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The Theoretical Description of Furfural and Lactic Acid Cathodic Determination in Bread and Milk

Volodymyr V. Tkach [1,*], Tetiana V. Morozova [2], Serhii V. Prymachenko [3], Iryna M. Korniienko [3], Larysa S. Yastremska [3], Olena O. Kuznetsova [3], Valentyna A. Chychun [4], José Inácio Ferrão da Paiva Martins [5], Lucinda Vaz dos Reis [6], Necdet Karakoyun [7], Marta V. Kushnir [1]

1 Chernivtsi National University, 58000, Kotsyubyns´ky Str. 2, Chernivtsi, Ukraine
2 National Transport University, 02000, Omelianovych-Pavlenko Str. 1, Kyiv, Ukraine
3 National Aviation University 03058, L. Huzar Ave., 1, Kyiv, Ukraine
4 Chernivtsi Institute of Trade and Economics of Kyiv National University of Trade and Economics, 58001, Central Sq. 6, Chernivtsi, Ukraine
5 Faculty of Engineering of the University of Porto, 4200-465, Rua Dr. Roberto Frias, s/n, Porto, Portugal
6 University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5001-801, Folhadela, Vila Real, Portugal
7 Yüzüncü Yil University of Van, Bardakçı, 65090, Tuşba/Van, Türkiye
* Correspondence: nightwatcher2401@gmail.com (V.V.T.);

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Abstract: The process of the electroanalytical cathodic determination of furfural and lactic acid in fermented bread and milk on vanadium oxyhydroxide-modified cathode has been developed and analyzed theoretically. The correspondent mathematical model analysis confirms this process's efficiency for furfural and lactic acid determination in a mildly acidic and neutral medium by a cathodic determination to propyleneglycol and furfuroic alcohol. Considering that both the compounds and their reduction products are less ionized in acidic media, cathodic reduction tends to be more efficient than anodic electrooxidation.

Keywords: furfural; lactic acid; electrochemical sensor; vanadium (III) oxyhydroxide; stable steady-state.

1. Introduction

The Ottoman Empire existed between 1299 and 1922. It was one of the major empires in the world, controlling, on its major extension, in 1687, nearly 5,2 million square kilometers, being home to nearly 30 000 000 people. In other words, one in every 25 people in the world lived in the Ottoman Empire [1 – 3]. It might be the most potent during the reign of Sultan Suleiman I, also known as Kanuni (Lawgiver). He is known as the author of the major Ottoman Law Code, known as Kanun-I Osmani or Kanunname. The law code inputs the legislative regulation to different areas, including bread production. The law foresaw that the flour had to be filtered by a sift with small pores and that the bread should be well done and should not smell another way than the common bread.

The bread scent is given by furfural (Figure 1 to the left) – a pento- and hexafuranose main fermentation product. It is an aldehyde formed during natural or artificial fermentation. [4 – 7]. Another side-product of the fermentation is lactic acid [8 – 10], a product of the glucose

fermentation by acils *L. bulgaricus*, *L. delbrueckii*, *L. acidophilus*, streptococ *S. thermophilus* (growing its activity if the bread is hot) and bifidobacteria *B. Infantis* and *B. Lactis*. The 5-hidroximetilfurfural, the main product of hexafuranose fermentations, appears in honey.

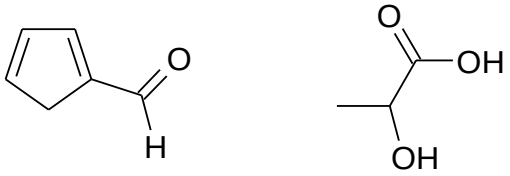

Figure 1. Furfural and lactic acid.

Besides bread fermentation, the bifidobacteria are used in pharmaceutical formulations [11, 12] to treat different gastrointestinal infections and diarrhea.

As for furfural, it is a nutriceutical and antioxidant, also serving as a starting point for different drugs like furosemide. Lactic acid, for its turn, besides being a food component, is also a human metabolism product. It is also used in pharmaceutical formulations as a main metabolism corrector. The concentration of both products is important to maintain homeostasis. Therefore, developing an efficient method for its quantification is actual [13 – 15]. Simultaneously determining furfural and lactic acid is important for the bread and milk products' organoleptic and alimentary properties determination.

Both of the compounds are electroactive and contain oxidative and reducing groups. [14 – 16]. Taking into account that the bread and milk pH is mildly acidic, the cathodic process, in which the protons participate in the reduction of the analyte, is preferable.

By this, the vanadium (III) oxyhydroxide, suitable as a cathode modifier for neutral and mildly acidic media, could be used as an electrode modifier [17 – 18]. So the goal of our work is to evaluate theoretically the VO(OH)-assisted furfural and lactic acid determination. This evaluation is made in electroanalytical and stability terms in order to foresee the behavior of the electroanalytical process and the conditions of the most efficient analytical signal interpretation. It also includes a comparison of the behavior of this system with that of similar ones [19 – 21].

2. System and its Modeling

Both furfural and lactic acid possess carbonyl groups. In the second case, it is linked directly to a hydroxyl, forming a carboxyl. Either way, the corresponding alcohols are formed during VO(OH)-assisted reduction. Further reduction with furan ring opening and alcoholic group transformation into alkan fragments is given by lower potentials.

Both vanadium dioxide and vanadyl ions may be formed as tetravalent vanadium forms. Either way, they are reduced, regenerating vanadium (III) oxyhydroxide as:

$$VO2 + H+ + e- \rightarrow VO(OH) \quad (1)$$

Or

$$VO2+ + H2O + e- \rightarrow VO(OH) + H+ \quad (2)$$

Considering the formation of vanadium dioxide as the main tetravalent vanadium form, we represent the electroanalytical process in Figure 2 schematically.

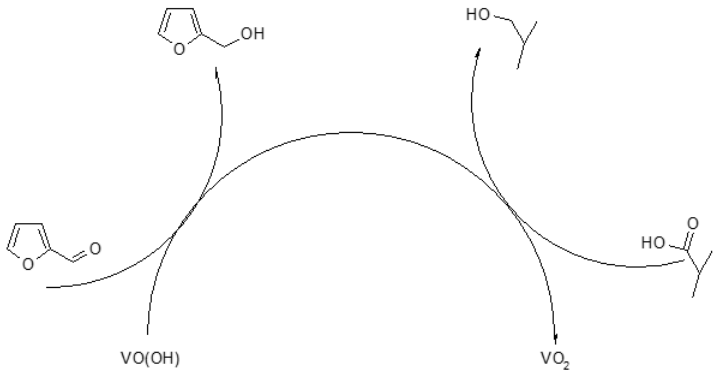

Figure 2. The schematic representation for the electroanalytical process.

Taking this into account and taking some assumptions [19 – 21], we describe the behavior of this system by the differential equation-set (3):

$$\begin{cases} \frac{df}{dt} = \frac{2}{\delta}\left(\frac{\Phi}{\delta}(f_0 - f) - f_1\right) \\ \frac{dl}{dt} = \frac{2}{\delta}\left(\frac{\Lambda}{\delta}(l_0 - l) - l_1\right) \\ \frac{dv}{dt} = \frac{1}{V}(f_1 + l_1 - v_1) \end{cases} \quad (3)$$

Being f and l the pre-surface concentration of furfural and lactic acid, Φ and Λ are their diffusion coefficients, f0, and l0 are their bulk concentrations, and f1 and l1 are their reduction rates (4 – 5), C is its maximal surface concentration, and v1 is its reduction rate (6).

$$f_1 = k_{f1} f (1 - v)^2 \quad (4)$$

$$l_1 = k_{l1} l (1 - v)^4 \quad (5)$$

$$v_1 = k_{v1} v \exp -\frac{F\varphi_0}{RT} \quad (6)$$

Herein, the parameters k are the correspondent reaction rate constants, 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 this case, the neutral or mildly acidic media favors the easy interpretation of the analytical signal. Moreover, the mildly acidic media favors the bread, and milk favors the reduction of both of the analytes. Nevertheless, highly acidic media will destroy the electrode modifier by (7):

$$VO(OH) + 3H+ \rightarrow V^{3+} + 2H_2O \quad (7)$$

or (8):

$$VO_2 + 4H+ + e- \rightarrow V^{3+} + 2H_2O \quad (8)$$

dissolving the modifier and making thereby unstable the electroanalytical process. Therefore, vanadium(III) oxyhydroxide is efficient for a cathodic reduction in the pH range of nearly 3<pH≤7. In this pH range, the process will be stable and efficient, as shown below.

3. Results and Discussion

To investigate the system with furfural and lactic acid VO(OH)-assisted determination in breads and milk, we analyze the equation-set (3) alongside the algebraic relations (4 – 6), by linear stability theory and write the steady-state Jacobian members as (9):

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (9)$$

in which:

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Phi}{\delta} - k_{f1}(1-v)^2\right) \quad (10)$$

$$a_{12} = 0 \quad (11)$$

$$a_{13} = \frac{2}{\delta}\left(2k_{f1}f(1-v)\right) \quad (12)$$

$$a_{21} = 0 \quad (13)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{\Lambda}{\delta} - k_{l1}(1-v)^4\right) \quad (14)$$

$$a_{23} = \frac{2}{\delta}(4k_{l1}(1-v)^3) \quad (15)$$

$$a_{31} = \frac{1}{V}\left(k_{f1}(1-v)^2\right) \quad (16)$$

$$a_{32} = \frac{1}{V}(k_{l1}(1-v)^4) \quad (17)$$

$$a_{33} = \frac{1}{V}\left(-2k_{f1}f(1-v) - 4k_{l1}(1-v)^3 - k_{v1}\exp\left(-\frac{F\varphi_0}{RT}\right) + jk_{v1}v\exp\left(-\frac{F\varphi_0}{RT}\right)\right) \quad (18)$$

Considering the elements (10), (14), and (18), we may conclude that in a mildly acidic medium, correspondent to milk and bread, the electrochemical oscillations, although possible, are less probable than in similar systems, due to the low ionization degree of each one of the analytes and their oxidation products.

The unique factor responsible for the oscillatory behavior is the influences of the electrochemical stage on the ionic force, capacitance, and impedance in DEL, provoking the cyclic changes in current. The oscillation frequency and amplitude will depend on electrode composition, such as observed experimentally [18 – 19] and theoretically [20 – 21]. This is also realized contrarily to the reduction in the alkaline media and contrarily to the anodic oxidation in the same conditions.

In order to investigate the steady-state stability via the Routh-Hurwitz criterion, we rewrite the determinant, introducing new variables (18):

$$\frac{4}{\delta^2 C}\begin{vmatrix} -\varphi - \Xi & 0 & P \\ 0 & -\lambda - T & \Sigma \\ \Xi & T & -P - \Sigma - \Omega \end{vmatrix} \quad (18)$$

avoiding thereby the cumbersome expressions.

Opening the brackets, applying the Det J<0 requisites, salient from the criterion, and changing the signs, we obtain the stability requirement as (19):

$$\varphi(\lambda P + \lambda\Sigma + \lambda\Omega + TP + T\Omega) + \Xi(\lambda\Sigma + \lambda\Omega + T\Omega) > 0 \quad (19)$$

Describing an efficient diffusion-controlled system. The kinetic influence enhances if the DEL is highly affected. As cited above, the steady-state stability of the analytes and the modifier aren't compromised at the working pH (3<pH≤7), corresponding to milk and bread. Therefore, the steady-state stability will correspond to the linear dependence between the analytes concentration and the current, which will permit the easy interpretation of the analytical signal.

As for the detection limit, it will be correspondent to the monotonic instability, defined by the Det J=0 condition, or (20):

$$\varphi(\lambda P + \lambda\Sigma + \lambda\Omega + TP + T\Omega) + \Xi(\lambda\Sigma + \lambda\Omega + T\Omega) > 0 \quad (20)$$

If vanadium hydroxide is used, the furfural will be reduced in two manners, including furan cycle destruction. This case will become more complicated and be described in our next works.

If a lactate ester is used, the system's behavior will be dependent on the alcoholic fragment present in it. If the corresponding alcohol contains the reducing groups, another scenario is added.

4. Conclusions

From the theoretical investigation of furfural and lactic acid cathodic determination on VO(OH), it was possible to conclude that this is an efficient electroanalytical process, more efficient than the anodic electrooxidation in the same conditions. As for milk and bread, in which the pH value is mildly acidic, it is foreseen to be more efficient, as the protons participate in the reduction process. The electroanalytical process is diffusion-controlled, although the kinetic factor plays an important role in the process stabilization. The unique factor of the electrochemical reduction influence to double electric layer electrophysical properties may cause the oscillatory behavior.

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Conflicts of Interest

The authors declare no conflict of interest.

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