



Anal. Bioanal. Chem. Res., Vol. 5, No. 2, 273-284, December 2018.

Determination of Mn^{2+} in Pharmaceutical Supplements by a Novel Coated Graphite Electrode Based on Zolpidem as a Neutral Ion Carrier

Mohammad Reza Jalali Sarvestani^{a,*} and Roya Ahmadi^b

^aYoung Researchers and Elite Club, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran

^bDepartment of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahr-e-rey Branch, Islamic Azad University, Tehran, Iran

(Received 24 February 2018, Accepted 12 May 2018)

Manganese plays a key role in the health of human beings, therefore, its determination is very important in medical fields. In this regard, for the first time, a novel coated graphite electrode was constructed for determination of manganese(II) by using zolpidem as an ionophore. The best performance was obtained for the membrane composition of PVC (32%), potassium tetrakis (4-chlorophenyl) borate (3%) as ionic additive, zolpidem (10%) as ionophore and dioctyl phthalate (55%) as plasticizer. The linear working range of the potentiometric sensor was from 1×10^{-7} - 1×10^{-2} M. The electrode shows an exquisite Nernstian slope value of 29.7 mV Decade⁻¹ and its limit of detection was 9×10^{-8} M. The potential response of the membrane sensor was also evaluated in non aqueous mediums, and it was found out that the electrode can also be used in systems containing 15% of ethanol and acetone organic solvents. The selectivity was also inspected through matching potential method for 20 different cations, and the electrode demonstrated a significant selectivity toward Mn^{2+} for all of the studied cations. In the end, the applicability of the electrode in the determination of Mn^{2+} in dietary supplements, as real samples, was investigated.

Keywords: Manganese, Zolpidem, Ion selective electrode, Potentiometry, Quality control of supplements

INTRODUCTION

Manganese is a chemical element with 25 atomic number, represented by Mn symbol. Manganese is a silvery-gray metal that is extremely hard and brittle. Mn is the 12th most abundant element in the earth's crust and forms 0.1 percent of it [1-3]. The human body is comprised of an average of 12 mg manganese, most of that accumulated in bones, liver and kidneys. Mn is a very strong antioxidant and it plays an important role in food digestion, bone growth, proper function of immune system and cellular energy supply, and this matter clarifies why this metal is an essential nutrient for human beings. Manganese deficiency can lead to the decreased density of bones and osteoporosis, delayed growth of children,

infertility, glucose intolerance, impaired lipid and carbohydrate metabolism, abnormal growth of bones (*Legg-Calvé-Perthes*) and high cholesterol [4-6]. In recent decades, the problem of counterfeit medicines has become a cosmopolitan concern and dilemma. The forged pharmaceutical products bear a lot of resemblance to the original ones apparently, but their quality is extremely low. In this regard, qualification control of drugs and supplements has been very controversial in the recent years [7]. Owing to the medicinal effects of manganese and its role as a micronutrient in the body, this mineral substance is one of the most widely used ingredients in therapeutic supplements and its determination is very important in diagnosis and treatment procedure of patients in the medical field and also pharmaceutical industry [8].

Ion-exchange chromatography, colorimetry, stripping voltammetry and Graphite furnace atomic absorption

*Corresponding author. E-mail: RezaJalali93@yahoo.com

spectroscopy are among the common methods to determine manganese [9-13]. However, the mentioned techniques have the main drawbacks such as lack of selectivity, considerable expenses, low reproducibility, and being time consuming. Fortunately, as a counterpoint of the mentioned complicated methods, we can refer to ion selective electrodes. Significant advantages of this type of electrochemical sensors make them ideal and unparalleled devices for determination of various analytes in analytical chemistry. Being economical, remarkable selectivity, short analysis time, wide linearity domain, high sensitivity and uncomplicated instrumentation are the main upsides of ion selective electrodes [14-31]. Despite the fact that numerous ISEs have been constructed for determination of various ionic species, few studies have been performed on manganese in this field. In addition, most of the reported Mn^{2+} selective electrodes have some drawbacks such as narrow working range, short lifespan and serious interferences. Therefore, extensive studies in this way seem logical and important [32-37].

Zolpidem is a drug that is widely prescribed for insomnia and sleep disorders [38]. Its IUPAC name and structure is given in Fig. 1. As shown, zolpidem has three nitrogen and one oxygen heteroatoms in its structure, no wonder that this molecule acts as a ligand and forms strong complexes with metals. Moreover, zolpidem has poor solubility in water. All the mentioned traits indicate that this drug could be a potential ionophore. Therefore, in this research, for the first time, the function of zolpidem as a novel neutral ion carrier was evaluated in the fabrication of a new Mn^{2+} selective coated graphite electrode. The main characteristics of zolpidem were also investigated, such as pH range, lifetime, selectivity and so on.

EXPERIMENTAL

Reagent and Materials

Diocetyl phthalate (DOP), nitrobenzene (NB), potassium tetrakis (4-chlorophenyl) borate (KTY), sodium hydroxide, acid nitric, acetone and ethanol were purchased from Sigma Aldrich. Zolpidem was supplied from Sobhan Darou pharmaceutical company. Nitrate salts of various metals, poly vinyl chloride (PVC) and tetrahydrofuran were bought from Merck and Fluka. Two dietary supplements

including Ginsaflex and Wellman were bought from Geriatric Pharmaton and Vitabiotics, respectively. All of the mentioned chemicals were utilized as received without any further purification. All of the solutions were supplied by doubly distilled deionized water (Kimia Tehran acid, Iran) and their activities were calculated by Debye-Huckel equation.

Apparatus

EMF measurements took place by SA-8515 potentiometer (which were procured from Sairan company, Iran) at $25\text{ }^{\circ}\text{C} \pm 0.1$. A saturated Calomel electrode (bought from Azar electrode company, Iran) was used as the reference electrode and a graphite rod (Karen atlas pazhoo, Iran) of 3 cm length and 3 mm diameter was employed for the preparation of the coated graphite electrode. The pH of solutions was adjusted by the glass electrode (Sentek Company, England). A Shimadzu 670/G atomic absorption spectrometer was utilized for determination of Manganese in real samples.

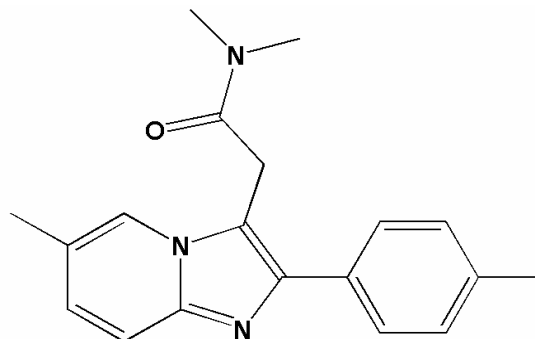
Membrane Preparation

Different amounts of plasticizers (NB and DOP), PVC, ionophore (Zolpidem) and KTY as ionic additive were weighed in a Petri dish. Then, 3 ml of THF was added to the mixture in order to solve all of the ingredients in it. Afterwards, the obtained solution was put under a hood to evaporate solvent and form an oily viscous solution. In this step, the graphite bar was plunged in the obtained solution for 15 s and a thin membrane of about 0.4 mm thickness was created on the surface of the graphite. Then, in order to dry the membranes, the acquired electrode was put in the room temperature for 12 h. In the end, the electrode was conditioned by drenching in a 1×10^{-3} M $Mn(NO_3)_2$ solution for 1 day.

RESULTS AND DISCUSSION

Membrane Optimization

Optimization the membrane composition is the most important step in the development of a potentiometric ion selective electrode. Because the potential response of the sensor can be influenced by various factors such as the dielectric constant of plasticizer, the amount and nature of



N,N-dimethyl-2-[6-methyl-2-(4-methylphenyl)imidazo[1,2-*a*]pyridin-3-yl]acetamide

Fig. 1. The structure and IUPAC name of zolpidem.

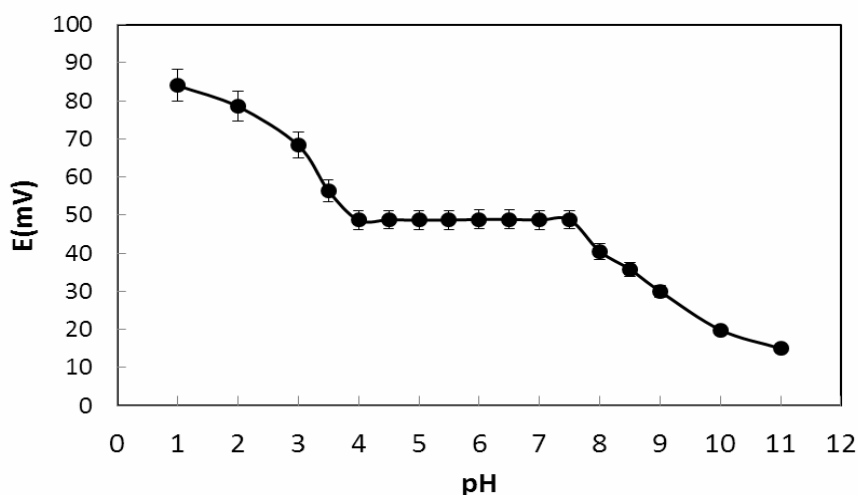


Fig. 2. The influence of pH on the potentiometric sensor based on zolpidem.

ionic additive. In this regard, 12 different compositions were prepared and their effect on the Nernstian slope and linear range was investigated. The amount of ion carrier was the first evaluated subject, according to the data that is provided by Table 1. Best performance was observed by the 9th composition that includes 10% ionophore, 3% KTY, 55% DOP and 32% PVC. As indicated, the slope of Nernstian plot and also dynamic range have been improved dramatically by increasing the amount of zolpidem. While the free ionophore membranes (no.1 and 2) exhibit low slopes (6.9 ± 0.4 and 10.1 ± 0.3 mV Decade⁻¹) and narrow linear ranges, by ascending the ligand amount up to 10% a

drastic increment takes place in the sensitivity and linearity domain of the sensor (No. 3-8). This matter substantiates that a strong complexation has occurred between the ionophore and manganese(II). It should be noted that adding higher amounts of ion carrier decreases the Nernstian slope (No. 11) from 29.7 ± 0.3 mV Decade⁻¹ to 26.8 ± 0.3 mV Decade⁻¹. Hence, in this study, 10 mg was chosen as the best amount of ion carrier.

The second variable affecting the traits of an ion selective electrode remarkably is the quiddity and the amount of plasticizer. For evaluating this parameter, six membranes (No. 4-6, 8-9) with different solvents (NB and

DOP) were prepared. The only discrepancy between these membranes is the nature of plasticizer. As it is obvious, DOP demonstrates better potential responses than NB and this phenomenon was not unexpected, because the dielectric constant of DOP is 5.1 which is significantly lower than the dielectric constant of NB (36.1). Moreover, NB is more polar than DOP, and these facts indicate that NB is able to decrease the performance of the sensor due to its tendency to extract other interfering ions. While DOP could improve the sensitivity of the membrane owing to its low polarity and dielectric constant which eventuate to a subtle affinity for extraction of interfering ions [39,40].

The influence of KTY as an outstanding ionic additive in the characteristics of the electrode was also inspected. This type of lipophilic anions usually improves the sensitivity and working range of ISEs by reducing the Ohmic resistance of the membrane. In addition, in some cases that the ligand used has a weak interaction with the analyte, ionic additives can catalyze the extraction procedure [41]. For this purpose, a membrane without ionic additive was prepared (No. 10) and the slope of Nernstian plot and dynamic range were measured. As can be observed, the slope of the free KTY membrane, 24.2 ± 0.4 mV Decade⁻¹, has risen to the Nernstian value, 29.7 ± 0.3 mV Decade⁻¹, by adding further amounts of KTY.

Applicable pH Range

Each ion selective electrode has a specific useful pH scope, and the potential response obeys the Nernst equation only in this span. Therefore, finding out the applicable pH range is an indispensable step in the development of an ion selective electrode. In this regard, a 1×10^{-4} M Mn(NO₃)₂ solution was made from a 1×10^{-2} M Mn(NO₃)₂ stock solution by diluting. Then, its pH value was justified by using small volumes of concentrated sodium hydroxide and nitric acid solutions in the range of 1.0-11.0. Then, the potential values were measured and recorded. As the acquired results, given in Fig. 2, illustrates clearly, the designed potentiometric sensor has an independent potential response from pH in the range of 4-7.5. It seems that in acidic solutions (pH < 4) hydronium ions can compete with the analyte in formation the complex with the utilized ion carrier and in basic solutions (pH > 7.5) hydroxyl anions take part in formation of the complex with

manganese cations. Both of the mentioned phenomena cause oscillations in potential out of the pH span of 4-7.5. Indeed, the accurate and precise function of the sensor is limited to this range.

Calibration Curve and Detection Limit

In most of the analytical methods depiction of the calibration plot is an inevitable and important step, because calibration curve reveals working range, limit of detection and sensitivity of analytical techniques. In this regard, several solutions of Mn(NO₃)₂ with different activities were prepared from a 1×10^{-2} M Mn(NO₃)₂ stock solution by diluting with doubly distilled deionized water. Afterward, their potentials were measured by the membrane sensor in optimum conditions, and finally, potential values were drawn *versus* the activity of the solutions. As Fig. 3. demonstrates obviously, the designed Mn²⁺ selective coated graphite electrode shows a wide linear working from 1×10^{-7} M to 1×10^{-2} M with a striking Nernstian slope of 29.7 ± 0.3 mV Decade⁻¹. The detection limit of the sensor was 9×10^{-8} M which was acquired by extrapolating two segments of the calibration graph.

The Effect of Organic Solvents

In order to investigate the electrode performance in partially non aqueous mediums, two series of Mn(NO₃)₂ solutions with different contents of ethanol and acetone were prepared. Then, the working linear range and Nernstian slope of the calibration graph were evaluated and the results are presented in Table 2. Clearly, the provided data indicate that the designed electrode keeps its sensitivity and wide dynamic range up to 15% of non aqueous content, while allocating more volume portion to organic solvents leads to a considerable decline in Nernstian slope and confines the linear range. This phenomenon that has occurred in the high concentration of organic solvents can be originated from leaking of ionophore from the membrane to the matrix of solutions.

Reproducibility

The precision of laboratory methods is defined as the proximity between the results of analyses performed in the same conditions. One of the best methods for measuring the precision of an analytical technique is the relative standard

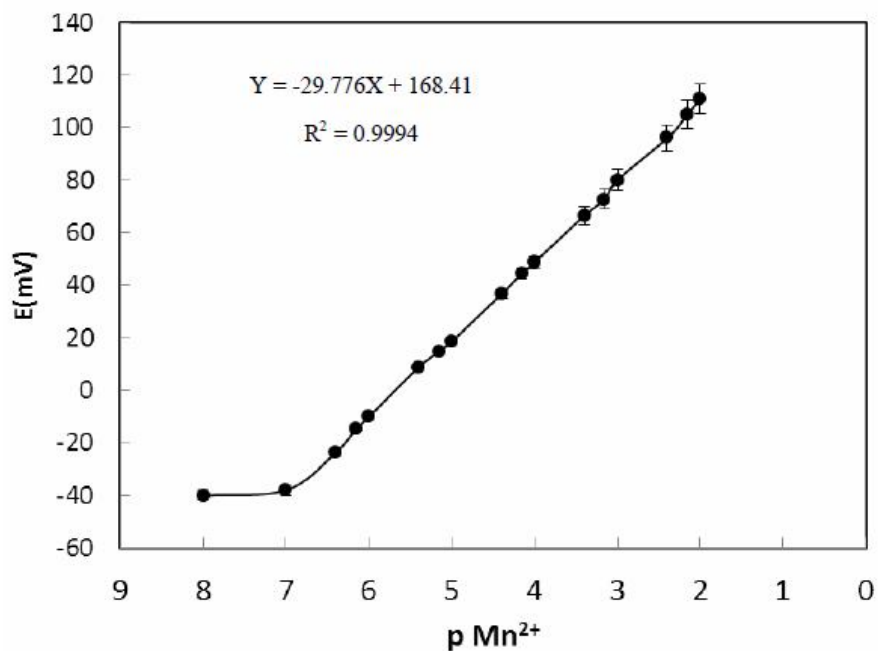


Fig. 3. Calibration graph of the Mn^{2+} selective coated graphite electrode.

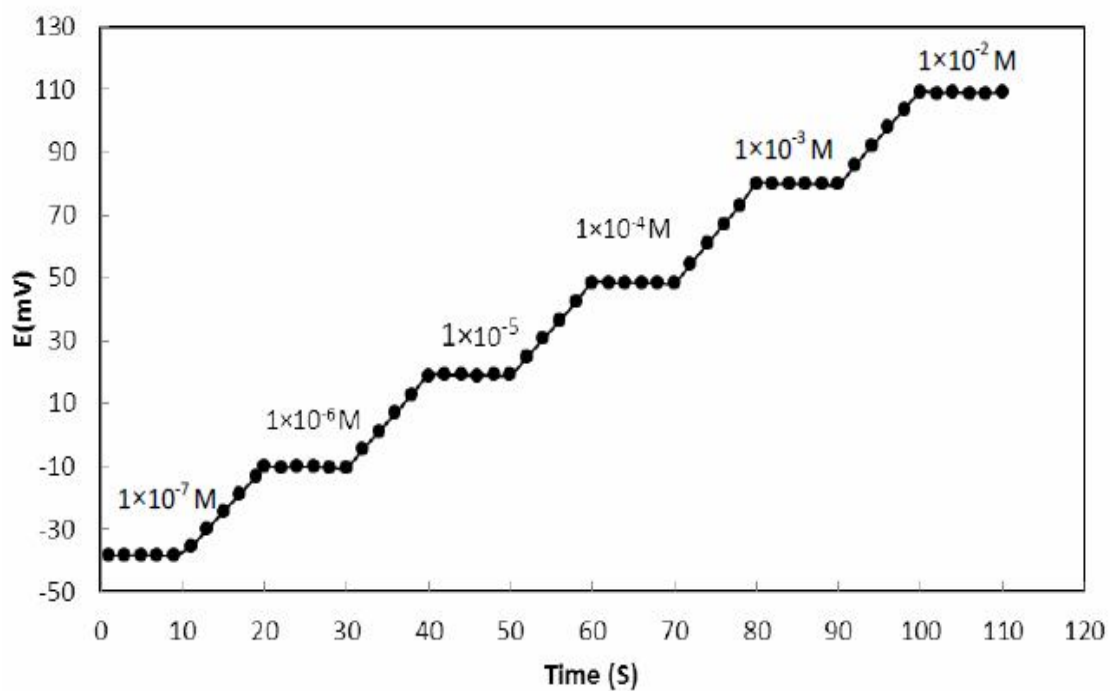


Fig. 4. Dynamic response time of the Mn^{2+} selective electrode for step alterations in concentration of Mn^{2+} over a concentration range from 1.0×10^{-7} - $1.0 \times 10^{-1} M$.

Table 1. Optimization the Membrane Composition

Membrane No.	Ionophore (%wt)	KTY (%wt)	PVC (%wt)	Plasticizer (%wt)		Slope (mV Decade ⁻¹)	Working range (M)
				DOP	NB		
				1	0		
2	0	3	40	57		1×10^{-4} - 1×10^{-2}	
2	2	2	32	64		1×10^{-5} - 1×10^{-2}	
3	4	2	32	62		1×10^{-5} - 1×10^{-2}	
4	6	2	30	62		1×10^{-6} - 1×10^{-2}	
5	6	2	30		62	1×10^{-6} - 1×10^{-2}	
6	8	2	30	60		1×10^{-6} - 1×10^{-2}	
7	8	2	30		60	1×10^{-6} - 1×10^{-2}	
7	10	2	32	56		1×10^{-7} - 1×10^{-2}	
8	10	3	32	55		1×10^{-7} - 1×10^{-2}	
9	10	3	32		55	1×10^{-7} - 1×10^{-2}	
10	10	0	35	55		1×10^{-6} - 1×10^{-2}	
11	12	2	31	55		1×10^{-7} - 1×10^{-2}	

deviation (RSD%) which is obtained by dividing the standard deviation to the average of the results. For investigating the repeatability of the proposed sensor, five 1×10^{-5} M $\text{Mn}(\text{NO}_3)_2$ solution was prepared and their potential was recorded by the designed electrode. Then, a calibration curve was plotted and used to determine unknown concentrations. Afterward, the obtained results were tabulated in Table 3, and the relative standard deviation was calculated from them. As indicated in Table 3, the calculated RSD (%) is 1.97 which proves that the fabricated electrode has an admissible reproducibility.

Selectivity

Selectivity is the most important trait of every analytical technique because it can affect the method accuracy and precision substantially. As the aim of this study was to develop a coated graphite electrode for determination of

trace amounts of Manganese in dietary supplements, the selectivity of the sensor was evaluated over 20 different cations by matched potential method (MPM). The most common mineral micronutrients that are widely used in pharmaceutical supplements were also considered in the studied interfering cations. The calculated selectivity coefficients, reported in Table 4, show that the designed electrode can discriminate between manganese(II) and other interfering ions remarkably, because all of the acquired selectivity coefficient values are about 100 to 1000 times smaller than the value of 1. If the calculated K_{MPM} is near to 1, it implies that the membrane exhibits a same potential response toward the primary ion and the interfering one. Closer selectivity coefficient values to zero connotes that the electrode has a weak tendency toward the interfering cation [42,43].

Table 2. The Influence of Organic Solvents on the Function of Potentiometric Sensor

Non aqueous content (%v/v)	Slope (mV Decade ⁻¹)	Dynamic range (M)
0	1×10^{-7} - 1×10^{-2}	29.7 ± 0.3
Ethanol		
5	1×10^{-7} - 1×10^{-2}	29.7 ± 0.2
10	1×10^{-7} - 1×10^{-2}	29.4 ± 0.3
15	1×10^{-7} - 1×10^{-2}	29.1 ± 0.4
20	6×10^{-6} - 1×10^{-2}	26.8 ± 0.3
Acetone		
5	1×10^{-7} - 1×10^{-2}	29.7 ± 0.3
10	1×10^{-7} - 1×10^{-2}	29.3 ± 0.4
15	1×10^{-7} - 1×10^{-2}	28.8 ± 0.5
20	3×10^{-6} - 1×10^{-2}	25.6 ± 0.4
Mixed 50:50 (Ethanol+ Acetone)		
5	1×10^{-7} - 1×10^{-2}	29.7 ± 0.4
10	1×10^{-7} - 1×10^{-2}	29.2 ± 0.5
15	1×10^{-7} - 1×10^{-2}	28.6 ± 0.3
20	8×10^{-6} - 1×10^{-2}	25.9 ± 0.3

Table 3. Calculating Relative Standard Deviation of the Proposed Electrode

Solution No.	Potential (mV)	Concentration (M)	RSD (%)
1	19.9	1.029×10^{-5}	1.97
2	20	1.037×10^{-5}	
3	19.7	1.013×10^{-5}	
4	19.5	9.997×10^{-6}	
5	19.4	9.900×10^{-6}	

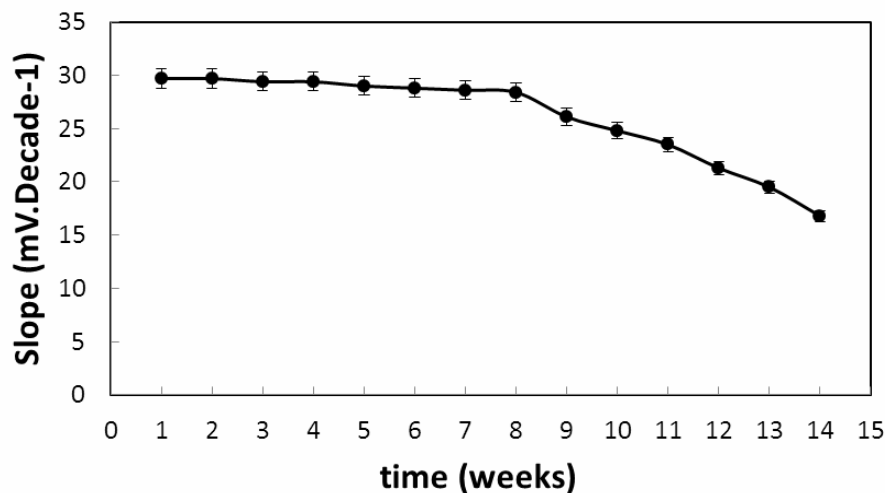


Fig. 5. The life time of the designed Mn²⁺ coated graphite electrode.

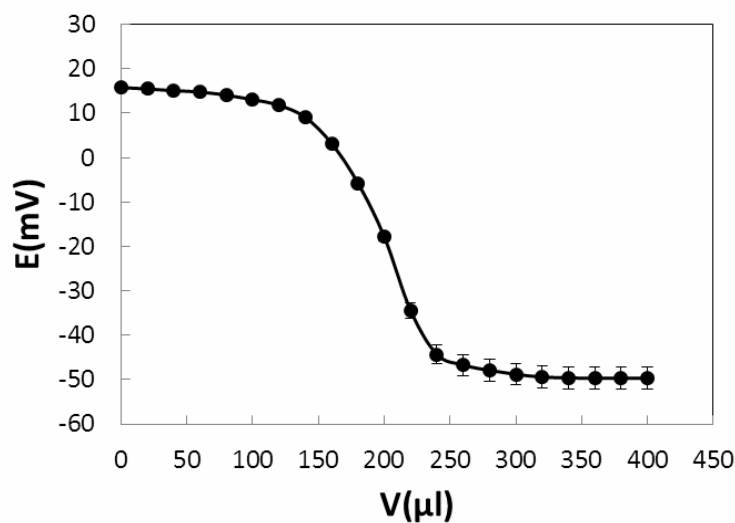


Fig. 6. Normal titration curve of 20 ml 1.0×10^{-5} M Mn²⁺ with 1.0×10^{-3} M EDTA, using the proposed sensor as an indicator electrode.

Response Time and Lifespan

The response time of an ion selective electrode usually is defined as the time required that an electrode system obtains a 90% value of its steady potential after being inserted into the test solution. The exchange kinetics speed of complexation-decomplexation of analyte ions with the utilized ion carrier at the membrane surface is the main factor affecting the response time of ISEs. For evaluating

this parameter, the reference and indicator electrodes were placed in a series of solutions of Mn(NO₃)₂ with 10 times discrepancy in activity, and the potential of the system was recorded in every second. The acquired results are displayed in Fig. 4. As indicated in this table, the response time of the constructed membrane sensor is 10 s in the whole dynamic range which is ideal and short. The lifetime of the electrode was also inspected by checking the linear

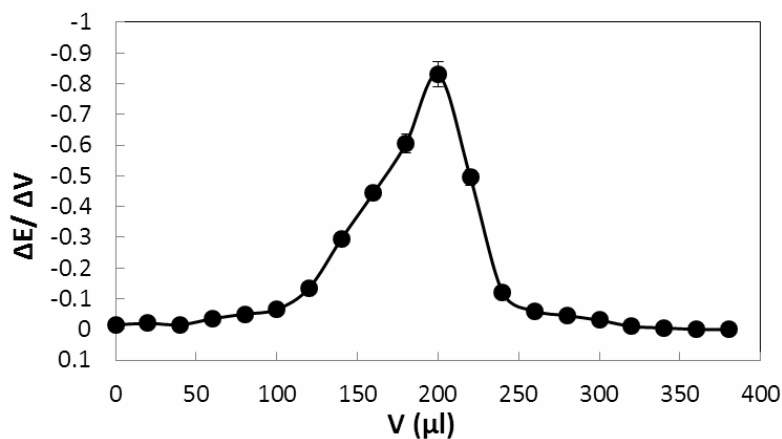


Fig. 7. The first derivative titration curve of 20 ml 1.0×10^{-5} M Mn^{2+} with 1.0×10^{-3} M EDTA, using the proposed sensor as an indicator electrode.

Table 4. Selectivity Coefficients of the Designed Electrode over Various Cations

Ion	K_{MPM}	Ion	K_{MPM}
Cu^{2+}	2.3×10^{-3}	Ag^{+}	9.8×10^{-3}
Mg^{2+}	7.4×10^{-3}	Cd^{2+}	4.1×10^{-2}
Ca^{2+}	9.1×10^{-4}	Pb^{2+}	3.8×10^{-3}
Fe^{2+}	1.6×10^{-2}	Hg^{2+}	2.6×10^{-2}
Fe^{3+}	5.7×10^{-2}	Ni^{2+}	7.9×10^{-3}
Zn^{2+}	6.3×10^{-3}	Al^{3+}	5.4×10^{-3}
Cr^{3+}	8.6×10^{-4}	Li^{+}	7.4×10^{-4}
Na^{+}	4.2×10^{-3}	Mo^{2+}	8.2×10^{-3}
K^{+}	7.1×10^{-4}	Se^{2+}	1.9×10^{-3}
Co^{2+}	3.2×10^{-3}	Bi^{3+}	6.7×10^{-4}

range and the slope of calibration plot in a 14 weeks period. As the obtained results in Fig. 5, demonstrates obviously, the potentiometric coated graphite electrode can be used at least for eight weeks or two months with high sensitivity and reproducibility, because, after the mentioned period the slope of the calibration curves has declined dramatically. Indeed, the sensor lost its sensitivity due to the leaking of

the membrane ingredients to the test solutions by passing time [44].

Potentiometric Titration

In order to evaluate the function of the recommended electrode in indirect potentiometry, 20 ml of a 1×10^{-5} M $Mn(NO_3)_2$ solution was prepared, and then titrated with

Table 5. Determination of Mn²⁺ in Two Pharmaceutical Specimens

Sample	Measured with FAAS (mg)	Measured with the recommended sensor (mg)
Ginsaflex supplement	0.199 (±1.52) ^a	0.203 (±1.33)
Wellman supplement	3.05 (±2.21)	3.21 (±1.91)

^a%RSD based on five replicate analysis.**Table 6.** Comparison of the Proposed Mn²⁺ Selective Electrode with some of the Prior Reports

Lifetime (months)	Detection limit (M)	Linear range (M)	Response time (S)	pH	Slope (mV decade ⁻¹)	Ref.
3	4 × 10 ⁻⁷	1 × 10 ⁻¹ -1 × 10 ⁻⁶	15	4-8	29.6	[47]
2	1 × 10 ⁻⁷	1.8 × 10 ⁻² -4 × 10 ⁻⁷	10	4.5-7.5	30.1	[35]
4	10 ⁻⁵ × 1.2	1 × 10 ⁻¹ -1.25 × 10 ⁻⁵	20	3-8	29.5	[37]
2	4 × 10 ⁻⁶	2 × 10 ⁻² -6 × 10 ⁻⁶	11	4-9.5	29	[36]
4	5.1 × 10 ⁻⁶	1 × 10 ⁻¹ -1 × 10 ⁻⁵	25	3.2-7	29.8	[33]
2	8 × 10 ⁻⁶	1 × 10 ⁻¹ -1 × 10 ⁻⁵	15	4-9	29.3	[34]
2	9 × 10 ⁻⁸	1 × 10 ⁻² -1 × 10 ⁻⁷	10	4-7.5	29.7	This work

EDTA 1 × 10⁻³ M. The resulting normal and the first derivative titration diagrams are given in Figs. 6 and 7 respectively. Obviously, the equivalent point and consequently the concentration of Mn²⁺ can be determined by potentiometric titration with a great precision and accuracy in both titration curves. This matter clarifies that the designed coated graphite electrode can be used as an ideal indicator electrode for determination the trace amounts of manganese(II) by potentiometric titration.

Analysis of Real Samples

Two Ginsaflex and Wellman dietary supplements were used as real samples. At the outset, 40 tablets were weighed in order to obtain the average tablet weight. Then, the

tablets were crushed and ground to a fine homogeneous powder with a mortar and pestle. Afterward, an average amount that was equivalent to one tablet's weight was weighed and transferred to a beaker, and 20 ml of 1 M HCl solution was added to the weighed powder. Then, the beaker was inserted in the ultrasonic bath for 10 min [45,46]. In the next step, the pH of the acquired solution was neutralized with small volumes of concentrated NaOH and the amount of manganese(II) in each tablet was determined by flame atomic absorption (FAAS) and the proposed coated graphite electrode. As the results in Table 5 exhibit clearly, the acquired results of the designed potentiometric membrane sensor and FAAS.

Comparison of the Designed Mn²⁺ Potentiometric Ion Selective Electrode with some of the Former Reports

The main properties of the constructed Mn²⁺ membrane sensor have been compared with some of the prior reported Mn²⁺ selective electrodes in Table 6. As indicated, the recommended electrode shows the widest linear working range and the lowest limit of detection among other sensors. In addition, it should be mentioned that other characteristics such as the response time and Nernstian slope are very close to the best former electrodes reported. All of the referred points illustrate that the designed electrode is superior to other potentiometric sensors.

CONCLUSIONS

In the recent decades, the matter of counterfeit pharmaceutical products has been very controversial. Manganese is a mineral micronutrient that is widely utilized in dietary supplements, owing to its prominent biological roles in the body. Hence, in this research, a coated graphite electrode was designed for determination of manganese(II) in medicinal supplements by using zolpidem as a neutral ion carrier. The electrode demonstrates a Nernstian slope (29.7 mV Decade⁻¹) over a wide concentration range of 1×10^{-7} - 1×10^{-2} M. The investigated membrane sensor shows a good selectivity toward Mn²⁺ over 20 interfering cations. Its performance in potentiometric titration and determination trace amounts of manganese(II) in dietary supplements was also evaluated, and the sensor could measure this cation with high accuracy and reproducibility in both cases. The lifespan and response time of the electrode were two months and 10 s, respectively. The sensor is also able to be used for detection of Mn²⁺ in non aqueous mediums containing 15% of organic solvents of ethanol and acetone.

ACKNOWLEDGEMENTS

The author appreciates the young researchers and elite club of Islamic Azad University of Yadegar-e-Imam Khomeini (RAH) Shahre-rey branch for the upholding of

this project.

REFERENCES

- [1] J. Roth, S. Ponzoni, M. Aschner, *Met. Ions Life Sci.* 12 (2013) 169.
- [2] J. Emsely, *Nature's Building Blocks: An A-Z Guide to the Elements*, OUP, Oxford, 2001.
- [3] E. Preisler, *Chem. J.* 14 (1980) 137.
- [4] A. Takeda, *Brain. Res. Rev.* 41 (2003) 79.
- [5] N.A. Law, T. Caudle, V.L. Pocararo, *Adv. Inorg. Chem.* 46 (1998) 305.
- [6] D.S. Avila, R.L. Puntel, M. Aschner, *Met. Ions Life Sci.* 13 (2013) 199.
- [7] J. Lenik, C. Wardak, *Proced. Eng.* 47 (2012) 144.
- [8] K.H. Thompson, M. Lee, *J. Nutr. Biochem.* 4 (1993) 476.
- [9] S. Schnell, S. Ratering, K.H. Jansen, *Environ. Sci. Technol.* 32 (1998) 1530.
- [10] B. Chiswell, G. Rauchile, M. Pascoe, *Talanta* 37 (1990) 237.
- [11] W.C. Purdy, D.N. Hume, *Anal. Chem.* 27 (1955) 256.
- [12] E.G.P. Dasilva, V. Hatjeh, N.L. Dossantos, M. Costa, R.A. Nogueira, L.C. Ferreira, *J. Food Comp. Anal.* 21 (2008) 259.
- [13] F.F. Lima, F. Tormin, M. Richter, A.A. Munoz, *Microchem. J.* 116 (2014) 178.
- [14] J. Miao, X. Wang, Y. Fan, J. Li, L. Zhang, G. Hu, C. He, C. Jin, *J. Food. Drug. Anal.* 26 (2018) 670.
- [15] Y. Fan, C. Xu, R. Wang, G. Hu, J. Miao, K. Hai, C. Lin, *J. Food Comp. Anal.* 62 (2017) 63.
- [16] J. HE, Y. LI, X. XUE, H. RU, X. HUANG, H. YANG, *J. Rare Earths* 35 (2017) 934.
- [17] M. Jeszke, K. Trzeciński, J. Karczewski, E. Luboch, *Electrochim. Acta* 246 (2017) 424.
- [18] G.A. Crespo, *Electrochim. Acta* 245 (2017) 1023.
- [19] E. Baghdar, M. Aghaie, H. Aghaie, *Arab. J. Chem.* 10 (2017) S2471.
- [20] T.A. Ali, G.G. Mohamed, M.M. Omar, N.M. Hanafy, *Ind. Eng. Chem.* 47 (2017) 102.
- [21] S.M. Hamza, N.M.H. Rizk, H.A.B. Matter, *Arab. J. Chem.* 10 (2017) S236.
- [22] A. Sharifi, L. Hajiaghababaei, S. Suzangarzadeh, M. R. Jalali Sarvestani, *Anal. Bioanal. Electrochem.* 9

- (2017) 888.
- [23] N. Rahman, S. Khan, *J. Electroanal. Chem.* 777 (2016) 92.
- [24] A. Pardakhty, S. Ahmadzadeh, S. Avazpour, V.K. Gupta, *J. Mol. Liq.* 216 (2016) 387.
- [25] H. Soltani, A. Pardakhty, S. Ahmadzadeh, *J. Mol. Liq.* 219 (2016) 63.
- [26] S. Ahmadzadeh, F. Karimi, N. Atar, E.R. Sartori, E. Faghih-Mirzaei, *Inorg. Nano-Met. Chem.* 47 (2017) 347.
- [27] S. Ahmadzadeh, M. Rezayi, E. Faghih-Mirzaei, M. Yoosefian, A. Kassim, *Electrochim. Acta* 178 (2015) 580.
- [28] M. Rezayi, L.Y. Heng, A. Kassim, S. Ahmadzadeh, Y. Abollahi, H. Jahangirian, *Sensors* 12 (2012) 8806.
- [29] M. Fouladgar, S. Ahmadzadeh, *Appl. Surf. Sci.* 370 (2016) 150.
- [30] S. Ahmadzadeh, M. Rezayi, A. Kassim, M. Aghasi, *RSC Adv.* 5 (2015) 39209.
- [31] V.K. Gupta, F. Golestani, S. Ahmadzadeh, H. Karimi-Maleh, G. Fazli, S. Khosravi, *Int. J. Electrochem. Sci.* 10 (2015) 3657.
- [32] Ai. Singh, Ar. Singh, K.C. Yadav, G. Singh, *Int. J. Chem. Appl.* 4 (2012) 127.
- [33] M. Sobhana, T. Divya, E.V. Anuja, K.G. Kumar, *Front Sci.* 1 (2013) 74.
- [34] M. Aghaei, M. Giahi, M. Zawari, *Bull. Korean Chem. Soc.* 31 (2010) 38.
- [35] M.H. Mashhadalizadeh, E.pourtaheri, I. Sheikhshoae, *Talanta* 72 (2007) 1088.
- [36] I. Sheikhshoae, T. Shamspur, Y. Ebrahimpour, *Arab. J. Chem.* 5 (2012) 201.
- [37] A.K. Singh, P. Saxena, A. Panwar, *Sens. Actuators B* 110 (2005) 377.
- [38] J.M. Monti, D.W. Spence, K. Buttoo, S.R. Pandi-Perumal, *Asian J. Psychiatr.* 25 (2017) 79.
- [39] M.K. Sahani, A.K. Singh, A.K. Jain, A. Upadhyay, A. Kumar, U.P. Singh, Sh. Narang, *Anal. Chim. Acta* 860 (2015) 51.
- [40] A.K. Singh, M.K. Sahani, K.R. Bandi, A.K. Jain, *Mater. Sci. Eng. C* 41 (2014) 206.
- [41] K.R. Bandi, A.K. Singh, A. Upadhyay, *Mater. Sci. Eng. C* 36 (2014) 187.
- [42] Y. Umezawa, K. Umezawa, H. Sato, *Pure. Appl. Chem.* 67 (1995) 507.
- [43] H.A. Zamani, M.R. Ganjali, P. Norouzi, M. Adib, *Sensor Lett.* 5 (2007) 522.
- [44] L. Hajiaghababaei, A. Sharafi, S. Suzangarzadeh, F. Faridbod, *Anal. Bioanal. Electrochem.* 5 (2013) 481.
- [45] Y.S. Chae, J.P. Vacik, W.H. Shelver, *J. Pharm. Sci.* 62 (1973) 1838.
- [46] S. Soriano, A.D.P. Netto, Ricardo J. Cassella, *J. Pharm. Biomed. Anal.* 43 (2007) 304.
- [47] V.K. Gupta, R. Jain, M.K. Pal, *Int. J. Electrochem. Sci.* 5 (2010) 1164.