Anal. Bioanal. Electrochem., Vol. 15, No. 11, 2023, 924-937
https://www.doi.org/10.22034/abec.2023.709094

Analytical & Bioanalytical Electrochemistry

2023 by CEE
www.abechem.com

Full Paper

Quantitative Determination of Quercetin in Black Tea and Beet Juice using SWAdSV onto The Pencil Graphite Electrode Surface

Nagihan Durmuş,[1] and İbrahim Ender Mülazımoğlu[2,*]

[1]*Necmettin Erbakan University, Institute of Science, Chemistry Department, Konya, Turkey*
[2]*Necmettin Erbakan University, Chemistry Department, Konya, Turkey*

*Corresponding Author, Tel.: +905061064651
E-Mail: iemulazimoglu@erbakan.edu.tr

Received: 25 August 2023 / Received in revised form: 25 October 2023 / Accepted: 16 November 2023 / Published online: 30 November 2023

Abstract- In this study, a new electroanalytical method has been developed for the determination of quercetin (Que), an important flavonoid derivative, in natural samples. Pencil graphite electrode (PGE) was used for the determination of Que in black tea and beet juice samples, these determinations were done by square wave adsorptive stripping voltammetry method (SWAdSV). When using the PGE, which has a wide and active surface, a significant increase was observed in the oxidation peak current of Que. Calibration graphs were drawn in the range from 9.67 ng mL^{-1} to 411 ng mL^{-1} (from 3.2×10^{-8} mol L^{-1} to 1.36×10^{-6} mol L^{-1}) using 0.1 M PBS at the optimum parameters determined for quantitative determination of Que. Thus, the amount of Que in beet juice and black tea samples was determined as 10.33 ng mL^{-1} (3.42×10^{-8} M) and 16.0 ng mL^{-1} (5.3×10^{-8} M), respectively. As a result of these processes using the SWAdSV technique, Limit of Detection (LOD) and Limit of Quantification (LOQ) values were calculated as 0.51 ng mL^{-1} (1.7×10^{-9} M) and LOQ 1.54 ng mL^{-1} (15.1×10^{-9} M), respectively. With this study, the determination of Que in natural samples without any interference effect has been demonstrated with the method developed using the PGE, which is very easy to access renewable and also cheap.

Keywords- SWAdSV; Quercetin; Flavonoid; PGE; Chemical Sensor Electrode

1. INTRODUCTION

Flavonoids are one of the major groups of phenolic compounds. Flavonoid term refers to a class of aromatic, oxygen-containing heterocyclic pigments widely distributed among higher plants as secondary metabolites. Flavonoids are known for being a prominent group of compounds characterized by the presence of hydroxyl groups attached to ring structures. These molecules belong to a large family of compounds with a common diphenylpropane structure ($C_6C_3C_6$) with different degrees of hydroxylation, oxidation, and substitution [1].

Flavonoids, which are found extensively not only in wine and tea but also in the fruits and vegetables from which these products are made, are also divided into different subtitles. Flavonols (3-hydroxy derivatives), of which quercetin (3,3′,4′,5,7-pentahydroxyflavone) can be given as an example, are one of them. Quercetin has a very dominant structure and is found in many medicinal plants and teas, especially dark-colored fruits, and vegetables [2].

In recent years, there has been a significant interest in Quercetin due to its anticancer, anti-allergic, anti-inflammatory, and antiviral properties. This molecule is an ingredient in supplements, beverages, and foods [3,4]. It also acts as an anti-mutagen which accelerates cell oxidative damage and protects human colonocyte DNA from oxidative attack in vitro.

Considering that quercetin is often used as a reference material for determining the antioxidant activity of various substances, there is an increase in its determination in various plant samples, foods, dietary supplements, and pharmaceutical preparations. In the last decade, several analytical methods have been reported in the literature for the determination of quercetin, either alone or simultaneously with other flavonoids in different matrices (natural sources, marketed food products, dietary supplements, biological fluids, etc.). In fact, several methods were reported for the determination of flavonoid compounds in natural sources including high-performance liquid chromatography (HPLC) [5], HPLC with UV detection [6], HPLC coupled with mass spectrometry (MS) [7], spectrophotometry [8], and solid phase extraction [9]. These methods are highly sensitive and effective but often require some complicated and time-consuming sample pretreatment.

Despite extensive research conducted over many years, it is well-established that PGE exhibits high surface activity. However, its utilization as a biosensor in new electroanalytical techniques has been sporadic, mainly due to a lack of comprehensive information on how to effectively harness its active surface. Achieving this requires a thorough stability and calibration study [10-13]. PGE has a larger active electrode surface area and is therefore efficient in detecting low concentrations and/or volume of the analyte [14]. The researcher concluded that the PGE is commonly a carbon-based electrode, it is less expensive, more useful, and more easily renewable compared to other electrodes such as CPE or GCE [15,16].

Anodic stripping voltammetry (ASV) is a versatile electroanalytical technique for trace metals determination in various environmental, clinical, and industrial samples. Stripping methods are important in trace analysis because the electrodeposition step concentrates the

analyte on the electrode surface, enabling its determination even in extremely low quantities with reasonable accuracy [17,18].

2. EXPERIMENTAL SECTION

2.1. Chemicals and reagents

Quercetin and other chemicals were of analytical-reagent grade purchased from Sigma-Aldrich. All reagents' solutions were prepared with ultra-pure quality water with a resistance of 18.2 MΩ cm (MP Minipure DestUp Ultra-Pure Water System, Ankara, Turkey). Since quercetin possesses poor aqueous solubility (60 mg mL^{-1} in water) with strong hydrophobic property [19] the stock solution of quercetin (0.04 mg mL^{-1}) was prepared by dissolving it in 5 ml ethanol and then diluting with redistilled water to 25 mL. The working solutions are stored at 4 °C when not in use. Two different buffer solutions, namely Britton-Robinson buffer (BR, pH=2–10) and phosphate buffer (0.1 M, pH=6.8-7.3) solutions were used. The PBS was prepared by mixing 0.05 mM Na_2HPO_4 and 0.05 mM NaH_2PO_4 and then adjusting the pH by the addition of NaOH or HCl. BR buffer solution, which was prepared from H_3PO_4 + CH_3COOH + H_3BO_3 according to preparation conditions in the literatures [20-23] and then adjusting the pH by the addition of 0.2 M or 1 M NaOH.

2.2. Apparatus

All voltammetric measurements have been performed on GAMRY Reference 600+ and PCI4/Series750 Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA) electrochemical analyzer. All electrochemical experiments were conducted in a three-electrode single-compartment glass cell with a volume of 10 mL. This cell consisted of a PGE saved as the working electrode. Ag/Ag^+ (10 mM $AgNO_3$) (BAS Model MF-2042) for non-aqueous media and an Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used as reference electrodes. Pt wire (BAS Model MW-1032) was used as a counter electrode. VWR pH 1100L pH meter (PA, USA) was employed for pH measurements.

Ultra-pure quality water with a resistance of 18.2 MΩ cm (MP MINIPURE purification system, DEST UP, USA) was used to prepare all aqueous solutions, measurements, cleaning of the glassware, and polishing the electrodes.

The body of the self-made PGE was a pencil lead. The pencil leads (Faber Castell, Germany, black lead of degree 2B) were purchased from a local bookstore. All leads had a total length of 60 mm and a diameter of 0.7 mm. The pencil leads were used as received. A crocodile clip was used as a holder. Electrical contact with the PGE was achieved by soldering a copper wire to the end of the crocodile clip that held the lead in place. A total of 10 mm of lead was immersed in solution per measurement. To obtain a more sensitive and stable analytical signal, the PGE was first subjected to SWAdSV between -0.3 V to 0.4 V

several times in the blank supporting electrolyte (SE), until reproducible behavior was observed [12].

2.3. Measurement procedures

The electrochemical behavior of Que was investigated in a PBS, dissolved 20% (v/v) ethanol, by cyclic voltammetry (CV), at PGE. In the study, PBS and 20% ethanol mixture were used as SE in the preparation of solutions of all flavonoid derivatives. The potential range was varied from -0.2 V to +0.75 V at a scan rate of 100 mV s^{-1} for CV analysis. SWAdSV was employed for the quantification of Que in real samples. The best electrode and the highest current of pH, PBS was used for quantitative analysis. Square wave voltammetry (SWV) was applied between -0.3 V and +0.4 V with the following instrumental parameters: pulse amplitude E_{sw} = 50 mV, frequency f = 25 Hz, and scan increment Ds = 1 mV.

The three-electrode system was immersed in a voltammetric cell. A selected pre-concentration potential was then applied to the previously treated PGE electrode surface for a selected pre-concentration period, while the solution was stirred at 450 rpm. Following this period, the stirring was stopped, and a 5 s rest period was allowed for the solution to become quiescent. Then the voltammogram was recorded by scanning the potential toward to positive direction from -0.3 V to +0.4 V using SWV form. All measurements were performed in triplicate at laboratory temperature.

2.4. Preparation of The Real Samples

Pickled beets were prepared completely natural. First, the beets were washed, chopped, and put in 3 liters of hot water. After the water cooled, 1 cup of apple cider vinegar, 10 cloves of garlic, and 3 tablespoons of rock salt were added. The prepared mixture was kept in a place that was not exposed to the sun for 10 days. After 10 days it was stored in a cool place. 1 mL of the sample was placed into a 25 mL flask, which was completed to the volume with 5 mL ethanol and 19 mL 0.1 M PBS.

Black tea, which is widely used on the market, was purchased and two small packages of tea were brewed for 20 minutes with 500 mL of hot water. 5 mL of the sample was placed into a 25 mL flask, which was completed to the volume with 5 mL ethanol and 15 mL 0.1 M PBS. 100 μL of prepared solutions were transferred to the voltammetric cells containing 2 mL ethanol and 8 mL 0.1 M PBS (pH 7.1). Que was added to the solutions by the standard addition method and the amount of Que present in the samples was calculated against the peak currents obtained.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric behavior of Que on PGE

CV was used to identify the electrochemical behavior of Que on PGE within the potential range from -0.3 V to +0.75 V at a scan rate of 100 mV s^{-1}. As can be seen in Figure 1 Que exhibits an anodic peak at about +0.027 V in 0.10 M PBS, dissolved in 20% (v/v) ethanol (pH=7.1).

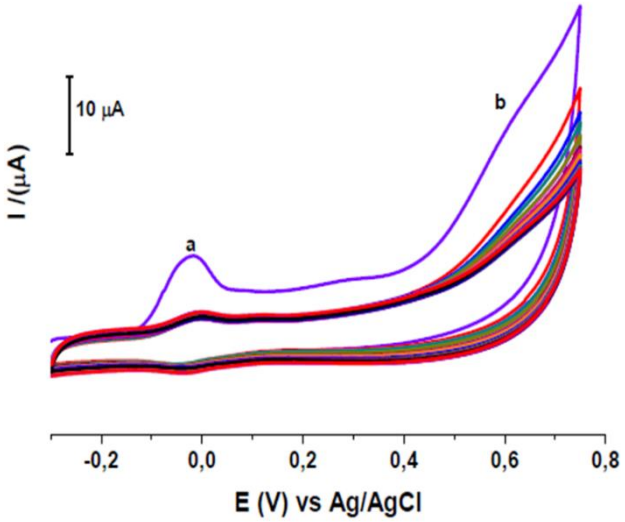

Figure 1. Cyclic voltammogram of PGE in 1.32×10^{-4} M Que in 5 mL EtOH + 20 mL PBS mixture, pH 7.1, *vs.* Ag/AgCl/(3 M KCl), 30 cycles; the sweep rate is 100 mV s^{-1}.

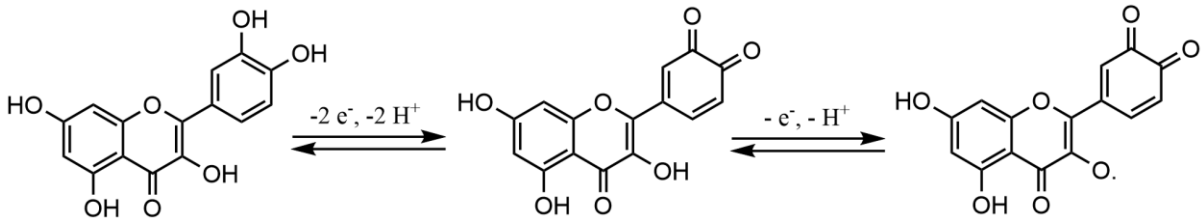

Figure 2. The oxidation mechanism proposed for quercetin onto the PGE electrode in 100 mM tetrabutylammonium tetrafluoroborate (NBu_4BF_4) (in CH_3CN) [23]

Although the number of peaks observed is different and depends on the experimental conditions, most of the authors have reported three peaks for the oxidation of Que. The first (the less positive potential) one has been attributed to the relatively reversible oxidation of hydroxyl groups in the B-ring-forming quinone species. The second peak is associated with the irreversible oxidation of the hydroxyl group in the C ring, while the third peak (the most positive potential) is linked to the irreversible oxidation of the 5,7-dihydroxy substituents in the A ring [24]. The observation of a single oxidation peak in Figure 1 compared to these known data indicates that Que is in very low potential and all active probes can be oxidized simultaneously in PBS and in the presence of a PGE. This suggests that PGE may be more susceptible to Que in PBS media.

3.2. Influence of SE and pH

Que is a substance with very low solubility in water. Therefore, as mentioned in the literature, to increase the solubility and to obtain a better result in quantitative determinations, we first dissolved Que in ethanol and supplemented the solution with SE. The voltammogram obtained by dissolving quercetin in ethanol in different proportions is shown in Figure 3. The highest peak current was obtained in a 20% ethanol solution.

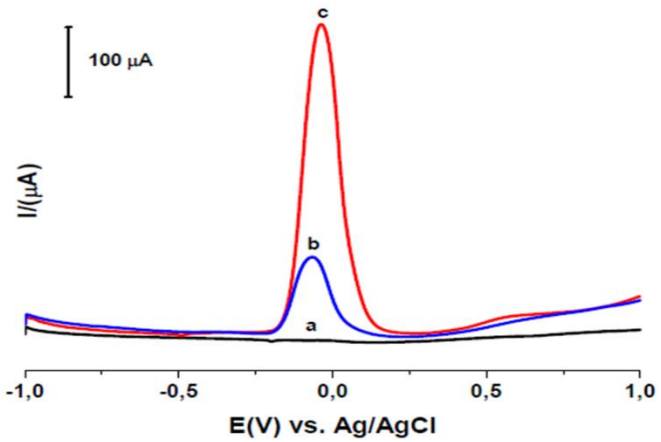

Figure 3. SWVs of PGE in different proportions of ethanol; (a) 80% ethanol-20% PBS, (b) 50% ethanol-50% PBS, (c) 20% ethanol-80% PBS

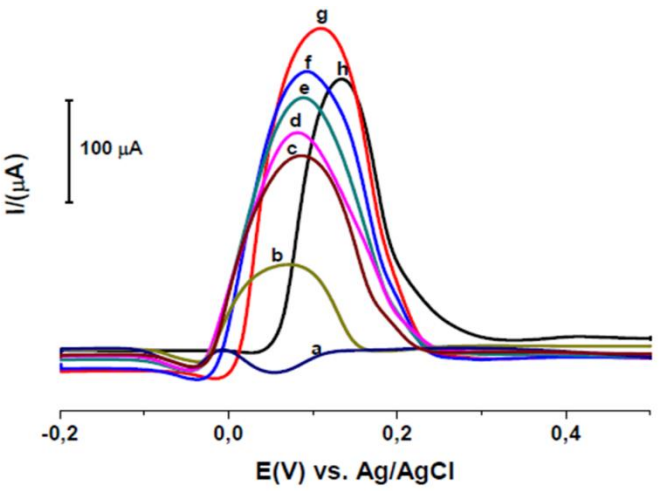

Figure 4. SWVs in different pH values in BR; (a) pH=9.0, (b) pH=8.0, (c) pH=7.0, (d) pH=6.0, (e) pH=5.0, (f) pH=4.0, (g) pH=3.0, (h) pH=2.0

In our study, two different buffer solutions (BR and PBS) were used. The pH between pH 2 and pH 9 was studied in BR buffer solution. Although the best results were obtained at pH 3 in BR buffer solution, it was observed that Que did not dissolve well in an acidic medium, and precipitation occurred in the solution in a short time. Precipitation was observed at all values below pH 6.5. Increasing of the basic properties of the solution also caused a

blackening of the solution. Therefore, the pH of the study was determined as close to neutral pH. The currents in PBS and BR buffer solution media at these pH values were compared and it was decided to continue the study with PBS, pH 7.1.

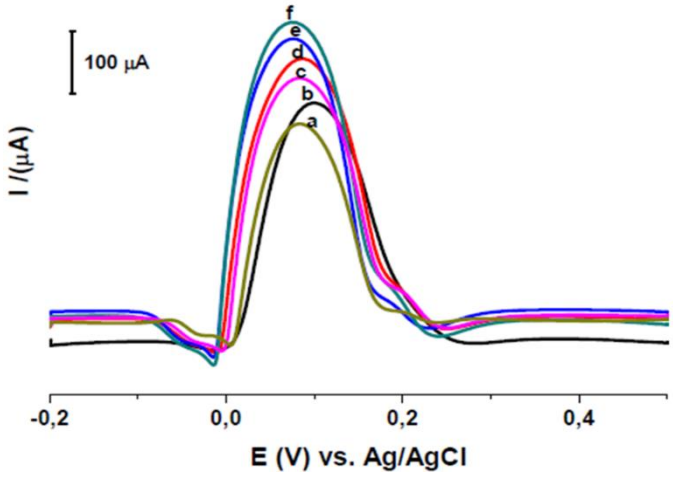

Figure 5. SWVs of Que in different pH values in PBS; (a) 7.3 (b) 6.8 (c) 7.2 (d) 6.9 (e) 7.0 (f) 7.1

3.3. Influence of Scan Rate

The obtained scan rate curve compared to the anodically obtained peak is shown in Figure 6. The change is linear in the range from 50 mV s^{-1} to 400 mV s^{-1}. This linearity tells us that the oxidation that takes place is diffusion-controlled.

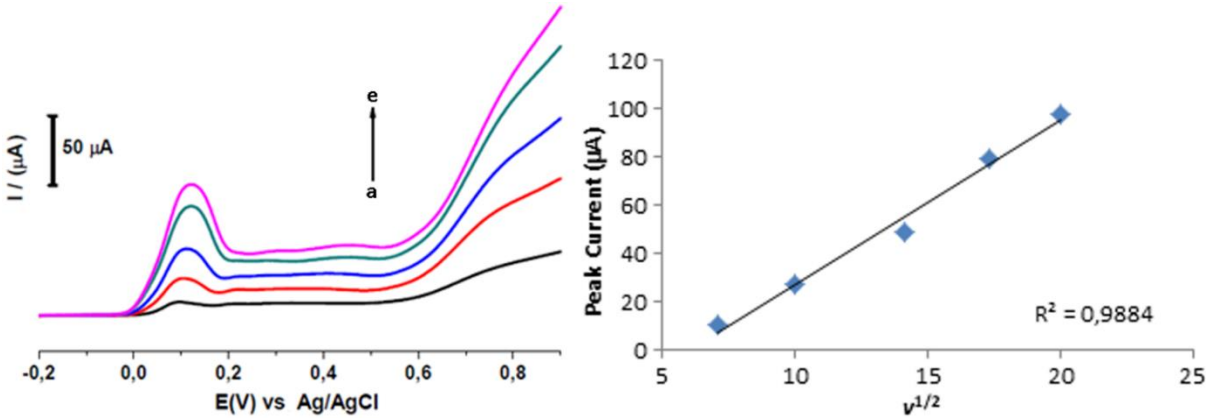

Figure 6. The overlayed images of Linear Sweep voltammograms (LSVs) of 1 mM Que with different scan rates for the PGE in 0.1 M PBS at pH 7.1. (a) 50 mV s^{-1}, (b) 100 mV s^{-1}, (c) 200 mV s^{-1}, (d) 300 mV s^{-1}, (e) 400 mV s^{-1}

The aim of the CV modification process is to attach the molecule to the surface in a diffusion-controlled manner. This method, which makes gluing easier, also gives a smooth

surface without stacking. Whether the binding was as intended was tested using different scan rates. According to the Randles-Sevcik equality from the two necessary conditions; First, the reciprocal $\boldsymbol{I_p}$ versus $\sqrt{\boldsymbol{\vartheta}}$ is linear; Second, it is enough to have a straight slope of 0.5 which is $\boldsymbol{logI_p}$ is plotted against $\boldsymbol{log\,\vartheta}$, only one of which is satisfied. In the study, the first of the conditions was evaluated [25-33]. The result of the first condition is shown in Figure 6.

3.4. Optimization of SWV Parameters

Next, it was attempted to optimize pulse parameters (frequency, f=5-30 Hz; scan increment, ΔEs =1-10 mV; square-wave amplitude, ΔEsw = 10-90 mV) on the stripping response for 40 μg mL^{-1} Que in PBS at pH 7.1 (not shown).

The frequency effect was studied in the range of 5 to 30 Hz. A peak current was obtained at each frequency studied. Peak currents increased as frequency increased. However, it was seen that voltammograms obtained from all frequency values except 25 Hz frequency were not a clear line. It was decided to work at a frequency of 25 Hz, considering that this negative effect would increase further if it was run at lower concentrations.

Pulse amplitude was examined in the range of 10 to 90 mV. As the amplitude increases, although the current obtained increases, it was decided to operate at 50 mV amplitude since the horizontal expansion of the peaks was observed at the potential values above 50 mV.

The influence of step potential was investigated between 1 and 10 mV. As with the amplitude of the pulse, a significant horizontal expansion of the peak was achieved and thus 1 step potential was studied.

Accumulation potential was examined between 0 mV and 50 mV and determined as 0 mV. Accumulation time was examined between 15 sec and 210 sec and determined as 150 sec.

3.5. Quantification of Que

In the optimum parameters determined for SWAdSV, analytical curves for quercetin in 20% ethanol 80% 0.1 M PBS at pH 7.1 using PGE. For this, aliquots from the Que standard solution were consecutively added to the electrochemical cell, and the SWV responses at a potential of +0.11 V were evaluated for each addition.

As seen from the illustration of Figure 7, the oxidation peak current value was proportional to its concentration from 9.67 ng mL^{-1} to 411 ng mL^{-1}, and the regression equation could be expressed by the equation: [I_p (μA) =0.035C (ng mL^{-1}) + 2.035 (r^2=0.984, n=13)] where I_p: is the adsorptive stripping peak current, C: Que concentration, r: the correlation coefficient, and n: the number of experiments. The LOD and LOQ values were found 0.51 ng mL^{-1} (1.7×10^{-9} M) and 1.54 ng mL^{-1} (15.1×10^{-9} M), respectively. They were calculated by using the formulas LOD=($C/_{S/N}$) ×3 and LOQ=3×LOD, where C: is the lowest

concentration of linearity range, S: is the peak current at the lowest concentration and N: is the noise of the voltammogram.

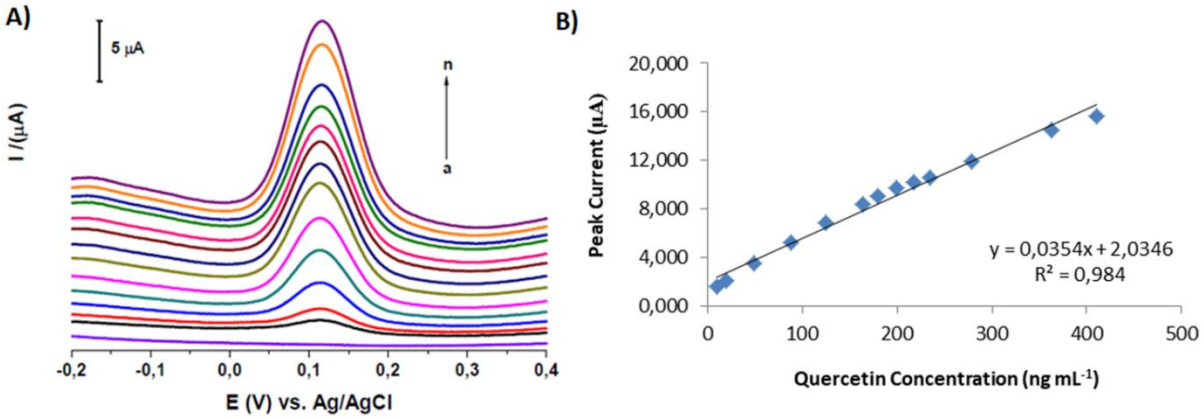

Figure 7. A) SWAdSVs for variation of Que concentration from 9.67 ng mL^{-1} to 411 ng mL^{-1} (32 nM to 1.36 µM) at the PGE in 0.1 M PBS at pH 7.1. Scan rate is 100 mV s^{-1}. B) Calibration Graph of the Ip vs. Que concentration in the range from 9.67 ng mL^{-1} to 411 ng mL^{-1}

As seen in the results; it is both cheaper and more practical to perform electrochemical measurements at relatively low concentrations with the PGE compared to more expensive commercial electrodes.

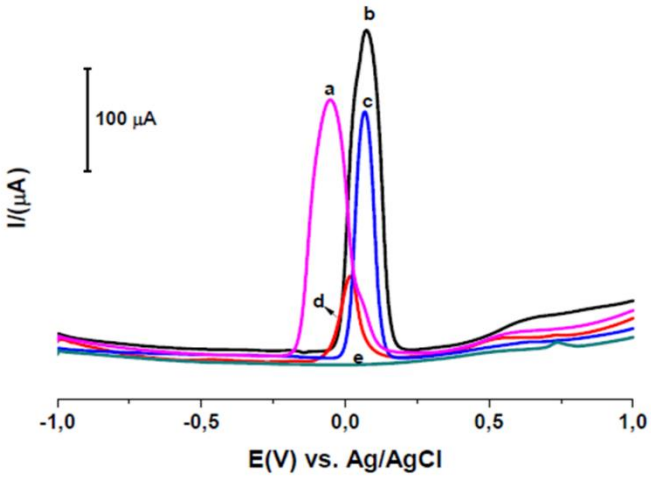

Figure 8. SWAdSVs for (a) Que, (b) Lut, (c) Rut and (d) Mor, and (e) SE at the PGE in 0.1 M PBS at pH 7.1 with scan rate 100 mV s^{-1}. The studied interfering agents were: Lut, Rut, and Mor (all concentrations are 1.32×10^{-4} M)

3.6. Interference effect

As shown in Figure 8 four different flavonoids were added to the SE. These flavonoids are Que, luteolin (Lut), rutin (Rut), and morin (Mor). All flavonoids contain two -OH groups

in ring B which are active in oxidation. These flavonoids are probably found together in foods and produce peak current at close potential values in voltammograms. Our aim in this study was to show whether Que can be separated from the mixture without pre-separation.

For this purpose, low concentrations were studied to prevent interference at high concentrations. At low concentrations, we also used flavone (Flv) which has a basic flavonoid skeletal structure. Que, Mor, Rut, Lut and Flv were added to the SE at specific concentrations, respectively.

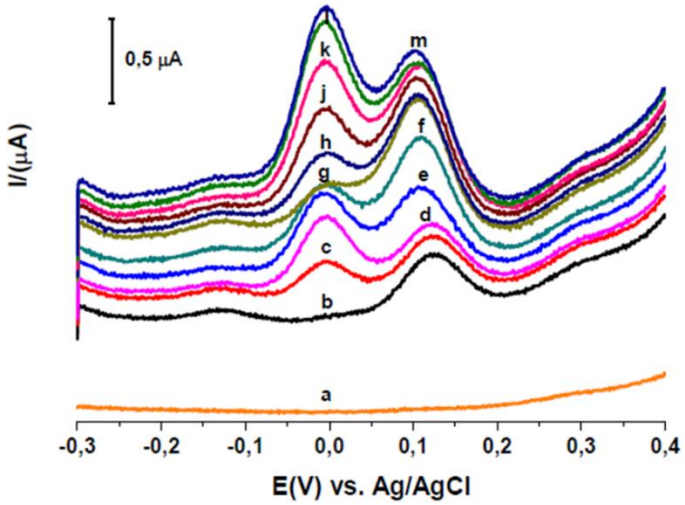

Figure 9. SWAdSVs by using the standard addition method for Que, Lut, Rut, Mor, and Flv on the PGE in 0.1 M PBS at pH 7.1, the scan rate is 100 mV s^{-1}. a) 10 mL SE, b) 50 µL 1.32×10^{-7} M Mor in SE, c) 50 µL 1.32×10^{-6} M Que in SE, d) 50 µL 1.32×10^{-6} M Que in SE, e) 50 µL 6.55×10^{-6} M Rut in SE, f) 50 µL 6.55×10^{-6} M Rut in SE, g) 50 µL 1.39×10^{-7} M Lut in SE, h) 50 µL 1.32×10^{-6} M Que in SE, j) 50 µL 1.32×10^{-6} M Que in SE, k) 50 µL 1.32×10^{-6} M Que in SE, l) 50 µL 1.32×10^{-6} M Que in SE, m) 50 µL 1.8×10^{-7} M Flv in SE

As seen from voltammograms, the addition of Mor, Rut, Lut, and Flv to the SE did not affect the peak current Que obtained at 0 V. Contrary to many studies in literature, this result showed that Que could be determined without any matrix effect from natural samples in the presence of these substances with the analytical method we developed.

3.7. Real Sample Analysis

The developed method was applied to the beet juice sample and black tea sample. SW voltammograms of the SE solution were taken. Then, the beet juice sample and black tee sample were added to the SE and SW voltammograms were taken and a peak of quercetin from beet juice and black tea was observed. It was observed that the Que peak increased by adding the standard solution of Que to the known concentration. Calibration graphs were

drawn using the peak currents obtained. Using the calibration graph, the amount of Que in beet juice and black tea samples was determined.

3.7.1 Determination of Que in Beet Juice

When we replaced the peak current value (Fig.10-B, Ip: 0.331 µA) obtained from beet juice in the equation of the calibration graph obtained using the standard addition method, the amount of Que in beet juice was determined as 10.33 ng mL^{-1} (3.42×10^{-8} M).

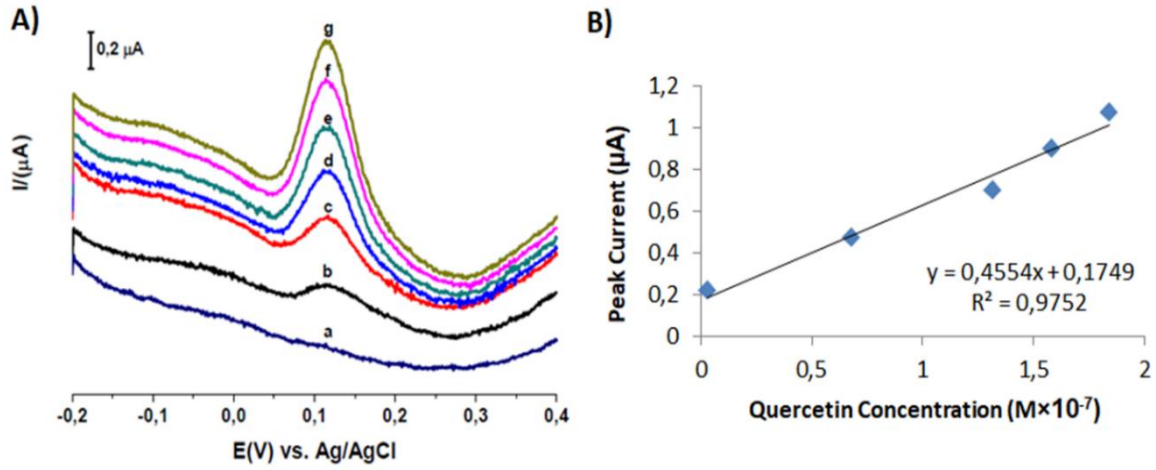

Figure 10. A) SWAdSVs of beet juice sample before (b) and after standard additions of c) 1, d) 20.5, e) 39.8, f) 47.8 and g) 55.6 ng mL^{-1} Que. (3.3×10^{-9}-1.84×10^{-7} M). a) SE; B) Calibration Graph of the I_p *vs.* Que concentration in beet juice

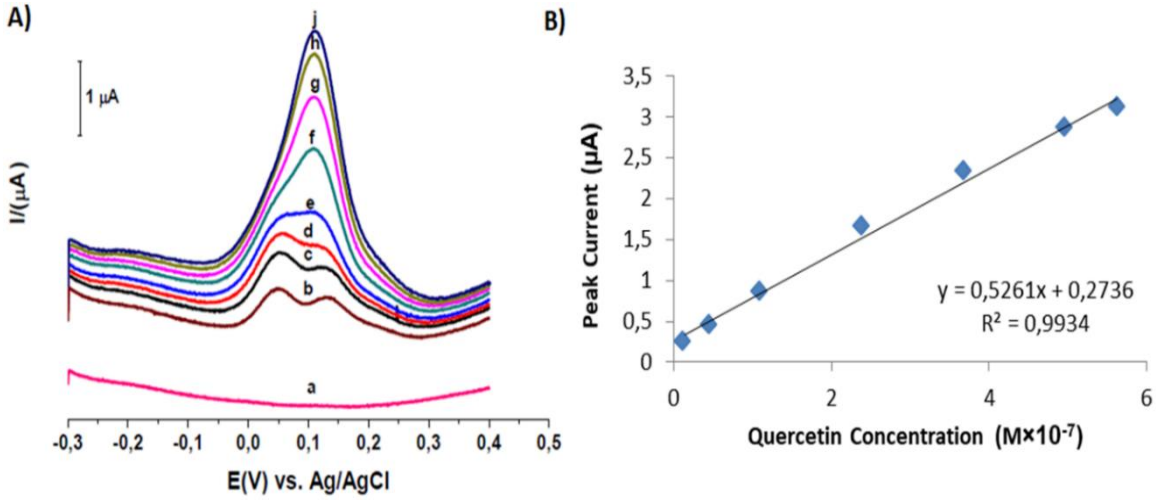

Figure 11. A) SWAdSVs of black tea sample before (b) and after standard additions of c) 3.93, d) 13.60, e) 33.2, f) 72.2, g) 111.2, h) 150.2 and j) 170 ng mL^{-1} Que. (1.32×10^{-8}-5.62×10^{-7}M). a) SE. B) Calibration Graph of the I_p *vs.* Que concentration in black tea

3.7.2 Determination of Que in black tea

When we replaced the peak current value (Fig.11-B, Ipa: 0.555 µA) obtained from black tea in the equation of the calibration graph obtained using the standard addition method, the amount of Que in black tea was determined as 16.0 ng mL^{-1} (5.3×10^{-8} M).

4. CONCLUSION

In this study, a new electroanalytical method was developed for the quantitative determination of Que, which is commonly found in natural products (especially colored fruits and vegetables), has many positive effects on human health, and is a powerful antioxidant. During the study, different buffer solutions were used as SE at different pH values, and optimum parameters were determined for the analysis. It was determined that the SWAdSV technique used during the studies was a very effective method for quantitative determination of Que. In this way, Que has been successfully determined in beet juice and black tea samples at very low concentrations under the optimum parameters determined. PGE, which has an economical, renewable, wide, and electroactive surface, was used as the working electrode throughout all analyses. Hence, PGE used in the quantification of Quercetin provided significantly superior results compared to other expensive modified electrodes with longer testing durations. So much so that the LOD and LOQ values were determined as 0.51 ng mL^{-1} (1.7×10^{-9} M) and 1.54 ng mL^{-1} (15.1×10^{-9} M), respectively, using the standard addition method and using the calibration graphs drawn between 9.67 ng mL^{-1} and 411 ng mL^{-1} (from 3.2×10^{-8} mol L^{-1} to 1.36×10^{-6} mol L^{-1}), the Que amounts in beet juice and black tea samples, were 10.33 ng mL^{-1} (3.42×10^{-8} M) and 16.0 ng mL^{-1} (5.3×10^{-8} M), respectively.

One of the biggest problems in the literature is that Que co-exists in natural samples with Rut, Lut, Mor, and Flv, which have the basic flavonoid skeletal structure, and these molecules create interference effects in quantitative determinations. Our study's developed method has demonstrated that these molecules, present in both the buffer solution used as the supporting electrolyte and the real sample, do not introduce any interference in the quantification of Que.

Consequently, quantitative Que determination was successfully performed in beet juice and black tea samples in a shorter period, without any pre-concentration, using a very economical method.

Acknowledgments

We would like to thank to the Research Foundation of Necmettin Erbakan University, Konya-TURKEY (BAP-191410001) for the financial support of this work.

Declarations of interest

The authors declare no conflict of interest in this reported work.

REFERENCES

[1] A. Demir Mülazımoğlu, and İ.E. Mülazımoğlu, Food Anal. Method 6 (2013) 141.
[2] A.A. Abdullah, Y. Yardım, and Z. Şentürk, Talanta 187 (2018) 156.
[3] X. Li, T. Zheng, S. Sang, and L. Lv, J. Agric. Food Chem. 62 (2014) 12152.
[4] K. Reddaiah, T.M. Reddy, P. Raghuand, and B.E.K. Swamy, Anal. Bioanal. Electrochem. 4 (2012) 122.
[5] M. Bittova, E. Krejzova, V. Roblova, P. Kuban, and V. Kuban, Cent. Eur. J. Chem. 12 (2014) 1152.
[6] E. Ranjbari, P. Biparva, and M.R. Hadjmohammadi, Talanta 89 (2012) 117.
[7] M. Jeszka-Skowron, and A. Zgola-Grzeskowiak, Food Anal. Method 7 (2014) 2033.
[8] G.D. Watson, and J.E. Oliveira, J. Chromatogr. B 723 (1999) 203.
[9] A. Molinelli, R. Weiss, and B. Mizaikoff, J. Agric. Food Chem. 50 (2002) 1804.
[10] M.R. Majidi, K.A. Zeynali, and B. Hafezi, Int. J. Electrochem. 6 (2011) 162.
[11] N. Aladag, L. Trnkova, A. Kourilova, M. Ozsoz, and F. Jelen, Electroanalysis 22 (2010) 1675.
[12] W. Gao, J. Song, and N. Wu, J. Electroanal. Chem. 576 (2005) 1.
[13] D. Demetriades, A. Economou, and A. Voulgaropoulos, Anal. Chim. Acta 519 (2004) 167.
[14] H. Karadeniz, B. Gulmez, F. Sahinci, A. Erdem, G.I. Kaya, N. Unver, B. Kivcak, and M. Ozsoz, J. Pharm. Biomed. Anal. 33 (2003) 295.
[15] U. Chandra, B.E.K. Swamy, O. Gilbert, M.P. Char, S. Reddy, S.S. Shankar, and B.S. Sherigara, Chin. Chem. Lett. 21 (2010) 1490.
[16] U. Chandra, B.E.K. Swamy, O. Gilbert, S. Reddy, S.S. Shankar, M.T. Shreenivas, and B.S. Sherigara, Anal. Bioanal. Electrochem. 3 (2011) 316.
[17] K. Keawkim, S. Chuanuwatanakul, O. Chailapakul, and S. Motomizu, Food Control. 31 (2013) 14.
[18] A.M. Bond, P.J. Mahon, J. Schiewe, and V. Vicente-Beckett, Anal. Chim. Acta 345 (1997) 67.
[19] K. Srinavas, J.W. King, L.R. Howard, and J.K. Monrad, J. Food Eng. 100 (2010) 208.
[20] İ.E. Mülazımoğlu, and A. Demir Mülazımoğlu, Food Anal. Method 5 (2012) 1419.
[21] İ.E. Mülazımoğlu, A. Demir Mülazımoğlu, and E. Yılmaz, Desalination 268 (2011) 227.
[22] N. Durmuş, E. Yılmaz, A. Demir Mülazımoğlu, B. Mercimek, A. Çukurovalı, İ. Yılmaz, A.O. Solak, and İ.E. Mülazımoğlu, Desalination and Water Treatment 112 (2018) 34.

[23] A. Demir Mülazımoğlu, E. Yılmaz, and İ.E. Mülazımoğlu, Sensors 12 (2012) 3916.
[24] A.M. Oliveira Brett, and V.C. Diculescu, Bioelectrochemistry 64 (2004) 133.
[25] A.J. Bard, and L.R. Faulkner, Electrochemical Methods, Wiley and Sons, New York, (1980).
[26] H.M. Shiri, A. Ehsani, and M.J. Khales, J. Colloid Interface Sci. 505 (2017) 940.
[27] A. Ehsani, M. Bigdeloo, M.Y. Ansari, B. Mirtamizdoust, A.A. Heidari, M. Hadi, and H.M. Shiri, Bull. Chem. Soc. Jpn. 91 (2018) 617.
[28] F.B. Ajdari, E. Kowsari, and A. Ehsani, J. Solid State Chem. 265 (2018) 155.
[29] F.B. Ajdari, E. Kowsari, A. Ehsani, M. Schorowski, and T. Ameri, Electrochim. Acta 292 (2018) 789.
[30] H.H. Çelik, S. Özcan, A. Demir Mülazımoğlu, E. Yılmaz, B. Mercimek, A. Çukurovalı, İ. Yılmaz, A.O. Solak, and İ.E. Mülazımoğlu, Inorg. Chem. Commun. 116 (2020) 107893.
[31] A. Demir Mülazımoğlu, and İ.E. Mülazımoğlu, Food Anal. Method 6 (2013) 845.
[32] A.D. Mülazımoğlu, S. Sağır, A. Durmuş, and İ.E. Mülazımoğlu, Eurasian J. Anal. Chem. 12 (2017) 15.
[33] N. İslamoğlu, İ.E. Mülazımoğlu, and A. Demir Mülazımoğlu, Anal. Methods 15 (2023) 4149.

Copyright © 2023 by CEE (Center of Excellence in Electrochemistry)

ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY (http://www.abechem.com**)**

Reproduction is permitted for noncommercial purposes.