ELECTROREDUCTION AT SOLID ELECTRODE MATERIALS AND VOLTAMMETRIC DETERMINATION OF POTASSIUM HYDROGENPEROXOMONOSULFATE

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The electrochemical behaviour of potassium hydrogenperoxomonosulfate (KHSO$_5$) at carbositall and Au, Ag electrodes using the square-wave voltammetry (SWV) with 0.2 mol L–1 KHSO$_4$ background solution (pH ~ 0.8) (Ep = 0.25 V vs Ag,AgCl/KCl(sat)) and differential pulse voltammetry (DPV) with 0.01 mol L–1 Na$_2$SO$_4$+8×10^{-3} H2SO4 background solution (pH = 0.9) (Ep = 0.14 V vs Ag,AgCl/KCl(sat)) correspondingly were studied. The voltammetric methods were developed and the possibility to determine the peroxomonosulfate in model solutions on the studied electrodes was shown.
Keywords: potassium hydrogenperoxomonosulfate, voltammetry, carbositall electrode, Ag electrode, Au electrode.

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Electrochemical analysis is a powerful analytical technique used in pharmaceutical industry and environmental applications. Electroanalysis is highly advantageous due to high sensitivity, reduction in solvent and sample consumption, high-speed, low operating cost and high scan rate in all cases.

An overview of development of electroanalytical chemistry demonstrates that solid electrodes represent the most rapidly growing class of electrodes. When surveying the current state of electroanalytical research and the ways of application of electroanalysis, one concludes that solid electrodes in general are widely used being practical electrode materials. In its broad sense electrochemistry involves a chemical phenomena associated with charge separation at an electrode surface. As voltammetric methods continue to develop, the range of working electrode materials continues to expand, and the analyst must remain aware of what is available. Both the geometry and composition of the working electrode material must be considered since they will influence the performance of the voltammetric method. Also, the physical form of the working electrode may influence the diffusion process, while the working electrode material will influence the chemical steps and the electron transfer process involved in the detection of the analyte.

A great variety of solid electrodes have been employed in different voltammetric techniques over the years. Among the many different solid materials that can be used as working electrodes, the most common are carbon, platinum and gold [1-8].

Potassium hydrogenperoxomonosulfate (KHSO$_5$) is one of the most widely used disinfectants in the medical practice, among well-known classes of chemical disinfectants – oxidants. It is included in the new generation of modern disinfection agents in the form of stable triple potassium salt 2KHSO$_5$•KHSO$_4$•K$_2$SO$_4$, such as "Perform" and the modified analogue of "Virkon"– "Ecocid S" (KRKA, Slovenia, Novo mesto).

The wide use of KHSO$_5$ demands a reliable analytical tool for its monitoring. Literature data provide the following methods of the KHSO$_5$ determination.

The procedure of polarographic determination of sulfuric acid peroxide derivatives such as peroxomonosulfate (Caro's acid) and peroxodisulfate (Marshal acid or persulfate) at dropping mercury electrode (DME) was described [9]. However, strong oxidant reduction such as persulfate in the background solution of 0.03 mol L-1 sulfuric acid at DME was observed at extremely positive potential area vs. saturated calomel electrode (SCE), where the anodic dissolution of electrode material occurred (+0.3 V). In the potential range of +0.3 to +0.15 V (vs. SCE) the diffusion current value maintained constant, and at 0.25 V was proportional to the concentration of potassium persulfate. If the peroxomonosulfate is present in the solution in the form of hydrogenperoxomonosulfate two waves will overlap, so only their total content can be defined by polarography at DME [10]. In addition to the low selectivity the proposed method is not sensitive, lower limit of detection was limited as absolute value and residual current fluctuations.

The hydrogenperoxomonosulfate was determined by voltammetry in the background of 1 mol L–1 perchloric acid solution using a smooth platinum rotated electrode as a working electrode at +0.214 V (vs SCE) after removal of oxygen during 15 minutes. Only platinum oxide dissolution peak was observed on the background voltammogram at +0.84 V. Platinized platinum electrode through relatively low resistance to oxidation by atmospheric oxygen (which leads to the formation of platinum oxide on its surface) requires advance preparation in order to obtain reproducible potentials, namely holding at +1.4 V for a few minutes to achieve the desired passivation of the electrode surface [11]. This method is not sufficiently sensitive: it allowed determining hydrogenperoxomonosulfate starting from the concentration of 5×10–5 mol L–1.

The determination of potassium monoperoxosulfate persisting in some disinfectants in the form of triple salt (2KHSO$_5$·KHSO$_4$·K2SO$_4$) based on titration by tin(II) chloride solution in the presence of potassium bromide at 70 °C with potentiometric registration by means of point platinum and glass pH electrodes was presented. The analysis of «Virkon» solution was performed [12]. The disadvantages of this technique are
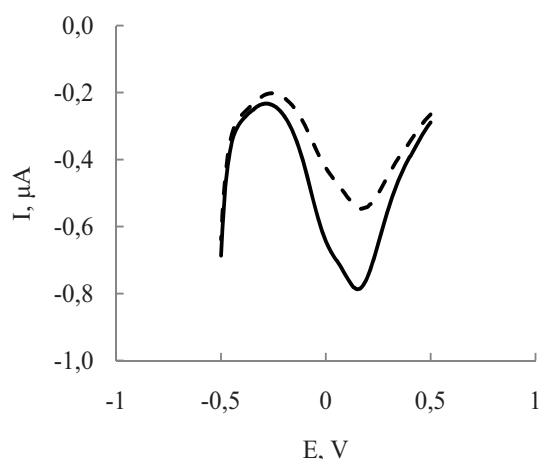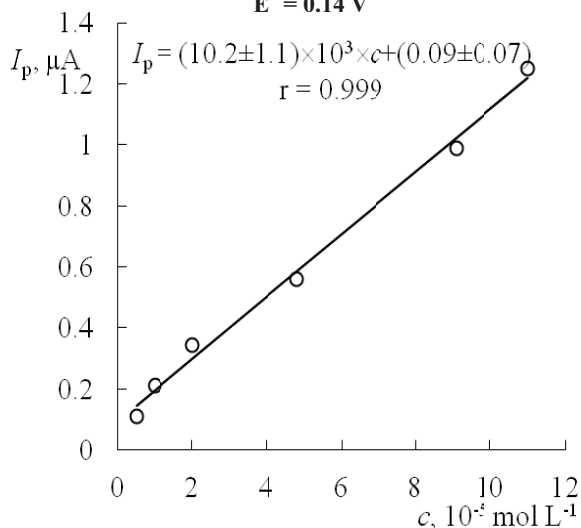
Fig. 1. Voltammogram of the KHSO$_5$ reduction obtained at Ag (dotted) and Au(straight) electrodes in N$_2$-saturated 0.01 mol L^{-1} Na$_2$SO$_4$+8×10^{-3} H$_2$SO$_4$ background solution (pH = 0.9) (reference electrode Ag,AgCl/KCl(sat)); E = 0.14 V

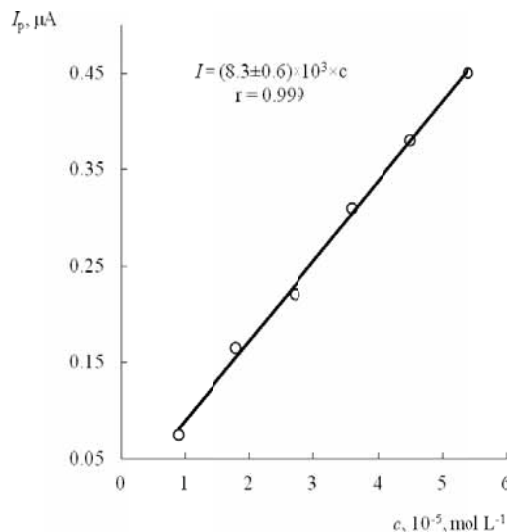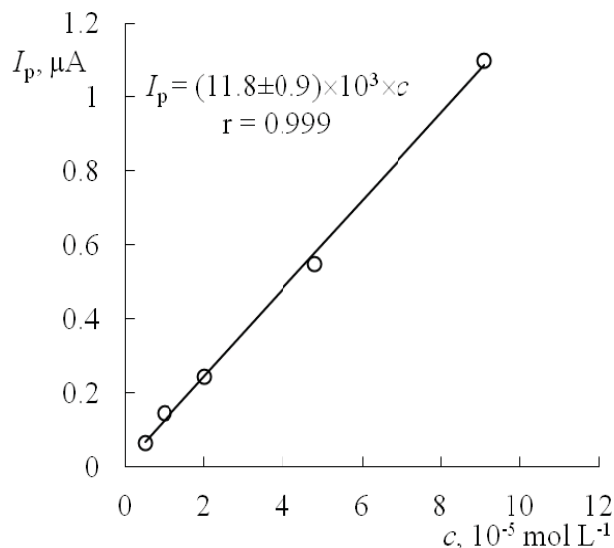**Fig. 2. The calibration plot of the KHSO$_5$ reduction current peak vs. concentration with 0.2 mol L^{-1} KHSO$_4$ background solution (pH ~ 0.8) at carbositall electrode (reference electrode Ag,AgCl/KCl(sat)); E$_p$ = 0.25 V**

$$I = (8.3\pm0.6)\times10^3\times c$$
$$r = 0.999$$

$$I_p = (10.2\pm1.1)\times10^3\times c+(0.09\pm0.07)$$
$$r = 0.999$$

$$I_p = (11.8\pm0.9)\times10^3\times c$$
$$r = 0.999$$

1

2

Fig. 3. The calibration plot of the KHSO$_5$ reduction current peak vs. concentration with 0.01 mol L^{-1} Na$_2$SO$_4$+8×10^{-3} H$_2$SO$_4$ background solution (pH = 0.9) at Ag (1) and Au (2) electrodes (reference electrode Ag,AgCl/KCl(sat)); E$_p$ = 0.14 V

the necessity to heat the solution of the test sample to a temperature of 70 °C, and the instability of the titrant solution.

To choose the electrode material, which would have had selectivity measurements in specific circumstances, it is necessary to know the mechanism of the electrode process, the degree of filling of the surface agents changed when the electrode material is changed. Also, notice that the behavior of the electrode is not determined by properties of the metal and thin oxide films on its surface, which strongly differ in electrical characteristics of metals. Common property of precious metals is good formation of conductive oxide films at anodic potentials.

Allowing for the disadvantages of existing methods, it became necessary to find other electrode materials, and therefore it is perspective to study the behavior of KHSO$_5$ on silver (Ag) and gold (Au) metal and carbositall electrodes because the data is not available in the literature.

In the present work the electrochemical behavior of KHSO$_5$ was examined at metal (i.e., Au, Ag) and carbositall electrodes using square wave and differential pulse rotating disk electrode voltammetry. The results of development of the procedure of KHSO5 quantitative determination using the calibration graph method were shown.

Experimental section

Materials and reagents

The solution of KHSO$_5$ («Oxone®», ACROS ORGANICS) was freshly prepared and standardized iodometrically.

Tab. 1.

Regression characteristics of KHSO$_5$ voltammetric determination procedure in pure substance

Parameters	Data		
	Carbositall	Ag	Au
Concentration ranges (mol L^{-1})	$(0.9-5.4)\times10^{-5}$	$(0.5-11.0)\times10^{-5}$	$(0.5-9.1)\times10^{-5}$
Regression equation	$I_p = (8.3\pm0.6)\times10^3\times c$	$I_p = (10.2\pm1.1)\times10^3\times c+$ $+(0.09\pm0.07)$	$I_p = (11.8\pm0.9)\times10^3\times c$
Slope (a)	8.3×10^3	10.2×10^3	11.8×10^3
Intercept (b)	0.006	0.09	0.009
Da	0.6×10^3	1.1×10^3	0.9×10^3
Db	0.05	0.07	0.04
S_a	0.6×10^3	0.4×10^3	0.3×10^3
S_b	0.02	0.02	0.013
Correlation coefficient (r)	0.999	0.997	0.999
LOD (mol L^{-1})	2.76×10^{-6}	7.26×10^{-6}	2.48×10^{-6}
LOQ (mol L^{-1})	9.19×10^{-6}	2.42×10^{-5}	8.26×10^{-6}

Stock solution was prepared by dissolving 0.1537 g of powder (triple potassium salt, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in 50 mL volumetric flask by double-distilled water to give a concentration of 9×10^{-2} mol L^{-1}. 10 mL of 9×10^{-2} mol L^{-1} solution of KHSO$_5$ was diluted in 100 mL volumetric flask with double-distilled water to obtain a 9×10^{-3} mol L^{-1} solution of KHSO$_5$. The stock solution was diluted with the appropriate buffer solution before use. Background solution for carbositall electrode was prepared by dissolving potassium hydrogensulfate (KHSO$_4$) in volumetric flask by double-distilled water. The background solution for metal electrodes consists of mixture of sulfuric acid (H$_2$SO$_4$) and sodium sulfate (Na$_2$SO$_4$) solutions.

Electrochemical measurements at carbositall electrode were carried out in the analyzer AVS-1.1 (Volta, St. Petersburg) with a three-electrode scheme by alternating the current mode with square wave modulation in potential range +1.0…–1.2 V, W = 1000 rpm, amplitude 40 mV, ν = 65 Hz. The values of potential peaks directly at a maximum are measured by the electrochemical sensor "Module EM-04" with the accuracy of ±5 mV. Carbositall electrode was used as a working and an auxiliary electrode, and Ag,AgCl/KCl(sat) electrode type EVL-1M4 - as a reference electrode.

Electrochemical measurements at Ag and Au electrodes were carried out in the Voltammetric measuring stand with the built-in three-electrode scheme potentiostat 797 VA Computrace (Metrohm, Switzerland) by differential pulse mode. For differential pulse voltammetry (DPV) operating conditions were the following: pulse amplitude 0.050 V; pulse width 0.040 s; and scan rate 0.010 V/s. Rotating disk electrodes (RDE) with exchangeable electrode tips made from Ag or Au were used as a working electrode. Platinum auxiliary electrode with plastic shaft was used as an auxiliary electrode, and Ag,AgCl/KCl(sat) electrode - as a reference electrode.

The pH was measured using the ionmeter type I-160M (Belarus) with the ESL-43-07 type glass electrode paired with Ag, AgCl/KCl (sat) electrode. All measurements were made at the room temperature.

Scheme of the reduction process is:

$$HSO_5^- + 2\bar{e} + 2H^+ \rightarrow HSO_4^- + H_2O$$
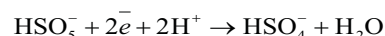
Activation of the electrode

An important factor in using solid electrodes is the dependence of the response on surface state of the electrode. Accordingly, the use of such electrodes requires precise electrode pretreatment and polishing in order to obtain reproducible results.

Tab. 2.

Evaluation of accuracy and precision of KHSO$_5$ voltammetric determination procedure (n = 5; P = 0.95%)

Electrode material	Taken (mol L^{-1})	Found (mol L^{-1})	Recovery (%±SD)	RSD, %	ε (%)	δ* (%)
Carbositall	3.6×10^{-5}	$(3.59\pm0.12)\times10^{-5}$	99.7±3.3	2.68	3.3	−0.27
	4.5×10^{-5}	$(4.52\pm0.14)\times10^{-5}$	100.4±3.2	2.55	3.2	+0.44
	5.4×10^{-5}	$(5.41\pm0.16)\times10^{-5}$	100.2±3.0	2.39	3.0	+0.19
Ag	0.99×10^{-5}	$(0.98\pm0.83)\times10^{-5}$	100.9±8.4	6.71	8.3	+0.01
	2.00×10^{-5}	$(2.04\pm0.15)\times10^{-5}$	101.8±7.5	5.95	7.4	+0.02
	11.0×10^{-5}	$(11.5\pm0.68)\times10^{-5}$	104.2±6.2	4.75	5.9	+0.04
Au	0.99×10^{-5}	$(1.10\pm0.86)\times10^{-5}$	111.5±8.7	6.26	7.8	+0.12
	2.00×10^{-5}	$(2.02\pm0.83)\times10^{-5}$	101.1±4.1	3.29	4.0	+0.01
	9.10×10^{-5}	$(9.19\pm0.32)\times10^{-5}$	101.0±3.5	2.88	3.5	+0.01

* relative to the average reference method of iodometric titration [15].

Metallic electrodes were pretreated electrochemically or chemically. The carbositall electrode was polished manually with aqueous slurry of alumina powder on a damp smooth polishing cloth (BAS velvet polishing pad), before measurement.

Results and discussion

Fig. 1 displays the differential pulse voltammetric responses of 2×10^{-5} mol L–1 $KHSO_5$ at Ag and Au electrodes in N_2-saturated 0.01 mol L–1 Na_2SO_4+8×10^{-3} H_2SO_4 background solution (pH = 0.9) (reference electrode Ag,AgCl/KCl(sat)); Ep = 0.14 V. Voltammetric behavior of $KHSO_5$ at carbositall electrode was shown in [13]. The study was conducted in solutions with concentration of KHSO5 from 0.9×10–5 to 5.4×10–5 mol L–1. Background solution was $KHSO_4$ (c = 0.2 mol L–1, pH ~0.8).

Procedure of obtaining results for the calibration graph

a) Ag and Au electrodes

Solutions of chosen supporting electrolytes were placed into the electrolytic cell at room temperature, and oxygen was removed by transmitting nitrogen through the solution during 2 min. A stock solution of the electroactive compound was added to the final concentration. Nitrogen was introduced for another 1 min and the current-voltage curve was recorded. In the supporting electrolytes used, the current-voltage curves remained unchanged for at least 72 h.

b) Carbositall electrode

Working solutions were prepared by diluting different volumes of stock solution and background solution each in 50 mL volumetric flask using double distilled water. 25 mL of the working solution of pure substance was transferred to the cell.

The voltammograms were recorded by scanning the potential toward the negative direction in the potential range from +1.0 V to –1.2V. The graph was plotted in the coordinates: the height of peaks Ip in μA on the ordinate axis and corresponding concentration of $KHSO_5$ c in mol L–1 on the abscissa axis.

The calibration curves were obtained based on the limiting currents for the reduction of $KHSO_5$ at carbositall

(Fig. 2) electrode (Ep = 0.25 V vs Ag,AgCl/KCl(sat)) and at Ag (Fig. 3.1) and Au (Fig. 3.2) electrodes (Ep = 0.14 V vs. Ag,AgCl/KCl(sat)).

Analytical characteristics of the calibration graphs of $KHSO_5$ voltammetric determination procedure are shown in Table 1.

Method validation

Precision and Accuracy

Precision is the degree of repeatability of an analytical method under normal operational conditions. The precision and accuracy were determined with standard quality control samples (in addition to calibration standards) prepared in triplicates at different concentration levels covering the entire linearity range. The precision of the assay was determined by repeatability (intraday) and intermediate precision (interday), and reported as RSD % for a statistically significant number of replicate measurements. The intermediate precision was studied by comparing the assays on three different days, and the results are documented as standard deviation and RSD %. Accuracy is the percent of analyte recovered by assay from a known added amount. Data from nine determinations over three concentration levels covering the specified range was obtained. The repeatability of the method was determined by assaying five sample solutions of the highest test concentration. The obtained results are summarized in Table. 2.

LOD and LOQ

In this study LOD and LOQ were based on the standard deviation of response and the slope of the corresponding curve using the following equations.

$$LOD = 3\ Sb/a; \qquad LOQ = 10\ Sb/a,$$

where Sb, the noise estimate, is the standard deviation of the absorbance of the sample, a is the slope of the related calibration graphs. The limit of quantification (LOQ) is defined as the lowest concentration of the standard curve that can be measured with acceptable accuracy, precision and variability (Table 1).

Conclusions

Thus, this report has demonstrated that carbositall and gold electrodes are the most perspective among the studied electrodes. A linear relationship between peak current and concentration was obtained in the range $(0.9\text{-}5.4)\times10^{-5}$ mol L–1 and $(0.5\text{-}9.1)\times10^{-5}$ mol L–1 (r=0.999) of the $KHSO_5$ concentrations at pH ~0.8. RSD were 2.68 %, 2.55 % and 2.39 % for the 3.6×10^{-5}, 4.5×10^{-5} and 5.4×10^{-5} mol L–1concentrations of $KHSO_5$ model solutions, respectively (δ = –0.27…+0.44 %); LOD = 2.76×10^{-6} mol L–1, LOQ = 9.19×10^{-6} mol L–1. While on Au and Ag electrodes this data was the following: RSD were 6.26 %, 3.29 % and 2.88 % for the 0.99×10^{-5}, 2.0×10^{-5} and 9.10×10^{-5} mol L–1concentrations of the KHSO5 model solutions, respectively (δ = +0.12…+ +0.01 %); LOD = 2.48×10^{-6} mol L–1, LOQ = 8.26×10^{-6} mol L–1 on Au electrode. These are the lowest values. On the Ag electrode this data was the following: for the concentrations of the $KHSO_5$ model solutions 0.99×10^{-5}, 2.0×10^{-5} and 11.0×10^{-5} mol L–1 RSD were 6.71 %, 5.5 % and 4.75 %, respectively (δ = +0.01…+0.04 %); LOD = 7.26×10^{-6} mol L–1, LOQ = 2.42×10^{-5} mol L–1 on Ag electrode. So $KHSO_5$ determination is more sensitive at carbositall and Au electrodes.

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