ISSN 1330-9862
doi: 10.17113/ftb.53.04.15.4176

original scientific paper

Sensitive Voltammetric Determination of Natural Flavonoid Quercetin on a Disposable Graphite Lead

Dai Long Vu[1], Simona Žabčíková[1], Libor Červenka[1], Bensu Ertek[2] and Yusuf Dilgin[2]*

[1]University of Pardubice, Studentska 573, CZ-53210 Pardubice, Czech Republic

[2]Canakkale Onsekiz Mart University, Mart University 18, TR-17100 Canakkale, Turkey

Received: March 18, 2015
Accepted: July 8, 2015

Summary

In this paper, a pencil graphite electrode was pretreated using chronoamperometry technique in phosphate buffer solution (pH=7.0) for sensitive determination of quercetin. Oxidation of quercetin was investigated using pretreated pencil graphite electrode and anodic stripping differential pulse voltammetry. Under optimal conditions, the anodic current of quercetin exhibited linear response to its concentration in the range from 0.001 to 1.5 μmol/L with the limit of detection of $0.3 \cdot 10^{-3}$ μmol/L. The proposed method was successfully applied for the determination of quercetin in cranberry and blackcurrant juices with recovery rate from 93.2 to 94.7 %. Solid-phase extraction was found to be necessary prior to voltammetric determination of quercetin in fruit juice samples using pretreated pencil graphite electrode.

Key words: pencil graphite electrode, voltammetry, quercetin, fruit juices

Introduction

Quercetin is one of the flavonoids of great importance due to its strong antioxidant effect that can be attributed to the high numbers of hydroxyl functional groups and to its conjugated orbitals by which quercetin is able to donate electrons or hydrogens (*1*). Besides their important biological roles in plant pigmentation, flavonoids possess anticancer, antiviral and anti-inflammatory properties, which are the consequence of their affinity to proteins and their antioxidant properties. They are well known for their antioxidant abilities and hold promise for preventing age-related diseases, including heart disease and cancer (*2,3*). These health-related effects make the determination of quercetin of great importance. Separation methods predominate as an analytical tool for determination and quantification of flavonoids including liquid chromatography, thin-layer chromatography and electrophoresis (*4*) together with gas chromatography (*5*), spectroscopic (*6*) and electrochemical methods (*7*). Compared with these methods, electrochemical techniques have some advantages such as high sensitivity, accuracy, simplicity, low costs and the possibility of miniaturisation. Among electroanalytical techniques, voltammetry is the most frequently used for the determination of readily oxidized species in food and pharmaceutical preparations (*8*). Various kinds of electrode materials, including platinum (*9–11*), gold (*12*), glassy carbon (*13–18*), carbon paste (*19–27*) or graphene oxide-based (*28–30*) electrodes, have been successfully used for the study of the electrochemical behaviour of quercetin. Some of them have been proposed for determination of quercetin in real food and beverage samples such as fruits, fruit juices and tea samples (*20–31*).

Quercetin is well known for its use as a redox mediator in carbon-based electrodes to enhance the electrocatalytic oxidation of some organic compounds such as dopamine (*31*), tyramine (*32*) or NADH (*33*). When compared with other carbon-based electrodes, pencil graphite electrodes have some advantages such as high electrochemical reactivity, commercial availability, good mechanical

*Corresponding author: Phone: +420 466 037 718; Fax: +420 466 037 068; E-mail: libor.cervenka@upce.cz

rigidity, disposability, renewability, low cost, low technology and ease of modification. Due to these useful and important characteristics, scientists have focused on the usage of pencil graphite electrodes for phenolic compound analysis (*34–37*). In this paper, we describe a simple and rapid method for the determination of quercetin using a pretreated pencil graphite electrode.

Materials and Methods

Reagents and equipment

All the reagents including quercetin (99.9 % purity) were purchased from Sigma-Aldrich (Prague, Czech Republic). Deionised water was used in this study ($G \leq 0.055$ μS). If necessary, dissolved oxygen was removed from the solutions by purging them with argon for 15 min (purity 99.99 %; Linde Technoplyn, Prague, Czech Republic).

A solution of quercetin (10^{-3} mol/L) was freshly prepared with absolute ethanol and kept in a dark bottle during the experiments. Britton-Robinson buffer (BRB; 0.1 M) solution was used as supporting electrolyte. A three-electrode system consisting of pencil graphite working electrode, Ag/AgCl/3.0 M KCl reference electrode and platinum wire (counter electrode) connected to a potentiostat (PalmSens, Ivium Technologies, Utrecht, The Netherlands) was used for electrochemical measurement. Pencil graphite lead with a diameter of 0.5 mm was obtained from A. W. Faber Castell, Prague, Czech Republic. A mechanical pencil (Rotring, Hamburg, Germany) was used as a holder for graphite lead in this study. Electrical contact was obtained by wrapping a metallic wire around the metallic part of the holder. For each individual measurement, a new graphite lead (fresh surface) was used with total of 10 mm of length immersed into the working solution. The term 'disposable' reflects the ability of the graphite lead to be used for one definite voltammetric measurement (regardless of the number of cycles) until the fouling of the lead surface occurs.

The preparation of the pretreated pencil graphite electrode

Pretreated pencil graphite electrodes were prepared by a chronoamperometric technique described in our previous study (*37*). The surface of pencil graphite electrode was pretreated by applying a potential of 1.45 V for 60 s in the supporting electrolyte (0.1 mol/L of phosphate buffer solution containing 0.1 mol/L of KCl, pH=7.0). After the pretreatment, the pencil graphite electrodes were used for the determination of quercetin using anodic stripping differential pulse voltammetry (ASDPV; potential range: 0–0.8 V, potential step: 25 mV, potential pulse: 25 mV, pulse time: 0.05 s, and scan rate: 100 mV/s). The effect of pH, accumulation potential and accumulation time were optimised. All of the pencil graphite electrodes were treated directly before each measurement.

Sample preparation

Blackcurrant and cranberry juices were purchased on the local market and stored at refrigerated temperature prior to analysis. The preparation of the sample consisted of centrifugation at 2650×*g* (Nüve, Ankara, Turkey) for 20 min followed by solid-phase extraction of 10 mL of the supernatant using solid-phase extraction columns Strata® C18-E (55 μm, 70 A; Phenomenex, Torrance, CA, USA). The target analyte was collected in 2 mL of methanol, then 50-μL aliquot was added to supporting electrolyte and measured. Any statistical differences were computed using a Student´s *t*-test at the probability level p=0.05 (OriginPro v. 9; OriginLab Corporation, Northampton, MA, USA).

Results and Discussion

The effect of pretreatment on the oxidation of quercetin

The responses of quercetin oxidation on the pretreated and bare pencil graphite electrode obtained using ASDPV technique in a BRB at pH=3.0 were compared. As can be seen in Fig. 1, the oxidation peak was obtained at the potential of 0.375 V using both pretreated pencil graphite electrode ((24.07±0.25) μA) and bare pencil graphite electrode ((10.03±0.12) μA) in the presence of 1.2 μmol/L of quercetin ($p<0.01$). Since the highest signal of quercetin oxidation was observed on the pretreated pencil graphite electrode, it was used in further experimental procedures. The oxidation of 3′,4′-dihydroxybenzoic moiety occurs at the potential of 0.375 V, as was confirmed in other studies (*9,13,18,20,27*).

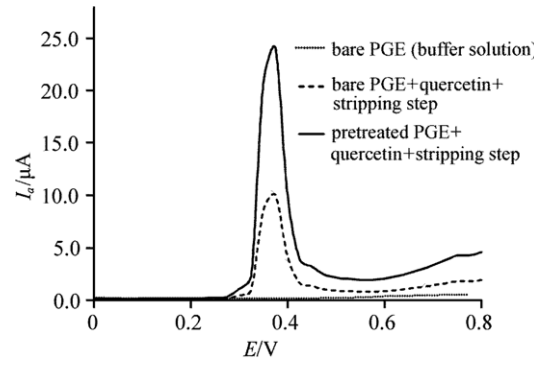

Fig. 1. Anodic stripping differential pulse voltammetry curves of 1.2 μmol/L of quercetin using bare pencil graphite electrode (PGE) and pretreated PGE in Britton-Robinson buffer (pH=3.0) accumulated at 0.1 V for 120 s (potential range from 0.0 to 0.8 V, potential step 25 mV, potential pulse 25 mV, pulse time 0.05 s and scan rate 100 mV/s). Bare PGE response in buffer solution served as control

The effect of the scan rate on the oxidation of quercetin

The electrochemical behaviour of pretreated pencil graphite electrode was investigated by recording differential pulse voltammetry in a BRB solution (pH=7.0) at various scan rates in the presence of 10^{-5} mol/L of quercetin. As indicated in Fig. 2, the oxidation currents increased linearly with the scan rate (Fig. 2, inset a), giving the following equation:

$$I_a = 0.012v + 0.059 \quad (R^2 = 0.996) \qquad /1/$$

where I_a is the oxidation current (μA), v is the scan rate (mV/s) and R^2 represents the coefficient of determination.

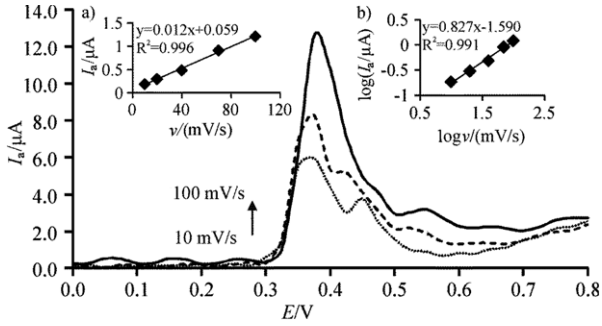

Fig. 2. Differential pulse voltammetry at various scan rates (from 10 to 100 mV/s) in the presence of 1.0 μmol/L of quercetin in Britton-Robinson buffer at pH=7.0. Inset: a) the oxidation current of quercetin at various scan rates, b) the plot of log I_a *vs.* log v, where I_a is oxidation current (μA) and v is the scan rate (mV/s). Potential range from 0.0 to 0.8 V, potential step 25 mV, potential pulse 25 mV, pulse time 0.05 s

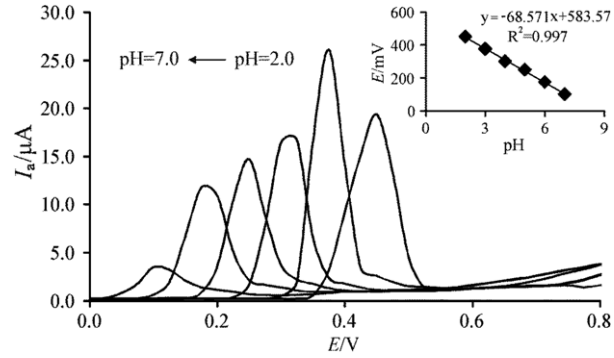

Fig. 3. Anodic stripping differential pulse voltammetry curves of 1.0 μmol/L of quercetin using pretreated pencil graphite electrode at various pH. Accumulation potential 0.1 V, accumulation time 120 s (potential range from 0.0 to 0.8 V, potential step 25 mV, potential pulse 25 mV, pulse time 0.05 s and scan rate 100 mV/s). Inset: the effect of pH on the oxidation potential of quercetin

This finding indicates that the electrochemical process of quercetin on pretreated pencil graphite electrode was surface controlled. Also, a plot of the logarithm of the peak current (μA) *vs*. the logarithm of the scan rate (mV/s) was examined. This relationship was found to be linear with a slope of 0.827 (Fig. 2, inset b). The value of the slope is close to the theoretical value of 1.0 of the adsorbed compound (*38*). Moreover, another oxidation peak at 0.450 V appeared at low scan rates (up to 50 mV/s) using both bare and pretreated pencil graphite electrodes (Fig. 2). Sokolová *et al*. (*13*) claimed that the second oxidation peak probably belongs to the oxidation product formed at the potential of the first oxidation wave using glassy carbon electrode; however, their experiment was performed under strict anaerobic conditions. On the contrary, Brett and Ghica (*9*) suggested that the oxidation of the hydroxyl group at position 3 at the ring C gave the second oxidation wave at more positive potential. A very small peak was explained by the formation of an intermolecular hydrogen bond of the hydroxyl group (C-3) with the oxygen at position 4 at ring C. This claim was also supported in a study of structural elucidation of the quercetin degradation products in ethanol-water solution (*17*).

The effect of some parameters on the determination of quercetin by ASDPV

The pH, accumulation potential and accumulation time have important effects on the determination of quercetin using ASDPV. As can be seen in Fig. 3, the pH influenced both the oxidation potential and the oxidation current. The oxidation potential shifted in the negative direction with increasing pH from 2.0 to 7.0, giving the following equation (Fig. 3, inset):

$$E_a = -68.571 \cdot pH + 583.570 \quad (R^2 = 0.997) \quad /2/$$

The shifting of the anodic potential with increasing pH at the rate of 68.6 mV per pH unit generally supports a reaction mechanism which involves equal number of protons and electrons. Oxidation of quercetin did not appear at pH≥8.0. It was found that the oxidation peak currents of quercetin on pretreated pencil graphite electrode gradually increased with the decrease of pH values, indicating the higher enhancement effect of pretreated pencil graphite electrode in more acidic conditions. However, the oxidation current of quercetin decreased after reaching the highest value at pH=3.0. The oxidation current depended on both accumulation potential and accumulation time (data not shown). Therefore, the optimum conditions were chosen as: supporting electrolyte BRB at pH=3.0, accumulation potential of 0.1 V and accumulation time of 120 s.

The enhancement of the electrochemical activity of pencil graphite electrode towards quercetin can be attributed to the increased formation of oxygen-containing groups, such as carbonyl and carboxyl on the graphite lead surface during the treatment (*39*). Quercetin as a molecule containing several hydroxyl groups bound to the aromatic rings (Fig. 4) acts as a weak acid.

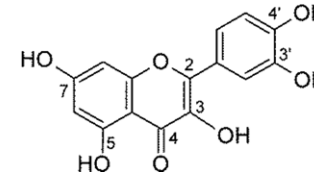

Fig. 4. The structure of quercetin

The value of pK_1=5.9 was reported in the solution under argon atmosphere (*40*). We assume that specific interactions among oxygen-containing groups at the surface of the electrode and hydroxyl groups of quercetin occurred under acidic conditions. With increasing pH, oxygen-containing groups in pencil lead were deprotonized and anionic forms of quercetin (QH^- and Q^{2-}) (*13*) were formed, leading to repulsion of negatively charged quercetin from the negatively charged surface. The same mechanism of interaction between tannic acid and the pretreated pencil graphite electrode was described in our previous study (*37*).

As can be seen in Fig. 5, the oxidation current of quercetin is proportional to its concentration in the range from 0.001 to 1.5 μmol/L with the calibration curve (Fig. 5, inset) calculated with the following equation:

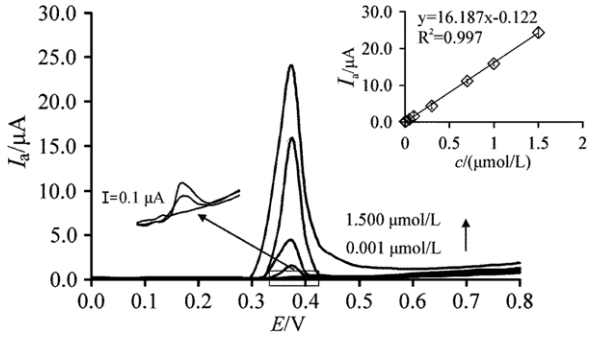

Fig. 5. Anodic stripping differential pulse voltammetry curves of various concentrations (from 0.001 to 1.500 μmol/L) of quercetin on pretreatment pencil graphite electrode in Britton-Robinson buffer at pH=3.0 after deposition at the potential of 0.1 V for 120 s. Potential range from 0.0 to 0.8 V, potential step 25 mV, potential pulse 25 mV, pulse time 0.05 s and scan rate 100 mV/s. Inset: the plot of oxidation current *vs*. concentration of quercetin

$$I_a = 16.187c - 0.122 \quad (R^2 = 0.997) \qquad /3/$$

where I_a is the oxidation current (μA) and c is the molar concentration (μmol/L). The limit of detection (LOD) was calculated using the equation:

$$\mathrm{LOD} = 3s_b/m \qquad /4/$$

where s_b is the standard deviation of the blank response and m is the slope of the calibration plot of $0.3 \cdot 10^{-3}$ μmol/L. Limit of quantification (LOQ) was 10^{-3} μmol/L (signal to noise ratio of 10). The repeatability of the method was investigated by the measurements of 50, 100 and 1200 nmol/L of quercetin (N=15) and the relative standard deviation (RSD) was found to be 3.9, 4.2 and 4.5 %, respectively. The linearity ranges and calculated LOD obtained from the pretreated pencil graphite electrode were compared with other methods. As can be seen in Table 1, two papers proposed methods for the determination of quercetin with LOD close to μmol/L using modified graphene oxide as an electrode material (*29*,*30*). Although the linear dynamic range was found to be better when using a glassy carbon electrode modified with graphene oxide (*29*), the preparation of graphene oxide is time-consuming procedure requiring strong oxidative compounds. The broadest working concentration range for determination of quercetin has been obtained in a study of Gupta *et al*. (*24*) with ionic liquid carbon paste electrode modified with the nanocomposite mixture of carbon nanotubes and nickel oxide. Even though the pencil graphite electrode is very cheap, extremely sensitive, and simple renewable tool for electrochemical determination of quercetin, it offers excellent results referenced in the above-mentioned studies.

Interference studies

The influence of potentially interfering species on the detection of quercetin was investigated. The criterion used for determining the presence of interference was the peak current change of 5 % or greater at 10^{-6} mol/L of

Table 1. Comparison of the efficiency of some modified electrodes used in the electrocatalysis of quercetin in real samples

Electrode	*c*(linear dynamic range) / μmol/L	*c*(limit of detection) / μmol/L	Sample (reference)
Au/MPA/CSH	0.5–12.2	n.d.	n.d. (*12*)
Pt-PDA@SiO_2/GCE	0.05–0.383	0.016	tea, apple, onion (*17*)
PVP-CPV	0.5–5.5	0.17	pharmaceutical (*19*)
CNTPE	0.1–1.0	0.03	blood serum (*20*)
Nafion/MWCNT/GPE	10.0–910.0	6.0/5.7	dry/frozen fruit (*21*)
Ac-Si/CPE	5.0–100.0*	*3.53	tea (*22*)
CNTPE-Cu	n.d.	0.543	apple juice (23)
ILs/NiO/CNT/CPE	0.08–400	0.03	onion, apple (*24*)
DNA-CPE	n.d.	0.0385	n.d. (*25*)
CPE/alumina	n.d.	0.001	tea (*26*)
MIP/GO/GC	0.60–15.0	0.048	fruit juices (*28*)
GCE/GO	0.006–10.000	0.0036	onion, apple (*29*)
AgNPs-AETGO	0.01–5.00	0.003	grape wine (*30*)
p-AMT/PGE	0.1–6.0*	2.2	n.d. (*35*)
Pre-PGE	0.001–1.5	0.0003	fruit juices (this study)

Au/MPA/CSH=gold electrode modified with 3-mercaptopropionic acid/L-cystein, Pt-PDA@SiO_2/GCE=glassy carbon electrode modified with platinum-polydopamine-coated silica nanocomposite, PVP-CPV=poly(vinylpyrrolidone)-modified carbon paste electrode, CNTPE=carbon nanotube-nujol paste electrode, Nafion/MWCNT/GPE=multiwalled carbon nanotube graphite paste electrode, Ac-Si/CPE=activated silica-gel carbon paste electrode, CNTPE/Cu=carbon nanotube paste electrode modified with copper nanoparticles, ILs/NiO/CNT/CPE=NiO carbon nanotube nanocomposite modified ionic liquid carbon paste electrode, DNA-CPE=carbon paste electrode modified with DNA, CPE/alumina=carbon paste electrode modified with alumina microfibres, MIP/GO/GC=molecularly imprinted polymer-incorporated graphene oxide-modified electrode with polypyrrole, GCE/GO=graphene oxide-modified glassy carbon electrode, AgNPs-AETGO=2-aminoethanethiol functionalized graphene oxide with silver nanoparticles, p-AMT/PGE=polymerized 5-amino-2-mercapto-1,3,4-thiadiazole pencil graphite electrode, Pre-PGE=pretreated pencil graphite electrode; n.d.=not determined; *originally expressed in μg/L

quercetin. It was found that 200-fold increase of concentration of K^+ and Na^+, 100-fold of glucose, 80-fold of tartaric acid, 70-fold of rutin, 60-fold of oxalic acid, 50-fold of citric acid, 40-fold of Ca^{2+}, Mg^{2+} and Ni^{2+}, 30-fold of ascorbic acid and Cr^{3+}, 25-fold of Fe^{3+} and Zn^{2+} and 15-fold of Cd^{2+} and Cu^{2+} did not interfere with the analysis of quercetin using pretreated pencil graphite electrode.

Analytical application

The proposed method was applied to determine the presence of quercetin in cranberry and blackcurrant juices with the results shown in Table 2.

Table 2. Determination of quercetin in fruit juice samples and the recovery data (N=8)

Sample	c(spiked) / mg/L	c(found) / mg/L	Recovery / %
Cranberry	0.00	0.59±0.11	n.d.
	0.34	0.92±0.08	94.72
Blackcurrant	0.00	0.16±0.05	n.d.
	0.34	0.48±0.10	93.24

n.d.=not determined

It was necessary to include cleaning steps because of the solid contents in both samples. The presence of colourful antocyanins in cranberry and blackcurrant juices significantly increased the background currents, thus decreasing the sensitivity of the pretreated pencil graphite electrode in this study (data not shown). The solid-phase extraction procedure successfully cleaned the sample from antocyanins and allowed to determine the presence of quercetin with a good recovery in the range of 93.24–94.72 %.

Conclusions

In this study the electrochemical determination of quercetin on the surface of pretreated pencil graphite electrode by anodic stripping differential pulse voltammetry has been investigated for the first time. It was shown that the pretreatment procedure remarkably enhanced the oxidation peak current of quercetin compared with that using bare pencil graphite electrode. Under optimal conditions, the anodic peak current is linearly proportional to the concentration of quercetin at a wide concentration range and at very low limit of detection in comparison with other studies. The electrode is proved to be of high sensitivity and reproducibility. The working electrode used in this study can be purchased in local market at the minimum cost and requires minor modification in phosphate buffer to be an excellent tool for voltammetric determination of quercetin. The method was successfully applied to the fruit juices; however, the cleaning and extraction steps are necessary for good recovery.

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