

## Determination of the Antioxidant Capacity of the Micellar Extracts of Spices in Brij® 35 Medium by Differential Pulse Voltammetry

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**Abstract**—It was established that the micellar extracts of spices are electrochemically active on a glassy carbon electrode modified with cerium dioxide nanoparticles in a 0.02 M Brij® 35 in the presence of a phosphate buffer solution (pH 7.4) under the conditions of differential pulse voltammetry. The number of oxidation steps and their potentials vary over a wide range depending on the type of spice. A number of the oxidation peaks of the micellar extracts of spices were identified based on the oxidation potentials of the following individual antioxidants: gallic acid, ferulic acid, *p*-coumaric acid, caffeic acid, rosmarinic acid, thymol, eugenol, vanillin, syringaldehyde, capsaicin, rutin, quercetin, catechin, tannin, and curcumin. The contribution of the main antioxidants to the amperometric response of the extracts was confirmed by the standard addition method. A procedure for the voltammetric determination of the antioxidant capacity of the extracts of spices based on the oxidation of their antioxidants was developed. The antioxidant capacity of spices was evaluated from the total area of the oxidation steps in units of gallic acid, whose analytical range, detection limit, and determination limit were 50–2490, 11.9, and 39.6  $\mu\text{M}$ , respectively. Twenty types of spices were analyzed. Positive correlations of the antioxidant capacity with the ferric reducing power and the antioxidant activity ( $r = 0.8971$  and  $0.9127$ , respectively at  $r_{\text{crit}} = 0.497$ ) were found.

**Keywords:** voltammetry, micellar media, Brij® 35, antioxidant capacity, spice, food analysis

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Food products are the main exogenous sources of biologically active substances that enter into the human body. Among the wide variety of these substances, antioxidants, which are capable of preventing the development of oxidative stress caused by chain radical reactions in the body and leveling its consequences, play an important role [1]. These compounds take up free radicals and thus actively suppress the lipids peroxidation in biological tissues and subcellular structures, such as mitochondria, microsomes, liposomes, and erythrocyte membranes [2].

Spices of plant origin contain a large number of various antioxidants, which can cause synergistic or antagonistic actions. Furthermore, depending on their concentration, structure, and mechanism of action, the low-molecular-weight antioxidants can exhibit prooxidant properties or prooxidant activity, which manifest themselves in an increase in the generation of reactive oxygen species [3].

Thus, the evaluation of the antioxidant properties of spices is a problem of considerable current interest. The most informative are integrated characteristics, which take into account the effects of all of the antioxidants contained in the test sample. Therefore, currently available standard spectrophotometric methods

for the determination of the total concentration of phenol compounds [4–6], ferric reducing power [7, 8], and antioxidant activity in reactions with 2,2-diphenyl-1-picrylhydrazyl (DPPH) [9–11] and 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonate) [12, 13]. A simple and sensitive method for the evaluation of antioxidant activity based on the reaction of antioxidants with DPPH in the micellar media of surfactants should be noted. It was shown that the reaction in a 2 mM micellar solution of cetyltrimethylammonium bromide in a 0.1 M acetate buffer solution (pH 4.6) occurs at a higher rate than that in methanol [14].

Electrochemical methods, in particular, voltammetry and coulometry, can be used for evaluating the antioxidant properties of spices because the reactions of antioxidants with radical species are related to electron transfer. Thus, methods for the coulometric determination of the ferric reducing power and the total antioxidant capacity of spices using the reactions of antioxidants with electrogenerated hexacyanoferrate(III) ions [15] and bromine, respectively, were developed. The applicability of the above approaches to the analysis of the micellar extracts of spices was demonstrated [16, 17]. Cyclic voltammetry on a glassy carbon electrode in an organic medium was proposed

for evaluating the antioxidant capacity of the methanol extracts of spices [18]. The total area of oxidation steps served as the parameter that characterizes antioxidant properties.

The aim of this study was to develop a method for the evaluation of the antioxidant capacity of the micellar extracts of spices under the conditions of differential pulse voltammetry on an electrode modified with cerium dioxide nanoparticles.

## EXPERIMENTAL

**Reagents.** The following reagents were used: 95% rutin trihydrate (Fluka, Germany), 98% quercetin dihydrate (Sigma, Germany), 98% catechin hydrate (Sigma, Germany), tannin of pharmacopoeial grade (Fluka, Germany), 99% gallic acid (Sigma, Germany), 98% caffeic acid (Sigma, Germany), 95% chlorogenic acid (Aldrich, Germany), 98% rosmarinic acid (Sigma, China), 98% *p*-coumaric acid (Sigma, Germany), 70% curcumin from *Curcuma longa* (Sigma, Germany), 50% capsaicin (Sigma, India), 99% eugenol (Aldrich, Germany), and 99.5% thymol (Sigma, Germany). The other reagents were of chemically pure grade.

The standard 1 mM solutions of antioxidants were prepared by dissolving an accurately weighed portion in 5.0 mL of 0.1 M Brij® 35 (Aldrich, Germany). The more dilute solutions were prepared directly before the measurements in 5.0-mL flasks by diluting with 0.1 M Brij® 35 to the mark.

**Extraction with 0.1 M Brij® 35.** An accurately weighed portion ( $0.1000 \pm 0.0005$  g) of spices was placed in a 15.0-mL flask, and from 2.0 to 10.0 mL of a 0.1 M solution of Brij® 35 was added; the flask was placed in an ultrasonic bath (Sonorex Super RK 100H, China) for 10 min. The extracts were filtered and used for evaluating the antioxidant properties [19].

**Voltammetric measurements.** The voltammetric measurements were performed on a  $\mu$ Autolab type III analyzer (Eco Chemie B.V., the Netherlands) equipped with the GPES-General Purpose Electrochemical System version 4.9.005 software (Eco Chemie B.V., the Netherlands). A 4.0-mL portion of a supporting electrolyte (phosphate buffer solution, pH 7.4) and an aliquot portion of a solution of the test compound or an extract of spices (0.25 or 1.0 mL) were introduced into a 5.0-mL electrochemical cell. The concentration of Brij® 35 in the cell was 0.02 M, and the solution volume in the cell was 5.0 mL. A working glassy carbon electrode (GCE) or the electrode modified with cerium dioxide nanoparticles (CeO<sub>2</sub>-Brij® 35/GCE), an auxiliary (platinum) electrode, and a saturated silver–silver chloride electrode were immersed, and differential pulse voltammograms were recorded from 0 to 1.2 V (pulse amplitude, 50 mV; pulse time, 50 ms; and potential scan rate, 10 mV/s). Baseline correction with the use of the GPES 4.9 soft-

ware was used for oxidation current measurements; this allowed us to better identify the peaks.

The working electrode was modified by the formation of a uniform layer of the homogeneous dispersion of CeO<sub>2</sub> nanoparticles (Aldrich, Germany) in 0.1 M Brij® 35 with a concentration of 1.0 mg/mL on the working surface and the dropwise evaporation of 6  $\mu$ L of the dispersion. The antioxidant capacity of spices was calculated from the total area of the oxidation steps and expressed in units of gallic acid weight per gram of dry spice.

**Photometric measurements.** The photometric measurements were carried out on a PE-5300 VI spectrophotometer (Ekros, Russia). Antioxidant activity was evaluated based on a reaction with DPPH (Sigma, Germany) [20]. The standard 100  $\mu$ M solution of DPPH (Aldrich, Germany) was prepared by the dissolution of an accurately weighed portion in methanol (chemically pure). For the estimation of antioxidant activity, 3.0 mL of the solution of DPPH and 5  $\mu$ L of an extract were placed in a test tube, and the contents were thoroughly stirred and incubated in the dark place at room temperature for 20 min; thereafter, the absorbance of the solution was measured at 517 nm ( $l = 1$  cm) relative to a reference solution (3.0 mL of methanol + 5  $\mu$ L of the extract). The antioxidant activity was expressed as a ratio between the DPPH absorption intensities before and after the reaction with the antioxidants of the extract.

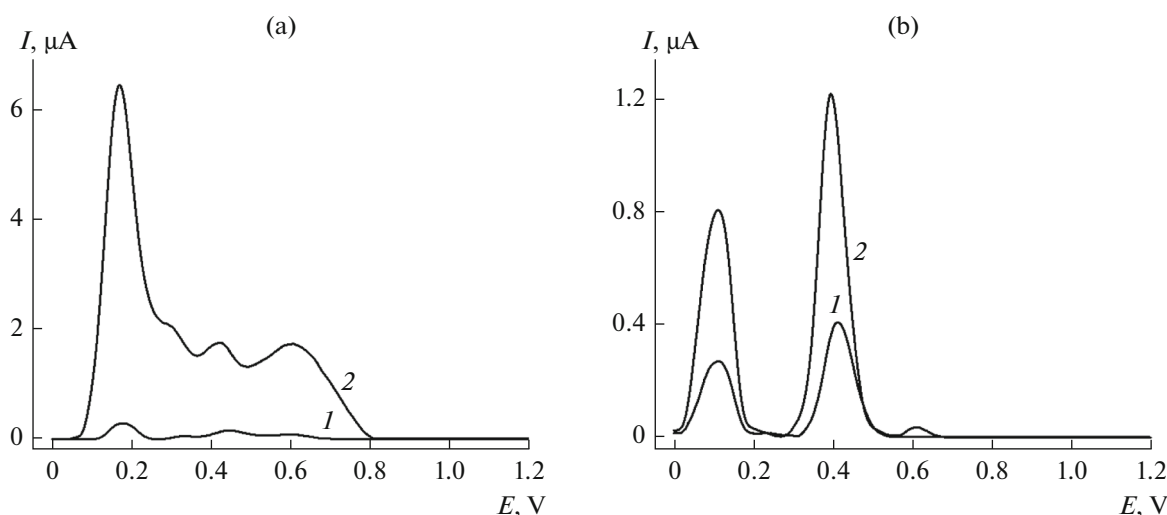
**Coulometric determination.** Coulometric analysis was performed on an Expert-006 analyzer (OOO Ekoniks-Expert, Russia). The ferric reducing power of the samples was evaluated based on a reaction with the electrogenerated Fe(CN)<sub>6</sub><sup>3-</sup> ions and calculated as the quantity of electricity (C) spent for titration per gram of dry spice [17].

**Statistical treatment.** The statistical processing of the results was conducted for  $n = 5$  or  $n = 3$  with a confidence coefficient of 0.95. The results were represented as  $x \pm \Delta x$ , where  $x$  is the average value and  $\Delta x$  is the confidence interval; the relative standard deviation ( $s_r$ ) was also given.

## RESULTS AND DISCUSSION

The voltammograms of the extracts on a GCE exhibited anodic steps, whose potentials depend on the type of spice. However, some spices cannot be reliably identified based on the shapes of curves and the values of signals. In order to improve the characteristics of the analytical signals of the extracts of spices, we used a GCE modified with CeO<sub>2</sub> nanoparticles.

Because the extracts of spices were prepared in a micellar medium of Brij® 35, we studied the nanoparticles of CeO<sub>2</sub> dispersed in this surfactant. The voltammograms of spices obtained on the modified electrode exhibited a notable increase in the anodic currents



**Fig. 1.** Differential-pulse voltammograms of the micellar extracts of (a) cinnamon and (b) ginger on (1) a GCE and (2)  $\text{CeO}_2$ -Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte. Pulse amplitude, 50 mV; pulse time, 50 ms; and potential scan rate, 10 mV/s.

(Fig. 1, curve 2) and an improvement in the shape of curves, as compared with the voltammograms obtained on the unmodified electrode (Fig. 1, curve 1). In connection with this, we used the GCE modified with  $\text{CeO}_2$  nanoparticles in 0.1 M Brij® 35 ( $\text{CeO}_2$ -Brij® 35/GCE) for the subsequent studies.

We studied the voltammetric behavior of the micellar extracts of spices on  $\text{CeO}_2$ -Brij® 35/GCE in 0.02 M Brij® 35 in the presence of a phosphate buffer solution with pH 7.4. All of the test extracts are electrochemically active in the test range of potentials (Table 1).

For establishing the nature of peaks observed in the voltammograms of the extracts of spices, the electrooxidation of the individual antioxidants of spices (gallic, ferulic, *p*-coumaric, caffeic, and rosmarinic acids; thymol; eugenol; vanillin, syringaldehyde; capsaicin; rutin; quercetin; catechin; tannin; and curcumin) in the micellar medium of Brij® 35 were studied. These compounds were oxidized in the test range of potentials (Table 2). The observed order of increasing  $E_{\text{ox}}$  gallic acid < eugenol < thymol is consistent with that described earlier for a GCE in an acetate–phosphate buffer solution with pH 7.0 [21] and 0.1 M  $\text{LiClO}_4$  in ethanol [18].

Gallic acid is oxidized in two steps, and the second step is expressed weakly. The first step corresponds to the formation of a semiquinone radical cation, which is converted into a radical by losing a proton. At the potentials of the second step, the detachment of the second electron occurs with the formation of a cation; *o*-quinone is formed upon the subsequent deprotonation of this cation [22].

Rosmarinic and caffeic acids are oxidized at 0.15 and 0.22 V, respectively. The oxidation occurs with the

participation of the OH groups of a pyrocatechol fragment with the formation of corresponding *o*- and di-*o*-quinones [23]. Ferulic and *p*-coumaric acids are oxidized in three steps. It is well known [24, 25] that they rapidly lose one electron with the formation of a phenoxyl radical, which is dimerized in the case of ferulic acid or converted into a carbocation upon losing an electron with the subsequent transformation into 3,4-dihydroxycinnamic acid in the case of *p*-coumaric acid. It is likely that, on the oxidation of thymol, a phenoxyl radical is formed with the subsequent dimerization and polymerization [18].

Eugenol, capsaicin, vanillin, and syringaldehyde [26, 27] are oxidized by a two-electron mechanism with the formation of corresponding *o*-quinones. Difference in the oxidation potentials may be caused by the steric and electronic effects of substituents. Rutin, quercetin, and catechin are oxidized due to the OH groups of ring B with the participation of two electrons in two steps; this is consistent with published data [28]. The shift of the oxidation potential of rutin at the first step to the anodic region can be explained by the presence of a glucoside group in its structure.

Based on the experimental data on the oxidation potentials of individual antioxidants, we identified the anodic peaks observed in the extracts of spices. Figure 2 shows some examples. Thus, five anodic peaks were observed in the voltammograms of an extract of cloves. Eugenol and gallic acid are the main components of cloves [29]. In the voltammograms of the extract of cloves, a peak at 0.38 V corresponds to the oxidation of eugenol, and peaks at 0.25 and 0.58 V correspond to the oxidation of gallic acid. The peak of an extract of oregano at 0.13 V is caused by the oxidation of rosmarinic acid and quercetin, whereas a peak at 0.52 V is due to thymol. Rosemary and red pepper

**Table 1.** Oxidation potentials of the micellar extracts of spices on CeO<sub>2</sub>-Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte

| Spice            | Trade mark     | $V_{\text{extractant}}$ , mL/g | $E$ , V                       |
|------------------|----------------|--------------------------------|-------------------------------|
| Cloves           | Appetita       | 30                             | +0.13; 0.25; 0.38; 0.58; 0.82 |
| Cinnamon         | Appetita       | 30                             | +0.17; 0.42; 0.63             |
| Nutmeg           | Interjarek     | 70                             | +0.13; 0.41                   |
| Rosemary         | Appetita       | 30                             | +0.14; 0.43; 0.62; 0.83       |
| Anise            | Appetita       | 30                             | +0.24; 0.44; 0.78             |
| Star anise       | Vietnam        | 60                             | +0.24; 0.94                   |
| Oregano          | Galeo          | 60                             | +0.13; 0.25; 0.52; 0.81       |
| Black pepper     | Magic tree     | 60                             | +0.17; 0.43; 0.59; 1.0        |
| Red pepper       | Galeo          | 40                             | +0.16; 0.26; 0.41; 0.66; 0.91 |
| White pepper     | Vietnam        | 120                            | +0.16; 0.30; 0.39; 0.97       |
| Sweet red pepper | Magic tree     | 110                            | +0.25; 0.43; 0.65             |
| Ginger           | Magic tree     | 100                            | +0.11; 0.39; 0.61             |
| Basil            | Appetita       | 40                             | +0.23; 0.44; 0.64             |
| Turmeric         | M&S            | 60                             | +0.19; 0.40; 0.54; 1.1        |
| Black curcuma    | Vietnam        | 30                             | +0.09; 0.40; 0.54             |
| Black cardamom   | Vietnam        | 60                             | +0.16; 0.57                   |
| Caraway          | Magic tree     | 20                             | +0.23; 0.44; 0.63             |
| Coriander        | Appetita       | 40                             | +0.24; 0.42; 0.63             |
| Cumin            | Magiya Vostoka | 40                             | +0.25; 0.70; 0.92             |
| Juniper berries  | Appetita       | 40                             | +0.11; 0.25; 0.72             |

**Table 2.** Oxidation potentials of the individual antioxidants of spices on CeO<sub>2</sub>-Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte

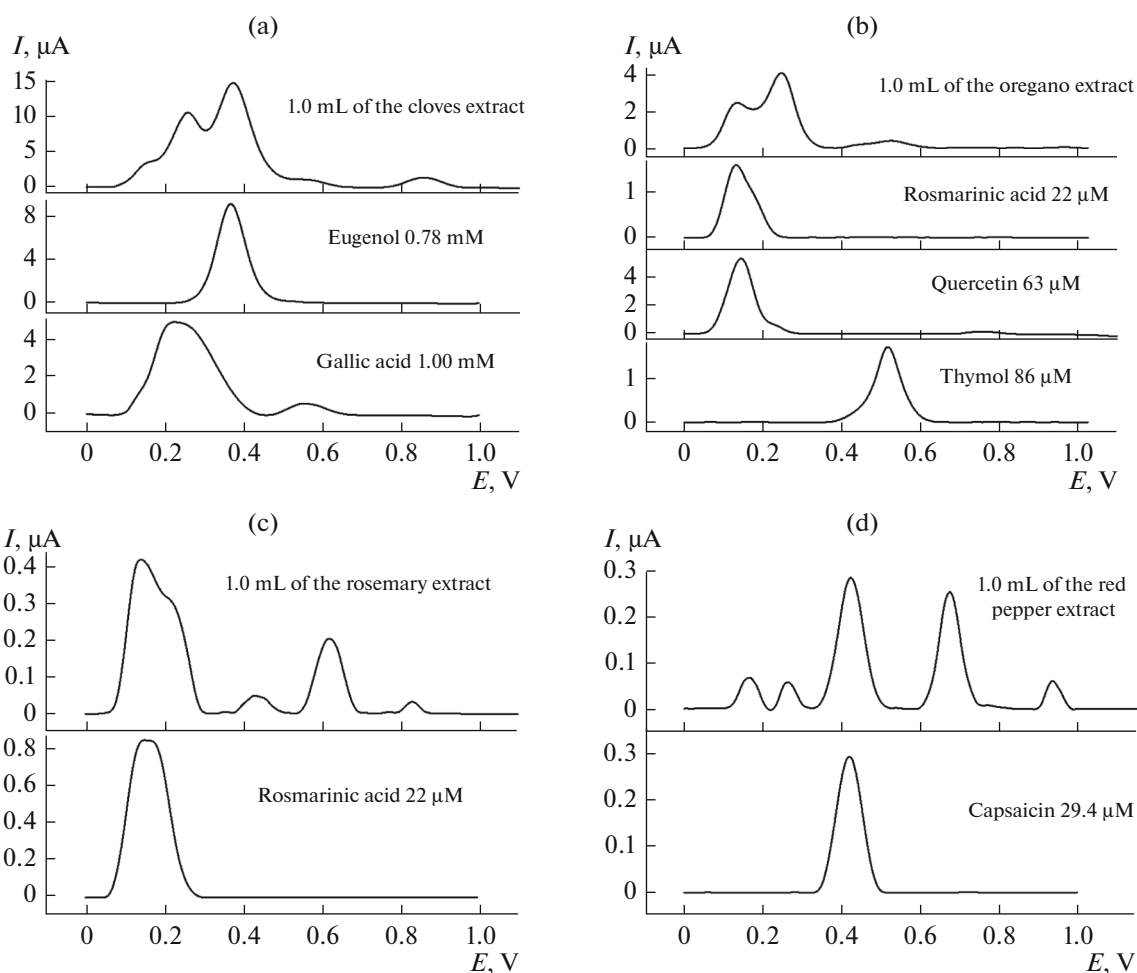
| Compound                | $E$ , V           |
|-------------------------|-------------------|
| Gallic acid             | +0.23; 0.54       |
| Rosmarinic acid         | +0.15             |
| Caffeic acid            | +0.22             |
| <i>p</i> -Coumaric acid | +0.24; 0.52; 0.68 |
| Ferulic acid            | +0.17; 0.36; 0.50 |
| Thymol                  | +0.52             |
| Eugenol                 | +0.37             |
| Vanillin                | +0.52             |
| Syringaldehyde          | +0.48; 0.67       |
| Capsaicin               | +0.41             |
| Rutin                   | +0.23; 0.78       |
| Quercetin               | +0.14; 0.76       |
| Catechin                | +0.16; 0.52       |
| Curcumin                | +0.20; 0.42       |
| Tannin                  | +0.14; 0.26       |

exhibit peaks due to their main components rosmarinic acid and capsaicin at 0.14 and 0.43 V, respectively.

Taking into account the published data on the composition of spices and the oxidation potentials of the test antioxidants, we evaluated the contributions of some of them to the analytical signals of the micellar extracts of spices by the standard addition method with the use of the individual antioxidants (Table 3). Upon the addition of the standard solutions of the individual antioxidants to the extracts of spices, the currents of the corresponding oxidation steps of the extracts proportionally increased (Table 3 summarizes the oxidation potentials).

The experimental results obtained made it possible to propose a method for the evaluation of the antioxidant capacity of spices with the aid of differential pulse voltammetry on CeO<sub>2</sub>-Brij® 35/GCE. Because gallic acid is most frequently used as a standard substance for plant materials, we preliminarily plotted a calibration function for its determination on CeO<sub>2</sub>-Brij® 35/GCE (Fig. 3). The area of the first anodic peak of gallic acid linearly depends on its concentration. The calibration graph was described by the equation

$$S = (-6.2 \pm 0.4) \times 10^{-8} + (101.0 \pm 0.7) \times 10^{-5} c_{\text{gallic acid}} (\text{M}), R^2 = 0.9997.$$



**Fig. 2.** Differential-pulse voltammograms of the micellar extracts of (a) cloves, (b) oregano, (c) rosemary, and (d) red pepper and their basic antioxidants on  $\text{CeO}_2$ -Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte. Pulse amplitude, 50 mV; pulse time, 50 ms; and potential scan rate, 10 mV/s.

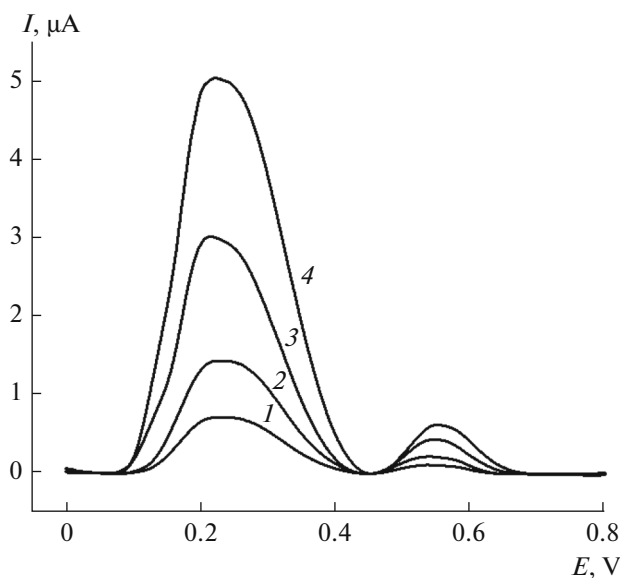
The analytical range of gallic acid was 50.0–2490  $\mu\text{M}$ ; the limit of detection ( $S/N = 3$ ) was 11.9  $\mu\text{M}$ , and the determination limit ( $S/N = 10$ ) was 39.6  $\mu\text{M}$ . Table 4 summarizes the results of the determination of gallic acid in model solutions. Their accuracy was evaluated by the standard addition method. The recovery was  $100 \pm 1\%$ , and the relative standard deviation did not exceed 4%.

The antioxidant capacity of spices was evaluated from the total area of the oxidation steps in units of gallic acid (Table 5). The obtained values of antioxidant capacity were caused by the presence of antioxidants from different classes, which are the constituents of spices. In this case, only the antioxidants whose concentrations were sufficiently high displayed themselves in the voltammograms. In general, the antioxidant capacities of extracts in a micellar medium of Brij® 35 correlate with the total antioxidant capacity based on a reaction with electrogenerated bromine [16] and the ferric reducing power of micellar extracts in the presence of Triton X100 [17]. An antioxidant

capacity maximum was obtained in cloves, which is consistent with published data on the total antioxidant content of cloves [8]. Black and white peppers are the effective sources of antioxidants from different classes, in particular, lignanes, alkaloids (piperine and its derivatives), flavonoids, and aromatic compounds [30] and also ascorbic acid, tocopherol,  $\beta$ -carotene, and retinol [31, 32]. The antioxidant capacity of the extract of cinnamon is caused by the presence of hydroxycinnamic acid and eugenol [33]. Ginger contains different phenolic antioxidants, in particular, gingerols, shogaols, paradols and zingerone [34]. Rosmarinic and hydroxycinnamic acids are the main antioxidants of basil and oregano [35, 36]. Oregano also contains flavonoids (luteolin, apigenin, dihydrokaempferol, and dihydroquercetin) [37–39]. Nutmeg contains phenolic antioxidants, in particular, eugenol and its derivatives, and also malabaricon B and C [40]; however, their concentration is small, which is reflected in the antioxidant capacity of the extract.

**Table 3.** Evaluation of the influences of individual antioxidants on the oxidation currents of the micellar extracts of spices ( $n = 5$ ;  $P = 0.95$ )

| Spice            | Antioxidant     | $E$ , V | Added, $\mu\text{g}$ | $I$ , $\mu\text{A}$ | RSD | $R^2$  |        |
|------------------|-----------------|---------|----------------------|---------------------|-----|--------|--------|
| Cloves           | Eugenol         | 0.38    | 0                    | $1.7 \pm 0.1$       | 5.9 | 0.9999 |        |
|                  |                 |         | 19.4                 | $1.9 \pm 0.1$       | 5.3 |        |        |
|                  |                 |         | 39                   | $2.1 \pm 0.1$       | 4.0 |        |        |
|                  | Gallic acid     | 0.25    | 0                    | $0.150 \pm 0.005$   | 2.7 |        | 0.9908 |
|                  |                 |         | 84.7                 | $0.26 \pm 0.02$     | 6.9 |        |        |
|                  |                 |         | 339                  | $0.59 \pm 0.02$     | 3.4 |        |        |
| Oregano          | Rosmarinic acid | 0.13    | 0                    | $0.31 \pm 0.01$     | 3.2 | 0.9999 |        |
|                  |                 |         | 7.6                  | $0.66 \pm 0.04$     | 4.5 |        |        |
|                  |                 |         | 15.1                 | $1.00 \pm 0.07$     | 6.0 |        |        |
|                  | Quercetin       | 0.13    | 0                    | $0.31 \pm 0.02$     | 6.4 |        | 0.9985 |
|                  |                 |         | 6.04                 | $0.99 \pm 0.06$     | 5.1 |        |        |
|                  |                 |         | 12.09                | $1.61 \pm 0.05$     | 2.5 |        |        |
|                  | Thymol          | 0.52    | 0                    | $0.012 \pm 0.001$   | 7.5 |        | 0.9975 |
|                  |                 |         | 3.3                  | $0.033 \pm 0.002$   | 5.8 |        |        |
|                  |                 |         | 6.5                  | $0.051 \pm 0.002$   | 3.2 |        |        |
| Red pepper       | Capsaicin       | 0.41    | 0                    | $0.18 \pm 0.01$     | 5.6 | 0.9990 |        |
|                  |                 |         | 7                    | $0.21 \pm 0.01$     | 4.8 |        |        |
|                  |                 |         | 13.9                 | $0.24 \pm 0.01$     | 4.2 |        |        |
| Sweet red pepper | Capsaicin       | 0.41    | 0                    | $0.0070 \pm 0.0004$ | 4.3 | 0.9965 |        |
|                  |                 |         | 3.48                 | $0.059 \pm 0.004$   | 5.1 |        |        |
|                  |                 |         | 7.0                  | $0.120 \pm 0.006$   | 4.2 |        |        |
| Rosemary         | Rosmarinic acid | 0.14    | 0                    | $0.037 \pm 0.001$   | 2.7 | 0.9999 |        |
|                  |                 |         | 7.6                  | $0.049 \pm 0.001$   | 2.0 |        |        |
|                  |                 |         | 15.1                 | $0.060 \pm 0.003$   | 4.6 |        |        |

**Fig. 3.** Differential-pulse voltammograms of gallic acid of different concentrations on  $\text{CeO}_2$ -Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte;  $c$ , mM: (1) 0.10, (2) 0.25, (3) 0.50, and (4) 1.00. Pulse amplitude, 50 mV; pulse time, 50 ms; and potential scan rate, 10 mV/s.

Capsaicinoids and flavonoids are the basic antioxidants of red pepper [41].

The experimental data on the antioxidant capacity of the micellar extracts of spices are consistent with other parameters, which characterize antioxidant properties, in particular, ferric reducing power in a reaction with electrogenerated hexacyanoferrate(III) ions and antioxidant activity in a reaction with DPPH. Positive correlations of antioxidant capacity with ferric reducing power and antioxidant activity were established ( $r = 0.8971$  and  $0.9127$ , respectively, at  $r_{\text{crit}} = 0.497$ ).

It should be noted that the method of determining antioxidant activity has a number of disadvantages, which do not always make it possible to reliably estimate the determined parameters. The main disadvantage is the instability of DPPH, in particular, its ability to be destroyed under the action of light and oxygen [42]; because of this, the intrinsic absorption of DPPH should be additionally determined at regular intervals. DPPH is soluble only in organic media, usually, lower alcohols, and its light absorption to a considerable extent depends on the water contents of the solvent and the test material. Many antioxidants,

**Table 4.** Results of the determination of gallic acid in model solutions on CeO<sub>2</sub>-Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte ( $n = 5$ ;  $P = 0.95$ )

| Added, µg | Found, µg | $s_r$  | $R, \%$    |
|-----------|-----------|--------|------------|
| 84.7      | 84 ± 4    | 0.040  | 99 ± 2     |
| 212       | 211 ± 3   | 0.012  | 99 ± 1     |
| 424       | 429 ± 5   | 0.010  | 101 ± 1    |
| 847       | 846 ± 6   | 0.0053 | 99.9 ± 0.6 |
| 2118      | 2124 ± 17 | 0.0064 | 100 ± 1    |

which interact with the radical forms of oxygen, do not react with DPPH [43]; this leads to errors in the estimation of integral characteristics.

The use of electrochemical methods makes it possible to remove the above complexities and disadvantages. Note that voltammetry is almost not used for the estimation of the integral antioxidant parameters of spices in actual practice. The only above method is based on the application of cyclic voltammetry in an organic medium at a sufficiently high potential scan rate, which leads to an increase in background currents [18]. In connection with this, only macro com-

ponents can be determined at high positive potentials. The proposed approach with the application of CeO<sub>2</sub>-Brij® 35/GCE under the conditions of differential pulse voltammetry is characterized by higher sensitivity, and it makes it possible to expand the number of the electrochemically active constituents of extracts in the accessible range of potentials.

\* \* \*

Thus, for the first time, we demonstrated the applicability of voltammetry in the micellar medium of surfactants to the evaluation of the antioxidant properties of spices. The correlation coefficients obtained allowed us to consider that the developed method adequately reflects the antioxidant properties of spices, and it is a suitable alternative method, which is characterized by simplicity, accessibility, and the reliability of the experimental results.

#### ACKNOWLEDGMENTS

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**Table 5.** Results of the voltammetric determination of the antioxidant capacity of spices on CeO<sub>2</sub>-Brij® 35/GCE in 0.02 M Brij® 35 with a phosphate buffer solution (pH 7.4) as a supporting electrolyte ( $n = 5$ ;  $P = 0.95$ )

| Spice            | Trade mark     | Antioxidant capacity, (mg gallic acid)/g | $s_r$ |
|------------------|----------------|--|-------|
| Cloves           | Appetita       | 153 ± 5                                  | 0.026 |
| Black pepper     | Magic tree     | 26 ± 2                                   | 0.078 |
| White pepper     | Vietnam        | 25.3 ± 1.5                               | 0.047 |
| Basil            | Appetita       | 24 ± 2                                   | 0.056 |
| Cinnamon         | Appetita       | 21 ± 2                                   | 0.080 |
| Turmeric         | M&S            | 20 ± 1                                   | 0.038 |
| Ginger           | Magic tree     | 19.7 ± 1.3                               | 0.052 |
| Oregano          | Galeo          | 18.7 ± 1.4                               | 0.060 |
| Cumin            | Magiya Vostoka | 16 ± 1                                   | 0.047 |
| Nutmeg           | Interjarek     | 12.6 ± 0.5                               | 0.031 |
| Black cardamom   | Vietnam        | 11.8 ± 0.6                               | 0.042 |
| Star anise       | Vietnam        | 11.0 ± 0.7                               | 0.054 |
| Anise            | Appetita       | 8.7 ± 0.8                                | 0.075 |
| Sweet red pepper | Magic tree     | 8.5 ± 0.2                                | 0.016 |
| Rosemary         | Appetita       | 7.3 ± 0.6                                | 0.064 |
| Juniper berries  | Appetita       | 6.8 ± 0.3                                | 0.038 |
| Coriander        | Appetita       | 4.4 ± 0.1                                | 0.027 |
| Black curcuma    | Vietnam        | 3.8 ± 0.1                                | 0.026 |
| Red pepper       | Galeo          | 3.7 ± 0.1                                | 0.017 |
| Caraway          | Magic tree     | 2.9 ± 0.3                                | 0.078 |

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