.0×10^{-1} M and detection limit 1.7×10^{-9} with a near-Nernstian slope of 28.4 mV/decade of activity.

The pH dependence of the electrode potential was tested over the range 1.0–9.5 for Mg^{2+} in this concentration 1.0×10^{-4} shown in Figure 3. The pH of the solutions was adjusted by the addition of dilute hydrochloric acid or sodium hydroxide. It is clear from Figure 3 that the useful pH range is 1.0–9.5, as the potentials remain constant in this range. The sharp change in potentials at higher pH values may be due to the hydrolysis of Mg^{2+} , while at lower pH values H^+ ions start contributing to the charge transport process of the membrane, thereby, causing interference.

The performance of the sensor (no. 4) was also investigated in partially nonaqueous medium using methanol-water, ethanol-water, and acetone-water mixtures. The membrane worked satisfactorily in nonaqueous medium up to

TABLE 1: Composition of PVC membrane of (MPS) and performance characteristics of Mg^{2+} -selective sensors based on them.

Sensor no.	Component in membranes (w/w)						Working Conc range (M)	Slope (\pm mv/decade of activity)
	MPS	PVC	NaTBP	DPB	NB	NTBP		
1	5	30	5				1.0×10^{-5} to 1.0×10^{-1}	35.5
2	5	30	5	60			1.0×10^{-4} to 1.0×10^{-1}	34
3	5	30	5		60		1.0×10^{-5} to 1.0×10^{-1}	22
4	5	30	5			60	1.0×10^{-8} to 1.0×10^{-1}	28.4

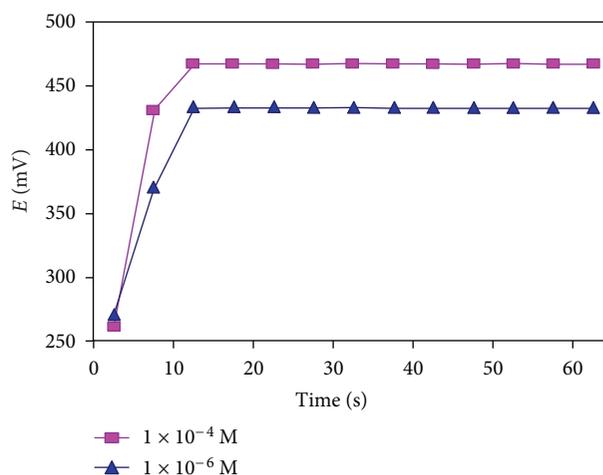
20% (v/v) nonaqueous content as in these mixtures; the working concentration range and slope remained unaffected as shown in Table 2. However, above 20% (v/v) nonaqueous content, slope, and working concentration range was reduced, and potentials show drift. It is worth mentioning that the lifetime of the membranes did not alter in nonaqueous solutions.

4.3. Potentiometric Selectivity. The selectivity is the most important characteristics, as it determines the extent of utility of a sensor in real sample measurement. The selectivity coefficient values were determined by fixed interference method (FIM) [28], which was proposed by Gadzekpo and Christian [29]. The selectivity coefficient values $K_{A,B}^{pot}$ indicate that the electrode is moderately selective to Mg^{2+} over a number of other cations (Table 3). The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, a_B , and varying activity of the primary ion, a_A . The potential values obtained are plotted in contrast to the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of a_A which is to be used to calculate $K_{A,B}^{pot}$ from the equation:

$$K_{A,B}^{pot} = \left(\frac{a_A}{a_B} \right)^{Z_A/Z_B}, \quad (1)$$

where both Z_A and Z_B have the same signs, positive or negative. A value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to primary as well as interfering ion. However, values smaller than 1.0 indicate that membrane sensor is responding more to primary ion than to interfering ions and in such a case the sensor is said to be selective to primary ion over interfering ion. Further, smaller is the selectivity coefficient, higher is the selectivity order. A perusal of Table 3 shows that selectivity coefficient values for the present sensor are much smaller than 1.0 over a number of mono-, di-, and trivalent cations being studied. Hence, the sensor is sufficiently selective over these ions and can therefore be used to estimate magnesium in presence of these ions by direct potentiometry.

4.4. Response and Lifetime. The average time required for the Mg^{2+} ion sensor to reach a potential within ± 1 mV of final equilibrium value after successive immersion of a series of magnesium(II) ion solutions, each having a 10-fold difference in concentration, was measured. The static response time of

FIGURE 4: The effect of the time on potentiometric response of Mg^{2+} electrode.

the membrane sensor thus obtained was < 10 s, for concentration $\geq 1.0 \times 10^{-4}$ and < 15 s for concentration of $\geq 10^{-6}$ (Figure 4). The life time of the proposed Mg^{2+} sensor was evaluated and tested for 40 weeks, while during this period the sensors were used extensively (one hour per weeks). The obtained results are given in Figure 5. As it obvious, the significant changes in the slope of the Mg^{2+} sensor were happen after 36 weeks. Thus, the proposed Mg^{2+} sensor can be used for at least 36 weeks. During this time a slight gradual decrease in the slopes (from 28.4 to 24.3 mV per decade) will be observed. The lifetime of the membrane sensor was about 8 months, during which it could be used without any measurable divergence.

The time of contact and concentration of the equilibrium solution was also optimized so that the sensor generated stable and reproducible potentials at relatively short response time. It was found that an equilibrating solution of 1.0×10^{-2} M and contact time of 2 days were appropriate for smooth functioning of the electrode. Membranes were stored in 1.0×10^{-2} M $Mg(NO_3)_2$ solution when being not used.

4.5. Comparison with Other Reported Electrodes. In Table 4, the response characteristics and the selectivity coefficients of the membrane electrode based on methyl phenyl acetophenonesemicarbazone of some potential interfering ions are compared with the corresponding values previously reported [18, 19, 23, 30–51] for magnesium ion-selective membrane

TABLE 2: Effect of partially nonaqueous medium on the working of Mg^{2+} selective sensors (sensor no. 4).

Non-aqueous content % (v/v)	Working concentration range (m)	Slope (± 0.1 mv/decade of activity)
Methanol		
10	1.0×10^{-8} to 1.0×10^{-1}	28.4
20	1.0×10^{-8} to 1.0×10^{-1}	28.4
30	1.0×10^{-8} to 1.0×10^{-1}	28.2
Ethanol		
10	1.0×10^{-8} to 1.0×10^{-1}	28.4
20	1.0×10^{-8} to 1.0×10^{-1}	28.4
30	1.0×10^{-8} to 1.0×10^{-1}	28.2
Acetone		
10	1.0×10^{-8} to 1.0×10^{-1}	28.4
20	1.0×10^{-8} to 1.0×10^{-1}	28.4
30	1.0×10^{-8} to 1.0×10^{-1}	28.3

TABLE 3: Selectivity coefficient values $K_{A,B}^{pot}$ for Mg^{2+} -selective sensor by fixed interference method.

S. No.	Interfering ion (B)	Selectivity coefficients
1	K^+	6.01×10^{-2}
2	NH_4^+	4.03×10^{-2}
3	Cd^{2+}	6.44×10^{-2}
4	Pb^{2+}	8.03×10^{-2}
5	Cu^{2+}	4.03×10^{-2}
6	Ni^{2+}	8.11×10^{-2}
7	Zn^{2+}	5.12×10^{-2}
8	Co^{2+}	2.01×10^{-2}
9	Ca^{2+}	1.06×10^{-2}
10	Str^{2+}	3.01×10^{-2}
11	Cr^{3+}	1.01×10^{-2}
12	Al^{3+}	6.01×10^{-2}

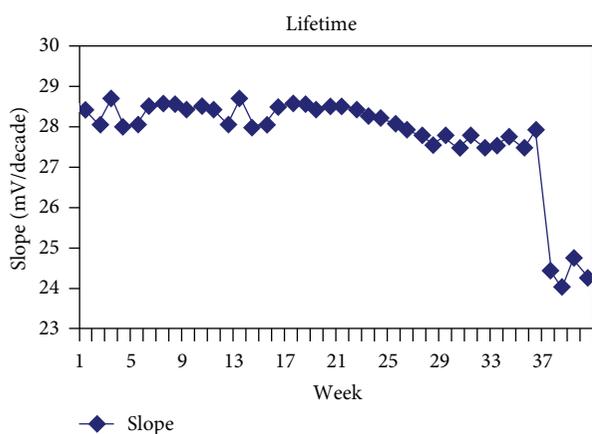
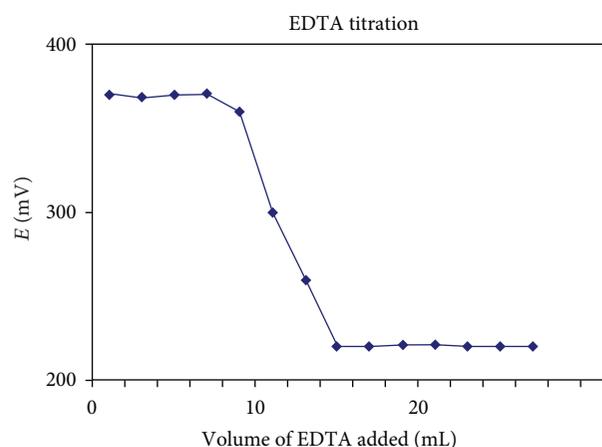


FIGURE 5: Lifetime of the proposed sensor.

electrodes based on a variety of different ionophores. As can be seen, the linear range and the response time of the proposed electrode are superior to those reported for magnesium ion-selective electrodes, and its selectivity behavior is among.

FIGURE 6: Potentiometric titration curve of Mg^{2+} ion (1.0×10^{-3} M, 20.0 mL) with EDTA (1.25×10^{-3} M), using the proposed sensor as an indicator electrode.

5. Analytical Applications

5.1. Potentiometric Titration. The membrane sensor could be successfully used in the potentiometric titration of Mg^{2+} with EDTA. A 20 mL (1.0×10^{-3} M) solution of Mg^{2+} was titrated with 1.25×10^{-3} M EDTA (Figure 6). On the addition of EDTA, the concentration of Mg^{2+} ions decreases, causing a decrease in potential in line. However, the break point is sharp and corresponds to the stoichiometry of Mg(II)-EDTA complex. After the end-point, potentials are almost constant because now the sensor is not responding to small changes in Mg^{2+} concentration. Thus the electrode assembly can be used for magnesium ions determination by potentiometric titration.

6. Conclusion

The plasticized PVC-based membrane incorporating methyl phenyl semicarbazone as an ionophore, TNBP as solvent mediator, and NaTBP as anion excluder in a PVC

TABLE 4: Comparison with other reported electrodes.

S. No.	Detection Limit	pH range	Slope	Liner range	Response (Sec)	life time	Reference
1	1.7×10^{-9}	1.0–9.5	28.4	1.0×10^{-8} to 1.0×10^{-1}	10	8 months	This work
2	—	2.2–9.8	31.1	1.0×10^{-5} to 1.0×10^{-5}	15.5	4 months	[18]
3	—	—	—	—	—	—	[30]
4	1×10^{-5}	—	28.6	—	—	1 week	[19]
5	—	—	30	0.1 to 3.2×10^{-5}	—	1 month	[23]
6	—	3.5–7.8	29.2	9.4×10^{-6} to 1.0×10^{-1}	13	—	[31]
7	—	2.5–6.5	29	1.9×10^{-6} to 1.0×10^{-1}	15	—	[32]

matrix could be used to determine Mg^{2+} in the concentration range 1.0×10^{-8} to 1.0×10^{-1} M. The membrane was prepared using the fixed ratio of 5:30:5:60 (w/w) (ionophore: PVC: NaTBP: NTBP). The detection limit was found to be 1.7×10^{-9} with a slope of 28.4 mV/decade of activity. The sensor works in a wide pH range 1.0 to 9.5 with a response time of 10 s. The selectivity of the electrode towards Mg^{2+} is quite well understood over the other cation. The lifetime of the assembly is 8 months in both aqueous and nonaqueous medium. In addition, the membrane sensor can also be used as an indicator electrode in potentiometric titration involving magnesium(II) ions against EDTA.

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