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Mn^{2+} Selective Electrode Based on 3-(6-Aminopyridin-2-Ylimino)-1, 3-Diphenylpropylidene) Pyridine-2, 6-Diamine

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The ion-selective electrode based on newly synthesized Schiff base 3-(6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6-diamine has been reported. Effect of various plasticizers; 2-nitrophenyloctylether (*o*-NPOE), dibutyl phosphonate (DBP), dioctylphthalate (DOP), tri-(2-ethylhexyl)phosphate (TEHP), chloronapthalin (CN), dibutyl butylphosphonate(DBBP) and anion excluder, Potassium tetrakis (p-chloropheny1)borate (KTpClPB) has been studied. The membrane with a composition of ionophore: KTpClPB : PVC : *o*-NPOE (w/w, mg) in the ratio of 10 : 8 : 120 : 250 exhibited best performance. The sensor exhibits a working concentration range of 1.0×10^{-6} - 1.0×10^{-1} M with a detection limit of 4.0×10^{-7} M and a Nernstian slope of 29.6 ±0.5mV $decade^{-1}$ activity in the pH range 4.0 to 8.0. The response time was as fast as < 15 s. The sensor has been found to work satisfactorily in partially non-aqueous media up to 10 % (v/v) content of methanol, ethanol, acetone or acetonitrile and could be used for a period of 3 months. The selectivity coefficients determined by using match potential method (MPM) and fixed interference method (FIM) indicated high selectivity for Mn^{2+}. The application of prepared sensor has been demonstrated in determination of Mn (II) ions in spiked water samples and in some natural plant and edible species.

Keywords: Ion selective sensor, manganese, Schiff base, poly (vinyl chloride) membranes.

1. INTRODUCTION

Manganese (Mn^{2+}) found as a free element in nature (often in combination with iron), and in many minerals. Due to free existence in nature it has many industrial applications. Manganese is essential to iron and steel production [1, 2] by virtue of its sulfur-fixing, deoxidizing, and alloying properties. Manganese is an alloying agent. Aluminium with a manganese content of roughly 1.5% has an increased resistance against corrosion due to the formation of grains absorbing impurities which would lead to galvanic corrosion [3]. Manganese is an essential trace nutrient in all forms of life [4].

The classes of enzymes that have manganese cofactors are very broad and include oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, lectins, and integrins. The reverse transcriptases of many retroviruses (though not lentiviruses such as HIV) contain manganese. The best known manganese-containing polypeptides may be arginase, the diphtheria toxin, and Mn-containing superoxide dismutase (Mn-SOD) [5].

The human body contains about 10 mg of manganese, which is stored mainly in the liver and kidneys. In the human brain the manganese is bound to manganese metalloproteins most notably glutamine synthetase in astrocytes [6]. Manganese is also important in photosynthetic oxygen evolution in chloroplasts in plants. The oxygen evolving complex (OEC) is a part of Photosystem II contained in the thylakoid membranes of chloroplasts; it is responsible for the terminal photooxidation of water during the light reactions of photosynthesis and has a metalloenzyme core containing four atoms of manganese [7]. For this reason, most broad-spectrum plant fertilizers contain manganese.

Beside lot of application in industry and as a being part of many biological enzymes, It is considered an essential element. But due to prolong exposure of manganese in industrial applications it might be toxic. Although manganese compounds are less toxic than those of other widespread metals such as nickel and copper. However, exposure to manganese dusts and fumes should not exceed the ceiling value of 5 mg/m^3 even for short periods because of its toxicity level.

Manganese poisoning has been linked to impaired motor skills and cognitive disorders. In 2005, a study suggested a possible link between manganese inhalation and central nervous system toxicity in rats [8]. It is hypothesized that long-term exposure to the naturally occurring manganese in shower water puts up to 8.7 million Americans at risk [9, 10].

A form of neurodegeneration similar to Parkinson's disease called "manganism" has been linked to manganese exposure amongst miners and smelters since the early 19th century [11]. Therefore its determination is very important for both industrial and health purposes. Considering these facts many analytical techniques for the determination of Mn are already reported; AAS [12-15], ICP-MS [16, 17], Fluorometry [18], etc.

All these techniques are costly and required pre-sample treatment of analyte and even required vey skilled person as a supervisor to handle the instrument. Beside this the technique; ion-selective electrode (ISEs) is simple, easy to handle and very cheaper to designed. Although a lot of work has been done on ISEs in determination of cations[19-29], anions[30-32] and drug molecules[33-46] still continuous research to improve the ion-selective electrode’s parameters; detection limit, working range, pH range and slope is required to increase the utility of electrode.

The present research describe the use of Schiff base; 3-(6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6-diamine as an ionophore in PVC-based sensor for the determination of Mn^{2+} in different natural samples.

2. EXPERIMENT

2.1. Reagent and material

Dibenzomethane, and 2, 6 diaminopyridine were purchased from Aldrich and used as received. Analytical grade *o*-nitrophenyloctylether (*o*-NPOE), Potassium tetrakis (p-chlorophenyl) borate (KTpClPB), tri-(2-ethylhexyl) phosphate (TEHP) and high molecular weight polyvinyl chloride (PVC) were purchased from Fluka and used as received. Chloronaphthalene (CN) and dioctylpththalate (DOP) were obtained from Hi-media laboratories (Mumbai, MH, India); di-n-butylphthalate (DBP) and dibutyl butylphosphonate (DBBP) were obtained from SD-Fine Chem. Limited (Mumbai, MH, India). Sodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) and tetrahydrofuran (THF) were used as received from Fluka. Manganese dichloride (KFO, Japan Co.Ltd.) was used without further purification. Doubly distilled water was used for the preparation of metal salts solutions of different concentrations by diluting stock solution (0.1 M).

2.2. Synthesis of 3-(6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6 diamine

The ionophore, 3-(6-aminopyridin-2-ylimino)-1,3-diphenylpropylidene)pyridine-2,6-diamine (Figure 1) was synthesized by refluxing 0.025 mol of dibenzoylmethane and 0.05 mol of 2,6 diaminopyridine in ethanol for 12 hour on a water bath and cooling the reaction mixture.

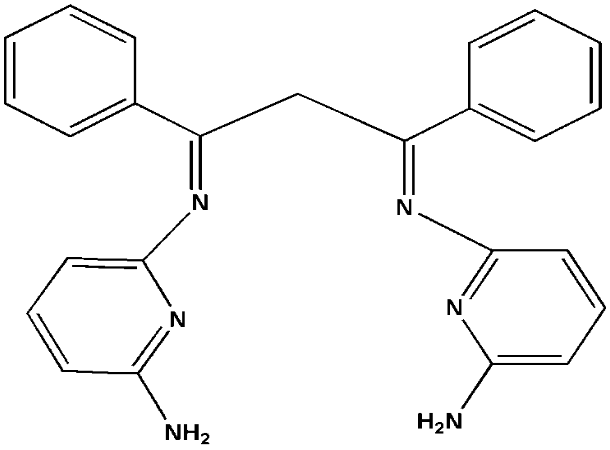

Figure 1 Structural formulae base 3-(6-aminopyridin-2-ylimino)-1, 3-diphenylpropylidene) pyridine-2, 6-diamine

A yellow colour reaction mixture was formed. The ionophore was extracted using n-hexane. The compound re-crystallized in ethanol and used for study. The compound obtained was re-crystallized in n-hexane. The compound was stable at room temperature. Anal. Calc. for [$C_{25}H_{22}N_6$]: C, 73.86, H, 5.45, N, 20.68 %. Found: C, 74.80, H, 5.48, N, 20.68. The ^{1}H-NMR ($CDCl_3$) exhibited signals at: δ(ppm)**:** 6.5 - 7.6 (m, 16H), 5.0 (s, 4H), 2.0 (2H,1s), $\upsilon_{C=N}$: 1640cm^{-1}.

2.3. Development of electrode

Of the various binders used for preparing heterogeneous solid state membranes, PVC has been most widely used due to its relatively cheap cost, good mechanical properties, inertness and amenability to plasticization. The PVC membranes were prepared by mixing of various components (ionophore, anion excluder, plasticizer and PVC) in tetrahydrofuran. Varying amounts of the ionophore and anion excluder were dissolved with an appropriate amount of PVC in 10 mL THF. To these, plasticizers viz. CN, DOP, DBBP, DBP, TEHP or *o*-NPOE were added to get membranes of different compositions. After thorough dissolution, the homogeneous mixture was concentrated by evaporating THF and it was then poured into polyacrylates rings placed on a smooth glass plate. The solution was poured gently so that bubbles could not form. After the evaporation of THF, a transparent membrane of was formed and it was removed carefully from the glass plate and glued to one end of Pyrex glass tube [47-66].

2.4. Equilibration of membranes and potential measurements

The membranes were equilibrated for two days in different concentration range (1.0×10^{-1} to 1.0×10^{-2} M) manganese chloride solution. The potentials were measured by varying the concentration of manganese in test solution in the range of 5.0×10^{-9} to 1.0×10^{-1} M. The best results were obtained when the concentration of inner electrolyte was 0.1 M Mn^{2+} + 1.0×10^{-1} Na_2EDTA M. This may be due to the decreasing zero-current ion fluxes from the membrane into the sample due to presence of Na_2EDTA as reported in literature [67, 68]. The potentials were measured at pH 4.0 with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode. SCE | test solution || PVC membrane || 0.1M Na_2^+ EDTA + 0.1M Mn^{2+}| SCE

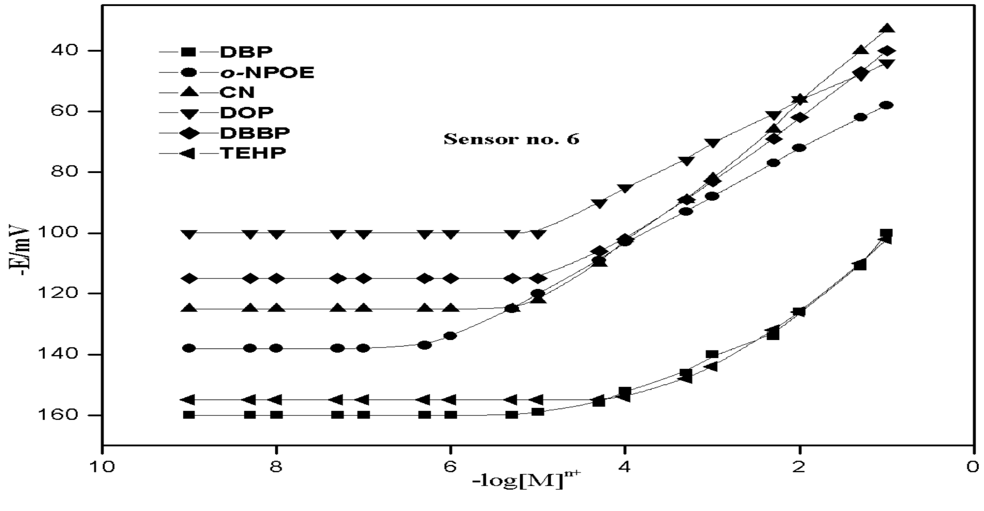

Figure 2 Response of different membrane sensors optimized with different plasticizers; *o*-NPOE, DBP, DOP, DBBP, CN and TEHP.

3. RESULT AND DISCUSSION

3.1. *Optimization of membrane compositions*

The sensitivity and selectivity of ion selective sensors is depended on the nature of ionophore, composition of the membrane and the amount of plasticizer used. Therefore, several membranes were prepared with different compositions. The best response was observed with the membrane prepared of the following ingredients: PVC: *o*-NPOE: ionophore: KTpClPB: 120: 250: 10: 8.

Table 1 Optimization of membrane ingredients for Mn^{2+} selective sensors.

Sensor no.	Composition (w/w, mg)				*Slope (mV decade^{-1} of activity)	Linear Range (M)	Detection Limit (M)	Response Time (S)
	Ionophore	KTpClPB	Plasticizer	PVC				
Mn-1	10	8	CN, 250	120	28.0 ± 0.6	4.5×1.0^{-5} - 1.0×10^{-1}	3.2×10^{-5}	23
Mn-2	10	8	DBBP, 250	120	28.5± 0.5	6.5×1.0^{-4} – 10×10^{-1}	5.7×10^{-5}	16
Mn-3	10	8	TEHP, 250	120	27.8 ± 0.7	7.0×1.0^{-4} – 10×10^{-1}	6.6×10^{-5}	18
Mn-4	10	8	DOP, 250	120	28.2 ± 0.6	4.7×10^{-5} - 1.0×10^{-1}	3.4×10^{-5}	16
Mn-5	10	8	DBP, 250	120	28.5 ± 0.4	1.0×10^{-5} - 1.0×10^{-1}	3.0×10^{-6}	15
Mn-6	10	8	*o*-NPOE, 250	120	29.6 ± 0.5	1.0×10^{-6} - 1.0×10^{-1}	4.0×10^{-7}	15

*Triplicate measurement

The effect of the plasticizes and concentration on the characteristics of the Mn^{2+} ion-selective sensors was investigated by using six plasticizers with different polarities including CN, DBP, DOP, DBBP, TEHP and *o*-NPOE. The electrode containing *o*-NPOE showed better sensitivity and linearity of the calibration plot. It is clear from Table 1 and Fig. 2 that *o*-NPOE as a high polarity compound among the plasticizers investigated provides more appropriate conditions for incorporation of the highly lipophilic manganese ion into the membrane. Therefore, we applied *o*-NPOE as suitable plasticizers for further studies.

3.2. Calibration curve

The potentiometric response of the prepared sensor was evaluated and presented in Table 1 and Fig. 3. The potential response of the sensor no. 6 exhibited a linear concentration range 1.0×10^{-6} - 1.0

× 10^{-1} M of Mn^{2+} ion in the calibration solution. The developed sensor displays a low detection limit. 4.0 × 10^{-7} M and slope 29.6 ±0.5mV $decade^{-1}$ activity.

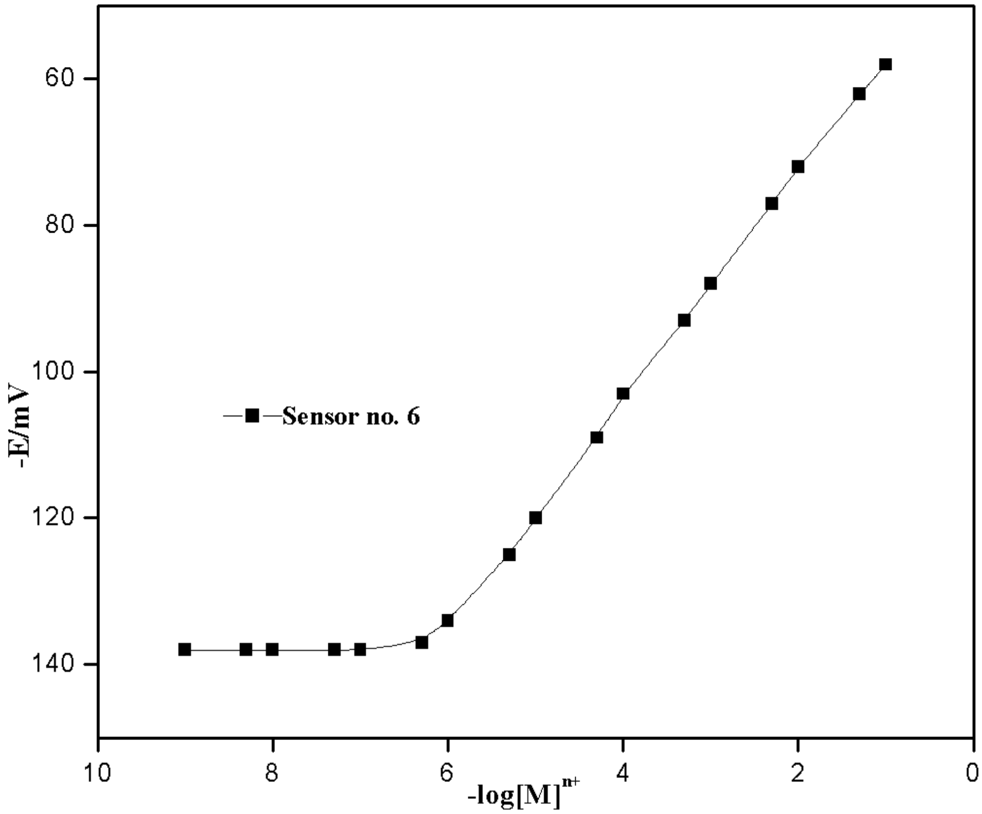

Figure 3 Calibration plot of Mn^{2+}-selective sensor

3.3. Response time and life time of proposed sensor

The time taken by the electrode to attain steady potential is taken as static response time. Response time for all the membranes is given in Table 1. It is seen from the Table 1 that the electrode no. 1 to 5 having membranes with plasticizers (DOP, DBP, TEHP, DBBP & CN) show high response time. The plasticizer *o*-NPOE is improved response time to the maximum extent. The response time of the electrode no. 6 with plasticizer *o*-NPOE is found to be 15s.

Among all the sensors, the life time of the membrane sensors comprising *o*-NPOE was maximum and found to be 3 months for sensor no. 6. It is clear from Table 2 that during this life time no significant drift in potential was noticed.

The electrodes were stored in 0.1 M Mn^{2+} solution when not in use. As the sensor no. 6 gave the best performance in terms of wide activity range, Nernstian slope, low response time and long life time, all further studies were carried out only on this electrode.

3.4. Effect of pH change and non-aqueous solvent

Table 2 Conditioning time of optimized Mn^{2+} ion selective sensor.

Time (days)	*Slope (mV $decade^{-1}$of activity)	Linear Range (M)
1	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
10	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
25	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
40	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
55	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
65	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
75	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
85	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
90	29.6 ±0.5	1.0×10^{-6} - 1.0×10^{-1}
95	28.6 ±0.5	1.0×10^{-4} - 1.0×10^{-1}
100	26.6 ±0.5	5.0×10^{-3} - 1.0×10^{-1}

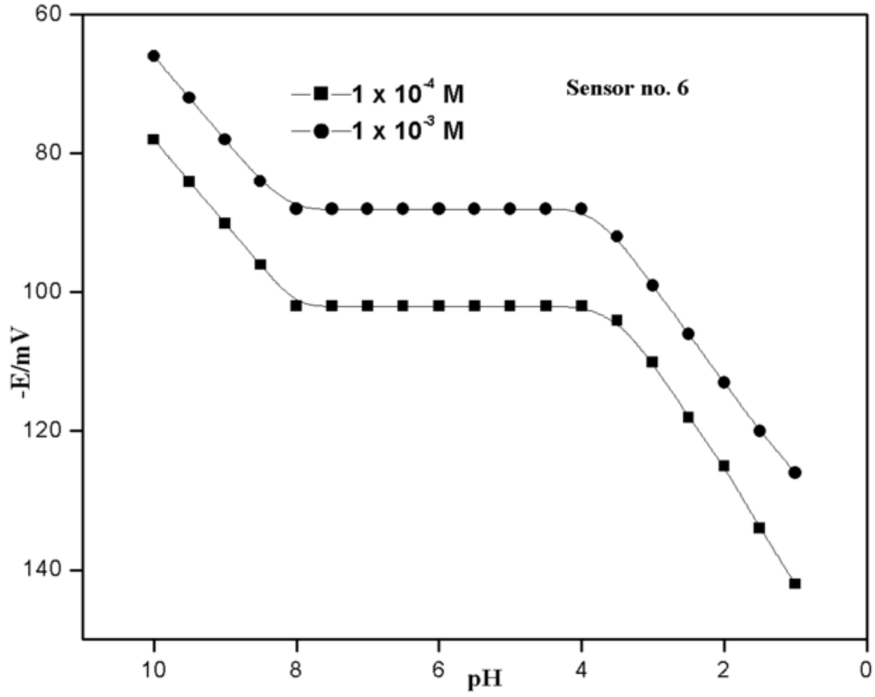

Figure 4 Effect of pH on potential response of manganese ion-selective sensor.

To evaluate the pH effect on sensor performance, the potentials were determined in the pH range 2.0 - 10 for 1.0 $\times 10^{-3}$ M and 1.0×10^{-4} M Mn^{2+} solutions [69-83]. The pH of the solution was adjusted by the addition of hydrochloric acid or sodium hydroxide. The respective results are depicted in Fig. 4, where the potentials remained constant from the pH range 4.0 to 8.0 for sensors no. 6. Beyond this range, a gradual change in potential was observed. Therefore, the pH range 4.0 to 8.0 was taken as the working pH range of the sensor.

The functioning of the sensor no. 6 was further investigated in partially non-aqueous media using methanol-water; ethanol-water and acetonitrile-water mixture and the obtained results are presented in Table 3.

Table 3 Performance of the membrane sensor no. 6 in partially non-aqueous medium.

Non-aqueous content (% v/v)	Working concentration range (M)	*Slope (mV decade^{-1} activity)
0	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
Methanol		
5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
10	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
15	$2.0 \times 10^{-5} - 1.0 \times 10^{-1}$	26.5±0.3
Ethanol		
5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
10	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
15	$4.0 \times 10^{-5} - 1.0 \times 10^{-1}$	26.0±0.8
Acetonitrile		
5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
10	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
15	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	27.5±0.1
Acetone		
5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
10	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	29.6±0.5
15	$4.5 \times 10^{-5} - 1.0 \times 10^{-1}$	28.0±0.2

*Triplicate mesuremnet

It is observed that the values of slope and working concentration range remain constant up to 10 % non-aqueous content. Therefore, the sensor can be satisfactorily used for the determination of Mn^{2+} in mixtures up to 10 % percentage of non-aqueous content.

3.5. Potentiometric selectivity

The most important characteristic of a membrane electrode is its response for the primary ion in the presence of other ions, which is measured in terms of potentiometric selectivity coefficient. The potentiometric selectivity coefficients ($K^{Pot}_{Pm^{3+},B}$) for electrode no. 6, toward different cationic species were evaluated by the fixed interference method (FIM) and match potential method (MPM). According to MPM, when the activity of the primary ion a_A increases to a'_A, the change in potential measured. When the interfering ion of activity a_B is added to the primary ion solution of activity a_A and the same change in potential occurs [84-95]. $K^{pot}_{A,B}$ is then determined from the following equation

$$K^{pot}_{A,B} = \frac{\Delta a_A}{a_B} = \frac{a'_A - a_A}{a_B} \qquad (1)$$

The values of a_A and a'_A for Mn^{2+} were taken as 1.0×10^{-3} M and 5.0×10^{-3} at pH 5.0. In the fixed interference method [96-122], the potential was measured for solutions containing varying concentration of Mn^{2+} and fixed interfering ion activity (1.0×10^{-3} M) and the emf values obtained were plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the value of a_A that is to be used to calculate $K^{Pot}_{Pm^{3+},B}$ from the following equation:

$$K^{pot}_{A,B} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad (2)$$

Where both Z_A and Z_B have the positive charges of both ions. A value of selectivity coefficient equal to 1.0 indicates that the membrane responds equally to primary as well as interfering ion. A value smaller than 1.0 indicates that it responds more to primary ion than interfering ion and in such a case the electrode is said to be selective to primary ion over interfering ion. It is seen from Table 4 that the selectivity coefficients values determined are much smaller than 1.0. Thus, sensor is substantially selective to Mn(II) ions over the all interfering ions studied.

3.6. Analytical application

The analytical application of proposed work was utilized in determination of Mn^{2+} ion in spiked water samples and in natural plant species or food items [123]. The proposed method application was comparatively analysed with AAS method.

Table 4 Selectivity coefficient of various interfering metal ions.

Interfering	Selectivity Coefficients $(-logK^{Pot}_{Mn^{2+}B})$	
ions	*MPM	**FIM
Al^{3+}	4.02	4.20
Ce^{3+}	3.89	3.93
Cr^{3+}	3.78	3.85
Be^{2+}	2.71	2.78
Mg^{2+}	2.67	2.73
Ca^{2+}	2.52	2.60
Ba^{2+}	2.48	2.42
Co^{2+}	2.36	2.40
Fe^{2+}	2.41	2.44
Ni^{2+}	2.80	2.86
Cu^{2+}	2.85	2.89
Zn^{2+}	2.88	2.98
Cd^{2+}	3.15	3.25
Ag^{+}	3.45	3.52
Li^{+}	4.12	4.15
Na^{+}	4.11	4.14
K^{+}	4.22	4.25

*Match Potential Method
**Fixed Interference Method

3.6.1. Mn^{2+} spiked water sample preparation for AAS.

The different natural water samples (River, Pond, Tap water) were collected from city (Roorkee, India). Natural water was preserved with conc. HNO_3 (0.25 ml 1000 ml^{-1}), filtered through a 0.45-µm membrane filter paper (Millipore) and collected in a polyethylene container carefully cleaned with nitric acid. The samples were stored at 4°C until analysis. Analyses were performed with the least possible delay.

3.6.2. Natural plant species sample preparation for AAS

The sample is washed with 0.1mol/1 HCl and then doubly washed with distilled water and dryed at 70 °C. A suitable weight of the sample previously ground (about 4g) is mineralized at 450 °C, the ashes extracted with 2-3 ml of water and 1 mL of cone. HCl and the volume made up to 25 ml with distilled water.

3.6.3. Procedure for AAS

An aliquot of the sample containing between 10 and 120 µg of manganese (II) was transferred into a 100 ml separating funnel. 3.0 ml of 5.0 $\times 10^{-3}$ tool/1 3BrBHA solution, 10 ml of HCO_3/CO_3^{2-} buffer solution pH 10.2 and the necessary amount of NaCl were added to bring the solution to 0.1 mol/1 and distilled water to 20.0 ml. The brownish-red chelate formed was extracted with 10.0 ml of 5.0 x 10^{3-} mol/1 Adogen solution in toluene by shaking vigorously for 10 min. The phases were allowed to separate; the organic phase was centrifuged and the absorbance was measured at 450 or 530 nm against a 5.0 $\times 10^{3-}$ tool/1 toluene solution of Adogen 464.

The standard addition method was followed for different water samples; (River, pond and Tap water) and obtained results were compiled in Table 5 with the proposed method. Similarly the results obtained for natural plant species were compiled in Table 6 with proposed method.

Table 5 Comparative analysis of different natural water samples (River, Pond and Tap water) after spiking different amounts of Mn^{2+}

Sample	Added (mg/L)	*Recovery%		t_{exp}.
		AAS method	Proposed method	
River water	1.5	100.21	99.87	2.21
Pond	2.3	99.98	98.78	2.23
Tap water	2.5	100.11	99.58	2.15

*Triplicate measurement

Table 6 Analytical application of the proposed method for the determination of Mn (II) in natural plant species and comparison with AAS.

Sample	*Amount of Mn^{2+} (µg g^{-1})		RSD% (n,5)
	AAS	Proposed method	
Beans	0.091	0.092	1.10
Butter	0.45	0.46	1.0
Corn flakes	0.52	0.52	0.90
Eggs	1.10	1.13	0.70
Flour	49.41	49.56	0.90
Tomatoes	24.0	24.52	0.95
Potato	0.053	0.054	1.20

*Triplicate measurement

4. CONCLUSION

The studies on membrane of 3-(6-aminopyridin-2-ylimino)-1,3 diphenylpropylidene)pyridine-2,6-diamine has shown that they act as Mn^{2+} selective sensor. The electrode no.6 having membrane composition (mg) of 10 : 8 : 120 : 250 (ionophore : KTpClPB: PVC : *o*-NPOE) was found to be best performance with a Nerstain slope 29.6 ± 0.5mV decade^{-1} activity, low response time 15s and better selectivity for Mn^{2+} ion. The electrode was found to perform satisfactory over the pH range 4.0 to 8.0 and even in the presence of 10 % non aqueous content. The proposed sensors show fairly good discrimination of manganese (II) ions from other cations. The proposed method was applied in determination of natural content of Mn^{2+} in different spiked water samples and plant species or food items

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