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ORIGINAL PAPER

MWNT-modified electrodes for voltammetric determination of lipophilic vitamins

Guzel Ziyatdinova · Mikhail Morozov · Herman Budnikov

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Abstract Multi-walled carbon nanotube modified graphite electrodes (MWNT-GEs) have been created for the voltammetric determination of α-tocopherol and retinol. The electrode surface was characterized by atomic force microscopy. The MWNT-GEs presented structured surfaces and a significant (26-fold) increase in roughness over unmodified graphite electrodes (8.2 vs. 0.32 nm for MWNT-GEs and GEs, respectively). Their surfaces consisted of aggregates with a highly regular "thorn-like" structure. α-Tocopherol and retinol were oxidized on the bare GEs and the MWNT-GEs in 0.1 M $HClO_4$ in acetonitrile. Decreases in the overpotential of 0.2 and 0.04 V for α-tocopherol and retinol, respectively, and increased oxidation currents were observed on the MWNT-GEs in comparison with the unmodified electrodes. The calibration graphs were linear in the range 0.065–2.00 mM for α-tocopherol and 0.05–1.50 mM for retinol. The detection limits were found to be 0.05 and 0.04 mM for α-tocopherol and retinol, respectively. The developed electrodes were applied to determine α-tocopherol and retinol in pharmaceuticals. The results obtained agreed well with coulometric titration data.

Dedicated to Dr. Nina F. Zakharchuk on the occasion of her 75th birthday.

G. Ziyatdinova (✉) · H. Budnikov
Department of Analytical Chemistry,
Kazan (Volga Region) Federal University,
Kremlyevskaya, 18,
Kazan 420008, Russian Federation
e-mail: Ziyatdinovag@mail.ru

M. Morozov
Department of Physics, Kazan (Volga Region) Federal University,
Kremlyevskaya, 18,
Kazan 420008, Russian Federation

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Introduction

Lipophilic vitamins, in particular α-tocopherol and retinol (Fig. 1), are important substances that regulate cell function.

Retinol and carotenoids are considered to be beneficial in the prevention of a variety of major diseases, including certain cancers and eye diseases [1]. The biological activity of retinol enhances the immune response, prevents photoinduced or chemically induced neoplasm formation, mutagenesis, and sister chromatid exchange, and inhibits micronucleation in epithelial cells [2, 3]. α-Tocopherol acts as a powerful antioxidant that counteracts the biological effects of reactive oxygen species and appears to be essential for maintaining immune system effectiveness, normal cellular metabolism, and for preventing cancer, atherosclerosis, cataracts, and aging [4, 5].

Different types of chromatography [6–9], spectrophotometry [10, 11], and chemiluminescence [12, 13] have been used to determine retinol and α-tocopherol in different samples, particularly wild plants [14]. Electrochemical methods, in particular voltammetry, represent a suitable technique, due to the relatively low cost of the instrumentation required, the possibility of miniaturization, and their fast and sensitive analytical performance.

Voltammetry has been applied for the study of α-tocopherol electrochemical oxidation [15–17], and the reaction of its diamagnetic cation with β-carotene [18]. The electrooxida-

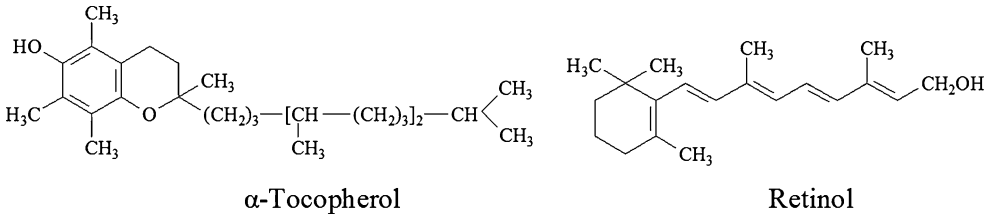

Fig. 1 Structure of lipophilic vitamins under investigation

tion of α-tocopherol in microemulsions stabilized by the anionic surfactant sodium dodecyl sulfate [19] and the redox reactions of α-tocopherol in 1,2-dichloroethane with NO and MnO_4^- in water at the water/1,2-dichloroethane interface [20] have been studied by different types of voltammetry. Differential pulse voltammetry (DPV) has been used to evaluate the antioxidant properties of tocopherol monoglucoside towards reactive oxygen species [21].

The reactivities of model tocopherol compounds with different degrees of methyl substitution around the phenolic ring have been investigated by variable scan rate cyclic voltammetry. The fully methylated derivative produces stable phenoxonium cations upon oxidation in acetonitrile. Compounds with less methyl substitution are more reactive following oxidation and form additional oxidation products (hemiketals and *p*-quinones) [22].

A simple and rapid voltammetric method for the quantitative determination of α-tocopheryl acetate in pharmaceutical preparations has been developed [23]. A well-defined irreversible oxidation wave/peak was obtained at 1.30 V (vs. Ag/AgCl) on platinum microelectrodes. Square wave voltammetry (SWV) or DPV allows for the precise determination of analyte using the multiple standard addition method. The quantification limits for both voltammetric techniques were found to be 6×10^{-5} M and 7×10^{-5} M of α-tocopheryl acetate in the SW and DP modes, respectively.

The voltammetric responses of retinol and α-tocopherol on a stationary platinum microelectrode in 0.1 M$HClO_4$ and 0.1 MCH_3COONa in acetonitrile have been investigated. The quantification limits were 2.7×10^{-4} M for α-tocopherol in 0.1 M$HClO_4$ and 4.1×10^{-5} M and 2.1×10^{-5} M for retinol in 0.1 M$HClO_4$ and 0.1 MCH_3COONa, respectively [24].

DPV was developed for determining silymarin/vitamin E acetate mixtures in pharmaceuticals [25]. Vitamin E acetate gave well-resolved, diffusion-controlled anodic peaks at +444 mV (versus Ag/AgCl) in Britton–Robinson buffer at pH 2.8. A linear response in the range 0.05–4.0 mg L^{-1} along with a detection limit of 0.01 mg L^{-1} for vitamin E acetate was obtained under the optimized conditions.

The conditions needed for vitamin E (α-tocopherol acetate) voltammetric detection in nonaqueous media using different carbon electrodes have been found. The application of differential voltammetry to the determination of vitamin E in multicomponent vitaminized mixtures has been developed and metrologically certified [26].

A voltammetric approach based on electrogenerated superoxide anion radical protonation with antioxidants has been developed for the determination of α-tocopherol and retinol in pharmaceuticals. The calibration graphs were linear in the concentration ranges 9.7×10^{-5} to 2.3×10^{-3} and 6.2×10^{-4} to 3.1×10^{-3} M of retinol and α-tocopherol, respectively. The detection limits were 4.8×10^{-5} M for retinol and 4.1×10^{-4} M for α-tocopherol [27].

The voltammetric behavior of vitamin E in the presence of olive oil has been studied at a glassy carbon electrode in a hexane–ethanol medium using sampled DC, DP, and SW techniques. PLS-1 multivariate calibration has been applied for the simultaneous determination of α-, β+γ-, and δ-tocopherols in vegetable oils [28].

Cyclic voltammetry of retinol in a sodium dodecyl sulfate medium has been applied for the analysis of pharmaceuticals, cosmetics, and foodstuffs. The calibration graph was linear in the range 29.4–980 μM of retinol with a detection limit of 15 μM in the presence of 1.1×10^{-4} M of sodium dodecyl sulfate. The application of a surfactant medium led to a decrease in the detection limit, an enlarged analytical range for retinol determination, and the capacity to perform retinol analysis in water media [29].

Chemically modified electrodes have also shown their applicability to the analysis of α-tocopherol. A polypyrrole-modified Pt electrode has been applied for the determination of total tocopherols in six vegetable oils [30]. A sensor based on a mixture of carbon nanotube powder, DNA (double-stranded calf thymus DNA), and mineral oil allowed the determination of DL-α-tocopherol in soybean oil [31]. However, only a few works have been devoted to the creation of modified electrodes. There is no information on the electrochemical behavior of lipophilic vitamins on carbon nanotube modified electrodes.

In the present report, MWNT-modified graphite electrodes were created and applied for the voltammetric determination of α-tocopherol and retinol in pharmaceuticals.

Material and methods

Reagents

MWNTs with a purity of 90% (OD 3–10 nm, ID 1–3 nm, length 0.1–10 μm) were obtained from Aldrich (Munich,

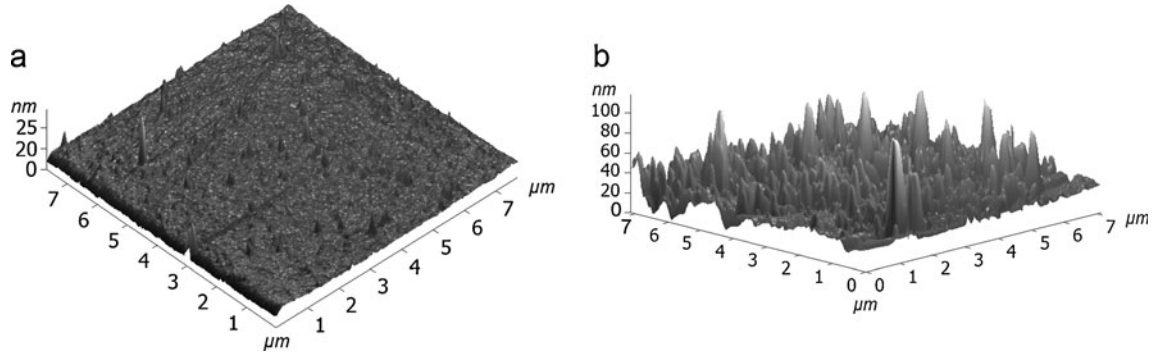

Fig. 2 AFM images of electrode surface morphology: **a** bare GE, **b** MWNT-GE

Germany). A homogeneous suspension of them was prepared by oxidation using a mixture of nitric and sulfuric acids (3:1) with ultrasonic dispersion and centrifugation. The precipitate obtained was washed at neutral pH with double-distilled water. The MWNTs were then dispersed in double-distilled water.

Retinol palmitate and α-tocopherol acetate oil solutions (both of pharmaceutical-grade purity) containing 55% and 97.7% of the substance of interest, respectively, were used for the measurements. Stock solutions of them were prepared by alkaline saponification of a sample (0.2 g) in ethanol by refluxing with a threefold excess of KOH alcoholic solution for 30 min on a water bath. The solution of retinol obtained was transferred to a volumetric flask, diluted to the mark with ethanol, and used for further investigations after coulometric standardization by titration with electrogenerated bromine [32]. The average degree of saponification was equal to 99%. The final concentrations of the stock solutions were 18 and 15 mM for α-tocopherol and retinol, respectively. More dilute solutions (test solutions) were prepared daily before performing measurements by exact dilution of the stock solutions.

Acetonitrile of HPLC grade (Panreac, Barcelona, Spain) and ethanol rectificate were used for the measurements. All other chemicals were of analytical reagent grade purity and used as received. The experiments were carried out at laboratory temperature (20–23 °C). All solutions were kept in glass vessels in the dark at laboratory temperature except for the retinol and α-tocopherol stock solutions, which were stored at +4 °C.

Procedures

Electrode preparation

The GE was carefully polished with alumina (0.05 μm) on a polishing cloth. It was then rinsed with acetone and double-distilled water before use. GE modification was performed by forming a homogeneous layer of MWNTs on the surface of the electrode after evaporating the 2 μL MWNT suspension to dryness.

Cyclic voltammetry

Voltammetric measurements were performed using an Ecotest-VA voltammetric analyzer (Econiks-Expert, Moscow, Russian Federation). The electrochemical cell (V= 25 ml) consisted of a graphite working electrode (3.14 mm^2 in geometric surface area), a silver–silver chloride saturated KCl reference electrode, and a counter electrode (platinum wire). 0.1 M$HClO_4$ in acetonitrile was chosen as the supporting electrolyte. After adding 15.0 ml of supporting electrolyte and an aliquot of the test solution of the analyte, linear potential sweep voltammograms were recorded under the following conditions: potential scan rate, 50 mV s^{-1}; potential range, 0–1.3 V.

Atomic force microscopy

Atomic force microscopy (AFM) of the electrode surfaces was performed using an NTegra Prima atomic force microscope (NT-MDT, Moscow, Russian Federation) and operated at room temperature under ambient conditions. An NSG03 silicon cantilever (NT-MDT) with a resonance frequency of 80 kHz was used to scan in semi-contact mode. The radius of curvature for the cantilever tip was close to 10 nm. Two microliters of MWNT suspension were dropped onto the surface of the graphite and allowed to

Table 1 Voltammetric characteristics of α-tocopherol and retinol oxidation

Compound	Oxidation potential (V)		$\frac{I_{mod}}{I}$
	GE	MWNT-GE	
α-Tocopherol	+0.52; 0.91	+0.32; 0.60	2.0
Retinol	+0.87; 1.12	+0.83; 1.10	2.3

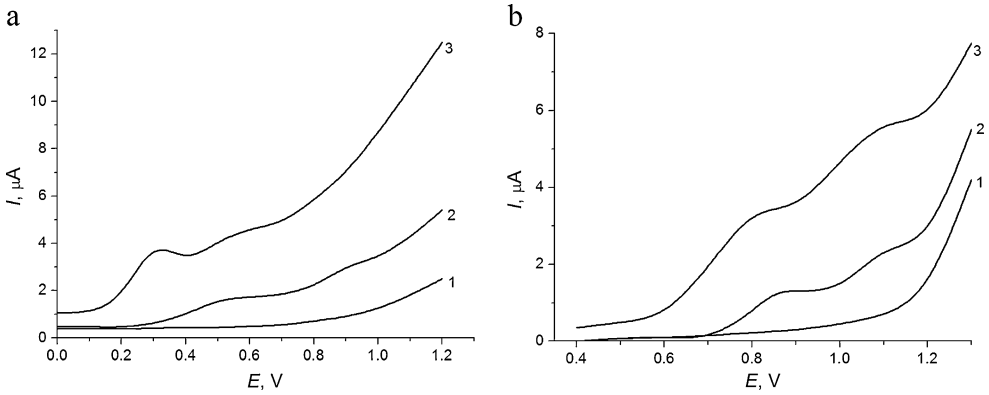

Fig. 3 Voltammograms of lipophilic vitamins on the bare GE (*curve 2*) and the MWNT-GE (*curve 3*) in 0.1 M $HClO_4$ in acetonitrile (*curve 1*). **a** 5.33×10^{-4} M α-tocopherol, **b** 3.73×10^{-4} M retinol. Potential scan rate was 50 mV s^{-1}

evaporate to dryness. The 7×7 μm AFM image of the surface was then scanned.

Coulometric titration

Electrochemical generation of bromine was carried out using a P-5827 M potentiostat (ZIP, Gomel, Belarus) at a current density of 5 mA/cm^2 from 0.2 M $(C_2H_5)_4NBr$ in 0.1 M $HClO_4$ in acetonitrile. The end point of the titration was measured amperometrically with two polarized platinum electrodes (ΔE=300 mV). A smooth platinum plate with a surface area of 1 cm^2 served as the working electrode, and a platinum coil separated from the anodic compartment with a semipermeable diaphragm as the auxiliary electrode.

Coulometric titration was carried out in a 50.0 mL cell. The supporting electrolyte (20.0 mL) and an aliquot of α-tocopherol or retinol solution (0.2–1.0 mL) was inserted into the cell. After the electrodes had been immersed, the generating circuit and timer were switched on simultaneously. Changes in the indicative current over time were noted. Titration curves showed the next view ⎯/. The end point of the titration corresponds to point of intersection of the indicative curves, and the mass of analyte was calculated using the Faraday formulae.

Sample preparation

The pharmaceuticals analyzed were commercially available oil solutions from different producers in the Russian Federation containing retinol or α-tocopherol acetate and palmitate in sunflower oil. They underwent the same procedure—saponification in alkaline ethanol solution—and were then used for the measurements. Taking into account the relatively low content of the active substance in a pharmaceutical, the sample weight for saponification was 1.0 g. An aliquot of the pharmaceutical alcoholic solution (0.5 mL) was inserted into the electrochemical cell with 15 mL of supporting electrolyte, and voltammograms were recorded in the range 0–1.3 V at a scan rate of 50 mV s^{-1}.

The standard addition method was employed to quantify the retinol, wherein 0.5 mL of the alcoholic solution of pharmaceutical were inserted into a cell containing 15.0 mL of the supporting electrolyte. Each addition of standard retinol solution was 0.1 mL.

Statistical analysis

Five replicates of all of the measurements were performed. Statistical evaluation was performed at a significance level

Scheme 1 Electrochemical oxidation of α-tocopherol

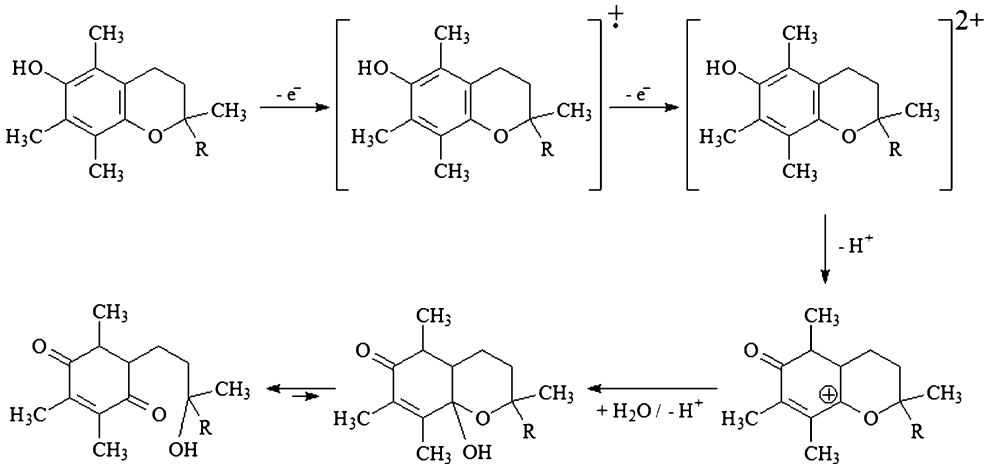

Table 2 Analytical characteristics of α-tocopherol and retinol determinations on bare and MWNT-modified GEs in 0.1 M $HClO_4$ in acetonitrile

Compound	Electrode	Detection limit (mM)	Analytical range (mM)	Calibration equation $y = a + bx$		R
				a (μA)	$b \times 10^{-3}$ (μA Lmol^{-1})	
α-Tocopherol	GE	0.16	0.22–1.34	−0.04±0.07	2.50±0.08	0.9983
	MWNT-GE	0.05	0.065–2.00	−0.07±0.07	4.33±0.06	0.9997
Retinol	GE	0.095	0.13–1.20	−0.03±0.09	3.4±0.1	0.9985
	MWNT-GE	0.04	0.05–1.5	0.52±0.05	5.70±0.06	0.9997

of 5%. All data given below are expressed as $X \pm \Delta X$ where X is the average value and ΔX is the confidence interval.

Results and discussion

Characterization of the electrode surface by AFM

Figure 2 represents the surface morphologies of the bare GE and the MWNT-GE, based on AFM measurements.

The bare GE shows an unstructured surface with nodular features and randomly distributed single spines of height 0.5–3.5 nm. The average and root mean square roughnesses are 0.32 and 0.38 nm, respectively. The MWNT-modified electrode is characterized by a structured surface and a significant (26-fold) increase in roughness. The surface consists of aggregates with a highly regular "thorn-like" structure. The heights of these structures are 10–35 nm and they are 80–400 nm in diameter. The average roughness is 8.2 nm, and the root mean square roughness is 11.5 nm.

Electrooxidation of lipophilic vitamins

The voltammetric behaviors of α-tocopherol and retinol on the bare GE and the MWNT-modified electrode were investigated in 0.1 M $HClO_4$ in acetonitrile.

Both substances are electrochemically active on the bare and the modified GEs. Their voltammetric characteristics are presented in Table 1.

Table 3 Voltammetric determinations of α-tocopherol and retinol in test solutions (n=5; P=0.95)

Analyte	Added (mg)	Found (mg)	RSD (%)
α-Tocopherol	0.422	0.421±0.003	0.66
	3.55	3.53±0.04	1.01
	14.90	14.89±0.05	0.29
Retinol	0.22	0.215±0.002	0.57
	0.57	0.565±0.003	0.48
	1.91	1.907±0.003	0.12
	7.06	7.03±0.05	0.53

A significant decrease in the overpotential of 0.2 V was observed for α-tocopherol in comparison to the unmodified electrode, as well as changes in the form of the analytical signal (Fig. 3a). ΔE=0.04 V was obtained for retinol (Fig. 3b).

The electrocatalytic effect of MWNTs is due to the oxygen-containing functional groups (carboxylic and other groups) formed during acid treatment when the MWNT suspension is being prepared [33, 34]. The number of oxygenated groups located on the tube ends and walls affect the electron transfer rate. The decrease in the overpotential for each analyte indicates an increased electron transfer rate in the oxidation reaction, which agrees well with literature data for phenolic compounds [35].

A twofold increase in the oxidation current was obtained on the MWNT-GE for both compounds under investigation due to the enhanced effective surface area of the modified electrode. The relationship between the oxidation currents on the GE and the MWNT-GE for both α-tocopherol and retinol indicates that the MWNTs play a mediator function.

α-Tocopherol contains a phenolic fragment, which explains its easy two-electron oxidation to *p*-tocopherylquinone

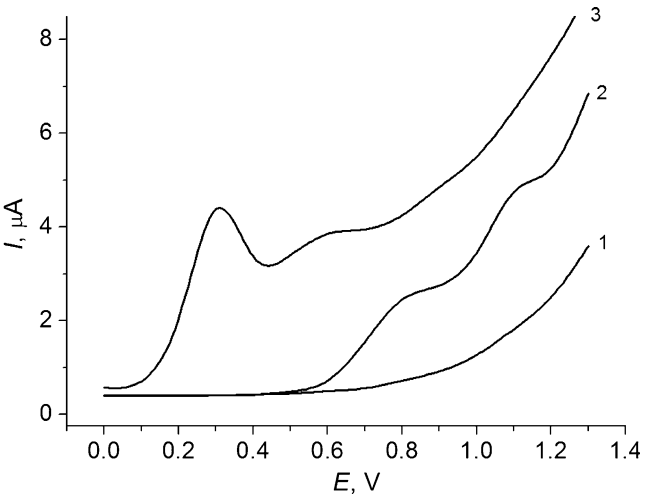

Fig. 4 Voltammograms of retinol (*curve 2*) and α-tocopherol (*curve 3*) from pharmaceuticals on the MWNT-GE in 0.1 M $HClO_4$ in acetonitrile (*curve 1*). Potential scan rate was 50 mV s^{-1}

Table 4 Recovery values for retinol in pharmaceuticals (n=5; P=0.95)

Sample	Spiked (mg)	Expected (mg)	Found (mg)	Recovery (%)
Retinol acetate oil solution	0.00		0.662±0.005	
	0.43	1.092	1.07±0.04	98.0
	0.86	1.522	1.51±0.02	99.2
Retinol palmitate oil solution	0.00		1.10±0.01	
	0.43	1.53	1.51±0.03	98.7
	0.86	1.96	1.94±0.04	99.0

[36, 37]. The overall reaction path involves several stages (Scheme 1). The first step on the voltammogram corresponds to the formation of a cation radical. In the presence of acid, this cation radical is able to undergo a further one-electron oxidation, leading to a dication. The corresponding signal on the voltammogram at approximately ±0.6 V is displayed in Fig. 3a. The dication immediately deprotonates to form a phenoxonium ion, which is stable in an acidic medium [16]. The water present in solvents and $HClO_4$ affects the lifetime of the phenoxonium ion, decreasing it as the proportion of water increases. Thus, phenoxonium ion undergoes a hydrolysis reaction, forming a hemiketal, which is rapidly converted into the quinone in the presence of acid [17].

The two oxidation steps on the retinol voltammogram correspond to the formation of retinal and retinoic acid, respectively, as confirmed by the approximately equal heights of the oxidation steps, and this agrees well with data described previously [24].

There are linear relationships between the oxidation currents and the concentrations of α-tocopherol and retinol. The analytical characteristics of phenol oxidation are presented in Table 2. The application of the MWNT-modified electrode allowed us to decrease the detection limits for the analytes as well as to significantly enlarge their analytical ranges of determination.

The quantitative determination of phenolic antioxidants in test solutions was carried out using MWNT-GE. The accuracy of the results obtained was evaluated by the added-found method (Table 3).

Analytical application

The results obtained allowed the determination of α-tocopherol and retinol in pharmaceuticals. The targets for this investigation were monocomponent forms containing the corresponding ester of retinol or α-tocopherol in sunflower oil. Well-defined oxidation steps for α-tocopherol and retinol were observed on the voltammograms (Fig. 4). Signal overlap could occur in the case of multicomponent pharmaceuticals.

The determination of retinol in pharmaceuticals is complicated by the matrix effect as well as the low content of the active substance. Therefore, the standard addition method was used to evaluate it. In order to check the accuracy of the determination, a known amount of retinol stock solution was spiked into the sample and the recovery was tested. The results are shown in Table 4. The recoveries were in the range from 98.0% to 99.2%, suggesting that the recovery and accuracy obtained with the MWNT-GE are satisfactory.

The results from α-tocopherol and retinol determinations in pharmaceuticals were reproducible and agreed well with the data obtained through coulometric titration with electrogenerated bromine (Table 5).

As shown in Table 5, the content of the ground substance in the pharmaceuticals corresponds to the labeled amount. The relative standard deviation for the voltammetric measurements did not exceed 3%.

Conclusion

MWNT-modified graphite electrodes were created for the detection of α-tocopherol and retinol. Both of them were electrochemically active at the electrode surface. Due to its large surface area and numerous active sites, the MWNT-modified electrode showed electrocatalytic activity with respect to α-tocopherol and retinol oxidation. The application of the modified electrode allowed us to enlarge the analytical ranges and decrease the detection limits for α-tocopherol and retinol determination. The analytical procedure was simple and rapid. The voltammetric

Table 5 α-Tocopherol and retinol determinations in pharmaceuticals (n=5; P=0.95)

Sample	Labeled amount (%)	Found by voltammetry (%)	RSD (%)	Found by coulometry (%)	RSD (%)
α-Tocopherol acetate oil solution	10	9.8±0.3	2.6	10.0±0.5	4.8
	30	29.5±0.5[a]	1.4	29±1[a]	3.2
		29.9±0.2[b]	0.60	29.5±0.9[b]	3.0
Retinol acetate oil solution	3.34	3.32±0.03	0.69	3.3±0.1	2.8
Retinol palmitate oil solution	5.55	5.51±0.03	0.48	5.5±0.1	1.6

[a] Manufacturer 1

[b] Manufacturer 2

approach developed here was used to determine α-tocopherol and retinol in monocomponent pharmaceuticals, and can be applied in practice as an alternative method for pharmaceutical quality control.

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