

Optimization of anethole determination using differential pulse voltammetry on glassy carbon electrode, boron doped diamond electrode and carbon paste electrode

Szymon Wójcik*, Małgorzata Jakubowska

AGH University of Science and Technology, Al. Adama Mickiewicza 30, 30–059 Kraków, Poland

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Abstract

Voltammetry is the general term for all techniques in which the current is measured as a function of electrode potential. The voltammetric techniques can be applied for the quantitative analysis of inorganic and organic species and are best suited for substances which can be either oxidized or reduced on electrodes. These techniques are characterized by high sensitivity which results in the possibility of performing determinations at a low concentration level. In voltammetry, many different types of working electrodes are applied. One of the important groups are solid electrodes, among which carbon electrodes play an important role. They represent a good alternative to mercury electrodes, however, surface preparation before the usage is required. In this work anethole determination will be presented using three types of carbon electrodes: glassy carbon electrode, boron doped diamond electrode and carbon paste electrode. Optimization process will be also described.

Keywords: Anethole, voltammetry

Introduction

Anethole is the main ingredient of anise and bardian oil and is found also in fennel oil. Anethole is widely used as a flavoring substance. On an industrial scale, it is obtained from anise fruit in a technological process where one of the stages is freezing. The *trans*-anethole obtained in the form of a solid is a crystalline white mass that melts already in 19°C and takes the form of a colorless liquid with a sweet taste and a characteristic odor. It has a bactericidal effect. One of the important features of anise oil is the lack of resistance to light and atmospheric oxygen, because in contact with these factors, photoanethole, a substance with a yellow color and unpleasant odor and taste is formed [1–4].

Voltammetry belongs to the group of electroanalytical techniques. During the voltammetric measurement current flowing through the electrode system, in relation to the applied potential, is measured. Mentioned experiment must be carried out under strictly defined conditions, because the speed of the redox reaction is related to the rate of transport of the analyte to the surface of the electrode. The voltammetric technique allows the analysis of both metal cations and non-metal anions, and with the use of appropriate techniques and electrodes gives the opportunity to study organic compounds. A prerequisite for an organic substance to be analyzed by electrochemical methods is to have a group that could be subject to oxidation or reduction [5–7].

The classic measuring system in voltammetry consists of three electrodes. The working electrode is the one on which the oxidation and reduction process takes place. It is a stationary electrode, that means surface does not change. The second electrode is a reference electrode whose potential is unchanged and the potential of the working electrode is measured against it. The last of the electrodes is an auxiliary electrode which is most often a platinum wire. Its role is to ensure the stability of the potential of the reference electrode [5, 8].

An extremely important step of the voltammetric measurement is the proper selection of the supporting electrolyte whose concentration should be much higher than the concentration of electroactive substance. The role of the supporting electrolyte is to carry the charge through the solution and to provide a constant ionic strength. The selection of appropriate measurement conditions is important, because the measured current should show useful, not the distorting processes [9].

Materials and Methods

In this work, Electrochemical Analyzer type M161 and CGMDE Electrode Stand type M164D (both mtm – anko, Poland) were applied. Also the following electrodes were used in determinations:

- GCE – Glassy Carbon Electrode, $\phi 3$ mm, type MF – 2012, BASi,
- BDDE – Boron Doped Diamond Electrode $\phi 3$ mm, type D – 565 – SA, Windsor Scientific,
- CPE – Carbon Paste Electrode with 20% addition of Y_2O_3 , $\phi 3$

*Corresponding author: szwojcik@agh.edu.pl

mm, self-made in our laboratory.

The reagent used for preparation of the standard solution was analytically pure *trans*-anethole, CAS: 4180-23-8 (Sigma–Aldrich). The supporting electrolyte was an acetate buffer with a concentration of 0.1 mol/dm³.

Results and Discussion

The key difference between the GC, CP and BDD electrodes is preparation of their surface before measurements. The surface of the GC electrode was prepared by polishing it onto the cloth with the use of an alumina polishing powder with an average particle size of 0.05 μm³. Polishing consisted in making 50 moves of the electrode in the shape of an ‘eight’ figure on the surface of the cloth. BDD electrodes cannot be polished because it can be damaged, therefore for the preparation of its surface, conditioning at a very positive potential and stabilization of the electrode at the starting potential of measurement were used. The described operation was carried out several times before the start of the measurement. The most intensive surface preparation concerned the CP electrode. Before the measurement, the electrode body should be filled with the electrode paste. After filling the electrode, the surface to be measured was prepared by polishing on a white paper with a weight of 70 g/m², and then by polishing on a weighing paper. Polishing consisted of making 50 moves of the electrode in the shape of an ‘eight’ figure on the surface of the page, and then also 50 moves on the surface of the weighing paper.

The optimization of the measurement parameters was carried out for GC and BDD electrodes, while the parameters of

the GC electrode were used also in the experiments with the CP electrode. In the optimization experiments, the anethole concentration was 7.0 mg/l, which corresponds to the addition of 10 μl of the standard solution. During the optimization values of only one parameter were changed with the unchanged remaining parameters. The starting potential (E_p), final potential (E_k), step potential (E_{step}), potential amplitude (d_E), sampling time (t_p) and waiting time (t_w) as well as electrode conditioning time were subject to optimization.

Each parameter was optimized according to the same strategy. As an example, optimization of the starting potential for the GC electrode is shown. For this purpose, three values of this parameter were selected, i.e. 500 mV, 600 mV and 700 mV. The results of the optimization are presented in Figure 1 and Table 1. Table 1 shows the number of repetitions (n) realized for the each parameter value, the average current peak height (i_H), the confidence interval of mean at the confidence level 0.95 (CI), the standard deviation of the peak height (SD), the relative standard deviation of the peak height (RSD) and coefficient of variation (CV).

As an optimum value of the initial potential in the anethole determination on GCE, 500 mV was chosen. The peak recorded assuming the initial potential of 500 mV had the highest amplitude and met also all of the assumed criteria. For each starting potential value, the repeatability of the signal was also tested. In each case, the value of CV did not exceed 1%, and so a typical acceptance criterion for repeatability i.e. 5% was met. It was also observed that the peak of the anethole has a symmetrical shape and at the stage of interpretation requires only a slight correction of the baseline.

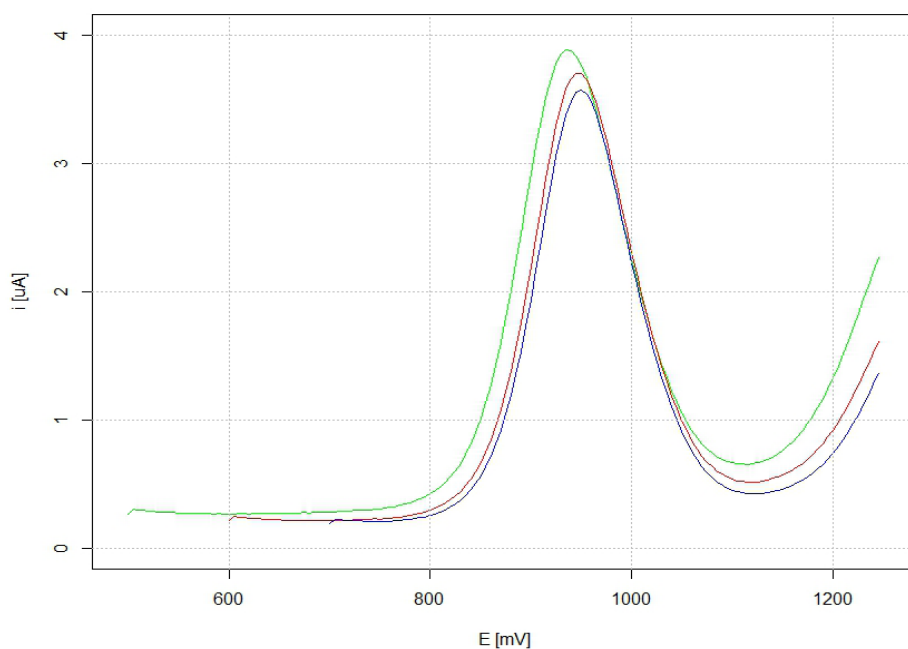


Figure 1. Optimization of the starting potential in measurement with GCE. Supporting electrolyte - acetate buffer with a concentration of 0.1 mol/dm³, pH = 6.0, anethole concentration – 7.0 mg/l. Green voltammogram - starting potential of 500 mV, red for 600 mV and blue for 700 mV.

Table 1. Statistical analysis of the results from Figure 1

E_p [mV]	n	i_H [μ A]	\pm CI [μ A]	SD [μ A]	RSD	CV [%]
500	3	3.524	0.085	0.034	0.010	1.0
600	3	3.489	0.054	0.022	0.006	0.6
700	3	3.368	0.045	0.018	0.005	0.5

After the optimization, the measuring parameters for experiments realized on each electrode were selected. The results are summarized in Table 2.

gram recorded on GC electrode are shown in Figure S1 while a calibration curve in Figure S2. During experiments on the GC electrode, the anethole concentration was in the range from 1.4

Table 2. Measuring parameters in DPV experiments. Supporting electrolyte – acetate buffer with a concentration of 0.1 mol/dm³ and pH = 6.0.

Parameter	GCE	CPE	BBDE
E_p [mV]	500	500	500
E_k [mV]	1250	1250	1200
E_{step} [mV]	5	5	5
d_E [mV]	50	50	50
t_p [ms]	10	10	10
t_w [ms]	10	10	10
electrode conditioning	-	-	2400 [mV] / 5 [s] 500 [mV] / 10 [s]

Using the optimum values of individual parameters, a set of signals to create a calibration relationship were recorded using the various anethole concentrations (Table 3). The voltam-

mg/l to 7.0 mg/l. Using similar parameters, a series of voltammograms depicted in Figure S3 was made for the CP electrode and based on them a calibration curve illustrated in Figure S4

Table 3. List of analytical method parameters obtained in optimal conditions for GC, CP and BDD electrodes. LOD is limit of detection, LOQ is limit of quantification

Parameter	GCE	CPE	BDDE
Sensitivity \pm SD [μ A \times mg/l]	0.721 \pm 0.009	1.34 \pm 0.10	0.460 \pm 0.060
Intercept \pm SD [μ A]	0.05 \pm 0.14	0.015 \pm 0.015	0.013 \pm 0.044
Linearity range [mg/l]	1.4 – 7.0	1.4 – 7.0	0.7 – 3.5
Correlation coefficient r	0.9972	0.9991	0.9975
Current peak position [mV]	959.8	1086.2	830.1
LOD [mg/l]	0.2	0.1	0.1
LOQ [mg/l]	0.6	0.4	0.3

was prepared. Also, when the optimal conditions for the BDD electrode were applied, a series of voltammograms was shown in Figure S5 and the calibration curve shown in Figure S6. However, with this electrode, the addition of the standard was 0.7 mg/l in the range from 0.7 mg/l to 3.5 mg/l.

If we combine voltammogram in the same figure for the same concentrations of anethole (Figure 3) obtained using different electrodes, we can notice different positions of peaks coming from anethole and significant differences in their heights.

Conclusions

Anethole was determined by the DPV technique using three electrodes, a glassy carbon electrode, a carbon paste electrode with 20% addition of Y_2O_3 and a boron-doped diamond electrode. Before starting the measurements, a procedure for surface renewal and preparation was developed for each electrode. The surfaces of GCE and CPE electrodes have been prepared by mechanical polishing. Activation of the surface in the case of BDDE

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Sensitivity \pm SD [$\mu A \times mg/l$]	0.721 ± 0.009	1.34 ± 0.10	0.460 ± 0.060
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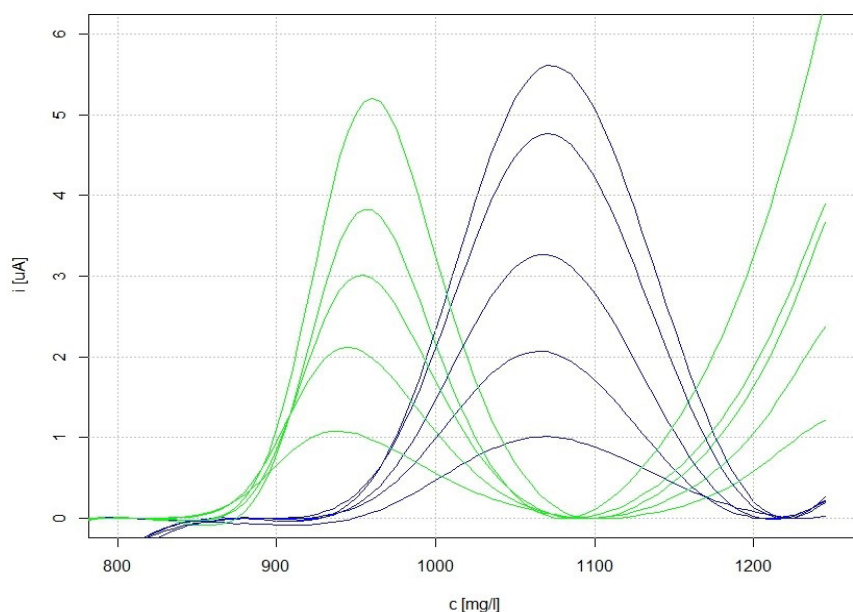


Figure 2. Comparison of anethole voltammograms in optimal measurement conditions after background correction, successive additions of the anethole standard from 2 μl to 10 μl , every 2 μl , green voltammograms correspond to the GC electrode, blue voltammograms correspond to the CP electrode.

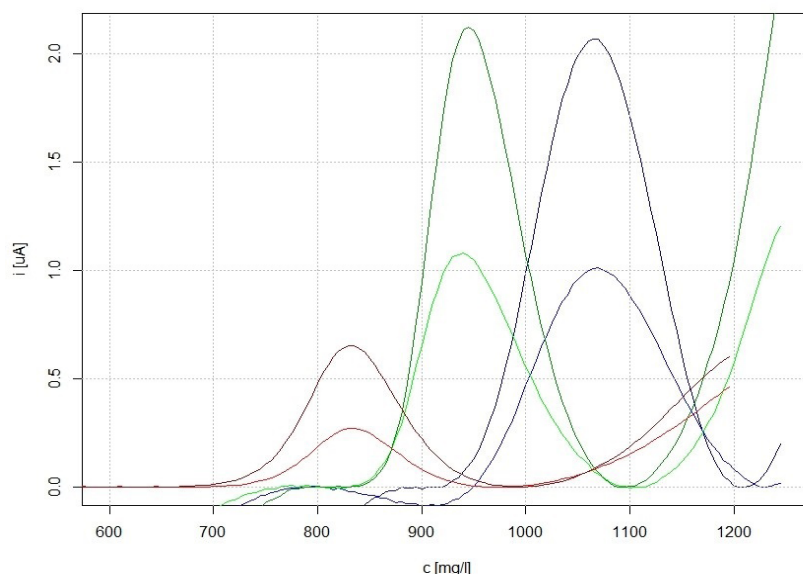


Figure 3. List of voltammograms from different electrodes. The voltammograms recorded on the BDD electrode are displayed in red, in green from GCE, in blue from CPE. Lower peaks are derived from the anethole concentration of 0.7 mg/l, while the higher peaks are derived from the anethole concentration of 1.4 mg/l.

based on application of high positive potential for 5 seconds and then stabilization at the starting potential for 10 seconds. This procedure was repeated before the registration of each curve. The measurement parameters have been optimized for each electrode. The calibration relationships for anethole have been constructed. The parameters of the analytical methods have also been indicated. The most favorable parameters were obtained for the CPE electrode for which the sensitivity was $1.34 \pm 0.10 \mu\text{A} \times \text{mg/l}$, and the correlation coefficient r was 0.9991. The second useful electrode with satisfactory functionality for the assay was a GCE electrode for which the sensitivity was $0.721 \pm 0.009 \mu\text{A} \times \text{mg/l}$, and the correlation coefficient r was 0.9972. Significant differences in the position of peaks derived from the same concentrations of anethole were also observed. In the case of the BDD electrode, the peaks are at the lowest potential, while in the case of the CP electrode, they are most shifted to a positive potential and are comparable to those of the GC electrode. Finally, it can be concluded that all three electrodes, despite significant differences in analytical parameters, can be used to determine anethole by the DPV technique.

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References

- Kołodziejczyk A, *Naturalne związki organiczne*, Wydawnictwo Naukowe PWN, Warszawa 2013.
- Klimek R, *Olejki eteryczne*, Wydawnictwo Przemysłu Lekkiego i Spożywczego, Warszawa 1957.
- Shahat AA, Ibrahim AY, Hendawy SF, Omer EA, Hammuda FM, Abdel-Rahman FH, Saleh MA, *Chemical Composition, Antimicrobial and Antioxidant Activities of Essential Oils from Organically Cultivated Fennel Cultivars*, *Molecules*, 2011; 16:1366–1377.
- Kowalcze M, Wyrwa J, Dziubaniuk M, Jakubowska M, *Voltammetric Determination of Anethole on $\text{La}_2\text{O}_3/\text{CPE}$ and BDD*, *Journal of Analytical Methods in Chemistry*, 2018, art. ID 2158407, 1–14.
- Ufnalska I, *Woltamperometria*, Politechnika Warszawska, Warszawa 2015.
- Molina A, Moreno MM, Serna C, Camacho L, *Additive differential pulse voltammetry, instead of double differential pulse voltammetry*, *Electrochemistry Communications* 2001; 3:324–329.
- Rogowska A, *Analiza woltamperometryczna wybranych substancji leczniczych w preparatach farmaceutycznych*, Akademia Medyczna, Gdańsk 2007.
- Kubiak W, Piech R, *Wstęp do polarografii i woltamperometrii*, Akademia Górniczo-Hutnicza, Kraków.
- Łuczak T, *Woltamperometrii cykliczna. Wyznaczenie parametrów procesu elektrodowego dla reakcji red-ox z udziałem kompleksu żelaza*, Zakład Chemii Fizycznej, Uniwersytet Adama Mickiewicza, Poznań 2010.

Supplementary information

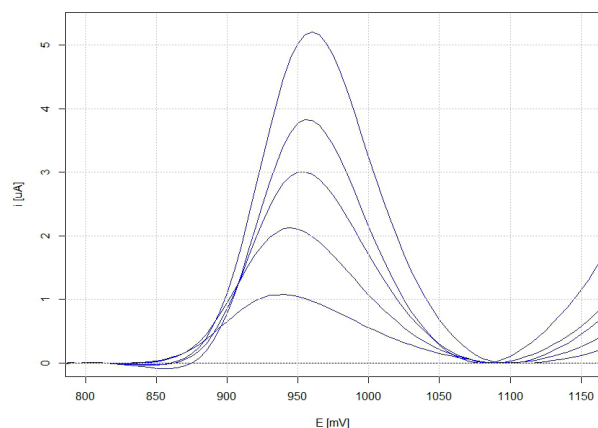


Figure S1. Voltammograms of the anethole in the concentration range of 1.4–7.0 mg/l with addition of 1.4 mg/l in optimal measurement conditions after background subtraction, GC electrode.

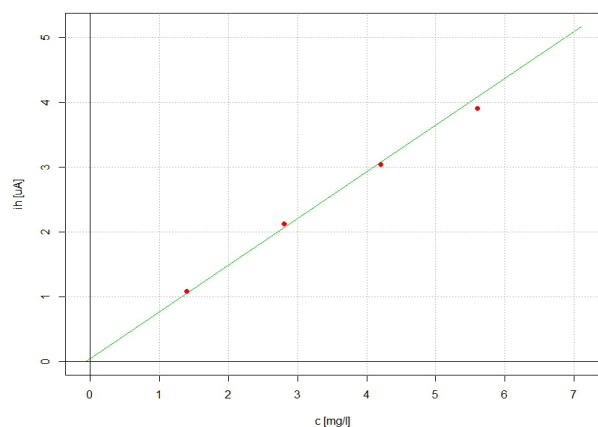


Figure S2. Calibration graph in the range of 1.4–7.0 mg/l of anethole at the GC electrode.

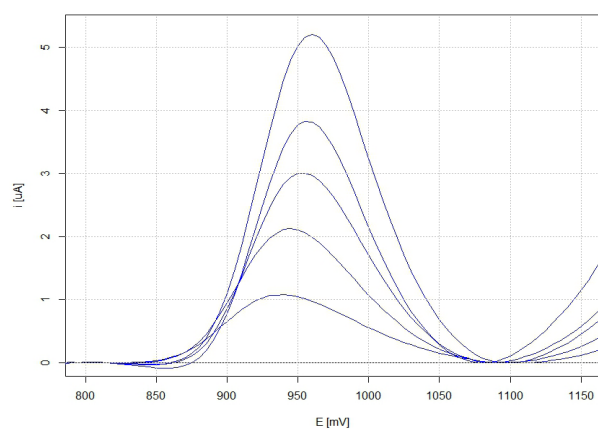


Figure S3. Voltammograms for anethole in the concentration range of 1.4–7.0 mg/l with addition of 1.4 mg/l in optimal measurement conditions after background subtraction, CP electrode.

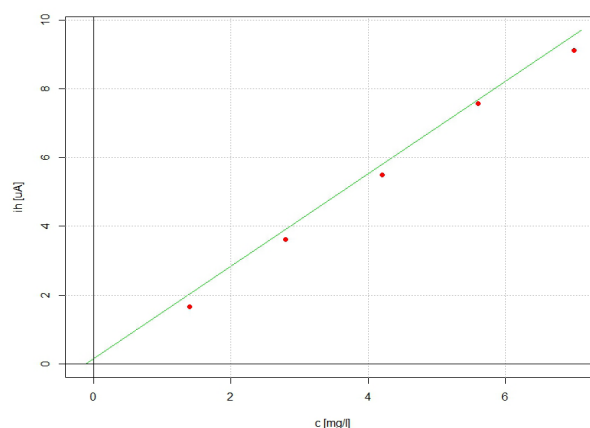


Figure S4. Calibration graph in the range of 1.4–7.0 mg/l of anethole at the CP electrode.

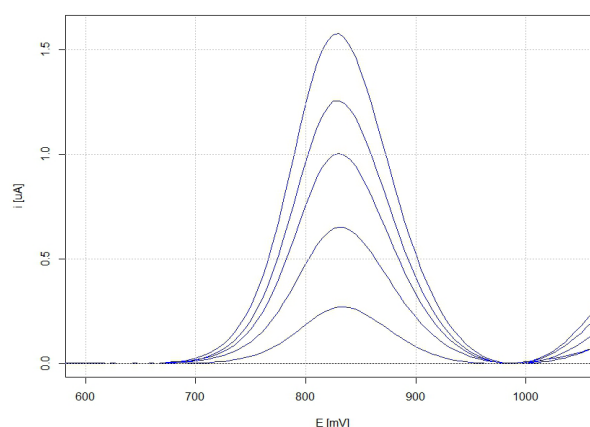


Figure S5. Voltammograms for anethole in the concentration range of 0.7–3.5 mg/l with addition of 0.7 mg/l in optimal measurement conditions after background subtraction, BDD electrode.

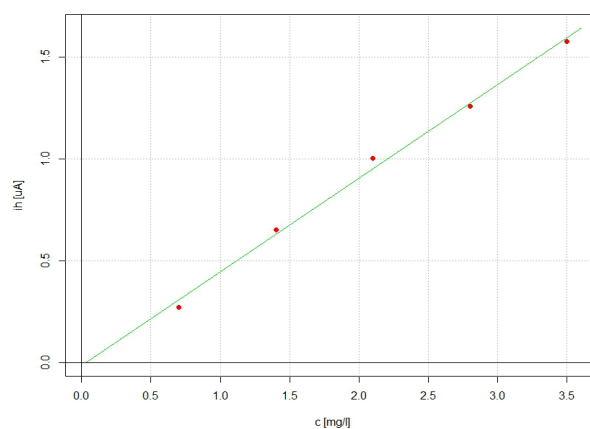


Figure S6. Calibration graph in the range of 0.7–3.5 mg/l of anethole on the BDD electrode.