

The Theoretical Description of Sucralose and Lugduname Electrochemical Determination in Beverages

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Abstract: The possibility of sucralose and lugduname electrochemical determination in beverages has been analyzed for the first time from a theoretical point of view. It has been shown that the electrochemical determination of sucralose and lugduname may be carried out efficiently by an anodic process due to the presence of electroactive groups in both substances despite the hybrid mechanism for lugduname electrooxidation. The stability analysis of the system from the steady-state formation and maintenance point of view confirms that the neutral or mildly acidic medium is favorable for the determination of both sweeteners.

Keywords: sucralose; lugduname; cobalt (III) oxyhydroxide; conducting polymer; electrochemical sensor; stable steady-state

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1. Introduction

Lugduname (Fig. 1) is one of the sweetest substances in the world [1]. It is estimated to be up to 300000 (three hundred thousand) times as sweet as common sugar, 37,5 times as sweet as neotame, the sweetest sugar substitute currently in widespread use, 300 times as sweet

as sucralose, and 600 times as saccharine. It was developed by the Université de Lyon (France) in 1996, and its name is derived from the Latin name of the city (Lugdunum). It is a part of the family of the guanidine derivatives of acetic acid, which are found to be potent sweeteners. It is also used to study animal taste responses [2].

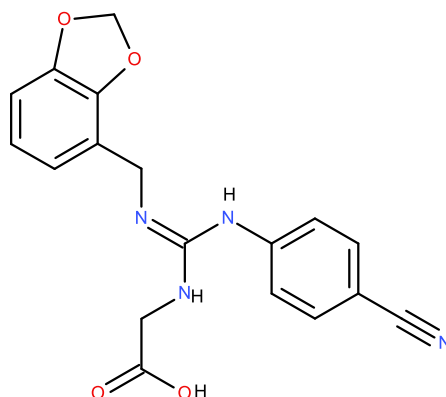


Figure 1. Lugduname.

It is limitedly used as a sweetener, as its toxicity essays have not been finished yet. Moreover, it contains toxic groups, like nitrile [3,4], the toxicity of which is dose-related. Therefore, developing a method for lugduname determination is actually [5], and electrochemical methods could provide a good service.

Adding two or more sweeteners to the beverage is frequently used to obtain certain taste combinations and/or mimic the real taste of certain beverage components. In this aspect, using lugduname and sucralose together in perspective would become very widespread in regulating the organoleptic properties of beverages and pharmaceutical forms.

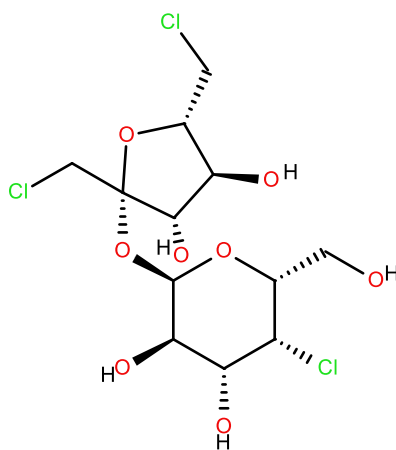


Figure 2. Sucralose.

As for sucralose [6 – 8] (Fig. 2), it is an extremely stable artificial sweetener up to 1000 times as sweet as common sugar. Its effects on human and animal organisms haven't been completely studied yet. 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 dioxines and tetrachlorodibenzofurans.

Moreover, lugduname metabolism in the presence of sucralose may become altered, which may provoke adverse effects. For this and other reasons, the development of the methods of determining lugduname and sucralose is actual.

Both substances are electroactive, 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. CoO/CoO(OH) and CoO(OH)/CoO₂ redox pairs may be used for this process. To stabilize the modifier, it is inserted into a conducting polymer matrix, acting also as a mediator.

Nevertheless, if sucralose is oxidized by a relatively simple mechanism[16–17], lugduname may be oxidized in different manners, including electropolymerization [18]. For this and other reasons, the *a priori* theoretical investigation, aimed to analyze the behavior of the electroanalytical system with sucralose and lugdunam electrochemical determination from the mechanical point of view, including the comparison to the similar processes [16–21], is necessary and this is the goal of the present study.

2. Materials and Methods

The composite material of conducting polymer with cobalt (III) oxyhydroxide may be obtained chemically or electrochemically, realizing it via the one-pot technique or in different stages. One of the typical manners to obtain it is to electropolymerize the monomer in the presence of the Co(II) salt as an additive to the background electrolyte.

Being oxidized by CoO(OH) lugduname will be transformed by three scenarios, including the nitrile group oxidation, heterocyclization, and electropolymerization (Fig. 3), whereas sucralose will be oxidized by the only hydroxymethyl group in its composition (Fig. 4).

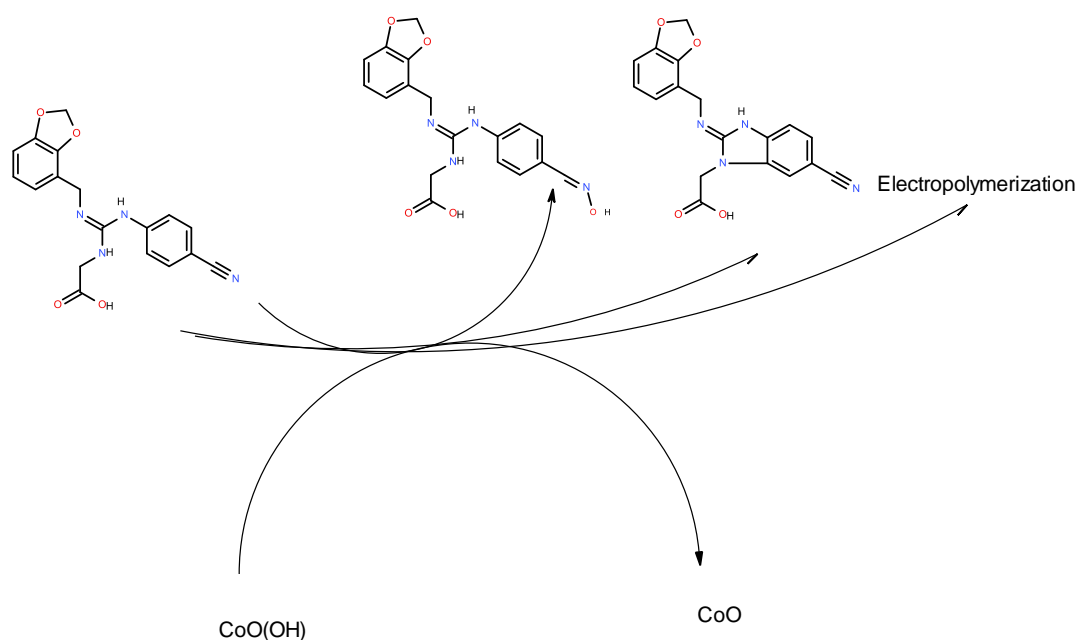


Figure 3. The scheme of the electroanalytical process.

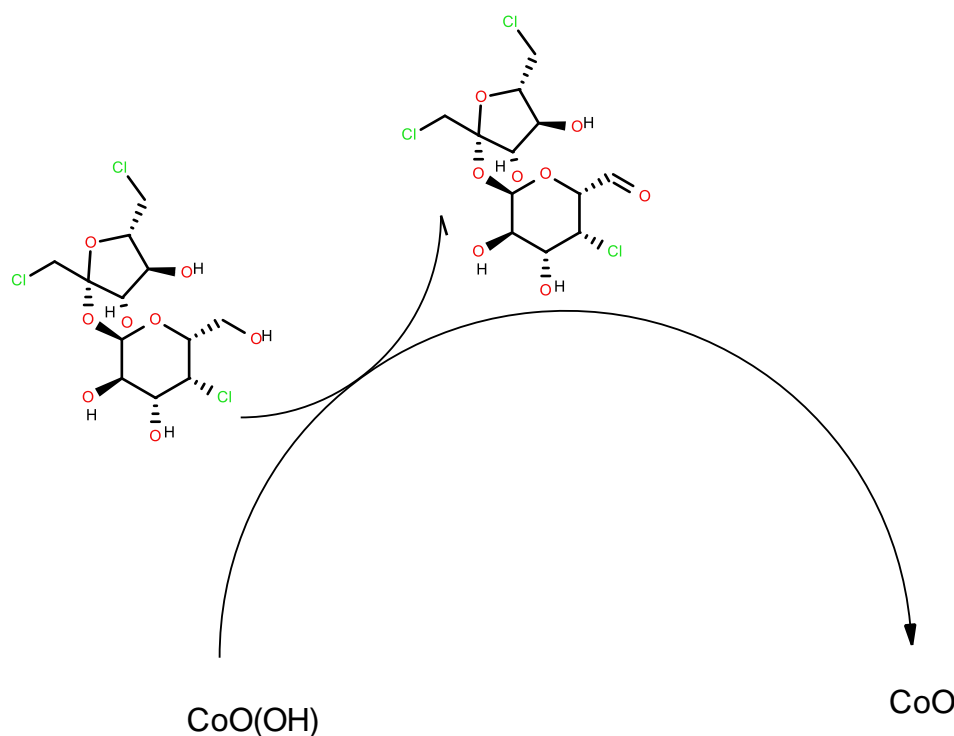


Figure 4. Sucralose CoO(OH)-assisted electroanalytical process.

So, taking into account the above-cited statements and accepting certain assumptions [16–21], we describe the behavior of this system by a trivariant equation-set (1):

$$\begin{cases} \frac{dl}{dt} = \frac{2}{\delta} \left(\frac{L}{\delta} (l_0 - l) - r_d - r_c - r_p \right) \\ \frac{ds}{dt} = \frac{2}{\delta} \left(\frac{S}{\delta} (s_0 - s) - r_s \right) \\ \frac{dc}{dt} = \frac{1}{c} (r_d + r_c + r_p + r_s - r_o) \end{cases} \quad (1)$$

in which l and s are lugdunam and sucralose pre-surface concentrations, l_0 and s_0 are their bulk concentrations, L and S are their diffusion coefficients, c is the cobalt (II) oxide surface coverage degree, C is its maximal matrix concentration, and the parameters r stand for the correspondent reaction rates, calculated as (2–6):

$$r_d = k_d l (1 - c) \exp(-al) \quad (2)$$

$$r_c = k_c l (1 - c)^2 \exp(-al) \quad (3)$$

$$r_p = k_p l^x (1 - c)^y \exp(-al) \exp(-bl) \quad (4)$$

$$r_s = k_s s (1 - c)^2 \quad (5)$$

$$r_o = k_o c \exp\left(\frac{F\varphi_0}{RT}\right) \quad (6)$$

Herein, the parameters k are the correspondent reaction rate constants, and parameter a describes the double electric layer (DEL) impact of the lugdunam ionic forms transformations in micromolecular scenarios (7)

$$a \begin{cases} = 0, & \text{if } pH \leq 7 \\ \neq 0, & \text{if } pH > 7 \end{cases} \quad (7)$$

b is the parameter describing the DEL influence of the ionic forms transformations during the polymer chain growth, and it isn't equal to nil in each pH, depending on the polymerization mechanism, typical for lugdunam in different conditions, F is the Faraday number, R is the universal gas constant, T is the absolute temperature and φ_0 is the potential slope related to the zero-charge potential.

In general, this system will resemble perillartine and sucralose. Nonetheless, the polymerization scenario is present, and it will have a strong impact on the system's stability. Either way, the electroanalytical process is considered efficient, as shown below.

3. Results and Discussion

Analyzing the equation-set (1) using 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 Jacobian members as (8):

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

wherein:

$$a_{11} = \frac{2}{\delta} \left(-\frac{l}{\delta} - k_d(1-c) \exp(-al) + ak_d l(1-c) \exp(-al) - k_c(1-c)^2 \exp(-al) + ak_c l(1-c)^2 \exp(-al) - xk_p l^{x-1}(1-c)^y \exp(-al) \exp(-bl) + (a+b)k_p l^x(1-c)^y \exp(-al) \exp(-bl) \right) \quad (9)$$

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

$$a_{13} = \frac{2}{\delta} (k_d l \exp(-al) + 2k_c l(1-c) \exp(-al) + yk_p l^x(1-c)^{y-1} \exp(-al) \exp(-bl)) \quad (11)$$

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

$$a_{22} = \frac{2}{\delta} \left(-\frac{s}{\delta} - k_s(1-c)^2 \right) \quad (13)$$

$$a_{23} = \frac{2}{\delta} (2k_s s(1-c)) \quad (14)$$

$$a_{31} = \frac{1}{c} (k_d(1-c) \exp(-al) - ak_d l(1-c) \exp(-al) + k_c(1-c)^2 \exp(-al) - ak_c l(1-c)^2 \exp(-al) + xk_p l^{x-1}(1-c)^y \exp(-al) \exp(-bl) - (a+b)k_p l^x(1-c)^y \exp(-al) \exp(-bl)) \quad (15)$$

$$a_{32} = \frac{1}{c} (k_s(1-c)^2) \quad (16)$$

$$a_{33} = \frac{1}{c} \left(-k_d l \exp(-al) - 2k_c l(1-c) \exp(-al) - yk_p l^x(1-c)^{y-1} \exp(-al) \exp(-bl) - 2k_s s(1-c) - k_o \exp\left(\frac{F\phi_o}{RT}\right) + jk_o c \exp\left(\frac{F\phi_o}{RT}\right) \right) \quad (17)$$

Similarly to [16–21], the *oscillatory behavior* is probable in this system. Moreover, it becomes more probable than for the perillartin and sucralose determination in the same conditions due to the presence of the polymerization factor, which influences the DEL ionic forms due to the cyclic changes of DEL structure caused by the growing radical-cation chain.

As known, the oscillatory behavior is realized in the case of the positive callback, described by the positivity of certain addendums in the Jacobian main diagonal (9), (13), (17).

Even in neutral or mildly acidic pH, two positive elements define the oscillatory behavior caused by DEL changes of CoO(OH) regeneration and lugdunam electropolymerization, described by the positivity of the elements $jk_o c \exp\left(\frac{F\phi_o}{RT}\right) > 0$ if $j > 0$ and $(a+b)k_p l^x(1-c)^y \exp(-al) \exp(-bl) > 0$, if $b > 0$. In the case of the basic medium, the oscillatory behavior probability augments as the elements $ak_d l(1-c) \exp(-al) > 0$ and $ak_c l(1-c)^2 \exp(-al) > 0$ becomes positive if $a > 0$. They describe the cyclic DEL impact of ionic form transformation. Therefore, the oscillatory behavior is more probable in a basic medium than neutral and mildly acidic.

The presence and the concentration of other ions (not only H⁺ and OH⁻) will define the form and frequency of the oscillations, such as observed experimentally [19–21] and theoretically [16– 8].

Rewriting the Jacobian determinant as (18):

$$\frac{4}{\delta^2 c} \begin{vmatrix} -\kappa - \mathcal{E} & 0 & \Sigma \\ 0 & -\xi - X & V \\ \mathcal{E} & X & -\Sigma - V - \Omega \end{vmatrix} \quad (18)$$

Opening the brackets and applying the Det J<0 requisite, salient from the Routh-Hurwitz criterion and changing the signs to the opposite, we obtain the steady-state stability requirement (19):

$$\kappa(\xi\Sigma + X\Sigma + \xi V + \xi\Omega + \Lambda\Omega) + \mathcal{E}(\xi V + \xi\Omega + X\Omega) > 0 \quad (19)$$

This describes either diffusion or kinetically controlled efficient electroanalytical process in which the steady-state stability topological region becomes narrower than perillartine and sucralose due to the polymerization factor. 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 sensitivity of the process.

As for the detection limit, it will correspond to the monotonic instability, which will thereby correspond to the nullity of the determinant (20):

$$-\kappa(\xi\Sigma + \Lambda\Sigma + \xi T + \xi\Omega + \Lambda\Omega) - \mathcal{E}(\xi T + \xi\Omega + \Lambda\Omega) = 0 \quad (20)$$

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

Considering this, it is possible to conclude that the electrochemical technique is suitable for lugdunam and sucralose determination in most beverages (with neutral and mildly acidic pH), including soft drinks, juices, and biological liquids). Therefore, using an anodic process for sucralose and lugdunam determination is viable. In the same manner, lugdunam may be quantified with perillartine. On the other hand, the cathodic process is recommended to quantify lugdunam with aspartame, saccharin, and acesulfame K. In the same manner, the cathodic process may also be realized for sucralose and perillartine.

4. Conclusions

From the analysis of the system with CoO(OH)-assisted sucralose and lugdunam electrochemical determination, it is possible to conclude that the electroanalytical CoO(OH)-assisted process is viable to detect both of the sweeteners at neutral and mildly acidic pH correspondent to the most of the drinks. The process is either diffusion or kinetically controlled, and 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 ionized; thereby, their ionic forms do not influence the DEL ionic force and related electrophysical properties. Nevertheless, the lugdunam electropolymerization does influence the DEL, making the oscillatory behavior in neutral media a bit more probable.

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Conflicts of Interest

The authors declare no conflict of interest.

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