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Chronoamperometric estimation of cognac and brandy antioxidant capacity using MWNT modified glassy carbon electrode

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ABSTRACT

Cognac and brandy components are electrochemically oxidized on multi-walled carbon nanotube modified glassy carbon electrode at 0.44 and 0.59 V in 0.1 M phosphate buffer solution pH 3.0. Voltammetric behavior of the main antioxidant constituents of cognac (ellagic and gallic acids, syringaldehyde, coniferaldehyde, vanillin, 5-hydroxymethylfurfural and furfural) has been investigated. The peak at the less positive potential of cognacs is caused by oxidation of gallic acid as well as syringaldehyde- and coniferaldehyde. The second peak corresponds to ellagic acid oxidation. One-step chronoamperometry at 0.59 V for 75 s has been applied for the cognac and brandy antioxidant capacity (AOC) evaluation. Ellagic acid, being the main antioxidant of cognac, has been used as a reference substance. The chronoamperometric response of ellagic acid is linear in the range of 0.66–52.8 μM with the limit of detection and quantification at 0.19 and 0.63 μM, respectively. AOC in ellagic acid equivalents per 100 mL of cognac and brandy for different denominations (11 cognacs and 11 ordinary and vintage brandies) has been estimated. AOC of cognacs and brandies increases with the age of the beverages. Positive correlations (r=0.9134–0.9703) with common parameters characterizing antioxidant properties of beverages, in particular antiradical activity, total phenolics content, total antioxidant capacity and ferric reducing power have been observed.

1. Introduction

Aged distilled beverages (cognac, armagnac and other aged brandies) are part of human diet and widely consumed all over the world. Epidemiological studies confirm that moderate consumption of alcoholic beverages has a positive influence on coronary heart disease improving metabolism of lipids, increasing anticoagulant and antioxidant activity and decreasing mortality from coronary disease, as well as from colorectal cancer [1–3].

Aged distilled beverages are rich in phenolic compounds due to their maturation in wooden barrels [4–6]. Phenolic compounds exhibit wide range of biological activity including the antioxidant effect [7]. The antioxidant activity of phenolic compounds depends on their chemical structure, nature of matrix, concentration and oxidation status. In the case of aged distilled beverages, the latter two factors are determined by the aging conditions including the wooden barrel characteristics such as wood botanical species [8–11], toasting level [8,12], barrel size [13] and the cellar environment [8,14]. Therefore, antioxidant properties are used as parameters characterizing the technological aspects of aged distilled beverages production as well as properties of final product [5,15,16].

Various approaches have been described for the evaluation of antioxidant properties of aged distilled beverages using spectrophotometric measurements [17–19]. From the other side, antioxidant effect of phenolic compounds from aged distilled beverages is associated with electron transfer that allows one to use methods of electroanalysis for its evaluation. First of all, antioxidant activity of aged distilled beverages has been studied using electrochemical properties of radical species that are usually used in spectrophotometric assays. Sherry brandies (Solera, Solera Reserva and Solera Gran Reserva) antioxidant activity has been estimated by amperometric reduction of 2,2-diphenyl-1-picrylhydrazyl (DPPH) [20] as well as antioxidant activity of several other commercial aged distillates (Cognacs, Armagnacs and Spanish, French and South African brandies) based on the electrochemical oxidation of 2,2″-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) [21].

An approach based on decrease of polarographic hydrogen peroxide anodic oxidation current has been applied for the determination of antioxidant activity of strong alcoholic beverages such as plum and wine brandies, whiskeys, bitters and sweet fruit liqueurs. Changes of antioxidant activity of some herbal liqueurs during storage under different conditions as well as a quarter century long aging of plum brandy in an oak barrel have been monitored [22].

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Constant-current coulometry with electrogenerated titrants – electrogenerated bromine and hexacyanoferrate(III) ions has been applied for estimation of cognac and brandy total antioxidant capacity (TAC) and ferric reducing power (FRP), respectively. Both parameters for cognacs are statistically significantly higher than for brandies and grow with the age increase [23].

Nevertheless, development of novel electrochemical procedures that are direct, less time-consuming and less expensive is of interest. Approaches based on simple and rapid experiment without sample pretreatment and usage of nonphysiological radical species are preferred. There is no such data about electrochemical behavior of cognacs and brandies. The aim of the present work is the investigation of aged distilled beverages' electrochemical behavior under conditions of voltammetry and chronoamperometry and development of the procedure for direct chronoamperometric evaluation of cognacs and brandies antioxidant capacity (AOC).

2. Material and methods

2.1. Samples and reagents

The cognacs and brandies analyzed were commercially available samples of different trademarks. A total 11 cognacs of 3 various commercial denominations (VS, VSOP and XO) as well as 11 ordinary and vintage brandies of Russian (Ru), Armenian (Am), Ukrainian (Ua) and Azerbaijanian (Az) origin have been analyzed. The commercial denomination indicates the minimum or average age of distillate which is used in the blend for cognac and brandy. Brandy denomination KV means an average age of 6 years, KS – 10 years and OS – 20 years.

Ellagic (95% purity) and gallic acids (99%), and vanillin (99%) were purchased from Sigma (Steinheim, Germany). Syringaldehyde (98%), coniferaldehyde (98%), 5-hydroxymethylfurfural (99%) and furfural of 99% purity were obtained from Aldrich (Steinheim, Germany). Their 0.4–5.0 mM stock solutions were prepared daily dissolving a definite amount of the substance in 10.0 mL of ethanol (rectificate). More dilute solutions (model solutions) were prepared before measurements in 10.0 mL volumetric flasks by dilution of the corresponding stock solution with a supporting electrolyte.

Multi-walled carbon nanotubes (MWNT) with OD 40–60 nm, ID 5–10 nm and length 0.5–500 μm were obtained from Aldrich (Steinheim, Germany). DPPH and Folin–Ciocalteu reagent were purchased from Aldrich (Steinheim, Germany). DPPH stock solution (61 μM) were prepared by dissolving a definite amount in methanol (chemical grade purity).

All other chemicals were analytical reagent grade purity and used as received. Double distilled water was used for measurements. The experiments were carried out at laboratory temperature (20–23 °C). All solutions of compounds under investigation were prepared exactly before measurements.

2.2. Instrumentation

Voltammetric and chronoamperometric measurements were performed on potentiostat/galvanostat μAutolab Type III with the software GPES-General Purpose Electrochemical System, version 4.9.005 (Eco Chemie B.V., Netherlands). A 15 mL glass electrochemical cell was used for the experiment. The three electrode system consisted of a working glassy carbon electrode (GCE) or MWNT-modified GCE (MWNT-GCE) (6.07 mm^2 surface geometric area), a silver–silver chloride saturated KCl reference electrode and a counter-electrode (platinum wire).

Coulometric measurements were carried out using P-5827M potentiostat (ZIP, Belarus) with four-electrode two-compartment electrochemical cell. A bare platinum foil with 1 cm^2 surface area was used as the working electrode, and a platinum wire separated from the anodic compartment with a semipermeable diaphragm as the auxiliary electrode. A pair of polarized platinum electrodes was used for detection of the titration end-point. Surface of platinum electrodes was cleaned by HNO_3 and then rinsed thoroughly with double distilled water.

Spectrophotometry was performed on a PE-5300 spectrophotometer (NPO Ecros, Russia). "Expert-001" pH meter (Econix-Expert Ltd., Russia) equippled with the glass electrode was used for pH measurements.

2.3. Procedures

2.3.1. Preparation of modified electrodes

The GCE was carefully polished with alumina (0.05 μm) on polishing cloth. Then it was rinsed with acetone and double distilled water before use. Homogeneous suspension of MWNT with final concentration of 0.5 mg mL^{-1} was achieved by ultrasonic dispersion for 18 min in 1% sodium dodecyl sulfate. Electrodes' modification was performed by coverage of GCE with 5 μL MWNT suspension without any electrochemical precondition of the electrode surface and evaporation to dryness.

2.3.2. Differential pulse voltammetry (DPV) and chronoamperometry

0.1 M phosphate buffer (PB) (pH 3.0) was used as the supporting electrolyte. Anodic DP voltammograms were registered within the potential range from 0.3 to 1.0 V using pulse amplitude of 50 mV, pulse width 50 ms and scan rate 10 mV s^{-1}. Baseline correction by moving average algorithm included in GPES software has been applied for better peaks' identification.

Chronoamperometric measurements were performed at potential 0.59 V. Amperometric signal was read for $t = 100$ s.

2.3.3. Coulometric titration

Electrochemical generation of titrants was carried out at a current density 5 mA cm^{-2} providing 100% current yield. Bromine was generated from 0.2 M KBr in 0.1 M H_2SO_4. Hexacyanoferrate (III) ions were generated from 0.1 M $K_4Fe(CN)_6$ in 2 M KOH. The titration end-point was measured biamperometrically ($\Delta E =$ 200 mV).

Coulometric titration was carried out in a 50 mL cell containing 20.0 mL of supporting electrolyte. The generating circuit was switched on and a certain value of indicator current was attained. Then an aliquot portion (500 μL) of cognac or brandy was added to the cell and timer was simultaneously started. The titration end-point was detected by the attainment of the initial value of the indicator current. The timer was stopped and the generating circuit was turned off. The time of titration was used for TAC and FRP calculation.

TAC and FRP were expressed in units of quantity of electricity (Coulombs (C)) spent for titration on 100 mL of cognac [23].

2.3.4. Antioxidant capacity (AOC) evaluation

500 μL of cognac or brandy sample were inserted into electrochemical cell containing 9500 μL of 0.1 M PB and chronoamperometric curves were recorded at 0.59 V. For AOC assay, current difference of sample and supporting electrolyte has been used after 75 s of electrolysis.

AOC of cognac and brandy was expressed in ellagic acid equivalents (EAE AOC) per 100 mL of beverage and calculated in

accordance with the following equation:

$$\mathrm{EAEAOC} = \frac{(I - I_0 - a)V_{cell}M_{EA} \times 100}{bV_{al}}$$

where I is the oxidation current of cognac or brandy at 75 s in μA; I_0 is the oxidation current of supporting electrolyte at 75 s in μA; a is the intercept of ellagic acid calibration plot, (0.01) μA; b is the slope of ellagic acid calibration plot, (11.6×10^3) μA M^{-1}; V_{cell} is the solution volume in the cell, (0.01) L; V_{al} is the cognac aliquot volume, (5×10^{-4}) L; M_{EA} is the molar mass of ellagic acid, (302.197) g mol^{-1}; 100 mL is the volume of cognac or brandy on which the EAE AOC is recalculated.

2.3.5. Antiradical activity assay

Antiradical activities of cognacs and brandies were determined using the free radical DPPH [24]. In its radical form, DPPH is absorbed at 515 nm but upon reduction by an antioxidant or radical species its absorption decreases.

A volume of 3.0 mL of 61 μM DPPH methanol solution was used. The reaction was started by the addition of 5 μL of cognac or brandy samples. After incubation at room temperature in dark for 30 min, the remaining DPPH was determined by absorbance at 515 nm and the radical scavenging activity of each sample was expressed using the ratio of the absorption decrease of DPPH (%) to that of the control DPPH solution (100%) in the absence of the sample. All samples were analyzed in triplicates.

2.3.6. Total phenolics by Folin–Ciocalteu assay

Total phenolic contents were determined by Folin–Ciocalteu colorimetric method with some modifications [25]. An aliquot (1.0 mL) of cognac (brandy) or gallic acid standard solution (20.0, 40.0, 60.0, 80.0, 100.0 and 300 mg L^{-1}) was added to a 25.0 mL volumetric flask containing 9.0 mL of distilled water. Folin–Ciocalteu reagent (1.0 mL) was added to the mixture and shaken. After 5 min, 10 mL of 7% Na_2CO_3 solution was added with mixing and solution was immediately diluted to 25.0 mL with distilled water. After incubation at room temperature for 1.5 h, the absorbance of the solution at 750 nm was measured. Total phenolic contents were expressed as mg of gallic acid equivalents (GAE) per 1 L of cognac. All samples were analyzed in triplicates.

2.4. Statistical analysis

All electrochemical measurements were performed in five replications. Statistical evaluation was performed at significance level of 5%. All data are expressed as $X \pm \Delta X$ with X as average value and ΔX as confidence interval.

AOC values for different denominations of cognac and brandy were expressed as $X \pm S$ with X as average value and S as standard deviation. The difference of parameters was measured by Student's t-test. $p < 0.05$ was considered as statistically significant. Correlation analysis was performed using OriginPro 8.0 (OriginLab, USA) software.

3. Results and discussion

3.1. DPV of cognacs

The voltammetric behaviors of cognac and brandy have been studied for the first time. Typical DP voltammogram of cognac (brandy) on GCE in PB (pH 3.0) is shown in Fig. 1A. There is a very weak oxidation step at 0.43 V and a well-defined peak at 0.57 V. The cognacs of VS denomination and ordinary brandies show just one oxidation peak at 0.57 V.

In the case of MWNT-GCE, there are well-defined oxidation peaks of cognac (brandy) components at 0.44 and 0.59 V on DP voltammograms (Fig. 1B) in PB (pH 3.0) for all samples under investigation. The second oxidation peak is 12-fold higher than that on GCE. Therefore, MWNT-GCE has been used in order to get reliable response of beverages. Variation of supporting electrolyte pH in the range of 3.0–7.0 has shown best forms of voltammograms and the highest peak currents at pH 3.0.

Taking into account the chemical content of cognacs, in particular phenolic compounds [5], voltammetric behavior of main antioxidant constituents (ellagic and gallic acids, syringaldehyde, coniferaldehyde and vanillin as well as 5-hydroxymethylfurfural and furfural) has been investigated in order to find signal forming substances.

Furfurals are electrochemically inactive in the range of potentials under investigation. Other antioxidants show well-defined oxidation steps on DP voltammograms (Fig. 2). Ellagic acid is oxidized to corresponding di-*o*-quinone (Scheme 1).

Gallic acid undergoes two-step oxidation and the second step is weakly defined. Pyrogallol group participates in the reaction. The first oxidation peak corresponds to formation of semiquinone cation radical which is further transformed to radical. The second step is caused by second electron elimination and formation of *o*-quinone [26] (Scheme 2). Vanillin and related compounds are oxidized by 2-electron mechanism to corresponding *o*-quinones [27,28] in accordance with Scheme 3.

As one can see in Fig. 2, only gallic acid is oxidized at 0.44 V but syringaldehyde and coniferaldehyde are oxidized at related potentials ($E_1 = 0.46$ and 0.41 V, respectively) and give contribution to DP response of cognac and brandy that is confirmed by a standard addition method. The second oxidation peak of cognac at 0.59 V coincides with ellagic acid oxidation potential. The standard addition method confirms the assumption noted above. Recovery

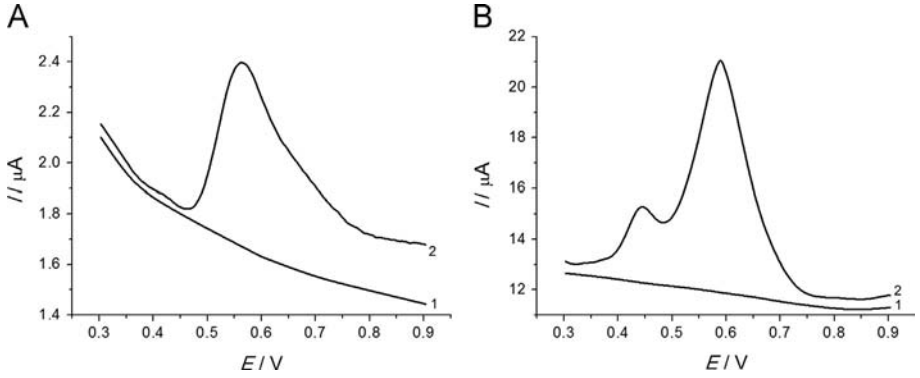


Fig. 1. Typical DP voltammograms of 2 mL cognac or brandy (curve 2) in 0.1 M phosphate buffer (pH 3.0) (curve 1): A – GCE; B – MWNT-GCE. Pulse amplitude is 50 mV, pulse width is 50 ms and scan rate is 10 mV s^{-1}.

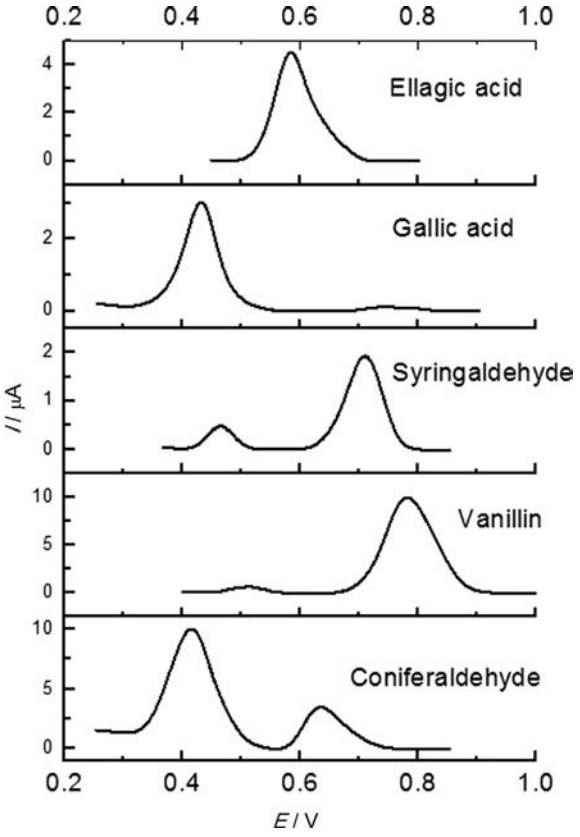
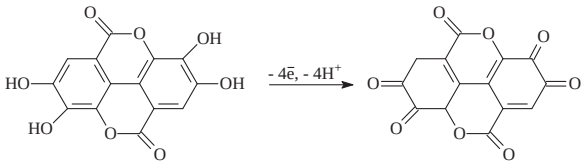
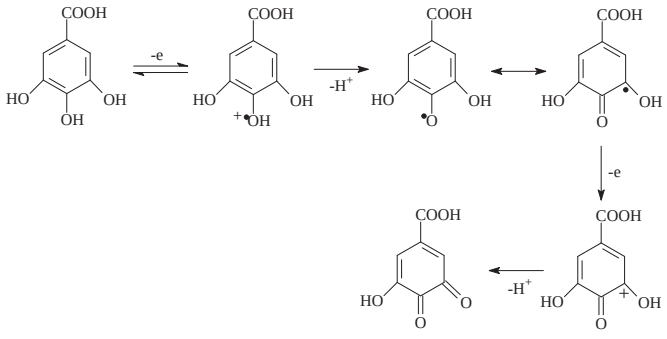


Fig. 2. Baseline corrected DP voltammograms of cognac antioxidants on MWNT-GCE in 0.1 M phosphate buffer (pH 3.0). Pulse amplitude is 50 mV, pulse width is 50 ms and scan rate is 10 mV s^{-1}.

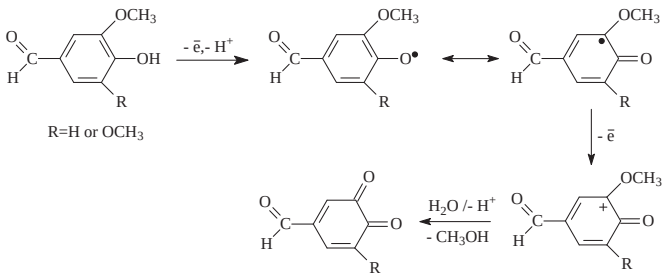


Scheme 1. Ellagic acid oxidation.



Scheme 2. Electrooxidation of gallic acid.

values of 13.4% and 96% have been observed for gallic and ellagic acids, respectively (Fig. 3). The low recovery of gallic acid confirms the integral nature of the first oxidation peak. The difference in gallic and ellagic acids' recovery is caused by their contents in aged distilled beverages. As known from HPLC data [5], ellagic acid contents in cognacs are 10-fold higher than gallic acid contents.



Scheme 3. Oxidation of vanillin and syringaldehyde.

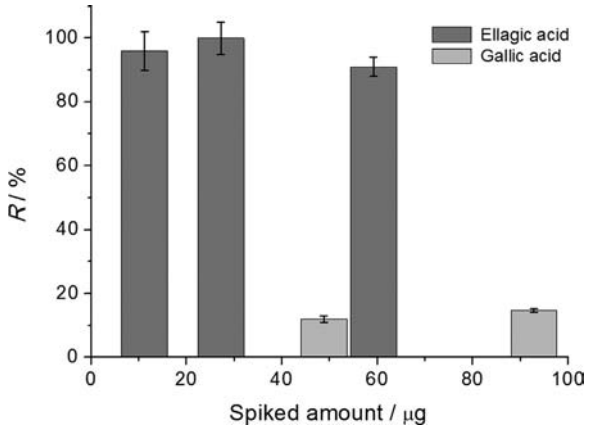


Fig. 3. Gallic and ellagic acids recovery test ($n=5$; $P=0.95$).

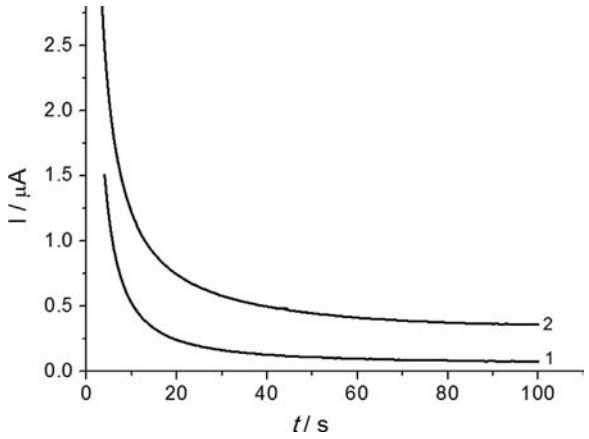


Fig. 4. Typical one-step chronoamperograms of 500 μL cognac or brandy (curve 2) on MWNT-GCE in 0.1 M phosphate buffer (pH 3.0) (curve 1) at 0.59 V.

3.2. Chronoamperometric response of cognacs and brandy

On the basis of voltammetric behavior of cognacs and brandy, chronoamperometry has been applied for the antioxidant properties' evaluation. One-step chronoamperometry at 0.59 V for 100 s has been used. Typical chronoamperogram of cognac is shown in Fig. 4. Electrolysis time of 75 s is enough to achieve the steady-state. The sample volume for chronoamperometric detection is 4-fold lower than that for DPV.

Ellagic acid being the main antioxidant of cognac has been used as a reference substance. Therefore, its chronoamperograms were preliminary recorded at 0.59 V and $t=75$ s (Fig. 5). The chronoamperometric response of ellagic acid is linear in the range of 0.66–52.8 μM. The calibration graph is $I(\mu A)=(0.01\pm0.01)+(11.6\pm0.6)\times10^3\times C(M)$ with $R^2=0.9951$.

The limits of detection (LODs) and quantification (LOQs) have been calculated using statistic treatment $3SD_a/b$ and $10SD_a/b$, respectively, where SD_a is the standard deviation of the average arithmetic of 10 voltammograms of the blank and b is the slope of the calibration curve. The LOD and LOQ are 0.19 and 0.63 μM of ellagic acid, respectively, indicating the satisfactory sensitivity of the approach developed.

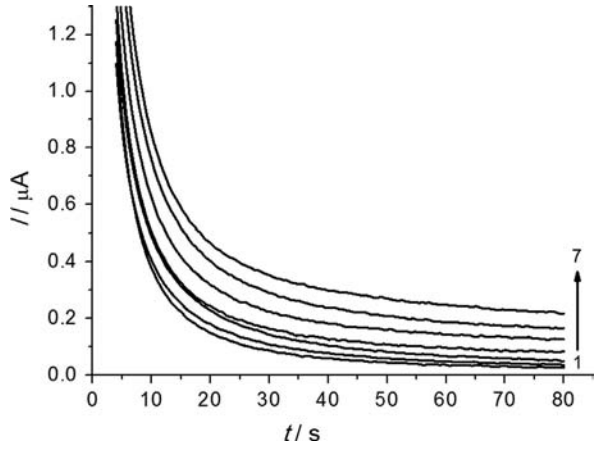


Fig. 5. Chronoamperograms of 0 (curve 1), 1.32 (2), 3.96 (3), 6.60 (4), 9.24 (5), 13.20 (6), and 26.4 μM (7) of ellagic acid on MWNT-GCE in 0.1 M phosphate buffer (pH 3.0) at 0.59 V.

Table 1
Cognac and brandy AOC in ellagic acid equivalents (EAE) based on chronoamperometric assay using MWNT-based GCE ($n=5$; $P=0.95$).

Beverage	Denomination	Sample	EAE AOC, mg per 100 mL	RSD (%)
Cognac	VS	F1	10.5 ± 0.8	6.1
		F2	2.97 ± 0.07	1.9
		F3	3.4 ± 0.3	9.7
		F4	9.6 ± 0.2	1.3
	VSOP	F1	13.8 ± 0.1	6.6
		F2	5.0 ± 0.3	5.5
		F4	7.4 ± 0.8	8.8
		F5	7.3 ± 0.7	7.3
	XO	F1	19.3 ± 0.2	6.1
		F2	8.4 ± 0.6	6.1
		F4	11.6 ± 0.2	1.4
Brandy	3-Star	Am1	4.3 ± 0.4	7.7
	4-Star	Am2	5.2 ± 0.4	7.7
	5-Star	Az	8.9 ± 0.2	2.0
		Ua	4.1 ± 0.1	2.6
		Ru1	2.8 ± 0.1	2.9
		Am3	3.5 ± 0.2	5.6
	KV	Ru2	2.4 ± 0.1	4.2
		Am4	9.8 ± 0.4	3.1
	KS	Am5	7.2 ± 0.6	6.6
		Ru3	6.2 ± 0.1	1.5
	OS	Am6	13.6 ± 0.6	3.4

3.3. Cognac and brandy AOC estimation

AOC of different denominations of cognac and brandy has been investigated and expressed in ellagic acid equivalents per 100 mL of beverage. The results are presented in Table 1.

The highest AOC has been obtained for cognac F1 in the range of the same denominations of the investigated brands. As for brandy, only vintage samples of KV, KS and OS denomination have shown to be comparable to cognac AOC values that was caused by technology of beverages production. Cognac and vintage brandy production includes stage of blending when very old distillates are added [29].

AOC of cognacs and brandy increases with the age of the beverage (Fig. 6) that is caused by longer aging in wood casks. Nevertheless, the difference between denominations is statistically insignificant ($p > 0.05$) due to different data for sample F1 for cognacs and different price range for brandy samples. It should be noted that Armenian brandies possess higher AOC than other brandies under investigation. So, the older beverages show higher AOC that agrees well with total antioxidant status of distilled spirits reported earlier [5].

Most common approaches to evaluation of alcoholic beverages antioxidant properties are spectrophotometric determination of total phenolic contents by Folin–Ciocalteu method and antiradical activity assay based on reaction with DPPH. Both procedures have been used for comparison of data obtained by a chronoamperometric method developed (Fig. 7A and B). In addition, TAC and FRP based on coulometric titration with electrogenerated bromine and hexacyanoferrate(III) ions have been used as independent parameters characterizing antioxidant properties of beverages (Fig. 7C and D). The correlation analysis results at $P=0.95$ are presented in Table 2.

The positive correlations observed confirm that the main antioxidants of cognacs and brandies have phenolic nature. The developed chronoamperometric approach adequately reflects antioxidant contents in cognacs and brandies that is confirmed by high correlation coefficients ($r=0.9134$–0.9703). At the same time, the method is simple, fast and allows one to avoid disadvantages like usage of unstable DPPH radical affected by light, oxygen, type of solvent and water presence [30] or time-consuming procedure and influence of nonphenolic reducing compounds [31] in Folin–Ciocalteu method. So, the chronoamperometric method can be successfully used for evaluation of cognac and brandy antioxidant properties as an alternative to spectrophotometry.

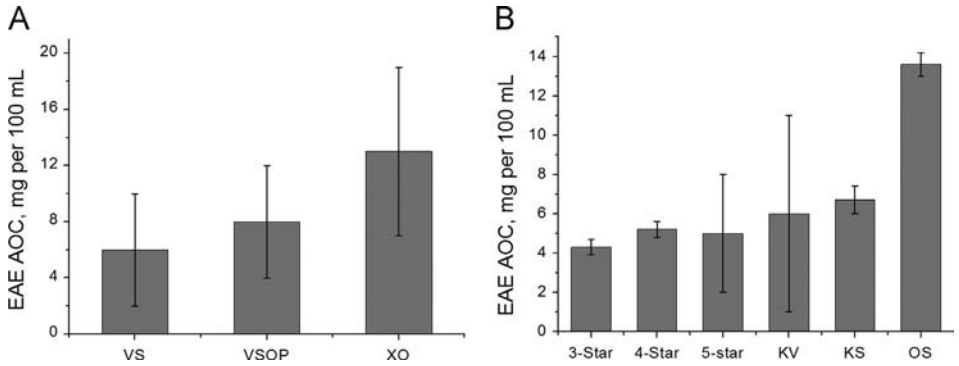


Fig. 6. Ellagic acid equivalent antioxidant capacity (EAE AOC) of cognac (A) and brandy (B) of different denominations.

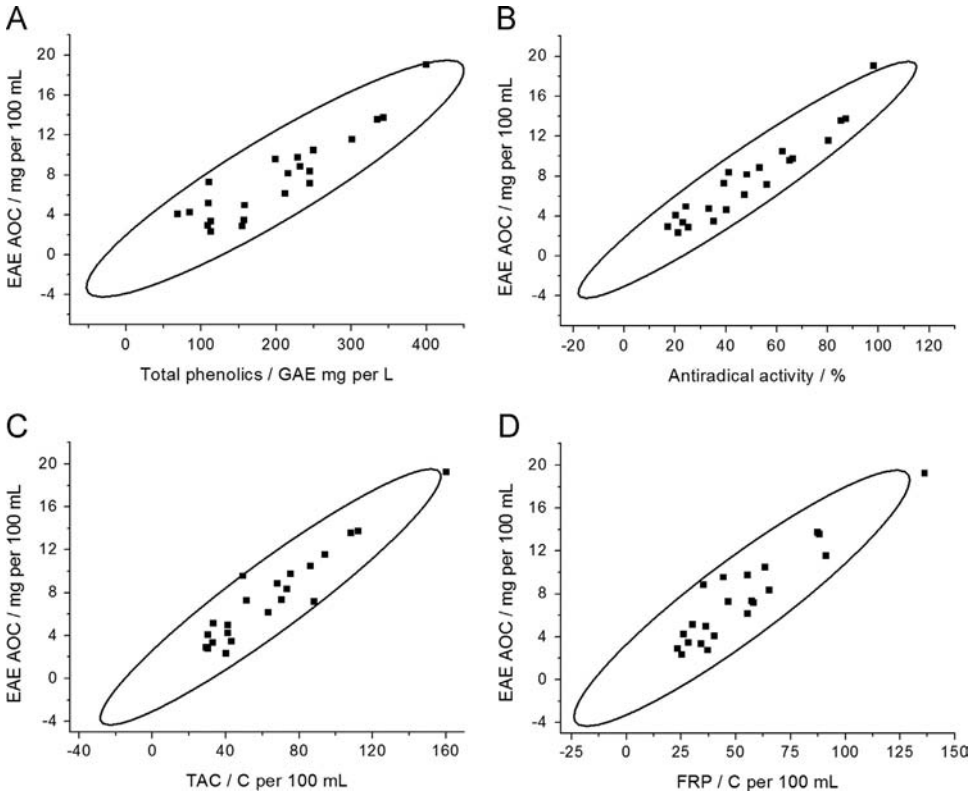


Fig. 7. Correlation plots of ellagic acid equivalent antioxidant capacity (EAE AOC) vs. total phenolics (A), antiradical activity (B), total antioxidant capacity (C) and ferric reducing power (D) of cognac and brandy (P=0.95).

Table 2
Correlation coefficients of parameters characterizing cognac and brandy antioxidant properties (n=22).

Parameter	EAE AOC, mg per 100 mL	Antiradical activity (%)	Total phenolics, GAE mg per L	TAC, C per 100 mL	FRP, C per 100 mL
EAE AOC, mg per 100 mL	–	0.9703	0.9134	0.9408	0.9223
Antiradical activity, %	0.9703	–	0.8912	0.8905	0.8311
Total phenolics, GAE mg per L	0.9134	0.8912	–	0.9566	0.9367
TAC, C per 100 mL	0.9408	0.8905	0.9566	–	0.9526
FRP, C per 100 mL	0.9223	0.8311	0.9367	0.9526	–

4. Conclusions

Electrochemical behavior of cognacs and brandies under conditions of voltammetry and chronoamperometry has been investigated for the first time. Ellagic and gallic acids as major signal forming substances have been established. It confirms that antioxidant properties of cognacs are mainly caused by lignin-derived phenolic antioxidants extracted from oak barrels. One-step chronoamperometric method for the evaluation of cognac and brandy AOC has been developed and characterized by reliability, simplicity, rapidity and cost-efficiency. Reliability of chronoamperometric assay is validated by comparison with two standard spectrophotometric assays and independent coulometric procedures. Thus, the approach developed can be successfully used for cognac and brandy AOC monitoring. The difference in AOC observed for different denominations of beverages confirms that their antioxidant properties strongly depend on aging time and production technology.

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