Bismuth Film Electrodes for Adsorptive Stripping Voltammetric Determination of *Sunset Yellow*

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Abstract: The suitability of bismuth film electrodes for the adsorptive stripping voltammetry of an azo dye – *Sunset Yellow* ("E110") has been examined. The effect of the glassy carbon support geometry, the plating solution concentration, and the optimal deposition potential were investigated and the results obtained discussed.

Keywords: Square-wave voltammetry; Bismuth film electrode; Azo dyes; *Sunset Yellow*.

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Introduction

Color is the first sensory quality by which food is judged and additionally it influences the perception of flavor. Colorings were being added to food as far back as ancient times to replace colors lost during preparation or storage, or to make food looking more attractive [1].

The natural food colorants are unstable and easily undergo degradation during the food processing. The synthetic dyes are less expensive, more stable, controllable, and intense in hue than natural color sources. The dyes are used as water soluble salts or insoluble aluminum lakes. Aluminum lakes are prepared by reacting dyes with alumina under aqueous conditions. The transformation from soluble dye to insoluble aluminum lake enhances the colorants usefulness, brings opacity and ability to be incorporated into products in the dry state,

enhance stability toward heat and light and in the end increase the shelf life of final product. Lake colors are used in almost every type of edible preparation, pharmaceutical and cosmetic products and plastic packaging materials but soluble salts are mainly used in drinks. Food colorings are tested for safety by various bodies around the world and in Europe the Council Directive 94/36/EC lays down detailed rules on colors.

Sunset Yellow (SY, *syn.* "E110") is one of widely used synthetic colors that belong among the azo dyes containing the functional group, $-N=N-$, in the molecular structure (see Scheme 1, below). Some azo dyes (*e.g.*, *Sudan I*) have been banned for food use due to toxic carcinogenic side effects. The azo linkage is the most labile fragment of the respective molecules and may easily undergo enzymatic breakdown in mammals. Azo dyes decompose to aromatic amines, causing frequent headaches in adults and potentially inducing hyperactivity and ADHD in children [2].
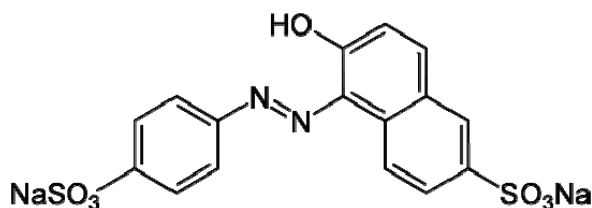
Scheme 1: *Sunset Yellow*; Disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate

Concerning health aspects of azo dyes and wide range of application of SY (drugs, cosmetics, orange drink and jelly, marzipan, apricot jam, citrus marmalade, sweets, hot chocolate mix, packet soups, breadcrumbs, cereals, baked goods, snack foods, ice cream, beverages, dessert powders, confections) there is a need to control its content. The synthetic food dyes are determined mainly using chromatographic techniques [3] or absorption spectrophotometry [4], but also electrochemical methods are reported including electrophoresis [5], polarography or voltammetry [6-12]. The reduction of azo dyes was extensively examined at a carbon paste [13-15], glassy carbon [16], mercury electrodes [17,18], or even with a BiFE [19].

In the frame of this work, a systematic study of voltammetric behavior of the *Sunset Yellow* at the bismuth film electrode was performed and sensitive methods for the determination of its trace amounts developed.

Experimental

Chemicals

The following reagents (of analytical grade; POCH, Poland) were used without further purification: Bi_2O_3, 70% $HClO_4$, 25% NH_3, NH_4Cl, and 35% HCl. An amount of 5,0 mg dye (CAS: 2783-94-0, lake pigment insoluble in water; Brenntag, Poland) was transferred using lab wash bottle into a 250-ml beaker containing 5 ml concentrated hydrochloric acid diluted with water to approximately 25 ml. The mixture was heated with stirring to dissolve the lake and then cooled to ambient temperature. The content of beaker was transferred to a 500-ml volumetric flask and made up to volume with water. The solution was stored in the refrigerator being renewed every two weeks. The concentration of *Sunset Yellow* (SY) was confirmed using UV-VIS spectroscopy (λ_{max} = 482 nm).

The solutions used for the *ex-situ* bismuth deposition were prepared by dilution of stock solution containing 0.17 M Bi(III) and 1.0 M $HClO_4$. The stock solution was prepared by mixing 4 g Bi_2O_3 with 9 ml 70 % $HClO_4$, heating up the mixture until it became clear, and filtering it to a 100 mL flask filled up to the mark with water. The bismuth solution of the above composition is recommended for electrolytic deposition of bismuth [19]. All solutions were prepared using deionized water from a deionzing device (model "Millipore Simplicity UV"; Millipore Corporation, USA).

Equipment

Electrochemical measurements were performed using a μAutolab (GPES 4.9 software) potentiostat (Ecochemie, Netherlands) with a standard three-electrode configuration. A coil of platinum wire served as the counter electrode, and an Ag/AgCl (3 M KCl) (Metrohm, Switzerland) acted as the reference one. The working electrode was a glassy carbon disc (d = 3 mm, BAS, USA; d = 1 and d = 2 mm Łomianki-Sadowa, Poland) polished successively with 0.3 and 0.05 μm aqueous alumina slurries (Buehler, USA) and rinsed with water after each polishing step. During preliminary study Control Growth Mercury Drop Electrode (CGMDE) was used (MTM, Poland).

Procedures

The bismuth deposits were prepared via electrolysis of a degased solution containing Bi(III) in 1.0 M $HClO_4$, using a freshly polished glassy carbon (GC) electrode. The electrolysis was carried out until the total charge that had passed during the experiment [20] and the corresponding values were: 1.1 mC (with GC disc of 1 mm in diameter), 4.4 mC (GC; d = 2 mm) and 10.0 mC (GC; d = 3 mm). After that, the BiFE and the reference and counter electrodes were washed thoroughly with diluted $HClO_4$ and then with water, and, finally, dried with a piece of filter paper.

Immediately after preparation, the BiFE was immersed in the tested solution, which was used without degasing. The square-wave voltammograms (SW) were recorded after pre-treatment including: electrode conditioning (-0.9 V, t = 1 s), deposition (-0.45 V, t = 20 s or t = 120 s) and equilibration (t = 10 s). The SW voltammograms were recorded between -0.45 V and -0.9 V using 0.002 V potential step and 0.050 V amplitude.

Results and Discussion

Voltammetric Characterization of *Sunset Yellow* at BiFE.

Sunset Yellow (SY), the synthetic dye from azo group, adsorbs at the surface of both mercury and bismuth film electrodes. In the preliminary experiment it was found that SY in 0.5 M ammonia buffer produces a distinct reduction peak at the potential of -0.55 V at Hg (Adsorptive stripping DPV, t_{acc} = 60 s) what was previously reported [7]. The voltammetric reduction of SY solution in 0.5 M ammonia buffer exploiting Bi electrodes and SWV polarization mode revealed the distinct peak at the potential of -0.53 V (Figure 1).
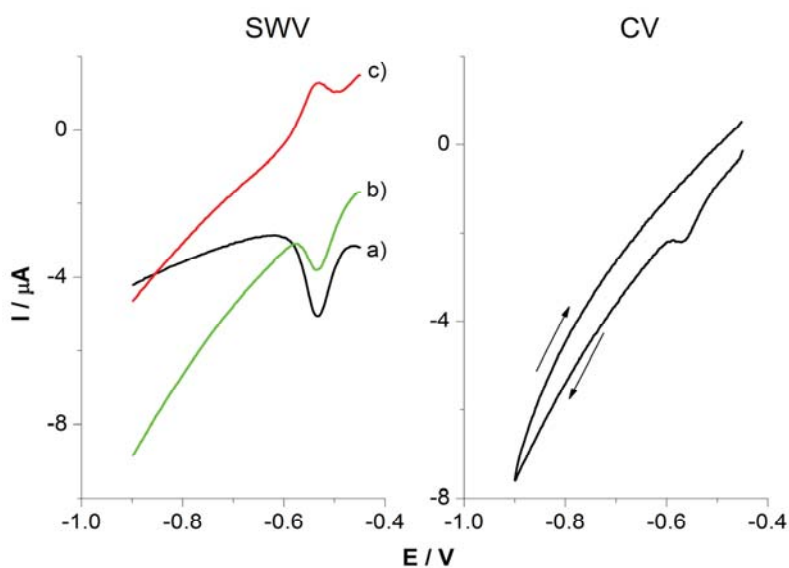

Fig. 1: *The SW and CV voltammograms for 108 µg/l SY recorded using a BiFE electrode plated at – 1.2 V in 0.01 M Bi(III) solution in ammonia buffer (0.5 M, pH 10.1).* Legend: a) net current, b) forward and c) backward current components. Instrumental parameters: E_{acc} = -0.45 V, t_{acc} = 60 s, t_{eq} = 10 s, SWV: f = 250 Hz, A = 50 mV, CV: v = 2 V/s; plating conditions: 0.01 M Bi(III) in 1 M HClO$_4$, without stirring, E_{plat} = -1.2 V, Q = 1.1 mC.

The factors influencing the SY signals could be classified into three categories: BiFE preparing (this category includes the size of the glassy carbon disc, concentration of plating solution, plating potential), supporting electrolyte composition (buffer type, buffer concentration and ionic strength, buffer pH) and instrumental parameters (accumulation time and potential, frequency, amplitude). The supporting electrolytes having the pH of 9 or higher

value were tested (ammonia buffer, carbonate – bicarbonate buffer, bicine buffer, Britton–Robinson buffer). The satisfactory results were obtained in the ammonia buffer only.

Background Characteristics of the BiFE

Bismuth deposits were plated from solution containing from 0. 1 mM to 100 mM Bi(III) in 1 M $HClO_4$ applying the specified potential in the -0.9 V to -1.35 V range. Electrodeposition of bismuth applying potentials from -0.9 V to -1.35 V results in formation of black velvet bismuth deposits (films plated at potentials less negative than -0.4 V are shiny 'bismuth mirrors'). The SW voltamograms of 0.5 M ammonia buffer recorded at such prepared electrodes regardless of the concentration of the plating solution reveal the presence of two cathodic distinct peaks (E_1 = -0.52 V, E_2 = -0.68 V). Their peak height depends on the time between measurements, when no potential is applied to the cell, and usually it amounts to several dozen microamperes for E_1 and several microamperes for E_2. After the application of conditioning potential (the value more negative than -0.75 V) for 1 second before accumulation of analyte these peak were no more observed and the voltammograms recorded in pure supporting electrolyte were unperturbated. During later examinations the conditioning potential of -0.9 V for 1 s was applied for every SWV or CV experiment.

The tests aimed at finding the optimal design of the bismuth film electrodes intended for SY determination started from the choice of glassy carbon dimension. The three GC disc electrodes with a diameter of 1 mm, 2 mm and 3 mm were selected. From the very first experiments it was obvious that the diameter of the glassy carbon used as a support for the bismuth film has a profound effect on the current response of the analyte (SY), which is well illustrated in Fig. 2.

The smaller surface area of the GC disc the better defined signals of SY were obtained taking into consideration peak shape, signal- to-noise ratio and sensitivity. The total net current measured at BiFEs increased along with the electrode diameter but the signal-to-noise value was on the decrease and peaks were getting less pronounced. The signal- to-noise ratio was estimated dividing the peak current by the noise's strength. The average noise strength was calculated as the difference between the bottom and top of the noise band. The signal-to-noise values calculated for curves obtained in the solution containing 70 µg/l of SY were 50, 40 and 30 for BiFEs with a diameter of 1 mm, 2 mm, and 3 mm, respectively.
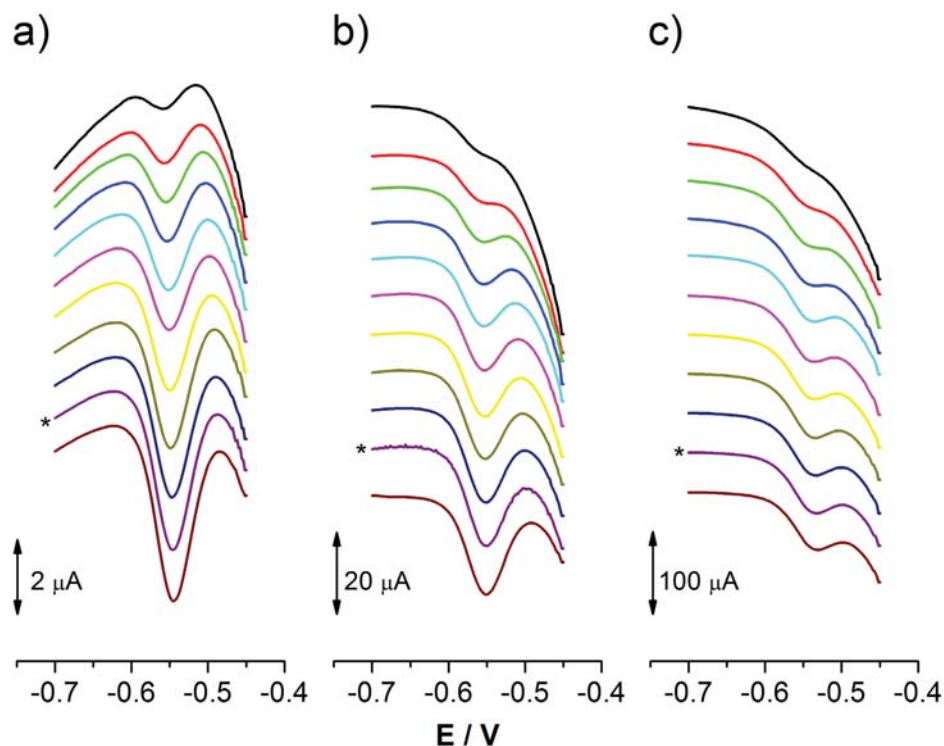
Fig. 2: *Square wave voltammograms for solutions containing increasing amount of Sunset Yellow recorded at the BiFE electrodes with a different diameter of glassy carbon support.* Legend: a) 1 mm, b) 2 mm, c) 3 mm. The concentration range of SY: a) 4 -70 µg/L, b) 4-87 µg/L, c) 26-250 µg/L. Supporting electrolyte: 0.5 M ammonia buffer. Instrumental parameters: E_{acc} = -0.45 V, t_{acc} = 120 s, t_{eq} = 10 s, f = 250 Hz, A = 50 mV; plating: 0.05 M Bi(III) in 1 M $HClO_4$ without stirring, E_{plat} = -1.1 V, a) Q = 1.1 mC, b) 4.4 mC and c) 10 mC.

The peak symmetry factors (SF) of signals observed at curves shown in Figure 2 and marked with star (*) were approximated in two ways: 1) by the calculation of the ratio of the peak area before the peak top (A) and the area after the peak (B) (Figure 3): SF = A/B; 2) by comparing distance from the point at peak midpoint to the trailing edge measured at 5% of the peak height: SF = a/b (see Fig. 3).

The term symmetry factor was adopted from chromatography - the peak asymmetry factor. The peak symmetry factor values were as follows: 0.97, 0.79 and 0.56 for electrodes with a diameter of 1 mm, 2 mm and 3 mm, respectively. The same ratio was obtained by comparing the midpoint distances at 5% of the peak height. Basing on the above mentioned data in further experiments the GC of 1 mm diameter was used.
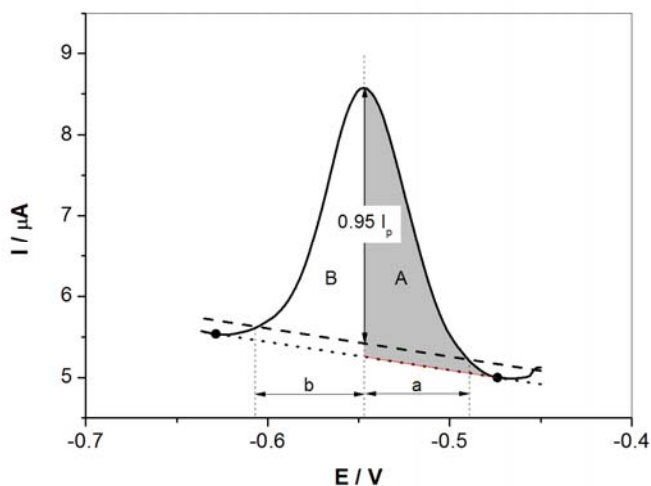
Fig. 3: *SW voltammogram of 44 µg/l SY in 0.5 M ammonia buffer showing the peak features during optimization of bismuth plating.* Support: glassy carbon disc $\phi = 1$ mm. $E_{plat} = -1.2$ V, $Q = 1.1$ mC. Instrumental parameters: $E_{acc} = -0.45$ V, $t_{acc} = 60$ s, $t_{eq} = 10$ s, $f = 250$ Hz, $A = 50$ mV.

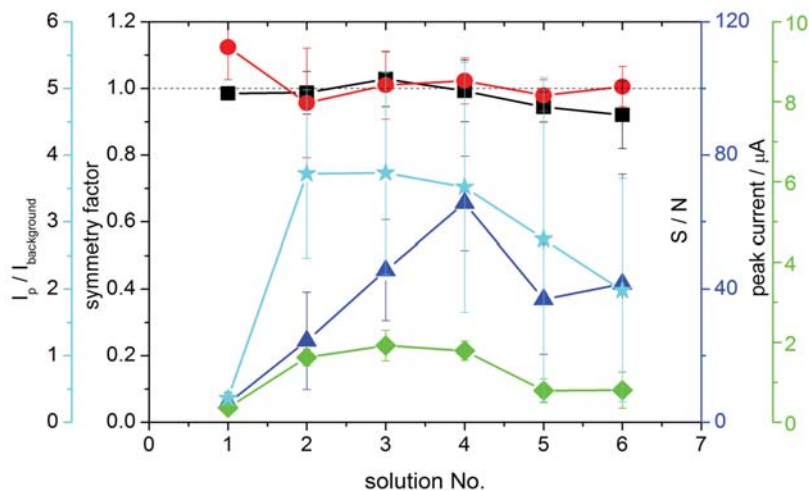**Fig. 4:** *The features of 44 µg/l Sunset Yellow signals recorded in 0.5 M ammonia buffer at BiFEs plated in solutions of different bismuth concentrations.* Legend: 1) 0.1 M, 2) 0.05 M, 3) 0.01 M, 4) 0.005 M, 5) 0.001 M, 6) 0.0005 M. Legend: circle – symmetry factor – the ratio of the peak area before the peak top and the area after the peak top; square – symmetry factor – the ratio of the peak widths at 5% of the peak height; triangle – signal to noise ratio; diamond – peak current value; star – the ratio of peak current (I_p) and the difference between current values ('$I_{background}$') for markers used for baseline construction (see Figure 2, the marker position selected using black circles).

After selection of the optimal GC support dimension the effect of the bismuth plating solution concentration on the response of SY was examined in order to select the optimal bismuth deposit which ensures good peak symmetry, maintaining at the same time a low 'flat' background current together with the most favorable signal-to-noise level. In order to accomplished this task seven bismuth plating solutions in 1 M $HClO_4$ was prepared and the plating charge of 1.1 mC was chosen. The concentration of the Bi(III) fell within the range from 0.1mM to 100 mM. The most diluted plating solution of 0.1 mM Bi(III) did not produce a film capable to develop the voltammogram of *Sunset Yellow* and it was excluded from further studies. In the case of most concentrated plating solution - 0.1 M Bi(III) - the charge exchanged during the plating was usually several tenths of milicoulombs higher than intended value of 1.1 mC because of intensive electrode processes what made it impossible to precisely control the plating process.

To assess the plating reproducibility the films were plated six times and at every film five SY voltammograms were recorded. Only in the case of bismuth solution of 0.5 mM Bi(III) twelve films were plated and examined due to very bad reproducibility of peak current (RSD = 56%) and even worse of signal-to-noise (RSD = 79%). The most favorable signals were attained using 0.01 M and 0.005 M Bi(III) plating solutions (see Fig. 4). The SY peaks recorded using these two plating solutions were almost symmetrical, with symmetry factors equal to 1. After exploiting the BiFEs plated from 0.01 M and 0.005 M Bi(III) solutions, the SY reduction peak currents were nearly the same and their current values were highest among tested BiFEs. The 0.005 M Bi(III) plating solution most proper for analytical purpose taking into consideration S/N characteristics. The variations in background current, geometry and value of voltammetric response during subsequent measurements were estimated in relation to plating conditions, support dimensions, and the value of $I_p/I_{background}$. '$I_{background}$' was calculated as the difference between current values for markers used for baseline construction (see Fig. 3; the marker position selected using black circles). The background current level depended on the 'history' of the film. The voltammogram recorded as the first one on the newly prepared bismuth film exhibited high background current that was rising substantially in the direction on negative potentials (Fig. 5, curve b). The tenth subsequent adsorptive stripping curve was more symmetric (the $I_p/I_{background}$ for 10th curve was equal to 7.15 and for 1st only 1.27) and it was easier to fix markers to generate the line to read the peak current or peak area value. Having in mind the BiFE background behavior during studies the fifth curve recorded at BiFE was consider appropriate.

Comparing the background current value in the case of electrodes plated in 0.01 M Bi(III) and 0.005 M Bi(III) it turned out that the use of 0.01 M Bi(III) makes it possible to prepare more efficient electrodes.

Using all *ex-situ* BiFEs plated from perchloric acid it was observed that the SY peak observed at subsequent voltammograms is getting smaller. Such small but noticeable decreasing trend was less pronounced for 0.005 M Bi(III) plating solution and for further study this concentration was used. The signal drop was linear and on average equal 0.056 µA/curve but the reproducibility estimated for 10 subsequent curves was satisfactory (RSD < 5% for electrodes plated in solution containing 0.005 M Bi(III).
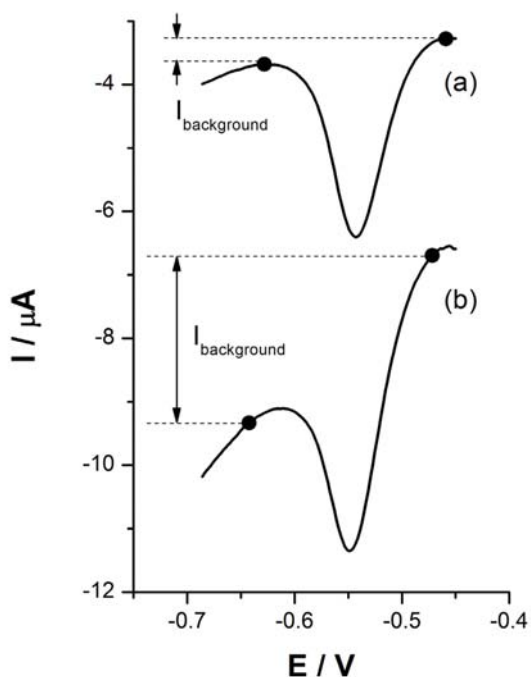

Fig. 5:
The first (b) *and tenth* (a) *SW voltammograms of 44 µg/l SY in 0.5 M ammonia buffer recorded at ex-situ plated BiFE*. Support: GC disc, ϕ = 1 mm. E_{plat} = -1.2 V, Q = 1.1 mC. Instrumental parameters: E_{acc} = -0.45 V, t_{acc} = 60 s, t_{eq} = 10 s, f = 250 Hz, A = 50 mV.

The effect of bismuth plating potential on the SY voltammetric response was tested by preparing the BiFE using different electrolysis potentials. Application of electrodes plated at potentials between -0.9 V and -1.35 V revealed that the SY signal increased linearly when electrodes were plated using potentials up to potential of -1.3 V. When BiFE were plated at more negative plating potentials, the SY signal dropped. Such tendency was observed at most of the tested BiFE plating solutions. The slump in SY peak current value observed at BiFEs plated at very negative plating potentials was caused by the competing release of hydrogen during electrolytic GC support coating of bismuth.

As optimal value the plating potential of -1.2 V was selected because at this potential the hydrogen generation was not as intensive (no bubbles were observed during electrolysis) and the process of electrode reduction was slow enough to precise control the plating charge.

The Effect of SW Instrumental Parameters on the Reduction of SY

The peak current (E_p) of SY is observed at the potential between -0.535 V and -0.559 V vs. ref. (average = -0.545 ± 0.006 V) and there is no any obvious relationship between the E_p value and the concentration of the plating solution.

The range potentials useful for SY accumulation is short and limited by the reduction of SY itself and the oxidation of the electrode material that was observed beginning from potential of -0.35 V vs. ref. The SY signal was almost independent of the accumulation potential over the range of 0.400 – 0.440 V vs. ref. and then increased by 20% when going to –0.450 V and this value was accept as optimal.

The prolongation of the accumulation time has conversely to accumulation potential very strong effect upon the SY signal. The results of tests performed at BiFE plated from 5 mM Bi(III) after 30 s of accumulation at – 0.45 V in solution of 22 µg/l of SY showed a linear increase of SY signal within the 0 – 60 s accumulation time range. A further prolongation of SY accumulation resulted in a slower increase of the SY signal, and, finally, when accumulation time reached 200 s a drop in the SY peak current was observed.

The effect of the frequency upon the signal of 0.1 mg/l SY over the 10 – 500 Hz range was examined using electrode plated from 0.001 M Bi(III). The measurable signal was observed starting from frequency of 50 Hz and it has risen in value up to 250 Hz and leveled off to 350 Hz. The higher frequency caused the drop of the SY signal. The increase of the frequency starting from 300 Hz leaded to a progressively more marked increase of the background noise and fall of S/N value (by 50% from 300 to 500 Hz).

Calibration Measurements

Under the optimized plating conditions, the BiFE provided well-defined peaks whose height had depended linearly on the SY concentration in a quite wide range. As found out, the SY adsorbed very readily at BiFEs and the main factors influencing their voltammetric response were the area of the electrode and the accumulation time.

By adjusting the electrode size and accumulation time, it was possible to obtain calibration with different sensitivity and dynamic range. Such examples are then given in Table I, showing the intercepts of regression line do not differ significantly from zero (for $\alpha = 0.05$).

Table I. *Sunset yellow calibration using BiFEs of different diameter.* To construct calibration curve, the peak area (A·V) was plotted against the SY concentration (µg/l)

ϕ / mm	Slope	Intercept	C_{min} / µg·L^{-1}	C_{max} / µg·L^{-1}	R^2
1	$(4.0\pm0.1)\cdot10^{-9}$	$-(4\pm2)\cdot10^{-9}$	4.4	35	0.9912
2	$(12.6\pm0.3)\cdot10^{-9}$	$-(2\pm1)\cdot10^{-8}$	4.4	87	0.9914
3	$(10.3\pm0.3)\cdot10^{-9}$	$-(9\pm3)\cdot10^{-8}$	26	169	0.9912

Interference Studies

To test the effect of the matrices of soft drinks on SY peak height several sweetening agents were tested (sucrose, fructose, *Aspartame*, *Acesulfam-K*, saccharin sodium salt) obtained from grocery shop in tablet or liquid form. When used according to the manufacturer recipe three of the above-mentioned artificial sweetener caused a small (5%) drop of SY signal. When their amount was four times higher than recommended the drop was more pronounced and the peak height retained only 30% of its initial value. The sucrose used in the amount equivalent to a level teaspoon of sugar (2 g) added to 250 ml of liquid almost suppressed the SY signal and the SY peak was barely observable (5% of initial I_p). While fructose was used in the same proportions the peak drop was also significant (30% of its initial value).

Conclusions

Our findings have illustrated that while the application of all tested electrodes BiFEs resulted in recording of measurable voltammetric signals of *Sunset Yellow* (SY), the BiFE plated at 1 mm GC disc electrode offered significantly higher selectivity and clearly most advantageous SY signal. The optimal concentration of bismuth plating solution used for BiFEs, design for SY characteristics, was between 0.01 M Bi(III) and 0.005 M Bi(III). Performance of BiFEs plated in both listed earlier solutions was very similar; the 0.01 M Bi(III) being more favorable with respect to the background current level.

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