Catalytic systems based on the organic nickel(II) complexes in chronoamperometric determination of urea and creatinine*

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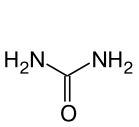
The organic nickel(II) complexes with catalytic activity in the electrochemical oxidation of creatinine and urea were synthesized and studied. The signals of electrocatalytic oxidation of the studied carbonyl-containing amines in model solutions were obtained. The detection limit (by the 3σ-criterion) is $8.7 \cdot 10^{-6}$ and $2.7 \cdot 10^{-5}$ mol L^{-1} for urea and creatinine, respectively.

Key words: urea, creatinine, organic nickel(II) complexes, chronoamperometry, voltammetry, electrocatalysis.

One of the key characteristics of human kidney and liver activity is the content of urea (**I**) and creatinine (**II**) in the blood serum. The content of these compounds in the dialysis liquid defines the degree of completion of the hemodialysis procedure.



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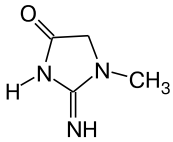

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Urea is determined using direct photometric methods based on the reaction of urea with diacetyl monoxime or the catalytic reactions with urease are used. The Jaffe reaction[1] or (very rarely) enzymatic hydrolysis by creatinine amidohydrolase using autoanalyzers[2] are used for the photometric determination of creatinine.

Conductometric,[3] potentiometric,[4—6] and amperometric variants of biosensors[7—11] or field transistors[12,13] with urease as a catalyst or recognizing compound are used for the determination of urea in biological fluids.

In biosensors for creatinine determination, creatininase[14—16] or a three-enzyme system consisting of creatinine amidohydrolase, creatinase, and sarcosine oxidase[17—24] are often used.

Drawbacks of colorimetric enzyme-free methods are instability of colored complexes and complexity and nonspecificity of analysis. Enzymatic optical methods are specific and sensitive, but their use for urea and creatinine determination is restricted by the instability of enzymes during storage and exploitation, complexity of the analytical procedure, and high cost of equipment and expendable materials.

Simplicity of electrochemical methods, on the one hand, and high sensitivity and selectivity of enzymes, on the other hand, increased the popularity of electrochemical biosensors in clinical diagnostics.

The active center of urease contains nickel(II) ions, and the active centers of creatininase and creatinine hydrolase contain zinc and/or manganese(II) ions. Metal ions in the enzyme composition act as cofactors, because protein molecules are catalytically inactive and manifest catalytic activity only in combination with metal ions.

Works on the electrocatalytic oxidation of phenols, alcohols, vitamins, amino acids, insulin, and urea in the presence of complexes of transition metal ions appeared in the recent years.[25—27] The $Ni(OH)_2$ films formed on the nickel anode in a strongly alkaline medium were used in the electrocatalytic oxidation of selected amines and alcohols.[28] The glassy carbon electrodes (GCE) modified by the macrocyclic nickel(II) complexes are used for the determination of hydroxy- and amino-containing organic compounds.[27,29—31] The modifier, *viz.*, nickel(II) complex, is immobilized on the working surface of the GCE by the

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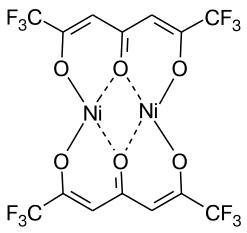

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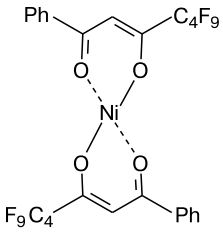

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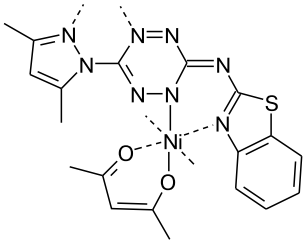

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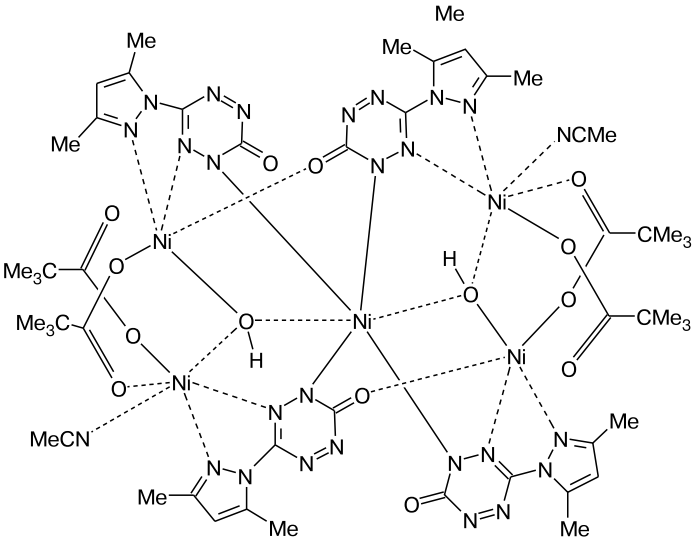

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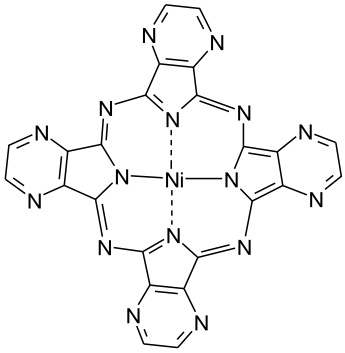

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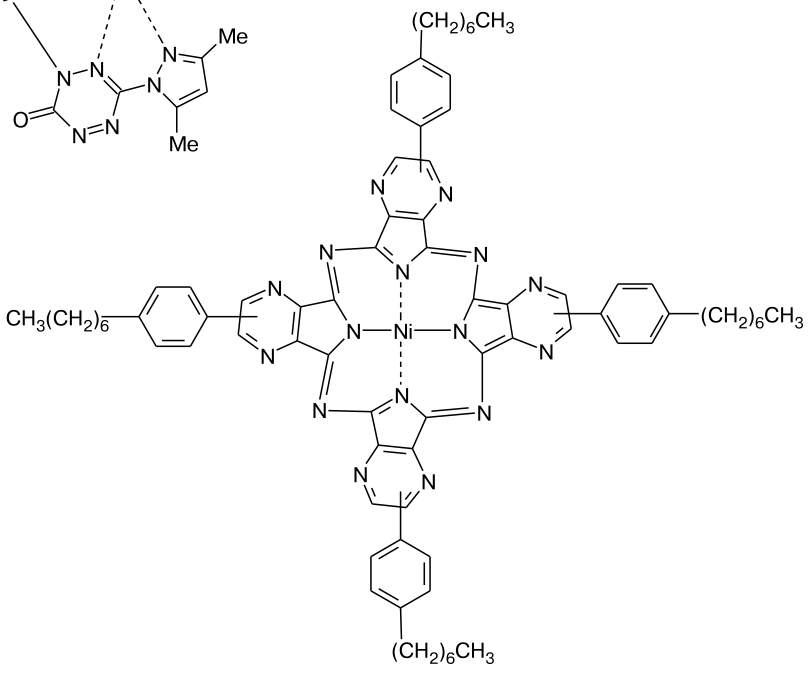

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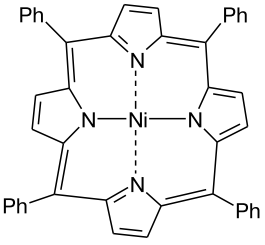

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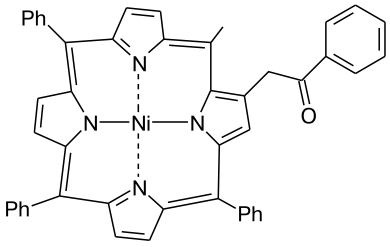

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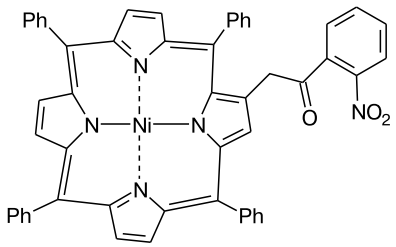

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electropolymerization of the corresponding nickel(II) complex from solution.[27,29–31]

The zinc complex of 1,4,7,10-tetraazacyclododecane (cyclen) incorporated into poly(ethylene glycol) dimethylacrylate was used in the potentiometric determination of creatinine.[32]

The voltammetric sensor sensitive to urea and consisting of the thick-film electrode modified by nickel(II) diethyl thiocarbamate based on carbon-containing ink "Metech" provides the stable and reproducible response to the urea content in the blood serum.[33]

The purpose of the present work is the study of the oxidation catalytic activity of some nickel(II) complexes based on di- and triketones, tetrazine derivatives, and macrocyclic derivatives of the porphyrin and tetraazaporphyrin series (**1—9**).

The compounds were chosen on the basis of available literature data[27,29–31] on the application of the macrocyclic complexes in the catalytic determination of amines and alcohols and due to the relative simplicity of the work with these compounds and their accessibility and stability in aqueous media.

Experimental

Bis(1,1,1,7,7,7-hexafluoroheptane-2,4,6-trionate)dinickel(II) tetrahydrate (**1**), bis(1-phenyl-4,4,5,5,6,6,7,7,7-nonafluoroheptadionate-1,3)nickel(II) dihydrate (**2**), [(3,5-dimethylpyrazol-1-yl)-6-(benzothiazol-2-ylamino)-*s*-tetrazinato](acetylacetonato)-nickel(II) (**3**), $Ni_5(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(\mu\text{-}N,N',N''\text{-}3,5\text{-}Me_2C_3HN_2C_2(O)N_4)_4(MeCN)_2$ (**4**), nickel(II) tetrapyrazinoporphyrazinate (**5**), nickel(II) 2,9,16,23-tetra(4-heptylphenyl)-tetrapyrazinoporphyrazinate (**6**), nickel(II) *meso*-tetraphenylporphyrinate (**7**), nickel(II) 2-phenacyl-5,10,15,20-tetraphenylporphyrinate (**8**), and nickel(II) 2-(2-nitrophenacyl)-5,10,15,20-tetraphenylporphyrinate (**9**) were synthesized at the I. Ya. Postovsky Institute of Organic Synthesis (Ural Division, Russian Academy of Sciences).

N,*N*-Dimethylformamide, dimethyl sulfoxide, 1,2-dimethoxyethane, acetonitrile, and NaOH were commercially available from Ecros and used as received. Poly(vinyl chloride) (PVC) (M_η = 75000, Dzerzhinsk, Russia) served as the polymeric basis of the protective film. Commercial dibutyl phthalate was used as a plasticiser. Weighed samples of sodium hydroxide, urea (Fluka), or creatinine (Merck) were dissolved in triply distilled water.

The structure of complex **3** was proposed by analogy to the earlier describe product of complex formation of 3-(5-amino-1,3,4-thiadiazol-2-ylamino)-6-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine with nickel cations[34] and was confirmed by the IR spectral data.

Voltammetric and chronoamperometric studies were carried out using an IVA-5 inversion voltammetric analyzer (IVA, Ekaterinburg) equipped with a three-electrode cell. The working electrodes (WE) were transducers modified by the nickel(II) complexes. Thick-film electrodes (IVA, Ekaterinburg) were used as transducers, and reference and auxiliary electrodes were a saturated silver—silver chloride electrode (SSCE) and a glassy carbon rod, respectively. Suspensions were prepared with a UD-20 automated ultrasonic disintegrator (Techpan, Poland).

Synthesis of the organic nickel(II) complexes. Complexes **2**, **4**, **5**, **6**, and **7** were synthesized at the I. Ya. Postovsky Institute of Organic Synthesis (Ural Division, Russian Academy of Sciences).[35–38] Purity of the reagents was checked by IR and NMR spectroscopy, mass spectrometry, and elemental analysis.

Bis(1,1,1,7,7,7-hexafluoroheptane-2,4,6-trionate)nickel(II) tetrahydrate (1). A solution of nickel(II) acetate (4.8 g, 0.012 mol) in distilled water (25 mL) was added to 1,1,1,7,7,7-hexafluoroheptane-2,4,6-trione (4.8 g, 0.012 mol), and the reaction mixture was stirred for 3—4 h until complex **1** precipitated. The precipitate was filtered off, washed on the filter with several portions of hot water, dried in air, and purified by sublimation *in vacuo*. The yield was 4.2 g (85%), m.p. 102—104 °C. Found (%): C, 27.31; H, 0.95; F, 37.12. $C_{14}H_4F_{12}Ni_2O_6$. Calculated (%): C, 27.41; H, 0.66; F, 37.16. IR, ν/cm^{-1}: 1608 (C=O).

[(3,5-Dimethylpyrazol-1-yl)-6-(benzothiazol-2-ylamino)-*s*-tetrazinato](acetylacetonato)nickel(II) (3). A solution of nickel acetylacetonate dihydrate (147 mg, 0.5 mmol) in benzene (10 mL) was added with stirring to a heated solution of 3-(3,5-dimethylpyrazol-1-yl)-6-(benzothiazol-2-ylamino)-*s*-tetrazine (162 mg, 0.5 mmol) in benzene (10 mL). The mixture was stirred for 3 h at 50 °C and then left to stand at room temperature for 8 h. A black precipitate formed was filtered off and washed on the filter with benzene and methanol. The yield was 191 mg (77%), m.p. > 350 °C. Found (%): C, 45.19; H, 3.63; N, 22.36; Ni, 10.86; S, 6.40. $C_{19}H_{18}N_8O_2SNi \cdot H_2O$. Calculated (%): C, 45.72; H, 4.04; N, 22.45; Ni, 11.76; S, 6.42. IR, ν/cm^{-1}: 1599, 1512, 1484, 1452, 1399, 1123, 1100, 1057, 1019, 986, 798, 754, 727.

Nickel(II) 2-phenacyl-5,10,15,20-tetraphenylporphyrinate (8). A mixture of acetophenone (90 μL, 0.15 mmol) and Cs_2CO_3 (250 mg, 0.11 mmol) in DMF (20 mL) was stirred for 30 min. Then nickel(II) 2-nitro-5,10,15,20-tetraphenylporphyrinate (110 mg, 0.77 mmol) was added, and the mixture was stirred for 72 h. The solvent was distilled off *in vacuo*, and the solid residue was dissolved in $CHCl_3$ (50 mL), washed with H_2O (3×50 mL), and dried with anhydrous Na_2SO_4. The residue was separated on silica gel eluting with a $CHCl_3$—hexane (1 : 1) mixture. Compound **8** was obtained as a violet powder. The yield was 40 mg (33%). MS, m/z (I_{rel} (%)): 787 $[M - 3\ H]^+$ (100), 788 $[M - 2\ H]^+$ (68), 789 $[M - H]^+$ (55), 790 $[M]^+$ (60), 791 $[M + H]^+$ (15), 831 $[M + CH_3CN]^+$ (20).

Nickel(II) 2-(2-nitrophenacyl)-5,10,15,20-tetraphenylporphyrinate (9). A mixture of 2-nitroacetophenone (173 mg, 0.11 mmol) and Cs_2CO_3 (341 mg, 0.11 mmol) in DMF (10 mL) was stirred for 30 min. Then 2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) (150 mg, 0.21 mmol) was added to the reaction mixture, and the latter stirred for 2.5 h. The solvent was distilled off *in vacuo*, and the solid residue was dissolved in $CHCl_3$ (50 mL), washed with H_2O (3×50 mL), and dried with anhydrous Na_2SO_4. The residue was separated on silica gel eluting with $CHCl_3$. Compound **7** was obtained as a violet powder. The yield was 81 mg (47%). ^1H NMR ($CDCl_3$), δ: 2.65 (s, 2 H, C$\underline{H}_2$); 7.17—7.36 (m, 12 H, Ar); 7.59—7.80 (m, 10 H, Ar); 7.81—7.88 (m, 5 H, Ar); 8.16—8.18 (m, 2 H, Ar); 8.28 (m, 1 H, Ar); 8.39 (m, 1 H, Ar). MS, m/z (I_{rel} (%)): 833 $[M - 2\ H]^+$ (100), 834 $[M - H]^+$ (37), 835 $[M]^+$ (8), 836 $[M + 2\ H]^+$ (91).

Procedure of preparation of the working electrode. Preparation of modifying solutions/suspensions. Solutions of the complexes were prepared by the dissolution of exact weighed samples of **1**

(50 mg), **5** (10 mg), **8** (5 mg), or **9** (5 mg) in 1 mL of DMSO, and weighed samples of **2** (200 mg) and **4** (4 mg) were dissolved in 1 mL of DMF and 1,2-DME, respectively. Suspensions were prepared by the ultrasonic treatment of exact weighed samples of complexes **3** (50 mg), **5** (40 mg), or **6** (40 mg) in 2 mL of DMF and complex **7** (23 mg) in 2 mL of THF.

Modification of transducers was carried out by the deposition of a solution or suspension on the surface of the working zone of the transducer followed by drying in air until the solvent evaporated completely. To prevent physical washing down of complex **1** with the supporting solution, a film of plasticized PVC was deposited on the working surface of the WE by the evaporation of 3 μL of polymer solution in THF.

Electrochemical preparation of the working electrode. The working surface of the WE was formed by cyclic voltammetry in a three-electrode cell against the background of 0.25 *M* NaOH as described earlier.[33]

Chronoamperometric determination of the catalytic activity of the organic nickel(II) complexes. To study the catalytic activity of the organic nickel(II) complexes, 10 mL of the background (0.25 *M* NaOH) and the WE were placed in the electrochemical cell. The potential was cycled from 0 to 0.8 V to form the working surface of the WE. The chronoamperogram of nickel oxidation was detected in the supporting electrolyte at the potential defined depending on the nature of the modifier used at 0.568±0.013 (**1**), 0.566±0.013 (**2**), 0.549±0.015 (**3**), 0.658±0.080 (**4**), 0.696±0.027 (**5**), 0.621±0.024 (**6**), 0.641±0.050 (**7**), 0.546±0.013 (**8**), and 0.543±0.010 V (**9**). A 0.1 *M* solution of urea or a 0.01 *M* solution of creatinine was added by portions of 0.1 mL, and the chronoamperometric signal was repeatedly detected.

In all cases, the current was measured 70 s after.

The efficiency of the catalytic systems was estimated using the "added—found" method.[33]

Results and Discussion

Voltammetric study of the catalytic activity of the nickel(II) complexes. The characteristic cyclic voltammograms obtained upon the formation of the WE surface are shown in Fig. 1. The shape of the first cyclic voltammogram is typical of the transducer. The further consecutive potential cycling results in the appearance and increase in the anodic—cathodic peak characteristic of the Ni^{II}—Ni^{III} system with E_a in the range from 0.45 to 0.60 V (anodic peak) and with E_C in the range from 0.3 to 0.4 V (cathodic peak), depending on the nature of the modifier used. Sixty cycles are enough for the complete formation of the working surface of the WE.

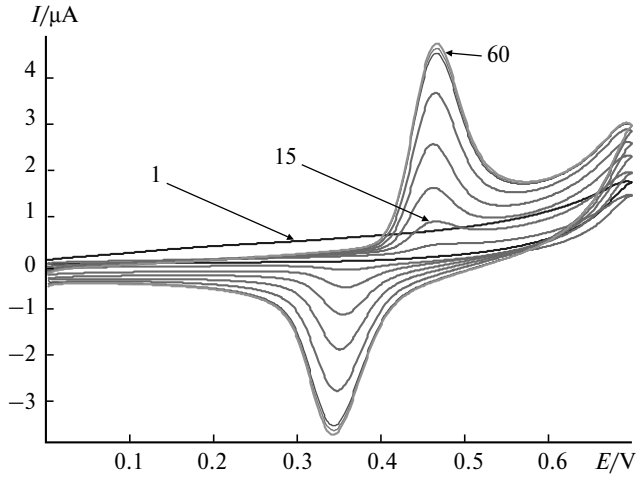


Fig. 1. Characteristic cyclic voltammograms for the working electrodes in 0.25 *M* NaOH (scan rate 0.1 V s^{-1}). Catalyst **2**; *1*, *15*, and *60*: respective numbers of cycles.

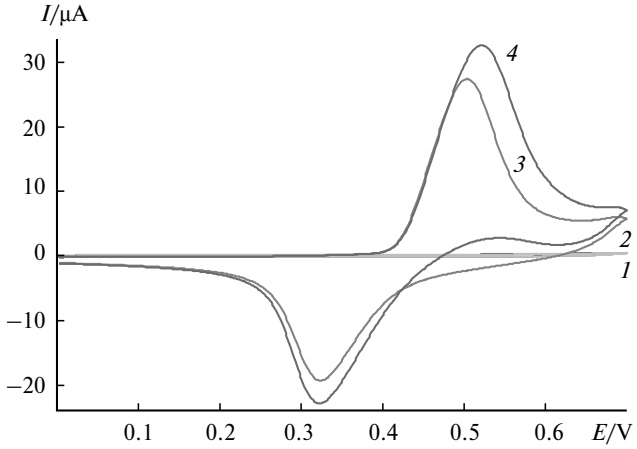


Fig. 2. Cyclic voltammograms for the transducer in the absence (*1*) and presence of $3 \cdot 10^{-3}$ *M* urea in a solution (*2*) and for the working electrode in the absence (*3*) and presence of $3 \cdot 10^{-3}$ *M* urea in a solution (*4*); catalyst **2**, background 0.25 *M* NaOH, and scan rate 0.1 V s^{-1}.

The cyclic voltammograms detected using the transducer and WE in the absence and presence of urea or creatinine are shown in Figs 2 and 3, respectively. The response of the oxidation current of urea or creatinine is observed only when the WE is used, indicating the electrocatalytic oxidation of the corresponding amines.

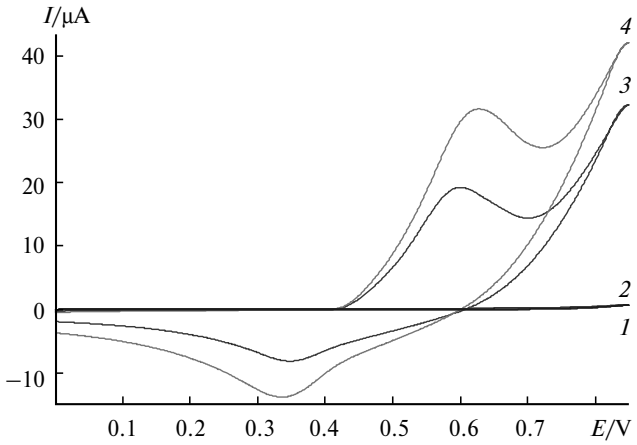


Fig. 3. Cyclic voltammograms for the transducer in the absence (*1*) and presence of $0.02 \cdot 10^{-3}$ *M* creatinine in a solution (*2*) and for the working electrode in the absence (*3*) and presence of $0.02 \cdot 10^{-3}$ *M* creatinine in a solution (*4*). Catalyst **2**, background 0.25 *M* NaOH, and scan rate 0.1 V s^{-1}.

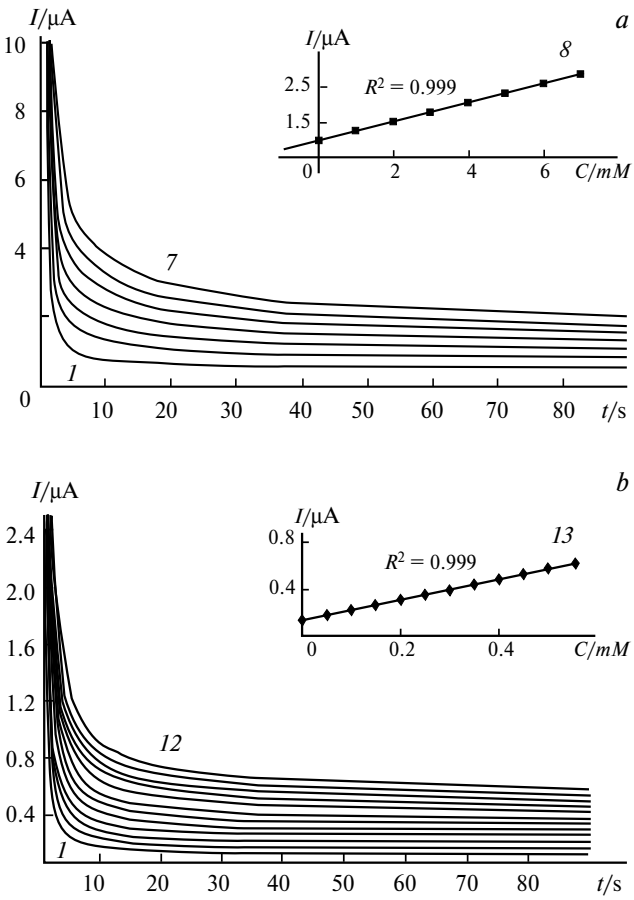
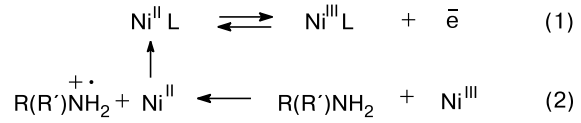


Fig. 4. Chronoamperograms of the oxidation of urea (*a*, curves *1—7*) and creatinine (*b*, curves *1—12*) obtained for the working electrodes at different concentrations of the analyte; background 0.25 *M* NaOH; catalyst **2**. Insets: dependences of the analytical signal on the concentration of urea (*a*, *8*) and creatinine (*b*, *13*).

A similar current increase in the presence of urea or creatinine was observed for the chronoamperometric determination of the corresponding analytes (Fig. 4).

Since the compounds containing the amino group form radical cations during electrochemical oxidation,[39] the electrochemical catalytic oxidation of urea or creatinine proceeds *via* Scheme 1.

Scheme 1



$R(R')NH_2$ is urea or creatinine, and L is an organic ligand.

Selection of the catalyst. Complexes **4** and **7** exhibit no electrochemical catalytic activity in the presence of urea. The phenyl substituents in **7** or 3-hydroxy-6-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine molecules in cluster **4** prevent the urea molecules to access the active sites of the modifiers. In the case of complexes **8** and **9**, the coordination of the urea molecules near the Ni^{2+} center through hydrogen bonding between the NH_2 groups of urea and the carbonyl group of the substituent competes with the steric factor of the phenyl groups. The electrochemical signal observed in this case in the presence of urea is at the level of measurement error.

In the case of other nickel(II) complexes under study, a distinct electrochemical response to the presence of urea in the solution is observed.

The analytical characteristics of urea and creatinine determination using the WE based on complexes **1—3**, **5**, and **6** are listed in Table 1. The WE based on complexes **6**

Table 1. Analytical characteristics of chronoamperometric determination of urea and creatinine using the working electrodes against the background of 0.25 mol L^{-1} NaOH

Complex Ni^{II}	C_{amine}/mol L^{-1}		Sr(%)	Parameters[a]		R	c/mmol L^{-1}
	Added	Found		a	b		
				Urea			
1		1.11±0.09	9.4	5.46	9.08	0.9951	
2		1.09±0.09	8.5	0.264	0.547	0.9991	
3	1	0.98±0.05	5.5	18.706	20.618	0.9923	0.01—10
5		0.85±0.12	6.7	5.729	9.565	0.9987	
6		0.95±0.08	7.0	0.040	0.647	0.9947	
				Creatinine			
1		0.54±0.09	13.6	1.88	0.38	0.9974	0.03—0.5
				1.45	0.79	0.9877	0.03—1
2	0.5	0.58±0.20	27.7	0.915	0.119	0.9987	0.05—0.55
				0.72	−0.04	0.9544	0.03—1
3		0.46±0.04	7.8	2.11	0.18	0.9972	0.03—0.5

[a]Parameters for the regression equation $I = aC + b$ (I/μA, C/mol L^{-1}).

generate the least pronounced (among the presented group of catalysts) analytical signals of urea oxidation in the range of the analyte concentrations studied. This is due, most likely, to the partial screening of the Ni^{2+} sites of the catalyst from the urea molecules by the heptylphenyl substituents.

The optimum results (the least value of the relative standard deviation (RSD) and closest values of the found additive) were obtained when the WE based on complexes **1—3** and **5** were used. The linear dependence of the analytical signal on the urea concentration for the presented WE ranges from 10^{-5} to 10^{-2} mol L^{-1}.

The detection limit is $8.7 \cdot 10^{-6}$ mol L^{-1} (by the 3σ-criterion), which is lower than the detection limit of urea in the blood serum ($C_{min} = 0.2 \cdot 10^{-3}$ mol L^{-1}) determined by the standard enzymatic method using a BUN/UREA Vitrous System colorimetric analyzer (Johnson and Johnson, Great Britain).[33]

The WE based on complexes **1—3**, **5**, and **6** were used for the electrochemical determination of creatinine. It is known that the catalytic activity of the nickel(II) compounds in electrochemical oxidation reactions decreases on going from the primary to secondary amine.[28] Since creatinine is a secondary amine, it is reasonable to expect a decrease in the electrocatalytic response of creatinine oxidation for the WE used compared to the electrocatalytic response of the current corresponding to urea oxidation. Indeed, in the case of using the WE based on complexes **5** and **6**, well pronounced signals for creatinine oxidation were not obtained.

However, when the WE based on complexes **1—3** are used in electrochemical oxidation, the analytical signal of creatinine is well pronounced. The optimum results (the least RSD value) were obtained when using these WE. The range of the linear dependence of the analytical signal on the creatinine concentration is from $5 \cdot 10^{-5}$ to 10^{-3} mol L^{-1}. The detection limit equal to $2.7 \cdot 10^{-5}$ mol L^{-1} is lower than the minimum content of creatinine in the blood serum of the healthy adults ($4.4 \cdot 10^{-5}$ mol L^{-1}).

The linear dependence of the analytical signal on the creatinine concentration with the correlation coefficient 0.999 and the low detection limit confirm that the method of additives can be used for the calculation of the creatinine concentration in body fluids.

Kinetics of amine oxidation. The dependence of the current of catalyst oxidation on the sweep rate obtained by cyclic voltammetry is shown in Fig. 5. The linear dependence of I on v indicates that an electroactive substance localized on the transducer surface participates in the rate-determining process. It is most likely that this process is the reversible electrochemical oxidation of $Ni^{II}L$ to $Ni^{III}L$.

The dependence of the current of urea oxidation on the detection time of the analytical signal obtained by chronoamperometry is shown in Fig. 6.

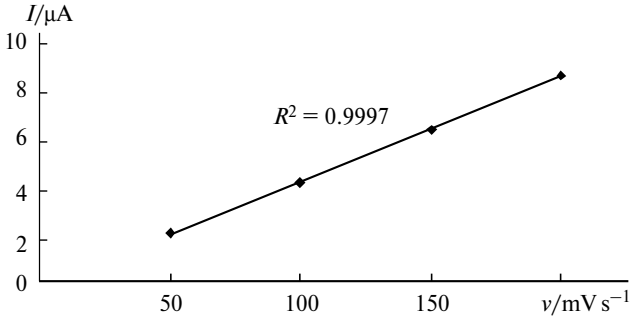


Fig. 5. Dependence of the maximum current of catalyst oxidation in the absence of area on the potential sweep rate; background 0.25 *M* NaOH; catalyst **2**.

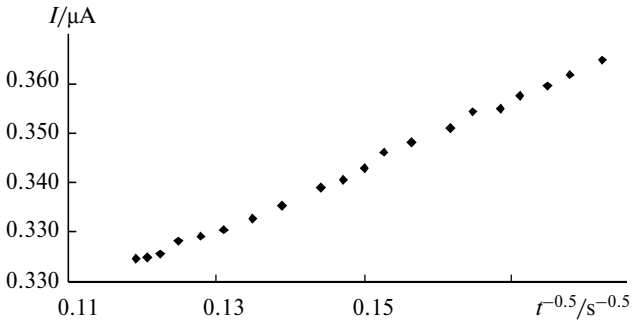


Fig. 6. Dependence of the analytical signal on $\sqrt{t}$, where t is the detection time of the chronoamperogram at the content of urea in the cell equal to $1 \cdot 10^{-3}$ mol L^{-1}; background 0.25 *M* NaOH; catalyst **2**.

The dependence of I on $t^{-0.5}$ is linear in the range of the detection time of the analytical signal from 30 to 70 s and corresponds to the Cottrell equation. This indicates that the oxidation of urea is limited by analyte diffusion from the solvent bulk.

The study of the electrochemical oxidation of creatinine also gave the linear dependence of I on $t^{-0.5}$.

It is most likely that the oxidation rate of the amines under study is limited by the diffusion of the analyte to the working surface of the WE.

The working electrodes with the supported nickel(II) complexes make it possible to obtain an analytical signal in the heterogeneous electrocatalytic oxidation of electrically inactive urea (complexes **1—3, 5**, and **6**) or creatinine (complexes **1—3**). The electrochemical oxidation of the carbonyl-containing amines under study occurs presumably with the intermediate formation of radical cations, and the rate-determining step is analyte diffusion to the working electrode surface. The linear dependence of the analytical signal on the analyte concentration with the correlation coefficient 0.999 and the low detection limit ($8.7 \cdot 10^{-6}$ and $2.7 \cdot 10^{-5}$ mol L^{-1} for the determination of urea and creatinine, respectively) make it possible to use these WE for the determination of the concentrations of studied amines in biological fluids.

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