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PVC Membrane Sensor and Wire Coated Electrode for Determination of Flurazepam

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Flurazepam is a benzodiazepine derivative which possesses anxiolytic, anticonvulsant, sedative and skeletal muscle relaxant properties. This research introduces two kinds of PVC membrane sensor (symmetric and asymmetric) for determination of flurazepam (FLZ) in pharmaceutical formulation. For the membrane preparation, flurazepam-tetraphenyl borate ion-pair was employed as a sensing material in the PVC membrane. Several plasticizers were studied in the membrane composition dibutyl phthalate (DBP), acetophenon (AP), nitrobenzene (NB) and nitrophenyloctyl ether (*o*-NPOE). After a series of experiments, the best electrode performance was made of a membrane composed of DBP. The electrodes illustrated a fast, stable and Nernstian response over a wide flurazepam concentration range of 1×10^{-5} to 1×10^{-2} M in case of PVC membrane electrode and 1×10^{-6} to 1×10^{-3} M in case of wire coated electrode, in the pH range of 4.0–7.0. Validation of the method shows suitability of the sensors for use in the analysis of flurazepam hydrochloride in pharmaceutical formulation.

Keywords: Flurazepam, potentiometric sensor, PVC membrane, wire coated electrode, ion-pair

1. INTRODUCTION

Flurazepam (Figure 1), 7-Chloro–1-[2-(diethylamino)ethyl]-5-(2–fluorophenyl)-1,3–dihydro–2H-1,4–benzodiazepin–2–one, is a benzodiazepine derivative which possesses anxiolytic, anticonvulsant, sedative and skeletal muscle relaxant properties [1,2]. All benzodiazepines are lipophilic amides which are rapidly and efficiently desorbed after oral administration [3] and most commonly used as hypnotics [4]. Flurazepam is a very efficient hypnotic of relatively low toxicity

which could be easily substituted for barbiturates and methaqualone/diphenhydramine4 in the treatment of long-term insomnia [5,6].

Previously this drug has been determined by gas-liquid chromatography [7], capillary gas chromatographic-negative chemical ionization mass spectrometric method [8] and high-performance liquid chromatography [9]. However, the official method for analysis of this drug is HPLC method [1].

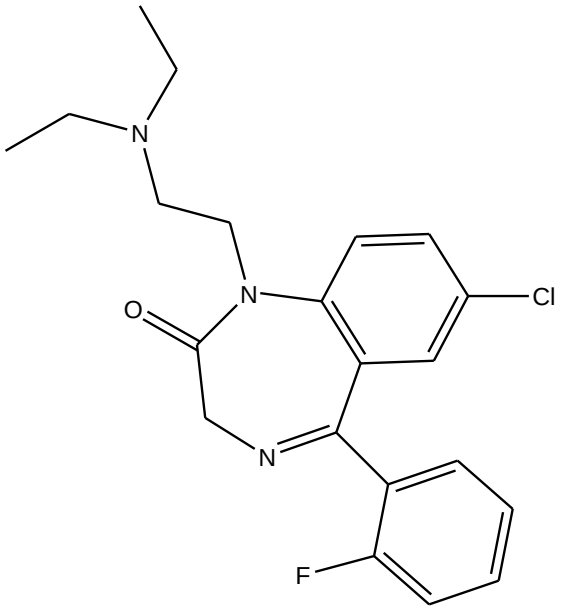

Figure 1. Chemical structure of flurazepam

Electrochemical techniques are recently used for analysis of drugs and poisons [10-13]. Potentiometric detection based on ion–selective electrodes (ISEs) offer the advantages of speed and ease of preparation and procedures, relatively fast response, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, portable and low cost [14,15]. These characteristics have inevitably led to the preparation of numerous sensors for several ionic species, and the list of available electrodes has grown substantially over the past years [16-26].

Literature survey shows that there is no report for flurazepam potentiometric electrode. Thus, in this work, we report a membrane sensor based on an ion-pair to determine flurazepam in its formulation samples with a nice Nernstian response over a relatively wide working range.

2. EXPERIMENTAL SECTION

2.1. Apparatus

R684 model Analion Ag/AgCl double junction reference electrode was used as internal and external reference electrode. The reference and indicator electrodes were connected to a Corning ion

analyzer with a 250 pH/mV meter with ±0.1 mV precision in order to measurement the potentials. The cell chamber was filled with an ammonium nitrate solution and 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

The necessary chemicals (of analytical reagent grade) were: high-molecular weight polyvinylchloride (PVC) (Fluka Co.), sodium tetraphenylborate (NaTPB), acetophenon (AP), dibutyl phthalate (DBP), nitrobenzene (NB), nitrophenyloctyl ether (o-NPOE) and tetrahydrofuran (THF) (Merck Co.). All the materials were at the highest available purity and were submitted to no further modification. Flurazepam hydrochloride and its pharmaceutical formulation were obtained from local pharmaceutical manufacturer (Tehran, Iran).

2.3. Preparation of sensing element

Ion-pair compound of flurazepam-tetraphenylborate (FLZ-TPB): About 10 mL of 0.01 M solution of Flurazepam hydrochloride was mixed with 10 mL of 0.01 M solution of tetraphenylborate under stirring. The resulting precipitate was filtered off, washed with water and dried [24, 27-31].

2.4. Preparation of the Electrodes

2.4.1. PVC membrane electrode

The general procedure to prepare the PVC membrane was as follow: Different amounts of the ion-pair along with appropriate amounts of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF), and the solution was mixed well.

The resulting 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 (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. The tube was then filled with an internal filling solution (1.0×10^{-3} M flurazepam hydrochloride). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M flurazepam hydrochloride solution [27-31].

2.4.2. Wire coated electrode

To make a wire coated electrode the same mixture as mentioned above was prepared. Then, wire electrode (from copper) was dipped into the mixture for about 5 s in order to form a transparent membrane. Then, they were removed from the mixture, retained at room temperature for at least 10 h. Then, it was soaked in a 10^{-3} M of flurazepam hydrochloride solution for 48 h [32-35].

2.5. Standard flurazepam solutions

A stock standard solution of 0.1 M flurazepam hydrochloride was prepared by dissolving 4.24 g of pure drug in 100 ml distilled water. The working solutions (1×10^{-7} to 1×10^{-2} M) were prepared by appropriate dilution of the stock solution with water.

2.6. emf Measurements

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

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

II: Copper (wire)-PVC membrane | sample solution || Ag-AgCl, KC1 (satd.)

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

3. RESULTS AND DISCUSSION

Since the sensitivity and selectivity degree of an ion-pair based electrode is greatly related to the membrane ingredients, the membrane composition influence on the potential responses of the flurazepam sensors was studied.

Actually, the operating characteristics of ISEs can be significantly modified by changing the relative proportions of the electrode membrane components. The main components of an electrode membrane of this type are PVC matrix, the plasticizer and the ion-pair. Each membrane component plays a special role in the membrane function [25-31].

3.1. PVC Membrane Composition Selection

The plasticizer mainly acts as a fluidizer, allowing homogeneous dissolution and diffusion mobility of the ion-pair inside the membrane. The nature and/or the amount of the plasticizer must be properly controlled in order to minimize the electrical asymmetry of the membrane and to limit fouling of the sensor.

The nature of the plasticizer has a marked influence on the response slope, linear domain and also on the selectivity of the PVC membrane electrodes. Here, many plasticizer types were tested, namely acetophenon (AP), dibutyl phthalate (DBP), nitrobenzene (NB) and nitrophenyloctyl ether (*o*-NPOE), as listed in Table 1.

After their evaluation, DBP, having the lower dielectric constant than other plasticizers was chosen to be employed in the sensor construction, because it provided an effective linear range and a

lower detection limit which is due to the better extraction of the flurazepam in the organic layer of the membrane [24-28].

Table 1. Optimization of the membrane ingredients

Membrane no.	PVC (% w)	Plasticizer (% w)	Ion-pair (% w)	Slope (mV/decade)	Linear range (M)	Detection Limit (M)
1	30	DBP, 66	4	53.6± 0.4	1.0×10^{-6} -1.0×10^{-2}	9.0×10^{-7}
2	30	DBP, 65	5	55.7± 0.3	1.0×10^{-6} -1.0×10^{-2}	7.0×10^{-7}
3	30	DBP,64	6	51.5± 0.3	5.0×10^{-6} -1.0×10^{-2}	2.0×10^{-6}
4	30	NB, 63	5	40.5± 0.3	1.0×10^{-5} -1.0×10^{-2}	1.0×10^{-5}
5	30	NPOE, 63	5	36.4± 0.2	5.0×10^{-5} -1.0×10^{-2}	5.0×10^{-5}
6	30	AP, 63	5	42.1± 0.4	1.0×10^{-5} -1.0×10^{-2}	8.5×10^{-6}
7	30	DBP, 70	-	4.3± 0.2	5.0×10^{-4} -5.0×10^{-3}	6.5×10^{-4}

As it can be seen from Table 1, the absence of the ion-pair in the membrane results a very poor response (membrane no. 7), which is shows the significance of the ion-pair. As a conclusion, the membrane no. 2 with the composition of 30% PVC, 5% ion-pair, and 65% DBP was the optimum one for the sensor design.

3.2. Wire coated electrode

Potentiometric membrane sensors, according to their construction, are categorized into two important group, symmetrical ion-selective electrodes, and asymmetrical ion-selective electrodes. Symmetrical ion-selective electrodes are classical electrodes in which the ion-selective membrane is placed between two solutions. In an asymmetrical ion-selective electrode, one side of the membrane is in contact with a solid phase while the other is exposed to the measured solution. Similar to the rest of the chemical sensors, a potentiometric wire coated electrode was composed of two basic parts; a transducer and an ion-sensitive receptor layer.

Table 2. Optimization of the membrane ingredients for wire coated electrode

No.	Composition, % (micro)				Slop (mV decade^{-1})	Linear Range (M)
	PVC	Plasticizer	FLZ-TPB	NaTPB		
1	25	DBP,70	5	--	32.7±0.5	5.0×10^{-6}-5.0×10^{-3}
2	25	DBP,68	5	2	54.6±0.4	1.0×10^{-6}-1.0×10^{-3}
3	25	DBP,69	5	1	43.6±0.3	5.0×10^{-6}-1.0×10^{-3}

The measurement of the electrochemical potential in the ion-selective membrane is conducted with the membrane incorporation into a transduction element. A transducer can be in the form of either a coated wire electrode or a device based on an ion-sensitive field effect transistor [32-35].

The best composition of the symmetric membrane was used for asymmetric one but the membrane concentration should be less viscose. As it can be seen from Table 2, the membrane no. 2 with the composition of 25% PVC, 5% ion-pair, 2% NaTPB and 68% DBP was the optimum one for the sensor design.

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 and 3 [34-40]. 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 [36-45]. Calibration graph slope for PVC membrane electrode is 55.7 mV per decade of the flurazepam concentration and a standard deviation of ±0.3 mV after eight replicate measurements (Figure 2). A linear response towards the flurazepam concentration was from 1.0×10^{-5}-1.0×10^{-2} M. Calibration graph slope for wire coated electrode is 54.6±0.4 mV per decade of flurazepam concentration in the range of 1.0×10^{-6}-1.0×10^{-3} M (Figure 3).

Detection limit was calculated from the intersection of two extrapolated segments of the calibration graph. In this work, detection limit of PVC membrane sensor was 1.0×10^{-5} M and in case of modified carbon paste electrode was 1.0×10^{-6} M which was calculated by extrapolating the two segments of the calibration curves.

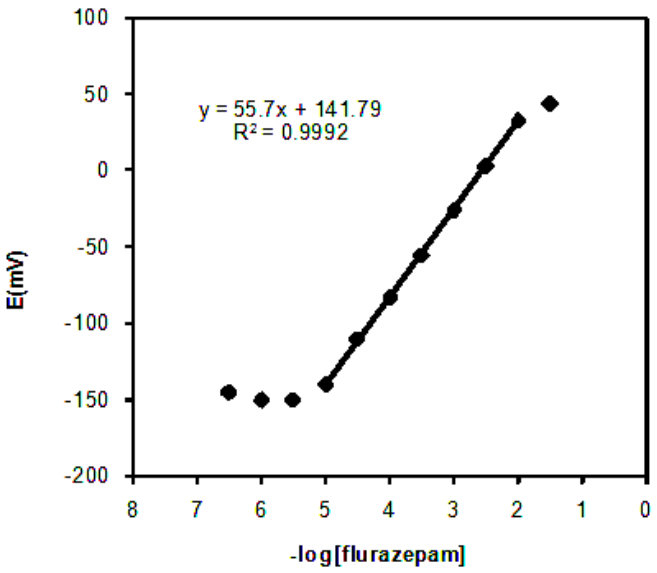

Figure 2. Calibration curve of the flurazepam PVC membrane electrode with the composition of the membrane no. 2. The results are based on 8 measurements.

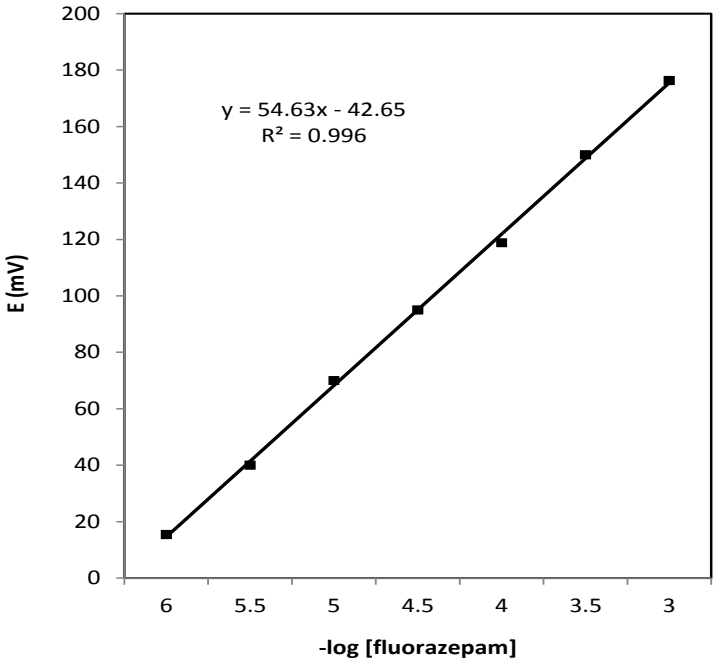

Figure 3. Calibration curve of the flurazepam wire coated with the composition of the membrane no. 2. The results are based on 8 measurements.

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 [46-52]. Its calculation involved the variation and the recording of the flurazepam concentration in a series of standard solutions. Both sensors were able to quickly reach its equilibrium response in the whole concentration range. The average time in the whole concentration range for wire coated electrode was about 15 seconds and for PVC membrane electrode was about 25 s.

3.5. pH Effect on the Electrodes Responses

To examine the effect of pH on both electrode responses, the potential was measured at a specific concentrations of the flurazepam solution (1.0×10^{-3} M) from the pH value of 2.0 up to 12.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment) [32-35]. The results showed that the potential remained constant despite the pH change in the range of 3.0 to 7.5, which indicates the applicability of this electrode in the specified pH range. The fluctuations above the pH value of 7.5 might be justified by removing the positive charge on the drug molecule. Fluctuations below the pH value of 3.0 were caused by removal of the ion-pair in the membrane 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 and calculation of its response slope. For this estimation, four electrodes were employed extensively (1 hour per day) for 10 weeks. After 6 weeks utilization of PVC membrane electrode, two changes were observed: a slight gradual decrease in the slope (from 55.5 to 44.1 mV/decade) and an increase in the detection limit (from 1.0×10^{-5} M to 9.3×10^{-4} M). This time in case of asymmetric membrane electrode was 6 weeks. In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response.

3.7. Analytical Applications

Linearity, limit of detection, recovery test, selectivity, precision, and accuracy were the parameters used for the method validation. As mentioned before, the sensors were measured between 1×10^{-5} and 1×10^{-2} M for PVC membrane electrode and 1×10^{-6} and 1×10^{-3} M for wire coated electrode. The calculated detection limit of the electrodes was 1.0×10^{-5} M (4.24 µg/mL) and 1.0×10^{-6} M (0.42 µg/mL), respectively.

3.7.1. Recovery Test from Tablet

The proposed sensor was evaluated by measuring the drug concentration in some pharmaceutical formulations (Table 3).

Table 3. Potentiometric determination of flurazepam in some pharmaceutical formulations

Samples	Labeled amount (mg/Cap.)	Found* (mg/Cap.) PVC membrane Electrode	Found* (mg/Cap.) Wire Coated Electrode
Sample I	15	14.7±0.4	14.6±0.6
Sample II	15	16.3±0.6	16.0±0.7
Sample III	15	15.7±0.6	15.5±0.8

* The results are based on triplicate measurements

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 97.7-108.8%.

3.7.2. Selectivity

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.

Table 4. Selectivity coefficients of various interfering compound for flurazepam sensor

Interference	Log K_{MPM} PVC membrane Electrode	Log K_{MPM} Wire Coated Electrode
Na^+	-3.13	-3.23
Cl^-	-4.31	-4.56
Br^-	-4.56	-4.41
I^-	-4.33	-4.26
Mg^{2+}	-4.24	-4.11
Ca^{2+}	-4.00	-4.06
K^+	-3.43	-3.51
glucose	-3.60	-3.63
ammonium	-3.22	-3.05

The potentiometric selectivity coefficients of the citalopram sensor were evaluated by the matched potential method (MPM) [53-55]. The resulting values of the selectivity coefficients are shown in Table 4. Note that all selectivity coefficients are about 1×10^{-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 of 4, 40, 400 µg/mL were measured. The mean concentrations by PVC membrane were 4.2±0.3, 44.6±2.7, 415.2±6.5 µg/mL with respective RSD values of 3.1, 4.5, and 1.8% and for wire coated electrode were 4.3±0.4, 45.3±3.0, 412.6±5.5 µg/mL with respective RSD values of 2.9, 4.2, and 1.5%.

4. CONCLUSIONS

Two kinds of potentiometric electrode were constructed for determination of flurazepam hydrochloride. The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 1.0×10^{-5} M (for PVC membrane electrode) and 1.0×10^{-6} M (for wire coated electrode) with potential responses across the range of 1.0×10^{-5}-1.0×10^{-2} M and 1.0×10^{-6}-1.0×10^{-3} M, respectively. The sensors enabled the flurazepam determination in pharmaceutical formulations. Both sensors respond based on ion-exchange mechanism. FlZ-TPB pair was employed as a sensing element in construction of both electrodes. The best PVC membrane electrode performance was achieved by a membrane composition of 30% PVC, 65% DBP and 5% ion-pair and in case of wire coated 25% PVC, 68% DBP, 2% NaTPB and 5% ion-pair.

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