Full Paper

Voltammetric Determination of Curcumin in Spices using Platinum Electrode Electrochemically Modified with Poly(Vanillin-co-Caffeic Acid)

Muammer Burç, Öznur Güngör, and Serap Titretir Duran[*]

Chemistry Department, Arts and Sciences Faculty, İnönü University, 44280, Malatya-Turkey

*Corresponding Author, Tel.: +904223773873; Fax: +904223410037
E-Mail: serap.titretir@inonu.edu.tr

Abstract- In this study a simple, highly sensitive, and selective electrochemical method was developed for determination of the low concentration curcumin (CUR) using a poly(vanillin-co-caffeic acid) *p*(Van-CA) modified platinum electrode. Electrode modification was carried out electrochemically with cyclic voltammetry (CV) method. For this purpose; a solution of 6 mM vanillin (Van) and 6 mM caffeic acid (CA) in phosphate buffer solution (PB) adjusted to pH 7.4 was used. Then, electrochemical behaviour of CUR on the platinum electrode modified with *p*(Van-CA) was investigated by using CV and differential pulse voltammetry (DPV) methods. Tween 20 as surfactant was used to increase the solubility and stability of CUR in this study. CUR responses of the modified electrode showed that it was selective, sensitive and stable. A linear calibration graph was acquired in the high concentration range of 0.1 to 1.0 mM CUR. Correlation coefficient (R^2) was calculated as 0.9951 from this linear calibration curve. The correlation coefficient for the low concentration range 0.01 to 0.07 mM was also calculated from 0.9950. LOD (limit of detection) and LOQ (limit of quantitation) of the developed method were determined as 0.005 mM and 0.015 mM, respectively. However, the detection of CUR in spices samples was made with this method. The recovery efficiency of the *p*(Van-CA) modified Pt electrode (*p*(Van-CA)/PtE) was calculated range of 96% and 102% for three different spices samples. Finally; developed method has been shown that it has fast, low cost, simple, reproducible, high accuracy and precision (99.6%) for sensitive and selective determination of CUR by using *p*(Van-CA)/PtE as effective novel electrode.

Keywords- Curcumin sensor; Antioxidant; Voltammetry; Copolymer; Vanillin; Caffeic acid

1. INTRODUCTION

Curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione) is a yellow substance obtained from *Curcuma longa Linnaeus* [1]. The chemical structure of curcumin was shown in Scheme 1.
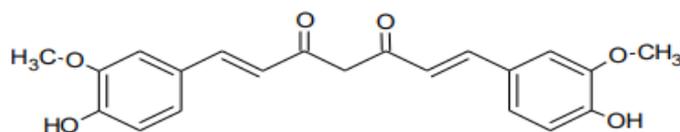
Scheme 1. Molecular formula of curcumin

CUR is yellow-orange antioxidant polyphenolic compound with bitter taste [2,3]. It is used both as food (spice) and colorant. Curcumin is commonly used as colouring agent as well as food additive. WHO stated the acceptable daily intake of curcumin as food additive in the range of 0-3 mg/kg [4]. CUR has ability to either prevent or induce cell apoptosis, antioxidant properties and anti-inflammatory effect [1,5]. It has been reported of traditional medicinal use in various diseases including influenza, colds and gastrointestinal system disorders for many years. Nowadays, it is used as both food supplement and spices in many countries. It has been indicated in studies that CUR has a wide range of biological and pharmacological effects through the impacts of antioxidant, anticancerogenic [6,7], antimutagenic, antidiabetic, antibacterial, antiviral, antiinflammatory, antinosiptive [7]. It has been suggested that CUR is effective and safe for the prevention and treatment of many diseases, including cancer such as breast cancer, genitourinary system cancer, gastrointestinal system cancer, ovarian cancer, lung cancer, melonom, neurological cancer and head cancer [8]. Although it is stated that CUR does not have as much cumulative effect as consumed at the recommended dosage level, it is stated that CUR can be toxic if it accumulates in tissues [9,10]. Also, it has been found combining curcumin-loaded hydrogels coatings with UV-A light gives good antimicrobial coatings to avoid cross-contaminations of L. innocua in refrigerated sausages [11]. Because of all above-mentioned properties, it is very important to develop easy, fast, low cost, precise, accurate, reliable, and sensitive method for the determination of CUR [12,13]. Therefore, control of the CUR concentration in biological fluids as well as in consumed food and therefore nutrients is highly necessary [14].

In the literature, many methods for the alone or simultaneously determination of CUR with other antioxidants, such as spectrometry (LC/MS), high performance liquid chromatography (HPLC) [15,16], liquid chromatography coupled with tandem mass spectroscopy (LCMS/MS) [17], high performance thin-layer chromatography [18], UV-Vis spectrophotometry [19], spectrofluorimetry [20], resonance light scattering (RLS) technique [21] have recently been reported. Nevertheless, these methods have too many disadvantages, such as complicated, lengthy procedures, expensiveness, and unsuitability for field use. In

recent years electrochemical methods developed have made great progress in overcoming the above-mentioned disadvantages. Polymer modified electrode studies in the field of biosensors and chemical sensors have received considerable attention due to their wide range of applications. [22-24]. Recently, electrochemical detection was used to detect CUR with good selectivity and high sensitivity. For example, dysprosium nanowires have been modified using carbon nanotube with adsorptive stripping voltammetry technique [25]. The suspended mercury drop electrode and carbon paste electrode were used together with differential pulse voltammetry for CUR detection [26]. Furthermore, determination of curcumin was successfully performed using the square wave voltammetry on palladium nanoparticles-polyproline modified graphite electrode by Arslan and Çakır [27]. Manaia and co-workers have been investigated CUR electrochemical oxidation behaviour at a glassy carbon [28]. Antioxidant activity and free radical scavenging ability of CUR, was investigated using two electrochemical methods and electron spin resonance (ESR) technique by Chen et al. [29].

Electrochemical sensor applications in the pharmaceutical [30-33] and food [34-36] industry for the selective detection of certain antioxidants [37] and important molecules such as drug [38] active substances in the last few decades have increased significantly.

Electrocatalysis at chemically modified electrodes is widely utilized for the determination of many inorganic and organic substrates [39]. CA has been incorporated in modified electrodes as an electrocatalyst to detect biologically important analytes [40]. In the literature, there is simultaneous voltammetric determination of ascorbic acid, epinephrine and uric acid with poly(caffeic acid) film electrode [41]. Nian Bing Li et al reported simultaneous voltammetric measurement of ascorbic acid and dopamine on poly(caffeic acid)-modified glassy carbon electrode [42]. On the other hand, caffeic acid modified glassy carbon electrode was used for the electrocatalytic oxidation of the reduced nicotinamide adenine dinucleotide (NADH) [39]. In several articles, electrochemical methods such as electrochemical oxidation of caffeic acid [43], electro-organic synthesis of new caffeic acid derivatives [44], and electrochemical synthesis of 6-arylsulphonyl caffeic acid derivatives [45].

Electrochemical synthesis of polvanillin, was performed in 2012 by Amarasekara and colleagues [46]. Polyvanillin modified electrode has been used for determination of adrenaline and uric acid [47]. The carbon nanotube/polyvanillin composite film has been used as a nitrite sensor [48]. However, no study was found using caffeic acid and vanillin as copolymers.

In this study, a new voltammetric sensor for electrocatalytic determination of CUR was designed by modifying PtE surface with Van-CA co-electropolymerization using CV method. Then, the developed sensor is intended to be used to determine the CUR content of spice samples and to prove the accuracy of the proposed method.

2. EXPERIMENTAL

2.1. Apparatus

The electrochemical behaviour of the CUR was investigated using two different voltammetric techniques (CV and DPV). In the initial studies in order to find the redox potential of CUR was used CV. Then, bare PtE was modified with Van and CA. In the ongoing studies, DPV technique was used for the optimization of analytical parameters of modified electrode for determination of CUR.

The reagents were used of analytical purity and purchased. CUR and acetonitrile (AcN) were obtained from Sigma-Aldrich Corporation. Bisphenol-A (BPA) and 4-aminobenzoic acid (PABA) were obtained from Fluka. Vanillin, dopamine (DOP), catechin (Ct), 4-hydroxybenzaldehyde, (PHB) calcium chloride, magnesium chloride, potassium chloride, potassium dihydrogen phosphate, potassium monohydrogen phosphate, sodium acetate, sodium bicarbonate, sodium borate, sodium carbonate, sodium chloride, sodium hydroxide, sodium citrate, tris HCl, acetic acid, caffeic acid (CA), citric acid, ethanol, phosphoric acid, and tween 20 were obtained from Merck Chemical Company. Sample of spices were purchased from local markets.

SEM analyzes were performed using the LEO-EVO 40 SEM instrument, and samples were analyzed with Au/Pd surface coating.

All electrochemical measurements were obtained at room condition using Bioanalytical Systems Electrochemical Analyzer (BAS 100B, Bioanalytical Systems, Inc.). The measurements were carried out in a three-electrode cell containing Ag/AgCl (3 M KCl) reference electrode, Pt wire counter electrode and platinum (MF-2014) working electrode. The Pt working electrodes were polished by gently pressing as if drawing the figure 8 until the electrode surface was as bright as a mirror after by first dropping 0.3 micrometer and then 0.05 micrometer alumina slurry (Johnson Matthey Catalog Comp., United States) into the velvet polishing pad of the electrode. Subsequently, each Pt working electrode was held in the ultrasonic bath (Branson model 3510) in distilled water and AcN for approximately 1 min., respectively, to remove residual abrasive particles, and gently dried with a paper towel. A Thermo Scientific STAR A-111 pH-meter was used to measure the pH of the prepared solution. The pH meter was calibrated with standard buffers (pH=10.00, pH=7.00 and pH=4.00) obtained from Merck. Weightlab Instrument WSA-224 model balance is used for weighing chemical substances. All aqueous solutions were prepared with ultrapure water from Millipore brand Elix 20.

2.2. Procedure

2.2.1. Preparation of monomer solution

Firstly, monomer solutions were prepared (Van, DOP, CA, Ct, PABA and PHB in 0.1 M

PB at pH 7.40 and BPA in ethanol). Then, the monomer solution was prepared by adding different amounts of both Van and CA to 0.1 M PB adjusted to pH 7.40.

2.2.2. Preparation of standard CUR solution

Curcumin does not dissolve in acidic and neutral pH in water, but can be dissolved in overly acidic solvents such as alkaline or glacial acetic acid, as in polar and non-polar organic solvents [4]. Therefore, in this study, stock standard curcumin solution was prepared by dissolved in AcN. 0.1% Tween 20 was added to the medium as a surfactant. Then, electrochemical measurements were made by adding appropriate amounts of curcumin to 0.1 M PB adjusted to pH 7.40.

2.2.3. Preparation of commercial spices samples

Three spice samples such as commercial curry powder and two different turmeric brands were purchased from supermarkets for the determination of CUR. Spice sample solutions were prepared by weighing 1.0 g of each sample, adding 10 mL of AcN, 0.1% Tween 20 and dissolving in an ultrasonic bath for 60 minutes. Filtration was not necessary, as these solutions were clear. Then, it was stored in the polyethylene bottles at +4 °C in the refrigerator up to analysis.

Taking 2.5 mL of this prepared solution was completed to 5.0 mL with PB and the differential pulse voltammograms were taken. Then it was analysed by adding 40 μM from standard stock solution with standard addition method.

3. RESULTS AND DISCUSSION

3.1. Optimization of the polymerization conditions

Monomer solutions such as Van, DOP, CA, Ct, PABA, PHB, Van-CA in PB on the other hand BPA in ethanol were prepared. Mentioned monomers were polymerized with CV method in the range of potential (-800) - (1000) mV at different segments (5 and 6) on bare PtE in 0.1 M PB pH 7.40. The monomers were polymerized in both 5 and 6 segments to determine which one responded higher by creating oxidized and reduced forms of the polymer. As a result of differential pulse voltammetric studies on the prepared electrodes, it has been understood that the 6-segment, i.e., reduced form of the polymer is suitable for CUR determination.

The effect of each polymer electrode on the CUR response was tested using the DPV technique. In Figure 1A, bar graphs are drawn using CUR oxidation peak currents on electrodes modified with the polymers mentioned above. As understood from Figure 1A, the CUR peak current of the modified electrode obtained with each monomer used is lower than that of the bare Pt electrode. In contrast, the peak current value of the copolymer coated

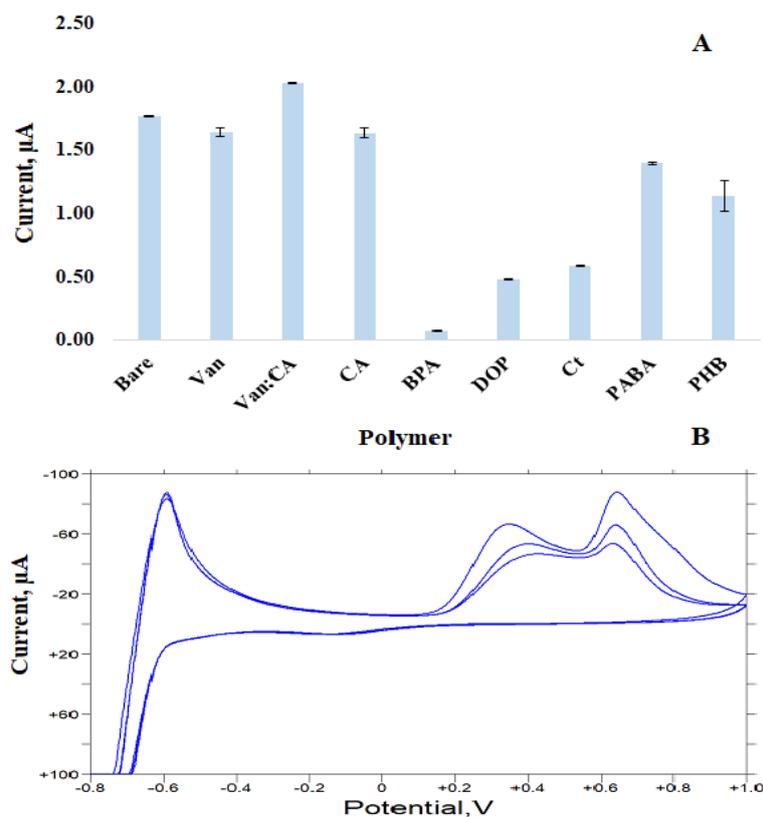electrode was higher than that of all other modified electrodes.

Fig. 1. Effect of polymer type **(A),** CV of the (Van-CA) polimerization in 0.1 M PB pH 7.40 **(B)**

For example, the CUR oxidation peak current was found as 1.6397 µA on the polyvanillin modified electrode and 1.6370 µA on the polycaffeic acid coated electrode. It is clearly seen from the figure that when the p(Van-CA) coated electrode obtained from these two monomer mixtures is used, the peak current increases to 2.0300 µA. The electrocatalytic effect of the p(Van-CA) modified electrode, whose polymerization CV is shown in Figure 1B, was found to be high.

The monomer solutions were prepared by stirring different concentration ratio of Van:CA (5:4, 5:5, 5:6, 4:5, 6:5, 3.3, 4:4, 6:6 and 8:8 mM) in 0.1 M phosphate buffer pH 7.40.

Polymerizations were carried out electrochemically by CV method on bare Pt electrode in the range of (-800) - (1000) mV potential. The effect of copolymers prepared using different Van:CA concentration ratios on CUR oxidation peak height was investigated. Optimum concentration ratio of Van:CA was selected as 6:6 (Fig. 2A). The effects of the monomer solution pH values on electrochemical signal of CUR were investigated in the range of 7.00-7.60 pH values. Finally, the highest peak current was obtained at pH 7.40.
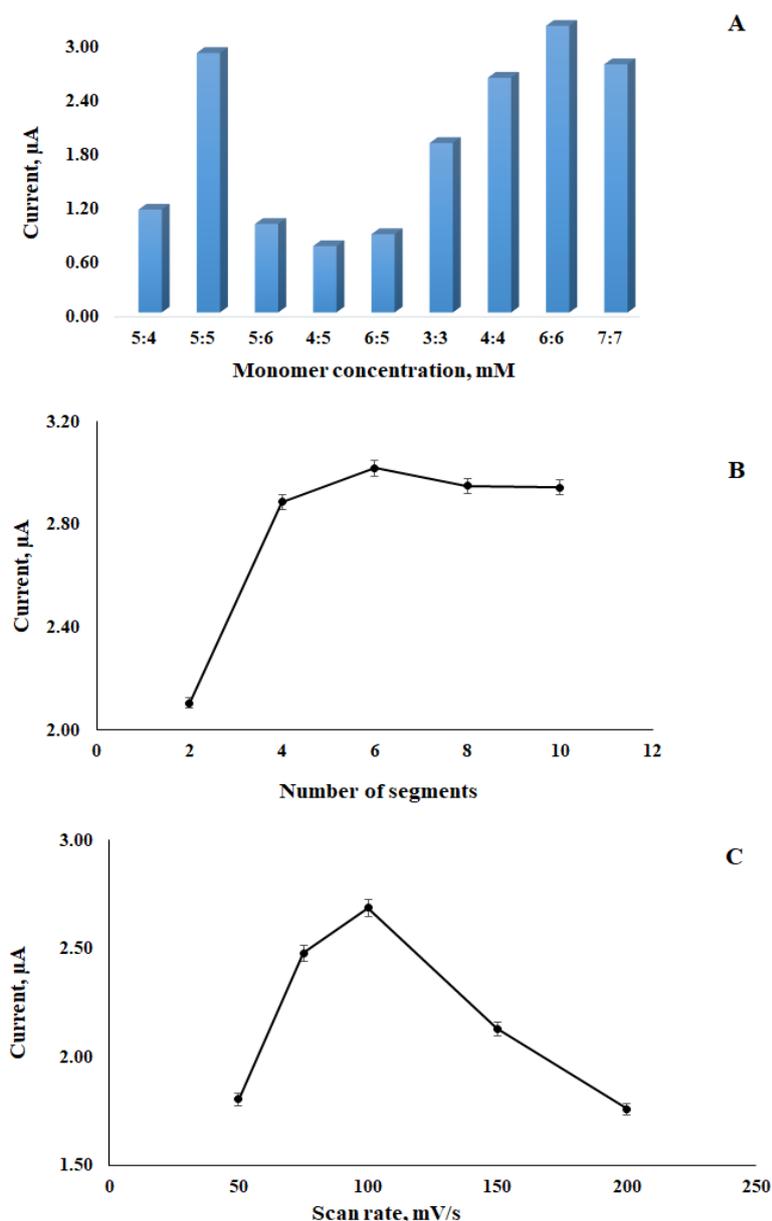
Fig. 2. Effect of the Van:CA concentration ratio **(A)**, number of segment **(B)** and scan rate **(C)**

The surface properties of modified electrode are generally affected by the film thickness, which may lead to a decrease in peak current after a certain thickness as the film thickness increases [49]. In present work, the thickness of polymer film layer was controlled through adjusting the number of segment during the electropolymerization process by CV method. The segment number has been changed from 2 to 10 to determine the maximum peak current. As shown in Fig. 2B, up to 6 segment film thickness increasing of the polymerization cycles, the current response of curcumin was increased. As the number of segments increased, thicker films were formed, resulting in decreased curcumin responses. In subsequent studies, film thickness was used as 6 segments.

The scan rate effect has been changed from 50 to 200 mV/s to determine the best scan rate for CUR oxidation. From Fig. 2C, it was clearly observed that best of the DPV response was occurred in the 100 mV/s scan rate.
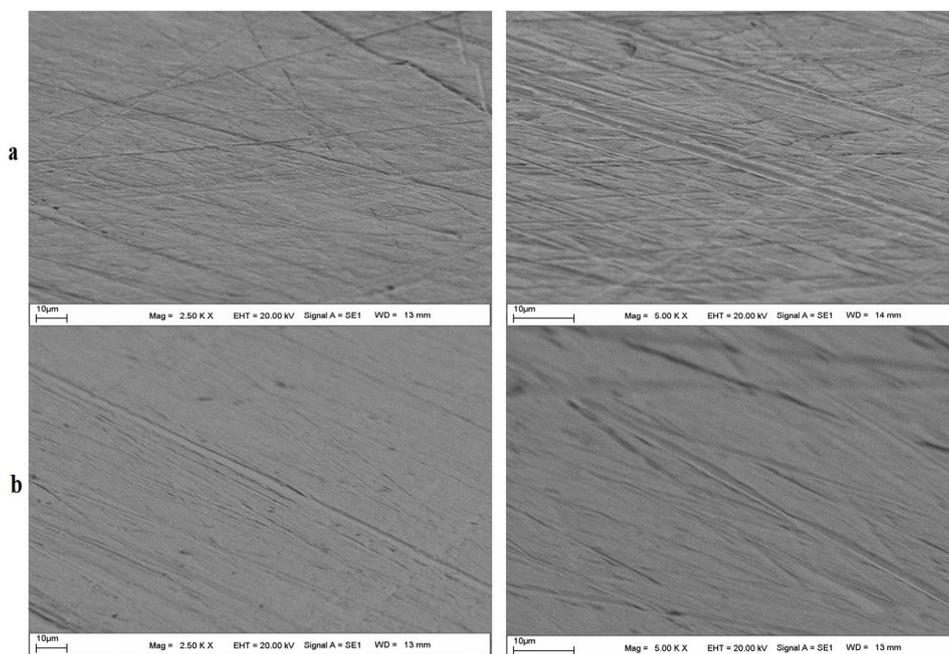

Fig. 3. SEM images of platinum electrode surfaces **a**: Bare, **b**: coated with *p*(Van-CA)

SEM analyses were performed to determine the effectiveness of the copolymer coating. SEM images of surfaces bare platinum electrode and platinum electrode coated with electropolymerization are given in Figure 3. The bare platinum surface is quite flat and smooth in the figures given in two different magnifications (Figure 3a). After the coating process, the polymeric film on the surface is clearly visible in two different magnifications too (Figure 3b). The surface images prove the smooth film structure.

3.2. Impedance study of the p(Van-CA)/Pt electrode

Electrochemical impedance spectroscopy (EIS) is a highly sensitive characterization technique that gives details about the interface properties after the surface modification [50]. Fig. 4 shows the EIS measurements. The Nyquist plots of the bare electrode represent at low frequency a straight line with a small semi-circle at high frequency region. Concerning, the Nyquist plots of the modified electrode it represent a semi-circle at high frequency which is related to an increase in the charge transfer resistance than it was estimated for the bare electrode, indicating the adhesion of the p(Van-CA) layer on the electrode surface. The increase in the resistance transfer charge is related to the formation of a dense layer of p(Van-CA) on the electrode surface. This increase could be also explained by repulsion between the deposited film on the surface of the electrode and the Ferricyanide present in the cell.
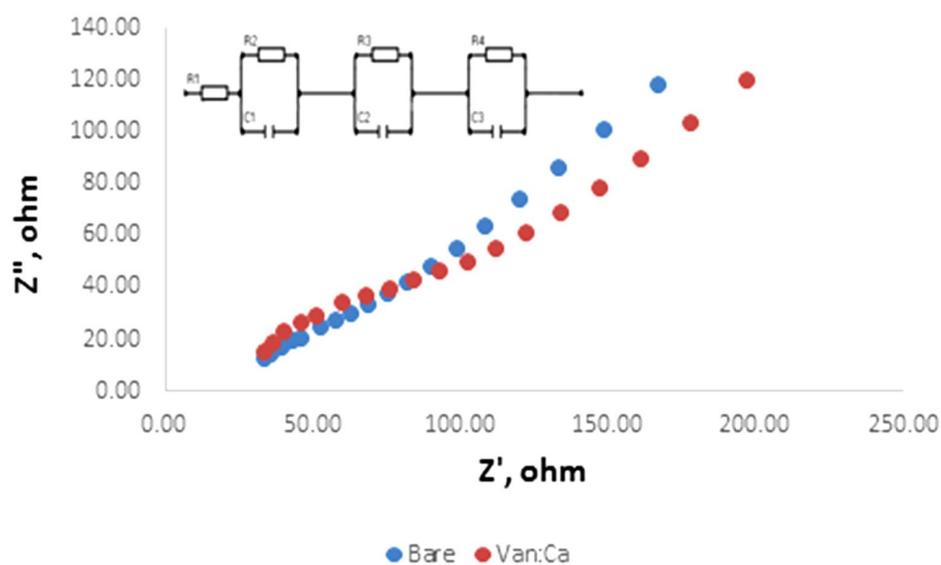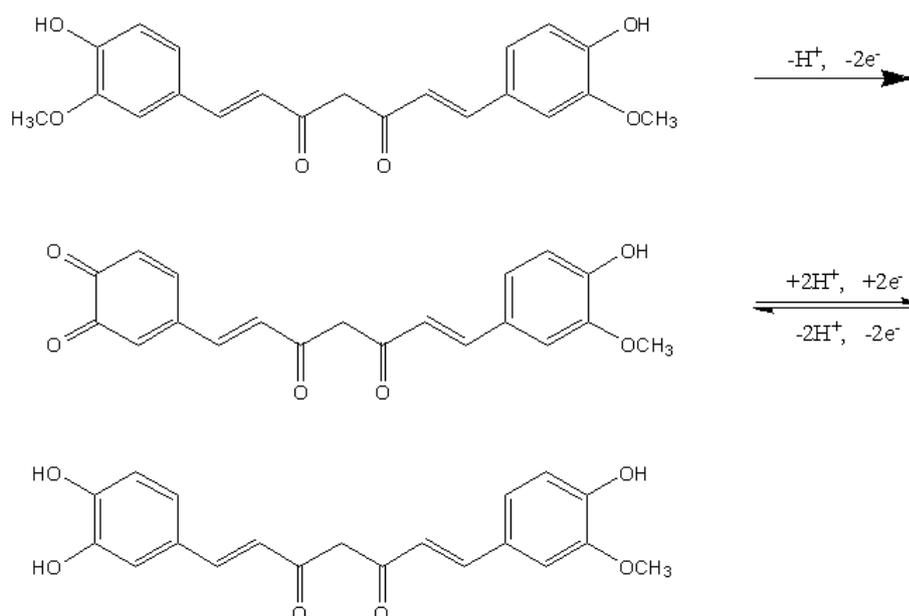
Fig. 4. Electrochemical impedance spectra for bare Pt electrode and p(Van-CA) coated electrode

3.3. Electrochemical behaviours of p(Van-CA) modified electrode

The voltammetric behaviour of CUR, shown in redox mechanism scheme 2, on bare and modified PtE was investigated in 0.1 M PB.
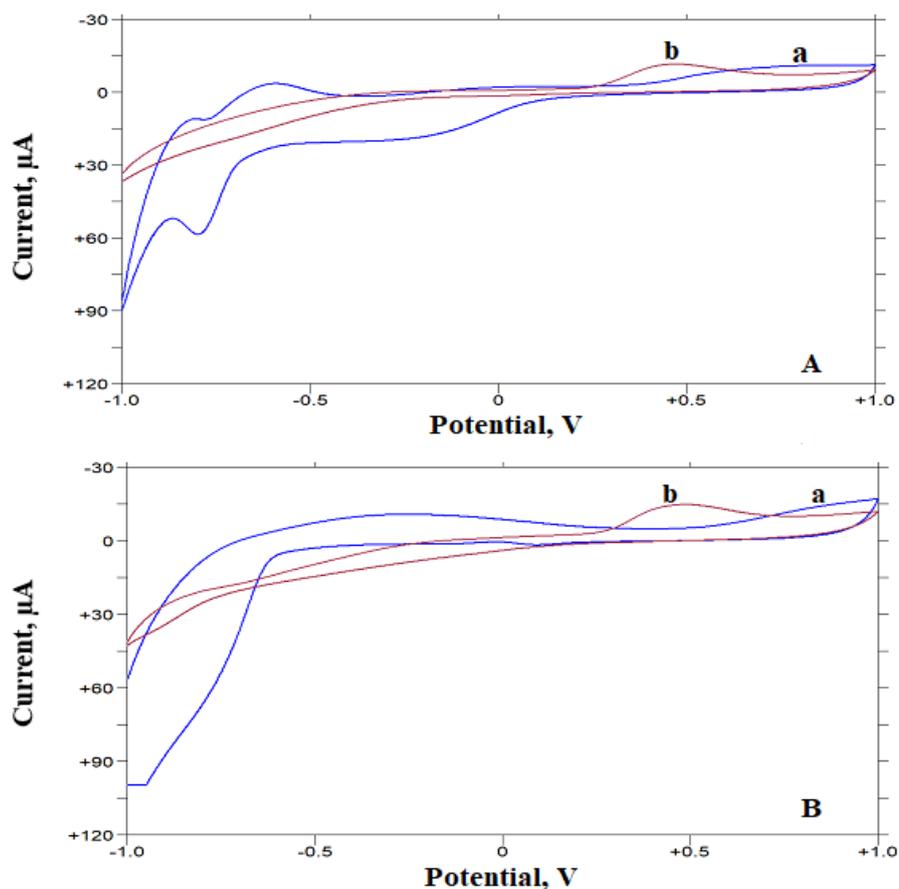

Scheme 2. Redox mechanism of CUR [1]

Fig. 5. Cyclic voltammograms of (a) background, (b) 0.3 mM CUR (in AcN) on bare PtE **(A)**; on *p*(Van-CA)/PtE **(B)** in PB, pH 7.40

The sensitivity of the modified electrodes is highly affected by the electrodeposition parameters, considering the strict relation between the electrodeposited film characteristics and the electrode response [47]. Therefore, voltammetric redox potential of CUR was first investigated in the range of (-1.0)-(1.0) V by CV method in 0.1 M PB at pH 7.40. Fig. 5 presents the CVs for both background and CUR in PB at the bare (Fig.5A) and *p*(Van-CA) coated Pt electrode (Fig. 5B) in 0.1 M PB at pH 7.40. When the voltammograms in Figure 5 are examined, the presence of an oxidation peak (Fig.5Ab and Fig 5Bb) with a potential of approximately 0.5 V on both bare PtE and *p*(Van-CA) modified PtE proves that this peak is a CUR, although it is not seen in the voltammogram of the background (Fig.5Aa and Fig 5Ba) solution. As a result of the CV experiments, the CUR oxidation pickup on the *p*(Van-CA) coated electrode was found to be higher compared with to the bare electrode response. Thus, it was understood that the copolymer used in the modification had an electrocatalytic effect.

Differential pulse voltammetry (DPV) is a more sensitive technique than the CV and was employed for detecting CUR on *p*(Van-CA)/PtE at the PB. For this reason, primarily analytical parameters optimized using the DPV technique to develop an electroanalytical

procedure for the determination of CUR. In this step; Optimum parameters were determined as potential operating range of 0.0 V to +0.8 V, pulse width 50 ms, sample width 20 ms, pulse amplitude 50 mV, and pulse time 200 ms, and were used in subsequent experiments. To determine the electrolyte type effect on the CUR oxidation peak current, each has a concentration of 0.1 M, carbonate buffer (CB), tris buffer (TrisB), citrate buffer (CitB), acetate buffer (AcB), Britton Robinson buffer (BRB), borate buffer (BB) and PB electrolyte solutions were used. When Figure 6A obtained from differantial pulse voltammograms is examined, it is seen that the highest peak current for CUR oxidation occurs in PB.

For determining curcumin in the literature, the optimum pH values obtained using different modified agents is quite different. For example; it has found 5.0 and 8.5 for CPE and HMDE, respectively by Stanic [26]. On the other hand, it was found to be 4.0 for dysprosium nanowires/CPE by Daneshgar et al. [25]. In our study, the effect of electrolyte pH on the CUR electrochemical signal was investigated using the DPV method with the *p*(Van-CA) modified PtE in 0.1 M PB in the range of pH 6.00 to 7.50, and the optimum pH was observed as 7.25 (Figure 6B).
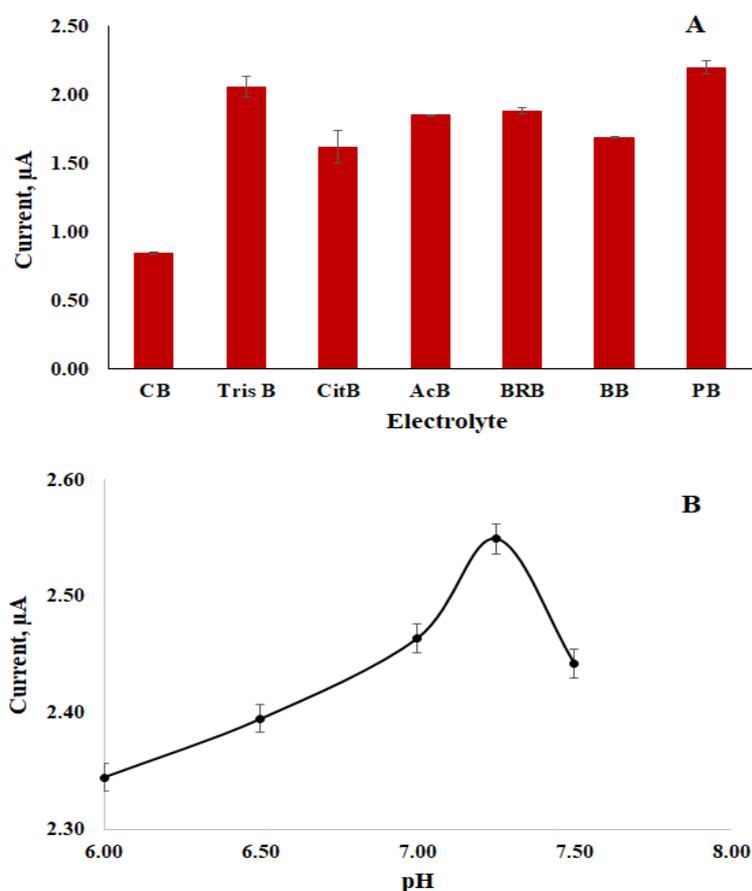

Fig. 6. Effect of the **(A)** support electrolyte type, **(B)** electrolyte pH on the CUR oxidation peak current in 0.1 M PB

The influence of pH on CUR oxidation peak potential (Ep) was illustrated in Fig. 7A. When it was investigated, it is seen that the regular increase in pH causes to decrease regularly of Ep. This state was seen that indicating the involvement of protons in the electrooxidation of CUR. As the pH values increased up to 7.00, the peak potential shifted to negative values. A linear decrease was observed in Ep-pH graph in acidic region. According to Nernst equation, the slope corresponding to 1 electron exchange was 59 mV, while it was found as 57.7 mV in this study (Eq. 1). This value is compatible with slope in the Nernst equation.

$$Ep = -57.7pH + 720.72 \qquad (E \text{ in mV}, R^2 = 0.9997) \qquad (Eq. 1)$$

The scan rate effect on the peak current of CUR in 0.1 M PB, pH 7.25 was studied by DPV in the range of 20-100 mV/s (Fig. 7B). The results indicated that the peak current was increased up to 80 mV/s then decreased. This value was used as the most appropriate scan rate in subsequent studies.
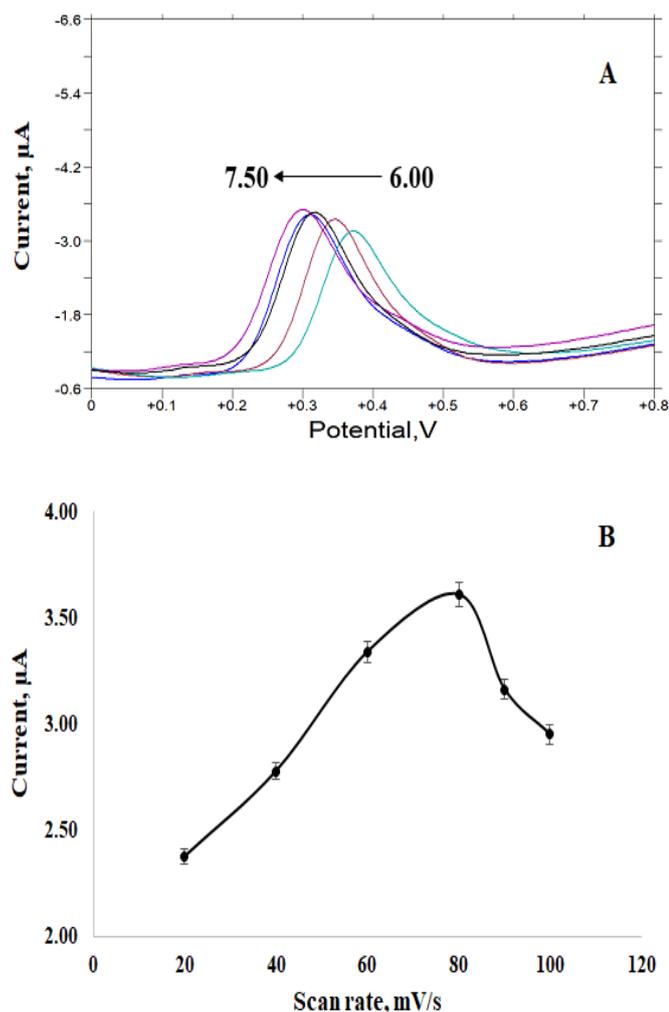

Fig. 7. Effect of the **(A)** electrolyte pH on the CUR oxidation peak potential, **(B)** scan rate on the CUR oxidation peak current in 0.1 M PB

Under optimal experimental conditions, DPV curves for different CUR concentrations in the presence of both electroactive (uric acid, ascorbic acid) and non-electroactive (glucose, lactose, maltose, sucrose) interferences (each of which is 100 µM) were shown in Fig. 8A. The peak currents increased with the increment of the concentration of CUR. The plot of calibration curve was linearly related to curcumin concentration with the regression equation of Eq. 2:

$$I_p(\mu A) = 20.207C \text{ (mM)} +0.0702 \tag{Eq. 2}$$

and the correlation coefficient was 0.9951.

The electrochemical performance and selectivity of the present modified electrode provides a sensitive and selective determination of CUR in the wide linear range of 0.01-1.0 mM with 5.0 µM *LOD*. Detection limit was calculated with the *LOD=3S/m* equation using the *S* (standard dev.) and *m* (slope) values obtained from the calibration curve in showed Fig. 8B.
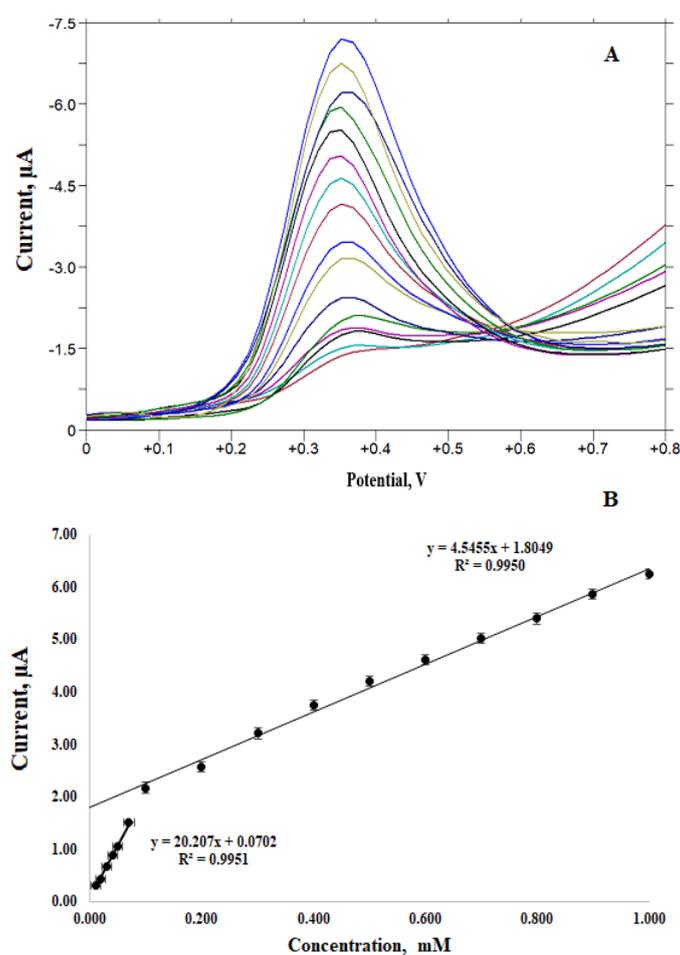

Fig. 8. Differential pulse voltammograms of CUR in 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90 and 1.00 mM concentrations (A), calibration curve (B), of 0.5 mM CUR oxidation on *p*(Van-CA)/PtE, in PB, pH 7.25

To test the stability of the method developed for CUR determination, the electrode was modified 10 times then differential pulse voltammograms in showed Fig. 9A were taken in 0.1 M PB containing 0.5 mM CUR. Figures 9A and 9B, the reproducibility of the differential pulse voltammetric responses obtained with ten measurements by using *p*(Van-CA) modified Pt electrode shows that the stability of the sensor prepared for the CUR assay is very good. Considering the *RSD* (relative standard dev.) 0.39 and standard deviation (0.016) calculated from the bar graph in Fig. 9B, the method was found to be reproducible, highly stable, and accurate (99.6%).
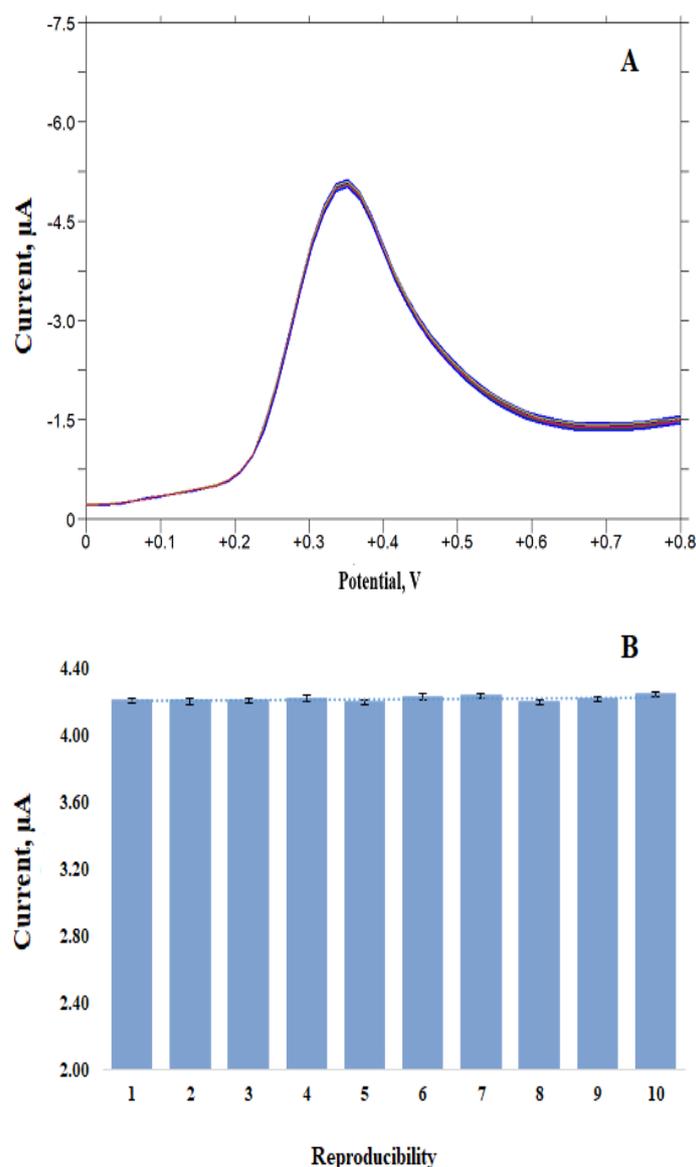

Fig. 9. (A, B) reproducibility of differential pulse voltammetric response, n=10 of 0.5 mM CUR oxidation on *p*(Van-CA)/PtE, in PB, pH 7.25

3.4. Curcumin determination in commercial spice samples

The analytical applicability of the developed modified electrode was confirmed by the use of this method for determination of CUR in three commercial spice samples (two different brand turmeric powder and curry powder). Just prior to analysis, appropriate amounts were taken from "Preparation of commercial spices samples" section-mentioned solution and analysed by diluting two fold. The recovery efficiency was then calculated using the standard addition method (Table 1).

"Preparation of commercial spices samples" section-mentioned solution and analyzed by double dilution.

Developed CUR detection technique was applied to commercially spice samples. *R* (Recovery) values for CUR determination in commercial spices were obtained using *p*(Van-CA) modified PtE in 0.1 M PB, pH 7.25. As shown in Table 1, the recovery efficiency in the range of 96% to 102% indicates that the sensor has been successfully applied to real samples. On the other hand, the RSD values for curcumin determination were found by Daneshgar et al. in the milk sample in the range of 0.05-0.25 using a dysprosium nanowire coated carbon paste electrode, and in the range of 0.03-0.31 using a carbon nanotube coated glassy electrode [25], Also, and Peng et al. RSD for curcumin in human urine in the range of 2.7-3.4% [51], and Ziyatdinova and colleagues in the spice samples in the range of 1.2-2.2% [14]. According to the RSD values in Table 1 and Table 2, we found are in accordance with the literature.

Table 1. Percents recovery yields of CUR in commercial spice samples obtained with *p*(Van-CA)/PtE in 0.1 M PB (n=3)

Sample	Original found in sample (μM)	Standard added (μM)	Total Found (μM)	RSD (%)	R (%)
Turmeric powder 1	< limit of detection	40	40.25±0.022	0.054	100.6
Turmeric powder 2	< limit of detection	40	40.80±0.102	0.250	102.0
Curry powder	< limit of detection	40	38.41±0.035	0.092	96.0

4. CONCLUSION

In summary, we were developed a sensor for the electrochemical detection of CUR by using a *p*(Van-CA) film. The results obtained in this study showed the potential of using *p*(Van-CA)/PtE combined with DPV technique for voltammetric determination of CUR in commercial samples such as spices.

This CUR sensor was prepared by a simple CV method and expanded sensing range, showed short response time, and high stability with a wide linear range of 0.01-1.0 mM and a

low detection limit of 0.005 mM. A lower passivation effect and better stability and reproducibility were shown with the modified electrode compared to the unmodified electrodes. Furthermore, the developed sensor has been successfully applied to the detection of CUR in three real sample of spices and exhibited good selectivity reproducibility and stability. However, the CUR responses of the sensor were not affected by the matrix in commercially real sample of spices. This new method offers great hope for the determination of CUR without a series of pre-treatments in various food sample applications. The electrocatalytic behaviour of *p*(Van-CA)/PtE was investigated carefully. As a result of this study, we notified that an electrochemical sensor was successfully developed and it was proven to have a low cost and a rapid response and to be very simple, reproducible, highly selective and sensitive for the detection of CUR in turmeric and curry powder spices.

The analytical parameters obtained are better than most of the advanced that modified electrodes reported in the literature (Table 2). Prepared polymer modified electrode for the determination of CUR exhibited extremely good analytical performance that it is with lower concentration levels and lower detection limit, wide linear range similar and/or better than those previous articles reported in literature. The advantages highlighted for this CUR sensor include low cost reproducibility, high stability, selectivity and fast analysis.

Table 2. The comparison of the presented sensor properties with the literature

Detection Method	Modification	Linear Range (M)	LOD (M)	R^2	RSD (%)	Ref.
DPV	poly-ACBK/GCE	1.0×10^{-7}-7.0×10^{-5}	4.1×10^{-8}	0.998	2.9	[51]
CV	GCE	9.9×10^{-6}-1.07×10^{-4}	4.1×10^{-6}	0.9987	-	[14]
FFTSWV	CNT/GCE	1.0×10^{-8}-1.0×10^{-6}	-	0.990	0.2-0.5	[28]
Fluorescence	-	2.0×10^{-3}-5×10^{-1}	4.3×10^{-4}	0.9973	-	[21]
DPV	*p*(Van-CA)/PtE	1.0×10^{-6}-1.0×10^{-3}	5.0×10^{-6}	0.9951	0.39	This Study

FFTSWV: Fast Fourier transform square wave voltammetry
CNT/GCE: Carbon nanotube/Glassy carbon electrode
poly-ACBK/GCE: Acid chrome blue K/Glassy carbon electrode

Compliance with ethical standards
The authors state that they have no competing financial interests or competing personal

relationships that could affect the work reported in this paper.

REFERENCES

[1] K. Li, Y. Li, L. Yang, L. Wang, and B. Ye, Anal. Methods 6 (2014) 7801.

[2] R. Zokhtareh, and M. Rahimnejad, Electroanalysis 30 (2018) 921.

[3] Y.J. Surh, Nature Reviews Cancer 3 (2003) 768.

[4] M.L.A.D. Lestari, and G. Indrayanto, Profiles of Drug Substances, Excipients and Related Methodology 39 (2014) 113.

[5] W.H. Chan, H.Y. Wu, and W.H. Chang, Food Chem. Toxicol. 44 (2006) 1362.

[6] B. Toptaş, and Z. Ateş Alagöz Journal of Faculty of Pharmacy Ankara 40 (2016) 58.

[7] M. Becit, S. Aydın, and N. Başaran, J. Pharm. Sci. 6 (2017) 126.

[8] P. Limtrakul, S. Lipigorngoson, O. Namwong, A. Apisariyakul, and F.W. Dunn, Cancer Lett. 116 (1997) 197.

[9] J.T. Piper, S.S. Singhal, M.S. Salameh, R.T. Torman, Y.C. Awasthi, and S. Awasthi, The International J. Biochem. Cell Biology 30 (1998) 445.

[10] P. Anand, C. Sundaram, S. Jhurani, A.B. Kunnumakkara, and B.B. Aggarwal, Cancer Lett. 267 (2008) 133.

[11] J.V. Tosati, E.F. de Oliveira, J.V. Oliveira, N. Nitin, and A.R. Monteiro, Food Control 84 (2018) 177.

[12] K. Mehta, P. Pantazis, T. McQueen, and B.B. Aggarwal, Anti-Cancer Drugs 8 (1997) 470.

[13] A.L. Cheng, C.H. Hsu, J.K. Lin, M.M. Hsu, Y.F. Ho, T.S. Shen, and J.Y. Ko, Anticancer Res 21 (2001) 2895.

[14] G.K. Ziyatdinova, A.M. Nizamova, and H.C. Budnikov, J. Anal. Chem. 67 (2012) 591.

[15] D.D. Heath, M.A. Pruitt, D.E. Brenner, and C.L. Rock, J. Chromatogr. B 783 (2003) 287.

[16] R.S.P. Singh, U. Das, J.R. Dimmock, and J. Alcorn, J. Chromatogr. B 878 (2010) 2796.

[17] V. Kakkar, S. Singh, D. Singla, S. Sahwney, A.S. Chauhan, G. Singh, and I.P. Kaur, J Chromatogr. B 878 (2010) 3427.

[18] A.K. Chavan, S.A. Nirmal, and S.R. Pattan, J. Liq. Chromatogr. Related Technol. 38 (2015) 1213.

[19] B. Tang, L. Ma, H.Y. Wang, and G.Y. Zhang, J. Agric. Food Chem. 50 (2002) 1355.

[20] F. Wang, W. Huang, and Y.W. Wang, J. Lumin. 128 (2008) 110.

[21] Z.G. Chen, L. Zhu, T.H. Song, J.H. Chen, and Z.M. Guo, Spectrochim. Acta Part A 72 (2009) 518.

[22] P. Wei, Z. Zhu, R. Song, Z. Li, and C. Chen, Electrochim. Acta 317 (2019) 93.

[23] B. He, and D. Yan, Food Control 103 (2019) 70.

[24] S. Titretir Duran, A. Paşahan, N. Ayhan, Ö. Güngör, M.A. Cengiz, and S. Köytepe

Polym Plast Technol Eng 56 (2017) 1741.

[25] P. Daneshgar, P. Norouzi, A.A. Moosavi-Movahedi, M.R. Ganjali, E. Haghshenas, F. Dousty, and M. Farhadi, J. Appl. Electrochem. 39 (2009) 1983.

[26] Z. Stanic, A. Voulgaropoulos, and S. Girousi, Electroanal. 20 (2008) 1263.

[27] E. Arslan, and S. Çakır, J. Solid State Electrochem. 18 (2014) 1611.

[28] M.A.N. Manaia, V.C. Diculescu, E. de S. Gil, and A.M. Oliveira-Brett, J. Electroanal. Chem. 682 (2012) 83-89.

[29] C. Chen, H. Xue, and S. Mu, J. Electroanal. Chem. 713 (2014) 22-27.

[30] M.M Ardakani, A.M. Dehghani-Tafti, and F. Sabaghian, Anal. Bioanal. Electrochem. 12 (2020) 277.

[31] M.M. Vinay, Y.A. Nayaka, K.V. Basavarajappa, P. Manjunatha, H.T. Purushothama, and R.O Yathisha, Anal. Bioanal. Electrochem. 12 (2020) 155.

[32] M. Burç, S. Köytepe, S. Titretir Duran, N. Ayhan, B. Aksoy, and T. Seçkin, Measurement 151 (2020) 107103.

[33] Ö. Güngör, İ. Özcan, M.A. Erdogan, B. Ateş, and S. Köytepe, Anal. Lett. 53 (2020) 228.

[34] A. Baytak Kutluay, and M. Aslanoğlu, Food Chem. 228 (2017) 152.

[35] S. Titretir Duran, Gazi University J. Sci. 32 (2019) 426.

[36] Â. Vilas-Boas, P. Valderrama, N. Fontes, D. Geraldo, and F. Bento, Food Chem. 276 (2019) 719.

[37] O.C Chikere, N.H Faisal, P.K.T Lin, and C. Fernandez, J. Solid State Electrochem. 23 (2019) 1795.

[38] H.R.S. Lima, E.A de O. Farias, P.R.S Teixeira, C.Eiras, and L.C.C. Nunes, J. Solid State Electrochem. 23 (2019) 3153.

[39] H.R. Zare, and S.M. Golabi, J. Solid State Electrochem. 4 (2000) 87.

[40] A. Rohanifar, A.M. Devasurendra, J.A. Young, and J.R. Kirchhof, Anal. Methods 8 (2016) 7891.

[41] W. Ren, H.Q. Luo, and N.B. Li, Biosens. Bioelectrons. 21 (2006) 1086.

[42] N.B. Li, W. Ren, and H.Q. Luo, J. Solid State Electrochem. 12 (2008) 693.

[43] P. Hapiot, A. Neudeck, J. Pinson, H. Fulcrand, P. Neta, and C. Rolando, J. Electroanal. Chem. 405 (1996) 169.

[44] A. B. Moghaddam, M. R. Ganjali, P. Norouzi, and M. Niasari, J. Electroanal. Chem. 601 (2007) 205.

[45] C.C. Zeng, C-F. Liu, J. Zeng, and R.G. Zhong, J. Electroanal. Chem. 608 (2007) 85.

[46] A.S. Amarasekara, B. Wiredu, and A. Razzaq, Green Chem. 14 (2012) 2395.

[47] H.D. Madhuchandra, and B.E. Kumara Swamy, Materials Science for Energy Technologies 2 (2019) 697.

[48] D. Zheng, C. Hu, Y. Peng, and S. Hu, Electrochimica. Acta 54 (2009) 4910.

[49] K.V. Özdokur, Electroanalysis 31 (2019) 1.

[50] J. Wang, Analytical Electrochemistry, Canada, 3rd ed. (2006) pp. 30.

[51] J. Peng, K. Nong, and L. Cen, J. Chin. Chem. Soc. 59 (2012) 1415.