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Sensitive and Selective Voltammetric Sensors for the Simultaneous Quantification of Natural Phenolic Antioxidants in Cognac and Brandy †

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Abstract: Aged distilled beverages (cognac and brandy) contain phenolic antioxidants being their quality markers. Novel voltammetric sensors based on the carbon nanotubes and electropolymerized pyrocatechol violet (PCV) or *p*-aminobenzoic acid (ABA) were developed for the simultaneous determination of phenolic antioxidants in cognac and brandy. Polymerization conditions of PCV and ABA were optimized. Sensor allow simultaneous sensitive determination of gallic and ellagic acids as well as syringaldehyde and vanillin. The analytical characteristics are improved *vs*. other modified electrodes. The sensors show selectivity in the presence of typical interferences and other natural phenolics. The sensors developed were tested on the cognac and brandy.

Keywords: electrochemical sensors; carbon nanomaterials; electropolymerization; phenolic acids; phenolic aldehydes; aged distilled beverages

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1. Introduction

Aged distilled beverages namely cognac and brandy contain natural phenolic antioxidants to be considered as one of the quality markers [1]. Phenolic acid (gallic and ellagic) as well as aromatic aldehydes (vanillin and syringaldehyde) are the major contributors to the antioxidant properties of aged distilled beverages [1-3]. Their simultaneus determination is of practical interest.

Different types of chromatography and capillary electrophoresis are usually applied for their quantification [2,4,5]. Nevertheless, less tedious and more simple methods are encouraged. Electrochemical sensors being simple, reliable and cost-effective could be an effective alternative tool for this purposes [6-8]. The only problem of the electrochemical approaches is the low selectivity of phenolics determination due to the structural similarity of analytes. This limitation can be overcome using chemically modified electrodes.

Nevertheless, simultaneous voltammetric detection of gallic and ellagic acids as well as aromatic aldehydes are almost out of consideration. Up to date, there is just one example of the gallic and ellagic acid quantification in mixture using multi-walled carbon nanotube (MWNT) modified carbon paste electrode [6]. Possibility of simultaneous determination of syringaldehyde and vanillin has been demonstrated on glassy carbon electrode (GCE) modified with carbon nanofibers and cationic surfactant cetylpyridinium bromide [7]. The analytical characteristics presented in Table 1 can be further improved. The disadvantage of both approaches is the absence of data on selectivity of electrode response to target analytes. Furthermore, the application to real samples was not realized.

Table 1. Analytical characteristics of simultaneous voltammetric determination of natural phenolic acids and aromatic aldehydes.

Electrode	Methods	Analyte	Detection limit, μM	Linear dynamic range, μM	Ref.
MWNT-Carbon paste electrode	AdDPV[1]	Gallic acid	–	2.50–21.25	[6]
		Ellagic acid	–	0.0075–0.019	
Cetylpyridinium bromide/Carbon nanofibers/GCE	DPV[2]	Syringaldehyde	0.53	2.5 – 30	[7]
		Vanillin	1.17	5.0 – 40	

[1] Adsorptive differential pulse voltammetry
[2] Differential pulse voltammetry

Thus, novel voltammetric sensors based on the carbon nanotubes and electropolymerized pyrocatechol violet (PCV) or *p*-aminobenzoic acid (ABA) have been developed for the simultaneous determination of phenolic antioxidants in cognac and brandy for the first time.

2. Materials and Methods

PCV and 99% ABA from Sigma-Aldrich (India and Germany, respectively) were used as monomers for the polymeric coverage obtaining. Their standard solutions (10 mM for PCV and 25 mM for ABA) were prepared in distilled water. Gallic (99%) and ellagic (95%) acids, vanillin (99%) from Sigma (Germany) and syringaldehyde (98%) from Aldrich (Germany) were used as standards. Their 10 mM (0.86 mM for ellagic acid) stock solutions in the methanol (ethanol in the case of aromatic aldehydes) were prepared in 5.0 mL flasks. The exact dilution with corresponding solvent was used for the preparation of less concentrated solutions.

MWNT (outer diameter 40–60 nm, inner diameter 5–10 nm and 0.5–500 μm length) and polyaminobenzene sulfonic acid functionalized single-walled carbon nanotubes (f-SWNT) ($d \times l$ is 1.1 nm×0.5–1.0 μm) were purchased from Aldrich and Sigma-Aldrich (Germany), respectively. MWNT (0.5 mg mL^{-1} homogeneous suspension in 1% sodium dodecylsulfate (Panreac, Spain) was prepared by sonication for 30 min in ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd, Republic of Korea). Homogeneous 1.0 mg mL^{-1} suspension of f-SWNT was got by ultrasonic dispersion for 30 min in dimethylformamide.

All reagents were chemical grade purity. Double distilled water was used for the measurements. The experiments were carried out at laboratory temperature (25 ± 2 °C).

Voltammetric measurements were carried out on the potentiostat/galvanostat Autolab PGSTAT 12 (Eco Chemie B.V., Netherlands) with the GPES software, version 4.9.005. Electrochemical impedance spectroscopy (EIS) was performed on the potentiostat/galvanostat Autolab PGSTAT 302N with FRA 32M module (Eco Chemie B.V., Netherlands) and NOVA 1.10.1.9 software. The 10 mL glassy electrochemical cell with working GCE with 7.07 mm^2 geometric surface area (CH Instruments, Inc., USA) or modified electrode, a silver-silver chloride saturated KCl reference electrode and a platinum wire as the counter electrode was used.

"Expert-001" pH meter (Econix-Expert Ltd., Russian Federation) equipped with the glassy electrode was applied for pH measurements.

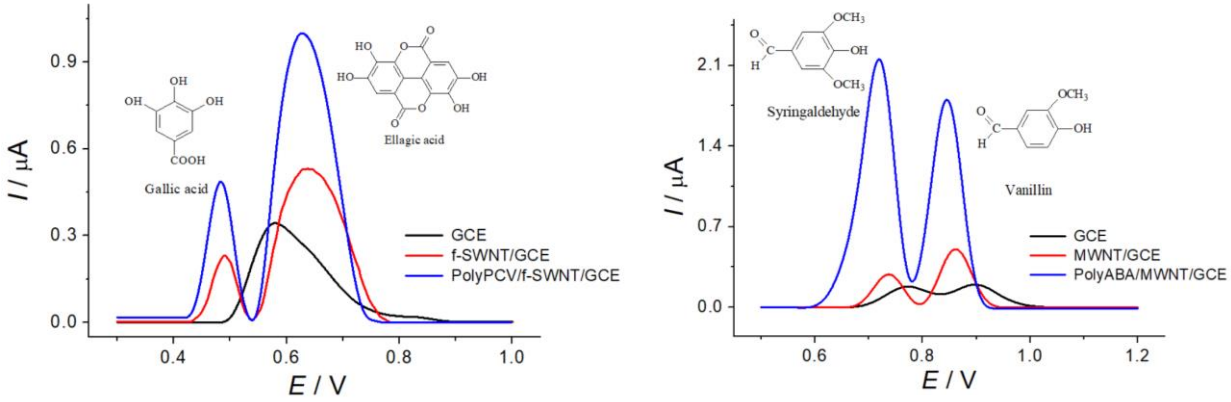
Scanning electron microscopy (SEM) was carried out on the high-resolution field emission scanning electron microscope MerlinTM (Carl Zeiss, Germany) at the accelerating voltage of 5 kV and emission current of 300 pA.

3. Results and Discussion

3.1. Polymer-Based Sensor Creation and Their Characteristics

Carbon nanotube-modified GCE has been used as a substrate for polymeric coverage electrochemical deposition. This approch provide high surface area and conductivity

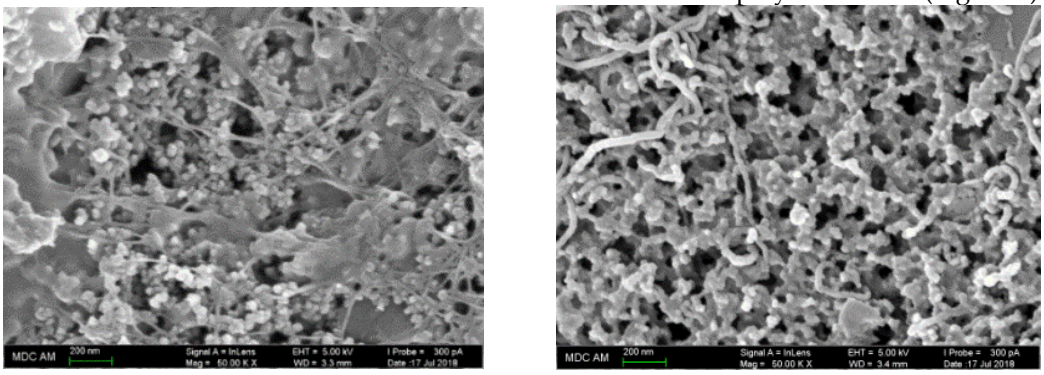
of the electrode. Both PCV and ABA form conductive polymers that is confirmed by the appearance of quasi-reversible redox peaks on the cyclic voltammograms which currents increase with the increase of the number of cycles. Polymerization conditions of PCV and ABA in potentiodynamic mode has been optimized on the basis of voltammetric response of pairs of target analytes. Peak potential separation for both types of analytes does not change on polymer-based sensor *vs*. carbon nanotube modified electrode (Figure 1) while oxidation currents are statistically significntly increased. Thus, electropolymerization of PCV should be performed from 50 μM monomer in 0.1 M H_2SO_4 by 10 cycles from −0.2 to 1.1 V at 50 mV s^{-1}. Optimum conditions for ABA electropolymerization are 20-fold potential cycling from −0.5 to 2.0 V at 100 mV s^{-1} from 100 μM monomer in Britton-Robinson buffer pH 2.0.



(**a**) (**b**)

Figure 1. Background subtracted differential pulse voltammograms of 10 μM mixture of (**a**) gallic and ellagic acids and (**b**) syringaldehyde and vanillin in Britton-Robinson buffer pH 2.0. ΔE_{pulse} = 50 mV, t_{pulse} = 50 ms, υ = 10 mV s^{-1}.

The sensors developed has been characterized with scanning electron microscopy (SEM), cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy (EIS). According SEM data, the polymeric coverages exhibit porous structure with the shape of particles and their aggregates deposited on the surface of carbon nanomaterials that confirms the successful electropolymerization (Figure 2).



(**a**) (**b**)

Figure 2. SEM images of (**a**) polyPCV/f-SWNT/GCE and (**b**) polyABA/MWNT/GCE.

Electroacitve surface area of the electrodes have been calculated on the basis of cyclic voltammetry and chronoamperometry (for GCE) of 1.0 mM $[Fe(CN)_6]^{4-}$. Statistically significant increase of the effective surface area (49.0±0.2 mm^2 for polyPCV/f-SWNT/GCE and 89±4 mm^2 for polyABA/MWNT/GCE *vs*. 38.9±0.6 mm^2 for f-SWNT/GCE, 75±3 mm^2 for MWNT/GCE and 8.2±0.3 mm^2 for GCE) explain well the increase of the analytes oxidation currents. EIS data show low charge transfer resistance of

the polymer-based sensors developed (26.0±0.4 and 4.9±0.3 kΩ for polyPCV/f-SWNT/GCE and polyABA/MWNT/GCE) in comparison to GCE (68±4 and 72±3 kΩ) and GCE modified with carbon nanotubes (19.2±0.8 kΩ for f-SWNT/GCE and 12.1±0.9 kΩ for MWNT/GCE) have been obtained. Thus, polymer-based sensor are characterized by higher electron transfer rate. SEM and electrochemical methods data confirm the effectivity of the developed modifier.

3.2. Simultaneous Quantification of Natural Phenolic Antioxidants

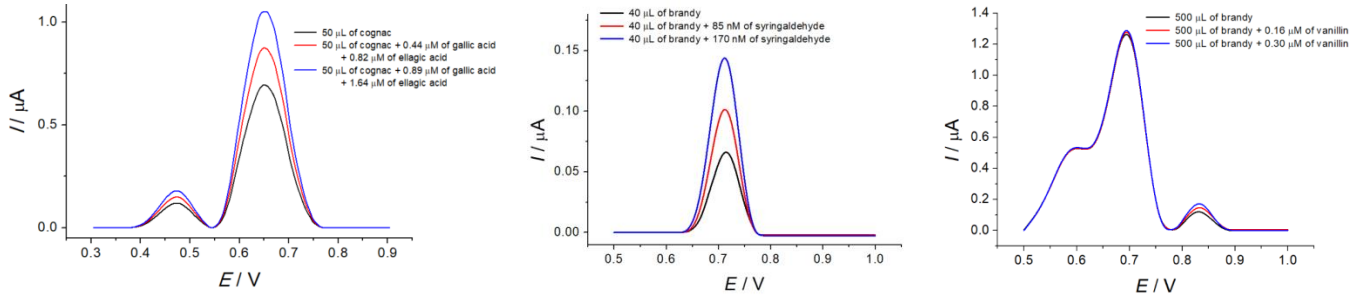
For the quantification of phenolics under consideration, the sensors created have been used under conditions of differential pulse voltammetry in Britton-Robinson buffer pH 2.0 medium providing the highest oxidation currents of the analytes (phenolic acids and aromatic aldehydes). The linear dynamic ranges of 0.75–10 and 10–100 μM for gallic acid and 0.75–7.5 and 7.5–100 μM for ellagic acid on polyPCV-based sensor have been obtained. The detection limits are equaled to 0.12 μM for gallic acid and 0.11 μM for ellagic acid. PolyABA-based sensor give linear response in the ranges of 0.075–7.5 and 7.5–100 μM of syringaldehyde and 0.50–7.5 and 7.5–100 μM of vanillin with the detection limits of 0.018 and 0.19 μM, respectively. The analytical characteristics obtained are improved *vs*. other modified electrodes [6,7]. The proved independent electrooxidation of the analytes pairs allows application of calibration graphs for the equimolar mixtures that is another advantage of the approaches developed. High accuracy of the sensors has been confirmed by recovery values (97.1–101%) for model solutions of phenolics.

The sensors selectivity in the presence of typical interferences and other natural phenolics has been obtained that is important advantage. 1000-Fold excess of inorganic ions (K^+, Mg^{2+}, Ca^{2+}, NO_3^-, Cl^-, and SO_4^{2}), glucose, rhamnose, sucrose as well as ascorbic acid (1000- and 100-fold excess in the case of phenolic acids and aromatic aldehydes, respectively) do not show interference effect. The absence of intereference effect of syringaldehyde and vanillin (< 2.5 and < 10 μM, respectively) on the oxidation peaks of phenolic acids has been proved. On contrary, gallic and ellagic acid are the major potential interferences for the determination of aromatic aldehydes under consideration. 10-Fold excess of gallic acid and < 1.0 μM of ellagic acid do not interfere with the determination of vanillin and syringaldehyde. The interference effect of ellagic acid which contents in cognac and brandy is high enough can be excluded via sample dilution. Thus, the sensors can be applied for the aged distilled beverages analysis.

3.3. Real Samples Analysis

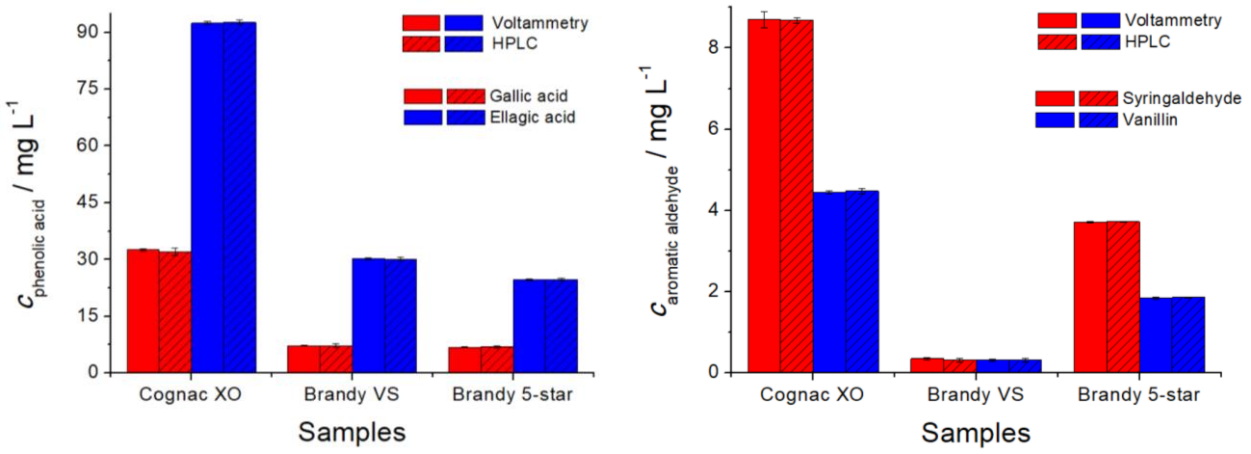
The sensors developed have been successfully tested on the cognac and brandy samples. There are resolved oxidation peaks of phenolic acids and aromatic aldehydes on the differential pulse voltammograms of cognac and brandy that is confirmed by standard addition method (Figure 3). Due to the low concentration of vanillin, the sample volume was varied for the quantification of syringaldehyde and vanillin (40 and 500 μL, respectively). The recovery of 98.9–102% indicates the absence of matrix effects in these determinations.

Quantification of natural phenolic antioxidants in cognac and brandy has been performed and compared with independent chromatographic determination (Figure 4). The results obtained agree well with each other. *t*-test data (0.0100–2.19) are less than critical value of 2.45 that means the absence of systematic errors in the determination. Similar, *F*-test results (1.00–17.36) are less than critical value 19.25 indicating uniform precision of the methods used.



(**a**) (**b**) (**c**)

Figure 3. Background subtracted differential pulse voltammograms of (**a**) 50 μL of cognac with additions on polyPCV-based sensor, (**b**) 40 μL and (**c**) 500 μL of brandy with additions on polyABA-based sensor. Supporting electrolyte is Britton-Robinson buffer pH 2.0. ΔE_{pulse} = 75 mV (50 mV for aromatic aldehydes), t_{pulse} = 25 ms, υ = 10 mV s^{-1}.



(**a**) (**b**)

Figure 4. Quantification of (**a**) gallic and ellagic acids and (**b**) syringaldehyde and vanillin in cognac and brandy (*n*=5; *P*=0.95).

Thus, the novel highly sensitive and selective voltammetric sensors for the simultaneous determination of structurally related phenolic antioxidants in cognac and brandy are characterized by simplicity of the fabrication, reliability, cost-efficiency and can be applied for the routine analysis as an alternative to chromatographic methods.

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Conflicts of Interest: The authors declare no conflict of interest

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