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Differential Pulse Polarographic Analysis of Glyburide in Pure form and Pharmaceutical Formulations

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A sensitive method is described for the determination of glyburide as antidiabetic in its pure form and dosage forms. The proposed method depends upon the polarographic activity of glyburide using cyclic voltammogram, direct current polarography, square wave polarography and differential pulse polarography in acetate buffer. At a sweep rate of 100 mV s^{-1} the cyclic voltammograms showed a well defined cathodic peak with high selectivity. The differential pulse polarography gave a reproducible well defined diffusion controlled peak for each drug at a sweep rate of 10 mVs^{-1}. The reduction peak was used to determine the tested drug concentrations. Whereby a well-defined cathodic wave is produced over the pH range 2-11. The current-concentration relationship was found to be rectilinear over the range 1-112, 2-80 and 1-40 µM with a RSD of 5.2, 4.4 and 4.8 % using droping mercury electrode, static droping mercury electrode and hanging droping mercury electrode, respectively. The limit of quantitation was 0.645 µM and the limit of detection 0.194 µM using droping mercury electrode. The proposed method was successfully applied to the determination of glyburide in tablets.

Key Words: Glyburide, Differential pulse polarographic analysis, Pharmaceuticals.

INTRODUCTION

Glyburide[1] (Fig. 1) is an oral antihyperglycemic drug of the sulfonylurea class, also referred as glibenclamide in British pharmacopoeia. The chemical name for glyburide is1-[[*p*-[2-(5-chloro-*o*-anisamido)ethyl]phenyl]sulfonyl]-3-cyclohexylurea. Glyburide is a white to off-white crystalline compound (m.f. $C_{23}H_{28}N_3O_5SCl$).

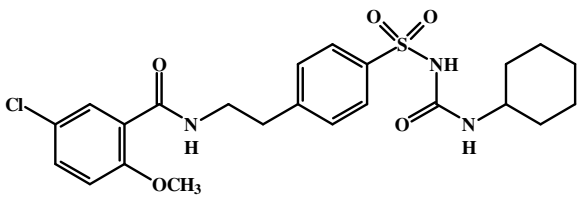

Fig. 1. Structural formula of glyburide

Glyburide is an effective, long-acting, second generation sulfonylurea used in the treatment of non-insulin-dependent diabetes mellitus (NIDDM). It functions by inhibiting ATP-sensitive potassium channels in pancreatic β-cells. This inhibition causes cell membrane depolarization, opening of voltage-dependent calcium channels, thus triggering an increase in intracellular calcium into the β-cell that stimulates insulin release. It occurs as a white or almost white, odorless crystalline powder. Solubility of the drug in water is approximately 4 µg mL^{-1} at pH 4 and 600 µg mL^{-1} at pH 9 and 3 mg mL^{-1} in alcohol. The drug has a pk_a of 6.8[2,3].

Literature data reports several methods for the determination of glyburide in biological samples. Most of them depends on HPLC methods with UV or fluorescence detector[4-14], mass spectrometry[15-17], fluorometric[18] and gas chromatographic[19] analysis. Voltammetric methods have been reported for the determination of some antidiabetic drugs at carbon paste and glassy carbon electrodes using cyclic and differential pulse voltammetry[20].

However, none of the reported methods for the determination of glyburide was used the polarographic analysis. Electrochemical methods were proved to be useful for sensitive and selective determination in pharmaceutical compounds. These methods do not require tedious pre-treatment and involve limited pre-separation and consequently reduce the cost of analysis[21-23].

The present work aimed to reconsider the electrochemical behaviour of the drug in acetate buffers at the dropping mercury electrode. It is also aimed here to optimize an electrochemical procedure for the direct determination of the drug in pharmaceutical formulations using differential pulse polarographic

technique. So that the investigated method can be applied to the analysis of glyburide in pharmaceutical preparation and they are characterized by simplicity and less running costs with high accuracy and precision.

EXPERIMENTAL

A Metrohm 797 VA processor was used; A Metrohm 797 VA stand with a multi-mode electrode (MME) comprising a dropping mercury electrode (DME), static mercury drop electrode (SMDE) and hanging mercury drop electrode as a working electrode, an auxiliary platinum electrode and a reference electrode [double junction type (Ag/AgCl) saturated with a 3.0M KCl solution] completed the three-electrode cell. All measurements were done at room temperature 25 ± 2 ºC, Nitrogen gas was used for deoxygenation. pH-Meter from radio meter company model ion check was used for the studying the pH effects.

Glyburide standard was supplied from Cadila Health Care Ltd., India, stock standard solutions were prepared daily by accurate weighing 24.7 mg of glyburide and dissolution it in 50 mL volumetric flask by acetonitrile to give a concentration of 0.494 mg mL^{-1} (1×10^{-3} M). Working standards were prepared daily by diluting different volumes of stock solution 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 4.0 and 5.0 mL diluting to 25 mL with 5 mM acetate buffer supporting electrolyte (pH 6.0) was prepared by dissolution 0.41015 g of CH_3COONa in 1000 mL volumetric flask by double-distilled deionized water, appropriate volume of CH_3COOH or NaOH (0.01 M) was added to give the desired pH. All solutions and reagents were prepared with double-distilled deionized water and analytical grade chemicals. Ultrapure mercury from Metrohm company was used throughout the experiments.

25 mL of working standard of glyburide was transferred to the cell. The solution was well mixed by automatic mixer and deoxygenated with nitrogen gas for 5 min. Current-voltage curves were recorded. Limiting currents were measured and calibration curves in electrolytes were constructed.

The polarograms of glyburide was recorded by using direct current polarography (DCP), cyclic voltammetry (CV) and differential pulse polarography positive polarity (DPPPP) and differential pulse polarography negative polarity (DPPNP) in the potential range from -600 mV to -1700 mV, sweep rate 10 mV/s with step voltage time 1s at DPP and 100 mV/s at cyclic voltammetry. The number of experiments (n = 5) according to this value the statistical calculations were done.

Sample preparation: Ten tablets containing glyburide and metformin HCl of pharmaceutical formulations: glibomet (2.5 and 5 mg gly./400 mg metf.HCl), glustate, (5 mg gly.), glyform (1.25 mg gly./250 mg metf. HCl, 2.5 and 5 mg gly./ 500 mg metf. HCl) gluvans (2.5 and 5 mg gly./500 mg metf. HCl), glicuformine (1.25 mg gly./250 mg metf. HCl), glymet (1.25 mg gly./250 mg metf. HCl, 5 mg gly./500 mg metf. HCl), glicoral (1.25 mg gly./250 mg metf. HCl, 2.5 mg gly./500 mg metf. HCl) and glyburine (2.5 and 5 mg gly./400 mg metf. HCl) tablets were weighed and ground to a fine powder. A quantity equivalent 5 mg of glyburide. was weighed and dissolved in10 mL volumetric flask by acetonitrile. The solution was slightly turbid, because of containing metf HCl which doesn't soluble in acetonitrile, but no further treatment was made. Known volumes 0.6 mL of the prepared solution were added to 25 mL aliquots of the electrolyte.

RESULTS AND DISCUSSION

Effect of polarographic method: Direct current polarography (DCP), cyclic voltammetry (CV), square wave (SqW), differential pulse polarography positive polarity and differential pulse polarography negative polarity of glyburide in presence of 5 mM acetate buffer at pH 6 as electrolyte by using dropping mercury electrode and hanging mercury drop electrode (HMDE) were studied. Differential pulse polarography positive polarity was found to give the greatest sensitivity. A cathodic peak was obtained at potential varying between-1.220 to -1.225V due to the reduction of glyburide (Fig. 2), a cyclic voltammogram of glyburide on hanging mercury drop electrode in presence of 5 mM acetate buffer at pH 6 as electrolyte. If the sweep rate is 100 mV/s, the voltammogram consists of an reduction peak at -1.222 V *versus* Ag/AgCl/3 M KCl, This peak is expected to be the reduction of the two carbonyl group. The fact that no peaks were observed in the anodic branch scans suggests that the process is an irreversible one. Square-wave voltammogram of glyburide on hanging mercury drop electrode is shown in Fig. 2. Frequency was varied from 60 to 300 Hz using a scan increment of 55 mV, pulse amplitude of 60 mV in 24 µM glyburide solution. The relationship was obtained between the peak current and the frequency of the signal up to 240 Hz, which is the frequency chosen to improve the sensitivity without any distortion of the peak or the baseline. A frequency of 240 Hz, of 60 mV amplitude and a sweep rate of 220 mV/s were used throughout the study (Fig. 3).

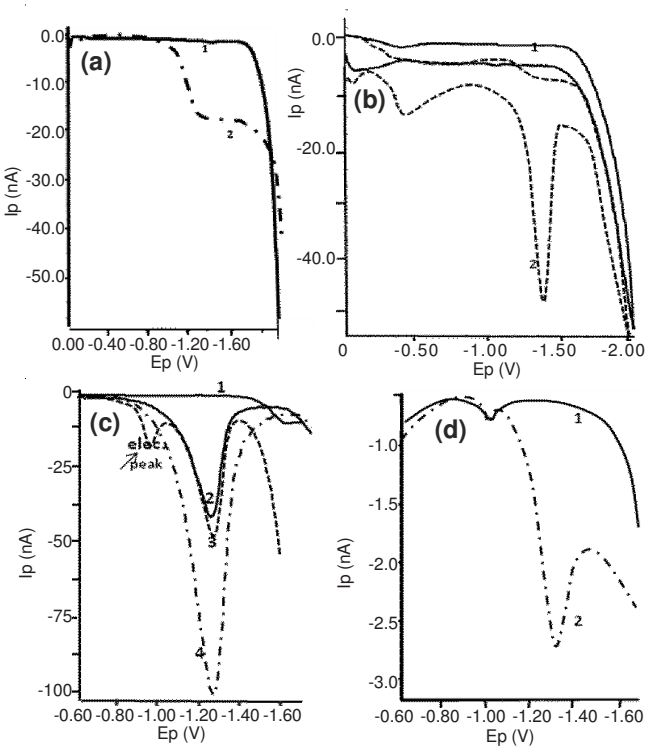

Fig. 2. Voltammetric Curves for the determination of glyburide in presence of 5 mM CH_3COONa at pH 6.0, (a) DC of glyburide (1- elec. 2-24 mM on HMDE), (b) CV of glyburide (1- elec. 2-24 mM on HMDE), (C) DPPPP of glyburide (1- elec. 2-24 mM on HMDE,3-24 mM on SMDE, 4-24 mM on DME), (d) SqW of glyburide (1- elec. 2-24 mM on HMDE)

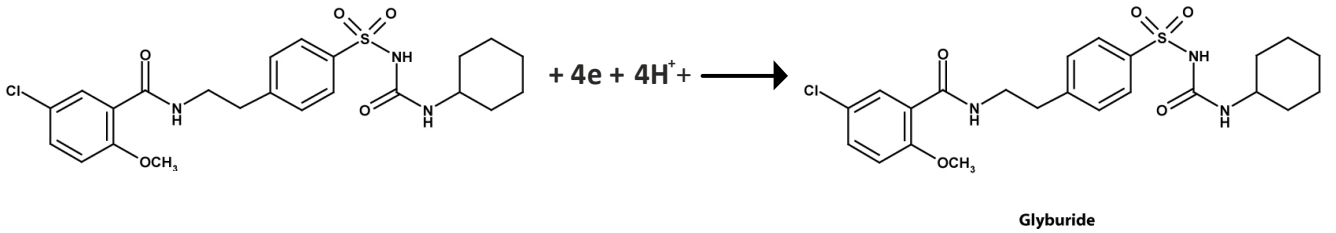

Fig. 4. Proposed mechanism for the reduction of carbonyl groups in optimal conditions of glyburide analysis

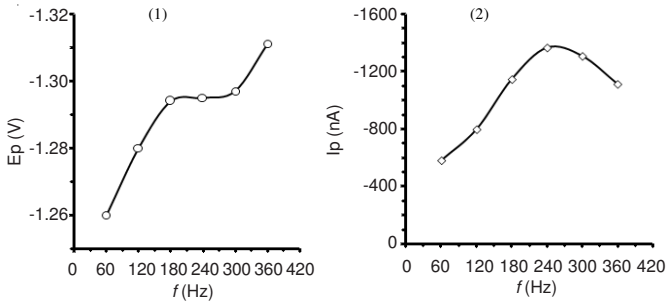

Fig. 3. Effect of frequency on square wave analysis using hanging mercury drop electrode of glyburide 24 mM in acetate buffer: 1-Ep. 2- Ip

Depending on the relationship between pulse amplitude and frequency, the number of electrons in half reaction will be 4 electrons and by comparison with natiglenide, the nateglinide containing one carbonyl group and the glyburide containing two carbonyl groups.The peak current of nateglinide is half of that obtained by glyburide at same concentration of material. Each of one carbonyl group exchange two electrons with electrode, so two ones of it exchange 4 electrons as shown in Fig. 4 accordance to the following equation by comparison with simvastatin[24]:

Effect of pH: The polarographic behaviour of the tested drug was found to be affected by the solution pH and the type of the supporting electrolyte. The effect of the above mentioned supporting electrolytes and the pH of the solution on the peak current of the tested drug were recorded. The different investigations were then carried out in the best supporting electrolyte, *i.e*. the acetate buffer over the pH range 2.0-11.0.

At pH ≤ 3 the drug precipitates and no well defined peak can be recorded. It was observed that the peak potential shifts to more negative direction when the solution pH was increased from 4 to 6 and then fixed between 6 to 8.5 and decreased after 8.5 to 11. At this values electrolyte peak appears again in high peak current referring to that the carboxyl groups reduced at this condition compared with nateglinide, it has two reduction peaks one refered to carbonyl group at E_p = -1.220 V and second to carboxyl groups at E_p = -0.998 V. The decrease of the peak current with the increase of the solution pH is attributed to the fact that the electroactive species of the drug occur in the basic form and the drug molecules. The dependence of peak potential (E_p) and peak current (I_p) on pH is shown in Fig. 5 curve 1 and 2, respectively.

Effect of electolyte concentration: Different supporting electrolytes, in different concentrations (0.0 - 0.015 M), namely HCl, H_2SO_4, acetic acid/sodium acetate, ammonium chloride/ aqueous ammonia, KCl, phosphate buffer, borate buffer and lithium perchlorate/perchloric acid buffer were investigated.

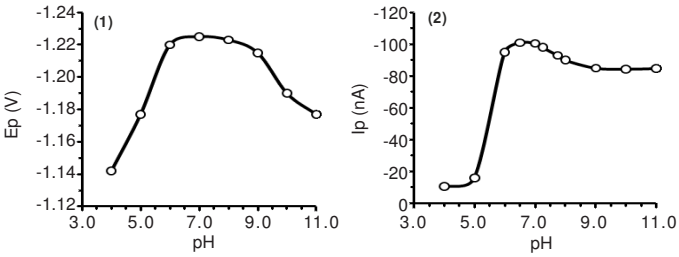

Fig. 5. Effect of pH values on differential pulse polarography positive polarity analysis using dropping mercury electrode-of glyburide 24 mM in acetate buffer: 1-Ep. 2 - Ip

From all those supporting electrolytes the acetate buffer solution was found to give the best and most reproducible results. It did not only give the highest peak current but it also gave the most symmetrical peak shape. The acidic buffer formed muddy solution with soluble drug in acetonitrile and the peak had gave completely disappeared. The optimum concentration of the acetate buffer at the respective pH was found to be 5 mM (Fig. 6).

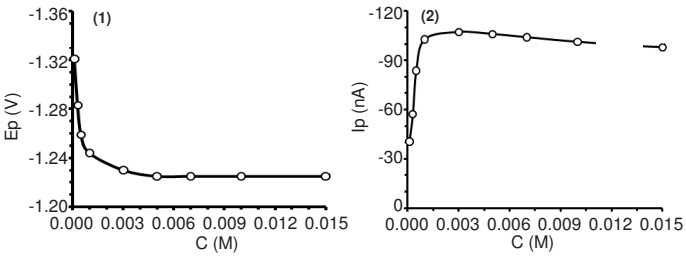

Fig. 6. Effect of concentration electrolytes on DPPPP analysis using DME of glyburide 24 mM at pH 6.0 : 1-Ep. 2 - Ip

Effect of pulse amplitude: The effect of pulse amplitude on DPP polarograms using dropping mercury electrode to determine of glyburide in acetate buffer pH 6.0 was studied. The peak current I_p increases proportional as a function to the increasing of differential pulse polarography negative polarity up to the value -30 mV. Therefore the value of pulse amplitude E = -20 mV was chosen as optimum value and the peak current I_p increases proportional as a function to the increasing of differential pulse polarography positive polarity up to the value +70 mV. Therefore the value of pulse amplitude E = +60 mV was chosen as optimum value.

Effect of electrodes sorts dropping mercury electrode, static mercury drop electrode and hanging mercury drop electrode: Differential pulse polarography was studied for standard solutions of glyburide on the potential range from -600 mV to -1700 mV in acetate buffer pH 6 by using dropping mercury electrode, static mercury drop electrode, hanging

TABLE-1
EVALUATION OF ACCURACY AND PRECISION OF THE PROPOSED METHODS FOR DETERMINATION OF GLYBURIDE ON DME, HMDE AND SMDE DPPPP

Electrode sort	$C_{Glyb.}$ taken (μM)	$C_{Glyb.}$ found, $\overline{x}^*$ (μM)	SD (μM)	Analytical standard error $\frac{SD}{\sqrt{n}}$ (μM)	Confidence limits $\overline{X} \pm \frac{SD}{\sqrt{n}} t$, (μM)	RSD (%)
Dropping mercury electrode (DME)	1.00	1.08	0.056	0.025	1.08 ± 0.070	5.2
	2.00	2.01	0.096	0.043	2.01 ± 0.119	4.7
	4.00	4.04	0.182	0.081	4.04 ± 0.225	4.5
	8.00	7.95	0.342	0.153	7.95 ± 0.424	4.3
	12.00	12.00	0.480	0.214	12.00 ± 0.594	4.0
	16.00	15.95	0.590	0.264	15.95 ± 0.733	3.7
	20.00	20.07	0.680	0.304	20.07 ± 0.844	3.3
	24.00	24.01	0.721	0.322	24.01 ± 0.893	3.0
	32.00	32.00	0.960	0.429	32.00 ± 1.191	3.0
	40.00	40.93	1.228	0.549	40.93 ± 1.524	3.0
	48.00	47.95	1.438	0.643	47.95 ± 1.785	3.0
	56.00	56.12	1.571	0.702	56.12 ± 1.948	2.8
	64.00	64.06	1.666	0.745	64.06 ± 2.068	2.6
	80.00	80.00	1.920	0.858	80.00 ± 2.382	2.4
	104.0	103.9	2.39	1.068	103.9 ± 2.964	2.3
	112.0	111.8	2.46	1.100	111.8 ± 3.053	2.2
Hanging dropping mercury electrode (HMDE)	1.00	1.05	0.050	0.022	1.05 ± 0.749	4.8
	2.00	2.06	0.093	0.041	2.06 ± 0.115	4.5
	4.00	4.10	0.135	0.060	4.10 ± 0.167	3.6
	8.00	7.98	0.287	0.128	7.98 ± 0.356	3.3
	12.00	12.00	0.396	0.177	12.00 ± 0.491	3.0
	20.00	19.92	0.498	0.222	19.92 ± 0.618	2.5
	24.00	24.04	0.553	0.247	24.04 ± 0.686	2.3
	32.00	31.92	0.670	0.299	31.92 ± 0.832	2.1
	40.00	39.94	0.799	0.357	39.94 ± 0.992	2.0
Static dropping mercury electrode (SMDE)	2.00	2.10	0.092	0.041	2.10 ± 0.114	4.4
	4.00	4.00	0.168	0.075	4.00 ± 0.208	4.2
	8.00	8.05	0.314	0.140	8.05 ± 0.389	3.9
	12.00	12.10	0.436	0.195	12.10 ± 0.541	3.6
	20.00	20.56	0.720	0.322	20.56 ± 0.894	3.5
	24.00	24.14	0.821	0.367	24.14 ± 1.019	3.4
	32.00	31.90	0.989	0.442	31.90 ± 1.228	3.1
	40.00	39.87	1.116	0.499	39.87 ± 1.385	2.8
	48.00	48.23	1.254	0.561	48.23 ± 1.557	2.6
	56.00	56.32	1.295	0.579	56.32 ± 1.607	2.3
	64.00	64.00	0.314	0.140	64.00 ± 0.389	2.0
	80.00	81.11	0.436	0.195	81.11 ± 0.541	1.8

* n = 5, t = 2.776

mercury drop electrode electrodes. Well-defined electrochemical reduction peak for glyburide was noticed at E_p range between -1220 mV to -1225 mV. It was found that the diffusion factor using dropping mercury electrode was greater than their values using hanging mercury drop electrode and using static mercury drop electrode:

$$K_{DME} = 3.000\ K_{HMDE} = 3.214\ K_{SMDE}$$

Calibration curves: Calibration curves for the determination of glyburide by differential pulse polarography using dropping mercury electrode, static mercury drop electrode and hanging mercury drop electrode electrodes were studied. The heights of current peaks I_p was proportional to the concentration of glyburide over the range 1.00-112.0 μM using dropping mercury electrode($y = -0.0045\ X + 1.6107$, $R^2 = 0.9999$; y: I_p, nA and X: $C_{Glyburide}$, nM), at pH = 6.00, 1.00-40.00 μM using hanging mercury drop electrode ($y = -0.0015X-1.899$, $R^2 = 0.9998$; and 2.00- 80.00 μM using static mercury drop electrode ($y = -0.0014X-0.367$, $R^2 = 0.9996$; electrodes by differential pulse polarography positive polarity method. The limits of quantifying glyburide were 1 μM and 2 μM with the relative standard deviation of 5.2, 4.8 and 4.4 % using dropping mercury electrode, static mercury drop electrode and hanging mercury drop electrode respectively. The lower limits of detection (LOD) and lower limits of quantification (LOQ) were calculated according to the following equations[25]:

$$LOQ = 10(SD/Slop),\ LOD = 3\ (SD/Slop).$$

where, SD is the standard deviation obtained from 5 different runs. The calculated values for each drug at dropping mercury electrode,static mercury drop electrode and hanging mercury drop electrode are presented in Tables 1 and 2.

Application to pharmaceutical preparations: The proposed method has been successfully applied for the analysis of glyburide in its commercial tablets. Pharmaceutical preparations glibomet, glymet, glicoral, glustate, glyform, gluvans, glicuformine, glyburine tablets contain 1.25 or 2.5 or 5.0 mg of glyburide) determined using differential pulse polarography

in acetate buffer pH 6.0. The results of quantitative analysis for glyburide were calculated by calibration curves and the standard addition methods, (Table-3).

TABLE-2
SUMMARY OF VALIDATION PARAMETERS FOR THE DETERMINATION OF GLYBURIDE IN PURE FORMS BY DPPPP METHODS ON DME, HMDE AND SMDE

Parameter	Data		
	DME	HMDE	SMDE
Linearity range (μM)	1.00-112.0	1.00-40.0	2.00-80.0
Correlation coefficient (R^2)	0.9999	0.9998	0.9996
Regression equation			
Slope	-0.0045	-0.0015	-0.0014
Intercept	1.6107	-1.899	-0.367
Limit of quantification (μM)	0.645	0.871	1.340
Limit of detection (μM)	0.194	0.262	0.402
RSD (%)	5.2	4.8	4.4

TABLE-3
DETERMINATION OF GLYBURIDE IN SOME PHARMACEUTICAL FORMULATIONS USING DPPPP METHODS ON DME AT PH = 6.00 USING STANDARD ADDITION METHOD

Commercial name	Contents in tablet (mg)	$\bar{x}$ (mg in tablet)	RSD (%)	Recovery (%)
Glibomet Tablet Unipharma (Damascus, Syria)	2.50	2.48	2.6	99.2
	5.0	5.13	2.2	102.6
Glustat Tablet Tamecco (Damascus, Syria)	5.00	5.38	2.3	107.6
Glymet Tablet Ruba Pharma (Damascus, Syria)	1.25	1.23	3.0	98.4
	5.00	5.18	2.1	103.6
Glicoral Tablet Racha Labs. (Damascus, Syria)	1.25	1.24	2.9	99.2
	2.50	2.52	2.5	100.8
	5.00	5.10	2.2	102.0
Glyform Tablet City Pharma Co. (Aleppo, Syria)	1.25	1.25	2.8	100.0
	2.50	2.60	2.5	104.0
	5.00	5.15	2.0	103.0
Gluvans Tablet El-Saad Pharma (Aleppo, Syria)	2.50	2.49	2.6	99.6
	5.00	5.20	2.1	104.0
Glicuformine Tablet Oubari Pharma (Aleppo, Syria)	1.25	1.23	3.0	98.4
Glyburine, Tablet National Co. for Pharma Indus. (Aleppo, Syria)	2.50	2.50	2.7	100.0
	5.00	5.14	2.0	102.8

After having the calibration curve, the pharmaceutical preparations of the drugs presented in Table-2, were then measured by the differential pulse polarographic method using dropping mercury electrode. The polarographic data were then compared with the data obtained by DPV as a standard reference method[20]. There were some significant differences between the porposed method besed on dropping mercury electrode and the reference electrochemical method based on the CPE and GCE electrodes.

Conclusion

In the proposed method, differential pulse polarographic analysis of glyburide in both pure form and pharmaceutical formulations at pH = 6.0 over the range of 1.00-112.0 μM (0.494-55.328 mg mL^{-1}) using dropping mercury electrode, 1.00-40.0 μM (0.494-19.76 mg mL^{-1}) using hanging mercury drop electrode and 2.00-80.0 μM (0.988-39.52 mg mL^{-1}) using static mercury drop electrode. Applying static mercury drop electrode and hanging mercury drop electrode over mentioned methods in this context were successfully carried out for the first time. The relative standard deviation (RSD) did not exceed of 5.2, 4.8 and 4.4 % using dropping mercury electrode, hanging mercury drop electrode and static mercury drop electrode, respectively. Therefore the proposed methods can be used for routine determination of glyburide in pharmaceutical formulations with high sensitivity.

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