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Mini Review

Electroanalytical Methods for Determination of Sunset Yellow— a Review

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The review highlights the electroanalytical methods used for the determination of the artificial dye Sunset Yellow, one of the most frequently used azo–dyes, with a very wide field of the application during the last two decades. As azo–dyes may have detrimental effects on living organisms, their content in food must be strictly controlled. Despite other analytical methods for determination of azo–dyes, the electroanalytical methods, especially voltammetric methods, offer many other advantages besides high sensitivity, selectivity, and reproducibility – e.g., less time for sample preparation and determination, low investment and running cost, electrode miniaturization and modifications, as well as use of eco–friendly materials. This critical review focuses on the electrode materials and their modifications since they are the deciding factor for a successful voltammetric determination of Sunset Yellow. In addition to this, the reaction mechanisms for determination and analytical performance are also presented in the paper.

Keywords: Azo–dyes, Sunset Yellow, Voltammetric methods, Modified electrodes, In food analysis

1. INTRODUCTION

All food dyes can be divided into two basic, general categories: natural dyes and artificial dyes. The natural food dyes are derived from grapes, saffron, paprika, carrots, beets, and algae, and are used to color a variety of foods. The artificial food dyes (AFCs), which are mostly derived from petroleum, contain a single, or more, azo functional group (–N=N–), which most frequently connects the two aromatic parts. People associate specific colors with specific flavors, therefore colors of food can affect their perception of taste, especially their perception of sweets and beverages. Artificial dyes may improve on natural variations in color, may enhance colors that occur naturally, or may provide color to colorless and "fun" food, thereby making it appear more attractive and appetizing – e.g. adding a red, yellow or green color to gummy sweets, which would naturally be colorless.

From the perspective of food producers, artificial dyes make the food more durable while also lowering the production costs [1]. Natural dyes, however, are unstable due to exposure to light, air, temperature, pH changes, moisture, and storage conditions [2, 3, 4].

Some of these substances, on the other hand, pose potential risks to human health, especially if consumed excessively. Some of the synthetic azo–dyes, especially those combined with some other azo–dyes or drugs, exhibit mutagenic effects [5] and may have significant potential of genotoxicity [6]. In addition, they may also be cancerous, may cause gastric annoyance, diarrhea, vomiting, urticaria, angioedema, rhinitis, nasal congestion, bronchial asthma symptoms, itching, headaches, or dizziness. The controversies concerning the use of AFCs date back to the 1920s, when they were related with hyperactivity [7], hypersensitivities, learning problems, and negative effects on cellular immune responses [8] in children.

Consequently, the use of AFCs in food products is strictly controlled by various national legislations [9, 10].

Despite the abovementioned side effects, the amount of AFCs used in foods has increased by 500 % in the last 50 years, with significant growth occurring during the last two decades.

As the use of artificial dyes has grown considerably, several analytical methods and techniques for determination of ACFs have been developed to prevent THE uncontrolled use of authorized dyes and their misapplication: i.e., high–performance liquid chromatography (HPLC) [11], liquid chromatography (LC) or thin–layer chromatography (TLC) [12], immunoassay techniques such as enzyme–linked immunosorbent assay (ELISA) [13], spectrophotometric techniques [14] or second derivative spectrophotometry for resolving binary system, tandem mass spectrometry, and capillary electrophoresis [15]. Most of the detection methods and techniques mentioned require several time–consuming steps, e.g. extraction of THE dye from a sample [16].

Spectrophotometric methods have been widely used for routine quantitative determination of synthetic dyes. Kaur et al. [14] review some of the spectrophotometric analytical techniques, e.g. Derivative Spectrophotometry, H–Point Standard Addition Method, Cloud Point Extraction Method for analyses of water–soluble and water–insoluble food dyes. The authors describe the best solution for qualitative and quantitative determination of AFCs, even for the binary dye mixtures with a strong spectral overlap. Although the use of spectrophotometric techniques is desirable, their application is limited due to the relatively low cost, in addition to issues related to low sensitivity and determination of dyes in complex product composition (isolation needed) [17]. In addition to this, some techniques, e.g. HPLC, LC or TLC, require an extraction step, which is both advantageous and disadvantageous in terms of their sensitivity, simplicity, rapidity, and cost–effectiveness.

In recent years, the electroanalytical approach has been found to be a very potent alternative for determination of dyes, due to their simplicity, low cost operations, and relatively short analysis time. Among other analytical methods, electroanalytical methods show both high sensitivity and high accuracy, making them ideally suited for the analysis of artificial dyes in food, pharmaceuticals, and cosmetics.

The objective of this paper is to summarize the results of the electroanalytical method used for determining of an artificial azo–dye, Sunset Yellow, during the last two decades. The Sunset Yellow FCF is disodium 2–hydroxy–1–(4–sulfonatophenylazo)naphthalene–6–sulfonate, also known as

Orange Yellow S, Yellow 6, denoted in Europe by E Number E110 or C.I. 15985 is a petroleum–derived orange food azo–dye, with structure shown below (Figure 1). Beside sodium salts, calcium and potassium, salts are also approved as food dyes in Europe.

The Sunset Yellow FCF is present in many common food products, such as bakery products, sugar candies, sugar–coated pills, jelly beans, powdered drinks, sweets, nutrient–enhanced sports beverages, ice creams, and gelatins [18]. The food categories most contributing to exposure are non–alcoholic beverages at maximum levels of 50 mg/L, as well as confectionary and fine bakery articles with a maximum level of 50 mg/kg [19]. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the European Commission's Scientific Committee on Food (SCF) established an acceptable daily intake (ADI) of 2.5 mg/kg for Sunset Yellow – yet lately, based on results from Mathur et al. (2005b) [20], the amount was reduced to 1 mg/kg.

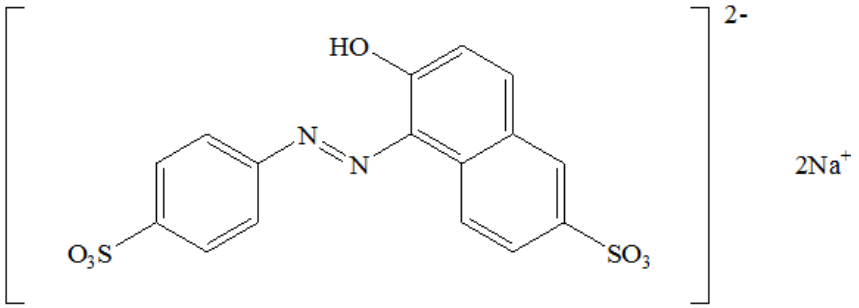


Figure 1 Structure of a water–soluble azo–dye, Sunset Yellow FCF (E 110).

Such strict regulations regulating the use of artificial dyes in the food industry, as reviewed by Solymosi [19], encourage the scientists to find a fast and simple monitoring method of Sunset Yellow in food.

First voltammetric method, based on hanging mercury drop electrode (HMDE), as reported by Fogg et al. [21, 22], dates back to the early 80's of the last century. Further papers present theoretical and general studies of the voltammetric behavior of several artificial dyes using cyclic voltammetry (reduction peak potentials and peak currents) and its determination by different differential pulse techniques used for determination [23, 24]. Sensitive methods for determination of several dyes using carbon paste electrode (CPE) in static systems or continuous flow systems have also been reported. Despite this, poor reduction peaks were observed in the analysis of some dyes in commercial samples; therefore, the sensitivity of the proposed method was found to be insufficient. When CPE was used instead of HMDE, the observed shifts of reduction potential, as well as the changes in current obtained, could be used for identifying an individual food dye [25, 26].

Table 1 summarizes the electrode materials (substrates), modifications, and methods used in the development of sensors, as well as the conditions, the limits of detections, and their application over past two decades used for determination of Sunset Yellow, displayed chronologically in accordance with the literature review ("Chronicle review").

As can be seen from "Chronicle review" presented in Table 1, a wide variety of different substrates and their modifications were used in order to achieve a satisfying analytical performance.

Figure 2 displays summary data from Table 1, as well as the number of appearances of the most common substrates, followed number of reported reaction for electrochemical determination. As can be seen from Figure 1, Sunset Yellow contains two potential electroactive groups (–OH and –N=N–). Therefore, the oxidation of the hydroxyl–group, or the reduction of the azo–group, can be used for electrochemical recognition.

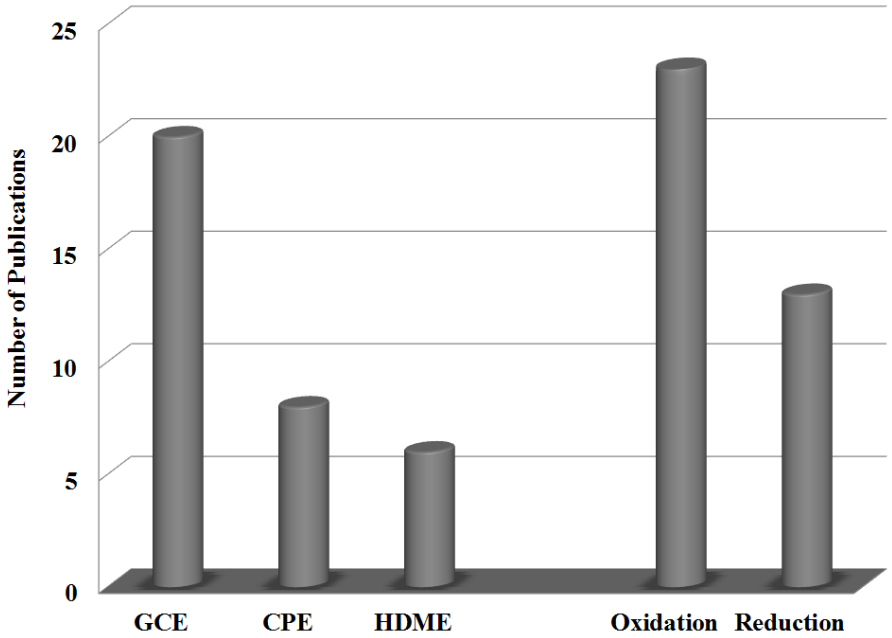


Figure 2 Publication activities in the field of the most frequently used substrates/electrodes for determination of Sunset Yellow, as well as by reaction for determination of Sunset Yellow for last two decades based on Table 1.

Table 1 Comparison of the electroanalytical and analytical performances reported for the electrochemical determination of Sunset Yellow.

Electrode–Modification/Substrate	Methods	Potential	pH Solution	Linear range (μg L^{-1})	LOD (μg L^{-1})	Analyzed samples	Year of publication/ Reference
ZnO/Cysteic acid on GCE	DPV	oxidation at 0.76 V vs. Ag/AgCl	5.0 PBS	45.2–1356	13.56	In soft drinks and peach jelly with Tartazine	2017 [27]
HMDE	AdSW	reduction of at –0.71 V vs. Ag/AgCl	12.3 PBS	N/A	1.5	Commercial drinks with Sudan I	2016 [28]
graphene oxide multi–walled carbon nanotubes on GCE	CV/LSV	oxidation at 0.8 V vs. SCE	5.0 PBS	3.6–40	11	With Tartazine	2016 [29]
β–cyclodextrin/ionic liquid/gold nanoparticles functionalized magnetic graphene oxide on GCE	CV/DPV	oxidation at 0.66 V vs. SCE	7.0 PBS	2.3– 90.5	0.9	In spiked water samples, mirinda drink and minute maid	2016 [30]
Copper with 1,3,5–Benzenetricarboxylate ion platform on CPE	DPV	oxidation at 0.61 V vs. SCE	8.0 PBS	0.14– 22.6	0.023	With Tartazine	2016 [31]

silver and poly(L–cysteine) composite film on GCE	DPV	oxidation at 0.86 V vs. Ag/AgCl	4.5 PBS	226–135708	34	With Tartazine in beverages	2016 [32]
CPE modified with nanostructured resorcinol–formaldehyde resin	DPV	oxidation at 0.67 V vs. SCE	7.0 PBS	0.14–56	40	In wastewater and drink samples	2015 [33]
gold nanoparticles/graphene electrode on GCE	CV/DPV/	oxidation at 0.75 V vs. SCE	4.0 PBS	0.91–49370	0.9	In soft drinks	2015 [34]
multi–walled carbon nanotubes/magnetic core– shell Fe_3O_4@SiO_2 nanoparticles/ CPE	AdSW	reduction at –0.2 V vs. Ag/AgCl	6.0 PBS	226–45236	22.6	With Tartazine	2015 [35]
CPE /montmorillonite calcium functionalized with cetyltrimethyl ammonium bromide	DPV	oxidation at 0.75 V vs. SCE	4.0 AcB	1.13– 90	0.32	In soft drinks	2015 [36]
Au nanoparticles/1–allyl–3–methyl imidazolium chloride on GCE	CV/SWV	oxidation at 0.65 V vs SCE	7.0	1.8–452	0.23	With Tartazine in beverages	2015 [37]
hexadecyl trimethyl ammonium bromide /graphene oxide/multiwalled carbon nanotubes/GCE	CV/ DPV	oxidation at 0.1 V vs SCE	6.0 PBS	14–271	2.26	With Tartazine in soft drinks	2015 [38]
bismuth film modified GCE	CV/DPV	reduction at –0.75 V vs. Ag/AgCl	7.0 PBS	2261–107662	4524	With carmoisine in food product	2014 [39]
poly(L–phenyl–alanine) on GCE	CV/DPV	reduction at –0.55 V vs. Ag/AgCl	7.0 PCB	181– 6333	18.1	With tartrazine in food and drug product	2014 [40]
hexadecyltrimethylammonium bromide functionalized grapheme/Pt–nanoparticles/GCE	CV/DPV	oxidation at 0.86 V vs. SCE	3.0 PBS	36–4524	1.9	In soft drinks	2014 [41]
bismuth film electrode on GCE	CV/SWV	reduction at –0.55 V vs. Ag/AgCl	9.26 AmB	4.4–87	1.0	In soft drinks	2014 [42]
highly dispersed polypyrrole and single–walled carbon nanotube on GCE	CV/DPV	oxidation at 0.68V vs. SCE	7.0 BR	0.9– 678.5	0.14	In soft drinks	2014 [43]
alumina microfiber/ CPE	CV/DPV	oxidation at 0.65 V vs. SCE	6.5 PBS	0.13–45.2	0.072	In soft drinks	2013 [44]
expanded graphite paste electrode modified with attapulgite	CV/SWV	oxidation at 0.656 V vs SCE	6.0 BR	1.13–679	0.45	In soft drinks	2013 [45]
poly (L–cysteine) modified GCE	CV/CA/DPV	oxidation at 0.733 V vs. Ag/AgCl	6.6 PBS	3.6–317	1.8	With lemon juice	2013 [46]
expanded graphite paste electrode	CV/SWV	oxidation at 0.66 V vs SCE	6.0 BR	22–904	2.26	In jelly and fruit juice	2013 [47]
β–cyclodextrin–coated poly (diallyldimethylammonium chloride)–functionalized graphene composite film/ GC–rotating disk electrode	DPV	oxidation at 0.81 V vs. SCE	5.0 PBS	23–9047	5.7	With tartrazine in food product	2013 [48]
graphene nanosheets with nickel nanoparticles on GCE	CV/SWV	oxidation at 0.69V vs. SCE	4.4 AcB	3–200	1.0	With tartrazine in food product	2013 [49]
Carbon–ceramic electrode/MWCNTs–ionic liquid	CV/DPV	oxidation at 0.68 V vs. SCE	7.0 PBS	181–49760	45	With tartrazine in food product	2013 [50]
BDDE	MPA–FIA		1.0 H_2SO_4	452–22619	6.0	With Tartazine and brilliant blue in gelatins, juice, beverages	2012 [51]
gold nanoparticles CPE	CV/SWV	oxidation at 0.75 V vs. Ag/AgCl	4 PBS	45–905	14	With Tartazine in soft drinks	2012 [52]
BDDE	DPV	reduction at –0.15 V vs. Ag/AgCl	1.0 H_2SO_4	45–2153	385	In gelatins, juice and beverages	2012 [10]
molecularly Imprinted Polypyrrole on GCE	CV	oxidation at 0.275 V vs. Ag/AgCl	7.0 PBS	181–3619	NA	In wine samples	2012 [53]
HMDE	CV/AdSW	reduction at –0.65 V vs. Ag/AgCl	9.8 BR	Up to 100	1.3	With Tartazine in gelatins and soft drinks	2012 [54]
graphene layer–wrapped phosphotungstic acid hybrid on GCE	CV/DPV	oxidation at 0.78V vs. SCE	4.4 AcB	1–300	0.5	With tartrazine in food product	2012 [55]
MWCNT on GCE	CV	reduction at –0.66 V vs. SCE	8.3 PBS	1200–125000	500	In soft drinks	2010 [56]
Platinum Wire–Coated Electrode with Sunset	Potentiom		7.0	143–	143	In commercial	2009

Yellow–cetyl ion pair as an ion exchanger	etric sensor		PBS	1430000		food products.	[57]
MWCNT on GCE	CV/DPV	oxidation at 0.60V vs. SCE	8.0 PBS	24–4976	0.01	With tartrazine in soft drinks	2009 [58]
polyallylamine modified tubular GCE	SWV	reduction at –0.20 V vs. SCE	<1 HCl	1583–67856	1583	With tartrazine and allura red in food product	2007 [59]
HMDE	CV/DPP	reduction at –0.63 V vs. Ag/AgCl	9.2 BR	22.6–452.4	5.0	With tartrazine and allura red	2002 [60]
HMDE	AdSW	reduction at –0.60 V vs. Ag/AgCl	10 AmB	5–90	5.0	In commercial refreshing drinks	1997 [18]
HMDE	AdSW	reduction at –0.50 V vs. Ag/AgCl	6.0 McIlvane BS	0.03–0.16	For trace level	With Amaranth in food product	1997 [61]
HMDE	AdSW	reduction at –0.46 V vs. Ag/AgCl	5.7 McIlvane BS	0.03–0.20	For trace level	With Amaranth, Tartrazine and Ponceau 4R in food product	1996 [62]

GCE glassy carbon electrode; CPE carbon paste electrode; HMDE hanging mercury drop electrode; MWCNT multi–walled carbon nanotubes, BDDE boron–doped diamond electrode.
PBS phosphate–buffered solution; AcB acetic–buffer; BR Britton–Robinson buffer; PCB Phosphate–citrate buffer; AmB ammonia buffer; McIlvane BS potassium phosphate, citric acid and potassium chloride buffered solution.
CV Cyclic voltammetry; CA Chronoamperometry; CC Chronocoulometry; DPV Differential pulse voltammetry; DPP Differential pulse polarography; AdSW Adsorptive stripping voltammetry; MPA–FIA flow injection system and multiple pulse amperometric determination; LSV Linear sweep voltammetry; SWV square–wave stripping voltammetry.

Despite the fact that determination of Sunset Yellow on unmodified ("bare") carbon electrodes has great advantages concerning simplicity, robustness, mechanical resistance, low price, and wide potential window in anodic and cathodic region (thus preventing evolution of hydrogen and oxygen), the electrochemical reactions of SY on "bare" carbon electrodes occur at high anodic and cathodic potentials on which other substances can be electrochemical active.

Electrode surface modifications have been introduced by many authors with the intention of solving or diminishing of the abovementioned problems, as well as to achieve improved selectivity and sensitivity.

As can be seen from Figure 2, a glassy carbon electrode is the most modified substrate. By introducing of different modifier (Table 1), in addition to better limits of detections, broader linear range, both high sensitivity and high selectivity for Sunset Yellow towards other dyes or excipient in food have been achieved.

One of the modification approaches deserving of our attention is the introduction of carbon nanotubes (CNT). Its unique features denote CNT as one of the intensely used carbon modifications during this century, the approach owing such use to its remarkable electrical (reduced capacitive current, high signal–to–noise rations), chemical (possibility of modification, inertness), mechanical, and structural properties. The exceptional sensitivity of CNT is a consequence of a hollow core, suitable for accumulation of different species, in addition to being well suited for in situ measurement as highly sensitive nanoscale sensor [63].

By modifying the GCE and by incorporating the MWCNT in the polymer matrix, a very low limit of detection (0.01 μg L^{-1}) was achieved [58] based on oxidation of azo–group. These results are

comparable with those obtained by HPLC, or any of other expensive and sophisticated methods. Interestingly, by performing similar GCE modifications, determination based on oxidation of the hydroxyl–group exhibits an improved sensitivity and limit of detection over those based on reduction of the azo–group [56]. Also, graphene, or graphene oxide, as an innovative electron transfer mediator, has been introduced, combined with MWCNT on GCE [29, 38], metallic modification [30, 34, 49], or polymeric modification [48] on GCE. Furthermore, modifications of GCE based on deposition of conducting polymer were reported: phosphotungstic acid hybrid [55], polyallylamine [59], poly(L–phenyl–alanine) [40], or polypyrrole [43, 53].

Other carbon–based electrodes following the latest trends are the carbon paste electrodes (CPE) (8 reports–see Figure 2). Due to the wide potential range for analysis, easily renewable surface, promotion of the electron transfer, as well as easier modification and simple construction, their use in the second decade was marked by significant growth, not solely due to their use in determining of Sunset Yellow, but also their wide application in analytical chemistry in general. Surprisingly, publications that report on this kind of electrode have been referred only during the last two years. The practical application of these electrodes is often limited by their mechanical instability. It is worth mentioning the modification of CPE with alumina microfibers [44]. The role of alumina was to provide a larger response area and porous structures with numerous adsorption sites for the oxidation of Sunset Yellow. By using this approach and its exceptional sensitivity, down to 0.13 μg L^{-1} in sample of soft drinks, was obtained.

The boron doped diamonds (BDD) are also carbon material, which gained special attention in the modern electroanalytical chemistry, owing to extremely broad potential window, high conductivity, low background currents, fast response, mechanical and chemically stability, biocompatibility, and above all, resistivity to passivation by reaction products. Thus, BDD is an electrode material superior to conventional carbon–based materials, including carbon paste, graphite, glassy carbon (GC); it is even superior to a carbon nanotube or microfiber [64]. By using BDD as a bare electrode for determination of Sunset Yellow, micromolar LOD was obtained, together with wide linear range, 452–22 619 μg L^{-1} or 45–2153 μg L^{-1} [10, 51].

The metals (as electrode material) in determination of Sunset Yellow have been very popular during 80's and 90's of the 20th century, mostly because of the use of mercury–based electrodes (mostly HDME). Until now, HDME, or other mercury–based electrodes, were the best materials available for voltammetric determination of various important analytes (organic, inorganic, organometallic, macromolecular substances, etc.), also including AFCs with excellent concentration range (from 10^{-3} to 10^{-11} mol dm^{-3}).

With the easy renewal of their surface, which minimizes passivation problems, their extremely broad potential window in the cathodic region, high sensitivity, low investment and running costs overshadow their non–environmentally friendly characteristics. Limitation of HDME is a narrow potential window in the anodic region and mercury toxicity. Other than the abovementioned limitation, excellent analytical performance was achieved with HMDE, in comparison with similar metal–based electrodes (amalgam, bismuth, or antimony electrodes) presented by Vyskočil and Barek [65], or various carbon–based electrodes [66, 67]. Determination of Sunset Yellow is strictly limited to the reduction of azo–group of Sunset Yellow, as is presented by Ni and Bai [60, 61]. The authors reported

a very low limit of detection and simple experimental procedure for use in food analysis. The possibility of simultaneous determination of Sunset Yellow and another azo–dye present, i.e. Tartazine, Allura Red, Ponceau 4R, Sudan I, over a wide potential range by AdSV or DPP, was elaborated on by a great number of independent authors and is presented in Table 1.

Not only do the mercury modified electrodes remarkably enhance the electron transfer and accumulation efficiency of Sunset Yellow, but also and Bi–modified electrodes [39, 42]. Bi is environmental friendly non–toxic element when compared to Hg and conventional and microbismuth film electrodes have been widely used in electrochemical analysis of various organic compounds [68-72].

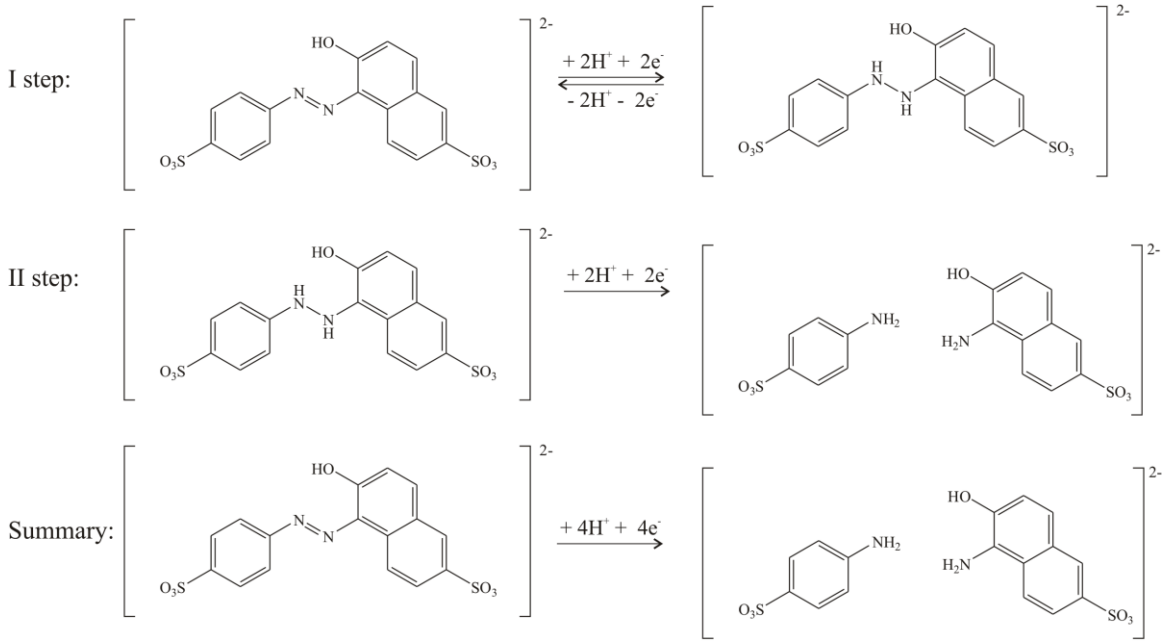
Also, a metal ion can be entrapped in complex frameworks and can be used as mediator of electrons from Sunset Yellow to the electrode surface, as is reported for Cu–BTC frameworks by Ji et al., [31].

The introduction of nanocrystalline metal particles leads to the improved chemical activity due to larger specific surface area, thereby consequently improving the sensitivity and selectivity of sensors. For this purpose, various metal nanoparticles were used: gold [34, 52] and nickel nanoparticals on GCE [49].

Recently, a more complex modification such as MWCNTs metal oxide–based electrode decorated with magnetic $Fe_3O_4@SiO_2$ nanoparticles with CPE was proposed for simultaneous determination of Sunset Yellow and TT in food products. The benefits of this method were inexpensive and less time–consuming pretreatments [35]. This approach integrates all of the gains that arise from properties of carbon nanotubes, porous structure and morphology of the metal oxide, together with easy preparation of carbon paste electrodes. As results of abovementioned modifications, faster electron–transfer kinetics and larger electroactive surface area lead to a lower limit of detection (22.6 μg L^{-1}) and wider linear range (226–45236 μg L^{-1}) based reduction of the azo–group [35].

As was mentioned earlier, Sunset Yellow contains two electroactive groups, (–N=N– and –OH). As it is presented in Table 1 and Figure 2, the dominant reaction used for electroanalytical determination of Sunset Yellow is oxidation of hydroxyl–group (23 papers compared to electroreduction 13 papers). However, which reaction will be dominant, and thus used in electroanalytical determination, will be mainly determined by modification materials and modification methods.

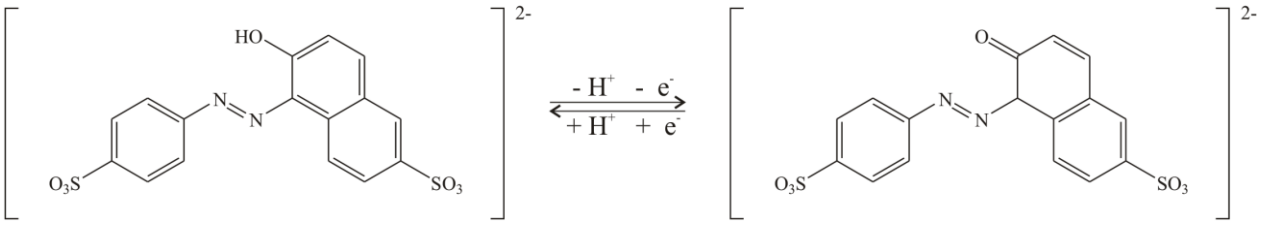
The mechanism of an azo–compounds electroreduction has been well known and reported on in the literature [73, 74]. The process on the electrode consists of two steps, similar to those occurring in the metabolic processes. Both of the steps include the transfer of two electrons (see Scheme 1) According to Florence et al. [74], at all pH values, the first step of reduction of azo–dye is a reversible 2 electron reaction in which azobenzene is reduced to hydrazobenzene. The second step is 2 electron irreversible reaction followed by breaking of the azo–group, which leads to the formation of aromatic amino compounds. Standard potentials of these two reactions are very close each other; consequently, overlapping of analytical signals (currents) can be noticed.



Scheme 1 The mechanism of the electrochemical reduction of Sunset Yellow.

Reduction potentials and signals are strongly influenced by pH of the media. At an approximately neutral pH, the electroreduction occurs with 4 electron–transfer irreversible reduction of azo–group, as a summary reaction.

The reaction that represents electrochemical oxidation of hydroxyl–group on Sunset Yellow, to keto–group includes transfer of one electron (see Scheme 2.) [29].



Scheme 2 The mechanism of the electrochemical oxidation of Sunset Yellow.

As was mentioned earlier, the two step reductions can be noticed when electroreduction takes place. Although all of the authors are consistent on the irreversibility of the second step, there is some disagreement in the explanation of the reversibility of the first step. Some authors [74] claim that the first step of reduction of an azo–compound is reversible, while other authors notice quasi–reversible behavior [27]. Among all the reports (based on electroreduction reaction), however, the lowest limit of detection has been observed with a bismuth film electrode on GCE (1.0 μg L^{-1}) [42].

Opposite to the slow kinetic of electroreduction of azo–group, a fast and reversible oxidation of hydroxyl–group ensures remarkably low limits of detection and provides an opportunity for the determination of very large number of azo–dyes that contain the hydroxyl–group. When compared to the lowest LOD based on electroreduction reaction, the limit of detection obtained by electrooxidation reaction using GCE modified with MWCNT shows a remarkable improvement (0.01 μg L^{-1}) [58]. This

makes voltammetric methods comparable to high–performance liquid chromatography (HPLC). Furthermore, by performing appropriate modification of the electrode, and due to an improved rate electron transfer and optimized conditions, a voltammetric determination of Sunset Yellow in real samples without any pretreatments can be performed.

2. CONCLUSION

Among all of the electroanalytical techniques, voltammetric methods are most widely used as a powerful tool for determination of Sunset Yellow.

Two mechanisms of determination are reported: first, based on electroreduction of azo–group, and, second, based on electroxidation of hydroxyl–group. By appropriate electrode modification one can prefer the first over the second reaction.

The most used substrate for voltammetric determination are glassy carbon electrodes, modified with different conducting polymers for electroxidation reaction, or electrodes based on metals for electroreduction reaction which exhibit excellent analytical performance, comparable with sophisticated analytical techniques.

Despite their excellent analytical performance, the main problem of all analytical techniques is the determination of Sunset Yellow in presence of complex matrices. The future investigations should therefore be focused on solving this problem by modification of electrodes being more specific, by miniaturizing them, and by introducing novel analytical procedures.

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