

Simple Electrochemical Determination of Sertraline Hydrochloride at Carbon Paste Electrode in Bulk, Tablets and Spiked Urine

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Abstract: In this work, the electrochemical behavior of sertraline hydrochloride (SRT) at carbon paste electrode (CPE) was studied using cyclic and square wave voltammetry in presence of micellar medium. Different experimental parameters were studied like pH, different surface active agents and scan rates. Britton-Robinson buffer of pH 7, scan rate of 100 mV s⁻¹ and Triton were found to be the optimum conditions for this study based on the peak current. SRT was found to be oxidized irreversibly through a diffusion controlled process. Under the optimum conditions, a linear relationship response was obtained from 1.99×10^{-7} to 1.38×10^{-5} mol L⁻¹ with correlation coefficient of 0.9995, limit of detection of 2.23×10^{-8} mol L⁻¹ and limit of quantification of 7.42×10^{-8} mol L⁻¹. The proposed method has been successfully applied to determine SRT in tablets as well as spiked urine.

Keywords: Voltammetry, Sertraline Hydrochloride, Micellar Medium, Urine

1. Introduction

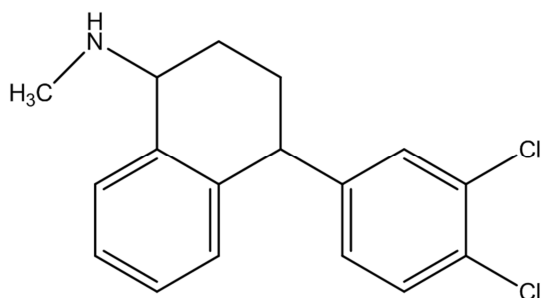


Figure 1. Chemical structure of SRT.

Sertraline hydrochloride (SRT) is a selective serotonin re-uptake inhibitor (SSRI) whose efficiency had been established in the treatment of depression, obsessive-compulsive disorder, depression relapse and social phobia [1]. Sertraline is cis (1S,4S)-N-methyl-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-1-naphthaleneamine and is available for pharmaceutical use as hydrochloride salt (Figure 1) [2].

Sertraline is a single stereoisomer and has a carbon side-chain containing an amino group. It is a secondary amine that exhibits two asymmetric centers, but has only one enantiomer which is formed by N-demethylation and was also introduced as an antidepressant [3]. It the most prescribed antidepressant and second most prescribed psychiatric medication in the United States [4].

One official analytical method was documented for determination of SRT in bulk and its active pharmaceutical preparation (APIs) in United States pharmacopeia 2017 [5].

The literature survey for SRT revealed variety of analytical methods including spectrophotometry [6-12], chromatography [13-27], electrochemistry [28-31], electrophoresis [32-34], GC-MS [35-39], electro kinetic chromatography [40], LC-MS/MS [41, 42], HPLC-ESI-MS [43], HPLC/ESI-MS/MS [44], NMR [45] and potentiometry [46].

It is worthy to mention that two out of the four electrochemical reported methods of sertraline focused on studying the electro reduction behavior of sertraline at

mercury electrodes [29, 30] whose use is unsafe due to its known toxicity [47], while the other two methods focused on studying the electro oxidation behavior of sertraline using glassy carbon electrodes one of them used bare glassy carbon electrode [28] and the other used rutin modified glassy carbon electrode [31]. The carbon paste electrode (CPE) used in this work is characterized by many advantages over all solid electrodes like the ease and speed of preparation and obtaining a new reproducible surface, low residual current, porous surface and low cost [48, 49].

In this work, a simple, rapid, safe and economic voltammetric method is described for the determination of SRT in bulk, dosage form and urine with good characteristics, such as simple preparation of electrode, high sensitivity, stability, and surface regeneration with excellent reproducibility, high selectivity and wide linear working range with lower detection limit compared to the reported electrochemical methods for SRT determination.

2. Experimental

2.1. Instrumentation

All voltammetric measurements were performed using a PC-controlled AEW2 electrochemistry work station and data were analyzed with EC-Lab electrochemistry software, manufactured by Bio-logic Science Instruments Pvt.ltd. (France). The one compartment cell with the three electrodes was connected to the electrochemical workstation through a C3-stand from BAS (USA). A platinum wire from BAS (USA) was employed as auxillary electrode. All the cell potentials were measured with respect to Ag/AgCl reference electrode from BAS (USA). Glass cell (5 mL) was used for electrochemical measurements. A JENWAY 3510 pH meter (England) with glass combination electrode was used for pH measurements. All the electrochemical experiments were performed at an ambient temperature of 25 °C.

2.2. Pure and Market Samples

SRT was kindly supplied from Memphis pharmaceutical company, Egypt, its purity was found to be 99.9% according to the supplier certificate. The dosage form, Zoloft® tablet, (produced by Pfizer pharmaceutical company, Egypt) labeled to contain 50 mg SRT was purchased from the local market.

2.3. Chemicals and Reagents

Britton-Robinson (BR) buffer solutions (pH 5-9) were used as supporting electrolytes. BR buffers were prepared by mixing a solution of 0.04 mol L⁻¹ phosphoric acid (Sigma-Aldrich), 0.04 mol L⁻¹ acetic acid (Loba Chemie Co., India) and 0.04 mol L⁻¹ boric acid which was obtained from El-Nasr pharmaceutical company, Cairo, Egypt. Buffer solutions were adjusted with the appropriate amount of 0.2 mol L⁻¹ sodium hydroxide (Winlab, Leicestershire, U.K.) to get the desired pH. Graphite powder and paraffin oil, Sodium dodecyl sulphate (SDS), Triton X-100 and

cetyltrimethyl ammonium bromide (CTAB) were provided from Sigma-Aldrich, Taufkirchen, Germany. All chemicals and reagents used throughout the work were of analytical reagent grade.

2.4. Standard and Working Solutions

The standard stock solution of SRT (1.0 x 10⁻² mol L⁻¹) was prepared by dissolving an accurately weighed amount of SRT in methanol. The stock solutions were stored in dark bottle and were stable when stored in a refrigerator at 4 °C for one week.

Working solutions were prepared by appropriate dilution of stock standard solutions with the same solvent to obtain a solution of 1.0 x 10⁻³ mol L⁻¹.

2.5. Preparation of Working Electrode

Carbon paste electrode (CPE) with was prepared by mixing graphite powder (0.5 g) with paraffin oil (approximately 0.3 mL) in a glassy mortar. The carbon paste was packed into the hole of the electrode body and smoothed on a filter paper until it had a shiny appearance without touching its surface.

2.6. Electrochemical Measurements

2.6.1. Electrochemical Behavior of SRT

For blank, 5 mL of BR buffer of pH 7, containing 70 µL Triton was transferred into the cell. Then the CPE, reference and auxillary were immersed and the cyclic voltammetry (CV) response was recorded.

For test solution, into the cell 4.5 mL BR buffer of pH 7 containing 70 µL Triton was introduced followed by 0.5 mL of 1.0 x 10⁻³ mol L⁻¹ of the drug and CV response was measured.

2.6.2. Recommended Procedure for Calibration Curve

Aliquots equivalent to, 1.99 x 10⁻⁷ - 1.38 x 10⁻⁵ mol L⁻¹ of SRT were transferred separately into a series of 5 mL volumetric flasks using micro pipette, then 70 µL of 10⁻² mol L⁻¹ Triton solution were added and the volume was completed to the mark with BR buffer of pH 7. The solution was transferred to the electrolytic cell then square wave voltammetry (SWV) was applied and voltammograms were recorded.

2.6.3. Applications

(i). Determination of SRT in Tablets

Five tablets were weighed, transferred to a clean mortar, grounded into fine powder and mixed well. An accurately weighed amount required to prepare SRT solution of concentration 1.0 x 10⁻³ mol L⁻¹ was transferred to a volumetric flask containing 60 mL methanol, sonicated for 10 min, completed to the volume with methanol and then filtered to separate out the insoluble excipients. Then the procedure mentioned under "2.6.2. Calibration curve" was followed.

(ii). Determination of SRT in Spiked Urine

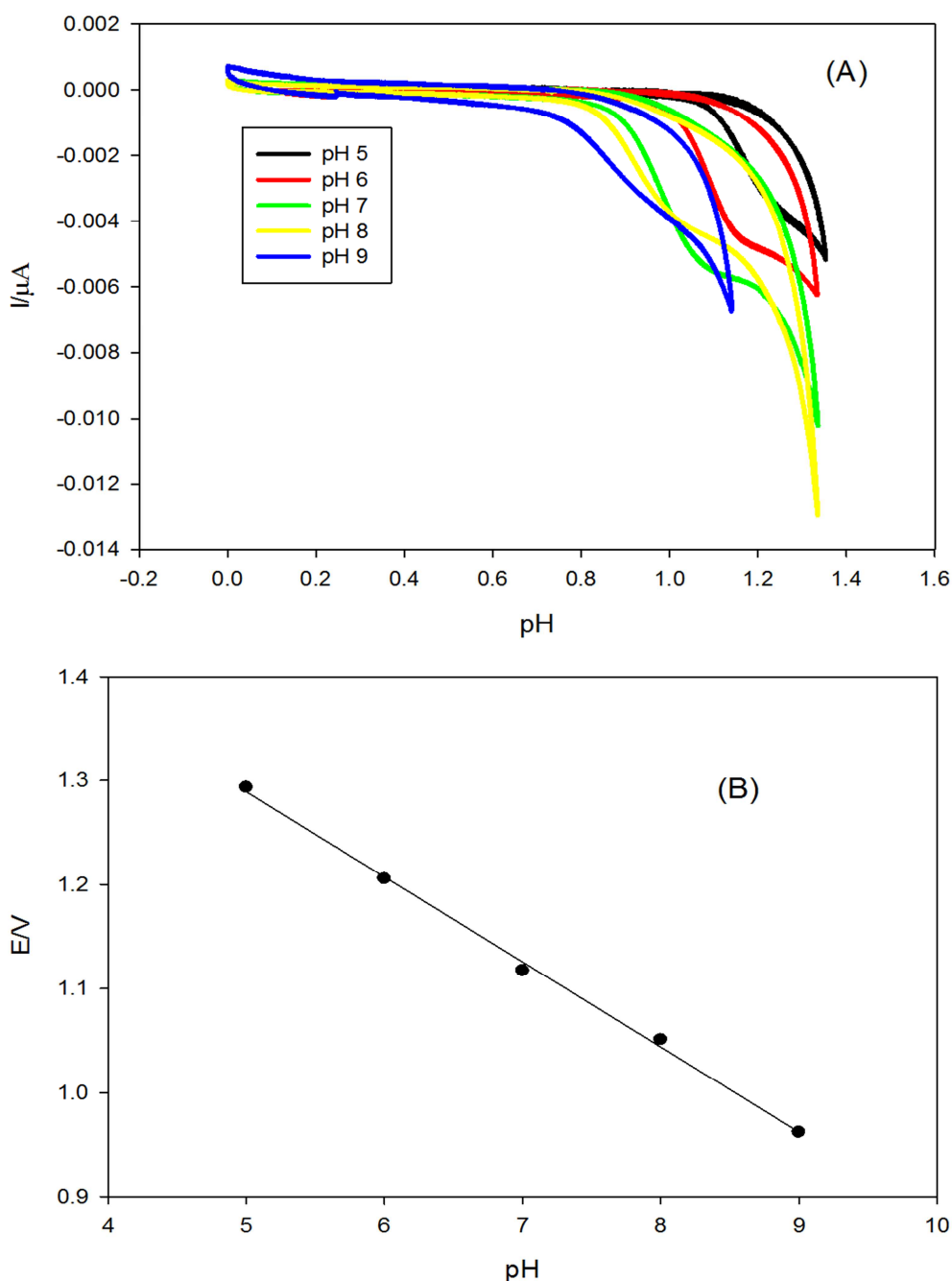
Urine sample (1.0 mL) was added to 9.0 mL of BR buffer of pH 7, mixed well, and then spiked with aliquots of SRT solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$). The procedure mentioned under “2.6.2. Calibration curve” was then followed and the calibration graph was constructed by plotting the peak currents against drug concentrations.

3. Results and Discussion

3.1. Electrochemistry of SRT

Figure 2A shows cyclic voltammograms of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT in BR buffer of pH ranging from 5.0 to 9.0, at scan rate of 100 mV s^{-1} at CPE in which anodic peaks were

produced due to the oxidation of the secondary amine group in SRT with no peaks on the reverse scan, suggesting the irreversibility of SRT oxidation reaction. In Figure 2B we notice shifting of the anodic peak potential negatively with the increase in the solution pH indicating that the oxidation process is pH dependent and protons have taken part in the electrode reaction processes. Below pH 5.0, no oxidation peak was observed for SRT while and by increasing the solution pH from 5.0 to 9.0 the anodic peak current increased gradually till pH 7.0 then decreased (Figure 2C) so pH 7.0 was chosen as for subsequent investigations. The peak potential for SRT oxidation varies linearly with pH over the pH range (5.0-9.0) according to the linear regression equation of $E (\text{V}) = 1.343 - 0.037 \text{ pH}$, with correlation coefficient (r^2) = 0.9968.



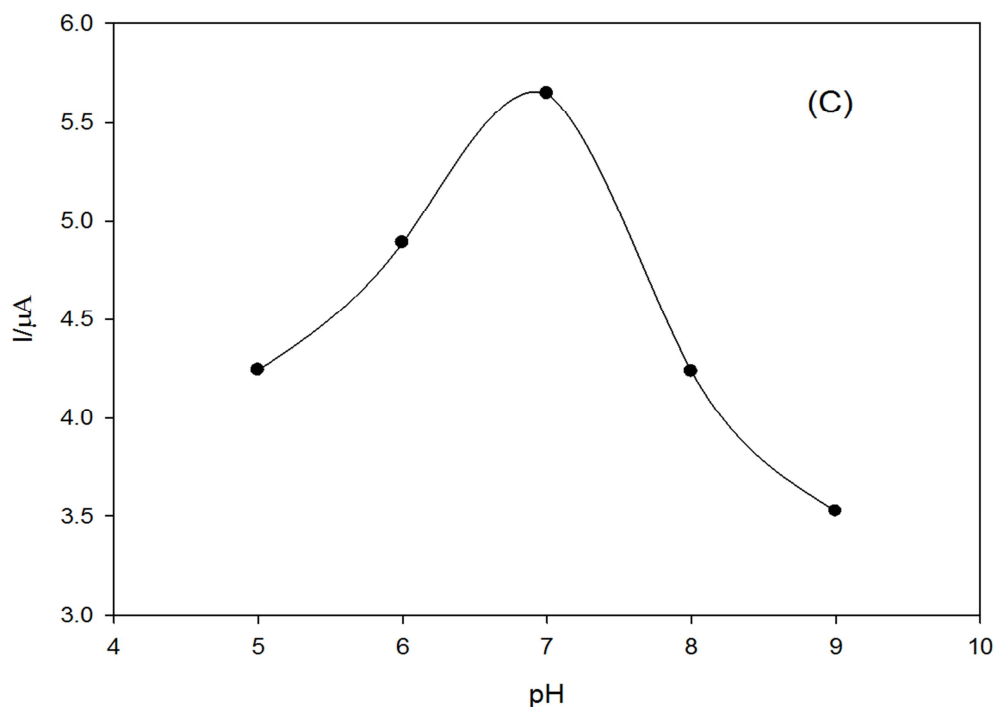


Figure 2. Cyclic voltammograms of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT at CPE in BR buffers of pH values from 5.0 to 9.0 at scan rate of 100 mV s^{-1} (A), the linear relations of peak potential (B) and current (C) as a function of pH.

3.2. Influence of Different Surfactants

The cyclic voltammograms of SRT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) in BR buffer of pH 7 were studied on CPE upon successive additions of the following surfactants: (SDS), (Triton) and (CTAB) of the same concentration of $1.0 \times 10^{-2} \text{ mol L}^{-1}$. Figure 3 shows that the oxidation peak current of SRT increased by increasing the volumes added of SDS, Triton and CTAB up to certain amount (50, 70 and 50 μL

respectively), after which any successive addition of surfactant causes decrease in the peak current. This is may be due to the adsorption of the surfactant molecules on the electrode surface followed by micelle formation leading to decreasing the distance between SRT and the electrode surface [50]. Form the figure we could conclude that Triton is the surfactant of the optimum response and should be used for subsequent investigations.

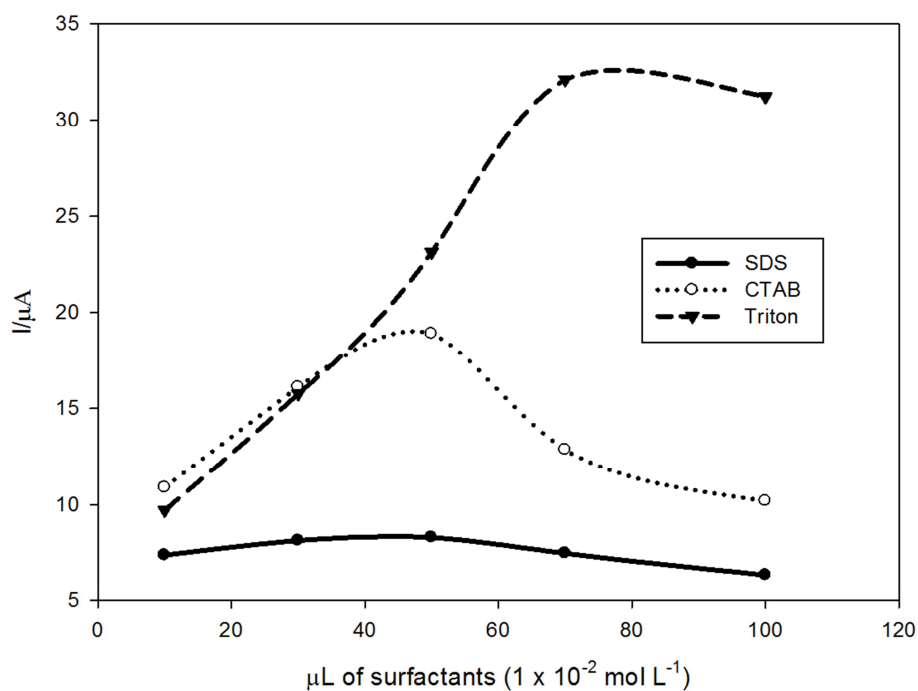


Figure 3. The linear relation of peak current of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT at CPE in BR buffers of pH 7.0 at scan rate of 100 mV s^{-1} as a function of different surfactants.

Figure 4 shows the cyclic voltammograms of SRT ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) in the presence of 70 μL Triton ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) and in absence of Triton. The oxidation peak current increased in the presence of Triton (32.1 μA) 5.68 fold its value without Triton (5.65 μA).

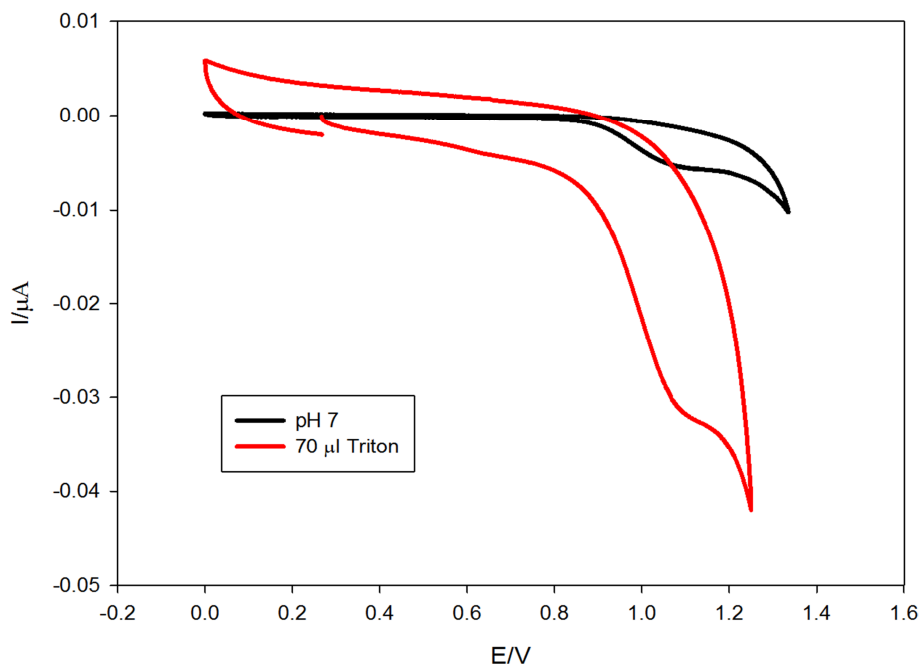


Figure 4. Comparison between cyclic voltammograms of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT at CPE in BR buffers of pH 7.0 with and without the addition of 70 μL of $1.0 \times 10^{-2} \text{ mol L}^{-1}$ Triton.

3.3. Influence of Scan Rate

The effect of scan rate (ν) ($25 - 450 \text{ mV s}^{-1}$) on the anodic peak current of SRT was investigated (Figure 6A). The oxidation reaction of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT in presence of 70 μL Triton ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) at CPE in BR buffer of pH 7.0 was identified by recording the cyclic voltammograms from which we got a linear relationship between the logarithm of the anodic peak currents and the logarithm of the scan rates. The direct proportionality between log current and log scan rate was according to the linear regression equation $\log I = 0.111 + 0.452 \log \nu$, $r^2 = 0.9929$ (Figure 6B). The value of the slope of the obtained linear relation is less than 0.5 which implies that the electro active species are

transported by a diffusion controlled process [51].

The number of electrons involved in reaction can be calculated using Laviron equation for an irreversible process [52]: $E = E^\circ + 2.303RT/\alpha nF [\log RTK^\circ/\alpha nF + \log \nu]$

where α is the electron transfer coefficient, n is the number of electrons, T is the temperature (298 K), R is the gas constant ($8.314 \text{ J K mol}^{-1}$) and F the Faraday constant (96485 C mol^{-1}), respectively. Thus we can calculate αn from the slope of the relation between E versus $\log \nu$. The slope was found to be 0.0587, generally, α (electron transfer coefficient) was assumed to be 0.5. Thus, the value of electrons number $n = 2$ which is found in agreement with the suggested electro oxidation mechanism of SRT as shown in Figure 5.

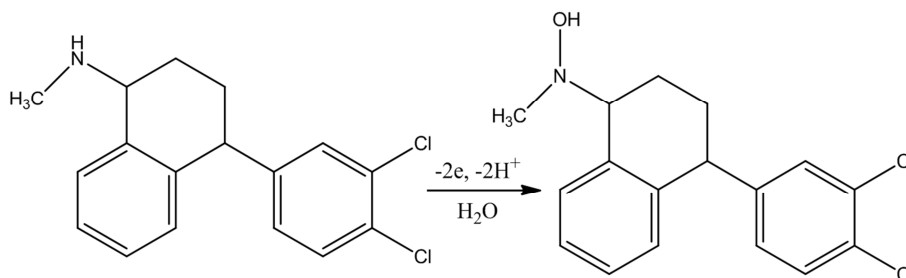


Figure 5. The suggested oxidation mechanism of SRT.

The relation between anodic peak current, diffusion coefficient of the electro active species, D ($\text{cm}^2 \text{ s}^{-1}$), and scan rate, ν (V s^{-1}), is given by Randles-Sevcik equation: [53]: $I = (2.99 \times 10^5) \alpha^{1/2} A C D^{1/2} \nu^{1/2}$, where n is the number of electrons involved in oxidation, α is the transfer coefficient,

A is the apparent electro active surface area of the electrode (cm^2) and C is the concentration of the electro active species (mmol L^{-1}). The diffusion coefficient was calculated was found to be $5.66 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ (Figure 6C).

The electro active surface area of CPE was calculated

through applying different scan rates on $1.0 \times 10^{-3} \text{ mol L}^{-1}$ $\text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 mol L^{-1} KCl. The diffusion coefficient of

$\text{K}_3\text{Fe}(\text{CN})_6$ is known and equals $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ consequently A was calculated to be 0.095 cm^2 .

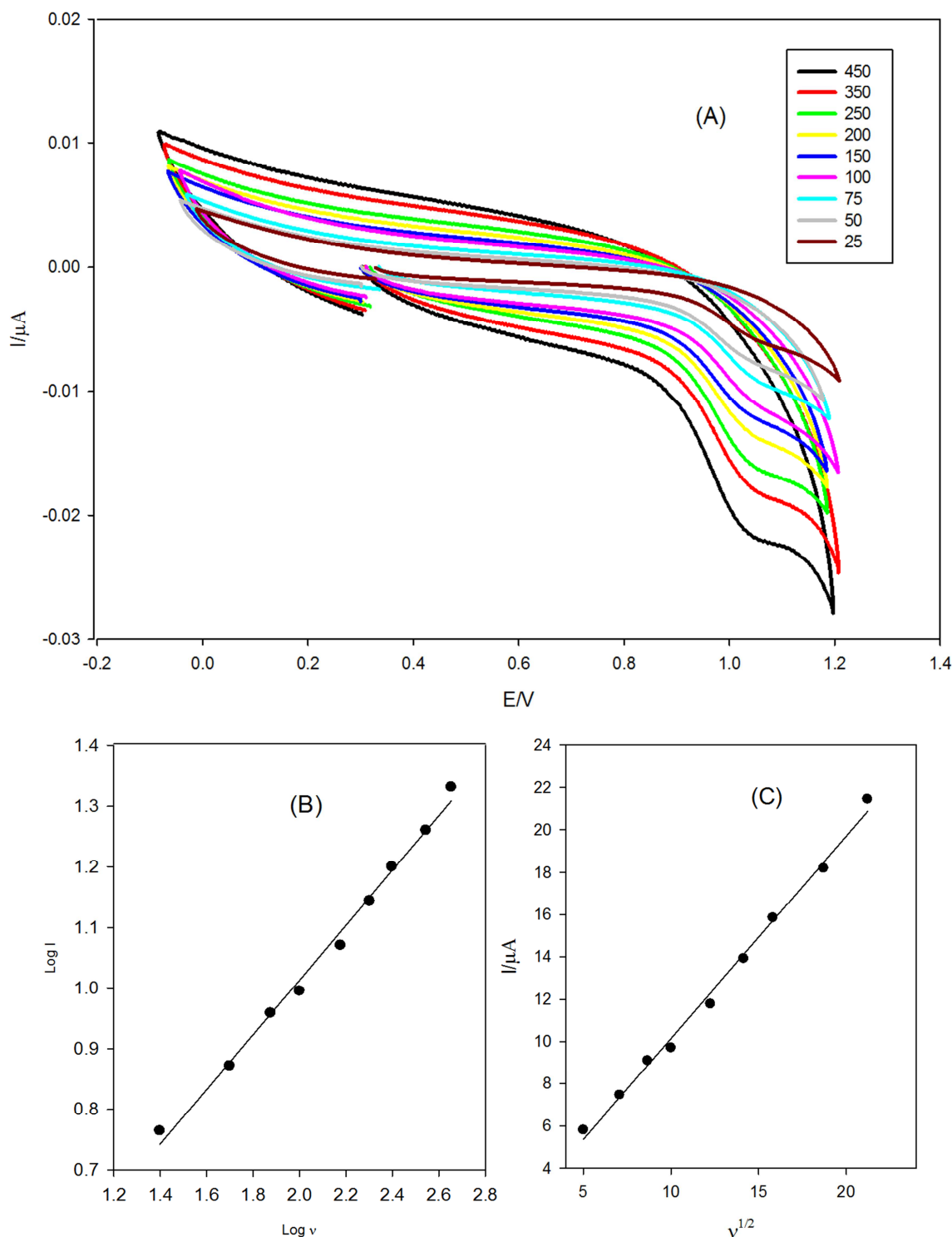


Figure 6. Cyclic voltammograms of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SRT at CPE in BR buffers of pH 7.0 at: 25-450 mV s^{-1} (A) in presence of 70 μL Triton ($1.0 \times 10^{-2} \text{ mol L}^{-1}$). Plot of log the anodic peak current versus log scan rate (B). Plot of square root of scan rate versus the anodic peak current (C).

3.4. Method Validation and Application

Validation of the proposed method was assessed according to the ICH Q2 (R1) recommendation [54]. The method was validated for specificity, linearity and range, limit of detection, limit of quantification, accuracy, precision and robustness.

3.5. Determination of SRT in Bulk

On the basis of the electrochemical oxidation of SRT at CPE, analytical method was developed using SWV for the determination of SRT in bulk. A linear response was

obtained in the range from 1.99×10^{-7} to 1.38×10^{-5} mol L⁻¹. The calibration plot (Figure 7) was described by the

following equation: $I (\mu A) = 0.23 C (\mu mol L^{-1}) + 20.91$, $r^2 = 0.9995$.

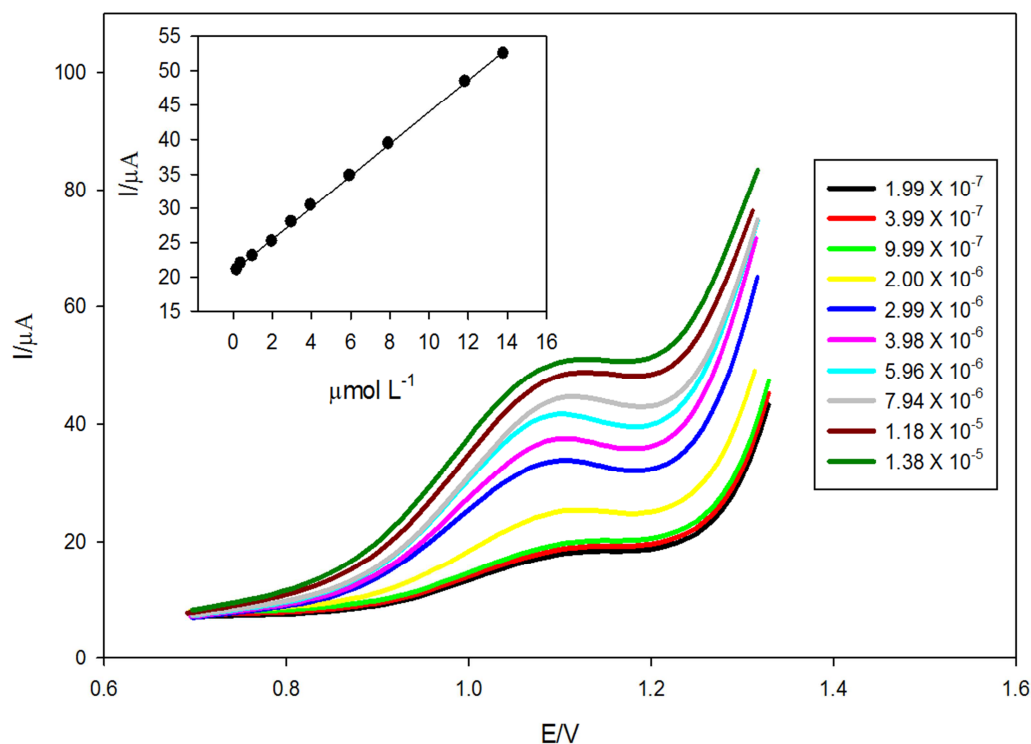


Figure 7. Square wave voltammograms of different concentrations of SRT at CPE in BR buffer of pH 7.0 in presence of 70 μL Triton (1.0×10^{-2} mol L⁻¹) at a scan rate of 100 mV s^{-1} . The inset: the calibration plot of the oxidation peak current versus the concentration range of SRT.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated using the following equations: $LOD = 3 \text{ SD}/m$ and $LOQ = 10 \text{ SD}/m$, where “SD” is the standard deviation of the intercept of the response ($n = 5$) and “m” is the slope of the regression line. The LOD and LOQ were found to be 2.23×10^{-8} mol L⁻¹ and 7.42×10^{-8} mol L⁻¹, respectively (Table 1). The proposed method was found to be more sensitive than all the reported electrochemical methods [28-31], potentiometric method [46] and spectrophotometric method [6-10] (Table 2).

Table 1. Regression data for quantitative determination of SRT in bulk and spiked urine.

Parameters	Bulk	Spiked Urine
Linearity range (mol L ⁻¹)	$1.99 \times 10^{-7} - 1.38 \times 10^{-5}$	$2.99 \times 10^{-6} - 1.76 \times 10^{-5}$
Slope	0.23	0.16
Intercept	20.91	17.77
r^2	0.9995	0.9982
LOD (mol L ⁻¹)	2.23×10^{-8}	4.70×10^{-8}
LOQ (mol L ⁻¹)	7.42×10^{-8}	1.57×10^{-7}

Table 2. Comparison of the proposed method with some reported methods for SRT.

Method	Linearity range	Reference
Voltammetry (mol L ⁻¹)	$1.99 \times 10^{-7} - 1.38 \times 10^{-5}$ (0.068 - 4.73)	This work
($\mu g \text{ mL}^{-1}$)	$4.0 \times 10^{-5} - 8.0 \times 10^{-4}$	[28]
	$2.33 \times 10^{-7} - 3.15 \times 10^{-6}$	[29]
	$2.0 \times 10^{-7} - 1.2 \times 10^{-6}$	[30]
	$3.0 \times 10^{-7} - 9 \times 10^{-6}$	[31]

Method	Linearity range	Reference
Potentiometry (mol L ⁻¹)	$1.0 \times 10^{-6} - 1.0 \times 10^{-5}$	[46]
	6 - 48	[6]
	8 - 46	[7]
Spectrophotometry ($\mu g \text{ mL}^{-1}$)	1 - 30	[8]
	1 - 10	[9]
	2 - 24	[10]

The precision and accuracy of the proposed method were assessed by repeating three different concentrations (9.99×10^{-7} , 5.96×10^{-6} , and 1.38×10^{-5}) on the calibration curve three times and the %Recovery was found to be in the range of 99.88-100.37% with relative standard deviation (%RSD) values in the range of 0.38-1.55%. The results listed in Table 3 show good precision and accuracy of the proposed method.

Table 3. Precision of the proposed SWV method for the determination of SRT in bulk.

Parameters	SRT (mol L ⁻¹)		
	9.99×10^{-7}	5.96×10^{-6}	1.38×10^{-5}
Repeatability	99.32	101.56	100.65
(%Recovery)	100.98	101.18	99.27
Mean	100.14	100.79	101.64
%RSD	100.15	101.18	100.52
	0.83	0.38	1.55

Robustness of the proposed method was performed using 3.98×10^{-6} mol L⁻¹ SRT solution and repeating the experimental with changing buffer pH 7.0 ± 0.2 , scan rate (mV s^{-1}) 100 ± 5 and volume of Triton $70 \mu L \pm 2$. The %RSD values were 0.788%, 0.809 and 0.832%, respectively.

confirming the robustness of the proposed method and that slight changes in the optimum parameters did not affect it.

3.6. Determination of SRT in Tablets

Table 4. Application of the standard addition method in determination of SRT in Zolofit Tablets.

Parameters	Added $\mu\text{mol L}^{-1}$	Taken $\mu\text{mol L}^{-1}$	Found $\mu\text{mol L}^{-1}$	%Recovery
Mean $\pm$ SD %RSD SE	5	10	15.10	100.67
	15		24.92	99.680
	30		40.08	100.20
	45		55.12	100.22
	60		70.40	100.57
				100.27 $\pm$ 0.389
				0.388
				0.174

The proposed method was successfully applied for the determination SRT in Zolofit tablets using the standard addition method without interference neither from

excipients nor preservatives that commonly present in the pharmaceutical matrix. Satisfactory mean recoveries $\pm$ RSD% (100.27 $\pm$ 0.388) were obtained. The obtained results were tabulated in Table 4.

3.7. Determination of SRT in Spiked Urine

The proposed method was used to determine SRT in urine samples. The results gives linear range of 9.99×10^{-7} - $1.38 \times 10^{-5} \text{ mol L}^{-1}$, $r^2 = 0.9982$ (Figure 8). The LOD was $4.70 \times 10^{-8} \text{ mol L}^{-1}$ and LOQ was $1.57 \times 10^{-7} \text{ mol L}^{-1}$. The precision and accuracy of the proposed method were assessed using three different concentrations (9.99×10^{-7} , 5.96×10^{-6} , and 1.38×10^{-5}) on the calibration curve that are repeated for three times and the % recovery was found to be in the range of 99.77-100.4% with mean recovery and %RSD of 100.09% and 0.3148%, respectively. The results listed in Table 5 show good precision and accuracy of the proposed.

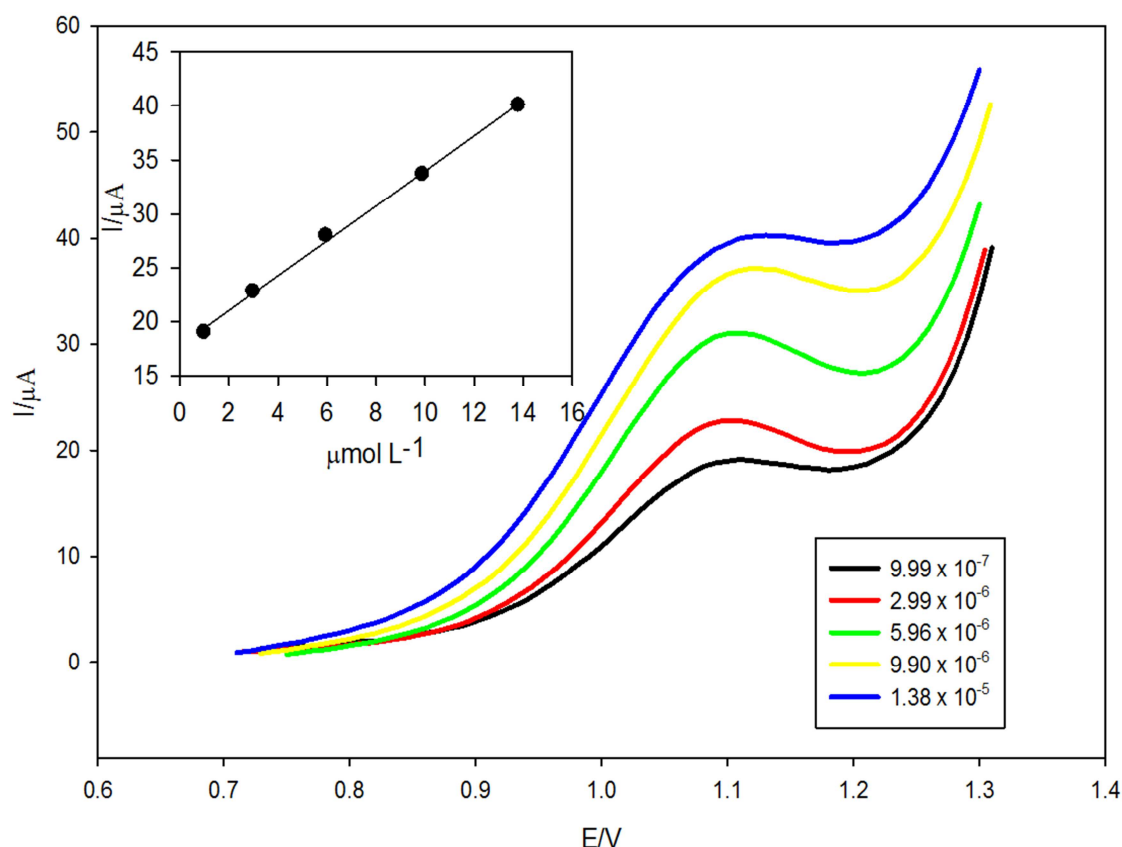


Figure 8. Square wave voltammogram of different concentrations of SRT spiked in urine at CPE in BR buffer of pH 7.0 in presence of 70 μL Triton ($1.0 \times 10^{-2} \text{ mol L}^{-1}$) at a scan rate of 100 mV s^{-1} . The inset: the calibration plot of the oxidation peak current versus the different concentrations of SRT.

Table 5. Evaluation of the accuracy and precision of the proposed method for the determination of SRT in urine.

Parameters	Added $\mu\text{mol L}^{-1}$	Found $\mu\text{mol L}^{-1}$	%Recovery
Mean	5	5.02	100.4%
$\pm$ SD %RSD	30	29.93	99.77%
SE	70	70.1	100.1%
			100.09 $\pm$ 0.3151
			0.3148
			0.1819

4. Conclusion

In the presented work, the electrochemical behavior of SRT is investigated using CV and SWV at CPE. The proposed procedure showed sensitive, rapid, and reproducible manner in the determination of SRT in bulk, pharmaceutical preparation and spiked urine. The analytical

procedure has been fully validated regarding linearity, precision, accuracy, reproducibility and sensitivity.

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