














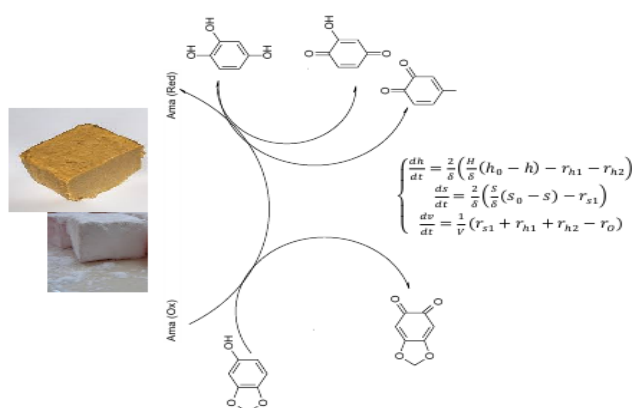
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The Theoretical Description for Fructose Fermentation Product Hydroxyquinol and its Ether Sesamol Amperometric Determination in Tahini Halva and Lokum

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For the first time, hydroxyquinol and sesamol electrochemical amperometric determination in *tahini halva* and *lokum* Turkish delights has been described. The electroanalytical process is given by amavadin-modified conducting polymer, in which both monomer and dopant may be natural compounds. Taking into account the ionic nature of the modifier, even in neutral medium the oscillatory behavior will be more probable in this system than in the simplest cases. Nevertheless, the amavadin-modified conducting polymer may be efficient electrode modifier for hydroxyquinol and sesamol electrochemical determination in Turkish delights like lokum and tahini halva.

Graphical abstract



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1. Introduction

Hydroxyquinol (1,2,4-trihydroxybenzene) [1 – 4] is one of three isomeric triphenolic compounds (Fig. 1). All of them are natural compounds, and hydroxyquinol is one of the most widespread among them. It is a product of fructose

dehydrative fermentation or termaldehydration product (Scheme 1).

The same phenolic compound is yielded while boiling or

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roasting fructose-containing products. Its ether sesamol [5 – 7] is also important, as one of the compounds responsible for the flavor, taste and antioxidant properties of Turkish delights including *halva* and *lokum* (Fig. 2). Both of the compounds are also used in other oriental delights including the Iranian

yoghurt-like drink *doug* and Turkish *simit* from Kastamonu region. For this and other reasons, the quantification of the two is really actual for fructose fermentation monitoring and food quality investigation (Fig. 2).

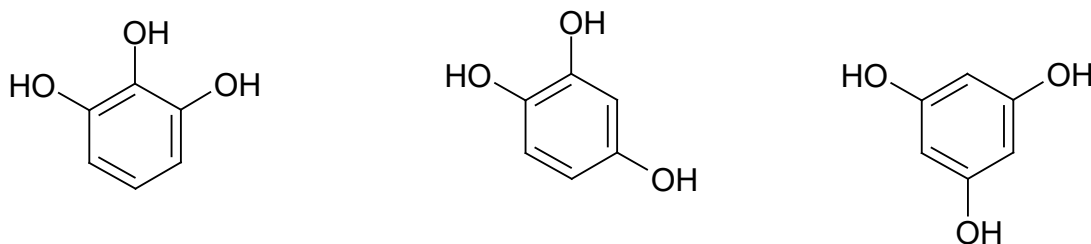
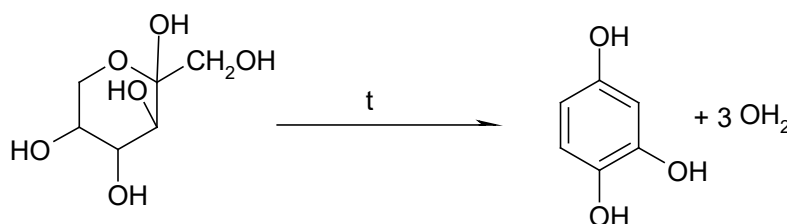


Fig. 1. From left to right pyrogallol, hydroxyquinol and phloroglucinol



Scheme 1.

The same phenolic compound is yielded while boiling or roasting fructose-containing products. Its ether sesamol [5 – 7] is also important, as one of the compounds responsible for the flavor, taste and antioxidant properties of Turkish delights including *halva* and *lokum* (Fig. 2). Both of the compounds are also used in other oriental delights including the Iranian yoghurt-like drink *doug* and Turkish *simit* from Kastamonu region. For this and other reasons, the quantification of the two is really actual for fructose fermentation monitoring and food quality investigation (Fig. 2).

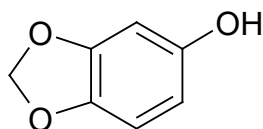


Fig. 2. Sesamol

Taking into account that the phenolic compounds are electrochemically active, the electroanalytical methods may be applicable to them [8 – 12]. Both hydroxyquinol and sesamol have been detected electrochemically [8, 10]. Nonetheless, as for now, no electrochemical method, capable to detect both of them has been reported till now. In this aspect, chemically modified electrodes (CME), in which the modifiers provide the excellent electroanalytical sensitivity and achieve the efficient peak separation. One of the most used organic CME are conducting polymers [13 – 15], also known as synthetic metals, which, combining the properties of plastics with metallic conductivity may provide an affinity to the analytes like key to the lock.

This affinity is provided by their modification flexibility, including the monomer and polymer transformation (by physical, chemical and electrochemical means) and polymer doping. For example, if a conducting polymer is doped by amavadin-ion (Fig. 3) [16 – 17], a natural oxidant from A.

muscaria, may easily enter the conducting polymer matrix, doping the polymer. The doped polymer will oxidize both of the phenolic compounds, which will thereby provide the analytical signal.

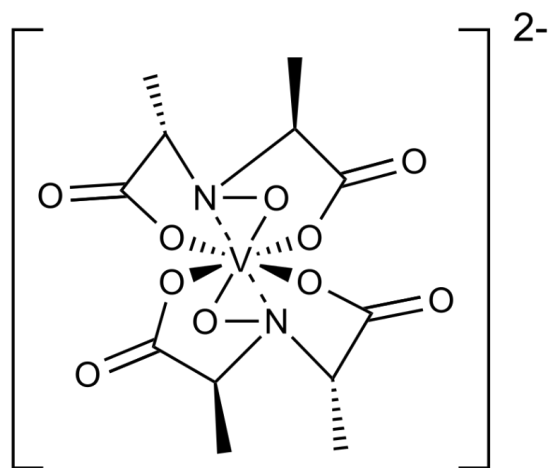


Fig. 3. Amavadin-ion.

Therefore, the goal of this work is to investigate theoretically the hydroxyquinol and sesamol electrochemical determination over amavadin-modified conducting polymer. This aims to find the condition of the parameter range for the best analytical signal interpretation, the oscillatory and monotonic instabilities condition and the comparison of the behavior of this system with that of the similar ones [18 – 21].

2. Material and Methods

On the first stage, the amavadin-ion, containing tetravalent vanadium form in the reduced state will be transformed to the

oxidized pentavalent form.

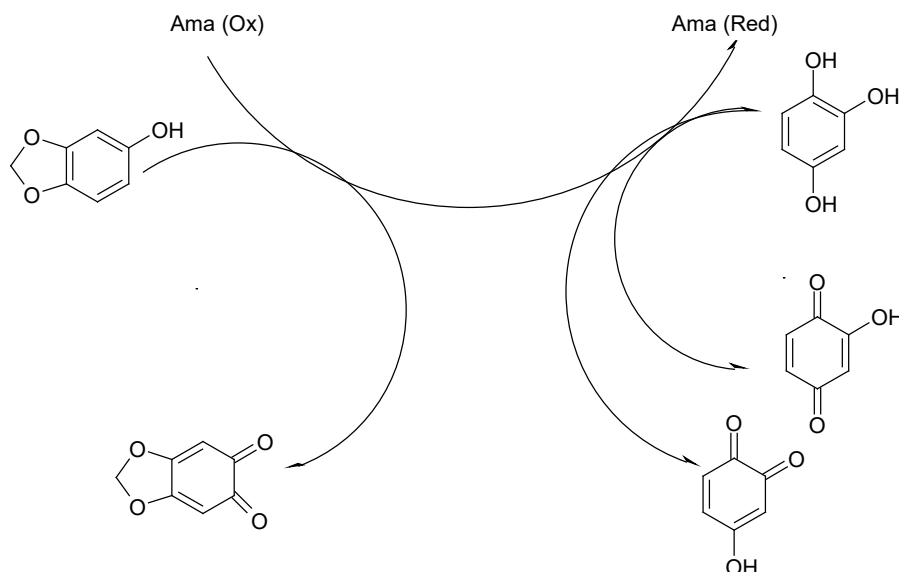
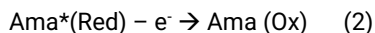


Fig. 4. Sesamol and hydroxyquinol determination process.

The modeling, including (co)polymerization scenarios will be described in our next works.

Therefore, taking some assumptions [18 – 21], we describe the behavior of this process by a trivariant equation-set (3).

$$\begin{cases} \frac{dh}{dt} = \frac{2}{\delta} \left(\frac{H}{\delta} (h_0 - h) - r_{h1} - r_{h2} \right) \\ \frac{ds}{dt} = \frac{2}{\delta} \left(\frac{S}{\delta} (s_0 - s) - r_{s1} \right) \\ \frac{dv}{dt} = \frac{1}{V} (r_{s1} + r_{h1} + r_{h2} - r_o) \end{cases} \quad (3)$$

Herein, h and s are hydroxyquinol and sesamol pre-surface layer concentrations, h_0 and s_0 their bulk concentrations, H and S are their diffusion coefficients, v is amavadin matrix coverage degree, V is its maximal matrix concentration and the parameters r are the correspondent reaction rates, calculated as:

$$r_{h1} = k_{h1} h (1 - v)^2 \exp(av) \quad (4)$$

$$r_{h2} = k_{h2} h (1 - v)^2 \exp(av) \quad (5)$$

$$r_s = k_s s (1 - v)^3 \exp(av) \quad (6)$$

$$r_o = k_o v \exp\left(\frac{F\phi_0}{RT}\right) \quad (7)$$

In which the parameters k are the correspondent reaction rate constants, a is the parameter, describing the influence of ionic transformations in matrix on DEL and surface ionic force, F is the Faraday number, ϕ_0 is the zero-charge related potential slope, R is the universal gas constant and T is the absolute temperature.

In neutral medium, the phenolic compounds are less ionized and thereby their chemical transformations DEL effect will be less expressed, than in the similar systems. Nevertheless, the amavadin ionic transformations will affect

Considering that the polymerization scenarios may require specific conditions, we conclude that the phenolic compounds will be oxidized according to the Fig. 4:

the DEL, provoking the oscillatory behavior.

These instability won't affect a generally stable and efficient electroanalytical process, as shown below, as it is realized beyond the detection limit.

3. Results and Discussion

We investigate the behavior of the hydroxyquinol and sesamol electrochemical determination over amavadin-doped conducting polymer by analyzing the equation-set (3) by means of linear stability theory and depict the Jacobian matrix members as (8):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (8)$$

in which:

$$a_{11} = \frac{2}{\delta} \left(-\frac{H}{\delta} (h_0 - h) - k_{h1} (1 - v)^2 \exp(av) - k_{h2} (1 - v)^2 \exp(av) \right) \quad (9)$$

$$a_{12} = 0 \quad (10)$$

$$a_{13} = \frac{2}{\delta} (2k_{h1} h (1 - v) \exp(av) - ak_{h1} h (1 - v)^2 \exp(av) + k_{h2} (1 - v)^2 \exp(av) - ak_{h2} h (1 - v)^2 \exp(av)) \quad (11)$$

$$a_{21} = 0 \quad (12)$$

$$a_{22} = \frac{2}{\delta} \left(-\frac{S}{\delta} - k_s (1 - v)^3 \exp(av) \right) \quad (13)$$

$$a_{23} = \frac{2}{\delta} (3k_s s (1 - v)^2 \exp(av) - ak_s s (1 - v)^3 \exp(av)) \quad (14)$$

$$a_{31} = \frac{1}{V} (k_{h1} (1 - v)^2 \exp(av) + k_{h2} (1 - v)^2 \exp(av)) \quad (15)$$

$$a_{32} = \frac{1}{V} (k_s (1 - v)^3 \exp(av)) \quad (16)$$

$$a_{33} = \frac{1}{v} \left(-2k_{h1}h(1-v)\exp(av) + ak_{h1}h(1-v)^2\exp(av) - k_{h2}(1-v)^2\exp(av) + ak_{h2}h(1-v)^2\exp(av) - 3k_s s(1-v)^2\exp(av) + ak_s s(1-v)^3\exp(av) - k_o \exp\left(\frac{F\phi_o}{RT}\right) + jk_o v \exp\left(\frac{F\phi_o}{RT}\right) \right) \quad (17)$$

In neutral medium, the phenolic compounds are less ionized than in alkaline solutions. On the other hand, the amavadin alternates between tetra- and pentavalent ionic forms during the electroanalytical process, which affects the surface and the DEL ionic forms. Therefore, the oscillatory behavior, despite of being less probable than for the alkaline medium, will remain more probable than for the simplest case [18 – 21].

The main condition for the Hopf bifurcation, responsible for the oscillatory behavior is the presence of the positive elements in the Jacobian main diagonal. They are responsible for the positive callback. As in [18 – 21], those elements are $j\tau_o > 0$, if $j > 0$ and $a(r_{h1} + r_{h2} + r_s) > 0$, if $a > 0$, defining the DEL influences of the ionic transformations in polymer matrix during the chemical and electrochemical stages. They describe the cyclic conductivity changes in the electroanalytical cell, caused by ionic form alternation in the polymer matrix, and correspond to the frequent and small-amplitude oscillations.

As for the steady-state stability, it will be warranted if $a \leq 0$, $j \leq 0$. It is possible to show this using Routh-Hurwitz criterion. In order to avoid cumbersome expressions during its application, we rewrite the determinant as (18):

$$\frac{4}{\delta^2 v} \begin{vmatrix} -\eta - \Xi & 0 & \Phi \\ 0 & -\sigma - T & \Lambda \\ \Xi & T & -\Phi - \Lambda - \Omega \end{vmatrix} \quad (18)$$

Opening the straight brackets and applying the Det $J < 0$ requisite, salient from the criterion, we obtain the stability condition, described as (19):

$$\eta(\sigma\Phi + \sigma\Lambda + \sigma\Omega + T\Phi + T\Omega) + \Xi(\sigma\Lambda + \sigma\Omega + T\Omega) > 0 \quad (19)$$

Which defines an electroanalytically efficient diffusion- and kinetically controlled system. Really, if $a \leq 0$ and $j \leq 0$, the kinetical parameters Ω , T and Λ will be positive, shifting the left side of the inequation (19) to more positive values, stabilizing the system. Moreover, as neither analyte nor electrode modifier stability is compromised by side reactions, the steady-state stability will be thereby correspondent to the linear dependence between the current and concentration.

As for the *detection limit*, it is defined by the monotonic instability, correspondent to the limiting point between the stable steady-states and unstable states. This instability is described by the principal conditions of Det $J = 0$ or (20):

$$\eta(\sigma\Phi + \sigma\Lambda + \sigma\Omega + T\Phi + T\Omega) + \Xi(\sigma\Lambda + \sigma\Omega + T\Omega) > 0 \quad (20)$$

If the solution conditions and potential applied to the anode correspond to the (co)polymerization chain initiation, the electron becomes transferred from the oxidized amavadin form to the polyphenolic compound, yielding the tetravalent form and cation-radical, provoking the chain growth. In this case, the equation-set (3) becomes modified to (21):

$$\begin{cases} \frac{dh}{dt} = \frac{2}{\delta} \left(\frac{H}{\delta} (h_0 - h) - r_{h1} - r_{h2} - r_c \right) \\ \frac{ds}{dt} = \frac{2}{\delta} \left(\frac{S}{\delta} (s_0 - s) - r_{s1} - r_c \right) \\ \frac{dv}{dt} = \frac{1}{v} (r_{s1} + r_{h1} + r_{h2} + r_c - r_o) \end{cases} \quad (21)$$

Describing a somehow more accomplished behavior, including homo- and copolymerization scenarios, which may yield a green conducting polymer. The structure of the resulting polymer depends on the analysis conditions.

This model is viable for neutral and mildly acidic medium. In alkaline medium, some corrections concerning phenolic compounds ionization have to be added [20 – 21]. These corrections include one more exponential multiplier, the presence of which will depict one more factor causing the oscillatory behavior. This factor has to be considered while using this sensor for the determination of hydroxyquinol and sesamol in other types of *halva*.

The interference of other polyphenolic compounds, including pyrogallol, phloroglucinol and their ethers is fixed by the presence of amavadin as modifier, as amavadin reacts with those compounds in a slightly different manner, which causes the voltammetric peak separation. As the matter of fact, it is also possible to use it for the determination of those compounds, and the behavior of this process will be described by a model, similar to the described above.

4. Conclusions

From the analysis of the system with hydroxyquinol and sesamol electrochemical determination, assisted by amavadin-doped conducting polymer, it was possible to conclude that that it is an efficient process, in which the linear dependence between the analyte concentration and electrochemical parameter is easy to form in an efficient diffusion and kinetically-controlled system. For its turn, the oscillatory behavior is expected to be less probable than in the alkaline medium, but even though more probable than in the simplest case, due to surface and double electric layer structure changes during the process on both chemical and electrochemical stage.

Author Contributions

Volodymyr V. Tkach (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing); Marta V. Kushnir (Data Curation, Conceptualization, Investigation); Iryna M. Kornienko (Conceptualization, Investigation, Supervision, Formal Analysis); Larysa S. Yastremska (Conceptualization, Investigation, Supervision, Formal Analysis), Larysa S. Yastremska (Conceptualization, Investigation, Supervision, Formal Analysis), Olena O. Kuznetsova (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Viktor V. Kryvetskyi (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Inna I. Kryvetska (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Igor V. Kryvetskyi (Investigation, Conceptualization, Data Curation, Methodology, Validation, Visualization), Petro I. Yagodynets' (Investigation, Conceptualization, Methodology, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing), Zholt O. Kormosh (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and

Editing), Dina V. Fedorova (Investigation, Conceptualization, Data Curation), Nadiia Yu. Chykun (Investigation, Conceptualization, Supervision, Validation, Writing – Original Draft, Writing – Review and Editing).

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