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Letrozole Potentiometric PVC membrane and Nano-Composite Carbon Paste Electrodes

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Two kinds of potentiometric electrodes, based on PVC membrane and nano-composite carbon paste electrodes have been introduced. The ion-pair, which was synthesized by the interaction of Letrozole and tetraphenyl borate, was used as a sensing element in both kinds of the electrode. The electrodes respond according to the ion-exchange mechanism. The best PVC membrane sensor response was obtained by a membrane composition of 30% PVC, 65% NB, and 5% ion-pair. Carbon paste electrode was then designed to have an electrode with the better mechanical resistance. The best electrode was composed of 20% ion-pair, 20% paraffin oil, 5% MWCNTs and 55% graphite powder. The proposed method was successfully applied in determination of Letrozole in some pharmaceutical formulations.

Keywords: Letrozole, Potentiometric Sensor, PVC membrane Electrode, Nano-composite Carbon Paste electrode, Ion-Pair

1. INTRODUCTION

Letrozole (Figure 1), antineoplastic compound, is an oral non-steroidal aromatase inhibitor for the treatment of hormonally-responsive breast cancer after surgery. Letrozole prevents the aromatase from producing estrogens by competitive, reversible binding to the heme of its cytochrome P450 unit. The action is specific, and letrozole does not reduce production of mineralo- or corticosteroids. Letrozole is approved by the United States Food and Drug Administration (FDA) for the treatment of local or metastatic breast cancer that is hormone receptor positive or has an unknown receptor status in postmenopausal women [1].

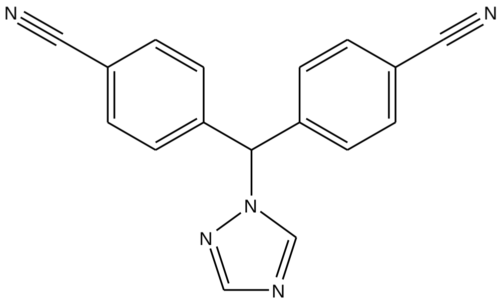

Figure 1. Chemical structure of Letrozole

Determination of Letrozole in tablet formulations have been previously reported by reversed phase high performance liquid chromatography [2], HPLC [3], ultraviolet (UV), first derivative, second derivative, and AUC-spectrophotometric methods [4], and micellar electrokinetic chromatographic method [5].

Recently various electrochemical methods was used in analysis drugs in their formulations [6,7]. Potentiometric measurements using indicator and reference electrodes are widely used in determination of active ingredients in a formulation [8-11]. Potentiometry has advantages of rapid and ease of preparation and procedures, fast response time, reasonable selectivity, wide linear dynamic range, and low cost. These characteristics have certainly led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown largely over the past years [12-18].

PVC membrane electrodes are one of the subdivisions of potentiometric sensors which are widely used and have different application in analysis of ionic species [19-24]. The major problem of PVC membrane sensors is their low physical and mechanical resistance for long-term usage. Besides, carbon paste electrodes (CPEs) are another category of potentiometric sensors [25-30] that have high mechanical stability. They have attracted more attention than PVC membrane electrodes because of some advantages such as improved renewability, more stable response, lower ohmic resistance, no need for internal solutions and suitable ability for modification.

In this work, two different kinds of potentiometric sensor were used. Both electrodes work based on ion-pair which was made from the interaction between Letrozole and sodium tetraphenyl borate and they respond according to the ion-exchange mechanism. First, PVC membrane electrode was made after series of experiments. Next, a carbon paste electrode based on multi wall carbon nanotubes (MWCNTs) was designed to improve the mechanical stability and analytical responses.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell, where the Letrozole indicator electrodes (PVC membrane or carbon paste electrodes) were placed, consisted of two Ag/AgCl double junction reference electrodes (Azar-Elelectrode Co., Iran) internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision.

2.2. Materials and Reagents

Chemicals (of analytical reagent grade) were: high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), benzylacetate (BA) and tetrahydrofuran (THF) (Merck Co., Germany). All materials were of the highest available purity without further modification. Letrozoleand its pharmaceutical formulation were obtained from local pharmaceutical manufacturer (Tehran, Iran) as gift samples. The multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, core diameter: 5-10 nm, SBET: 40-600 m^2/g, V_{total}: 0.9 cm^3/g, bulk density 0.1 g/cm^3, true density 2.1 g/cm^3 and with 95% purity were purchased from a local company (Iran).

2.3. Preparation of the sensing element (ion-pair)

Sensing element used in both sensors was an ion-pair compound made from the interaction of Letrozole and sodium tetra phenyl borate. It was prepared by mixing about 20 mL of 0.01 M acidic solution of Letrozole with 20 mL tetraphenyl borate solution. The resulting precipitate was then filtered, washed with water and dried in room temperature [8-11].

2.4. Preparation of the Electrodes

2.4.1. PVC membrane electrode

General procedure to prepare PVC membrane was as follow: different amounts of ion-pair along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and the solution was mixed well into a glass dish of 2 cm diameter. Followed by THF was evaporated slowly until an oily concentrated mixture was obtained. A plastic tube (about 3 mm o.d.) was dipped into the mixture for about 10 s so a transparent membrane of about 0.3 mm in thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 5 h. Afterwards, the tube was filled with an internal filling solution (1.0×10^{-3} M of Letrozole acidic solution (pH=4.0)). The electrode was finally conditioned for 18 h by soaking in the same solution [8-11].

2.4.2. Carbon Paste Electrodes (CPEs)

General procedure for preparation of carbon paste electrode was as follows: various amounts of ion-pair along with appropriate amount of graphite powder, MWCNTs, paraffin oil, were thoroughly mixed. After homogenization of the mixture, the resulting paste was transferred into a plastic tube with 6 mm o.d. and a height of 3 cm. The paste was carefully packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistant. A copper wire was inserted into the opposite end of the CPE to establish electrical contact. External surface of the carbon paste was smoothed with soft paper. The electrode was finally conditioned for about 48 h by soaking it in a 1.0×10^{-3} M of Letrozole acidic solution [25-30].

2.5. Standard Letrozole solutions

A stock solution of 0.02 M Letrozole acidic solution (pH=4.0) was prepared. The working standard solutions (1×10^{-7} to 1×10^{-2} M) were prepared by appropriately dilution of the stock solution with distilled water.

2.6. The emf Measurements

Following cell assembly for the conduction of emf (electromotive force) measurements were used:

A: Ag-AgCl || internal solution, 1×10^{-3} M Letrozole solution | PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

B: CPE | sample solution || Ag-AgCl, KC1 (satd.)

These measurements were done using calibration of the electrodes with several standard solutions.

3. RESULTS AND DISCUSSION

3.1. PVC Membrane Composition Selection

Membrane composition effect on the potential responses of the electrode was tested. The operating characteristics of PVC membrane sensor can be significantly modified by changing the relative amount of the electrode membrane components [31-36].

Table 1. Optimization of PVC membrane ingredients

No.	Composition (%)			Slope (mV per decade)	LR (M)	DL (M)
	PVC	Plasticizer	Ion-pair			
1	30	NB, 67	3	15.6±0.4	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}
2	30	NB, 65	5	19.0±0.3	5.0×10^{-6}-1.0×10^{-2}	3.0×10^{-6}
3	30	NB, 63	7	17.0±0.3	1.0×10^{-5}-1.5×10^{-2}	1.0×10^{-5}
4	30	DBP, 65	5	14.2±0.3	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}
5	30	BA, 65	5	16.5±0.2	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}
6	30	NB, 70	0	4.2±0.5	5.0×10^{-4}-5.0×10^{-3}	-

The main components of a membrane are PVC matrix, plasticizer and the ion-pair as a sensing material. Each membrane component plays a special role in the membrane function and electrode response [37-42]. Previous studies shows that the membrane prepared with a plasticizer/PVC ratio about 2.2 can show the best performance [37,43]. As it can be seen in Table 1, the optimum amount of PVC was selected 30 mg.

Plasticizer mainly acts as a membrane solvent allowing homogeneous dissolution and diffusional mobility of the ion-pair inside the membrane. The plasticizer should be water-immiscible liquid of low vapor-pressure, compatible with PVC, no functional groups which can undergo protonation reactions. The selectivity of such electrode can be drastically influenced by the choice of the membrane solvent [44-49]. Nature of the plasticizer has a marked effect on analytical responses e.g. slope, linear domain and selectivity of PVC membrane electrodes. Here, three plasticizers with different polarity (dielectric constant) were tested, dibutyl phthalate (DBP with DC of 6.4), nitrobenzene (NB with DC of 35.7) and benzylacetate (BA with DC of about 5.7), as listed in Table 1. The electrode responses showed that membrane had NB better respond. NB had the lowest dielectric constant among the used plasticizers, and provided an effective linear range and a lower detection limit due to the better extraction of the polar Letrozole ions in the organic layer of the membrane.

As it can be seen from Table 1, absence of ion-pair in the membrane causes a very poor response (membrane no. 6), which confirm significance of the ion-pair. The electrodes behavior show that the best Nernstian slope is 19.0±0.3 mV per decade. It can conclude that Letrozole behave like a trivalent ion. This is expected from the structure of the Letrozole. As a conclusion, membrane no. 2 with the composition of 30% PVC, 5% ion-pair, and 65% NB was the optimum one for the sensor design.

3.2. Carbon Paste Composition Selection

Two kinds of carbon paste were made; modified and unmodified CPEs with a variety of compositions. The results for these CPEs are given in Table 2. The electrode composed of 20% paraffin oil, 20% ion-pair, and 60% graphite powder (no. 5) was found to be optimal for Letrozole carbon paste electrode.

This composition was selected for further examination. Multi-wall carbon nanotubes (MWCNTs) have been also used in the compositions of carbon paste electrodes due to their surprising physicochemical properties, such as ordered structures with high aspect ratios, ultra-light weight, high thermal conductivity, metallic or semi-metallic behavior, high surface area, high electrical conductivity and remarkable mechanical strength [27-30]. High conductivity of MWCNTs increases the dynamic working range and response time of the electrode. Addition of 5% MWCNT to the composition was found to increase the response to a Nernstian slope of about 19.7±0.3 mV per decade (no. 5). From Table 2, it was obvious that in the absence of ion-pair and presence of other components (no. 1), the response of the modified CPE was very low (slope of 2.1±0.6 mV per decade).

Table 2. Optimization of nano-composite carbon paste electrode composition

No.	**Composition (%)**				**Slope (mV per decade)**	**LR (M)**	**DL (M)**
	Graphite	Paraffin	Ion-pair	MWCNTs			
1	80	20	-	-	2.1±0.6	-	-
2	70	20	10	-	13.1±0.5	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}
3	60	20	20	-	16.9±0.3	5.0×10^{-6}-1.0×10^{-2}	5.0×10^{-6}
4	55	20	25	-	16.1±0.4	5.0×10^{-6}-5.0×10^{-2}	6.0×10^{-6}
5	55	25	20	-	15.4±0.4	1.0×10^{-5}-1.0×10^{-2}	1.0×10^{-5}
6	57	20	20	3	19.3±0.2	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}
7	55	20	20	5	19.7±0.3	1.0×10^{-6}-1.0×10^{-2}	1.0×10^{-6}
8	53	20	25	7	19.0±0.4	5.0×10^{-6}-1.0×10^{-2}	5.0×10^{-6}

3.3. Calibration Graph and Statistical Data

The measuring range of a potentiometric sensor is the linear part of the calibration graph as shown in Figure 2.

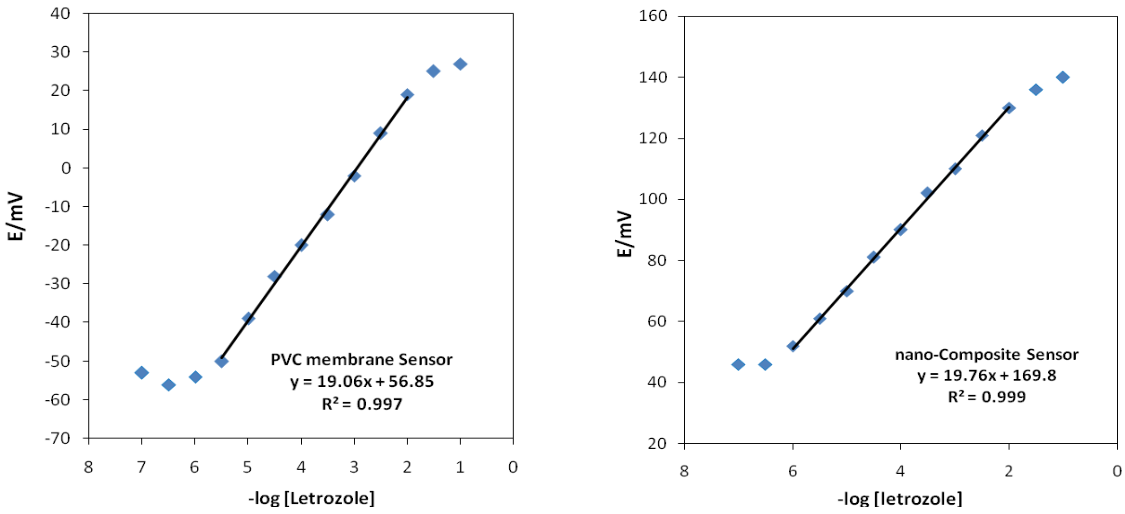

Figure 2. Calibration curves of CPE and PVC membrane electrode. The results are based on 5 replicate measurements.

Measurements could be performed in this lower range, but noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar to 10^{-6} or even 10^{-7} molar concentrations [39-48]. Calibration graph slope for PVC membrane electrode is 19.0 mV per decade of the Letrozole concentration and a standard deviation of ±0.3 mV after five replicate measurements. A linear response towards the Letrozole concentration was from 5.0×10^{-6}-1.0×10^{-2} M. Calibration graph slope for CPEs is 19.7 mV per decade of Letrozole concentration in the range of 1.0×10^{-6}-1.0×10^{-2} M with a standard deviation of ±0.3 mV after eight replicate measurements. Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of the PVC membrane sensor was 3.0×10^{-6} M and in case of nano-composite carbon paste electrode was 1.0×10^{-6} M which was calculated by extrapolating the two segments of the calibration curves.

3.4. Dynamic Response Time

Dynamic response time is the required time for the electrode to achieve values within ±1 mV of the final equilibrium potential, after successive immersions in the sample solutions [48-51]. Its calculation involved the variation and the recording of the Letrozole concentration in a series of solutions from 1.0×10^{-6} to 1.0×10^{-2} M. Both sensors were able to quickly reach its equilibrium response in the whole concentration range. This time for CPE was about 15 seconds and for PVC membrane electrode was about 20 s in concentrated solutions.

3.5. pH Effect on the Electrodes Response

To examine the effect of pH on both electrode responses, the potential was measured at specific concentration of the Letrozole solution (1.0×10^{-4} M) from the pH value of 1.0 up to 9.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment).

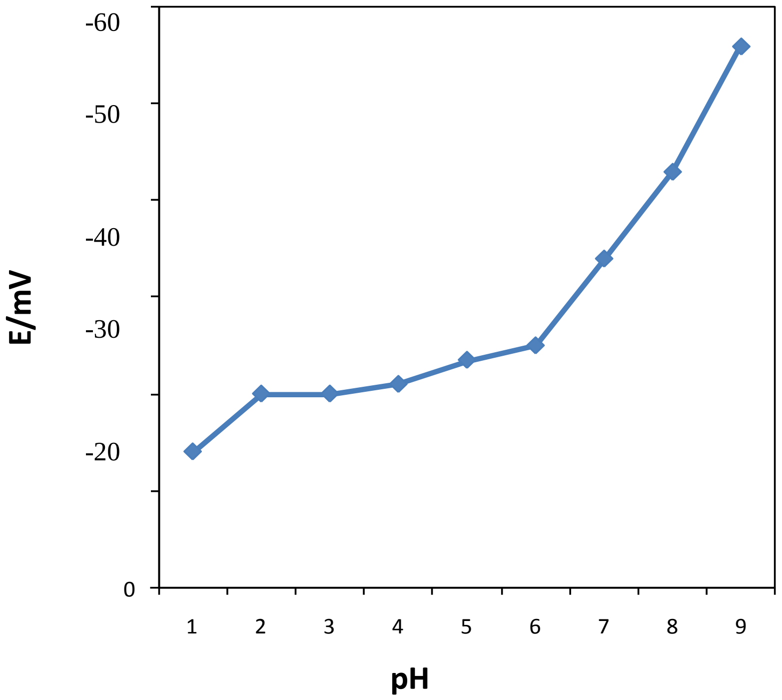

Figure 3. Applicable pH of the electrodes in the test solution of 1.0×10^{-4} M

The results showed that the potential remained constant despite the pH change in the range of 2.0 to 5.0, which indicates the applicability of this electrode in the specified pH range.

Relatively noteworthy fluctuations in the potential *vs.* pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 5.0 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 2.0 were caused by removal of the membrane ingredients or analyte in the solution. In both electrodes the same trend were observed.

3.6. Life-time Study

Both electrodes lifetime was estimated with the calibration curve, periodical test of a standard solution (1.0×10^{-6}-1.0×10^{-2} M) and calculation of its response slope.

Table 3. Lifetime of CPE and PVC membrane electrode

Week	PVC membrane Slope (mV per decade)	DL (M)	Nano-composite CPE Slope (mV per decade)	DL (M)
First	19.0	5.0×10^{-6}	19.7	1.0×10^{-6}
Second	18.9	5.5×10^{-6}	19.6	1.5×10^{-6}
Third	18.4	7.5×10^{-6}	19.5	2.0×10^{-6}
Fourth	18.0	8.9×10^{-6}	19.4	3.5×10^{-6}
Fifth	17.6	1.0×10^{-5}	19.2	5.8×10^{-6}
Sixth	15.4	5.7×10^{-5}	19.0	9.5×10^{-6}
Seventh	14.1	1.0×10^{-4}	18.5	2.8×10^{-5}
Eighth	13.0	3.5×10^{-4}	16.8	5.6×10^{-5}
Ninth	11.8	6.5×10^{-4}	15.0	7.1×10^{-5}
Tenth	9.9	9.0×10^{-4}	14.2	9.5×10^{-5}

For this estimation, three electrodes were employed extensively (1 hour per day) for 10 weeks. After 5 weeks utilization of PVC membrane electrode, two changes were observed: a slight gradual decrease in the slope and an increase in the detection limit. As it can be seen from Table 3, this time in case of carbon paste was 7 weeks which shows the long-term stability of this kind of sensor in comparison with PVC membrane electrodes.

In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response. While in CPEs the surface of the electrode are renewable and can be used for longer time.

3.7. Analytical Applications

Linearity, limit of detection, recovery test, selectivity, precision, accuracy, and ruggedness/robustness were the parameters used for the method validation of a sensor [45-51].

3.7.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 4). 10 tablets of Iran-Hormone Company (2.5 mg Letrozole/tablet) were thoroughly powdered. Then, the amount of 3 tablets was weighed carefully and was dissolved in 100-mL of acidic solution (pH=4). Then, the solution was centrifuged and the above solution was analyzed by the proposed sensors. The drug concentration was determined using calibration method. The results are in satisfactory agreement with the labeled amounts. The corresponding recovery percentage value varied from 93.2-97.5%.

Table 4. Potentiometric determination of Letrozole in pharmaceutical formulations

Sample	Labeled amount (mg/tab.)	Found by PVC membrane electrode* (mg/tab.)	Found by Nano-composite CPE* (mg/tab.)
Tablet 1	2.5	2.40±0.07	2.42±0.04
Tablet 2	2.5	2.32±0.08	2.37±0.05
Tablet 3	2.5	2.38±0.05	2.44±0.04

* The results are based on five replicate measurements

3.7.2. Selectivity

Table 5. Selectivity coefficients of various interfering compounds for Letrozole sensors

Interfering ion	Log K_{MPM} (PVC membrane electrode)	Log K_{MPM} (Nano-composite CPE)
Na^+	-3.5	-3.6
K^+	-4.0	-3.9
NH_4^+	-3.6	-3.5
Ca^{2+}	-4.1	-4.0
Mg^{2+}	-4.3	-4.4
Cl^-	-3.8	-3.9
NO_3^-	-4.3	-4.4
Lactose	-4.0	-4.1
Glucose	-4.1	-4.0

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices. The potentiometric selectivity coefficients of the Letrozole sensor were evaluated by the matched potential method (MPM). This method was described previously [52-58]. The resulting values of the selectivity coefficients are shown in Table 5. Note that all selectivity coefficients are about 10^{-3}, suggesting were interferences negligible in the performance of the electrode assembly.

3.7.3. Precision and accuracy

For repeatability monitoring, 5 replicate standard samples were measured. The RSD values by PVC membrane were 3.2, 4.1, and 3.4% and for nano-composite CPE were 3.8, 3.9, and 4.0%.

3.7.4. Ruggedness/Robustness

For ruggedness of the methods a comparison was performed between the intra- and inter-day assay results for Letrozole obtained by two analysts.

The RSD values for the intra- and inter-day assays in the cited formulations performed in the same laboratory by the two analysts did not exceed 4.7%. On the other hand, the robustness was examined while the parameter values (pH of the solution and the laboratory temperature) changed slightly. Letrozole recovery percentages were good under most conditions, and not showing any significant change when the critical parameters were modified.

4. CONCLUSIONS

In the present work, two types of potentiometric electrodes were constructed for determination of Letrozole. The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 3.0×10^{-6} M for PVC membrane electrodes and of 1.0×10^{-6} M potential responses across the range of 5.0×10^{-6}-1.0×10^{-2} M and 1.0×10^{-6}-1.0×10^{-2} M. The sensors enabled the Letrozole determination in pharmaceutical formulations. Both sensors respond based on ion-exchange mechanism. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 65% NB, and 5% ion-pair. Then, a carbon paste electrode was designed to improve the analytical responses. The best electrode was composed of 20% ion-pair, 20% paraffin, 5% MWCNTs and 55% graphite.

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