

# Analytical capabilities of the electrochemical sensors based on the transition metal oxide nanomaterials <sup>†</sup>

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**Abstract:** Voltammetric sensors based on the CeO<sub>2</sub>, SnO<sub>2</sub>, CeO<sub>2</sub>:Fe<sub>2</sub>O<sub>3</sub> nanoparticles (NPs), and MnO<sub>2</sub> nanorods (NRs) have been developed for the quantification of various organic substances. Surfactant media have been applied as dispersive agents for metal oxide nanomaterials providing high stability of the dispersions after sonication, decrease of the NPs size as well as preconcentration of the target analytes at the sensor surface due to the hydrophobic interactions between the surfactant and analyte molecules. Natural phenolics (quercetin, rutin, gallic acid, taxifolin, eugenol, vanillin, hesperidin), propyl gallate,  $\alpha$ -lipoic acid and synthetic food colorants (tartrazine, brilliant blue FCF and sudan I) have been studied as analytes. The effect of the nature and concentration of surfactant on the target analyte response has been evaluated. Cationic surfactants (cetylpyridinium (CPB) or cetyltriphenylphosphonium bromides (CTPPB)) show the best effect for the majority of the analytes. The wide linear dynamic ranges and low detection limits have been obtained and are improved vs. reported to date. Simultaneous quantification of tartrazine and brilliant blue FCF has been achieved with high selectivity. The practical applicability of the sensors is shown on the real samples and is validated by comparison to independent methods.

**Keywords:** electrochemical sensors; voltammetry; chemically modified electrodes; metal oxide nanomaterials; surfactants; antioxidants; food colorants; azo dyes

## 1. Introduction

Electrochemical sensors based on the transition metal oxide nanomaterials have got attention recently [1]. Nanostructured CeO<sub>2</sub>, ZnO, CdO, SnO<sub>2</sub>, MnO<sub>2</sub>, TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> are typical semiconductors demonstrating large surface area, chemical and electrochemical inertness, high sorption ability, and biocompatibility [1,2]. Nanoparticles (NPs), nanorods (NRs), nanowires, nanoflowers, etc. synthesized by various techniques have been used as an effective electrode surface modifiers [3].

The porous structure of the nanomaterials increases the mass transport and electron transfer rate that improves the sensitivity of target analyte determination. Another advantage of this type of modifier is simple procedure of the electrode fabrication. The most common approach is the drop casting of metal oxide nanomaterial dispersion or suspension in the appropriate solvent. Surfactants are among the perspective dispersive agents due to the low costs, high stability under ambient conditions, easiness of use, and lower toxicity compared to organic solvents [4]. On the other hand, the presence of surfactant at the electrode surface makes it co-modifier affecting the target analyte response. The effect can be attributed to electrostatic and/or hydrophobic interaction between the surfactant and analyte depending on their nature and experimental conditions.

Thus, the target analyte response can be controlled and changed depending on the metal oxide nanomaterial and surfactant choice that is shown on example of various classes of organic compounds in current work.

## 2. Materials and Methods

Natural phenolic antioxidants (95% quercetin, 94% hesperidin, 99% gallic acid, from Sigma (Steinheim, Germany), 97% rutin trihydrate (Alfa Aesar, Heysham, UK), taxifolin (analytical standard purity) from Fluka (Steinheim, Germany), eugenol (Aldrich, Steinheim, Germany), 99% vanillin from Sigma-Aldrich (Steinheim, Germany)), propyl gallate (Sigma, Steinheim, Germany), 99%  $\alpha$ -lipoic acid (Sigma, Steinheim, Germany), and synthetic food colorants (85% tartrazine (Sigma, St. Louis, MO, USA), 85% brilliant blue FCF and 95% sudan I from Sigma-Aldrich (Steinheim, Germany)) were used as standards. Their 10 mM solutions (1.0 mM for rutin) were prepared in the appropriate solvent (ethanol (rectificate), methanol (c.p.) for antioxidants or distilled water for synthetic food colorants). An exact dilution was used for the preparation of less concentrated solutions prior to measurements.

The following metal oxide nanomaterials were used as electrode surface modifiers:

- 10% aqueous dispersion of CeO<sub>2</sub> NPs (particle size < 25 nm) from Sigma-Aldrich, (St. Louis, MO, USA);
- SnO<sub>2</sub> NPs powder ( $\phi$  < 100 nm) from Aldrich (Steinheim, Germany);
- 20% aqueous dispersion of CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> NPs (50:50 wt.%) from Alfa Aesar Cerion (Rochester, NY, USA)
- MnO<sub>2</sub> NRs (99%,  $\phi \times L = 5\text{--}30 \text{ nm} \times 80\text{--}100 \text{ nm}$ ) from Sigma-Aldrich (Steinheim, Germany).

Their 0.25–2.0 mg mL<sup>-1</sup> dispersion (1.0 mg mL<sup>-1</sup> suspension for MnO<sub>2</sub> NRs) in surfactant media were obtained by sonication for 10 min (40 min for MnO<sub>2</sub> NRs) in ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea). Working dispersions of CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> NPs were obtained by exact dilution with distilled water.

Sodium dodecyl sulfate (SDS) of Ph. Eur. grade (Panreac, Barcelona, Spain), 98% cetylpyridinium bromide (CPB), sodium lauroyl sarcosinate (SLS), Triton X-100 from Aldrich (Steinheim, Germany), 99 % cetyltrimethylammonium bromide (CTAB) and Brij® 35 (Acros Organics, Geel, Belgium), cetyltriphenylphosphonium bromide (CTPPB) synthesized in the Department of Organoelement Compounds Chemistry of Kazan Federal University were used for the preparation of dispersing media by dissolving of the exact weight of surfactant in distilled water.

Other reagents were of c.p. grade and used as received.

Electrochemical measurements were performed at ambient temperature (25 ± 2 °C). Potentiostat/galvanostat PGSTAT 302N with FRA 32M module (Metrohm B.V., Utrecht, The Netherlands),  $\mu$ Autolab Type III (Eco Chemie B.V., Utrecht, The Netherlands), and PGSTAT 12 (Eco Chemie B.V., Utrecht, The Netherlands) supplied with NOVA 1.10.1.9, or GPES 4.9 software. A three-electrode electrochemical cell with bare glassy carbon electrode (GCE) of 3 mm diameter (CH Instruments Inc., Bee Cave, TX, USA or BASi® Inc., West Lafayette, IN, USA), Ag/AgCl/3M KCl reference electrode, and platinum wire auxiliary electrode was used.

An "Expert-001" pH meter (Econix-Expert Ltd., Moscow, Russia) with the glass electrode was used for the pH measurements.

Conditions of voltammetric determination of the antioxidants and real samples preparation are presented in the Table S1 and subsection S2.1, respectively.

## 3. Results and Discussion

### 3.1. Electrochemical Sensors Fabrication and their Characteristics

Metal oxide nanomaterial-based electrochemical sensors were created by drop casting method. The choice of nanomaterial concentration, nature and concentration of surfactant medium used as dispersing agent was performed on the basis of the target analyte response, i.e., oxidation potential and oxidation peak current obtained. Anionic

(SDS and SLS), cationic (CPB, CTAB, and CTPPB) and non-ionic (Triton X-100 and Brij® 35) surfactants in the concentration range of 1.00–1000  $\mu\text{M}$ . The optimal conditions are summarized in Table 1.

**Table 1.** Optimal parameters of metal oxide nanomaterial-based electrochemical sensors creation depending on the analyte.

| Analyte                                    | Electrode modifier                                   | Modifier concentration ( $\text{mg mL}^{-1}$ ) | Drop-casted amount ( $\mu\text{L}$ ) | Surfactant concentration ( $\mu\text{M}$ ) | A ( $\text{mm}^2$ ) |
|--|--|--|--------------------------------------|--|---------------------|
| Quercetin and rutin                        | CeO <sub>2</sub> NPs–SDS                             | 1.0  | 5                                    | 10   | 18.5 $\pm$ 0.1      |
| Gallic acid and hesperidin                 | SnO <sub>2</sub> NPs–CPB                             | 1.0  | 4                                    | 500  | 34.7 $\pm$ 0.3      |
| Taxifolin                                  | SnO <sub>2</sub> NPs–CPB                             | 1.0  | 2                                    | 1000                                       | 25.2 $\pm$ 0.2      |
| Eugenol                                    | CeO <sub>2</sub> NPs–CPB                             | 1.0  | 6                                    | 450  | 30 $\pm$ 1          |
| Vanillin                                   | SnO <sub>2</sub> NPs–CPB                             | 1.0  | 5                                    | 500  | 29.3 $\pm$ 0.7      |
| Propyl gallate                             | CeO <sub>2</sub> NPs–CPB                             | 1.0  | 4                                    | 500  | 32.4 $\pm$ 0.5      |
| $\alpha$ -Lipoic acid                      | SnO <sub>2</sub> NPs–CTPPB                           | 1.5  | 5                                    | 500  | 13.7 $\pm$ 0.2      |
|  | CeO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> NPs | 0.5  | 6                                    | —  | 38.9 $\pm$ 0.6      |
| Tartrazine                                 | CeO <sub>2</sub> NPs–CTPPB                           | 1.0  | 3                                    | 100  | 21.3 $\pm$ 0.2      |
| Tartrazine, brilliant blue FCF and sudan I | MnO <sub>2</sub> NRs–CPB                             | 1.0  | 5                                    | 1000                                       | 70 $\pm$ 2          |

Comparison of the voltammetric characteristics for various nature of surfactants showed that oxidation peak currents are more or less increased for the majority of the analytes. This means that hydrophobic interactions are the main contributors to the changes observed. Cationic surfactants provided the best response of all types of analytes excluding quercetin and rutin, for which the supporting electrolyte pH affected stability of the CeO<sub>2</sub> NPs in dispersion, i.e. electrostatic repulsion between NPs bearing partial positive charge and cationic surfactants. Among the cationic surfactants, the highest oxidation currents of the analytes were obtained for CPB and CTPPB containing aromatic rings in the structure that is probably allowed to realize  $\pi$ -stacking with the aromatic rings in the structure of analytes. In the case of tartrazine at GCE/CeO<sub>2</sub> NPs–CTPPB, the electrostatic interaction occurred. In both cases, the analyte preconcentration at the electrode surface was achieved and electrooxidation was controlled by the surface or mixed processes (excluding gallic and  $\alpha$ -lipoic acids, and guaiacol derivatives) as was confirmed by cyclic voltammetry at the various potential scan rate.

Another aspect leading to the increase of the oxidation peak currents of the analytes is statistically significant increase of the effective surface area (Table 1) vs. bare GCE (8.9  $\pm$  0.2 or 8.2  $\pm$  0.3  $\text{mm}^2$  depending on the electrode producer) as has been calculated using cyclic voltammetry data for [Fe(CN)<sub>6</sub>]<sup>4-</sup> oxidation and Randles–Ševčík equation.

In general, the oxidation currents of the various antioxidants and synthetic food colorants at the metal oxide nanomaterial modified electrodes are 1.6–72.5-fold increased vs. those ones at the bare GCE indicating improvement in the sensitivity of the response.

Electrochemical impedance spectroscopy indicated dramatic decrease (16.8–2132-fold) of the charge transfer resistance for the modified electrodes confirming significant increase in the electron transfer rate (Table S2). Furthermore, the application of the surfactant media provided stabilization of nanomaterial dispersions (the lifetime was more than 1 month) and smaller size of the NPs at the electrode surface (Table S3) as scanning electron microscopy data indicated.

### 3.2. Analytical Capabilities of the Sensors

Quantification of the target analytes was performed using differential pulse or linear sweep voltammetry. The supporting electrolyte pH (phosphate (PB) or Britton-Robinson buffer (BRB)) and voltammetry conditions (pulse parameters, potential sweep rate, elec-

trochemical window) were preliminary optimized. The analytical characteristics achieved are presented in Table 2.

**Table 2.** Figures of merit of the electrochemical sensors based on the metal oxide nanomaterials.

| Analyte                          | Sensor   | Method   | Supporting electrolyte | $E_{ox}$ (V) | Detection limit ( $\mu\text{M}$ ) | Linear dynamic range ( $\mu\text{M}$ ) |
|----------------------------------|--|----------|------------------------|--------------|-----------------------------------|--|
| Quercetin<br>Rutin               | CeO <sub>2</sub> NPs–SDS/GCE                             | DPV*     | BRB pH 2.0             | 0.44<br>0.51 | 0.0029<br>0.028                   | 0.010–1.00 and 1.00–250<br>0.10–100    |
| Gallic acid                      | SnO <sub>2</sub> NPs–CPB/GCE                             | DPV      | BRB pH 4.0             | 0.31         | 0.044                             | 0.10–2.5 and 2.5–75                    |
| Hesperidin                       | SnO <sub>2</sub> NPs–CPB/GCE                             | AdADPV** | PB pH 7.0              | 0.52         | 0.077                             | 0.10–10 and 10–75                      |
| Taxifolin                        | SnO <sub>2</sub> NPs–CPB/GCE                             | DPV      | BRB pH 6.0             | 0.25         | 0.071                             | 0.075–25                               |
| Eugenol                          | CeO <sub>2</sub> NPs–CPB/GCE                             | DPV      | PB pH 7.0              | 0.40         | 0.019                             | 0.075–75                               |
| Vanillin                         | SnO <sub>2</sub> NPs–CPB/GCE                             | DPV      | BRB pH 2.0             | 0.81         | 0.020                             | 0.10–100 and 100–500                   |
| Propyl gallate                   | CeO <sub>2</sub> NPs–CPB/GCE                             | DPV      | BRB pH 2.0             | 0.48         | 0.067                             | 0.10–2.5 and 2.5–50                    |
| $\alpha$ -Lipoic acid            | SnO <sub>2</sub> NPs–CTPPB/GCE                           | DPV      | BRB pH 4.5             | 0.84         | 0.13                              | 0.50–50 and 50–400                     |
|                                  | CeO <sub>2</sub> ·Fe <sub>2</sub> O <sub>3</sub> NPs/GCE |          | PB pH 7.0              | 0.83         | 0.053                             | 0.075–7.5 and 7.5–100                  |
| Tartrazine                       | CeO <sub>2</sub> NPs–CTPPB/GCE                           | LSV***   | PB pH 7.5              | 1.17         | 0.40                              | 1.0–15 and 15–250                      |
| Tartrazine<br>Brilliant blue FCF | MnO <sub>2</sub> NRs–CPB/GCE                             | DPV      | PB pH 7.0              | 0.77         | 0.043                             | 0.10–2.5 and 2.5–15                    |
|                                  |  |          |                        | 0.97         | 0.041                             | 0.25–2.5 and 2.5–15                    |
| Sudan I                          | MnO <sub>2</sub> NRs–CPB/GCE                             | DPV      | PB pH 6.5              | 0.68         | 0.0135                            | 0.050–2.5 and 2.5–25                   |

\* Differential pulse voltammetry. \*\* Adsorptive anodic differential pulse voltammetry ( $t_{acc} = 120$  s).

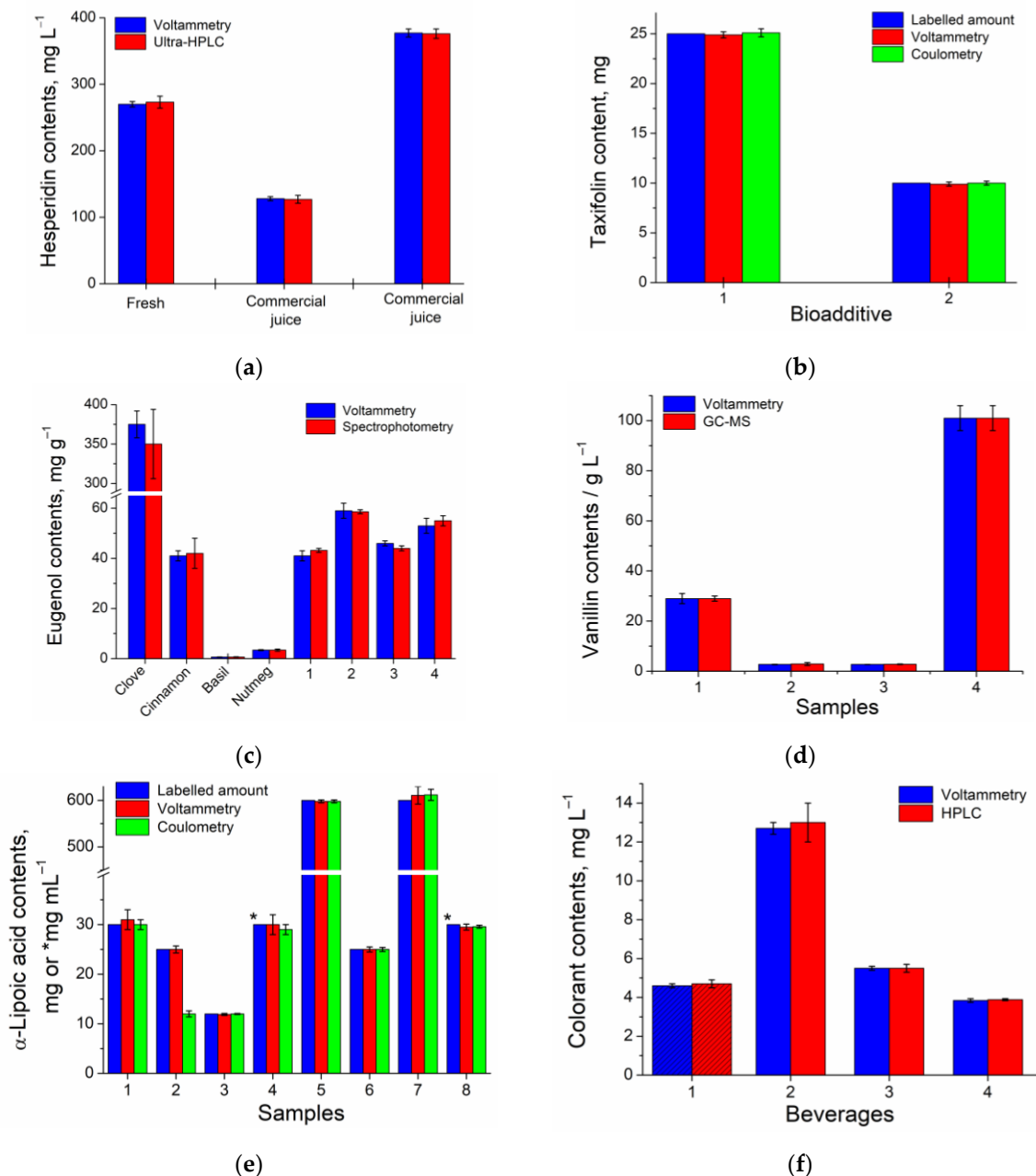
\*\*\* Linear sweep voltammetry ( $v = 250$  mV s<sup>-1</sup>).

The analytical characteristics are comparable or significantly improved vs. reported for other electrochemical sensors [5-13]. CeO<sub>2</sub>·Fe<sub>2</sub>O<sub>3</sub> NPs/GCE provides the best linear range for  $\alpha$ -lipoic acid among all existing to date electrochemical approaches. Simultaneous quantification of colorants tartrazine and brilliant blue FCF has been achieved. High selectivity of the sensors toward target analyte (excluding gallic acid) in the presence of typical interferences (inorganic ions, saccharides, ascorbic acid) and structurally related compounds (natural phenolics of various classes, other colorants, and S-containing antioxidants) is one of the significant advantages. Moreover, the sensors are easy and fast in fabrication (only one step of drop casting) and require a simple and cheap modifier. The direct determination excludes adsorptive preconcentration, i.e. reduces measurement time and does not lead to co-adsorption of other components contained in real samples.

### 3.3. Practical Application

The sensors created were applied to real samples that are typical for the analytes under study. Quercetin and rutin were quantified in water and ethanol extracts from medicinal plant material (St. John's wort herb, marigold flowers, and bearberry leaves), hesperidin – in commercial and fresh orange juices, taxifolin – in bioadditives, eugenol – in essential oils of clove, cinnamon, basil, and nutmeg as well as clove spices, vanillin – in perfumes and vanilla essential oils, propyl gallate – in spiked ethanolic extract of vegetable oils (sunflower and sesame),  $\alpha$ -lipoic acid – in pharmaceutical dosage forms. Synthetic food colorants were determined in food stuff. Soft and isotonic sports drinks were tested for tartrazine and brilliant blue FCF. Sudan I was determined in the spiked samples of red hot pepper, smoked paprika, and salmon. The recovery tests showed the absence of matrix effects as far as recovery values were in the range of 97.1–103%. Sensor for gallic acid was used for the evaluation of the antioxidant capacity of fruit juices in gallic acid equivalents. The positive correlations with standard parameters (antioxidant capacity by reaction with 2,2-diphenyl-1-picrylhydrazyl ( $r = 0.7477$  at  $r_{crit} = 0.6319$ ) and total phenolic contents by Folin-Ciocalteu ( $r = 0.7489$  at  $r_{crit} = 0.6319$ )) were obtained.

Several typical examples of real sample analysis are presented in Figure 1. The accuracy of the sensors developed is confirmed by the independent methods. A good agreement of the data was obtained. Moreover, the *t*- and *F*-test values are less than critical indicating the absence of systematic errors and similar precision of the methods.



**Figure 1.** Application of metal oxide nanomaterial based electrochemical sensors in real samples analysis: (a) Determination of hesperidin in the orange juices using SnO<sub>2</sub> NPs-CPB/GCE; (b) Determination of taxifolin in the bioadditives using SnO<sub>2</sub> NPs-CPB/GCE; (c) Determination of eugenol in the essential oils and clove spices (samples 1–4) using CeO<sub>2</sub> NPs-CPB/GCE; (d) Determination of vanillin in the perfumes (samples 1 and 2) and essential oils (samples 3 and 4) using SnO<sub>2</sub> NPs-CPB/GCE; (e) Determination of α-lipoic acid in the pharmaceutical dosage forms using SnO<sub>2</sub> NPs-CTPPB/GCE (samples 1–5) and CeO<sub>2</sub>·Fe<sub>2</sub>O<sub>3</sub> NPs/GCE (samples 6–8); (f) Determination of Brilliant blue FCF (samples 1) and tartrazine (samples 2–4) in the beverages using MnO<sub>2</sub> NRs-CPB/GCE.

#### 4. Conclusions

Metal oxide nanomaterial-based electrochemical sensors have been shown to be an effective tool in organic electroanalysis. The application of surfactants as dispersing me-

dia provides stabilization of the electrode surface modifier dispersions and suspensions. On the other hand, the surfactants provide preconcentration of the analytes at the electrode surface. The developed electrochemical sensors give a highly sensitive and selective response to a wide range of organic compounds of different classes (natural and synthetic phenolic antioxidants, cyclic disulfide, and azo- and triarylmethane dyes) allowing consideration of this type of electrode as universal sensors.

**Supplementary Materials:** The following supporting information can be downloaded at: [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1), Table S1: Conditions of voltammetric determination of the antioxidants at the metal oxide nanomaterial modified electrodes; Subsection S2.1. Sample preparation; Table S2: Electrochemical impedance parameters of the bare GCE and modified electrodes; Table S3: Scanning electron microscopy based size and shape of the NPs at the electrode surface after drop casting of dispersion in water or surfactant media ( $n = 5$ ;  $P = 0.95$ ).

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