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Electrode Modified with Manganese Dioxide Nanorods for the Simultaneous Voltammetric Determination of Food Colorants

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Featured Application: Direct voltammetric determination of brilliant blue FCF and tartrazine in soft and isotonic sports drinks.

Abstract: Synthetic colorants in particular tartrazine and brilliant blue FCF are widely used in food chemistry and technology although can give negative health effects of various severities. Therefore, sensitive, selective, simple, and reliable methods for the quantification of these dyes are required. Glassy carbon electrode (GCE) modified with manganese dioxide nanorods (MnO_2 NR) dispersed in cetylpyridinium bromide gives a sensitive response to tartrazine and brilliant blue FCF in mixtures. Electrode modification provides a 7.9-fold increase of the electroactive surface area and a 72-fold decrease of electron transfer resistance. Simultaneous voltammetric quantification of colorants has been performed in phosphate buffer pH 7.0 in differential pulse mode. The linear dynamic ranges of 0.10-2.5 and 2.5-15 μM of tartrazine and 0.25-2.5 and 2.5-15 μM of brilliant blue FCF have been obtained with the limits of detection 43 and 41 nM, respectively. The advantage of the sensor developed is the high selectivity of response in the presence of typical interferences (inorganic ions, saccharides, ascorbic and sorbic acids) and other food colorants (riboflavin, indigo carmine, and sunset yellow). The practical applicability of the approach is shown on the soft and isotonic sports drinks and is validated by comparison to chromatography.

Keywords: electrochemical sensors; voltammetry; chemically modified electrodes; metal oxide nanomaterials; food colorants

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1. Introduction

Synthetic colorants in particular tartrazine and brilliant blue FCF are widely used in food chemistry and technology, although they can give negative health effects of various severities [1,2]. Both tartrazine and brilliant blue FCF are used as colorants for alcoholic and non-alcoholic beverages, candies, jellies, ice cream, etc. [3]. The average daily intake of tartrazine and brilliant blue FCF is regulated at 7.5 mg/kg_{bw} [4] and 6 mg/kg_{bw} [5]. Therefore, colorants contents in foodstuff have to be controlled.

Sensitive and selective, simple and reliable methods for the quantification of these dyes are required. Voltammetric sensors suit well for such purposes. A wide range of electrochemical sensors has been developed for the determination of tartrazine. Brilliant blue FCF is seldom studied colorant in electroanalytical chemistry. Most sensors are based on the application of surface modifiers, such as carbon nanomaterials [6–8], metal [9,10] and metal oxide [11] nanoparticles, polymeric coverages [12,13], and a combination of various modifiers [14–18].

Tartrazine and brilliant blue FCF are often used together for the production of green-colored foodstuffs and beverages. Therefore, simultaneous voltammetric determination of these colorants is of practical interest. However, this topic did not receive enough attention. Just three voltammetric approaches have been reported [19–21]. All of them are based on the application of modified electrodes (carbon black–polyethylene composite electrode [19], ionic liquid-modified expanded graphite paste electrode [20], and multi-walled carbon nanotube paste electrode [21]).

Electrochemically inert metal oxide nanomaterials (TiO_2, In_2O_3, CeO_2, ZnO, Fe_3O_4, etc.) are perspective modifiers of the electrode surface [22]. Their effectivity has been successfully demonstrated on example of antioxidants [23–25], pharmaceuticals [26], and pollutants [27,28]. Almost no application of such electrodes to food colorants excluding recent works focused on the tartrazine determination on CeO_2 [29] and TiO_2 [30,31] nanoparticles modified electrodes. Thus, the development of voltammetric method based on the oxidation of tartrazine and brilliant blue FCF at the metal oxide nanomaterials-based electrodes is actual. In current work, manganese dioxide nanorods (MnO_2 NR) dispersed in surfactant have been successfully applied as electrode surface modifier. The electrode created provides well-resolved oxidation peaks of tartrazine and brilliant blue FCF allowing their simultaneous quantification.

2. Materials and Methods

Tartrazine (85% purity) was obtained from Sigma (St. Louis, MO, USA) and 85% brilliant blue FCF from Sigma-Aldrich (Steinheim, Germany). Ascorbic acid of 99% purity (Sigma, Steinheim, Germany), 9% sunset yellow and 99% vanillin (Aldrich, Steinheim, Germany), 99% sorbic acid, 98% riboflavin, and 85% indigo carmine (Sigma-Aldrich, Steinheim, Germany) were used for the interference study. 10 mM standard solutions of all compounds were prepared in distilled water. Other reagents were c.p. grade. The laboratory temperature was (25 ± 2 °C).

MnO_2 NR (99%, diameter × L = 5–30 nm × 80–100 nm) from Sigma-Aldrich (Steinheim, Germany) were used as electrode surface modifier. Their 1 mg mL^{-1} suspension was prepared in 1.0 mM cetylpyridinium bromide using sonication for 40 min in an ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea). A standard surfactant solution with a concentration of 1.0 mM was prepared from 98% cetylpyridinium bromide (Aldrich, Steinheim, Germany) by dissolving in distilled water.

Voltammetric measurements were conducted on the potentiostat/galvanostat μAutolab Type III (Eco Chemie B.V., Utrecht, The Netherlands) and NOVA 1.7.8 software. Electrochemical impedance spectroscopy (EIS) was performed on the potentiostat/galvanostat Autolab PGSTAT 302N with the FRA 32M module (Eco Chemie B.V., Utrecht, The Netherlands) and the NOVA 1.10.1.9 software. A glassy electrochemical cell of 10 mL volume was used for electrochemical measurements. The tree-electrode system consisted of a working glassy carbon electrode (GCE) of 3 mm diameter (CH Instruments, Inc., Bee Cave, TX, USA), or a modified electrode, an Ag/AgCl reference electrode, and a platinum wire as an auxiliary electrode. After polishing on 0.05 μm alumina slurry, working electrode surface modification was performed by drop casting of 5 μL of MnO_2 NR suspension.

The pH measurements were carried out using the "Expert-001" pH meter (Econix-Expert Ltd., Moscow, Russian Federation) with a glassy electrode.

A MerlinTM (Carl Zeiss, Oberkochen, Germany) high-resolution field emission scanning electron microscope was applied for the electrode surface morphology characterization and operated at 5 kV accelerating voltage and a 300 pA emission current.

3. Results and Discussion

3.1. Voltammetric Characteristics of Colorants at Bare and Modified Electrodes

Tartrazine and brilliant blue FCF are electrochemically active on bare GCE in phosphate buffer pH 7.0. Single-step oxidation proceeds irreversibly that is typical for these colorants. The corresponding voltammetric characteristics are summarized in Table 1.

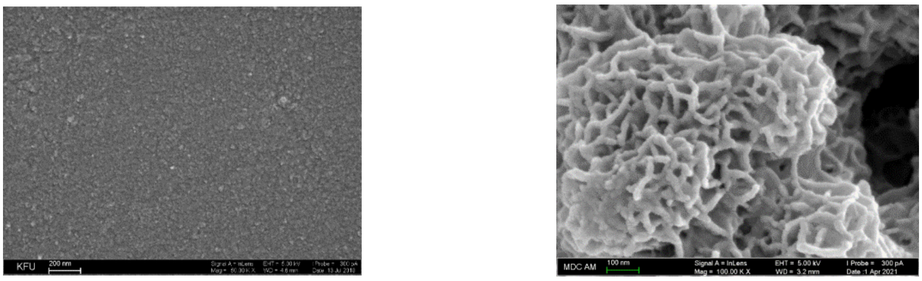
Table 1. Voltammetric characteristics of 10 μM tartrazine and brilliant blue FCF in phosphate buffer pH 7.0.

Electrode	Tartrazine		Brilliant blue FCF	
	E_{ox} (V)	I_{ox} (μA)	E_{ox} (V)	I_{ox} (μA)
Bare GCE	0.94	0.07 ± 0.01	0.94	0.07 ± 0.01
MnO_2 NR/GCE	0.81	0.42 ± 0.01	1.02	0.40 ± 0.04

Simultaneous detection of tartrazine and brilliant blue FCF at the bare GCE is impossible due to the full overlap of the oxidation peaks. Oxidation currents are low in spite of relatively high concentration of colorants. Modified with MnO_2 NR electrode has been used to solve this problem. The oxidation potential of colorants at the modified electrode are significantly changed (Table 1). The difference in oxidation potential achieves 210 mV, making it possible to detect colorants simultaneously. There are two well-defined oxidation peaks on the voltammograms of the colorant's mixture with the peak potential separation of 180 mV. Furthermore, oxidation currents at the modified electrode are statistically significantly increased that confirms higher sensitivity of the colorant's response and effectivity of the suggested modifier.

3.2. Morphology, Effective Surface Area, and Electron Transfer Properties of the Modified Electrode

Scanning electron microscopy data confirm the presence of a modifier on the GCE surface (Figure 1). A sponge-like structure from the intertwined nanorods with a width of 15-20 nm included in the surfactant film has been obtained for MnO_2 NR (Figure 1b).



(**a**) (**b**)

Figure 1. Morphology of the electrode surface by scanning electron microscopy data: (**a**) bare GCE; (**b**) MnO_2 NR/GCE.

Electrochemical investigation of redox peaks of 1.0 mM $[Fe(CN)_6]^{4-}$ ions has shown that the modified electrode demonstrates a significant increase in the effective surface area compared to bare GCE (70 ± 2 mm^2 *vs*. 8.9 ± 0.3 mm^2 for bare GCE). This explains the increase of the colorant's oxidation currents at the modified electrode.

EIS in the presence of 1.0 mM $[Fe(CN)_6]^{4-/3-}$ as a redox probe has been used for the characterization of the electron transfer properties of the electrodes. The 72-fold decrease (72 ± 3 kOhm *vs*. 1.0 ± 0.2 kOhm for GCE) of the charge transfer resistance clearly confirms the increase of the electron transfer rate at the modified electrode. The constant phase element is 29-fold increased compared to bare GCE that is caused by porous structure of the modified electrode surface as well as by the increase of the total surface charge due to the presence of cationic surfactant.

The data obtained confirms once more the effectivity of MnO_2 NR as electrode surface modifier.

3.3. Simultaneous Determination of Tartrazine and Brilliant Blue FCF

Differential pulse voltammetry has been used for the simultaneous quantification of tartrazine and brilliant blue FCF in phosphate buffer pH 7.0. Well-resolved oxidation peaks of colorants at 0.77 and 0.97 V for tartrazine and brilliant blue FCF, respectively, have been observed on the voltammograms (Figure 2). Oxidation currents increases linearly with the growth of the colorant's concentration in the ranges of 0.10–2.5 and 2.5–15 μM for tartrazine and 0.25–2.5 and 2.5–15 μM for brilliant blue FCF with detection limits of 0.043 and 0.041 μM, respectively. The limits of detection are worse than for the other electrodes for the determination of tartrazine and brilliant blue FCF [19,20], but improved vs. multi-walled carbon nanotubes-carbon paste electrode [21]. Nevertheless, the simultaneous determination is impossible at the carbon ink film modified carbon black-polyethylene composite electrode [19] as far as detection is performed at the various pH for tartrazine and brilliant blue FCF. Method [20] requires pre-concentration for 500 s complicating the measurement procedure.

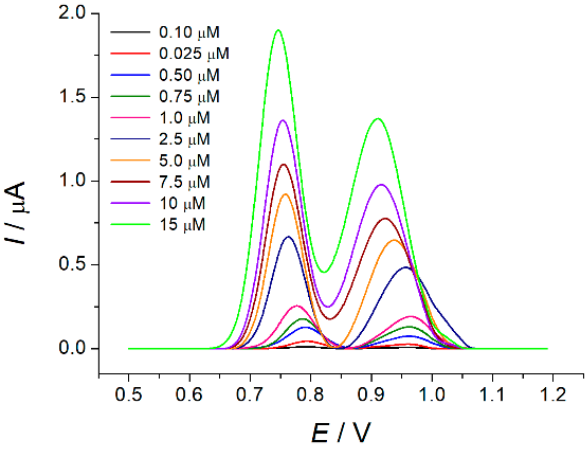


Figure 2. Baseline-corrected differential pulse voltammograms of equimolar mixtures of tartrazine and brilliant blue FCF at the MnO_2 NR/GCE in phosphate buffer pH 7.0. ΔE_{pulse} = 75 mV, t_{pulse} = 25 ms, υ = 20 mV s^{-1}.

Voltammograms for the non-equimolar mixtures of colorants indicate their independent oxidation in the first linear range. Therefore, calibration graphs obtained for equimolar mixtures are universal and can be used independently of the colorant's concentration ratio in the sample. Simple dilution can be applied in the case of high contents of the colorants in real samples.

The accuracy of the method developed has been shown on the model mixtures of colorants at five concentration levels. Relative standard deviation of the determination does not exceed 3% confirming high reproducibility of the electrode response (electrode was renewed before each measurement). The recovery value is in the range of 99–100% confirms high accuracy of the sensor developed.

Foodstuffs are characterized by multi-component composition which can affect response of colorants. The selectivity test has shown that typical interferences (inorganic ions (1000-fold excess of K^+, Mg^{2+}, Ca^{2+}, NO_3^-, Cl^-, and SO_4^{2-}), saccharides (100-fold excess of glucose, rhamnose, and sucrose), 10-fold excess of ascorbic acid, and electrochemically silent sorbic acid), equimolar level of vanillin, and other food colorants (50-fold excess of riboflavin, 10-fold excess of indigo carmine, and equimolar level of sunset yellow) do not affect response of tartrazine and brilliant blue FCF. Thus, the high selectivity of the electrode created towards tartrazine and brilliant blue FCF is an important advantage over other electrodes [19–21].

Practical application of the electrode has been demonstrated on the soft and isotonic sports drinks. Sample 1 is free of tartrazine while samples 2–4 contain both colorants but concentration of brilliant blue FCF is too low and cannot be determined by voltammetry. Standard addition method data confirm that oxidation peaks of real samples belong to the colorants. The results of soft and isotonic sports drinks analysis are presented in Figure 3. Voltammetric data agree well with that obtained by high-performance liquid chromatography [32]. *t*- and *F*-tests confirm the absence of systematic errors of determination and similar precision of both methods.

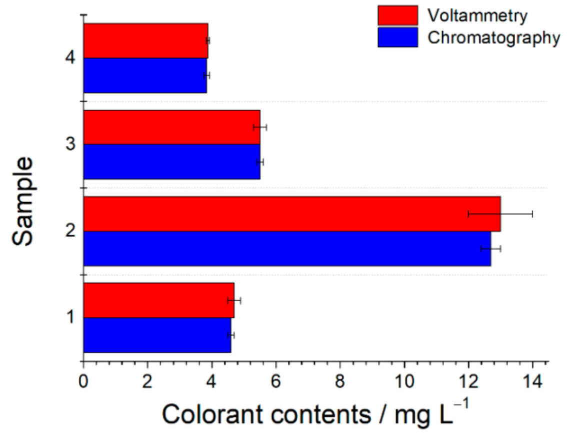


Figure 2. Brilliant blue FCF (sample 1) and tartrazine (samples 2-4) contents in the soft and isotonic sports drinks.

4. Conclusions

Electrode modified with MnO_2 NR has been developed for the determination of tartrazine and brilliant blue FCF for the first time. The simultaneous determination of colorants in the ranges of 0.10-2.5 and 2.5-15 μM of tartrazine and 0.25-2.5 and 2.5-15 μM of brilliant blue FCF has been achieved using electrode created. High selectivity of the electrode response to target colorants is a major advantage of the approach developed. The voltammetric method developed is simple, highly selective, express, and reliable and can be used for the beverages quality control.

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