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Original scientific paper

Rapid and sensitive electrochemical determination of flavonoids in Albanian wines using zeolite X and Prrenjasi clay as carbon paste modifiers

Nensi Isak[1], Muhamed Farruku[1], Xhensiana Ndreka[1], Sara Dervishi[1], Magdalena Cara[2], Edlira Baraj[3], Avni Berisha[4], Arjan Korpa[1] and Kledi Xhaxhiu[1,✉]

[1]*Faculty of Natural Sciences, University of Tirana, Boulevard "Zogu I", 1001, Tirana, Albania*
[2]*Department of Plant Protection, Faculty of Agriculture and Environment, Agricultural University of Tirana, Albania*
[3]*Departmentof Chemistry, Faculty of Mathematical Engineering and Physical Engineering, Polytechnic University of Tirana, Albania*
[4]*Faculty of Natural and Mathematics Science, University of Pristina, Pristina 10000, Kosovo*
Corresponding author: ✉kledi.xhaxhiu@fshn.edu.al

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Abstract

This study investigated the electrochemical determination of flavonoids in Albanian wines using carbon paste electrodes modified with various materials. We employed an ex-situ method to minimize interferences from complex wine matrices, focusing on catechins as flavonoids representatives. The modifiers included Zeolite type X, and clay from the Prrenjasi region in Albania. Differential pulse voltammetry, cyclic voltammetry, electrochemical impedance spectroscopy, and scanning electron microscopy were utilized to characterize the modified electrodes. Results indicated that the carbon paste electrode modified by Prrenjasi clay (PCME) exhibits the highest sensitivity, with the lowest electron transfer resistance and largest active surface area. Also, PCME was chosen for its linear background, low cost, and excellent sensitivity for total flavonoid determinations in Albanian wines. The method demonstrated a limit of detection of 99.3 nM and a limit of quantification of 331 nM. The catechin equivalent flavonoids in the analysed Albanian wine samples ranged between 513.13 and 2156.07 mg L^{-1}. The diffusion coefficient of catechin was determined to be 1.38×10^{-5} cm^2 s^{-1}. A comparative analysis was also performed using UV-VIS spectrophotometry, which determined the total flavonoid content in each analysed wine. The study demonstrated the potential of using PCME carbon paste electrodes for reliable flavonoid quantification in Albanian wines.

Keywords

Wine analysis; polyphenolic compounds; catechin oxidation; aluminosilicate solid; Albanian clay

Introduction

Antioxidants encompass a wide range of chemical compounds that counteract oxidative processes, which can lead to the degradation of dietary nutrients, materials like rubber and plastic, and essential molecules in biological systems [1]. Recently, with the increasing focus on identifying safe food antioxidants, there has been a growing preference for natural antioxidants, particularly those derived from plants [2]. The main bioactive compounds in natural sources are phenolic compounds, including flavonoids and non-flavonoids [3]. They play a crucial role in scavenging reactive oxygen species, effectively countering lipid oxidation, reducing peroxide formation in vivo, and enhancing the activity of the body's antioxidant enzymes [4]. Catechins represent a class of polyphenolic compounds categorized within the flavanol subfamily of flavonoids. These compounds find their most abundant dietary sources in green tea, cocoa products, and wine [5].

According to the latest data from the International Organization of Vine and Wine (IOV), global wine consumption in 2023 was 221 million hectolitres [6]. Wine production in Albania is thought to have begun in the Bronze Age, approximately 3,000 years ago. Between 2000 and 2016, grape production in Albania increased by over 250 percent. In 2022, the country produced 3.03 million litres of wine, with 46.4 percent exported, primarily to other European countries, according to Albania's Ministry of Agriculture and Rural Development [7].

The quality of wine, particularly red wine, is heavily influenced by the amount of polyphenolic compounds present [8]. Instead of producing wine from tropical fruits, some manufacturers use artificial or natural colorants, such as roselle calyces, flavourings, or various inexpensive ingredients (colourants, water, sugars, flavourings, and ethanol) to adulterate wine [9]. As a result, the quality and authenticity of wines on the market have become a concern for reputable wine producers, government authorities, and discerning consumers. While attributes like colour, mouthfeel, and taste serve as indicators of wine quality, the presence of phenolic compounds and other wine components is widely used to provide reliable information about the authenticity of the wine [10].

The determination and quantification of flavonoids have become highly attractive. Successful quantification of them has been reported based on electromigration methods such as capillary electrophoresis (CE) [11,12], micellar electrokinetic chromatography (MEKC) [13], thin-layer chromatography [14], separation with high-performance liquid chromatography (HPLC) coupled with UV [15], spectrophotometric methods [16], mass spectrometry (MS) detection [17] or electrochemical detection [18]. The use of electroanalysis for the quantitative analysis of phytopharmaceuticals is increasingly recognized for its significant advantages, including low equipment costs, minimal reagent consumption, excellent sensitivity, and suitable selectivity [19].

The electrochemical determination of flavonoids represented by catechin relies on the oxidation/reduction peak caused by catechin oxidation, which occurs in two steps: initially, the catechol undergoes oxidation at a low positive potential to form semiquinone, followed by the oxidation of the resorcinol hydroxyl group at a higher potential, resulting in quinone [20].

Electrodes with different modifications were already applied for the determination of catechins, such as glassy carbon electrodes modified with single-walled carbon nanotubes and cetyltrimethylammonium bromide [21], single-walled carbon nanotubes/poly(hydroxymethylated-3,4-ethylenedioxythiophene) composite modified electrode [22], beta-cyclodextrin-modified carbon paste electrode [23,24], self-assembled monolayer of nickel (II) complex and thiol on gold electrode [25], and electrodes modified with enzymes [26,27]. Several studies have reported the determination of flavonoids in wine samples. An electrochemical sensor, utilizing a glassy carbon electrode modified with a nanocomposite of graphene aerogel, chitosan, and zirconium oxide nanoparticles, coupled with

solid-phase extraction, was developed for the determination of flavonoids in real samples, including red wine, and demonstrated high sensitivity, selectivity, and accurate recovery rates [28]. Also in 2019, based on a nanocomposite of functionalized reduced graphene oxide, mercapto-β-cyclodextrin, and gold nanoparticles, an electrochemical sensor was developed for flavonoid determination in wine [29]. In addition, electrochemists have shown particular interest in inorganic materials, such as zeolites, silica-based hybrid materials, and clays, among the wide variety of electrode modifiers [30], especially for their analytical applications [31].

Zeolite type X is a laboratory-synthesized zeolite composed of fly ash (FA) as raw material. According to previous studies, Zeolite-X has exhibited outstanding adsorptive properties. Our research group previously described the XRD pattern of zeolite type X and the synthesis process [32]. Due to their advanced properties, including large surface area, uniform porosity, thermal stability, and ion exchange capacity, zeolites have found various applications, such as electrode materials, supercapacitors, sensors, catalysts, and adsorbents [33]. In 1996, Wang and Walcarius [34] used Zeolite-Y-modified carbon paste electrodes for selective dopamine monitoring. Additionally, Paredes-Doig *et al.* [35] have successfully modified gas sensors with zeolite type Y to detect volatile compounds in wine.

Clay minerals possess a significant adsorption capacity, driven by Coulombic forces and, due to their extensive surface area, by Van der Waals forces. They offer several advantages over other adsorbents, such as large specific surface areas resulting from their small particle size, low cost, and widespread availability [36]. X-ray diffraction powder measurements and chemical composition and physicochemical properties of several Albanian clays were previously reported [37]. The surface area of Prrenjasi clay (175 m^2 g^{-1}) is approximately three times higher than most natural Albanian clays, which is strongly related to the high montmorillonite content [38]. Clay materials have also been widely used as carbon paste modifiers in the detection of flavonoids [39-41].

This research study is the first to assess carbon paste electrodes modified with Zeolite type X for selective detection and quantification of flavonoids expressed as catechin equivalents in wine samples. Besides zeolite type X, the present research introduces Prrenjasi clay as a novel material for determining total flavonoids in wine, demonstrating its potential as an effective adsorbent in electrochemical applications. The chosen modifiers were implemented into carbon paste electrodes, forming zeolite type X modified electrode (ZME), and Prrenjasi clay modified electrode (PCME). These modifiers are easily synthesized or found in nature with minimal cost, and they exhibit outstanding performance in enhancing electrode sensitivity.

The novelty of this research lies in applying the *ex-situ* (extractive stripping voltammetry) method for electrochemical determination of total flavonoids in Albanian wine samples. This method effectively avoids potential interferences from compounds such as ascorbic acid, hydroquinone, and gallic acid, which are present in the highly complex matrices of wine. Analytical performance of modified electrodes is followed by using techniques such as differential pulse voltammetry (DPV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), together with UV-Vis spectrophotometry method ($AlCl_3$ assay) as a comparative technique and SEM for surface characterization.

Experimental

This article uses a novel approach instead of the traditional *in-situ* method (direct voltammetry), where the electrode is placed in the analyte solution and differential pulse voltammetry (DPV) is recorded. The *ex-situ* method for determination and quantification involves two steps:

The electrode is placed in the analyte solution (diluted wine) and continuously stirred with a magnet. No potential is applied during this step, allowing the analyte (catechin) to adsorb onto the carbon paste electrode (CPE).

After a time period of 3 to 30 minutes, optimized for each experiment, the electrode is removed from the solution, rinsed with ultrapure Mili-Q water, and then transferred to the measuring solution (buffer acetate, pH 5.5). DPV is then used to detect flavonoids.

The *in-situ* DPV method results in two oxidation peaks for catechin, but it suffers from poor selectivity, especially in real sample analysis, where complex matrices can interfere with the results. Non-flavonoids, including monocyclic acids, are the main interfering compounds. The *ex-situ* measurement of the catechin standards has been used to avoid the abovementioned complications. Our experience with this method has shown considerable adsorption/extraction of catechin onto the paste surface due to the hydrophobic-hydrophobic interaction [42].

Unlike the *in-situ* method, which often shows partial or complete overlap of interference peaks with catechin peaks in direct voltammograms, the *ex-situ* method remains unaffected by interfering compounds, even at high concentrations. This is due to the adsorption/extraction properties of the carbon paste electrode (CPE), including the polarity of the binding oil, hydrophobicity, and its modifications, as well as the differing adsorbing characteristics of catechin and the interfering compounds [43]. In this research, the spectrophotometric method ($AlCl_3$ assay) was used as a reference method for determining catechin (CAT)-equivalent flavonoids in wines.

Reagents, solvents and standards

(+)-Catechin analytical standards ($C_{15}H_{14}O_6$) were obtained from Sigma-Aldrich. Sodium acetate (CH_3COONa), acetic acid (CH_3COOH), and silicone oil 47 V 100 with a density of 0.86 g cm^{-3} at 20°C were obtained from VWR Chemicals. High-purity graphite micron powder (99.9 %) with a particle size range of 5 to 10 µm was purchased from Nanography Nano Technology, Germany.

Carbon paste preparation

The carbon paste is manually homogenized using an agate mortar. Graphite powder is mixed with binding oil for at least one hour until a uniform mixture is achieved. This paste is placed into a Teflon tube, making the working electrode with a diameter of 3.5 mm and a geometrical area of 0.0962 cm^2. Before each new measurement, it is crucial to clean the working electrode surface and remove a thin layer to eliminate any adsorbed analyte. The bare CPE was composed of 26 % silicon oil concentration in the paste.

Carbon paste modifiers

Zeolite type X and Albanian Clay from the Prrenjasi region were chosen as carbon paste modifiers. Each modifier at a concentration of 5 %, was incorporated into a paste composed of 26 % silicon oil and graphite micron powder, with a purity of 99.9 % and particle sizes ranging from 5 to 10 µm.

Preparation of standard catechin solution

Catechin is not entirely soluble in water; therefore, an organic solvent such as ethanol must be used to achieve its complete dissolution. After the 1 mM stock solution of (+)-catechin was prepared, dilutions were made in acetate buffer solution with pH of 5.5 during the measurements. The external standard calibration and standard addition method determined each selected wine's total flavonoids concentration (expressed as equivalent catechin) and the recovery, % of each tested

electrode. Calibration curves were obtained from triplicate injections of each concentration. Each wine was diluted in a 1:500 ratio.

Apparatus

Voltametric measurements were carried out by a Potentiostat/Galvanostat/Impedance Analyzer PalmSens 4 controlled by PSTrace 5 (version 5.11.913). The electrochemical cell contains a reference electrode (Ag/AgCl electrode in 3 M KCl solution), an auxiliary electrode (platinum wire), and a working electrode (carbon paste electrode). Spectrophotometric measurements were carried out with Jenway 6800 Double-Beam Spectrophotometer purchased from Bibby Scientific Ltd. United Kingdom with spectrum scanning range 190 to 1100 nm with resolutions up to 0.1 nm, and scan speeds up to 3600 nm/sec. The surface of the electrodes was characterized with scanning electron microscope (SEM) Zeiss EVO MA10.

Electrochemical characterization of catechin-equivalent flavonoids

Differential pulse voltammetry (DPV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry were employed to investigate the electrochemical properties of electrode interfaces. DPV was conducted in acetate buffer (pH 5.5) within a 0.0 to 1.2 V potential range, with pulse amplitude 0.025 V and scan rate 0.01 V s^{-1}, utilizing the peak current for total flavonoid quantification. CV explored redox mechanisms in 0.1 M KCl mixed with 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$, applying a potential range of -0.5 to 1 V at 100 mV s^{-1}. EIS characterized bare and modified electrode interfaces in 0.1 M KCl mixed with 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$, employing sinusoidal perturbations (±5 mV) across frequencies (100 kHz to 0.1 Hz), at open circuit potential. The equivalent circuit fitting of experimental data was done using PSTrace5 software version 5.11.913 from Palmsens. Chronoamperometry was performed in acetate buffer (pH 5.5) at 1.1 V *vs.* Ag/AgCl/KCl (3.0 M), and catechin concentrations were evaluated based on diffusion-controlled currents.

Spectrophotometric determination of total flavonoids

The total flavonoid content in Albanian wines was determined using an $AlCl_3$ assay [44]. In brief, 0.25 mL of the wine was combined with 1.25 mL of ultrapure Mili-Q water and 75 µL of 5 % $NaNO_2$ solution. The mixture was rested for 6 minutes. Subsequently, 150 µL of 10 % $AlCl_3$ solution was added and left to react for 5 minutes. Then, 0.5 mL of 1 M NaOH was introduced, and the total volume was adjusted to 2.5 mL with ultrapure Mili-Q water. The absorbance of the solution was measured at 510 nm using a UV/Vis spectrophotometer (Jenway 6800 manufacturer by Bibby Scientific Ltd). A calibration curve was constructed using (+)-catechin, and the results obtained from three replicates were expressed as mg of catechin equivalents per litre of beverage.

Results and discussion

The morphological characterization of bare and modified electrodes is shown in Figures 1a to 1c.

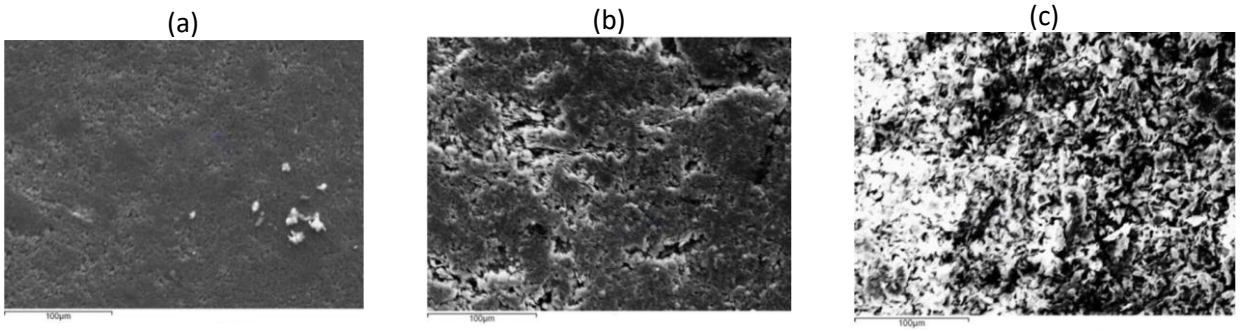

Figure 1. *SEM images of (a) bare CPE, (b) ZME and (c) PCME*

It is observable that the surface of bare CPE (Figure 1a) is the most homogenous, indicating a lower surface area. The surfaces of ZME and PCME (Figure 1b and 1c) exhibit a similar surface roughness, indicating an increased potential for analyte adsorption compared to the unmodified electrode. Overall, PCME reveals the highest distribution of active sites capable of absorbing the analyte.

Active surface area study

The determination of the electrochemical active surface area is done through CV measurement in the solution of 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl at different scan rates (v) (30 to 600 mV s^{-1}) for each electrode under study. The electrode active surface areas (A) were calculated from the slope obtained from the plots of I_p *vs.* $v^{1/2}$ shown in Figure 2, through Randles-Ševčik Equation (1) [45]:

$$I_p = \pm 2.69\times10^5 n^{2/3} A D^{1/2} C\, v^{1/2} \quad (1)$$

where I_p is the peak current, n is the number of electrons transferred (1 e^- for $[Fe(CN)_6]^{3-/4-}$ redox couple), D is diffusion constant (7.6×10^{-6} cm^2 s^{-1} for this redox probe solution) and C is the concentration of the redox probe solution (5 mM equimolar $[Fe(CN)_6]^{3-/4-}$). The respective active surface areas for bare CPE, ZME, and PCME were found as 1.91×10^{-3}, 2.05×10^{-3} and 2.11×10^{-3} cm^2, which are comparable to the geometrical area of working electrodes and indicate an increase in the electroactive area for the modified *vs.* bare electrodes.

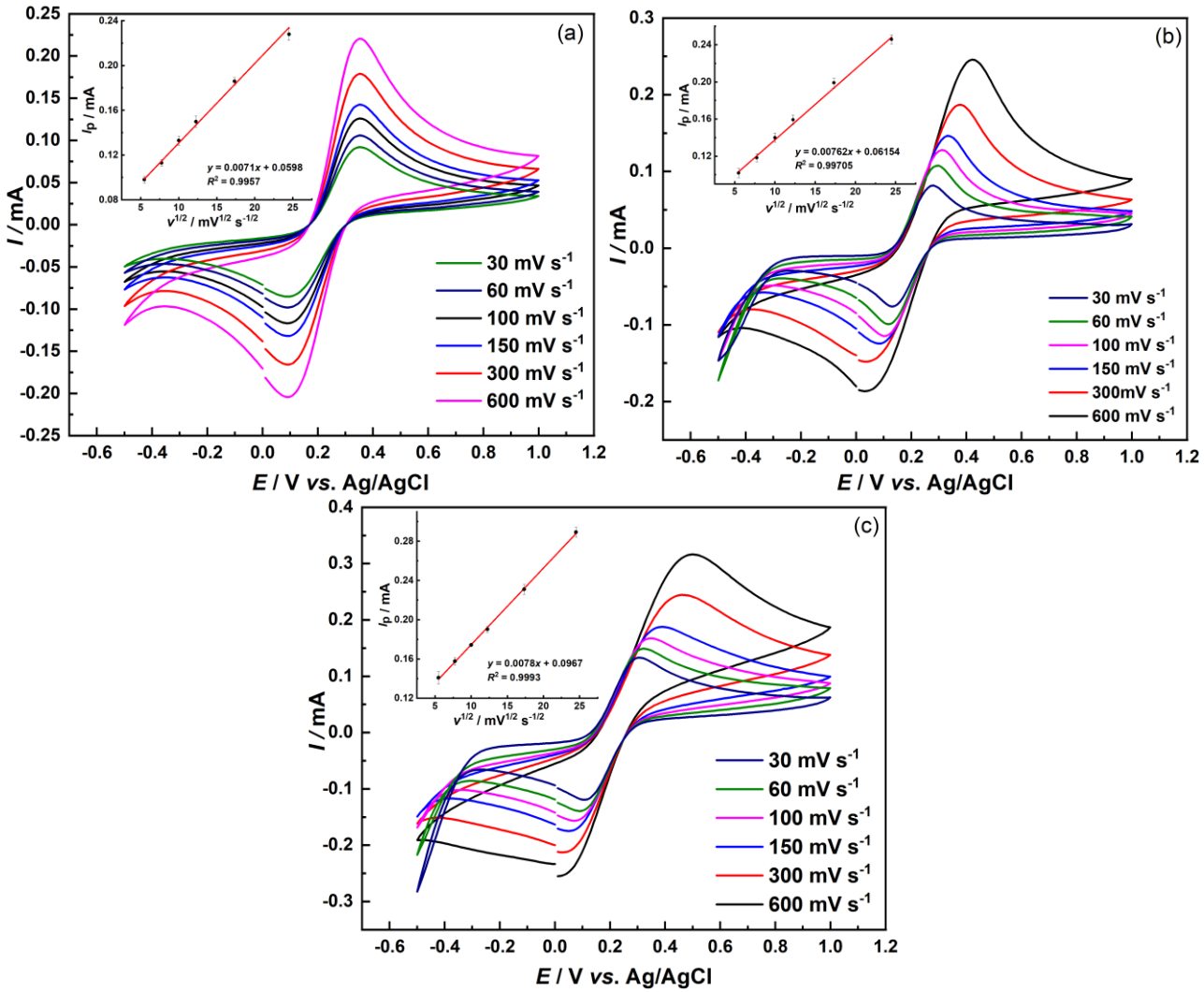

Figure 2. *CVs of carbon paste electrodes in the presence of 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$ solution in aqueous 0.1 M KCl at various scan rates: (a) bare CPE, (b) ZME, (c) PCME, accompanied by corresponding plots of peak current* vs. *$v^{1/2}$ as insets*

CV analysis of bare and modified carbon paste electrodes

The electrochemical behaviour of bare and modified carbon paste electrodes is evaluated *via* the CV technique. The comparison of bare and modified electrodes through CV measurements is shown in Figure 3. The redox probe was the solution of 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl. Bare CPE shows the weakest redox peak current. The increased current peaks for the others appear to be in the following order: ZME< PCME. In terms of ΔE_p, they show similar values in a range of 0.12 to 0.15 V. From the CV measurement, Prrenjasi clay modifier appears to have the best response.

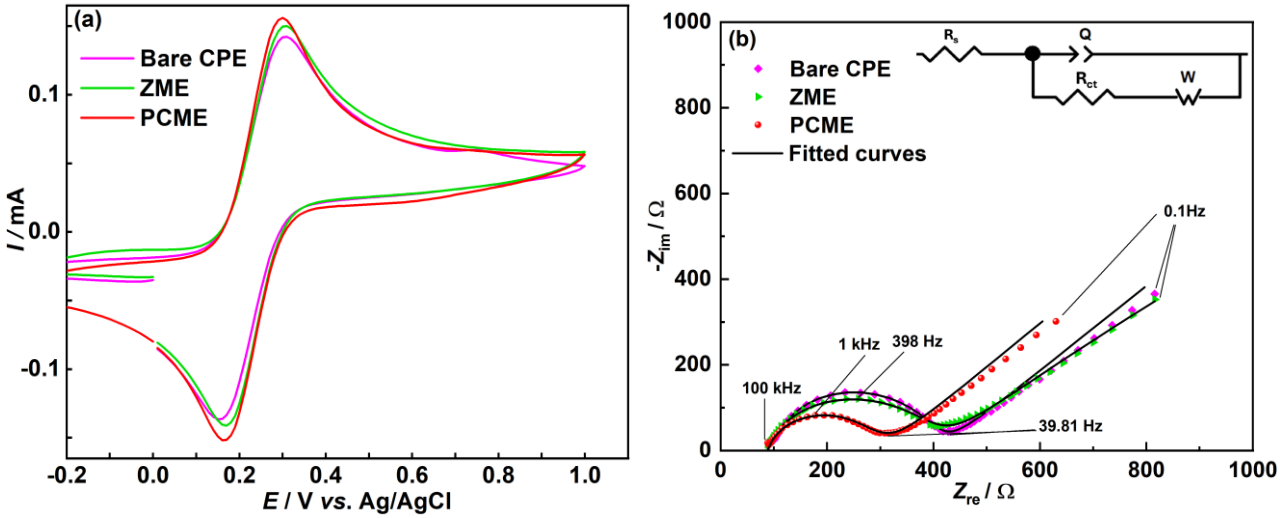

Figure 3. *(a) CVs at 100 mV s^{-1} for bare and modified CPEs, (b) Nyquist plots and EEC of bare and modified carbon paste electrodes in the presence of 5 mM $[Fe(CN)_6]^{3-/4-}$ solution in aqueous 0.1 M KCl*

Electrochemical impedance spectroscopy analysis

To characterize interfacial processes at bare and modified electrodes, EIS measurements were carried out in the presence of $[Fe(CN)_6]^{3-/4-}$ redox probe.

Figure 3(b) shows the Nyquist plots for bare and modified electrodes recorded in a solution of 5 mM equimolar $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl, at open circuit potential. Each recorded EIS measurement contains one depressed semicircle in the high-frequency range and a straight line of about $\pi/4$ slope in the low-frequency range. The capacitive loops represent the interfacial electron transfer resistance coupled with double-layer capacitance, and the straight line is attributed to Warburg impedance, which indicates the diffusion process (*i.e.* mass transfer) to the electrode surface [46]. The EIS records are on par with CV measurements. The solid lines represent the fitted spectra with the electrochemical equivalent circuit (EEC) model shown in the inset of Figure 3(b), which is selected to produce the lowest possible fitting curve error (χ^2). The model contains the solution resistance (R_s), electron transfer resistance (R_{ct}), Warburg element (W) and constant phase element (CPE). The impedance of CPE is defined by Equation (2) [47]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (1)$$

where Q is non-ideal capacitance, ω is the angular frequency ($\omega = 2\pi f$), j is imaginary number ($j^2 = -1$), and n is the exponent that represents the value of deviation from an ideal semicircle of capacitance loops. The system behaviour when $n \neq 1$ is attributed to the time constants characterized by continuous distribution in charge-transfer reactions, surface heterogeneity, and porosity of the electrode surface [47,48]. The double layer capacitance (C_{dl}) was further calculated using equation (3) [49]:

$$C_{dl} = \frac{(R_{ct}Q)^{1/n}}{R_{ct}} \quad (2)$$

Table 1 displays the fitted data from the EEC model. The electron transfer resistance (R_{ct}) is the most essential parameter extracted from the EIS spectrum that determines electrode sensitivity. The lower the R_{ct}, the easier is transfer of electrons to the electroactive species in the solution. This results in higher CV peaks that are translated to higher method sensitivity. The R_{ct} values displayed in Table 1 reveal that bare CPE and ZME have similar sensitivity (≈312 Ω), while PCME has the lowest R_{ct} value (213.55 Ω), indicating the highest electrode sensitivity compared to the ZME and bare CPE. The *n* values for ZME and PCME are lower compared to bare CPE, indicating higher porosity of the electrode surface for modified electrodes [47]. ZME has a slightly lower *n* value (0.8169) compared to PCME (0.8322), but overall, PCME has a smaller semicircle diameter compared to ZME, achieving higher sensitivity. The C_{dl} values confirm that PCME has the thinnest double layer compared to other electrodes tested in this paper, indicating higher electrode sensitivity. The Warburg coefficient (σ_w) values appear to be in the same range for all three electrodes. Electron transfer resistance data from fitted EIS spectra were used to calculate the standard heterogeneous rate constant (k^0) using Equation (3) [50]:

$$k^0 = RT / F^2 R_{ct} AC \quad (3)$$

where *R* is the standard gas constant (8.314 J mol^{-1} K^{-1}), *T* / K is absolute temperature, F is the Faraday constant (96485C mol^{-1}), R_{ct} / Ω is electron transfer resistance, A is the electrochemical active surface area found from Equation (1), and C is the concentration of the redox probe solution (5 mM). The calculated values of k^o for bare CPE, ZME and PCME are 8.28×10^{-5}, 8.87×10^{-5} and 11.82×10^{-5} cm s^{-1}, respectively. The larger the k^0 value, the faster the electron transfer at the electrode surface.

Table 1. *Fitted experimental parameter values of EIS spectra (Figure 3b) measured for bare and modified carbon paste electrodes at OCP and 298 K*

Electrode	R_s / Ω	R_{ct} / Ω	C_{dl} / μF	*n*	σ_w / Ω s$^{-1/2}$	χ^2
Bare CPE	95.23	312.51	0.4602	0.8946	522.17	0.0017
ZME	86.25	312.47	0.9374	0.8169	424.80	0.0016
PCME	87.97	213.55	1.0738	0.8322	424.75	0.0015

Comparison of differential pulse voltammetry results

Differential pulse voltammetry measurements shown in Figure 4 were performed using modified electrodes and compared with the unmodified electrode.

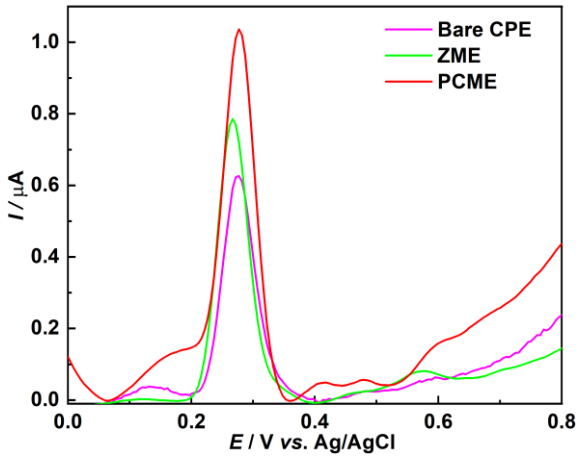

Figure 4. *DPV for each carbon paste electrode type with catechin standard concentration 5×10^{-6} M in acetate buffered solution (pH 5.5) using ex-situ method*

Each modified electrode has a graphite base with 5 *to* 10 µm particle dimensions and silicone oil. The method applied in each case is *ex situ*. The tests were conducted using standard catechin in acetate buffer solution (pH 5.5) and electrochemical determination methods such as DPV. It was found that the most effective modifier in enhancing the analytical signal is Prrenjasi clay.

Chronoamperometric measurements

Figure 5a shows the chronoamperometric measurements for different concentrations of catechin as the electroactive compound, which were carried out with a PCME electrode at 1100 mV *vs.* Ag/AgCl/KCl (3M) in the acetate buffered solution (pH 5.5). Cottrell equation (Equation ***Error! Reference source not found.***) is used to describe the current response for the electroactive material in electrochemical reaction at mass-transport limited conditions [51]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \quad (4)$$

where n, F, D, C_b / mol cm^{-3}, and t / s are the number of electrons transferred from the electroactive compound (*i.e.* catechin in this study), Faraday constant (96485 C), diffusion coefficient, analyte bulk concentration and time, respectively.

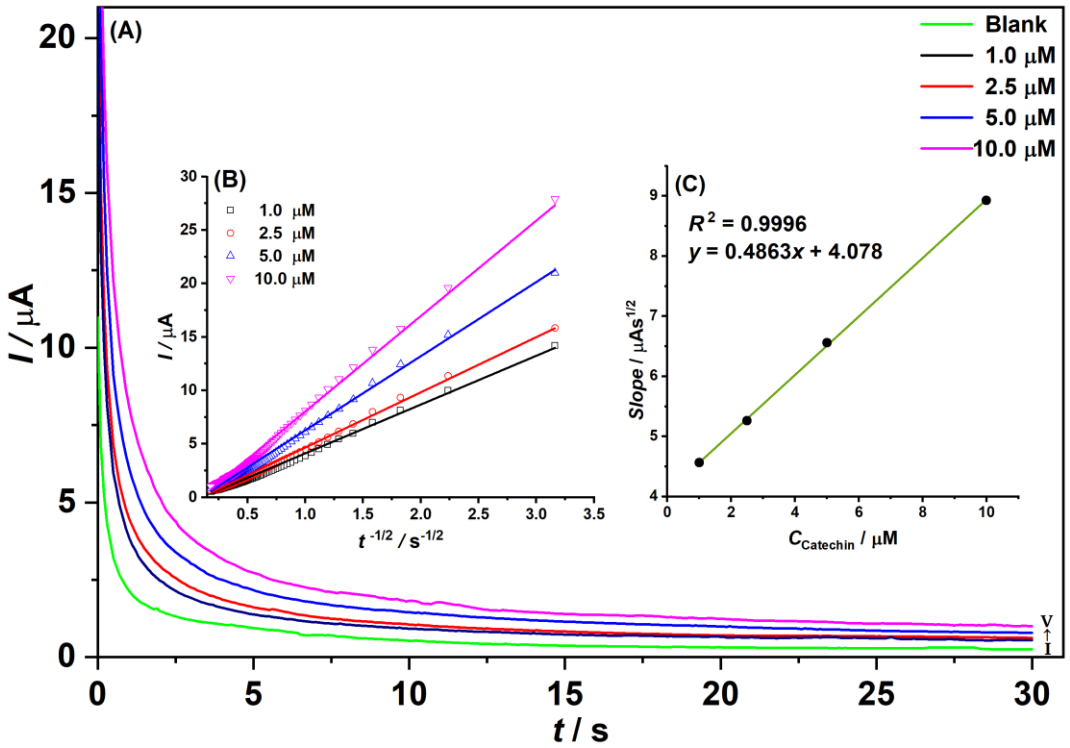

Figure 5. *(A) Chronoamperograms for PCME in the acetate buffered solution (pH 5.5). Insets: (B) plots of* I vs. $t^{-1/2}$ *obtained from chronoamperograms, (C) plot of the slope of the straight lines against catechin concentration*

The plot of I *vs.* $t^{-1/2}$ in Figure 5b was used to determine the slopes for each concentration of catechin used. Moreover, the slope *vs.* concentration plot is constructed in Figure 5c. From the resulting slope, the Cottrell equation is used to calculate the mean value of D (diffusion coefficient of analyte), which was found to be 1.38×10^{-5} cm^2 s^{-1} for catechin, similar to previously published papers [50].

Analytical performance of the method

Precision and accuracy were evaluated from the RSD and recovery values, respectively. At least six measurements were performed, and the average recovery and RSD values are reported. The obtained recovery values (Table 2) indicate the efficiency of each modified electrode in detecting flavonoids. Higher recovery rates suggest minimal matrix effects and reliable quantification, while

lower values may indicate signal suppression or interference. The results demonstrate that the PCME electrode exhibited the best recovery performance, likely due to its improved surface characteristics and enhanced electron transfer properties.

***Table 2**. Analytical performance of bare CPE, ZME, and PCME*

Electrode	Amount, µM		Recovery, %	RSD, % (n = 6)	LOD, nM	LOQ, nM
	Added	Found				
Bare CPE	5	5.525	109.3	6.28	369.0	1230
ZME	5	4.865	97.5	4.12	178.8	596
PCME	5	5.135	102.4	3.56	99.3	331

Representative DPV measurements at PCME in various concentrations of catechin with the corresponding calibration curve are shown in Figure 6. The voltammograms reveal a slight shoulder on the higher-potential side of the catechin peak, likely due to surface heterogeneity of the PCME [52]. However, this does not compromise the analytical performance, as peak height is determined at more negative potentials, well separated from the shoulder region.

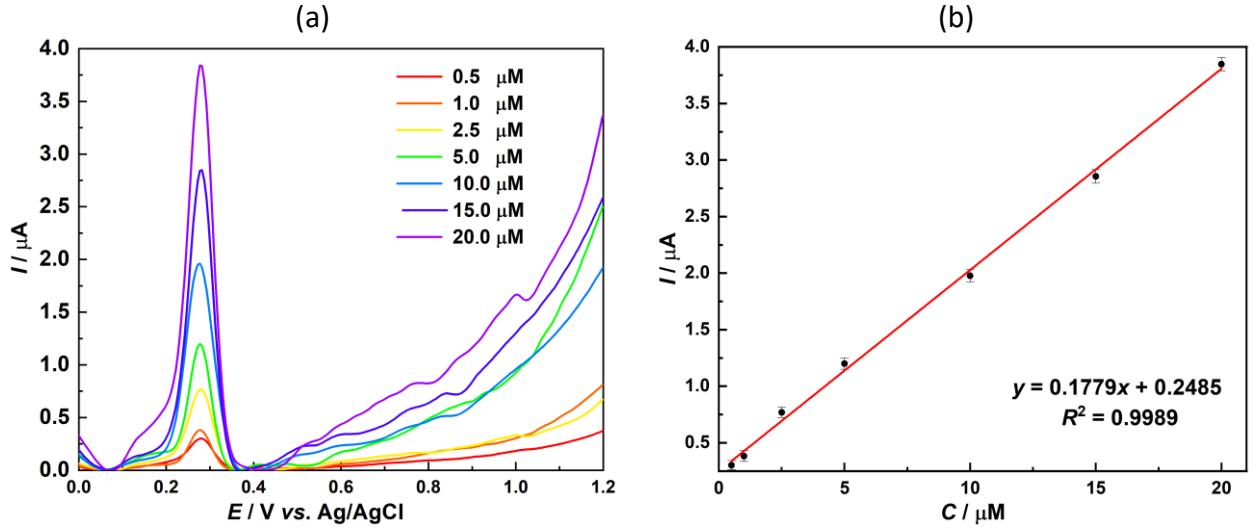

***Figure 6**. (a) DPVs of PCME in acetate buffered solution (pH 5.5) for different concentrations of catechin and (b) corresponding calibration curve*

The limit of detection (LOD) and limit of quantification (LOQ) were determined using 3.3 σ/s and 10 σ/s formulas, where σ represents the intercept standard deviation in the calibration curve and s represents the slope of the calibration curve [53]. LOD and LOQ were determined to be 99.3 and 331 nM, respectively, for the PCME electrode. Table 3 compares the performance of various previously reported electrochemical methods for catechin detection. It highlights differences in linear detection range, detection limits (LOD) and quantification limits (LOQ).

***Table 3.** Analytical performance of some previously reported electrodes for catechin detection by DPV*

Compound	Working electrode	Linear detection range, µM	LOD, nM	LOQ, nM	Ref.
Catechin	CPE by electropolymerized methylene blue	1 to 10 0.001 to 0.1	4.9	14	[54]
Epigallocatechin gallate	Natural glassy CPE	1 to 12.5	80	242.42	[55]
Catechin	MWCNTs	0.1 to 2.69	17	51.51	[56]
Epigallocatechin gallate	Ionic liquid, n-octylpyridinium hexafluorophosphate CPE	0.5 to 12.5	132	435	[57]
Catechin	Prrenjasi clay-modified CPE	0.5 to 20	99.3	331	This work

Electrochemical measurements of wine samples

This work uses DPV to determine the total flavonoid content of some common Albanian wines using a PCME electrode. Two representative DPVs (W2-white wine and W5-red wine) are shown in Figure 7, while results obtained for all wine samples (W1-W7) are displayed in Table 4.

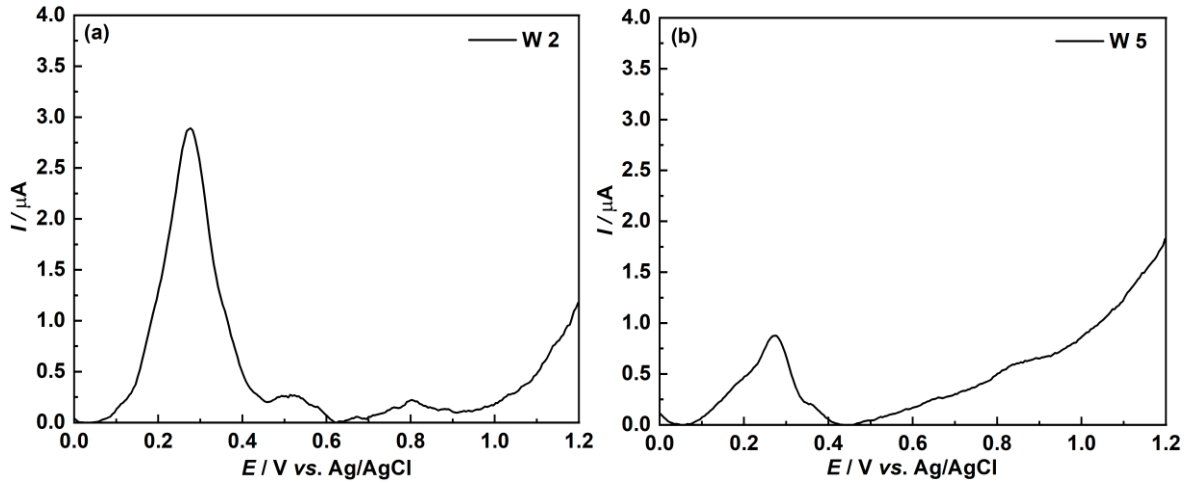

***Figure 7**. DPVs of wine samples diluted (1:500), a) red wine and b) white wine*

The total flavonoid content in the analysed Albanian wines (7 bottles giving W1-W7 samples) ranged between 513.13 and 2156.07 mg L^{-1} in agreement with Braga *et al.* [58], who found values between 947.03 and 2431.77 mg L^{-1} in Vitis labrusca wines, and in agreement with Woraratphoka *et al.* [59], with reported values between 1184 and 2647 mg L^{-1} in Vitis vinifera wines. The reference spectrophotometric method ($AlCl_3$ assay) results are shown in Table 4, showing the range from 686.57 to 2299.24 mg L^{-1} for the analysed wines. These results validate our proposed method (ex-situ) for total flavonoid determination in wines. As expected, red wines resulted in a higher total flavonoid concentration compared to white wines (W5). This difference arises primarily from the customary practice of fermenting red grapes along with their skins, whereas white wine production involves the removal of grape skins prior to fermentation. Soil composition, including mineral content and pH levels, exposure to sunlight, temperature, rainfall, and general growing conditions, can affect the synthesis and accumulation of flavonoids in grape seeds. Additionally, the total flavonoid content in wine is significantly influenced by the geographical region in which the grapes were grown. Regions with abundant sunlight and moderate temperatures tend to have higher levels of flavonoids. This is the reason why wines that are produced from grape crops that grow in warmer areas of Albania tend to be richer in antioxidants.

***Table 4.** Real sample measurement of Albanian wines with the developed and reference methods (spectrophotometric)*

Wines	Total flavonoid content, mg L^{-1}		RSD, %	
	DPV	$AlCl_3$ assay	DPV	$AlCl_3$ assay
W1	2059.28	2113.45	1.40	1.26
W2	2156.07	2299.24	2.22	2.10
W3	1985.88	1898.33	1.25	2.56
W4	1489.16	1656.81	3.59	3.36
W5	513.13	686.57	2.14	1.51
W6	1535.11	1608.94	3.88	1.48
W7	1877.94	1782.54	1.72	1.33

Conclusions

This study demonstrated the electrochemical determination of total flavonoid content, expressed as catechin equivalent flavonoids, in Albanian wines, using Prrenjasi clay modified carbon paste electrode (PCME). The ex-situ method employed proved effective in minimizing interference from complex wine matrices, allowing for a more accurate analysis of total flavonoids in wines. PCME exhibited the highest sensitivity among the tested modifiers, characterized by the lowest electron transfer resistance and the largest active surface area. This can be attributed to its higher cation exchange capacity, larger surface area, and more adaptable layered structure, which facilitates enhanced interactions with the modifying agents. Additionally, the presence of a higher proportion of montmorillonite in Prrenjasi clay contributes to increased adsorption efficiency due to its expandable interlayer spacing and enhanced functionalization potential. This enhanced performance resulted in a limit of detection of 99.3 nM and a limit of quantification of 331 nM, with a calculated diffusion coefficient of 1.38×10^{-5} cm^2 s^{-1}. The total flavonoid content in the analysed Albanian wine samples ranged between 513.13 and 2156.07 mg L^{-1}. Notably, red wines displayed higher catechin concentrations compared to white wines, consistent with previous literature. Additionally, the study included a comparative analysis using UV-VIS spectrophotometry to measure the total flavonoid content in the wine samples, further validating the electrochemical method.

Due to the superior signal quality of the modified electrodes, the PCME electrode was chosen for ongoing research due to its exceptionally linear and clean background, lower production costs, and excellent sensitivity. This practical approach is particularly suited for determining of total flavonoid content in Albanian wines, demonstrating the effectiveness of the PCME in this application.

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