Voltammetric Studies for Detection and Degradation Assessment of some Synthetic Food Dyestuffs
II. Sunset Yellow - E-110

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The electrochemical behaviour of the synthetic food dyestuff Sunset Yellow-E 110 is discussed in comparison with our Tartrazine previous data [1]. Voltammetric experiments obtained by cyclic voltammetry and differential pulse voltammetry were performed on glassy carbon electrode in buffered aqueous solutions at different pH values. The influence of SUN concentration, scan rate and pH, on the currents and peak potentials have been studied. The electrode processes are controlled by diffusion. Both applied voltammetric methods showed a good matching of the electrochemical parameters, and any of this simple, high-performance, and inexpensive methods can be recommended for the determination of trace SUN levels in commercial soft drinks. In the same time, an assessment of SUN degradation process can be achieved by the interpretation the voltammetric data.

Keywords: Sunset Yellow, Tartrazine, voltammetry, food dyestuff

The electrochemical behaviour of the synthetic food dyestuff Sunset Yellow-E 110 (disodium 6-hydroxy-5-[(4-sulphonyl)azo]-2-naphthalenesulfonate) is discussed in comparison with our Tartrazine previous data [1]. Sunset Yellow (SUN) was chosen for this voltammetric study because of its wide use in various products, such as: foods, soft drinks, drugs and cosmetics. This synthetic food dyestuff is used either alone or in mixtures with other synthetic dyestuffs, but especially with Tartrazine (TAR). Although SUN and TAR are permitted food colorants, due to their possible harmful human health issues, their maximum accepted values in foods are internationally regulated [2-4] and much attention has been paid for the detection and analysis of these substances by high-performance analytical techniques [5-11].

The electrochemical behaviour of TAR in both anodic and cathodic potential domains was previously studied [1]. The characterization by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods allowed the assessment of the electrochemical properties of this dye and the evaluation of parameters which can be exploited in TAR analysis by using one of these simple, sensitive and inexpensive methods.

This work presents experimental data concerning the electrochemical characterisation of SUN (fig.1) by CV and DPV methods. The study allowed the establishment of the diffusion controlled processes and the determination of analytical parameters in view of simultaneous determination of SUN and TAR synthetic food dyestuffs.

Fig. 1. Chemical structure of Sunset Yellow

Experimental part

The electrochemical experiments were carried out using glassy carbon electrode in buffered aqueous solutions of SUN at different pH values, concentrations and scan rates, under the previously reported experimental conditions [1]. A PAR283 potentiostat and a three-electrode cell have been used for electrochemical measurements. A glassy carbon disk (3-mm diameter from CH Instruments), a platinum wire and a Ag/AgCl/saturated KCl reference electrodes, respectively. All reagents were of analytical purity and the solutions were prepared using bidistilled water. SUN was purchased from SIGMA-Aldrich. Buffer solutions (citrate for pH = 3.0 and 4.0, acetate for pH = 5.0) were prepared according to standard procedures. Bidistilled water was obtained from an Elgastat water purification system (5 Ω cm).

Results and discussion

CV and DPV experiments have been conducted in aqueous buffer solutions as supporting electrolyte in milimolar concentrations of SUN (1-10mM), at different pH values, selected within the pH range of the commercial soft drinks samples, between 3 and 7. In order to establish the reversible character of the involved electrochemical processes and SUN degradation, the CV curves have been recorded at different scan rates and potential ranges. In the following, only the results concerning the electrochemical behaviour of SUN at pH 3, a value where all the electrochemical processes are best highlighted, are presented.

Electrochemical characterization of SUN at pH 3

The electrochemical behaviour of SUN has been investigated in solutions of SUN in 0.1M aqueous buffer solutions as supporting electrolyte. DPV and CV studies
have been performed at different concentrations of SUN, and at different scan rates and potential ranges in CV.

Figure 2 shows the DPV curves for SUN at different concentrations. A single anodic peak (1a) and a single cathodic peak (1c) can be observed (in comparison with TAR DPV curves, where two cathodic peaks appeared [1]). The peak potentials vary linearly with the logarithm of the SUN concentration (upper inset in fig. 2) and the peak currents vary linearly with the SUN concentration (lower inset in fig. 2). These dependences can be used in analytical determinations of SUN by DPV method. The corresponding equations of these lines are given in table 1.

The anodic peak identified in the DPV curves could be attributed to the oxidation of SUN to its stable radical cation. After ionization the positive charge is mainly delocalized on the whole molecule. The oxidation potential of the peak 1a is in the range characteristic for azo compounds. The cathodic peak 1c identified in the DPV curves could be attributed to the reduction of SUN to its stable radical anion. After ionization, the negative charge is also delocalized on the whole molecule. The reduction potential values are also in the range characteristic for these azo compounds (SUN and TAR). It is very likely that both oxidation and reduction of SUN involve electrochemical and chemical steps. In case of SUN, at pH value in the experiment (pH = 3), there is not a second multielectron transfer as in the case of TAR curves at very negative potentials.

The same processes are identified for SUN in the CV curves (fig. 3) with anodic and cathodic peaks situated at potential values in agreement with those obtained by DPV. The processes are electrochemically irreversible, showing the electrochemical degradation of SUN during the potential scanning, as in the case of TAR. The peak potentials vary linearly with the logarithm of SUN concentration (upper inset in fig. 3) and the peak currents vary linearly with SUN concentration (lower inset in fig. 3). These dependences can be used in analytical determination of SUN by CV method. The equations of these dependences are given in table 2.

Figure 4 shows the CV curves at different scan rates in the domains of the anodic and cathodic processes. Anodic and cathodic scans are plotted on the same graph. The electrochemical reversibility of the anodic (1a) and cathodic (1c) processes has been carefully evaluated from the CV curves obtained at different scan rates. As it can be seen in figure 4, these processes are both irreversible. Linear dependences of the peak potentials on the logarithm of the scan rate have been experimentally obtained (upper inset in fig. 4). Linear dependences of the peak currents (1a, 1c) on the square root of the scan rate have been obtained (lower inset in fig. 4) demonstrating diffusion controlled processes. The values of ip/(vs) ratio of around 96 and 128 μA/(V/s)(1/2)(mM)(1/2) have been calculated for peaks 1a and 1c, respectively. They are lower than the corresponding values obtained for TAR (200 and 300 μA/(V/s)(1/2)(mM)(1/2), respectively). It can be noticed that in the range of investigated scan rates and concentrations of SUN, the processes are irreversible. The diffusion coefficient of ~3×10⁻⁷ cm²/s for SUN species has been calculated using Randles-Sevcik equation by supposing a single electron transfer. However, the lower inset in figure 4 shows that the slope of the peak current dependence on the scan rate is 33% higher for (1c) than for (1a).

### The pH influence

The influence of pH on the peak potentials for both anodic and cathodic processes has been studied from the CV curves (fig. 3) with anodic and cathodic peaks situated at potential values in agreement with those obtained by DPV. The processes are electrochemically irreversible, showing the electrochemical degradation of SUN during the potential scanning, as in the case of TAR. The peak potentials vary linearly with the logarithm of SUN concentration (upper inset in fig. 3) and the peak currents vary linearly with SUN concentration (lower inset in fig. 3). These dependences can be used in analytical determination of SUN by CV method. The equations of these dependences are given in table 2.
Experiments have about the same slopes as in DPV experiments (around 14mV and 123mV, respectively). Also, the data analysis expresses the difference between the numbers of electrons involved in these electrode processes, which are not simple electrochemical transfers, but complex processes. Analyzing the data from table 3 it can be observed that for E1a and E1c, the two voltammetric methods present similar dependences on the solution pH. Consequently, to determine SUN content in a drink sample, it is recommended to perform the measurements at a given potential E1a, because it is more stable than E1c potential in respect with the pH variation.

Table 4 displays the results concerning pH influence on peak currents for both anodic peak (1a) and cathodic peak (1c). It can be seen that there are differences in the variations with the pH of solution. For instance, in DPV experiments, the slope is of around -3.9mA and 0.39mA, for i1a and i1c, respectively. The corresponding values from CV experiments are of around -2.2μA and -2μA, respectively. However, in this case, the correlation coefficients have quite smaller values and this explains their disagreement with DPV values. Nevertheless, a given value for i1a from DPV can be also used as analytical signal for SUN analysis.

Conclusions

The voltammetric study of SUN has evidenced a different electrochemical behaviour in comparison with that of TAR both in anodic and cathodic potential domains. Thus, while TAR presents two cathodic peaks, SUN displays only one. This can be attributed to the electrochemical reduction in two steps of TAR in respect to SUN. The first reduction step of both SUN and TAR leads to rather stable radicals form.

DPV and CV curves obtained for SUN solutions in different buffer solutions. These dependences are all linear (fig. 5). DPV curves show generally better correlation coefficients than CV curves, as it can be seen in tables 1–4.

It can be seen from table 1 that, in DPV experiments, the E1a peak dependence on pH has around the same slope as E1c peak (around 8.5mV). The corresponding values from CV are a little bit higher than the DPV values (around 10mV, respectively). These data express that the numbers of electrons involved in the corresponding electrode processes are the same in the case of SUN. This represents a difference in respect to TAR, where a different number of electrons involved in anodic and cathodic processes occur.

It can be seen from table 2 that in DPV measurements, i1a peak current has a slope of its dependence on pH is lower than that of i1c peak current (around 7.8mA and 11.5mA, respectively). The corresponding values from CV measurements are less different, around 40μA and 45μA, respectively but, both higher than the DPV values, as normally is expected, at each pH studied. From analytical point of view, the CV method offers better possibilities than DPV method for the detection of SUN. However, in the case of dye mixtures the DPV method could be a preferred choice due to its higher selectivity.

From table 3 it can be seen that, in DPV experiments, the E1a peak potential has a negative slope of its dependence in respect to pH, a value of around -19mV, showing that the electrochemical oxidation has a slower rate at acidic pH, and therefore, the SUN degradation is slowed down in acidic media. The slope value of E1a from DPV experiments is around six times smaller than that for E1c peak (119mV). The corresponding values from CV experiments have about the same slopes as in DPV experiments (around 14mV and 123mV, respectively). Also, the data analysis expresses the difference between the numbers of electrons involved in these electrode processes, which are not simple electrochemical transfers, but complex processes. Analyzing the data from table 3 it can be observed that for E1a and E1c, the two voltammetric methods present similar dependences on the solution pH. Consequently, to determine SUN content in a drink sample, it is recommended to perform the measurements at a given potential E1a, because it is more stable than E1c potential in respect with the pH variation.

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the OH groups, while the second cathodic peak of TAR is due to the reduction of the heterocyclic ring which occurs slowly at higher negative potential, being favoured by a small pH (the second cathodic peak is shifted towards more negative potentials).

The characterization by CV and DPV methods allowed the assessment of SUN electrochemical properties and the evaluation of parameters. The experimental data show that both methods are suitable for SUN detection, although DPV method is more sensitive. In order to determine SUN content in a drink sample, it is recommended to perform the measurements at the anodic peak potential, because it is more stable than the cathodic one in respect with the pH variation.

The present electrochemical study also shows that SUN degradation appears during the potential scanning, all electrochemical processes being irreversible.

The characterization by CV and DPV methods allowed the assessment of SUN and TAR electrochemical properties and the evaluation of parameters which lead to the optimum choice of analytical parameters. For instance, the oxidation and reduction peaks appear at different potentials for each of these dyestuffs. This fact can be further exploited for the simultaneous determination of these colours in the soft drinks and possible interference that may occur when both colors are present in the sample matrix can be eliminated.

References
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