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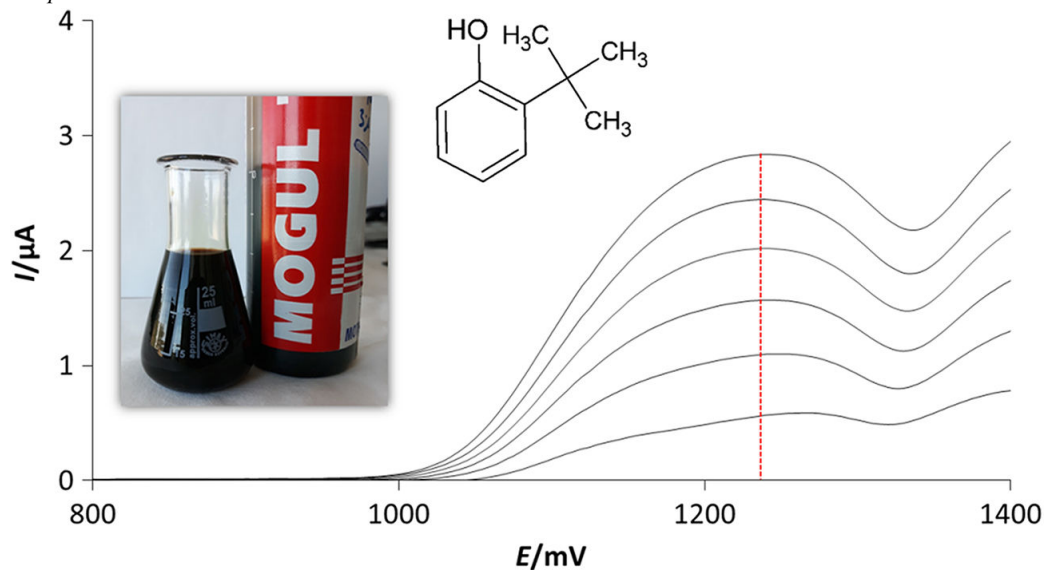
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Abstract:

Simple voltammetric method for practical determination of an antioxidant 2-*tert*-butylphenol (2-TBF) was developed using gold disk working electrode and linear sweep voltammetry. 2-*tert*-Butylphenol provided one anodic signal at about +1300 mV in the environment of ethanolic solution of H₂SO₄. A non-linear growth of the response with added amount of 2-*tert*-butylphenol was observed, and low detection (LOD = 0.67 µg cm⁻³) and quantification limit (LOQ = 2.22 µg cm⁻³) were obtained. Applicability was verified by analysis of samples of mineral and synthetic oils.

Graphical Abstract:



Keywords (separated by '-') Antioxidant - 2-*tert*-Butylphenol - Voltammetry - Gold disk electrode - Electrochemistry - Cyclic voltammetry

Footnote Information



New voltammetric method for rapid determination of phenolic antioxidant 2-*tert*-butylphenol in synthetic oils using gold electrode

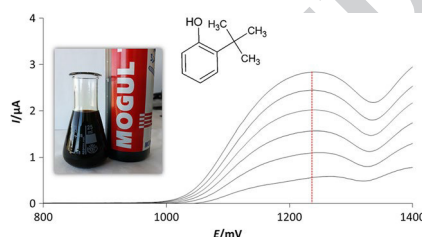
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Abstract

Simple voltammetric method for practical determination of an antioxidant 2-*tert*-butylphenol (2-TBF) was developed using gold disk working electrode and linear sweep voltammetry. 2-*tert*-Butylphenol provided one anodic signal at about +1300 mV in the environment of ethanolic solution of H₂SO₄. A non-linear growth of the response with added amount of 2-*tert*-butylphenol was observed, and low detection (LOD = 0.67 μg cm⁻³) and quantification limit (LOQ = 2.22 μg cm⁻³) were obtained. Applicability was verified by analysis of samples of mineral and synthetic oils.

Graphical Abstract



Keywords Antioxidant · 2-*tert*-Butylphenol · Voltammetry · Gold disk electrode · Electrochemistry · Cyclic voltammetry

Introduction

Commercially available fuels like gasoline, aviation fuel, or biodiesel, and other petroleum products such as lubricating oils, are unstable without additives. The main reason of their degradation is oxidation caused especially by the air oxygen. The oxidatively degraded petroleum products lose very fast their utility features; therefore, suitable additives including antioxidants (AOs) are commonly employed to ensure the stable properties [1–3]. One of the synthetic phenolic

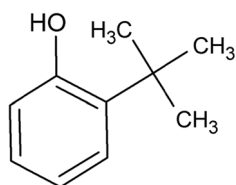
AOs—2-*tert*-butylphenol (2-TBF, Fig. 1) [4–7], which is applied in, e.g., navy mobility fuels, aviation fuels, or bio-diesels [8–10] in mixture with other AOs, was studied in the present paper. Some analytical tools like negative ion mobility spectrometry–mass spectrometry [7], gas chromatography–mass spectrometry [8, 11, 12], and high-performance liquid chromatography [13], have been already utilized for 2-TBF determination. As we described in our previous papers, e.g. [14–19], electrochemical techniques, especially voltammetry in combination with solid electrodes, represent simple, time- and costs-saving approach for determination of AOs even in mixtures or in samples with complicated matrices like mineral and synthetic oils or biofuels. Voltammetric behavior of 2-TBF and simple method for its determination are for the first time described in the present paper. Moreover, resolution of voltammetric signals of the most applied antioxidant BHT (butylated hydroxytoluene), which has similar structure as 2-TBF, and 2-TBF is examined as well. Gold disk electrode was chosen

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Fig. 1 The structure formula of 2-*tert*-butylphenol



44 as an indicative electrode due to its favorable user properties
45 and wide applicable utilization.

46 Results and discussion

47 Choice of the supporting electrolyte

48 The choice of the supporting electrolyte plays a crucial
49 role in the optimization process. Ethanolic solutions (86%)
50 of different pH ensured by 0.16 mol dm⁻³ H₂SO₄, 0.1 and
51 0.01 mol dm⁻³ NaOH, and 0.1 mol dm⁻³ acetate buffer of pH
52 5.5, respectively, were examined for analysis of 2-TBF. Linear
53 sweep voltammetry was applied for this set of experiments. It
54 was found that 9.63 μg cm⁻³ 2-TBF provided one significant
55 anodic signal, corresponding to the oxidation of the hydroxyl
56 group, in all of the tested supporting electrolytes. One poorly
57 developed signal could be observed more positively, espe-
58 cially at higher concentration levels, but due to its shape and
59 position, it was not suitable for analytical purposes and was
60 not further examined. Next, concentration dependence from
61 9.63 to 35.53 μg cm⁻³ (0.1 mol dm⁻³ NaOH), 57.22 μg cm⁻³
62 (0.16 mol dm⁻³ H₂SO₄), and 85.33 μg cm⁻³ 2-TBF (acetate
63 buffer, 0.01 mol dm⁻³ NaOH), respectively, was recorded.
64 The highest, the best developed, reproducible, stable, and
65 easily evaluable wave was recorded in the acidic medium of
66 sulfuric acid. Stable and reproducible response was also mea-
67 sured in the acetate buffer but its shape did not allow correct
68 evaluation. The alkaline medium was ensured by two differ-
69 ent concentrated solutions of NaOH. Non-reproducible and
70 only poorly evaluable signal of 2-TBF was recorded in both of
71 them. Moreover, turbidity of the solution in the polarographic
72 cell, which increased with concentration of NaOH and time
73 of the analysis, was observed. The less concentrated solution
74 of NaOH allowed to register the concentration dependence of
75 2-TBF but in rapid sequence. Non-linear course of the con-
76 centration dependence was observed in all cases; therefore,
77 the software **Nonlinear** [19] was applied for the correct evalua-
78 tion. The calibration curves could be described by following
79 Eq. (1) for H₂SO₄, Eq. (2) for acetate buffer, and Eq. (3) for
80 0.01 mol dm⁻³ NaOH, where *c* is in μg cm⁻³ and *I_p* is in μA:

$$I_p = 9.54 \times 10^{-5} c^2 + 5.42 \times 10^{-2} c + 7.64 \times 10^{-2}, \quad (1)$$

$$I_p = 1.18 \times 10^{-4} c^2 + 4.62 \times 10^{-2} c + 4.93 \times 10^{-2}, \quad (2)$$

$$I_p = 1.35 \times 10^{-4} c^2 + 4.17 \times 10^{-2} c + 1.19 \times 10^{-1}. \quad (3)$$

84 Calculated LOD and LOQ are summarized in Table 1. It
85 is obvious that the best results were obtained from measure-
86 ments in the environment of sulfuric acid as well. LOD and
87 LOQ, respectively, obtained for acetate buffer are compar-
88 able but the obtained signal was poorly evaluable. Consider-
89 ing the above-mentioned facts, the supporting electrolyte
90 consisting of 86% ethanol and 0.16 mol dm⁻³ H₂SO₄ was
91 selected for further examination.

92 Quantitative analysis of 2-*tert*-butylphenol in oil 93 samples

94 In our previous research [16], we found, that direct analysis
95 of the oils containing AOs is impossible due to the cover-
96 age of the working surface of the indicative electrode by
97 the matrix. Thus, the extraction is a necessary step before
98 the analysis. Determination of 2-TBF in model samples of
99 the oils was 5 times repeated and the obtained results are
100 summarized in Table 2. The outcomes confirmed properly
101 designed extraction and determination procedure, respec-
102 tively. Example of the determination of 2-TBF in ethanolic
103 extract of the oil matrix of N10H is displayed in Fig. 2.

104 Identification of 2-TBF in the presence of BHT

105 BHT is one of the most applied antioxidants in general. Thus,
106 we decided to study influence of its presence on voltammetric
107 response of 2-TBF and its possible identification. BHT (tested
108 concentration range of 9.12–80.83 μg cm⁻³) provided one sig-
109 nal at ca. +940 mV under our used conditions of analysis.
110 Its response could be found about 200 mV more positively
111 than 2-TBF response. After addition of 2-TBF on the same

Table 1 LOD and LOQ of 2-TBF determination in the used support-
ing electrolytes

	0.16 mol dm ⁻³ H ₂ SO ₄	Acetate buffer pH 5.5	0.01 mol dm ⁻³ NaOH
LOD/μg cm ⁻³	0.670	0.730	1.10
LOQ/μg cm ⁻³	2.22	2.46	3.68

Table 2 Results of 5 repeated determinations of 2-TBF in ethanolic
extracts of the oils

Analyzed sample	Added/ (g/100 g oil)	Determined/ (g/100 g oil)	Recovery/ %	RSD/ %
N10A	0.97	0.97 ± 0.08	91.75–108.3	7.87
N10H	1.02	1.09 ± 0.03	103.9–109.8	4.12
MES15	1.04	1.02 ± 0.03	95.19–100.9	3.80

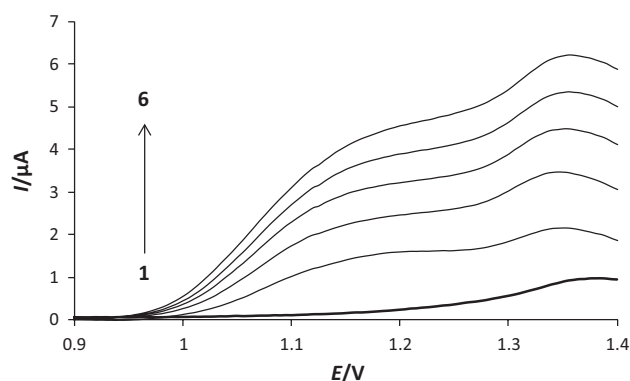


Fig. 2 Linear sweep voltammetric curves of determination of 2-TBF in the ethanolic oil extract of N10H recorded on gold disk electrode in ethanolic solution of $0.16 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. 1—curve of the sample; 2–6—curves of the standard additions of 2-TBF, all curves are after baseline correction

concentration level as BHT, it was obvious that the resolution of both compounds is possible. Moreover, 2-TBF wave (non-linearly) increased with its added amount. The ethanolic extract of the oil sample OL-J3 containing BHT was prepared using the procedure described in “Experimental” part. The determined amount of BHT (0.2%), which was obtained as a result of 5 repeated determinations (RSD=4.6%) was confirmed by the producer of the oil as accurate. After addition of 2-TBF, a new significant and well-separated signal of its oxidation was observed. Thus, it could be concluded that oxidation of 2-TBF could be recorded even in the presence of BHT.

Conclusion

Voltammetric method for precise and accurate determination of the antioxidant 2-*tert*-butylphenol was presented in the paper. It was found that 2-TBF provided one anodic signal suitable for analytical purposes, which could be recorded in wide pH range. Ethanolic solution of $0.16 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was selected for further measurements due to the obtained stable, repeatable, and easily evaluable response of 2-TBF. Applicability of the developed approach was verified by analysis of model oil samples with excellent results. The proposed method is a simple but sensitive tool for routine analysis of AOs in the petroleum products. Moreover, it allows recognition of 2-TBF in the presence of one of the most used antioxidants—BHT.

Experimental

The stock solutions of 2-TBF and BHT (both Sigma Aldrich, purity of $\geq 99\%$), respectively, were prepared by dissolution of the solid substance in 96% ethanol (Penta, Prague, Czech Republic) every week. Supporting electrolytes were created

by mixture of ethanol (Penta, Prague, Czech Republic) and diluted sulfuric acid (prepared from 96% H_2SO_4 from Penta, Prague, Czech Republic), solution of NaOH (prepared from the solid substance of 98% purity originated from Penta, Prague, Czech Republic) or acetate buffer of pH 5.5 (mixture of sodium acetate (Penta, Prague, Czech Republic) and diluted acetic acid (99%, Lach-ner, Neratovice, Czech Republic)). All solutions were stored in refrigerator at about 4°C .

Preparation of samples

Model samples of oils were prepared by adding about 200 mg of solid 2-TBF into 25 cm^3 volumetric flask with ca. 20 g of an oil, particularly 180.0 mg of 2-TBF and 18.56 g of base oil N10A, 204.4 mg of 2-TBF and 20.04 g of N10H oil, and 202.0 mg of 2-TBF and 19.42 g of MES 15 oil. Samples prepared this way were homogenized for 10 min in the ultrasonic bath and were stored in a refrigerator overnight. Extraction of the prepared samples and of the oil OL-J3 containing BHT was performed in the following way. About 4 g of the sample, particularly 3.747 g of N10A, 3.924 g of N10H, 3.944 g of MES15, and 4.008 g of OL-J3, respectively, were added to 25-cm^3 volumetric flask with 20 cm^3 of 96% ethanol and placed in the ultrasonic bath for 10 min. The created emulsion was left at rest. After 1 h, the upper ethanolic layer was transferred into a glass tube. Anhydrous Na_2SO_4 (2–3 g, p.a. purity, Lachema, Brno, Czech Republic) was put into the glass tube to break down the emulsion. The glass tube with the emulsion was left at rest in a refrigerator overnight and the last residues of the oil were removed by filtering through a paper filter.

Instrumentation

All of the voltammetric measurements were carried out by computer-controlled electrochemical analyzer EP 100 (HSC Servis, Bratislava, Slovak Republic) in three electrode set-up, where a gold disk electrode with diameter of 3 mm (AuDE, HSC Servis, Bratislava, Slovak Republic) served as a working electrode, saturated Ag|AgCl|KCl as a reference and platinum wire as an auxiliary electrode (both Monokrystaly, Turnov, Czech Republic).

Measurement procedure

Linear sweep voltammetry (LSV) was utilized as a measuring method. The oxidation of 2-TBF was recorded from 0 mV to +1200—+1600 mV (depending on the position of the response). The other parameters of analysis were set up as follows: scan rate (v) 40 mV s^{-1} , scan step 5 mV, and current range $40 \mu\text{A}$. Standard addition method and software Nelinear [19] was employed for the quantitative analysis.

189 The statistical parameters like LOD and LOQ were calcu-
190 lated using software Nelin (personal consultation to assoc.
191 prof. V. Jehlička). The baseline correction was applied to
192 simplify the evaluation.

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