Int. J. Electrochem. Sci., 15 **(2020)** 7214 – 7227, doi: 10.20964/2020.08.06

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Determination of Gallic Acid with a Glassy Carbon Electrode modified with Reduced Graphene Oxide

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Received: 9 April 2020 / *Accepted:* 25 May 2020 / *Published:* 10 July 2020

Gallic acid is a valuable compound that is present or incorporated in a variety of foods, beverages, cosmetics, and other chemical formulations. However, the cost-efficient determination of gallic acid over a wide range of concentrations is an unsolved problem. In this work, we propose a reduced graphene oxide (rGO)-modified electrode design that is easy to manufacture in a highly repeatable manner, does not involve toxic chemicals or fragile components, and offers superior sensitivity and linear dynamic range. Application of the electrode is demonstrated and optimized with common cyclic voltammetry and square-wave voltammetry system; the latter being recommended for quantification. The electrode is reusable, very robust to common interferents, and is shown to yield precise determinations in real samples, even at very low gallic acid concentrations.

Keywords: voltammetry; reduced graphene oxide; glassy carbon electrode (GCE); gallic acid; square-wave voltammetry

1. INTRODUCTION

Phenolic acids and polyphenols are secondary metabolites produced by some plants that are receiving increasing attention by industry and society due to their health implications [1]. Gallic acid (GA, 3,4,5-trihydroxybenzoic acid) is one of the most abundant phenolic acids in plants and is the building block of many polyphenols (hydrolysable tannins) [2]. GA is abundant in foods like tea, wine, and berries. Fast and simple determination of GA is essential in the quality control and authentication of

foods. The total phenolic content or antioxidant capacity of a sample is typically expressed as gallic acid equivalents. Gallic acid is also extracted to produce food additives and nutraceuticals [3] and, because of its bioactive properties -namely antioxidant but also antimicrobial, hepatoprotective, anti-HIV-1, etc. [4, 5], it is also widely used in the cosmetic industry and pharmaceutical research.

In research, a variety of methods have been used for the detection of gallic acid [6]. A common approach involves liquid chromatography separation followed by UV or electrochemical detection (ED) [6, 7]. However, for industrial applications, it is desirable to develop quick and easy methods that can provide determinations requiring less capital investment, involving few or no reagents and using simple sample preparation. This makes electrochemical sensors very attractive. Multiple electrochemical sensors have been proposed [8-15], which often would be used after sample pretreatment with liquid-liquid or solid-phase extraction. Despite the advances, there is still room to improve the sensitivity, linear range, cost, and especially, to minimize interferences by other compounds present in the matrix, which would simplify sample processing and improve accuracy. In addition, a better understanding of the effect of matrix and instrumental variables is necessary for the sensors to be applicable in a variety of samples and laboratories.

In this work, we propose a novel electrode design based on reduced graphene oxide (*r*GO). The *r*GO holds many benefits, including low cost, excellent electrical properties, and ease of modifications due to its controlled amount of oxygen-containing functional groups on its surface [16]. As the *r*GO prepared by electrochemical reduction has advantages over the one made by chemical reduction in terms of simplicity and avoidance of hazardous chemicals for the reduction of graphene oxide (GO) [17], we applied the electrochemical method for the electrode preparation in this work. Next, the electrode was tested under a variety of conditions, such as pH and measurement parameters, to find the best conditions for the determination of GA. The interference study and the stability over repeated measurement cycles of the electrode were then evaluated in acidic buffer solutions. This *r*GO-modified electrode also demonstrated a wide analytical range for the GA determination with a low limit of detection. Finally, the capability of this electrode for GA detection has been investigated in real samples, such as drinking water and tea, to ensure its real-life applications.

2. EXPERIMENTAL

2.1 Reagents and Solutions

Gallic acid was obtained from Sigma-Aldrich (Missouri, USA). Potassium ferricyanide was purchased from Acros (Geel, Belgium). Citric acid and nitric acid were obtained from Carlo-Erba (Milan, Italy). Nitric acid, sulfuric acid, hydrogen peroxide, potassium permanganate, and sodium acetate were purchased from QRëC (New Zealand). All chemicals used in this work were of analytical grade purity. Graphite was obtained from ChemPUR (Karlsruhe, Germany). All the solutions were prepared with deionized (DI) water (R = 18.2 MΩ·cm).

2.2 Apparatus

A potentiostat/galvanostat Autolab model PGSTAT 204 (Metrohm Autolab B.V., Netherlands) was employed for the electrochemical measurements. Voltammetric experiments were carried out with a three-electrode system at room temperature. The reference electrode was an Ag/AgCl electrode, and the auxiliary electrode was a platinum sheet electrode. A glassy carbon electrode (3 mm diameter) was employed as the conductive substrate before GO modification. The chemical functionalities in GO and *r*GO were investigated with a Spectrum 100 FT-IR spectrometer (PerkinElmer, USA).

2.3 Synthesis of Graphene oxide

Graphene oxide was prepared by adapting Hummers' method [18]. 1 g of graphite was added and dispersed in 36 mL 98% H_2SO_4. The mixture was continually stirred for 1 h. Then, the mixture was kept in an ice bath while 56 % HNO_3 was slowly added under agitation. Next, 5 g $KMnO_4$ was gradually added to the mixture while keeping the mixture in the ice bath. The resulting mixture was stirred at room temperature for 12 h. Then, 120 mL of deionized water was added and stirred for 2 h. Next, 6 mL of H_2O_2 was added to the mixture and further stirred for 2 h. After this step, the mixture was left for at least 24 at room temperature. The mixture was separated into two layers: a colorless supernatant and a yellow precipitate. The supernatant was removed from the mixture, and the yellow precipitate was washed with 250 mL deionized (DI) water. Finally, 1 mL 37% HCl and 10 mL 3% H_2O_2 were added sequentially to the mixture and stirred for 2 h. The resulting mixture was centrifuged to obtain the precipitate. The recovered precipitate was washed with 600 mL DI water and centrifuged to remove the supernatant. This washing was repeated several times until the pH of the supernatant was 6.7. The precipitate of GO was kept in a freezer at -10 °C for 12 h. Then, the frozen precipitate was kept in a lyophilizer for 24 h before storing it in a fridge at -4 °C.

2.4 Reduced Graphene Oxide-modified Electrode

A glassy carbon electrode (GCE) (Metrohm, diameter 3mm) was successively polished on a polishing cloth using alumina powders of size 5, 1, and 0.5 microns, respectively. The electrode surface was rinsed with DI water and sonicated in ethanol for 3 min to remove the alumina. GO was electrochemically reduced to *r*GO using cyclic voltammetry by adapting the approach from [19]. 5 μL of graphite oxide 0.5 mg/mL was drop-casted on the electrode surface, and the electrode was allowed to dry for 2 h at room temperature. The obtained GO-modified glassy carbon electrode was immersed in an acetate buffer at pH 5. To obtain *r*GO, the potential of the GO-modified glassy carbon was scanned between -1.5 and 1.5 V (vs. Ag/AgCl electrode) with the scan rate of 100 mV/s for 30 cycles. The resulting *r*GO-modified glassy carbon electrode was thoroughly rinsed with deionized water before performing the voltammetric measurements.

To confirm the active surface area of the electrode, cyclic voltammetry was carried out in the solution containing 5 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl as a supporting electrolyte [20]. The electroactive

surface area of the electrodes was calculated by using the oxidation peak current obtained from the CV using the Randles-Sevcik equation as following:

$$I_p = 2.69 \times 10^5 AD^{1/2}n^{3/2}\upsilon^{1/2}C$$

where A is the electroactive surface area of the electrode (cm^2), n is the number of the electron involved the redox reaction, D is the diffusion coefficient (cm^2/s), υ is the scan rate applied to the electrode (V/s), and C is the concentration of the electroactive species (mol/L). By using the value for the diffusion coefficient of $[Fe(CN)_6]^{3-}$ of 6.30×10^{-6} cm^2 s^{-1}, the electroactive surface area of each electrode was obtained.

2.5 Analytical procedure and sample preparation

The modified electrodes were used to study the electrochemical oxidation of gallic acid at varying concentrations in 0.1 M citrate buffer at pH 1.8. Cyclic voltammetry was demonstrated as a possible method, which is widely available. Subsequently, square-wave voltammetry (SWV) was demonstrated as a superior method for gallic acid determination with optimized SWV parameters (a pulse size of 10 mV, a potential step of 2.5 mV and a frequency of 15 Hz) in the potential range between 0.4 to 0.7 V. The accumulation time for allowing the gallic acid to adsorb on the electrode surface before the SWV measurement was 180 s at the open-circuit potential.

Drinking water (brand 'Crystal') was directly analyzed by the standard addition method after spiking in known concentrations of gallic acid. For a green tea sample (purchased from the local market in Chiang Rai), the procedure was adapted from [11] 50.4 mg of green tea powder was dissolved in 10 mL DI water and boiled at 80 °C for 10 min under stirring. The tea sample was allowed to cool down before filtrating through a Whatman filter paper no.1 and then DI water was added to a volume of 50 mL. GA quantification in tea was performed by 25-fold dilution of the green tea sample with the citrate buffer at pH 1.8 using the standard addition method. Percentual recovery and percentual relative standard deviation were calculated for method validation.

3. RESULTS AND DISSCUSSION

3.1 Characterization of the electrodes prepared

FT-IR spectroscopy was used to confirm the formation of *r*GO by electrochemical reduction. The IR spectra of graphene oxide (GO) and the prepared reduced graphene oxide (*r*GO) are shown in Fig. 1 The broad peak found in both GO and *r*GO at 3350 cm^{-1} is assigned to the -OH stretching vibration. In the GO spectrum, the band at 1735 cm^{-1} corresponds to -COOH (carboxylic acid group), while the peak at 1625 cm^{-1} is assigned to -C=O (carbonyl group). The bands at 1411 and 1226 cm^{-1} correspond to the stretching of $-COO^-$ and -CO (epoxy group), respectively. By contrast, in *r*GO, the transmittance of these bands significantly increased relative to GO. This is because the electrochemical reduction process decreases the amount of functional groups, including -OH, -C=O, -COOH, $-COO^-$ and -CO. These results are consistent with previous reports [21-25].

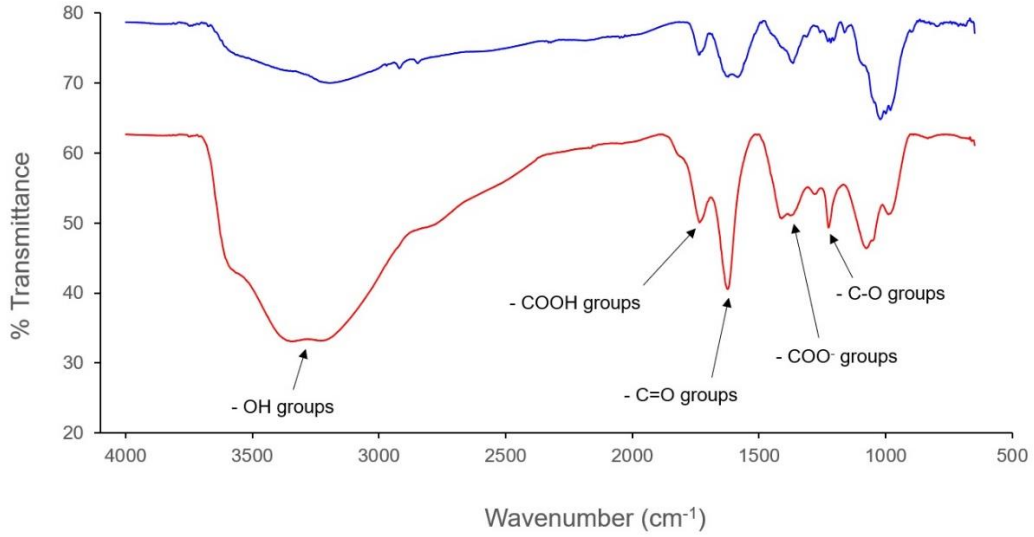

Figure 1. FT-IR absorption spectra of *r*GO (blue) and GO (red).

Evaluating the oxidation and reduction of $K_3[Fe(CN)_6]$ is commonly used as a test reaction to characterize the electrochemical properties of new electrode designs. The effects of modifying the GCE with GO and *r*GO were investigated by measuring the cyclic voltammograms of the bare GCE, GO/GCE, and *r*GO/GCE electrodes in 5 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl as supporting electrolyte. The results are shown in Fig 2. The *r*GO/GCE showed the highest peak current (I_p) as well as the smallest peak-to-peak separation (ΔE_p), which indicates a fast electron transfer for the reversible redox-couple $[Fe(CN)_6]^{3-/4-}$ [26]. The estimates of electroactive surface area (Table 1) indicate that the *r*GO-modified electrode had the highest electroactive surface area. This may be due to a lower degree of structural disorder compared to that of GO, which possesses higher numbers of defects and functionalities and leads to poor electrical conductivity [16].

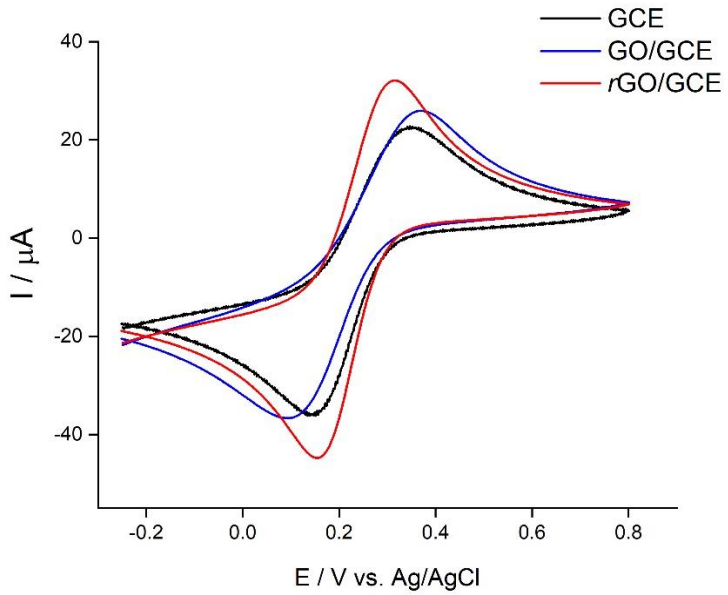

Figure 2. Cyclic voltammograms of GCE (black); GO/GCE (blue); *r*GO/GCE (red) in **(A)** 5 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl at the scan rate 50 mV s^{-1}.

Table 1. Comparison of the peak current, peak separation, and electroactive surface area for the electrodes with different modifications.

Electrode	Peak current (μA)	Peak-to-peak separation (V)	Electroactive surface area (cm^2)
GCE	29.125	0.200	0.0235
GO/GCE	29.750	0.276	0.0295
rGO/GCE	38.656	0.161	0.0422

3.2 Electrochemical oxidation of gallic acid on the electrodes prepared

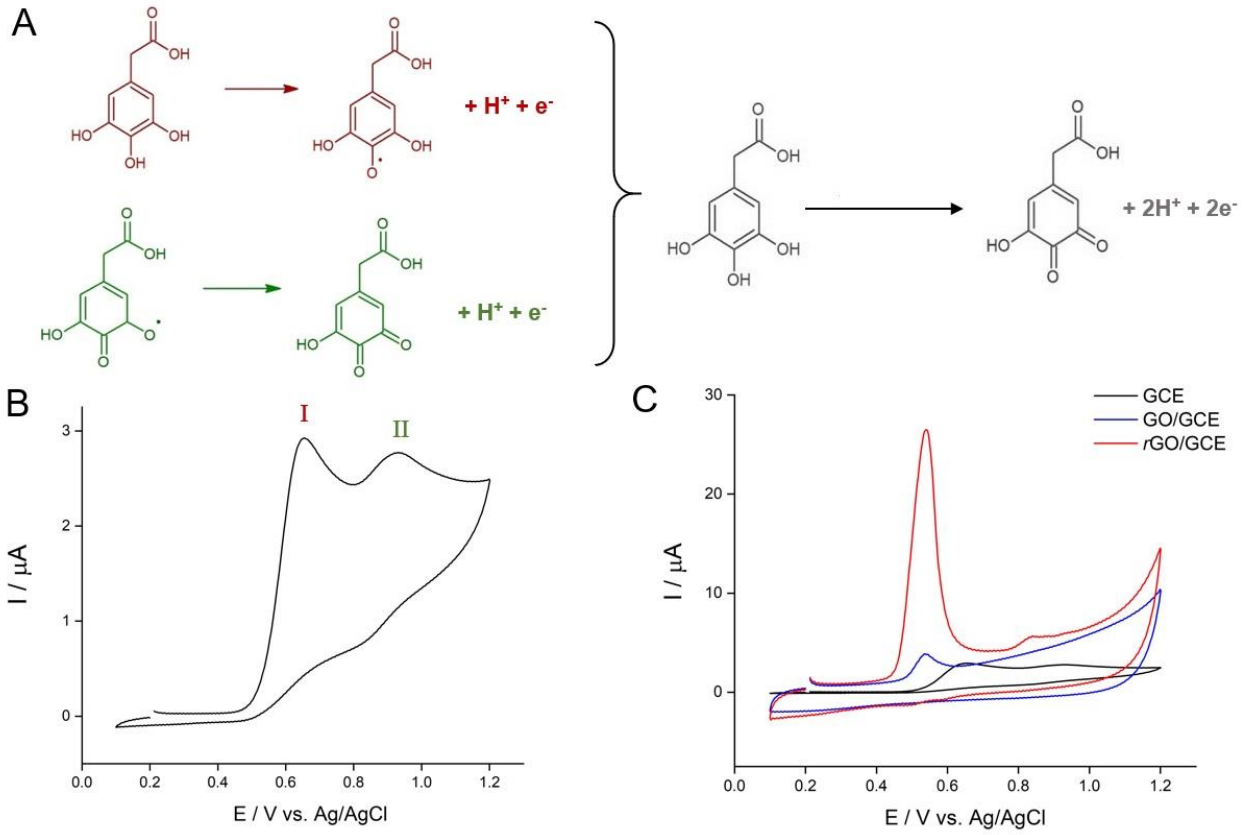

Figure 3. (A) Chemical structure of gallic acid and its two-step oxidation [27]. **(B)** Cyclic Voltammogram of 1 mM gallic acid at the scan rate of 100 mV/s in citrate buffer pH 1.8 with a glassy carbon electrode (GCE). **(C)** Cyclic voltammograms of the electrocatalytic oxidation of 1 mM gallic acid in 0.1 M citrate buffer (pH 1.8) at a scan rate 100 mV/s over the different electrodes.

The oxidation of gallic acid consists of two steps, as shown in the cyclic voltammogram in Fig. 3(A-B). Oxidation peak I corresponds to the first oxidation of gallic acid, involving the loss of a proton and an electron from the *para*-hydroxy group, resulting in a semiquinone product. The second oxidation peak corresponds to the loss of a proton and an electron at the *meta*-hydroxy group, which leads to the formation of the quinone [27]. When the scan direction was reversed towards negative potential values

(cathodic scan), no reduction peak was observed, indicating that the electrochemical oxidation of gallic acid is an irreversible process [28].

The electrochemical oxidation of 1 mM gallic acid was studied on the different electrodes. As shown in Fig. 3 (C), the CV for gallic acid obtained from *r*GO/GCE showed much higher oxidation peak current compared to those of GO and bare GCE (a value 12-fold higher than that of bare GCE). The essential benefit of using *r*GO for gallic acid detection is a significant decrease in the amounts of carboxyl and hydroxyl groups on GO. These groups are likely to cause a repulsive interaction with carboxylic acid groups of the substrate. As a result, the electrochemical oxidation rate toward gallic acid obtained with the *r*GO-modified electrode was remarkably improved. Upon using the *r*GO-modified electrode, the most distinct oxidation peak observed corresponded to the first peak (I), while the second peak (II) evidenced lesser oxidation compared to the first peak. This may be attributed to the instability of the semiquinone radicals, which could quench to a significant extent, forming oxidized products by recombination, before the potential reaches sufficiently high values for their electrochemical oxidation on the electrode surface [29]. Indeed, other studies have shown that increasing the scan rate over GCE increases the ratio of peak currents II to I [28], which agrees with this interpretation.

3.3 Optimizing the study of gallic acid by cyclic voltammetry

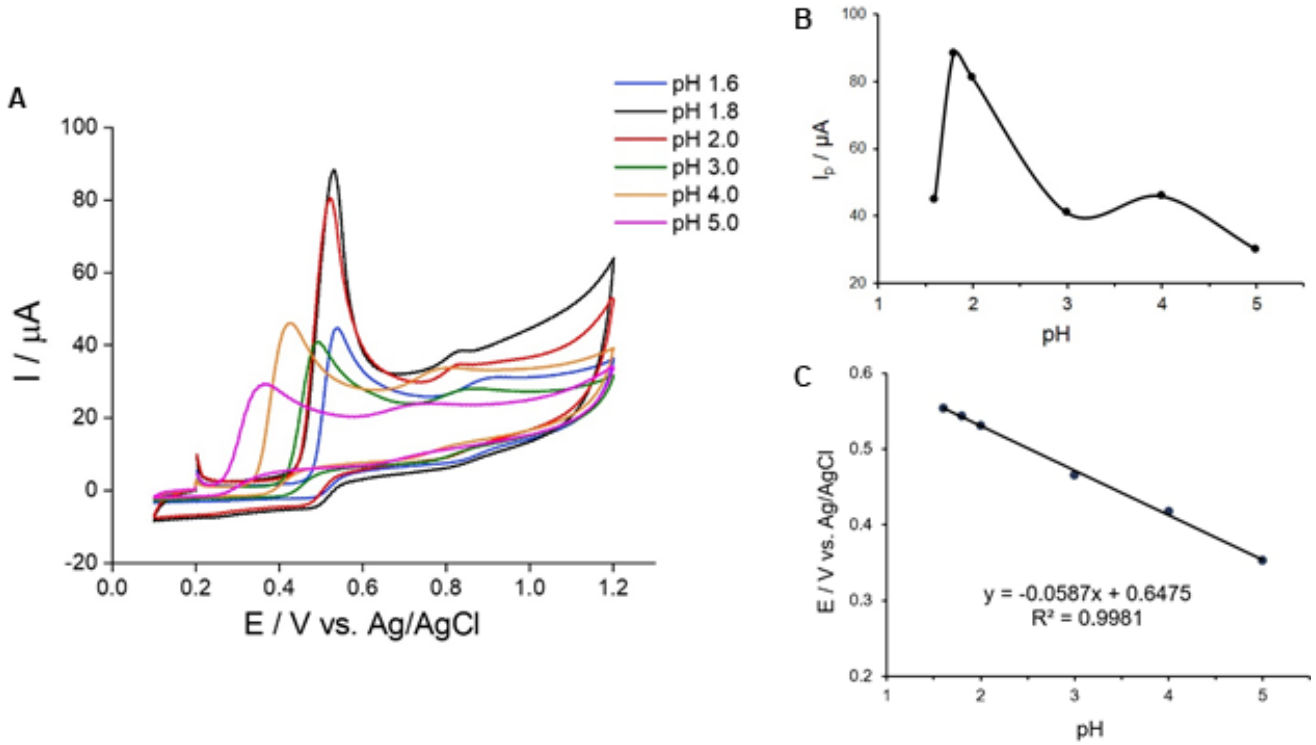

Figure 4. (A) Cyclic voltammograms of 1 mM gallic acid at various pH ranging from 1.6 to 5.0 with the *r*GO/GCE electrode at a scan rate of 100 mV s^{-1}. **(B)** Effect of pH on the anodic peak current, and **(C)** dependence of peak potential on pH.

The effect of pH on the anodic peak of 1 mM gallic acid was investigated in citrate buffer in the pH range from 1.6 to 5.0 by cyclic voltammetry at a scan rate of 100 mV/s. As depicted in Fig. 4(A-B), the peak current increased from pH 1.6 to 1.8, and then declined as the pH was further increased from

1.8 to 5.0. The oxidation of gallic acid is strongly dependent on the pH of the solution and explicitly occurs at pH 2, as previously reported [30]. Therefore, pH 1.8 was chosen in the rest of the study, as it yielded the highest oxidation current from gallic acid. The anodic peak potential (E_{pa}) of gallic acid decreased linearly with an increase in pH, as shown in Fig. 4(C). The linear dependency between peak potential and pH was E_{pa} (V) = -0.0587pH + 0.6475 (R^2 = 0.9981). The slope value obtained, 58.7 mV, is very close to the theoretical Nernst value of 58 mV at 25 °C for a two-electron and two-proton process and is in agreement with previous works [12, 31].

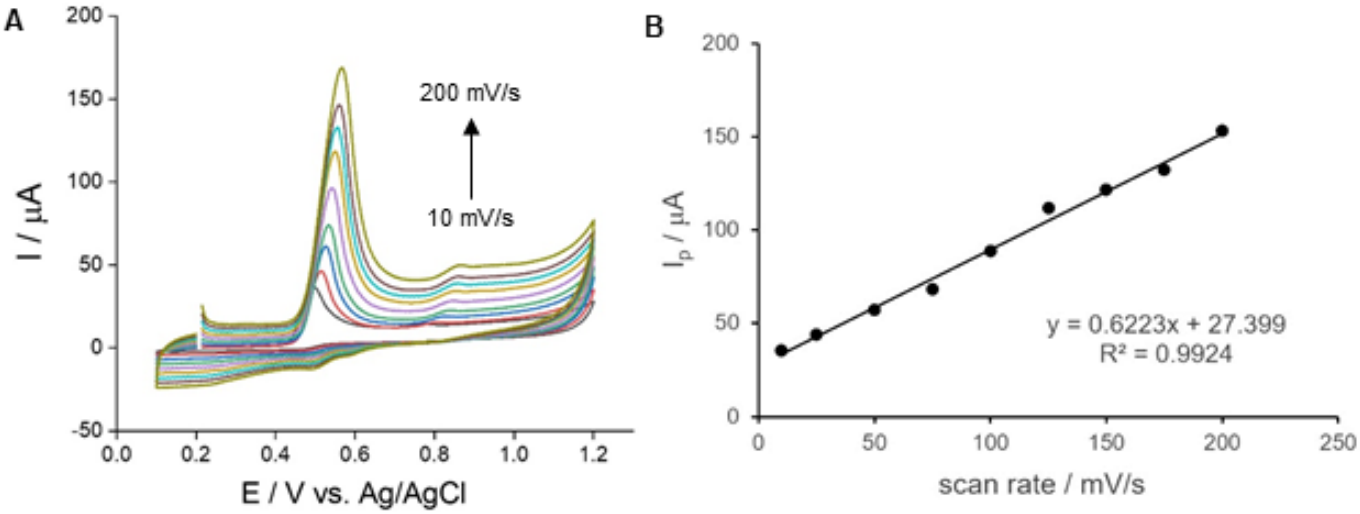

Figure 5. (A) Cyclic voltammograms of *r*GO/GCE for 1 mM gallic acid in 0.1 M citrate buffer pH 1.8 at the scan rates of 10, 25, 50, 75, 100, 125, 150, 175 and 200 mV s^{-1} (from inner to outer). **(B)** Relationship between the scan rate and the peak current.

The effect of the scan rate on the electrochemical oxidation peak of gallic acid for *r*GO/GCE was investigated in citrate buffer at pH 1.8 using cyclic voltammetry. The results are presented in Fig. 5(A). The oxidation process was studied by plotting the peak current against the scan rate used in the oxidation of gallic acid. A plot of the peak current vs. the square root of the scan rate was not linear (results not shown), suggesting that the process was not diffusion-controlled. By contrast, the peak current showed a linear dependence with the scan rate in the range 10 to 200 mV s^{-1} (R^2 of 0.9924), the dependence being I_p = 0.6223υ + 27.399 (I_p: μA, υ: mV/s) (Fig. 5(B)). Such linearity demonstrates that the electrochemical oxidation of gallic acid over the *r*GO-modified glassy carbon electrode prepared in this work is an adsorption-controlled process rather than a diffusion-controlled process [32].

3.4 Determination of gallic acid by square-wave voltammetry

To enhance the sensitivity for the detection of gallic acid, Square-Wave Voltammetry (SWV) was chosen, as it offers high sensitivity and enables the measurement with lower charging current than cyclic voltammetry [33]. A series of the SWV parameters including pulse size, potential step, and frequency was investigated, the optimum values for the parameter were as follows: pulse-height of 10 mV, the potential step of 2.5 mV and frequency of 15 Hz and were used for all SWV experiments. Under

the optimum condition, the corresponding voltammograms related to the electro-oxidation was obtained. The *r*GO/GCE electrode was applied to the quantification of gallic acid by SWV. Fig. 6(A) shows the SWV voltammograms obtained from gallic acid in the concentration range from 8 to 400 μM. The peak current increased linearly with gallic acid concentration, yielding two linear ranges depicted in Fig. 6 (B)-(C). The corresponding linear regression for the low concentrations ranging from 8 to 20 μM is: *Ip* (μA) = 0.3356μM +47.199 (R^2 = 0.9948) (Fig. 6(B)), while the one for high concentrations varying from 20 to 400 μM is: *Ip* (μA) = 0.1136μM +52.917 (R^2 = 0.9978) (Fig. (6C)). The limit of detection for GA determination was calculated as 0.42 μM.

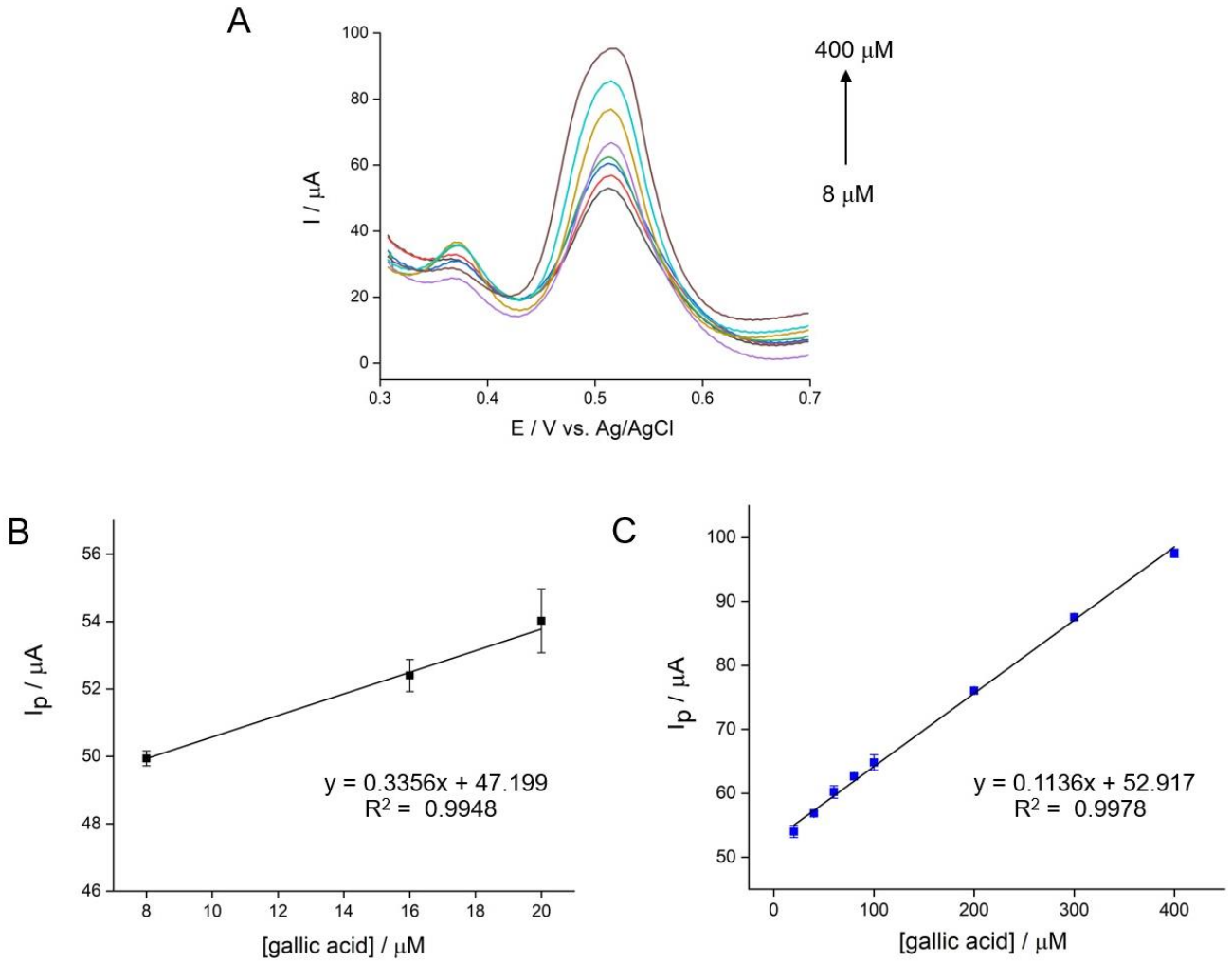

Figure 6. (A) SW Voltammograms for different concentrations from 8 to 400 μM of gallic acid at pH 1.8 with *r*GO/GCE. **(B)** Calibration curves for the quantification of gallic acid in the concentration range 8-20 μM and **(C)** in the concentration range 20-400 μM; SW pulse size 10 mV; SW frequency 15 Hz; potential step 2.5 mV.

The analytical characteristics of different methods published recently for the voltammetric detection of gallic acid are shown in Table 2. The *r*GO electrochemically modified glassy carbon proposed in this work shows a wide dynamic range as well as a low LOD compared to other proposals.

Table 2. Comparison of the analytical performance of different electrochemical methods for gallic acid determination.

Electrode	Method	Linear Range (µM)	LOD (µM)	Ref
*r*GO/carbon ceramic electrode	SWV	0.51 - 46.46	0.0867	[34]
Polyaminobenzene sulfonic acid functionalized SW-CNT /poly(pyrocatechol violet)/ GCE	DPV	10 -100	0.11	[35]
Polyepinephrine/GCE	SWV	1.0 – 20.0	0.66	[11]
Poly(glutamicacid)/*r*GO/GCE	DPV	0.03-480	0.01	[31]
Polymelamine/graphene/GCE	Amperometry	0.1 - 728.9	0.027	[36]
Hexagonal-prism-ZnO/GCE	Amperometry	0.1-130	0.02	[37]
Graphene/GCE	DPV	0.08-20	0.0012	[38]
ZrO_2 nanoparticles/CPE	DPV	1-1000	0.124	[39]
*r*GO/GCE	SWV	8 - 400	0.42	This work

DPV: Differential pulse voltammetry SWV: Square-wave voltammetry

SW-CNT: Single-walled carbon nanotubes CPE: Carbon paste electrode

3.6 Repeatability, Reproducibility and Interference Studies

The repeatability of the measurements with the *r*GO-modified GCE was investigated by measuring the peak current from SWV of 1 mM gallic acid for 5 replicates (Fig. 7A). The relative standard deviation (%RSD) observed from the 5 peak currents was 0.50%, which is relatively low, indicating that the *r*GO/GCE can be employed for measuring the electrochemical signal of the gallic acid with good repeatability. The reproducibility of the proposed electrode design was evaluated by freshly preparing 5 electrodes modified with *r*GO and measuring the oxidation peak current of 1 mM gallic acid from the individual electrodes (Fig. 7B). The %RSD for peak currents obtained was 0.85%. The results demonstrate that the electrode prepared in a simple manner from electrochemically reduced GO can produce highly reproducible results for gallic acid detection.

An interference study was carried on by comparing the peak current response from the oxidation of 60 µM gallic acid to those obtained in the presence of interfering species. The results for the influence of foreign substances are shown in Table 3. For example, ascorbic acid and caffeine are widely used in the food and beverage industry and contain ionizable and polar groups that could interfere with the determination. When ascorbic acid and caffeine were introduced at 30-fold higher concentrations than gallic acid, the peak currents for gallic acid observed were still maintained within $\pm$ 6.0%.

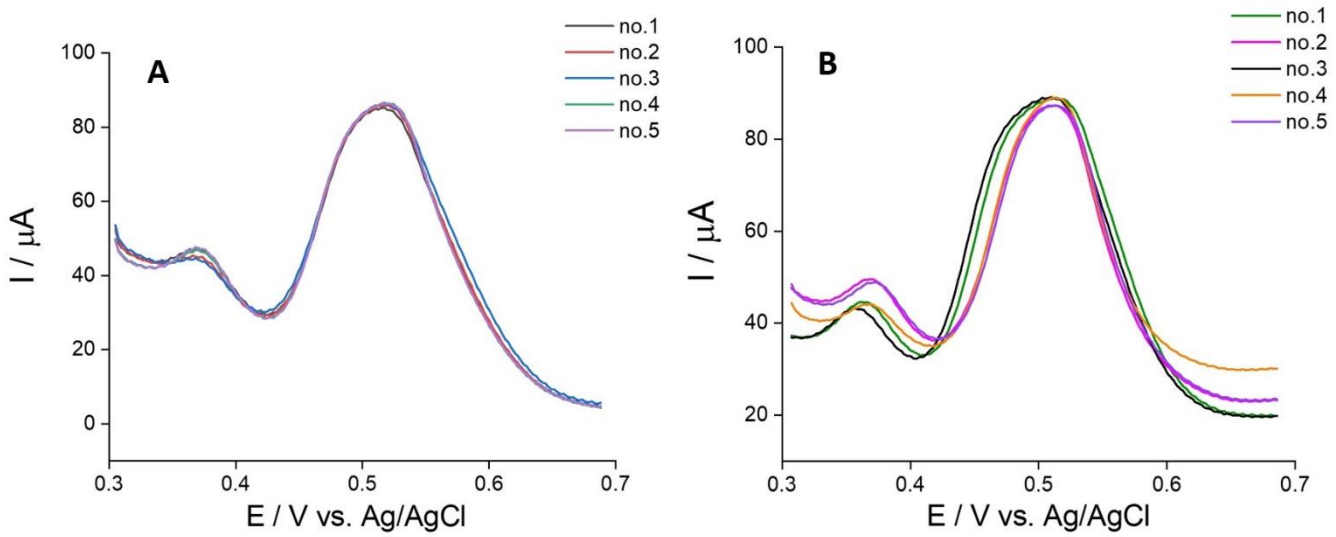

Figure 7. (A) SW Voltammograms acquired as part of the repeatability study and (B) of the reproducibility study in the electrochemical oxidation of 1 mM gallic acid at pH 1.8 over *r*GO/GCE; SWV pulse size 10 mV; frequency 15 Hz; potential step 2.5 mV.

We also reasoned that some cations, including Ni^{2+}, Zn^{2+}, Na^{+}, and K^{+}, could potentially interfere with the signal of gallic acid due to the formation of complexes, and were also investigated. The results also indicated that the presence of these metal ions, even at concentrations 300-fold higher than those of gallic acid, did not cause any considerable change in the peak current of gallic acid. The results demonstrate that despite the presence of these common interferents, the *r*GO/GCE electrode can still be used for the determination of gallic acid thanks to its good selectivity**.**

Table 3. Effect of various interferents on the peak current in gallic acid determination with the *r*GO/GCE electrode in this work.

Substance	**Amount (mM)**	**Peak current (µA)**	**% Deviation**
60 µM gallic acid	-	95.14	-
$NiSO_4$	18	96.28	+1.20
$ZnCl_2$	18	89.50	-5.93
Na_2CO_3	18	99.00	+4.06
KNO_3	18	90.63	-4.74
Caffeine	0.54	99.44	+4.52
Ascorbic acid	0.54	92.89	-2.36

3.6 Validation of the rGO-modified electrode design for gallic acid determination

The validity of the proposed method for gallic acid determination was then examined in water and tea samples, which contained 0.1 M citrate buffer pH 1.8. Gallic acid standards of known concentrations were also spiked into the samples in order to evaluate the percentual recovery. The determination of gallic acid in the samples was performed by the standard addition method. No gallic acid was found in the drinking water sample, while the concentration of gallic acid in the green tea sample was 8.77$\pm$ 0.17 µM (n =3), which corresponds to 0.037 mg gallic acid/mg green tea. The recoveries for gallic acid in the beverage samples are close to 100%, showing the suitability of the electrode for the quantitative analysis of gallic acid.

Table 4. Recovery test for gallic acid in drinking water and green tea samples (n = 3).

Sample	Original conc. measured (µM)	Added (µM)	Detected (µM)	%Recovery	%RSD
Drinking water	-	5	5.21	104.2	2.88
Green tea	8.77	5	14.91	108.27	1.94

4. CONCLUSION

In this work, an electroanalytical method for gallic acid quantification using reduced graphene oxide (*r*GO) on glassy carbon electrode (GCE) was demonstrated. *r*GO can be prepared by the electrochemical reduction of graphene oxide, thus improving the electrical conductivity and chemical surface for this determination. The electrochemical behavior of the *r*GO-modified electrode for the oxidation of gallic acid was investigated by cyclic voltammetry and square-wave voltammetry. The *r*GO-modified electrode displayed high sensitivity, a wide linear analytical range, as well as a low detection limit for gallic acid determination. The proposed method was successfully applied to the quantification of gallic acid in beverage samples, including tea and drinking water. The results obtained were reproducible with %RSD less than 5% and yielded a good percentual recovery, making it suitable for real applications.

ACKNOWLEDGEMENTS
The authors thank the Thailand Research Fund (TRF) and Office of the Higher Education Commission (MRG) Grant No. MRG6180072 for financial support.

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