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New voltammetric strategy for determination and electrochemical behaviors of Metformin by pencil graphite electrode in the NaOH

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In this study, the electrochemical properties and determination of Metformin (MET), which is one of the drugs used as an antidiabetic agent, was carried out using pencil graphite electrode (PGE) in NaOH (0.1 *M*) medium. This compound gave an irreversible peak of oxidation at about +1.28 V. Using square wave voltammetry in NaOH environment, the current showed a linear correlation with a concentration of 2.76–24.8 μM. At a concentration of 2.76 μM (n = 9), the limit of detection (LOD) of 9.03 nM (1.495 ng L^{-1}) and a relative standard deviation of 3.25% were calculated. The developed voltammetric method has been successfully applied in pharmaceutical preparations and urine samples for the determination of MET.

Keywords: Metformin, pencil graphite electrode, voltammetry, drug, urine.

1. Introduction

Diabetes, which is a disease called blood sugar and occurs when blood sugar is very high, it always significantly affects today's public health and quality of life. Diabetes types can generally be classified as Type 1, Type 2 and Gestational diabetes. People suffering from this disease should properly use these drugs.

The drugs used in the treatment of diabetes are generally divided into insulins and oral tablets[1]. Metformin (MET), which is one of the oral antidiabetic drugs commonly used in the treatment of Type 2 diabetes, is a drug that increases insulin sensitivity[2–4].

In the literature, several analytical methods have been reported on MET. Most of these studies, generally using UV[5], HPLC[6–10], mass spectroscopy[7–8], electrophoresis[11], Raman spectroscopy[12] and FTIR[13]; it relates to the determination of MET in biological fluids and pharmaceutically. Although these techniques show high sensitivity and accuracy, they have disadvantages such as the need for very expensive devices, time consuming due to various routine analysis steps, high cost, and having an experienced analyst.

Electrochemical methods are generally easy and do not require expertise. In addition, the sample to be determined can be analyzed directly without any pre-processing[14–16]. Voltammetric, one of the electrochemical methods can confidently meet the needs in this field because they provide safe, accurate, sensitive and reproducible results in the long term[17–20].

In the literature research, it is seen that electrochemical techniques recommended for the analysis of MET in biological fluid and drug forms. Furthermore, it is appearing that the electrodes used in these studies were modified. In the study using CuMW/CNT/PE electrode, it is seen that it gives two oxidation peaks in BR (pH 7.2)[21]. For the determination of MET, it was oxidized at +0.95 V in NH_3/NH_4Cl (pH 8.9) by using cyclic voltammetry (CV) technique and MWCNT/PE[22]. In another study in which MET was examined using CPE in 100 mM NaOH with CV technique, the oxidation peak was observed around +0.7 V[23]. In another study investigating the electrochemical behavior of MET using CPE in PBS (pH 12.0)

with CV technique, its oxidation potential was recorded as approximately +0.85 V[24]. Hadi *et al*. observed a detection limit of 0.12 μM in the BR (pH 2.59–12.65) with modified GC electrode, and also evaluated the electrochemical properties of MET by CV technique[25]. In another study, they stated that the reduction properties of MET were examined with CV technique and modified GC electrode, and gave a reduction peak at –0.15 V in PBS (pH 9.0)[26].

The sensitivity and repeatability losses take place on the surface of the electrode of GC used in electrochemical studies as a result of coating some molecules with oxidation products during analysis. The repeatability and sensitivity of the electrode response is quite high, since the pencil graphite electrodes (PG) are disposable and do not have electrode cleaning procedures. In addition to these properties it has, PG electrodes have become an alternative to GC electrodes due to their low cost, especially in simple and sensitive determinations of toxic, pharmaceutical and other compounds. PG electrodes are very attractive electrodes in terms of environmental sensitivity due to their high electrochemical reactivity, mechanical strength, low cost, low technology, easy preparation, and easy storage for disposal after use[29–35].

In this study, electrochemical properties of MET were investigated by using PG electrode in 0.1 *M* NaOH medium with CV and square wave voltammetry (SWV) techniques. In this study, a suitable voltammetric method on PG electrode is proposed for the first time as the electrochemical properties and determination of MET. The proposed method has been successfully applied to urine and drug forms.

2. Experimental

2.1. Chemicals:

Metformin (PHR1084) was obtained from Sigma-Aldrich. The tablet form of the drug (GLİFOR® 1000 mg) were purchased from a pharmacy in Turkey. Britton-Robinson (BR; pH 2.0–12.0), phosphate buffer (PBS; pH 2.0, 3.0, 7.4, 9.0), acetate buffer (ABS; pH 4.8) and 0.1 *M* NaOH solutions were used as supporting electrolyte solutions. The desired pH values of the supporting electrolytes were adjusted with 5 *M* NaOH and 5 *M* HCl. Stock solutions prepared by dissolving MET (1 mM) and GLİFOR® tablet (5.51 mM) in water were stored in refrigerator at +4°C. All experiments were carried out at room temperature in the laboratory.

2.2. Materials:

In electroanalytical studies, Autolab PGSTAT 128N electrochemical analyzer of EcoChemie company, Bioanalytical System Inc. (BAS) company was used with a three-electrode cell unit and electrochemical analysis was controlled with Nova 1.11 software.

The cell stand has three electrode systems; PG as a working electrode; a platinum wire (BAS MF 1032) as counter electrode; an Ag/AgCl saturated KCl (BAS MF 2052) was used as the reference electrode. Since PG electrodes are disposable, there is no need for cleaning. However, the PG electrode was electrochemically activated for 1.6 V/30 s in the supporting electrolyte. Electrochemical measurements were carried out after the PG electrode was activated. pH measurements were made using WTW Inolab pH 720.

2.3. Sample preparation:

10 GLİFOR tablets (each tablet containing 1000 mg Metformin) were accurately weighed and ground into a homogeneous fine powder. 1 mM stock tablet solution was prepared after mixing for 30 min in an ultrasonic bath. Measurements were taken by adding the desired amount of MET to the support electrolyte solution. Recovery calculations were made using the standard addition method. Measurements were repeated 3 times.

Urine sample was collected from a healthy non-smoking and drug-free volunteer on an empty stomach and just before the experiments. The sample was centrifuged at 5000 rpm for 10 min to remove unknown endogenous chemicals. 250 μL of urine sample taken from the upper clear part was diluted to 10 mL with the support solution and electrochemical measurements were performed as described in Section 2.2. Recovery calculations were made using the standard addition method. Measurements were repeated 3 times.

3. Results and discussion

3.1. Cyclic voltammetry:

In the first step of the electrochemical analysis, CVs of 0.551 mM MET (0.0 V) – (+1.5 V) – (0.0 V) direction at 100 mV s^{-1} scan rate are recorded on the PG electrode in 0.1 *M* NaOH medium (Fig. 1A). It is seen that the anodic peak potential (1.272 V/1.287 V) and current (0.771 μA/0.565 μA peak currents) change in the cycles, respectively.

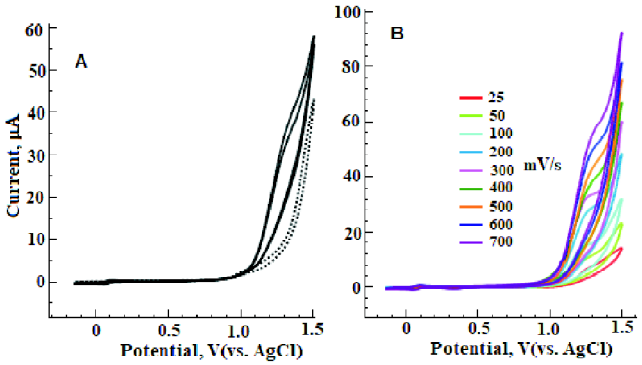

Fig. 1. Cyclic voltammograms for 0.551 mM Metformin at PG electrode in 0.1 *M* NaOH: (A) Repeat cycle voltammograms; scan rate, 100 mV s^{-1}. Dashed line, supporting electrolyte, (B) different scan rates.

In order to examine the electrochemical oxidation effect of potential scan rate on MET, CVs of 0.551 mM MET solution in 0.1 *M* NaOH at potential scan rates between 25–700 mV s^{-1} were recorded (Fig. 1B).

Examining Fig. 1B in detail, as the scan rate increased, the anodic peak potentials shifted slightly to the more negative region. This phenomenon is characteristic for an irreversible or semi-reversible electrochemical reaction[36]. When the potential scan rate results obtained on the PG electrode are evaluated, the relation between E_p and log ν is as follows; E_p (V) = 0.0511 log ν (mV s^{-1}) + 1.1201 (r = 0.998). For an irreversible electrode process, the relationship E*p*/ν is defined as [$E_p = E^0 + (2.303\,RT/\alpha nF)\log(RTk^0/\alpha nF) + (2.303\,RT/\alpha nF)\log \nu$][37].

In the equation, α is the charge transfer coefficient and n is the number of electrons transferred in the redox reaction. R (8.314 J K^{-1} mol^{-1}), T (298 K) and F (96480 C mol^{-1}) are known constants. The slope value in the E_p–log ν relationship is 0.0511. Using the equation above, the value of αn is calculated as 1.16. In the case of the fully-irreversible electrode, it can be accepted as α = 0.5 for most systems. Thus, a value of n = 2.32 (≈2) is obtained. Based on the data obtained, it is seen that the electrochemical pathway of MET is as in Fig. 2 and compatible with the mechanisms suggested in the literature[21–28].

3.2. pH effect:

The electrochemical behavior of MET has been investigated in different supporting electrolytes and pH's [BR (pH 2–12), PBS (pH 2.0, 3.0, 7.4, 9.0), ABS (pH 4.8), 0.1 *M* H_2SO_4 and 0.1 *M* NaOH]. From the electrochemical results obtained, it was seen that MET was not electroactive on the PG electrode surface, except for BR (pH 11–12) and 0.1 *M* NaOH mediums. According to the literature information and as can be seen from the results summarized in Table 1, it is seen that the electrodes are coated with a modified agent in order to be active on the electrode surface in electrochemical studies related to MET. In addition, as can be seen in these studies, it is observed that the working medium is mostly basic. In our study, it is observed that MET is electroactive on the PG electrode surface in BR (pH 11–12) and 0.1 *M* NaOH mediums (Fig. 3). As can be seen from Fig. 3, it is fixated that the anodic peak signal intensity obtained in 0.1 *M* NaOH medium is quite high. It was decided to use 0.1 *M* NaOH in the next steps of the study.

As can be seen from Fig. 3, as the pH value increases, the peak potential shifts to more negative values. When the relationship of E_p/pH [E_p (mV) = –0.0685 pH + 1.9733 (r = 0.983)] on the electrode surface during the electrochemical process is examined; the slope value (–68.5 mV–pH) of MET in the working pH range was obtained. According to these results, it can be said that the proton contribution in the oxidation process is equal to the number of electrons.

3.3. Optimization of SW parameters:

In order to set down the optimum device variables to obtain the most sensitive and symmetrical voltammograms in

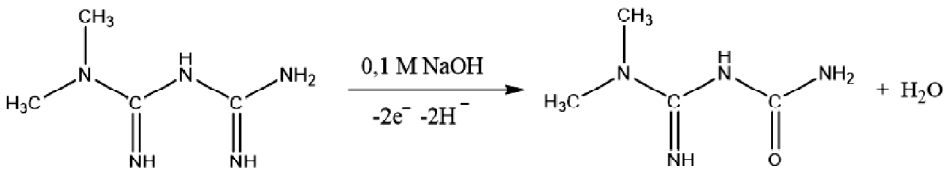

Fig. 2. Possible oxidation mechanism of Metformin.

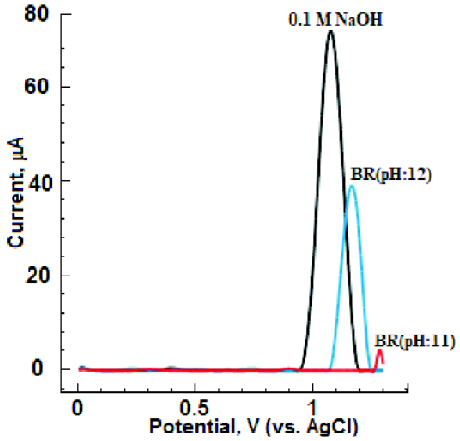

Fig. 3. Square-wave voltammograms for 0.551 mM Metformin in BR (pH 11–12) and 0.1 *M* NaOH supporting electrolytes using PG electrode. SW parameters: frequency, 40 Hz; step potential, 8 mV; amplitude, 50 mV.

electrochemical studies; the effects of square-wave parameters, which is amplitude(ΔE_{sw}), step potential(ΔE_s) and frequency (*f*), on the peak current signal were investigated. Electrochemical measurements were carried out using PG electrode in 0.551 mM MET 0.1 *M* NaOH as supporting electrolyte.

First, the effect of ΔE_{sw} on the peak current signal was investigated in the potential range of 10–90 mV. The peak current signal intensity increased up to 50 mV and then decreased. Later, when the measurements made in the range of 1–9 mV to detect the optimum ΔE_s value by keeping ΔE_{sw} = 50 mV constant, it was observed that the peak signal intensity increased up to 8 mV and then the peak intensity decreased. In order to detect the best frequency value under conditions, which is ΔE_{sw} = 50 mV and ΔE_s = 8 mV, measurements were made in the range of 10–100 Hz. It was observed that the peak current signal intensity increased up to 40 Hz and at higher *f*, a broadening and a distortion in the voltammograms were observed (data not shown). An excellent compromise between voltammetric profile and sensitivity was obtained at the ΔE_{sw} = 50 mV, ΔE_s = 8 mV and *f* = 40 Hz. As an optimum, these values were chosen for use in subsequent experiments.

3.4. Analytical application:

In order to investigate the effect of MET concentration on anodic peak current under optimum operating conditions, voltammograms were recorded with PG electrode in 0.1 *M* NaOH medium in the concentration range of 2.76–24.8 µM. It was observed that the current density linearly increased with the increasing proportionally to the MET concentration [i_p (µA) = 0.1916 C (µM) – 0.2858 (*r* = 0.9988, *n* = 9)] (Fig. 4). From this plot, the limit of detection (LOD) and the limit of quantification (LOQ) values; it was calculated as 9.03 nM and 30.1 nM, respectively.

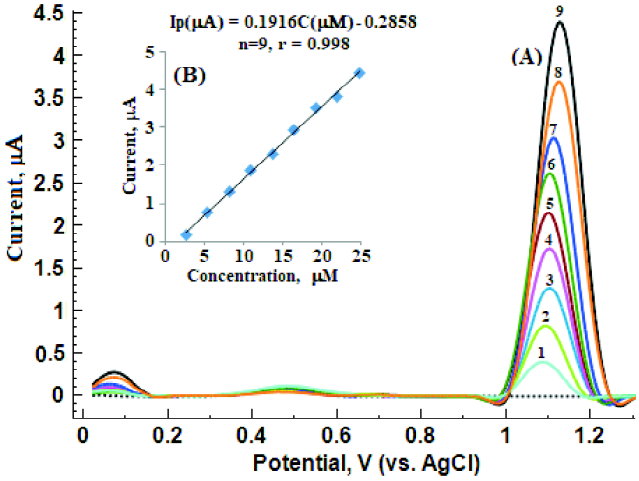

Fig. 4. Square-wave voltammograms for (A) Metformin [(1) 2.755, (2) 5.51, (3) 8.265, (4) 11.02, (5) 13.775, (6) 16.53, (7) 19.285, (8) 22.04, (9) 24.795 µM] in 0.1 *M* NaOH solution using PG electrode. (B) $i_p/C_{Metformin}$ curve. Dashed line, supporting electrolyte. SW parameters as indicated in Fig. 3.

The results obtained for the determination of MET in 0.1 *M* NaOH using the PG electrode were compared with the voltammetric measurement results made before (Table 1). As well as low the LOD values were obtained from the measurements made with electrodes such as CuMW/CNT/PE[23], MWCNT/PE[24], CPE[26] and PYCPE[28]; there is a waste of time in the preparation of modified electrodes, the cost of the method is increasing, and the environment is harmed by the use of toxic chemicals. Low LOD values were obtained in the unmodified electrodes such as CPE[25], GCE[27] and GCE[30]. In addition, the cost of unmodified electrodes and the inconvenience of cleaning the electrodes before each measurement are seen as disadvantages in studies. PG electrode used in the voltammetric method developed for the electrochemical properties evaluation and determination of MET; it has extremely important features such as environmentally

Table 1. Comparison of dates obtained from voltammetric methods applied to determination of MET with analytical values obtained at PG electrode

Electrode	Technique	Supporting electrolyte	Linear range (μM)	LOD (mM/μM)	Samples	Reference
CuMW/CNT/PE	SWV	BR (pH 7.2)	0.9–50	0.65 μM	Pharmaceutical	21
MWCNT/PE	SWV	NH_3-NH_4Cl (pH 8.9)	0.2–10	67 nM	Pharmaceutical	22
CPE	Amperometric	NaOH (100 mM)	4.0–63	0.45 μM	Urine, blood serum and breast milk	23
CPE	DPV	PBS (pH 12.0)	50–60 nM	9 nM	Pharmaceutical and human urine	24
Cu-BTC/CNT	CV	KOH (0.1 *M*)	0.5–25	0.12 μM	Pharmaceutical	25
GCE	CV	PBS (pH 9.0)	15–200	0.076 μM	Rainwater	26
GCE	CV	TBAH (0.1 *M*)				27
PYCPE Pyrogallol (PY)	DPV	BR (pH 2.0)	0.8–6	0.0663 μM	Pharmaceutical and human urine	28
PG	SWV	NaOH (0.1 *M*)	2.76–24.8	9.03 nM	Pharmaceutical and human urine	This work

friendly, cheap, disposable and very good analytical performance.

In order to determine the repeatability level of PG electrode with the developed voltammetric method, 13.77 μM MET in 0.1 *M* NaOH medium was recorded 9 times SW voltammograms on the same day. Anodic peak current and potentials values were read on these voltammograms, and these values were evaluated as intra-day precision. The relative standard deviations (RSD) values for anodic peak current and potential were determined as 1.20% and 0.78%, respectively. These results demonstrate that the measurement of the current density and peak potential, recommended voltammetric method using PG electrode, show excellent reproducibility, repeatability and sensitivity for MET determination.

3.5. Analysis of real samples:

To test the analytic performance of the developed method in real samples, its applicability to commercial drug forms has been studied. Recovery experiments were carried out to check the accuracy and precision of the method developed. For this purpose, successive additions were made on the prepared tablet solution, on the condition of not exceeding the linearity limits from the standard MET solution, and voltammograms were recorded again after each addition. Measurement of the anodic peak currents was registered both from the original tablet solution and after successive additions. Then, how much of the pure substance added to the tablet solution sample could be determined was calculated. The results obtained are given in Table 2. The results demonstrate that the accuracy of the voltammetric method developed on the PG electrode with the recovery ranged from 94.16 to 108.19% is scientifically valid.

Table 2. Voltammetric method analysis results in tablets containing Metformin

Sample	Found (mg)[a,b]	Recovery[b](%)±%RSD
1	1081.9	108.19±3.46
2	1066.9	106.69±3.91
3	941.6	94.16±4.69
4	987.9	98.790±3.97
5	968.70	96.87±2.79

[a]Each tablet contains 1000 mg of Metformin.

[b]Results are the average of three analyzes.

Due to the high sensitivity and reproducibility of the voltammetric method developed on a single-use PG electrode in 0.1 *M* NaOH medium for MET determination, the conditions of its use in complex matrix media such as urine sample have been investigated.

Voltammograms of urine samples without added MET were recorded according to the sample preparation protocol described in Section 2.4. No anodic signals were observed for biomolecules (uric acid, ascorbic acid, dopamine) likely to be present in the urine, in where the potential range in the

anodic peak current signal of the MET was observed. As can be seen in Fig. 5, it was decided that it belongs to the uric acid, anodic signal observed around +0.78 V. It was observed that this anodic peak take place in urine samples did not interfere for determination of MET.

As seen clearly in Fig. 5, the anodic peak observed at around +1.14 V steadily increased with the addition of standard MET solution. The analytical curve (inset Fig. 5) shows a linear response in the range of 2.755 to 19.285 μM.

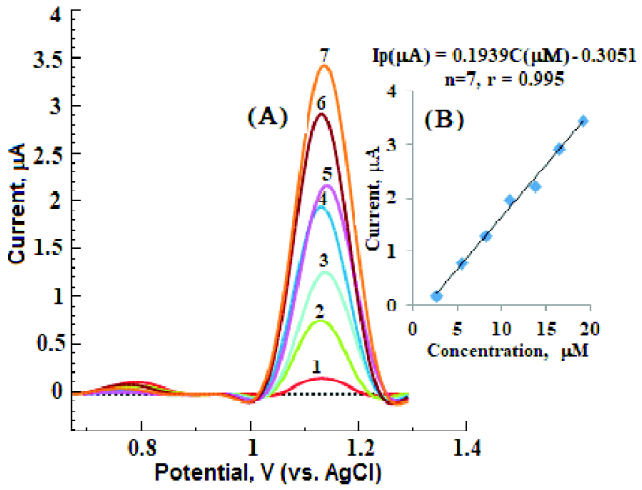

Fig. 5. Square-wave voltammograms for urine sample: (A) Metformin not added (dashed line), (1) 2.755 μM, (2) 5.51 μM, (3) 8.265 μM, (4) 11.02 μM, (5) 13.775 μM, (6) 16.53 μM, (7) 19.285 μM. (B) The inset depicts the corresponding analytical curve. SW parameters as indicated in Fig. 3.

As shown in Table 3, the correspondence between the found value and the MET concentration added to the urine (with sufficient recovery value) showed that the proposed method can also be correctly determined from urine samples of the MET.

Table 3. Voltammetric analysis findings of Metformin-added urine sample

Added (μM)[a]	Found (μM)[a]	Recovery[b](%)±%RSD
2.755	2.711	98.403±2.92
5.510	5.652	102.577±4.13
8.265	8.152	98.633±3.70
11.020	11.506	104.410±3.57
13.775	13.231	96.051±3.96
16.530	16.473	99.655±3.76
19.285	18.889	97.946±3.32

3.6. Interference study:

Since the sensitivity, accuracy and repeatability results of the developed voltammetric method were quite good, a selectivity study was also conducted. The selectivity study was carried out on compounds likely to be in biological fluids. By keeping 0.551 mM MET constant, interfering species (Na^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, uric acid, dopamine, epinefrin, norepinefrin) with a concentration of 10 times were added and voltammograms were recorded under optimum operating conditions. As can be seen from in Fig. 6, it has been shown that the voltammetric method developed in 0.1 *M* NaOH medium in biological fluids except Co^{2+}, Cu^{2+} and Ni^{2+} can be determined selectively on the PG electrode.

Results demonstrated that the proposed voltammetric method can be successfully applied in control processes and MET determinations in urine samples.

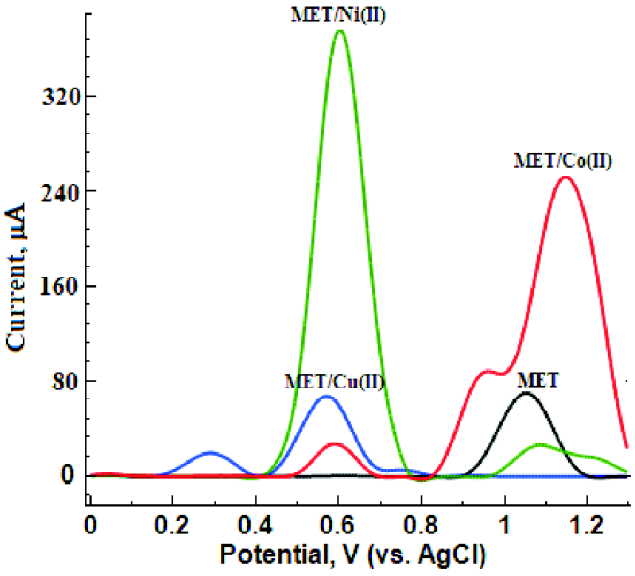

Fig. 6. Square-wave voltammograms for 0.551 mM Metformin mixed with Cu(II), Ni(II) and Co(II) in 0.1 *M* NaOH using PG electrode.

4. Conclusion

In this study, electrochemical properties of MET were examined using PG electrode and an economical, simple, fast, sensitive and selective voltammetric method was developed for MET determination. The electrochemical behavior of MET was found to be the most suitable 0.1 *M* NaOH solution among different supporting electrolyte. Under optimized conditions of the developed method, a good linearity

and LOD and LOQ values were found to be 9.03 nM and 30.1 nM, respectively, in the range of 2.76–24.8 μM using PG electrode in NaOH medium. The applicability of the developed voltammetric method was evidenced in the pharmaceutical dosage and urine samples for MET determination, and the accuracy, precision, selectivity, sensitivity and intra-day repeatability of the method were clearly demonstrated. Proposed electrochemical method, it has the advantages of being much less time consuming and much cheaper than other analytical techniques. In addition, the analytical performance of the PG electrode used in the voltammetric method has been found to be more advantageous in many respects than the studies summarized in Table 1.

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