

Manganese(II) Ion-Selective Membrane Electrode Based on *N*-(2-picolinamido ethyl)-Picolinamide as Neutral Carrier

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A new poly (vinyl chloride) (PVC) membrane electrode that is highly selective to Mn^{+2} ions was prepared using *N,N'*-bis(2'-pyridinecarboxamide)-1,2-ethane (bpenH₂) as a suitable neutral carrier. This concentration range (1.0×10^{-5} to 1.0×10^{-1} M) with Nernstian slope of 29.3 ± 0.5 mV per decade. The detection limit and the response time of electrode were 8.0×10^{-6} M and (≤ 15 s) respectively. The membrane can be used for more than two months without observing any divergence. The electrodes exhibited excellent selectivity for Mn^{+2} ion over other mono-, di- and trivalent cations. Selectivity coefficients were determined by the matched potential method (MPM). The electrode can be used in the pH range from 4.0 - 9.0. The isothermal coefficient of this electrode amounted to 0.0023 V/°C. The stability constant ($\log K_s$) of the Mn^{+2} - bpenH₂ complex was determined at 25 °C by potentiometric titration in mixed aqueous solution. The proposed electrode was applied to the determination of Mn^{+2} ions in real samples.

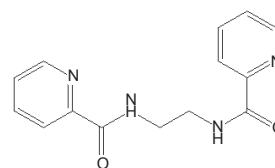
Key Words: Mn^{+2} -selective electrode, PVC membrane *N,N'*-bis(2'-pyridinecarboxamide)-1,2-ethane, Potentiometry

Introduction

The utility of ion sensors is being increasingly realized in view of the rapid growth of industry and technology. Good ion-selective electrodes (ISEs) possess many advantages over the traditional methods of analysis as they provide accurate, reproducible, fast and often selective determination of various ionic species. Not only this, the ion-selective electrodes (ISEs) allow non-destructive, on line monitoring of particular ion in small volume of sample without any pretreatment. ISEs are utilized in many fields, including physiology, process control, and environmental analysis. So, they form one of the most important groups of chemical sensors.¹⁻¹⁰

After extensive efforts some of the commercial sensors are available for alkali, alkaline earth metals, halides, nitrates, etc. Efforts are required to develop ion-selective electrodes for heavy metal ions, which are toxic in very low concentration. The EPA recommends 0.05 mg/L as the maximum allowable manganese concentration in drinking water.¹¹ Consequently, the determination of manganese in environmental resources becomes an important task. Various techniques have been used for the determination of trace manganese in biochemical and environmental resources.¹²⁻¹⁴ Most of techniques have problems such as, high detection limit, narrow working concentration range, high response time, poor selectivity and significant interfering cations.¹⁵ For this purpose, ion selective sensors are the best tools as they permit quick and convenient determination at low cost. In spite of this important requirement, only little work on manganese selective electrodes has been done.^{16,17}

In this paper we have reported a new ISE for determination of Mn^{2+} ion based on *N,N'*-bis(2'-pyridinecarboxamide)-1,2-ethane (bpenH₂) as a suitable ionophore (Scheme 1). It was shown that the new ISE has a relatively wide working concentration range, fast response time and gives reproducible results.



Scheme 1. Structure of ionophore

Experimental

Reagents and materials. All the reagents, with the exception of (bpenH₂) were of analytical reagent grade but the ionophore (bpenH₂) that its preparation had been published previously.^{18,19}

Reagent grade dibutyl phthalate (DBP), acetophenone (AP), *o*-nitrophenyl octyl ether (*o*-NPOE), oleic acid(OA), sodium tetraphenylborate (NaTPB), Potassium tetrakis[*p*-chlorophenyl]borate (KTpCIPB), and tetrahydrofuran (THF) (all from Fluka) were used as received. High relative molecular weight PVC was purchased from Fluka and used as such. Nitrate and chloride salt of all cations were of the highest purity available (all from Merck or Fluka) and used without any further purification. Double distilled deionized water was used throughout. Working solutions of different concentrations were prepared as required by suitable dilution with the same water.

Preparation of the electrodes. The general procedure used to prepare the PVC membrane was mixing thoroughly 28 mg of powdered PVC, 5 mg of ionophore (bpenH₂), 62 mg of plasticizer *o*-NPOE and 5 mg of additive KTpCIPB until the PVC was wet. The mixture was then dissolved in 3 mL of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 10 s so that a non-transparent membrane of about 0.3 mm thickness was

formed. The tube was then pulled out of the mixture and kept at room temperature for about 2 h before filling with internal solution 1.0×10^{-3} M MnCl_2 . The electrode was finally conditioned for 10h by soaking into a 1.0×10^{-2} M MnCl_2 solution.

Emf measurements. All emf measurements were carried out with the following assembly:

Ag-AgCl | KCl (3 M) | internal solution 1×10^{-3} M MnCl_2 | PVC membrane | test solution | Hg-Hg₂Cl₂, KCl (standard).

The potentials were measured by varying the concentration of the test solution in the range of 1.0×10^{-7} to 1.0×10^{-1} M.

Preparation of the sample. A first a 10 mL volume of Minadex tonic syrup (0.38 mg per 5 mL) directly and then a Multiple vitamins with minerals tablet (3.5 mg) which it was dissolved distilled water and transferred into 100-mL volumetric flask after that 10-mL of this solution were applied for determination of Mn^{2+} ions by standard addition method Table 4.

Results and Discussion

Effect of membrane composition. BpenH₂ was used as a carrier to prepare PVC membrane electrodes for a number of metal ions including alkali, alkaline earth and transition metal ions. Characterization of the selectivity of Mn^{2+} sensor over other metal ions is shown in Fig. 1. It is shown that the membrane electrode responds to Mn^{2+} with near Nernstian slope and over a wide concentration range, while other metal ions showed poor response.

The sensitivity and selectivity of an ion selective electrode depends significantly on the membrane composition and the nature of solvent mediator and additives.²⁰ Thus, the influences of the membrane composition, nature and amount of plasticizer and additive and amount of ionophore on the potential response of the Mn^{2+} sensor were investigated and the results are summarized in Table 1. It is shown that, the use of 62% (w/w) *o*-NPOE in the presence of 28% (w/w) PVC, 5% (w/w) ionophore and 5% (w/w) KTpCIPB results in acquiring the best sensitivity, with Nernstian slope of 29.3 ± 0.5 mV/decade over a relatively wide concentration range of Mn^{2+} ions and the characteristics performance of the electrode was the best (No. 10).

Calibration curve and statistical data. The measurements were performed in the concentration range of 1.0×10^{-7} to 1.0×10^{-1} M. The electrode showed linear response in the concentration range from 1.0×10^{-5} to 1.0×10^{-1} M MnCl_2 . The sensor showed nearly Nernstian slope of 29.3 ± 0.5 mV per decade. The detection limit obtained from the intersection of the extrapolated linear regions in the plot, is 8×10^{-6} M; additionally, the standard deviation of 7 replicate measurements was ± 0.5 mV. The membrane electrodes prepared could be used for more than 2 months without any measurable change in potential.

Effect of pH. The pH dependence of the electrode potentials was tested at 1.0×10^{-2} M and 1.0×10^{-3} M Mn^{2+} solutions by varying the pH in the range of 2.0 - 10.0. The potentials remained constant in the pH range 4.0 - 9.0 (Fig. 2) and the same may be taken as the working pH range of the sensor. The sharp changes in potential below pH 4.0 may be ascribed to H^+ co-fluxing and above pH 9.0 due to the hydrolysis of Mn^{2+} ions.

Response time. Dynamic response time is an important factor for an ion-selective electrode.²¹ In this study, the practical response time was recorded by changing solution with different

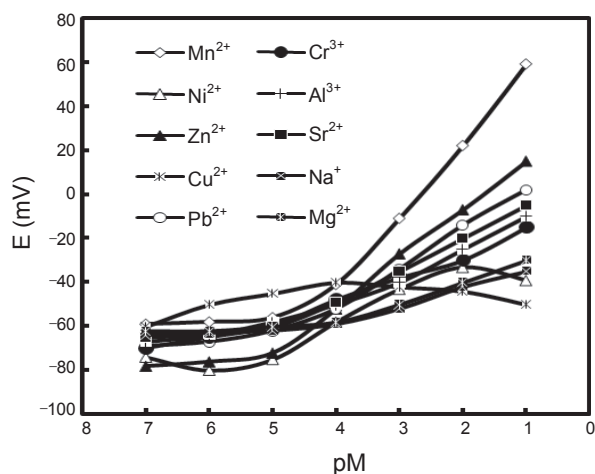


Figure 1. Potential response of various metal ion-selective electrodes based on (bpenH₂) as ionophore.

Table 1. Optimization of the membrane ingredients

No	Composition (%)				Slope (mV/decade)	Linear Range [M]
	PVC (mg)	Ionophore (mg)	Additive (mg)	Plasticizer (mg)		
1	30	5	5 (OA)	60 (AP)	8.1	1.0×10^{-4} - 1.0×10^{-1}
2	30	5	5 (OA)	60 (DBP)	9.1	1.0×10^{-4} - 1.0×10^{-1}
3	30	5	5 (NaTPB)	60 (<i>o</i> -NPOE)	24.8	1.0×10^{-5} - 1.0×10^{-1}
4	30	5	5 KTpCIPB	60 (<i>o</i> -NPOE)	29.1	1.0×10^{-5} - 1.0×10^{-1}
5	30	5	3 KTpCIPB	62 (<i>o</i> -NPOE)	28.1	1.0×10^{-5} - 1.0×10^{-1}
6	30	3	5 KTpCIPB	62 (<i>o</i> -NPOE)	26.8	1.0×10^{-4} - 1.0×10^{-1}
7	30	1	5 KTpCIPB	64 (<i>o</i> -NPOE)	23.1	1.0×10^{-4} - 1.0×10^{-1}
8	30	-	5 KTpCIPB	65 (<i>o</i> -NPOE)	18.5	1.0×10^{-4} - 1.0×10^{-1}
9	30	5	5 (OA)	60 (<i>o</i> -NPOE)	17.2	1.0×10^{-4} - 1.0×10^{-1}
10	28	5	5 KTpCIPB	62 (<i>o</i> -NPOE)	29.3	1.0×10^{-5} - 1.0×10^{-1}
11	30	5	5 KTpCIPB	60 (DBP)	20.5	1.0×10^{-4} - 1.0×10^{-1}
12	30	5	5 KTpCIPB	60 (AP)	19.9	1.0×10^{-4} - 1.0×10^{-1}

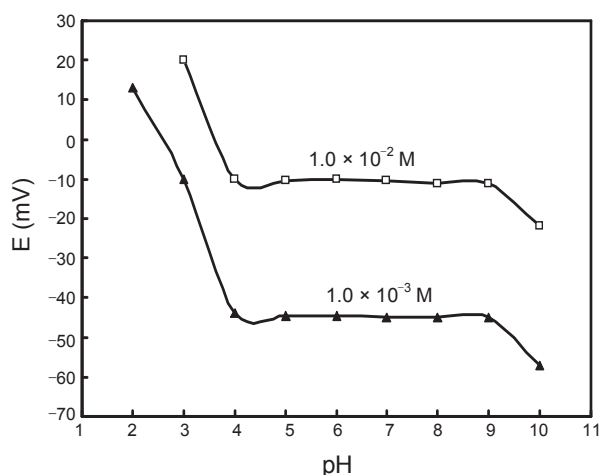


Figure 2. Effect of pH of the test solutions on the potential response of the Mn^{2+} ion-selective electrode.

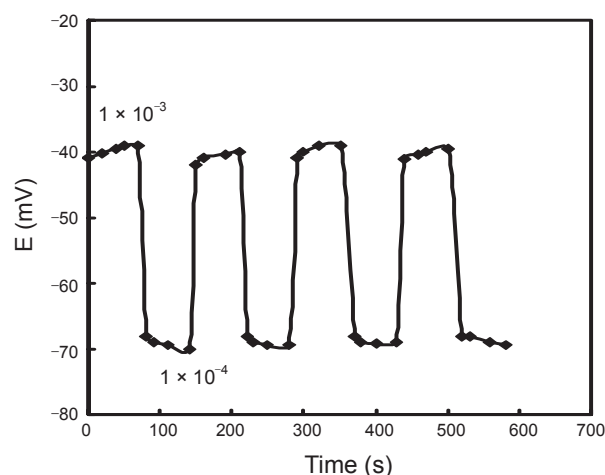


Figure 4. Dynamic response characteristics of the Mn^{2+} -electrode for several high-to-low sample cycles.

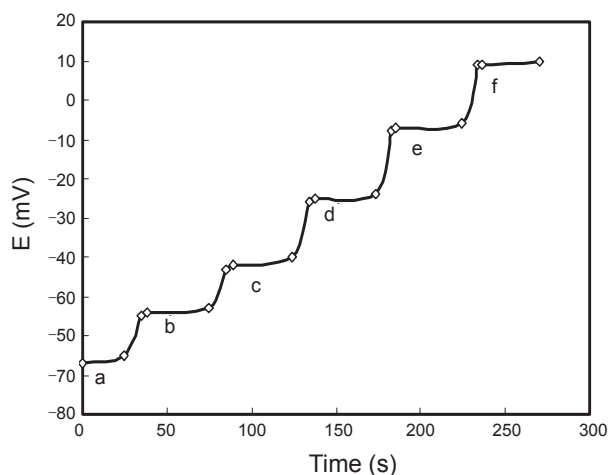


Figure 3. Dynamic response of membrane electrode for step changes in concentration (low to high) of Mn^{2+} . (a) 1.0×10^{-4} M, (b) 5.0×10^{-4} M, (c) 1.0×10^{-3} M, (d) 5.0×10^{-3} M, (e) 1.0×10^{-2} M, (f) 5.0×10^{-2} .

Mn^{2+} concentration from 1.0×10^{-4} to 5.0×10^{-2} M (low-to-high). The actual potential *versus* time traces is shown in Fig. 3. As can be seen, the electrode reaches the equilibrium response in a very short time of about ≤ 15 s. To evaluate the reversibility of the electrode, a similar procedure with opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results are shown in Fig. 4. It is shown that the potentiometric response of the electrode is reversible and had no memory effect.²²

Potentiometric selectivity. The potentiometric selectivity coefficients of the electrode ($K_{\text{Mn}^{2+},\text{M}}^{\text{pot}}$) towards different cationic species were determined by IUPAC recommended matched potential method²³ at a 1.0×10^{-1} concentration of interfering ions. The resulting selectivity coefficients summarized in Table 2 indicates that the sensor is selective for Mn^{2+} ion in presence of interfering ions. As can be seen for most ions used ($K_{\text{Mn}^{2+},\text{M}}^{\text{pot}}$) values were of the order of 10^{-2} or smaller, indicating that they would not significantly disturb the functioning of the Mn^{2+} ion-selective electrodes. However, Zn^{2+} , Cu^{2+} , Ni^{2+} and

Table 2. Selectivity coefficients of various interfering cations

$\text{M}^{\text{n}+}$	$K_{\text{Mn}^{2+},\text{M}}^{\text{pot}}$
Na^+	5.2×10^{-3}
Mg^{2+}	4.7×10^{-3}
Cu^{2+}	1.0×10^{-1}
Cr^{3+}	7.5×10^{-2}
K^+	9.2×10^{-3}
Al^{3+}	1.8×10^{-2}
Ni^{2+}	2.2×10^{-1}
Pb^{2+}	6.8×10^{-2}
Cd^{2+}	1.0×10^{-1}
Zn^{2+}	3.2×10^{-1}
Ca^{2+}	6.3×10^{-3}
Sr^{2+}	8.6×10^{-3}

Table 3. Trend of changes of electrode performance with temperature

Temperature ($^{\circ}\text{C}$)	Slope (mV/decade)	E° (mV)	Linear range (M)
20	28.6	59.8	1.0×10^{-5} - 1.0×10^{-1}
30	30.9	68.3	1.0×10^{-5} - 1.0×10^{-1}
40	34.6	77.2	1.0×10^{-5} - 1.0×10^{-1}
50	36	86.4	1.0×10^{-5} - 1.0×10^{-1}

Cd^{2+} have relatively higher values and may cause interference at higher concentrations.

Effect of temperature. The trend of changes of electrode performance with temperature, at test solution temperatures 20, 30, 40 and 50 $^{\circ}\text{C}$ for the Mn^{2+} electrodes are represented in Table 3. The electrode exhibits good Nernstian behavior in the temperature range (20 - 50 $^{\circ}\text{C}$). The standard cell potentials, (E_{cell}°), were determined at different temperatures from the respective calibration plots as the intercepts of these plots at $\text{pMn}^{2+} = 0$, and were used to determine the isothermal temperature coefficient (dE°/dt) of the cell with the aid of the following equation²⁴:

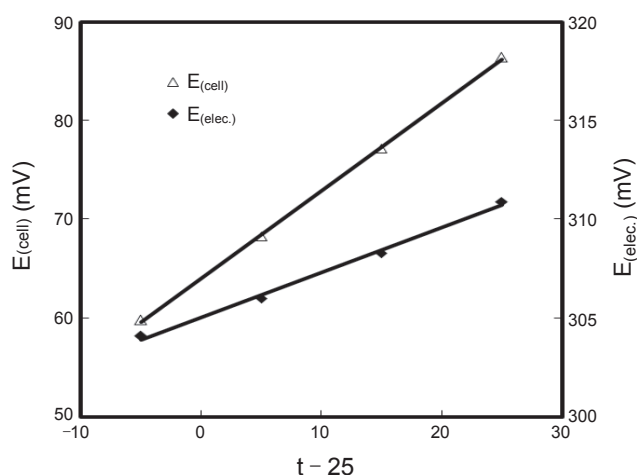


Figure 5. Variation of standard potential of the cell and the electrode with changes of test solution temperatures.

$$E_{\text{cell}}^{\circ} = E_{\text{cell}}^{\circ}(25^{\circ}\text{C}) + (dE^{\circ}/dt)_{\text{cell}}(t - 25) \quad (1)$$

Plot of E_{cell}° versus $(t - 25)$ produced a straight line, as shown in Fig. 5.

The slope of this line was taken as the isothermal temperature coefficient of the cell. It amounts to $0.00089 \text{ V}^{\circ}\text{C}$. The standard potentials to the SCE were calculated using the following equation:

$$E_{\text{Hg}/\text{Hg}_2\text{Cl}_2}^{\circ} = 0.241 - 6.6 \times 10^{-4}(t - 25) \quad (2)$$

The values of the standard potentials of Mn^{+2} -electrode were calculated at the different temperatures from the following relationship:

$$E_{\text{cell}}^{\circ} + E_{\text{ref.}}^{\circ} = E_{\text{elec.}}^{\circ} \quad (3)$$

Plot of $E_{\text{elec.}}^{\circ}$ versus $(t - 25)$ gave a straight line, as shown in Fig. 5. The slope of the line was taken as the isothermal temperature coefficient of the Mn^{+2} -electrode. It amounts to $0.00023 \text{ V}^{\circ}\text{C}$. The small values of $(dE^{\circ}/dt)_{\text{cell}}$ and $(dE^{\circ}/dt)_{\text{elec.}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

Determination of stability constant and thermodynamic parameters. Potentiometric titrations were performed to measure the complexation behavior of (bpenH₂) with Mn^{2+} directly in mixed aqueous solution of water and dioxane. Using the experimental set-up described in,²⁵ a salt solution ($1.0 \times 10^{-3} \text{ M}$) was titrated with a solution containing the ligand ($1.0 \times 10^{-2} \text{ M}$). The activity of uncomplexed cation $[\text{Mn}^{2+}]$ in solution is calculated from the measured potential E according to the following equation:

$$[\text{Mn}^{2+}] = C_{\text{M}} \times 10^{(E - E_i)/D} \quad (4)$$

where E_i is the potential between the Mn^{+2} -electrode and the

reference electrode before titration. The constant D is defined as:

$$D = -\frac{2.303RT}{nF} = -\frac{59.16}{n}(\text{mV}) \quad (5)$$

Since the total concentrations of the cation C_{M} and ligand C_{L} are known, the concentration of the complex, $[\text{MnL}^{2+}]$, can be expressed as:

$$[\text{MnL}^{2+}] = C_{\text{M}} - [\text{Mn}^{2+}] \quad (6)$$

The concentration of free ligand $[\text{L}]$ is:

$$[\text{L}] = C_{\text{L}} - [\text{MnL}^{2+}] \quad (7)$$

As ligand (bpenH₂) is added, the concentration of Mn^{2+} is expected to change due to complex formation. The accompanied potential changes from $C_{\text{L}}/C_{\text{M}}$ ratio were measured and used to calculate the stability constant for 1: 1 complex as 99040.21 (i.e. $\log K_f = 4.996$) at 25°C .

The Isochore-VanHoff equation is used to obtain the thermodynamic parameters such as ΔG° , ΔH° and ΔS° of the complex in water solution.

$$d \ln K_f = -[d(1/T)] \Delta H^{\circ}/R \quad (8)$$

The slope of a graph of $\ln K_f$ vs. $1/T$ gives ΔH° (ΔH° is almost constant over a small range of temperature). ΔG° and ΔS° could be calculated from $-RT \ln K_f = \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ equation. The results obtained are for ΔG° , ΔH° and ΔS° are $-28499.5 \text{ J.mol}^{-1}$, 63494 J.mol^{-1} and $308.7 \text{ J.mol}^{-1}.\text{K}^{-1}$, respectively. More negative value of ΔG° indicates more interaction between cation and ligand.

Analytical application. The proposed electrode was successfully applied to the determination of Mn^{+2} ions in tablet and syrup by standard addition method. An electrode was immersed into a sample of 10 cm^3 with unknown concentration (C_x) and the equilibrium potential of E_1 was recorded. 0.1 cm^3 of $1.0 \times 10^{-2} \text{ M}$ of Mn^{+2} standard was then added into the testing solution and the equilibrium potential of E_2 obtained. From the potential change of ΔE ($E_2 - E_1$) the concentration of the testing sample was determined using the following equation:

$$C_x = \frac{C_s V_s}{(V_x + V_s)10^{-\Delta E/S} - V_x} \quad (9)$$

Where C_x and C_s are the Mn^{+2} concentration of test and the standard samples respectively, V_x and V_s are the corresponding volumes, S is the slope of the electrode response, and ΔE the change in potential.²⁶ In the determination of Mn^{+2} in multiple vitamins with minerals tablet and Minadex tonic syrup, the electrode showed almost identical behavior. The results are given in Table 4.

Table 4. Results of determination of Mn²⁺ in different samples

Sample	Amount of real sample (molL ⁻¹)	Founded by standard addition method (molL ⁻¹)
^a Multiple vitamins with minerals tablet	6.37 × 10 ⁻⁴	6.28 × 10 ⁻⁴
^b Minadex tonic	1.38 × 10 ⁻³	1.43 × 10 ⁻³

^aMade in England. ^bMade in USA.

Conclusion

The membrane sensor incorporating (bpenH₂) as an ionophore can be used to determine Mn⁺² in the wide working concentration range. The main advantages of this sensor are its simplicity of preparation, short conditioning time, wide dynamic range, Nernstian behavior, low detection limit, good selectivity and reasonable long-term stability and low cost. The sensor shows a wide pH range, an adequate shelf life, a fast response time and good stability constant of complexion Mn⁺² with (bpenH₂). The selectivity of the electrode towards Mn⁺² is quite good over other cations. The proposed sensor was successfully applied to direct determination of Mn⁺² in real samples.

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References

1. Srivastva, S. K.; Gupta, V. K.; Jain, S. *Analyst* **1995**, *120*, 495.
2. Mahajan, R. K.; Kumar, M.; Sharma, V.; Kaur, I. *Analyst* **2001**, *126*, 505.
3. Mahajan, R. K.; Parkash, O. *Talanta* **2000**, *52*, 691.
4. Buhlmann, P.; Pretsch, E.; Bakker, E. *Chem.Rev.* **1998**, *98*, 1593.
5. Aghaie, H.; Giahhi, M.; Monajjemi, M.; Arvand, M.; Nafissi, G. H.; Aghaie, M. *Sens. Actuators B* **2005**, *107*, 756.
6. Giahhi, M.; Pournaghdy, M.; Rakhshae, R. *J. Anal. Chem.* **2009**, *64*, 188.
7. Assubaie, F. N.; Moody, G. J.; Thomas, G. J. *Analyst* **1989**, *114*, 1545.
8. Liu, Y.; Zhao, B. T.; Chen, L. X.; He, X. W. *Microchemical J.* **2000**, *65*, 75.
9. Giahhi, M.; Arvand, M.; Mirzaei, M.; Bagherinia, M. A. *Anal. Lett.* **2009**, *42*, 870.
10. Mahajan, R. K.; Kumar, M.; Sharma, V.; Kaur, I. *Talanta* **2002**, *58*, 545.
11. US EPA (US Environmental Protection Agency). Integrated Risk Information System (IRIS) on Manganese, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH, 1993.
12. Maniasso, N.; Zagatto, E. A. G. *Anal. Chim. Acta* **1998**, *366*, 87.
13. Lal, U. S.; Chattopadhyaya, M. C.; Ghosh, K.; Dey, A. K. *Indian Agriculturist (Spec. vol.)* **1982**, 139.
14. Su, Y. *Fenxi Huaxue* **1983**, *11*, 905.
15. Midgley, D.; Mulcahy, D. E. *Talanta* **1985**, *32*, 7.
16. Agarwala, V.; Chattopadhyaya, M. C. *Anal. Lett.* **1989**, *22*, 1451.
17. Singh, A. K.; Saxena, P.; Panwar, A. *Sens. Actuators B* **2005**, *110*, 377.
18. Barnes, D. J.; Chapman, R. L.; Vagg, R. S.; Watton, E. C. *J. of Chemical & Engineering Data* **1978**, *23*, 349.
19. Barnes, D. J.; Chapman, R. L.; Stephens, F. S.; Vagg, R. S. *Inorganic Chimica Acta* **1981**, *51*, 155.
20. Tavakkoli, N.; Shamsipur, M. *Anal. Lett.* **1996**, *29*, 2269.
21. Matysik, S.; Matysik, F. M.; Mattusch, J.; Einicke, W. D. *Electroanalysis* **1998**, *10*, 98.
22. Bakker, E.; Pretsch, E.; Buhlmann, P. *Anal. Chem.* **2000**, *72*, 1127.
23. Bakker, E. *Electroanalysis* **1997**, *9*, 7.
24. Antropov, L. I. *Theoretical Electrochemistry*; Mir Publishers: Moscow, 1972; pp 180-183.
25. Gutknecht, J.; Schneider, H. *J. Stroka. Inorg. Chem.* **1978**, *17*, 3326.
26. Buck, R. P.; Lindner, E. *Pure Appl. Chem.* **1994**, *66*, 2527.