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Differentiation between phenol- and amino-substances in voltammetry determination of synthetic antioxidants in oils

Research Article

Jaromíra Chýlková[1], Renáta Šelešovská[1]*, Jaroslava Machalíková[2] and Libor Dušek[1]

[1]*Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*

[2]*Department of Transport Means and Diagnostics, Jan Perner Transport Faculty, University of Pardubice, CZ-53210 Pardubice, Czech Republic*

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Abstract: The paper describes a method of voltammetric determination of antioxidants in lubricating oils developed with the use of Linear Sweep Voltammetry (LSV) and Fast Scan Differential Pulse Voltammetry (FSDPV). Experimental conditions have been found for simultaneous determination of phenol-based antioxidants and amino-antioxidants: the phenols can be electrochemically oxidized using the polarisation of gold disc electrode (AuDE) in the potential range of 0–1400 mV in 0.2 M H_2SO_4 in the presence of ethanol and acetonitrile at the ratio of 3:1. Secondary aromatic amines can be determined directly in this supporting electrolyte; the presence of phenolic antioxidants does not interfere with this analysis. On the other hand, secondary aromatic amines interfere with the determination of phenolic substances; therefore, the amines present have to be eliminated in a suitable way. A procedure for masking the aromatic amines using their reaction with nitrous acid has been suggested and optimised. The nitrosamines thus formed can be used for sensitive and selective determination of amino-antioxidants by means of cathodic reduction on the hanging mercury drop electrode (HMDE) using Fast Scan Differential Pulse Voltammetry. The method was applied in analysis of real samples of lubricating oils.

Keywords: *Antioxidants • Lubricating oils • Voltammetry • Gold disc electrode*

1. Introduction

Lubricating oils can satisfy the present high demands only if they contain modern additives, which improve their original properties. Antioxidants belong to the group of additives that ensure oxidation stability of oils, slow down their ageing, and restrict formation of undesired substances. During the use of lubricating oils in machines, their antioxidant content decreases, which results in degradation of the oil and, possibly, damage of the lubricated surfaces. Therefore, monitoring the decrease in content of antioxidants in lubricating oils provides a significant parameter for determining their "wear" and/or working life. The low-temperature antioxidants that interrupt the oxidation chain reactions in oils, include substances containing an active hydrogen atom in their molecules. There are antioxidants based on substituted phenols and aromatic amines [1,2]. These and other antioxidants and their mixtures play an important role also in a number of biological processes characterised by the presence of free radicals [3]. Due to their properties, they are also used in the food processing industry, production of pharmaceuticals and cosmetics, where they prevent product decomposition [4,5]. Recently, it has been found that phenol-based antioxidants can exhibit undesirable toxic effects [3,6,7]. Therefore, in a number of countries, the application of some of them was restricted and their content and quality must be tested, particularly in foodstuffs, which requires the necessity of developing precise analytical methods for their determination [8].

* *E-mail: renata.selesovska@upce.cz*

Various analytical methods can be used for determination of antioxidants. A number of published papers described their spectrophotometric [9–13] or spectrofluorimetric determination [14]. Liquid chromatography [15–18] mostly in combination with electrochemical detection [19–21], with diode array detector [22,23] and also with mass spectrometer [24–26] has been applied for these purposes also. Gas chromatography with various detection methods [27–30] is an alternative available way for antioxidants determination. The GC-MS technique [31] or micellar electrokinetic capillary chromatography [32,33] was applied successfully. All the above-mentioned methods were developed in order to determine antioxidants in samples of foodstuffs, pharmaceuticals and cosmetics. They are sufficiently sensitive, but also demanding with regard to instrumentation and costs, they require complex procedures of sample preparation, and they are not suitable for field analyses.

Electrochemical methods represent a suitable alternative because of the relatively low costs of instrumentation, possibility of miniaturization, and particularly the fast and sensitive performance of analysis. Moreover, antioxidants are substances that can be oxidised electrochemically very easily [34,35]. The analysis is to be always performed in an acidic medium, using *e.g.* sulphuric acid [36], perchloric acid [37,38], hydrochloric acid [39] or acetic acid [40], in the presence of an organic solvent, such as ethanol, methanol, benzene, acetone or acetonitrile, or their mixtures [36–40]. Literature also describes applications of various working electrodes. Most papers deal with applications of a glassy carbon electrode both for determination of phenolic antioxidants in foodstuffs, pharmaceuticals and cosmetic [37,41–44] and for determination of synthetic antioxidants in lubricating oils [36,45–49]. Another possibility lies in an application of a platinum electrode [50,51], gold electrode [52,53], carbon-paste electrode [54] or composite electrode [55]. A relatively extensive group of papers deals with applications of miniaturized electrodes, both the carbon-based ones and platinum ones [39,40,56–58]. Independently the working electrodes with chemically modified surfaces have been developed. Modification of carbon electrodes [8,59,60], carbon-paste electrodes [38,61] or polypyrrol electrode [62,63] were described for determination of antioxidants in various types of samples, most often using the complex of nickel phthalocyanine or various polymers. In contrast to chromatography, the electrochemical methods can have the drawback of insufficient selectivity of determination in analyses of antioxidant mixtures. In particular, problems can be encountered if amino- and phenol-based substances have to be determined in their mixture, because the presence of amines in the sample significantly affects the quantitative determination of phenols.

In this paper, we have studied the conditions for reliable determination of particular amino- and phenol-based antioxidants in their mixture in samples of lubricating oils using the gold disc working electrode (AuDE) and hanging mercury drop electrode (HMDE). A procedure for masking aromatic amines in the sample before the determination of phenolic substances has been suggested and optimised.

2. Experimental Procedure

The voltammetric analyses of two selected antioxidants, namely 2,6-di-tert-butyl-4-methylphenol (BHT, 99% purity, AppliChem) and N-phenyl-1-naphthylamine (PNA, 98% purity, Acros Organics), were carried out by means of an electrochemical analyser EP 100 (HSC service, Bratislava) in a three-electrode arrangement. D.C. technique with linear change of potential (linear sweep voltammetry) was utilized for the electrochemical oxidation of antioxidants. The working electrode was in the form of a gold disc (AuDE). It was polarised in the potential range of 0–1400 mV at the scan rate of 40 mV s^{-1}. The cathodic reduction of the nitrosamines, formed in the reaction of secondary aromatic amines with nitrous acid, was carried out using fast scan differential pulse voltammetry (FSDPV) on hanging mercury drop electrode (HMDE). The used indication electrode was polarised in the potential range from -100 mV to -900 mV at the scan rate of 40 mV s^{-1}; pulse amplitude 30 mV, pulse length 60 ms. The reference electrode was silver/silver chloride electrode with a liquid bridge filled with 1M $NaNO_3$; the auxiliary electrode was made of platinum wire.

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

3. Results and Discussion

The acidic medium proved to be the most suitable for determination of analysed antioxidants, because the concentration of analysed substances could be decreased in an alkaline medium due to the enhanced reactivity of phenols and aromatic amines

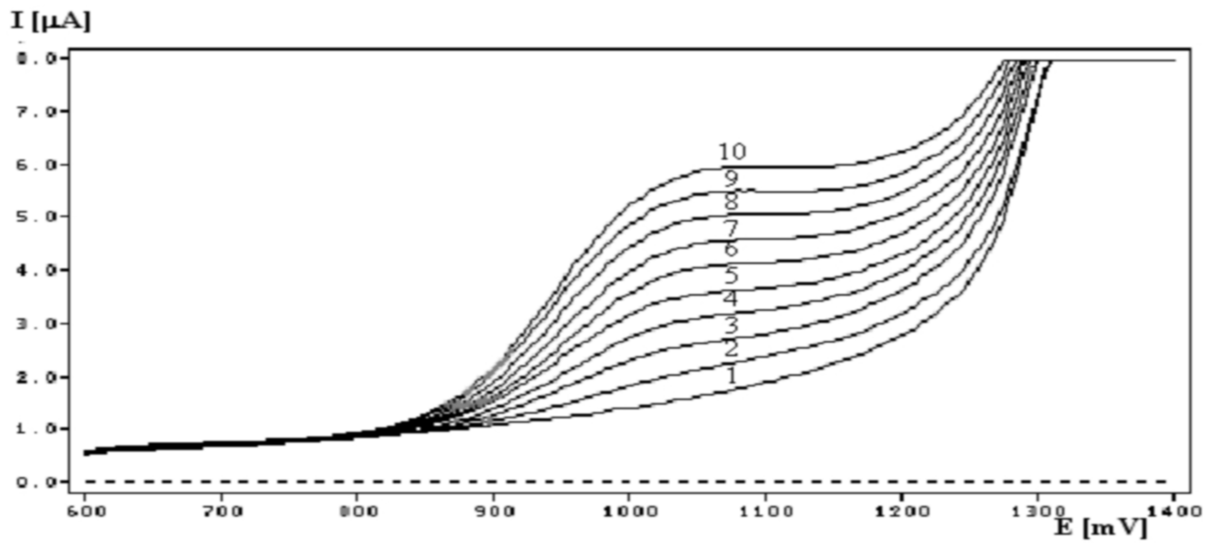

Figure 1. Dependence of oxidation peak height on concentration of BHT. Experimental conditions: LSV-AuDE, supporting electrolyte – 0.2 M H_2SO_4 + ethanol:acetonitrile (3:1), E_{in} = 0 mV, E_{fin} = + 1400 mV, v = 40 mV s^{-1}, 1 – pure supporting electrolyte, 2 – 7.3 μg BHT mL^{-1}, 3 – 14.6 μg BHT mL^{-1}, 4 – 21.9 μg BHT mL^{-1}, 5 – 29.2 μg BHT mL^{-1}, 6 – 36.5 μg BHT mL^{-1}, 7 – 43.8 μg BHT mL^{-1}, 8 – 51.1 μg BHT mL^{-1}, 9 – 58.4 μg BHT mL^{-1}, 10 – 65.7 μg BHT mL^{-1}.

in their reactions with other components of the sample. Furthermore, it was necessary to ensure the solubility of the analysed substances in the supporting electrolyte by the presence of a suitable organic solvent.

3.1. Determination of phenolic antioxidants

At first, the determination of BHT was tested in the media containing from 0.03 M of H_2SO_4 to 0.33 M of H_2SO_4 in the presence of ethanol. Concentration of the analysed BHT was increased from the value of 7.33 μg mL^{-1} to the value of 66 μg mL^{-1} of the solution in the polarographic vessel. The sensitivity of determination did not substantially change with the acidity of the electrolyte; however, the half-wave potential, $E_{1/2}$, shifted from the value of +1100 mV (in 0.03 M of H_2SO_4) to the value of +825 mV (in 0.33 M of H_2SO_4). At the same time, the anodic curves in more acidic media exhibited a more distinct maximum corresponding to the oxidation of BHT. Linear dependence of the height of waves on the concentration of BHT was recorded in the concentration range of sulphuric acid from 0.17 to 0.27 mol L^{-1}. Secondly, the influence of ethanol content in electrolyte was investigated. Its amount was changed in range from 93 wt% to 64 wt% (under constant acidity of the solution - 0.2 M of H_2SO_4). For the following analyses, the supporting electrolyte with the composition of 0.2 M of H_2SO_4 and 77 wt% ethanol was chosen as the optimum. Under these conditions, the measured waves were well developed and evaluated, the equation of calibration curve had the following form: I = 2471c – 0.59, where I is the wave height in μA, and c is the concentration of BHT in μg mL^{-1}. The correlation coefficient was amounted to 0.9988.

Similarly, we also tested the voltammetric determination of BHT in the other organic solvent – acetonitrile. The achieved sensitivity of the determination is somewhat higher, the waves were found near to more positive potentials (about 1100 mV) and the half-wave potential, $E_{1/2}$, was only slightly dependent on acidity of the solution analysed. The linearity of the dependence between wave height and analysed concentration of BHT was found in a broader interval of acidities of the supporting electrolyte, from the concentration as low as 0.03 M of H_2SO_4 to the concentration of 0.23 M of H_2SO_4. The concentration range of acetonitrile was from 66 wt% to 96 wt%. The waves from ethanolic media were evaluable in an easier way in comparison with acetonitrile medium. However, acetonitrile seems to be more suitable solvent for the analysed substances. The most suitable ratio of ethanol:acetonitrile was experimentally tested too. On the basis of all results, we chose the following supporting electrolyte for the determination of phenolic antioxidants as the most suitable: 0.2 M of H_2SO_4 in the mixture of ethanol and acetonitrile in the ratio of 3:1. Under these conditions, the recorded waves can be evaluated easily, their heights depend linearly on the BHT concentration in the sample. The equation of the calibration curve had the following form: I = 2352c + 0.1673, where I is the wave height in μA, and c is the concentration of BHT in μg mL^{-1} of the solution analyzed. The correlation coefficient was amounted to 0.9998. Fig. 1 presents an example of the concentration dependence of BHT in the concentration interval from

7.33 μg mL^{-1} to 66.00 μg mL^{-1} of the solution, which was recorded under suggested conditions on the gold disc electrode.

Accuracy and precision of voltammetric determination of BHT under the conditions suggested were tested by means of ten repeated analyses of a model solution of known concentration, 18.33 μg mL^{-1}, using the method of two standard additions. The results were evaluated according to the wave heights as well as according to the peak areas. The statistical evaluation using the Adstat program [64] showed that the evaluation of results based on the wave heights is more precise and accurate because the average calculated value is 17.67 μg of BHT mL^{-1}, the standard deviation has the value of 0.93 μg of BHT mL^{-1}, the 95% confidence interval has the lower limit at 17.0 μg of BHT mL^{-1} and the upper limit at 18.4 μg of BHT mL^{-1}. The evaluation of results by means of the peak areas gives the average determined value of 20.0 μg of BHT mL^{-1}, the standard deviation of 1.3 μg of BHT mL^{-1}, and the 95% confidence interval has the lower limit at 19.1 μg of BHT mL^{-1} and the upper limit at 21.0 μg of BHT mL^{-1}. These results show that the method of evaluation using the peak areas (which is recommended in a number of published papers) is encumbered with a systematic error. The calculated mean lies outside the confidence interval.

The method developed was also verified using a model real sample prepared by adding a known amount of BHT (namely 200 mg per 100 g) to oil. The analyses of the original oil gave an average of 104 mg of BHT per 100 g, while the analysis of the oil after the addition gave a value of 315.5 mg per 100 g. The difference of these values shows that the amount of BHT added to the oil was determined with an error of +5.8%, which is acceptable for such a demanding process that includes the isolation of BHT from the oil.

3.2. Determination of phenolic antioxidants and amino-antioxidants in their mixture

Real samples of oils often contain several types of antioxidants. In the model mixtures studied, we chose BHT as the representative of phenolic antioxidants, and PNA (N-phenyl-1-naphthylamine) as the representative of secondary aromatic amines.

A series of experiments carried out showed that in the case of analysis of a mixture of antioxidants, it is more appropriate to work in an acidic medium in the presence of acetonitrile, because the waves of anodic oxidation of the antioxidants mentioned above are distinguished more clearly in this medium, which facilitates the evaluation. The half-wave potentials, $E_{1/2}$, are +805 and +1070 mV for PNA and BHT, respectively, in the supporting electrolyte containing 0.2 M of H_2SO_4 in the presence of the 79.2 wt% acetonitrile, while in the medium of 0.2 M of H_2SO_4 and 76.8 wt% ethanol, the waves are closer to each other, namely $E_{1/2}^{PNA}$ is +815 mV and $E_{1/2}^{BHT}$ is +970 mV. The determination of the antioxidants based on secondary aromatic amines mixed with BHT in the suggested supporting electrolyte can use the equation of the linear calibration curve in the following form: $I = 1131c + 1.38$, where I is the wave height in μA, and c is the concentration of PNA in μg mL^{-1} of the analysed solution. The correlation coefficient is 0.9931. An example of the anodic oxidation curves obtained for the PNA concentration is presented in Fig. 2 and shows an increase from 34.7 μg mL^{-1} to 246.7 μg mL^{-1} at a constant concentration of BHT, 16.1 μg mL^{-1}.

Furthermore, a more detailed inspection of the curves obtained from a voltammetric analysis of a mixture of low-temperature antioxidants showed that the presence of a comparable concentration of amino-antioxidant affects the determination of BHT. This is caused by the fact that the wave of PNA exhibits a distinct maximum with a descending section superimposed onto the ascending section of the BHT peak. The result is a less developed wave corresponding to the oxidation of BHT with the height being decreased, which leads to a negative error in the quantitative determination of phenolic antioxidants. Therefore, our next research activity was focused on the specification of conditions that would eliminate the effect of amino-antioxidants upon the determination of BHT. It was found that in this case that it is possible to solve this problem by application of the reaction of secondary aromatic amines with $NaNO_2$ in an acidic medium, which produces the corresponding nitrosamines: these have different electrochemical properties and do not interfere with the analysis of BHT. The reaction course is presented schematically in Fig. 3. The resulting reaction product (N-nitroso derivative of secondary aromatic amine) is yellow.

This experimental approach is documented in Fig. 4, which gives the voltammetric curve of anodic oxidation of a mixture of PNA and BHT (curve 2) and also the time-dependence curves obtained after the addition of $NaNO_2$. The figure demonstrates that the wave corresponding to PNA decreases with time until it completely disappears. At the same time, it is obvious that the wave of the nitrite present overlaps with the wave of anodic oxidation of BHT. Therefore, it is necessary to remove the excess nitrous acid after its reaction with PNA is completed,: this is achieved for example by means of bubbling, purging

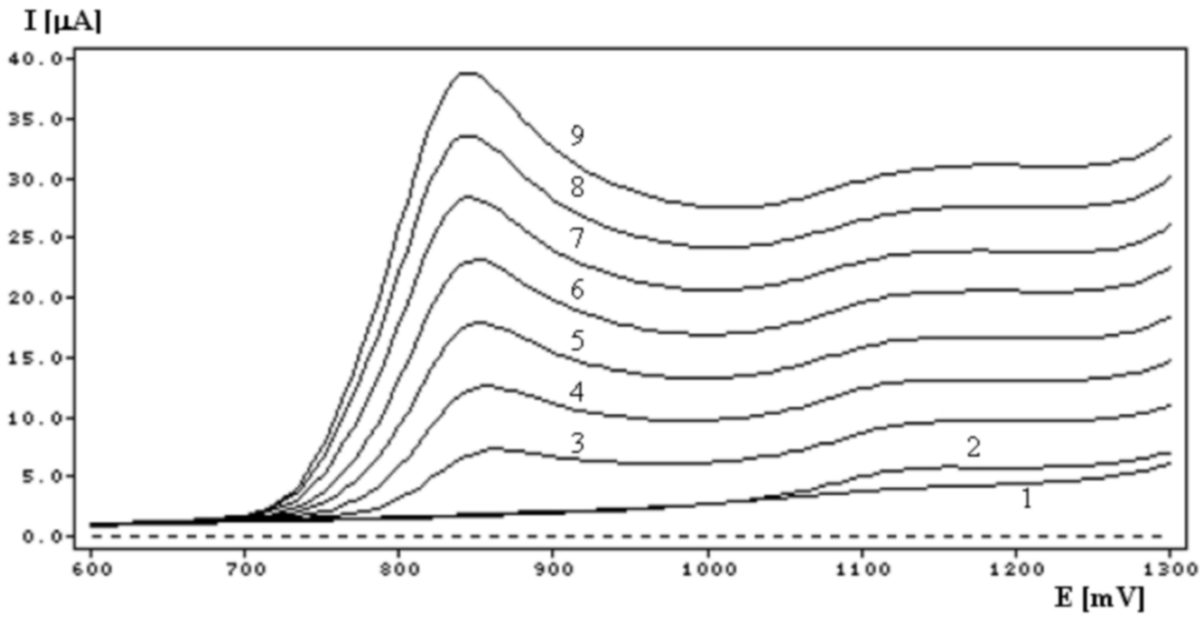

Figure 2. Dependence of oxidation peak height on concentration of PNA. Experimental conditions: LSV-AuDE, supporting electrolyte – 0.2 M H_2SO_4 + 79.2 wt% acetonitrile, E_{in} = 0 mV, E_{fin} = +1400 mV, v = 40 mV s^{-1}, 1 – pure supporting electrolyte, 2 – 16.1 µg BHT mL^{-1}, 3 – 16.1 µg BHT mL^{-1} + 34.7 µg PNA mL^{-1}, 4 – 16.1 µg BHT mL^{-1} + 69.4 µg PNA mL^{-1}, 5 – 16.1 µg BHT mL^{-1} + 104.1 µg PNA mL^{-1}, 6 – 16.1 µg BHT mL^{-1} + 138.8 µg PNA mL^{-1}, 7 – 16.1 µg BHT mL^{-1} + 173.5 µg PNA mL^{-1}, 8 – 16.1 µg BHT mL^{-1}+ 208.2 µg PNA mL^{-1}, 9 – 16.1 µg BHT mL^{-1} + 242.9 µg PNA mL^{-1}.

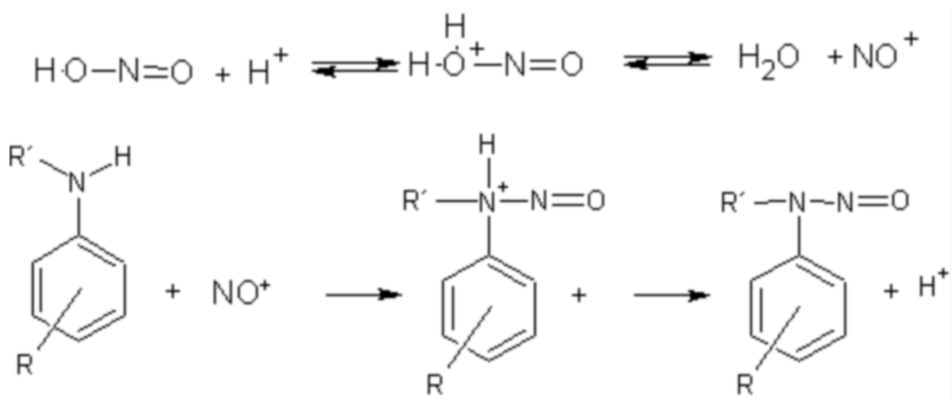

Figure 3. Scheme of reaction of secondary aromatic amines with nitrous acid

of the analysed solution with an inert gas, such as argon. The voltammetric analysis of a sample modified in the way described above provides a wave that represents the oxidation of BHT only. The determination was carried out in the supporting electrolyte containing 0.2 M of H_2SO_4 and acetonitrile; c_{BHT} was 32.0 µg mL^{-1}, c_{PNA} was 69.3 µg mL^{-1}. The amount of nitrite added to the solution analysed was 92.7 µg of $NaNO_2$ mL^{-1}. Curve 1 represents the record of the supporting electrolyte, curve 2 is the voltammogram of the mixture of BHT and PNA: this curve clearly shows the influence of the amino-antioxidant present on the BHT wave. The curves without numbers show a gradual decrease in the PNA oxidation wave with time (the time of reaction with nitrous acid), and curve 3 corresponds to the anodic oxidation of BHT after complete elimination of PNA from the analysed solution.

The suitable amount of nitrite needed for the elimination of PNA from the sample containing BHT in the medium of the supporting electrolyte composed of 0.2 M of H_2SO_4 and 79.2 wt% acetonitrile was found through experimentation. Fig. 5 presents the dependences of the rate of decrease in the PNA wave for various added amounts of nitrite. The figure shows that the larger this amount is, the faster the PNA wave decreases. Complete removal of 73.3 µg of PNA mL^{-1} requires 93.3 µg of $NaNO_2$ per ml of the solution analysed, but it is worth mentioning that a successful determination of BHT does not require the 100% elimination of PNA. It is sufficient if the PNA effect is only minimised.

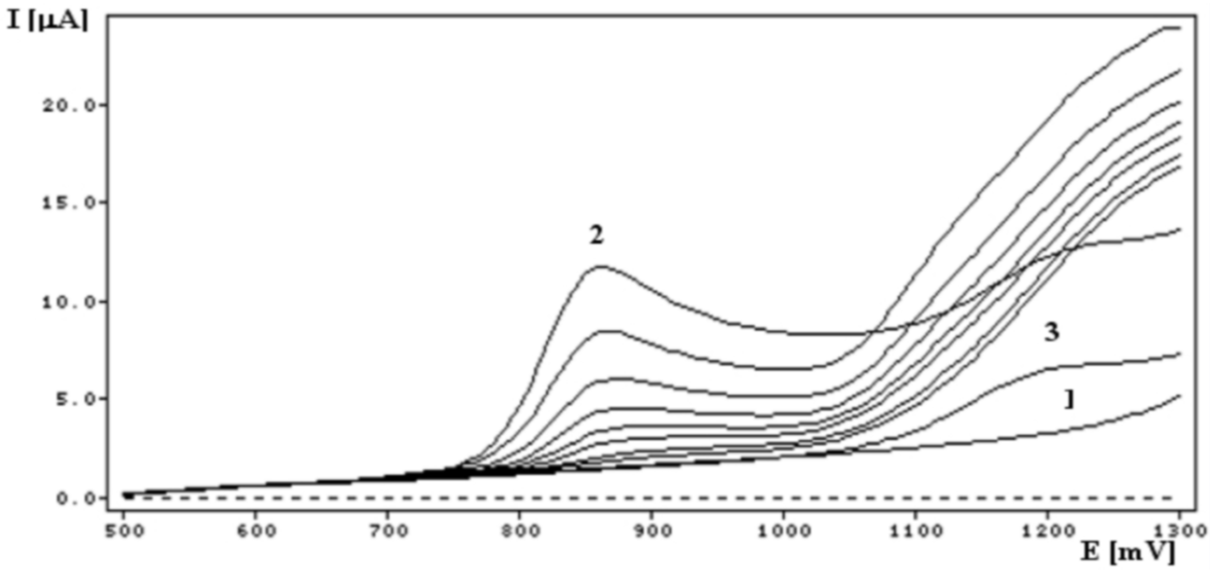

Figure 4. Evolution of anodic curves during the process of PNA elimination. Experimental conditions: LSV-AuDE, supporting electrolyte – 0.2 M H_2SO_4 + 79.2 wt% acetonitrile , E_{in} = 0 mV, E_{fin} = +1400 mV, v = 40 mV s^{-1}, c(BHT) = 32.0 μg mL^{-1}, c(PNA) = 69.3 μg mL^{-1}, c($NaNO_2$) = 92.7 μg mL^{-1}; 1 – pure supporting electrolyte, 2 – mixture of BHT and PNA, 3 – the same mixture after the complete elimination of PNA by addition of $NaNO_2$ and after the bubbling the solution with argon, unnumbered – curves after the addition of $NaNO_2$, gradual decrease in the PNA oxidation wave with time.

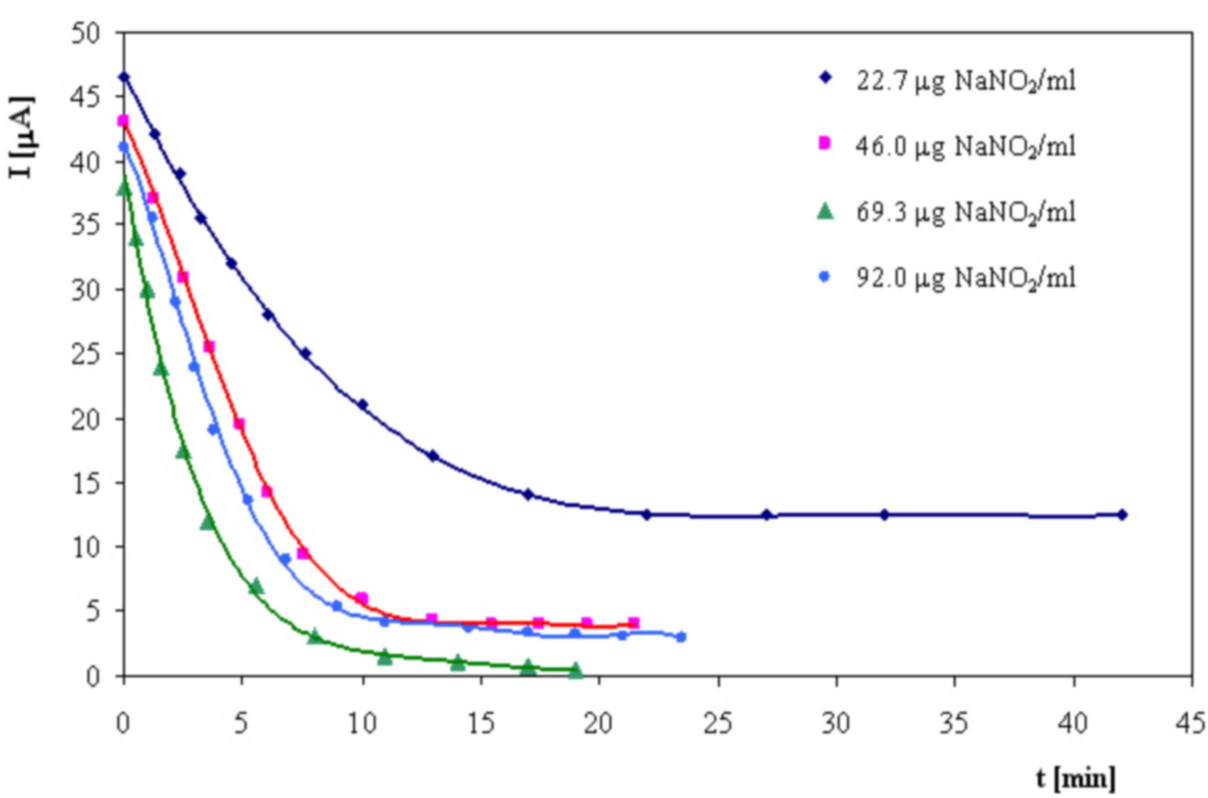

Figure 5. Time-dependence of peak height of anodic oxidation of PNA with various amounts of added $NaNO_2$

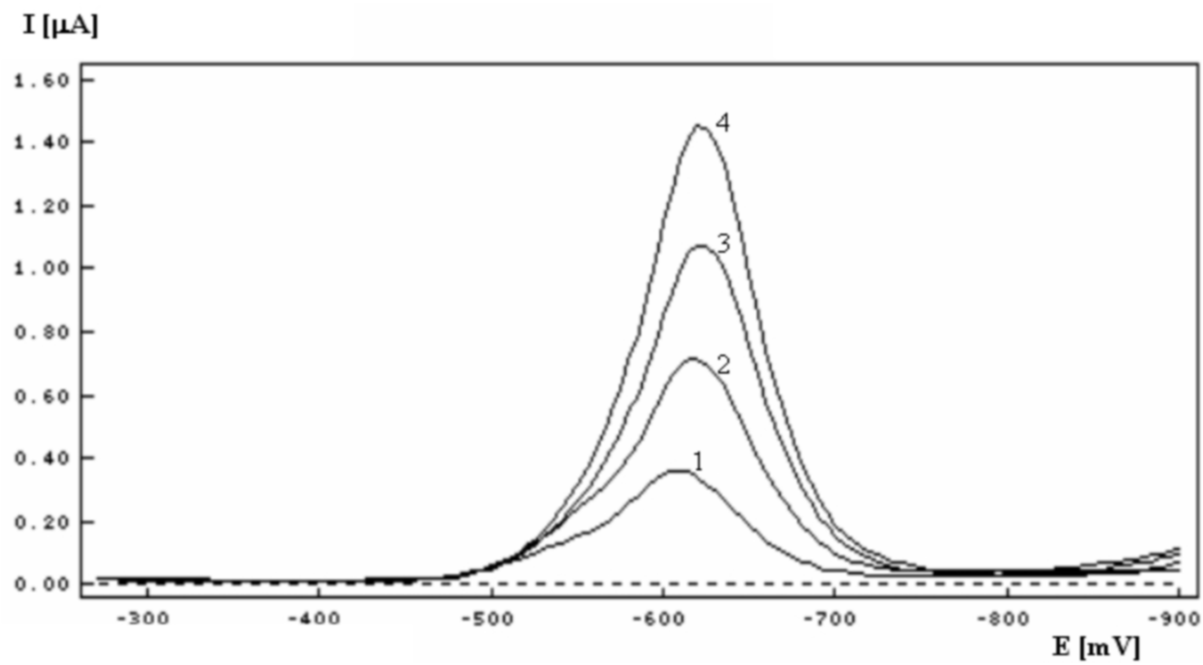

Figure 6. Dependence of reduction peak height of N-nitroso-N-phenyl-1-naphthylamine on concentration of PNA. Experimental conditions: FSDPV-HMDE, supporting electrolyte – 0.2 M H_2SO_4 + 79.2 wt% acetonitrile, E_{in} = -100 mV, E_{fin} = -900 mV, v = 40 mV s^{-1}, c($NaNO_2$) = 92.7 µg mL^{-1}, 1 – 14.9 µg PNA mL^{-1}, 2 – 29.8 µg PNA mL^{-1}, 3 – 44.8 µg PNA mL^{-1}, 4 – 59.6 µg PNA mL^{-1}.

Table 1. Results of determination of BHT in the presence of an increasing concentration of PNA without the elimination of the amino-antioxidant and after its removal

Number of measurement	Concentration of PNA in solution [µg mL^{-1}]	Error of determination of BHT in the presence of PNA [%]	Error of determination of BHT after elimination of PNA [%]
1	18.3	–19.2	–9.62
2	36.5	–30.0	8.93
3	54.8	–31.8	–11.7
4	73.1	–35.4	5.96
5	91.3	–56.0	–1.4
6	109.6	–53.7	0.02

Table 1 gives the results of determining the model solution of BHT with the concentration of 64.1 µg mL^{-1} in the presence of increasing concentrations of PNA without its removal and after an addition of nitrite. The table indicates an unambiguous conclusion that the presence of an amino-antioxidant in an amount comparable with that of BHT in the analysed sample affects the determination of BHT; the obtained results are lower. Therefore, the procedure of an amino-antioxidant elimination suggested above is inevitable for obtaining correct values of the content of the phenolic antioxidant.

3.3. Determination of amino-antioxidants after their transformation into nitrosamines

The reaction of antioxidants of the type of secondary aromatic amines with nitrous acid can also be used for a sensitive and selective determination of these amines. The nitrosamines formed can be reduced on the mercury drop electrode making use of modern voltammetric techniques. Fig. 6 presents voltammetric curves obtained by means of the FSDPV method using mercury drop indication electrode (HMDE) for increasing amounts of PNA, which varied from 14.9 µg mL^{-1} to 59.5 µg mL^{-1} of the solution analysed in the polarographic vessel. The supporting electrolyte was composed of 0.2 M of H_2SO_4 and 79.2 wt% acetonitrile. Together with the additions of PNA, $NaNO_2$ was added to the analysed solution as well. After completing the reaction, the excess nitrous acid was removed by means of bubbling with inert gas.

Table 2. Comparison of results of voltammetric and IR-spectrophotometric determination of BHT in samples of real oils (A – bearing oil, B – turbine oil)

Number of oil sample	BHT determined voltammetrically [mg/100 g of oil]	BHT determined by IR spectrometry [mg/100 g of oil]	Note
1	95.6	90	A
2	130.5	130	A
3	67.7	90	A
4	265.6	230	B
5	183.7	170	A

Both the figure and subsequent statistical treatment show that both the peak height and the peak area exhibit a linear dependence on the amount of analysed substance, so they can be used for the determination. The equation of the calibration curve using the peak height has the following form: I = 3647c – 0.85, where I is the peak height of cathodic reduction of N-nitroso-N-phenyl-1-naphthylamine in μA and c is the concentration of PNA in μg mL^{-1}. The correlation coefficient is 0.9998. The equation of the calibration curve using the peak area has the following form: S = 1869c + 0.49, where S is the peak area and c is the concentration of PNA in μg mL^{-1}. The correlation coefficient is 0.9999.

The suggested method of voltammetric determination of antioxidants in oils was applied to five real samples of oils. These samples were found to contain the antioxidant BHT only. Therefore, AuDE was used for its determination. Found amounts are summarised in Table 2. The table also presents the results obtained by using an independent method of IR spectrophotometry. The differences that appear in some results can be caused for example by the way of collecting the samples or by imperfect homogenization of samples.

4. Conclusions

The aim of this work was to suggest and optimise the procedure of determination of phenolic antioxidants and amino-antioxidants in their mixtures present in lubricating oils. Conditions were optimised for the determination of the phenolic antioxidant BHT on gold disc electrode in acidic medium of 0.2 M H_2SO_4 with the addition of ethanol and acetonitrile in the ratio of 3:1. The results were verified by a repeated determination of BHT in the sample prepared from a standard solution (ten repeated analyses gave the relative standard deviation RSD = 5.3%) and also by a determination of known additions of BHT to a real oil sample after its extraction with ethanol (the error varied around 5%). The same experimental conditions can also be used for the determination of amino-antioxidants, in particular of PNA.

Since the antioxidants in oils can be present as mixtures, analyses were also performed with a mixture of phenolic antioxidants (BHT) and amino-antioxidants (PNA). It was found that the presence of amino-compounds affects the determination of BHT significantly: the amounts determined by the analyses are lower than the actual ones. A procedure has been suggested for eliminating the aromatic amines from the sample before performing the proper determination of phenolic substances. This elimination is based on the known reaction of amines with sodium nitrite in an acidic medium giving the corresponding nitrosamines. Since nitrosamines have electrochemical properties that are significantly different from those of the amino-antioxidants, they do not interfere with the determination of BHT. In addition to that, nitrosamines easily undergo a reduction on the hanging mercury drop electrode, which can be used for a very sensitive and selective determination of amino-antioxidants. The whole procedure of elimination of the interfering amino-compounds, determination of phenolic antioxidants on a gold disc electrode, and subsequent determination of nitrosamines (*i.e.*, amino-antioxidants) on the mercury electrode can be performed in a single solution by merely exchanging electrodes.

In conclusion, it can be stated that the developed method of voltammetric determination of antioxidants in oils, is be useful in practice. It can be used by manufacturers for checking the quality of their products or, in broader context, for monitoring the "wear" and/or working life of oils, which can contribute to better economy, decreasing the amount of waste, and burden to the environment.

Acknowledgments

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