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Araştırma Makalesi - Research Article

Türk ve Filtre Kahve Örneklerindeki Toplam Antioksidan Kapasitelerin Elektrokimyasal Yöntemlerle Belirlenmesi

Sevinç Yıldırım[1], Ersin Demir[2*], İlkay Gök[3]

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ÖZ

Bu çalışmada, az, orta ve koyu gibi değişik derecelerde farklı kavrulmuş kahve çekirdekleriyle demlenen Türk ve Filtre kahvelerindeki toplam antioksidan kapasitesinin (TAC) belirlenmesi için dönüşümlü (CV), kare dalga sıyırma (SWSV) ve diferansiyel puls sıyırma (DPSV) voltametrik yöntemlerle kullanıldı. Voltametrik parametreleri, karbon pasta elektrotu (CPE) kullanılarak pH 4.0 Britton-Robinson tampon çözeltisinde optimize edildi. Standart antioksidan maddeleri olarak gallik asit ve kuersetin'in elektrokimyasal davranışı CPE üzerinde optimum koşullar altında CV, SWSV ve DPSV teknikleri ile incelendi. Her üç elektrokimyasal tekniklerle (CV, SWSV, DPSV) gallik asit için yaklaşık 350 mV ve 700 mV'ta olmak üzere iki oksidasyon piki görülürken, kuersetin için ise 340 mV, 725 mV ve 1015 mV'larda anodik pikleri elde edildi. Bununla birlikte, kahve örneklerindeki toplam antioksidan kapasitelerini eşdeğer gallik asit ve kuersetin cinsinden belirlemek için CPE kullanılarak pH 4.0'da her iki maddeye ait yaklaşık 350 mV'de anodik pik akımları tercih edildi. Az kavrulmuş kahve çekirdekleriyle hazırlanan kahve örneklerinde maksimum antioksidan kapasite (TAC) gösterdiği bulundu. Az kavrulmuş kahve çekirdekleri ile hazırlanan Türk kahvesi için TAC değeri, CV yöntemi kullanılarak 17.868 ± 0.281 g/L ve 65.165 ± 1.024 g/L eşdeğer gallik asit ve kersetin olarak hesaplandı. Ayrıca, Filtre kahvesi için, TAC değerleri sırasıyla 32.290 ± 0.839 g/L ve 118.471 ± 3.529 g/L olarak bulundu. Dahası, tüm kahve örneklerindeki TAC değerleri CV'nin yanı sıra DPSV ve SWSV ile analiz edildi. Sonuç olarak, elektrokimyasal yöntemlerle, hızlı, ucuz ve ön işlemlere tabi tutulmadan doğrudan gıda örneklerinde TAC analizi edilmektedir.

Anahtar Kelimeler- Kahve, Antioksidan, Elektrokimya, Voltametri

[1]İletişim: sevinc.yildirim@okan.edu.tr (https://orcid.org/0000-0001-57933-2333)
Uygulamalı Bilimler Fakültesi, Gastronomi Bölümü, İstanbul Okan Üniversitesi, İstanbul Türkiye
[2]*Sorumlu yazar iletişim: dr.ersindemir@yahoo.com (https://orcid.org/0000-0001-9180-0609)
Eczacılık Fakültesi, Analitik Kimya Ana Bilim Dalı, Afyonkarahisar Sağlık Bilimleri Üniversitesi, Afyonkarahisar, Türkiye
[3]İletişim: ilkay.gok@okan.edu.tr (https://orcid.org/0000-0002-4871-8981)
Uygulamalı Bilimler Fakültesi, Gastronomi Bölümü, İstanbul Okan Üniversitesi, İstanbul Türkiye

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Determination of Total Antioxidant Capacities in Turkish and Filter Coffee Samples by Electrochemical Methods

ABSTRACT

In this study, cyclic (CV), square wave stripping (SWSV) and differential pulse stripping voltammetric (DPSV) methods were used to determine total antioxidant capacity (TAC) in Turkish and Filter coffees brewed with differently roasted coffee beans such as light, medium and dark. Voltammetric parameters were optimized in pH 4.0 Britton-Robinson buffer solution using carbon paste electrode (CPE). Electrochemical behavior of gallic acid and quercetin as standard antioxidant substances were investigated on CPE under optimum conditions by CV, SWSV and DPSV. With all three electrochemical techniques (CV, SWSV, DPSV), two oxidation peaks were observed for gallic acid approximately at 350 mV and 700 mV, while anodic peaks were obtained for quercetin at 340 mV, 725 mV and 1015 mV. However, anodic peak currents at 350 mV for both substances were preferred using CPE to determine total antioxidant capacities in coffee samples in terms of equivalent gallic acid and quercetin. It was found that coffee samples prepared by light roasted coffee beans showed maximum antioxidant capacity (TAC). TAC values for Turkish coffee prepared with less roasted coffee beans were calculated as 17.868±0.281 g/L and 65.165±1.024 g/L equivalent gallic acid and quercetin using CV method. Also, TAC values for filter coffee were 32.290±0.839 g/L and 118.471±3.529 g/L, respectively. Moreover, TAC values in all coffee samples were also analyzed with DPSV and SWSV as well as CV. As a result, TAC analysis is carried out directly on food samples with electrochemical methods, fast, cheap and without pre-treatment.

Keywords- Coffee, Antioxidant, Electrochemistry, Voltammetry

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I. INTRODUCTION

Antioxidants can be described briefly as substances that stop or negate the adverse effects and formation of free radicals in the human body and foods [1-2]. Oxidative stress caused by free radicals adversely affects human health [3]. The oxidative stress can seriously damage lipids, proteins, enzymes, carbohydrates and DNA. Furthermore, they cause random breaks in DNA chains, damage to enzymes and structural proteins, cancer, neurodegenerative and cardiovascular diseases [3-5]. Therefore, antioxidants are one of the most important food sources for healthcare individuals [6-7]. Both endogenous (natural) and exogenous (artificial) origin antioxidants intake is of great importance for human health [8]. The endogen (natural) antioxidants are produced by the organism, while exogenous antioxidants are herbal sources [9-10]. Antioxidant substances that only organisms can produce are not enough for human health. In addition, the human body needs plant-based antioxidants [11]. For these reasons, antioxidant-rich food materials and their consumption has become the basic need for healthy individuals. Many natural beverages, especially fruits and vegetables, are known to contain antioxidant substances [12]. Coffee, a soft drink, comes at the beginning of these beverages which are contains a large amount antioxidant according due to their rich components [13-15].

Coffee, belonging to the Rubiaceae family and of the genus Coffea, was named after Kaffa, a city in Ethiopia [16]. It is one of the oldest soft drinks globally. A near history of 1000 years, coffee is one of the most consumed beverages in the world [17]. The most efficient coffee growing places are tropical regions and maximum coffee bean harvest is obtained in moist and cool regions. Coffee, which is a very delicate and fragile plant species, has now been identified as nearly 100 plant types in the main floor [17]. Coffee contains more than 1000 nutrients and flavors, mainly caffeine, carbohydrates, lipids, vitamins, nitrogenous compounds and micronutrients [18-19]. Many studies are carried out by scientists in coffees, which are quite remarkable in terms of antioxidants [20-22]. Most of these studies are spectrophotometric and chromatographic methods. The antioxidants determinations in coffee samples have been carried out by oxygen radical absorbance capacity (ORAC)[23], total radical-trapping antioxidant parameter (TRAP) [14], trolox equivalent antioxidant capacity method (TEAC) [24], 2,2-diphenyl-1-picrilhydrazyl (DPPH) radical scavenging capacity method [25], copper (II) ion reduction based antioxidant capacity method (CUPRAC) [26], iron (ii) ion reducing antioxidant power method (FRAP) [27] and Folin-Ciocalteu reactive (FCR) method [28]. However, cheaper, faster, more precise and reliable new methods are required for antioxidant determinations due to the use of many non-environmentally friendly solvents, long pretreatment and expensive equipment are required from these classical methods. While this is the case, electrochemical methods are successfully used in the determination of numerous drugs, pesticides, amino acids and antioxidant substances [29-31]. Moreover, considering important validation parameters such as time, cost, precision and portable, electrochemical methods show great superiority. In addition, countless new sensors have been constructed nowadays for many trace levels of antioxidant determinations in food samples [32-36].

The antioxidant determinations in differently roasted coffee varieties with the electrochemical methods rarely used in antioxidant determinations were performed for the first time with this study. In this work, the total antioxidant capacities (TAC) of Turkish and Filter coffee samples brewed using roasted coffee beans such as light, medium and dark were investigated voltammetric methods on a carbon paste electrode (CPE). Electrochemical behaviors of gallic acid and quercetin as references antioxidant agents were explored in detail cyclic (CV), square wave stripping (SWSV) and differential pulse stripping (DPSV) voltammetric methods in pH 4.0 Britton-Robinson buffer solutions. TAC values in two coffee samples by prepared with three different beans were calculated in terms of equivalent to gallic acid and quercetin by using CV, SWSV and DPSV methods on CPE. Consequently, TAC values in coffee samples were successfully analyzed using fast, economical and environmentally friendly voltammetric methods. Therefore, novel analytical methods have been developed for antioxidant determinations in coffee samples and contribution of this manuscript will be made to the literature in terms of determination TAC in coffee sample.

II. EXPERIMENT

A. Apparatus

All data were collected by using Vertex®One (Ivium) electrochemical analyzer combined with a solid electrode cell stand. This system consists of three electrodes such as reference (Ag/AgCl; BASi, MF-2052), counter (platinum wire; BASi, MW-1032). and working electrodes (Carbon paste electrode (CPE); BASi MF-2010). For the determination of antioxidant in coffee, cyclic voltammetry (CV), differential pulse stripping voltammetry (DPSV) and square wave stripping voltammetry (SWSV) methods were applied on CPE in pH 4.0 Brittion-Robinson (B-R) buffer solutions. Mettler Toledo brand pH meter with an accuracy of ± 0.05.

B. Reagents

Gallic acid and quercetin were obtained from Aldrich-Sigma at as analytical standard. The stock solutions of gallic acid and quercetin were prepared as a concentration of 500 mg/L by water and ethanol, respectively. Britton Robinson buffer solution used for support electrolyte was prepared with acetic acid, ortho-phosphoric and boric acid to be 0.04 M. To adjust the buffer to pH 4.0, 2.0 M NaOH or 2.0 M HCl solutions were preferred. Distilled water was used in all processes such as solution preparation and washing.

C. Preparation of working electrode

In the construction of carbon paste electrode (CPE) as an indicator electrode, 70% graphite powder (<150 µm) by mass was treated with 30% mineral oil. These two mixtures were mixed until homogeneous. The formed homogeneous carbon paste was placed in the 3 mm diameter area at BASi-MF 2010 electrode with a syringe. Before using CPE, polishing was applied to the electrode surface with soft sandpaper. Finally, after polishing, the electrode was washed with distilled water and dried at room temperature.

D. Process preparation of coffee samples

All coffee beans were obtained from the commercial coffee producer company. Coffee beans were roasted light, medium and dark at three different temperatures. Filter and Turkish coffees are ground according to the brewing type. For Turkish coffee samples, 7.0 grams of finely weighed coffee beans ground into fine powder were obtained by using the Arzum Okka machine. Brewed Turkish coffees were cooled at room temperature and centrifuged for 5 minutes. The coffee beans used in making filter coffee were weighed precisely as 7.0 grams as in Turkish coffee. Three types of filter coffee samples were obtained using SINBO SCM 2938 machine. The coffee samples were then cooled to room temperature and centrifuged at 3000 rpm for 5 minutes. All coffee samples were stored at –20 ° C in the freezer when not in use.

III. RESULTS AND DISCUSSION

A. Cyclic Voltammetry

Firstly, the electrochemical behavior of gallic acid and quercetin at 2 mg/L was examined with a carbon paste electrode (CPE) in a pH 4.0 Britton-Robinson buffer solution. Cyclic voltammograms were obtained for these standard antioxidant compounds between –200 and +1400 mV at a scanning rate of 100 mV/s (Figure 1). Gallic acid exhibited two anodic peaks at 360 mV and 727 mV by CV. For the quercetin, three oxidation peaks were observed, 350 mV, 735 mV and 1025 mV on CPE in pH 4.0. In the cathodic scanning, no reduction peak was obtained for both items. Therefore, it can be said that it has an irreversible electrode reaction for both substances. In addition, predominant anodic peak currents of approximately 350 mV for both substances were taken as reference for the antioxidant determinations in coffee samples ((pH 4.0 BR buffer solution, scan rate = 100 mV/s, CPE).

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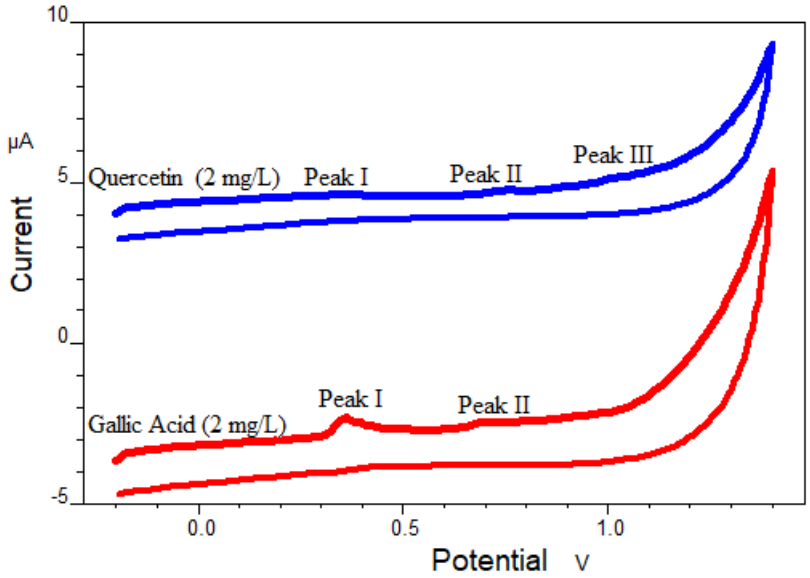

Figure 1. Cyclic voltammograms for the gallic acid and quercetin (pH 4.0 BR buffer solution, scan rate = 100 mV/s)

CV measurements for the Turkish and Filter coffee samples brewed with different roasted beans were taken under optimum conditions determined for reference antioxidant substances on CPE in pH 4.0 BR buffer solution (Figure 2).

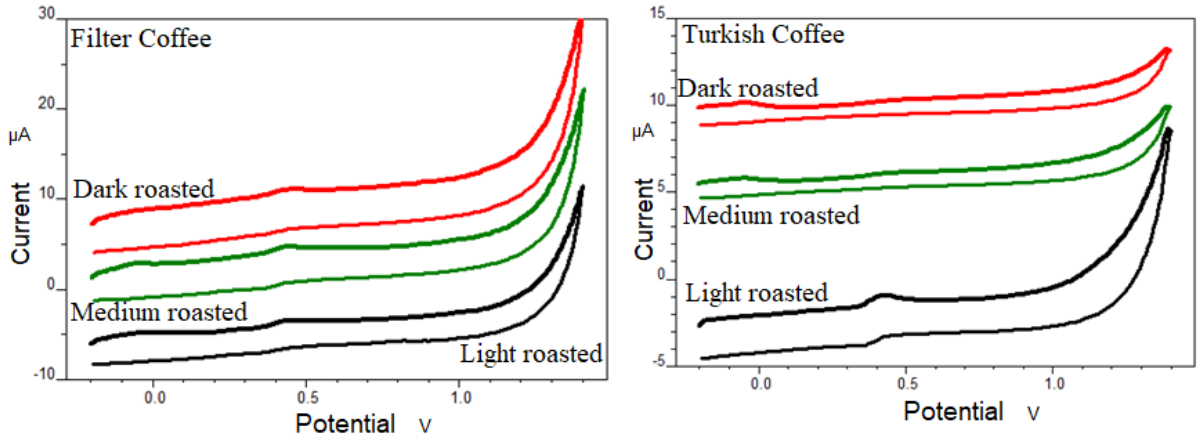

Figure 2. Cyclic voltammograms of Turkish and Filter Coffee samples prepared with different coffee beans (pH 4.0 BR buffer solution, scan rate = 100 mV/s, CPE)

According to the results of the CV, it has been found that it contains the most antioxidant capacity (TAC) in Turkish and Filter coffees prepared with low roasted coffee beans (Table 1). For Turkish coffee, the TAC in terms equivalent of gallic acid and quercetin was as 17.868±0.281 and 65.165±1.024, respectively. These values for filter coffee were found as 13.290±0.419 and 48.471±1.529. According to the method of roasting, there was a significant decrease in the amount of antioxidants in both coffees prepared with medium and dark coffee beans.

Table 1. Total TAC values as equivalent gallic acid and quercetin by CV for Turkish and Filter coffee samples, n = 3.

Coffee Bean	Equivalent Gallic Acid (g/L)		Equivalent Quercetin (g/L)	
	Brewing technique		Brewing technique	
	Turkish coffee	Filter coffee	Turkish coffee	Filter coffee
Light roasted	17.868±0.281	32.290±0.839	65.165±1.024	118.471±3.529
Medium roasted	0.997±0.019	8.880±0.226	3.635±0.071	32.389±0.824
Dark roasted	---	0.580±0.012	---	2.106±0.048

B. Square Wave Stripping Voltammetry

Square wave stripping voltammetry (SWSV) is the most frequently used and highly sensitive, selective and fast method among electrochemical methods has been used in qualitative and quantitative analysis of many electro-active analytes. Optimal experimental conditions of SWSV, another analytical chemistry method which is more sensitive, selective and precision were determined for the determination of gallic acid and quercetin (Table 2).

Table 2. Optimum module parameters of SWSV technique on carbon paste electrode (CPE)

Parameters	Optimum Values
Pulse Amplitude (ΔE)	50 mV
Frequency (*f*)	100 Hz
Step Potential (ΔE_b)	5 mV
Accumulation Potantial (E_b)	0 mV
Accumulation Time (t_b)	30 s
Support Electrolyte	pH 4.0 Britton-Robinson buffer

Two oxidation peaks at 350 mV and 675 mV were observed for 0.5 mg/L gallic acid on carbon paste electrode (CPE) under experimental conditions of SWSV (Figure 3). For the quercetin, three anodic peaks were obtained at 350 mV, 735 mV and 1020 mV in pH pH 4.0 Britton-Robinson buffer solutions on CPE. However, since the density of anodic peaks at 675 mV for gallic acid and 735 mV and 1025 mV for quercetin is very low, the peak currents at 350 mV were used when calculating the total antioxidant capacity (TAC) as equivalent gallic acid and quercetin in coffee samples.

Table 3. Total TAC values as equivalent gallic acid and quercetin by SWSV for Turkish and Filter coffee samples, n = 3.

Coffee Bean	Equivalent Gallic Acid (g/L)		Equivalent Quercetin (g/L)	
	Brewing technique		Brewing technique	
	Turkish coffee	Filter coffee	Turkish coffee	Filter coffee
Light roasted	40.143±1.143	92.869±2.613	19.580±0.558	45.298±1.274
Medium roasted	7.254±0.285	42.006±1.757	3.538±0.139	20.489±0.857
Dark roasted	1.519±0.019	14.072±0.446	0.741±0.009	6.864±0.218

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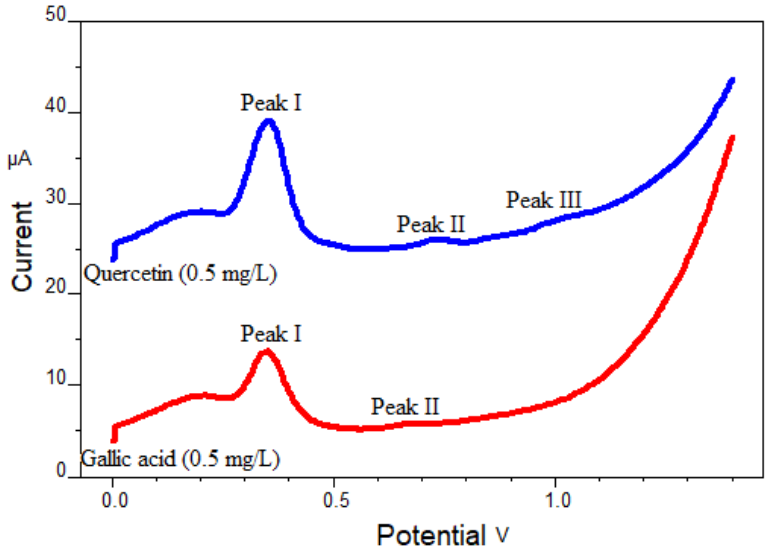

Figure 3. SWS voltammograms for the gallic acid and quercetin (CPE, pH 4.0 BR buffer solution, t_b = 30 s, E_b = 0 mV, ΔE = 50 mV, $ΔE_b$ = 5 mV ve *f* = 100 Hz)

SWS voltammograms of Turkish and Filter coffee samples brewed with different roasted beans under SWSV operating conditions for the standard antioxidant compounds as gallic acid and quercetin were taken on CPE in pH 4.0 BR buffer solution (Figure 4). According to the results of the SWSV, it has been found that it contains the most antioxidant capacity (TAC) in Turkish and Filter coffees prepared with low roasted coffee beans (Table 3). For Turkish coffee, the TAC in terms equivalent of gallic acid and quercetin was as 40.143±1.143 and 19.580±0.558, respectively. These values for filter coffee were found as 92.869±2.613 and 45.298±1.274. According to the method of roasting, there was a significant decrease in the amount of antioxidants in both coffees prepared with medium and dark coffee beans. In addition, while total antioxidant capacity (TAC) cannot be determined by CV in Turkish coffee prepared with dark roasted coffee beans, TAC analysis was performed in same sample with the SWSV method.

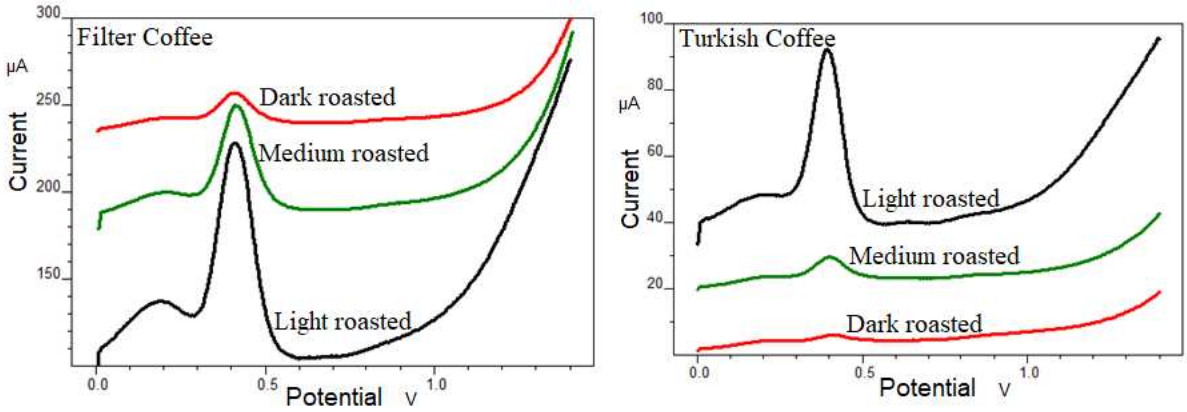

Figure 4. SWS voltammograms for Turkish and Filter Coffee samples prepared with different coffee beans (CPE, t_b = 30 s, E_b = 0 mV, ΔE = 50 mV, $ΔE_b$ = 5 mV ve *f* = 100 Hz)

C. Differential Pulse Stripping Voltammetry

Differential Pulse Stripping Voltammetry (DPSV) is the most commonly has been used in qualitative and quantitative analysis of many electro-active analytes such as antioxidant, drug, pesticide and heavy metal etc. Due to the fact that it is very sensitive and the waste current (noise) is very low, the DPSV technique makes it possible to analyze even many trace materials at nano–molar level. For these reasons, the DPSV technique has attracted great interest from scientists. It was one of the first preferred techniques among electrochemical analysis methods. Here, optimal experimental conditions of DPSV were initially assigned for the determination of Gallic acid and Quercetin on CPE in pH 4.0 buffer solutions (Table 4).

Table 4. Optimum module parameters of DPSV technique on carbon paste electrode (CPE)

Parameters	**Optimum Values**
Pulse Amplitude (ΔE)	50 mV
Pulse period (E_t)	10 ms
Scan rate	50 mV/s
Step Potential (ΔE_b)	5 mV
Accumulation Potantial (E_b)	0 mV
Accumulation Time (t_b)	30 s
Support Electrolyte	pH 4.0 Britton-Robinson buffer

DPS voltammograms were collected using CPE in the presence of 5 mg/L standard quercetin and gallic acid under the optimal experimental conditions of DPSV (Figure 6). While for the gallic acid, two anodic peaks at 320 mV and 665 mV were obtained, quercetin exhibited tree oxidation peaks at 320 mV, 705 mV and 995 mV on CPE in pH 4.0 Britton-Robinson buffer solutions. However, since the peak currents at 675 mV for gallic acid and 735 mV and 1025 mV for quercetin are very low. So that peak currents for the both agent at 320 mV were used when calculating the total antioxidant capacity (TAC) as equivalent gallic acid and quercetin in coffee samples.

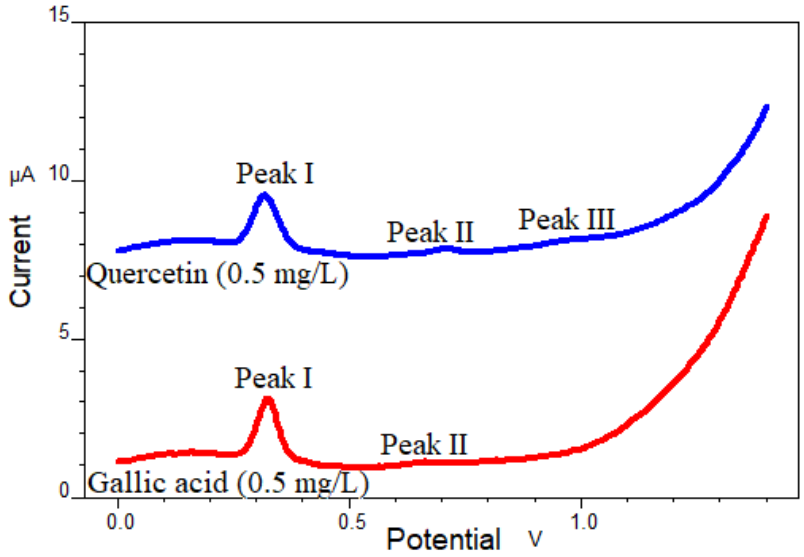

Figure 5. DPS voltammograms for the gallic acid and quercetin (CPE, pH 4.0 BR buffer solution, t_b = 30 s, E_b = 0 mV, ΔE = 50 mV, ΔE_b = 5 mV ve scan rate = 50 mV/s, E_t = 10 ms)

DPS voltammograms of Turkish and Filter coffee samples brewed with different roasted beans under operating conditions for the standard antioxidant compounds as gallic acid and quercetin were taken on CPE in pH 4.0 BR buffer solution (Figure 4). According to the results of the DPSV for the coffee sample, it has been found that it contains the most antioxidant capacity (TAC) in Turkish and Filter coffees prepared with low roasted coffee beans (Table 5). For Turkish coffee, the TAC in terms equivalent of gallic acid and quercetin was as 30.711±0.976and 36.634±1.166, respectively. These values for filter coffee were found as 58.993±1.14 and 70.373±1.816. According to the method of roasting, there was a significant decrease in the amount of antioxidants in both coffees prepared with medium and dark coffee beans. In addition, while total antioxidant capacity (TAC) cannot be determined by CV in Turkish coffee prepared with dark roasted coffee beans, TAC analysis was performed in same sample with the DPSV method.

Table 5. Total TAC values as equivalent gallic acid and quercetin by DPSV for Turkish and Filter coffee samples, n = 3.

Coffee Bean	**Equivalent** Gallic Acid (g/L)		**Equivalent** Quercetin (g/L)	
	Brewing technique		Brewing technique	
	Turkish coffee	Filter coffee	Turkish coffee	Filter coffee
Light roasted	30.711±0.976	58.993±1.14	36.634±1.166	70.373±1.816
Medium roasted	1.669±0.064	9.853±0.234	1.991±0.076	11.753±0.280
Dark roasted	0.676±0.018	5.879±0.099	0.807±0.021	7.013±0.118

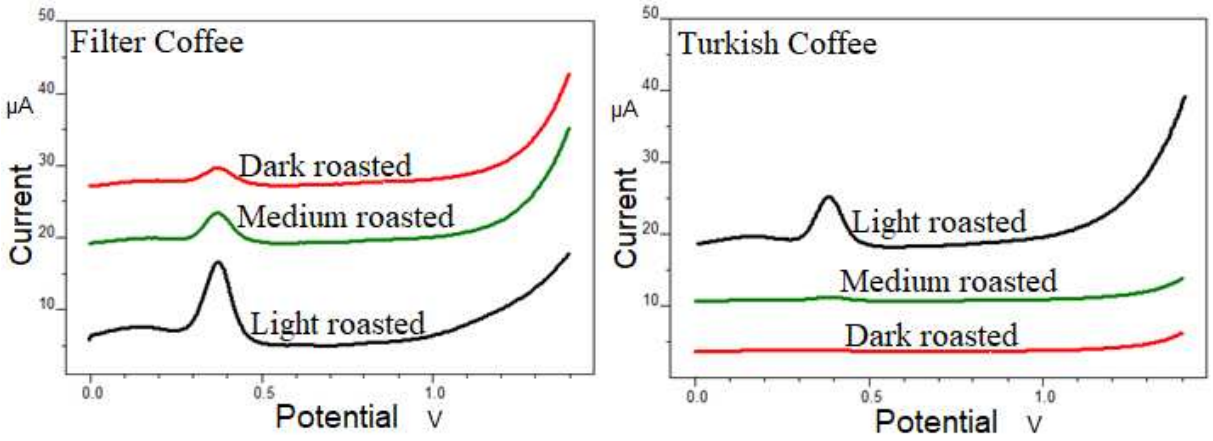

Figure 6. DPS voltammograms for Turkish and Filter Coffee samples prepared with different coffee beans (CPE,t_b = 30 s, E_b = 0 mV, ΔE = 50 mV, ΔE_b = 5 mV ve scan rate = 50 mV/s, E_t = 10 ms)

IV. CONCLUSIONS

In the present study, electrochemical applications such as cyclic (CV), square wave stripping (SWSV) and differential pulse striping (DPSV) voltammetric techniques for determination of total antioxidant capacity (TAC) in Turkish and Filter coffee samples were carried using carbon paste electrode (CPE). The operating models of SWSV and DPSV were evaluated for the gallic acid and quercetin as reference antioxidant agents in pH 4.0 Britton-Robinson buffer solutions. The anodic peak for the both agents at 350 mV was taken a reference point for the analysis of TAC. TAC values were successfully calculated as equivalent gallic acid and quercetin in Turkish and Filter coffee samples prepared with different beans such as light, medium and dark by using all the recommended electrochemical methods (CV, SWSV and DPSV). The maximum antioxidant capacity in coffee samples was found by prepared the light roasted beans for the two coffee types. Consequently, electrochemical

methods such as CV, SWSV and DPSV can be alternative to evaluate TAC in food samples to conventional analytical methods due to they are fast, reliable, fully validated and without any pretreatment.

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