Original scientific paper

Characterization of wine polyphenols with a carbon/nanoparticle TiO₂ electrode

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Abstract

The positive effects of polyphenolic compounds on the sensory characteristics of wine and human health indicate a great need for a simple, fast and easily accessible method to determine the content of polyphenols in wine. The aim of this study is the electrochemical characterization of polyphenolic compounds in natural wine samples using a modified carbon paste electrode with TiO₂ nanoparticles (MCPE/npTiO₂) and improved voltammo-gram processing to obtain indicative data for polyphenols. The most marked influence of the modification of CPE with TiO₂ nanoparticles was an increased sensitivity to electrooxi-dation, which is reflected in an increase of the anodic peak current. Of the five tested poly-phenols, i.e., gallic acid (GA), caffeic acid (CA), catechin (CT), quercetin (QV) and resveratrol (RE), the current maximum of the first two oxidation peaks increased only for GA by a factor of about 2 and for CT by a factor of about 1.5. Of the three red wines, Vranac (VR), Merlot (ME), Cabernet Sauvignon (CS); three white wines, Graševina (GR), Temjanika (TE), Char-donnay (CS) and one rose wine, Belrose Mediterranée Rosé (RO) tested, an increase by a factor of about 2.5 was observed for two red wines (VR, CS) and by a factor of 1.5 for one red wine (ME), one white wine (GR), and the rose wine (RO), while no increase in the current signal was observed for one of the white wines (CS). The most significant increase in the voltammetric signal of GA at the MCPE/npTiO₂ compared to other studied polyphenols can be explained by its higher affinity for adsorption on TiO₂ nanoparticles. The investigated modified electrode provides an improved, linear and reproducible voltammetric response in wine samples. Consequently, MCPE/npTiO₂ represents a good basis for the further deve-lopment of an integrated sensor/data system with the possibility of a broader application for the detection of polyphenols, especially GA, as an aroma and visually relevant parameter in winemaking.

Introduction

Compounds with a large number of phenolic structural units, known as polyphenols, have a significant impact on the quality of wine in terms of organoleptic properties and effects on human health [1,2]. This class of compounds not only influences the sensory properties of wine and the stability of subsequent oxidative processes but also causes the activation of antioxidant and anti-inflammatory processes that lead to inhibition of platelet aggregation and reduce the risk of heart disease and stroke [3]. Recent studies suggest that polyphenol-containing substances have a small direct antioxidant effect in the human body and that the metabolites formed by the consumption of polyphenol rich foods play a significant positive role [4]. Due to the above-mentioned benefits of polyphenolic compounds, there is a growing interest in the development and application of various analytical methods for their characterization in real samples: colorimetric, gravimetric, precipitation and chromatographic methods, vibrational spectroscopy, electrochemical methods, mass spectrometry, nuclear magnetic resonance and surface plasmon resonance [5,6]. Previous studies have shown that electrochemical methods have considerable potential due to the simplicity of the procedure, rapid detection, cost efficiency, high sensitivity and selectivity. In particular, voltammetric techniques using electrodes made of carbon paste and various modifiers and binders have shown improved properties compared to unmodified carbon electrode material.

As far as we know, the application of voltammetric methods using carbon paste electrodes modified with TiO$_2$ nanoparticles is rather limited. Carbon electrodes with TiO2 nanoparticles have been used mostly for quantitative and qualitative analysis of various inorganic, organic and biologically active substances. Mao *et al.* [7] demonstrated the possibility of mercury detection using a glassy carbon electrode modified with TiO$_2$ nanoparticles and multi-walled carbon nanotubes dispersed in a cationic surfactant. The tested electrode showed high selectivity for mercury in the presence of other interfering metal ions [7]. The study by Hassaninejad-Darzi *et al.* [8] presented the development of a carbon electrode modified with TiO$_2$ nanoparticles for the voltammetric characterization of pramipexole (a pharmaceutical formulation) in biological samples. The proposed electrode showed good selectivity and sensitivity to the analyte under investigation [8]. A carbon electrode modified with a nanocomposite modifier (TiO$_2$ nanofibers, graphene oxide nanosheets) was used for the electrochemical characterization of adenine. Upon oxidation of adenine on the surface of the tested electrode, an increase in peak current and electron transfer kinetics, as well as a decrease in overpotential, was observed [9]. Mashhadizadeh and Afshar determined clozapine in blood plasma samples using an electrode paste containing 33 wt.% kerosene oil and 6 wt.% TiO$_2$ nanoparticles [10]. The test results showed that the presence of TiO$_2$ nanoparticles in the electrode material caused an increase in the electroactive surface area of the electrode, improved sensitivity and increased the intensity of the anodic current maximum.

In general, it can be stated that the properties of the carbon electrode modified with TiO$_2$ nanoparticles are significantly influenced by the type and quantity of the binding material and the fraction of TiO$_2$ nanoparticles in the electrode paste. Carbon electrodes modified with TiO$_2$ nanoparticles using paraffine oil are characterized by good sensitivity, selectivity of the tested substances, reproducibility and repeatability with a low detection limit [11]. In a previous work, Mićin *et al.* [12] have shown that the optimal composition of the modified electrode material is

40 vol.% paraffin oil and 8 wt.% TiO_2 nanoparticles in terms of morphological, physicochemical and electrochemical properties of the tested electrode materials

As far as we know, the possibility of using a sensor based on carbon and paraffin oil modified with TiO_2 nanoparticles ($MCPE/npTiO_2$) for the characterization of polyphenolic compounds in wines has not yet been investigated. However, a modified carbon paste electrode with TiO_2 nanoparticles has been used for the electrochemical characterization of gallic acid [13], the most important wine polyphenol. Cyclic voltammetry and differential pulse voltammetry tests showed lower resistance to electron transfer and significant improvement in the oxidation current peak. The high analytical performance was attributed to the good biocompatibility and high conductivity of the TiO_2 nanoparticles. The width of the linear voltammetric response range and the detection limit indicated good sensitivity of the electrode [13].

The aim of this work is to advance the characterization of selected polyphenolic compounds in a model wine solution and a series of natural wine samples using cyclic voltammetry at a TiO_2-modified CPE electrode. The data processing approach developed by Espinoza *et al.* is applied, which allows a physical interpretation of the electrochemical behavior of such complex systems [14]. The purpose of our work is to pave the way for an integrated sensor/data processing system for the quantitative characterization of polyphenolic compounds in wine, which are related to the sensory properties of wine and could contribute to a more comprehensive characterization of polyphenols in winemaking.

Experimental

Chemicals

Unmodified and modified carbon pastes were prepared using extra purity graphite powder, particle size <50 μm, Merck, Germany, paraffin oil, Merck, Germany, diethyl ether *p.a.*, Lachner, Czech Republic and TiO_2 nanoparticles ($npTiO_2$), trade name AER-OXIDE® TiO_2P, Evonik Industries AG, Germany. The size of nanoparticles was 10-50 nm, predominantly distributed in the range of 15 to 25 nm [15].

Ethyl alcohol, 99.8%, LACH:NER, Czech Republic, tartaric acid Sigma-Aldrich, Germany, sodium hydroxide, LACH:NER, Czech Republic, (+)-catechin, Roth, Germany, caffeic acid (≥ 98 %), Sigma-Aldrich, Germany, trans-resveratrol (≥ 98 %), Cayman chemical, USA, quercetin (≥ 98 %), Molecule group, England and gallic acid (98 %), Acros organics, Belgium, were used in electrolyte solutions for the characterization of polyphenolic compounds. Three commercially available red wine varieties were tested: Cabernet Sauvignon (CS, pH 3.41, alcohol content 13.5 vol.%; Merlot (ME, pH 3.19, alcohol content 13.5 vol.%), Vranac (VR, pH 3.19, alcohol content 11.5 vol.%). In addition, three types of white wine were tested: Temjanika (TE, pH 3.14, alcohol content 11.5 vol.%), Graševina (GR, pH 2.92, alcohol content 10.5 vol.%), Chardonnay (CH), pH 3.07, alcohol content 12.5 vol.%) and one type of rose wine (Belrose Mediteranee Rose (RO, pH 3.1, alcohol content 12.5 vol.%). Distilled water with a conductivity of 4 μS m^{-1} was used for the preparation of all solutions.

Preparation of unmodified carbon paste

The unmodified carbon paste was prepared by manually mixing graphite powder (3 g) and paraffin oil (1.09 mL) in a bowl and stored in a closed plastic container at room temperature. The paste was used 24 hours after preparation.

Preparation of modified carbon paste

The modified carbon paste was prepared by dispersing a mixture of graphite powder (4.6 g) and TiO$_2$ nanoparticles (0.4 g) in 50 mL of diethyl ether with constant stirring and heating to a temperature of 40 °C. The mixture was then evaporated. After evaporation of the diethyl ether, the graphite powder (3 g), where the TiO$_2$ particles were dispersed, was mixed with paraffin oil (1.09 mL). Homogenization was carried out by manual mixing in a ceramic bowl according to the procedure described [10]. The prepared modified carbon paste was stored in a closed plastic box at room temperature and used 24 hours after preparation.

The body of the working electrode was made of commercially available Teflon in the form of a tube (length 200 mm, diameter 20 mm) with a cavity at the end of the electrode body (length 10 mm, diameter 2.4 mm, surface area 0.045216 cm^2). The electrical contact was made with a copper wire (diameter 1 mm) fixed in the electrode body. The prepared unmodified/modified paste was pressed into the body of the working electrode. The active surface of the electrode was polished to obtain a smooth electrode surface. Pressing a new amount of paste and polishing the electrode surface was performed immediately before each experimental measurement.

Electrochemical characterization of polyphenolic compounds

The predominant polyphenols in wine, such as gallic acid (GA), caffeic acid (CA), catechin (CT), quercetin (QV) and resveratrol (RE) [16], were selected as polyphenolic model compounds and used for electrochemical characterization. The measurements were performed by cyclic voltammetry (CV) on a potentiostat/galvanostat device (PAR 273A, Princeton Applied Research, USA), using an electrochemical cell with a volume of 50 mL, consisting of a working electrode, a reference electrode (Ag/AgCl 3.5 M KCl) and a counter electrode (platinum plate, surface area 2.4 cm^2). The unmodified carbon paste electrode (CPE) and the modified carbon paste electrode (MCPE/npTiO$_2$) were used as working electrodes. The experiments were performed without mixing at room temperature 23±1 °C with three consecutive measurements. The cyclic voltammograms were analyzed using Powersuite 2.40 software. All potentials are given relative to the reference electrode. The working electrolyte solution was a 0.3 mM solution (unless otherwise stated) of a polyphenolic compound in a model wine solution (tartaric acid 0.033 M, 12 vol.% ethanol) with a pH 3.6 (quercetin solution pH 2.6). A model wine solution was used to determine the oxidation potentials of phenolic compounds in wine [17]. The pH of the working electrolyte was corrected by adding solid NaOH and checked with a pH meter (CONSORT C861). The measurement of real wine samples was carried out without prior processing of the sample. The change in the concentration of polyphenolic compounds in natural wine samples was carried out by diluting the wine sample with a model wine solution. Unless otherwise stated, cyclic voltammograms were recorded in the potential range from -100 mV to 1500 mV with a potential change rate of 200 mV s^{-1}.

Mathematical analysis of voltammograms

The formal electrooxidation potential of the polyphenolic compounds was determined by identifying the inflection point obtained by the first derivative of the cyclic voltammogram function. Specifically, the potentials where the first derivative function is zero (*i.e.*, where it intersects the *x*-axis) correspond to the potential values of the anode current peaks. In addition, the potentials where the first derivative function reaches its maximum coincide with the inflection points [14]. The application software EXCEL 2016 and MATH 10 were used to process the cyclic voltammograms to determine the inflection point.

Results and discussion

Five selected polyphenolic compounds, *i.e*., GA, CA, CT, QV, and RE, were characterized in model wine solutions. Figure 1 shows a cyclic voltammogram recorded for GA in a model solution for different potential scan rates.
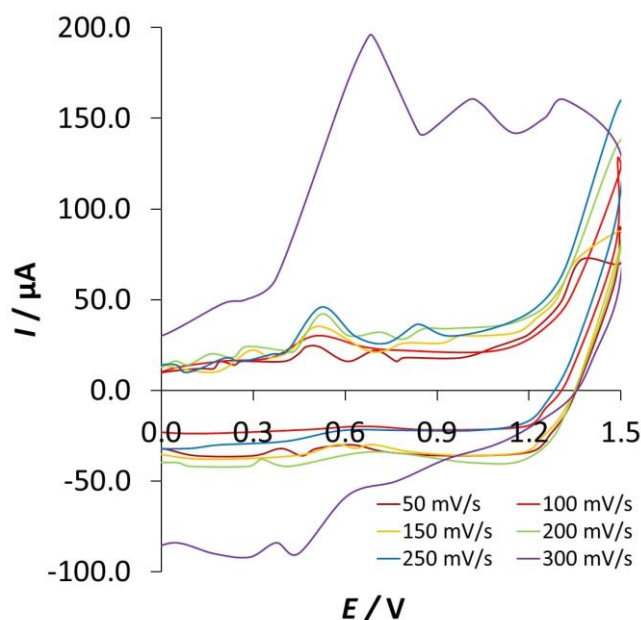

Figure 1. *Cyclic voltammograms recorded at CPE in the model wine solution of 0.3 mM GA (pH = 3.6) with scan potential rates of 50, 100, 150, 200, 250, 300 mV s^{-1}*

Figure 2 shows the cyclic voltammograms of the tested polyphenolic compounds recorded with CPE and MCPE/npTiO$_2$. The values of the formal oxidation potential and the anodic peak potentials and currents listed in Table 1 were determined from the derivative function of the cyclic voltammograms for GA, CT, QV and RE. Considering the reversible character of the electrooxidation of CA, the value of the formal potential for CA was determined from the half-wave potential.

Table 1. *Estimated values of oxidation potential, and anodic peak potential and current intensity calculated from the derivative function of the cyclic voltammograms obtained at CPE and MCPE/npTiO$_2$ for 0.3 mM solutions of GA, CT, QV, RE and QV, and the half-wave potential for 0.3 mM solution of CA*

Polyphenolic compound	Electrode	Oxidation potential, V			Anodic peak potential, V			Anodic peak current, μA		
		Anodic peak number								
		1	2	3	1	2	3	1	2	3
GA	CPE	0.42±0.01	0.71±0.02	--	0.50±0.01	0.80±0.03	--	20±1.0	14±1.0	--
	MCPE/npTiO$_2$	0.39±0.03	0.81±0.01	1.16±0.05	0.53±0.04	0.85±0.02	1.21±0.03	40±0.8	26±0.8	30±0.5
CA	CPE	0.47±0.01	--	--	0.50±0.02	--	--	28±0.7	--	--
	MCPE/npTiO$_2$	0.47±0.02	--	--	0.50±0.02	--	--	28±1.0	--	--
CT	CPE	0.49±0.03	0.94±0.02	--	0.60±0.01	1.07±0.02	--	12±0.7	14±0.9	--
	MCPE/npTiO$_2$	0.48±0.01	0.79±0.04	--	0.58±0.02	0.90±0.01	--	16±0.6	20±0.8	--
QV	CPE	0.48±0.02	--	--	0.54±0.01	--	--	22±0.8	--	--
	MCPE/npTiO$_2$	0.42±0.02	0.69±0.03	0.89±0.02	0.53±0.01	0.73±0.05	1.00±0.02	26±0.6	14±0.5	14±0.7
RE	CPE	0.50±0.01	0.79±0.06	--	0.59±0.03	1.02±0.02	--	14±0.8	24±1.0	--
	MCPE/npTiO$_2$	0.48±0.02	0.84±0.02	--	0.57±0.01	1.00±0.05	--	16±1.0	26±0.7	--

The voltammogram of GA recorded at CPE shows two anodic peaks at the potentials of 0.50 and 0.80 V, whereas the voltammogram of GA recorded at MCPE/npTiO$_2$ shows two anodic peaks at the potentials of 0.53 and 0.85 V. In addition, the voltammogram recorded with MCPE/npTiO$_2$ shows a third anodic peak of lower intensity at a potential of 1.21 V.
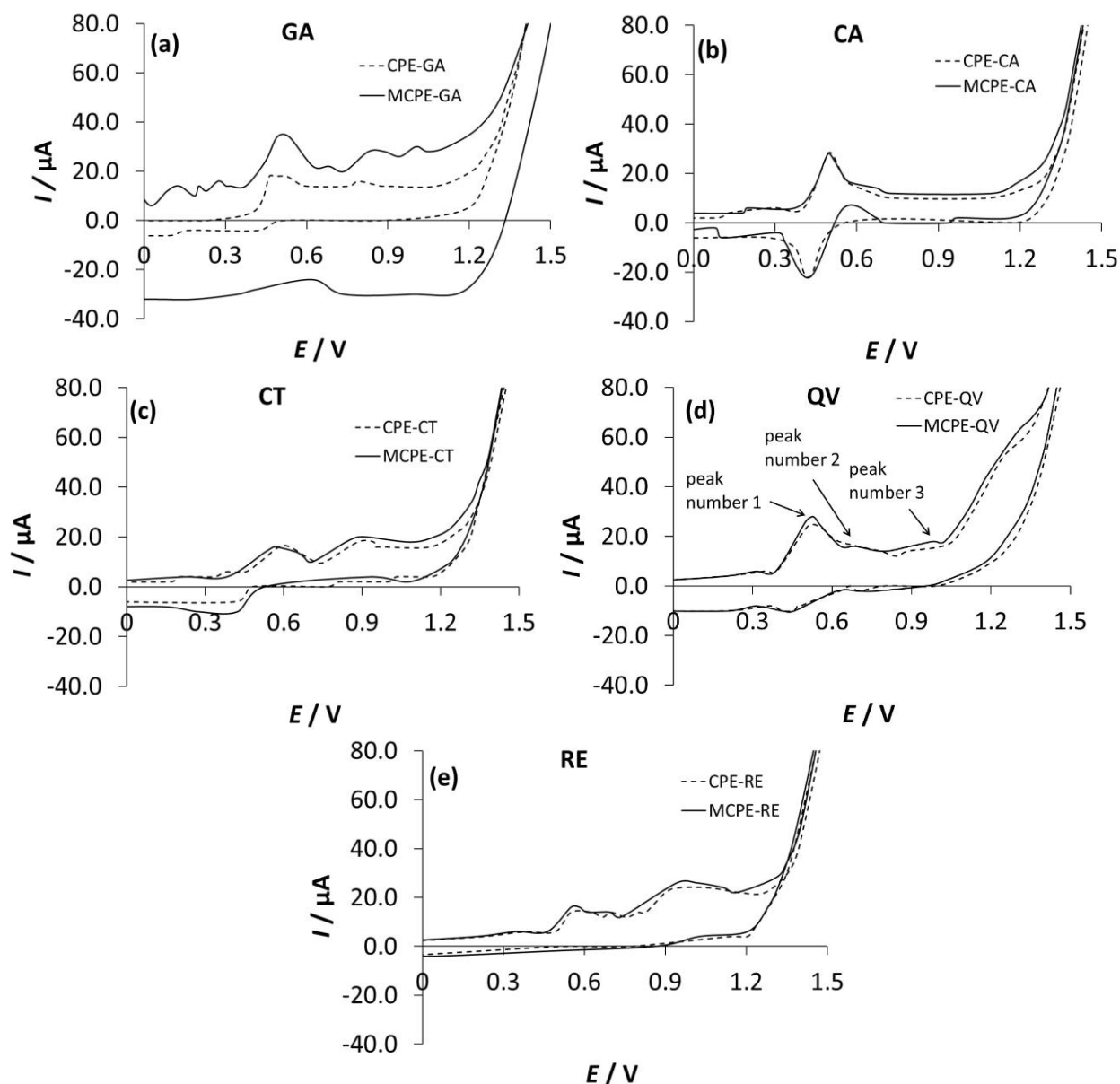
Figure 2. *Cyclic voltammograms (200 mV s^{-1}) recorded at CPE (dotted line) and MCPE/npTiO$_2$ (solid line) in a model wine solution with 0.3 mM of: (a) GA; (b) CA; (c) CT; (d) QV; (e) RE*

The estimated formal oxidation potential of GA recorded at MCPE/npTiO$_2$ is shifted slightly towards more negative values at 0.39 V compared to the estimated potential of 0.42 V obtained with CPE. The intensity of the GA anodic current peaks increases significantly when using the modified electrode. No pronounced cathodic current peak can be observed in the GA voltam-mograms, which indicates the predominant irreversibility of the reaction.

The cyclic voltammogram recorded in a 0.3 mM CA solution in the potential range from -0.1 to 1.0 V using CPE shows identical values of the formal potential and the potential of the anodic wave peak compared to the voltammogram recorded using MCPE/npTiO$_2$, where the intensity of the anodic peak current did not increase. The results show a pronounced anodic current peak at a potential of 0.50 V and a cathodic current peak at a potential of 0.43 V. The oxidation potential has a value of 0.47 V. The shape of the recorded voltammogram shows the reversibility of the electrochemical oxidation process of CA.

For CT, QV and RE solutions, the difference between peak current intensities of CPE and MCPE/npTiO$_2$ is much smaller than in GA solution, and the effect of CPE modification on oxidation

potentials and current peak potentials is mixed and in the range of tens of mV. Similar to GA, the electrooxidation of these compounds is predominantly irreversible. For QV, two additional anodic current peaks at more positive potential were observed in the voltammogram recorded at MCPE/npTiO$_2$ compared to CPE.

Based on the dependence of the anodic current peak on the rate of potential change, an assessment was made of the type of electrode process influencing the rate of electrochemical oxidation of the tested polyphenolic compounds on the MCPE/npTiO$_2$ electrode (Figure 3).
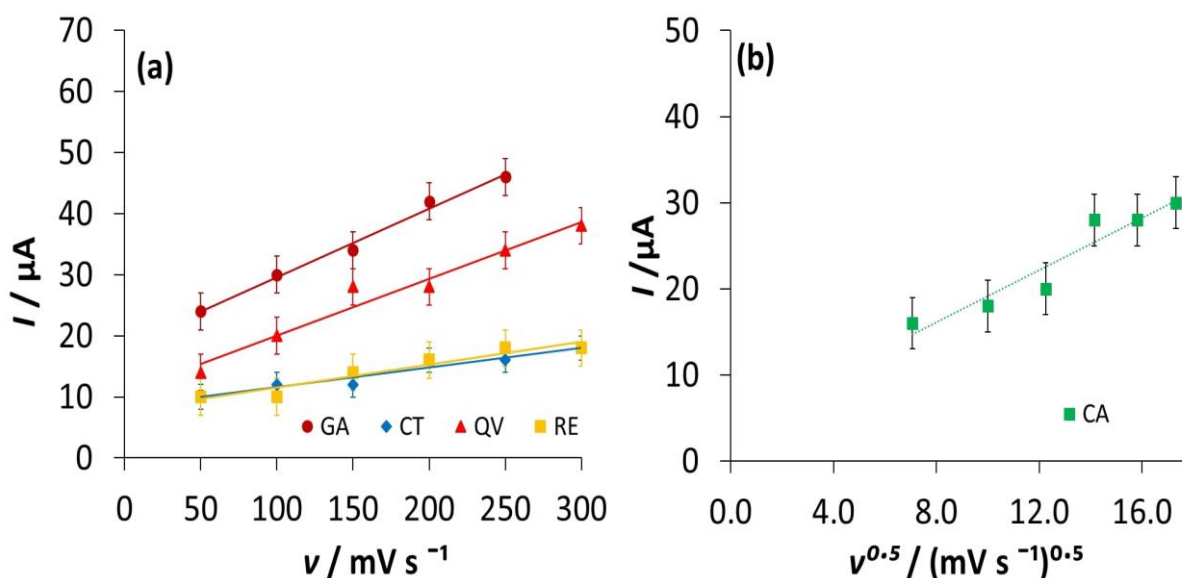

Figure 3. (a) Dependence of the first anodic peak current of GA, CT, QV, RE at MCPE/npTiO$_2$ on the potential scan rate, (b) dependence of the first anodic peak current of CA on the square root of the potential scan rate

The dependence of the first anodic peak current (I_{pa}) on the potential scan rate are for five tested polyphenolic compounds described by the linear expressions in Table 2.

Table 2. Linear regression line equations for the first anodic peak current at MCPE/npTiO$_2$ on the potential scan rate for GA, CA, CT, RE, and square root of the potential scan rate for CA

Polyphenolic compound	Linear fit
GA	$I_{pa} = 0.11\ v + 18.60\pm0.31;\ R^2 = 0.99$
CA	$I_{pa} = 1.51\ v^{0.5} + 4.05\pm0.40;\ R^2 = 0.92$
CT	$I_{pa} = 0.03\ v + 8.66\pm0.28;\ R^2 = 0.96$
QV	$I_{pa} = 0.09\ v + 10.80\pm0.55;\ R^2 = 0.96$
RE	$I_{pa} = 0.03\ v + 8.40\pm0.37;\ R^2 = 0.94$

For all investigated polyphenols except CA, the first anodic peak current depends linearly on the rate of potential change, which indicates that the electrode reactions of the tested polyphenols take place under the influence of adsorption. Electrode reaction of CA shows a linear dependence of the anodic peak current on the square root of the rate of potential change, which points to diffusion control of the reaction.

The dependence of the anodic peak current on the concentration of polyphenolic compounds on the MCPE/npTiO$_2$ electrode (Figure 4) shows the linearity represented by the expressions given in the Table 3.

The reproducibility of the results was examined by recording five cyclic voltammograms of 0.3 mM solutions of GA, CA, CT, QV and RE in a model wine solution. The analysis was based on the values of the first anodic peak current. The relative standard deviation (RSD) values are RSD$_{GA}$ = 13.1 %,

RSD_{CA} = 5.44 %, RSD_{CT} = 1.41 %, RSD_{QV} = 11.78 %, RSD_{RE} = 5.73 %, which indicates the degree of reproducibility of measurements using MCPE/npTiO$_2$. The representative graph showing reproducibility of measurements is shown for CA in Figure 5.
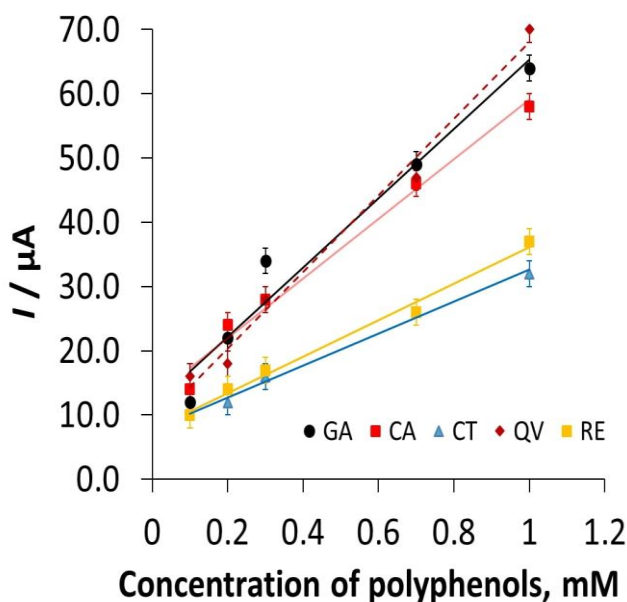

Figure 4. *Dependence of the first anodic peak current at the MCPE/npTiO$_2$ on the concentration of different polyphenols*

Table 3. *Linear regression line equations for the first anodic peak current at MCPE/npTiO$_2$ vs. concentration of different polyphenols*

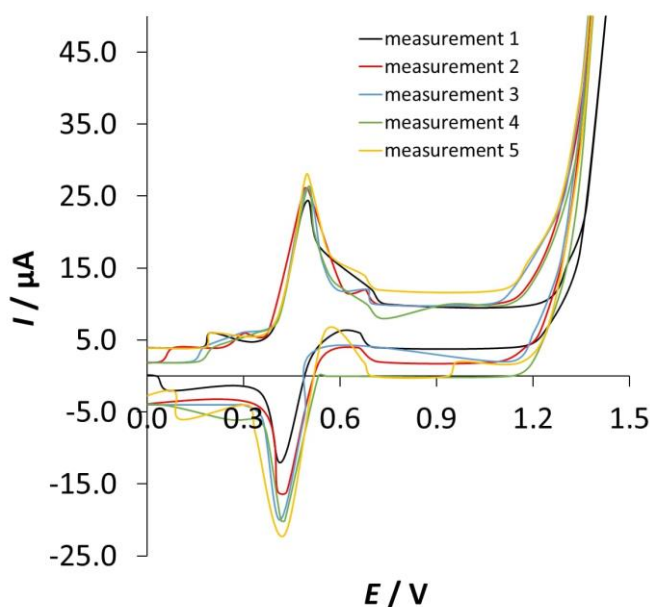| Polyphenolic compound	Linear fit
GA	I_{pa} = 53.91 C_{GA} + 11.39±0.28; R^2 = 0.96
CA	I_{pa} = 46.50 C_{CA} + 12.60±0.44; R^2 = 0.98
CT	I_{pa} = 24.89 C_{CT} + 7.74±0.36; R^2 = 0.99
QV	I_{pa} = 59.72 C_{QV} + 8.33±0.25; R^2 = 0.99
RE	I_{pa} = 28.42 C_{RE} + 7.72±0.33; R^2 = 0.99

Figure 5. *Cyclic voltammograms (200 mV s^{-1}) recorded at MCPE/npTiO$_2$ in a model solution of wine with 0.3 mM CA (pH 3.6) during five consecutive measurements (black line indicates the first measurement, yellow line the last measurement)*

As was declared in the Experimental section, three red wines (VR, CS, ME), three white wines (CH, TE, GR) and one rose (RO) wine were analyzed. Figure 6 shows cyclic voltammograms recorded in natural wine samples with unmodified and modified carbon paste electrodes.
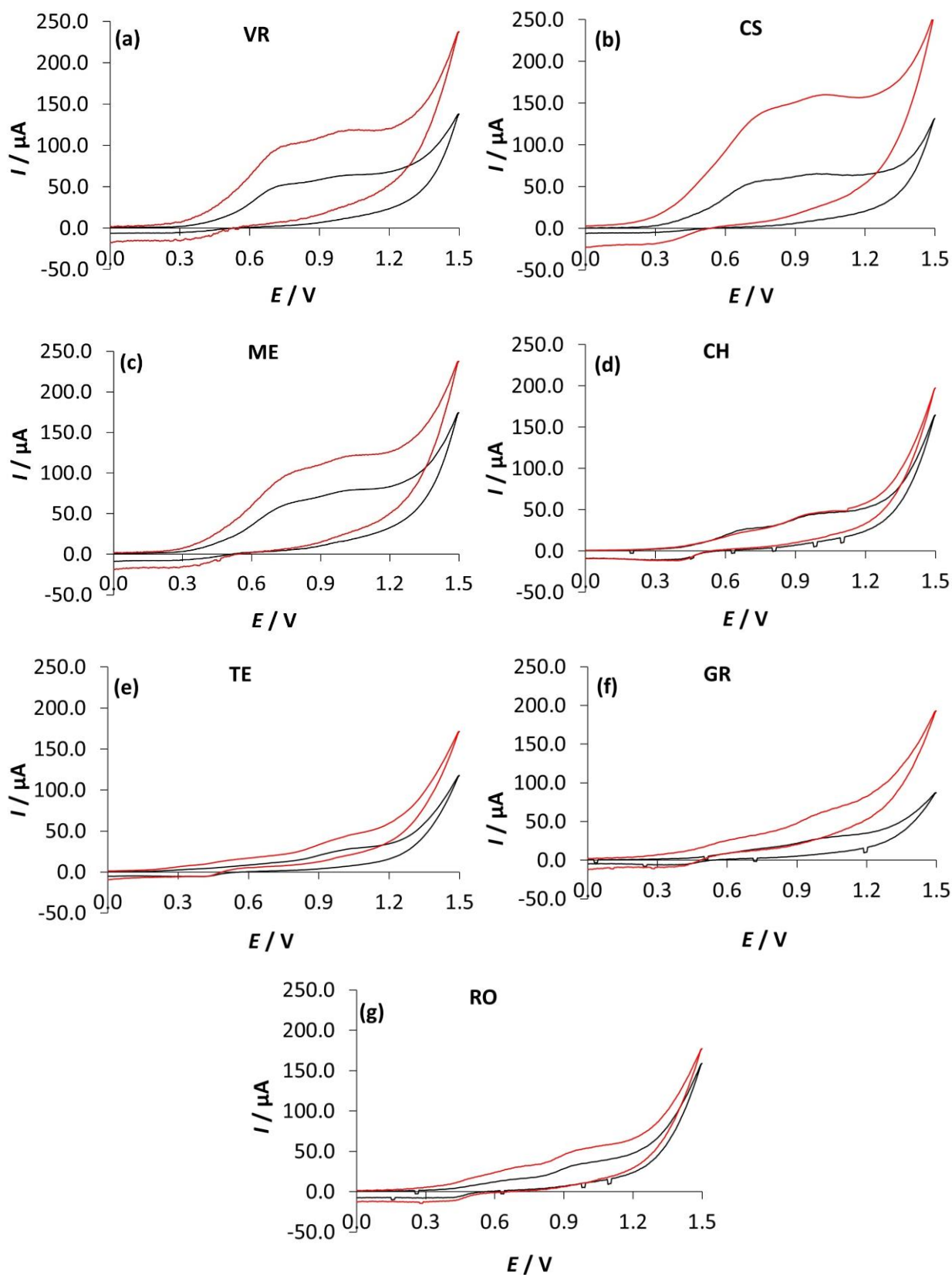

***Figure 6.** Cyclic voltammograms (200 mV s⁻¹) recorded at CPE (black line) and MCPE/npTiO₂ (red line) in real wine samples: (a) VR; (b) CS; (c) ME; (d) CH; (e) TE; (f) GR; (g) RO*

Estimated values of oxidation potential, and anodic peak potentials and current intensities on CPE and MCPE/npTiO$_2$, calculated from the derivative function of the cyclic voltammograms, are for different wine samples shown in Table 4.

Table 4. Estimated values of oxidation potential, and anodic peak potential and current intensity, calculated from the derivative function of the cyclic voltammograms of CPE and MCPE/npTiO$_2$, obtained for different wine samples

Wine sample	Electrode	Oxidation potential, V		Anodic peak potential, V		Anodic peak current, µA	
		Anodic peak number					
		1	2	1	2	1	2
VR	CPE	0.63±0.01	0.90±0.01	0.86±0.02	1.07±0.01	37.3±0.2	58.9±0.9
	MCPE/npTiO$_2$	0.62±0.02	0.92±0.04	0.86±0.02	1.06±0.03	104.29±0.8	111.6±0.7
ME	CPE	0.60±0.03	0.92±0.02	0.83±0.01	1.09±0.05	67.3±0.6	80.2±0.7
	MCPE/npTiO$_2$	0.63±0.01	0.94±0.03	0.85±0.04	1.09±0.01	106.7±0.8	122.4±0.9
CS	CPE	0.56±0.06	0.89±0.02	0.80±0.06	1.00±0.03	58.7±0.5	62.16±0.4
	MCPE/npTiO$_2$	0.62±0.02	0.93±0.03	0.83±0.02	1.03±0.04	146.31±0.6	154.5±0.7
CH	CPE	0.63±0.01	-	0.69±0.03	1.10±0.01	23.11±0.6	47.61±0.7
	MCPE/npTiO$_2$	0.51±0.05	-	0.79±0.01	1.10±0.02	11.34±0.8	48.66±0.8
TE	CPE	-	0.90±0.04	-	1.12±0.05	-	33.23±0.4
	MCPE/npTiO$_2$	0.40±0.03	0.89±0.02	0.62±0.01	1.10±0.03	17.56±0.3	49.26±0.4
GR	CPE	0.62±0.02	0.91±0.05	0.70±0.02	1.10±0.04	28.78±0.3	31.71±0.7
	MCPE/npTiO$_2$	0.51±0.04	0.92±0.02	0.71±0.02	1.06±0.03	31.77±0.6	67.22±0.5
RO	CPE	0.58±0.01	0.83±0.04	0.72±0.04	1.07±0.02	16.70±0.4	39.20±0.6
	MCPE/npTiO$_2$	0.63±0.02	0.87±0.03	0.75±0.01	1.06±0.01	32.40±0.7	57.23±0.8

The voltammograms of all wines showed two anodic current peaks, except CH, which showed one peak. Also, a more intense current response at MCPE/npTiO$_2$ compared to CPE was observed in all wines except CH. The shape of the voltammograms of all wine samples indicates that the oxidation process of the tested samples is predominantly irreversible.

The values of the estimated formal oxidation potential of the first anodic wave for red and rosé wine samples (VR, ME, CS, RO) obtained at CPE are in the potential range of 0.56 to 0.63 V, and at MCPE/np TiO$_2$ in the potential range of 0.62 to 0.82 V. The potentials of the first anodic current peak are between 0.72 and 0.86 V and between 0.75 and 0.86 V when unmodified or modified electrodes are used.

For white wine samples (CH, TE, GR) on CPE, the formal oxidation potential of the first anodic wave is in the range of 0.62 to 0.63 V, while at MCPE/npTiO$_2$ the formal oxidation potential is in the range of 0.40 to 0.51 V. The potentials of the first anodic current peak are between 0.69 and 1.01 V and 0.62 to 0.79 V when unmodified or modified electrodes are used.

The linearity of response was investigated by recording cyclic voltammograms of wine samples with different concentrations of polyphenols. The concentration of the electroactive substances in the real wine samples was changed by adding an appropriate amount of model wine solution. The anodic branch of the cyclic voltammograms for different proportions of wine for CS is shown in Figure 7.

The first anodic peak current showed a linear dependence on the concentration of the electroactive species in all natural wine samples examined. The highest degree of linear dependence in the range of wine content from 10 to 100 % was observed for CS (R^2 = 0.9947). The samples TE and CH showed a similar degree of linear dependence (R^2 =0.9885; R^2 =0.9833). The lowest degree of linear dependence is shown by samples ME, VR, GR and RO (R^2 =0.9500 to 0.9734).
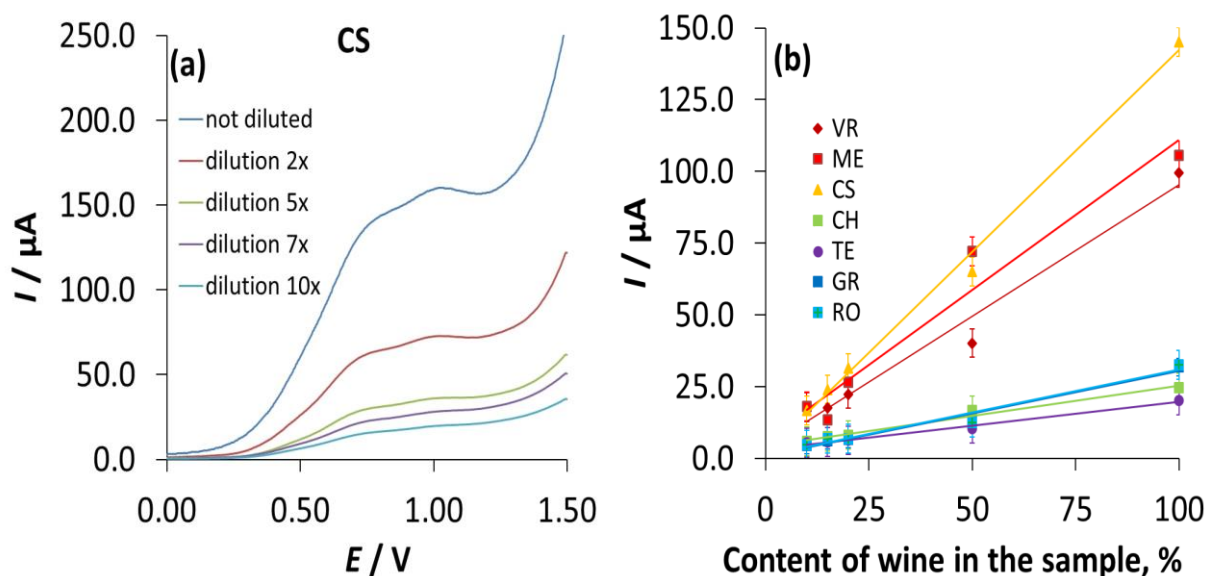
Figure 7. *(a) Anodic branch of cyclic voltammograms (200 mV s^{-1}) at MCPE/npTiO$_2$ recorded in undiluted and diluted samples of red wine CS; (b) intensity of anodic current peak depending on the proportion of wine for VR, ME, CS, CH, TE, GR, RO*

The results showed that the voltammetric response of anodic oxidation of GA at MCPE/npTiO$_2$ exhibits much more pronounced current maxima than at CPE. In addition, the voltammogram of the electrolytic oxidation of GA at MCPE/npTiO$_2$ shows a third anodic current peak, which is consistent with previous results. According to the studies of Chikere *et al*. [18], the first anodic peak corresponds to the formation of the semiquinone radical, while the second current peak is caused by the oxidation of the third -OH-galloyl group. Ziyatdinova *et al*. [19] discovered that the observed third anodic peak is due to the dimerization of the semiquinone radical to ellagic acid.

Regarding the effect of electrode modification on the anodic current, mixed effects on the oxidation potential and anodic peak potential were observed and lies in the range of just a few tens of mV. The shifts in potential, both negative and positive, were attributed to the catalytic and adsorptive effects of the modified electrodes. Carbon electrodes modified with nanoparticles showed an increased Faraday current and a shift of electrochemical reaction potential compared to unmodified carbon electrodes [20]. It has already been shown that TiO$_2$ nanoparticles cause a shift in the GA electrooxidation potential toward negative values, lowering the energy barrier during electron transfer [21]. Similarly, using a glassy carbon electrode modified with reduced graphene oxide, anodic oxidation of gallic acid occurs under the influence of adsorption. This modification shows a displacement of the peak potential of the anodic current towards more positive values [22].

Electrode modification has no effect on the electrooxidation of CA. The potential values of the anodic and cathodic current peaks during the electrooxidation of CA are consistent with previous studies by Manikandan *et al*. [23], who showed that the anodic current peak represents the orthoquinone formation reaction that accompanies the electrooxidation of CA, and that the oxidation reaction of CA occurs through the transfer of two electrons.

The cyclic voltammogram of CT electrooxidation at MCPE/npTiO$_2$ shows a slightly more intense anodic peak current compared to that obtained at CPE. Two anodic and one cathodic current maxima were observed. The mechanism of electrochemical oxidation of CT proposed by Janeiro *et al*. is based on two-step one-electron oxidation of ortho-phenolic groups bound to the B-ring in the structure of CT. The reaction mechanism is significantly influenced by the concentration of CT and pH of the electrolyte. It was shown that the first anodic peak corresponds to the first stage of the

oxidation of the 3,4-dihydroxyl groups of catechol and is fully reversible, which explains appearance of the cathodic current peak. The second anodic peak is related to the second oxidation step, the oxidation of the hydroxyl groups on the resorcinol unit of the CT structure and is completely irreversible, with CT being strongly adsorbed on the electrode surface [24]. The linear dependence of the anodic peak current on the potential scan rate suggests that the CT electrooxidation process at the modified electrode is controlled by adsorption. Similar results were presented in the study by Şenocak *et al.* [25], who showed that the anodic oxidation of catechins at a glassy carbon electrode modified with single-walled carbon nanotubes functionalized with subphthalocyanine, takes place under the influence of adsorption.

In the voltammogram of the anodic oxidation of QV at MCPE/npTiO$_2$, a slightly higher first peak current and the occurrence of the second and third anodic peaks indicate that the modified electrode has higher sensitivity compared to the unmodified electrode. According to studies by Sokolová *et al.* [26], the first oxidation peak corresponds to the two-electron oxidation of the 3´,4´-dihydroxy-benzo group, which is quasi-reversible. The second anodic wave corresponds to the oxidation of the product formed at the potential of the first anodic wave. The third anodic peak corresponds to the oxidation of the hydroxyl groups at positions C5 and C7 of the benzo ring. The process of electrooxidation of the product formed at the potential of the first anodic wave and of the hydroxyl groups at positions C5 and C7 of the benzene ring is characterized by irreversibility [26]. The dependence of the anodic peak current on the potential scan rate shows a linear dependence, indicating the adsorption control of the QV oxidation process. In the study by Saritha *et al.* [27] the adsorption control of the QV electrooxidation process was observed on the surface of a carbon electrode modified with ZnO nanoparticles and carbon nanosheets.

The observed anodic current peaks in the cyclic voltammogram of RE electrooxidation are in agreement with the results of Corduneanu *et al.* [28]*,* who showed that the first anodic current peak corresponds to the oxidation of the phenolic part, while the second anodic current peak corresponds to the oxidation of the resorcinol part of the RE structure . The dependence of the intensity of the anodic peak current on the potential scan rate showed a linear dependence, indicating that the RE electrooxidation process is controlled by adsorption. Similar results were shown in a study by Liu *et al.* [29] using a graphene-modified glassy carbon electrode.

Cyclic voltammograms of natural wine samples recorded with a modified carbon paste electrode are characterized by an increasingly more pronounced current wave compared to voltammograms recorded with an unmodified electrode, starting from CH, which showed no improvement to CS, which showed the most improvement. Improved characteristics of the TiO$_2$ nanoparticle-modified electrode material were also observed in the study by Manjunatha *et al.* [30]. The modified electrode showed better redox kinetics in the electrooxidation of paracetamol, a substituted monophenol, manifested in a more pronounced anodic current wave and potential shift [30].

Furthermore, the observed linear relationship between the peak current of the examined wine polyphenols and the potential scan rate suggests that the rate of adsorption and desorption at the electrode does not depend on the potential scan rate. This behavior results from the interaction of the electrochemical reaction kinetics and the adsorption process. The slopes from Table 2 that describe the linear relationship of the first anodic peak current of polyphenolic compounds on the potential scan rate at the MCPE/npTiO$_2$ electrode are RE / GA : (QV, CA, CT) : RE, respectively, and are approximately 3:2:1. This suggests that GA and QV adsorb with similar kinetics, while other polyphenols adsorb more slowly. However, GA has the highest current.

The significant increase in the GA voltammetric signal on the MCPE/npTiO$_2$ electrode compared to other studied polyphenols can be explained by the higher affinity for adsorption on TiO$_2$ nanoparticles. Titanium dioxide particles in aqueous solutions are known to interact with dihydroxy aromatic compounds, resulting in well-defined surface complexes. Arajuo *et al*. reported that catechol and GA bind to TiO$_2$ *via* two adjacent -OH groups and that the -COOH moiety of GA plays no role in Ti atom complexation [31]. Adsorption across neighboring -OH groups can be represented schematically using the following equations (1) and (2):

$$(\equiv Ti - OH)_2 + H_2L = (\equiv Ti)_2 - L + 2H_2O \tag{1}$$

$$(\equiv Ti - OH)_2 + L^{2-} + 2H^+ = (\equiv Ti)_2 - L + 2H_2O \tag{2}$$

whereby the equilibrium is described by the Langmuir-type stability constants. For GA and catechol, deprotonated species showed much higher stability constants of 27.1 and 24.7 than protonated species, which had stability constants of 4.9 and 4.7. This illustrates that the polyphenol's ability to deprotonate at the pH of the testing solution, which in this case is 3.6 for the model wine solution, has a significant influence on its adsorption affinity.

Deprotonation is indicated by the pKa values of the -OH groups. GA has the lowest pKa$_1$ constant and the highest degree of deprotonation at a model wine solution pH of 3.6, which, combined with the dependence of the stability constant on pH, explains its higher adsorption affinity compared to other compounds [31]. Arajuo *et al*. [31] found that deprotonating the carboxyl group increases affinity in the pH range of 3.2 to 5.2, owing to increased Lewis basicity of the anion. Indeed, the isotherms of gallic acid overlap at pH 3.75 and 6.15, indicating that GA adsorption is facilitated near the model wine's pH of 3.6. Further, they have also demonstrated that the maximum surface coverage by the adsorbed compound varies as a result of different adsorption affinities, and it is reasonable to assume that compounds with higher adsorption affinity produce a stronger voltammetric signal [31].

The shape of the voltammogram recorded in natural wine samples indicates the irreversible character of the oxidation process of electroactive polyphenols, which can be attributed to the pronounced tendency of polyphenolic compounds and their electrooxidation products to adsorb on the electrode surface of MCPE/np TiO$_2$ and CPE [24,26].

Cyclic voltammograms recorded in wine samples with a modified electrode exhibit an increasingly noticeable current wave compared to voltammograms recorded with an unmodified electrode, progressing from CH, which showed no improvement over CPE, to CS, which showed the most improvement. Manjunatha *et al*. [30] found improved properties of the TiO$_2$ nanoparticle-modified electrode material. The modified electrode demonstrated better redox kinetics in the electrooxidation of paracetamol, a substituted monophenol that manifested itself in a more pronounced anodic current wave [30].

The anodic current peaks in the voltammograms of white wines are significantly less amplified by the electrode modification than the current peaks in the voltammograms of red and rose wines, which is consistent with the higher gallic acid concentrations in red wines compared to white wines. These results are consistent with the study by Gutiérrez-Escobar *et al.*, in which significantly lower concentrations of polyphenolic compounds, including GA, were found in natural samples of white wines compared to red wines [1].

For all wine samples, the average estimated oxidation potential of the first current wave is 0.603±0.028 V on CPE and 0.560±0.089 V on MCPE/npTiO$_2$. For both the modified and unmodified electrodes, the average estimated oxidation potential of the second current wave was 0.911±0.026 V and 0.891±0.031 V, respectively. For the CPE electrode, the average estimated potential of the first current peak was 0.844±0.10 V, and for the MCPE/npTiO$_2$ electrode, 0.768±0.095 mV. For both the

modified and unmodified electrodes, the average second anodic peak potential is at 1.066±0.025 V and 1.075±0.041 V, respectively. The positive and negative shifts are in the range of several tens of millivolts and are possibly the result of the phenomenon of heterogeneous catalysis with adsorption of the reactants on the catalyst surface. It can be assumed that several polyphenolic compounds, in addition to those tested separately in this work, are co-adsorbed on the surface of the working electrode. As Mahotkina and Kilmartin have shown, the presence of substances used in the production process, whose function is to inhibit the oxidation process of polyphenolic compounds present in wine, has a significant influence on the potential value and intensity of the peak of the anodic current wave of wine samples [32]. Cyclic voltammograms of solutions of individual polyphenols (CA, CT, QV) in a model solution and cyclic voltammograms of natural red and white wine samples recorded using a glassy carbon electrode are shown along with the effects of glutathione, ascorbic acid, and sodium metabisulfite (which dissociates into SO$_2$ in solution). Sulfur dioxide increases anodic current while decreasing cathodic current due to its interaction with quinones formed during the oxidation of polyphenols. A similar effect has been observed with glutathione [32].

Based on the results presented in this study, it can be assumed that the enhancement of gallic acid oxidation occurs selectively on TiO$_2$ nanoparticles when introduced into the carbon paste. We hypothesize that the selective signal enhancement is proportional to the GA concentration in the solution, allowing a measurement in an undiluted sample that shows a linear decrease of the anodic current signal with dilution. A similar effect was observed on cobalt oxide nanoparticles by Chikere *et al.* [33]. This hypothesis should be confirmed by independent gallic acid measurements in wine samples, which is beyond the scope of this study. However, the basis for the operating principle of a wine sensor that selectively enhances the reaction of the mixture component based on adsorption affinity has been established.

The use of a sensor that selectively enhances the reaction of GA could be very interesting for wine production. A recent study investigated how gallic acid imparts an astringent flavor to white and red wine and affects gastric acid secretion by activating the bitter taste receptor [34]. Zhang *et al*. [35] investigated how the addition of gallic acid and ellagic acid before fermentation affects wine quality and composition during the aging process. They found that the addition of gallic acid improved the extraction of total anthocyanins and the co-pigmentation effect, resulting in wines with greater blackness, redness, yellowness and saturation [35].

Conclusions

In this work, the electrochemical characterization of polyphenolic compounds in a model wine solution and selected natural wine varieties was performed using cyclic voltammetry at CPE and CPE modified with TiO$_2$ nanoparticles. The modified CPE showed a significantly increased sensitivity for the electrooxidation of gallic acid, which was reflected in an increase in the anodic peak current. A very small increase in sensitivity was observed for caffeic acid, quercetin, and resveratrol, and none was observed for catechin. No clear trends were observed in the shift of the oxidation potential of the anodic waves and the potentials of the anodic peaks. The potentials were consistent with the known mechanisms for the electrooxidation of the studied polyphenols.

Cyclic voltammograms of real wine samples recorded with a modified CPE were characterized by an increasingly pronounced wave current, ranging from no improvement observed for unmodified CPE in one of the white wines to a current almost three times higher than CPE in one of the red wines. This study provides a good basis for the development and possible application of an amperometric sensor based on a carbon paste electrode modified with TiO$_2$ nanoparticles for the

selective enhancement of GA in wine samples. The simplicity of preparing the electrode material, the use of the analyte without prior sample preparation, the speed and ease of performing measurements with a satisfactory level of accuracy and reliability, and the algorithm for objective determination of the quantitative parameters provide a solid basis for the development of an integrated sensor/data processing system that could find wide application in winemaking.

Conflicts of interest: *The authors declare to have no competing financial interest or personal relation that could influence the results of this work.*

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