Int. J. Electrochem. Sci., 11 **(2016)** 7990 – 8001, doi: 10.20964/2016.09.64

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Pramipexole Symmetric and Asymmetric Potentiometric PVC Membrane Sensors

Farnoush Faridbod[1,*], *Tahereh Jamshidpour*[1], *Mohammad Reza Ganjali*[1,2]

[1] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
[2] Biosensor Research Center, Endocrinology and Metabolism Molecular-Cellular Sciences Institute, Tehran University of Medical Sciences, Tehran, Iran
[*]E-mail: faridbodf@khayam.ut.ac.ir

Received: 12 May 2016 / *Accepted:* 21 July 2016 / *Published:* 7 August 2016

Pramipexole is one of the prescribed medication for Parkinson's disease, which is a dopamine agonist of the non-ergoline class. Due to the importance of the drug, the analysis of its active ingredient in formulation is of great importance. Here, a PVC membrane sensor was made for the measurement of Pramipexole active ingredient in some pharmaceutical tablets. The PVC membrane containing ion-pair compound of Pramipexol-tetraphenyl borate as a sensing material was placed at the end of a plastic tube (as symmetric electrode) and coated on a graphite and a copper wire electrodes (as asymmetric electrodes). The polymeric membrane was plasticized by dibutyl phthalate (DBP). A wide linear range of 1.0×10^{-6}-1.0×10^{-1} mol L^{-1} were provided by three sensors. Applicable pH range of the sensor is 3.0–6.8. Finally, the method was validated in the analysis of Pramipexole in pharmaceutical formulation.

Keywords: Pramipexole, Potentiometry, PVC membrane, Sensor, Coated wire electrode, Coated graphite electrode

1. INTRODUCTION

Pramipexole (Fig. 1) is a Parkinson medication that binds with high affinity to both native and expressed dopamine D2 family receptors [1]. It is a dopamine agonist of the non-ergoline class. Because of the significant of this drug in treatments of Parkinson disease, analysis of pharmaceutical formulation is of great importance. Pramipexole dihydrochloride is used as the active ingredients of the formulations. Tablets of 0.7 mg, 0.18 and 0.35 mg are dosage form of this drug in Iran. Generally chromatographic methods are dominant methods in analysis of drugs especially in biological fluids because of their high accuracy and precision. Pramipexole also analyzed by high performance liquid chromatography (HPLC) methods [2-4]. By progress in electrochemical techniques in analysis of

drugs, some of them played an important role in pharmaceutical analysis due to their advantages of ease, speed and inexpensively over spectrophotometric and chromatographic methods [5-11]. Determination of drug molecules by potentiometric sensors can be a new way in pharmaceutical analysis [12-19].

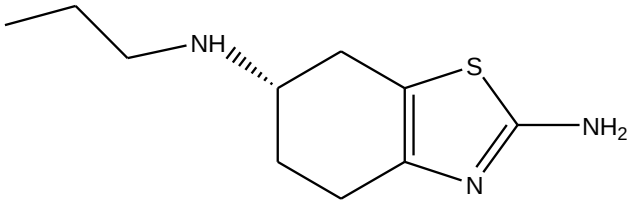

Figure 1. Chemical structure of Pramipexole

The simplicity of working with potentiometric electrodes, make them suitable devices in analysis of various species [20-23]. Based on the method which the polymeric membrane is immobilized on the electrode, symmetric and asymmetric sensors can be made. In general PVC membrane electrodes (PMEs) which are so common, there is a need to an internal reference electrode and internal filling solution. In fact, the membrane was placed between two solutions from both sides. In this way, the probability of the leaching of the membrane ingredients to the aqueous solution are increased. Also, the mechanical stability of the indicator electrode is decreased. While, by coating the polymeric membrane on to the surface of a conducting wire or graphite rod [24-26], there is no need to the internal reference electrode as transducer. Removal the internal solution also decreases the leaching process and reduce the lower detection limit. Perhaps, only the weakness of the asymmetric electrodes are lack of response in high concentrations of the analyte. Both electrodes with each others can provide a wide linear range.

In designing a drug potentiometric sensor, an ion-pair complex of the drug ions with a suitable ionic additive are used. The response mechanism is based on an ion-exchanging. In the present work, a Pramipexole potentiometric membrane electrode is developed based on ion-pair compound of Pramipexole-tetraphenylbroate (PXL-TPB) as a sensing substance in the membrane. Pramipexole dihydrochloride was interacted by sodium tetraphenyl borate to form the ion-pair which was then applied in the membrane [16-18]. The membrane was plasticized with a suitable plasticizer and then placed on the plastic tubes, copper wire and graphite rode to make the polymeric membrane sensors. The performance of both kinds of sensor were considered in analysis of Pramipexole in some tablets.

2. EXPERIMENTAL SECTION

2.1. Apparatus

Two Ag/AgCl reference electrode from Azar electrode (Iran) were used as internal and external reference electrodes. To measurement the potentials, both reference and indicator electrodes were

linked to a multi-meter having a volt-meter with ±0.1 mV precision (Japan). The measurement cell was assembled as follow:

Symmetric Sensor: Ag-AgCl || internal solution, 1×10^{-3} mol L^{-1} pramipexole.2HCl | PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

Asymmetric Sensor: Coated graphite or wire-PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

2.2. Materials

Analytical reagent grade of the materials including high-molecular weight poly(vinylchloride) (PVC) (Fluka Co., USA), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), tetrahydrofuran (THF) (Merck Co., Germany) and sodium tetraphenyl borate (NaTPB) were used. Pramipexole ((S)-2-Amino–4,5,6,7–tetrahydro–6-(propylamino)benzothiazole) and its pharmaceutical formulation were obtained from local pharmaceutical manufacturer (Tehran, Iran) as gift samples.

2.3. Synthesis of the Sensing-material

As mentioned above, ion-pair compound of Pramipexole-tetraphenylborate (PXL-TPB) was used as a sensing material in the polymeric membrane. To preparing the compound, about 20 mL of 0.01 mol L^{-1} solution of tetraphenyl borate was added to 10 mL of 0.01 mol L^{-1} solution of Pramipexole dihydrochloride in water. The result participate were filtered, washed with distilled water and dried to be used as sensing material.

2.4. Preparation of the Electrodes

For making PVC membrane electrode, the ion-pair compound, PVC with a plasticizer and ionic additive, with the ratio presented in Table 1, were dissolved in tetrahydrofuran (THF), and the solution was mixed into a small beaker of 2 cm diameter. Then, THF was gradually evaporated up to a honey concentrated solution was achieved.

Now for general PVC membrane electrode, the membrane placed at the end of a plastic tube (about 3mm o.d.) by dipping the tube head into the prepared solution for about 10 s till a transparent membrane of about 0.3 mm in thickness was formed at the end. Then the plastic tube was kept at room temperature for about 5 h. Next, the tube was filled with 10×10^{-3} mol L^{-1} of Pramipexole solution. After for 15 h conditioning by soaking in the 10×10^{-3} mol L^{-1} solution, the indicator electrode is ready to measure.

For Wire coated electrode, the same honey solution of membrane ingredients was prepared. Then, a copper wire was dipped into the mixture for about 5 s to form a transparent membrane at the

end surface. After drying at room temperature for at least 5 h, it was soaked in a 1.0×10^{-3} mol L^{-1} of Pramipexole dihydrochloride solution for 24 h.

In case of coated graphite electrode, the polymeric membrane coated on a graphite rods of 3 mm diameter and 15 mm long by dipping method. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated well in distilled water and dried in room temperature. The membrane which was formed on the graphite surface, dried in the air for 5 h and the electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} solution of Pramipexole.

2.5. Standard Pramipexole Solutions

Pramipexole dihydrochloride Monohydrate is soluble in aqueous solutions. A stock solution of 0.1 mol L^{-1} Pramipexole.2HCl was prepared by dissolving appropriate amount of pure drug in 100 mL distilled water. The standard solutions (1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}) were then prepared by proper dilution of the stock solution with distilled water.

2.6. Sample Preparation

For the preparation of the tablet solution, 10 tablets (0.7 mg Pramipexole in each tablet) were thoroughly powdered and mixed. Then, apportion amount equal to the average weight of one tablet, was carefully weighted, move in to a 10 ml volumetric flask and diluted by adjusting the pH to 4.5. This solution was completely stirred for 15 min and then filtered.

3. RESULTS AND DISCUSSION

Response of a potentiometric PVC membrane sensor significantly depends on the composition of the polymeric membrane as a sensing element and the transducer used to transduce the chemical signal to electrical ones. After finding the best composition and the response, the analytical performance of the prepared sensor is studied.

3.1. Sensing Element Composition

The sensing element of the proposed sensors is a polymeric matrix contain ion-pair compound. PVC was used as a best polymer for the matrix since introducing the PMEs. 30%wt. PVC was selected for all PMEs [27-31]. The most important element of the membrane, which plays a main roles in potential response of the sensor, is the amount of the ion-pair. The plasticizer generally acts as a solvent mediator, tolerating uniform dispersion and moving of the ion-pair inside the membrane. The type and the quantity of the plasticizer must be appropriately controlled. Three plasticizers were tested, dibutyl phthalate (DBP), nitrobenzene (NB) and benzyl acetate (BA), as shown in Table 1. Among them, DBP, having a rather lower dielectric constant provided the best plasticizing role. Addition of 3% ionic additive to the composition of the membrane improves the potential response of the sensor

remarkably. Also, the presence of ionic additive to the membrane can decrease the Ohmic resistance of the membrane significantly. As it is obvious from Table 1, the presence of 3% NaTPB provided the electrode with a nice Nernstian potential response.

Table 1. PVC membrane ingredients optimization

No.	PXL-TPB (%wt.)	PVC (%wt.)	Plasticizer (%wt.)	NaTPB (%wt.)	Linear range (mol L^{-1})	Slope (mV/decade)	R^2
1	4	30	66 DBP	0	1×10^{-5}-1×10^{-1}	16.5±0.6	0.983
2	5	30	65 DBP	0	1×10^{-5}-1×10^{-1}	18.0±0.7	0.987
3	6	30	64 DBP	0	1×10^{-5}-1×10^{-1}	15.0±0.6	0.974
4	5	30	64 DBP	1	1×10^{-5}-1×10^{-1}	21.6±0.5	0.978
5	5	30	63 DBP	2	1×10^{-5}-1×10^{-1}	22.4±0.7	0.991
6	5	30	62 DBP	3	1×10^{-5}-1×10^{-1}	26.1±0.4	0.994
7	5	30	62 NB	3	1×10^{-5}-1×10^{-2}	10.24±0.3	0.993
8	5	30	62 BA	3	1×10^{-4}-1×10^{-2}	7.84±0.5	0.985
9	0	30	67 DBP	3	1×10^{-4}-1×10^{-3}	3.95±0.6	0.978

In conclusion, the membrane no. 6 with the composition of 30% PVC, 5% ion-pair, 3% NaTPB and 62% DBP was selected as the optimum amounts for the preparation of the sensor. The membrane having no ion-pair compound (membrane no. 9), has the lowest response.

3.2. Coated Wire Electrode

To enhance the linear range of the Pramipexole sensor, the best composition of the membrane was immobilized on the surface of the copper wire. In this way, i.e. the asymmetrical electrode, one side of the membrane is in contact with a solid state while the other side is encountered to the aqueous solution. The membrane which was used for PMEs, also was used for coating on the copper wire.

Table 1. Optimization of the membrane ingredients for wire coated electrode

No.	PXL-TPB (%wt.)	PVC (%wt.)	DBP (%wt.)	NaTPB (%wt.)	Linear range (mol L^{-1})	Slope (mV/decade)	R^2
1	4	30	66	0	1×10^{-5}-1×10^{-2}	13.7±0.7	0.963
2	5	30	65	0	1×10^{-5}-1×10^{-2}	24.2±0.3	0.987
3	6	30	64	0	1×10^{-5}-1×10^{-2}	19.8±0.5	0.984
4	5	30	64	1	1×10^{-6}-1×10^{-2}	26.3±0.3	0.989
5	5	30	63	2	1×10^{-6}-1×10^{-2}	27.7±0.4	0.994
6	5	30	62	3	1×10^{-6}-1×10^{-2}	24.6±0.5	0.993

However, to find a best response in case of CWE, amount of ion-pair and ionic additive was a little bit changed. The obtained results were listed in Table 2. As it can be seen from Table 2, the sensor can detect lower concentration of Pramipexole. Lower amount of ionic additive, NaTPB, used in the membrane may decrease the effect of other interference.

Finally, the membrane no. 5 with the composition of 30% PVC, 5% ion-pair, 2% NaTPB and 63% DBP was the optimum one for the CWE.

3.3. Coated Graphite Electrode

Another choice for making an asymmetric potentiometric sensor is using graphite rod as transducer. The membrane, like coated wire, can placed at the end of a graphite rod [32, 33]. The same best membrane composition was applied in this case too. However, to find a better performance of the indicator electrode, a small changes in ingredients ratio was done. The characteristics of several membranes having various ingredients are summarized in Table 3.

Table 2. Membrane ingredients optimization for coated graphite electrode

No.	PXL-TPB (%wt.)	PVC (%wt.)	DBP (%wt.)	NaTPB (%wt.)	Linear range (mol L^{-1})	Slope (mV/decade)	R^2
1	4	30	66	0	1×10^{-5}-1×10^{-2}	24.6±0.3	0.989
2	5	30	65	0	1×10^{-5}-1×10^{-2}	28.5±0.5	0.985
3	6	30	64	0	1×10^{-5}-1×10^{-2}	25.5±0.5	0.994
4	5	30	64	1	5×10^{-6}-1×10^{-2}	26.5±0.4	0.982
5	5	30	63	2	5×10^{-6}-1×10^{-2}	28.7±0.4	0.971
6	5	30	62	3	1×10^{-6}-1×10^{-2}	28.4±0.6	0.992

It was found that membrane no. 6 with the composition of 30% PVC, 5% ion pair, 62% DBP, and 3% NaTPB results in the best sensitivity with a Nernstian slope of 28.4 mV per decade concentration of Pramipexole over a very wide dynamic range. Using graphite rode in the sensor, causes an improvement in the Nernstian response and increase the mechanical stability of the sensor.

3.4. Calibration Curves

Linear range of a the membrane sensor is indicate by the linear section of the calibration curve as can be seen in Figure 2, 3 and 4 for Pramipexole determination by PME, CWE and CGE, respectively. The slope for PME is obtained 26.1 mV per decade of the Pramipexole concentration and a standard deviation of ±0.4 mV for five replicants (Figure 2). The obtained linear range for Pramipexole was 1.0×10^{-5}-1.0×10^{-1} mol L^{-1}. In case of CWE, calibration graph slope was 27.7 mV per decade of Pramipexole concentration in the range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1} (Figure 3). The slope for coated graphite electrode was 28.4 mV per decade in the linear range of 1.0×10^{-6}-1.0×10^{-2} mol L^{-1}

(Figure 4). Here, detection limit of PME was 1.0×10^{-5} mol L^{-1}, CWE was 1.2×10^{-6} mol L^{-1} and in case of coated graphite electrode was 1.0×10^{-6} mol L^{-1} which was determined by extrapolation of two parts of the calibration graph.

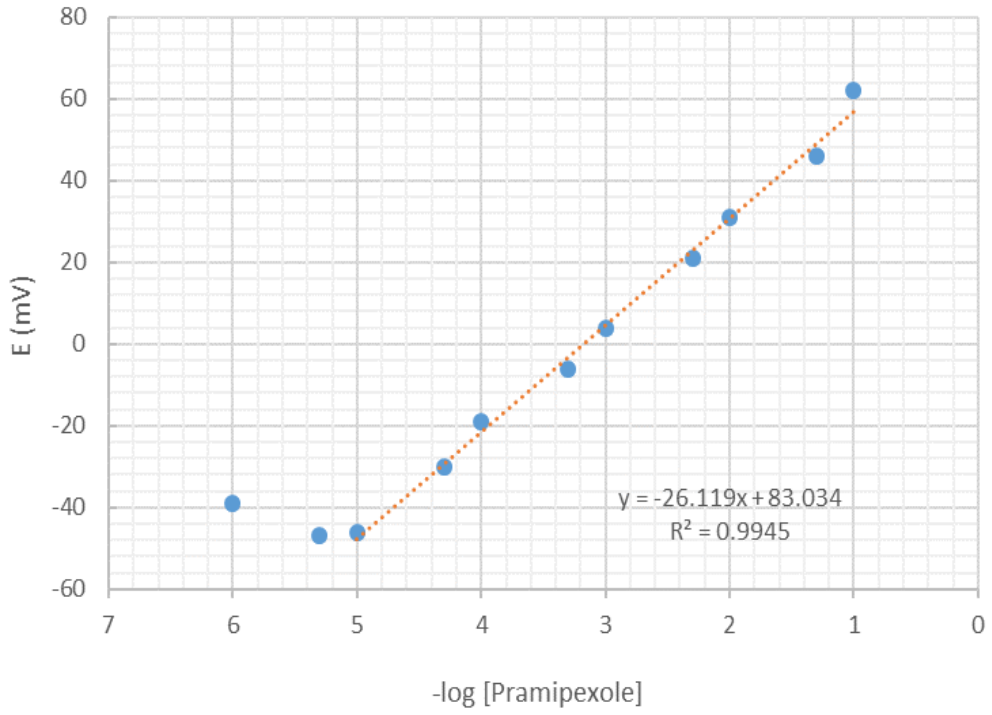

Figure 1. Calibration curve of PME for determination of Pramipexole (membrane no. 6)

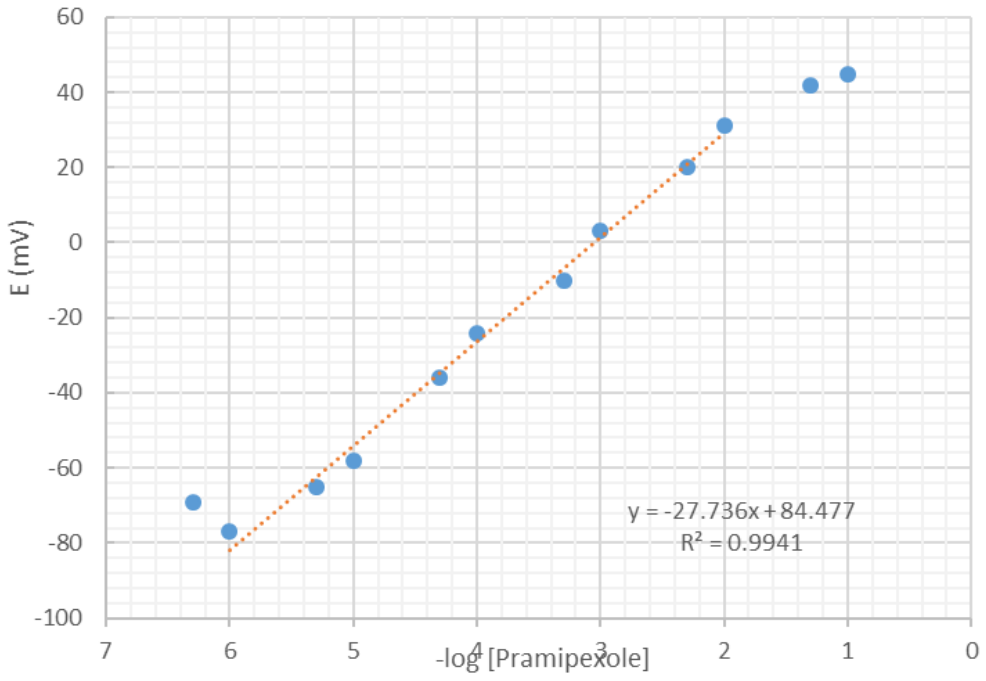

Figure 2. Calibration curve of CWE for determination of Pramipexole (membrane no. 5)

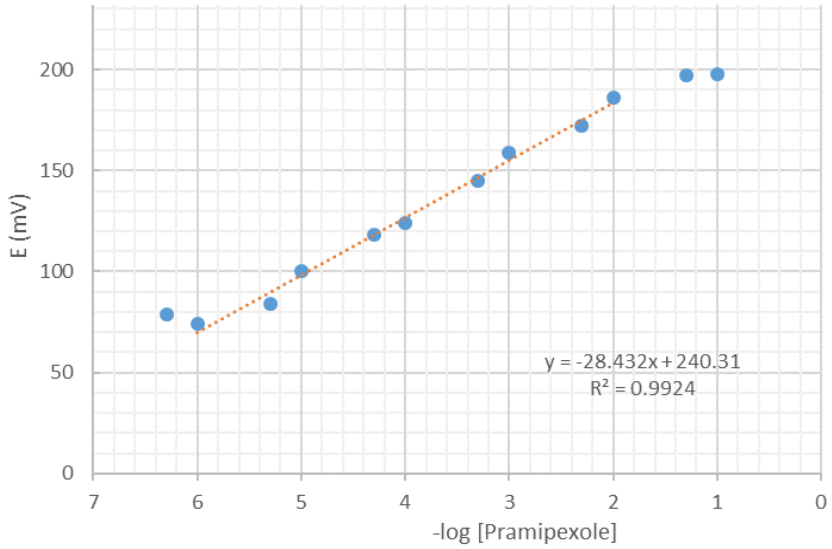

Figure 3. Calibration curve of CGE (membrane no. 6)

3.5. Response Times of the Sensors

Response time is one of the required parameter for characterization of each sensor. It is indicated as the time needed the potential response to achieve values within ±1 mV of the final equilibrium potential [34-37]. It is obtained by recording the potential changes of the Pramipexole series of standard solutions while recording the time. All three sensors were able to quickly reach its equilibrium response in the whole concentration range. The average time in the whole concentration range for coated wire electrode was about 15 second, graphite coated electrode was about 18 s and for PVC membrane electrode was about 20 s.

3.6. pH study

pH effect on three types of electrodes responses was tested as follow: the potential was determined at a specific concentrations of the Pramipexole solution (1.0×10^{-3} mol L^{-1}) from the pH of 2.0 to 10.0 (the pHs was adjusted by concentrated NaOH or HCl solutions). The results showed that the potential is constant in the pH range of 3.0 to 6.8, which showed the performance of the sensors in this pH range. The fluctuations above the pH value of 6.8 might be justified by removing the positive charge on the drug molecule and removal of the ion-pair in the membrane. Variations below the pH 3.0 were because of the removing the analyte in the test solution and response to proton ions. In all three types of sensors the same trend were observed.

3.7. Selectivity

Selectivity of the sensor is the indicator electrode response to the target ion in the presence of interfering ions. It is the most important characteristic of the sensor. The selectivity coefficients of the

Pramipexole sensors were evaluated by the well-known Matched Potential Method (MPM) [38-40]. The resulting values of the selectivity coefficients are shown in Table 4.

Table 4. Selectivity coefficients of various interfering species for Pramipexole sensors

interference	**log K_{MPM}**
Ca^{2+}	-2.65
Mg^{2+}	-2.66
K^{+}	-2.63
NH_4^{+}	-2.67
Na^{+}	-2.65
NO_3^{-}	-2.67

In MPM, the selectivity coefficient is the activity ratio of the primary ion (A, 10^{-4} mol L^{-1} Pramipexole ions) and the interfering ion (B = 10^{-4}–10^{-2} mol L^{-1}) which gives the same potential change in a reference solution (1.0×10^{-5} mol L^{-1} Pramipexole ions). Accordingly, first the change in the potentials, upon changing the primary ion activity is measured, and then the interfering ion is added to an identical reference solution until the same potential change is obtained. The selectivity coefficient K_{MPM} is obtained as:

$$K_{MPM}= \Delta a_A/a_B$$

where $\Delta a_{A=}a'_A-a_{A,}$ a_A is the initial primary ion activity and a'_A the activity of A, in the presence of interfering ion, a_B.

3.8. Stability and Lifetime of the Sensors

The stability and lifetime of the sensors were studied. Three similar sensors from each types were selected and their slopes and detection limits were recorded within 10 weeks. The obtained results revealed that the PME can be used for at least 6 weeks without significant change in its slope, in case of CWE and CGE was 7 weeks. After this time reduction in the Nernstian slope and increase in detection limits was observed.

3.9. Real Sample Analysis

The proposed sensors were used for measuring the active ingredients of Pramipexole dihydrochloride in some pharmaceutical Tablets (Table 5). As it can be seen from Table 5, the results obtained by graphite coated electrodes have the better recoveries values.

Table 5. Analysis of Pramipexole in pharmaceutical formulations by the proposed sensors

Sample	Stated Content (mg/tablet)	Found (mg/tablet)*	RSD%
Sample 1	0.7	PME: 0.730 CWE: 0.728 CGE: 0.724	PME: 4.3% CWE: 4.0% CGE: 3.4%
Sample 2	0.7	PME: 0.727 CWE: 0.725 CGE: 0.724	PME: 3.8% CWE: 3.6% CGE: 3.4%
Sample 3	0.7	PME: 0.675 CWE: 0.678 CGE: 0.681	PME: 3.6% CWE: 3.1% CGE: 2.7%

*The results are average of three replicates measurements

In the next experiment, to test the accuracy of the proposed drug sensor, two samples from a same batch was taken, analyzed by the CWE and by HPLC method [41]. Then, the results were compared by student t-test. According to this statistical test, there is no significant changes between the results of two methods by confidence interval of 95%.

Also, to test repeatability of the proposed sensors, 3 standard solutions of Pramipexole were measured each one for five times by a same sensor. The RSD values by PME were 4.3%, CWE 3.8% and 3.5%. For reproducibility of the methods was done by making the sensors from each types for three times and analyzed a standard solution of Pramipexole for five times. The RSD values for the assays did not exceed 4.7% for each type of sensors.

4. CONCLUSION

In this work, three kinds of potentiometric sensors was produced for determination of Pramipexole dihydrochloride. Pramipexole is a medication for Parkinson's disease, which is a dopamine agonist of the non-ergoline class. Because of the significance of the drug, the analysis of its active ingredient in formulations is of great importance. Three kinds of PVC membrane sensors were made for the measurement of Pramipexole ingredient in some pharmaceutical tablets. The PVC membrane having Pramipexol-tetraphenyl borate ion-pair was placed at the end of a plastic tube (as symmetric electrode) and coated on a graphite and a copper wire electrodes (as asymmetric electrodes). A wide linear range of 1.0×10^{-6}-1.0×10^{-1} mol L^{-1} were provided by three sensors. Applicable pH range of the sensor is 3.0–6.8. Finally, the method was validated in the analysis of Pramipexole in some tablets.

ACKNOWLEDGEMENTS
The authors thank the research Council of University of Tehran for financial support of this work.

References

1. K. Shannon, and J. Bennett, J. Friedman, *Neurology,* 49 (1997) 724.
2. Y. Lau, G. D. Hanson, and N. Ichhpurani, *J. Chromatogr. A,* 683 (1996) 217.
3. V. M. Panditrao, A. P. Sarkate, J. N. Sangshetti, P. S. Wakte, D. B. Shinde, *J. Brazilian Chem. Soc.*, 22 (2011) 1253.
4. E. Ghasemi, S. Kheradmand, and O. G. Dadrass, *Biomed. Chromatogr.*, 28 (2014) 486.
5. V. Arabali, M. Ebrahimi, M. Abbasghorbani, V. K. Gupta, M. Farsi, M. R. Ganjali, and F. Karimi, *J. M. Liq.*, 213 (2016) 312.
6. H. Beitollah, M. Goodarzian, M. A. Khalilzadeh, and H. Karimi-Maleh, *J. Mol. Liq.*, 173 (2012) 137.
7. E. Afsharmanesh, H. Karimi-Maleh, A. Pahlavan, and J. Vahedi, *J. Mol. Liq.*, 181 (2013) 8.
8. S. Jafari, F. Faridbod, P. Norouzi, A. S. Dezfuli, D. Ajloo, F. Mohammadipanah and M. R. Ganjali, *Anal. Chim. Acta,* 895 (2015) 80.
9. J. B. Raoof, R. Ojani, and H. Karimi-Maleh, *Electroanalysis,* 20 (2008) 1259.
10. H. Yaghoubian, H. Karimi-Maleh, M. A. Khalilzadeh, and F. Karimi, *Int. J. Electrochem. Sci*., 4 (2009) 993.
11. M. R. Shahmiri, A. Bahari, H. Karimi-Maleh, R. Hosseinzadeh, and N. Mirnia, *Sens. Actuators B,* 177 (2013) 70.
12. M. R. Ganjali, T. Razavi, F. Faridbod, S. Riahi, and P. Norouzi, *Curr. Pharm. Anal*., 5 (2009) 28.
13. F. Faridbod, M. R. Ganjali, R. Dinarvand, S. Riahi, P. Norouzi, and M. B. A. Olia, *J. Food Drug Anal.*, 17 (2009) 264.
14. F. Faridbod, *Anal. Bioanal. Electrochem.*, 4 (2012) 315.
15. M. R. Ganjali, B. Larijani, and E. Pourbasheer, *Int. J. Electrochem. Sci.*, 11 (2016) 2119.
16. F. Faridbod, *Anal. Bioanal. Electrochem.*, 8 (2016) 92.
17. F. Faridbod, F. Mizani, M. R. Ganjali, and P. Norouzi, *Int. J. Electrochem. Sci.*, 7 (2012) 7643.
18. F. Faridbod, M. R. Ganjali, B. Larijani, E. Nasli-Esfahani, S. Riahi, and P. Norouzi, *Int. J. Electrochem. Sci.*, 5 (2010) 653.
19. M. R. Housaindokht, N. Ashraf, and E. Sheikhzadeh, *Sens. Lett*., 12 (2014) 1341.
20. M.M. Khalil, Y.M. Issa, and A.G. Mohamed, *Electroanalysis,* 26 (2014) 2789.
21. H.A. Zamani, M. Nekoei, M. Mohammadhosseini, and M.R. Ganjali, *Mater. Sci. Eng. C,* 30 (2010) 480.
22. M. R. Ganjali, H. A. Zamani, P. Norouzi, M. Adib, and M. Accedy, *Acta Chim. Slov.*, 52 (2005) 309.
23. F. Faridbod, M. Khamseh-Nejad, M. R. Ganjali, P. Norouzi, and L. Hajiaghababaei, L., *Int. J. Electrochem. Sci.*, 7 (2012) 1917.
24. F. Faridbod, M. R. Ganjali, B. Larijani, P. Norouzi, S. Riahi and F. S. Mirnaghi, *Sensors,* 7 (2007) 3119.
25. M. R. Ganjali, Z. Memari, F. Faridbod and P. Norouzi, *Int. J. Electrochem. Sci.*, 3 (2008) 1169.
26. M. R. Ganjali, A. Daftari, P. Nourozi and M. Salavati-Niasari, *Anal. Lett.*, 36 (2003) 1511.
27. M. Shamsipur, S. Rouhani, M. R. Ganjali, H. Eshghi and H. Sharghi, *Microchem. J.*, 63 (1999) 202.
28. M. R. Ganjali, A. Roubollahi, A. R. Mardan, M. Hamzeloo, A. Mogimi and M. Shamsipur, *Microchem. J*., 60 (1998) 122.
29. M. Shamsipur, M. Javanbakht, M. F. Mousavi, M. R. Ganjali, V. Lippolis, A. Garau and L. Tei, *Talanta,* 55 (2001) 1047.
30. M. R. Ganjali, T. Poursaberi, M. Hosseini, M. Salavati-Niasari, M. Yousefi and M. Shamsipur, *Anal. Sci.*, 18 (2002) 289.
31. H. A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M. S. Zabihi, M. R. Ganjali and M. Salavati-Niasari, *Mater. Sci. Eng. C,* 30 (2010) 917.

32. M. R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour and M. Emami, *Electroanalysis*, 16 (2004) 1002.
33. M. R. Ganjali, M. Rezapour, M. R. Pourjavid and S. Haghgoo, *Anal. Sci.*, 20 (2004) 1007.
34. H. A. Zamani, G. Rajabzadeh, M. R. Ganjali and S. M. Khatami, *Electroanalysis*, 17 (2005) 2260.
35. T. A. Ali, G. G. Mohamed, and A. R. Othman, *Int. J. Electrochem. Sci.*, 10 (2015) 7275.
36. I. H.A. Badr, G. A. Saleh, S. M. Sayed and D. A. M. Nour El-Deen, *Int. J. Electrochem. Sci*., 9 (2014) 1621.
37. O. Galovic, M. Samardzic, S. Petrusic, and M. Sak-Bosnar, *Int. J. Electrochem. Sci.*, 9 (2014) 3802.
38. H. A. Zamani, M. R. Ganjali and M. J. Pooyamanesh, *J. Brazil Chem. Soc.*, 17 (2006) 149.
39. Y. Umezawa, K. Umezawa, H. Sato, *Pure Appl. Chem.*, 67 (1995) 507.
40. H. A. Zamani, F. Malekzadegan and M. R. Ganjali, *Anal. Chim. Acta*, 555 (2006) 336.
41. US Pharmacopoeia; Pramipexole dihydrochloride, Official monographs; USP 35.