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. 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-sulfophenyl)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.

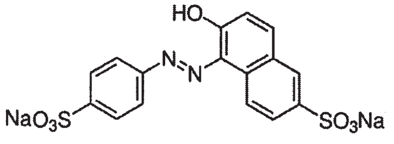

Fig. 1. Chemical structure of Sunset Yellow

Experimental part

The electrochemical experiments were carried out using glassy carbon electrode in buffered aqueous solutions of **SUN** at different *p*H 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 aqueous solution were used as working, auxiliary, and 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 *p*H = 3.0 and 4.0, acetate for *p*H = 5.0) were prepared according to standard procedures. Bidistilled water was obtained from an Elgastat water purification system (5 MΩ 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 *p*H 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 *p*H 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

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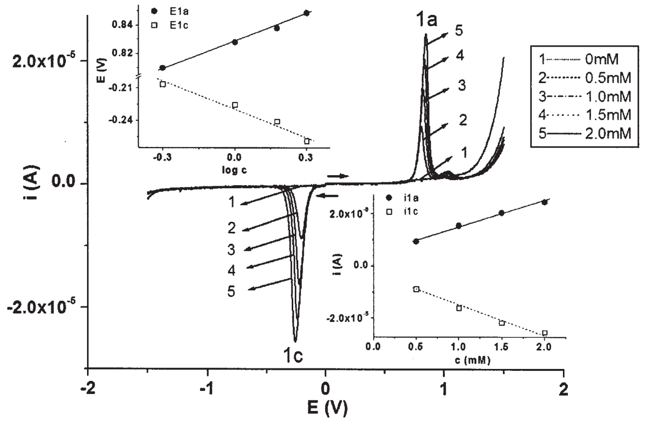

Fig. 2. DPV curves for **SUN** at different concentrations on glassy carbon disk electrode (3mm in diameter) at pH 3; upper inset - Linear dependences of anodic peak potential (E1a) and cathodic peak potential (E1c) *vs* the logarithm of **SUN** concentration (log c); lower inset - Linear dependences of anodic (i1a) and cathodic peak currents (i1c) *vs* **SUN** concentration (c); c is expressed in mM.

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.

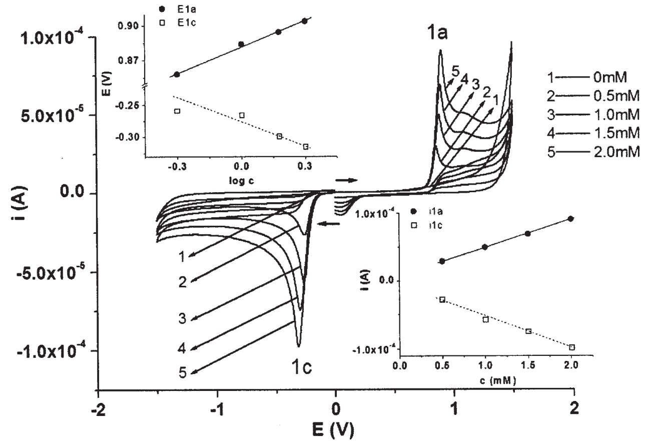

Fig. 3. CV curves (0.1V/s) for **SUN** at different concentrations on glassy carbon disk m electrode (3mm in diameter) at pH 3; upper inset - Linear dependences of the anodic peak potential (E1a) and cathodic peak potential (E1c) *vs* **SUN** concentration logarithm (log c); lower inset - Linear dependences of the anodic (i1a) and cathodic peak currents (i1c) *vs* **SUN** concentration (c); c is expressed in mM

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 *p*H value in the experiment (*p*H = 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/($v^{1/2}$c) ratio of around 96 and 128 μA(V/s)$^{-1/2}$(mM)$^{-1}$ 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)$^{-1}$, 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^{-5}cm^{2}s^{-1} for **SUN** species has been calculated using Randless-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 *p*H on the peak potentials for both anodic and cathodic processes has been studied from the

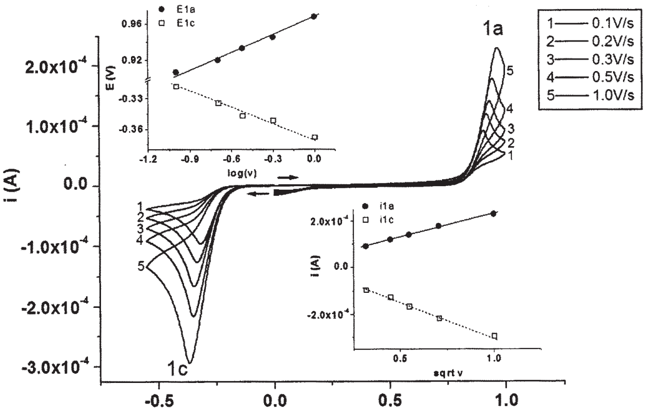

Fig. 4. CV curves in anodic and cathodic scans at different scan rates (v in V/s) on glassy carbon disk electrode (3mm in diameter) in a **SUN** solution (2 mM); upper inset - Linear dependences of anodic peak (E1a) potential and cathodic peak (E1c) potential *vs* the logarithm of the scan rate (log v); lower inset - Linear dependences of the anodic (i1a) and cathodic (i1c) peak currents *vs* the square root of the scan rate (sqrt v)

Table 1
PARAMETERS OF THE LINEAR DEPENDENCES OF THE PEAK POTENTIAL E (in V) FOR THE ANODIC PEAK 1a AND CATHODIC PEAK 1c *vs* **SUN** CONCENTRATION LOGARITHM log c (c in mM) (R^2 IS THE CORRELATION COEFFICIENT)

pH	DPV: $E = m \cdot \log c + n$					
	E1a			E1c		
	$m \cdot 10^2$	$n \cdot 10$	R^2	$m \cdot 10^2$	$n \cdot 10$	R^2
3	6.27	8.28	0.995	-8.41	-2.29	0.966
4	8.95	8.11	0.958	-8.17	-3.38	0.989
5	11.5	7.89	0.990	-7.53	-4.66	0.995
Mean slope	8.91	-	-	-8.04	-	-
pH	CV: $E = m \cdot \log c + n$					
	E1a			E1c		
	$m \cdot 10^2$	$n \cdot 10$	R^2	$m \cdot 10^2$	$n \cdot 10$	R^2
3	7.53	8.82	0.994	-9.49	-2.80	0.860
4	9.16	8.65	0.982	-14.8	-3.84	0.984
5	11.1	8.53	0.997	-8.64	-5.25	0.844
Mean slope	9.26	-	-	-10.98	-	-

Table 2
PARAMETERS OF THE LINEAR DEPENDENCES OF THE PEAK CURRENTS (in A) FOR THE ANODIC PEAK i1a AND THE FIRST CATHODIC PEAK i1c *vs* **SUN** CONCENTRATION c (c in mM) (R^2 IS THE CORRELATION COEFFICIENT)

pH	DPV: $i = m \cdot c + n$					
	i1a			i1c		
	$m \cdot 10^6$	$n \cdot 10^6$	R^2	$m \cdot 10^5$	$n \cdot 10^6$	R^2
3	9.99	4.99	0.993	-1.13	-3.99	0.978
4	7.73	3.79	0.992	-1.15	-3.19	0.990
5	5.74	2.46	1.000	-1.17	-2.70	0.987
Mean slope	7.82	-	-	-1.15	-	-
pH	CV: $i = m \cdot c + n$					
	i1a			i1c		
	$m \cdot 10^5$	$n \cdot 10^6$	R^2	$m \cdot 10^5$	$n \cdot 10^6$	R^2
3	4.08	8.48	0.999	-4.62	-6.42	0.989
4	3.95	7.59	0.999	-3.73	-13	0.990
5	3.91	6.07	1.000	-5.16	-3.81	0.998
Mean slope	3.98	-	-	-4.50	-	-

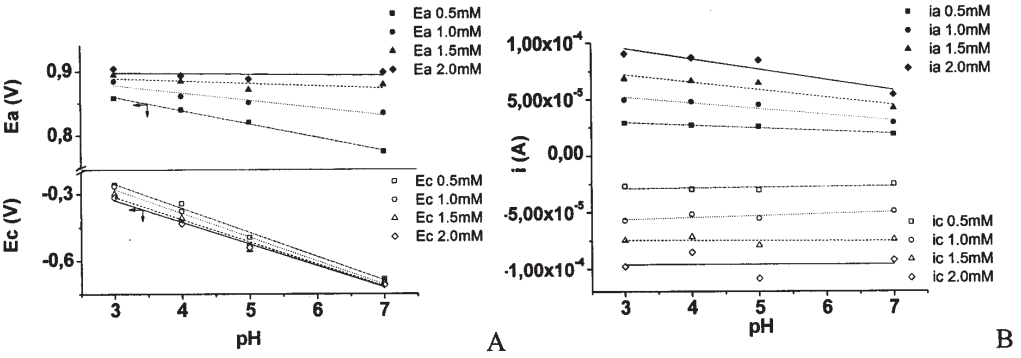

Fig. 5. Dependences on pH for different concentrations of **SUN** from DPV curves:
A – of the anodic (E1a) and cathodic (E1c) peak potentials;
B – of the anodic (i1a) and cathodic (i1c) peak currents

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 *p*H 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 *p*H 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 *p*H 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 *p*H, a value of around -19mV, showing that the electrochemical oxidation has a slower rate at acidic *p*H, 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 *p*H. 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 *p*H variation.

Table 4 displays the results concerning *p*H 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 *p*H 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

Table 3

PARAMETERS OF THE LINEAR DEPENDENCES *vs* pH OF THE PEAK POTENTIAL E (in V) FOR THE ANODIC PEAK E1a AND CATHODIC PEAK E1c AT DIFFERENT **SUN** CONCENTRATIONS c (c in mM) FROM DPV AND CV EXPERIMENTS. (R^2 IS THE CORRELATION COEFFICIENT)

c	DPV: E = m·pH + n					
	E1a			E1c		
	$m\cdot10^2$	n·10	R^2	$m\cdot10^2$	n·10	R^2
0.5	-2.69	8.91	0.999	-11.8	1.53	0.996
1.0	-2.16	8.95	0.979	-12.2	1.41	0.999
1.5	-1.49	8.81	0.985	-11.9	1.18	0.999
2.0	-1.12	8.84	0.931	-11.5	9.07	0.996
Mean slope	-1.87	-	-	-11.9	-	-
c	CV: E = m·pH + n					
	E1a			E1c		
	$m\cdot10^2$	n·10	R2	$m\cdot10^2$	n·10	R2
0.5	-1.88	9.15	1.000	-11.8	1.08	0.973
1.0	-1.65	9.31	0.948	-13.3	1.40	0.992
1.5	-1.17	9.30	0.995	-12.6	0.86	0.994
2.0	-0.81	9.27	0.968	-11.3	0.23	0.999
Mean slope	-1.38	-	-	-12.3	-	-

Table 4

PARAMETERS OF THE LINEAR DEPENDENCES OF THE PEAK CURRENTS (in A) FOR THE ANODIC PEAK i1a AND THE FIRST CATHODIC PEAK i1c *vs* pH AT DIFFERENT **SUN** CONCENTRATIONS c (c in mM) FROM DPV AND CV EXPERIMENTS. (R^2 IS THE CORRELATION COEFFICIENT)

c	DPV: i = m·pH + n					
	i1a			i1c		
	$m\cdot10^6$	$n\cdot10^5$	R^2	$m\cdot10^6$	$n\cdot10^5$	R^2
0.5	-2.09	1.58	0.997	0.40	-0.99	0.971
1.0	-3.64	2.62	0.991	0.65	-1.80	0.874
1.5	-4.66	3.45	0.999	0.33	-2.28	0.869
2.0	-5.29	4.03	0.999	0.16	-2.61	0.836
Mean slope	-3.92	-	-	0.39	-	-
c	CV: i = m·pH + n					
	i1a			i1c		
	$m\cdot10^6$	$n\cdot10^5$	R^2	$m\cdot10^6$	$n\cdot10^5$	R2
0.5	-1.55	3.35	0.980	-1.78	-2.18	0.870
1.0	-2.21	5.63	0.980	-	-	-
1.5	-2.16	7.50	0.994	-2.21	-6.63	0.820
2.0	-2.90	9.89	0.973	-	-	-
Mean slope	-2.21	-	-	-2.00	-	-

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 *p*H (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 *p*H 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.

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