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Screening of the Essential Oils Antioxidant Capacity Using Electrode Modified with Carboxylated Multi-Walled Carbon Nanotubes †

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Abstract: Essential oils are of interest in analytical chemistry due to their bioactive constituents and wide application area. Voltammetric behavior of essential oils (from 15 types of plant material) at the electrode modified with carboxylated multi-walled carbon nanotubes was studied for the first time. Oxidation peaks at 0.0–0.75 and 0.75–1.5 V were obtained on the differential pulse voltammograms in neutral medium caused by electrooxidation of phenolic constituents and terpenoids. Two-step chronoamperometric method was developed for the evaluation of the essential oils antioxidant capacity. Screening of 37 samples of essential oils was performed. The data agree with the standard antioxidant parameters.

Keywords: electrochemical sensors; carbon nanotubes; modified electrodes; essential oils; antioxidants; antioxidant capacity

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1. Introduction

Essential oils are of great interest in analytical chemistry due to their bioactive properties and wide application area (in the aromatherapy, medicine, and food industry) [1–3]. Gas chromatography with mass-spectrometric detection is the golden standard in their characterization and investigation [1,4]. On the other hand, the presence of volatile phenolics and terpenoids make it possible to use electrochemical methods for the characterization and screening of essential oils using antioxidant parameters in particular antioxidant capacity. Unfortunately, essential oils are almost out of consideration in modern electroanalysis from this point of view. The only example is voltammetric method for *Mentha* species antioxidant properties estimation based on the reaction of the antioxidants with superoxide anion radical [5]. Therefore, simple, reliable, and cost-effective electrochemical approaches for the evaluation of the total antioxidant parameters of essential oils are of practical interest.

The current work is focused on the development of an electrochemical approach for the evaluation of the antioxidant capacity of essential oils using the electrooxidation of their antioxidants at the electrode modified with carboxylated multi-walled carbon nanotubes. The practical applicability of the method developed is shown on the screening of the 37 samples of essential oils from 15 types of plant material. The comparison of data obtained with standard parameters (antioxidant activity by reaction with 2,2-diphenyl-1-picrylhydrazyl and total phenolic content by the Folin-Ciocalteu method) has been performed.

2. Materials and Methods

Commercially available essential oils from various plant materials (clove, cinnamon, nutmeg, lavender, ginger, anise, basil, bergamot, jasmine, ylang-ylang, marjoram, neroli, rosemary, thyme and clary sage) of various trademarks were studied. Their ten-fold dilution with ethanol was used exactly before the measurements.

Thymol of 99.5% purity (Sigma, Steinheim, Germany), 98% carvacrol, 99% eugenol (Aldrich, Steinheim, Germany), 97% phythol (Sigma-Aldrich, Steinheim, Germany), 99% benzyl alcohol, 96% limonene, 98% α-pinene, 98% β-pinene, 98% D-carvone, 75% camphene, as well as α-fenchene, myrcene, 99.5% L-menthol, and 97% L-borneol (Acros Organics, Geel, Belgium) were used. Their 10 mM stock solutions were prepared by dissolving an accurately weighed portion in 5.0 mL of ethanol (rectificate). Other reagents were of chemical purity and used as received.

Carboxylated multi-walled carbon nanotubes (diameter 9.5 nm, length 1.5 μm and carboxylation degree >8%) from Aldrich (Steinheim, Germany) were used as electrode surface modifier. Their 1.0 mg mL^{-1} suspension in 1% sodium dodecylsulfate (Panreac, Barcelona, Spain) was obtained by sonication for 30 min in an ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd., Wonju-si, Korea).

Potentiostats/galvanostats μAutolab Type III (Eco Chemie B.V., Utrecht, The Netherlands) with GPES 4.9.005 software and 10 mL glassy electrochemical cell were used for the electrochemical measurements. Working glassy carbon electrodes (GCE) of 3 mm diameter (BASi® Inc., West Lafayette, IN, USA), or modified electrodes, an Ag/AgCl reference electrode, and a platinum wire as an auxiliary electrode were used.

GCE modification was performed by drop casting of 2 μL of carboxylated multi-walled carbon nanotube suspension.

The pH measurements were performed using "Expert-001" pH meter (Econix-Expert Ltd., Moscow, Russia) and a glassy electrode.

3. Results and Discussion

The voltammetric behavior of essential oils (from 15 types of plant material) at the electrode modified with carboxylated multi-walled carbon nanotubes has been studied. All samples are electrochemically active in neutral medium (phosphate buffer pH 7.0) under conditions of differential pulse voltammetry. There are well-pronounced signals on the voltammograms in the ranges of 0.0–0.75 and 0.75–1.5 V (Table 1). Clear oxidation peaks for nine essential oils are registered in the range of 0.75–1.5 V only.

Table 1. Essential oil oxidation potentials.

Essential Oil	Oxidation Potential (V)
Clove	0.13; 0.39
Cinnamon	0.14; 0.41; 1.33
Nutmeg	0.14; 0.41; 0.64; 0.96; 1.36
Lavender	1.30
Ginger	1.31
Anise	0.96; 1.25; 1.35
Basil	1.21
Bergamot	0.94; 1.14; 1.33
Jasmine	0.14; 0.43; 0.80; 1.22
Ylang-Ylang	1.31
Marjoram	1.01; 1.36
Neroli	0.89; 1.33
Rosemary	1.17; 1.35
Thyme	0.56; 1.4
Clary sage	1.29

Investigation of the voltammetric characteristics of individual antioxidants has shown that thymol and carvacrol are oxidized at 0.53 and 0.54 V, respectively. Eugenol shows two oxidation steps at 0.13 and 0.40 V. Among the terpenoids considered, only limonene and *α*-pinene are electrochemically active at 1.27 and 1.09 V, respectively. Phythol, β-pinene, D-carvone, camphene, *α*-fenchene, myrcene, L-menthol, benzyl alcohol, and L-borneol are silent on the voltammograms under conditions of the experiment. Thus, oxidation peaks of essential oils in the range of 0.0–0.75 V are caused by oxidation of phenolic antioxidants while the terpenoids are oxidized in the second range of 0.75–1.5 V.

On the basis of data obtained, two-step chronoamperometric method has been developed for the evaluation of the essential oils antioxidant capacity. Two anodic potentials of 0.80 and 1.4 V have been chosen for these purposes. The electrolysis steady-state is achieved at 75 s of electrolysis. A typical view of the chronoamperogram is shown in Figure 1.

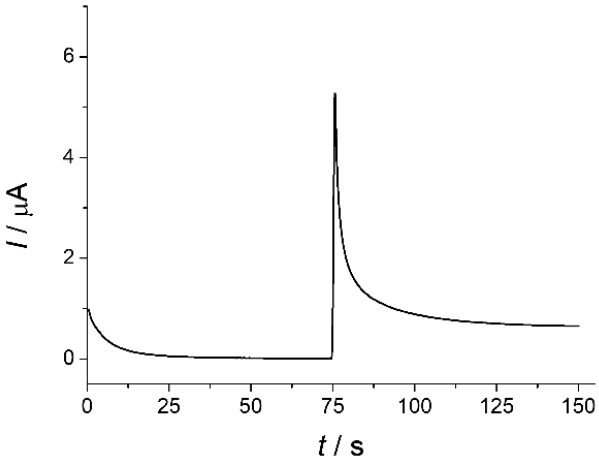

Figure 1. Typical view of the background subtracted chronoamperogram on example of 10 μL of 10-fold diluted rosemary essential oil. E_1 = 0.8 V, E_2 = 1.4 V.

The antioxidant capacity has been expressed as a current at 0.8 V reflecting the contents of phenolics ($AOC_{0.8}$) and the total current at 1.4 V (AOC_{total}) recalculated per 1 mL of essential oil. The antioxidant capacity screening of 37 essential oil samples from 15 types of plant material has been performed (Figure 2).

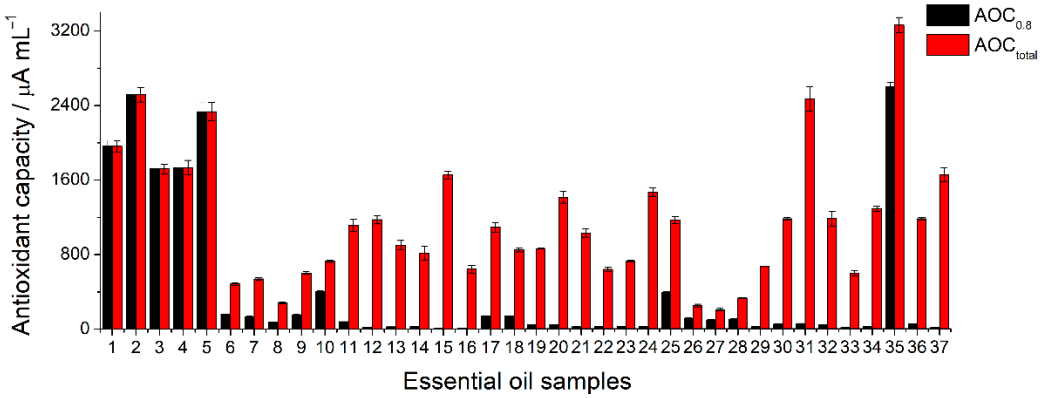

Figure 2. Antioxidant capacity of the essential oils based on chronoamperometric data. Samples 1–5—clove, 6–10—cinnamon, 11—nutmeg, 12–15—lavender, 16—ginger, 17 and 18—anise, 19 and 20—basil, 21–24—bergamot, 25–28—jasmine, 29—ylang-ylang, 30 and 31—marjoram, 32—neroli, 33 and 34—rosemary, 35—thyme, 36 and 37—clary sage essential oils.

The data obtained have been compared to the standard antioxidant parameters (antioxidant activity towards 2,2-diphenyl-1-picrylhydrazyl [6] and total phenolics [7]). Statistically significant correlations have been found. Comparison of total antioxidant capacity with antioxidant activity towards 2,2-diphenyl-1-picrylhydrazyl has been performed for all studied samples and has shown positive correlation with $r = 0.4458$ that is more than critical value of 0.3245. Antioxidant capacity at 0.8 V correlates with the total phenolic content by the Folin-Ciocalteu method ($r = 0.7969$ at $n = 12$). It should be noted that the spectrophotometric approach was applicable for clove, cinnamon, nutmeg, and thyme essential oils only. The turbid systems were obtained for other oils after the addition of photometric reagents. Chronoamperometric approach successfully overcomes this limitation that can be considered as a significant advantage.

Thus, the data obtained clearly demonstrated the applicability of electrochemical methods on carbon nanotubes modified electrode, in particular, the two-step chronoamperometry for the evaluation of essential oil antioxidant capacity and samples screening. Simplicity, rapidity, cost-efficiency, and reliability of the method as well as possibility of miniaturization make it an attractive tool for such purposes as alternative to chromatography for the fast screening of the essential oils.

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