

## ORIGINAL ARTICLE

## King Saud University

## Arabian Journal of Chemistry

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# Potentiometric and surface topography studies of new carbon-paste sensors for determination of thiamine in Egyptian multivitamin ampoules

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Received 24 August 2016; accepted 22 November 2016 Available online 30 November 2016

#### **KEYWORDS**

Carbon-paste; Sensor; Thiamine; Potentiometry; Microscopy; Topography Abstract We report here for the first time two potentiometric carbon-paste sensors for determination of thiamine chloride hydrochloride in aqueous solutions. The proposed sensors use the ion-pair of thiamine with tetraphenylborate as an electro-active species and dibutyl phthalate (sensor I) or o-nitrophenyloctyl ether (sensor II) as solvent mediators. The effect of solvent mediator was studied using dibutyl phthalate, o-nitrophenyloctyl ether, ethylhexyl adipate, dioctyl phthalate, tricresyl phosphate and paraffin oil. The slopes of the calibration graphs are  $29.49 \pm 0.24$  and 29.60 $\pm$  0.15 mV/decade for sensors (I) and (II), respectively. The sensors are able to detect down to  $5.25 \times 10^{-6}$  and  $3.57 \times 10^{-6}$  for (I) and (II), respectively. Both sensors show reasonable thermal stability and fast response time. The selectivity coefficients obtained from the matched potential method indicate high selectivity of the proposed sensors toward thiamine over commonly interfering cations. Sensor (I) has a lifetime of only 1-2 days; however, sensor (II) remains usable for up to one month. Analytical applications to pure solutions and Egyptian multivitamin ampoules show excellent recovery values ranging from 97.92 to 103.72% and 97.21 to 102.19% for sensors (I) and (II), respectively. Moreover, the precision and reproducibility of the sensors are indicated from the low values of %RSD of five replicate measurements. In addition, the surface topography of the sensors was studied using scanning electron microscopy to investigate the effect of chemical modification on the surface structure.

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#### 1. Introduction

Vitamins are important biological molecules which play the role of cofactors in enzyme catalyzed reactions inside the bodies of the living organisms. They cannot be synthesized inside the human body and must be taken from an external source (Li, 2014). Thiamine hydrochloride (TH) is the first identified vitamin (Brumback, 2012). It belongs to

#### http://dx.doi.org/10.1016/j.arabjc.2016.11.012

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a group of vitamins called the B-complex family. It is also known as vitamin B1 and its IUPAC name is 3-[(4-amino-2-methylpyrimidin-5-yl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium chloride hydrochloride (Abiola et al., 2011). TH acts as a co-enzyme in many enzymatic processes inside the human body such as the biosynthesis of neurotransmitters, production of pentoses for nucleic acid synthesis and the production of the reducing agents which is used in the defense against oxidative stress (Guilland, 2013).

Sodium tetraphenylborate (STPB) is the sodium salt of the tetraphenylborate (TPB) anion which has a molar mass of 342.2 g/mol. This organic compound is usually used as a precipitating agent due to its high molecular weight. It also plays an important role in chemical synthesis (Ciattini et al., 1992; King and Bryant, 1992). Moreover, STPB is used as a precipitating agent for preparing the electrode materials of electrochemical potentiometric sensors (Abu Shawish et al., 2016b; Issa et al., 2017; Shao et al., 2016). Scheme 1 shows the chemical structures of TH and STPB.

Many researchers proposed analytical methods for determination of TH such as spectrophotometry and spectrofluorimetry based on thiochrome-formation reaction (Fujiwara and Matsui, 1953; Karlberg and Thelander, 1980; Weber and Kewitz, 1985). In addition, high performance liquid chromatography (HPLC) methods were developed to determine TH (Dinc et al., 2000; Marszałł et al., 2005; Tang et al., 2006; Weber and Kewitz, 1985; Yantih et al., 2011). Hassan et al. proposed a membrane sensor based on thiamine-picrolonate ion-pair complex for the determination of thiamine (Hassan et al., 1985). Moreover, Hassan and Elnemma used thiamine-reineckate in nitrobenzene to prepare a membrane sensor selective for thiamine (Hassan and Elnemma, 1989). Another membrane sensor was recently developed by Hosseinzadeh and Khorsandi. The sensor is based on the ion-pair of thiamine and the anti-inflammatory drug, diclofenac sodium (Hosseinzadeh and Khorsandi, 2015). From the abovementioned methods, it is clear that there are few electrochemical methods developed for determination of TH and, to the best of our knowledge. there are no carbon-paste sensors (CPSs) used for determination of TH. The spectrophotometric methods have the disadvantages of relatively high detection limit compared with the other methods and the consumption of a massive amount of chemicals. On the other hand, HPLC usually requires the use of toxic organic solvents and expensive columns. Moreover, the previously proposed potentiometric membrane sensors have the disadvantages of the use of organic solvents, tedious preparation procedures and the use of a filling solution for electrical conduction. Consequently, it is necessary to prepare carbon-paste sensors (Wei et al., 2013; Yan et al., 2013a, 2013b) for estimating TH potentiometrically.

The main objective of this work was to prepare and characterize ion-selective CPSs for thiamine determination in pure solution and multivitamin ampoules for the first time. The sensors are based on TH-TPB ion-pair as an electrode material. Different parameters were investigated to characterize the proposed sensors such as the type of solvent mediator, the percentage of the ion-pair, effect of interfering ions and test solution temperature. The proposed sensors were applied to the determination of TH in pure solutions and different Egyptian multivitamin ampoules.

#### 2. Experimental

The materials used to perform this study are of chromatographic grade purity. Solutions were prepared using double distilled water from a glass distillation instrument.

#### 2.1. Apparatus

Accurate weighing was performed using a four-digit Scientech SA 210 balance throughout the work. Potential measurements were achieved with the aid of a Jenway 3010 pH meter against an Ag/AgCl electrode as an external reference. Scanning electron microscopy images were taken by a Quanta FEG 250 electron microscope, Desert Research Center, El-Matareya, Cairo, Egypt.

#### 2.2. Materials and reagents

Pure TH powder (337.27 g/mol) was obtained from Amriya Pharm. Ind., Egypt. STPB, carbon powder, paraffin oil, dioctyl phthalate (DOP), dibutyl phthalate (DBP), tricresyl phosphate (TCP), ethylhexyl adipate (EHA) and orthonitrophenyloctyl ether (NPOE) were purchased from Sigma– Aldrich, Germany. Sodium chloride, potassium chloride, magnesium sulfate heptahydrate, zinc acetate, and calcium chloride are Adwic Chemical Company products, Cairo, Egypt. Amino acids (D-alanine and DL-serine) and sugars (lactose and fructose) were obtained from Sigma–Aldrich, Germany. Neurovit<sup>®</sup> (Amriya Pharm. Ind., Egypt), Neuroton<sup>®</sup> (Amoun, Egypt), Bécozyme<sup>®</sup> (Bayer AG, Germany) and B-Com<sup>®</sup> (Amoun, Egypt) are the multivitamin ampoules used in the application of the sensors to the analysis of TH in its pharmaceutical form.

#### 2.3. Ion-exchanger preparation

The ion-pair of TH with TPB was used as the ion-exchanger (electrode material) in the sensing carbon-paste. TH solution was prepared by dissolving 84.32 mg of TH in 25 mL of bidistilled water (solution A). A solution of STPB was prepared by dissolving 85.55 mg of STPB in 25 mL of bidistilled water (solution B). Thereafter, solution A was added to solution B



Scheme 1 Chemical structures of TH (a) and STPB (b).

and the mixture was left for 48 h for complete coagulation. The mixture was filtered and the obtained precipitate was washed several times with bidistilled water. The precipitate was covered and left to dry for one week at room temperature.

#### 2.4. Preparation of the sensors

The sensing carbon-paste was prepared by mixing the appropriate amounts of graphite, ion-exchanger and plasticizer. The components were made homogeneous by mechanical mixing in an Agate mortar. Thereafter, the obtained paste was fixed in a hollow Teflon holder having a stainless steel rod inside its body for electrical conductance. The length of the rod is tuned (and hence ejecting the paste outside the holder body) with the aid of a rotatable screw at the upper end of



Figure 1 Effect of variable ion-exchanger ratios on the potentiometric performance of the proposed carbon-paste sensors.

the rod. The surface of the paste is smoothed against a smooth piece of paper to give a clean shiny surface. After their preparation, the sensors were stored in a dry and cold place until use.

#### 2.5. Calculation of the selectivity coefficients

The selectivity of ion-selective sensors (ISSs) toward interfering ions can be investigated by measuring their corresponding selectivity coefficients ( $K_{TH,J^{z+}}^{Pot}$ ). Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, D-alanine, DL-serine, fructose and lactose were used as interfering ions to investigate the selectivity of the prepared sensors using the matched potential method (Horvai, 1997). In this method, the selectivity coefficient is defined as the activity ratio of the primary ion and the interfering ion which gives the same potential change in a reference solution. 50 mL of  $1.0 \times 10^{-5}$  mol/L TH solution was used as a reference solution. Furthermore, 0.1 mL of  $1.0 \times 10^{-2} \text{ mol/L} (a_{TH})$  of TH solution was added to the reference solution and the corresponding potential change ( $\Delta E$ ) was recorded. In a separate experiment,  $1.0 \times 10^{-2}$  mol/L solution of the interfering ion  $(J^{Z^+})$  was successively added to an identical reference solution until the same potential change value ( $\Delta E$ ) was reached. The values of  $K_{TH,J^{z+}}^{Pot.}$  are then calculated using Eq. (1):

$$K_{TH,J^{z+}}^{Pot.} = \frac{a_{TH}}{a_{J^{z+}}}$$
(1)

where  $a_{J^{2+}}$  is the activity of the added interfering ion.

#### 2.6. Standard addition method

The standard addition method is a method applied in the analytical applications of the proposed sensors. In this method, known volumes of the TH standard solution were added to the analyte solution (containing the pure form or pharmaceutical multivitamin ampoules). The change in potential reading is recorded and the unknown concentration can be calculated by substitution in Eq. (2) (Brand and Rechnitz, 1970; Issa and Khorshid, 2011):

$$C_x = C_s \left(\frac{V_s}{V_x + V_s}\right) \left(10^{n(\Delta E/s)} - \frac{V_x}{V_x + V_s}\right)^{-1}$$
(2)

Table 1	Potentiometric	characteristics of	chemically n	nodified TH	CPSs,	average of	5 replica	te measurements at	t room tem	perature
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Composition (w%)			Slope $\pm$ SE <sup>a</sup>	Linear range	LOD	LOQ	RSD <sup>b</sup>	$r^2$
TH-TPB	Plast.	С	(mV/decade)	(mol/L)			(%)	
2 <sup>c</sup>	49.0 DBP	49.0	$29.49 \pm 0.24$	$5.96 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$5.25 \times 10^{-6}$	$1.73 \times 10^{-5}$	1.43	0.9988
3	48.5 DBP	48.5	$34.61 \pm 0.19$	$1.18 \times 10^{-5}$ $-1.0 \times 10^{-2}$	$7.33 \times 10^{-6}$	$2.42 \times 10^{-5}$	1.22	0.9985
5	47.5 DBP	47.5	$33.74 \pm 0.17$	$6.31 \times 10^{-6}$ $-1.0 \times 10^{-2}$	$8.18 \times 10^{-6}$	$2.70 \times 10^{-5}$	0.61	0.9969
7	46.5 DBP	46.5	$33.81 \pm 0.22$	$1.10 \times 10^{-5}$ $-1.0 \times 10^{-2}$	$1.00 \times 10^{-5}$	$3.30 \times 10^{-5}$	0.52	0.9960
$2^{\rm c}$	49.0 NPOE	49.0	$29.60 \pm 0.15$	$3.98 \times 10^{-6}$ - $1.0 \times 10^{-2}$	$3.57 \times 10^{-6}$	$1.18 \times 10^{-5}$	0.46	0.9998
2	49.0 TCP	49.0	$28.03 \pm 0.28$	$3.98 \times 10^{-6}$ $-1.0 \times 10^{-2}$	$3.74 \times 10^{-6}$	$1.31 \times 10^{-5}$	1.26	0.9986
2	49.0 EHA	49.0	$24.84 \pm 0.18$	$5.96 \times 10^{-6}$ - $8.4 \times 10^{-4}$	$9.28 \times 10^{-6}$	$1.97 \times 10^{-5}$	2.11	0.9929
2	49.0 DOP	49.0	$17.72 \pm 0.59$	$3.98 \times 10^{-6}$ - $8.4 \times 10^{-4}$	$3.89 \times 10^{-6}$	$1.31 \times 10^{-5}$	2.35	0.9944
2	49.0 Paraffin Oil	49.0	$24.91 \pm 0.91$	$7.94 \times 10^{-6}$ - $9.09 \times 10^{-5}$	$8.38  imes 10^{-6}$	$2.62 \times 10^{-5}$	2.09	0.9973

Plast.: plasticizer; C: graphite; SE: standard error;  $r^2$ : correlation coefficient.

<sup>°</sup> The selected sensors for subsequent measurements.

SE: Standard Error.

<sup>&</sup>lt;sup>b</sup> Relative standard deviation of 5 replicate measurements.

Temperature	Slope	Linear range	LOD	LOQ	$r^2$	$\rm E^{\circ}_{cell}$	$\mathrm{E}^{\circ}_{\mathrm{sen}}$
(°C)	(mV/decade)	(mol/L)				(mV)	
2% + DBP							
25	31.06	$3.98 \times 10^{-6} - 10^{-2}$	$3.73 \times 10^{-6}$	$12.31 \times 10^{-6}$	0.998	256.5	544.7
30	26.8	$9.90 \times 10^{-6} - 10^{-2}$	$1.17 \times 10^{-6}$	$3.86 \times 10^{-6}$	0.996	228.7	511.6
35	32.95	$5.96 \times 10^{-6} - 10^{-2}$	$4.20 \times 10^{-6}$	$13.86 \times 10^{-6}$	0.998	247.5	526.9
40	29.57	$5.96 \times 10^{-6} - 10^{-2}$	$5.88 \times 10^{-6}$	$19.40 \times 10^{-6}$	0.999	228.3	504.2
45	36.98	$5.96 \times 10^{-6} - 10^{-2}$	$6.42 \times 10^{-6}$	$21.19 \times 10^{-6}$	0.998	255.2	527.5
2% + NPOE							
25	30.12	$5.96 \times 10^{-6} - 10^{-2}$	$3.71 \times 10^{-6}$	$12.24 \times 10^{-6}$	0.999	233.1	519.3
30	40.37	$5.96 \times 10^{-6} - 10^{-2}$	$4.27 \times 10^{-6}$	$14.09 \times 10^{-6}$	0.999	280.2	563.1
35	42.51	$7.94 \times 10^{-6} - 10^{-2}$	$4.25 \times 10^{-6}$	$14.02 \times 10^{-6}$	0.996	235.6	515.0
45	47.77	$5.96 \times 10^{-6} - 10^{-2}$	$4.91 \times 10^{-6}$	$16.20 \times 10^{-6}$	0.994	317.2	589.5





**Figure 2** Changing standard sensor potential ( $\blacktriangle$ ) and standard cell potential ( $\blacklozenge$ ) with changing the test solution temperature.

where  $C_x$  is the concentration to be determined,  $V_x$  is the volume of the original sample solution,  $V_s$  and  $C_s$  are the volume and concentration of standard solution added to the sample to be analyzed, respectively,  $\Delta E$  is the change in potential after addition of a certain volume of standard solution and s is the slope of the calibration graph.

#### 3. Results and discussion

#### 3.1. Amount of the ion-exchanger

The amount of the ion-exchanger is one of the most important parameters which affect the performance of ISSs. This is because it strongly affects the sensitivity of the sensors in addition to their selectivity and limits of detection (LOD). Consequently, we have studied the effect of changing the amount of the ion-exchanger (2%, 3%, 5% and 7% using DBP as a solvent mediator) on the performance of the proposed sensors and the obtained calibration graphs are illustrated in Fig. 1. Moreover, Table 1 shows the obtained potentiometric characteristics of the CPSs prepared with varying compositions. It is clear from the obtained data that the best performance was obtained by using 2% of the ion-exchanger as it gives the nearest slope to the Nernstian value (29.49  $\pm$  0.24 mV/decade), the widest linear range  $(5.96 \times 10^{-6} - 1.00 \times 10^{-2} \text{ mol/L})$  and the lowest LOD ( $5.25 \times 10^{-6}$  mol/L). As a result, 2% TH-TPB was used as the best paste composition for the preparation of the sensors throughout the work procedures.

#### 3.2. Solvent mediator

Ethers and some fatty acid esters are usually used as solvent mediators in ISSs preparation because they improve electrical conductivity and mechanical properties of either the carbonpaste or the polymeric membrane. In addition, they can extend the lifetime of ISSs as reported by Zahran et al. (2014). The effect of different types of plasticizers (paraffin oil, DBP, DOP, TCP, EHA, NPOE) was studied and the obtained results can be found in Table 1. The calibration curves using the selected composition and solvent mediators are shown in Fig. S1 in the supporting information. The resulting calibration graphs were used to evaluate the potentiometric performance of the sensor in each case by following up the changes in their slopes, LODs and linear ranges. In addition, the lifetime of the sensors was taken into consideration during choosing the most suitable sensor. The obtained results reveal that DBP (slope of  $29.49 \pm 0.24 \text{ mV/decade}$ ) and NPOE (slope of  $29.60 \pm 0.15 \text{ mV/decade}$ ) are the most suitable sensors for potentiometric determination of TH in aqueous

solutions. These results agree with the expected trend of sensitivity from the dielectric constant values of these solvent mediators (Table S1). The highest sensitivity is obtained using the NPOE (dielectric constant  $\sim$ 24). Based on the above results, two sensors were prepared using DBP (sensor I) and NPOE (sensor II), characterized and applied to the determination of TH in aqueous media.

#### 3.3. Effect of temperature

Changes in test solution temperature can affect the potentiometric performance of ISSs. These effects are mainly attributed to two reasons. Firstly, the solubility of the ion-exchanger in water is enhanced by temperature rise causing leaching of the ion-exchanger or the electro-active species from the carbon-paste. Secondly, since adsorption depends on weak chemical forces between the analyte molecules and the ionexchanger molecules in the carbon-paste such, thermal energy which can overcome these chemical forces are able to inhibit the analyte adsorption on the surface of the sensor. Different test solution temperatures, 25, 30, 35, 40 and 45 °C for sensor (I) and 25, 30, 35 and 45 °C for sensor (II), were used to investigate the effect of temperature on the sensors behavior. The results (Table 2) show that sensor (I) does not show a significant change upon changing the test solution temperature as the slope values remain near Nernstian. However, the performance of sensor (II) is affected, to some extent, by temperature changes as the slope values increase by increasing test solution temperature. Calibration curves of the two sensors at different test solution temperatures are illustrated in Figs. S2 and S3. Both sensors can be used for TH determination at room temperature. Moreover, this conclusion can be supported by the calculated values of the thermal coefficients  $[(dE^{\circ}/dt)_{cell}]$  and  $(dE^{\circ}/dt)_{sen}$ ]. Thermal coefficients are numerical values representing the slope of a linear function between E° versus (t - 25) for the electrochemical cell or the sensor. Low values of thermal coefficients indicate thermal stability of the sensors.

Thermal coefficients can be obtained from Fig. 2 which was plotted using Eq. (3) (Abu Shawish et al., 2016a; Issa and Khorshid, 2011; Khorshid and Issa, 2014). Standard cell and sensor potentials can be obtained from Figs. S4 and S5 in the supplementary material.

$$E^{\circ} = E^{\circ}_{25 \circ C} + (dE^{\circ}/dt)(t - 25)$$
(3)

#### 3.4. Selectivity of the sensors

Complex samples may contain large number of interfering ions, especially metal ions. These ions are able to interfere with the analyte ions and give false results during analytical procedures. Furthermore, many multivitamin pharmaceuticals are combinations of vitamins and minerals especially those used as general tonics. Accordingly, TH may be found associated with different metal cations, sugars and amino acids when we are talking about pharmaceutical and/or biological samples. Selectivity of the proposed sensors toward TH is measured by calculating the selectivity coefficients in the presence of various interfering ions such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, D-alanine, DL-serine, fructose and lactose. The selectivity coefficients were calculated by applying the matched potential method (Horvai, 1997). The *p*-function of the selectivity coefficient values of sensors (I) and (II) is tabulated in Table S2. The higher these values are, the higher is the selectivity of the sensor toward the corresponding ion. The values in the table are small enough (2.2-3.8)indicating high selectivity of the sensors toward TH over the studied cations. The calibration curves of the interfering ions and TH using sensor (I) and sensor (II) are plotted in Fig. 3 from which we can notice that the sensors are nearly not sensitive toward the studied interfering ions.

#### 3.5. Hysteresis and response time

Response time of an ISS is defined as the length of time which elapses between the instant at which an ISS and a reference



Figure 3 Calibration graphs for TH and possible interfering metal ions, amino acids and sugars showing the response of the proposed CPSs towards TH over the interfering ions. (a) 2% TH-TPB + DBP; (b) 2% TH-TPB + NPOE.



Figure 4 Time-trace calibration plot (a), response time (b) and hysteresis (c) of the proposed CPSs. (A) 2% TH-TPB + DBP; (B) 2% TH-TPB + NPOE.

electrode are brought into contact with a sample solution (or at which the concentration of the ion of interest in a solution in contact with an ISS and a reference electrode is changed) and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV (Buck and Lindner, 1994). However, hysteresis is known as the sensor memory. It is said to occur if there is a different potential reading is observed after the concentration has been changed and restored to its original value. The reproducibility of the sensor will consequently be poor. The systematic error is generally in the direction of the concentration of the solution in which the electrode was previously immersed (Buck and Lindner, 1994). Fig. 4 shows the response time and the memory of sensors (I) and (II). Sensor (I) responds to changes in analyte concentration within 10-12 s while the response time of sensor (II) is about 5 s. It is obvious from the figure that sensor (I) has almost no memory allowing the use of the sensor several times for analysis of different successive samples without need to renew the surface. On the other hand, sensor (II) shows some memory toward the concentration of the previous solution in



Figure 5 SEM micrographs of CPSs. The magnification is  $2000 \times$ . (A) bBare paste + DBP, (B) 2%TH-TPB + DBP, (C) bare paste + NPOE and (D) 2%TH-TPB + NPOE.

	CPS + DBP			CPS + NPOE			
Taken (mg)	Found	Recovery <sup>a</sup>	RSD <sup>b</sup>	Found	Recovery <sup>a</sup>	RSD	
	(mg)	(%)	(%)	(mg)	(%)	(%)	
Pure solution							
0.1686	0.1730	102.63	1.23	0.1639	97.21	0.84	
0.8432	0.8576	101.71	1.38	0.8494	100.74	1.29	
1.686	1.717	101.85	0.96	1.649	97.81	0.74	
8.432	8.456	100.29	1.19	8.518	101.02	0.62	
16.86	17.26	102.37	1.20	16.69	98.99	1.73	
Neurovit <sup>®</sup> (ampou	les 50 mg/mL)						
0.1686	0.1676	99.38	0.77	0.1676	99.43	0.85	
0.8432	0.8486	100.64	0.37	0.8399	99.61	1.36	
1.686	1.749	103.72	0.59	1.6671	98.88	0.81	
8.432	8.284	98.24	0.36	8.459	100.32	0.42	
16.86	17.05	101.13	0.94	17.23	102.19	1.49	
Neuroton <sup>®</sup> (ampou	$(les \ 100 \ mg/mL)$						
0.1686	0.1668	98.99	0.97	0.1714	101.67	1.21	
0.8432	0.8670	102.82	1.19	0.8409	99.73	0.94	
1.686	1.675	99.35	1.23	1.654	98.13	1.53	
8.432	8.738	103.63	0.82	8.419	99.85	0.37	
16.86	16.94	100.49	0.93	16.95	100.54	0.67	
Bécozyme <sup>®</sup> (ampo	ules 5 $mg/mL$ )						
0.1686	0.1651	97.92	1.10	0.1694	100.48	0.33	
0.8432	0.8419	99.84	0.78	0.8360	99.15	0.56	
1.686	1.735	102.89	0.97	1.669	99.00	1.48	
8.432	8.629	102.34	0.47	8.514	100.97	0.84	
16.86	16.98	100.70	0.60	17.00	100.83	0.77	
					(continu	ed on next page	

**Table 3** Determination of TH.HCl in pure sample solutions and different ampoules from the Egyptian market by applying thestandard addition method using the proposed CPSs.

Table 3(continued)

	CPS + DBP			CPS + NPOE			
Taken (mg)	Found (mg)	Recovery <sup>a</sup> (%)	RSD <sup>b</sup> (%)	Found (mg)	Recovery <sup>a</sup> (%)	RSDb (%)	
B-Com <sup>®</sup> (ampoule	s 5 mg/mL)						
0.1686	0.1655	98.14	0.65	0.1689	100.18	0.45	
0.8432	0.8414	99.79	0.46	0.8619	102.22	0.74	
1.686	1.674	99.28	0.69	1.676	99.40	0.86	
8.432	8.442	100.12	0.36	8.294	98.36	1.20	
16.86	17.01	100.88	0.82	16.43	97.45	1.07	

<sup>a</sup> Mean % recovery of 5 replicate measurements.

<sup>b</sup> Relative standard deviation for 5 replicate measurements.

 Table 4
 A comparison between the proposed sensors and some of the previously reported methods.

Method	Determination range (µg/mL)	LOD (µg/mL)	$r^2$	Recovery (%)	References
Sensor (I)	2-3372	1.77	0.9988	97.92-103.72	Current study
Sensor (II)	1.34-3372	1.20	0.9998	97.21-102.19	Current study
Micellar electrokinetic	5–15	0.3-125	> 0.9990	99.0-101.2	Okamoto et al. (2002)
chromatography					
Orion liquid membrane electrode	16.86-3372	1.0	Not	96.5-99.2	Hassan et al. (1985)
(model 92)			indicated		
Fluorescent sensor	3.37-16-86	0.094	0.9974	97.11-97.13	Purbia and Paria (2016)
Reverse-phase HPLC	489.9-1469.6	Not indicated	0.9997	99.8-100.2	Poongothai et al. (2010)
Capillary zone electrophoresis	5-200	0.9–9.0	0.9952	97.0-101.4	Franco et al. (2012)
Thiamine-reineckate liquid	0.337-337.27	0.3	0.9980	98.1	Hassan and Elnemma (1989)
membrane electrode					
Whole cell immobilized	0.0016-0.0337	0.0016	0.9956	97.2-102.5	Akyilmaz et al. (2006)
amperometric biosensor					
Flow-through biparameter system	2-30	0.10	0.9999	97.00-100.3	Ortega Barrales et al. (2001)
UV photometric sensor	2.0-33.0	0.16	0.9999	95.83-102.88	Ortega Barrales et al. (1998)
CdSe quantum dots	5.00-40.0	0.070	0.9963	99.35–99.85	Sun et al. (2008)

which it was immersed. Actually, this is a non-issue because this problem can be resolved by renewing the surface of the carbon-paste between each two successive runs.

#### 3.6. Lifetime

Following up the performance of the ISSs prepared using the same carbon-paste, it was found that the carbon-paste of sensor (I) has a lifetime of only 1–2 days. On the other hand, the lifetime of the carbon-paste of sensor (II) is about one month. These results are in line with the previously reported work concerning the influence of the type of solvent mediator on the lifetime of ISSs (Zahran et al., 2014).

#### 3.7. Surface topography

The amount of defects present in the surface of an adsorbent strongly affects the amount of the adsorbed species (Pan, 1992). As a result, it would be useful to study the surface topography of the proposed sensors to investigate the effect of chemical modification on the amount of defects and consequently on the adsorption capacity of the surface. Scanning electron micrographs of both sensors (I) and (II) are illustrated

in Fig. 5. The topographies of the unmodified sensors are smoother and show fewer defects than the surfaces of the modified ones. In addition, the modified sensors have rough surfaces due to the presence of plate-like parts arranged in different elevations causing the appearance of many pores which act as active sites for TH adsorption (Atta et al., 2012). As a result, the active surface area available for adsorption of TH is also increased.

#### 3.8. Assay of pure solutions and multivitamin ampoules

Different concentrations of TH were estimated in pure solution and a number of Egyptian multivitamin ampoules using the standard addition method and satisfactory results were obtained. The solutions of the ampoules were diluted as required and the appropriate volumes were taken and completed to 50 mL for standard addition measurements. Table 3 summarizes the recovery values obtained from the analytical application of sensor (I) and (II). The found recovery values are 97.92–103.7% and 97.21–102.2% for sensors (I) and (II), respectively. In addition, the relative standard deviation (RSD) values for five replicate measurements are low indicating the reproducibility and precision of the proposed sensors. Both pure solution and ampoule recovery values are excellent and acceptable. As a result, the proposed sensors can be used for accurate and precise determination of TH in aqueous solutions.

#### 4. Conclusions

The present work presents the potentiometric and surface topography studies of two CPSs designed for the first time to estimate TH in aqueous solutions. Different characterization parameters were investigated to evaluate the sensors performance. The most worth noting advantages of the sensors are their ease of preparation, Nernstian behavior, low limits of detection, high accuracy and reproducibility. In addition, the sensors show fast response to changes in TH concentration and low interference from common interfering ions. Sensor (I) shows higher thermal stability than sensor (II). It was found that changing the type of plasticizer strongly affects the lifetime of CPSs as NPOE extends the lifetime of sensor (II) to one month instead of 1 or 2 days in case of sensor (I) which was prepared using DBP. SEM was used to characterize the prepared sensors in comparison with the chemically unmodified ones. The proposed sensors were successfully applied to the determination of TH in pure aqueous solution and four multivitamin ampoules obtained from the Egyptian market using the standard addition method. The results are rather better than or similar to the previously reported methods in the literature (Table 4). It is highly recommended to use the proposed sensors for TH determination in drug control laboratories.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc. 2016.11.012.

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