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The Analytical Capabilities of Electrochemical Sensors Based on Transition Metal Oxide Nanomaterials [†]

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Abstract: Voltammetric sensors based on CeO_2, SnO_2, $CeO_2 \cdot Fe_2O_3$ nanoparticles (NPs) and MnO_2 nanorods (NRs) were developed for the quantification of various organic substances. Surfactant media were applied as dispersive agents for metal oxide nanomaterials, providing a high stability of the dispersions after sonication and a decrease in the NPs' size, as well as the preconcentration of the target analytes at the sensor surface due to the hydrophobic interactions between the surfactant and the analyte molecules. Natural phenolics (quercetin, rutin, gallic acid, taxifolin, eugenol, vanillin, and hesperidin), propyl gallate, α-lipoic acid, and synthetic food colorants (tartrazine, brilliant blue FCF, and sudan I) were studied as analytes. The effect of the nature and concentration of the surfactant on the target analyte response was evaluated. Cationic surfactants (cetylpyridinium (CPB) or cetyltriphenylphosphonium bromides (CTPPB)) showed the best effect for the majority of the analytes. Wide linear dynamic ranges and low detection limits were obtained and were improved vs. reported to date. The simultaneous quantification of tartrazine and brilliant blue FCF was achieved with a high selectivity. The practical applicability of the sensors was shown on the real samples and was validated by comparison to independent methods.

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

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1. Introduction

Electrochemical sensors based on transition metal oxide nanomaterials have received attention recently [1]. Nanostructured CeO_2, ZnO, CdO, SnO_2, MnO_2, TiO_2, In_2O_3, and Fe_3O_4 are typical semiconductors demonstrating a large surface area, chemical and electrochemical inertness, a high sorption ability, and biocompatibility [1,2]. Nanoparticles (NPs), nanorods (NRs), nanowires, and nanoflowers, etc., synthesized using various techniques have been used as effective electrode surface modifiers [3].

The porous structure of the nanomaterials increases the mass transport and electron transfer rate, which improves the sensitivity of target analyte determination. Another advantage of this type of modifier is the 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 their low costs, high stability under ambient conditions, ease of use, and lower toxicity compared to organic solvents [4]. On the other hand, the presence of a surfactant at the electrode surface makes it a co-modifier affecting the target analyte response. This effect can be attributed to the 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, which is shown on examples of various classes of organic compounds in the current work.

2. Materials and Methods

Natural phenolic antioxidants (95% quercetin, 94% hesperidin, and 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% α-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 a 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 the measurements.

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

- A 10% aqueous dispersion of CeO2 NPs (particle size < 25 nm) from Sigma-Aldrich, (St. Louis, MO, USA);
- SnO2 NPs powder (ø < 100 nm) from Aldrich (Steinheim, Germany);
- A 20% aqueous dispersion of CeO2·Fe2O3 NPs (50:50 wt.%) from Alfa Aesar Cerion (Rochester, NY, USA);
- MnO2 NRs (99%, ø × L = 5–30 nm × 80–100 nm) from Sigma-Aldrich (Steinheim, Germany).

Their 0.25–2.0 mg mL^{-1} dispersions (1.0 mg mL^{-1} suspension for MnO_2 NRs) in surfactant media were obtained via sonication for 10 min (40 min for MnO_2 NRs) in an ultrasonic bath (WiseClean WUC-A03H (DAIHAN Scientific Co., Ltd., Wonju-si, Republic of Korea). Working dispersions of $CeO_2 \cdot Fe_2O_3$ NPs were obtained via 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), Brij® 35 (Acros Organics, Geel, Belgium), and cetyltriphenylphosphonium bromide (CTPPB) synthetized in the Department of Organoelement Compounds Chemistry of Kazan Federal University were used for the preparation of the dispersion media through dissolving the exact weight of the surfactant in distilled water.

The other reagents were of c.p. grade and were used as received.

Electrochemical measurements were performed at ambient temperature (25 ± 2 °C). Potentiostat/galvanostat PGSTAT 302N with an FRA 32M module (Metrohm B.V., Utrecht, The Netherlands), μAutolab Type III (Eco Chemie B.V., Utrecht, The Netherlands), and PGSTAT 12 (Eco Chemie B.V., Utrecht, The Netherlands) was supplied with NOVA 1.10.1.9 or GPES 4.9 software. A three-electrode electrochemical cell with a bare glassy carbon electrode (GCE) of a 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 were used.

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

The conditions for the voltammetric determination of the antioxidants and real sample preparation are presented in Table S1 and Section S2.1, respectively.

3. Results and Discussion

3.1. Electrochemical Sensors Fabrication and Their Characteristics

Metal oxide nanomaterial-based electrochemical sensors were created using the drop casting method. The choice of nanomaterial concentration, nature, and concentration of the surfactant medium used as a dispersing agent was performed on the basis of the target analyte response, i.e., the oxidation potential and oxidation peak current obtained. There were 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 μM. 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 (mg mL^{-1})	Drop-Casted amount (μL)	Surfactant Concentration (μM)	A (mm^2)
Quercetin and rutin	CeO_2 NPs–SDS	1.0	5	10	18.5 ± 0.1
Gallic acid and hesperidin	SnO_2 NPs–CPB	1.0	4	500	34.7 ± 0.3
Taxifolin	SnO_2 NPs–CPB	1.0	2	1000	25.2 ± 0.2
Eugenol	CeO_2 NPs–CPB	1.0	6	450	30 ± 1
Vanillin	SnO_2 NPs–CPB	1.0	5	500	29.3 ± 0.7
Propyl gallate	CeO_2 NPs–CPB	1.0	4	500	32.4 ± 0.5
α-Lipoic acid	SnO_2 NPs–CTPPB	1.5	5	500	13.7 ± 0.2
	$CeO_2 \cdot Fe_2O_3$ NPs	0.5	6	—	38.9 ± 0.6
Tartrazine	CeO_2 NPs–CTPPB	1.0	3	100	21.3 ± 0.2
Tartrazine, brilliant blue FCF and sudan I	MnO_2 NRs–CPB	1.0	5	1000	70 ± 2

A comparison of the voltammetric characteristics for the various natures of surfactants showed that the oxidation peak currents were more or less increased for the majority of the analytes. This means that hydrophobic interactions were 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 the stability of the CeO_2 NPs in dispersion, i.e., electrostatic repulsion between NPs bearing a 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, which probably allowed for the realization of π-stacking with the aromatic rings in the structure of the analytes. In the case of tartrazine at GCE/CeO_2 NPs–CTPPB, 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 α-lipoic acids, and guaiacol derivatives), as was confirmed by cyclic voltammetry at the various potential scan rate.

Another aspect leading to the increase in the oxidation peak currents of the analytes was a statistically significant increase in the effective surface area (Table 1) vs. bare GCE (8.9 ± 0.2 or 8.2 ± 0.3 mm^2 depending on the electrode producer), as was calculated using cyclic voltammetry data for $[Fe(CN)_6]^{4-}$ oxidation and the Randles–Ševčík equation.

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

Electrochemical impedance spectroscopy indicated a dramatic decrease (16.8–2132-fold) in the charge transfer resistance for the modified electrodes, confirming a significant increase in the electron transfer rate (Table S2). Furthermore, the application of the surfactant media provided the stabilization of the 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

The 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, and electrochemical 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 (μM)	Linear Dynamic Range (μM)
Quercetin	CeO_2 NPs–SDS/GCE	DPV *	BRB pH 2.0	0.44	0.0029	0.010–1.00 and 1.00–250
Rutin				0.51	0.028	0.10–100
Gallic acid	SnO_2 NPs–CPB/GCE	DPV	BRB pH 4.0	0.31	0.044	0.10–2.5 and 2.5–75
Hesperidin	SnO_2 NPs–CPB/GCE	AdADPV **	PB pH 7.0	0.52	0.077	0.10–10 and 10–75
Taxifolin	SnO_2 NPs–CPB/GCE	DPV	BRB pH 6.0	0.25	0.071	0.075–25
Eugenol	CeO_2 NPs–CPB/GCE	DPV	PB pH 7.0	0.40	0.019	0.075–75
Vanillin	SnO_2 NPs–CPB/GCE	DPV	BRB pH 2.0	0.81	0.020	0.10–100 and 100–500
Propyl gallate	CeO_2 NPs–CPB/GCE	DPV	BRB pH 2.0	0.48	0.067	0.10–2.5 and 2.5–50
α-Lipoic acid	SnO_2 NPs–CTPPB/GCE	DPV	BRB pH 4.5	0.84	0.13	0.50–50 and 50–400
	$CeO_2{\cdot}Fe_2O_3$ NPs/GCE		PB pH 7.0	0.83	0.053	0.075–7.5 and 7.5–100
Tartrazine	CeO_2 NPs–CTPPB/GCE	LSV ***	PB pH 7.5	1.17	0.40	1.0–15 and 15–250
Tartrazine	MnO_2 NRs–CPB/GCE	DPV	PB pH 7.0	0.77	0.043	0.10–2.5 and 2.5–15
Brilliant blue FCF				0.97	0.041	0.25–2.5 and 2.5–15
Sudan I	MnO_2 NRs–CPB/GCE	DPV	PB pH 6.5	0.68	0.0135	0.050–2.5 and 2.5–25

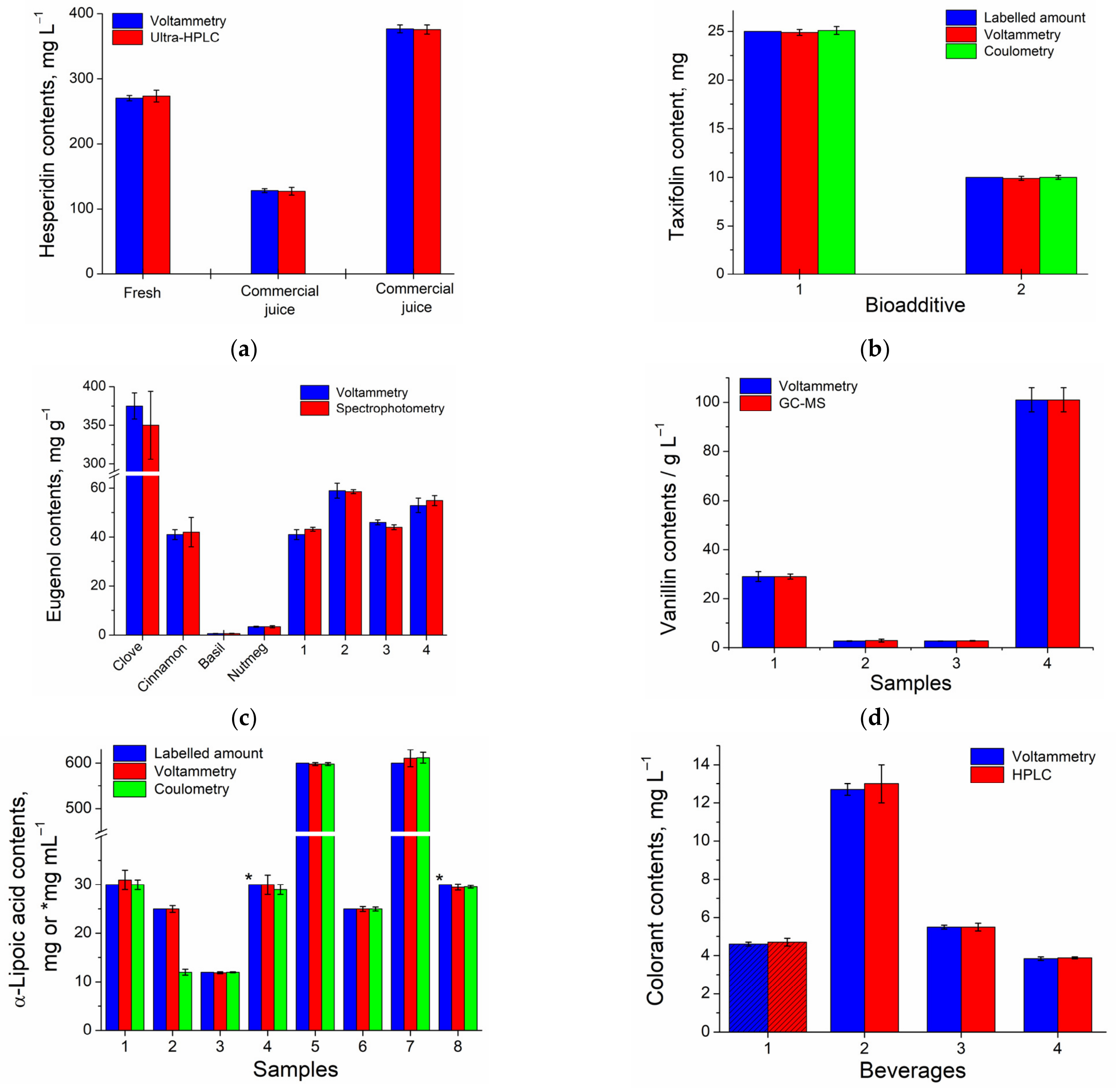
* Differential pulse voltammetry. ** Adsorptive anodic differential pulse voltammetry (t_{acc} = 120 s). *** Linear sweep voltammetry (υ = 250 mV s^{-1}).

The analytical characteristics were comparable or significantly improved vs. those reported for other electrochemical sensors [5–13]. $CeO_2{\cdot}Fe_2O_3$ NPs/GCE provided the best linear range for α-lipoic acid among all the electrochemical approaches existing to date. The simultaneous quantification of the colorants tartrazine and brilliant blue FCF was achieved. The high selectivity of the sensors toward the target analyte (excluding gallic acid) in the presence of typical interferences (inorganic ions, saccharides, and 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 terms of fabrication (only one step of drop casting) and require a simple and cheap modifier. The direct determination excludes adsorptive preconcentration, i.e., reduces the measurement time and does not lead to the co-adsorption of the 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, nutmeg, and clove spices, vanillin—in perfumes and vanilla essential oils, propyl gallate—in spiked ethanolic extracts of vegetable oils (sunflower and sesame), and α-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 spiked samples of red hot pepper, smoked paprika, and salmon. The recovery tests showed the absence of matrix effects as long as the recovery values were in the range of 97.1–103%. A sensor for gallic acid was used for the evaluation of the antioxidant capacity of fruit juices in gallic acid equivalents. 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 was confirmed by the independent methods. A good agreement of the data was obtained. Moreover, the *t*- and *F*-test values were less than critical, indicating the absence of systematic errors and a similar precision of the methods.



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

(**c**) (**d**)

(**e**) (**f**)

Figure 1. Application of metal oxide nanomaterial-based electrochemical sensors in real samples analysis: (**a**) determination of hesperidin in the orange juices using SnO_2 NPs–CPB/GCE; (**b**) determination of taxifolin in the bioadditives using SnO_2 NPs–CPB/GCE; (**c**) determination of eugenol in the essential oils and clove spices (samples 1–4) using CeO_2 NPs–CPB/GCE; (**d**) determination of vanillin in the perfumes (samples 1 and 2) and essential oils (samples 3 and 4) using SnO_2 NPs–CPB/GCE; (**e**) determination of α-lipoic acid in the pharmaceutical dosage forms using SnO_2 NPs–CTPPB/GCE (samples 1–5) and $CeO_2{\cdot}Fe_2O_3$ NPs/GCE (samples 6–8); and (**f**) determination of brilliant blue FCF (samples 1) and tartrazine (samples 2–4) in the beverages using MnO_2 NRs–CPB/GCE.

4. Conclusions

Metal oxide nanomaterial-based electrochemical sensors were shown to be an effective tool in organic electroanalysis. The application of surfactants as dispersing media provided the stabilization of the electrode surface modifier dispersions and suspensions. On the other hand, the surfactants provided a preconcentration of the analytes at the electrode surface. The developed electrochemical sensors gave 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 for the consideration of this type of electrode as a universal sensor.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/CSAC2023-14916/s1, Table S1: Conditions of voltammetric determination of the antioxidants at the metal oxide nanomaterial modified electrodes; Section 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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