



Adsorptive stripping voltammetric determination of gallic acid using an electrochemical sensor based on polyepinephrine/glassy carbon electrode and its determination in black tea sample



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ABSTRACT

An efficient adsorptive stripping voltammetric (AdSV) method for determination of gallic acid, GA, was developed by using an electrochemical sensor based on polyepinephrine/glassy carbon electrode, PEP/GCE. Modification of GCE with PEP was done by electropolymerization of epinephrine, EP, in 0.2 M phosphate buffer solution using cyclic voltammetry, cv. A well-defined redox cv wave of epinephrine in potential range of -0.10 to 0.70 V was obtained. It corresponds to oxidation of EP to PEP. The formed PEP was characterized by cv, FE-SEM and in situ UV–vis spectroelectrochemistic spectral methods. Gallic acid at the modified electrode shows an irreversible well-defined adsorption-controlled redox cv wave. At optimal conditions, the anodic square wave, SW, peak current correlates linearly with GA concentration from 1.0 to 20.0 μM with detection limit of 6.63×10^{-7} M. It was found that ascorbic and caffeic acids do not interfere with the voltammetric response of GA. Gallic acid content in black tea sample was successfully determined on applying the prepared sensor.

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1. Introduction

Gallic acid, GA, is one of the main phenolic components found in black tea, grapes, and several other plants [1]. Recently, polyphenols, especially those naturally present in foods, have been a subject of increasing interest due to their biological properties, including anti-inflammatory, antihistaminic, and antitumor activities, scavenging of free radicals, and protecting against cardiovascular diseases [2]. Several methods allow determination not only of GA but also of other polyphenols. Each method has its advantages and disadvantages in analyzing different samples. In most cases, analysis follows sample pretreatment. However, there is still a need for alternative analytical methods for the determination of individual polyphenols, in particular gallic acid. Many electroanalytical methods have been described for direct determination GA at a carbon paste electrode modified with carbon nanotubes [3], at hanging mercury drop electrode [4], with some polyphenols at carbon–polyvinylchloride composite electrodes [5] and in plant extracts, food and beverage samples [6]. Abdel-Hamid and Newair [7] investigated the electrochemical behaviour of GA in an aqueous solution. They suggested that the electrochemical oxidation occurs via two irreversible diffusion-controlled cyclic voltammetric waves

at the entire range of pH. The electrochemical oxidation mechanism was proposed to be an ECEC, first-order reaction. The two cv waves involves each an electron transfer step followed by an irreversible chemical follow-up deprotonation reaction. Di Fusco et al. [8] developed and characterized an electrochemical biosensor using laccases as the biocatalytic material for the determination of GA content in wines. Polymer-modified electrodes, PMEs, have shown to be a powerful tool [9,10]. Because characteristics like film thickness, permeation and charge transport can be controlled by adjusting the electrochemical parameters. Therefore, PMEs have many advantages such as improved electro catalysis, absence of surface fouling and prevention of undesirable reactions competing kinetically with the desired electrode process.

The objective of the work was to develop and applying an efficient simple sensor for rapid adsorptive stripping voltammetric determination of GA at low concentration. It uses a glassy carbon electrode modified with polyepinephrine, PEP/GCE. To validate the proposed procedure, the determination of total gallic acid content in black tea sample was performed.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

All solutions were prepared using deionized water purified in a Millipore (Milli-Q) system. All chemicals were of analytical reagent

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grade and used without further purification. 0.2 M Phosphate buffer solutions, PBS, supporting electrolyte was prepared with various pH values from monosodium phosphate and disodium phosphate in deionized water. Fresh stock standard solution of depolarizers (10 mM) was prepared from the dry pure substances in the phosphate buffer. The subject solutions were prepared on dilution to the convenient concentration just prior to use.

2.1.2. Instruments

Cyclic and square wave voltammetric measurements were carried out with a potentiostat/galvanostat microAUTOLAB (Ecochemie) controlled by a personal computer using GPES 4.9 Software. A conventional three-electrode electrolytic cell was employed. The working electrode was glassy carbon electrode modified with polyepinephrine, PEP/GCE. Ag/AgCl, KCl saturated and platinum wire electrodes were used as reference and counter electrodes, respectively. Test solutions, contain gallic acid and buffer solution, were degassed with pure nitrogen prior to the voltammetric measurements. The nitrogen flow was stopped and the solution was stirred. Then the stirring was switched off and a quiescence time of 10 s was allowed. A nitrogen blanket was maintained thereafter. The potential scan was carried out and voltammograms were recorded. Background data were stored and subtracted from the experimental data set, minimizing side effects such as double layer charging current. All potentials quoted are relative to Ag/AgCl reference electrode. A 780 pH Meter (Metrohm), equipped with a combined Ag/AgCl glass electrode was used for pH measurements.

UV–vis absorption spectroelectrochemistry were measured using UV-JASCO V-500/V-600 spectrophotometer. Field emission scanning electron microscope (FE-SEM) image was obtained on a JSM-600 Field Emission Scanning Electron Microanalyzer (JEOL, Japan). All experiments were performed at room temperature, 25 °C.

2.1.3. Preparation of the modified electrode

Glassy-carbon electrode GC, surface area of 0.0079 cm², working electrode was freshly polished to a smooth surface, using fine (0.5 µm) grades of SiC paper and washed with deionized water. After sonication cleaning in water for 15 min, the electrode was modified with polyepinephrine, PEP, by cyclic voltammetric method in 0.2 M phosphate buffer solution containing 1.0 mM epinephrine, EP, at pH 7.01. The electrode was then rinsed with ethanol and deionized water. The modified electrode, PEP/GCE, was stored in the PBS (pH 7.01). High-purity nitrogen was used for de-aeration.

2.1.4. Spectroelectrochemistry

A 1.0 mL of 1.0 mM epinephrine solution was injected into the spectroelectrochemical cell through its reference electrode chamber. A similar cell was set in the reference beam of the spectrophotometer for background subtraction during in situ measurement of UV–vis absorption spectra. The absorption spectra were recorded while the applied potential to the working electrode was 1.0 V to oxidize epinephrine. During the electrolysis of EP in the spectroelectrochemical cell, a series of successive spectra were recorded.

2.1.5. Sample preparation

The black tea sample was prepared on addition of deionized water to 50.4 mg dry tea in a 50 mL conical flask and stirred on a hot plate at 80 °C for 10 min. Then, tea solution was filtered off through a Whatman paper (No. 1). The tea solution was cooled to room temperature and diluted to 50 mL with deionized water.

3. Results and discussion

3.1. Electropolymerization of EP at GCE

The electrochemical sensor based on glassy carbon electrode modified with polyepinephrine, PEP/GCE, was prepared by successive cycling voltammograms of 0.2 M phosphate buffer solution, PBS at pH 7.01, containing 0.67 M EP in a potential range of –0.1 to 0.6 V, c.f. Fig. 1A. EP shows an irreversible cyclic voltammogram, cv, with anodic peak potential at 0.205 V versus Ag/Ag⁺ at scan rate of 50 mV s^{–1}. The cv is attributed to oxidation of epinephrine to the epinephrine *quinone*. On successive cycling, the intensity of the cv peak decreases progressively and at 10 cycles, it levels off. On continuous cyclic sweep to 100 cycles, the cv has the same response. This behaviour is due to the formation of polyepinephrine, PEP on coupling of EP [11]. On recording cv of PEP/GCE, reversible redox peaks are seen at 0.352/0.314 V at various scan rates, c.f. Fig. 1B. It is found that the anodic peak current, i_p^a , depends linearly on scan rate, v . This dependence is represented by a regression equation with correlation coefficient of 0.999 as follows:

$$i_p^a \text{ (A)} = 2.37 \times 10^{-8} + 7.98 \times 10^{-7} v \text{ (V s}^{-1}\text{)} \quad (1)$$

This indicates that the response is of an adsorption-controlled nature.

3.2. Characterization of polyepinephrine, PEP/GCE, modified electrode

Scanning electron microscopy, SEM, is an excellent technique for investigating the surface morphology of polyepinephrine, PEP. Fig. 2 shows the surface morphology of PEP. Fig. 2A is a typical FE-SEM image of the deposited PEP using chronoamperometric method at 1.0 V to 20 h, while Fig. 2B is a typical FE-SEM image using cyclic voltammetric method in –0.1 to 0.7 V range at scan rate of 50 mV s^{–1} for 5 cycles. As shown in Fig. 2A, the surface has very weak cavities. This illustrates that the electrodeposition of EP is irregularly gather due to rapid reaction. On the other hand, Fig. 2B shows a surface with very strong irregular cavities. Thus, the cyclic voltammetric method is the suitable way for formation of irregular porous film which was used for modification.

To study the electrochemistry of EP in detail, the oxidation product of EP in solution was investigated by using UV–vis Spectroelectrochemistic spectra. A series of spectra was recorded on applying a potential of 1.0 V for 60 cycles in PBS to monitor any absorbing species as intermediates or products, c.f. Fig. 3. Two absorption bands at $\lambda_{\text{max}} = 220$ and 290 nm are seen for EP before oxidation, curve 1. These absorption bands are attributed to EP itself, which was confirmed by a separate absorption spectrum of EP solution. Two absorption bands are developed on continuous scanning. A sharp absorption maximum, at $\lambda_{\text{max}} = 310$ nm and a broad band at 485–505 nm indicating formation of a new reaction product, curve 60. These spectra match the characteristic spectrum of open chain catecholamine–quinone [12]. The open chain *quinone* is rapidly cyclized to form PEP. Thus, the gradual enhancement of the longer wavelength absorption bands and the decrease of the shorter ones in subsequent scans are attributed to the proceeding of the polymerization reaction.

3.3. Electrochemical behaviour of gallic acid at polyepinephrine/glassy carbon electrode

Cyclic voltammograms of 0.2 M phosphate buffer solution, PBS, (pH 1.88) containing 1.13 mM gallic acid, GA, at the modified and bare GCE are recorded in Fig. 4. Gallic acid shows an irreversible well-defined redox cv wave on both electrodes. A negative shift

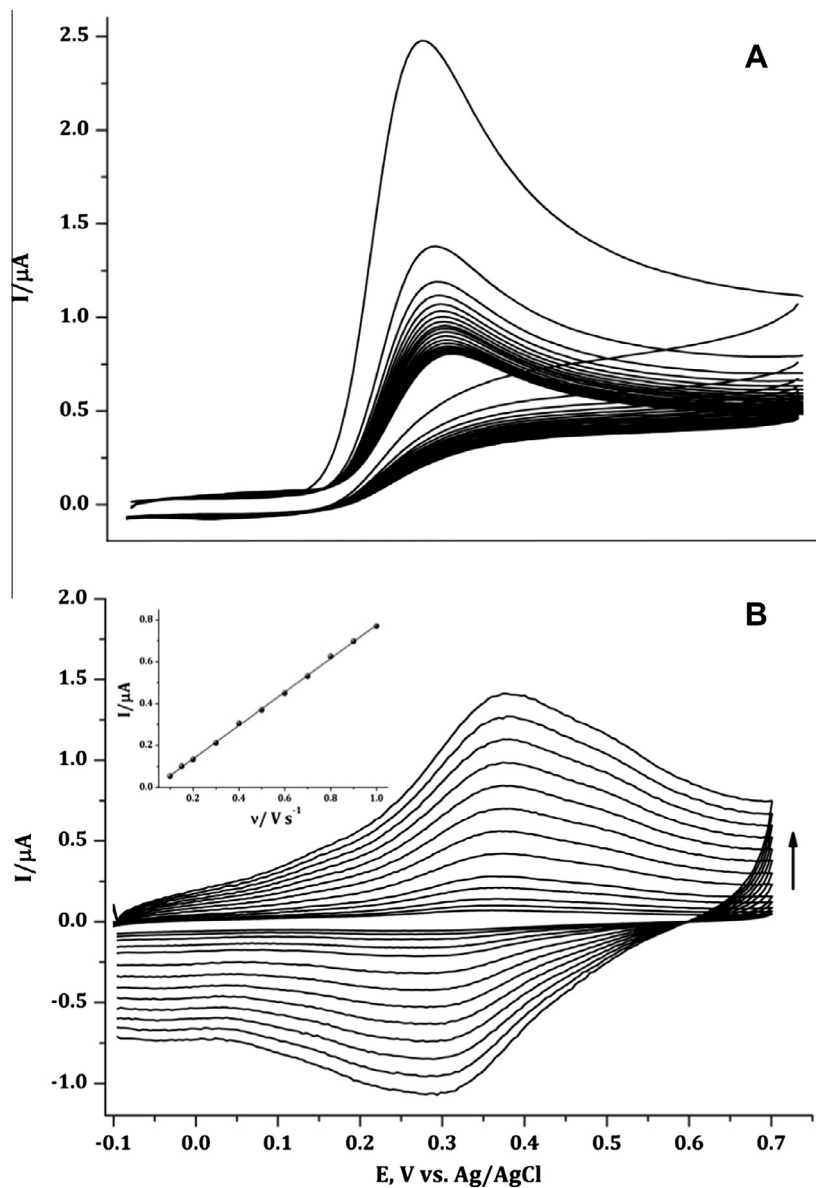


Fig. 1. (A) Cyclic voltammograms of 0.67 mM EP at GCE in 0.2 M PBS (pH 7.01) with continuous scans at scan rate of 50 mV s⁻¹, and (B) CVs of PEP/GCE modified electrode at different scan rates. Inset: the linear regression plot of the anodic peak current i_p^a versus ν .

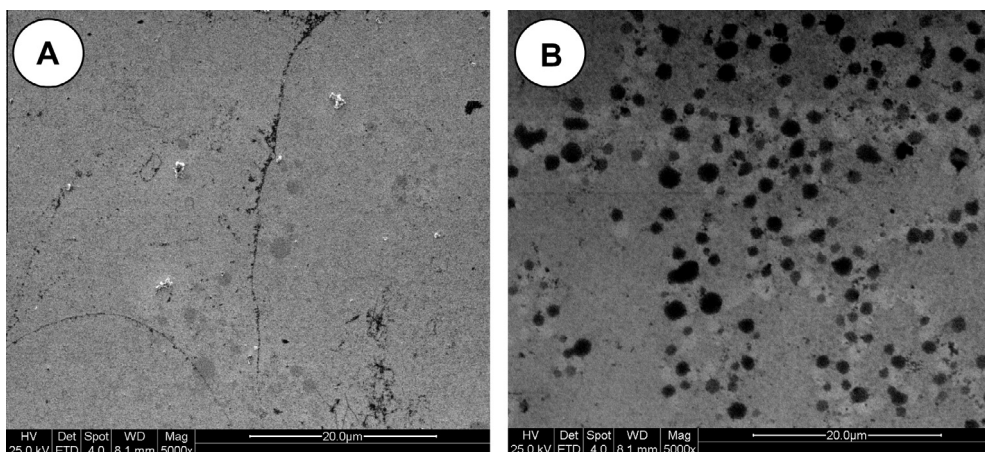


Fig. 2. (A) Typical FE-TEM image of polypinephrine, PEP, deposited using chronoamperometric method at 1.0 V for 20 h, and (B) PEP deposited using cyclic voltammetric method in -0.1 to 0.7 V range at scan rate of 50 mV s⁻¹ for 5 cycles.

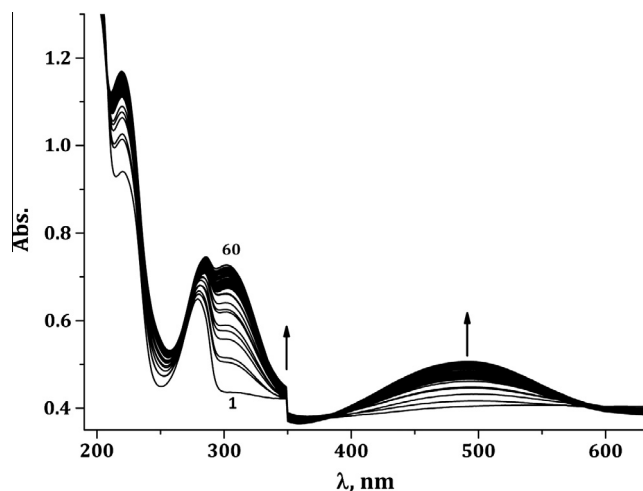


Fig. 3. UV-spectroelectrochemical absorption spectra of 0.1 μM EP at Pt for 60 cycles at 1.0 V in 0.2 M PBS, pH 7.01.

of oxidation peak potential and an enhancement of peak current are obtained on modification, c.f. Fig. 4A. This indicates that PEP/GCE effectively improve the electron-transfer kinetics of GA. On increasing scan rates, v , the oxidation and reduction peak currents

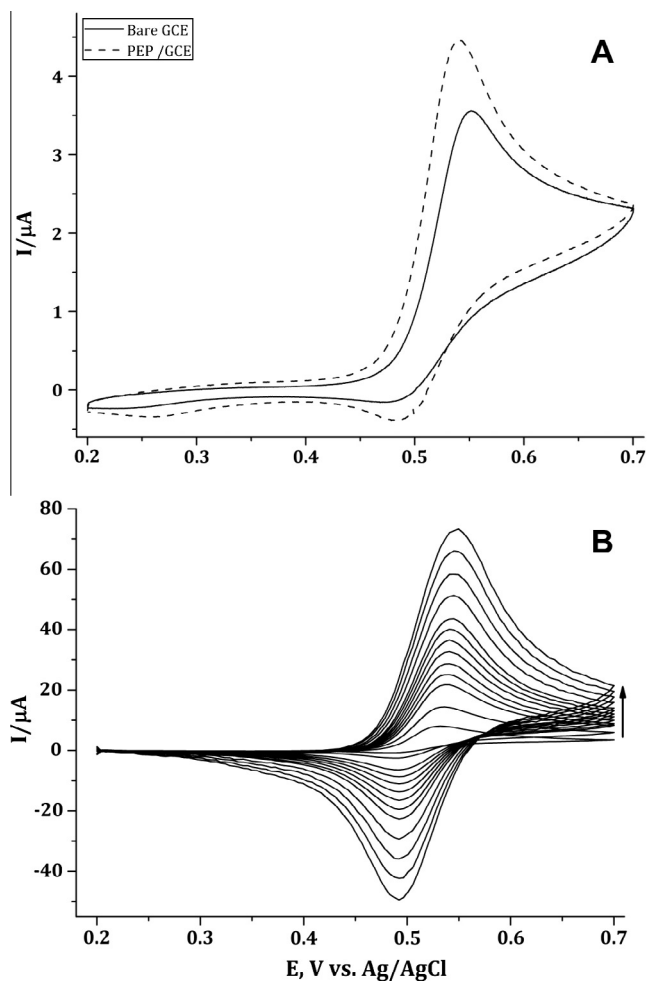


Fig. 4. (A) Cyclic voltammograms of 1.13 mM GA in 0.2 M PBS (pH 1.88) at PEP modified and bare glassy carbon electrodes at scan rate of 100 mV s^{-1} . (B) CVs of 0.2 mM GA at PEP/GCE in 0.2 M PBS (pH 1.88) at different scan rates.

increase c.f. Fig. 4B. At low scan rates GA shows an irreversible cv wave, while at higher ones, the wave becomes quasi-reversible. On plotting the oxidation peak current, i_p^a versus scan rate, v , from 0.01 to 1.80 V s^{-1} , a linear increase of i_p^a with v rather than $v^{1/2}$ is seen. This indicates that the electrode process is controlled by adsorption. Furthermore, on plotting logarithm i_p^a versus logarithm v , a straight line with a slope of 0.81 was obtained. This confirms that electrode process is an adsorption-controlled process.

3.4. Square wave adsorptive stripping voltammetric determination of gallic acid

For electrochemical determination of gallic acid, a square wave adsorptive stripping voltammetric method, SWAdSV was performed at PEP/GCE. The SWAdSV method is effective and rapid electroanalytical technique with well-established advantages, including good discrimination against background currents and low detection limits. For electrochemical determination of GA, optimal conditions such as pH, accumulation potential, accumulation time and concentration of GA were investigated.

3.4.1. Effect of pH

The pH value of the base solution has a significant influence on the oxidation of GA at the PEP/GCE. The effect of solution pH on the SWAdSV response of 50 μM gallic acid was investigated over the pH range of 1.88–6.6. Fig. 5A shows that the anodic peak current of GA decreases with increasing the pH of solution. On increasing of pH, the protonated degree of GA decreases, thus, the static attraction interaction between GA and polyepinephrine decreases with increasing of pH. So the anodic peak current decreases with the increasing of pH. Since pH 1.88 was chosen for the electrochemical determination of GA.

3.4.2. Effect of accumulation potential

Effect of the accumulation potential, from 0.0 to 0.7 V, on the SWAdSV signal at PEP/GCE was studied for 50 μM GA solution. Fig. 5B displays the variation of peak current versus accumulation potential. It is clear that peak current increases with increasing of accumulation potential till a maximum value at potential of 0.2 V. On further increase of accumulation potential to more anodic value, a decrease in the SWAdSV signal is observed. Therefore, the accumulation potential of 0.2 V was chosen in all the subsequent work.

3.4.3. Effect of accumulation time

Effect of accumulation time on anodic peak current was investigated at different time range of 0–60 s c.f. Fig. 5C. On increasing time, the peak current increases to a maximum value at 10 s and scales off at longer accumulation time. This indicates that, GA on the modified electrode surface is rapidly adsorbed. Further increase of accumulation time did not increase the response of GA on the electrode. This is due to a complete coverage of electrode surface and the peak current remains almost scale off. For practical purposes, a 10 s accumulation time is sufficient for adsorptive stripping voltammetric determination of GA.

3.4.4. Effect of gallic acid concentration

Effect of gallic acid concentration on the square wave voltammetric, SWV, response at PEP/GCE in 0.2 M PBS solution, pH 1.88, was investigated. On optimal operating conditions, SWAdSV measurements were carried out in solutions containing different concentrations of GA (10×10^{-7} to 2×10^{-5} M). The square wave voltammograms obtained and the respective analytical curve (inset) are recorded in Fig. 6. The anodic peak current corresponding to the oxidation of GA correlates linearly with GA concentration in the entire range of investigation, see inset of Fig. 6. A linear

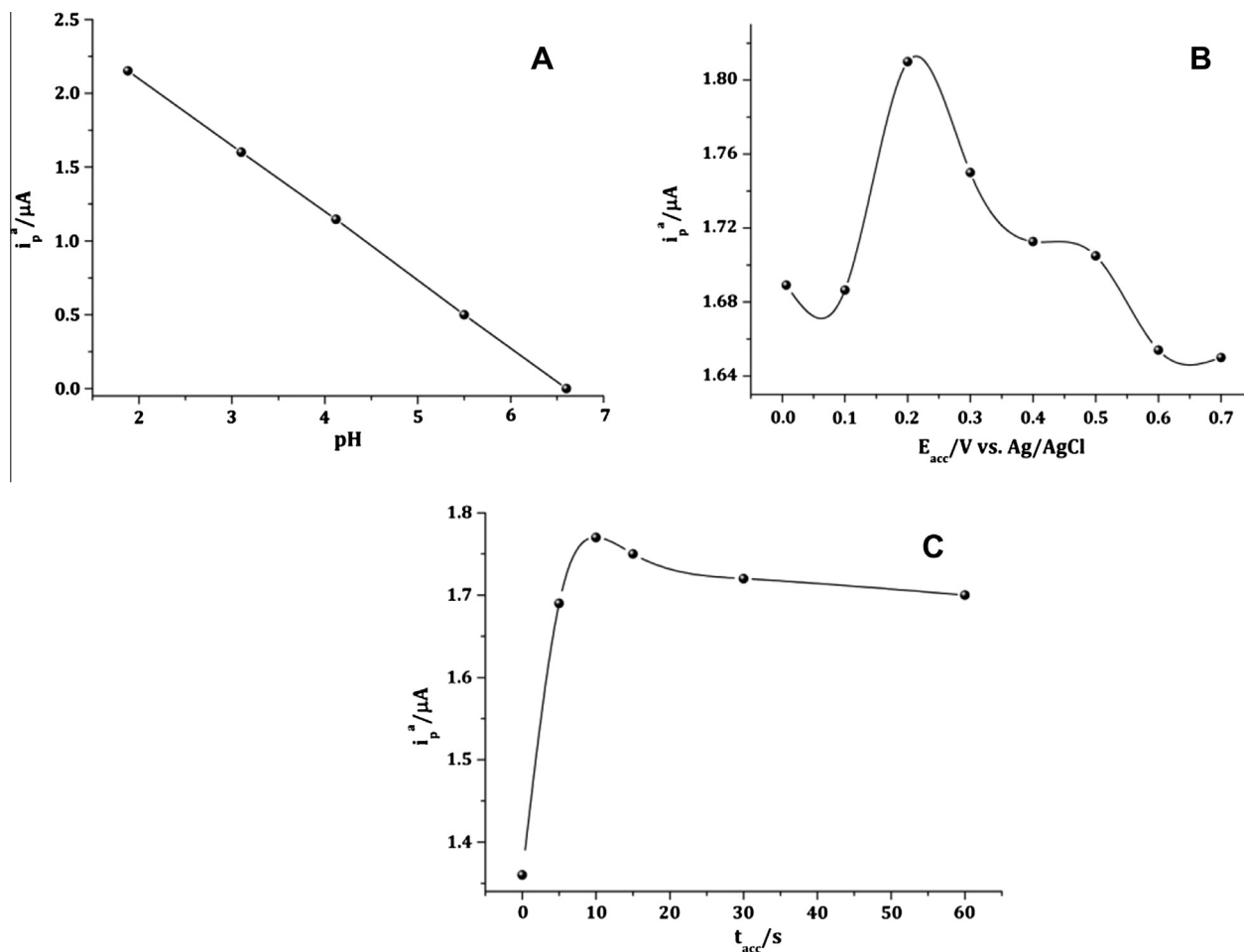


Fig. 5. Effect of pH (A), accumulation potential (B) and accumulation time (C) on anodic peak current of 50 μ M GA in 0.2 M PBS at step potential 5 mV, SW amplitude 25 mV and SW frequency 25 Hz.

regression relationship between peak current and the concentration of GA is represented by following equation:

$$i_p (\mu A) = 1.71 \times 10^{-8} + 9.40 \times 10^{-3} C_{GA} (nM) \quad r = 0.999 \quad (2)$$

The detection limit for gallic acid is $6.63 \times 10^{-7} \text{ mol L}^{-1}$ at a signal-to-noise ratio (S/N) of 3. It is found that, the obtained results reveal that the present method is more sensitive and has short time than the previous Ghoreishi method [13].

3.4.5. Analytical application

To investigate the concomitant effects of compounds usually present in tea, SW voltammograms at PEP/GCE were carried out in a 0.2 M phosphate buffer solution, pH 1.88, containing $5.0 \times 10^{-6} \text{ M}$ GA in the absence and presence of caffeic and ascorbic acids. No significant interference is found for the voltammetric response for GA. For determination GA in black tea sample, the gallic acid content was determined by using the standard addition method at the optimal parameters. Square wave voltammograms for an aliquot of 10 μ L of black tea added directly to the electrochemical cell containing 5 mL of PBS, were recorded. Concentration of gallic acid is estimated to be $7.0 \pm 0.05 \times 10^{-6} \text{ M}$. This value corresponds to 2.36% of the black tea sample. The given values corresponds to the mean value of three determinations. The results show that the polyepinephrine electrochemical sensor based on PEP/GCE can be used successfully to give a good estimate of the gallic acid content in foods.

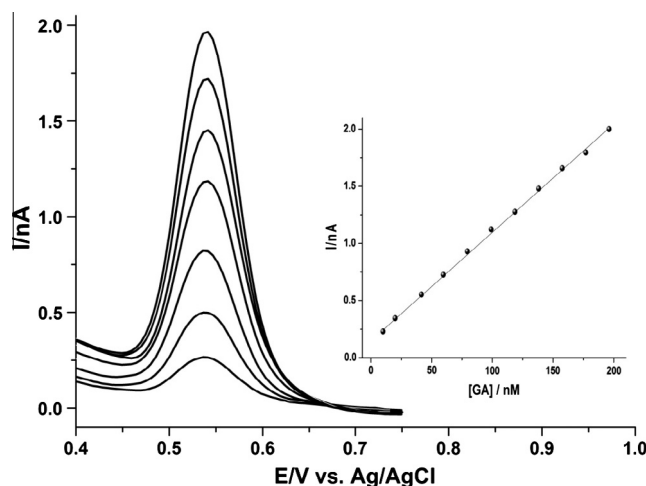


Fig. 6. Square wave voltammograms obtained under optimal conditions in 0.2 M PBS containing different concentration of GA, from 10×10^{-7} to $2 \times 10^{-5} \text{ M}$. Inset, the relationship between oxidation peak current and GA concentration at PEP/GCE.

4. Conclusion

Glassy carbon electrode, GCE, modified with polyepinephrine, PEP, film was prepared and used as a sensor based on PEP/GCE in phosphate buffer solution for detection of gallic acid, GA. Cyclic and square wave voltammetric techniques were used. It was

shown that PEP/GCE exhibits remarkable electrochemical effects towards oxidation of GA. The modified electrode, PEP/GCE, enhances the oxidation peak current of GA. The results can be applied for the adsorptive stripping voltammetric determination of GA concentrations in real samples, black tea, with satisfactory results.

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