Bulgarian Chemical Communications, Volume 56, Special Issue D (pp. 116-120) 2024 DOI: 10.34049/bcc.56.D.S1P43

Electrochemical response of gallic acid on activated glassy carbon electrode

D. T. Hadzhiev, T. M. Dodevska*, I. G. Shterev

Department of Organic Chemistry and Inorganic Chemistry,
University of Food Technologies, 26, Maritsa Blvd., Plovdiv 4002, Bulgaria

Received: November 3, 2023; Revised: April 11, 2024

A simple and sensitive electrochemical method for the quantitative determination of gallic acid (GA) using an electrochemically activated glassy carbon electrode (EAGCE) is reported. The electrochemical pre-treatment of the electrode was carried in 0.1M H_2SO_4 by cycling between 0.0 and 1.5 V (*vs*. Ag/AgCl, 3M KCl) for 10 cycles using cyclic voltammetry technique. The electrochemical properties of the suggested electrode and the voltammetric behavior of GA were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The prepared electrode EAGCE exhibited good sensitivity, selectivity and reliability in the electroanalysis of GA. Interference studies indicate that common ions (Na^+, NH_4^+, Mg^{2+}, Cu^{2+}, Cl^-, NO_3^-, CO_3^{2-}, and PO_4^{3-}), as well as some organic acids (ascorbic, oxalic, citric, salicylic, and tartaric acid) do not interfere with the GA assay. The proposed metal-free catalyst has cost-effective and good performance to GA determination.

Keywords: gallic acid; sensor; electrochemical sensor; electrochemical analysis; electrochemical activation, electrocatalysis

INTRODUCTION

Recently, gallic acid (3,4,5-trihydroxybenzoic acid, GA) has received considerable attention because of its multiple applications. GA is a strong natural antioxidant present in a wide variety of fruits, vegetables, green tea, black tea and several other plants. A number of studies confirmed that GA possesses various biological functions such as scavenging of free radicals, anti-inflammatory and antitumor activity, protection against cardiovascular diseases, which lead to its popularity and rapid adoption in medical and pharmaceutical industries [1-5]. Additionally, GA is generally accepted as a reference standard when determining the total polyphenolic content in plants, and the resultant GA equivalents are used to indicate the antioxidant level of the plant extracts. Thus, GA content in many natural products and beverages is considered as a benchmark for their quality.

Owing to the bioactive and pharmacological importance of GA, the development of new reliable, sensitive, easy to use, and time-saving analytical methods for GA determination is of great interest [6]. The presence of three hydroxyl groups (-OH) and one carboxylic group (-COOH) in GA molecule make it highly electroactive, thus electroanalytical methods are appropriate for its assessment [7]. Several research papers report on the application of electrochemical methods for the quantification of GA using, in particular, carbon-based electrodes modified with different electrocatalytic materials: metal nanoparticles [8], metal oxide nanoparticles [9, 10], carbon nanotubes [11, 12], graphene [13, 14], graphene oxide [15, 16], metal-organic frameworks [17, 18], conductive polymers [19].

Herein, we report a cost-effective, simple and sensitive electrochemical method for the quantitative detection of GA using an electrochemically activated glassy carbon electrode (EAGCE). The electrochemical activation process may generate various oxygen-containing functional groups (hydroxyl, carbonyl, carboxyl, quinone, etc.) on the surface of the glassy carbon. These functional groups could act as electron acceptors in the target reaction of oxidation of GA that can improve the sensitivity and selectivity of the sensing platform. In fact, the sensing platform is non-expensive, no hazardous or highly pure solvents are required, and no modifications are necessary. The electro-activation method used in this work only requires the application of a potential on the bare GCE immersed in the supporting electrolyte before measurements. The electrochemical activation of the GCE is fast, easy and reproducible, and the measurement of GA by DPV shows considerable sensitivity and reliability.

EXPERIMENTAL

Materials and Apparatus

H_2SO_4, $NaNO_3$, NaCl (Merck); NH_4Cl, $MgCl_2$, $CuSO_4.5H_2O$, Na_2CO_3, Na_3PO_4, $Na_2HPO_4.12H_2O$,

* To whom all correspondence should be sent:
E-mail: dodevska@mail.bg

$NaH_2PO_4.2H_2O$, (Fluka). Gallic acid, ascorbic acid, oxalic acid, citric acid, salicylic acid, and tartaric acid were purchased from Sigma-Aldrich. All the chemicals were of analytical grade and used without any further purification. Double distilled water was used to prepare aqueous solutions. Phosphate buffer solutions (pH = 1.0, 3.0, and 7.0) were ready by mixing of 0.1M NaH_2PO_4 and 0.1M Na_2HPO_4 and adjusting the solution pH to the required value with H_3PO_4 and/or NaOH.

EmStat2 potentiostat (PalmSens BV, The Netherlands) controlled by a PC running PSTrace software version 5.5. The electrochemical cell was composed of a common three-electrode system: GCE with a surface diameter of 3 mm (Metrohm Autolab BV, The Netherlands) as a working electrode, platinum wire as a counter-electrode, and Ag/AgCl (3M KCl) as a reference electrode. All potentials in this study were reported *vs*. this reference electrode.

Procedures

The surface of the GCE was mechanically cleaned *via* polishing using 0.05 μm alumina slurry on a microcloth, sonicated in double distilled water for 5 min, followed by thorough rinsing with ethanol and double distilled water. The cleaned GCE was immersed in 0.1 M H_2SO_4 and conditioned by cyclic voltammetry. The activation process was carried out by sweeping the GCE in the potential range between 0.0 V and +1.5 V (*vs*. Ag/AgCl, 3M KCl) for 10 cycles at a scan rate of 100 mV s^{-1}. The electrochemically activated electrode (EAGCE) was then directly used for the measurements.

The measurements were carried out at ambient temperature (25 ± 3 °C). The experimental data analysis was performed using software package 'OriginPro 2015'. For the calibration curve, each point was obtained by the average peak intensity of three consecutive DPV measurements. The linearity was evaluated using the least-square regression method.

RESULTS AND DISCUSSION

Electrooxidation of GA on bare GCE

The electrochemical behavior of GA on bare GCE was initially investigated in 0.1M H_2SO_4 using cyclic voltammetry at a scan rate of 100 mV s^{-1}. As shown in Fig. 1, in the presence of GA (500 μM) one oxidation peak appears at about 0.63 V, but no reduction peak can be detected over the whole potential range. This finding suggests irreversibility of the GA oxidation process at the GCE surface.

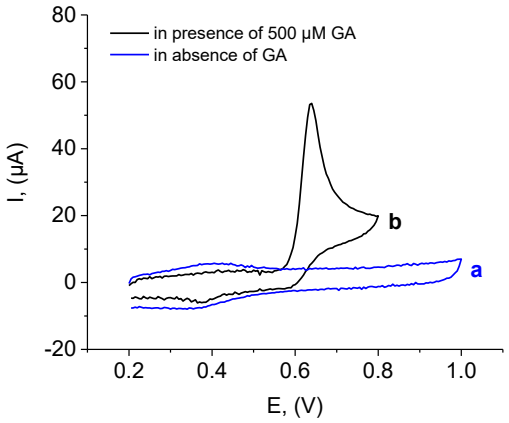


Figure 1. CVs of the bare GCE in the absence (curve a) and presence of 500 μM GA (curve b). Supporting electrolyte 0.1M H_2SO_4; scan rate 100 mV s^{-1}.

The effect of pH value of the supporting electrolyte on the electrochemical response of GCE toward GA oxidation was investigated by DPV in phosphate buffer of different pHs (1.0, 3.0, and 7.0) in the presence of GA. The obtained results are presented in Fig. 2. The anodic peak potentials of GA are shifted toward the more negative direction with decreasing proton concentration. It can be observed that the relationship of peak potential Ep *vs.* pH is linear and described by equation Ep (V) = −0.05214 pH + 0.5899. According to the Nernst equation, the slope of 0.0521 V pH^{-1} is close to the expected theoretical value of 0.0591 V pH^{-1} which indicates the transfer of an equal number of electrons and protons in the electrooxidation process. The oxidation mechanism of GA in acidic solutions occurs *via* two electrons and two protons transfer. The results were in line with the findings of previous studies [9-12].

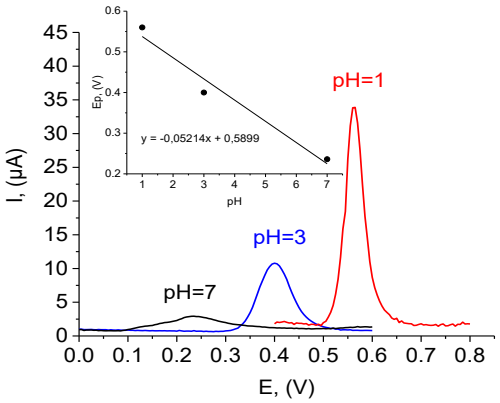
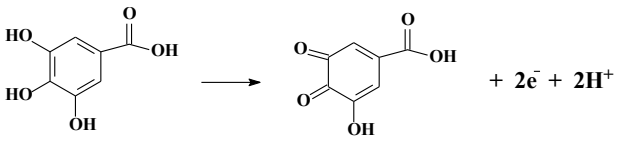


Figure 2. DPVs obtained at the bare GCE in the presence of 300 μM GA in supporting electrolyte phosphate buffer of various pHs. Inset: the relationship of the anodic peak potential for GA oxidation as a function of pH of the buffer solution.

Direct electrochemical oxidation of GA at the GCE is facile; at pH ≤ 4.24 GA undergoes a $-2e^-$, $-2H^+$ process to form quinone (Scheme 1). As can be seen from the results presented in Fig. 2, the oxidation peak of GA becomes lower with the increase of pH from 1.0 to 7.0. It was found that at pH 1.0 the well-shaped, the most symmetrical and intense peak of GA oxidation was obtained.



Scheme 1. Oxidation of GA.

Electrooxidation of GA on EAGCE

The electrochemical oxidation of GCE altered the surface chemistry of the electrode because of the increased number of different oxygen functionalities which affect hydrophilicity. This procedure activates the electrode surface, leading to faster electron transfer kinetics.

Immediately after the electrochemical activation, the electrode EAGCE was directly used for the measurements in the same electrolyte (0.1M H_2SO_4 solution). The experimental results clearly show that the electrochemical signals of GA were increased by the application of the electro-activation procedure. Fig. 3 presents CV curves of GCE and EAGCE in supporting electrolyte 0.1M H_2SO_4 in the presence of 300 µM GA under certain testing conditions (pH = 1.0; potential range from 0.2 to 0.8 V; scan rate of 100 mV s^{-1}). It can be clearly observed that the peak current at EAGCE (curve b) is twice as high as that at GCE (curve a). Owing to the specific oxygen-containing functional groups and the outstanding conductivity of EAGCE, the proposed sensing platform exhibits an enhanced oxidation peak current of GA when compared with non-activated GCE. This indicates that the electrochemical activation of GCE can facilitate the electron transfer at the electrode surface and enhance the adsorption of GA. Thus, the peak current enhancement at EAGCE is attributed to the increased adsorption active sites and effective surface area, as well as to the improvement of electron transfer ability and high electrocatalytic activity of the EAGCE.

Using EAGCE a series of DPVs for increasing concentrations of the analyte GA were recorded. The measurement signal was the current value read at 0.59 V, which corresponds to the potential of the GA peak maximum. The peak height was used for quantification, and each analytical signal was recorded in triplicate.

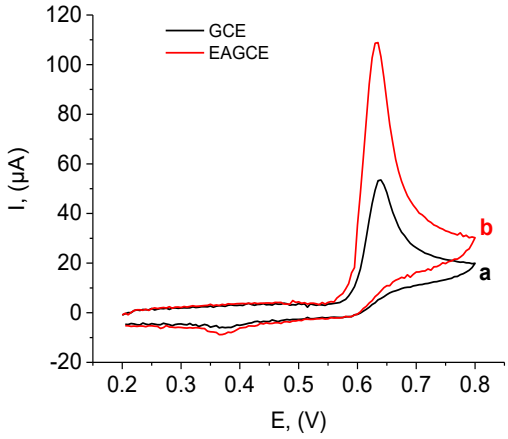


Figure 3. CVs of 500 µM GA in 0.1M H_2SO_4 on bare GCE (a) and EAGCE (b).

From the records presented in Fig. 4 it can be observed that the current linearly increases with the concentration of GA in two ranges. The first one is up to 0.5 mM GA with a linear regression equation I (µA) = 0.1154C (µM) + 4.3622 and a correlation coefficient of 0.988. The electrode shows electrochemical sensitivity of 1.6323 µA $µM^{-1}$ cm^{-2} (normalized to the electrode geometric surface area). In the concentration range from 0.5 to 1.5 mM GA the linear regression equation is I (µA) = 0.03063C (µM) + 48.16; the sensitivity and the correlation coefficient are 0.4332 µA $µM^{-1}$ cm^{-2} and 0.999, respectively. The limit of quantification (LOQ) was calculated to be 8 µM (S/N = 10).

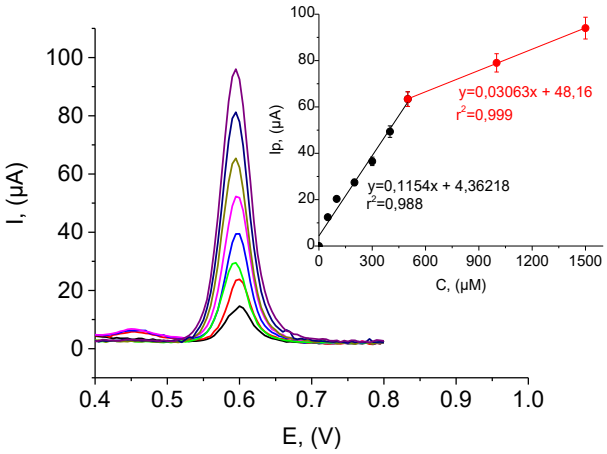


Figure 4. DPV response for various concentrations of GA at EAGCE. Inset: corresponding calibration plot (n=3). Supporting electrolyte: 0.1M H_2SO_4.

The selectivity of the EAGCE-based sensing platform was examined with common interfering organic substances and inorganic ions that may alter the registered DPV signals. The influence of each possible interfering compound was examined by the comparison between peak current of 500 µM GA

and peak current of GA in the presence of interfering ion/molecule. Results indicated that 6-fold amounts of ascorbic acid (AA), oxalic acid (OA), citric acid (CA), salicylic acid (SA), and tartaric acid (TA) and 30-fold amounts of $NaNO_3$, NaCl, NH_4Cl, $MgCl_2$, $CuSO_4$, Na_2CO_3, and Na_3PO_4 did not practically affect the detection of GA (signal change below 5%). Fig. 5 shows the effect of 6-fold addition of AA, OA, and CA on the DPV-response toward 500 µM GA. These findings suggest that the proposed electrode EAGCE has a good selectivity for GA and could be used as a reliable and cost-effective sensing platform for selective detection of GA in real samples.

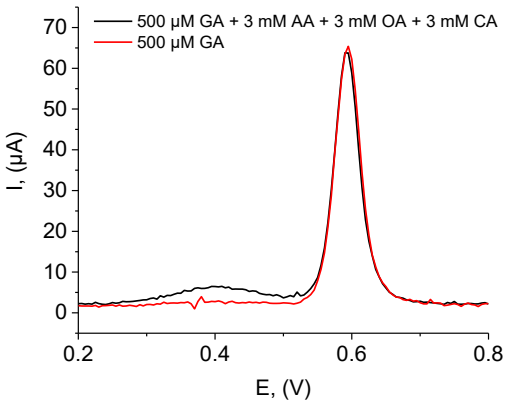


Figure 5. Effect of addition of 3 mM AA, OA, and CA on DPV response toward 500 µM GA. Supporting electrolyte: 0.1M H_2SO_4.

Usually, poor reproducibility of the current signal was encountered when carbon-based electrodes were applied in the determination of phenol derivatives by means of electrochemical oxidation, and the same electrode could not be used for the next measurement. In regard to the electrochemical oxidation of GA, a number of researchers reported a severe surface fouling accompanied by the adsorption of oxidized products.

In this work potential cycling was employed as a regeneration and activation process, i.e. the electrode surface could be renewed by activation process and it was found to give reproducible results. Good reproducibility (RSD of 4.2%) was observed for 5 replicate DPV measurements in the presence of 100 µM GA. The low RSD value reveals the fact that EAGCE used in this work provides precise measurements for GA sensing. The sensitivity could be restored even after an intensive fouling of electrode surface using the electrochemical activation procedure to generate new active sites for use in subsequent experiments.

Here we outline future research directions in the upcoming study. Our future work will be oriented toward optimization of the various parameters such as electrolyte concentration, number of cycles, and oxidation potential window to achieve the best performance against GA. The second direction of the research will be to demonstrate the application of the proposed platform for direct electrochemical sensing of GA in a real sample (green tea extract).

CONCLUSION

Electrochemical oxidation is a simple, controllable and reproducible method for processing a GCE. In the present work, an electrochemically activated GCE was proven to be a useful sensing platform for GA quantitative detection. The electroanalytical properties were improved after the working electrode was activated which was ascribed to the attribution of surface oxygen containing functional groups and increased hydrophilicity. By incorporating electrochemical activation of GCE as a part of the analysis procedure, the effect of fouling of electrode surface was sufficiently minimized to achieve reliable measurements. The benefits of using the EAGCE presented here instead of the more complex modified ones are based on the absence of obstructions related to long-term stability. As the working electrode can be regenerated by a fast, simple electrochemical procedure *in situ*, this method of reactivating the electrode surface will keep the catalyst active in long-term experiments and repeated measurements. Furthermore, the use of EAGCE avoids the use of costly and time-consuming surface functionalization procedures.

REFERENCES

1. B. Badhani, N. Sharma, R. Kakkar, *RSC Adv.*, **5**, 27540 (2015).
2. N. Nayeem, S. M. B. Asdaq, H. Salem, S. Ahei-Alfqy, *J. App. Pharm.*, **8**, 213 (2016).
3. J. Bai, Y. Zhang, C. Tang, Y. Hou, X. Ai, X. Chen, Y. Zhang, X. Wang, X. Meng, *Biomed. Pharmacother.*, **133**, 110985 (2021).
4. N. Jabbari, M. Feghhi, O. Esnaashari, H. Soraya, J. Rezaie, *BioImpacts*, **12(6)**, 549 (2022).
5. M. S. Bhuia, M. M. Rahaman, T. Islam, M. H. Bappi, M. I. Sikder, K. N. Hossain, F. Akter, A. A. S. Prottay, M. Rokonuzzman, E. S. Gürer, D. Calina, M. T. Islam, J. Sharif-Rad, *Chin. Med.,* **18**, 27 (2023).
6. F. H. Fernandes, H. R. Salgado, *Crit. Rev. Anal. Chem.*, **46**, 257 (2016).
7. M. Badea, F. Di Modugno, L. Floroian, D. M. Tit, P. Restani, S. Bungau, L. Aleya, *Sci. Total Environ.*, **672**, 129 (2019).
8. S. A. Shahamirifard, M. Ghaedi, Z. Razmi, S. Hajati, *Biosens. Bioelectron.*, **114**, 30 (2018).
9. F. Gao, D. Zheng, H. Tanaka, F. Zhan, X. Yuan, F. Gao, Q. Wang, *Mater. Sci. Eng. C*, **57**, 279 (2015).
10. J. Tashkhourian, S. F. Nami-Ana, *Mater. Sci. Eng. C*, **52**, 103 (2015).

11. H. Zhao, Q. Ran, Y. Li, B. Li, B. Liu, H. Ma, S. Komarneni, *J. Mater. Res. Technol*., **9(4)**, 9422 (2020).
12. H. Zhao, Y. Liu, F. Li, G. Zhu, M. Guo, J. Han, M. Zhao, Z. Wang, F. Nie, Q. Ran, *Ceram. Int.*, **49(16)**, 26289 (2023).
13. M. Chen, H. Lv, X. Li, Z. Tian, X. Ma, *Int. Electrochem. Sci*., **14**, 4852 (2019).
14. Z. Liang, H. Zhai, Z. Chen, H. Wang, S. Wang, Q. Zhou, X. Huang, *Sens. Actuat. B: Chemical*, **224**, 915 (2016).
15. J. Węgiel, B. Burnat, S. Skrzypek, *Diam. Relat. Mater*., **88**, 137 (2018).
16. R. Abdel-Hamid, A. Bakr, E. F. Newair, F. Garcia, *Beverages*, **5(1)**, 11 (2019).
17. J. Chen, Y. Chen, S. Li, J. Yang, J. Dong, *Colloid. Surface.,* **650**, 129318 (2022).
18. J. Li, Y. Yang, Y. Li, P. Zhao, J. Fei, Y. Xie, *Food Chem.*, **429**, 136900 (2023).
19. V. Krishnan, E. Gunasekaran, C. Prabhakaran, P. Kanagavalli, V. Ananth, M. Veerapandian, *Mater. Chem. Phys.*, **295**, 127071 (2023).