Available online at www.sciencedirect.com
ScienceDirect
Journal of Pharmaceutical and Biomedical Analysis 47 (2008) 177–182
JOURNAL OF PHARMACEUTICAL AND BIOMEDICAL ANALYSIS
www.elsevier.com/locate/jpba

Short communication

Determination of pyridoxine hydrochloride in pharmaceutical preparations by calixarene based potentiometric sensor

V.D. Vaze, A.K. Srivastava *

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai 400098, India

Received 8 June 2007; received in revised form 3 December 2007; accepted 4 December 2007
Available online 19 February 2008

Abstract

A simple, rapid and sensitive sensor for the assay of pyridoxine hydrochloride has been developed. The method is based upon the use of calix-8-arene as a neutral carrier in the presence of phosphotungstic acid as an ion extruder and di isooctyl phthalate as plasticizer. The sensor was found to have a short response time of 20 s to pyridoxine concentration. Perfectly Nernstian slope of 60.4 ± 3.1 mV/decade of activity between pH 3.0 and 7.2 for the monovalent pyridoxine hydrochloride over a wide concentration range of 1×10^{-1} M to 6.2×10^{-6} M was observed. The detection limit observed was 1.6×10^{-6} M. The selectivity coefficients of the developed sensor indicated excellent selectivity for pyridoxine hydrochloride over a number of species, which normally accompany pyridoxine in various pharmaceutical formulations. The mediator *o*-nitrophenyl octyl ether significantly increased the lifetime of the sensor. The results obtained for pharmaceutical sample analysis using this sensor were satisfactory with excellent recovery percentage comparable and sometimes even better than the ones obtained by other routine methods for the assay.

Keywords: Pyridoxine; Vitamin B_6; Calixarene; Ion-selective electrode; Electrochemical sensor

1. Introduction

Pyridoxine is an essential vitamin for human beings. Deficiency of pyridoxine (Vitamin B_6) is known to affect Central Nervous System inducing seizures similar to epileptic seizures [1]. The vitamin is administered in various forms to treat such ailments. Therefore, assaying the vitamin from different pharmaceutical formulations (multivitamin or single) becomes a necessity. Many methods have been developed for the assay of pyridoxine. Some methods like flow injection analysis [2] high performance liquid chromatography [3–5], capillary zone electrophoresis [6,7], spectrophotometry [8,9], fluorimetry [10–12] and voltammetry [13–18] are being widely used for quantification of pyridoxine from different sources. Simultaneous determination of pyridoxine has also been reported using expensive techniques like high performance liquid chromatography [19,20] and capillary electrophoresis [7]. Electrochemical and spectroelectrochemical [21] studies have also been performed on pyridoxine using modified electrodes. Determination of pyridoxine hydrochloride in pharmaceutical preparations by potentiometric membrane sensor has also been reported [22]. Some of these methods and some of the official methods available for assaying of pyridoxine are cumbersome, time consuming and expensive.

Calixarenes have attracted a lot of interest as a kind of key receptors in supramolecular chemistry [23–31]. Calixarenes have been found to be suitable for the purpose [23] because of the ease in their large-scale synthesis and the different ways in which they can be selectively functionalized at the lower rim (polar) or at the upper rim (non-polar). Because of these properties calixarenes can form inclusion complexes with a wide range of guest species. Functionalized calixarenes have been used for investigating the interaction with organic amines spectroscopically [32] and thermogravimetrically [33].

Potentiometric sensors for the determination of various ions have gained a lot of importance over past few years due to low operational cost and considerable reliability of the results. Buck and Lindner [34] have summarized the status of these sensors and their applications in clinical chemistry. A successful attempt was made in our laboratory at designing coated

* Corresponding author. Tel.: +91 22 26526119; fax: +91 22 26528547.
E-mail addresses: aks@mail.mu.ac.in, akschbu@yahoo.com (A.K. Srivastava).

0731-7085/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpba.2007.12.030

wire Fe(III)-selective electrodes [35] based on iron complex of 1,4,8,11-tetraazacyclotetradecane.

In the present paper we describe the use of calixarenes for development of a novel sensor for the determination of pyridoxine hydrochloride in pharmaceutical preparations, potentiometrically. The sensor is based upon the incorporation of a neutral ionophore, *viz*. calix-8-arene in the PVC-membrane matrix with solvent mediator *o*-nitrophenyl octyl ether (*o*-NPOE). The sensor was found to display a very stable, fast and linear response over a wide concentration and pH range.

2. Experimental

2.1. Chemicals and materials

All the chemicals and reagents were of analytical reagent grade unless otherwise stated. Low molecular weight poly vinyl chloride (PVC), dibutyl sebacate (DBS), di isooctyl phthalate (DIOP), *o*-nitrophenyl octyl ether, sodium tetraphenyl borate (NaTPB), phosphotungstic acid (PTA), pyridoxine hydrochloride, 4-*tert*-butyl calix-*n*-arenes ($n = 4, 6, 8$), tetrahydrofuran (THF) were purchased from Fluka. Pharmaceutical formulations containing pyridoxine hydrochloride were purchased from local drug stores and were of IP grade.

Double distilled de-ionized water was used to prepare all the solutions.

A standard stock solution (1×10^{-1} M) of pyridoxine hydrochloride was prepared and dilute solutions, in the concentration range 10^{-2} M to 10^{-8} M, were prepared by appropriately diluting the stock solution with double distilled deionized water.

2.2. Apparatus

All potentiometric measurements were carried out at $25 \pm 1\,^{\circ}$C. A Cyberscan 2500 pHmeter (Eutech instruments, Singapore) having an accuracy of ± 0.1 mV with a saturated calomel electrode (SCE) as reference electrode was used for potential measurements. The electrochemical cell used for the potentiometric measurements is:

$$\mathrm{Hg, Hg_2Cl_{2(S)}, KCl_{(S)}, |sample\ solution|membrane}$$
$$\mathrm{||0.1\,M\,Py + 0.1\,M\,KCl|AgCl_{(S)}, Ag}$$

where Py is the pyridoxine hydrochloride.

2.3. Procedures

2.3.1. Fabrication of pyridoxine-selective PVC membrane sensors

Fifty milligram of calixarene was mixed with 300 mg PVC powder, 600 mg of a selectophore/plasticizer and 50 mg of an ion extruder in a 5 cm diameter glass petri dish. The mix was dissolved in 5 ml double distilled THF. The petri dish was covered with a filter paper and left overnight at room temperature to allow slow evaporation of the solvent. A transparent PVC membrane with an average thickness of 0.3 mm was obtained. The membrane was then cut into circular pieces of 10 mm diameter and glued to one end of Teflon tube (7 mm o.d.) The tube was then kept at room temperature for 12 h. The electrode was then filled with an internal solution of 0.1 M pyridoxine hydrochloride solution containing 0.1 M KCl. An Ag/AgCl coated wire was used as an internal reference electrode. The membrane was conditioned in a 0.1 M pyridoxine hydrochloride solution for 24 h prior to its use for the determination of pyridoxine hydrochloride. The sensor was stored in double distilled deionized water when not in use.

2.3.2. Sensors calibrations

The developed sensors were calibrated by transferring 25 ml aliquots of an aqueous solution (10^{-1} M to 10^{-8} M) of pyridoxine hydrochloride to 50 ml beakers. The pyridoxine-PVC membrane sensor in conjunction with a SCE as reference electrode was then immersed in the above test solutions. The potential was recorded after stabilizing to ± 0.2 mV and the emf was plotted as a function of negative logarithm of pyridoxine hydrochloride concentration. The slope of the calibration graph was then used to determine the unknown pyridoxine concentrations.

2.3.3. Sensor selectivity

The potentiometric selectivity coefficients ($K_{A,B}$) were determined by fixed interference method [34] using 0.1 M solution of the interfering drug component and varying the concentration of primary ion. The emf values obtained were then plotted against the logarithm of the concentration of primary ion. The intersection of extrapolation of linear portions indicates the value of a_A to be used for finding the selectivity coefficients using the Nikolsky–Eisenmen equation [34].

The potentiometric selectivity coefficients were also determined by unbiased fixed interference method [36,37]. Here, the lower detection limit [a_I(DL)] is determined using the calibration curve for the primary ion. The calibration curve for the primary ion is then measured in the presence of an interfering ion and the lower detection limit [a_J(BG)] is determined. The selectivity coefficients are determined using the following equation:

$$\log K_{IJ}^{\mathrm{pot}} = \log [a_I(\mathrm{DL})/a_J(\mathrm{BG})^{z_I/z_J}]$$

where z_I and z_J are the charge on the primary ion and the charge on the interfering ion, respectively [37].

2.4. Determination of pyridoxine hydrochloride in a pharmaceutical preparation

Pharmaceutical preparation containing pyridoxine equivalent to 50 mg was weighed and 50 ml water was added. The solution was stirred for about 20 min. It was then diluted to 100 ml. The supernatant liquid was filtered through filter paper and 25 ml of the solution was used for emf measurement.

Table 1
Composition and response characteristics of PVC based membranes having *p-tert*-butyl calix-4-arene, having, *p-tert*-butyl calix-6-arene and *p-tert*-butyl calix-8-arene as ionophores

Electrode no.	Calix-n-arene	Ion extruder	Selectophore/plasticizer	Slope mV/decade	Correlation coefficient	Linear range (M)
1.	Calix-4-arene	NaTPB	DIOP	1.0	–*	–*
2.	Calix-4-arene	NaTPB	DBS	1.2	–*	–*
3.	Calix-4-arene	NaTPB	*o*-NPOE	20.5	0.9942	10^{-1} to 10^{-7}
4.	Calix-4-arene	PTA	DIOP	40.1	0.9898	10^{-1} to 10^{-5}
5.	Calix-4-arene	PTA	DBS	17.5	0.9931	10^{-1} to 10^{-8}
6.	Calix-4-arene	PTA	*o*-NPOE	1.6	0.4997	10^{-1} to 10^{-8}
7.	Calix-6-arene	NaTPB	DIOP	17.7	0.9853	10^{-1} to 10^{-4}
8.	Calix-6-arene	NaTPB	DBS	1.6	0.8923	10^{-5} to 10^{-7}
9.	Calix-6-arene	NaTPB	*o*-NPOE	3.9	0.9969	10^{-1} to 10^{-5}
10.	Calix-6-arene	PTA	DIOP	51.6	0.9997	10^{-1} to 10^{-5}
11.	Calix-6-arene	PTA	DBS	32.7	0.9895	10^{-1} to 10^{-5}
12.	Calix-6-arene	PTA	*o*-NPOE	28.3	0.9823	10^{-1} to 10^{-5}
13.	Calix-8-arene	NaTPB	DIOP	51.8	0.9666	10^{-3} to 10^{-5}
14.	Calix-8-arene	NaTPB	DBS	41.4	0.9835	10^{-1} to 10^{-7}
15.	Calix-8-arene	NaTPB	*o*-NPOE	27.1	0.9805	10^{-1} to 10^{-5}
16.	Calix-8-arene	PTA	DIOP	60.4	0.9996	10^{-1} to 6.2×10^{-6}
17.	Calix-8-arene	PTA	DBS	40.3	0.9870	10^{-1} to 10^{-7}
18.	Calix-8-arene	PTA	*o*-NPOE	39.4	0.9805	10^{-1} to 10^{-6}

NaTPB: sodium tetraphenyl boron, PTA: phosphotungstic acid, DIOP: di isooctyl phthalate, DBS: dibutyl sebacate, *o*-NPOE: *o*-nitrophenyl octyl ether.
* No proper response.

3. Results and discussion

3.1. Performance characteristics of pyridoxine sensor

Calixarenes are well known as selective ligands for various ions. A calixarene, with an ion extruder in a PVC membrane containing a plasticizer was used as electrical carriers for the determination of pyridoxine hydrochloride after conditioning the membrane in a 0.1 M pyridoxine hydrochloride solution for 24 h. Such membranes are then electrochemically evaluated under a static mode of operation according to IUPAC recommendations [34]. Membranes of different compositions were prepared as shown in Table 1. The responses of all these sensors have also been tabulated in Table 1. Sensor no. 10 has a reasonably good slope but falls short in the limit of linearity while sensor no.5 has a wider linear range but is far from Nernstian behavior. Sensor no. 14, too, exhibited a sub-Nernstian behavior despite having a good linear range. This also proves that the 4-*tert*-butyl calix-4-arenes and 4-*tert*-butyl calix-6-arenes could not accommodate the pyridoxine hydrochloride ion. The overall trend was found to favor the use of phosphotungstic acid over sodium tetraphenyl borate as the ion extruder. Of the 18 sensors constructed the sensor no. 16, based on calix-8-arene containing *o*-NPOE as plasticizer and PTA as ion extruder shows the best response towards pyridoxine hydrochloride. Table 2 summarizes response characteristics of the selected sensor no.16, e.g. slope, response time, linear range and detection limit. The sensor exhibits a Nernstian slope of 60.4 ± 3.1 mV/decade over a concentration range of 0.1 M to 6.2×10^{-6} M with a detection limit of 1.6×10^{-6} M. The sensor exhibited a short response time of 20 s. These parameters did not change significantly for over a period of 6 weeks. The sensor also exhibits good behavior with respect to reproducibility of the emf values. A typical calibration curve is shown in Fig. 1. The sensors displayed constant potential readings for day-to-day measurements over a period of 4 weeks. The slope of the calibration plot did not change significantly for at least 6 weeks and then exhibited a gradual decrease in the sensitivity. However, it could be effectively used for 3 month. Thus, it can be inferred that the lifetime of the investigated sensor is 3 months.

The sensor showed excellent reproducibility after it is conditioned for 24 h, before use, in a 0.1 M solution of pyridoxine hydrochloride. After reconditioning, the sensor exhibited the same Nernstian slope, linear concentration range, and detection limit.

3.2. Dynamic response time

For analytical applications, dynamic response time is an important factor for an ion-selective electrode. In this study, practical response time was recorded by immediate changing of the pyridoxine hydrochloride concentration from 1×10^{-6} M to

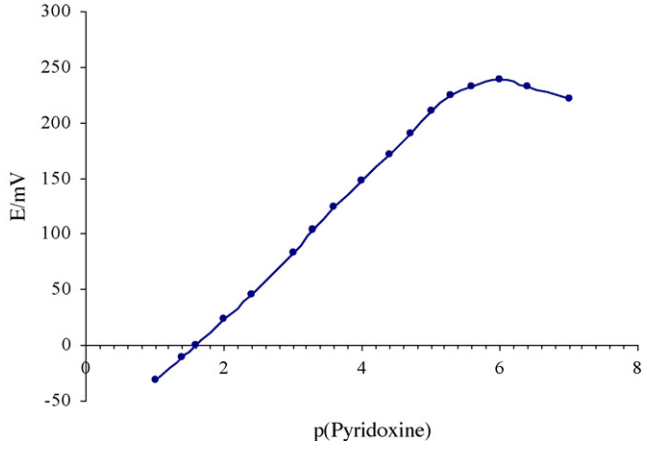

Fig. 1. Potential response of the pyridoxine-selective electrode based on calix-6-arene.

Table 2
Response characteristics of the proposed sensor based on calix-8-arene and its comparison with the reported sensor

Parameter	Present PVC membrane sensor response	Sensor response reported [22]
Slope (mV/decade)	60.4 ± 3.1	54 ± 0.4
Intercept (mV)	94.3	287 ± 0.5
Correlation coefficient, (r) ($n = 6$)	0.9996	0.9980
Limits of linearity (M)	10^{-1} to 6.2×10^{-6}	1×10^{-2} to 6×10^{-5}
Lower limit of detection (M)	1.6×10^{-6}	4.0×10^{-5}
Response time (s)	20	60
Working pH range	3.0–7.2	2–4

1×10^{-2} M. The actual potential time trace is shown in Fig. 2. As is seen from the graph the sensor reaches its equilibrium potential in a very short time of 10 s.

3.3. Effect of pH

Measurement of pH dependence of the pyridoxine hydrochloride sensor was studied over a pH range from 2 to 8. The pH was adjusted using 0.1 M sodium carbonate and/or hydrochloric acid solution. The potential-pH profile for 10^{-3} M solution of pyridoxine hydrochloride using this sensor is summarized in Fig. 3. The data revealed a linear potential *versus* pH relationship in the range of 3.0–7.2 from the point of view of sensor function. It is apparent that below pH 3.0 the pyridoxine hydrochloride ionization is progressively suppressed due to increase in the hydrogen ion concentration. This results in gradual decrease in the sensitivity of the proposed sensor. Beyond pH 7.2, again the sensor exhibited a fall in the sensitivity that can be due to the formation of pyridoxinium hydroxide, which is a weak electrolyte.

3.4. Effect of foreign ions

The potentiometric selectivity coefficient of the pyridoxine sensor depends on the selectivity of ion exchange process at the membrane-solution interface and the mobility of the respective ions in the membrane as well as the hydrophobic interactions

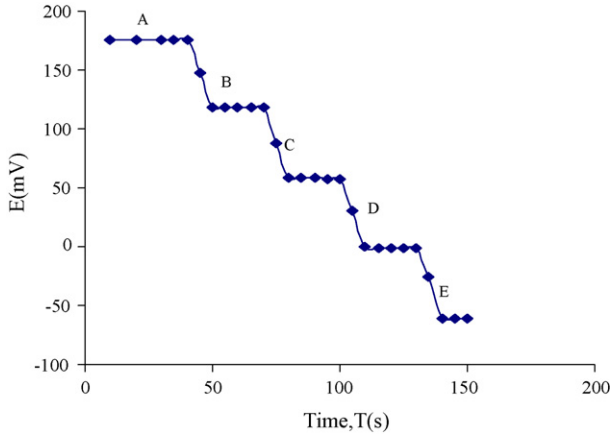

Fig. 2. Dynamic response of the pyridoxine-selective membrane electrode for step changes in concentration of pyridoxine hydrochloride: (A) 1×10^{-6} M, (B) 1×10^{-5} M, (C) 1×10^{-4} M, (D) 1×10^{-3} M, (E) 1×10^{-2} M.

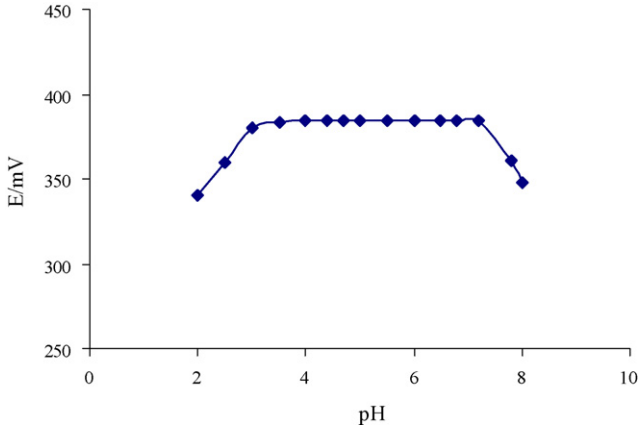

Fig. 3. Effect of pH of the test solution on the potential response of the pyridoxine-selective electrode at 1×10^{-3} M solution.

of the primary ions and the organic membrane. The selectivity of the pyridoxine membrane sensor is also related to the free energy of transfer of pyridoxine hydrochloride cation between the aqueous and the organic phases. The selectivity studies were performed at concentrations above 100-fold molar excess over pyridoxine concentration. The potentiometric selectivity of the sensor towards different substances was determined using biased or conventional fixed interference method [34] and unbiased fixed interference method [36,37] with 0.1 M solution of the interfering species at pH 6.5. The selectivity coefficients for pyridoxine hydrochloride obtained by towards various species thus determined are given in Table 3. Good selectivity for pyridox-

Table 3
Selectivity coefficients of various interfering ions

Interfering species	Selectivity coefficients	
	$K_{A,B}$ [FIM][a]	log $K_{A,B}$ [FIM][b]
Ca^{2+}	2.00×10^{-05}	-4.8 ± 0.1
Cu^{2+}	1.26×10^{-04}	-4.4 ± 0.2
Cyanocobalamin	6.00×10^{-05}	-4.7 ± 0.2
Thiamine hydrochloride	2.52×10^{-04}	-4.7 ± 0.2
Nicotinamide	1.00×10^{-03}	-4.6 ± 0.3
Zn^{2+}	1.00×10^{-04}	-4.5 ± 0.1
p-Amino benzoic acid	2.00×10^{-03}	-3.6 ± 0.2

Conditions: Primary (pyridoxine hydrochloride) ion concentration 1×10^{-1} M; interfering ion concentration: 1×10^{-3} M for conventional fixed interference method.

[a] Conventional fixed interference method.
[b] Unbiased fixed interference method [36,37].

Table 4
Results of determination of pyridoxine in different samples

Name of the formulation	Composition (mg/ml)		Observed pyridoxine content ± RSD/mg ($n = 5$)	
			By the present method using the developed sensor	By an established method*
Tab. Benedon	Pyridoxine HCl	40 mg	40.1 ± 0.2	40.9 ± 1.7
Inj. trineurosole-H	Hydroxocobalamin	1000 mcg		
	Thiamine HCl	0.1 g		
	Pyridoxine HCl	50 mg	50.3 ± 0.5	50.9 ± 1.5
	D-Panthenol	50 mg		
	Methyl Paraban	0.1% (w/v)		
	Water	qs		
Cap. Becosule	Thiamine mononitrate	10 mg		
	Riboflavin	10 mg		
	Pyridoxine HCl	3 mg	3.0 ± 0.5	3.1 ± 0.6
	Cyanicobalamin	15 mcg		
	Nicotinamid	100 mg		
	Ca-pantothenate	50 mg		
	Folic acid	1.5 mg		
	Biotin	100 mcg		
	Ascorbic acid	150 mg		
Cap. Polybion	Thiamine mononitrate	10 mg		
	Riboflavin	10 mg		
	Pyridoxine HCl	3 mg	2.7 ± 0.2	2.2 ± 1.6
	Ascorbic acid	150 mg		
	Nicotinamide	100 mg		
	Cyanocobalamin	15 mcg		
	Ca-pantothenate	50 mg		
	Folic acid	1.5 mg		
	Biotin	100 mcg		

* A standard HPLC method [38].

ine was achieved in the presence of many species that normally accompany pyridoxine hydrochloride in pharmaceutical multivitamin formulations.

3.5. Potentiometric determination of pyridoxine hydrochloride in formulations

The proposed sensor was successfully employed for the analysis of pyridoxine hydrochloride in multivitamin formulation using standard addition method [34]. The results for the analysis of pyridoxine hydrochloride in pharmaceutical multivitamin formulations are summarized in Table 4. The data obtained are in good agreement with the claimed values and compare favorably with those obtained by a standard HPLC method [38] used in the quality control division of multinational company. The quantity of pyridoxine is calculated using the following formula [39],

$$[X]_A = \frac{[X]_B}{[10^{\Delta E/S}[1 + (V_A/V_B)] - (V_A/V_B)]}$$

where $[X]_A$ is the concentration of the standard (M); $[X]_B$ the concentration of the determinand (M); ΔE the change in potential (mV); S the slope of the calibration plot (mV/decade); V_A the initial volume of the sample (ml); V_B the initial volume of the sample (ml).

The proposed method was validated against the HPLC method [38] using t-test with multiple samples. The calculated t-value was found to be 0.61. The tabulated t-value at 95% confidence level for 3 degrees of freedom is 3.182 and that at 99.5% confidence level is 7.453. Therefore, $t_{calc} \ll t_{tab}$ and there is no significant difference between the two methods at both the confidence levels.

The proposed sensor gives a Nernstian slope of 60.4 ± 3.1 mV/decade with correlation coefficient of 0.9996 as against 54 ± 0.4 mV/decade with correlation coefficient of 0.9980 as reported in literature [22]. The limits of linearity, the lower detection limit, the response time and the working pH range of the proposed sensor are superior to those for the sensor reported, as shown in Table 2. The proposed sensor, thus, has better performance characteristics as compared with the one reported earlier [22].

The proposed sensor can be successfully used for the selective determination of pyridoxine hydrochloride in the presence of other components that normally accompany pyridoxine in multivitamin formulations.

4. Conclusion

The developed sensor is selective, sensitive and low cost for routine control analysis. The proposed sensor exhibits favorable performance characteristics of pH, low detection limit, Nernstian calibration slope and fast response. The vitamin does not need any pretreatment or separation step and yields highly selective measurements. The sensor can be easily pre-

pared on a large scale and may be regarded as a disposable one.

Acknowledgement

The Department of Science and Technology, Government of India, is thanked for providing the financial assistance for this work.

References

[1] E.E. Conn, P.K. Stumpf, Outlines of Biochemistry, Wiley, New York, 1963, pp. 145.
[2] A.A. Alwarthan, F.A. Aly, Talanta 45 (1998) 1131–1138.
[3] E.D. Dinc, G. Kokdil, F. Onur, J. Pharm. Biomed. Anal. 22 (2000) 915–923.
[4] A. El-Gindy, F. El-Yazby, A. Mostafa, M.M. Maher, J. Pharm. Biomed. Anal. 35 (2004) 703–713.
[5] R. Gatti, M.G. Gioia, V. Cavrini, Anal. Chim. Acta 512 (2004) 85–91.
[6] W. Jin, J. Zhang, Electroanalysis 12 (2000) 465–467.
[7] M. Schreiner, E. Razzazi, W. Lui, Nahrung/Food 47 (2003) 243–247.
[8] A.J. Nepota, P.C. Dmiani, A.C. OliVieri, J. Pharm. Biomed. Anal. 31 (2003) 621–627.
[9] A.R. Medina, M.L.F. Cordora, A.M. Diaz, J. Anal. Chem. 363 (1999) 265–269.
[10] G.m. Escander, A.J. Bystol, A.D. Campiglia, Anal. Chim. Acta 466 (2002) 273–283.
[11] N.R. Martos, A.M. Diaz, A.O. Navalon, I.D. Paya, L.F.C. Vallrey, J. Pharm. Biomed. Anal. 23 (2000) 837–844.
[12] A. El-Gindy, J. Pharm. Biomed. Anal. 32 (2003) 277–286.
[13] P. Soderhjelm, J. Lindquist, Analyst 100 (1975) 349–354.
[14] S.R. Hernandez, G.G. Ribero, H.C. Goicoechea, Talanta 61 (2003) 743–753.
[15] I. Siddiqui, K.S. Piter, J. Pharm. Biomed. Anal. 26 (2001) 1009–1015.
[16] M.F.S. Teixeira, A. Segnini, F.C. Moraes, L.H. Marcolino-Junior, O. Fatibello-Filho, E.T.G. Cavalheiro, J. Braz. Chem. Soc. 14 (2003) 316–321.
[17] M.F.S. Teixeira, G. Marino, E.R. Dockal, E.T.G. Cavalheiro, Anal. Chim. Acta 508 (2004) 79–85.
[18] W. Qu, K. Wu, S. Hu, J. Pharm. Biomed. Anal. 36 (2004) 631–635.
[19] H. Okamoto, T. Nakajima, Y. Ito, J. Pharm. Biomed. Anal. 30 (2002) 815–822.
[20] C.K. Markopoulou, K.A. Kagkadis, J.E. Koundorellis, J. Pharm. Biomed. Anal. 30 (2002) 1403–1410.
[21] L. Tan, Q. Xie, S. Yao, Electroanalysis 16 (2004) 1592–1597.
[22] G.A.E. Mostafa, J. Anal. Chem. 58 (2003) 1073–1077.
[23] C.D. Gutsche, Calixarenes, The Royal Society of Chemistry, Cambridge, 1989.
[24] J. Vicens, V. Bohmer, Calixarenes: A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, 1990.
[25] D. Diamond, K. Nolan, Anal. Chem. 73 (2001) 22A–29A.
[26] V.K. Gupta, R.N. Goyal, M. Al Khayat, P. Kumar, N. Bachheti, Talanta 69 (2006) 1149–1155.
[27] A.K. Jain, V.K. Gupta, L.P. Singh, J.R. Raisoni, Electrochim. Acta 51 (2006) 2547–2553.
[28] V.K. Gupta, R. Ludwig, S. Agarwal, Anal. Chim. Acta 538 (2005) 213–218.
[29] A.K. Jain, V.K. Gupta, L.P. Singh, P. Srivastava, J.R. Raisoni, Talanta 65 (2005) 716–721.
[30] A.K. Jain, V.K. Gupta, J.R. Raisoni, Sensors 4 (2004) 115–124.
[31] V.K. Gupta, R. Mangla, S. Agarwal, Electroanalysis 14 (2002) 1127–1132.
[32] I. Mohammed-Ziegler, B. Poor, M. Kubinyi, A. Grofcsik, A. Grun, I. Bitter, J. Mol. Struct. 650 (2003) 39–44.
[33] M. Lazzarotto, F.F. Nachtigall, E. Schnitzler, E.E. Castellano, Thermochim. Acta 429 (2005) 111–117.
[34] R.P. Buck, E. Lindner, Pure Appl. Chem. 66 (1994) 2527–2536.
[35] A. Sil, V.S. Ijeri, A.K. Srivastava, Sens. Actuators B 106 (2005) 648–653.
[36] A. Radu, S. Peper, E. Bakker, D. Diamond, Electroanalysis 19 (2007) 144–154.
[37] E. Bakker, E. Pretsch, P. Buhlmann, Anal. Chem. 72 (2000) 1127–1133.
[38] Indian Phamacopoiea, Ministry of Health and Family Welfare, Government of India, 1996, pp. 646.
[39] P.L. Bailey, Analysis with Ion Selective Electrode, Heyden and Son Ltd., 1976, pp. 187.