

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
19 (2013)

**VOLTAMMETRIC DETERMINATION
OF BUTYLATED HYDROXYANISOL IN BIODIESEL,
MINERAL AND SYNTHETIC OILS USING GOLD
ELECTRODE**

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Received September 30, 2013

Voltammetric determination of butylated hydroxyanisol (BHA) antioxidant in propan-2-ol containing 0.1 mol l⁻¹ H₂SO₄ using DC voltammetry with gold working electrode was tested. The developed method is designed for determination of BHA in biodiesel, mineral, and synthetic oils. There were compared the results obtained by nonlinear and linear regression of recorded data. The program OK-nelin was applied in evaluation by nonlinear regression. This method was applied to analysis of real model samples. Analyses in biodiesels can be performed directly, without necessity of sample pretreatment or extraction. The extraction is necessary for analyses in oils.

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Introduction

Lubricants are commercial products and due to their impact on environment it is necessary to analyse them, similarly as in case of any other product [1]

The users of lubricants have to take into account that they deteriorate during their use. They are degraded by evaporation, oxidation, and contamination. The composition of a lubricant, used for a defined application, is influenced by the way of its deterioration during time, work, distance, or operation. The deterioration of a lubricant can be either planned and controlled by various means or uncontrolled.

Lubricants are composed of a base oil mixture and an additive pack. The base oil is usually a mixture of base oils and additives chosen for their physical and chemical properties. Oxidation is the most important of all chemical causes of lubricant deterioration. It is related to the formation of organic acids, usually carboxylic acids, sludges, etc. The inhibition of the oxidative processes of petroleum substances represents the major technological problem. The oxidation resistance is increased by addition of various synthetic antioxidants [1-3].

The most commonly used synthetic antioxidants are: butylated hydroxytoluene (BHT) butylated hydroxyanisole (BHA), tertbutylhydroquinone (TBHQ), propyl gallate (PG) and pyrogallol (PA) [4].

Many methods for determination of BHA, separately or in mixtures, have been recently reported. They are based on utilization of spectrophotometry [5-8], of liquid chromatography [9-13] mostly in combination with electrochemical detection [14,15], and also with mass spectrometer [16,17], and of gas chromatography with various detection methods [18-20]. On the other hand, electrochemical determinations of synthetic antioxidants exhibit many advantages. Electrochemical methods represent a suitable alternative due to their relatively low costs, to the possibility of miniaturization, and particularly, to the fast and sensitive analysis. However, it is known that the quantitative and qualitative evaluation is sometimes complicated by overlapping of electroanalytical signals in mixtures of synthetic phenolic antioxidants.

In papers [21-23], the authors used voltammetric methods at the disc ultramicroelectrodes for determination of BHA, BHT or PG in vegetable and corn oils. In papers [24,25], the authors studied the conditions for reliable determination of particular amine- and phenol-type antioxidants in their mixtures in samples of lubricating oils using gold disc working electrode (AuDE) and hanging mercury drop electrode (HMDE) in acidic medium of $0.2 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ with addition of ethanol and acetonitrile in the ratio 3:1. A procedure was suggested for elimination of aromatic amines from the sample before determination of phenol type substances and for study of reaction kinetics of the reaction of *N*-phenyl-1-naphthylamine with nitrous acid which leads to a desired concentration reduction of this disturbing antioxidant. Medeiros *et al.* in [26] describe a method for simultaneous determination of BHA and BHT in food using multiple pulse

amperometry with flow injection analysis. Antioxidants were determined with a cathodically pretreated boron-doped diamond electrode in 10 mmol l⁻¹ KNO₃ in aqueous ethanolic solution (30 %, v/v). Ameye *et al.* [27] present extraction-based sample treatment for analysis of amine and phenolic antioxidants in motor and turbine oil. The oil sample was extracted in solution of supporting electrolyte (sodium perchlorate solution in acetone or potassium hydroxide solution in ethanol) in the presence of sand. Whereas soluble species, together with antioxidants, were extracted into the solution and analyzed, the suspension adhered at the sand. Robledo *et al.* [28] determined four antioxidants, namely BHA, BHT, TBHQ, and PG, in olive oil. In this case, square-wave voltammetry (SWV) with platinum ultramicroelectrode in the supporting electrolyte containing acetonitrile (AcN) and 0.1 M (C₄H₉)₄N PF₆ was used. The analysis was done either directly in oil matrix dissolved in the mixture of benzene-ethanol (1:2) in the presence of 0.1 M or 1 M H₂SO₄, or the antioxidants were isolated with double extraction using AcN. The authors of the paper [29] developed a simple electrochemical method for separate and simultaneous determination of BHA and BHT in food using square wave voltammetry. A carbon composite electrode modified with copper(II) phosphate immobilized in polyester resin was proposed.

In this present work, we describe the voltammetric determination of BHA in petroleum products (biodiesel, mineral and synthetic oils) at gold electrode. This method was successfully used for determination of BHT [30]. The parameters of determination were optimized and the main attention was paid to the experimental testing of this method in analyses of selected spiked real samples.

Experimental

Chemicals and Reagents

All chemicals used were of analytical reagent grade and purchased from Penta or Sigma Aldrich. Stock solution of BHA (4 g l⁻¹) was prepared by dissolving of appropriate amount of BHA (Sigma Aldrich, CAS: 121-00-6) in 96% solution of ethanol.

BHA was determined in matrix of biodiesel which is a mixture of standard diesel fuel and 30 % fatty acid methyl esters (rapeseed oil methyl ester). The real samples of mineral and synthetic oils were extracted with 96% ethanol. Sodium sulfate anhydrous — Na₂SO₄ (Sigma Aldrich, CAS: 239313) was used to remove the rest of oils from the extract.

Apparatus and Accessories

Voltammetric analyses were performed using electrochemical analyzer EP 100VA (HSC Servis; Bratislava, Slovak Republic) in a three-electrode cell which was composed of the gold disc (AuDE, Ø2 mm, HSC servis, Bratislava, Slovak Republic) as working electrode, the Ag|AgCl|3 M KCl as the reference, and the Pt-plate (3×5 mm) as the counter electrode. Prior to each measurement, the electrode was conditioned by applying a potential of – 1 V for 2 s.

Procedure

The determinations of antioxidants were performed in propan-2-ol in dependence on the amount of added analyte. This amount was from 50 µl to 350 µl of BHA with concentration 4.3 µg ml⁻¹. All analyses were performed in propan-2-ol containing 0.1 mol l⁻¹ H₂SO₄.

Biodiesel samples were analyzed directly as we describe above. The determined antioxidants in mineral and synthetic oils had to be isolated by extraction. BHA was extracted from 4-5 g synthetic or mineral oil matrix by means of 96% ethanol under application of ultrasonic field for 10 min. After the suspension settled, the upper layer was separated, and free oil residue analyzed.

The limits of decision (L_C), detection (L_D) and quantification (L_Q) were calculated as described in [31] and the parameters of calibration curves (e.g., slope, intercept) and other statistical data were calculated using software Excel 2003 (Microsoft, USA).

Results and Discussion

Voltammetric Behavior of BHA and Optimization of Conditions

We investigated the electrochemical behavior of BHA using cyclic voltammetry. It was found out that this compound undergoes anodic oxidation in potential range of 640-770 mV (see Fig. 1).

The process is irreversible. Since, in view of the fact that the studied antioxidant is used in mixture with BHT, and the paper [30] using DC voltammetry for determination of BHT was published, in this present paper we chose the same method. It was found out by experiments that the choice of the initial potential from 0 mV to 500 mV has no effect on the curve of anodic oxidation. Potential 400 mV was chosen for next work.

The next parameter, which was investigated, was scan rate. The determination of concentration of BHA 28.8 µg ml⁻¹ was performed in rate range from 1 mV s⁻¹ to 125 mV s⁻¹. Measured curves are presented in Fig. 2.

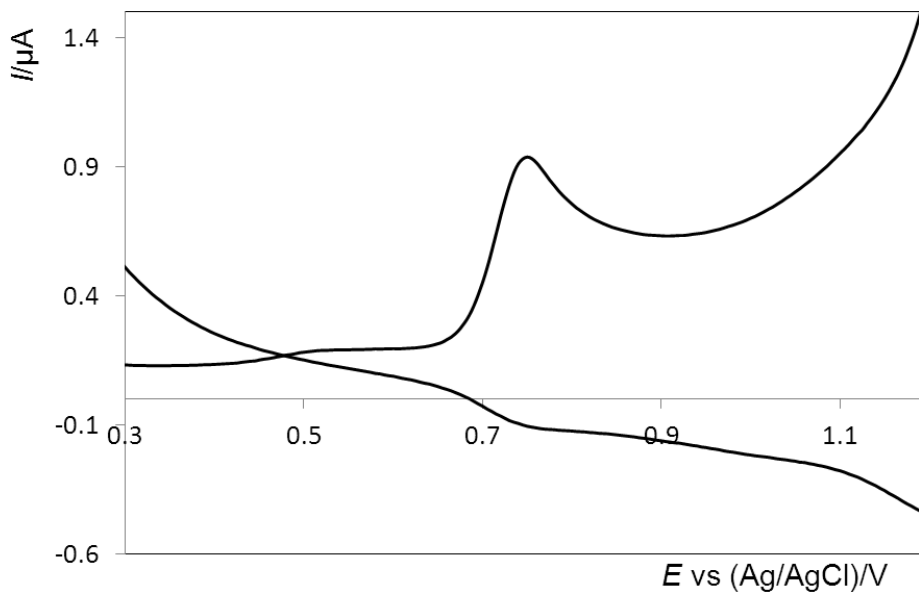


Fig. 1 CV-voltammograms of BHA in propan-2-ol containing $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. Experimental conditions: scan rate: 40 mV s^{-1} , concentration of BHA: $28.8 \text{ } \mu\text{g ml}^{-1}$

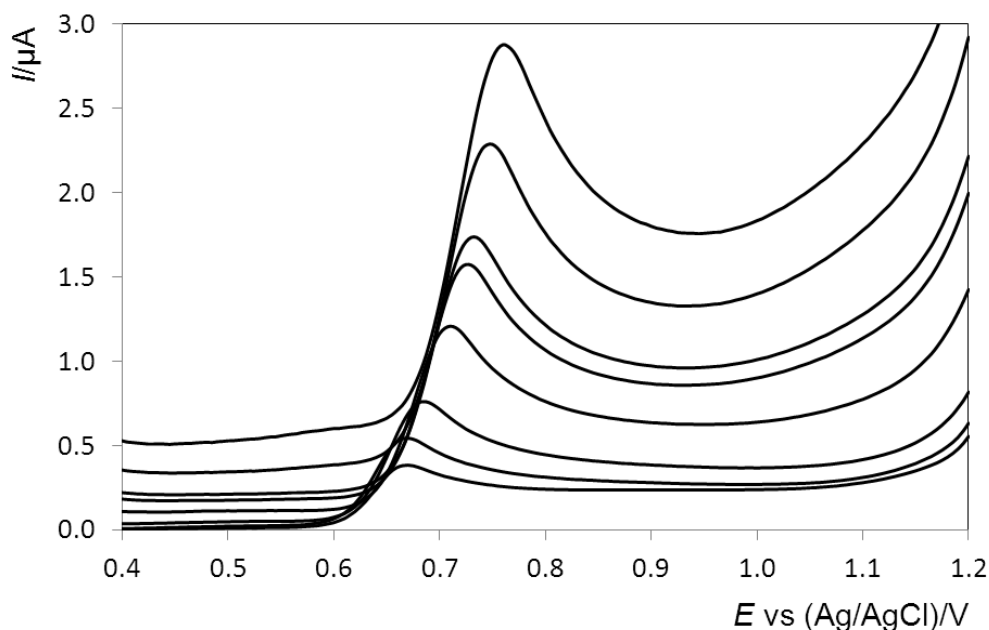


Fig. 2 DC-voltammograms of BHA in propan-2-ol containing $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$. Experimental conditions: LSV, $E_{\text{in}} = +0.4 \text{ V}$, $E_{\text{fin}} = +1.2 \text{ V}$, scan rate: 1 mV s^{-1} – 125 mV s^{-1} , concentration of BHA: $28.8 \text{ } \mu\text{g ml}^{-1}$

In Fig. 2, the peak height is on the increase with increasing rate, but nonlinearly, and the background increases also. This fact can have an influence during analyses of real samples. The scan rate was chosen 40 mV s^{-1} for this

reason. From presented curves: higher rates causes the shift of peak maximum. The process on electrode is driven kinetically. The dependence of peak height on second power of polarization rate is linear and has the form: $y = 0.29x - 3.4 \times 10^{-3}$. The low value of segment means that the process is driven by diffusion.

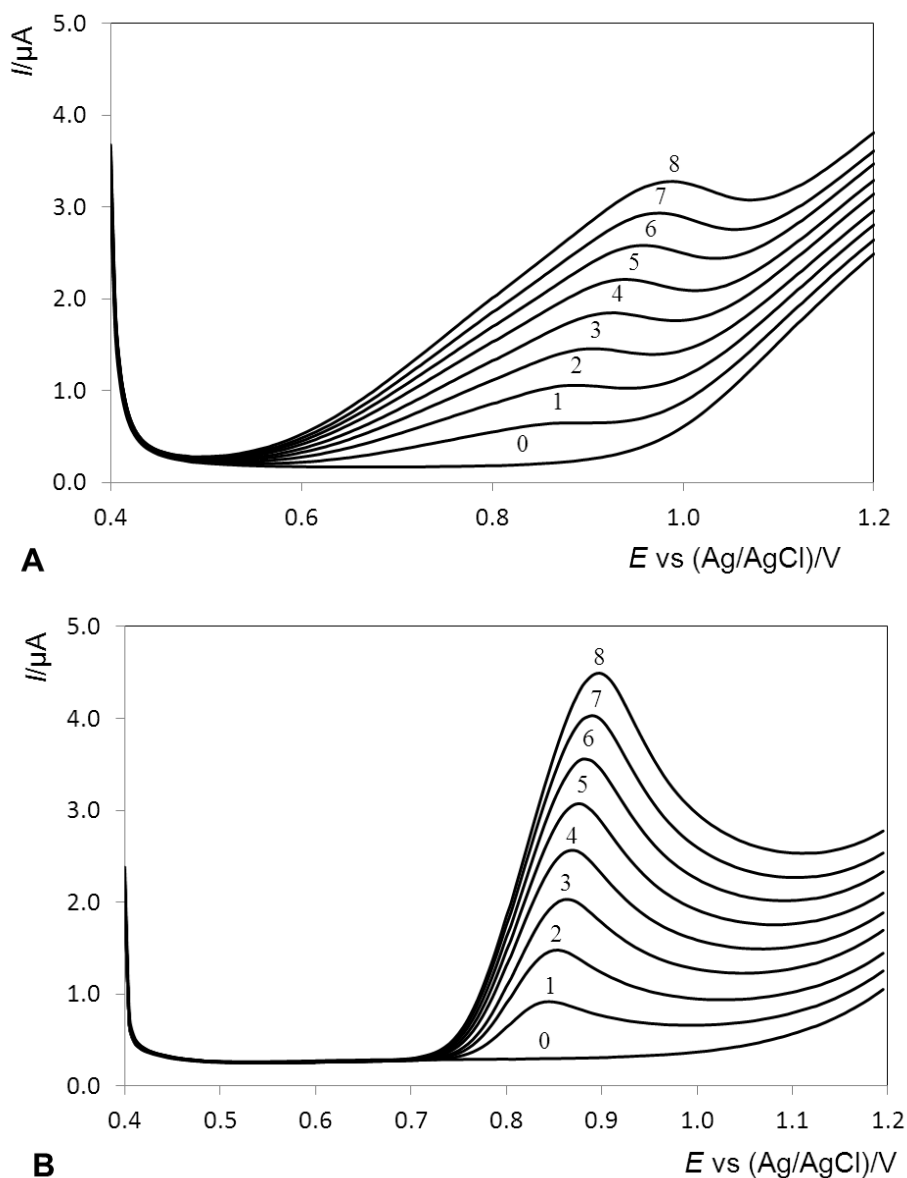


Fig. 3 DC voltammograms of BHA in propan-2-ol containing A. $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ B. 0.007 mol l^{-1} acetate buffer (pH 5). $E_{\text{in}}: +0.4 \text{ V}$, $E_{\text{fin}} = +1.2 \text{ V}$, scan rate: 40 mV s^{-1} , concentration range of BHA: Curve 0 – $0 \text{ } \mu\text{g ml}^{-1}$; Curve 1 – $14.9 \text{ } \mu\text{g ml}^{-1}$; Curve 2 – $29.9 \text{ } \mu\text{g ml}^{-1}$; Curve 3 – $44.8 \text{ } \mu\text{g ml}^{-1}$; Curve 4 – $59.7 \text{ } \mu\text{g ml}^{-1}$; Curve 5 – $74.7 \text{ } \mu\text{g ml}^{-1}$; Curve 6 – $89.6 \text{ } \mu\text{g ml}^{-1}$; Curve 7 – $104.5 \text{ } \mu\text{g ml}^{-1}$; Curve 8 – $119.5 \text{ } \mu\text{g ml}^{-1}$

DC voltammetric determination of BHA, by application of parameters as previously found, was in different supporting electrolytes. As it was found in Ref.

[30], an addition of propan-2-ol can be used as solvent assuring higher solubility of target analyte. Anodic voltammetric signal corresponding to BHA oxidation was not registered in potential range from +0.4 V to +1.2 V in alkaline medium with the concentration of 0.007 mol l⁻¹ NaOH (BHA concentration was below 119.5 µg ml⁻¹). However, anodic oxidation curves of BHA in propan-2-ol containing 0.007 mol l⁻¹ acetate buffer (pH 5) with concentration 0.007 mol l⁻¹ were already evident and are presented in Fig. 3A. The peak potential shifts with increasing BHA concentration to more positive values (from $E_p = 0.89$ V corresponding to BHA concentration 14.9 µg ml⁻¹ to $E_p = 0.98$ V for BHA concentration 119.5 µg ml⁻¹). Figure 1B shows voltammograms in BHA concentration range from 6.5 µg ml⁻¹ to 51.8 µg ml⁻¹, which was analyzed in 0.1 mol l⁻¹ H₂SO₄. In this case the peak potential shifts to more positive values from E_p 0.84 V for BHA concentration 6.5 µg ml⁻¹ to E_p 0.9 V for BHA concentration 51.8 µg ml⁻¹. Therefore, it is possible to conclude that this shift is smaller than in the case of acetate buffer (Fig. 3A vs. Fig. 3B).

It was proved that an acidic medium is more suitable for BHA analysis (see Fig. 3B) due to more sensitive responses and well developed peaks. The influence of H₂SO₄ concentration (in concentration range from 0.05 to 0.45 mol l⁻¹) on voltammetric signals of BHA in model samples was studied in more detail (Fig 4). Peak potentials, corresponding to the anodic oxidation of BHA, decrease with decreasing pH of supporting electrolyte. They are shifted from 0.920 V for sulfuric acid concentration 0.05 mol l⁻¹ to 0.880 V for acid concentration 0.45 mol l⁻¹.

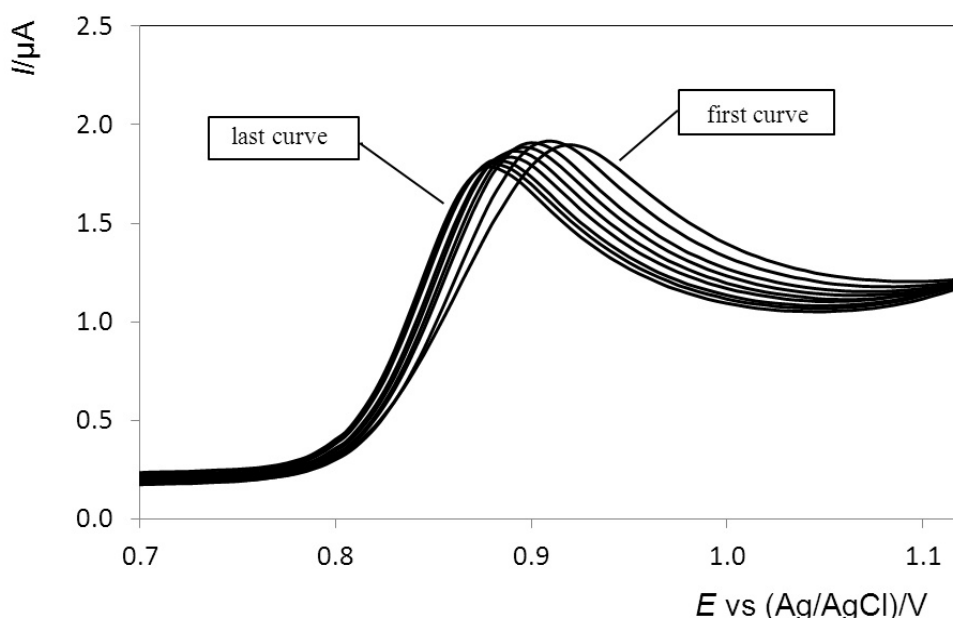


Fig. 4 DC voltammograms of BHA in different concentrations of H₂SO₄. E_{in} : +0.4 V, E_{fin} = +1.2 V, scan rate: 40 mV s⁻¹, concentration of BHA: 43.2 µg ml⁻¹, concentration range of H₂SO₄: from 0.05 to 0.45 mol l⁻¹

Due to the highest registered voltammetric signals of analyzed BHA in model solutions ($43.2 \mu\text{g ml}^{-1}$), the $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ with propan-2-ol was chosen as the most suitable medium for the following experiments.

In the following experiments, the concentration dependence was investigated. Concentrations of samples were evaluated using standard addition method. The optimum number of standard addition was investigated for different BHA concentration ranges. The results are summarized in Table I. The calculated determination errors for one standard addition are listed in column A, for two standard additions in column B and for seven standard additions in column C, D, E., For evaluation of results in column A, B and C, the linear approximation was used, for results in column D, the parabolic dependence (second-degree polynomial) was used and for results in column E, the hyperbolic dependence (third-degree polynomial) was used.

The peak height depends linearly on concentration in the concentration range from $6.5 \mu\text{g ml}^{-1}$ to $71.1 \mu\text{g ml}^{-1}$. Determination error, which is calculated on the basis of linear regression, does not exceed 7.7 %, L_D amounts to 9.9 ng ml^{-1} and L_Q amounts to 20 ng ml^{-1} for this concentration range and limit of detection. However, the dependence of the peak height on concentration exhibits the nonlinear shape in wider range ($15\text{-}123 \mu\text{g ml}^{-1}$). In this case, the polynomial of degree 3 provides optimum results. The calculated error differs from real value in the range $-1.6 - +2.8 \%$.

Table I Errors of determination in different concentration ranges of BHA in H_2SO_4 0.1 mol l^{-1} and in propan-2-ol in dependence on number of additions and on method of evaluation

No.	Concentration range μgml^{-1}	Determination error, %				
		A	B	C	D	E
1	6.5-51.8	-0.61	0.46	4.81	1.04	-0.15
2	8.6-45.0	4.16	-0.44	3.18	1.97	-3.81
3	10.9-49.2	1.07	-0.58	3.79	0.02	-5.42
4	11.5-51.8	1.2	2.59	3.73	-0.24	7.09
5	13.7-71.1	-2.87	-0.99	7.68	-2.64	-6.26
6	14.9-119.4	7.37	10.24	35.29	4.36	-1.61
7	27.3-123.0	11.96	10.3	11.46	8.83	2.79

Notes: Determined errors assuming applicability of linear dependence $I = f(c)$: A – one addition; B – two additions; C – seven additions with approximation of polynomial of degree 1; D – seven additions with approximation of polynomial of degree 2; E – seven additions with approximation of polynomial of degree 3

Determination of BHA in Model Samples of Biodiesel

The developed method of BHA determination was applied in case of biodiesel samples. This matrix, as it was already published [30], can be dosed directly into the supporting electrolyte containing propan-2-ol as a solvent. Three model mixtures containing BHA (concentrations 1 %, 0.5 %, and 0.1 %) were prepared. These concentration levels correspond to real situations: The initial concentration of BHA in biodiesel is about 1 % and it decreases with time. It was necessary to find appropriate amount of sample, which can be dosed directly into the supporting electrolyte. Furthermore, it was necessary to characterize the influences of biodiesel matrix on the waveform and shape of anodic oxidation curves of studied antioxidant BHA and on the determination error. Therefore, various amounts of samples were added to the supporting electrolyte (from 0.1 ml to 1.0 ml, total volume was 15 ml) and analyzed. It was found that increasing amount of biodiesel in supporting electrolyte decreases the peak current and shifts the peak potential to more positive potentials. This effect of matrix is presented in Table II.

Table II Influence of biodiesel matrix on maximum position of BHA peak and the sensitivity of determination

Volume of biodiesel, ml	Percentage (v/v) of biodiesel in analyzed volume, %	E_p V	I_p $\mu\text{A g}^{-1}$
0.1	0.7	0.93	2.7
0.5	3.3	0.93	2.02
1	6.7	0.995	1.82

It follows from Table II that one order increase in the matrix content caused a not significant shift of the peak potential (65 mV), and the peak current decreased by 30 %. Therefore, it can be concluded that the smaller sample addition is more suitable. However, changes are not significant and the volume of sample can be chosen arbitrarily in a range of 0.1-1.0 ml according to the expected concentration of sample (according to old or wear and tear of products).

The example of real analysis of BHA in a biodiesel sample is presented in Fig. 5.

The quantitative evaluation was performed assuming linear or nonlinear dependence of current on the BHA concentration. The first peak from Fig. 5 is taken as a model sample which is evaluated using linear and nonlinear standard addition method. The obtained results are presented in Table III. The meanings of data presented in column A-E are identical with similar data in Table I.

The data in Table III shows that the linear part of dependence $I = f(c)$ provides the results with error smaller than 10 %, which cannot be found within

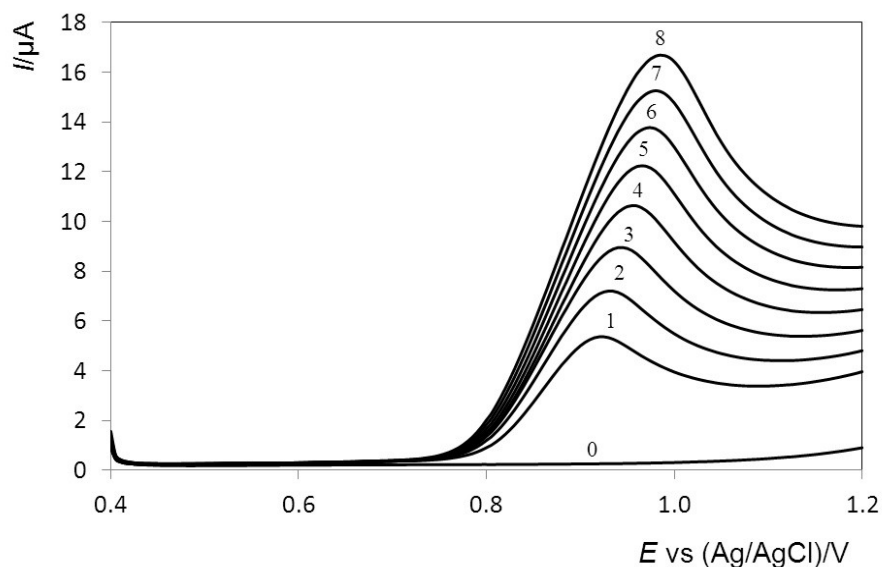


Fig. 5 DC-voltammograms of BHA in propan-2-ol containing $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ and biodiesel. Experimental conditions: LSV, $E_{\text{in}}: +0.4 \text{ V}$, $E_{\text{fin}} = +1.2 \text{ V}$, scan rate: 40 mV s^{-1} , concentration of BHA in sample (curve 1): $147.3 \text{ } \mu\text{g ml}^{-1}$; concentration range of BHA (curves 2-8): from 207.0 to $565.4 \text{ } \mu\text{g ml}^{-1}$

Table III Errors of determination in different concentration ranges of BHA in supporting electrolyte ($\text{H}_2\text{SO}_4 0.1 \text{ mol l}^{-1}$ and propan-2-ol) containing biodiesel in dependence on number of additions and on method of evaluation

No.	Concentration range $\mu\text{g ml}^{-1}$	Determination error, %				
		A	B	C	D	E
1	31.9-120.8	-0.9	1.3	11.3	3.4	-7.8
2	62.4-240.1	-10.3	-8.2	13.2	-1.5	-7.7
3	90.7-445.8	9.6	9.8	24.1	2.5	-7.6
4	33.7-117.3	-3.2	-1.3	12.9	-7.2	-9.3
5	153.1-571.2	4.1	6.8	26.2	-0.9	-6.3
6	299.7-1136	9.7	13.2	42.1	1.4	3
7	62.5-229.8	-0.4	5.6	16.6	1.9	-4.9
8	286.7-1123	6.9	10.4	38.1	0.2	2.5
9	557.1-2334	9.7	17.7	29.8	-8.4	-9.2

Notes: Error of determination assuming applicability of linear dependence $I = f(c)$ in columns A-C: A – one addition; B – two additions; C – seven additions with approximation of polynomial of degree 1; D – seven additions with approximation of polynomial of degree 2; E – seven additions with approximation of polynomial of degree 3.

the experiments and in the wide concentration range of BHA. Hence, it was approached to the nonlinear regression which was applied as follows: in the graph of Fig. 6, there are given the heights of individual peaks in dependence on the addition of BHA. The first peak is taken as the zero value of standard addition, thus the concentration of first peak is the concentration of model sample. The measured data was approached using polynomials of degrees from 1 to 4.

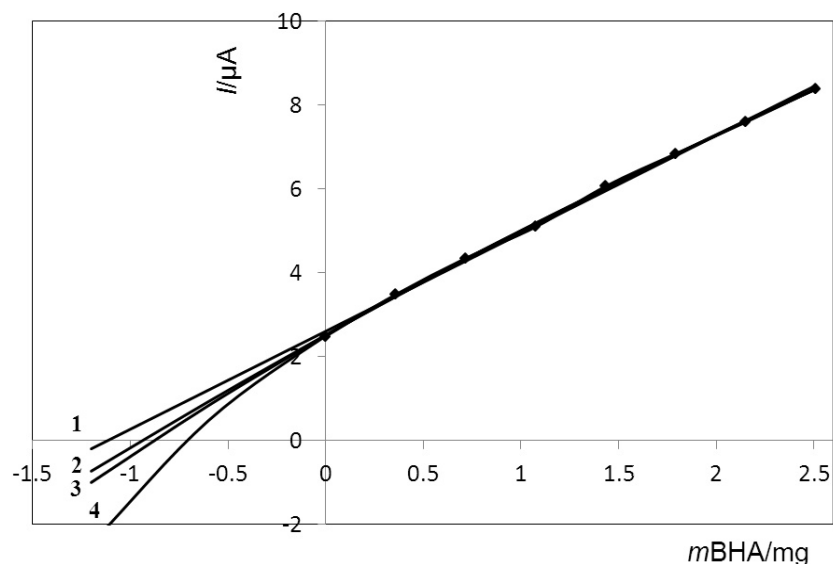


Fig. 6 The approximation of measured data, y (◆) – measured values, 1 – approximation of polynomial of degree 1, 2 – approximation of polynomial of degree 2, 3 – approximation of polynomial of degree 3, 4 – approximation of polynomial of degree 4

The correct degree of approximation by polynomial is selected for the calculation of the concentration, and the corresponding curve must be moved in the argument in such a way that the curve passes through the coordinate origin. This concentration can be determined from the regression curve on the basis of the measured current value for a sample; this is, therefore, a calibration curve. The approximation function allows interpolation between measured data in the measured range for all three polynomials with approximately the same quality. The extrapolation and search for a point of intersection of the curve with the horizontal axis of the coordinate system is focused in the area, which is important for determination of the concentration. In view of the fact that the area with an extrapolated course of dependence of peak height on the concentration of BHA contains no measured data, the correct degree of approximation polynomial can be obtained only on the basis of experimental measurement and evaluation of sufficient quantity of samples with known concentrations of the analyzed substance. Altogether 25 model samples with known concentrations were analyzed. In the next Table IV, there are presented averages, medians and standard

deviations for relative errors of calculated concentrations of samples with known amounts using approximation polynomials of degree from 1 to 3.

Table IV Results of average errors of 25 model samples for different degrees of polynomials

Degree of polynomial	Average – error %	Median – error %	Standard deviation %
1	22.09	17.75	12.17
2	-1.54	0.18	7.07
3	-8.74	-9.01	8.42

From Table IV, the nonlinear dependence of peak height on the concentration (example Fig. 5) is optimally approached using the polynomial of degree 2.

The next algorithm to calculate the concentration of analyzed model sample was proposed and tested experimentally. The algorithm is a part of the program OK-nelin [32].

1. Measured data are approached polynomial of degree 2 using the method of least squares. The first peak is taken as the zero value of standard addition and other peaks are assigned to corresponding increases in concentrations.
2. Roots of approximation polynomial are calculated using resolution of quadratic equation.
3. The seeking concentration of the sample is numerically equal to negative value of the root of approximation polynomial. The second calculated root of approximation polynomial, that is greater than zero, has no real significance. The resulting nonlinear dependence of peak height on the concentration of analyte (Fig. 5), that is in argument moved with the value of root of approximation polynomial including measured data, is presented in the graph in Fig. 7.

Fitting experimental points, where is also a point zero (zero concentration belong to zero current), is identical with the theoretically calculated curve. The calculated dependence can be used for quantitative evaluation of results (Fig. 7). This evaluation method of BHA in the case of nonlinear dependence was applied to samples of biodiesel. The results with values obtained using linear dependence are summarized in Table V.

The values in Table V show that the developed method of BHA analysis with suggested conditions in biodiesel needs evaluation of results according nonlinear model. The achieved errors are in the range of ± 10 rel. %. It is acceptable. When linear model is used for evaluation, the obtained results are very different from the correct ones. Data in Table V confirmed the introduced facts:

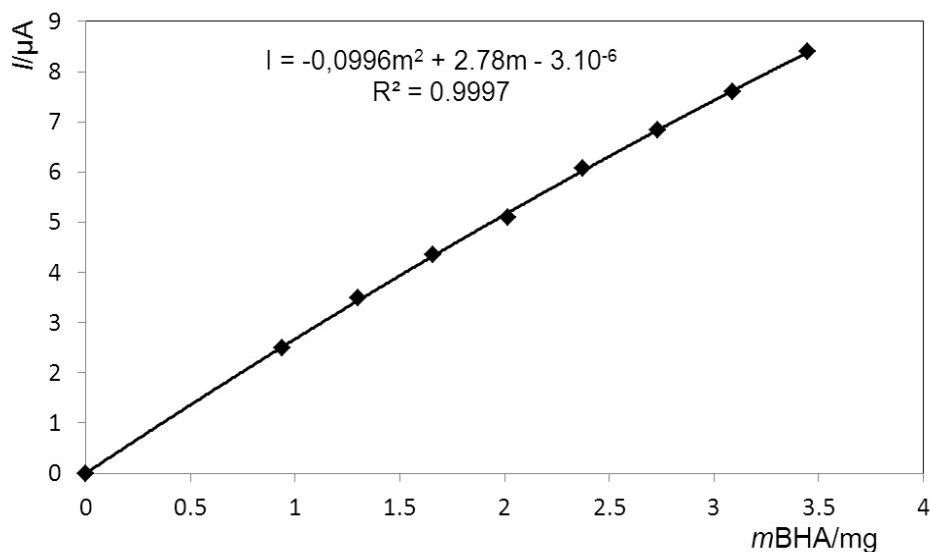


Fig. 7 Measured data with approximation of polynomial of degree 2

Table V Determined values for samples of biodiesel by linear and nonlinear regression. Determined concentration: model 0.1 % – 1.099 g kg⁻¹; model 0.5 % – 5.281 g kg⁻¹; model 1 % – 9.817 g kg⁻¹

Amount of BHA in sample	Volume of sample ml	Linear regression		Nonlinear regression	
		Determined g kg ⁻¹	Error %	Determined g kg ⁻¹	Error %
1 %	0.1	11.447	16.6	10.006	-1.9
	0.5	13.559	38.1	9.836	0.2
	1	12.746	29.8	8.995	-8.4
0.5 %	0.1	5.964	12.9	4.9	-7.2
	0.5	6.664	26.2	5.234	-0.9
	1	7.505	42.1	5.353	1.4
0.1 %	0.1	1.223	11.3	1.136	3.4
	0.5	1.244	13.2	1.083	-1.5
	1	1.364	24.1	1.126	2.5

volumes in range 0.1-1.0 ml for analysis BHA can be dosed in supporting electrolyte according to the expected concentration. The dosed volume has no significant influence on the determination of errors. The accuracy and precision of voltammetric determination of BHA under the conditions suggested were tested by means of 5 repeated analyses of a model solution of known concentration, 0.5

% BHA (2.28 g kg^{-1}). The volume of sample was 0.5 ml. The average determined value was 2.37 g kg^{-1} with standard deviation 0.328 g kg^{-1} ; 95 % interval of reliability with lower limit 1.96 g kg^{-1} and upper limit 2.77 g kg^{-1} . The average value differs by 3.9 % from the real value.

Determination of BHA in Model Samples of Oils

Oils are another important type of samples, where it is necessary to monitor the content of antioxidants. It was found that this matrix makes impossible the voltammetric determination of antioxidant BHA using working gold electrode. It is necessary to realize the sample pretreatment using extraction. Ethanol (96%) was used for extraction of BHA from oil. This operation was performed in ultrasonic bath, which helps to homogenize the sample. The sonication time was 10 min (similarly, as it was published in [25]). The oil matrix was kept to sediment for 30 min after antioxidant dissolution in the polar solvent. Then the upper ethanolic layer was separated. However, this solution contains traces of oil in the suspension form. When this solution is analyzed, the surface of the working electrode gets coated with a thin film. This complicates the measurement substantially. Therefore, attention was directed to development of more reliable process of oil residual removal from the extract. Different procedures were tested: repeated filtration, longtime sedimentation, increase in the ionic strength of ethanolic solution using Na_2SO_4 , and the combination of these procedures. The obtained results are summarized in Fig. 8.

Anodic oxidation curve No. 1 (Fig. 8) for single filtration is shifted to more positive potentials. The peak potential is at 1.16 V. Conditions of oxidation are difficult. Anodic oxidation curve No. 2 (Fig. 8) corresponding to the longtime sedimentation, No. 3 (Fig. 8) corresponding to the 2-times repeated filtration and No. 4 (Fig. 8) corresponding to the increased ionic strength of ethanolic are almost similar. The peak potentials of these curves are in the range from 0.945 V to 0.965 V.

Application of ionic strength increase and in combination with other filtration exhibited the highest peak current (No. 5, Fig. 8). Therefore, this procedure was selected as the most effective and it was tested in more detail.

The results of realized analyses by application of the last mentioned pretreatment method (increase in the ionic strength and filtration after ethanolic extraction) are presented in Table VI. For evaluation using two standard additions only, the linear model is fully acceptable (determination error is in the range of ± 5 %). In case of more standard additions, application of a nonlinear regression is more suitable (in our case realized with program OK-nelin). The polynomial of degree 2 gives correct results for this type of sample. The variance of results (presented in Table VI) is probably caused by consuming processing of oil samples.

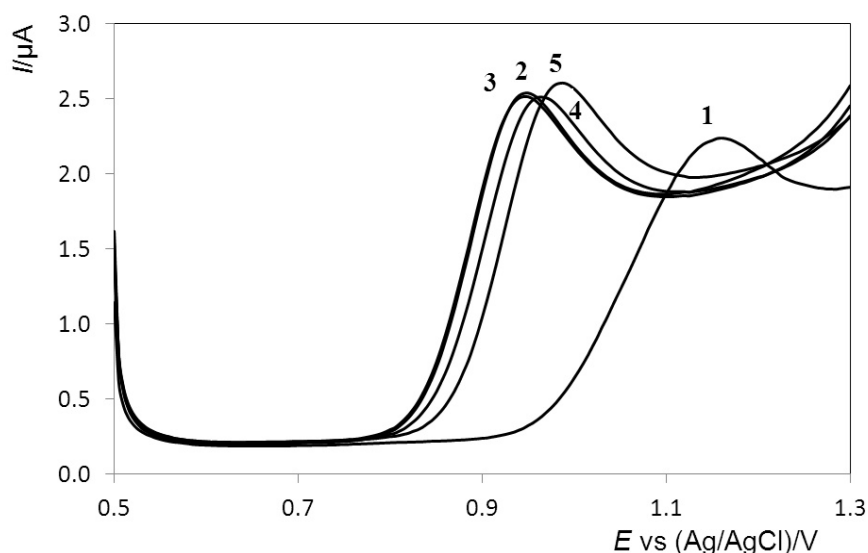


Fig. 8 DC voltammograms of BHA solution, extracted with 96% ethanol and treated by different procedures for different treatment of extractions. Experimental conditions, E_{in} : +0.4 V, E_{fin} = +1.3 V, scan rate: 40 mV s⁻¹. Extraction with 96% ethanol, concentration of BHA: 44.8 μg ml⁻¹. Curve 1 – single filtration, Curve 2 – longtime sedimentation, Curve 3 – repeated filtration, Curve 4 – salting of oil, Curve 5 – combination of filtration and salting

Table VI Errors of determination in different concentration ranges of BHA in a supporting electrolyte containing ethanolic extract of oils after ionic strength increase and filtration

No.	Concentration range μgml ⁻¹	Determination error, %				
		A	B	C	D	E
1	34.2-164.1	-0.69	-0.04	14.86	-8.32	-2.97
2	34.2-164.1	4.3	3.77	10.01	-1.00	4.71
3	47.9-229.7	-2.97	-0.67	9.2	-6.62	-1.90
4	47.9-229.7	-2.14	-1.29	11.42	-8.80	-2.50
5	68.4-328.1	-4.81	-2.91	9.19	-6.82	-12.47
6	82.1-393.8	4.29	4.6	28.57	-1.05	-10.92
7	82.1-393.8	-3.53	-2.13	17.68	-10.27	-9.30
8	61.6-451.8	1.51	1.83	20.43	-4.44	-9.38

Notes: Error of determination assuming applicability of linear dependence $I = f(c)$ in columns A-C: A – one addition; B – two additions; C – seven additions with approximation of polynomial of degree 1; D – seven additions with approximation of polynomial of degree 2; E – seven additions with approximation of polynomial of degree 3.

Analytical Application

The developed method of BHA determination was applied to 5 spiked real samples which were prepared by dissolving of known amount of antioxidant, pure oil or biodiesel. The samples were homogenized using ultrasound. The results are summarized in Table VII. It is possible to conclude that the determined concentrations of BHA in real samples were in good agreement with the declared values.

Table VII Results of voltammetric determination of BHA in spiked real samples

Sample #	Specification of sample	Declared g kg ⁻¹	Determined g kg ⁻¹	Error %
1	Biodiesel	5.28	5.46 ± 0.13	3.4
2	Mineral oil	5.09	5.13 ± 0.18	0.8
3	Mineral oil	2.61	2.61 ± 0.18	0
4	Synthetic oil	2.5	2.55 ± 0.12	2
5	Synthetic oil	1.17	1.120 ± 0.025	-4.3

From values in Table VII it can be stated that the method of voltammetric determination of BHA provides reliable results in complicated matrix of oils or biodiesel. The suggested method is applicable in practical laboratories that deal with effective using of lubricants and fuels.

Conclusion

In this paper, the voltammetric method of BHA determination in oils and biodiesel using disc gold working electrode was investigated. For these purposes, the gold electrode chosen has offered reproducible response and propan-2-ol containing 0.1 mol l⁻¹ H₂SO₄ as supporting electrolyte was used. The program OK-nelin was applied in evaluation by nonlinear regression.

Analyses in biodiesels can be performed directly, without necessity of sample pretreatment or extraction. The extraction is necessary for analyses of oils. The analytical results obtained by DC voltammetry are sufficiently accurate and precise and show good agreement with declared values.

Finally, the analysis of spiked real samples has shown that the content of BHA in biodiesel and oils is sufficiently high and hence, it is not necessary to use special procedures for trace analysis; e.g., combination with highly sophisticated

electroanalytical instrumentation. In conclusion, the method presented seems to be convenient and fully recommendable for routine analysis in laboratories of refineries and similar industrial service units.

Acknowledgement

Financial support was provided by the project SGFChT05/2013, by the Czech Science Foundation (the Czech Republic) (project No. P208/12/1645 and project No. 13-21409P).

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