Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(11):489-496

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Voltammetric determination of potassium hydrogenperoxomonosulfate in pure substance and disinfectant "Ecocide S"

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ABSTRACT

The behavior of potassium hydrogenperoxomonosulfate ($KHSO_5$) has been studied using alternating current voltammetry with square wave modulation in potential range +1.0…–1.2 V at carbositall electrode as indicating and auxiliary electrode (reference electrode Ag, AgCl/KCl(sat)) (E_p = +0.25 V). A linear relationship between peak current and concentration was obtained in the range 0.9×10^{-5} mol L^{-1} to 5.4×10^{-5} mol L^{-1} of the $KHSO_5$ concentrations at pH ~ 0.8 for pure substance. It is $I_p = (8.3 \pm 0.6)\times10^{3}\times c$ ($r = 0.999$). 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^{-1}concentrations of $KHSO_5$ model solutions, respectively (δ = –0.28…+0.44 %). The addition method was used for $KHSO_5$ determination in disinfectant "Ecocid S", RSD were 2.01 % and 1.88 % for c($KHSO_5$) = 4.65×10^{-5} and 7.75×10^{-5} mol L^{-1}, respectively. The obtained results have good agreement with those obtained by using the reference method of iodometric titration, with an accuracy lower than –0.42 %.

Keywords: potassium hydrogenperoxomonosulfate, voltammetry, carbositall electrode, disinfectant

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INTRODUCTION

Potassium hydrogenperoxomonosulfate ($KHSO_5$) is one of the most widely used disinfectants in a medical practice, among well-known class of chemical disinfectants – oxidants. It is included in the new generation of modern disinfection agents in the form of a stable triple potassium salt $2KHSO_5\cdot KHSO_4\cdot K_2SO_4$, such as "Virkon" and its modified analogue "Ecocid S". Potassium hydrogenperoxomonosulfate is also used as analytical reagent for quantitave analysis of different pharmaceutical substances such as penicillins, phenothiazines, cephalosporins and etc. [1].

Ecocid S (KRKA, Slovenia, Novo mesto) is a well known universal combination highly active broad-spectrum disinfectant of the new generation of the oxidant class, which has virulicidal, bactericidal, fungicidal and sporocidal activity, comprising $KHSO_5$ (50 %) in the form of a triple potassium salt – $2KHSO_5\cdot KHSO_4\cdot K_2SO_4$ (500 mg to 1 g of drug) (mass fraction of active oxygen in terms of active chlorine 9.5-15.0 %) as active ingredient and excipients: surfactant – sodium dodecylbenzenesulfonate, organic acids (malic and sulfamic acids), inorganic buffer systems (sodium polyphosphate, sodium chloride), an indicator of activity – azo dye and flavor of citron scent. $KHSO_5$ is an effective biocide; it works against all 18 known families of pathogenic for humans and animals viruses, Gram-positive and Gram-negative bacteria, some yeasts and fungi [2-9]. Organic acids in combination with inorganic buffer creates an acidic environment and optimize the biocidal activity of $KHSO_5$. Sodium dodecylbenzenesulfonate acts as a surfactant, thus ensuring oxidizer contact with pathogens.

The drug is intended for disinfection of all surfaces that require safe and effective disinfection. It is used for disinfection of livestock and poultry premises vivariums, pet cages, aquariums, plants for the processing of poultry and eggs, slaughter and meat processing plants, grain storage, feed mills, vehicles, containers, equipment, surfaces, appliances, instruments, systems supply drinking water, milk, air sanitation, drinking water and other facilities are subject to veterinary supervision.

It is used as aqueous solutions in the working concentrations of 0.1 to 4 %. To disinfect the hands 0.5 % solution is recommended.

Determination (mass fraction) of active oxygen (in terms of active chlorine) in the preparation is carried out by iodometric titration [10].

$KHSO_5$ in the preparation "Virkon" is determined by the technique of pH-potentiometric titration with standard solution of tin (II) chloride in the presence of potassium bromide using a point platinum and glass electrode [11].

Extensive literature survey reveals that various electrochemical methods have been reported for the determination of electrochemically active compounds of various classes, including hydrogen peroxide and inorganic peroxides analysis [12-16]. Among them the method of voltammetry with linear potential scan using a drop mercury electrode or its other modifications and solid platinum or gold electrodes is most commonly used. These electrodes are characterized by satisfactory reproducibility of research results and simple methods for their preparation. However, mercury is a toxic substance and other metals rather expensive. Also is known, that the oxygen chemosorbs on Au, as well as on Pt, and forms oxide film. Adsorbed oxygen is involved in the anodic process, and Au oxides inhibit processes of analyte electrooxidation. As a consequence the electrodes based on cheap carbon materials such as carbon glass, carbon paste, carbositall are widely used [17-20]. They are characterized by high overpotential (low adsorption capacity in relation to O_2 and H_2 in the work potential area) of hydrogen and/or oxygen (the ability to track multiple regeneration to obtain reproducible surface). In addition, these electrodes offer the ability to perform such analytical definitions which mercury or other electrodes are not always possible to. It has been very popular because of its excellent electrical and mechanical properties, wide potential range, extreme chemical inertness and relatively reproducible performance [21-27].

The aim of the present work is to determine the feasibility of quantitative determination of potassium hydrogenperoxomonosulfate in pure substance and disinfectant "Ecocid S" by cathodic voltammetry using carbositall electrode (Russia) as indicating (working) electrode.

EXPERIMENTAL SECTION

Instrumentation

Electrochemical measurements were carried out in the analyzer AVS-1.1 (Volta, St. Petersburg) with a three-electrode scheme by alternating 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 electrochemical sensor "Module EM-04" with an 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.

Scheme of the reduction process is:

$$\mathrm{HSO_5^-} + 2\bar{e} + 2\mathrm{H^+} \rightarrow \mathrm{HSO_4^-} + \mathrm{H_2O}$$

Reagents and Chemicals

All the materials were of analytical reagent grade, and the solutions were prepared with double-distilled water.

Background solution

Background solution is prepared by dissolving 68.1 g of potassium hydrogensulfate ($KHSO_4$) in 500 mL volumetric flask by double-distilled water to give a concentration of 1 mol L^{-1}.

Stock solution of pure substance

The solution of potassium hydrogenperoxomonosulfate («Oxone®», ACROS ORGANICS) was freshly prepared and standardized iodometrically. Stock solution were 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^{-3} mol L^{-1}. 10 mL of 9×10^{-3} mol L^{-1} $KHSO_5$ was diluted in 100 mL volumetric flask with double-distilled water to obtain a solution of 9×10^{-4} mol L^{-1} $KHSO_5$.

Working solutions of pure substance

Working standards were prepared by diluting different volumes of stock solution 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL with 10 mL of 1 mol L^{-1} background solution in 50 mL volumetric flask by double-distilled water.

Stock solution of the sample preparation

The sample preparation which was subjected to the analytical procedures for the analysis of $KHSO_5$ was disinfectant "Ecocid S" (KRKA, Slovenia, Novo mesto). This solution was prepared by dissolving 0.5 g of preparation (accurate weight) in 100 mL volumetric flask by double-distilled water to give a concentration of preparation 5 % (concentration of $KHSO_5$ in mass was 7.75×10^{-3} mol L^{-1}). 10 mL of this solution was diluted in 100 mL volumetric flask with double-distilled water to obtain a solution of 7.75×10^{-4} mol L^{-1} $KHSO_5$.

Working solutions of the sample preparation

Working solutions were prepared by diluting 3.0 and 5.0 mL of stock solution of the sample preparation with 10 mL of 1 mol L^{-1} background solution in 50 mL volumetric flask by double-distilled water.

Analytical procedure

Procedure of pure substance

25 mL of 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. All data were obtained at room temperature. The number of experiments (n = 5) according to this value, the statistical calculations were done for 3.6×10^{-5}, 4.5×10^{-5} and 5.4×10^{-5} mol L^{-1} solutions of $KHSO_5$.

Procedure for sample preparation

A typical procedure involves preparing several solutions containing the same amount of unknown, but different amounts of standard. For example, five 50 mL volumetric flasks are each filled with 3 mL or 5 mL of the unknown and then the standard is added in differing amounts, such as 0, 1, 2, and 3 mL. The flasks are then diluted to the mark and mixed well. 25 mL of each prepared solutions were 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 –1.2 V. All data were obtained at room temperature.

RESULTS AND DISCUSSION

Effect of nature and pH of background solution

The effect of pH on the reduction process was investigated by recording voltammograms of $KHSO_5$ at a 5.4×10^{-5} mol L^{-1} concentration at several pH values ranging from 0.80 to 7.17 (Fig. 1). A mixture of 0.5 mol L^{-1} Na_2SO_4 + 0.05 mol L^{-1} $KHSO_4$ was used as background solution and the pH of the solution from 0.80 to 7.17 was changed gradually adding NaOH 0.2 mol L^{-1}. The pH was measured using ionmeter type I-160M (Belarus) with a glass electrode type ESL-43-07 paired with Ag, AgCl/KCl (sat) electrode.

As can be seen, height of $KHSO_5$ reduction peak at the carbositall electrode surface decreases and potential of reduction peak is shifted toward more electronegative values with increasing of background electrolyte pH from 0.80 to 7.17.

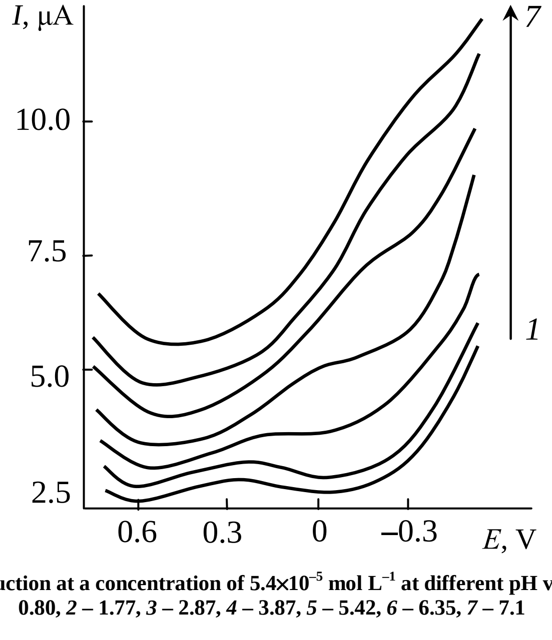

Fig. 1. Voltammogram of $KHSO_5$ reduction at a concentration of 5.4×10^{-5} mol L^{-1} at different pH values of the background solution: *1* – 0.80, *2* – 1.77, *3* – 2.87, *4* – 3.87, *5* – 5.42, *6* – 6.35, *7* – 7.1

The maximum peak (I_p) occurs at approximately pH 0.8 and at a pH around 5 analytical signal almost disappears (Fig. 2). The effect of pH on peak potential (E_p) shows the following: when pH value increases in the interval from 0.8 to 2, E_p remains almost constant, but E_p decreases sharply to negative value with pH increasing (Fig. 3). That is why the optimum pH for analysis is ≤ 2.

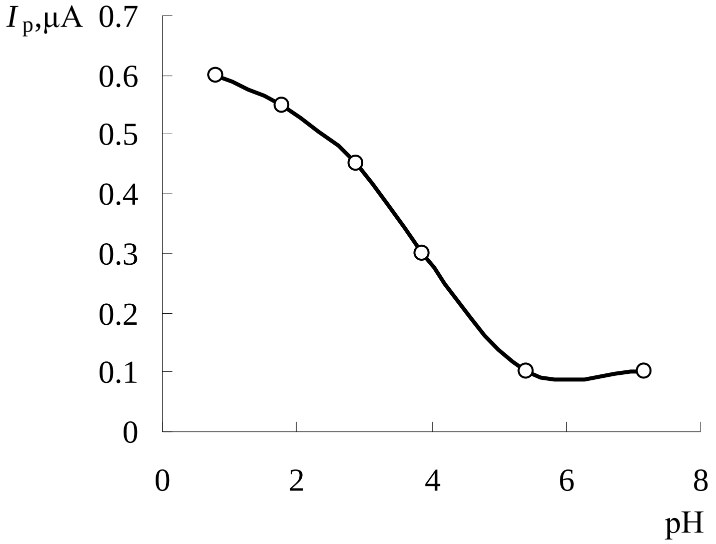

Fig. 2. Influence of pH on the peak intensity of the reduction process of $KHSO_5$ at the carbositall electrode (reference electrode Ag,AgCl/KCl(sat))

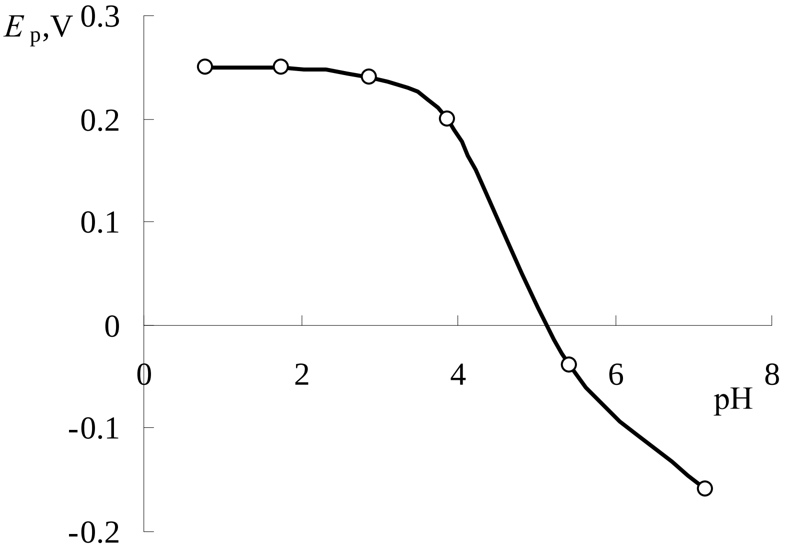

Fig. 3. Influence of pH on the peak potential of the reduction process of $KHSO_5$ at the carbositall electrode (reference electrode Ag,AgCl/KCl(sat))

Effect of surfactant

Surfactants are a kind of amphiphilic molecule with a polar group on one side and a long hydrophobic tail on the other. The variety of currently available surfactants and hence their properties makes it possible to use this group of compounds for controlling analytical signals in voltammetry and, consequently, to increase the sensitivity and selectivity of the analyte response. The applications of surfactants in electrochemistry and electroanalytical chemistry have been widely reported [28,29].

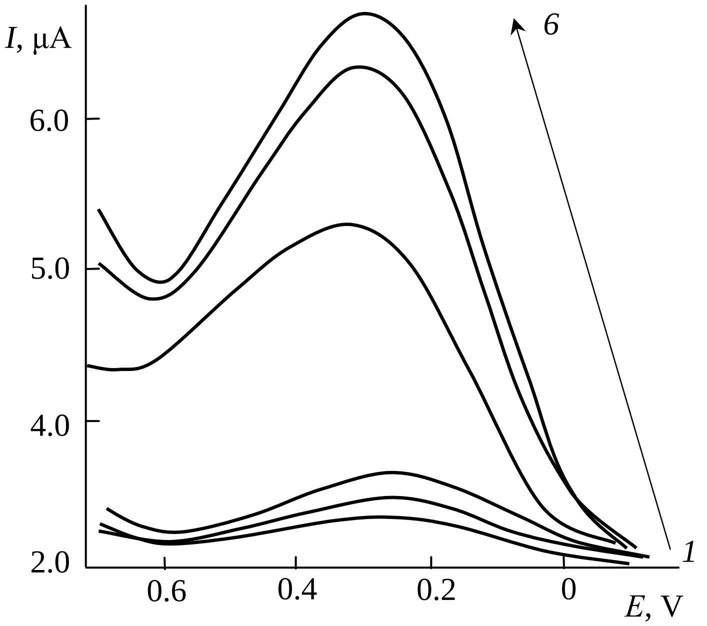

Fig. 4. Voltammogram of $KHSO_5$ reduction depending on the concentration in the absence (curves *1-3*) and in the presence of surfactants (0.05 % solution of SDBS) (curves *4-6*). *c*($KHSO_5$), 10^{-5}, mol L^{-1}: *1, 4* – 1.8, *2, 5* – 5.4, *3, 6* – 9.2, with SDBS: *4* – 1.8, *5* – 5.4, *6* – 9.2 (background – 0.2 mol L^{-1} $KHSO_4$) at carbositall electrode(reference electrode Ag,AgCl/KCl(sat))

The electrochemical responses of $KHSO_5$ at carbositall electrode were shown in Fig. 4 (curves 1-3) with 0.2 M $KHSO_4$ as background solution. The voltammetric response is apparently improved in the presence of 0.05% sodium dodecylbenzenesulfonate (SDBS), reflected by the enlargement of current peak (Fig. 4, curves 4-6) and the reduction peak shifted to more electropositive side from +0.25 V to +0.3 V. The peak current enhancement was undoubtedly attributed to the interaction of SDBS with $KHSO_5$ and carbositall electrode. It is well known that surfactants can be adsorbed on hydrophobic surface to form surfactant film, which may alter the overvoltage of the electrode and influence the rate of electron transfer [30,31]. The probable mechanism is following: the SDBS surfactant molecule diffuses into the carbositall electrode along with the $KHSO_5$ signal.

Method of quantitative determination of $KHSO_5$ in pure substance

Voltammetric behavior of $KHSO_5$ at carbositall electrode was shown in Fig. 5. The study was conducted in solutions with a concentration of $KHSO_5$ 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).

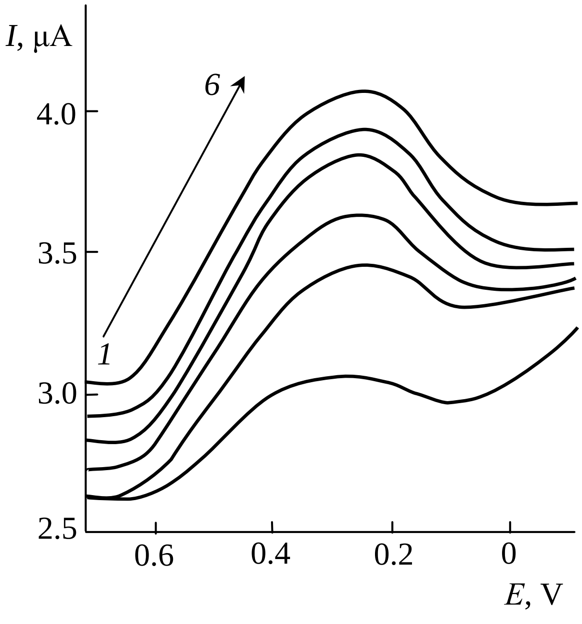

Fig. 5. Voltammogram of $KHSO_5$ reduction at carbositall electrode according to the concentration. *c* ($KHSO_5$), 10^{-5}, mol L^{-1} *1* – 0.9, *2* – 1.8, *3* – 2.7, *4* – 3.6, *5* – 4.5, *6* – 5.4; pH ~0.8 (background is $KHSO_4$, *c* = 0.2 mol L^{-1}); E_p = 0.25 V (reference electrode Ag, AgCl/KCl(sat))

The calibration curves method is used to quantify the concentration of $KHSO_5$. The graph was plotted in the coordinates: the height of peaks I_p in μA at 0.25 V on the ordinate axis and corresponding concentration of $KHSO_5$ c in mol L^{-1} on the abscissa axis (Fig. 6).

Regression characteristics of $KHSO_5$ voltammetric determination procedure in pure substance was shown in Tab. 1.

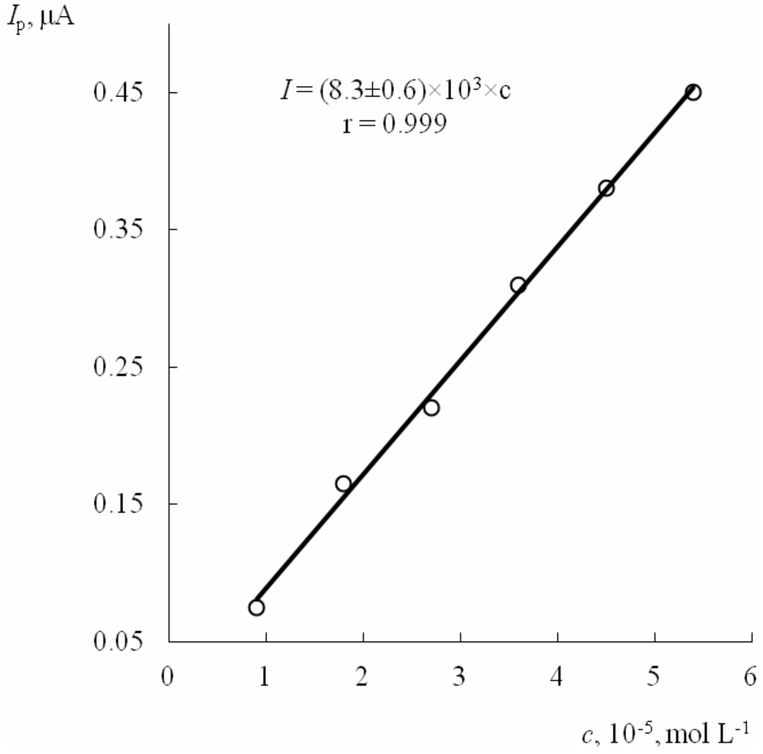

Fig. 6. The calibration plot of the $KHSO_5$ reduction current peak vs. concentration with 0.2 mol L^{-1} $KHSO_4$ background solution (pH ~ 0.8) at carbositall electrode (reference electrode Ag,AgCl/KCl(sat)); E_p = 0.25 V

Table 1: Regression characteristics of $KHSO_5$ voltammetric determination procedure in pure substance

Parameters	Data
Concentration ranges (mol L^{-1})	$(0.9\text{-}5.4)\times10^{-5}$
Regression equation	$I_p = (8.3 \pm 0.6)\times10^3\times c$
Slope (a)	8.3×10^3
Intercept (b)	0.006
Δa	0.6×10^3
Δb	0.02
S_a	0.2×10^3
S_b	0,007
Correlation coefficient (r)	0.999
LOD (mol L^{-1})	2.76×10^{-6}
LOQ (mol L^{-1})	9.19×10^{-6}

The reproducibility was evaluated from 5 repeated electrochemical signal measurements of model solutions with 3.6×10^{-5}, 4.5×10^{-5} and 5.4×10^{-5} mol L^{-1} concentrations of $KHSO_5$. The precision of the developed method in terms of the relative standard deviation (RSD) were 2.68 %, 2.55 % and 2.39 % (δ = –0.28…+0.44 %), respectively. The obtained results are summarized in Tab. 2.

Table 2: Evaluation of accuracy and precision of $KHSO_5$ voltammetric determination procedure in model solution of pure substance (n = 5; P = 0.95%)

Taken (mol L^{-1})	Found (mol L^{-1})	Recovery (%±SD)	RSD, %	ε (%)	δ (%)
3.6×10^{-5}	$(3.59\pm0.12)\times10^{-5}$	99.7±3.3	2.68	3.3	–0.28
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

Method of quantitative determination of $KHSO_5$ in "Ecocid S"

It was found that SDBS, which is the part of the test solution of sample preparation, cause the $KHSO_5$ reduction current peak increase, so it was decided to use the addition method for analysis of the preparation.

At first voltammogram of test solution was recorded and then a solution of known aliquots of standard solution C_{st} was added and again voltammogram was recorded. The concentration of the test solution C_x is given by the equation:

$$C_x = C_{st} \frac{I_x}{I_{x+st} - I_x},$$

where I_x – current peak of test solution; I_{x+st} – current peak of test solution with the addition of a standard substance. The high sensitivity of this method is accompanied by very good reproducibility. During the determination of 4.65×10^{-5} and 7.75×10^{-5} mol L^{-1} $KHSO_5$ in test solutions RSD were 2.01 % and 1.88 % (δ = –0.42…–0.30%), respectively ($n = 5$, $P = 0.95$). The obtained results are summarized in Tab. 3.

Table 3: The results of voltammetric determination of potassium hydrogenperoxomonosulfate in Ecocid S (n = 5; P = 0.95%)

Taken		Found		Recovery (%±SD)	RSD, %	ε (%)	δ** (%)
mol L^{-1}	% *	mol L^{-1}	%*				
4.65×10^{-5}	11.01	$(4.63\pm0.12)\times10^{-5}$	10.96	99.57±2.49	2.01	2.5	–0.42
7.75×10^{-5}	11.01	$(7.72\pm0.18)\times10^{-5}$	10.95	99.64±2.32	1.88	2.3	–0.30

** in terms of active chlorine in preparation [10]*

*** relative to the average reference method of iodometric titration [10]*

CONCLUSION

So, new voltammetric method of aqueous solutions of potassium hydrogenperoxomonosulfate determination in pure substance and disinfectant "Ecocid S" using carbositall electrode as indicating electrode was developed and the possibility of its quantitative determination was shown.

Linear concentration ranges for pure substance varies from $(0.9\text{-}5.4)\times10^{-5}$ mol L^{-1}. Calibration graph is $I_p = (8.3 \pm 0.6)\times10^3\times c$ (r = 0.999). 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^{-1}concentrations of $KHSO_5$ model solutions, respectively (δ = –0.28…+0.44 %). The addition method was used for $KHSO_5$ determination in disinfectant "Ecocid S", RSD were 2.01 % and 1.88 % for $c(KHSO_5) = 4.65\times10^{-5}$ and 7.75×10^{-5} mol L^{-1}, respectively. The obtained results have good agreement with those obtained by using the reference method of iodometric titration, with an accuracy lower than –0.42 %.

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