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An adsorptive stripping voltammetric study based on disposable pencil graphite sensor for the determination of caffeine in local brand ice tea

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Abstract

In this study, voltammetric methods were developed for the quantification of caffeine (CAF) analysis based on a practical, economical, sensitive, and eco-friendly pencil graphite electrode (PGE). Initially, the electrochemical behavior of CAF was investigated by cyclic voltammetry (CV), and the results reveal that CAF has an irreversible oxidation signal. The optimum analytical parameters such as, supporting electrolyte, pH, accumulation potential, and accumulation time for the determination of CAF analysis were investigated to develop differential pulse (AdsDPV) and square wave adsorptive stripping voltammetric (AdsSWV) methods. In order to examine the nature of the buffer, Britton Robinson (BR), phosphate buffer (PBS), and 0.1 M H_2SO_4 solutions were tested in the appropriate pH ranges. The best electrolyte and pH were determined as PBS buffer and pH 1.5. The optimum values for accumulation potentials and times were optimized, and under optimized conditions, the oxidation peak current of CAF was proportional to its concentration. The PGE used exhibited wide linear working range for AdsDPV (2.36-1000 µM) and AdsSWV (3.69-1600 µM) methods with the detection limits of 0.71 µM for AdsDPV and 1.107 µM for AdsSWV. The developed methods were applied to the analysis of CAF in an ice tea beverage sample with acceptable recoveries.

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1. Introduction

Caffeine (CAF), called 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione, also known as mateine or guaranine, is an alkaloid, and it can be found in coffees, teas, guarana, and in cacao [1, 2]. CAF was discovered in 1819 by the German chemist Friedich Ferdinand Runge [3]. It affects the central nervous system and accelerates the messages to and from the brain [4]. CAF has some physiological effects on human metabolisms, such as increasing blood pressure [5], stimulating the respiratory system [6], and being diuretic [7].

CAF is widely used in pharmaceutical preparations promote diuresis and a positive effect on the cardiovascular system [8]. Also, some drug combinations with CAF have existed for the treatment of migraine [9, 10]. As well as drug formulations, CAF can be found in some commercially available soft drinks such as energy drinks, ice tea, and some kind of cokes. The U.S. Food and Drugs Administration determined the maximal amount of CAF in soft drinks was approximately lower than 200 mg/L and specified the lethal dose only 10 g of CAF (about 170 mg/kg body weight) per people [11]. Since high concentration levels of CAF are toxic for human beings, it can lead to depression, hyperactivity, nausea and nervousness, heart diseases, kidney failure, asthma, vomiting, trembling, seizures, and DNA modification effects [12-15]. Therefore, developing a fast, sensitive, selective, and reliable method for analyzing CAF is an essential role in human health. Numerous analysis methods have been developed for the analysis of CAF, including spectrophotometry, infrared spectroscopy, chromatography, and voltammetry. These methods, excluding voltammetry, are often time-consuming and require expensive equipment. Also, requiring pretreatment steps, such as extraction and

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*Corresponding author. *Email address: zdurmus@science.ankara.edu.tr* separation steps are needed in an organic environment. Voltammetric methods are based on the redox reaction of organic agents in a wide range of industrials, pharmaceutical, and cosmetic products. Among them, adsorptive stripping voltammetry-based adsorption phenomena can be preferred for the electrochemical detection of some organic compounds in the term of sensitivity, trace level analysis, and simplicity [16, 17].

In voltammetry, many types of carbon-based working electrodes have been used for years [18, 14, 19]. The working electrodes such as carbon paste, boron-doped diamond, glassy carbon, and screen-printed electrodes required complicated surface cleaning processes since the surfaces of these electrodes are deactivated rapidly. As well as having a problematic cleaning process, the renewability of these surfaces is too hard. Pencil lead graphite electrode (PGE) is cheap, disposable, and easy to use [20-23]. Besides, it has excellent electrochemical reactivity, good mechanical rigidity, low technology, and ease of modification [24-26]. Furthermore, it was described that PGEs offer a renewable surface simpler and faster than polishing procedures [26]. Generally, PGEs consist of graphite, clay, and binder. The chemical and structural properties of the pencil graphite leads were explored in detail by Kariuki [27].

The current study is aimed to develop AdsDPV and AdsSWV voltammetric methods for the determination of CAF at disposable PGE surface in an ice tea beverage. The voltammetric methods developed have a wide linear working range and comparatively low detection limits. To demonstrate the applicability of the proposed methods, CAF analysis was carried out using the standard addition method in real-life samples with satisfactory results. To the best of our literature knowledge, this paper is the first time voltammetric study about the CAF analysis in an ice tea sample using the PGE electrode.

2. Materials and Methods

2.1. Reagents and apparatus

The standard caffeine (CAF) powder was purchased from Sigma Aldrich Company, St. Louis, Missouri, ABD. The 0.01 M CAF stock solution was prepared by dissolving an appropriate quantity of standard CAF powder in double-distilled water and stored in the fridge at +4 ºC. 0.2 M phosphate buffer solution (PBS) was used as the supporting electrolyte, and the pH of the solution was adjusted by 5.0 M NaOH solution. Cyclic voltammetry (CV) and AdsSWV and AdsDPV experiments were performed by using CHI 660C (USA, Texas) and C3 cell stand (Bioanalytical Systems, Inc., USA, BASi) with a solid electrode unit. Ag/AgCl (in 3.0 M NaCl, BAS MF-2052) as reference electrode and platinum wire (BASi MW-1032) as auxiliary electrode were used for electrochemical measurements. Faber Castel brand PG electrode of the dimensions 0.7 × 75 mm (diameter × length) and the active surface area 0.393 (±0.032) cm^2 [28] was used as a working electrode and supplied from local stationery in Ankara, Turkey, and used as such without any pretreatment procedure. Double distilled water was supplied from the mpMINIpure water distillation system (MES, Ankara, Turkey). All pH measurements were carried out using HANNA/HI2211 pH/ORPmeter (LABOR, Istanbul, Turkey). All experiments were performed at room temperature.

2.2 Analytical procedure

The stock solution of CAF (1.0×10^{-2} M) was used in all experiments. In all voltammetric methods, PBS buffer and CAF stock solution were added to the electrochemical cell with a total volume of 10.0 mL. The PGE, reference, and counter electrodes were immersed in the cell. After arranging all the electrode connections, the working solutions were purged with nitrogen gas (99.99% purity) to remove the oxygen, and then the voltammograms were recorded in the potential window of 1.0 V – 1.90 V by using CV, AdsDPV and AdsSWV.

2.3 Real sample preparetion

A regional brand of ice tea (Didi) sample content of 80.0 mg/L CAF was regarded to substitute for the stock solution, and in the analytical part of the voltammetric studies, the experiment solution was prepared by mixing the stock solution and the PBS buffer of the desired pH in a 1: 1 ratio and the total volume was completed to 10 mL. Then, the AdsDPV and AdsSWV voltammograms were recorded.

3. Results and Discussion

3.1 Electrochemical behavior of CAF on PGE electrode

The oxidation behaviour of CAF was first studied by CV technique in phosphate buffer pH 1.5 (optimized response) in potential range from 1.0 V to 1.90 V at scan rate 0.1 V/s (Fig. 1). As can be seen, CAF exhibits the oxidation signal at the potential of about 1.5 V. Also, there is no appearance of any reduction peak in the reverse scan, indicating that the electrochemical process is irreversible in nature.

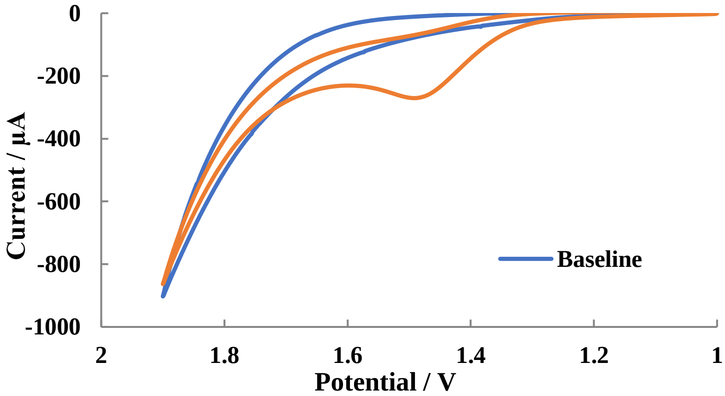

Figure 1. CV voltammograms of baseline (blue line) and 1.0 mM CAF (orange line) in PBS pH 1.5, scan rate: 0.1 Vs^{-1}.

The effect of scan rate on oxidation peak of 1.0 mM CAF on the PGE electrode surface was investigated by CV in phosphate buffer, pH 1.50 at different scan rates within the range 0.1 – 0.6 V/s (Fig. 2). As the scan rate was increased, the oxidation signal of CAF shifted towards more positive potential, confirming the irreversible redox behavior of the electrode reaction of CAF [29]. On the other hand, to monitor the electrochemical process (adsorption or diffusion-controlled) of CAF, logi_p-logυ, and i_p-υ graphs were plotted and given in the inset of Figure 2. The slope value of the logi_p-logυ graph is about 0.60, indicating that the electrode reaction of CAF was both adsorption and diffusion-controlled process [30-32]. Also, the peak current of CAF depicted linear dependence on the scan rates (inset of Fig. 2) and the regression equation was $i_p = 0.0005\upsilon + 0.0001$ ($R^2 = 0.9899$). This result confirms the adsorption-controlled oxidation process of the CAF on the PGE surface [33].

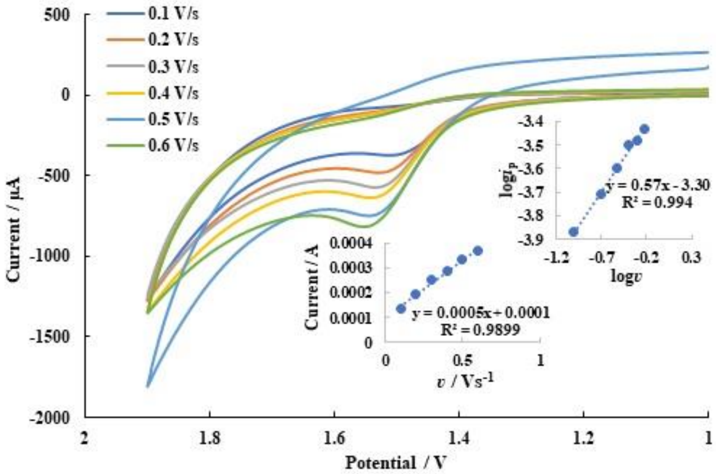

Figure 2. CVs of 1.0 mM CAF with increasing scan rates in PBS buffer solution, pH 1.5. Insets: i_p-υ and logi_p-logυ graphs.

3.2 Effect of supporting electrolyte and pH

The pH value and components of electrolyte solutions are important factors affecting the redox behavior of electroactive species. For this reason, to investigate the effect of supporting electrolyte and pH, PBS (1.5-3.0 with the interval of 0.5), 0.1 M H_2SO_4 (1.0-2.5 with the interval of 0.5) and 0.04 M Britton Robinson (2.0-7.0 with the interval of 1.0) buffer solutions at different pH values for the oxidation of CAF were explored in different pH ranges by using CV technique (Fig. 3). It can be seen that the oxidation peak current of CAF has a maximum value in the PBS buffer solution (pH 1.5) (Fig. 3). This indicated that the best electrolyte for the oxidation of CAF was chosen to be the PBS buffer at the pH of 1.5.

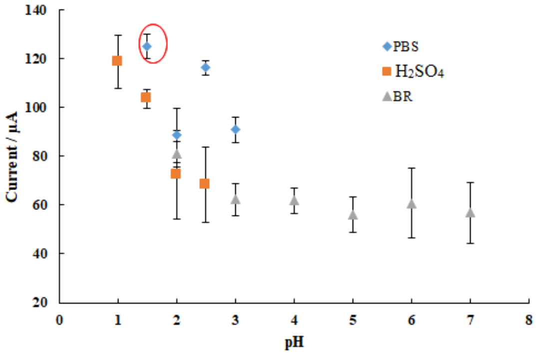

Figure 3. pH-Current results of 1.0 mM CAF obtained by CV in different supporting electrolytes (BR, PBS, and H_2SO_4).

3.3 Optimization of analytical parameters

In adsorptive stripping voltammetric methods, experimental conditions such as accumulation potential and accumulation time are critical parameters that are affected by the electrochemical signal of organic compounds. In this context, to develop AdsDPV and AdsSWV methods for analyzing of CAF, the effect of the accumulation potential and accumulation time on the peak current were investigated for both adsorptive stripping methods. Accumulation potential was changed in the potential ranges, 0.0 - 1.0 V (with 0.1 V increments) (Fig. 4A and 4B). According to Figure 4A, the peak current value of CAF increases in the potential range, 0.0 to 0.2 V, then decreases in the range 0.3 to 1.0 V. Hence, optimum accumulation potential was selected as 0.2 V for the AdsDPV method. Parallel trials for AdsSWV were done, and the accumulation potential was changed in the range of 0.0 to 1.0 V, and the optimum accumulation potential was selected as 0.3 V. To optimize the accumulation times for AdsDPV and AdsSWV, the accumulation times were changed in the range of 0.0-240 s with 30 s increments. According to the AdsDPV results in Figure 4C, the peak current of CAF increases up to 180.0 s and then decreases, so the best accumulation time for the AdsDPV method was chosen as 180.0 s under these conditions. Similar experiments were also carried out for AdsSWV, and the results were represented in Figure 4D. In the Figure, the peak current of CAF increases with increasing accumulation time up to 120.0 s; then, it decreases slightly. Therefore, the best accumulation time for the AdsSWV method was chosen to be 120.0 s.

3.4 The voltammetric determination of CAF

The practicability of the AdsDPV and AdsSWV methods for the quantitative determination of CAF was studied by measuring the anodic currents of CAF as a function of the increasing concentration levels. Under the optimum conditions, CAF concentration was changed in the range of 0.1 - 1000.0 µM and 0.1 - 1600 µM for AdsDPV and AdsSWV, respectively. The voltammograms in increasing concentrations and the peak current versus concentration of CAF calibration graphs were given in Figure 5A(a) and B(b). The linear regression equations for AdsDPV and AdsSWV were found to be as follows:

$i_{p\,(CAF)} = 0.1978C_{CAF} + 1.1545$ ($R^2 = 0.9958$) for AdsDPV;

$i_{p\,(CAF)} = 0.1947C_{CAF} + 5.4664$ ($R^2 = 0.9975$) for AdsSWV.

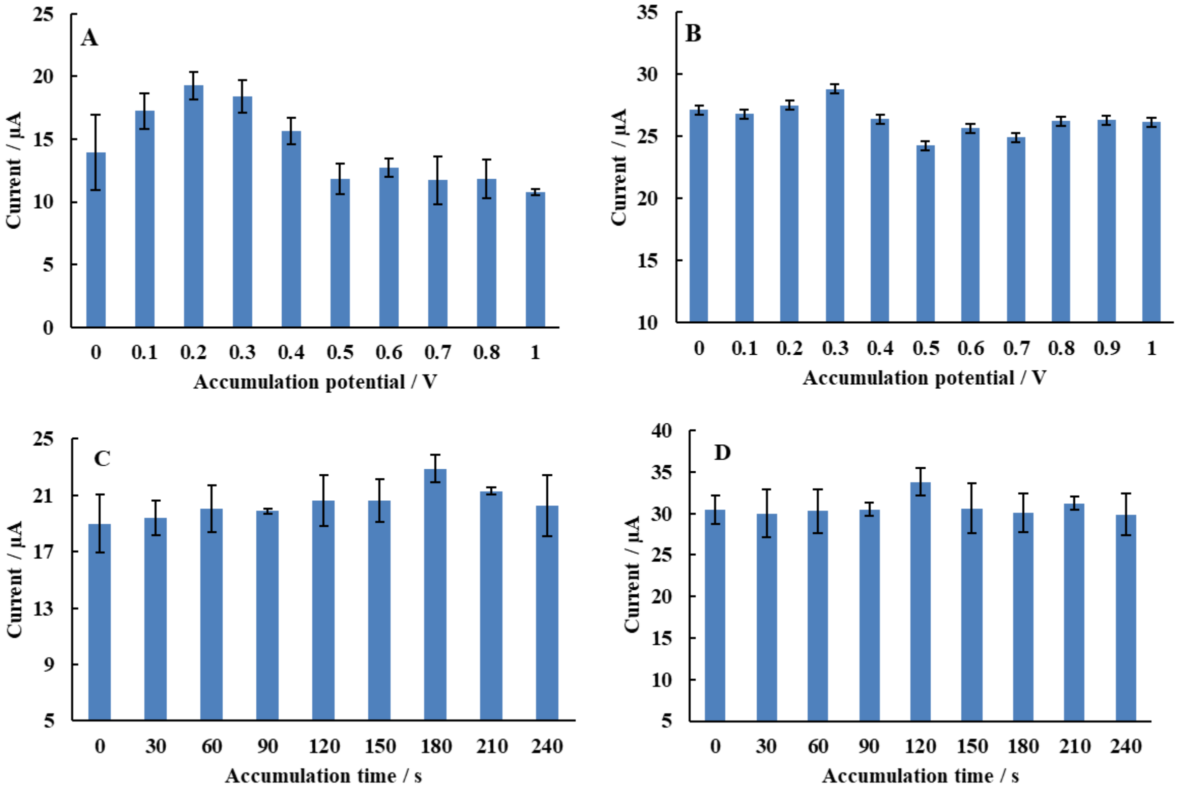

Figure 4. Effect of accumulation potential **(A, B)** and accumulation time **(C, D)** on the peak currents of 0.1 mM CAF using AdsDPV **(A, C)** and AdsSWV **(B, D)** methods in PBS (pH 1.5).

3.5 The voltammetric determination of CAF

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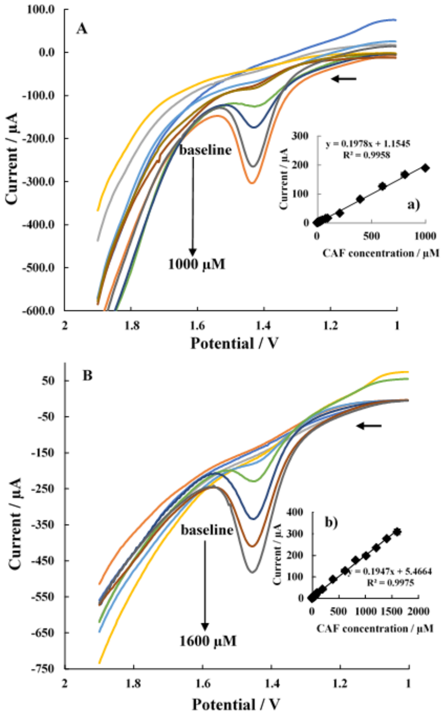

Figure 5. A. AdsDPV and **B.** AdsSWV voltammograms of CAF at the different concentrations on the PGE surface in the PBS (pH 3.0). Insets **a)** and **b)** are the calibration plots for CAF.

The slopes of the calibration curves of CAF obtained by AdsDPV and AdsSWV methods were used to compute the detection (LOD) and the quantification (LOQ) limits with the equations as follows;

$$\mathrm{LOD}=\frac{3s}{m},\ \mathrm{LOQ}=\frac{10s}{m}$$

where s is the standard deviation calculated for the lowest CAF concentration (0.1 μM), and m is the slope of the calibration graphs. The LODs were found to be 0.71 and 1.11 μM for AdsDPV and AdsSWV, respectively; the LOQs were found to be 2.36 and 3.69 μM for AdsDPV and AdsSWV, respectively. Besides, the linear working ranges were found in the range of 2.36 - 1000 μM for AdsDPV and 3.69-1600 μM for AdsSWV.

The comparison of the analytical performances of the other voltammetric methods for the determination of CAF in different samples was presented in Table 1. As seen in the Table, the detection limits for CAF are in the range of 0.01 - 47.3 μM and the LOD value obtained for the AdsDPV method is comparable with the literature reports. Besides, the linear working range of CAF obtained by the AdsSWV method is among the best ones in the literature reports given in Table 1. In addition, the PGE electrode was used directly without any pretreatment and modification processes.

3.6 CAF analysis in commercial ice tea beverage

In order to demonstrate the applicability of the proposed AdsDPV and AdsSWV methods for CAF analysis based on PGE, local commercial ice tea beverage (80 mg/L) was used. The content of CAF in ice tea beverage was determined by the standard addition and recovery tests using proposed methods under optimum experimental conditions. The results obtained are summarized in Table 2, and the recovery values obtained were found in the range from 99.19% to 115.59% with the RSD % of 6.56 for AdsDPV and AdsSWV 97.62% - 103.41% with the RSD% of 2.58. These show the applicability of the method developed in the real sample on the PGE electrode surface without any interference.

3.7 CAF analysis in commercial ice tea beverage

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Table 2. Recovery results for CAF from *Didi* ice tea sample using the standard addition method

Method	Claimed, mg/L CAF	Found*, mg/L CAF	Recovery, %	RSD, %
AdsDPV	80.0	83.30; 92.47; 79.35; 83.38	105.79(± 8.63)	6.56
AdsSWV	80.0	79.37; 82.73; 78.77; 78.10	99.68(± 3.19)	2.58

*each value is the average of five experiments, t=2.78 for 95% confidence level, $ts/\sqrt{N}$

Table 1. The comparison of some voltammetric results for the determination of CAF

Electrode	Analyte	Method	Linear working range, μM	LOD, μM	Application	Literature
PGE	CAF	AdsSWV	0-2574	47.3	Tea samples	[22]
MIP/CP[a]	CAF	DPV	0.06-25	0.015	Cola	[34]
Nafion/MWNTs/GCE[b]	CAF	DPV	0.6-400	0.23	Cola	[35]
MWCNT-Nafion/GCE[c]	CAF	AdsDPV	2.945-377 377-2356	0.513	Drug and Cola	[36]
Nafion–Gr/GCE[d]	CAF	DPV	0.4-40 40-600	0.12	Cola	[37]
Nafion/GO/GCE[e]	CAF	DPV	0.4-80	0.2	Cola, Tea and Energy drink	[38]
SWCNT/CCE[f]	CAF	DPV	0.25-100	0.12	Mineral water	[39]
CF-UME[g]	CAF	FSV*	10-200	3.33	Drug	[40]
BDD[h]	CAF	DPV	0.4-25	0.15	Cola, Tea, Coffee and Energy drink	[41]
CPE[i]	CAF	SWV	2-1000	0.35	Coffee, Tea, Cola and Drug	[42]
SPE/Nafion/Graphene[j]	CAF	AdsDPV	0.10-0.90 1.0-10	0.021	Cola, Ice tea, Coffee and Energy drink	[43]
GORGCP[k]	CAF	DPV	8-800	0.153	Energy drink and Drug	[44]
PCE/CNFs[l]	CAF	AdsDPV	0.2-1.0	0.056	Energy drink and Cola	[45]
NCOMCP[m]	CAF	DPV	5-600	0.016	Energy drink and Drug	[46]
Fullerene/MWCNT/Naf/GCE[n]	CAF	DPV	10-1000	0.072	Drug	[15]
PGE	*CAF*	*AdsDPV* *AdsSWV*	*2.36-1000* *3.69-1600*	*0.71* *1.11*	*Ice tea*	*This work*

[a] MIP/CP: molecularly imprinted polymer modified carbon paste electrode; [b] Nafion/MWNTs/GCE: Nafion/multi-wall carbon nanotubes composite film coated glassy carbon electrode; [c] Multi-Walled Carbon Nanotubes and Nafion modified glassy carbon electrode; [d] Nafion–Gr modified glassy carbon electrode; [e] glassy carbon electrode modified with Nafion and graphene oxide; [f] single-walled carbon nanotubes on carbon-ceramic electrode; [g] carbon fiber ultramicroelectrode; [h] BDD: Boron doped diamond electrode; [i] Carbon paste electrode; [j] Nafion and graphene modified screen printed electrode; [k] graphene oxide-reduced glutathione modified carbon paste; [l] screen-printed carbon electrode; coated with carbon nanofibers; [m] Nano-Cobalt (II, III) oxide modified carbon paste; [n] fullerene/multiwalled carbon nanotube/Nafion modified glassy carbon electrode; * FSV: Fast scan voltammetry.

4. Conclusion

This research paper demonstrates the PGE electrode surface without any surface modification was tried as a sensor for CAF determination in ice tea samples. The sensitive detection of CAF was carried out by using adsorptive anodic stripping methods. The effect of scan rate, supporting electrolyte, pH, accumulation time, and accumulation potential values were investigated for the determination of CAF. The linear working ranges, LOD, and LOQ values obtained by the developed methods were found to be comparable to the methods reported in the literature. The acceptable recovery values for CAF in the *real sample* by using the standard addition method demonstrated that the applicability of the developed methods was satisfactory. The methods proposed may be found as a cheap alternative method for future uses in the beverage industry.

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Conflicts of interest

The authors state that did not have conflict of interests.

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