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The Theoretical Description for CoO(OH)-Assisted Electrochemical Determination of Sucralose and Perillartine in Beverages

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Abstract: This work gives the possibility for sucralose and perillartine electrochemical determination over cobalt (III)-oxyhydroxide-modified electrodes. It is shown that the neutral and mildly acidic medium is the most convenient for perillartin electrochemical determination on CoO(OH) due to the less expressed ionization of both of the analytes. The analysis of the correspondent mathematical model confirms the efficiency of the electroanalytical process in the detection of both sweeteners in beverages. This process may be used in food quality tests or falsification investigations.

Keywords: food safety; perillartine; sucralose; cobalt (III) oxyhydroxide; electrochemical sensor; electrochemical oscillations; stable steady-state.

1. Introduction

Perillartine (Figure 1) (perillaldehyde anti-aldoxime) is a natural sugar substitute [1–6] extracted from Japanese perilla (shiso) leaves. As mentioned below, it is considered twice as sweet as sucralose, four times as sweet as saccharine, and 2000 times as sweet as sucrose, so it may serve as a viable alternative to synthetic sweeteners. It may be used alongside its ether adduct (Figure 1).

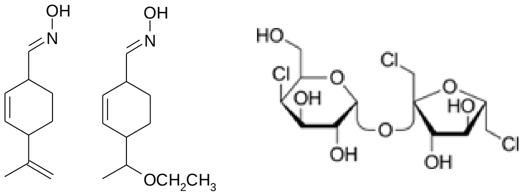

Figure 1. Perillartine, its ether derivative and sucralose

Nevertheless, it may be allergic for people allergic to shiso herb. Also, some toxic nitrogen derivatives like hydroxylamine may form during its metabolism in some people [3–6]. Thus, developing an efficient, exact, and rapid method for perillartine determination is really a task, and electroanalytical methods would provide a good service.

Sucralose [7–12] (Figure 1 to the right) is an extremely stable artificial sweetener up to 1000 times as sweet as common sugar. Its effects on human and animal organisms have not yet been completely studied. Moreover, being hardly metabolized, it is accumulated in the environment. A recent 2023-dated study has shown that the use of sucralose by pregnant women can influence the neonates' gut microbiota [9]. Also, the organisms capable of metabolizing it transform sucralose into toxic chloroorganic derivatives like dioxins and tetrachlorodibenzofurans.

Moreover, sucralose may be added in the double dose to mimic perillartine presence in the products, pretending to be Japanese. For this reason, the sucralose and perilartine determination is also actual.

Both substances are electroactive, being both anodic and cathodic processes applicable to them. In the case of anodic oxidation, cobalt (III) oxyhydroxide [13–15] may be used as an efficient electrode modifier for this purpose.

In our previous works, the theoretical description for CoO(OH) action as an electrode modifier for the determination of sucralose [17] and perillartine [18] separately has been proven as efficient. Nevertheless, both of them may be used together in beverages, pharmaceutical formulations, food, and cosmetics, and the relative concentration between the two may be very important to verify the product composition, safety, and origin.

Therefore, this work investigates the possibility of CoO(OH)-assisted determination and quantification of sucralose and perillartine in beverages. This includes developing and analyzing the correspondent mathematical model in stability terms and comparing the system's behavior with similar systems [16–21]. This analysis aids us in the sensor development.

2. Materials and Methods

The electroanalytical process in this system is given in a neutral medium. By this, the chlorine atoms in sucralose do not hydrolyze. Therefore, the electrooxidation of sucralose will be only given by the hydroxymethyl group. As for perillartine, two oxidation scenarios are possible, one of them hydroxylation via Wagner reaction and another oxyme group oxidation to nitroform. By this, the electroanalytical process will be realized as in Figure 2.

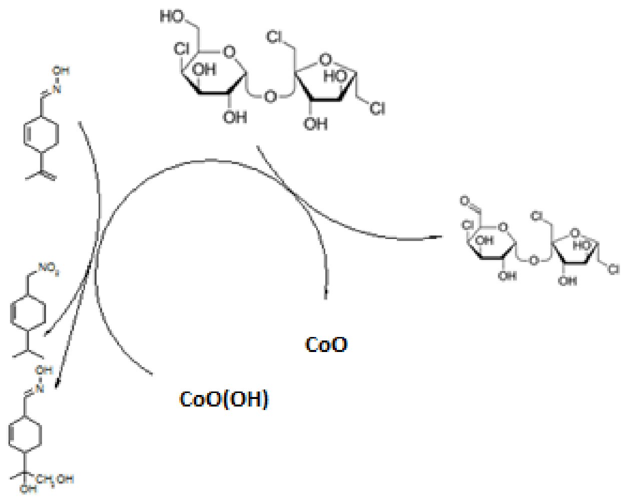

Figure 2. Sucralose and perillartine CoO(OH)-assisted determination.

Taking some assumptions, we describe the electroanalytical process by a trivariant equation-set (1):

$$\begin{cases} \frac{dp}{dt} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(p_0 - p) - r_{11} - r_{12}\right) \\ \frac{ds}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(s_0 - s) - r_{21}\right) \\ \frac{dc}{dt} = \frac{1}{C}(r_{11} + r_{12} + r_{21} - r_3) \end{cases} \quad (1)$$

in which p and s are perillartine and sucralose pre-surface concentrations, p_0 and s_0 are their bulk concentrations, Δ and D are the diffusion coefficients, c is the cobalt oxide matrix coverage degree, and C is its maximal matrix concentration.

As for the parameters r, they stand for the correspondent reaction rates, calculated as:

$$r_{11} = k_{11}p(1-c)^4 \quad (2)$$

$$r_{12} = k_{12}p(1-c)^3 \quad (3)$$

$$r_{21} = k_{21}s(1-c)^2 \quad (4)$$

$$r_3 = k_3 c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (5)$$

in which the parameters k stand for 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 an alkaline medium [17, 18], both sucralose and perillartine will be hydrolyzed and ionized, which will have a great impact on the DEL ionic force and related factors. As for the neutral medium, the ionization factor may be neglected for both of the analytes, which favors the electroanalytical function of the sensor, as shown below.

3. Results and Discussion

Analyzing equation-set (1) by means of linear stability theory, we investigate the behavior for CoO(OH)-assisted electrochemical determination of sucralose and perillartine in beverages in a neutral medium. We expose the steady-state stability of Jacobian members as (6).

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \quad (6),$$

wherein

$$a_{11} = \frac{2}{\delta}\left(-\frac{\Delta}{\delta} - k_{11}(1-c)^4 - k_{12}(1-c)^3\right) \tag{7}$$

$$a_{12} = 0 \tag{8}$$

$$a_{13} = \frac{2}{\delta}\left(4k_{11}p(1-c)^3 + 3k_{12}p(1-c)^2\right) \tag{9}$$

$$a_{21} = 0 \tag{10}$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{D}{\delta} - k_{21}(1-c)^2\right) \tag{11}$$

$$a_{23} = \frac{2}{\delta}\left(2k_{21}s(1-c)\right) \tag{12}$$

$$a_{31} = \frac{1}{C}\left(k_{11}(1-c)^4 + k_{12}(1-c)^3\right) \tag{13}$$

$$a_{32} = \frac{1}{C}\left(k_{21}(1-c)^2\right) \tag{14}$$

$$a_{33} = \frac{1}{C}\left(-4k_{11}p(1-c)^3 - 3k_{12}p(1-c)^2 - 2k_{21}s(1-c) - k_3 \exp\left(\frac{F\varphi_0}{RT}\right) + jk_3 c \exp\left(\frac{F\varphi_0}{RT}\right)\right) \tag{15}$$

Contrarily to the works [17, 18], neither additional ionization nor side reactions in a neutral medium, leading to DEL impact, are realized. Therefore, the system will be much more stable, and the electroanalytical process will be easier to realize and interpret, as confirmed by the stability analysis below.

Rewriting the Jacobian determinant as (16):

$$\frac{4}{\delta^2 C}\begin{vmatrix} -\kappa - \Xi & 0 & \Sigma \\ 0 & -\xi - \Lambda & T \\ \Xi & \Lambda & -\Sigma - T - \Omega \end{vmatrix} \tag{16}$$

Opening the brackets and applying the Det J<0 requisite, salient from the Routh-Hurwitz criterion, we obtain the steady-state stability requirement (17):

$$-\kappa(\xi\Sigma + \Lambda\Sigma + \xi T + \xi\Omega + \Lambda\Omega) - \Xi(\xi T + \xi\Omega + \Lambda\Omega) < 0 \tag{17}$$

Which, contrarily to diffusion and kinetically controlled processes described in [17, 18], will correspond to the mostly diffusion-controlled process, in which the electroanalytical process will be even more efficient. This will correspond to the linear dependence between the electrochemical parameter (current) and concentration, which will be realized in a vaster parameter region, thereby augmenting the process's sensitivity.

As for the detection limit, it will correspond to the monotonic instability, which will thereby correspond to the nullity of the determinant (18):

$$-\kappa(\xi\Sigma + \Lambda\Sigma + \xi T + \xi\Omega + \Lambda\Omega) - \Xi(\xi T + \xi\Omega + \Lambda\Omega) = 0 \tag{18}$$

This will delimit a margin between the stable steady-states and unstable states, in which multiple steady-states, each one unstable, coexist.

The oscillatory behavior will be less probable than in an alkaline medium [17 – 18], in which the ionization factor and its influence on the DEL ionic force and related parameters becomes important. The unique factor responsible for the positive callback necessary for this system's oscillatory behavior is the electrochemical stages' DEL influences. They are described by the positivity of the parameter Ω, requiring the positivity of $jk_3 c \exp\left(\frac{F\varphi_0}{RT}\right)$, if j>0. Even in a neutral medium, the oscillation frequency and amplitude depend on the background electrolyte composition.

As for the cathodic process, perillartin and sucralose determination are also possible. Other electrode modifiers, like conducting polymers and vanadium (III) oxyhydroxide, must be used in this process. On the other hand, determining other sweeteners (saccharin, aspartame, acesulfame K) with perillartine is preferable on the cathode, as shown in our next works.

4. Conclusions

From the analysis of the system with CoO(OH)-assisted sucralose and perillartine electrochemical determination, it is possible to conclude that this process is a highly efficient diffusion-controlled process, in which the linear dependence between the electrochemical parameter and concentration is easily obtained and maintained. The easy interpretation of the analytical signal is given mostly in a neutral medium, in which neither the analytes nor their oxidation products are not ionized and, thereby, their ionic forms do not influence the DEL ionic force and related electrophysical properties, making it less probable the oscillatory behavior.

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Conflicts of Interest

The authors declare no conflict of interest.

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