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Voltammetry with a carbon paste electroactive electrode used for the quality assessment of vegetable oils

Anna Horská, Ivan Švancara, and Milan Sýs*

Department of Analytical Chemistry,
The University of Pardubice, CZ−532 10 Pardubice, Czech Republic

This article introduces carbon paste electroactive electrodes in combination with voltammetric measurements as a useful tool for simple, low-cost, efficient, and semi-quantitative assessment of the quality of various vegetable oils. The respective method is based on anodic oxidation of electroactive organic compounds (namely: phenolic compounds and lipophilic vitamins) that naturally occur in the samples of interest and, in this case, being admixed in a small quantity directly into the carbon paste bulk. All the experiments were performed in 0.1 mol L^{-1} acetate buffer (pH 4.5) in the square-wave voltammetric mode. The results obtained have shown that the proposed procedure can be applied in food control to authenticate — as an electrochemical fingerprinting — the kind and the quality of a vegetable oil, including its freshness.

Introduction

Solid phase voltammetry (SPV) is a lesser known but very interesting variant of traditional electrochemical measurements [1–4]. It utilises a specific approach when the substance of interest is an integral part of the working electrode, being either contained directly in the electrode bulk or attached onto its surface.

Due to the heterogeneous character and manual preparation, the so-called carbon pastes are defined as mixtures of graphite powder and a liquid binder [5]. They represent a nearly ideal platform for adopting yet another component.

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* Corresponding author, ✉ milan.sys@upce.cz

In a great majority of practical realisations, the third constituent is modifier (or even a mixture of modifiers) admixed to purposely change the properties of the native paste. The respective configuration is known as chemically or biologically modified carbon paste (CMCPE [5,6] or a CP-biosensor [5,7], respectively).

The initial pioneering attempts with SPV employed the electrodes from carbon pastes that had consisted of graphite powder and an electroactive solid dissolved in a strong electrolyte acting as the binder, thus representing a new configuration – "carbon paste electroactive electrode" (CPEE [1–4]). According to some sources, the very first report came from the former USSR [8]; however, because of its publication in a regional and hardly accessible journal, the priority in use of a CPEE is often being attributed to Bauer and Gaillochet [9]. Since the mid-1970s, these electrodes had experienced a rapid development, when the substances studied were various minerals and ores, synthetic pigments and dyes, catalysts, semiconductors, or ceramics, including the fragments from archaeological finds; see e.g. [5]. (*Note:* There are also some other approaches how to perform a SPV experiment with inorganic solids. For instance, Scholz et al have introduced a technique called abrasive voltammetry, AbV [10] where a common disc electrode from pyrolytic graphite or glassy carbon [2–4], and later also boron-doped diamond [11] bears a thin layer of powdered sample attached onto the surface by mechanical wiping of the original compact material.)

Although the domain of SPV with CPEEs are the above-mentioned inorganic substances, the same approach is applicable also to study some organic compounds. In this case, the native paste has a traditional composition with non-polar and highly viscous paraffin or silicone oil, in which the substance of interest can be dissolved or at least dispersed. Such configurations had been the first three-component carbon pastes ever used and reported by Kuwana et al [12–14] in the mid-1960s, i.e., already in the early era of carbon paste-based electrodes.

Rather dense VOs can be considered as representatives of liquid lipids [15], where main components are usually triacylglycerols (TGC) rich with linoleic acid whereas other constituents are various electroactive substances, such as a mixture of tocopherols and tocotrienols (vitamin E [16]), carotenoids [17], phenolic compounds (oleuropein, tyrosol and hydroxytyrosol [18]), or phylloquinone (vitamin K1 [19]). Moreover, they can be fortified with synthetic analogues of vitamin A, namely all-*trans*-retinyl acetate and all-*trans*-retinyl palmitate.

Thus, one can assume that these electroactive substances can serve as biological markers for the analytical evaluation of VOs, including the subsequent discrimination of the individual products. When using the CPEEs, this was for the first time shown in a paper by Spanish electrochemists who have analysed a set of virgin olive oils [20]. Although these authors had not tried to identify the individual electroactive substances responsible for typical broad voltammetric

signals, their experiments were sufficient to characterise different types of commercial products, thus offering a way for an electrochemical mapping or fingerprinting, respectively.

In this article, the Kuwana's concept [12–14] has been adopted, when the samples were either dissolved in mineral oil or they replaced it completely. These configurations have then represented an analytical tool for studying different kinds of vegetable oils (VOs), such as olive, rapeseed, linseed, pumpkin, chia, and sunflower oils, were selected as the samples embedded in CPEEs. In addition, some comparative experiments were also made when using carbon pastes containing different lipophilic vitamins that typically occur in VOs.

Experimental

Chemicals and Reagents

Graphite powder "CR-2" (natural product grinded and chemically purified, with average particle size of 2 µm; Graphite, Týn nad Vltavou, Czech Republic), graphite powder "RW-B" (synthetic product for spectroscopy, Ringsdorff Werke, Germany), glassy carbon powder "Sigradur-G" (particle size: 5–20 µm; HTW Hochtemperatur-Werkstoffe, Maintingen, Germany), and multi-wall carbon nanotubes (MWCNTs, diameter: 10–30 nm, length: 5–15 µm, specific surface area: 40–300 m^2 g^{-1}; Nanotech Port Co., Shenzhen, China) were used as the carbon moieties for preparation of native carbon pastes. In the role of a binder or pasting liquid, respectively, paraffin / mineral oil ("MO"; Merck, Darmstadt, Germany) was chosen based on the previous experience; see [21] and refs. therein.

Analytical standards of (±)-α-tocopherol (α-TOH), phylloquinone (VK1), ≥98% (*w/w*) cholecalciferol (VD3), all-*trans*-retinyl acetate, all-*trans*-retinyl palmitate, and β-carotene were purchased from Merck. For preparation of aqueous working media, the respective packaging of 65% HNO_3, 98% H_2SO_4, 35% HCl, 85% H_3PO_4, 99.8% acetic acid, 99% boric acid, NaOH, and CH_3COONa were obtained from Lach-Ner (Neratovice, Czech Republic). A deionized water (with minimal electric resistivity of 18.2 MΩ cm and maximal content of 3 µg L^{-1} of total organic carbon) was obtained in a Milli-Q® water purification unit (Merck Millipore; Burlington, MA, USA).

Instrumentation and accessories

All voltammetric measurements were carried out in a conventional electrochemical cell always containing 10 mL of 0.1 mol L^{-1} acetate buffer (pH 4.5) with the three-electrode system, comprising the working CPEE, an Ag/AgCl (3M KCl) reference with salt bridge, and a Pt-sheet as the auxiliary electrode.

All the electrodes were connected to an AUTOLAB PGSTAT101 potentiostat / galvanostat operated by the NOVA 1.11 software (all from Metrohm Switzerland / Division Czech Republic, Prague, Czech Republic).

The pH of the supporting electrolytes was controlled using an InoLab device (model "pH 720"; WT Werke, Germany) with the combined glass electrode ("Sen Tix 41" type) calibrated on a set of three commercial buffers of pH 3.01, 7.00, and 10.0, all from the same manufacturer.

Carbon paste electroactive electrodes

The individual carbon pastes containing the same quantity of graphite powder (80 %; *w/w*) and mineral oil, and/or selected vegetable oil (20 %; *w/w*) were prepared by thorough hand-mixing the respective components for ca. 10 min. when using a pestle and mortar (both from ceramics of high purity).

The resultant carbon paste mixtures were packed into a cavity (with diameter of 3 mm) of Teflon® electrode piston-holders designed in the workshops at the University of Pardubice [22]. After leaving the filled electrode bodies for one day to self-homogenise under laboratory conditions, all the CPEEs were ready to use for voltammetric measurements.

Procedures

Square-wave voltammetry (SWV) was used as the technique of choice for the measurement and detection of electroactive substances present in selected vegetable oils. Operational parameters of the SWV ramp were set as follows: deposition potential (E_{dep}) of -0.4 V, deposition time (t_{dep}) of 30 s, potential range from -0.4 to $+1.6$ V, potential step (E_{step}) of 5 mV, pulse amplitude (E_{ampl}) of 25 mV, and frequency (f) of 40 Hz.

Typically, each voltammetric analysis was made in five replicates. Eventual changes in the working conditions and instrumental parameters are specified in the legends of the corresponding figures.

Vegetable oils

Commercially available vegetable oils of different kinds were purchased in common Czech stores. These samples included (i) extra-virgin olive oils marketed by Amway Česká Republika a Slovensko (Prague, Czech Republic), Gourmet Partners (Prague, Czech Rep.), Biolevante (Andria, Italy), Oro Bailen (Jaén, Spain), then (ii) rapeseed and sunflower oils produced by Glencore Agriculture

Czech (Ústí nad Labem, Czech Rep.), (iii) linseed and pumpkin oils from Agro-El, (Znojmo, Czech Rep.), and, finally, (iv) a chia (seed) oil from Green Idea (Kuřim, Czech Republic).

Results and discussion

Effect of the type of the carbon powder moiety

Fig. 1 makes comparison of a quartet of CPEEs made of four different carbon materials in the powdered form and containing the same sample – extra-virgin olive oil; here, acting also as a binder.

As can be seen, each CPEE had behaved individually, exhibiting different voltammograms and the corresponding signals superimposed upon. This can be explained by unequal properties of the respective carbons; namely, possible adsorption capabilities (e.g., some synthetic graphites), or electrocatalytic effects (typical e.g. for MWCNTs), including their combinations [5,23].
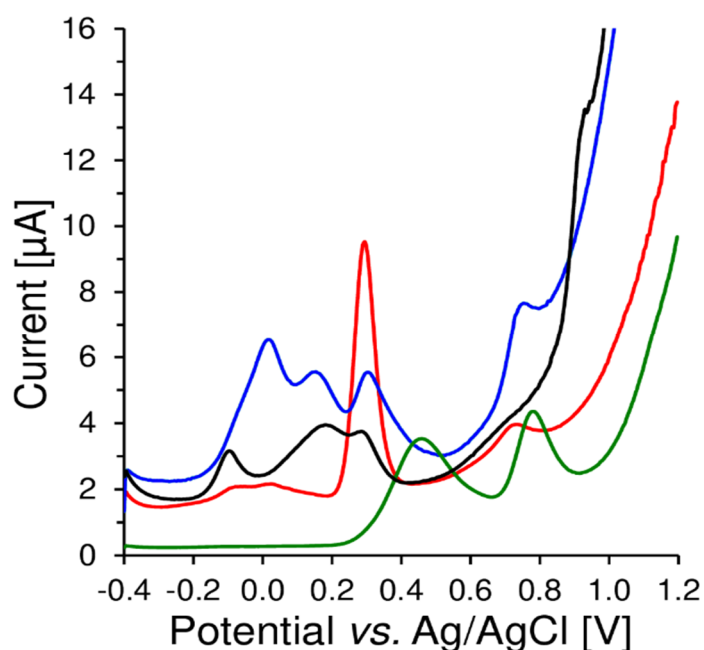

Fig. 1 Square-wave voltammograms for a quartet of CPEEs prepared from the selected carbonaceous material (80%, w/w) and a binder – extra virgin olive oil (product from Amway; 20%, w/w)

Legend: black curve: graphite powder CR-2, green: graphite powder RW-B, red: glassy carbon powder Sigradur, blue: MWCNTs

Experimental conditions: 0.1 M acetate buffer (pH 4.5), scan: from −0.4 V vs. ref. to positive direction (see figure), SW-parameters: $E_{dep} = -0.4$ V, $t_{dep} = 30$ s, $E_{step} = 5$ mV, $E_{ampl} = 25$ mV, and $f = 40$ Hz

From a practical point of view and when following the results of some special studies that had confirmed only insignificant adsorption capabilities (see again [23] and refs. therein), as well as thanks to favourable price and accessibility, graphite CR-2 was found the most suitable candidate for the proper carbon material in CPEE configurations and therefore used in all further studies.

Composition of the working medium

The above-mentioned oxidation peaks can be attributed to electrode reactions of the nutrients, such as lipophilic vitamins, provitamins, and phenolic compounds (natural antioxidants). Except the type of carbon selected, their electrochemical behaviour depends on the choice of detection medium, especially upon pH value. In our previous reports [24,25], it has been shown that most of these substances provide high current yields in acidic solutions.

Hence, a set of common aqueous working media (buffers and diluted solutions of mineral acids) was compared in the SPV/CPEE mode with model composition of three lipophilic vitamins as illustrated in Fig. 2. For the respective experiment, the main criterion was the shape of the individual anodic peaks; namely, to obtain them fairly narrow, without any overlap(s). Due to higher background currents at the baseline in the working media with pH < 2, a solution of 0.1 mol L^{-1} acetate buffer (pH 4.5) was chosen as optimum.
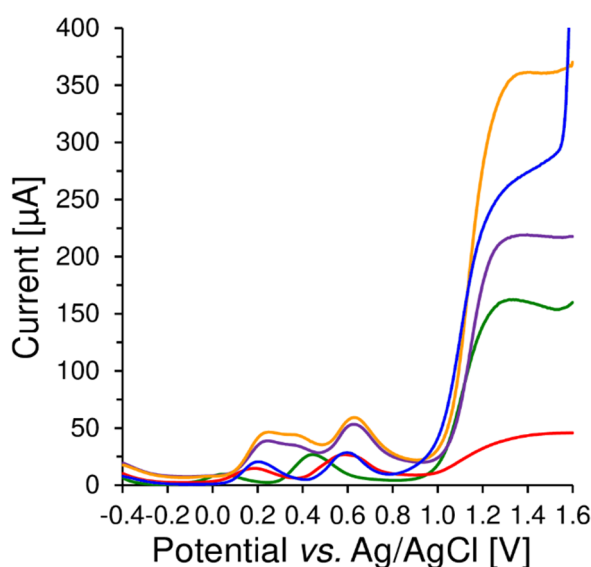

Fig. 2 A set of square-wave voltammograms obtained in different supporting media

Legend: 0.1 mol L^{-1} acetate buffer (pH 4.5, green), 0.1 mol L^{-1} Britton-Robinson buffer (pH 2, red), 0.05 mol L^{-1} H_2SO_4 (violet), 0.1 mol L^{-1} HNO_3 (blue), and 0.1 mol L^{-1} HCl (orange)

Experimental conditions: CPEE: 80% (*w/w*) CR-2 graphite +17 % (*w/w*) MO +1 % (*w/w*) VK1, α-TOH, and VD3; SWV parameters: E_{dep} = −0.4 V, t_{dep} = 30 s, E_{step} = 5 mV, E_{ampl} = 25 mV, and f = 10 Hz

Optimisation of electrochemical detection of phylloquinone

Usually, VK1 comes into VOs by pressing plant seeds together with green residues and thus its content varies widely [26]. Because of its natural occurrence in the oxidation form as a naphthoquinone, VK1 cannot be electrochemically oxidized. In order to monitor vitamin K along with other electroactive essential nutrients, it was necessary to reduce phylloquinone to phyllohydroquinone with the involvement of two protons and electrons. Other substances in VOs occur in the reduction forms; hence, it can be assumed that application of the negative deposition potential for certain time has caused no electrochemical changes.

Fig. 3 shows that the deposition potential (E_{dep}) and the deposition time (t_{dep}) have both a principal effect on the VK1 current response. It was observed that the oxidation peak VK1 increases and, also, gets broader with more negative E_{dep} values and with longer t_{dep}, which may cause a deterioration in the recognition with other accompanying analytes. For that reason, E_{dep} of −0.4 V and t_{dep} of 30 s could be considered as sufficient.
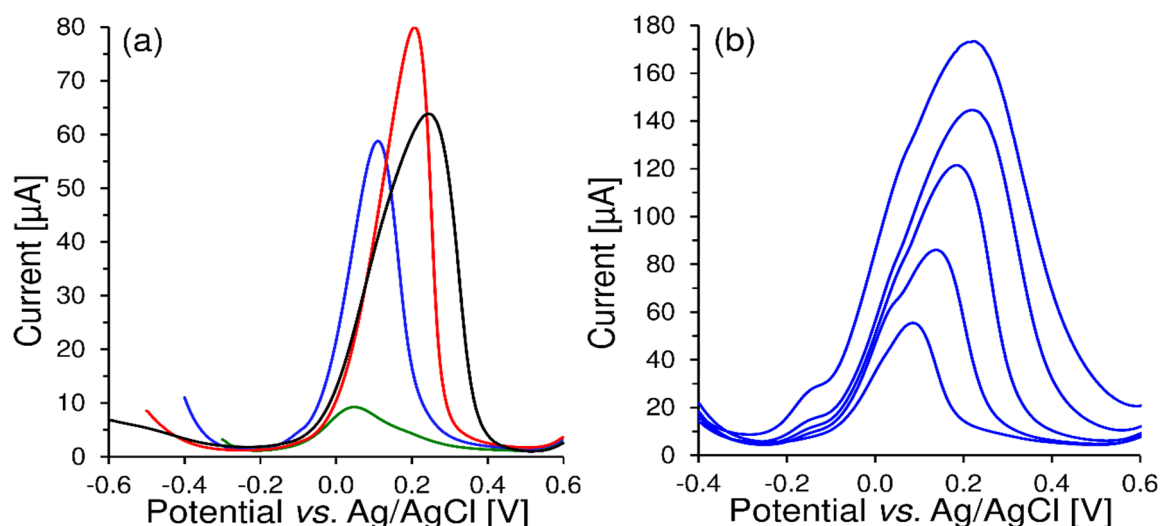

Fig. 3 Square-wave voltammograms obtained in 0.1 mol L^{-1} acetate buffer (pH 4.5) at various CPEEs containing vitamin K1

Experimental conditions: CPEE: 80% (*w/w*) CR-2 graphite powder, 18% (*w/w*) MO and 2% (*w/w*) VK1. Set (a): E_{dep} = −0.3, −0.4, −0.5, and −0.6 V; t_{dep} = 60 s, E_{step} = 2.5 mV, E_{ampl} = 25 mV, and f = 10 Hz. Set (b): t_{dep} = 30, 60, 120, 240, and 300 s; E_{dep} = −0.4 V, E_{step} = 2.5 mV, E_{ampl} = 25 mV, and f = 10 Hz

The choice of the key parameters for square-wave voltammetry

The optimization of the SWV potential ramp was focused on finding the proper pulse amplitude (E_{ampl}) and frequency (f) at constant potential step (E_{step}) of 5 mV; all affecting the peak current significantly. The effects of two mentioned parameters had been investigated for intervals of 10–100 mV and of 2–100 Hz.

It was found that, in model CPEE, the setting the pulse amplitude higher than 25 mV did not cause significant broadening of the respective responses for lipophilic vitamins VK1, α-TOH, and VD3. Furthermore, their peak heights increased with higher values of frequency when noticeable increase of the baseline (background currents) was also observed. Hence, a frequency of 40 Hz was chosen as a compromise and together with optimised values of the pulse amplitude and frequency consequently selected for next measurements.

Analytical performance of the SPV-CPEE combination

Before starting the actual analysis of various VOs and semi-quantitative determination of selected electroactive substance (serving as a biological marker), it was necessary to define the accuracy and precision of repeated measurements. Fig. 4 offers a comparison between five replicated measurements with CPEE containing 20% (*w*/w) an extra-virgin olive oil obtained at the same electrode surface [set (a)] and after regular surface renewal [set (b)].

At first glance, it is evident that all the analyses have to be carried out at always renewed surface (with RSD of about 9.9 % for oxidation peak at +0.3 V *vs*. ref.). In the previous case (a), an increasing trend of all signals was observed; probably, due to the accumulation of analytes onto the CPE surface, representing a special type of liquid-liquid interface (formed by nonpolar oil and polar supporting electrolyte) where their electrochemical reactions may take place.
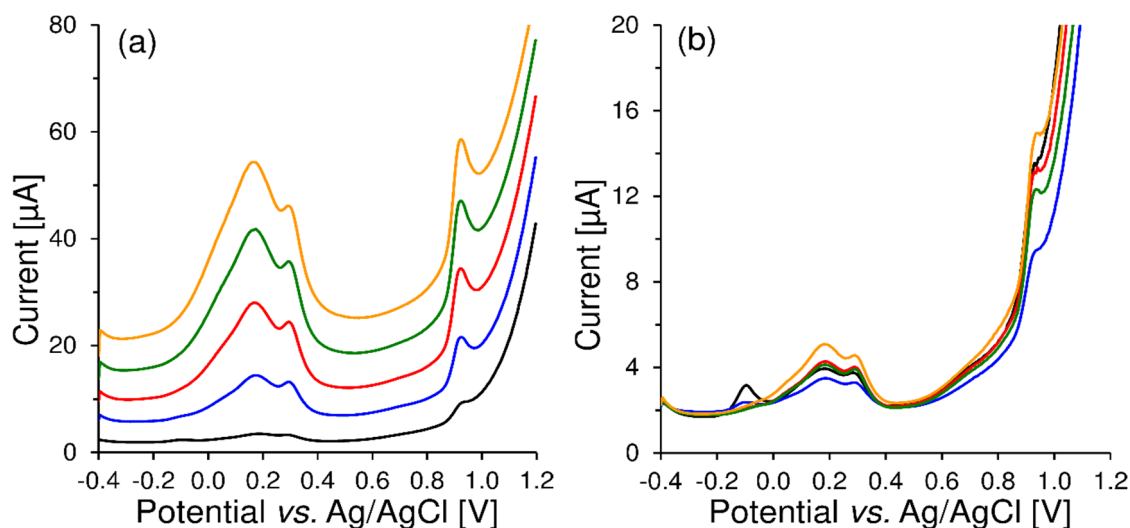

Fig. 4 Five repeated analyses performed at the same surface (a) and always renewed surface of CPE (b)

Experimental conditions: SWV, 0.1 mol L^{-1} acetate buffer (pH 4.5); CPEE: 80% (*w*/w) graphite CR-2 +20 % (*w*/w) extra-virgin olive oil (Amway); E_{dep} = −0.4 V, t_{dep} = 30 s, E_{step} = 5 mV, E_{ampl} = 25 mV, and f = 40 Hz

From the literature [27], it is known that vitamin E (VE), especially α- and γ-tocopherol (α-TOH and γ-TOH, resp.), represents the main electroactive nutrient with a high content. For example, fully refined rapeseed oils contain up to 80 mg per 100 g although the oil refining can cause losses up to 70 % VE [28]. Then, a minimal content of 0.1 % (*w/w*) VE can also be assumed even for the refined oil. Fig. 5 gathers anodic voltammograms recorded on model CPEEs differing in the α-TOH content (*w/w*).

A linear dependence between the anodic current response (I_p^a) and α-TOH content (*w/w*) described by a regression equation: $I_p^a = -0.6691 + 8.8263$ (*w/w*) with the coefficient of determination $R^2 = 0.9978$, was achieved for the concentration range from 0.5 to 2.5 % (*w/w*) α-TOH. With a relative high RSD of about 10 %, one could predict a limit of detection (LOD) of 0.15 % and limit of quantification (LOQ) of 0.45 % (both as *w/w*).
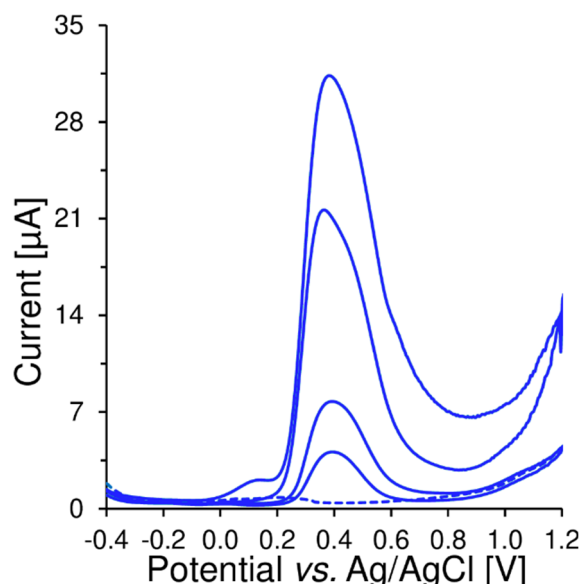

Fig. 5 Square-wave voltammograms at CPEEs varying in the content and in mutual ratio of mineral oil and α-tocopherol

Experimental conditions: 80% (*w/w*) graphite CR-2; 20, 19.5, 19, 17.5, and 15% (*w/w*) MO and correspondingly 0, 0.5, 1.0, 2.5, and 5.0% (*w/w*) α-TOH; 0.1 mol L^{-1} acetate buffer (pH 4.5); SWV ramp: $E_{dep} = -0.4$ V, $t_{dep} = 30$ s, $E_{step} = 5$ mV, $E_{ampl} = 25$ mV, and $f = 40$ Hz

Analysis of selected vegetable oils using SPV with CPEEs

Because of the fact, the technique of SPV with CPEEs is being only scarcely capable of precise quantitative analysis [2–4], it was necessary to test whether newly proposed CPEEs containing vegetable oils as a binder can be utilised at least for semi-quantitative determinations or only for qualitative analysis of the individual constituents in VOs, i.e., for identification. Fig. 6 (given overleaf) surveys of the

voltammetric curves obtained for four different samples of extra-virgin olive oils. As seen, up to five anodic signals — in figure, denoted by Roman symbols — could be observed. (*Note:* To present all four sub-figures in the desired way allowing one a comfortable criss-cross comparison, relatively low zoom has been used; nevertheless, all the signals of interest can be clearly noticed.)

According to the literature, the contents of electroactive compounds per 100 g virgin olive oil vary in the following intervals: 9.7–78.5 mg TOHs [28], 12.7–18.9 µg VK1 [29], 3.4–4.0 mg *β*-carotene [30], 0.4–0.48 mg oleuropein [31], and, finally, from 5 to 20 mg hydroxytyrosol [32].

Based on the subtracted values of the anodic peak potentials (E_p^a) and average content of the individual components, one can attribute the peak I to the electro-chemical oxidation of hydroxytyrosol, overlapping peaks II and III to tocopherols and tocotrienols, a broad peak IV to carotenoids, and the peak V to tyrosol.
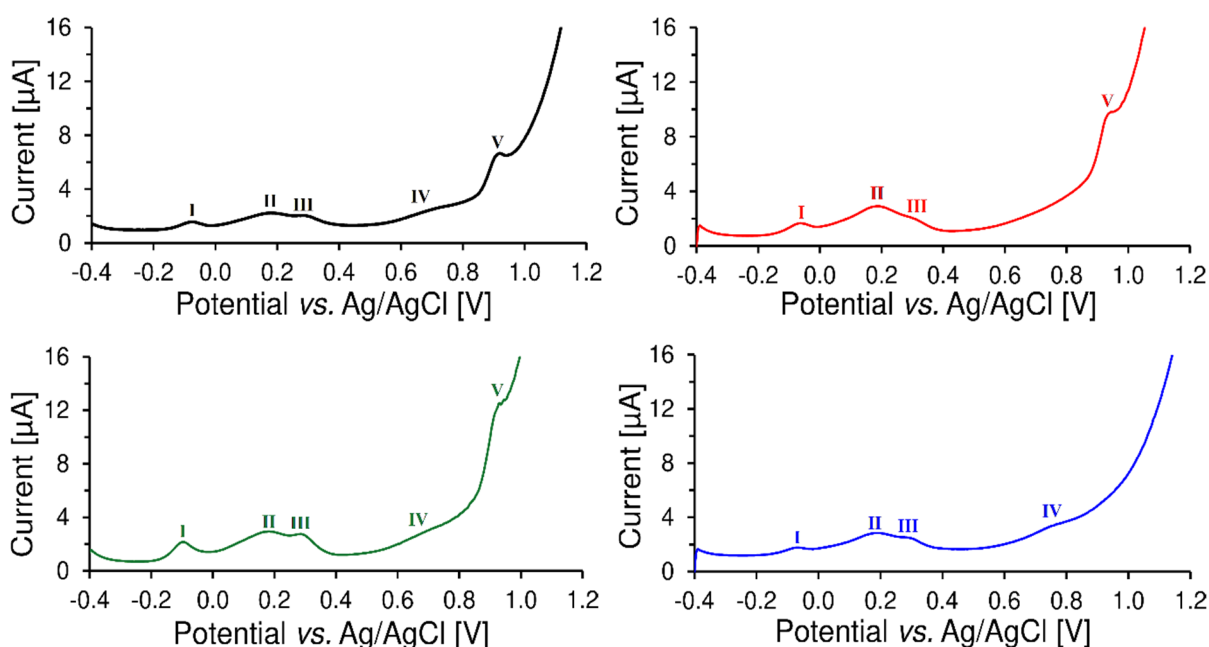

Fig. 6 Square-wave voltammograms obtained at CPEEs with four different extra-virgin olive oils

Legend: CPEE containing 20% (*w/w*) of the product by Oro Bailen (**black** curve), Gourmet Partners (red), Amway (green), and Biolevante (blue)

Experimental conditions: all CPEEs prepared from graphite CR-2 (80%, *w/w*); 0.1 mol L^{-1} acetate buffer (pH 4.45); SWV ramp: $E_{dep} = -0.4$ V, $t_{dep} = 30$ s, $E_{step} = 5$ mV, $E_{ampl} = 25$ mV, and $f = 40$ Hz

Very similar shapes of all the voltammograms for samples of olive oils was confirmed. As shown in Fig. 7, the situation was completely different when comparing various types of VOs.
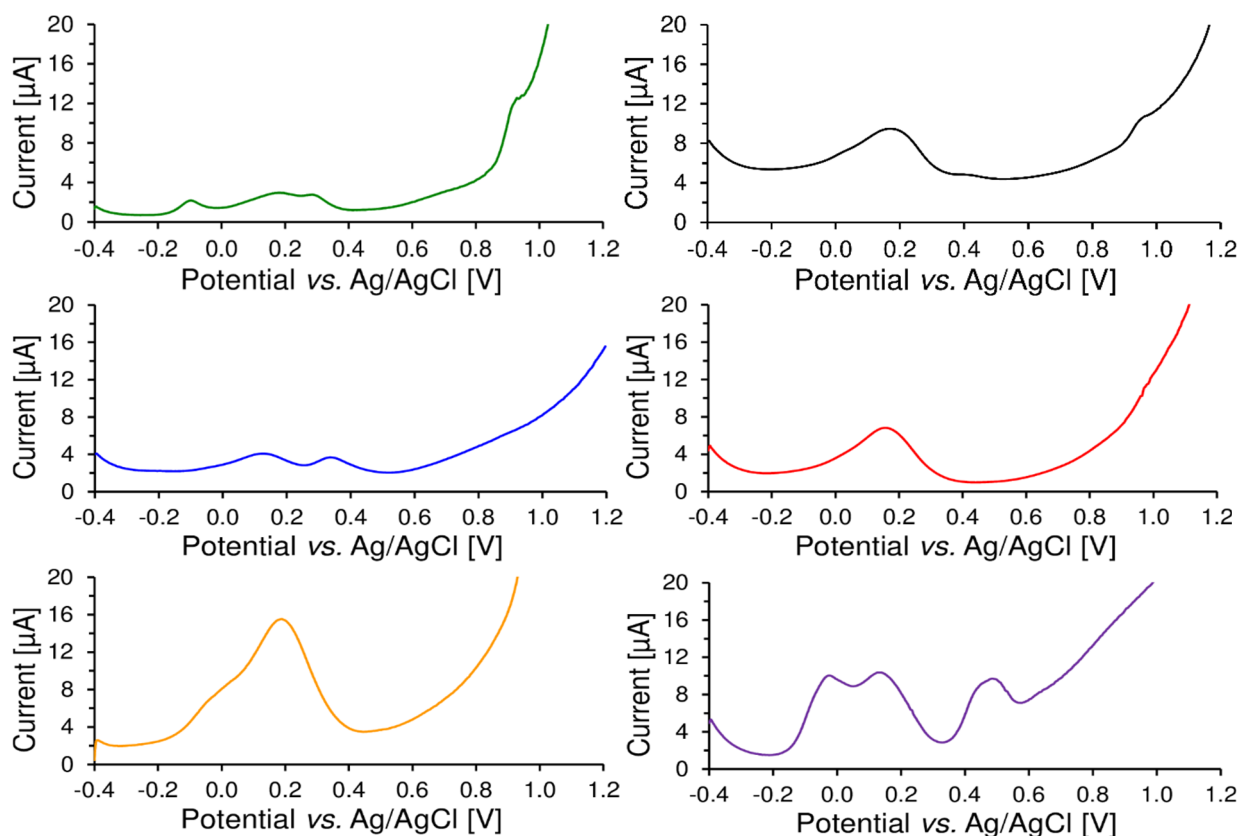
Fig. 7 Square-wave voltammograms obtained with CPEEs, prepared from various vegetable oils

Legend: The carbon paste was formed from 80% (*w/w*) graphite CR-2 and 20% (*w/w*) extra virgin olive (green curve), pumpkin (black), sunflower (blue), linseed (red), rapeseed (orange), and chia oil (violet)

Experimental conditions: 0.1 mol L^{-1} acetate buffer (pH 4.5); SWV ramp: $E_{dep} = -0.4$ V, $t_{dep} = 30$ s, $E_{step} = 5$ mV, $E_{ampl} = 25$ mV, and $f = 40$ Hz

In the case of SPV with CPEE, the mutual confrontation of the shapes of the voltammetric records obtained is more important than monitoring of the content of the individual electroactive organic substances. It seems that such a comparison of voltammograms enables to determine the types of VOs, when a voltammogram recorded for the known product can be archived as a specimen, together with the key experimental conditions, and thus functioning analogically as a fingerprinting in forensic analyses.

As expected from the data reported in the literature [28,33,34], the samples of rapeseed oil and chia oil had a significantly higher content of tocopherols and phenolic compounds than that of the others. Notwithstanding this fact, selected samples of extra-virgin olive oils and of pumpkin oil were richer in the occurrence of carotenoids and tyrosol [32,35].

Study on possible degradation of vegetable oils (forming the CPEEs)

In VOs, it is known that mainly tocopherols are sensitive to higher temperatures when they may undergo a gradual or even total disintegration [27]. This feature was thus utilised as a test on degradability of commercial products. The respective assay was accomplished in a way when the sample of rapeseed oil had been heated at constant temperature of 150 °C and the aliquot volume at defined time interval (every 5 min) then taken for voltammetric analysis.
Herein, it should be added that each aliquot was cooled down to laboratory temperature before preparation of the corresponding CPEE to keep the constant working conditions.

As demonstrated in Fig. 8, a typical decrease of the anodic peak current at +0.215 V vs. ref. was observed. This phenomenon probably corresponds to the above-mentioned degradation of tocopherols and/or the accompanying phenolic compounds, which is caused by oxidation with atmospheric oxygen [36] and their reaction with the free radicals formed [37,38]. To compare our observations with the literature data, for example, a report by Polish authors [39] states that about 7% of γ-TOH and 12% of α-TOH disappeared when refined rapeseed oil had been heated at 180 °C for 15 min. And after 8 hours at the same temperature the content of both isomers of tocopherols decreased correspondingly to 29% and 30%.

Thus, it can be deduced that SPV with CPEEs can also be used to reveal the degradation of electroactive compounds in VOs and to evaluate the quality of VOs via a dependence upon the storage time.
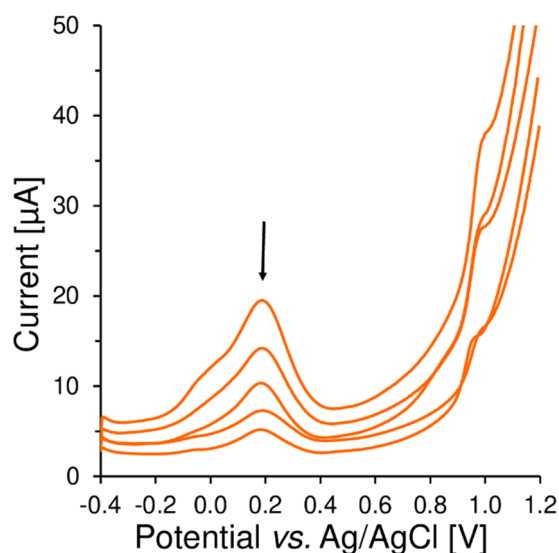

Fig. 8 Square-wave voltammograms obtained with CPEE prepared from temperature-pretreated vegetable oil

Experimental conditions: carbon paste, 80% (*w/w*) graphite CR-2 + 20% (*w/w*) rapeseed oil (Lukana); oil pre-heated at 150 °C for 0, 5, 10, 15, or 20 min and cooled down; 0.1 mol L^{-1} acetate buffer (pH 4.5); SWV ramp: $E_{dep} = -0.4$ V, $t_{dep} = 30$ s, $E_{step} = 5$ mV, $E_{ampl} = 25$ mV, and $f = 40$ Hz

Conclusions

A simple, low-cost, efficient, and semi-quantitative electroanalytical method for screening and evaluation of the quality of vegetable oils has been developed using the concept of solid-phase voltammetry with carbon paste electroactive electrodes prepared from graphite powder and a small portion of sample of VO.

All essential experimental conditions, including selection of the proper carbon material, composition of the working medium, as well as the key parameters of the SWV ramp were investigated and optimised. The voltammetric detection of electroactive organic compounds in VOs gave rise to a spectrum of anodic signals whose number and overall shape have been found to be typical for a certain type of vegetable oil, thus serving like "electrochemical fingerprinting"; in other words, "electrochemical spectroscopy" [10], or even "electrochemical clocks" [40] being capable to countdown the quality with respect to time.

It can be concluded that the proposed method employing SPV with CPEE can be recommended as a useful tool for simple, rapid, and low-cost quality evaluation of vegetable oils in specialised laboratories dealing with their post-production control or with serial routine analysis of commercially marketed products, including indicative assessment of their actual freshness.

Acknowledgements

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