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Voltammetric Determination of Different Antioxidants in Petroleum Products by Working Gold Electrode

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The present paper deals with the problem of voltammetric determination of a mixture of amine-type antioxidant *N*-phenyl-1-naphthylamine (PNA) and phenol-type antioxidant butylated hydroxytoluene (BHT) in oil matrix by the method of linear sweep voltammetry using gold working electrode. Attention was focused on the effect of large excess of PNA on the curves of anodic oxidation of BHT. It was found that only more than tenfold excess of PNA disturbs the determination of the phenol-type antioxidant in the adopted supporting electrolyte. In such case it is necessary to reduce its content by its transformation into the corresponding nitrosamine by reaction with nitrous acid. The rate constants of this reaction were determined for two different concentrations of PNA.

Keywords: Linear Sweep Voltammetry; Antioxidants; Mineral Oil; Synthetic Oil; Gold Disc Electrode

1. INTRODUCTION

At present great attention is being focused on monitoring the effect of traffic on the environment. Inhibition of oxidative conversions of petroleum substances represents the major

technological problem. The resistance to oxidation is increased by addition of various synthetic antioxidants [1].

The most common phenol-type antioxidants include BHT, butylated hydroxyanisol (BHA), *tert*-butylhydroquinone (TBHQ), propyl gallate (PG) and pyrogallol (PA); a common amine-type antioxidant is PNA [2].

Various analytical methods can be used for determination of antioxidants. A number of published papers describe their spectrophotometric determination [3-14]. Liquid chromatography [15-20] mostly in combination with electrochemical detection [10,21-28], with diode array detector [29-31] and also with mass spectrometer [32-34] has been also applied for this purpose. The GC-MS technique [35] or micellar electrokinetic capillary chromatography [36,37] were applied successfully, too.

Most of these methods are quite expensive or require a rather complicated preparation of sample prior to the analysis: in other words, they are not suitable for field analysis. Electrochemical methods represent a relatively cheap and effective alternative with portable instrumentation and with possibility of further miniaturization. Moreover, antioxidants are substances that can be electrochemically easily oxidized [38].

The problem of determination of antioxidants was dealt with also in previous years, the phenol-type antioxidants (as most frequently used) having been studied predominantly. Antioxidants are commonly used, alone or in commercial mixtures, as additives in oils or fats, in order to prevent oxidative rancidity [39]. In practice, a mixture of two or more antioxidants is found to be more effective than the application of a single compound. Since these substances are chemically similar, the analysis becomes difficult at trace levels without previous separation [40].

S. N. Robledo *et al.* [41] worked on the determination of four antioxidants in olive oil, namely of BHA, BHT, TBHQ and PG. A simple electroanalytical method was proposed: it adopts square wave voltammetry with a Pt band ultramicroelectrode to perform a qualitative and quantitative analysis of mixtures of synthetic antioxidants that are allowed by official regulations for the use in edible oils. Antioxidants were extracted from olive oil by acetonitrile. Their electrochemical responses were then studied in acetonitrile with 0.1 M $(C_4H_9)_4NF_6P$ and compared with changes produced by successive additions of $(C_4H_9)_4NOH$. The analyses were performed either directly in oil matrix dissolved in a mixture of benzene-ethanol (1:2) in presence of 0.1 M or 1 M H_2SO_4, or the antioxidants were isolated by double extraction using acetonitrile.

Medeiros *et al.* in their paper [42] describe the method for determination of BHA and BHT in mixture. The method was developed for simultaneous determination of antioxidants in samples of mayonnaise: it uses multiple pulse amperometry with flow injection analysis. It was carried out by extraction of samples of mayonnaise with ethanol before determination of antioxidants. The phenol-type antioxidants were determined with a cathodically pretreated boron-doped diamond electrode in aqueous ethanolic (30% ethanol, v/v) 10 $mmol.L^{-1}$ KNO_3 solution as supporting electrolyte.

In paper [43], the authors worked with the same antioxidants. A simple electrochemical method was developed for single and simultaneous determination of BHA and BHT in food samples using square wave voltammetry. A carbon composite electrode modified with copper(II) phosphate immobilized in a polyester resin was proposed. The procedure developed was effective for

simultaneous determination of BHA and BHT in complex food samples such as mayonnaise, without the use of any chemometric approaches or prior treatments.

Hanging mercury drop electrode (HMDE) [26,44,45], solid composite electrodes [27,46,47], solid amalgam electrodes [48-54], glassy carbon electrodes [55,56] and screen printed electrodes [57] are most frequently used for electrochemical determination of antioxidants. The gold electrode, mono-crystalline, poly-crystalline, composite or in form of amalgam, has been also frequently used in electrochemical detections of various compounds (e.g. [27,58-60]). In paper [45], 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 HMDE in acidic medium of 0.2 mol.L^{-1} H_2SO_4 with addition of ethanol and acetonitrile in the ratio of 3:1. It was found that the presence of amino-compounds significantly affects the determination of BHT: the amounts determined by the analyses are lower than the actual values. A procedure was suggested for eliminating the aromatic amines from the sample before performing the determination of phenol-type substances.

The aim of the present work is a detailed investigation of the effect of various amounts of amine-type antioxidant on the determination of BHT and a study of reaction kinetics of the reaction of *N*-phenyl-1-naphthylamine (PNA) with nitrous acid which leads to a desired concentration reduction of this disturbing antioxidant.

2. EXPERIMENTAL PART

2.1. Chemicals and Reagents

The stock solution of BHT (4 g.L^{-1}) was prepared by dissolving the appropriate amount of BHT (AppliChem; CAS: 128-37-0) in 96% ethanol, and the stock solution of PNA (4 g.L^{-1}) was prepared by dissolving the appropriate amount of PNA (Acros Organics; CAS: 90-30-2) also in 96% ethanol. The real samples of mineral and synthetic oils were extracted with 96% ethanol. Solution of 1 mol.L^{-1} $NaNO_2$ (Lachema, CZ) was used to eliminate the effect of amine-type antioxidants on the BHT determination.

2.2. Apparatus and Accessories

The voltammetric analyses of antioxidants were performed by means of an electrochemical analyzer EP 100VA (HSC service, Bratislava, Slovak Republic) using a three-electrode arrangement. The working electrode had the form of gold disc (AuDE, 2 mm in diameter, HSC service, Bratislava, Slovak Republic). The reference electrode was a silver/silver chloride electrode with a liquid bridge filled with 1 M KNO_3, and the auxiliary electrode was made of platinum (Pt-plate: 3×5 mm). D. C. technique with linear change of potential (linear sweep voltammetry) was adopted for the electrochemical oxidation of antioxidants.

2.3. Procedure

The antioxidants were extracted from 1-2 g of oil matrix by means of 96% ethanol with the application of ultrasonic field for 5 min, from 4-5 g of oil matrix for 10 min. After the suspension settled, the upper layer was separated by filtration through a white ribbon filter and analyzed.

The determination of antioxidants was performed in a mixture of ethanol and acetonitrile in the ratio of 2.5:1 containing 0.1 mol.L^{-1} H_2SO_4. The oxidation of antioxidants was recorded by LSV method within the potential range from +400 mV to +1300 mV at scan rate of 40 mV.s^{-1}.

3. RESULTS AND DISCUSSION

The voltammetric determination of the above-mentioned antioxidants can make use of their anodic oxidation, which proceeds at considerably positive potentials. However, in practice the stabilization of oils is carried out by simultaneous addition of both amine-type and phenol-type antioxidants: i.e., there emerges the necessity of their determination side by side. Acidic medium was proved to be most suitable for this determination [45]. Furthermore, it was necessary to ensure the solubility of analyzed substances in supporting electrolyte by the presence of suitable solvent. The supporting electrolyte (chosen on basis of a number of experiments) has the following composition: 0.1 mol.L^{-1} H_2SO_4 in ethanol-acetonitrile mixture of ratio 2.5:1. In this medium, the response of the method was sufficiently sensitive with concomitant satisfactory differentiation between the two types of antioxidants. At the same time, the presence of organic solvents ensured perfect solubility of the analyzed substances. If the method is adopted for analytical purposes, its monitored response should be straight-line dependent on the concentration determined. Figures 1 and 2 present the curves of anodic oxidation of PNA and BHT in ranges of the concentrations studied (from 5 mg.L^{-1} to 45 mg.L^{-1} in the case of PNA, and from 5 mg.L^{-1} to 44 mg.L^{-1} in the case of BHT).

Fig. 1 shows that the heights of curves corresponding to anodic oxidation of PNA are straight line to analyzed amounts. Using of dependence in Fig. 1, the equation calculated is as follows:

$$I[\mu A] = (0.06291 \pm 0.00032)\, c_{PNA}[mg.L^{-1}] + (0.1714 \pm 0.0090)$$

The Adstat program [52] was used for the statistical evaluation. From statistical analysis, which also provided the linear calibration model, LoD 0.21 mg.L^{-1},LoQ 0.15 mg.L^{-1} and the correlation coefficient 0.9977 were evaluated by direct method for the experiment given.

The equation which express the dependence of peak height on BHT concentration for its anodic oxidation we also have calculated (see Fig. 2) as follows:

$$I[\mu A] = (0.0391 \pm 0.00059)\, c_{BHT}[mg.L^{-1}] + (0.0058 \pm 0.00162).$$

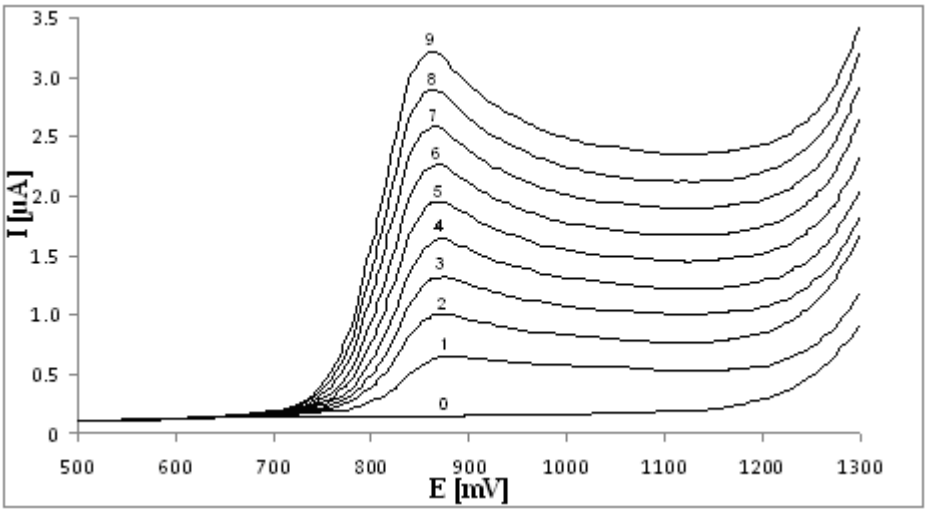

Figure 1. Anodic oxidation curves in voltammetric determination of PNA. Exp. conditions: LSV, supporting electrolyte: ethanol-acetonitrile mixture in ratio 2.5:1 containing 0.1 mol.L^{-1} H_2SO_4; initial volume: 17.4 mL; E_{in}: +0.4 V, E_{fin} = +1.3 V; scan rate: 40 mV.s^{-1}; concentration range of PNA: from 5 mg.L^{-1} to 45 mg.L^{-1}. Curve 0 – 0 mg.L^{-1}; curve 1 – 5 mg.L^{-1}; curve 2 – 10 mg.L^{-1}; curve 3 – 15 mg.L^{-1};curve 4 – 20 mg.L^{-1}; curve 5 – 25 mg.L^{-1}; curve 6 – 30 mg.L^{-1}; curve 7 – 35 mg.L^{-1}; curve 8 – 40 mg.L^{-1}; curve 9 – 45 mg.L^{-1}.

LoD was 0.08 mg.L^{-1}, LoQ was 0.27 mg.L^{-1}, and the correlation coefficient was 0.9993. The reliability and accuracy of determination of both antioxidants in the electrolyte recommended were tested by analysis of model solutions of 24.9 mg.L^{-1} PNA and 24.4 mg.L^{-1} BHT. Analysis was repeated for six times (n = 6).

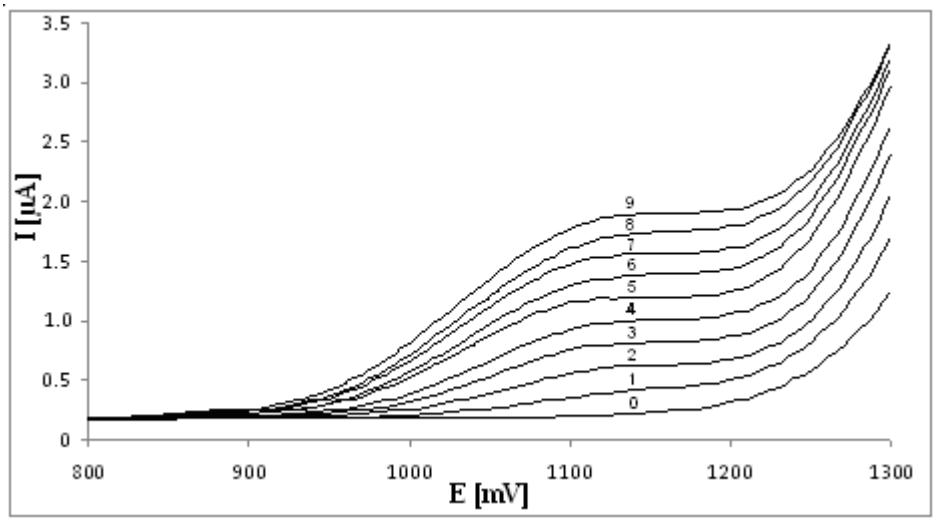

Figure 2. Anodic oxidation curves in voltammetric determination of BHT. Exp. conditions: LSV; supporting electrolyte: ethanol-acetonitrile mixture in ratio 2.5:1 containing 0.1 mol.L^{-1} H_2SO_4; initial volume: 17.4 mL; E_{in}: +0.4 V, E_{fin} = +1.3 V; scan rate: 40 mV.s^{-1}; concentration range of BHT: from 5 mg.L^{-1} to 44 mg.L^{-1}. Curve 0 – 0 mg.L^{-1}; curve 1 – 5 mg.L^{-1}; curve 2 – 10 mg.L^{-1}; curve 3 – 15 mg.L^{-1}; curve 4 – 20 mg.L^{-1}; curve 5 – 24 mg.L^{-1}; curve 6 – 29 mg.L^{-1}; curve 7 – 34 mg.L^{-1}; curve 8 – 39 mg.L^{-1}; curve 9 – 44 mg.L^{-1}.

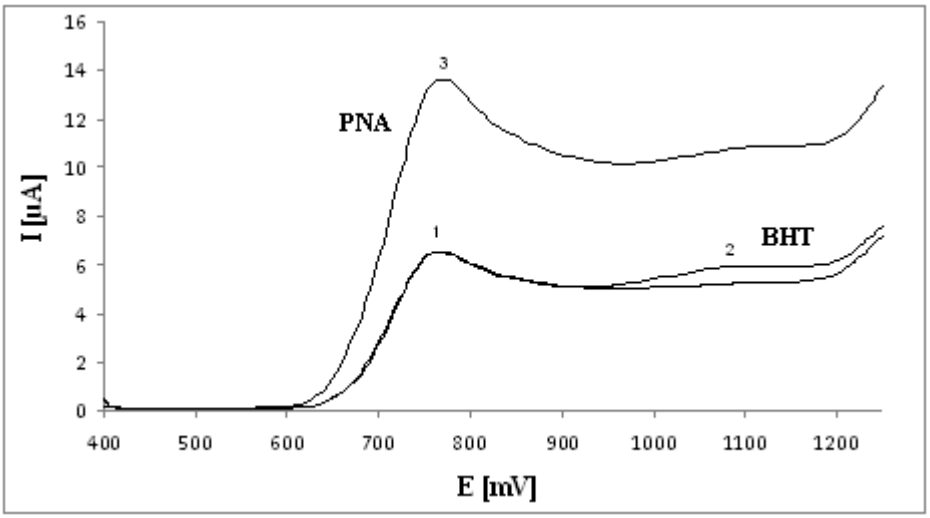

Figure 3. Anodic oxidation curves of mixture of the antioxidants PNA and BHT (10:1) in the sample. Exp. conditions: LSV; E_{in}: +0.4 V, E_{fin} = +1.3 V; scan rate: 40 mV.s^{-1}; 1 mL of extract of model oil was analyzed; supporting electrolyte: 0.1 M H_2SO_4 in ethanol-acetonitrile mixture 2.5:1, initial volume: 17.4 mL; Curve 1 – anodic oxidation of extract of synthetic oil; curve 2– addition of 50 µl BHT (1.35 mg.L^{-1}); curve 3 – addition of 400 µl PNA (104.2 mg.L^{-1}).

The average values 26.3 mg.L^{-1} for PNA and 23.4 mg.L^{-1} for BHT were found within the 95% confidence interval. They differ from the real values by +5.6% (PNA) and –4.1% (BHT), respectively. The standard deviations were 0.37 mg.L^{-1} for PNA and 1.17 mg.L^{-1} for BHT. The above-given results show that the determination of representatives of individual types of antioxidants presents no problems. However, problems are encountered if both types are present in a sample. Regarding the fact that the positions of peaks of anodic oxidation of PNA and BHT do not differ too much under the conditions given (the maximum of PNA is +865 mV, that of BHT varies in the interval from +1110 mV to +1140 mV according to concentration), it can be presumed that superposed curves (which will affect subsequent evaluation of results) will be provided during measurement (an example is presented in Fig. 3).

Fig. 3 shows that the decrease in PNA peaks is superposed onto the increasing BHT peak, which eventually distorts the overall height of response of this antioxidant, and its determination exhibits a negative error. Similar facts were also described in Ref. [45], where the procedure suggested for analyses of such mixtures consisted of three steps and gave correct results: the PNA content is determined in the first step, then this antioxidant is removed, i.e. converted into the corresponding *N*-nitrosamine by reaction with nitrous acid, and finally the BHT content is determined.

This approach was retained in the present study; however, attention was focused on detailed investigation of effects of various amounts of the amine-type antioxidant on the determination of BHT and, furthermore, on the reaction between nitrous acid and the substances tested. From the results of analyses of model mixtures in which the concentration ratio PNA:BHT varied in the interval from 1:1 to 10:1 it can be stated (Table 1) that under the given conditions the BHT values are affected only in the presence of tenfold excess of PNA. The average error of BHT determination in this case is –31.3%

(n = 9). These results are more favorable than those described in Ref. [45] thanks to the adopted evaluation system which does not process the absolute peak heights, but their derived records, which is enabled by software of the electrochemical analyzer used.

Fig. 4 presents the anodic oxidation curves of PNA-BHT mixture in dependence on equally increasing concentrations of the two antioxidants. Their mutual ratio 1:1 is kept constant. The evaluation of this dependence provided the equation of straight line for PNA as follows:

$$I[\mu A] = (0.06361 \pm 0.00076)c_{PNA}[mg\ L^{-1}] + (0.283 \pm 0.017)$$

The evaluation of this dependence provided the equation of straight line for BHT as follows:

$$I[\mu A] = (0.0333 \pm 0.0010)c_{BHT}[mg\ L^{-1}] \pm (-0.051 \pm 0.022)$$

Table 1. Determination of PNA-BHT mixtures with various ratios of antioxidants.

	PNA:BHT ratio					
	1:1	2:1	3:1	4:1	5:1	10:1
Determined concentration of BHT [mg.L^{-1}]	12.12	11.96	11.97	11.92	12.5	8.38
Relative error [%]	–0.6	–2.0	–1.9	–2.3	+2.4	–31.2

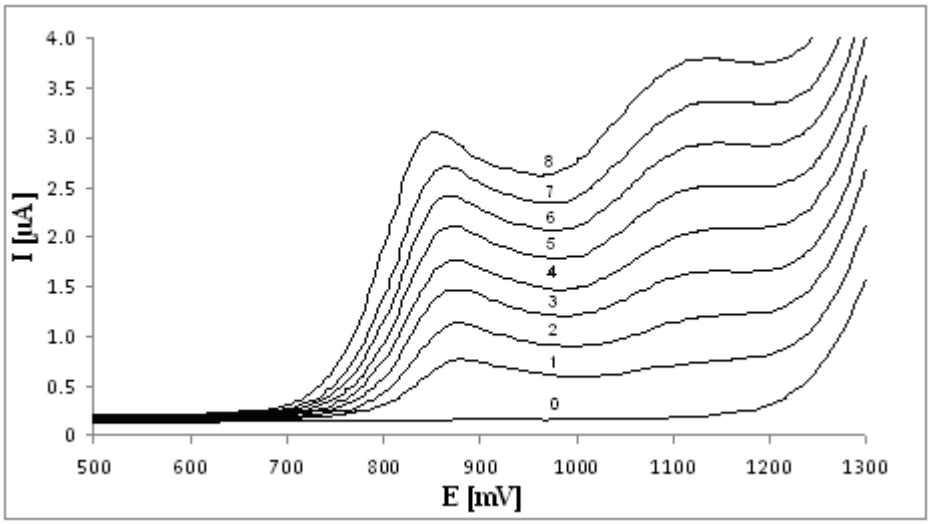

Figure 4. Anodic oxidation curves of PNA-BHT mixtures. Exp. conditions: LSV; supporting electrolyte: ethanol-acetonitrile in the ratio of 2.5:1 containing 0.1 mol.L^{-1} H_2SO_4, initial volume: 17.4 mL; E_{in} +0.4 V, E_{fin} = +1.3 V; scan rate: 40 mV.s^{-1}; concentration range of PNA and BHT: from 5 mg.L^{-1} to 40 mg.L^{-1}; curve 0 – 0 mg L^{-1}; curve 1 – 5 mg L^{-1} PNA and BHT; curve 2 – 10 mg L^{-1} PNA and BHT; curve 3 – 15 mg L^{-1} PNA and BHT; curve 4 – 20 mg L^{-1} PNA and BHT; curve 5 – 25 mg L^{-1} PNA and BHT; curve 6 – 30 mg L^{-1} PNA and BHT; curve 7 – 35 mg L^{-1} PNA and BHT; curve 8 – 40 mg L^{-1} PNA and BHT.

These equations can be applied to analyses of unknown samples. In the case of voltammetric analyses of the above-mentioned mixtures containing equal amounts of the two substances, LoD are 0.27 $mg.L^{-1}$ (PNA) and 0.34 $mg.L^{-1}$ (BHT), LoQ are 0.37 $mg.L^{-1}$ (PNA) and 0.05 $mg.L^{-1}$ (BHT), and the correlation coefficients are 0.9993 (PNA) and 0.9954 (BHT). For all statistical evaluation was used the Adstat program [52].

Since a large excess of amine-type antioxidant has to be removed by the above-described reaction with nitrous acid before the BHT analysis proper, the reaction rate of this reaction was investigated in more detail.

In the kinetic study of elimination of the primary amine PNA of concentration 5.76×10^{-5} $mol.L^{-1}$ with sodium nitrite in acidic medium, the reaction was carried out with the amine dissolved in organic solvents mixture (ethanol-acetonitrile 2.5:1) in the presence of 0.1 M H_2SO_4. Sodium nitrite was used in excess. The 17.4 mL volume of reaction mixture contained 13.8 mg $NaNO_2$ but only a part of it was dissolved, while the rest remained as solid in the given medium. The evaluation of reaction kinetics made use of monitoring of the concentration decrease of amine PNA with time, and the reaction scheme of irreversible bimolecular reaction with rate constant k was applied (Eq. 1). The reaction rate (r) is expressed by Eq. 2, where the exponents α, β are reaction orders with respect to the concentrations of PNA and HNO_2. By calculating the logarithm of Eq. 2 we obtain Eq. 3, which represents an equation of straight line as far as the actual concentration of nitrous acid [HNO_2] does not change very much, i.e. [HNO_2]~*const*.

$$PNA + HNO_2 \xrightarrow{k} Products \tag{1}$$

$$r = -\frac{d[PNA]}{dt} = k[HNO_2]^{\beta}[PNA]^{\alpha} \tag{2}$$

$$\ln r = \alpha \ln[PNA] + \ln k[HNO_2]^{\beta} \tag{3}$$

Equation ln(r) = 1.9257ln[PNA]+5.6374 (the correlation coefficient was 0.8683) presents the dependence of logarithm of reaction rate (r) on logarithm of concentration [*PNA*] according to Eq. 3. The found value of reaction order with respect to PNA, $\alpha = 1.93$, corresponds to a situation in which the reaction mixture at the beginning contains virtually equal concentrations of the two starting reagents (PNA and HNO_2), and the reaction order with respect to HNO_2 is $\beta = 0$. The experimental dependence of reaction rate on the amine concentration under the given conditions is virtually expressed by Eq. 4, where the parameter k is rate constant. Hence under the given conditions it can be stated that the nitrous acid concentration in the solution is constant and comparable with the starting concentration of amine (i.e. the excess of solid $NaNO_2$ ensures the constant concentration of reagent [HNO_2] in the solution). Integration of Eq. 4 provides experimental dependence of the amine PNA concentration on time (Eq. 5).

$$r = k[PNA]^2 \tag{4}$$

$$[PNA] = \frac{PNA_0}{PNA_0 kt + 1} \quad (5)$$

Fig. 5 presents a comparison of the measured experimental dependence of concentration of starting substance PNA on time with the regression curve calculated according to Eq. 5. The parameters of regression curve in Fig. 5 enable an assessment of rate constant on the basis of the kinetic equation

$$[\text{PNA}] = 5.76 \times 10^{-5}/(0.0389t + 1) \quad (6)$$

under given conditions at room temperature, k = 679 L $mol^{-1} \cdot s^{-1}$. Moreover, it was confirmed that the reaction rate depends on the square of PNA concentration.

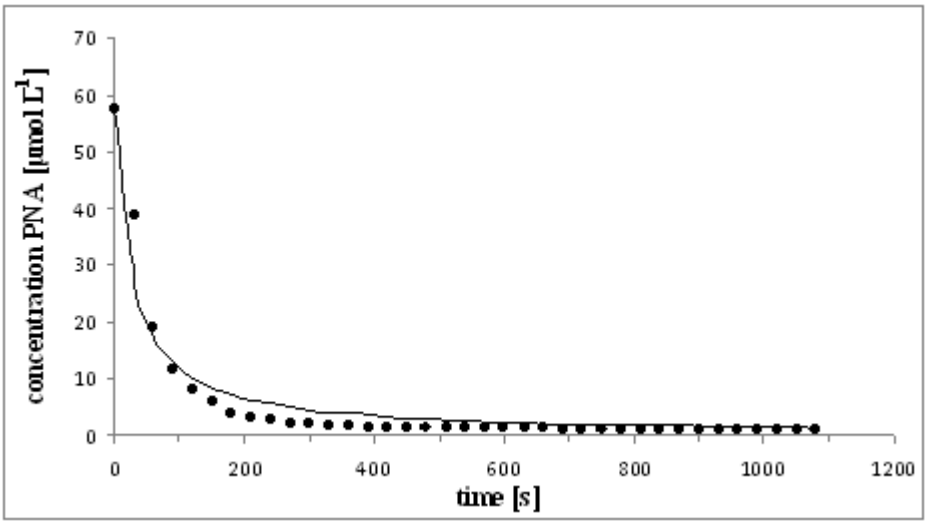

Figure 5. Experimental points (●) and regression curve (solid line) of the dependence PNA concentration – time (Eq.6)

For determination of BHT in mixtures containing a large excess of PNA which has to be removed it was important to find reaction conditions (the amount of nitrite added, acidity of medium, reaction time) that would ensure a sufficient removal of PNA without affecting the amount of BHT. On basis of numerous experiments, in which a mixture of PNA-BHT antioxidants (10:1) was treated with excess $NaNO_2$ in presence of various concentrations of sulfuric acid, (1.72×10^{-2} mol.L^{-1} H_2SO_4, 2.29×10^{-2} mol.L^{-1} H_2SO_4, and 2.87×10^{-2} mol.L^{-1} H_2SO_4), the time dependence of concentrations of the studied substances was determined (Fig. 6). The results show that increasing acidity of the reaction mixture causes a marked decrease in PNA concentration: 50 % of this substance is removed within 3-5 min. During this time period, the BHT concentration still oscillates around the starting value. Its mild decrease is observed only after 7 min with the lowest acidity tested. The time interval of BHT stability is shortened with increasing acidity of reaction medium. The given facts indicate that a 5 min presence of excess nitrite is sufficient for elimination of the disturbing effect of tenfold excess of PNA (13.8 mg/5 mL of reaction solution) in the medium containing from 1.72×10^{-2} mol.L^{-1} H_2SO_4 to $2.29 \times 10^{-}$

^{2} mol.L^{-1} H_2SO_4. The results of above-described kinetic study were also applied to the course of elimination of PNA in a real sample in mixture with BHT in the ratio of 10:1 under the conditions suggested. The starting concentration of PNA was ca 4.7×10^{-4} mol.L^{-1}, the overall amount of added $NaNO_2$ was 13.8 mg/5 mL of the solution. It was found out that the decrease in PNA concentration with time - even under these conditions - formally obeys the same kinetic equation (see Eq. 5) as in the previous case. The measured experimental data and the calculated regression curve of the dependence of PNA concentration on time are depicted in Fig. 6. The rate constant is equal to k = 10.1 L.mol^{-1}.s^{-1}.

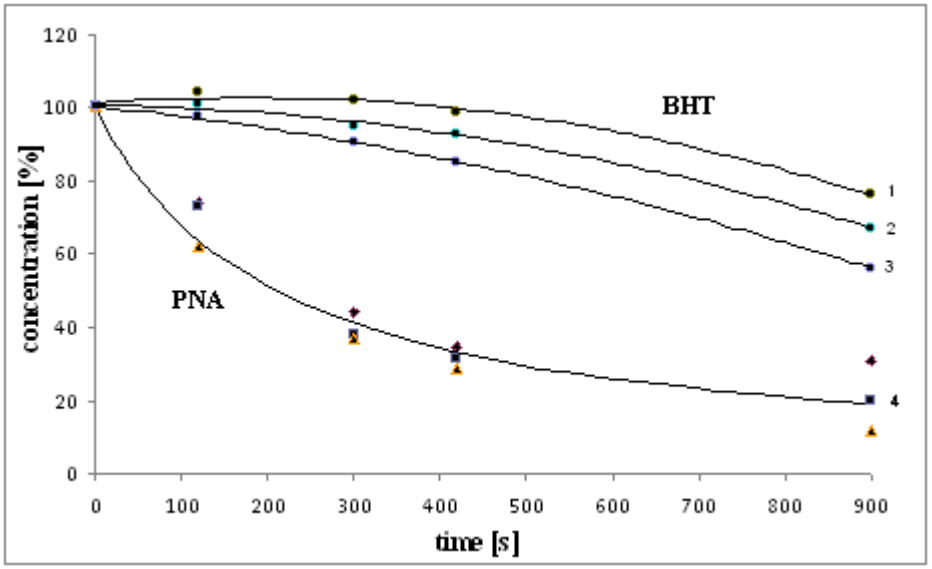

Figure 6. The dependence of PNA and BHT concentrations on time in the reaction with nitrite at three acidity levels of the medium. Experimental conditions: $NaNO_2$ amount added: 13.8 mg/5 mL of reaction solution. The curves of dependences of BHT concentration on time for various acidity levels: curve 1 – 1.72×10^{-2} mol.L^{-1} H_2SO_4; curve 2 – 2.29×10^{-2} mol.L^{-1} H_2SO_4; curve 3 – 2.87×10^{-2} mol.L^{-1} H_2SO_4: curve 4 – regression curve [PNA] = 4.71×10^{-4}/(0.0048t + 1) for 2.29×10^{-2} mol L^{-1} H_2SO_4. Experimental points of the dependence of PNA concentration on time in a model sample PNA-BHT 10:1 with H_2SO_4 concentrations: 1.72×10^{-2} mol.L^{-1} (◆), 2.29×10^{-2} mol.L^{-1} (■), and 2.87×10^{-2} mol.L^{-1} (▲).

The developed analytical procedure for antioxidant mixtures in base oils, both mineral and synthetic, was applied to model mixtures that contained known amounts of the tested antioxidants PNA and BHT in various ratios, in the c_{PNA}:c_{BHT} interval from 1:1 to 10:1. The samples were homogenized by means of ultrasound. In the case of samples 4 and 7 (which contained tenfold excess of amine-based antioxidant) the PNA content was decreased (after its determination) by application of nitrous acid, and only then the phenol-type antioxidant BHT was analyzed. The results (Table 2) were obtained by repeated determination (n = 3) using the method of standard addition. An example of records of anodic oxidation curves of PNA and BHT in sample 7 (both before and after the elimination of PNA) is given in Fig. 3 and Fig. 7. The graphs clearly show that a decrease in amine-type antioxidant results in a more distinct BHT curve and in concomitant arriving at a correct result, which is also confirmed by the data in Table 2.

The error in results which is due to the complete processing of samples, inclusive the extraction of analytes, the analysis itself, and the subsequent evaluation within a broad range of concentrations of both amine-based antioxidant and phenol-based antioxidant, did not exceed 10%. The suggested method is applicable in practice.

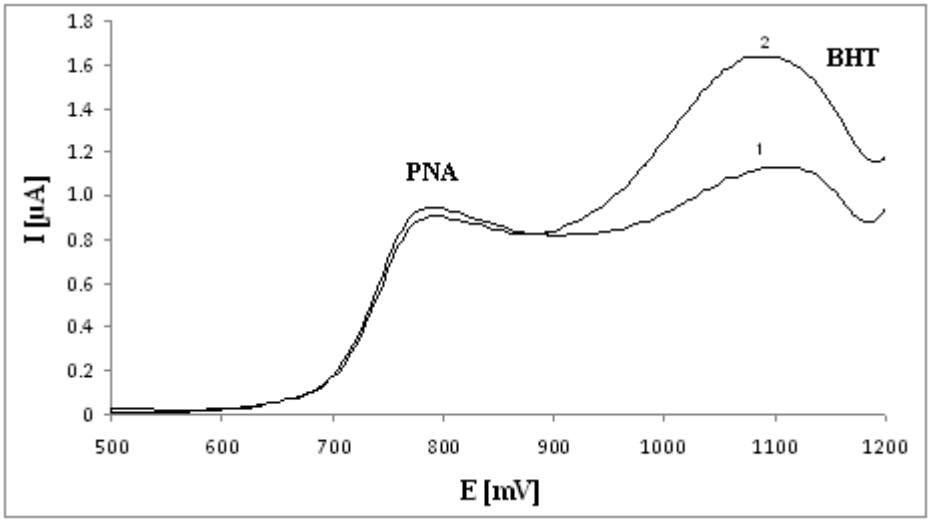

Figure 7. Anodic oxidation curves of PNA and BHT after elimination of PNA by means of reaction with nitrous acid. Exp. conditions: LSV; E_{in}: +0.4 V, E_{fin} = +1.3 V, scan rate: 40 $mV.s^{-1}$; supporting electrolyte: 0.1 M H_2SO_4 in ethanol-acetonitrile solution 2.5:1; initial volume: 17.4 mL; 1 mL extract of model sample of synthetic oil was analyzed; amount of added $NaNO_2$ 13.8/5 mL solution; curve 1 – anodic oxidation of synthetic oil extract after elimination of PNA component; curve 2 – addition of 50 µl BHT (1.35 $mg.L^{-1}$).

Table 2. Results of voltammetric determination of PNA and BHT antioxidants in model samples of mineral and synthetic oils.

Sample no.	Added [$g.kg^{-1}$] PNA / BHT	Determined [$g.kg^{-1}$] PNA / BHT	Error[%] PNA / BHT
1	5.49	5.37	–2.2
	5.80	6.18	+6.6
2	8.41	7.81	–7.0
	2.60	2.73	+5.0
3	9.51	9.01	–5.3
	2.00	1.90	–5.0
4	10.20	10.20	0.0
	1.00	0.94	–6.0
5	5.22	4.92	–5.8
	4.92	4.95	+0.6
6	8.17	8.70	+6.5
	1.82	1.92	+5.5
7	9.35	9.76	+4.4
	0.97	0.92	–5.2

Note: Samples 1-4 – mineral oil; samples 5-7 – synthetic oil

4. CONCLUSIONS

The developed method enables simultaneous voltammetric determination of mixtures of antioxidants based on secondary aromatic amines and BHT up to a tenfold excess of PNA with the use of anodic oxidation on gold disc electrode in a single supporting electrolyte.

Any large excess of PNA affecting the determination of BHT has to be eliminated by transformation of PNA into the corresponding nitrosamine (by reaction with nitrous acid). It was found that under certain conditions this reaction also decreases the BHT concentration, which depends on the H_2SO_4 concentration in the reaction medium. The reaction of amine-type antioxidant with nitrous acid proceeds - under the conditions suggested for its elimination - according to kinetic model of the second-order reaction with the rate constant $k = 10.1$ L.mol^{-1}.s^{-1}. The method is quick, easily realizable, and has applications in practice.

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References

1. F. Vlk, Alternative drive of motor vehicles (In Czech), Vlk, Brno, 2004.
2. G. Karavalakis, D. Hilari, L. Givalou, D. Karonis and S. Stournas, *Energy*, 36 (2011) 369.
3. L. F. Capitan-Vallvey, M. C. Valencia and E. A. Nicolas, *Analytica Chimica Acta*, 503 (2004) 179.
4. J. Kulys and I. Bratkovskaja, *Talanta*, 72 (2007) 526.
5. J. Tabart, C. Kevers, J. Pincemail, J. O. Defraigne and J. Dommes, *Food Chemistry*, 120 (2010) 607.
6. A. Versari, G. P. Parpinello, F. Scazzina and D. Del Rio, *Food Control*, 21 (2010) 786.
7. M. Laguerre, L. J. Lopez-Giraldo, J. Lecomte, B. Barea, E. Cambon, P. F. Tchobo, N. Barouh and P. Villeneuve, *Analytical Biochemistry*, 380 (2008) 282.
8. A. Kleckerova, P. Sobrova, O. Krystofova, J. Sochor, O. Zitka, P. Babula, V. Adam, H. Docekalova and R. Kizek, *International Journal of Electrochemical Science*, 6 (2011) 6011.
9. J. Sochor, H. Skutkova, P. Babula, O. Zitka, N. Cernei, O. Rop, B. Krska, V. Adam, I. Provaznik and R. Kizek, *Molecules*, 16 (2011) 7428.
10. M. Medvidovic-Kosanovic, M. Samardzic, N. Malatesti and M. Sak-Bosnar, *International Journal of Electrochemical Science*, 6 (2011) 1075.
11. T. Navratil, E. Kohlikova, M. Petr, M. Heyrovsky, D. Pelclova, K. Pristoupilova, T. I. Pristoupil and Z. Senholdova, *Food Chemistry*, 112 (2009) 500.
12. T. Navratil, E. Kohlikova, M. Petr, D. Pelclova, M. Heyrovsky and K. Pristoupilova, *Physiological Research*, 59 (2010) 431.
13. T. Navratil, M. Petr, Z. Senholdova, K. Pristoupilova, T. I. Pristoupil, M. Heyrovsky, D. Pelclova and E. Kohlikova, *Physiological Research*, 56 (2007) 113.
14. M. Petr, T. Navratil, M. Heyrovsky and E. Kohlikova, *Current Organic Chemistry*, 15 (2011) 3029.
15. J. Karovicova and P. Simko, *Journal of Chromatography A*, 882 (2000) 271.
16. D. Pezo, J. Salafranca and C. Nerin, *Journal of Chromatography A*, 1178 (2008) 126.
17. B. Saad, Y. Y. Sing, M. A. Nawi, N. Hashim, A. S. M. Ali, M. I. Saleh, S. F. Sulaiman, K. M. Talib and K. Ahmad, *Food Chemistry*, 105 (2007) 389.

18. H. Kelebek, S. Selli, A. Canbas and T. Cabaroglu, *Microchemical Journal*, 91 (2009) 187.
19. S. Ramesova, R. Sokolova, I. Degano, M. Hromadova, M. Gal, V. Kolivoska and M. P. Colombini, *Collection of Czechoslovak Chemical Communications*, 76 (2011) 1651.
20. R. Sokolova, I. Degano, S. Ramesova, J. Bulickova, M. Hromadova, M. Gal, J. Fiedler and M. Valasek, *Electrochimica Acta*, 56 (2011) 7421.
21. M. A. Ruiz, E. Garcia-Moreno, C. Barbas and J. M. Pingarron, *Electroanalysis*, 11 (1999) 470.
22. M. Skrinjar, M. H. Kolar, N. Jelsek, A. R. Hras, M. Bezjak and Z. Knez, *Journal of Food Composition and Analysis*, 20 (2007) 539.
23. L. Bianchi, M. A. Colivicchi, L. DellaCorte, M. Valoti, G. P. Sgaragli and P. Bechi, *Journal of Chromatography B*, 694 (1997) 359.
24. V. Shestivska, V. Adam, J. Prasek, T. Macek, M. Mackova, L. Havel, V. Diopan, J. Zehnalek, J. Hubalek and R. Kizek, *International Journal of Electrochemical Science*, 6 (2011) 2869.
25. G. Ziyatdinova, J. Galandova and J. Labuda, *International Journal of Electrochemical Science*, 3 (2008) 223.
26. C. V. Krishnan and M. Garnett, *International Journal of Electrochemical Science*, 6 (2011) 3607.
27. T. Navratil, *Current Organic Chemistry*, 15 (2011) 2996.
28. C. Barus, F. Wetz-Torond, Y. Brunel and P. Gros, *International Journal of Electrochemical Science*, 7 (2012) 5429.
29. D. W. M. Sin, Y. C. Wong, C. Y. Mak, S. T. Sze and W. Y. Yao, *Journal of Food Composition and Analysis*, 19 (2006) 784.
30. I. G. Zigoneanu, L. Wilhams, Z. Xu and C. M. Sabliov, *Bioresource Technology*, 99 (2008) 4910.
31. S. Komorsky-Lovric and I. Novak, *International Journal of Electrochemical Science*, 6 (2011) 4638.
32. M. R. Lee, C. Y. Lin, Z. G. Li and T. F. Tsai, *Journal of Chromatography A*, 1120 (2006) 244.
33. G. H. Shui and L. P. Leong, *Journal of Chromatography A*, 1022 (2004) 67.
34. P. P. Hao, J. R. Ni, W. L. Sun and W. Huang, *Food Chemistry*, 105 (2007) 1732.
35. W. Y. Zhang, C. Y. Wu, C. Y. Wang, Z. J. Yang and L. Liu, *Se Pu*, 20 (2002) 178.
36. Y. Q. Guan, Q. C. Chu, L. Fu, T. Wu and J. N. Ye, *Food Chemistry*, 94 (2006) 157.
37. M. M. Delgado-Zamarreno, I. Gonzalez-Maza, A. Sanchez-Perez and R. C. Martinez, *Food Chemistry*, 100 (2007) 1722.
38. E. I. Korotkova, Y. A. Karbainov and A. Shevchuk, *Journal of Electroanalytical Chemistry*, 518 (2002) 56.
39. O. Bruggemann, A. Visnjevski, R. Burch and P. Patel, *Analytica Chimica Acta*, 504 (2004) 81.
40. K. Robards and S. Dilli, *Analyst*, 112 (1987) 933.
41. S. N. Robledo, M. A. Zon, C. D. Ceballos and H. Fernandez, *Food Chemistry*, 127 (2011) 1361.
42. R. A. Medeiros, B. C. Lourencao, R. C. Rocha and O. Fatibello, *Analytical Chemistry*, 82 (2010) 8658.
43. K. H. G. Freitas and O. Fatibello, *Talanta*, 81 (2010) 1102.
44. S. Abbasi, A. Daneshfar, S. Hamdghadareh and A. Farmany, *International Journal of Electrochemical Science*, 6 (2011) 4843.
45. J. Chylkova, R. Selesovska, J. Machalikova and L. Dusek, *Central European Journal of Chemistry*, 8 (2010) 607.
46. J. Barek, J. Fischer, T. Navratil, K. Peckova, B. Yosypchuk and J. Zima, *Electroanalysis*, 19 (2007) 2003.
47. T. Navratil and J. Barek, *Critical Reviews in Analytical Chemistry*, 39 (2009) 131.
48. B. Yosypchuk, T. Navratil, A. N. Lukina, K. Peckova and J. Barek, *Chemia Analityczna (Warsaw)*, 52 (2007) 897.
49. R. Selesovska-Fadrna, T. Navratil and M. Vlcek, *Chemia Analityczna (Warsaw)*, 52 (2007) 911.
50. L. Bandzuchova and R. Selesovska, *Acta Chimica Slovenica*, 58 (2011) 776.

51. L. Bandzuchova, R. Selesovska, T. Navratil and J. Chylkova, *Electrochimica Acta*, 56 (2011) 2411.
52. R. Selesovska, L. Bandzuchova and J. Chylkova, in T. Navratil, J. Barek (Editors), Modern Electrochemical Methods XXX, Lenka Srsenova-Best Servis, Usti Nad Labem, 2010, p. 163.
53. R. Selesovska, L. Bandzuchova and T. Navratil, *Electroanalysis*, 23 (2011) 177.
54. R. Selesovska, L. Bandzuchova, T. Navratil and J. Chylkova, *Electrochimica Acta*, 60 (2012) 375.
55. M. I. Sabela, N. J. Gumede, P. Singh and K. Bisetty, *International Journal of Electrochemical Science*, 7 (2012) 4918.
56. K. Bisetty, M. I. Sabela, S. Khulu, M. Xhakaza and L. Ramsarup, *International Journal of Electrochemical Science*, 6 (2011) 3631.
57. M. Buckova, J. Labuda, J. Sandula, L. Krizkova, I. Stepanek and Z. Durackova, *Talanta*, 56 (2002) 939.
58. T. Navratil, M. Kopanica and J. Krista, *Chemia Analityczna (Warsaw)*, 48 (2003) 265.
59. T. Navratil, S. Sebkova and M. Kopanica, *Analytical and Bioanalytical Chemistry*, 379 (2004) 294.
60. T. Navratil, B. Yosypchuk and J. Barek, *Chemia Analityczna (Warsaw)*, 54 (2009) 3.