

Full Paper

Quantitative Determination of Duloxetine Hydrochloride in Biological Samples of Blood Serum and Urine Using a Novel Potentiometric Sensor

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Abstract- In this work, a potentiometric sensor was developed based on polyvinyl chloride (PVC), duloxetine tetraphenylborate ion pair, various plasticizers of dioctyl phthalate (DOP), benzyl butyl phthalate (BBP), di(2-ethylhexyl)phthalate (DEPH), tris(2-ethylhexyl) phosphate (TEPH), dibutyl butyl phosphonate (DBBPh), dibutyl phthalate (DBP), dioctyl sebacate (DOS), dibutyl sebacate (DBS), 2-nitrophenyl octyl ether (NPOE) and di-octyl phthalate (DOPH) and THF as membrane solvent. The electrode responses at various contents of PVC and plasticizer were recorded to optimize their percentage compositions, and the best Nernst response (59.7) was obtained. The linear concentration range for this electrode made by optimal composition is 0.7 μM to 0.1 M with a detection limit of 0.3 μM . The response time of the ion-selective electrode based on the duloxetine-tetraphenylborate ion pair was determined. The effect of pH on the potential of duloxetine hydrochloride (DHCl) solution with a concentration of 1.0 mM was studied. Moreover, the performance of the prepared electrode was studied over two months to investigate the constructed membrane electrode's stability. The selectivity coefficients of the electrode for determination of DHCl in the presence of some ions and molecules including Na^+ , K^+ , Li^+ , Ni^+ , Mg^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} , Fe^{2+} , Ca^{2+} , Cu^{2+} , Co^{2+} , Cr^{2+} , ascorbic acid, D-fructose, sucrose, aspartic acid, L-H-histidine, dopamine, glucose, uric acid, propranolol, dexamethasone and melatonin were determined using a separate solution method (SSM) and an adapted potential method. The application of the proposed sensor to determine DHCl in two biological matrices, including blood serum and urine samples, was also investigated.

Keywords- Potentiometric sensor; Ion selective electrode; Duloxetine hydrochloride (DHCl); Duloxetine tetraphenylborate ion pair; Polyvinyl chloride (PVC)

1. INTRODUCTION

Major depressive disorder is treated with duloxetine hydrochloride (DHCl, see Figure 1), also known chemically as (+)-(S)-N-methyl-(1-naphthoxy)-2-thiophenepropylamine hydrochloride (MDD). It is a selective inhibitor of norepinephrine and serotonin reuptake (SSNRI) [1]. The US Food and Drug Administration has approved this medication to treat diabetic polyneuropathy. The indications for this medication include treating fibromyalgia, generalized anxiety disorder, and, most recently, stress urine incontinence [2].

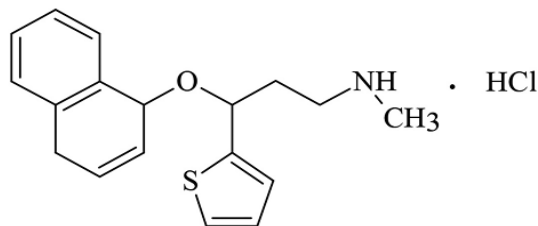


Figure 1. Chemical structure of duloxetine hydrochloride

There are numerous quantitative analytical techniques for detecting DHCl in biological fluids and human medicinal products that have been documented, some of which are: Reverse phase chromatography method [2,3], high-performance liquid chromatography [4,5], potentiometric methods [6], mass spectrometry (MS) and sequential liquid chromatography-mass spectrometry (LC-MS) [7] and spectrofluorometry method [8,9]. Although these techniques are not delicate, complex, or expensive, they involve sample preparation and laborious liquid-liquid or solid-phase extraction processes before analysis. It should be said that some chromatographic methods are time-consuming, costly, and incompatible with the environment. The cheaper, simpler, and more accessible electrochemical methods can be used instead. On the other hand, due to their rapid reaction, high sensitivity, and low cost, electroanalysis techniques might be seen as practical and straightforward for determining pharmaceutical substances in various matrices [10].

Ion-selective electrodes (ISEs) are an essential class of chemical sensors widely used in several typical applications, including laboratory medical devices. The potential difference between two electrodes in no-current situations is measured by potentiometric ion sensors or ion selective electrodes (ISE), and it should be highlighted. The potentiometric cell consists of an ISE whose potential is very sensitive to a specific ion to be measured and less or no sensitivity to other interferences. ISEs allow quick, low-volume assessments of these clinically significant analytes that are sensitive, trustworthy, and affordable [11]. Cellulose acetate (CA), polysulfone (PSF), polyvinylidene fluoride (PVDF), polyether sulfone (PES), polyacrylonitrile (PAN), polyetherimide (PEI), polypropylene (PP), and polyvinyl chloride (PVC) are the most popular polymer materials used to produce membranes [12]. PSF, PVDF, and PES cannot be regarded as inexpensive components for producing universal membranes out of this group of

polymers. However, when utilizing organic solvents, membranes made of inexpensive polymers, like PP, have poor chemical resistance. PVC is a cheap membrane material with suitable chemical characteristics, physical stability, and thermal stability. The ability of PVC to produce films, its outstanding resistance to acids, bases, and solvents, and its good solubility in various organic solvents, make it a desirable material. Using PVC-based membranes in membrane separation processes is particularly cost-effective because PVC is a reasonably inexpensive polymer [13]. As a result, PVC-based membranes for use in numerous membrane separation processes, including liquid filtration, ion exchange, gas separation, evaporation, and PVC-based polymer membranes, have drawn much interest [13]. Also, electrodes modified with nanomaterials have been considered due to increased sensitivity, amplified response signals, and more acceptable reproducibility [14-16]. In 2012, Ammar et al. prepared a PVC membrane using a duloxetine-silicomolybdate ion pair complex and dioctyl phthalate plasticizer for designing DHCl ion-selective membrane electrode. This electrode has a fast, stable, and Nernst response in a wide concentration range of DHCl (10 μM to 10 mM) with a concentration gradient of 59.140 mV dec^{-1} , a wide working pH range (4.3 to 8.4) and fast response time (< 15 s) [14]. Alarfaj et al. (2012) designed a disposable electrode system to determine DHCl using screen printing technology. The proposed sensors worked satisfactorily in the concentration range of 1.0 μM to 10.0 mM with a detection limit of 50 μM and a lifetime of 6 months [6]. In 2018, Attia et al. introduced and validated a rapid voltammetric method for determining DHCl through a new electrochemical sensor applying square wave voltammetry and cyclic voltammetry. The response was obtained in the linear range of 3.0 μM to 0.2 mM, and the detection limit of 0.4 μM was obtained [15]. The proposed method successfully determined DHCl's active pharmaceutical preparation and spiked urine. Manrique et al. (2020) used a cathode-pretreated boron-doped diamond electrode to determine small amounts of DHCl by differential pulse voltammetry. This drug was determined with the detection limit of 5.87 nM to the concentration range of 0.030 to 0.333 μM [16].

2. EXPERIMENTAL SECTION

2.1. Chemicals

In this work, all chemicals were of analytical quality, and all solutions were made with double-distilled (deionized) water. The pure form of duloxetine hydrochloride was purchased from Iran's Daru Parseh Company. Poly vinylchloride (PVC), dioctyl Phthalate (DOP), benzyl butyl phthalate (BBP), di(2-ethylhexyl)phthalate (DEPH), tris(2-ethylhexyl) phosphate (TEPH), dibutyl butyl phosphonate (DBBPh), dibutyl phthalate (DBP), dioctyl sebacate (DOS), dibutyl sebacate (DBS), 2-nitrophenyl octyl ether (NPOE) and di-octyl phthalate (DOPH) and tetrahydrofuran (THF) solvent were obtained from Merck company.

2.2. Apparatus

Potentiometer/pH meter device of Zag-Shimi company (model 162) made in Iran was used to measure the potential difference between the manufactured electrode and the reference electrode (Ag/AgCl|KCl(sat)|). Metrohm potential/pH meter model 827 (Switzerland) was applied to adjust and measure pH. A polymer pipe with an aperture diameter of 2 mm and a length of 5-7 cm was utilized to deposit a PVC membrane, and a magnetic stirrer (Zag-Shimi Company, Iran) was employed to mix samples.

2.3. Preparation of sensor

About 50 ml of 0.01 M DHCl solution and 50 ml of 0.01 M sodium phenylborate solution were combined to create the ion pair. A white precipitate was obtained, washed with distilled water after filtering, and stored at 50 °C dried up. The resulting residue was used in the preparation of the DHCl ion-selective electrode. To prepare a sensor sensitive to DHCl hydrochloride, desired amounts of PVC, duloxetine tetraphenylborate ion pair, various plasticizers such as Dioctyl Phthalate (DOP), benzyl butyl phthalate (BBP), di(2-ethylhexyl)phthalate (DEPH), tris(2-ethylhexyl) phosphate (TEPH), dibutyl butyl phosphonate (DBBPh), Dibutyl phthalate (DBP), Dioctyl sebacate (DOS), Dibutyl sebacate (DBS), 2-nitrophenyl octyl ether (NPOE) and di-octyl phthalate (DOPH)) and 3-5 ml of THF as membrane solvent were mixed by stirring for 15 minutes until a uniform solution was obtained. Next, a polymer tube with an aperture diameter of 2 mm and a length of 5-7 cm was immersed in the mixture for 10 seconds to obtain an opaque membrane of about 0.2 mm thickness. The polymer tube was then removed from the mixture, and the membranes prepared this way were allowed to dry completely. Then the tube inside was filled with the internal solution of 10 mM DHCl. After that, the fabricated electrode was immersed in a solution of 10 mM of DHCl for 4 hours to reach equilibrium. It should be mentioned that a silver/silver chloride electrode was used as an internal reference. The necessary solutions were prepared through successive dilution of stock solution (0.01 M). It should be noted that double distilled water was used in all cases. Thus, the concentration range of 100 μ M–10 mM DHCl was used for the experiments.

3. RESULTS AND DISCUSSION

3.1. Optimization of the membrane components

In this study, the required solutions in the concentration range used were prepared through successive dilution. Double distilled water was used in all cases. Thus, the concentration range of 100 μ M–10 mM M DHCl was used for the experiment. Optimizing the ingredients is essential, considering the direct effect of the membrane components' composition on the electrode response. So, electrode responses at various contents of PVC and plasticizer were recorded to optimize their percentage compositions. It was observed that the electrode in the

20 μM –10 mM concentration range has a linear response with a slope of 59.7 mV/decade (Table 1). According to Table 1, the best Nernst response (59.7) was obtained for electrode 5 with DOP (63%) and PVC (30%) plasticizer; the calibration diagram for this composition is presented in Figure 2.

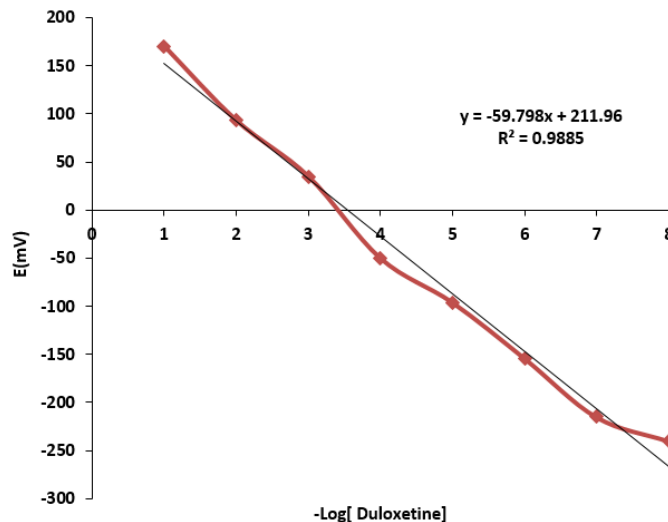


Figure 2. Duloxetine-tetraphenylborate membrane electrode response at optimal condition

The linear concentration range for this electrode made by mentioned composition is 0.7 μM to 10 mM, which has Nernstian behavior in this range. The detection limit derived by extrapolating the linear parts of the calibration curve is 0.3 μM .

Table 1. Responses of membrane electrodes with different membrane compositions to DHCl

Electrode number	PVC (%)	IP (%)	plasticizer (%)	SLOPE (mV/decade)	Linear range
1	30	7	DBS (63)	23.8±1.17	50 μM –0.1 M
2	34	5	DBS (61)	24.0±1.14	10 μM –0.1 M
3	34	6	DOP (60)	35.7±0.72	10 μM –0.1 M
4	32	7	DOS (61)	53.6±0.22	3.0 μM –0.1 M
5	30	7	DOP (63)	59.7±0.43	0.2 mM–0.1 M
6	33	6	DOP (61)	61.1±0.17	2.0 μM – 0.1 M
7	32	8	DOP (60)	47.7±0.22	0.1 μM –0.1 M
8	33	6	DOP (61)	60.9±0.12	1.0 μM –0.1 M
9	34	6	DBP (60)	56.2 ±0.12	2.0 μM –0.1 M
10	32	6	DBBPh (60)	47.8±0.52	30 μM –0.1 M
11	33	7	2-NPOE (60)	56.9± 0.15	2.0 μM –0.1 M
12	30	8	DEPh (62)	52.9±0.21	0.2 μM –0.1 M
13	29	6	DOP (65)	50.5±0.21	3.0 μM –0.1 M
14	29	6	DOP (65)	47.9±0.21	1.0 μM –0.1 M
15	31	6	DOP (63)	43.9±0.22	2.0 μM –0.1 M
16	34	1	DOP (65)	43.0±0.20	1.0 μM –0.1 M
17	33	5	DOPH (62)	48.9±0.18	2.0 μM –0.1 M
18	32	5	TEPh (65)	50.9±0.23	5.0 μM –0.1 M

3.2. Effect of internal filling solution

In this work, the duloxetine-tetraphenylborate electrode response was investigated in various concentrations of internal solution (0.01 M, 10 mM, and 1.0 mM). It was discovered that the electrode response was only considerably affected by differences in the intercept of the curves and not by changes in the internal solution concentration. This feature is because the activity of the internal filling solution remains unchanged during the test; its contribution to the electrode response equation is in the constant sections of the Nernst equation (intercept of response equation). Therefore, for two different concentrations, this difference is shown in the intercept of the diagram (Figure 3).

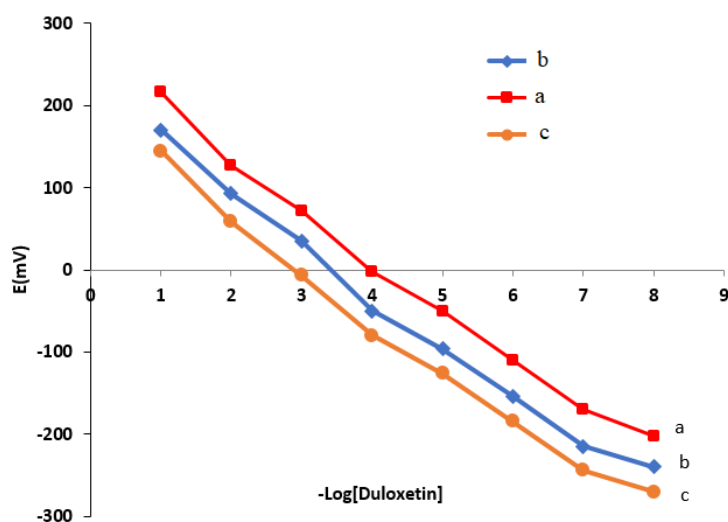


Figure 3. Calibration curves of duloxetine-tetraphenylborate membrane electrode with different internal solutions: a) 1.0 mM b) 10.0 mM c) 0.10 M

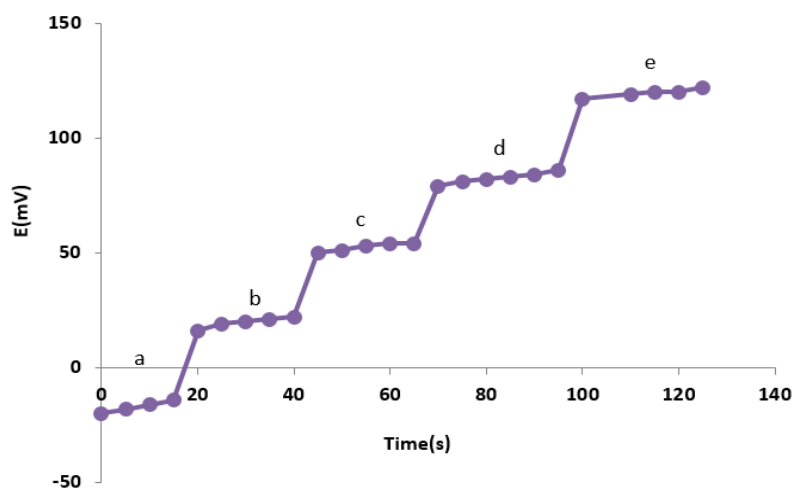


Figure 4. Response time of duloxetine-tetraphenylborate membrane electrode during step-by-step change of concentration: a) 1.0 μ M b) 10.0 μ M c) 0.1 mM d) 1.0 mM e) 10.0 mM

3.3. Response time

The time taken for the electrode potential to reach 90% of the final equilibrium value was calculated by measuring the potential of solutions with varied concentrations of DHCl to evaluate the electrode's useful response time. Figure 4 depicts the ion-selective electrode's response time to a change in the concentration of the duloxetine solution from 1.0 μM to 10.0 mM using the duloxetine-tetraphenylborate ion pair. Measurements were performed from the lowest to the highest concentration, and the electrode potential changes were plotted versus the time. The electrode reaches equilibrium sooner in higher concentrations. This electrode's response time is approximately five seconds.

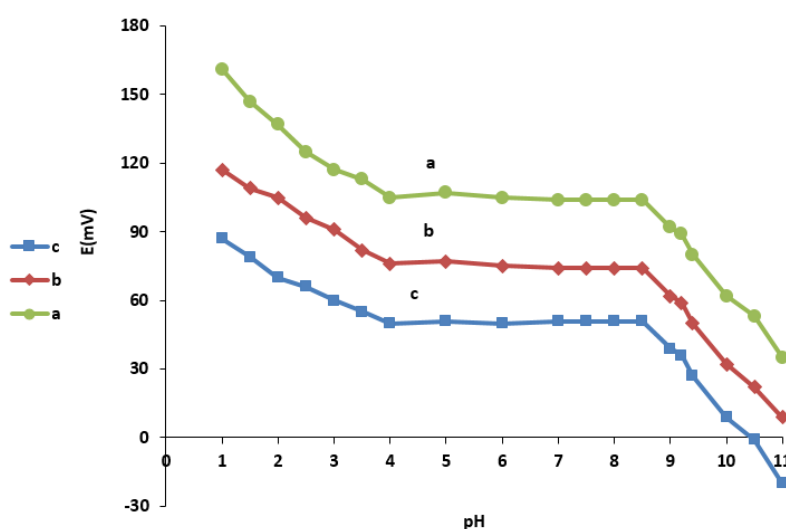


Figure 5. The effect of pH on the potential response of duloxetine-tetraphenylborate membrane electrode with optimal membrane combination of three concentrations: a) 10.0 mM b) 1.0 mM c) 0.1 mM

3.4. The effect of pH

Considering the importance of the pH factor on the electrode response, the effect of pH was investigated after optimizing the membrane composition. Nitric acid and sodium hydroxide solutions were used to adjust the concentration of DHCl solution to 1.0 mM, and the potentials were measured at each pH. Figure 5 shows that the potential is constant between 4.0 and 8.5; this pH range was chosen as the sensor's usable pH range. The rise in the concentration of hydroxide ions in the solution and the potential for the formation of a neutral complex between duloxetine and hydroxide ions may both contribute to the varied values of the potential at higher pH. This causes the membrane to permit the non-transverse passage of duloxetine ions, decreasing the potential response.

3.5. Electrode lifetime

The performance of the prepared electrode was studied over two months to investigate the constructed membrane electrode's stability. For this purpose, the electrode's response to DHCl

solutions with a specific concentration was checked daily, and the electrode was then kept in DHCl solution 0.01 M. The electrode has been tested almost every day since its construction and the data obtained during the study period are presented in Table 2. According to this table, no significant change has been observed in the electrode's response during the two months. The parameters such as slope, working potential range, and response time have good repeatability. It should be noted that the lifetime of the electrodes is limited due to the leakage of plasticizer and ion into the sample solution.

Table 2. Electrode response and linear response range in the time interval of 1 to 60 days

Time (day)	Slope (mV/decade)	Linear response range
1	59.7±0.5	0.2 μM–0.1 M
10	59.3±0.3	0.1 μM–0.1 M
20	59.0±0.6	0.2 μM–0.1 M
30	59.1±0.3	0.2 μM–0.1 M
30	59.4±0.2	0.2 μM–0.1 M
50	59.6±0.2	0.2 μM–0.1 M
60	59.5±0.1	0.3 μM–0.1 M

3.6. Selectivity of the electrode

The selectivity of the electrode for determination of DHCl was investigated in the presence of some ions and molecules, including Na⁺, K⁺, Li⁺, Ni⁺, Mg²⁺, Cd²⁺, Zn²⁺, Mn²⁺, Fe²⁺, Ca²⁺, Cu²⁺, Co²⁺, Cr²⁺, ascorbic acid, D-fructose, sucrose, aspartic acid, L-H-histidine, dopamine, glucose, uric acid, propranolol, dexamethasone, and melatonin. A modified potential approach and a separate solution method (SSM) were used to calculate the selectivity coefficients (MPM).

The selectivity coefficient is then determined by the following formulas [17]:

$$\log K_{Drug,J^{X+}}^{Pot} = \frac{E_2 - E_1}{S} + \log[Drug] - \log[J^{X+}]^{1/X} \quad (1)$$

$$\log K_{Drug,J^{C+}}^{Pot} = \frac{a_{Drug}}{a_J} \quad (2)$$

DHCl solution with a concentration of 0.1 mM was selected to study, and the coefficients for DHCl electrode are shown in Table 3. The results of this table show that the duloxetine electrode has very low selectivity to anions such as Na⁺ and K⁺, as well as to biological compounds such as D-fructose and melatonin, and it has a reasonable selectivity to other ions and biological species. The figures of merit of the ion selective electrode, such as the linear concentration range and Nernst slope of the sensor designed in this research, show that the

interference of these species in the measurement of DHCl is insignificant, and DHCl can be measured in the presence of these species without interference.

Table 3. selectivity coefficients for DHCl membrane electrode using separate solution method (SSM) and adapted potential method (MPM)

Interfering agent	K(SSM)	K(MPM)	Interfering agent	K(SSM)	K(MPM)
Na ⁺	2.3×10^{-5}	2.2×10^{-5}	K ⁺	4.7×10^{-5}	1.6×10^{-5}
Li ⁺	2.1×10^{-3}	3.4×10^{-4}	Ni ⁺	3.9×10^{-4}	4.1×10^{-4}
Mg ²⁺	7.4×10^{-4}	4.2×10^{-4}	Ca ²⁺	4.2×10^{-3}	7.8×10^{-4}
Cd ²⁺	1.8×10^{-2}	6.6×10^{-4}	Cu ²⁺	3.2×10^{-3}	7.3×10^{-4}
Zn ²⁺	2.5×10^{-4}	5.2×10^{-4}	Co ²⁺	6.6×10^{-3}	6.2×10^{-4}
Mn ²⁺	2.3×10^{-3}	6.3×10^{-4}	Cr ²⁺	2.2×10^{-4}	4.3×10^{-4}
Fe ²⁺	2.3×10^{-3}	2.4×10^{-4}	Ascorbic acid	5.4×10^{-5}	4.2×10^{-5}
D-fructose	2.4×10^{-6}	-	Glucose	3.7×10^{-5}	-
Sucrose	6.7×10^{-5}	3.3×10^{-5}	Uric acid	6.3×10^{-3}	6.7×10^{-3}
Aspartic acid	4.2×10^{-4}	5.1×10^{-4}	Propranolol	5.3×10^{-5}	6.4×10^{-4}
L-H-histidine	5.2×10^{-2}	4.2×10^{-3}	Dexamethasone	6.2×10^{-3}	3.2×10^{-4}
Dopamin	3.2×10^{-4}	3.6×10^{-4}	Melatonin	4.4×10^{-6}	3.3×10^{-4}

3.7. Analysis in real samples

The application of the proposed sensor to determine DHCl in two biological matrices, including blood serum and spiked urine samples, was also investigated. To prepare samples, 5 ml of human serum (or urine) was transferred to a 50 ml balloon and phosphate buffer solution (pH=7). Next, the solution was shaken for 5 minutes, and 25 ml was transferred to a 50 ml beaker. Different amounts of the drug were spiked separately in the mentioned solution. It should be noted that the standard addition method was used to measure recovery values. The results are shown in Table 4. According to the experiments performed and the comparison of the measured values with the added values, it can be said that the suggested duloxetine electrode is a good measurement tool [18].

Table 4. Measurement of DHCl in urine and blood plasma samples by direct potentiometric method

Tissue sample	Added DHCl (M)	Measured DHCl (M) *	Recovery (%)
Plasma	1.0 mM	0.990 (± 0.06) mM	98.78
	0.1 mM	0.097 (± 0.04) mM	96.95
	10.0 μ M	10.20 (± 0.05) μ M	103.26
Urine	1.0 mM	0.970 (± 0.05) mM	96.76
	0.1 mM	0.098 (± 0.05) mM	97.85
	10.0 μ M	10.60 (± 0.06) μ M	106.24

* \pm standard deviation for four times of measurement

4. CONCLUSION

In this work, a new ion-selective electrode was used for designing a potentiometric sensor to measure DHCl. PVC-based DHCl sensor was equipped using duloxetine-tetraphenylborate ion pair, various plasticizers (DOP, BBPA, DEPH, BA, TEPH, DOS, DBP, O-NPOE, DBBPH, DOPH, and DBS) and THF as membrane solvent. Different percentages of plasticizer, ion pair, and polymer were used to prepare the membrane. The best Nernst response (59.7) was obtained for the electrode with DOP (63%) plasticizer and PVC (30%). The linear concentration range for this electrode made by optimal composition is 0.7 μM to 0.01 M with a detection limit of 0.3 μM . It was also found that the change in the concentration of the internal solution does not significantly affect the electrode's response. This electrode's response time is approximately 5 s; its lifetime is predicted to be two months. The potential remains constant in the pH range of 4.0-8.5; hence this range is considered the practical pH range of the used sensor. The selectivity coefficients of this electrode for the ions such as Na^+ and K^+ and especially biological species such as D-fructose and melatonin are very small. Therefore, DHCl can be determined without any disturbance in the presence of these species. According to the conducted experiments and comparing the obtained values with the added values, it can be concluded that the DHCl electrode can be used as a suitable measuring tool.

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Declarations of interest

The authors declare no conflict of interest in this reported work.

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