*Anal. Bioanal. Electrochem., Vol. 12, No. 1, 2020, 93-106*

*Analytical &*
*Bioanalytical*
*Electrochemistry*

2020 by CEE
www.abechem.com

*Full Paper*

# Simultaneous Electrochemical Determination of Paracetamol and Caffeine using Activated Glassy Carbon Electrode

**Tilahun Yai Feyisa,[1,*] Shimeles Addisu Kitte,[1,*] Dereje Yenealem[2]**
**and Gebru Gebretsadik[1]**

[1]*Department of Chemistry, College of Natural science, Jimma University, P.O. Box 378, Jimma, Ethiopia*

[2]*Department of Chemistry, College of Natural and Computational Science, University of Gondar, P.O. Box: 196, Gondar, Ethiopia*

*Corresponding Author, Tel.: +251-47 1121252; Fax: +251-47 1121252

E-Mail: tilahunyai@gmail.com; shimeles.addisu1@gmail.com, shimeles.addisu@ju.edu.et

*Received: 4 October 2019 / Received in revised form: 21 December 2019 /*
*Accepted: 25 December 2019 / Published online: 31 January 2020*

---

**Abstract-** Herein, we report simultaneous electrochemical determination of Paracetamol (PAR) and Caffeine (CAF) at activated glassy carbon electrode (aGCE) using cyclic voltammetry (CV) and square wave voltammetry (SWV). Comparison was made for cyclic voltammetric response of PAR and CAF at bare glassy carbon electrode (bGCE) and aGCE in 0.1 M phosphate buffer solution (PBS) of pH 7.0. The experimental result showed that the redox process of PAR was both diffusion and adsorption controlled, whereas the oxidation reaction of CAF is diffusion controlled at aGCE. The aGCE showed a linear response to PAR in the concentration range of 10-180 µM when the concentration of CAF was kept constant (25 µM). Similarly, the linear range for CAF was from 10 -95 µM at a constant concentration of 10 µM PAR. The detection limit (LOD) of PAR and CAF was found to be 2.55 µM, 2.36 µM (3σ/m), respectively. The validity of the demonstrated method was checked by using commercial tablet which contain different amount of PA and CAF and satisfactory percent recoveries were obtained.

**Keywords-** Paracetamol, Caffeine, Activated Glassy Carbon Electrode, Electrochemical determination, Square wave voltammetry, Cyclic voltammetry

---

## 1. INTRODUCTION

Paracetamol (PAR), also called acetaminophen, $C_8H_9NO_2$, which is N-acetyl-*p*-aminophenol, an acylated aromatic amide discovered in 1877 [1] and it was used as a medicine by Von Mering in 1893 for the first time as a painkiller [2]. PAR is the most commonly used oral painkiller for the relief of postoperative pain, fever, headache, arthritis and so on [3, 4]. PAR is well-known to have outstanding safety profile at recommended healing doses, but consumption above the limit or misused is also known to show some side effects such as mortal hepatotoxicity, alcohol use may enhance toxicity [5,6].

Whereas, Caffeine (CAF), $C_8H_{10}N_4O_2$, which is 1,3,7-trimethylxanthine, alkaloid of nitrogen containing organic metabolite produced by plants [7]. It is world's most widely used psychotropic drug and a stimulant to the central nervous system [8-10]. CAF is present naturally in different plants like coffee, tea and cocoa beans and synthetically prepared for the use of foods, beverages, dietary supplements, and drugs [11,12]. Excessive consumption of CAF causes a variety of physiological effects such as cardiovascular problem, kidney diseases and hyperactivity [13-15]. The mean consumption of CAF suggested is about 165 mg/day [16]. Its excessive intake leads to death [15,17]. As a result of the aforementioned facts determination of PAR and CAF is important for food and clinical significance.

Various methods have been reported for the determination of PAR and CAF separately or together. Most commonly used methods were spectroscopic [18,19] and different chromatographic methods [20,21]. Because of expensive apparatus and time consuming procedures are needed in the above techniques, a method which inexpensive, simple, sensitive and reliable is of substantial importance [22-25]. Considerable experimental findings were reported for the simultaneous electrochemical determination of PAR and CAF by help of various modified electrodes [25-31].

Glassy carbon electrode (GCE) is commonly used carbon based electrode for electrochemical studies of oxidizable compounds. It exhibits good electrochemical stability, high chemical inertness, very low permeability of gas, good biocompatibility and extremely low thermal expansion coefficient [32-34]. Surface treatment is the commonly used method to improve the surface electrochemical behavior of GCE. Activation of GCE takes place by electrochemical pretreatment, such as cleaning and activating the electrode surface by galvanostatic oxidation, application of a fixed anodic potential or by repeated scanning potential in a wide range [35-37]. During surface activation of GCE, the electrode surface can be oxidized, thus, more functional groups can be introduced at the surface of electrode that facilitate the redox reaction. So electrochemically activated GCEs are demonstrating fast electron transfer rate and low background current, better sensitivity, reversibility, reproducibility, stability and reduced overpotential compared with their precursors [38-42]. Therefore, in this study the aGCE was used for simultaneous electrochemical determination of PAR and CAF. The cyclic voltammetric response of the PAR and CAF was studied before and after the activation of GCE. The aGCE exhibits better electrochemical performance than the traditional electrodes. Therefore, the aGCE has been used for the electrochemical investigations of PAR and CAF.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals and Reagents

CAF (Godrej industries, India), PAR (APF, Ethiopia), anhydrous di-potassium hydrogen orthophosphate (BDH, England), potassium dihydrogen phosphate (Sigma-Aldrich Switzerland), hydrochloric acid (Riedel-deHaen, Germany), sodium hydroxide (BDH, England), and uric acid (Godrej industries, India) were used as received. The stock solution of PAR and CAF was prepared and kept in a refrigerator until used. 0.1 M phosphate buffer solutions (PBS) (pH 7.0) were prepared by mixing appropriate amount of 0.2 M $KH_2PO_4$ and $K_2HPO_4$ each and were used as supporting electrolyte throughout the experiments.

### 2.2. Instrumentation

CV-CHI760E electrochemical workstation [Bioanalytical Systems (BAS), USA] connected to a desktop computer was used for the CV and SWV experiments with three-electrode configuration. Besides using aGCE (3.0 mm in diameter) as the working electrode and Ag/AgCl (KCl (sat.)) electrode and platinum wire were used as reference and auxiliary electrode, respectively.

### 2.3. Preparation of the aGCE

Before activation, 3 mm bGCE was polished with 0.5 μm alumina slurry on polishing pad and carefully washed and sonicated in distilled water to remove remaining impurities. The GCE was activated by applying a potential of 1750 mV for 200 s (optimum condition for electrochemical anodization) in time-based technique in PBS [43-45]. CV of the activated electrode was run between 0 to 700 mV until a stable voltammogram attained.

### 2.4. Preparation of Stock and Standard Solutions

A stock solution of PAR and CAF was prepared by dissolving 0.0750 g PAR and 0.0971 g CAF in 500 mL of PBS of pH 7.0. A standard solutions with the required concentration were prepared from the stock solution by serial dilution with the 0.1 M PBS of pH 7.0.

### 2.5. Preparation of Calibration Curve

To prepare a calibration curve of PAR and CAF, different concentration of PAR (10 µM-180.0 µM) at 25 µM CAF was prepared in 0.1 M PBS of pH 7.0. In same way different concentration of CAF (10 µM-95 µM) at 10 µM PAR was prepared by 0.1 M PBS of pH 7.0. SWV at pulse wave amplitude 25 mV, Frequency 15 Hz and with potential window -200 to 1600 mV of each prepared solution was measured. Finally, the calibrations curves were drawn.

### 2.6. Sample Preparation from Tablets

Commercially available tablets known as SNIP pain which contains 0.50 mg PAR and 0.065 mg CAF per tablet was purchased from local pharmaceutical drug shop. Five tablet formulations were precisely weighed and crushed in to fine powder using mortar and pestle. This powder was accurately weighed and dissolved into a 500 mL volumetric flask with 0.1 M PBS pH 7.0. Concentration of PAR and CAF in the stock solutions were 1.7 mM and 0.17 mM, respectively. And then working sample solutions were prepared in 0.1 M PBS of pH 7.0.

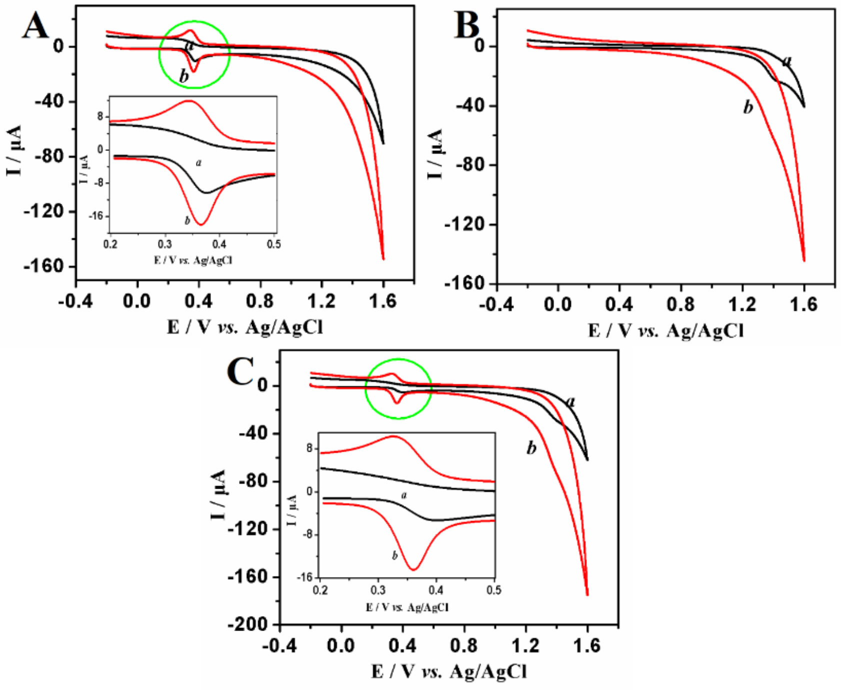

**Fig. 1.** A) CV of 0.3 mM PAR; B) CV of 0.3 mM CAF; C) CV of 0.3 mM mixture of PAR and CAF at a) bGCE and b) aGCE in 0.1 M PBS of pH 7.0 at scan rate of 100 mVs$^{-1}$. (Inset: Enlarged CV for PAR)

## 3. RESULTS AND DISCUSSION

### 3.1. CV of PAR and CAF at bGCE and aGCE

CV of 0.3 mM PAR and CAF was studied at bGCE and aGCE in 0.1 M PBS, pH 7.0 at a scan rate of 100 $mVs^{-1}$ and the result was shown in Figure 1A. PAR exhibits an irreversible behavior at bGCE with oxidation peak potential at 0.37 mV. Whereas at aGCE, the well resolved reversible oxidation and reduction peaks were appeared at 0.365 mV and 0.345 mV, respectively with $\Delta E_p$ of 0.02 mV. Moreover, enhanced peak current was observed at aGCE which can be a clear indication of the electrocatalytic phenomenon of the aGCE for the oxidation of PAR as a result of fast rate of electron transfer at aGCE.

Activation of an electrode can be shown a good electrocatalytic effect on the oxidation of PAR in which oxidation potential was moved to negative value and the magnitude of oxidation current was increased. As shown in Figure 1B weak anodic peak current of CAF was observed at aGCE, indicating that the weak interaction between CAF and surface of aGCE, this might be because the surface of the GCE is blocked by the oxidation product [46]. Moreover, the anodic potential of CAF was moved to negative value.

The mixture of PAR and CAF were also studied at both bGCE and aGCE. As shown in Figure 1C the definite reversible redox peak current was observed at aGCE for PAR, with slight shift of oxidation peak potential toward negative value. Similarly, the oxidation peak potential of CAF was shift to negative value which shows the good electrocatalytic effect of aGCE. Therefore, aGCE was used for simultaneous electrochemical determination of both PAR and CAF in a mixture.

#### *3.1.1. Effect of pH on Electrochemical Behavior of PAR and CAF*

PH of the supporting electrolyte is one of the parameters that can highly influence the response of the electrode in electroanalysis. The pH range was studied from 4 to 10 in PBS for the simultaneous voltammetric determination of PAR and CAF by CV. As seen in Figure 2A both the redox peak current and peak potential varied with pH of the solution.

As depicted in Figure 2B, the anodic peak current of PAR increases as the pH increase from 4.0 to 7.0 and then decrease up to pH 10.0. Therefore, pH 7.0 was chosen as the optimum pH for PAR oxidation. On the contrary, the oxidation peak current of CAF decreases up on increasing the pH from 4.0 to 7.0 then slowly increases when increasing the pH from 7.0 to 10.0 (Figure 2C). Therefore, it is impossible to use the oxidation peak current as evidence to judge the optimum pH. Compared to other pH value, CAF has well defined oxidation peak and in good separation with PAR at pH 7.0. Therefore, pH 7.0 was selected as optimum pH for simultaneous determination of CAF and PAR for subsequent work.

The oxidation peak potentials ($E_{pa}$) of PAR was moved to negative value with increasing the pH of the solution at aGCE from 4.0 to 8.0 (Figure 2D), which indicates that the oxidation at the aGCE is a pH dependent reaction and that protons have involved in their electrochemical processes [37].

Similarly, the peak potential of CAF shift to negative value as the pH varies from 4.0 to 7.0 as shown in Figure 2E. This indicates good electrocatalytic effect of aGCE toward CAF with involvement of proton. The gradual raise of oxidation current of CAF from pH 7.0 to 10.0 indicates the absence of proton in their electrode reaction as PBS was in more basic condition [47].

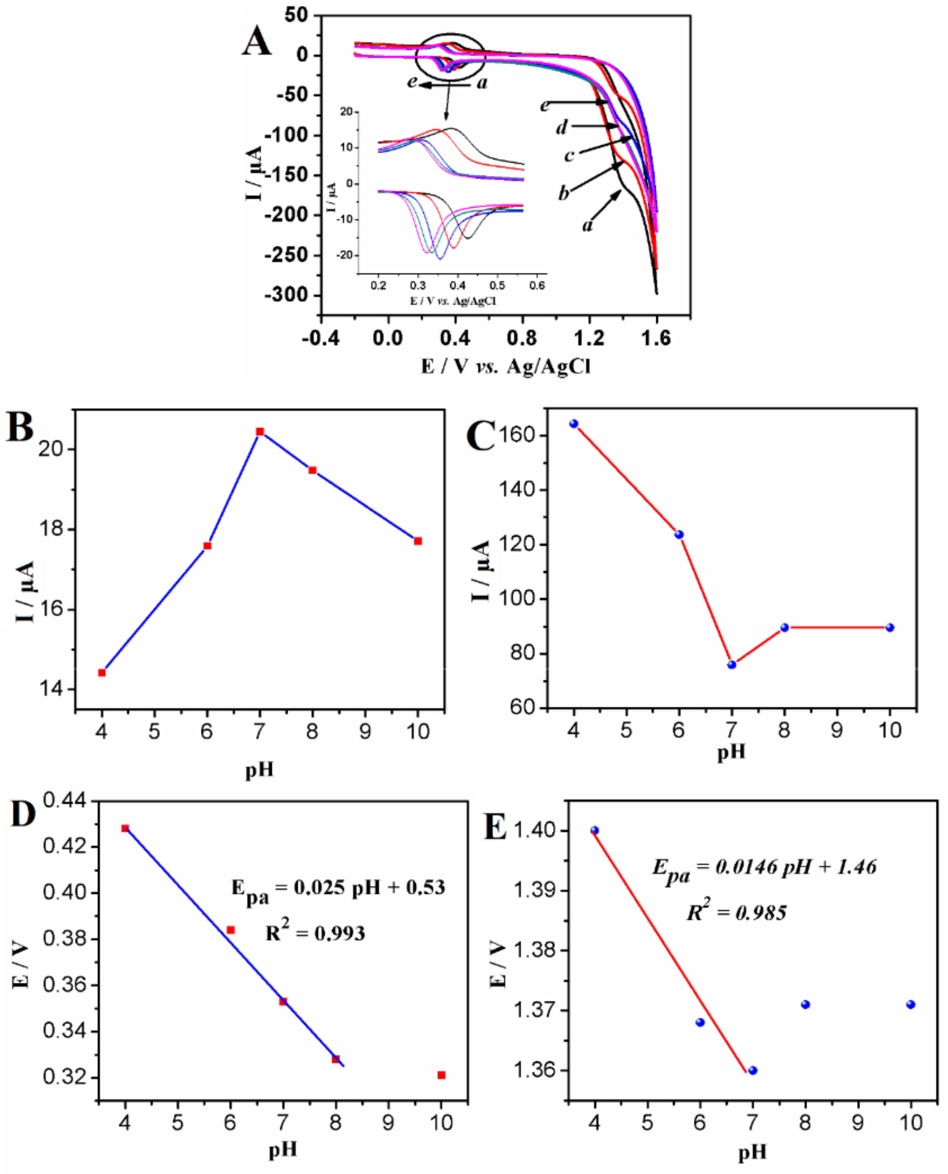

**Fig. 2.** A) CV of 0.3 mM PAR and CAF at aGCE in 0.1 M PBS of different pH (a) 4, (b) 6, (c) 7, (d) 8, and (e) 10 at 100 $mVs^{-1}$; Effect of pH on oxidation currents of B) PAR and C) CAF at aGCE in 0.1 M PBS, from a pH of 4.0 to 10.0 at a scan rate of 100 $mVs^{-1}$; Linear variation range of oxidation peak potential with pH of 0.1 M PBS; D) PAR and E) CAF

The plot of $E_{pa}$ *vs.* pH gave straight line with slopes of 0.025 V/pH and 0.0146 V/pH for PAR and CAF, respectively shown in Figure 2D and E. It is known that two protons and two electrons are involved for the oxidation of PAR, so the slope would likely be 0.059 V/pH.

But the slope obtained in this study was 0.025 V/pH, which indicates more complex redox process takes place at the surface of the electrode resulting small amount of PAR is oxidized. Therefore, this study was shown that electrode reaction process was close to one proton and two electron process [48].

For CAF the slope obtained was 0.0146 V/pH which indicates that more complicated redox process is taking place at the surface of the electrode in the studied pH range.

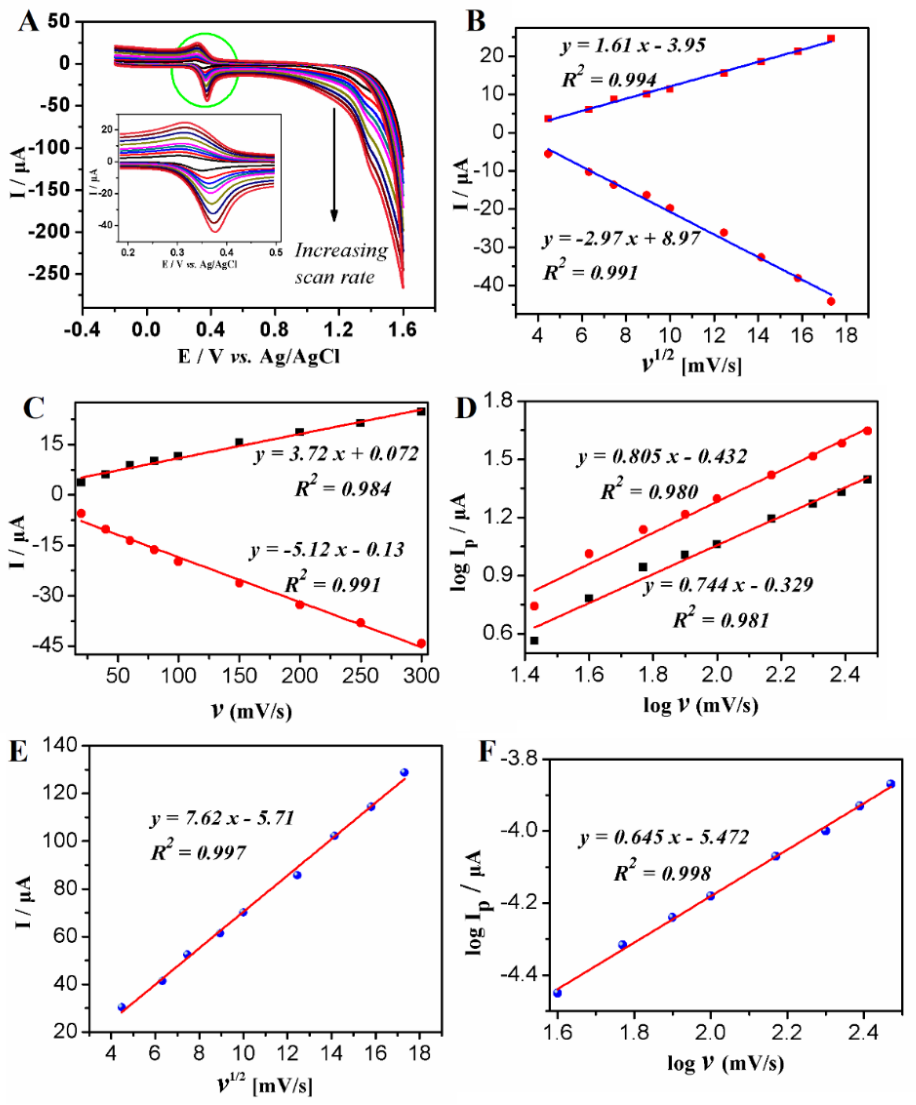

**Fig. 3.** A) CVs of aGCE at scan rates of 20, 40, 60, 80, 100, 150, 200, 250, 300 $mVs^{-1}$ on redox current of 0.3 mM PAR and CAF 0.1 M PBS of pH 7.0 (Inset: the enlarged CVs for PAR); Plot of B) oxidation and reduction currents *vs.* square root of scan rate of PAR; C) oxidation and reduction currents *vs.* scan rate of PAR; D) log $I_p$ vs. log υ of PAR; E) oxidation current *vs.* square root of scan rate of CAF F) log $I_p$ *vs.* log υ of CAF

Moreover, the ratio of number of protons and electrons involved in this electrode process is not equal to 1, a greater number of electrons involve than protons. In the oxidation process of CAF, unequal number of protons and electrons are involved. Though the explanations for this behavior is uncertain, this is probably because of oxygen evolution or the deprotonation of oxidation product [46,48,49].

### *3.1.2. Effect of Scan Rate on Electrochemical Behavior of PAR and CAF*

The effect of scan rate on the peak current at aGCE was carried out for PAR and CAF recorded at different scan rates within the range of 2 mVs$^{-1}$ to 300 mVs$^{-1}$. Figure 3A shows the CVs in the presence of 0.3 mM PAR and CAF in 0.1 M PBS pH 7.0. The relationships of the oxidation and reduction currents with the scan rate and square root of scan rate for PAR were constructed and the results are shown in Figure 3B and C. The oxidation and reduction currents have linear relationship to scan rates (υ) as well as their square root (υ$^{1/2}$) in the above scan rate ranges, meaning that the redox process is controlled by both diffusion and adsorption. Additionally, Figure 3D demonstrates the plot of the logarithm of redox peak currents (log $I_p$) *vs.* logarithm of scan rate (log υ). It is clearly observed that log $I_p$ is linearly corelated with log υ with a slope values of 0.744 and 0.805 for oxidation and reduction, respectively.

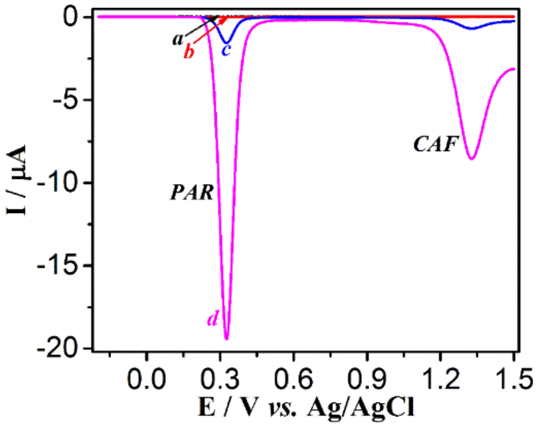

**Fig. 4.** SWV curve of a) bGCE in 0.1 M PBS b) aGCE in 0.1 M PBS at pH 7.0 c) bGCE in 50 μM PAR and 20 μM CAF in 0.1 M PBS at pH 7.0 and d) aGCE in 50 μM PAR and 20 μM CAF in 0.1 M PBS at pH 7.0 (SW amplitude of 25 mV, Frequency 15 Hz, scan increment 4 mV and quiet time 2 s)

Moreover, the experimentally obtained slope is greater than the theoretical value of 0.5 for redox process controlled by diffusion, but less than 1 which is theoretical value for a redox process controlled by adsorption. It indicates that the redox peaks arise not only from PAR species reaching by diffusion but also the adsorbed PAR on the surface of aGCE. On the contrary, the plot of oxidation current of CAF against the square root of scan rate shown in

Figure 3E exhibiting a linear relationship suggests that the oxidation reaction of CAF is controlled by diffusion.

Moreover, the slope of log $I_p$ *vs.* log υ (Figure 3F) is 0.64, which was very close to 0.5 which is the theoretically predicted value for redox process controlled by diffusion. This further confirms the oxidation of CAF at aGCE is controlled by diffusion [50-52].

### 3.2. Simultaneous voltammetric Determination of PAR and CAF by SWV

SWV was used for the simultaneous voltammetric determination of PAR and CAF in 0.1 M PBS of pH 7.0 at aGCE. As shown in the SWV curve in Figure 4 the oxidation peaks were observed at 0.32 V and 1.32 V *vs.* Ag/AgCl for PAR and CAF, respectively. The oxidation peak separation is about 1.0 V which can allow the simultaneous voltammetric determination of PAR and CAF. Moreover, the oxidation peak currents of 50 µM PAR and 20 µM CAF in 0.1 M PBS at pH 7.0 were compared at both bGCE (curve c) and aGCE (curve d). As it is clearly observed aGCE shows higher oxidation peak current than bGCE. Thus, aGCE was used for the simultaneous voltammetric determination of PAR and CAF.

Figure 5A demonstrates the SWV curves for various concentrations of PAR by keeping the concentration of CAF constant (25 µM). The oxidation peak currents of PAR are directly proportional to the concentration of PAR in the range of 10 and 180 µM with a regression equation of: $I_p$ (µA)=0.185$C$ (µM)+1.918, $R^2$=0.991. The limit of detection (LOD) of PAR was 2.55 µM (3$\sigma$/$m$).

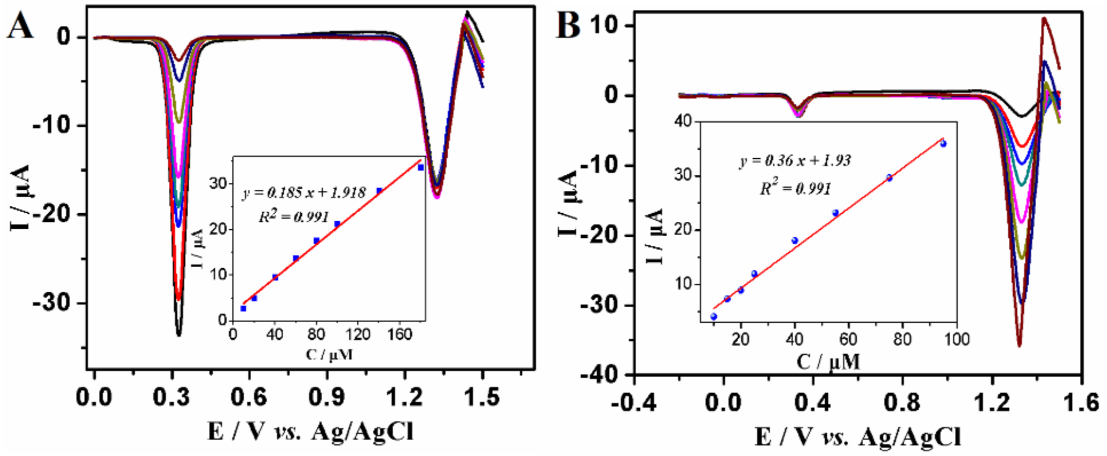

**Fig. 5.** SWV curves of various concentrations of A) PAR at fixed concentration CAF (25 µM) (Inset: calibration curve of PAR); B) CAF at constant concentration of PAR (10 µM) (Inset: calibration curve of CAF), in 0.1 M PBS of pH 7.0 at aGCE (SW amplitude of 25 mV, Frequency 15 Hz, scan increment 4 mV and quiet time 2 s)

Likewise, as revealed in Figure 5B, at constant concentration of PAR which is 10 µM, the oxidation peak current of CAF increases proportionally with concentration in the range of 10 to 95 µM. The regression equation of the calibration curve of CAF was: $I_p$ (µA)= 0.36C (µM)+1.93, $R^2$=0.991 and the LOD is 2.36 µM (3*σ/m*). The calculated limits of quantification (LOQ) were 8.49 µM for PAR and 1.21 µM (10*σ/m*) for CAF. (Where *σ* and *m* are standard deviation of blank and the slope of the curve, respectively).

Evaluation was made between the analytical performance of aGCE and other similar electrochemical sensors reported for the simultaneous voltammetric determination of PAR and CAF and shown in Table 1. The experimental findings suggest that aGCE shows reasonable linear range and acceptable LOD. Compared with the other electrochemical methods, this method has shown comparable analytical performance.

### 3.3. Real Sample Analysis

The demonstrated method was studied for the simultaneous electrochemical determination of both PAR and CAF pharmaceutical tablets (SNIP pain) as described in section 2.6 for the application of real sample analysis. Briefly, five tablet formulations were precisely weighed and crushed using mortar and pestle. 0.172 g of the fine powder of the tablet was weighed and dissolved in 0.1 M PBS into 500 mL flask. Concentration of PAR and CAF present in the solution was 1.7 mM and 0.17 mM, respectively. And then a more diluted sample solution was prepared in PBS pH 7.0 with 51 µM PAR and 790 µM CAF.

**Table 1.** Linear range and LOD for PAR and CAF with other reported electrochemical methods

| **Electrode** | **Method** | **Linear range / µM** | | **LOD / µM** | | **Ref.** |
|---|---|---|---|---|---|---|
| | | **PAR** | **CAF** | **PAR** | **CAF** | |
| Boron doped diamond electrode | DPV | 0.5-83 | 0.5-83 | 0.49 | 0.035 | [27] |
| Carbon films modified multi walled carbon nanotubes electrode | SWV | 0.99-36.7 | 9.98-91.7 | 0.334 | 0.367 | [28] |
| Reduced grapheneoxide-GCE | DPASV | 0.2-4.4 | 0.2-4.4 | 0.24 | 0.26 | [31] |
| Carbon ionic liquid electrode | DPV | 1-200 | - | 0.3 | - | [53] |
| Poly(4-amino-3-hydroxynaphthalene sulfonic acid)-GCE | SWV | 10-125 | 10-125 | 0.45 | 0.79 | [54] |
| Cobalt ferrite-GCE | DPV | 0.2-4.4 | 0.2-4.4 | 0.267 | 0.226 | [55] |
| Copper nanoparticles -carbon black-graphene oxide-poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)-GCE | SWV | 0.9-7 | 11-64 | 0.23 | 3.4 | [56] |
| Poly(taurine)/$TiO_2$-graphene-GCE | DPV | 0.05-100 | 0.05-100 | 0.034 | 0.5 | [57] |
| aGCE | SWV | 10-180 | 10-95 | 2.55 | 2.36 | This work |

**Table 2.** Recovery of PAR and CAF in drug sample

| **Matrix (Tablet)** | **Added (µM)** | | **Found (µM)** | | **Recovery (%)** | |
|---|---|---|---|---|---|---|
| | **CAF** | **PAR** | **CAF** | **PAR** | **CAF** | **PAR** |
| SNIP pain | - | - | 788 | 50 | - | - |
| | 55 | 30 | 840 | 79 | 94.54 | 96.66 |

DPV-Differential Pulse Voltammetry, SWV-Square Wave Voltammetry, DPASV-Differential Anodic Stripping Voltammetry

The SWV response for tablet sample solution containing 790 µM CAF and 51 µM PAR was spiked with 50 µM CAF and 30 µM PAR were recorded. As indicated in Table 2, the recovery results for PAR and CAF were 96.66% and 94.54%, respectively confirmed that the proposed method can be applied for the analysis of PAR and CAF in real samples.

### 3.4. Interference Study

There are various possible interferents which inhibit the selectivity of aGCE for the simultaneous voltammetric determination of PAR and CAF. Different interfering substances were added as an interferent into a solution containing PAR and CAF. Equimolar amounts of ascorbic acid (AA), glucose (GL), $K^+$, $Na^+$, $Cl^-$, and $NO_3^-$ have no interfering effect with the detection of PAR and CAF. But equimolar uric acid (UA) was moderately affect the oxidation peak current of both PAR and CAF, and with slight shift of peak potential of CAF toward negative side. The signal change caused by addition of UA was greater than 5% which indicate the positive interference effect.

## 4. CONCLUSION

We have reported the results from using aGCE as an electrode material for simultaneous voltammetric sensor for PAR and CAF. The electrochemical behavior of the studied analyte was improved at aGCE as compared to bGCE. Moreover, the redox behavior of the PAR and CAF were studied in variable pH and scan rates. The information about the electrode processes were comprehended from these behaviors. The experimental result revealed that the oxidation and reduction process for PAR was controlled by both diffusion and adsorption but the oxidation reaction of CAF is controlled by diffusion at aGCE. The simultaneous electrochemical detection of PAR and CAF was studied by using SWV at aGCE. The calibration curves obtained for PAR and CAF were linear from 10 to 180 µM and from 10 to 95 µM, respectively. The LODs of PAR and CAF were found to be 2.55 µM and 2.36 µM. The method shows comparable analytical performance with similar works reported before. Finally, this method was used successfully to the simultaneous voltammetric detection of PAR and CAF in pharmaceutical tablets. The recovery obtained were 96.66% for PAR and 94.54% for

CAF. From the studied interferences UA has moderate interfering effect on determination of PAR and CAF.

## REFERENCES

[1] B. C. Mangus, and M. G. Miller, Pharmacology application in athletic training, F. A. Davis, Philadelphia, Pennsylvania (2005).

[2] A. Bertolini, A. Ferrari, A. Ottani, S. Guerzoni, R. Tacchi, and S. Leone, CNS Drug Rev. 12 (2006) 250.

[3] M. de Martino, and A. Chiarugi, Pain Ther. 4 (2015) 149.

[4] M. Amare, Heliyon 5 (2019) e01663.

[5] A. M. Larson, J. Polson, R. J. Fontana, T. J. Davern, E. Lalani, L. S. Hynan, J. S. Reisch, F. V. Schiødt, G. Ostapowicz, A. O. Shakil, W. M. Lee, and T. A. L. F. S. Group, Hepatology 42 (2005) 1364.

[6] M. Boopathi, M. Won, and Y. Shim, Anal. Chim. Acta 512 (2004) 191.

[7] C. Benjamin, F. Paul, and T. Fidel, Encyclopedia of Food and Health, Academic Press (2015).

[8] A. Nehlig, J. L. Daval, and G. Debry, Neurosci. Biobehav. Rev. 17 (1992) 139.

[9] T. M. McLellan, J. A. Caldwell, and H. R. Lieberman, Neurosci. Biobehav. Rev. 71 (2016) 294.

[10] D. C. Mitchell, C. A. Knight, J. Hockenberry, R. Teplansky, and T. J. Hartman, Food Chem. Toxicol. 63 (2014) 136.

[11] D. Turnbull, J. V. Rodricks, G. F. Mariano, and F. Chowdhury, Regul. Toxicol. Pharmacol. 89 (2017) 165.

[12] D. Wikoff, B. T. Welsh, R. Henderson, G. P. Brorby, J. Britt, E. Myers, J. Goldberger, H. R. Lieberman, C. O'Brien, J. Peck, M. Tenenbein, C. Weaver, S. Harvey, J. Urban, and C. Doepker, Food Chem. Toxicol. 109 (2017) 585.

[13] K. Tyszczuk-Rotko, and I. Bęczkowska, Food Chem. 172 (2015) 24.

[14] W. D. J. R. Santos, M. Santhiago, I. V. P. Yoshida, and L. T. Kubota, Sens. Actuators B 166-167 (2012) 739.

[15] T. Ören, and Ü. Anık, Measurement 106 (2017) 26.

[16] D. C. Mitchell, J. Hockenberry, R. Teplansky, and T. J. Hartman, Food Chem. Toxicol. 80 (2015) 247.

[17] W. Y. H. Khoo, M. Pumera, and A. Bonanni, Anal. Chim. Acta 804 (2013) 92.

[18] X. Zhang, W. Li, B. Yin, W. Chen, D. P. Kelly, X. Wang, K. Zheng, and Y. Du, Spectrochim. Acta A 114 (2013) 350.

[19] M. Sayed, M. Ismail, S. Khan, and H. M. Khan, Phys. Chem. 17 (2015) 1.

[20] S. S. Narwade, J. Appl. Chem. 7 (2014) 46.

[21] S. S. Verenitch, C. J. Lowe, and A. Mazumder, J. Chromatogr. A 1116 (2006) 193.

[22] L. U. Švorc, P. Tomčík, J. Svítková, M. Rievaj, and D. Bustin, Food Chem. 135 (2012) 1198.

[23] J. Li, J. Liu, G. Tan, J. Jiang, S. Peng, M. Deng, D. Qian, Y. Feng, and Y. Liu, Biosens. Bioelectron. 54 (2014) 468.

[24] Y. Dai, X. Li, X. Lu, and X. Kan, Microchim. Acta 183 (2016) 2771.

[25] Z. M. Khoshhesab, RSC Advances 115 (2015) 95140.

[26] A. J. Jeevagan, and S. A. John, Electrochim. Acta 77 (2012) 137.

[27] B. C. Lourenção, R. A. Medeiros, R. C. Rocha-Filho, L. H. Mazo, and O. Fatibello-Filho, Talanta 78 (2009) 748.

[28] T. A. Silva, H. Zanin, E. J. Corat, and O. Fatibello-Filho, Electroanalysis 29 (2017) 907.

[29] T. T. Minh, N. H. Phong, H. Van Duc, and D. Q. Khieu, J. Mat. Sci. 53 (2018) 2453.

[30] T. R. Saciloto, P. Cervini, and É. T. G. Cavalheiro, J. Braz. Chem. Soc. 24 (2013) 1461.

[31] N. H. Phong, T. T. T. Toan, M. X. Tinh, T. N. Tuyen, T. X. Mau, and D. Q. Khieu, J. Nanomater. 2018 (2018) 15.

[32] A. Dekanski, J. Stevanović, R. Stevanović, B. Ž. Nikolić, and V. M. Jovanović, Carbon 39 (2001) 1195.

[33] W. E. Van der Linden, and J. W. Dieker, Anal. Chim. Acta 119 (1980) 1.

[34] T. Bystron, E. Sramkova, F. Dvorak, and K. Bouzek, Electrochim. Acta 299 (2019) 963.

[35] T. S. Sunil Kumar Naik, and B. E. Kumara Swamy, J. Electroanal. Chem. 826 (2018) 23.

[36] K. R. Mahanthesha, and B. E. Kumara Swamy, J. Electroanal. Chem. 703 (2013) 1.

[37] A. Hailemichael, and H. Lebohang, Bull. Chem. Soc. Ethiop. 21 (2007) 1.

[38] A. Rana, N. Baig, and T. A. Saleh, J. Electroanal. Chem. 833 (2019) 313.

[39] J. X. Qiao, H. Q. Luo, and N. B. Li, Colloids Surf. B 62 (2008) 31.

[40] I. F. Hu, D.H. Karweik, and T. Kuwana, J. Electroanal. Chem. 188 (1985) 59.

[41] M. Hadi, A. Rouhollahi, M. Yousefi, F. Taidy, and R. Malekfar, Electroanalysis 18 (2006) 787.

[42] Y. Li, J. Zhou, J. Song, X. Liang, Z. Zhang, D. Men, D. Wang, and X. Zhang, Biosens. Bioelectron. 144 (2019) 111534.

[43] M. Santhiago, C. M. Maroneze, C. C. C. Silva, M. N. L. Camargo, and L. T. Kubota, ChemElectroChem 2 (2015) 761.

[44] M. Morita, R. Arizono, N. Yoshimoto, and M. Egashira, J. Appl. Electrochem. 44 (2014) 447.

[45] M. Noel, and P. N. Anantharaman, Surf. Coat. Tech. 28 (1986) 161.

[46] S. Chitravathi, and N. Munichandraiah, J. Electroanal. Chem. 764 (2016) 93.

[47] G. Gopu, P. Manisankar, B. Muralidharan, and C. Vedhi, Int. J. Electrochem. 2011 (2011) 11.

[48] A. A. Ensafi, H. Karimi-Maleh, S. Mallakpour, and M. Hatami, Sens. Actuators B 155 (2011) 464.

[49] M. H. Pournaghi-Azar, and A. Saadatirad, Electroanalysis 22 (2010) 1592.

[50] Y. Zhang, L. Wu, W. Lei, X. Xia, M. Xia, and Q. Hao, Electrochim. Acta 146 (2014) 568.

[51] R. Esmaili, and D. Nematollahi, J. Electrochem. Soc. 159 (2012) H792.

[52] W. Lei, W. Si, Q. Hao, Z. Han, Y. Zhang, and M. Xia, Sens. Actuators B 212 (2015) 207.

[53] X. Shang Guan, H. Zhang, and J. Zheng, Anal. Bioanal. Chem. 391 (2008) 1049.

[54] M. Tefera, A. Geto, M. Tessema, and S. Admassie, Food Chem. 210 (2016) 156.

[55] P. T. K. Thu, N. D. Trinh, N. T. V. Hoan, D. X. Du, T. X. Mau, V. H. Trung, N. H. Phong, T. T. T. Toan, and D. Q. Khieu, J. Mater. Sci.: Mater. Electron. 30 (2019) 17245.

[56] A. Wong, A.M. Santos, T.A. Silva, and O. Fatibello-Filho, Talanta 183 (2018) 329.

[57] X. XiaoQin, H. KeJing, X. ChunXuan, J. ChunXue, and Z. QiuGe, Chem. Ind. Chem. Eng. Q 19 (2013) 359.