

Flow Injection Potentiometric Determination of Terazosin Hydrochloride Using Modified Carbon Paste Electrodes

Sayed I M. Zayed^{1,2,*}, Mohamed M. Khalil³, Yousry M. Issa⁴, and Huda R. Khalefa³

¹Faculty of Industrial Education, Beni Suef University, Beni Suef, Egypt

²Chemistry Department, Faculty of Science, Taif University, Taif, KSA

³Chemistry Department, Faculty of Science, Beni Suef University, Beni Suef, Egypt,

⁴Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

*E-mail: simzayed2011@hotmail.com

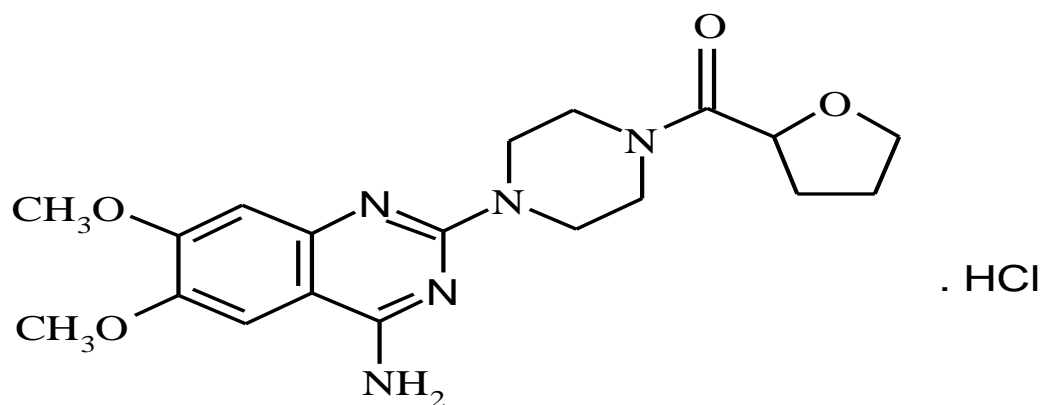
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Three carbon paste electrodes for determination of terazosin hydrochloride (TerazCl) were prepared based on ion association complexes with sodium tetraphenylborate (NaTPB), ammonium reineckate and phosphotungstic acid (PTA), using dibutyl phthalate as solvent mediator. The developed sensors showed a near-Nernstian response over the concentration range 3.98×10^{-5} - 1.00×10^{-2} mol L⁻¹ TerazCl with detection limits of 2.18×10^{-5} , 3.60×10^{-5} and 1.26×10^{-5} mol L⁻¹ TerazCl, in case of tetraphenylborate, reineckate, and phosphotungstate, respectively. The proposed sensors exhibit good selectivity for terazosin with respect to a large number of inorganic cations, sugars, amino acids and vitamins. The sensors were successfully applied for the potentiometric determination of TerazCl in pharmaceutical preparation in batch and flow injection conditions. The sensors were also applied for the determination of TerazCl in spiked human urine samples by using the standard addition method.

Keywords: Terazosin hydrochloride, modified carbon paste electrodes, flow injection analysis, potentiometry.

1. INTRODUCTION

Terazosin hydrochloride (TerazCl), 1-(4-Amino-6,7-dimethoxyquinazolin-2-yl)-4-(tetrahydro-2-furoyl) piperazine hydrochloride [63074-08-8], (Scheme 1). It is an α_1 -adrenoceptor blocker with actions similar to those of prazosin, but a longer duration of action. It is used in the management of hypertension and in benign prostatic hyperplasia to relieve symptoms of urinary obstruction [1].



Scheme 1. Structural formula of terazosin hydrochloride

Several methods for determination of this drug have been reported in the literature, including, high performance liquid chromatography [2-13], spectrophotometry [14,15], spectrofluorimetry [15-17], capillary zone electrophoresis [18], and voltammetric methods [19,20]. Plastic PVC ion selective electrodes potentiometric methods based on terazosin-tetraphenylborate, terazosin-reineckate and terazosin-silicotungstate have been reported [21,22].

The aim of this work is to describe the construction, performance characteristics of terazosin modified carbon paste electrodes based on terazosin-tetraphenylborate, terazosin-reineckate and terazosin-phosphotungstate as electroactive materials and dibutyl phthalate as solvent mediator and using the developed carbon paste selective electrodes for determination of TerazCl in its pharmaceutical preparation and biological fluids.

2. EXPERIMENTAL

2.1. Reagents and materials

All chemicals were of analytical grade. Double distilled water was used throughout all experiments. Pure grade terazosin hydrochloride and the pharmaceutical preparation Terazin tablets (2 mg TerazCl/tablet) were provided by Pharaonia pharmaceuticals, Co., Borg El-Arab, Alexandria, Egypt. Sodium tetraphenylborate (NaTPB), ammonium reineckate, phosphotungstic acid (PTA), dioctyl sebacate (DOS), and tricresyl phosphate (TCP) were from Fluka, dibutyl phthalate (DBP) and dioctyl phthalate (DOP) from Merck (Germany). Graphite powder (1-2 micron) was from Aldrich (USA)

2.2. Apparatus

Potentiometric and pH measurements were carried out using a Seibold G-103 digital pH/mV meter (Vienna, Austria). A Techne circulator thermostat Model C-100 was used to control the temperature of the test solutions. A saturated calomel electrode (SCE) was used as the external

reference. The electrochemical system of the electrode may be represented as follows: Teraz-carbon paste electrode/test solution//KCl salt bridge//saturated calomel electrode.

The flow injection setup is that previously reported [23,24]. Figure 1 represents the schematic diagram of the flow injection system used in the measurements.

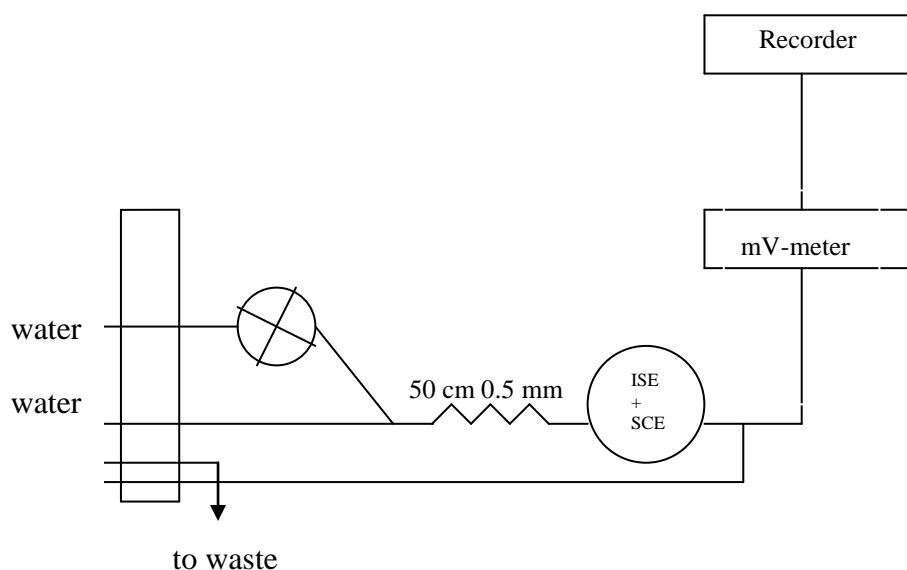


Figure 1. Schematic diagram of the flow injection system used in the measurements

2.3. Preparation of the ion pair

The ion pair, Teraz-TPB and Teraz-reineckate were prepared by mixing 50 mL 10^{-2} mol L $^{-1}$ TerazCl solution and 50 mL 10^{-2} mol L $^{-1}$ solution of each of sodium tetraphenylborate (NaTPB) or ammonium reineckate, in case of Teraz-PT mixing 150 mL 10^{-2} mol L $^{-1}$ TerazCl solution with 50 mL 10^{-2} mol L $^{-1}$ of PTA solution. The formed precipitates were filtered, washed thoroughly with bidistilled water and dried at room temperature. The composition of ion pair was found to be 1:1 both in case of Teraz-TPB or Teraz-reineckate, and 3:1 in case of Teraz-PT, as confirmed by elemental analysis data done at microanalytical research laboratory in National Research Centre (Dokki, Cairo, Egypt). The percentage values found are 70.64, 6.20 and 9.22 and the calculated values are 69.55, 6.11 and 9.43 for C, H and N in case of Teraz-TPB. In case of Teraz-reineckate, the percentage values found are 36.81, 5.04 and 20.14 and the calculated values are 36.36, 4.91 and 20.28 for C, H and N, respectively, while in case of Teraz-PT the percentage values found are 16.45, 1.90 and 5.05 and the calculated values are 16.51, 1.82 and 5.07 for C, H and N, respectively.

2.4. Preparation of the electrode

Carbon paste was prepared by mixing weighed amount of ion pair, graphite powder (Aldrich, 1-2 micron), and dibutyl phthalate as a pasting liquid (ratio of graphite powder to pasting liquid was 1:1) in a mortar until it was uniformly wetted. The carbon paste electrode was prepared by successive

packing of the carbon paste into the tip end of home made Teflon holder (2 mm), and electrical contact was achieved by stainless steel rod (2 mm) connecting the paste to the mV meter.

2.5. Potentiometric determination of TerazCl

TerazCl has been determined using the proposed electrodes by the standard addition method [25]. In this method small increments of 1×10^{-1} mol L⁻¹ standard TerazCl solution were added to 50 mL aliquot samples of various concentrations (1.84-11.50 mg TerazCl). The change in millivolt readings was recorded for each increment and used to calculate the concentration of TerazCl sample solution using the following equation:

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

Where C_x and V_x are the concentration and the volume of the unknown solutions, respectively, C_s and V_s the concentration and the volume of the standard solutions, respectively, S the slope of the calibration graph and ΔE is the change in millivolt due to the addition of standard.

2.6. Determination of TerazCl in Terazin tablets

Twenty terazin tablets, were ground to a fine powder in a mortar, and the required amounts from the powder was dissolved in about 30 mL bidistilled water and filtered in a 50-mL measuring flask. The residue was washed three times with bidistilled water; the volume was completed to the mark by the same solvent. The contents of the measuring flask were transferred into 100-mL beaker, and subjected to potentiometric determination of TerazCl

In FI, a series of solutions of different concentrations was prepared from the tablets and the peak heights were measured, and then compared with those obtained by injecting a standard solutions of the same concentration prepared from pure TerazCl

2.7. Determination of TerazCl in spiked human urine samples

Different amounts of TerazCl and 5 mL urine of a healthy person were transferred to a 50 mL measuring flask, and completed to the mark by bidistilled water to give solutions of concentrations ranging 1.84-11.50 mg TerazCl/50 mL. The contents of the measuring flask were transferred to a 100-mL beaker, and subjected to potentiometric determination of TerazCl by the standard addition method.

2.8. Potentiometric titration of TerazCl

An aliquot of TerazCl solution containing (23-68.99 mg TerazCl) was transferred into 100-mL beaker, diluted to approximately 50 mL with bidistilled water, and then titrated against a standard

solution of NaTPB using the investigated electrodes as indicator electrodes. The same method was applied for determination TerazCl in terazine tablets.

3. RESULTS AND DISCUSSION

3.1. Optimization of the electrodes in batch conditions

3.1.1 Composition of carbon paste electrodes

Table 1. Composition of terazosin carbon paste electrodes and the slope of the calibration graphs at $25 \pm 1^\circ\text{C}$

| Electrode | Ion associate | Composition / (% w/w) | | Slope / (mV decade ⁻¹) | RSD / % |
|------------------|---------------|-----------------------|------|---------------------------------------|---------|
| | | graphite | DBP | | |
| Teraz-TPB | | | | | |
| I | 3 | 48.5 | 48.5 | 38.6 | 0.33 |
| II | 5 | 47.5 | 47.5 | 50.3 | 0.60 |
| III | 7 | 46.5 | 46.5 | 45.1 | 0.44 |
| IV | 9 | 45.5 | 45.5 | 40.3 | 0.80 |
| Teraz-reineckate | | | | | |
| I | 3 | 48.5 | 48.5 | 42.0 | 0.60 |
| II | 5 | 47.5 | 47.5 | 52.5 | 0.60 |
| III | 7 | 46.5 | 46.5 | 37.0 | 0.90 |
| IV | 9 | 45.5 | 45.5 | 30.0 | 0.30 |
| Teraz-PT | | | | | |
| I | 3 | 48.5 | 48.5 | 34.8 | 0.36 |
| II | 5 | 47.5 | 47.5 | 54.0 | 0.60 |
| III | 7 | 46.5 | 46.5 | 39.4 | 0.72 |
| IV | 9 | 45.5 | 45.5 | 38.7 | 0.20 |

Four electrodes were prepared that contains the electroactive complex Teraz-TPB, Teraz-reineckate or Teraz-PT in the ratios 3, 5, 7 and 9%, and the ratio of graphite to liquid mediators is 1:1 (Table 1). The result reveal that at 25°C , the electrodes with ratio of 5% have the best performance characteristics (slope, 50.3 mV concentration decade⁻¹; usable concentration range, 3.98×10^{-5} - 1×10^{-2} mol L⁻¹ TerazCl; detection limit [26,27], 2.18×10^{-5} mol L⁻¹, and response time ≤ 10 s), for Teraz-TPB electrode, (slope, 52.5 mV concentration decade⁻¹, usable concentration range, 3.98×10^{-5} - 1×10^{-2} mol L⁻¹ TerazCl; detection limit, 3.6×10^{-5} mol L⁻¹ TerazCl, and response time ≤ 10 s) for Teraz-reineckate electrode, while the characteristics are (slope, 54.0 mV concentration decade⁻¹, usable concentration

range, 3.98×10^{-5} - 1×10^{-2} mol L⁻¹ TerazCl; detection limit, 1.26×10^{-5} mol L⁻¹ TerazCl, and response time ≤ 10 s) for Teraz-PT electrode. The effect of solvent mediators on the performance characteristics of carbon paste electrodes was investigated by using four plasticizers of different polarities (DBP, DOP, DOS and TCP). The effect of plasticizers on the performance characteristics of ion-selective electrodes are due to their influence on migration, ion pair formation and diffusion coefficient [28]. The results show that DBP is the best of the plasticizers used, (Table 2). Poor sensitivities for the electrodes plasticized by DOP, DOS and TCP are due to low distributions of electroactive complex (Teraz-TPB, Teraz-reineckate or Teraz-PT) in these solvents [29]. The response characteristics of the proposed electrodes were evaluated according to IUPAC recommendations [30].

Table 2. Effect of plasticizers on terazosin responsive electrodes and the slopes of the calibration graphs at 25 ± 1 °C

| plasticizer | Slope / (mV decade ⁻¹) | Usable concentration range / mol L ⁻¹ | Limit of detection / mol L ⁻¹ | RSD / % |
|-------------------------|---------------------------------------|--|---|------------|
| Teraz-TPB | | | | |
| DBP | 50.3 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 2.18×10^{-5} | 0.6 |
| DOP | 41.9 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 2.75×10^{-5} | 1.0 |
| DOS | 42.7 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 3.23×10^{-5} | 1.0 |
| TCP | 30.3 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 3.38×10^{-5} | 0.9 |
| Teraz-reineckate | | | | |
| DBP | 52.5 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 3.60×10^{-5} | 0.6 |
| DOP | 40.0 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 8.66×10^{-6} | 1.1 |
| DOS | 35.0 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 2.41×10^{-5} | 1.0 |
| TCP | 42.0 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 1.82×10^{-5} | 1.2 |
| Teraz-PT | | | | |
| DBP | 54.0 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 1.26×10^{-5} | 0.6 |
| DOP | 41.6 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 9.77×10^{-6} | 1.0 |
| DOS | 30.5 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 9.33×10^{-6} | 1.0 |
| TCP | 47.4 | $3.98 \times 10^{-5} - 1 \times 10^{-2}$ | 9.12×10^{-6} | 1.2 |

3.1.2. Effect of pH

The effect of pH on the response of terazosin electrodes was investigated using two concentrations of TerazCl (1×10^{-3} and 1×10^{-4} mol L⁻¹), by following the variation in potential with change in pH by addition of small volumes of hydrochloric acid and sodium hydroxide (each 0.1-1.0 mol L⁻¹) in TerazCl solution. The results indicate that the investigated electrodes showed no pH response over the range 2.0-6.9 for all the proposed electrodes. Representative curves for Teraz-PT electrode are shown in Fig. 2. The decrease in potential at pH higher than 6.9 is most probably

attributed to the gradual increase in the concentration of the unprotonated terazosin, resulting in the precipitation of terazosin base in the solution, leading to decrease in concentration of terazosin cation.

3.1.3. Life time of the electrodes

The electrode life time was investigated by performing the calibration graphs periodically and calculating the response slope after the electrode left in air without soaking in the drug. The electrode was preconditioned by soaking in 1×10^{-3} mol L⁻¹ of the drug for 30 minutes before use. The results indicate that in case of Teraz-TPB electrode, the slope of the calibration graph remains at 50.3 mV concentration decade⁻¹ for 4 days, then slightly decreased reaching 47.0 and 42.0 mV concentration decade⁻¹ after 8 and 12 days, respectively. In case of Teraz-reineckate electrode, the slope of the calibration graph remains at 52.5 mV concentration decade⁻¹ after 1 day, then decreased reaching 50.0, 49.0, 45.0 and 42.0 mV concentration decade⁻¹ after 2, 4, 8 and 10 days, respectively, while in case of Teraz-PT electrode the slope of the calibration graph remains at 54.0 mV concentration decade⁻¹ after 1 day, then decreased reaching 53.0, 50.0, 48.0 and 45.0 mV concentration decade⁻¹ after 2, 4, 7 and 10 days, respectively.

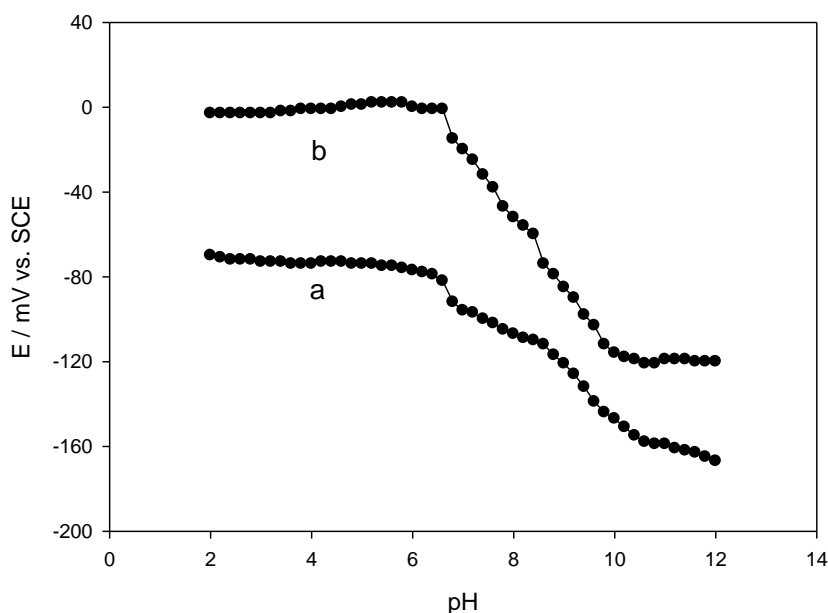


Figure 2. Effect of pH of the test solution on the potential response of Teraz-PT electrode, (a) 1×10^{-4} M, (b) 1×10^{-3} M TerazCl

3.1.4. Effect of temperature

To study the thermal stability of the electrodes, calibration graphs were constructed at different test solution temperature (25-70 °C), and the thermal coefficients (dE/dt) of the selected electrodes were calculated [31], to be -0.0017, -0.0012 and -0.0011 V/°C, for Teraz-TPB, Teraz-reineckate, and

Teraz-PT electrodes, respectively. These values indicates fairly good thermal stability of the electrodes.

3.2. Optimization of the electrodes response in FI conditions

Flow injection analysis becomes a wide spread of methods which are characterized by its versatility, minium sample treatment prior to injection into the system, reduced time of analysis and low consumption of reagent compared to the batch procedure. To obtain the best signal sensitivity, FI parameters must be optimized. The dispersion coefficients were found to be 1.31, 1.18 and 1.27 for Teraz-TPB, Teraz-reineckate and Teraz-PT electrodes, respectively, these limited dispersion coefficients aids the optimum sensitivity, and fast response of the electrodes [32]. The effect of sample loope size on the response of the electrodes was studied by injecting samples of different volumes (4.7-500.0 μL) of 10^{-3} mol L^{-1} TerazCl at constant flow rates. (9.70 mL/min for Teraz-TPB electrode, and 17.85 mL/min for Teraz-reineckate and Teraz-PT electrodes). The higher the sample volume, the higher the peak height and the longer the residence time of the sample at the electrode surface; such samples require a longer time to reach a steady state, and greater consumption of sample [33].

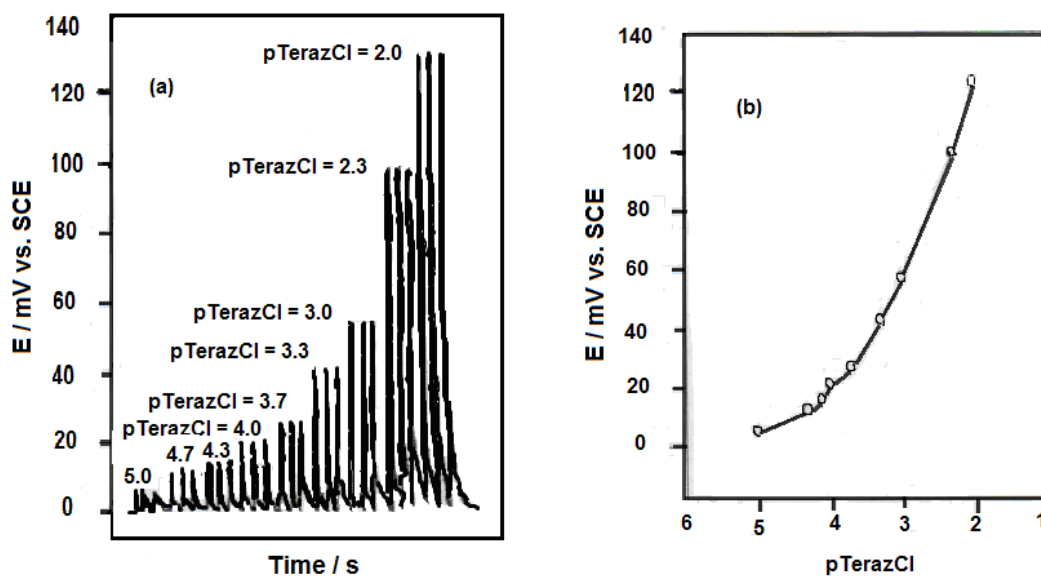


Figure 3. Recording (a) and their corresponding calibration graph (b) obtained for Teraz-TPB electrode at optimum FI conditions

The optimum sample loop size was found to be 150, 150, and 75 μL for Teraz-TPB, Teraz-reineckate and Teraz-PT electrodes, respectively, giving maximum peak height, less consumption of reagents, and shorter time to reach the base line. The effect of flow rates on the electrode response was studied at different flow rates (4.15-30.00 mL/min), using constant sample loop size of 150 μL in case of Teraz-TPB and Teraz-reineckate electrodes or 75 μL in case of Teraz-PT electrode. It was stated that, the residence time of the sample is inversely proportional to the flow rate [34]. It was found that, as

the flow rate increases, the peak becomes higher and narrower until flow rates of 9.70 mL/min in case of Teraz-TPB electrode, and 17.85 mL/min in case of Teraz-reineckate and Teraz-PT electrodes. The peaks obtained above these flow rates were nearly the same. These flow rates were used throughout this work providing maximum peak height, a shorter time to reach the base line, and less consumption of the carrier solution. Under these conditions, the performance characteristics are: slope, 73.2, 61.6 and 53.5 mV concentration decade⁻¹ for Teraz-TPB, Teraz-reineckate, and Teraz-PT electrodes, respectively, linear range, 3.98x10⁻⁵-1.00x10⁻² mol L⁻¹ TerazCl for all the developed electrodes. Figure 3 represents a typical recording and the calibration graph for Teraz-TPB electrode as representative figure.

3.3. Selectivity of the electrodes

Table 3. Selectivity coefficients for Teraz electrodes in batch and FI conditions

| Interferent | $-\log K_{\text{Teraz}, J^{z+}}^{\text{pot}}$ | | | | | | | | |
|------------------------------|---|------|------------------|------|-------|----------|------|------|------|
| | Teraz-TPB | | Teraz-reineckate | | | Teraz-PT | | | |
| | Batch | FI | Batch | FI | Batch | FI | | | |
| | SSM | MPM | SSM | MPM | SSM | MPM | SSM | MPM | |
| Na ⁺ | 2.40 | - | 2.30 | 1.00 | - | 0.90 | 2.40 | - | 2.35 |
| K ⁺ | 2.30 | - | 2.04 | 1.50 | - | 1.10 | 2.84 | - | 2.73 |
| Ca ²⁺ | 3.20 | - | 3.20 | 2.20 | - | 2.10 | 3.98 | - | 2.43 |
| Mg ²⁺ | 3.30 | - | 3.20 | 2.50 | - | 2.00 | 5.03 | - | 3.42 |
| Zn ²⁺ | 3.30 | - | 2.58 | 3.00 | - | 2.50 | 3.86 | - | 3.79 |
| Co ²⁺ | 3.40 | - | 2.98 | 3.00 | - | 2.20 | 5.32 | - | 3.89 |
| NH ₄ ⁺ | 1.80 | - | 1.52 | 2.50 | - | 2.30 | 2.74 | - | 2.63 |
| VitaminB ₁ | 1.60 | - | 1.00 | 1.10 | - | 0.90 | 1.95 | - | 1.61 |
| VitaminB ₆ | 1.60 | - | 1.40 | 1.30 | - | 1.00 | 1.92 | - | 1.71 |
| Vitamin C | - | 1.40 | - | - | 1.70 | - | - | 1.49 | - |
| Glucose | - | 2.80 | - | - | 2.40 | - | - | 2.89 | - |
| Fructose | - | 2.60 | - | - | 2.30 | - | - | 2.96 | - |
| Lactose | - | 2.60 | - | - | 2.40 | - | - | 2.89 | - |
| Maltose | - | 2.80 | - | - | 2.10 | - | - | 2.64 | - |
| Glycine | - | 2.90 | - | - | 2.40 | - | - | 2.52 | - |
| Alanine | - | 2.90 | - | - | 2.20 | - | - | 2.52 | - |

The effect of some inorganic cations, sugar, amino acids, and vitamins were investigated. The selectivity coefficients were evaluated according to IUPAC guidelines by the separate solution method (SSM) [35], in which the Nicolsky- Eisenman equation was used:

$$\log K_{\text{Teraz}, J^{z+}}^{\text{pot}} = (E_2 - E_1)/S + \log [\text{Teraz}] - \log [J^{z+}]^{\frac{1}{z}}$$

Where E₁ and E₂ are the electrode potential in 1x10⁻³ mol L⁻¹ TerazCl solution and interfering ions J^{z+}, respectively, and S is the slope of the calibration graph in mV concentration decade⁻¹. In FI conditions, a series of standard solutions of TerazCl of concentration between 3.98x10⁻⁵-1.00x10⁻² mol L⁻¹ were prepared, their corresponding potentials were measured and used to determine the slope of the

calibration graph. Solutions of 1×10^{-3} mol L⁻¹ of interfering ions were prepared, their corresponding peak heights were measured. The selectivity coefficients $K_{Teraz,J^{z+}}^{pot}$ were calculated using the above equation. In cases of ion without charges the selectivity coefficients were determined using the matched potential method [36]. The selectivity coefficients values $-\log K_{Teraz,J^{z+}}^{pot}$ of the developed carbon paste electrodes presented in Table 3 indicate that these electrodes are highly selective to terazosin cation under both batch and flow injection conditions. The inorganic cations do not interfere because of the difference in their mobility and permeability as compared to terazosin cation. In case of sugars and amino acids the non interference behavior is related to the difference in polarity and lipophilic nature of their molecules relative to terazosin cation.

3.4. Analytical applications

Table 4. Determination of TerazCl in pure form and in terazine tablets by applying standard addition, potentiometric titration and FI method

| | Teraz-TPB | | | | Teraz-reineckate | | | Teraz-PT | | |
|--------------------------|------------|------------|--------------|---------|------------------|--------------|---------|------------|--------------|---------|
| | Taken / mg | Found / mg | Recovery / % | RSD / % | Found / mg | Recovery / % | RSD / % | Found / mg | Recovery / % | RSD / % |
| Pure solution | | | | | | | | | | |
| Standard addition | | | | | | | | | | |
| | 1.84 | 1.87 | 101.63 | 0.84 | 1.84 | 100.00 | 0.64 | 1.79 | 97.28 | 0.76 |
| | 2.30 | 2.26 | 98.26 | 1.02 | 2.30 | 100.00 | 0.53 | 2.26 | 98.26 | 1.04 |
| | 4.60 | 4.48 | 97.39 | 0.75 | 4.55 | 98.91 | 0.82 | 4.57 | 99.35 | 1.02 |
| | 11.50 | 11.46 | 99.65 | 0.27 | 11.50 | 100.00 | 1.00 | 11.39 | 99.04 | 0.39 |
| Potentiometric titration | | | | | | | | | | |
| | 23.00 | 22.52 | 97.91 | 0.34 | | | | | | |
| | 46.00 | 45.08 | 98.00 | 0.78 | 44.16 | 96.00 | 0.90 | | | |
| | 68.99 | 68.23 | 98.90 | 0.95 | 67.61 | 98.00 | 0.95 | | | |
| Terazin tablets | | | | | | | | | | |
| Standard addition | | | | | | | | | | |
| | 1.84 | 1.83 | 99.46 | 0.89 | 1.82 | 98.91 | 0.98 | 1.82 | 98.91 | 0.98 |
| | 2.30 | 2.32 | 100.87 | 0.87 | 2.25 | 97.83 | 1.30 | 2.25 | 97.83 | 1.30 |
| | 4.60 | 4.59 | 99.78 | 1.00 | 4.55 | 98.91 | 1.50 | 4.55 | 98.91 | 1.50 |
| | 11.50 | 11.46 | 99.65 | 0.75 | 11.27 | 98.00 | 1.00 | 11.5 | 100.00 | 1.00 |
| Potentiometric titration | | | | | | | | | | |
| | 23.00 | 22.31 | 97.00 | 0.98 | | | | | | |
| | 46.00 | 45.31 | 98.50 | 1.00 | 45.08 | 98.00 | 1.00 | | | |
| | 68.99 | 67.61 | 98.00 | 0.70 | 67.61 | 98.0 | 0.90 | | | |
| FI | | | | | | | | | | |
| | 2.30 | 2.35 | 102.17 | 1.98 | 2.33 | 101.30 | 0.53 | 2.29 | 99.57 | 0.980 |
| | 4.60 | 4.65 | 101.09 | 1.98 | 4.62 | 100.43 | 0.60 | 4.59 | 99.78 | 1.300 |
| | 11.50 | 11.52 | 100.17 | 1.47 | 11.48 | 99.83 | 0.98 | 11.53 | 100.26 | 1.500 |
| | 22.99 | 23.10 | 100.48 | 1.83 | 23.2 | 100.91 | 0.88 | 23.00 | 100.04 | 1.110 |

The usefulness of the developed carbon paste electrodes was examined by using in the potentiometric determination of TerazCl in pure solutions, and in pharmaceutical preparation Terazin tablets (2 mg TerazCl/tablet) in batch and FI conditions. The mean recovery, and the relative standard deviation values are summarized in Table 4. The data indicate that there is no interference from the excipients used in the formulations of the tablets. Figure 4 represents potentiometric titration curves for determination of TerazCl in Terazin tablets using Teraz-TPB electrode as representative figure. The results obtained were compared with UV spectrophotometric published reference method [14] (Table 5). The obtained results are in good agreement with those obtained from the reference method. Statistical comparison of the accuracy and precision of the developed methods with the reference UV spectrophotometric method was performed using Students t- and the F-ratio tests at 95% confidence level [37].

Table 5. Statistical comparison between the results of the pharmaceutical preparation Terazin tablets on applying the proposed and reference methods

| Parameter | Proposed methods | | | Ref method ^[14] |
|-------------------------|-------------------|---------------|--------|----------------------------|
| | Standard addition | Pot titration | FI | |
| Teraz-TPB | | | | |
| Mean recovery / % | 99.94 | 97.83 | 100.98 | 98.11 |
| S.D / % | 0.88 | 0.87 | 0.80 | 1.77 |
| R.S.D / % | 0.88 | 0.89 | 0.79 | |
| F-ratio (9.28) | 4.046 | 4.139 | 1.023 | |
| t-Test (2.447) | 1.849 | 0.396 | 2.280 | |
| Teraz-reineckate | | | | |
| Mean recovery / % | 98.41 | 98.00 | 100.62 | |
| S.D / % | 1.18 | 0.93 | 0.75 | |
| R.S.D / % | 1.20 | 0.95 | 0.75 | |
| F-ratio (9.28) | 2.25 | 3.622 | 5.570 | |
| t-Test (2.447) | 0.282 | 0.110 | 2.414 | |
| Teraz-PT | | | | |
| Mean recovery / % | 98.91 | - | 99.91 | |
| S.D / % | 1.18 | - | 1.22 | |
| R.S.D / % | 1.19 | - | 1.22 | |
| F-ratio (9.28) | 2.25 | - | 2.105 | |
| t-test (2.447) | 0.752 | - | 1.675 | |

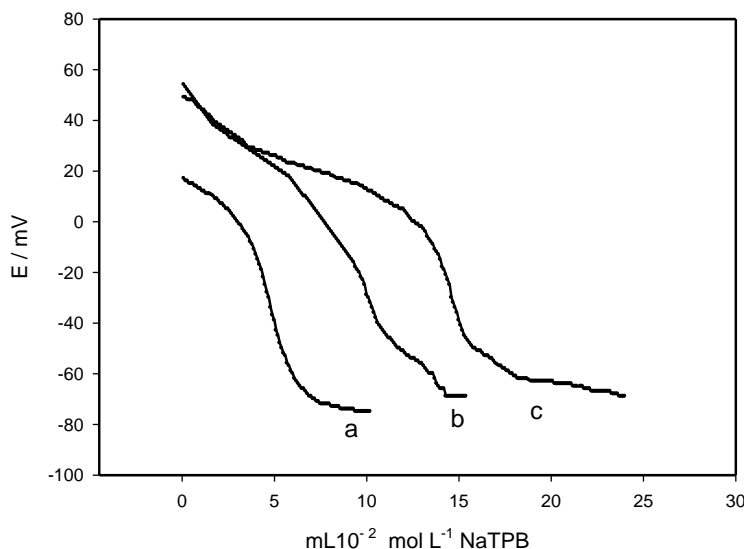


Figure 4. Potentiometric titration of 5 ml (a), 10 ml (b), and 15 ml (c) of 1×10^{-2} M terazin tablets against 1×10^{-2} M NaTPB solution using Teraz-TPB carbon paste electrode

The t- and F-values did not exceed the theoretical values, there is no significant difference in accuracy or precision between the proposed and reference methods.

Terazosin hydrochloride is administrated orally, it is rapidly and almost completely absorbed from the gastrointestinal tract after oral doses, the bioavailability is reported to be about 90%. Peak plasma concentrations are achieved in about 1 h. It is metabolized in the liver, the half-life in plasma is about 12 h, and it excreted in faeces via the bile, and in the urine as unchanged drug and metabolites [1]. Determination of TerazCl in spiked human urine samples was carried out at three different levels of concentrations (1.84-11.50 mg TerazCl/50 mL), in batch conditions using standard addition method. The mean recovery, and relative standard deviations are summarized in (Table 6).

Table 6. Determination of TerazCl in spiked human urine samples using standard addition method

| Electrode | Taken / mg | Found / mg | Recovery / % | RSD / % |
|------------------|------------|------------|--------------|---------|
| Teraz-TPB | 1.84 | 1.89 | 102.72 | 2.00 |
| | 4.60 | 4.48 | 97.39 | 1.90 |
| | 11.50 | 11.78 | 102.43 | 1.00 |
| Teraz-reineckate | 1.84 | 1.80 | 97.83 | 0.70 |
| | 4.60 | 4.65 | 101.09 | 1.60 |
| | 11.50 | 11.73 | 102.00 | 1.10 |
| Teraz-PT | 1.84 | 1.86 | 101.09 | 1.50 |
| | 4.60 | 4.73 | 102.83 | 1.00 |
| | 11.50 | 11.39 | 99.04 | 0.90 |

4. CONCLUSIONS

The developed terazosin modified carbon paste electrodes based on Teraz-TPB, Teraz-reineckate and Teraz-PT as electroactive materials and DBP as solvent mediator offers simple, rapid, accurate, and selective tools for the determination of TerazCl in bulk solution, pharmaceutical formulation, and spiked human urine samples. The novelty of this work is based on using modified carbon paste electrodes as new sensors, using Teraz-PT electrode as a new electrode, using FI technique for determination of the drug in its pharmaceutical formulation and determination of the drug in spiked human urine samples.

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