

Full Paper

Monitoring of Risperidone in Pharmaceutical Formulations by a Novel Solid-Contact PVC Membrane Potentiometric Sensor

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Abstract- Risperidone (RSP) is an antipsychotic medication commonly used in the treatment of schizophrenia, schizoaffective and some forms of bipolar disorder. A novel RSP all-solid-state potentiometric membrane electrode (ASS-PME) was introduced for assay of risperidone active ingredient in dosage forms. The ASS-PME was made of a copper wire coated with a layer of conductive graphite-epoxy resin, a layer of carbon dots and finally a PVC sensing layer. The PVC layer was composed of 30% of PVC, 61% of dibutylphthalate (DBP) as solvent mediator, 2% of an ionic additive (sodium tetraphenyl borate (NaTPB)) and 7% of an ion-pair of RSP-TPB as a sensing material. The device worked well under laboratory condition and showed a Nernstian response of 58.2 ± 0.4 mV/decade from 1.0×10^{-7} M to 1.0×10^{-3} M of the analyte with lower detection limit of 8.3×10^{-8} M. The ASS-PME has excellent selectivity toward RIS in presence of excipients in its pharmaceutical dosage forms.

Keywords- Risperidone, Sensor, All-solid-state electrode, Potentiometry, Pharmaceutical formulations, Carbon dots

1. INTRODUCTION

Risperidone (RSP) is an antipsychotic drug which is commonly used in the treatment of schizophrenia, schizoaffective and some forms of bipolar disorder [1-4]. This medication is also used to treat irritability in individuals with autism. It is a special monoaminergic antagonist with a high affinity for dopamine type 2 and serotonin type 2 receptors [4-8].

As shown in Fig. 1. RSP contains the functional groups of benzisoxazole as part of its structural formula which is important antipsychotic medication chemical group [9-10].

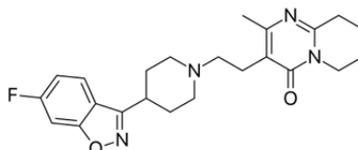


Fig. 1. Chemical structure of Risperidone (RSP)

Risperidone is available as a tablet, an oral solution, and an ampule. Numerous analytical methods have been applied for RSP assay in pharmaceutical formulations and biological fluids, such as ultraviolet spectrometry [11], FT-Raman spectroscopy [12], polarography [13], chemiluminescence [14], colorimetry [15], capillary electrophoresis [16], high performance liquid chromatography [17], solid phase extraction [18] and electrochemical methods [19]. Most of these techniques are valid methods which have enough accuracies and precisions to be applied for analysis of RSP in complex matrixes such as urine or plasma samples. For active ingredient analysis of a dosage form, which is a simpler matrix, however, there can be some faster, simpler and cost-effective methods. Also, in many cases such as dissolution study of a formulation, there is a need to online and continuous monitoring of the active ingredient release from a formulation. One successful offer is potentiometric sensor.

Potentiometric sensors have been introduced and reported for many medications and ions from many years ago [20-35]. They can be used in a rather wide linear range, normally from 10 μM to 1 M. This range may not be suitable for low concentration levels of drugs in biological fluids but can be accurately used for analyses of dosage forms. Recently, by using some materials or nanomaterials, or even changing the indicator electrode structure extension of the linear range has been possible. One kind of electrodes in this regard are all-solid-state (ASS) electrodes. Normally in making potentiometric sensors, two trends can be used. In first one, a PVC membrane placed between two solutions (standard internal solution and unknown external solution). This kind of assembly is called symmetric electrodes. In second trends, the membrane placed on a conducting solid material such as a graphite rod or a copper wire. However, to have a better contact interface for sticking the polymeric membrane, epoxy-resin is used. And for keeping up the conduction, graphite powder is mixed with epoxy-resin. Sometimes a layer of conducting polymer is used instead. Lack of internal solutions in

asymmetrical electrodes leads to lowering detection limits, increasing mechanical stability and life time due to the decreasing the risks of its leaking membrane ingredients. The enhanced mechanical stability on the other hand makes it possible to make more flexible electrodes, and makes it possible to produce disposable sensors.

In this work, we tried to make a potentiometric sensor, both symmetric and asymmetric ones, for risperidone chemical medication. The best membrane composition obtained by symmetric PVC membrane electrode (PME), was immobilized on a solid contact. The solid contact is a copper wire coated with a layer of conductive polymeric composite of graphite-epoxy-resin and a layer of carbon dots (CDs) as the ASS part. Then, a layer of a PVC membrane covered on ASS to provide the membrane sensor. CDs is a term used for nano-sized carbonic materials. CDs have been generally used for photoluminescence applications. However, additional exceptional properties of CDs including easily preparation and functionalization, larger surface area, more active site and accessible edge, high speed of electron transport leads to their applications in designing electrochemical sensors as better transducer materials. The proposed sensor, finally was applied for the RSP active ingredients analysis of some pharmaceutical formulations.

2. EXPERIMENTAL SECTION

2.1. Reagents

Analytical reagent grade, tetrahydrofuran (THF), dibutyl phthalate (DBP), and sodium tetrapenyl borate (NaTPB), graphite powder (1–2 μm particle size) and all nitrate or chloride salts of the cations used were from Merck Co. and used without any further treatment. High molecular-weight polyvinylchloride (PVC) was obtained from Fluka Co. and Macroplast Su 2227 epoxy and the desmodur RFE hardener were from Henkel Co. and Bayer Ag (Germany).

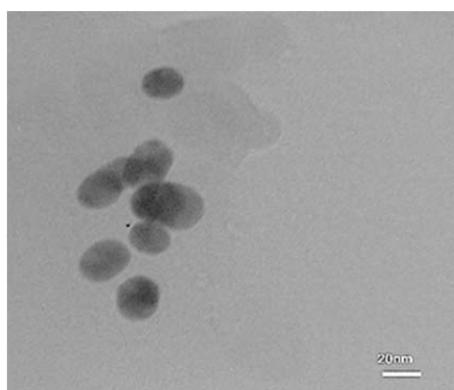


Fig. 2. CDs TEM image

Risperidone active ingredient was obtained as a gift sample from a local pharmaceutical Company in Iran. Its pharmaceutical samples were bought from local pharmacy. Carbon dots were synthesized as explained elsewhere [36]. Briefly, 2 g of citric acid was heated up to 200 °C while stirring. After 5 min, citric acid was melted and its color gradually changed from colorless to pale yellow. After 20 min, the liquid converted to a light orange which is CDs. The related TEM image of the produced CDs was shown in Fig. 2.

2.2. Ion-pair preparation

The ion-pair material was prepared through mixing acidic solution of RSP in HCl (0.01 M) and a solution of a suitable organic salt, here, sodium tetraphenyl borate (NaTPB). The organic salts which have hydrophobic large anions and small inorganic cations are usually applied as a precipitating reagent in inorganic or organometallic studies. Ion-pair compound was synthesized by adding of the organic salt solution (40 mg in 5 mL distilled water) to RSP solution (40 mg in 15 mL acidic solution). The formed precipitate was filtered, and washed with distilled water, then dried in room temperature.

2.3. Preparation of PME and ASS-PME

For construction of both kind of symmetric and asymmetric sensors, a polymeric membrane is needed. The membrane was composed of a certain amount of ion-pair, and appropriate amount of PVC, a plasticizer and ionic additive. They were mixed in about 2 mL of tetrahydrofuran (THF). Then, by heating slowly, THF was evaporated and an oily concentrated solution was formed.

For PME, a plastic tube (with ~3 mm o.d.) was dipped into this oily solution kept about 10 s till a transparent membrane formed. Then, the tube was pulled out and kept at room temperature for 5 h to dry the membrane at the end of tube. Following, the tube was filled by an internal filling solution (1.0×10^{-3} mol L⁻¹ of RSP.HCl) and conditioned in the same solution for about 15 h [35-40].

For ASS-PME, surface of a copper wire was covered with a conductive polymeric composite layer made of graphite-incorporated epoxy resin. Graphite powder, epoxy, and hardener were mixed in various amounts. The best all solid-state contact material was prepared by mixing 0.30 g (30% w/w) of epoxy resin, 0.15 (15% w/w) of hardener and 0.55 g (55% w/w) of graphite powder in THF solvent and after mixing, the solution was left to stand about 20-30 min in air for aging. Then, the viscose mixture was put on the surface of a copper wire (0.5 mm diameter and 15 cm length) which was polished well through dipping in to the solution for about 10 times. Thus, the wire was covered with the black mixture, and then let it dried for about 10 h [26-29]. Next, a layer of CDs was placed on the prepared electrode by dropping 5 µl of CDs aqueous solution and let it dried under IR-lamp. The solid-state contact material was then immersed into the polymeric membrane solution

as described above for 3 times and then allowed to dry in air for 24 h. Finally, prepared ASS-PME was conditioned in a 10^{-3} M solution of RSP.HCl.

2.4. Preparation of RSP solutions

Since RSP is a practically insoluble in water, but freely soluble in dilute acidic solutions, and because for potentiometric measurements, cationic form of RSP is needed, a solution of 0.1 M of the drug was prepared in HCl 0.01 M and used as stock solution. Then, by appropriate dilution of this solution, and adjusting the pH, working standard solutions from 1×10^{-8} to 1×10^{-2} M were prepared. The solutions were kept in refrigerator (4 °C) when not in use.

For pharmaceutical dosage analysis, 20 tablets of RSP were thoroughly powdered. Amounts equivalent to the weight of 5 tablets (each tablet contain 4, 2, 1 mg RSP) were weighed carefully and transferred into a 100-mL volumetric flask, shaken and diluted with acetate buffer (0.1 mol L⁻¹; pH=4). Suitable amounts of this solution were filtered through a Millipore filter (0.45 mm). This solution was used as a stock solution.

2.5. Potentiometric measurements

PME or ASS-PME were used as indicator electrodes in a potentiometric measurement by calibration method. A reference electrode (Ag/AgCl; Azar-Electrode Co., Iran) were connected to an ion analyzer (with a 250 pH/mV meter with ± 0.1 mV precision) also used. The below cell assembly shows the potentiometric measurements:

For PME:

Ag-AgCl || internal solution, 1×10^{-3} M RSP.HCl solution | PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

And For ASS-PME:

Cu wire | ASS layer/CDs | PVC membrane | sample solution || Ag-AgCl, KCl (satd.)

3. RESULTS AND DISCUSSION

The main part of a potentiometric polymeric membrane sensor is the composition of the membrane. Here, also the most important part of PME and ASS-PME is their polymeric membrane composition which contain the sensing material. The ingredients used in the membrane can directly affect the performance of the sensor.

3.1. Composition of Polymeric Membrane

Constituents of a membrane are a sensing material, a plasticizer, a polymeric matrix and

sometimes a suitable ionic additive. Type, amount and the ratio of each components should be optimized to achieve a best sensor response. Table 1 lists the various membrane compositions tested to find the best one. PVC is used as polymeric matrix. The ratio of the plasticizer to the polymer is normally something between 2 to 2.2 [20-35]. According to the previous studies on drug potentiometric sensors, 30%wt. PVC, and dibutyl phthalate (DBP) were used for all the membranes presented in Table 1.

Table 1. Compositions of the membranes used in preparation of RSP sensor

No	Composition of the membrane			Characterization of PME			
	Plasticizer	Ion-pair	Ionic Additive	Slope (mV/decade)	Linear Range (M)	Detection Limit (M)	Response time
1	DBP,67	3	-	12.7±0.7*	2.5×10 ⁻⁴ -1.0×10 ⁻³	3.0×10 ⁻⁴	1.5 min
2	DBP,65	5	-	30.2±0.5	1.0×10 ⁻⁴ -1.0×10 ⁻²	8.0×10 ⁻⁴	1 min
3	DBP,63	7	-	44.7±0.6	5.0×10 ⁻⁴ -5.0×10 ⁻¹	4.0×10 ⁻⁴	53 s
4	DBP,61	10	-	45.1±0.7	5.0×10 ⁻⁴ -5.0×10 ⁻¹	5.0×10 ⁻⁴	62 s
5	DBP,62	7	1 NaTPB	44.5±0.6	3.2×10 ⁻⁴ -5.0×10 ⁻¹	2.0×10 ⁻⁴	45 s
6	DBS,61	7	2 NaTPB	57.3±0.5	1.0×10 ⁻⁴ -1.0×10 ⁻¹	5.0×10 ⁻⁵	32 s
7	DBS,60	7	3 NaTPB	57.2±0.5	1.0×10 ⁻⁴ -1.0×10 ⁻¹	8.0×10 ⁻⁵	35 s
8	DBS,68	0	2 NaTPB	3.5±0.7	1.0×10 ⁻⁴ -1.0×10 ⁻³	5.0×10 ⁻⁴	2 min

*standard deviation of five repeated measurements

Membrane solvent called plasticizer is an ingredient used to plasticize the membrane. It is a water-immiscible organic solvent which has low vapor-pressure. The mobility of the sensing material in the membrane can be affected by the nature of the plasticizer. The plasticizer should be compatible with PVC and has no functional groups to protonate during the interactions. Variety of plasticizers having different dielectric constants can be used in the membrane. Dibutyl sebacate (DBS; DC: 4.5), dibutyl phthalate (DBP; DC: 6.4), nitrophenyloctyl ether (*o*-NPOE; DC: 24), nitrobenzene (NB; DC: 35.7) and benzylacetate (BA; DC: 5.7) were used. However for drug molecule which are hydrophobe ions, as studied in previous works, DBP showed the better response in the membrane. RSP cation is also a hydrophobic cation, thus, DBP helps the better extraction of this organic cation in to the membrane. Ionic additives are components of the membrane can be used to reduce the Ohmic resistance of the membrane. They should be used as small amounts if higher amounts are added to the membrane, it may acts as ion-exchanger to and lower the limit of detection of the sensor. As seen from data in Table 1, a membrane which has no sensing material, has no response (membrane no. 8). Therefore, membrane no. 6 with 7% ion-pair, 61% DBP, 30% PVC, and 2% NaTPB shows the Nernstian behavior with slope of 55.8±0.6 mV per decade.

This membrane composition was used for next studies and in preparation of ASS-PME.

3.2. Calibration curves

Different concentrations of the RSP HCl (one decade difference in concentration) were measured by the proposed sensors. Based on the Nernst equation, E vs. $-\log [\text{RSP}]$ was drawn (Fig. 3). The linear section of the curves is the linear range (LR) of the sensor response. Most of the PME sensors for pharmaceutical compounds have a linear range of 10^{-2} to 10^{-5} M. Here, in case of PME, the linear range of the sensor was 1.0×10^{-4} – 1.0×10^{-1} M of the RSP concentration with a Nernstian slope of 57.3 ± 0.5 mV/decade. In case of ASS-PME, which is an asymmetric sensor as explained in introduction, a LR of 1.0×10^{-7} to 1.0×10^{-3} M with slope of 58.2 ± 0.4 mV/decade. Through extrapolating two sections of the calibration curves, DL of the polymeric membrane sensors were calculated 5.0×10^{-5} M and for PME and 8.3×10^{-8} M for ASS-PME.

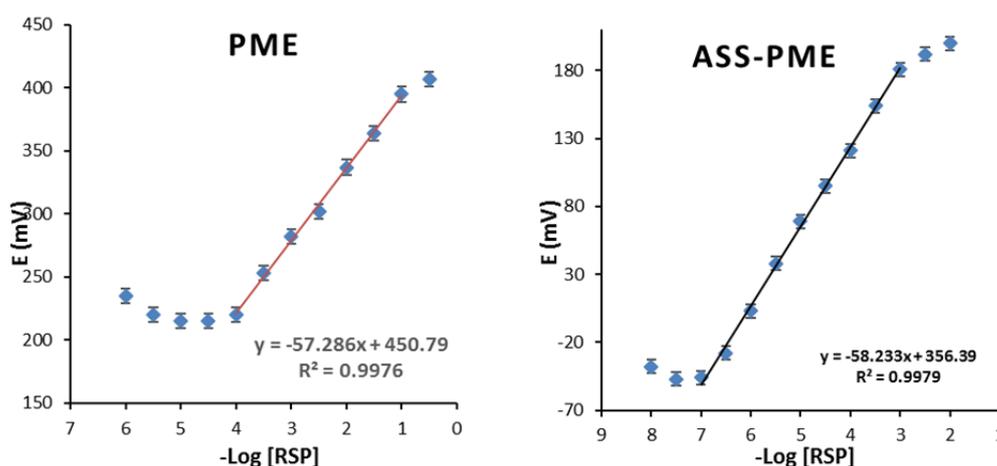


Fig. 3. Calibration curves of RSP potentiometric sensors; each points are averaged of five replicate measurements

3.3. Response Time

Response time of a potentiometric sensor is the time takes to reach the ± 1 mV of the final potential. It can be obtained after successive immersions of the sensors in the analyte solutions. Here, the RSP concentration was changed from 1.0×10^{-7} to 1.0×10^{-3} M continuously and the times were recorded. Sensor was able to quickly reach its equilibrium response in the whole concentration range. The response time was about 15 s in case of PME and about 22 s for PME-ASS.

3.4. pH Effect on the potential response of the sensors

PH effect on the potential responses of the sensors was tested in the RSP solution (1.0×10^{-5} M) when the pH was changed from 1.0 to 10.0 (adjusted by concentrated NaOH or HCl solutions). As can be seen in Fig. 4, potentials stayed constant upon pH changes in the range of 3.0 to 7.0, in both types of sensor which shows the applicability of these electrodes in the this pH range.

Changes in the potential above and below the pH ranges can be due to the removing the positive charge on the cations of the drug molecule and lessening the solubility of the drug in the solution and by removing of the membrane components or the analyte in the solution, respectively.

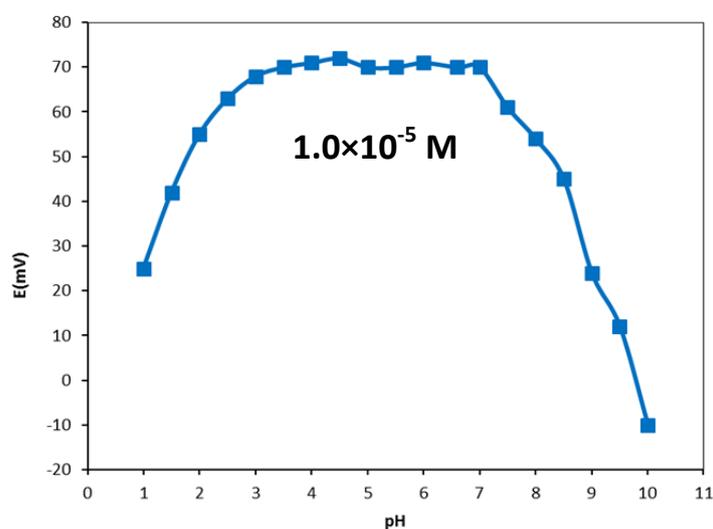


Fig. 4. pH range of the electrodes performance in the solutions of 1.0×10^{-5} M for ASS-PME

3.5. Life-time

Lifetime of a potentiometric sensor can be evaluated using the Nernstian slope and detection limit. For this purpose, three electrodes were used for 1 h per day within 10 weeks. The common lifetime of the reported potentiometric sensors is in the range of 4–10 weeks [37]. The results have been summarized in Table 3.

As it can be seen, after 7 weeks usage of the sensor, the slope gradually decreased and the detection limit were increased. ASS-PME shows a longer life-time than PME sensors. The changes can be seen after 9 weeks. In general the mechanical stability of the PME are too less than ASS-PME. Losing of the membrane ingredients into the solution by several times of usage, causes such limitation of the sensors.

Table 3. Lifetime of ASS-PME

Week	ASS-PME	
	Slope (mV/decade)	DL (M)
First	57.2±0.5	8.3×10 ⁻⁸
Second	57.2±0.6	8.5×10 ⁻⁸
Third	56.8±0.4	9.0×10 ⁻⁸
Fourth	56.7±0.5	9.6×10 ⁻⁸
Fifth	56.8±0.3	9.5×10 ⁻⁸
Sixth	56.5±0.3	1.5×10 ⁻⁷
Seventh	56.1±0.6	3.0×10 ⁻⁷
Eighth	55.7±0.4	4.2×10 ⁻⁷
Ninth	55.0±0.6	7.3×10 ⁻⁷
Tenth	41.5±0.7	1.0×10 ⁻⁵

3.6. Analytical characterization of the sensors

To show the analytical applicability of the prepared sensors, they were used in the determination of RSP in pure solution and in pharmaceutical tablets. There are some parameters which should be applied for validation a sensor including linear range, detection limit, selectivity, precision, accuracy, and ruggedness/robustness.

Table 4. Measurement of RSP.HCl in pharmaceutical formulations by the proposed sensors and standard methods

Sample	Labeled amount (mg/tab.)	Found by the ASS-PME* (mg/tab.) n=5	Standard method n=5	t-test (p-value: 0.05; t _{theoretical} : 2.31)
Sample 1	2	1.91±0.22	1.88±0.17	t _{experimental} = 0.24
Sample 2	2	2.10±0.24	2.05±0.14	t _{experimental} = 0.40
Sample 3	2	2.21±0.31	2.17±0.22	t _{experimental} = 0.23

* Averages of five repeated measurements

The proposed sensors were used in analysis of RSP in some tablets (Table 4). Calibration method was used to determine RSP content of tablets. There is no significant difference among the results of the proposed method and labeled amounts and HPLC standard method.

One of the most important parameter of each sensor is its selectivity. The selectivity of

an ion-selective electrode is tendency of the sensing element to the analyte in the presence of interfering species. The selectivity is stated as selectivity coefficient in potentiometric sensors. Various methods have been reported for determination of the selectivity coefficients. Here, they were calculated by the matched potential method (MPM) [48,49]. The obtained selectivity coefficients are presented in Table 5. According to the resulted data, the interferences from ionic and non-ionic species in RSP determination are not significant.

Table 5. Selectivity coefficients obtained for RSP ASS-PME

Interfering species	ASS-PME
	Log (K_{MPM})
Na ⁺	-3.2
K ⁺	-3.3
NH ₄ ⁺	-2.5
Ca ²⁺	-3.5
Mg ²⁺	-3.6
Cl ⁻	-3.2
NO ₃ ⁻	-4.3
Lactose	-4.7
Glucose	-4.5

Repeatability of the sensors was calculated using three standard synthetic samples. The samples were measured repeatedly. RSD% obtained for PME was 3.55 and for ASS-PME 3.11%. Ruggedness of the method was performed by comparing the results of the experiments which done by two analysts intra- and inter-day in the same laboratory. RSD% calculated for two analyses did not exceed 4.6% for PME and 3.7% for ASS-PME. Robustness was obtained while the important parameters (i.e. pH of the solution and the laboratory temperature) changed slightly. RSP recovery% were good under most conditions, and show no significant change when the critical parameters were changed.

4. CONCLUSION

Paroxetine which is a selective serotonin reuptake inhibitors (SSRIs) prescribed as an antidepressant compound was measured by a PVC membrane electrode (PME), and all solid state polymeric membrane electrodes (ASS-PME). An ion-pair based polymeric membrane was used in construction of the both sensors and the best membrane composition was obtained by a liquid membrane composed of 7% RSP-TPB, 61% DBP, 2% NaTPB, 30% PVC. The all-solid-state electrode is made based on a layer of CDs, a layer of conductive composite of graphite, and epoxy resin on a copper wire. A thin layer of PVC membrane is then coated on the surface of the new conducting transducer. The Nernstian behavior (slope

of 57.3 ± 0.5 mV/decade in case of PME and 58.2 ± 0.4 mV/decade for ASS-PME) can be seen in a wide concentration range of 1.0×10^{-4} to 1.0×10^{-2} M for PME, 1.0×10^{-7} to 1.0×10^{-3} M for ASS-PME. Validation of the method was done and showed applicability of the sensors for the quality control analysis of risperidone in pharmaceutical formulations.

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