ISSN 1070-4272, Russian Journal of Applied Chemistry, 2011, Vol. 84, No. 4, pp. 620−627. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © L.G. Shaidarova, A.V. Gedmina, I.A. Chelnokova, G.K. Budnikov, 2011, published in Zhurnal Prikladnoi Khimii, 2011, Vol. 84, No. 4, pp. 582−590.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Selective Determination of Paracetamol and Acetylsalicylic Acid on Electrode Modified with a Mixed-Valent Film of Ruthenium Oxide–Ruthenium Cyanide

L. G. Shaidarova, A. V. Gedmina, I. A. Chelnokova, and G. K. Budnikov

Kazan State University, Kazan, Tatarstan, Russia

Received April 16, 2010

Abstract—Catalytic activity exhibited by a mixed-valent film of ruthenium oxide– ruthenium cyanide deposited on the surface of a glassy-carbon electrode in electrooxidation of paracetamol and acetylsalicylic acid was used to develop a high-sensitivity selective method for determination of these compounds in the case of their joint presence under flow-injection conditions.

DOI: 10.1134/S1070427211040112

Because of the increased amount of pharmaceutical preparations containing paracetamol (PC, N-(4-hydrophenyl)acetamide and acetylsalicylic acid (AC, 2-acetyloxybenzoic acid) and threat of their falsification, development and implementation of new, more perfect and rapid methods for determination of these organic compounds is an important and topical task.

PC and AC are commonly determined by various methods, such as titrimetry, spectrophotometry, voltammetry, and high-performance liquid chromatography [1–5]. Most of these techniques are complicate by the necessary sample preparation and include extraction or a preceding chemical reaction. The results obtained when determining PC by the titrimetric and spectrophotometric methods are affected by presence of ascorbic or acetylsalicylic acid in a medicinal preparation, which impairs the metrological characteristics of determination in their joint presence. Use of direct voltammetric methods for determination of PC and AC on metallic and graphite electrodes is hindered by the lacking reproducibility of their results. In addition, determination of simultaneously present PC and AC by voltammetry is hindered by the fact that their electrooxidation potentials are close. Use of chemically modified electrodes (CMEs), including those operating on electrocatalysis principles, makes it possible to overcome these difficulties. As immobilized catalysts for determination of PC and AC are commonly used boron-doped diamond [6], nanoparticles of gold [7] and nickel oxide [8], metal-polymeric films [9], and carbon nanotubes [10]. However, use of CMEs fails to always improve the reproducibility of the analytical signal. Combination of voltammetry on CMEs and flow-through methods of analysis frequently improves the metrological characteristics of determination of organic compounds [11].

We studied the electrooxidation of PC and AC on a glassy carbon (GC) electrode covered with an inorganic film of a mixed-valent ruthenium oxide–ruthenium cyanide (RuO–RuCN) and developed a selective method for determination of PC and AC on a modified electrode of this kind under conditions of a flow-injection analysis (FIA).

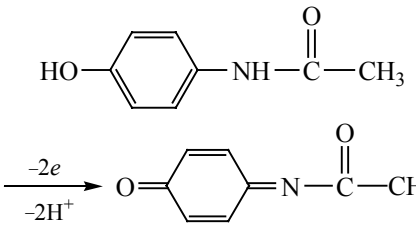
EXPERIMENTAL

We recorded cyclic voltammograms using a PI-50-1.1 potentiostat with a PU-1 programming unit in a three-

electrode cell. A GC electrode with a surface area of 0.096 cm^2 and a GC electrode coated with a RuO–RuCN film as working electrodes. A silver chloride electrode served as reference, and a platinum wire as auxiliary electrode. The cyclic voltammograms were recorded at a potential application rate of 20 mV s^{-1}. The inorganic film was formed on the GC surface by potentiodynamic deposition from an aqueous solution containing 1 mM $RuCl_3$ and $K_4[Ru(CN)_6]$ (Aldrich), with a 0.1 M H_2SO_4 solution as supporting electrolyte. The electrode surface was refreshed mechanically.

Solutions of PC and AC were prepared by dissolution of their precisely weighed portions in an aqueous solution. Sets of solutions with lower concentrations were prepared by successive dissolution of the starting solution immediately before measurements. Measurements under FIA conditions were made on an installation including a peristaltic pump of the DLV type, injector, flow-through electrochemical cell, and a recording device [12]. Solutions were delivered and discharged via flow-through lines fabricated from silicone pipe with an inner diameter of 2.0 mm. The injection was performed with a microsyringe through a sealing membrane.

Paracetamol is irreversibly oxidized on GC on the background of a 0.1 M H_2SO_4 solution, with a peak formed at a potential E_a = 0.90 V (Fig. 1a). By analogy with published data on electrooxidation of aminophenols [13], it can be assumed that a compound with a quinoid fragment is formed as a product of a chemical reaction. The electrode reaction is the following:



(1)

It should be noted that it is impossible to obtain a well-reproducible voltammogram. This is due to adsorption of substrate oxidation products on the graphite surface. Thus, a graphite electrode cannot be used to determine PC by direct voltammetry.

Acetyl salicylic acid is oxidized in a complicated way, with a preliminary stage of AC hydrolysis to salicylic acid, which is oxidized on the electrode. Preliminary

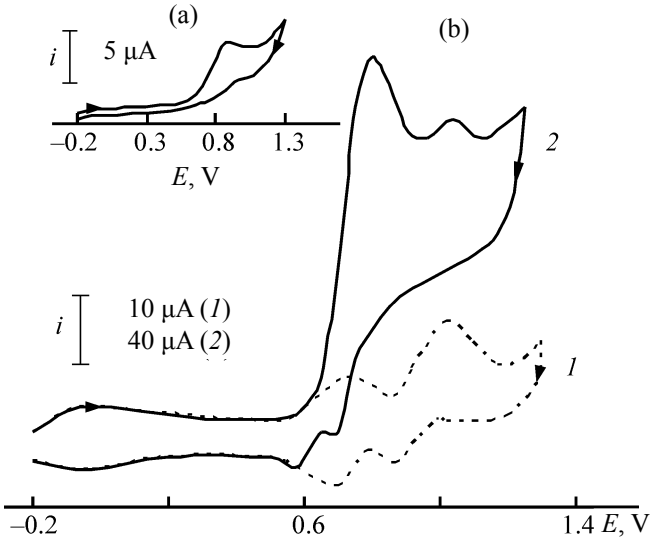
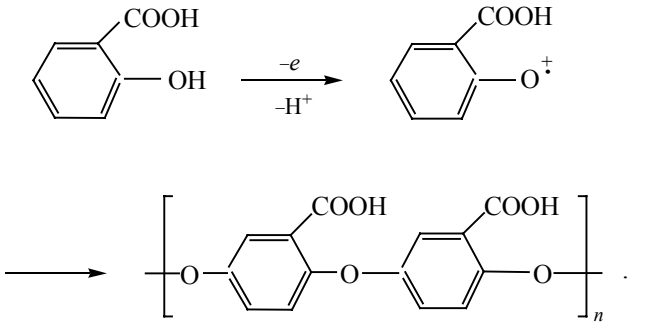


Fig. 1. Cyclic voltammograms for oxidation of paracetamol on (a) GC and (b, curve *2*) CME with a RuO–RuCN film on the background of a 0.1 M H_2SO_4 solution. Paracetamol concentration 5 × 10^{-3} M; the same for Figs. 3 and 4. Dashed line *1* is the background curve obtained on CME; the same for Fig. 2. (*E*) Potential; the same for Fig. 2.

hydrolysis was performed by the method described in [5]. Similarly to PC, salicylic acid is oxidized irreversibly with a peak formed in a more remote range of potentials, at E_p = 1.15 V (Fig. 2a). The oxidation scheme of this compound is complex [14] and includes formation of a cation radical, with its subsequent dimerization to give an oligomeric product:



(2)

The voltammogram of oxidation of PC and AC in their joint presence shows a single broad peak (Table 1), which hinders use of unmodified graphite electrodes for selective voltammetric determination of these compounds. Use of CMEs with electrocatalytic properties makes it possible to diminish the overvoltage of the reaction and make higher the determination

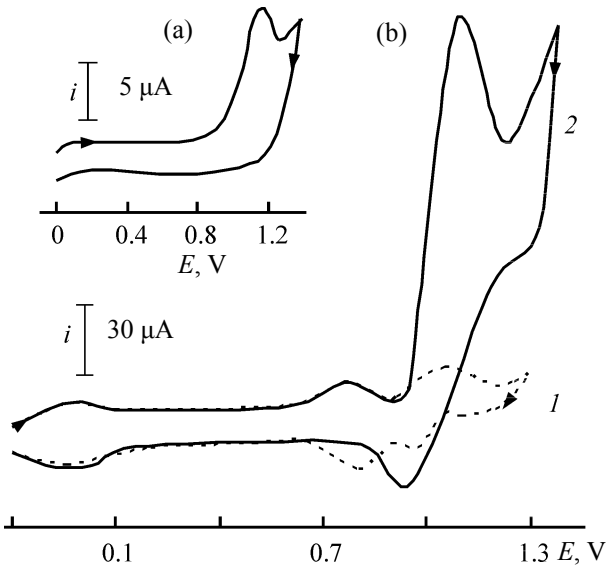


Fig. 2. Cyclic voltammograms for oxidation of acetylsalicylic acid on (a) GC and (b, curve *2*) CME with a RuO–RuCN film on the background of a 0.1 M H_2SO_4 solution. Acetyl salicylic acid concentration 5×10^{-3} M; the same for Figs. 3 and 4.

sensitivity of PC and AC, and the presence of several mediator centers in the composition of the inorganic film improves the selectivity of their determination. The electrochemical behavior of PC and AC on a CME with a RuO–RuCN film was studied.

Previously, the electrochemical behavior of a film of heterovalent ruthenium oxide– ruthenium cyanide has been studied [15]. A cyclic voltammogram obtained on the CME is presented in Fig. 1b (curve *1*). The voltammetric curve shows three well-pronounced anodic and reverse cathodic peaks. The electrochemical reactions occurring at a potential of 0.05 V are commonly related to the Ru(III/II) redox pair, and peaks at potentials of 0.80 and 1.10 V, to oxidation of mixed-valence ruthenium species bound to oxo and cyano groups to higher degrees of oxidation. The difficulty in determining the precise degree of oxidation is due to the formation of numerous redox centers and to the polymeric nature of the immobilized metal-complex. Spectral methods, including X-ray photoelectron spectroscopy, fail to reliably identify the degree of ruthenium oxidation, which is due to overlapping of the energy levels of carbon in the cyano group with the electron levels Ru($d_{3/2}$) and Ru($d_{5/2}$) [16]. Taking into account the similarity of the voltammograms obtained on electrodes modified with a ruthenium deposit [17] and a RuO–RuCN film [18] and comparing the results of a study of these films in [19], we can attribute the anodic-cathodic peaks to the following redox pairs: Ru(III)/Ru(II) (E = 0.05 V), Ru(IV)/Ru(III) (E = 0.80 V), and Ru(VI)/Ru(IV) (E = 1.05 V).

The RuO–RuCN film has a high chemical and electrochemical stability, which is indicated by the

Table 1. Voltammetric characteristics[a] of oxidation of paracetamol and acetylsalicylic acid on GC and CME with a RuO–RuCN film on the background of a 0.1 M H_2SO_4 solution

Electrode	E_s, V	i_s, μA	E_{med}, V	i_{med}, μA	E_{cat}, V	i_{cat}, μA	i_{cat}/i_{med}
Paracetamol							
GC	0.90	21	–	–	–	–	–
CME	–	–	0.80	11	0.80	172	15.6
			1.05	20	–	–	–
Acetyl salicylic acid							
GC	1.15	9	–	–	–	–	–
CME	–	–	0.80	11	–	–	–
			1.05	20	1.10	150	7.5
Mixture of paracetamol and acetylsalicylic acid							
GC	1.00	32	–	–	–	–	–
CME	–	–	0.80	11	0.80	172	15.6
			1.05	20	1.10	150	7.5

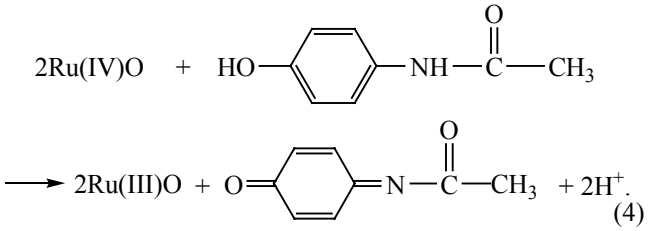
[a] E_s and i_s are the potential and current of the peak of substrate oxidation on GC; E_{med} and i_{med}, potential and current of the peak of mediator oxidation; E_{cat} and i_{cat}, potential and current of the peak of catalytic oxidation of the substrate on CME.

good reproducibility of voltammograms obtained upon a cyclic variation of the potential during a month, with a 0.1 M H_2SO_4 solution as a background. Raising the pH of the supporting electrolyte makes the voltammograms worse. In alkaline solutions, the film disintegrates and voltammograms take the form of a background curve characteristic of GC without a film.

We compared the electrochemical behaviors of PC and AC on a CME with a RuO–RuCN film. In electrooxidation of PC and AC, voltammograms show well-pronounced peaks (Figs. 1b and 2b, curves *2*). The current of the oxidation peak of the mediator increases at E = 0.80 V in oxidation of PC (Fig. 1b, curve *2*) and at E = 1.05 V in oxidation of AC (Fig. 2b, curve *2*). The background curve shows at the same potentials (0.80 and 1.05 V) current peaks corresponding to the transitions –Ru(III)O → –Ru(IV)O and –Ru(IV)O → –Ru(VI)O, respectively, i.e., the substrates are oxidized in the oxidation range of various forms of the modifier. The many-times increase in the height of these peaks and the linear dependence of the recorded currents on the concentration of PC and AC enable us to identify this process as a catalytic process. The catalytic effect is manifested in that the oxidation potentials of the substrates on CMEs are lower, compared with the unmodified electrode, by 100 and 150 mV for PC and AC, respectively, and the mediator oxidation current is many times higher. The ratios between the catalytic oxidation current i_{cat} of the substrates to the oxidation current i_{med} of the mediator are i_{cat}/i_{med} = 15.6 and 7.5 for PC and AC, respectively.

When studying the dependence of the PC oxidation peak current i_p on the potential application rate ν, we observed a linear dependence of $i_p/\sqrt{\nu}$ on $\sqrt{\nu}$, with a negative slope (Fig. 3a, curve *1*). According to the Reynolds–Shevchik equation, this dependence indicates that the substrate electrooxidation is complicated by a chemical reaction [20, 21]. By changing the initial potential E_{in} from which voltammograms were recorded and the delay time t_d of this potential (Figs. 3b and 3c, curves *1*), we found that the height of the peak remains unchanged as E_p decreases and t_d increases. This indicates that there is no adsorption component in the oxidation of PC [20, 21]. The scheme of catalytic electrooxidation of PC on CME can be represented as

$$\text{–Ru(III)O} \rightleftharpoons \text{–Ru(IV)O} + e, \qquad (3)$$



(4)

The plot of the dependence of $i_p/\sqrt{\nu}$ on $\sqrt{\nu}$ in oxidation of AC has a positive slope (Fig. 3a, curve *2*), and the current of the peak grows with increasing t_d and decreasing E_{in} (Figs. 3b and 3c, curves *2*), which is indicative of the adsorption contribution to the process of AC electrooxidation on this CME by the scheme

$$\text{–Ru(IV)O} \rightleftharpoons \text{–Ru(VI)O} + 2e, \qquad (5)$$

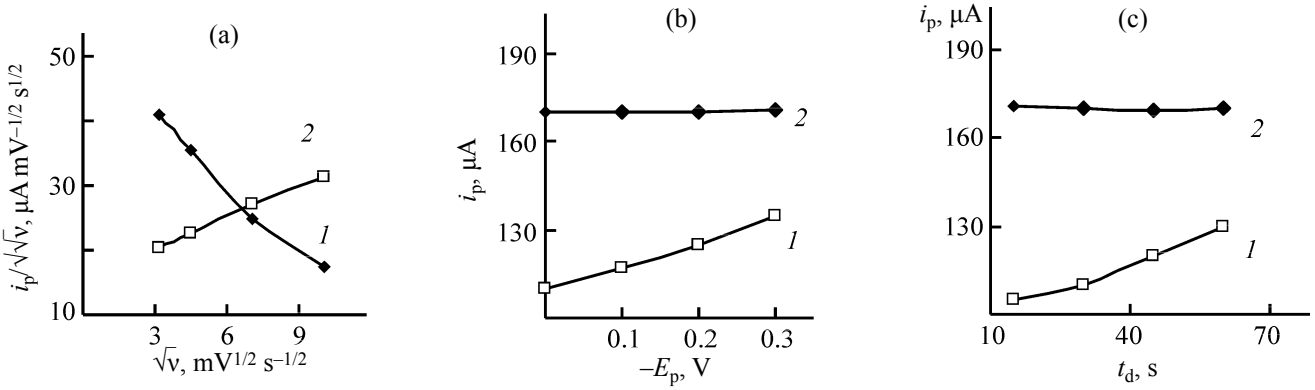
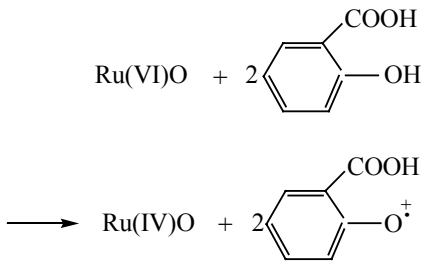


Fig. 3. Catalytic current i_p of the oxidation peak for (*1*) paracetamol and (*2*) acetylsalicylic acid on CME vs. (a) potential application rate ν, (b) initial potential from which a voltammogram is recorded, and (c) the delay time t_d of the initial potential from which a voltammogram is recorded.



(6)

The cyclic voltammogram for electrooxidation of jointly present PC and AC on a CME with a RuO–RuCN film shows in its anodic branch two well-pronounced peaks at E = 0.80 and 1.05 V, which correspond to the catalytic oxidation of PC and AC, respectively (Table 1).

The magnitude of the electrocatalytic response of CMEs depends on the method by which a RuO–RuCN film is deposited onto the GC surface. The film was produced electrochemically. We varied the electrolysis duration and potential in the case of a potentiostatic deposition, and the range and rate of a cyclic variation of the potential, in potentiodynamic deposition. A pronounced catalytic effect is observed in oxidation of PC and AC when the film is deposited by cyclic variation of the potential in the range from –0.10 to +1.10 V at a potential application rate of 100 mV s^{-1} in the course of 15 min.

Thus, the electrocatalytic oxidation of PC and AC occurs on a CME with a RuO–RuCN film at different potentials (the potential difference ΔE is 300 mV), which makes it possible to develop a method for selective voltammetric determination of these compounds. However, the adsorption nature of the AC oxidation current results in that the reproducibility of the currents measured is unsatisfactory. Amperometric detection of PC and AC under FIA condition eliminates this disadvantage. A chemically modified electrode based on a RuO–RuCN film was used to determine PC and AC under the FIA conditions, with FIA signals recorded in the potentiostatic mode. Preliminarily, the effect of hydrodynamic parameters of the system on the intensity of the analytical signal was considered. We studied the dependence of the current on the volume V of a sample being injected and flow rate u. The strongest FIA signal is observed for PC and AC for a 0.15-ml injected sample (Fig. 4a). The dependence of i on u for PC and AC passes through a maximum at u = 16 ml min^{-1} (Fig. 4b). With these hydrodynamic parameters, we studied the dependence of the current on potential. The maximum current is observed in detection on CME at E = 0.75 V for PC and E = 1.05 V for AC (Fig. 4c). Based on the dependences obtained, we chose the working conditions for recording the FIA signal: V = 0.5 ml, u = 17 ml min^{-1}, and E = 0.75 V for PC; and V = 0.5 ml, u = 17 ml min^{-1}, and E = 1.05 V for AC.

The method of flow-injection determination of PC and AC on a CME with a RuO–RuCN film consists in that the FIA signal is recorded at E = 0.75 V for PC and E = 1.05 V for AC after a sample with a volume of 0.5 ml is injected into a carrier (0.01 M solution of H_2SO_4) at its flow rate of 17 ml min^{-1}. The dependence of the FIA signal on the PC and AC concentrations is linear in logarithmic coordinates in the range from 5 × 10^{-3} to 5 × 10^{-8} M and is described by Eqs. (7) and (8), respectively:

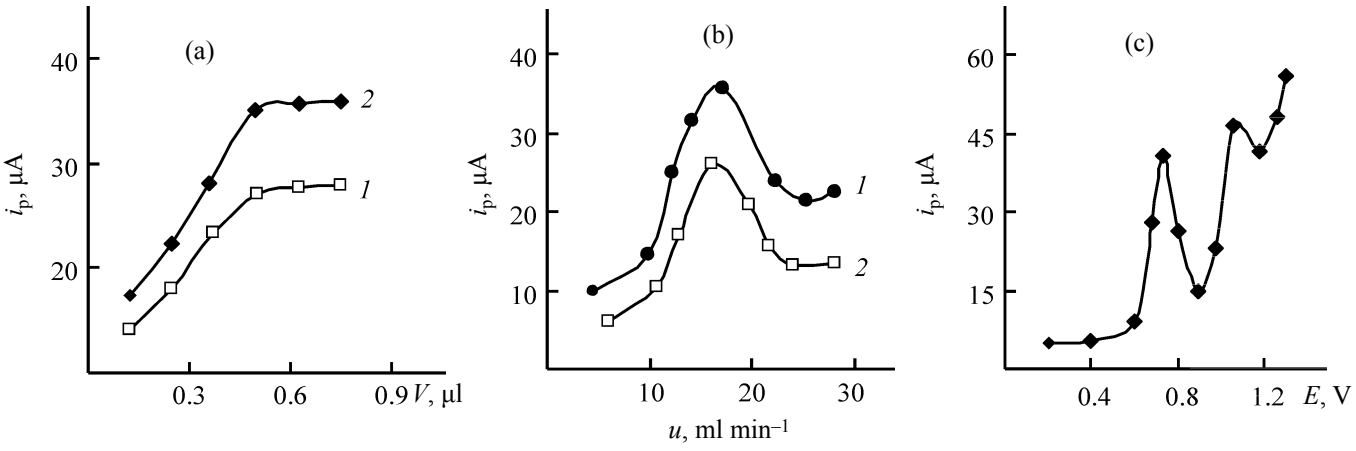


Fig. 4. Catalytic response of CME under FIA conditions to (*1*) paracetamol and (*2*) acetylsalicylic acid vs. (a) volume V of an injected sample, (b) flow rate u, and (c) applied potential E on the background of an H_2SO_4 solution with pH 2.0. (i_p) Current.

Table 2. Metrological characteristics of the flow-through–injection determination of paracetamol and acetylsalicylic acid on a CME with a RuO–RuCN film; $n = 6$, $P = 0.95$

Analyte	Content of an analyte, μM		S_r
	introduced	found $x \pm \Delta x$	
PC	0.5	0.51 ± 0.02	0.05
	5.0	4.9 ± 0.2	0.04
	10.0	10.2 ± 0.3	0.03
	100	99 ± 1	0.01
AC	0.5	0.49 ± 0.02	0.05
	5.0	4.8 ± 0.2	0.05
	10.0	9.9 ± 0.4	0.04
	100	101 ± 2	0.02

$$\log i_p = (2.44 \pm 0.09) + (0.46 \pm 0.01)\log c,\ R = 0.997 \quad (i_p, \mu A;\ c, M); \quad (7)$$

$$\text{Log } i_p = (2.72 \pm 0.04) + (0.57 \pm 0.03)\text{l0g } c,\ R = 0.999 \quad (i_p, \mu A;\ c, M); \quad (8)$$

The detection limit calculated using the 3*s* criterion [21] is 2×10^{-8} M. The adequacy of the procedure was verified by the introduced–found method (Table 2). An assessment of the metrological characteristics revealed a good accuracy of the results of voltammetric determination of PC and AC in a flow-through system. The improved reproducibility of the analytical signal in a low is due to the absence of sorption of the substrate and its oxidation production the CME surface. The suggested method for amperometric detection of PC and AC with a CME based on a RuO–RuCN film under FIA conditions is distinguished by simplicity, high sensitivity, selectivity, and fast determination.

We used a chemically modified electrode with a RuO–RuCN film to determine PC and AC in pharmaceutical preparations. It was found that there is no mutual influence of PC and AC on the results of their determination (Table 3). In addition, we examined the influence of various components present in medicinal materials on the determination of the analytes. Table 3 lists results we obtained when determining PC and AC in the presence of a number of compounds, such as caffeine, phenobarbital, cacao, codeine, citric acid, and codeine phosphate, which are contained in the corresponding preparations, but do not hinder determination of PC and AC. It was found that, in the presence of their compounds, a good reproducibility of

Table 3. Determination of paracetamol and acetylsalicylic acid on a CME with a RuO–RuCN film in the presence of matrix components of pharmaceutical preparations; $n = 6$, $P = 0.95$, $t_{tab} = 2.57$

Preparation	Analyte	Matrix component	Ratio	Introduced	Found	S_r
				g		
Ascofen	PC	AC	1 : 1	0.20	0.22 ± 0.01	0.04
		Caffeine	1 : 5	0.15	0.140 ± 0.007	0.05
	AC	PC	1 : 1	0.20	0.190 ± 0.006	0.03
		Caffeine	1 : 5	0.30	0.28 ± 0.01	0.04
Citropar	PC	Caffeine	1 : 6	0.3	0.29 ± 0.01	0.04
		Cacao	1 : 8	0.4	0.398 ± 0.008	0.05
		Citric acid	1 : 4	0.25	0.242 ± 0.008	0.03
	AC	Caffeine	1 : 8	0.500	0.470 ± 0.005	0.01
		Cacao	1 : 10	0.15	0.146 ± 0.005	0.03
		Citric acid	1 : 5	0.2	0.19 ± 0.01	0.05
Sedalgin-N	PC	Phenobarbital	1 : 8	0.180	0.176 ± 0.009	0.05
		Caffeine	1 : 4	0.250	0.255 ± 0.008	0.03
		Codeine phosphate	1 : 20	0.4	0.42 ± 0.01	0.03
	AC	Phenobarbital	1 : 8	0.0750	0.0747 ± 0.0008	0.01
		Caffeine	1 : 4	0.300	0.297 ± 0.006	0.02
		Codeine phosphate	1 : 20	0.240	0.242 ± 0.003	0.01

Table 4. Results of determination of paracetamol and acetylsalicylic acid on a CME with a RuO–RuCN film in pharmaceutical preparations; $n = 6$, $P = 0.95$, $t_{tab} = 2.57$

Preparation (in pellets)	Analyte	Certified value of m, g	Found m, g	S	t_{cal}
Paracetamol	PC	0.500	0.495 ± 0.006	0.006	2.04
Ascofen		0.200	0.196 ± 0.007	0.007	1.40
Sedalgin-N		0.300	0.306 ± 0.007	0.007	2.10
Citropar		0.180	0.173 ± 0.008	0.008	2.14
Ascofen	AC	0.20	0.204 ± 0.005	0.005	1.96
Sedalgin-N		0.200	0.194 ± 0.007	0.007	2.10
Citropar		0.240	0.242 ± 0.003	0.003	1.63

measurement results is observed ($S_r < 0.05$).

Results of analyses for PC and AC in selected pharmaceutical preparations are listed in Table 4. As certified values serve the contents of PC and AC, specified in the medicine instruction sheets. A statistical assessment of the results by the value of the *t*-criterion demonstrated that there is no statistically significant systematic error: $t_{cal} < t_{tab}$.

CONCLUSIONS

(1) It was found that heterovalent ruthenium oxide– ruthenium cyanide deposited on the surface of a glassy carbon electrode exhibits a catalytic activity in electrooxidation of paracetamol and acetylsalicylic acid. The catalytic oxidation of paracetamol is observed at $E = 0.890$ V in the oxidation range of Ru(III) oxo species, and that of acetylsalicylic acid, at $E = 1.05$ V in the oxidation range of Ru(IV) oxo species.

(2) A method was suggested for amperometric determination of paracetamol and acetylsalicylic acid on a modified electrode under conditions of a flow-through–injection analysis. The electrochemical and hydrodynamic conditions in which the flow-injection signal should be recorded were found. It was demonstrated that a linear dependence of the catalytic current on the concentration of the analytes under consideration is observed in the range from 5 × 10–8 to 5 × 10–3 M.

(3) A chemically modified electrode based on a RuO–RuCN film was used for selective determination of paracetamol and acetylsalicylic acid jointly present in pharmaceutical preparations. The determination is not hindered by accompanying components present in the preparations under study, which is confirmed by the good reproducibility of the determination results ($S_r <$ 5%).

ACKNOWLEDGMENTS

The study was supported by the Russian Foundation for Basic Research (grant no. 08-03-00749).

REFERENCES

1. *Farmatsevticheskii analiz lekarstvennykh sredstv* (Pharmaceutical Analysis of Medicinal Preparations), Shapovalova, V.A., Ed., Kharkov: IMP Rubikon, 1995.
2. Sadic, G., Abu Hena Mostofa Kamal, M., Helal Uddin Biswas, M., et al., *J. Medical Sci.*, 2001, vol. 1, no. 2, pp. 61–62.
3. Bloomfield, M.S., *Talanta*, 2003, vol. 58, no. 6, pp. 1301–1310.
4. Githiga, I.M., Muchohi, S.N., Ogutu, B.R., et al., *J. Chromatogr. B*, 2004, vol. 805, no., pp. 365–369.
5. Supalkova, V., Petrek, J., Havel, S., et al., *Sensors*, 2006, vol. 6, no. 11, pp. 1483–1497.
6. Lourencao, B.C., Medeiros, R.A., Rocha-Filho, R.C., et al., *Talanta*, 2009, vol. 78, no. 3, pp. 748–752.
7. Goyal, R.N., Gupta, V.K., Oyama, M., and Bachheti, N., *Electrochem. Commun*., 2005, vol. 7, no. 8, pp. 803–807.
8. Batchelor-McAuley, C. and Wildgoose, G.G., *Electrochem. Commun.*, 2008, vol. 10, no. 8, pp. 1129–1131.
9. Boopathi, M., Won, M.-S., and Shim, Y.-B., *Anal. Chim. Acta,* 2004, vol. 512, no. 2, pp. 191–197.
10. Kachoosangi, R.T., Wildgoose, G.G., and Compton, R.G., *Anal. Chim. Acta*, 2008, vol. 618, no. 1, pp. 54–60.
11. Silva, M.L.S., Garsia, M.B.Q., C.Lima, J.L.F., and Barrado, E., *Portugal. Electrochim. Acta*, 2006, vol. 24, no. 2, pp. 261–271.

12. Shaidarova, L.G., Zaripova, S.A., Tikhonova, L.N., et al., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 5, pp. 728–732.
13. *Organic Electrochemistry: An Introduction and a Guide*, Baizer, M.M. and Lund, H., Eds., New York: Marcel Dekker, 1983, 2nd ed.
14. Vedenyapina, M.D., Rakishev, A.K., Vedenyapin, A.A., et al., *Kondens. Sredy Mezhfazn. Granitsy*, 2007, vol. 9, no. 1, pp. 26–31.
15. Shaidarova, L.G., Gedmina, A.V., Chelnokova, I.A., and Budnikov, G.K., *Zh. Prikl. Khim*., 2004, vol. 77, no.12, pp.1974–1979.
16. Kulesza, P.J., Grzybowska, B., Malic, M.A., et al., *J. Electroanal. Chem.,* 2001, vol. 512, nos. 1–2, pp. 110–118.
17. Shaidarova, L.G., Gedmina, A.V., Chelnokova, I.A., and Budnikov, G.K., *Zh. Anal. Khim*., 2005, vol. 60, no. 6, pp. 603–609.
18. Kumar, A.S. and Zen, J.-M., *Electroanalysis,* 2004, vol. 16, no. 15, pp.1211–1220.
19. Chen, S.-M. and Hsueh, S.-H., *J. Electroanal. Chem.,* 2004, vol. 566, no. 2, pp. 299–303.
20. Budnikov, G.K., Maistrenko, V.N., and Vyaselev, M.R., *Osnovy sovremennogo elektrokhimicheskogo analiza* (Fundamentals of Modern Electrochemical Analysis), Moscow: Mir, Binoms LZ, 2003.
21. Budnikov, G.K., *Printsipy i primenenie vol'tampernoi ostsillograficheskoi polyarografii* (Principles and Application of Voltammetric Oscillographic Polarography), Kazan: Kazan. Gos. Univ., 1975.