Anal. Bioanal. Electrochem., Vol. 9, No. 8, 2017, 1044-1056

Analytical & Bioanalytical Electrochemistry

www.abechem.com

Full Paper

Eco-friendly Stability-Indicating Potentiometric Method for the Determination of Ropinirole Hydrochloride

Hanan A. Merey[1] and Shimaa A. Atty[2]

[1]*Analytical Chemistry Department, Faculty of Pharmacy, Cairo University, Kasr-El-Aini 11562-Cairo, Egypt*
[2]*National Organization for Drug Control and Research (NODCAR), 6 Abu Hazem Street, Pyramids Ave, P.O. Box 29, Giza, Egypt*

*Corresponding Author, Tel.:+202/01003617394
E-Mail:hanan.merey@pharma.cu.edu.eg

Received: 20 May 2017 / Received in revised form: 5 October 2017 / Accepted: 31 October 2017 / Published online: 31 December 2017

Abstract- A new fabricated ion selective electrode was described for the determination ropinirole HCl by direct potentiometry in pure drug substance and in pharmaceutical formulation. The proposed sensor was fabricated using ammonium reineckate (AR) as a cationic exchanger and 2-nitrophenyl octylether as a plasticizer in a polymeric matrix of polyvinyl chloride (PVC). Nernstian response of 55.1 mV/decade was obtained by the proposed sensor over a wide RP concentration range (10^{-5} to 1×10^{-2} mol/L) in the pH range of 3–7. The proposed sensor was stable for two weeks without any change in sensitivity. The proposed electrode shows good selectivity for the analysis of RP in the presence of up to 30% of its induced alkaline degradation product and in the presence of common inorganic and organic species commonly present in pharmaceutical dosage form. Statistical comparison between the results obtained by the proposed sensor for the analysis of ropinirole HCl in dosage form and the reported one shows no significant difference with respect to accuracy and precision.

Keywords - Ion-selective electrodes, Ammonium reineckate, Ropinirole hydrochloride

1. INTRODUCTION

Parkinson's disease is the most common degenerative disorder in central nervous system which affects the motor system. The most obvious clinical symptoms are rigidity, shaking,

slowed movement and difficulty with waking. These symptoms respond well to dopaminergic therapy as ropinirole HCl [1]. Ropinirole HCl (RP) chemically is known as 4-[2-dipropylamino) ethyl]-1, 3-dihydro-2H-indol-2-one [2]. RP is D_2, D_3, and D_4 dopamine receptor agonist with the highest affinity for D_2. It is used alone or in combination with levodopa for treatment of early and advanced Parkinson disease [3].

Literature survey reported few analytical methods for the determination of RP in pharmaceutical dosage form or in biological fluids. These methods include HPLC [4-9], TLC [10], spectrophotometric [8, 10-12], spectrofluorimetric [11] and voltammetric methods [13-17]. Analytical determination of Rp in the presence of its impurities was done using HPLC method [18,19]. Stability indicating methods were reported for the determination of RP in pharmaceutical dosage form using conventional methods of analysis such as HPLC and TLC [20-23]. These methods need sample pre-treatment, higher solvent consumption and expensive equipment. Therefore, they are neither economic nor eco-friendly. A recently emerged approach for developing analytical methods are of global interest to reach greenest analytical methodologies as no hazardous reagents or organic solvents will be needed [24]. Green Analytical Chemistry aims to the development of greener analytical methods through minimizing sample preparation, handling, solvent and reagent consumption, energy consumption and waste. By this way, the developed methods reduce the undesirable environmental side effects of chemical analysis, while preserving the accuracy, sensitivity, selectivity and precision of the analytical determination. One of the most environmentally friendly methods of analysis is potentiometry that depends on fabricated ion selective electrodes [25].

Potentiometric method based on material transport across a selective membrane as ion selective electrodes (ISEs) are now usually used in the quantitation of drugs in pure form, pharmaceutical dosage form and biological fluids [26]. The material transport includes charged complex species and simple ions [27]. The electrochemical sensors show good selectivity towards the transported material that imparts a great advantage over other techniques [28]. In addition, they do not need sample pre-treatment and are characterized by a limited reagent consumption, easy automation and good environmental impact. Therefore, it can be used as bench-top real-time analyzer for in process tracking of the concentration of active species in pharmaceutical forms and showed many advantages over traditional methods [29,30].

The aim of this work is to introduce the first contribution of new, economic and portable ion selective electrode that can be used as a sensor in the eco-friendly stability indicating potentiometric method for the determination of ropinirole HCl in pharmaceutical dosage form with the same analytical performance of conventional methods parameters.

2. EXPERIMANTAL

2.1. Apparatus

Jenway digital ion analyzer Model 3330 (Spectronic Camspec Ltd, Garforth, UK) with Ag/AgCl double junction reference electrode No. Z113107-1EAPW (Aldrich Chemical Co., St. Louis, MO) was used. The influence of pH on the response of the electrodes was studied using a glass pH electrode (Jenway No. 924005-BO3-Q11C).

2.2. Chemicals and Reagents

All chemicals and reagents used were of analytical reagent grade. Water was bi-distilled. Handling of all chemicals and solvents all over the procedure of experiment was done in the fuming cupboard. Wearing gloves and masks were done before measuring solvent with the aid of pipettes.

Ropinirole HCl (RP) was kindly obtained from The Egyptian Co. for Pharmaceutical &Chemical Industries (EPCI), Beni Suef, Egypt and its purity was found to be 100.1±0.6% according to the reported method [23].

Ropinirole Tables labeled to contain 2mg ropinirole HCl and manufactured by The Egyptian Co. for Pharmaceutical &Chemical Industries (EPCI), Beni Suef, Egypt and purchased from Egyptian markets. Batch numbers for dosage forms were 457108 and 92308 for valid and expired dosage forms, respectively.

Nitrophenyl octyl ether (NPOE), dibutyl sebacate (DBS), sodium phosphotungestate tribasic (PT) were purchased from Aldrich (Steinhein, Germany). Ammonium reineckate (AR), sodium tetraphenylborate (TPB), tetrahydrofuran (THF), poly (vinyl chloride) (PVC) of high molecular weight were purchased from BDH (Poole, England). Sodium hydroxide, HCl and potassium chloride were purchased from Prolabo (Pennsylvania, USA).

RP stock solution (1.0×10^{-2} M) was prepared using water as a solvent. RP working solutions (1.0×10^{-6} to 1.0×10^{-2} M) were prepared by serial dilutions from RP stock solution using water as a solvent

2.3. Procedures

2.3.1. Preparation of the Degradation Products

Alkaline-degradate prepared by dissolving 100 mg of pure RP powder in 10 mL methanol followed by addition of 75 mL of 0.1 N sodium hydroxide. The produced solution was refluxed for 12 hours. Complete degradation was checked by TLC using toluene-ethyl acetate-6M ammonia solution (5:6:0.5, by volume) as a developing system according to the reported method [23]. After complete degradation, the produced degradation solution was neutralized using 0.2 N HCl and the volume was adjusted with distilled water to produce solution of concentration 1 mg/mL which was subjected to concentration under pressure to

produce solution of 4 mg/mL. This solution used for preparation of 10^{-2} M of derived degradation product.

2.3.2. Preparation of the Membrane Sensors

For the preparation of the suggested sensor, a portion (10 mg) of ammonium reineckate was thoroughly mixed with 0.19 g PVC and 0.35 mL NPOE in a glass petri dish (5 cm diameter) then dissolved in 5 mL THF [31,32].

The petri dish was covered with a filter paper and left to stand overnight to allow solvent evaporation at room temperature. A master membrane with thickness of 0.1 mm was obtained and used for the construction of the electrodes.

2.3.3 Preparation of the Electrode Assembly

A disk (≈3 mm diameter) was cut using from the prepared master membrane (sensor) and pasted using THF to an interchangeable PVC tip that was clipped into the end of the glassy electrode body. Equal volumes of 1×10^{-2} M RP and 1×10^{-2} M KCl were mixed and this solution was used as internal solution for the proposed sensor. An internal reference electrode Ag/AgCl wire (1 mm diameter) was immersed in the internal solution of the proposed sensor. The cell, Ag–AgCl/internal solution, 10^{-2} M RP, 10^{-2} M KCl/PVC membrane sensor/test solution/Ag–AgCl, KC1 (saturated), was assembled for measuring the electromotive force. The proposed sensor was conditioned by soaking in 1×10^{-2} M RP solution for one day and stored in it when not in use.

2.3.4. Potentiometric Determination of RP in its Pure Samples

The proposed sensor was calibrated by transferring 25 mL aliquots of solutions covering the concentration range of (1.0×10^{-6} to 1.0×10^{-2} M) RP, into a series of 50 mL beakers. The system was immersed in each solution, in conjunction with a double junction Ag/AgCl reference electrode. The Proposed sensor was washed with distilled water between measurements. The recorded potential was plotted versus each negative logarithmic concentration of RP standard solutions. The regression equation of the obtained calibration plot was used for subsequent measurements of unknown samples.

2.3.5. Direct Potentiometric Determination of ropinirole HCl in its Expired and valid Pharmaceutical Formulations

Ten tablets of pharmaceutical formulations (valid and expired) were weighted and finely powdered in a small dish. The accurately weighed portions of the pharmaceutical formulations powder equivalent to 0.074 mg of ropinirole HCl were transferred into two separated 50 mL volumetric flasks (to prepare 1.0×10^{-3} M valid and expired pharmaceutical

formulations) and completed to the mark with water. The potentials of the prepared solutions were recorded by immersing the proposed sensor in conjunction with the double junction Ag/AgCl reference electrode. The concentration of RP was calculated from the corresponding regression equation.

2.3.6. Determination of ropinirole HCl in the Presence of its Alkaline Degradation Product

Different volumes from stock solutions of RP and its alkaline degradation (1.0×10^{-2} M) were quantitatively transferred into three separated volumetric flasks (50 mL) to prepare laboratory prepared mixtures containing 5: 0.1, 5: 0.25 and 5: 2.5 RP: degradation product ratios. The volumes were completed to the mark with distilled water. The potentials of the laboratory prepared mixtures were recorded and the concentration of RP was calculated from the corresponding regression equation.

2.3.7. Determination of ropinirole HCl in aqueous solution during 21 days

Direct potentiometric determination of RP was done on two aqueous solutions series of RP (10^{-4}-10^{-2} M) for 21 days. The first series was store in a tightly capped volumetric flasks protected from light at 25 ^{o}C and the other one stored in refrigerator at 4 ^{o}C (measurement was done when its temperature=25 ^{o}C). The concentration of RP was calculated from the corresponding regression equation.

3. RESULTS AND DISCUSSION

Potentiometric determination using ion selective electrodes is a very important analytical technique due to their accuracy, rapidity, simplicity, eco-friendly and wide application in analysis of different compounds including pharmaceutical drugs in dosage forms and biological fluids [33-35] or pollutants in water [36-38]. The important advantages of using ion selective electrodes over other analytical methods are accurate determination of colored, turbid and viscous samples. In addition, it shows rapid response to changes in the concentration, can be used for the measurement over a wide concentration range and ecofriendly method [39]. Therefore, the aim of our work is to develop simple, accurate, rapid and precise stability indicating method using ion selective electrode to ropinirole HCl in raw materials and pharmaceutical dosage form.

Screening the literature we find that, there is no reported publication for the analysis of ropinirole HCl using ion selective electrode. So, the proposed method is the first contribution for the analysis of RP using ion selective electrode.

3.1. Sensor composition and Response Characteristics

RP behaves as a cation drug due to protonation of tertiary amine (Figure 1); therefore, cationic exchanger was used for preparation of the proposed sensor. The response of the sensor depend mainly on the type of ion exchanger [35]. Therefore, three cationic exchangers, namely TPB, PT and AR were incorporated with a suitable solvent mediator in poly (vinyl chloride) matrix for the preparation of different membrane sensors. From Table 1, we found that the sensor containing AR has the best tendency to exchange with RP (best Nernestian response).

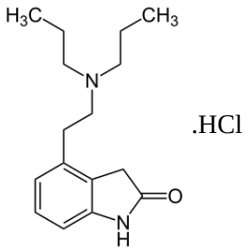

Fig. 1. Chemical structure of ropinirole HCl

Table 1. Effect of the type of electro-active species and plasticizer on the slope and concentration range for potentiometric determination of RP

Electro-active species	Plasticizer	Slope	Correlation coefficient (r)	Concentration range (M)
TPB	DBS	47.5±3.0	0.9987	10^{-5}-10^{-2}
TPB	NPOE	50.0±2.7	0.9991	10^{-5}-10^{-2}
AR	DBS	52.5±2.0	0.9994	10^{-5}-10^{-2}
AR	NPOE	55.1±1.7	0.9998	10^{-5}-10^{-2}
PT	DBS	45.3±2.3	0.9991	10^{-5}-10^{-2}
PT	NPOE	52.9±1.8	0.9998	10^{-5}-10^{-2}

The second important factor is the type of solvent mediator (plasticizer) that allows the extraction of RP from aqueous phase to sensor membrane (RP Log p=3.06). The viscosity and dielectric constant of plasticizer play an important role in adjusting the polarity of sensor to reduce the rate of exudation and therefore decrease the migration of sensor component to aqueous phase. This effect will increase the selectivity and sensitivity of the prepared sensor. So, two types of plasticizers, namely NPOE and DBS (as examples for plasticizer from nitroaromatic compounds and diesters of dicarboxylic acids, respectively) were used for construction of sensors. Table 1 shows that NPOE (a high-polar solvent mediator) exhibits

slightly better response than DBS (a low-polar solvent mediator). NPOE has a high dielectric constant value leading to the best membrane permeability and mobility of the cationic-exchanger sites to facilitate extraction of polar ions (RP) from aqueous solution. The more selective membranes were obtained when fabricated with polar solvent mediators than that fabricated with less polar one [40]. The designed sensor and the response characteristics were evaluated according to IUPAC recommendations [41]. The slop, linearity range and validation parameters of the proposed sensor were listed in Table 2. The suggested sensor shows a Nernestian slope of 55.1 mV/ decade in RP concentration range 10^{-5}-10^{-2} (Figure 2).

Table 2. Response characteristics of the proposed sensor

Parameter	**Sensor**
Slope (mV/decade) *n*=5	55.1±1.7
Intercept (mV) *n*=5	209.49
Correlation coefficient	0.9998
Concentration range (M)	10^{-5}-10^{-2}
Response time (s)	10
Working pH range	3-7
Stability, [Life time] (weeks)	2
Average accuracy[a] (% ±SD)	99.98±1.035
Precision[b]	
Repeatability[b1]	0.656
Intermediate precision [b2]	1.268
Robustness[c]	1.518
Ruggedness[d]	1.671

[a]Average recovery (%) of five concentration levels (from 10^{-5} to 10^{-2}) each repeated three times. [b1]Three concentration levels (10^{-5}, 10^{-4} and 10^{-3}) each repeated three times within the same day. [b2]Three concentration levels (10^{-5}, 10^{-4} and 10^{-3}) each repeated three times in three successive days. [c] Relative standard deviation (RSD %) of determining 1×10^{-5} - 1×10^{-2} M solutions using membrane containing 0.4 mL of NPOE instead of 0.35 mL, [d] (RSD %) of determining 1×10^{-5} - 1×10^{-2} M solutions using Jenway 3505 digital ion analyzer instead of 3330.

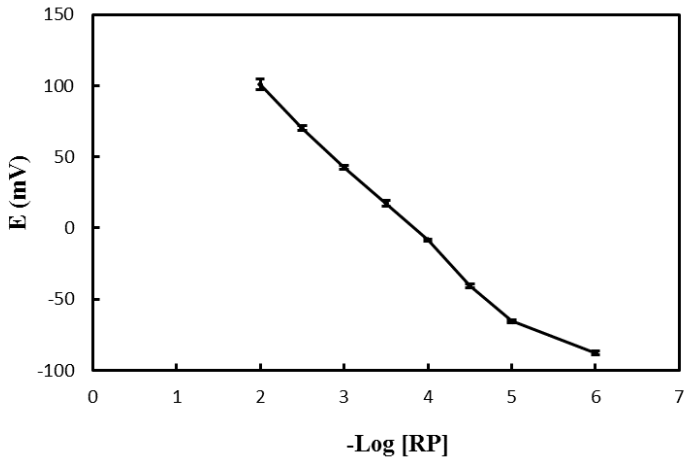

Fig. 2. Potentiometric profile of the proposed sensor

The deviation from the ideal Nernestian slope (60 mV/ decade), is due to the fact that the electrode responds to activities of the drug rather than the concentration. The fast response was obtained within 10±5 seconds. The life time of the suggested sensor was done by periodically recalibrating the potentiometric RP response in the standard RP solutions. The proposed sensor performance shows no significant change over 2 weeks.

The proposed sensor was equilibrated before using by soaking in 1×10^{-2} M RP for 24 h and stored in it when not in use. The precision of the suggested method was evaluated by measuring three concentrations (1×10^{-5}, 1×10^{-4} and 1×10^{-3} M solutions) of RP. Three solutions of each concentration were prepared and analyzed in triplicate (repeatability assay). The intermediate precision of the suggested method was assessed by measuring the same concentrations used for repeatability but on three successive days (Table 2). The robustness was carried out by measuring the concentrations of RP solutions in range 1×10^{-5} - 1×10^{-2} using another fabricated sensor has the same composition but using 0.4 mL of NPOE instead of 0.35 mL. For the ruggedness study, the concentrations of RP solutions in range 1×10^{-5}-1×10^{-2} M were determined by the suggested sensor using Jenway 3505 digital ion analyzer instead of 3330 Model. Satisfactory results were obtained and proved the stability of the suggested method upon changing the instrument (Table 2).

3.2. The Effect of pH on the sensor Response

The effect of pH on the response of the suggested sensor was studied on two concentrations 10^{-4} and 10^{-3} M. Figure 3 shows a typical pH response curve for the suggested sensor, over a pH range 2.0–10.0, where the pH was adjusted with hydrochloric acid and sodium hydroxide solutions.

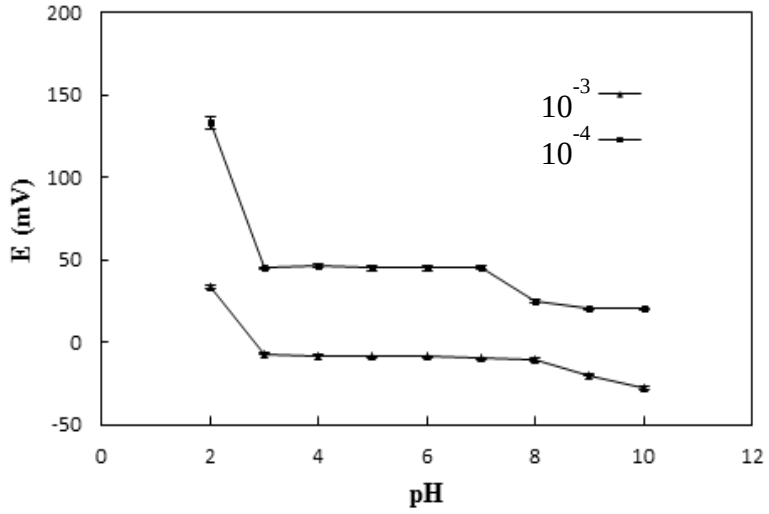

Fig. 3. Effect of pH on the response of the proposed sensor on 10^{-3} and 10^{-4} M of RP

The sensor response was stable over the pH change from 3 up to 7 (RP pKa=10.17), this is due to the presence of RP in ionized form, therefore working was done in distilled water without using a buffer solution (eco-friendly method). Below pH 3, the electrode response increased with the increase in solution acidity as the membrane may extract H^+ leading to a noisy response [40]. The gradual decrease in potential at pH>7.0 was due to the gradual decrease in the concentration of the RP mono cation due to the formation of the non-protonated amino group.

3.3. Sensor Selectivity

The potentiometric selectivity factor $K^{Pot}_{\text{Primary ion interferent}}$ of the proposed sensor was determined for different pharmaceutical additives and diluents commonly used in pharmaceutical formulations by the separate solution method and calculated from the following equation [35].

Table 3. Potentiometric selectivity coefficients (K^{pot}_{RP}) of RP for the proposed sensor by separate solution method (*n*=3)

Interferent 10^{-3} M	**Selectivity Coefficient** (K^{pot}_{RP})
Urea	1.19×10^{-3}
Starch	5.31×10^{-3}
Glucose	5.62×10^{-3}
Lactose	6.68×10^{-4}
Talc	1.68×10^{-3}
$(NH_4)_2SO_4$	1.68×10^{-3}
$MgCl_2$	7.08×10^{-4}
NaCl	2.12×10^{-3}
KCl	2.66×10^{-3}
$CaCl_2$	3.98×10^{-3}
Alkaline degradate	2.11×10^{-3}

$$-log\left(K^{Pot}_{Primary\ ion\ interferent}\right) = \left[\frac{(E_M - E_{RP})}{2.303RT/Z_{RP}F}\right] + \left[1 + \frac{Z_{RP}}{Z_M}\right] log[RP]$$

Where E_{RP} and E_M are the potential readings recorded after exposing the sensor to the same concentration of the studied drug and the interferent, respectively, Z_{RP} and Z_M are the charges on RP and the interfering ion, respectively and $2.303RT/Z_{RP}F$ represents the slope of the investigated sensor (mV/decade). The results were listed in Table 3 showed that, the proposed sensor display high selectivity towards RP over different interferent ions including the induced alkaline degradation product. Another way to assess the selectivity of the

proposed sensor is the determination of RP in laboratory prepared mixture containing different ratios of RP and its alkaline degradation, varying from 5: 0.1 to 5: 2.5. Table 4 shows that the proposed sensor was successfully applied for the selective determination of RP in the presence of up to 30% of its degradation product. The proposed potentiometric method was also used for the determination of RP in expired tablets and the obtained results were listed in Table 5.

Table 4. Determination of RP in laboratory prepared mixtures containing different ratios of RP and its induced alkaline degradation product by the proposed sensor

Drug: Drug degradate ratio	% recovery*±SD (*n*=3)
5: 0.1	101.70±0.605
5: 0.25	100.09±0.349
5: 2.5	99.09±0.924

- Average of three determinations

Table 5. Determination of RP in Ropinirole® tablets by the proposed potentiometric and reported [23] methods

Parameters	Valid tablets	Expired tablets	Reported method	
			Valid tablets[a]	Expired tablets[b]
Found % (*n*=3)	100.73	60.20	99.74	61.55
SD	0.953	1.438	0.873	1.562
Variance	0.908	2.068	0.762	2.44
F test (6.39)*	1.19	1.18		
Student's t test (2.306)*	1.713	1.743		

*Figures between parenthesis are the corresponding tabulated values (*p*=0.05)
[a]Batch no. 457108
[b]Batch no. 92308

3.4. Determination of RP in pharmaceutical dosage form.

As shown in Table 3, the most common tablet additives show no significant interference with the determination of RP, therefore the proposed sensor was successfully applied for RP determination in tablets (valid formulation) without prior extraction as shown in Table 5. Statistical comparison between the results obtained from the analysis of (expired and valid) tables by the suggested potentiometric method and the reported one was done [23] and no significant difference was found at p=0.05, Table 5.

3.5. Stability of aqueous solution

By studying the stability of aqueous solution over 21 days we found that, aqueous solution at 25 ^{o}C was stable over 10 days (recovery% 99.83±1.533) while, the stability of the stored solutions in refrigerator was 17 days (recovery% 100.53±1.763). After specified time, gradual decrease in recovery was observed which indicates starting of degradation of RP in aqueous solution.

4. CONCLUSION

An eco-friendly potentiometric method was described as a stability indicating method for the determination of ropinirole hydrochloride using an ion selective electrode. The method was validated and found to be sufficiently simple, selective and accurate for the quantitative determination of RP in pure form and pharmaceutical formulation without separation steps. The method was found to be selective for determination of ropinirole HCl in the presence of its hydrolytic degradation product and common additives and excipients. The suggested method was applied for the determination of ropinirole HCl in valid and expired samples. According to the obtained results the proposed method can used for monitoring ropinirole HCl offers advantages of fast response, eco-friendly quantitative determination of ropinirole HCl and therefore can be used without the need of preliminary derivatization, extraction or separation steps.

REFERENCES

[1] S. Sveinbjornsdottir, J. Neurochem. 139 (2016) 318.
[2] C. Sean Sweetman, Martindale, The Complete Drug Reference. The Pharmaceutical Press, London UK, 38th, (2014).
[3] R. Barker, J Neurol. Neurosurg. Psychiatry. 68 (2000) 538.
[4] J. Bhatt, A. Jangid, R. Shetty, B. Shah, S. Kambli, G. Subbaiah, and S. Singh, J. Pharm. Biomed. Anal. 40 (2006) 1202.
[5] A. Önal, Chromatographia 64 (2006) 459.
[6] D. V. Bharathi, B. Jagadeesh, S. S. Kumar, R. N. Lakshmi, K. K. Hotha, A. Naidu, and R. Mullangi, Biomed. Chromatogr. 23 (2009) 557.
[7] N. Sreekanth, C. Rao, and K. Mukkanti, Int. J. Pharm. Pharm. Sci. 1 (2009) 186.
[8] L. P. Kothapalli, M. E. Choudhari, A. B. Thomas, R. K. Nanda, A. D. Deshpande, and P. S. Gaidhani, Der Pharma Chem. 3 (2011) 1.
[9] C. Krishnaiah, M. V. Murthy, A. R. Reddy, R. Kumar, and K. Mukkanti, J. Chin. Chem. Soc. 57 (2010). 348.
[10] J. Susheel, S. Malathi, and T. Ravi, Indian J. Pharm. Sci. 69 (2007) 589.
[11] Z. Aydoğmuş, Spectrochim. Acta Part A 70 (2008) 69.

[12] A. Önal, and S. Çağlar, Chem. pharm. bull. 55 (2007) 629.
[13] M. Sadiković, B. Nigović, S. Jurić, and A. Mornar, J. Electroanal. Chem. 733 (2014) 60.
[14] J. Wang, and A. Walcarius, J. Electroanal. Chem. 407 (1996) 183.
[15] B. Nigović, S. Jurić, A. Mornar, and I. Malenica, J. Chem. Sci. 125 (2013) 1197.
[16] B. Bozal-Palabiyik, and B. Uslu, Ionics 22 (2016) 115.
[17] N. N. Salama, H. E. Zaazaa, S. M. Azab, S. A. Atty, N. M. El-Kosy, and M. Y. Salem, Sens. Actuators B 240 (2017) 1291.
[18] A. Kakouris, V. Samara, A. Kalaskani, and I. Panderi, Chromatographia 77 (2014) 447.
[19] P. Coufal, K. Štulík, H. A. Claessens, M. J. Hardy, and M. Webb, J. Chromatog. B 732 (1999) 437.
[20] A. Azeem, Z. Iqbal, F. A. Ahmad, R. K. Khar, and S. Talegaonkar, Acta chromatographica 20 (2008) 95.
[21] G. Parmar, S. Sharma, K. Singh, and G. Bansal, Chromatographia 69 (2009) 199.
[22] G. Mustafa, S. Baboota, J. Ali, and A. Ahuja, J. Pharm. Innovation 7 (2012) 47.
[23] G. Mustafa, A. Ahuja, S. Baboota, and J. Ali, Saudi Pharm. J. 21 (2013) 93.
[24] M. Tobiszewski, A. Mechlińska, and J. Namieśnik, Chem. Soc. Rev. 39 (2010) 2869.
[25] M. Guardia, and S. Garrigues, Hand Book of Green Analytical Chemistry, John Wiley & Sons. (2012).
[26] F. Metwally, J. Yakugaku Zasshi 127 (2007) 1267.
[27] Y. Elsaharty, F. Metwally, M. Refaat, and S. El-Khateeb, J. Pharm. Biomed. Anal. 41 (2006) 7200
[28] G. Mostafa, and A. Al-Majed, J. Pharm. Biomed. Anal. 48 (2008) 57.
[29] M. K. A. EL-Rahman, H. E. Zaazaa, N. B. El Din and A. A. Moustafa, Talanta 132 (2015) 52.
[30] M. K. A. EL-Rahman, and M. Y. Salem, Sens. Actuators B 220 (2015) 255.
[31] S. S. M. Hassan, and S. A. M. Marzouk, Talanta 41 (1994) 891.
[32] T. S. Ma, and S. M. Hassan, Organic Analysis Using Ion Selective Electrodes, Academic Press, Place (1982).
[33] M. A. El-Sayed, Sens. Actuators B 190 (2014) 101.
[34] B. V. Noronha, E. H. Bindewald, M. C. de Oliveira, M. A. Papi, M. F. Bergamini, and L. H. Marcolino-Jr, Mater. Sci. Eng. 43 (2014) 517.
[35] E. S. Elzanfaly, H. E. Zaazaa, and H. A. Merey, Acta Chimica Slovenica 60 (2013) 256.
[36] M. Ganjali, F. Faridbod, N. Davarkhah, S. Shahtaheri, and P. Norouzi, Int. J. Environ. Res. 9 (2015) 333.
[37] T. A. Ali, A. M. Eldidamony, G. G. Mohamed, and D. M. Elatfy, Int. J. Electrochem. Sci. 9 (2014) 2420.
[38] T. A. Ali, A. A. Farag, and G. G. Mohamed, J. Ind. Eng. Chem. 20 (2014) 2394.

[39] N. K. Ramadan, and H. A. Merey, Acta Chimica Slovenica 59 (2012) 870.

[40] H. A. Merey, M. I. Helmy, S. M. Tawakkol, S. S. Toubar, and M. S. Risk, Port. Electrochim. Acta 30 (2012) 31.

[41] IUPAC Analytical Chemistry Division Commission on Analytical Nomenclature, Pure Applied Chemistry 72 (2000) 1851.