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ARTICLES

Chronoamperometric Determination of Synthetic Phenolic Antioxidants in Brij® 35 Micellar Medium

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Abstract—*tert*-Butylhydroquinone (TBHQ) and *tert*-butylhydroxyanisole (BHA) are oxidized on a glassy carbon electrode modified with multiwalled carbon nanotubes in a 0.1 M $LiClO_4$ supporting electrolyte in the medium of 1 mM Brij®35 at 0.27 and 0.47 V, respectively. A method for their chronoamperometric determination is developed. It is shown that a steady-state electrolysis is achieved within 100 s. The analytical range is 2.50–1000 μM for TBHQ and 1.50–100 and 250–1000 μM for BHA with the detection limits ($S/N = 3$) 0.64 and 0.38 μM, respectively. The relative standard deviation in the determination of TBHQ and BHA in model solutions does not exceed 6%. The method was tested on micellar extracts of linseed oils. The accuracy measure is 100 ± 1%, which points to the absence of matrix effects in the determination of TBHQ and BHA.

Keywords: chronoamperometry, sterically hindered phenols, micellar media, surfactants

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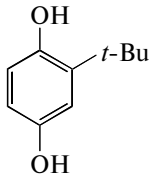
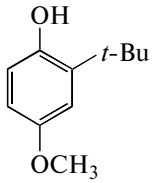
Synthetic phenolic antioxidants, such as *tert*-butylhydroquinone and *tert*-butylhydroxyanisole, are often used as stabilizing additives to prevent oxidation of food [1, 2] and industrial oils [3] and thermo-oxidative degradation of polymers and plastics [4]. The concentration of these components is strictly regulated and requires monitoring, which is especially important for food, since phenolic compounds at high concentrations may have a toxic effect, depending on dose [5, 6].



tert-Butylhydroquinone



tert-Butylhydroxyanisole

In view of the phenolic nature of TBHQ and BHA, electrochemical methods are often used for their determination; these methods are characterized by simplicity, availability, and efficiency, combined with the possibility of miniaturization of equipment and the reliability of results.

Both TBHQ and BHA are insoluble in water; so that polar organic [7, 8] and aqueous–organic [9–12] media are required for their electrochemical determination, which is undesirable from the standpoint of green chemistry. It is known that aqueous micellar media based on surface-active substances (surfactants) have been actively used in analytical chemistry, including electroanalysis, as an alternative to organic solvents [13–15]. The use of surfactants for solubilizing organic compounds is of great practical importance. This increases their concentration in solution and decreases the fraction of organic solvent, as demonstrated in the voltammetric determination of α-tocopherol [16, 17], carotenoids [18, 19], and menadione [20] and in the coulometric determination of a number of antioxidants [21]. The use of micellar media of nonionic surfactants Brij® 35 and Triton X-100, and anionic surfactant sodium dodecyl sulfate in the voltammetric measurements of eugenol [22] and α-tocopherol [23, 24], respectively, enables the determination of these analytes in an aqueous medium.

Information about using micellar media to determine TBHQ and BHA is insufficient. The published data are mainly devoted to the application of aqueous–organic media. For example, voltammetry using printed electrodes modified with multiwalled carbon nanotubes (MWNT) in a medium of 500 μM cationic cetyltrimethylammonium bromide in 2% methanol in a 0.4 M Britton–Robinson buffer solution was applied for the simultaneous determination of TBHQ and BHA in biofuel. The analytical range was 0.5–10 μM

for both analytes with the detection limit of 3.4×10^{-7} and 1.8×10^{-7} M for TBHQ and BHA, respectively [25].

Methods for determining TBHQ in biodiesel are developed based on its oxidation in a medium of methanol and a Britton–Robinson buffer solution with low concentrations of cetyltrimethylammonium bromide [26] and Triton X-100 [27]. The addition of surfactants increases the oxidation currents. The range of linearity of the calibration curve in the medium of the cationic surfactant is 1.05–10.15 μM with the detection limit of 7.11×10^{-8} M and the limit of quantification of 2.37×10^{-7} M [26]. In the medium of Triton X-100, the oxidation current of TBHQ in the square-wave voltammogram is proportional to the concentration in the range of 1.05–10.10 μM with the detection limit of 3.43×10^{-8} M and the limit of quantification of 1.14×10^{-7} M [27].

It is shown that micellar media of Triton X-100, Brij® 35, and sodium dodecyl sulfate affect the oxidation of TBHQ, BHA, and *tert*-butylhydroxytoluene on a glassy carbon electrode (GCE) against a mixture (1 : 9) of acetonitrile and the Britton—Robinson buffer solution pH 3.0. In the presence of nonionic surfactants, splitting and suppression of the oxidation steps of sterically hindered phenols are observed. An anion of sodium dodecyl sulfate greatly increases the anodic currents and shifts the peaks to less positive potentials. For the differential pulse voltammetric determination in the presence of 0.1 M sodium dodecyl sulfate, the analytical ranges for TBHQ, BHA, and *tert*-butylhydroxytoluene are 2.02–1010, 2.34–1170, and 6.15–615 μM with the detection limits of 0.23, 0.18, and 3.5 2 μM, respectively. The possibility of determination of phenols in binary mixtures of TBHQ–*tert*-butylhydroxytoluene and BHA–*tert*-butylhydroxytoluene is shown in a wide range of concentrations of the components [28].

TBHQ, BHA, and propylgallate can be simultaneously determined by means of cyclic voltammetry in the micellar medium of sodium dodecyl sulfate with the use of chemometric data processing by the least squares method or the method of artificial neural networks [29].

To determine BHA in foods, a tyrosinase amperometric biosensor is developed, the response of which upon flow-injection analysis is linearly dependent on the concentration of the analyte in the range of 0.1–1 mM in a medium of phosphate buffer solution containing reverse micelles of dioctylsulfosuccinate in ethyl acetate [30].

The present work is devoted to the further development of the methodology of electrolysis based on the use of surfactants, in particular, the chronoamperometric determination of TBHQ and BHA on a glassy carbon electrode modified with multiwalled carbon nanotubes in Brij® 35 micellar medium.

EXPERIMENTAL

We used *tert*-butylhydroquinone (97%, Aldrich, Germany) and *tert*-butylhydroxyanisole (98%, Aldrich, Germany), reference 0.01 M solutions of which were prepared by dissolving their accurate weighed portions in Brij® 35 micellar medium (0.01 M). An aqueous 0.01 M solution of Brij® 35 (Panreac, Spain) was prepared by dissolving its accurately weighed portion. Other reagents were of cp grade.

Multiwalled carbon nanotubes (40–60 nm in outer diameter, 5–10 nm in inner diameter, and 0.5–500 μm in length) from Aldrich (Germany) were used as a modifier of the electrode surface. Their homogeneous suspension with a concentration of 0.5 mg/mL was prepared in 0.01 M Brij® 35 by ultrasonic dispersion for 40 min. A GCE was modified through the formation of a uniform MWNT layer on the working electrode surface, by applying 2 μL of suspension and evaporating the solvent at room temperature. Prior to modification, the GCE working surface was renewed mechanically, by polishing it with alumina with a particle size of 0.05 μm. Then, the electrode was rinsed with acetone and distilled water.

Voltammetric measurements were performed using a μAutolab electrochemical analyzer (Eco Chemie, Netherlands). Ten milliliters of a supporting electrolyte (0.1 M $LiClO_4$) or an aliquot portion of a phenolic antioxidant solution and a supporting electrolyte were placed in a 20.0-mL electrochemical cell. The fraction of Brij® 35 in the cell was adjusted to 10%; that is, the Brij® 35 concentration in the cell was 1 mM. The volume of solution in the cell was 10.0 mL. The working glassy carbon electrode modified with multiwalled carbon nanotubes (MWNT/GCE), an auxiliary (platinum) electrode, and a saturated Ag–AgCl electrode were placed in the cell. The differential pulse voltammograms were recorded from 0 to 1.0 V (pulse amplitude, 50 mV; pulse duration, 25 ms; and potential sweep rate, 20 mV/s).

Chronoamperograms were recorded in a similar cell for 200 s at the potentials of oxidation of TBHQ and BHA. To assess the matrix effect, 250 μL of an extract of linseed oils and 750 μL of 0.01 M Brij® 35 were added in the electrochemical cell and diluted to 10 mL with the supporting electrolyte; the chronoamperograms were recorded for 100 s at 0.27 V for TBHQ and 0.47 V for BHA.

We performed the statistical treatment of the results for $n = 5$ and $P = 0.95$. Results are presented as $X \pm \Delta X$, where X is the mean value and ΔX is the confidence interval.

RESULTS AND DISCUSSION

In the differential pulse voltammograms of synthetic phenolic antioxidants in Brij® 35 micellar medium, clear oxidation peaks are observed at potentials of 0.27 and 0.47 V for TBHQ and BHA, respec-

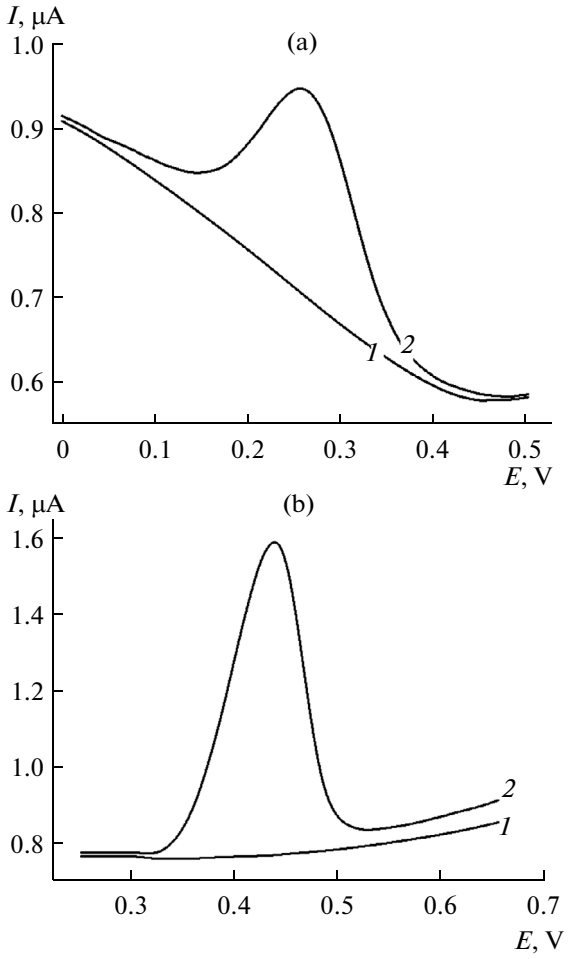


Fig. 1. Differential pulse voltammogram of (*2*) 50 μM of (a) *tert*-butylhydroquinone and (b) *tert*-butylhydroxyanisole in 1 mM Bri® 35 in (*1*) a 0.1 M $LiClO_4$ supporting electrolyte; pulse amplitude, 50 mV; pulse duration, 25 ms; potential sweep rate, 20 mV/s.

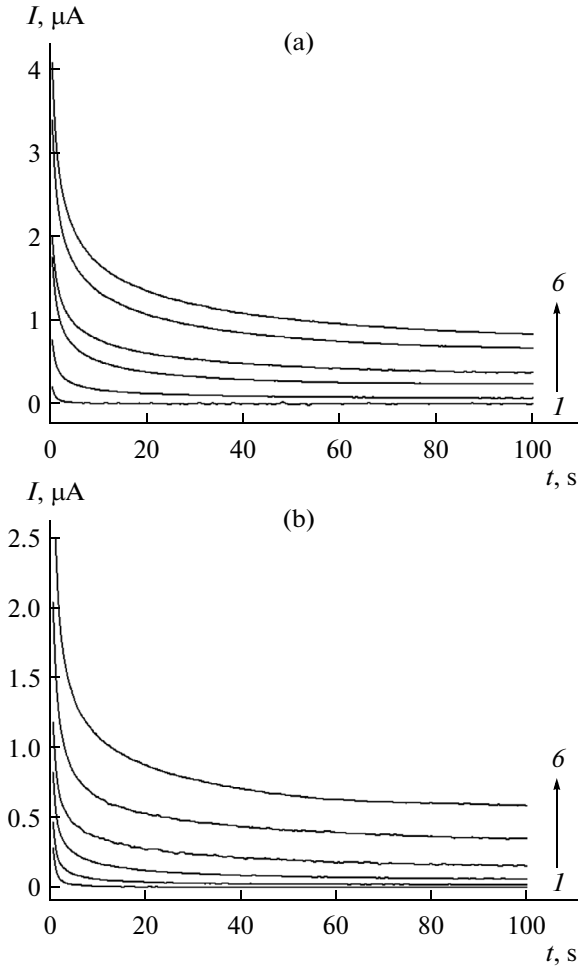


Fig. 2. Chronoamperograms of synthetic phenolic antioxidants in 1 mM Brij® 35 in a 0.1 M $LiClO_4$ supporting electrolyte: (a) (*1*) 0, (*2*) 75.0, (*3*) 250, (*4*) 500, (*5*) 750, and (*6*) 1000 μM of *tert*-butylhydroquinone at $E = 0.27$ V; (b) (*1*) 0, (*2*) 25.0, (*3*) 75.0, (*4*) 250, (*5*) 750, and (*6*) 1000 μM of *tert*-butylhydroxyanisole at $E = 0.47$ V.

tively (Fig. 1). It is known that the process proceeds by two-electron mechanism to form the corresponding quinones [31–33]. Based on these data, we developed a chronoamperometric method for determining TBHQ and BHA. For this purpose, changes in the anodic currents with time were recorded at 0.27 and 0.47 V, respectively, for 200 s. It was found that 100 s is a sufficient electrolysis time, for which a steady state is reached (Fig. 2). It was shown that the chronoamperometric signal increases as the concentration of analyte in the cell. The analytical characteristics of the chronoamperometric determination of sterically hindered phenols are given in Table 1.

Sterically hindered phenols are determined in model solutions using chronoamperometry (Table 2). The accuracy of the results is evaluated by the standard addition method. The relative standard deviation does not exceed 6%. The accuracy is 99.8 ± 0.6%, indicating a high accuracy of the determination. Since the electrode surface was renewed before each measurement, the values of the relative standard deviation evidence a high reproducibility.

The method was tested on micellar extracts of oils. Linseed oil, into which synthetic phenolic antioxidants are added to prevent the oxidation of vitamins A, D, and E and unsaturated fatty acids, were the object of analysis [34]. Extracts of oils were obtained by a single ultrasonic extraction with 0.01 M Brij® 35 for 15 min at a volume ratio of oil–extractant of 1 : 2.5 [29]. It should be noted that the investigated linseed oil did not contain TBHQ and BHA; *tert*-butylhydroxytoluene is added to stabilize them [28], which is practically insoluble in 0.01 M Brij® 35 and, thus, is not extracted from the oils. Furthermore, its oxidation is observed at more positive potentials and does not overlap with the peaks of oxidation of TBHQ and BHA.

Table 1. Analytical characteristics of the chronoamperometric determination of synthetic phenolic antioxidants at a MWNT/GCE in 1mM Brij® 35 in a 0.1 M $LiClO_4$ supporting electrolyte ($n = 5$, $P = 0.95$)

Analyte	c_{min}, μM	c_l, μM	Analytical range, μM	$I = a + bc$		R^2
				a, μA	$b \times 10^2$, μA M^{-1}	
TBHQ	0.64	2.12	2.50–1000	0.006 ± 0.004	8.4 ± 0.1	0.9982
BHA	0.38	1.28	1.50–100	0.0 ± 0.0	9.0 ± 0.3	0.9910
			250–1000	0.04 ± 0.01	4.5 ± 0.2	0.9958

Table 2. Chronoamperometric determination of synthetic phenolic antioxidants, μg, in model solutions ($n = 5$, $P = 0.95$)

Analyte	Added	Found	RSD, %	R, %
TBHQ	8.31	8.31 ± 0.06	5.7	100.0 ± 0.9
	41.6	41 ± 1	2.3	99 ± 3
	125	125 ± 4	2.5	100 ± 3
	831	832 ± 9	0.83	100 ± 1
	1662	1659 ± 11	0.54	99.9 ± 0.7
BHA	9.00	9.0 ± 0.2	1.6	100 ± 2
	45.0	44 ± 3	5.8	98 ± 7
	180	180 ± 7	3.1	100 ± 4
	900	905 ± 19	1.7	101 ± 2
	1800	1808 ± 51	2.3	100 ± 3

Table 3. Chronoamperometric determination of synthetic phenolic antioxidants, μM, in the presence of extracts of linseed oil ($n = 5$, $P = 0.95$)

Sample	Analyte	Added	Found	RSD, %	R, %
Extract of 100% linseed oil	TBHQ	50	49.1 ± 0.3	0.52	98.2 ± 0.6
		100	100 ± 2	1.9	100 ± 2
	BHA	50	50.2 ± 0.4	0.59	100.4 ± 0.7
		100	100 ± 2	1.7	100 ± 2
Extracts of unrefined food linseed oil	TBHQ	50	49.5 ± 0.2	0.27	99.1 ± 0.3
		100	101 ± 2	1.4	101 ± 2
	BHA	50	50.8 ± 0.6	0.97	102 ± 1
		100	99.2 ± 0.2	0.20	99.2 ± 0.2

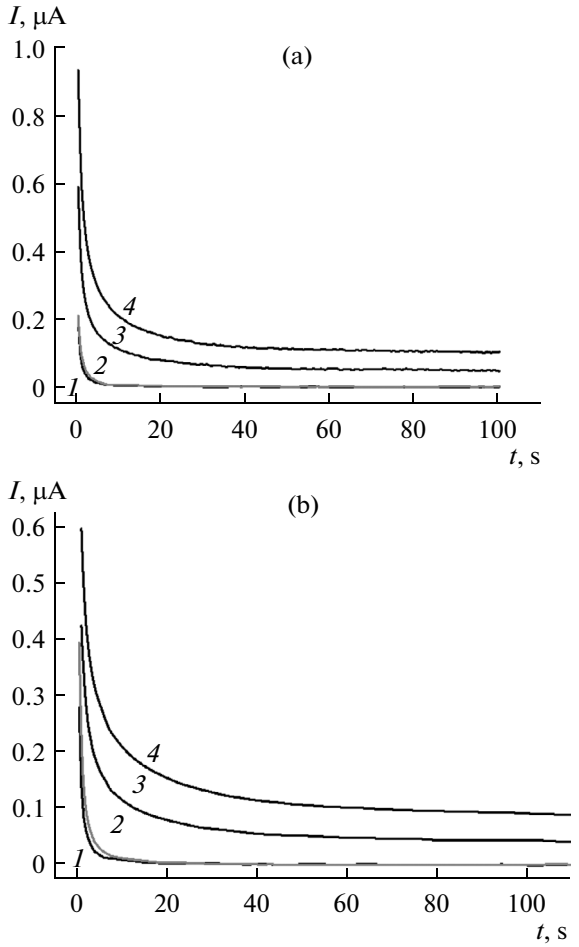


Fig. 3. Chronoamperograms of (a) TBHQ and (b) BHA in 1 mM Brij® 35 in a 0.1 M $LiClO_4$ supporting electrolyte: (*1*) background, (*2*) 250 μL of extract of linseed oil, (*3*) 250 μL of extract of linseed oil + 50 μM of phenolic antioxidant, (*4*) 250 μL of extract of linseed oil + 100 μM of phenolic antioxidant; $E = 0.27$ V for TBHQ and 0.47 V for BHA; electrolysis time, 100 s.

The chronoamperograms of its extracts are statistically insignificantly different from the curves of supporting electrolyte (Fig. 3, curves *1* and *2*). This signal is probably due to the oxidation of vitamins A and E, contained in the linseed oil and extracted with Brij® 35. However, considering the low concentration of these antioxidants in linseed oil, and, therefore, in extracts and the effect of dilution in the electrochemical cell, this signal can be neglected. After introducing standard additions of TBHQ and BHA, the currents increase proportionally to the amount of phenolic antioxidants added (Fig. 3, curves *3* and *4*).

The results of determination of TBHQ and BHA in the presence of extracts of linseed oil are shown in Table 3. Accuracy is 100 ± 1%, which indicates that matrix effects are absent in the determination of TBHQ and BHA.

The proposed chronoamperometric method for determining synthetic phenolic antioxidants in Brij® 35 micellar medium using an electrode modified with multiwalled carbon nanotubes electrode is characterized by simplicity, availability, and reliability of the results obtained and ensures the determination of analytes in an aqueous medium.

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REFERENCES

1. Hudson, B.J.F., *Food Antioxidants*, London: Elsevier, 1990.
2. Gülçin, I., *Arch. Toxicol.*, 2012, vol. 86, no. 3, p. 345.
3. *Lubricant Additives: Chemistry and Applications*, Rudnick, L.R., Ed., New York: CRC Press, 2009.
4. Roginskii, V.A., *Fenol'nye antioksidanty. Reaktsionnaya sposobnost' i effektivnost'* (Phenolic Antioxidants: Reactivity and Efficiency), Moscow: Nauka, 1988.
5. Yu, R., Mandlekar, S., and Kong, A.N.T., *Mol. Pharmacol.*, 2000, no. 2, p. 431.
6. Sherwin, E.R., in *Food Additives*, Branen, A.L., Davidson, P.M., and Salminen, S., Eds., New York: Marcel Dekker, 1990, p. 139.
7. Ziyatdinova, G., Khuzina, A., and Budnikov, H., *Anal. Lett.*, 2012, vol. 45, no. 12, p. 1670.
8. Tormin, T.F., Cunha, R.R., Richter, E.M., and Munoz, R.A.A., *Talanta*, 2012, vol. 99, p. 527.
9. Zhao, P. and Hao, J., *Food Chem.*, 2013, vol. 139, nos. 1–4, p. 1001.
10. Freitas, K.H.G. and Fatibello-Filho, O., *Talanta*, 2010, vol. 81, no. 3, p. 1102.
11. Prabakar, S.J.R. and Narayanan, S.S., *Food Chem.*, 2010, vol. 118, no. 2, p. 449.
12. Tomaskova, M., Chylkova, J., Jehlicka, V., Navratil, T., Svancara, I., and Selesovska, R., *Fuel*, 2014, vol. 123, p. 107.
13. Ziyatdinova, G.K., Ziganshina, E.R., and Budnikov, G.K., *J. Anal. Chem*, 2012, vol. 67, no. 11, p. 869.
14. Pramauro, E. and Pelizzetti, E., *Surfactants in Analytical Chemistry: Applications of Organized Amphiphilic Media*, Amsterdam: Elsevier, 1996.
15. Shtykov, S.N., *J. Anal. Chem*, 2000, vol. 55, no. 7, p. 608.
16. Jaiswal, P.V., Ijeri, V.S., and Srivastava, A.K., *Anal. Chim. Acta*, 2001, vol. 441, no. 2, p. 201.
17. Ziyatdinova, G.K., Giniyatova, E.R., and Budnikov, G.K., *J. Anal. Chem*, 2012, vol. 67, no. 5, p. 467.
18. Ziyatdinova, G., Giniyatova, E., and Budnikov, H., *Electroanalysis*, 2010, vol. 22, no. 22, p. 2708.
19. Ziyatdinova, G., Ziganshina, E., and Budnikov, H., *Talanta*, 2012, vol. 99, p. 1024.
20. Ziyatdinova, G., Ziganshina, E., and Budnikov, H., *J. Solid State Electrochem.*, 2013, vol. 17, no. 10, p. 2679.

21. Ziyatdinova, G., Ziganshina, E., and Budnikov, H., *Anal. Chim. Acta*, 2012, vol. 744, p. 23.

22. Ziyatdinova, G., Ziganshina, E., and Budnikov, H., *Anal. Methods*, 2013, vol. 5, no. 18, p. 4750.

23. Ghanem, M.A., Compton, R.G., Coles, B.A., Canals, A., and Marken, F., *Analyst*, 2005, vol. 130, no. 10, p. 1425.

24. Ghanem, M.A., Marken, F., Coles, B.A., and Compton, R.G., *J. Solid State Electrochem.*, 2005, vol. 9, no. 12, p. 809.

25. Caramit, R.P., Andrade, A.G.D., de Souza, J.B.G., de Araujo, T.A., Viana, L.H., Trindade, M.A.G., and Ferreira, V.S., *Fuel*, 2013, vol. 105, p. 306.

26. de Araujo, T.A., Barbosa, A.M.J., Viana, L.H., and Ferreira, V.S., *Colloids Surf., B,* 2010, vol. 79, no. 2, p. 409.

27. de Araujo, T.A., Barbosa, A.M.J., Viana, L.H., and Ferreira, V.S., *Fuel*, 2011, vol. 90, no. 2, p. 707.

28. Ziyatdinova, G.K., Ziganshina, E.R., Os'kina, K.S., and Budnikov, H.C., *J. Anal. Chem*, 2014, vol. 69, no. 8, p. 750.

29. Ziyatdinova, G.K., Saveliev, A.A., Evtugyn, G.A., and Budnikov, H.C., *Electrochim. Acta*, 2014, vol. 137, p. 114.

30. Ruiz, M.A., Reviejo, A.J., Parrado, C., and Pingarron, J.M., *Electroanalysis*, 1996, vol. 8, no. 6, p. 529.

31. Ershov, V.V., Nikiforov, G.A., and Volod'kin, A.A., *Prostranstvenno-zatrudnennye fenoly* (Sterically Hindered Phenols), Moscow: Khimiya, 1972.

32. Medeiros, R.A., Rocha-Filho, R.C., and Fatibello-Filho, O., *Food Chem.*, 2010, vol. 123, p. 886.

33. Jayasri, D. and Narayanan, S.S., *Food Chem.*, 2007, vol. 101, no. 2, p. 607.

34. *Food Fortification to End Micronutrient Malnutrition: State of the Art,* Ottawa: Stylus, 1998.

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