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Tin(IV) Oxide Nanoparticles and Surfactants Modified Electrode as Sensitive Sensor for Hesperidin †

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Abstract: Tin(IV) oxide nanoparticles in combination with surfactants have been used as sensitive layer of the sensor for hesperidin. The effect of surfactants nature and concentration on hesperidin response has been evaluated. The best parameters have been registered in the case of 500 μM cetylpyridinium bromide (CPB) as dispersive agent. The SEM and electrochemical data confirm the increase of sensor surface effective area and electron transfer rate. Sensor gives linear response to hesperidin in the ranges of 0.10-10 and 10-75 μM with the detection limit of 77 nM. The approach has been successfully tested on orange juices and validated with ultra-HPLC.

Keywords: electrochemical sensors; metal oxide nanoparticles; surfactants; flavonoids; food analysis

1. Introduction

Hesperidin (Figure 1) is the major flavonoid of *Citrus* L. fruits [1] with a wide spectrum of biological activity that is caused its application in medicine [2]. On the other hand, it can show prooxidant effect when high concentration is applied that is typical for the phenolic antioxidants [3].

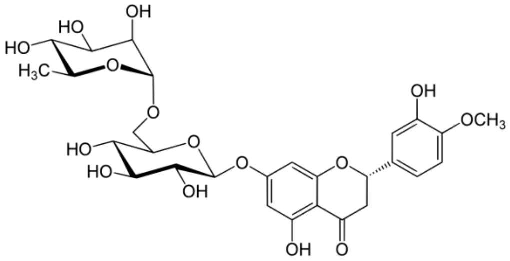

Figure 1. Hesperidin structure.

Therefore, simple, sensitive and selective methods for hesperidin determination are required. Electrochemical sensors can be successfully used for these purposes due to ability of hesperidin to be oxidized on the electrode surface [4,5]. At present time, the chemically modified electrodes are applied in the hesperidin analysis [6–11] as far as provide higher sensitivity and selectivity of response. Nevertheless, further development in the field is required as far as selectivity of the sensors response is often out of consideration and limited applicability to real samples occurs.

Current work is focused on the creation and application of novel voltammetric sensor for hesperidin based on glassy carbon electrode (GCE) modified with the tin(IV) oxide nanoparticles and surfactants. The attention is paid to the evaluation of surfactant nature

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and concentration effect on the hesperidin voltammetric response. The electrodes under investigation have been characterized by SEM and electrochemical methods. The analytical aspects of hesperidin detection are discussed.

2. Materials and Methods

Hesperidin (94% purity) form Sigma (Germany) was used as a standard. Its 0.40 mM stock solution was prepared in methanol (c.p. grade). Naringin (95% purity), 99% ascorbic and 98%caffeic acids, 95% quercetin trihydrate, 85% morin hydrate from Sigma (Germany), 95% chlorogenic acid from Aldrich (Germany) and 97% rutin trihydrate from Alfa Aesar (UK) were used in interference test. Their 10 mM stock solutions in the methanol were prepared in 5.0 mL flasks. Less concentrated solutions were obtained by exact dilution.

Tin(IV) oxide nanoparticles (D < 100 nm) were purchased from Aldrich (Germany). Their 1 mg mL^{-1} dispersions in water and surfactants were prepared by sonication for 10 min in ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd, Republic of Korea). Cetylpyridinium bromide (CPB) (98% purity), 97% *N*-lauroylsarcosine sodium salt (LSS) and Triton X-100 from Aldrich (Germany), 99% cetyltrimethylammonium bromide (CTAB) and Brij® 35 from Acros Organics (Belgium), sodium dodecylsulfate (SDS) (Ph. Eur.) from Panreac (Spain) and cetyltriphenylphosphonium bromide (CTPPB) synthetized in the Department of Organoelement Compounds Chemistry of Kazan Federal University have been used as dispersive agents. Their 1.0 mM solutions were prepared in distilled water.

Other reagents were chemical grade purity. Double distilled water was used for the measurements. The experiments were carried out at laboratory temperature (25±2 °C).

Voltammetric measurements were carried out on the potentiostat/galvanostat Autolab PGSTAT 12 (Eco Chemie B.V., Netherlands) with the GPES software, version 4.9.005. Electrochemical impedance spectroscopy was performed on the potentiostat/galvanostat Autolab PGSTAT 302N with FRA 32M module (Eco Chemie B.V., Netherlands) and NOVA 1.10.1.9 software. The 10 mL glassy electrochemical cell with working GCE with 7.07 mm^2 geometric surface area (BASi® Inc., USA) or modified electrode, a silver-silver chloride saturated KCl reference electrode and a platinum wire as the counter electrode was used.

“Expert-001” pH meter (Econix-Expert Ltd., Russian Federation) equipped with the glassy electrode was applied for pH measurements.

Scanning electron microscopy (SEM) was carried out on the high-resolution field emission scanning electron microscope MerlinTM (Carl Zeiss, Germany) at the accelerating voltage of 5 kV and emission current of 300 pA.

3. Results and Discussion

3.1. Voltammetric Characteristics of Hesperidin on Modified Electrodes

Voltammetric behavior of hesperidin on bare GCE and modified electrodes has been studied in 0.1 M phosphate buffer pH 7.0. Hesperidin irreversibly oxidized on two steps. The second step is worse pronounced. Therefore, the first oxidation peak has been considered (Table 1). Modification of the electrode surface with tin(IV) oxide nanoparticles provide insignificant increase of the hesperidin oxidation currents. Nevertheless, these values are still insufficient for the sensitive hesperidin quantification. Application of surfactants provides stabilization of nanoparticles dispersions and preconcentration of the hesperidin on the electrode surface via hydrophobic interaction as far as increase of the oxidation currents has been obtained for all surfactants under investigation. The effect of surfactants concentration in the range of 10-500 μM on hesperidin response has been evaluated. The oxidation potentials are cathodically shifted. The oxidation currents are statistically significantly increased. The higher oxidation currents are obtained in the case of cationic surfactants. The best hesperidin response has been registered on the sensor based on the tin(IV) oxide nanoparticles dispersed in 500 μM cetylpyridinium bromide that agree well with literature data for other natural phenolics [12,13].

Table 1. Voltammetric characteristics of hesperidin on GCE and modified electrodes ($n = 5$; $P = 0.95$)

Electrode	$c_{surfactant}$, mM	E_{ox_1}, V	I_{ox_1}, μA
GCE	0	0.623	0.100 ± 0.004
SnO_2-H_2O/GCE	0	0.603	0.120 ± 0.003
SnO_2-SDS/GCE	0.1	0.573	0.300 ± 0.006
SnO_2-LSS/GCE	0.1	0.553	0.254 ± 0.005
SnO_2-Triton X100/GCE	0.1	0.573	0.333 ± 0.008
SnO_2-Brij® 35/GCE	0.1	0.573	0.171 ± 0.004
SnO_2-CPB/GCE	0.1	0.583	0.440 ± 0.009
SnO_2-CTAB/GCE	0.1	0.563	0.271 ± 0.006
SnO_2-CTPPB/GCE	0.1	0.593	0.323 ± 0.008

3.2. Electrodes Characterization by SEM and Electrochemical Methods

SEM shows the presence of spherical and rhomboid structure and their aggregates of 30-200 nm for SnO_2-H_2O/GCE on contrary to relatively smooth surface of GCE. Application of CPB as dispersive agent provides more uniform coverage consisted of spherical particles of 20-40 nm forming porous surface leading to increase of the electrode surface area.

The electroactive surface area for modified electrode is significantly increased *vs.* bare GCE (34.7 ± 0.3 mm^2 for SnO_2-CPB/GCE in comparison to 8.9 ± 0.3 mm^2 for GCE) as confirmed by cyclic voltammetry (for SnO_2-CPB/GCE) and chronoamperometry (for GCE and SnO_2-H_2O/GCE) using $[Fe(CN)_6]^{3-}$ ions as a standard. Electrochemical impedance spectroscopy has been performed in the presence of $[Fe(CN)_6]^{4-/3-}$ as a redox probe at 0.23 V. Data obtained by Randles equivalent circuit fitting for charge transfer resistance for modified electrode is 554-fold less than for GCE indicating dramatic increase of the electron transfer rate. Thus, sensor developed can be considered as a perspective for the analytical applications.

3.2. Analytical Characterization of the Sensor

Hesperidin quantification using sensor developed has been performed in adsorptive differential pulse mode as far as surface-controlled electrooxidation has been proved. The variation of preconcentration time at the open circuit potential has shown the highest oxidation currents for 120 s of accumulation. Evaluation of pulse parameters effect has shown that the best response is registered at pulse amplitude of 100 mV and pulse time of 50 ms.

Sensor gives linear response to hesperidin in the ranges of 0.10–10 and 10-75 μM (Figure 2) with the detection limit of 77 nM. The analytical characteristics obtained are comparable to other sensors based on the modified electrodes [6–11] but the sensor developed is simpler, relatively chiper and less tedious in preparation. The accuracy of the hesperidin determination has been tested on the model hesperidin solutions using added-found method. The relative standard deviation is less than 3.5% meaning the absence of random errors of quantification. The recovery of 98.4-100% confirms high accuracy of the sensor developed.

The sensor selectivity in the presence of 1000-fold excess of inorganic ions (K^+, Mg^{2+}, Ca^{2+}, NO_3^-, Cl^-, and SO_4^{2}), glucose, rhamnose, sucrose as well as 1000- fold excess of ascorbic acid has been shown. Another important advantage is the high selectivity to hesperidin in presence of other flavonoids and phenolic acids. 10-Fold excess of naringin, quercetin, rutin, morin, caffeic and chlorogenic acids in spite of being electroactive do not show interference effect on hesperidin quantification.

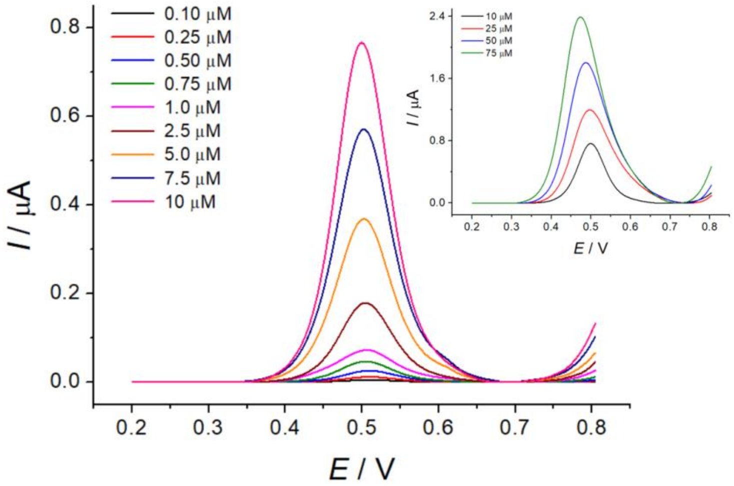

Figure 2. Differential pulse voltammograms of hesperidin on SnO_2-CPB/GCE in 0.1 M phosphate buffer pH 7.0. t_{acc} = 120 s, ΔE_{pulse} = 100 mV, t_{pulse} = 50 ms, υ = 10 mV s^{-1}.

3.2. Application to Real Samples

The sensor applicability to real samples analysis has been successfully tested on the orange juices. There is well-defined oxidation peak of hesperidin on the differential pulse voltammograms of orange juices (commercial and fresh ones) that is confirmed by standard addition method. Recovery values of 99-100% indicate the absence of matrix effects in the determination.

Results of hesperidin quantification in orange juices using sensor developed are presented on Figure 3. Validation with independent ultra-HPLC with mass-spectrometric detection results has been performed (Figure 3). The relative standard deviation for both methods does not exceed 2% that proves the absence of random errors. *t*-Test values (0.290–1.08) are less than critical value of 2.45 that confirms the absence of systematic errors in the determination. Similar, *F*-test results (1.17–2.57) are less than critical value 6.59 indicating uniform precision of the methods used.

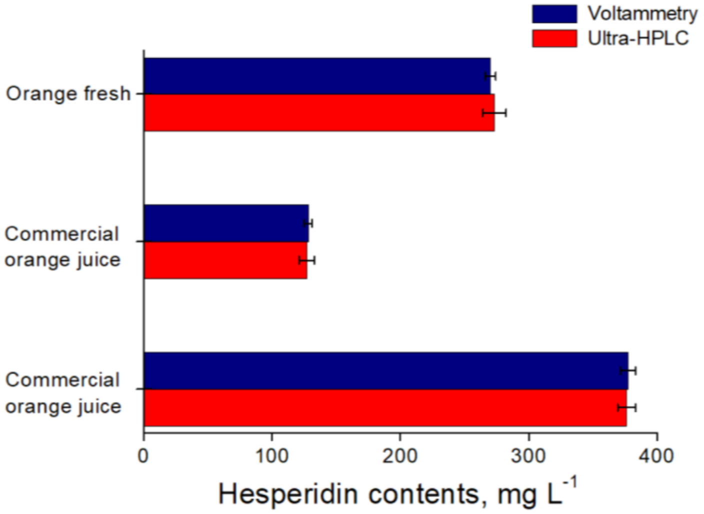

Figure 3. Quantification of hesperidin in orange juices using electrochemical sensor and ultra-HPLC.

4. Conclusions

Tin(IV) oxide nanoparticles and CPB based sensor provides improvement of the voltammetric and analytical characteristics of hesperidin. Surfactant provides stabilization of nanomaterial dispersion and accumulation of analyte on the sensor surface. Novel voltammetric sensor is highly sensitive and selective, reliable and can be recommended for the preliminary screening of citrus juices as an alternative to chromatography.

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Conflicts of Interest: The authors declare no conflict of interest.

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