Anal. Bioanal. Electrochem., Vol. 5, No. 3, 2013, 368 - 380

Analytical & Bioanalytical Electrochemistry

Full Paper

Ion Selective Membrane Electrodes for the Determination of Xylometazoline Hydrochloride in Rabbit Aqueous Humor using 2-Hydroxy Propyl β-cyclodextrin and Calix[6]arene as Ionophores

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Received: 27 March 2013 / Received in revised form: 29 May 2013: Accepted: 1 June 2013 / Published online: 30 June 2013

Abstract- Three novel Xylometazoline Hydrochloride (XYLO) selective electrodes were investigated with Dioctyl phthalate (DOP) as a plasticizer in a polymeric matrix of polyvinyl chloride (PVC). Sensor 1 was fabricated using Phosphomolybdic acid (PMA) as an anionic exchanger without incorporation of an ionophore. Sensor 2 used 2-hydroxy propyl β-cyclodextrin (hpβ-CD) as an ionophore while sensor 3 was constructed using calix[6]arene as an ionophore. Linear responses of XYLO within the concentration ranges of 10^{-4} to 10^{-2}, 10^{-5} to 10^{-2} and 10^{-5} to 10^{-2} mol L^{-1} were obtained using sensors 1, 2 and 3, respectively. Nernstian slopes of 49.78, 56.21 and 46.20 mV/decade over the pH range of 5–9 for sensors 1, 2 and 5-7 for sensor 3 were observed. The selectivity coefficients of the developed sensors indicated excellent selectivity for XYLO. The utility of 2-hydroxy propyl β-cyclodextrin and calix[6]arene as ionophores had a significant influence on increasing the membrane sensitivity and selectivity of sensors 2 and 3 compared to sensor 1. The proposed sensors displayed useful analytical characteristics for the determination of XYLO in bulk powder, different pharmaceutical formulations, and biological fluids (Rabbit aqueous humor) and in the presence of its degradation product (2, 6- dimethyl-4-tert-butyl-phenylacetic acid) and thus could be used as stability-indicating method.

Keywords- Xylometazoline, Hydroxypropyl β cyclodextrine, Calix[6]arene, Rabbit Aqueous Humor

1. INTRODUCTION

Xylometazoline-HCl (XYLO) 2-(4-tert-butyl-1,2-dimethylbenzyl)-2-imidazoline is an imidazoline derivative. It is a sympathomimetic agent with marked alpha adrenergic activity. It constricts the smaller arterioles of the nasal passage, affecting a decongesting action. It is used in 0.1% and 0.05% solutions for the relief of nasal congestion caused by rhinitis and sinusitis. A 0.05% may be instilled into the eye as a conjunctive decongestant [1].

There are different techniques were reported for XYLO determination in pharmaceutical preparations and in biological fluids. Gas chromatography [2,3], HPTLC for simultaneous determination of XYLO and dexamethasone in nasal drops [4], solid-phase extraction and liquid chromatography-tandem mass spectrometric methods [5], chemometric analysis based on chromatographic data [6], HPLC [7–11], application of atomic-emission and atomic-absorption spectrometry [12]. First derivative spectrophotometry by using picrate derivative [13] Colorimetric determination [14–17], Spectrofluorimetry [18].

There is no ion selective electrode was reported for determination of XYLO. So this work was the first in this branch for XYLO.

Cyclodextrins (Fig. 1) are chiral, toroidal-shaped enzymatic products formed by the action enzyme cyclodextrin transglycosylase on hydrolyzed starch. The obtained glucose units bonded together forming a characteristic sleeve-like cavity which exhibits a hydrophobic behavior. These cavities are known to accommodate a wide variety of organic, inorganic and biologic guest molecules to form stable host–guest inclusion complexes [19–21].Cyclodextrins, are commercially available and have been previously applied as sensor ionophores in potentiometric ion selective electrodes [21-23].

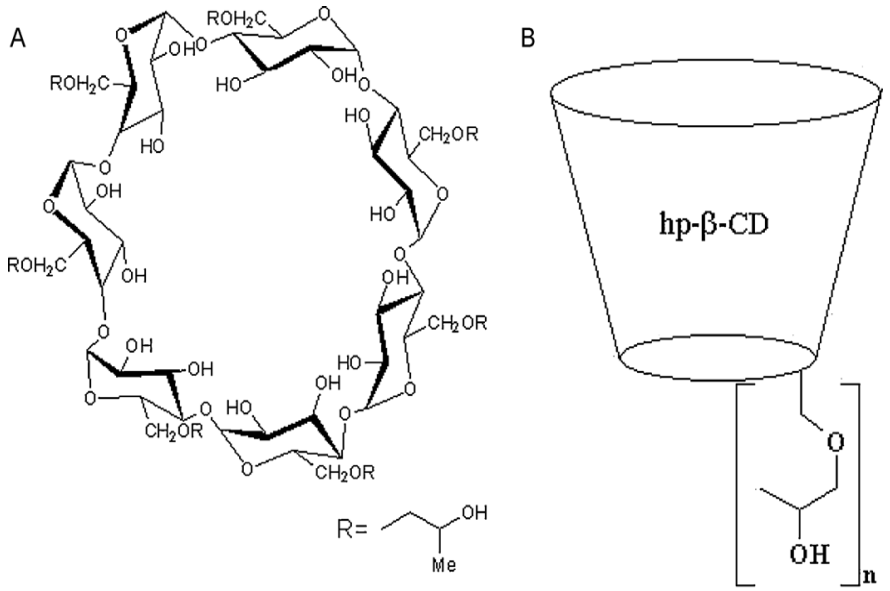

Fig. 1. Chemical structure and toroidal shape of cyclodextrin hydroxyl propyl β-cyclodextrine molecule

Calixarenes (Fig. 2) have attracted a lot of interest as a kind of key receptors in supramolecular chemistry [24]. They are cavity-shaped cyclic oligomers made up of phenol units linked via alkylidene groups. They can be selectively functionalized at the narrow rim (polar) or at the wide rim (non-polar), so calixarenes can form inclusion complexes with a wide range of guest species as used in applications in ion-selective membranes and electrodes [23,25-27].

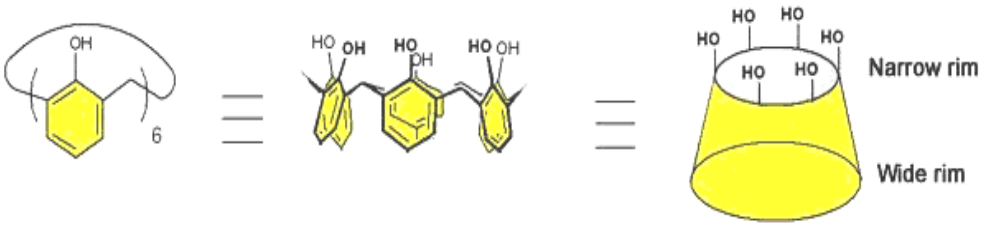

Fig. 2. Chemical structure of calix[6]arene molecule showing the narrow rim (polar) and the wide rim (non-polar)

The present work describes the use of functionalised cyclodextrin derivatives (hpβ-CD) and calix[6]arene as neutral ionophores in presence of PMA as ion exchange, for the development of novel sensors for the determination of XYLO. These sensors were used for the determination of XYLO in bulk powder, different pharmaceutical formulations, and biological fluid (rabbit aqueous humor) and in the presence of its degradation product.

2. EXPERIMENTAL

2.1. Apparatus

A Jenway digital ion analyser model 3330 (Essex, UK) with Ag/AgCl double junction reference electrode (Aldrich, Germany) was used for potential measurements. A Jenway pH glass electrode (Essex, UK) was used for pH adjustments.

2.2. Chemicals and reagents

XYLO was kindly supplied by Cid Company, Egypt. Its purity was checked in our laboratory according to the HPLC method [28] and was found to be 101.77±1.29%. Rhinex nasal drops containing XYLO 0.1% Adults and 0.05% Infants was manufactured by Cid Company and was purchased from local markets.

All chemicals and reagents used were of analytical reagent grade. PVC, hpβ-CD, calix[6]arene, PMA, DOP and Tetrahydrofuran (THF) were obtained from Aldrich, Germany. Potassium chloride Merck (USA). Phosphate buffer solution: prepared according

to B.P. using 0.2 M potassium dihydrogen phosphate (El-Nasr pharmaceutical chemicals, Cairo, Egypt.) and 0.2 M NaOH aqueous solution.

Fresh rabbit apueous humour: from rabbits that were purchased from EL Nile pharmaceutical company.

2.3. Procedures

2.3.1. Fabrication of membrane sensors

For the preparation of sensor 1, in a glass Petri dish (5 cm diameter) 400 mg DOP as a plasticizer was mixed with 190 mg of PVC and 30 mg PMA. The mixture was dissolved in 5 ml of THF. For sensor 2 preparation, the same composition as sensor 1 but with addition of 50 mg of hpβ-CD while for sensor 350 mg calix[6]arene were added instead. The Petri dishes were covered with a filter papers and left to stand overnight to allow solvent evaporation at room temperature. These ratios of components added will form a master membrane with a thickness of 0.1 mm which is wanted.

From each master membrane, a disk (about 8 mm diameter) was cut using a cork borer and pasted using THF to an interchangeable PVC tip that was clipped into the end of the electrode glass body. Equal volumes of 10^{-2} M XYLO and 10^{-2} M potassium chloride were mixed and this solution was used as an internal reference solution. Ag/AgCl wire (1 mm diameter) was immersed in the internal reference solution as an internal reference electrode. The sensors were conditioned by soaking each sensor into 10^{-2} M aqueous XYLO solutions for 24 h and storing in the same solution when not in use.

2.3.2. Sensors calibration

The conditioned sensors were calibrated by separately transferring 50 ml aliquots of solutions covering concentration range of (1×10^{-7}–1×10^{-2} M) of XYLO into a series of 100 ml beakers starting from the low to the high concentrations. The membrane sensors in conjunction with a reference electrode were immersed in each solution, allowed equilibrating with constant stirring, then recording the stable potential with in ±2 mV. The electrode potential (EMF) was plotted versus each negative logarithmic concentration of XYLO.

2.3.3. Effect of pH

The effect of pH on the potential values of the three investigated sensors was studied over pH range of 3-10 at 1 pH interval by using 10^{-4} M and 10^{-3} M XYLO solutions.

The pH was gradually increased or decreased by adding aliquots of dilute sodium hydroxide or dilute hydrochloric acid solutions respectively. The potential obtained at each pH value was recorded. The obtained platue region was selected as pH range of use in the procedure and covered by appropriate buffer.

2.3.4. Sensors selectivity

The potentiometric selectivity coefficient –log $K^{pot.}_{(Primary\ ion,\ interferent)}$ was used to evaluate the extent to which a foreign ion would interfere with the response of an electrode to its primary ion. Selectivity coefficients were calculated by the separate solutions method, where potentials were measured for 10^{-3} M aqueous XYLO solution and then for 10^{-3} M aqueous interferent solution separately then potentiometric selectivity coefficients were calculated using the following equation:

$$- \log K^{pot.}_{(Primary\ ion,\ interferent)} = (E_{xylo.} - E_M) / Slope$$

Where E_{XYLO} is the potential measured in 10^{-3} M XYLO solution.
E_M is the potential measured in 10^{-3} M interferent solution.

2.3.5. Determination of XYLO in pharmaceutical preparations

From the content of Rhinex nasal drops bottles (0.1% adult and 0.05% infant), aliquot mL were transferred separately into 25 mL volumetric flask, dissolved with the appropriate chosen buffer, then completed to mark to obtain 1×10^{-4} M aqueous solution of XYLO, procedure was then completed as described under 2.3.2. From the recorded potential calculate the concentration of XYLO from the corresponding regression equation.

2.3.6. Determination of XYLO in the presence of its alkaline degradate

A degraded sample of XYLO was prepared by adding 25 ml of 2 M NaOH solution to pure XYLO (100 mg) in a 150 mL flask and then reflux the solution at 100 °C for 3 h. Test for complete degradation by TLC using benzene: acetone: NH_3 (3:25: 3 by volume) as the developing system [1]. Oily droplets were separated on the surface, can be physically separated by using separating funnel. Add 2 M HCl solution to the aqueous degraded solution till pH was adjusted to about 7. Extract the degredate in the aqueous solution by shaking with 30 mL chloroform 3 times 10 mL each, then evaporate the chloroformic solution slowly just to dryness under ambient temperature. Test the purity of the degradation product obtained by dissolving a small portion in methanol, applying onto TLC plates and developing using the previously mentioned solvent system. Elucidate the structure of the isolated degradation product using the IR and mass spectrometry.

Prepare from the degradate10^{-4}, 10^{-3} M in 100 mL volumetric flasks. Aliquots of standard drug solution (10^{-4}, 10^{-3} M) were mixed with its degraded sample (10^{-4},10^{-3} M) respectively in different ratios. The EMF values of these laboratory-prepared mixtures were recorded and results were compared with the calibration plot.

2.3.7. Determination of XYLO in Rabbit aqueous humor

Three to five albino rabbits were used to obtain a fresh aqueous humor. Two drops of 0.4% solution of oxybuprocaine HCl (Local anesthetic) were instilled into rabbit's eye. Samples of aqueous humor were immediately removed from the anterior chamber of each eye using a 26- gauge needle attached to 1 ml tuberculin syringe. The procedure was repeated 2 times a day for about 3-5 days till the wanted volume was collected. The samples were stored frozen until the experiment was carried out [29]. After removal of aqueous humor samples at each time interval, the rabbits were scarified. The ocular surface was irrigated with isotonic phosphate buffered saline and dried with soft tissue.

Add 0.5 ml of 10^{-3} standard drug solution into 25 ml beaker containing 4.5 ml of the collected aqueous humor, and vortex for 1 min. Immerse the membrane sensors in this solution. Measure the EMF produced by the proposed sensors and determines the concentration of XYLO from the corresponding regression equation.

3. RESULTS AND DISCUSSION

The molecular recognition and inclusion complexation are of current interest in host guest and supramolecular chemistry and offer a promising approach to chemical sensing [30,31]. The use of selective inclusion complexation and complementary ionic or hydrogen bonding are two main strategies for preparing synthetic host molecules, which recognize the structure of guest molecules [32].

Modified cyclodextrins (CDs), either natural or synthetic, are viewed as molecular receptors. In the case of natural CD, cooperative binding with certain guest molecules was mostly attributed to intermolecular hydrogen bonding between the CD molecules, while intermolecular interactions between the host and guest molecules (hydrogen bonds, hydrophobic interactions and Van der Waals forces) contributed to cooperative binding processes when synthetic CDs were used [33]. Although the size and geometry of the guest mainly govern the binding strength, it is possible to influence the host guest interactions by modifying the three hydroxyl groups on each glucose unit. Indeed, the use of hpβ-CD enhanced the interaction properties between host and guest molecules [23].

Calixarenes are characterized by a three-dimensional basket, cup or bucket shape. They are representative for the study of host guest interactions either with various metals [24] or variety of cation substrates [23]. They have electron rich interior cavities and possessing the ability to complex through dipole–dipole interactions with metal ion of compatible dimensions or with cationic compounds.

The present work evaluates the possibility of quantitative determination of XYLO by using selective electrode 1 with only ion exchanger PMA in its composition or accompanied by hpβ-CD or calix[6]arene as sensor ionophores in selective electrodes 2 and 3,

respectively, using PVC as a polymeric matrix to immobilize the sensors and to attain the formation of highly stable complexes.

3.1. Performance characteristics of XYLO sensors

The positive XYLO ion prefers the high donation sites OH-groups of hpβ-CD structures rather than the methyl groups. Thus, sensor 2 shows the higher slope value than others. The presence of ionophores in sensors 2, 3 affect the enhancement of sensitivity and selectivity as showing larger linearity range with lower selectivity values. Sensor 1 with no ionophore shows higher selectivity coefficient values that correspond with more attack by interfering cations on the electrode membrane [23].

The results reveal that, as ionophores, hpβ-CD and calix[6]arene provide high stability to the complexes formed with cationic drug present in solution; thus, the membrane selectivity and sensitivity are substantially enhanced. The electrochemical performance characteristics of the proposed sensors were systematically evaluated according to IUPAC standards [34]. Table 1 shows the results obtained for each sensor.

Table 1. Electrochemical response characteristics of the three investigated XYLO sensors

Parameters	**Sensor 1**	**Sensor 2**	**Sensor 3**
Slope(mv decade^{-1})*	49.78	56.21	46.20
Intercept (mv)	180.02	271.39	193.75
Response time (sec.)	15-20	15-20	15-20
Working pH range	6-9	5-9	5-7
Concentration range (M)	10^{-4}-10^{-2}	10^{-5}-10^{-2}	10^{-5}-10^{-2}
Stability (days)	45 days	45 days	7 days
Correlation coefficient	0.9995	0.9995	0.9996

*Average results of three determinations

Typical calibration plots are shown in Fig. 3. The slopes of the calibration plots are 49.78, 56.21 and 46.20 mV/decade for sensors 1, 2 and 3, respectively. Deviation from the ideal Nernstian slope (60 mV) is due to the electrodes responding to the activity of the drug cations rather than its concentration. The sensors displayed constant potential readings for day to day measurements, and the calibration slopes did not change by more than ±2 mV/decade over a period of 45, 45 and 7 days for sensors 1, 2 and 3, respectively. The detection limits of the three sensors were estimated according to the IUPAC definition [34]. Table 1 shows that sensor 2, 3 can detect XYLO in dilute solutions down to 10^{-5} M. sensor 3 exhibits a sub-Nernstian behavior despite having a good linear range while sensor 1 has a

reasonably good slope but falls short in the limit of linearity. Sensor 2 is the best due to the use of derivative cyclodextrin.

The slopes of the calibration plot did not change significantly but show a gradual decrease in sensitivity.

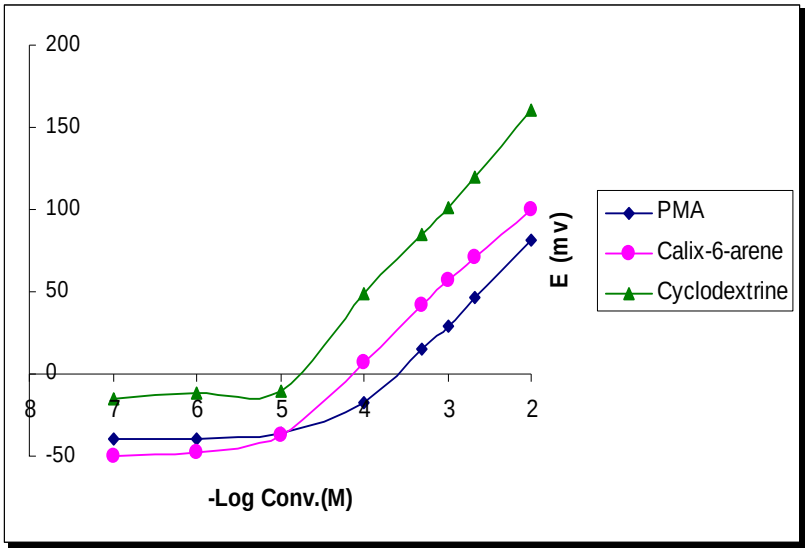

Fig. 3. Profile of the potential in mV *vs.* −log concentrations of XYLO in M obtained with sensors 1, 2 and 3

3.2. Dynamic response time

Dynamic response time is an important factor for analytical applications of ion-selective electrodes. In this study, practical response time was recorded by increasing XYLO concentration by up to 10-fold. The required time for the sensors to reach values within ±2 mV of the final equilibrium potential was 15-20 sec. for the sensors. The response time increases with increasing the concentrations.

3.3. Effect of pH

For quantitative measurements with ion selective electrodes, studies were carried out to reach the optimum experimental conditions. The potential pH profile obtained indicates that the responses of the sensors 1, 2 are fairly constant over the pH range 5–9. Therefore, the pH range from 5 to 9 was assumed to be the working pH range of these sensors. While for sensor 3 the working pH is 5-7.

3.4. Sensors selectivity

The higher the selectivity coefficient value, the more the electrode membrane is attacked by the interferent cations. Table 2 shows the potentiometric selectivity coefficients of the proposed sensors in the presence of degradates, other inorganic cations (K^+, Na^+ and Ca^{++})

that are usually found in biological fluids. Glucose, lactose and starch those are usually present in dosage forms. The results reveal that the proposed membrane sensors display high selectivity sensors 2 and 3 are at least 10–100 times more selective than sensor 1.

Table 2. Potentiometric selectivity coefficients of the three proposed sensors by separate solutions method (SSM)

Interferent**	PMA	HPβ-CD	Calix[6]arene
Glucose	$4.35*10^{-1}$	$6.31*10^{-4}$	$4.90*10^{-4}$
Lactose	$6.30*10^{-1}$	$2.51*10^{-3}$	$2.19*10^{-3}$
Starch	$2.61*10^{-1}$	$1.41*10^{-3}$	$1.55*10^{-3}$
NaCl	$5.96*10^{-2}$	$8.31*10^{-4}$	$3.63*10^{-4}$
KCl	$2.7*10^{-2}$	$5.13*10^{-4}$	$1.26*10^{-3}$
$CaCl_2$	$1.2*10^{-2}$	$4.57*10^{-4}$	$6.61*10^{-4}$
urea	$8.22*10^{-2}$	$8.32*10^{-4}$	$5.13*10^{-5}$

** 1×10^{-3} M aqueous solutions were used

3.5. Potentiometric determination of XYLO in pharmaceutical formulations

The proposed sensors were applied for the analysis of XYLO pharmaceutical formulations in buffered solutions. The results prove the applicability of the three sensors for the determination of pharmaceutical formulations containing XYLO. These data are shown in Table 3.

To examine the validity of the proposed sensors, the obtained results were compared to HPLC method [28] and no significant difference was observed. Moreover, the proposed sensors do not require preliminary drug extraction.

Table 3. Determination of XYLO in pharmaceutical formulations Rhinex nasal drops by the three proposed sensors

Pharmaceutical formulation	Recovery % of XYLO		
	Sensor 1	Sensor 2	Sensor 3
Rhinex(0.1%) Batch No. 113658D	98.64	103.13	100.00
Rhinex(0.05%) Batch No. 111456D	103.84	100.00	102.08

3.6. Potentiometric determination of XYLO in the presence of its alkaline degradate

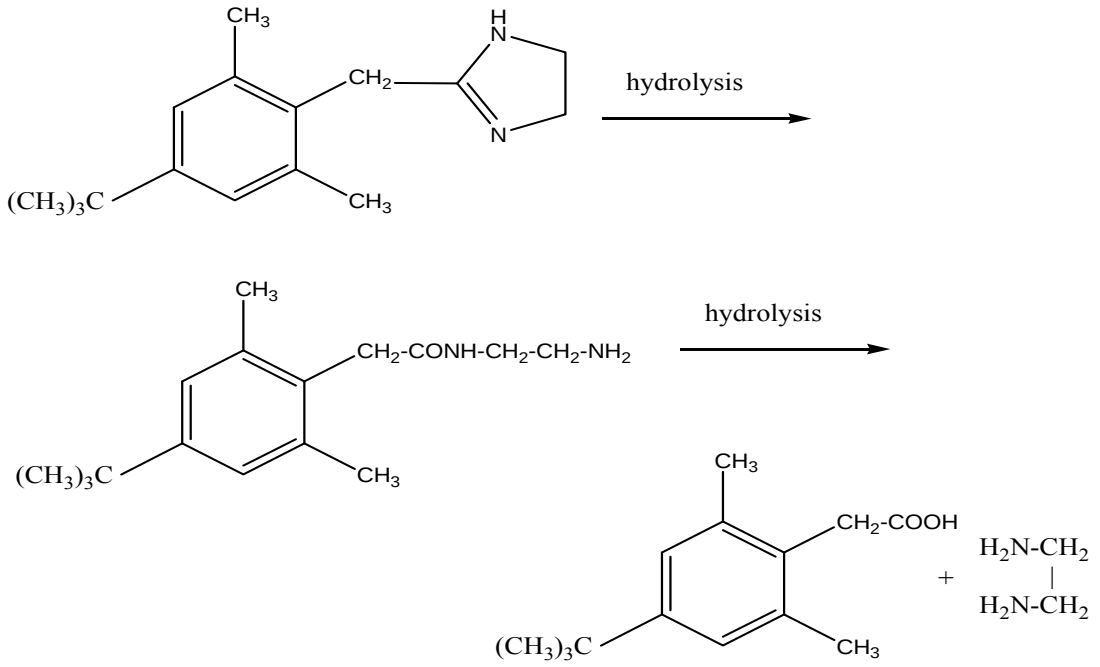

Fig. 4. Degradation pathway of XYLO

Complete degradation of XYLO was induced by boiling with 2 M NaOH for 3 h, Fig. 4 shows the reported alkaline degradation of the drug [1]. The final degradation products are

2,6-dimethyl-4-tert-butyl-phenylacetic acid and ethylenediamine.

The induced alkaline degradation was tested by TLC till complete degradation products were obtained. Table 4 shows the results obtained upon analysis of synthetic mixtures containing different ratios of intact drug and degraded sample varying from 100:0 to 10:90. The result shows that three sensors can be successfully used for selective determination of intact drug in the presence of >90% of it's degradate. So they are recommended for use in stability-indicating methods.

Table 4. Determination of XYLO in laboratory prepared mixtures containing different ratios of XYLO and its induced alkaline degradation product by the proposed sensors using either 10^{-3} M or 10^{-4} M solution

Ratio % XYLO: Degredate	Recovery % of XYLO					
	Sensor1		Sensor2		Sensor3	
	10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M	10^{-3} M	10^{-4} M
90: 10%	99.50	103.33	99.00	97.00	97.67	101.96
70: 30%	100.50	99.50	97.00	98.50	97.73	100.93
50: 50%	100.00	100.50	98.50	97.30	100.00	102.80
30: 70%	100.50	100.00	100.00	97.00	97.78	103.51
10: 90%	100.33	99.50	98.00	100.00	97.33	100.00

3.7. Potentiometric determination of XYLO in Rabbit aqueous humor

For determination of XYLO in spiked rabbit aqueous humor, it was found that the three sensors are reliable and give stable results with very good accuracy and high percentage recovery without preliminary extraction procedures, which is shown in **Error! Reference source not found.**.

The response times of the proposed sensors are instant (within 15 s), so the sensors are rapidly transferred back and forth between the biological samples and the distilled water between measurements to protect the sensing component from adhering to the surface of some matrix components.

It is concluded that the proposed sensors can be successfully applied to in vitro studies and for clinical use.

Table 5. Determination of XYLO in spiked rabbit aqueous humor by the proposed sensors

XYLO added (M) in rabbit aqueous humor	Recovery % of XYLO		
	Sensor1	Sensor2	Sensor3
10^{-4} M	97.37	100.00	102.38

4. CONCLUSION

The described sensors are sufficiently simple and selective for the quantitative determination of XYLO in pure form, pharmaceutical formulations, in the presence of its degradate and in rabbit aqueous humor. Both calix[6]arene and 2-hydroxy propyl β-cyclodextrin as ionophores increased the membrane sensitivity and selectivity of sensors 2 and 3 in comparison with sensor 1. Sensor 2 shows advance over the other two sensors as the use of derivative of cyclodextrin improve its performance. The proposed sensors offer advantages of fast response and elimination of drug pretreatment or separation steps. They can therefore be used for routine analysis of XYLO in quality control laboratories.

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