QUANTITATIVE DETERMINATION OF POTASSIUM HYDROGENPEROXOMONOSULFATE IN “ECOCID S” DISINFECTANT BY CATHODIC VOLTAMMETRY

M.Ye.Blazheyevskiy, O.O.Mozgova
National University of Pharmacy

Key words: potassium hydrogenperoxomonosulfate; voltammetry; carbositall electrode; SDBS; disinfectant

The electrochemical behaviour of potassium hydrogenperoxomonosulfate (KHSO₄) in the presence of sodium dodecylbenzenesulfonate (SDBS) has been studied using cathodic voltammetry at the carbositall electrode as indicating in the potential range of +1.0…–1.2 V (the reference electrode Ag, AgCl/KCl(sat)) (E₀ = +0.3 V). It has been experimentally proven that the height of KHSO₄ reduction peak decreases and the potential of the reduction peak is shifted toward more electronegative values with increasing of the background electrolyte pH from 0.80 to 7.17. The maximum peak (Iₚ) occurs at a pH of approximately 0.8 and at a pH around 5 the analytical signal almost disappears. The effect of pH on the peak potential (Eₚ) shows the following: when the pH value increases in the interval from 0.8 to 2, Eₚ remains almost constant, but Eₚ decreases sharply to the negative value with pH increasing over 2. It has been experimentally proven that SDBS leads to increase of the current peak and the peak potential shifts to the more electropositive side (+0.25→+0.3V). The influence of the present SDBS has been examined. The current peak increases with the concentration of the surfactant up to 1.2×10⁻⁵ mol L⁻¹ and then stays almost constant with the increase in the concentration of SDBS above 3.0×10⁻⁴ mol L⁻¹. The linear relationship was observed in the KHSO₄ concentration range of (1.8–9.0)×10⁻⁵ mol L⁻¹, the calibration curve equation was Iₚ = (4.3±2.1)×10⁻⁶ c (⁰ = 0.998). When determining KHSO₄ in the test solution of “Ecocid S” disinfectant with the concentrations of 4.65×10⁻⁵, 6.20×10⁻⁵ and 7.75×10⁻⁵ mol L⁻¹ the RSDs were 0.025, 0.023 and 0.021, respectively (⁰ = –0.64 ... +0.16%); LOD = 6.50×10⁻⁶ mol L⁻¹, LOQ = 2.17×10⁻⁵ mol L⁻¹.

Potassium hydrogenperoxomonosulfate (KHSO₄) is one of the most widely used disinfectants in 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 a stable complex disinfectant in the form of a stable granulated water-soluble powder, which contains KHSO₄ (50%) and such excipients as a surfactant – sodium dodecylbenzenesulfonate (SDBS to 15%), organic acids (malic and sulfamic acids), inorganic buffer systems (sodium polyphosphate, sodium chloride), an indicator of activity – azo dye and flavour with a citron odour. It is characterized by the broad-spectrum antimicrobial activity to bacteria, viruses, fungi, as well as to Mycobacterium tuberculosis [2, 4, 7–9]. It does not have the sensitizing and local irritative effect to the skin and is slightly irritating to the mucous membranes in regulated concentrations (0.5–4% by the active substance). Working solutions remain active for 7 days. It does not have the corrosive action and the negative impact on the surface treated. It is applied for preventive and forced disinfection. SDBD acts as a surfactant, thus providing a contact with the pathogen oxidant; reacts with membrane lipids and proteins causing denaturation of the cell membranes.

Determination (mass fraction) of active oxygen (in terms of active chlorine) in the product is carried out by iodometric titration [15].

Scientific literature describes quantitative determination of KHSO₄ in “Virkon” disinfectant by the method of pH-potentiometric titration with the standard solution of tin (II) chloride in the presence of potassium bromide using a point platinum and glass electrode [5].

Extensive literature survey reveals that various electrochemical methods have been reported for determination of electrochemically active compounds of various classes, including hydrogen peroxide and inorganic peroxides analysis [11, 13, 14, 20, 21]. Among them the method of voltammetry with the 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 are rather expensive. It is also known that oxygen chemosorbs on Au, as well as on Pt, and forms oxide films. Adsorbed oxygen is involved in the anodic process, and Au oxides inhibit processes of the analyte electrooxidation. Thus, the electrodes based on cheap carbon materials such as carbon glass, carbon paste, carbositall are widely used [6, 12, 19]. They are characterized by high overpotential (low adsorption capacity in relation to O₂ and H₂ in the poten-
tial work 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 determinations, which mercury or other electrodes are not always possible to do. It has been very popular because of its excellent electrical and mechanical properties, a wide potential range, extreme chemical inertness and relatively reproducible performance [10, 16, 17].

It has been previously proven that SDBS leads to increase of the KHSO₄ reduction peak at the carbotissalt electrode and the addition method was used for KHSO₄ determination in “Ecocid S” disinfectant, which contains SDBS surfactant [3].

In the present work the results of elaboration of the quantitative determination method for KHSO₄ in the presence of SDBS by cathodic voltammetry at the carbotissalt electrode using the method of the calibration graph are presented.

Experimental Part
The solution of KHSO₄ (“Oxone®”, ACROS ORGANICS) was freshly prepared and standardized iodometrically. The stock solution was prepared by dissolving 0.1537 g of the powder (triple potassium salt, 2KHSO₄-K₂SO₄) in a 50 mL volumetric flask by double distilled water to give the concentration of 9×10⁻² mol L⁻¹. 10 mL of 9×10⁻¹ mol L⁻¹ solution of KHSO₄ was diluted in a 100 mL volumetric flask with double distilled water to obtain 9×10⁻³ mol L⁻¹ of KHSO₄ solution.

The solution of SDBS was prepared by dissolving 6.96 g of the powder in a 100 mL volumetric flask by double distilled water to give the concentration of 0.2 mol L⁻¹. The background solution was prepared by dissolving 68.1 g of potassium hydrosulfate (KHSO₃) in a 500 mL volumetric flask by double distilled water to give the concentration of 1 mol L⁻¹.

The pH was measured using an ionmeter of I-160M type (Belarus) with a glass electrode of ESL-43-07 type paired with Ag, AgCl/KCl (sat) electrode.

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

The scheme of the reduction process is as follows:

\[ \text{HSO}_3^- + 2e^- + 2H^+ \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} \]

Results and Discussion
The effect of the nature and pH of the background solution
It has been experimentally proven that the height of KHSO₄ reduction peak at the carbotissalt electrode surface decreases, and the potential of the reduction peak is shifted toward more electronegative values with increasing of the background electrolyte pH from 0.80 to 7.17. The maximum peak (Iₚ) occurs at the pH of approximately 0.8, and at the pH around 5 the analytical signal almost disappears. The effect of pH on the peak potential (Eₚ) shows the following: when the pH value increases in the interval from 0.8 to 2, Eₚ remains almost constant, but Eₚ decreases sharply to a negative value with pH increasing over 2. That is why the optimum pH for analysis is ≤7 [3].

The effect of a surfactant
It has been experimentally proven that SDBS leads to increase of the current peak and the peak potential shifts to more electropositive side (+0.25 → +0.3V) (Fig. 1).

The current increases probably due to alleviation of desorption of reduction products from the electrode surface, and acceleration of the electron transfer in the course of electrochemical reactions is caused by the ability of SDBS to adsorb on the hydrophobic surface of the electrode and to form a surface film that changes the over-pressure [1, 19, 23].

The influence of the present SDBS was examined. The current peak increases with the concentration of the surfactant up to 1.2×10⁻³ mol L⁻¹ and then stays almost constant with the increase in the concentration of SDBS above 3.0×10⁻³ mol L⁻¹ (Fig. 1). That is why the optimum SDBS concentration for analysis is ≥3.0×10⁻³ mol L⁻¹.

It is known that Ecocid S disinfectant contains SDBS in the amount of 15% of the total content, i.e. in 0.5% of the working solution the concentration of SDBS is about 7.5×10⁻⁴ mol L⁻¹. So, it was decided to use the method of the calibration graph to quantify the concentration of KHSO₄ in “Ecocid S” in the presence of SDBS excess (4.0×10⁻⁴ mol L⁻¹).

The procedure of obtaining results for the calibration graph
Working solutions were prepared by diluting 1.00, 2.00, 3.00, 4.00 and 5.00 mL of the stock solution with 10 mL of 1 mol L⁻¹ background solution and 1 mL of
0.2 mol L⁻¹ SDBD each in a 50 mL volumetric flask by double distilled water. 25 mL of the working solution of a pure substance was transferred to the cell. The voltamgrams 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.

The graph was plotted in the following coordinates: the height of peaks \( I_p \) in μA at 0.3 V on the ordinate axis and the corresponding concentration of KHSO₅ \( c \) in mol L⁻¹ on the abscissa axis (Fig. 2).

Analytical characteristics of the calibration graph of the KHSO₅ voltammetric determination procedure are given in Tab. 1.

The procedure for quantitative determination of KHSO₅ in “Ecocid S”

The test solution was prepared by dissolving 0.5 g of the powder in a 100 mL volumetric flask by double distilled water to give the concentration of 7.75×10⁻³ mol L⁻¹. 10 mL of 7.75×10⁻³ mol L⁻¹ KHSO₅ was diluted in a 100 mL volumetric flask with double distilled water to obtain 7.75×10⁻⁴ mol L⁻¹ of KHSO₅ solution.

Working solutions were prepared by diluting 3.00, 4.00 and 5.00 mL of the stock solution with 10 mL of 1 mol L⁻¹ background solution and 1 mL of 0.2 mol L⁻¹ SDBD each in a 50 mL volumetric flask by double distilled water. 25 mL of the working solution of a pure substance was transferred to the cell. The voltammo-

grams were recorded by scanning the potential toward the negative direction in the potential range from +1.0 V to −1.2 V.

The KHSO₅ content \( C_s \) mol L⁻¹ was calculated by:

\[
C_s = \frac{I_p - b}{a}
\]

The high sensitivity of this method is accompanied by a very good reproducibility. The reproducibility was evaluated by 5 repeated electrochemical signal measurements of model solutions with the concentrations of KHSO₅ of 3.6×10⁻⁵, 4.5×10⁻⁵ and 5.4×10⁻⁵ mol L⁻¹. The precision of the method developed in terms of the relative standard deviation (RSD) was 0.025, 0.023 and 0.021 (δ = 0.64...+0.16 %), respectively. The results obtained are summarized in Tab. 2.

CONCLUSIONS

Thus, a new voltammetric method of PMS determination in the presence of SDBS at the carbositall electrode using the method of the calibration graph has been developed and the possibility of its quantitative determination has been shown.

The linear dependence is observed in the PMS concentration range (1.8-9.0)×10⁻⁴ mol L⁻¹, the calibration curve equation is \( I = (4.3±1.1)×10^c \) (r = 0.998); RSD = 0.025...0.021 and δ = 0.64...+0.16% (n = 5; P = 0.95%), LOD = 6.50×10⁻⁶ mol L⁻¹, LOQ = 2.17×10⁻⁵ mol L⁻¹.

### Table 1

| Parameters                        | Value          |
|----------------------------------|----------------|
| Concentration ranges (mol L⁻¹)   | (1.8-9.0)×10⁻⁵|
| Regression equation              | \( I_p = (4.3±1.1)×10^c \) |
| \( a \)                          | 4.3×10⁴        |
| \( b \)                          | 0.04           |
| \( S_a \)                        | 2.6×10⁳        |
| \( S_b \)                        | 0.09           |
| δ\( a \)                         | 1.1×10⁴        |
| δ\( b \)                         | 0.41           |
| Correlation coefficient (r)      | 0.998          |
| LOD (mol L⁻¹)                    | 6.50×10⁻⁶      |
| LOQ (mol L⁻¹)                    | 2.17×10⁻⁵      |

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

### Table 2

| Taken, mol L⁻¹ | Found, mol L⁻¹ | Reproducibility (%±SD) | RSD, % | ε (%) | δ (%) |
|----------------|----------------|------------------------|--------|-------|-------|
| 4.65×10⁻⁵      | (4.63±0.14)×10⁻⁵ | 99.57±2.49            | 0.025  | 3.1   | -0.43 |
| 6.20×10⁻⁵      | (6.21±0.13)×10⁻⁵ | 100.22±3.01           | 0.023  | 3.0   | +0.16 |
| 7.75×10⁻⁵      | (7.70±0.20)×10⁻⁵ | 99.64±2.32            | 0.021  | 2.55  | -0.64 |
КІЛЬКІСНЕ ВИЗНАЧЕННЯ ГІДРОГЕНПЕРОКСОМОНОСУЛЬФАТУ КАЛІЮ У ДЕЗІНФЕКЦІЙНОМУ ЗАСОБІ “ЕКОЦИД С” МЕТОДОМ ВОЛЬТАМПЕРОМЕТРІЇ

М.Є.Блажеєвський, О.О.Мозгова

Ключові слова: калію гідрогенпероксомоносульфат; вольтамперометрія; вуглеситаловий електрод; NaДБС; дезінфекційний засіб

Методом катодної вольтамперометрії з використанням як індикаторного вуглеситалового електрода вивчено електрохімічну поведінку калію гідрогенпероксомоносульфату (KHSO₅) у присутності поверхнево-активної речовини натрію додецилбензенсульфонату (NaДБС) на фоні 0,2 моль/л розчину KHSO₄ в інтервалі потенціалів Еₚ = +1,0… –1,2 В (відн. нас. ХСЕ) (Eₚ = +0,3 В).

Було встановлено, що зі збільшенням рН середовища фонового електроліту від 0,80 до 7,17 висота піку відновлення KHSO₅ зменшується, а потенціал піку відновлення зсувається у бік більш електронегативних значень, причому при рН біля 5 аналітичний сигнал практично зникає. Максимальний пік (Iₚ) спостерігався при pH 0,8-2, а також за цих умов потенціал піку практично не змінювався. Експериментально встановлено, що NaДБС, котрий входить до складу випробовуваного засобу, призводить до збільшення сили струму у максимумі піку та зсуває потенціал піку у більш електропозитивний бік (+0,25→+0,3 В). Вивчення впливу концентрації NaДБС на висоту піку відновлення KHSO₅ показало, що при ростанні концентрації NaДБС до 1,2·10⁻³ моль/л висота піку стрімко зростає, а при досягненні 3,0·10⁻³ моль/л залишається практично незмінною. Лінійна залежність спостерігалася у діапазоні концентрацій KHSO₅ (1,8-9,0)·10⁻³ моль/л, рівняння градуального графіка: Iₚ = (4,3±1,1)·10⁻⁶р (r = 0,998). При визначенні KHSO₅ у розчинах дезінфекційного засобу “Екоцид С” з концентраціями 4,65·10⁻⁵, 6,20·10⁻⁵ і 7,75·10⁻⁵ моль/л RSD дорівнювало 0,025, 0,023 та 0,021, відповідно (δ = –0,64...+0,16%); LOD = 6,50·10⁻⁶ моль/л, LOQ = 2,17·10⁻⁵ моль/л.
КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ ГИДРОГЕНПЕРОКСОМОНОСУЛЬФАТА КАЛИЯ В ДЕЗИНФЕКЦИОННОМ СРЕДСТВЕ «ЭКОЦИД С» МЕТОДОМ ВОЛЬТАМПЕРОМЕТРИИ Н.Е.Блажеевский, Е.А.Мозговая

Ключевые слова: гидрогенпероксомоносульфат калия; вольтамперометрия; углеситаловый электрод; NaДБС; дезинфирующее средство

Методом катодной вольтамперометрии с использованием катионного углеситаллового электрода изучено электрохимическое поведение гидрогенпероксомоносульфата калия (KHSO₅) в присутствии поверхностно-активного вещества додецилбензенсульфоната натрия (NaДБС) на фоне 0,2 моль/л раствора KHSO₄ в интервале потенциалов Е = +1,0...–1,2 B (отн. нас. ХСЕ) (Eₚ = +0,3 B). Было установлено, что при увеличении рН среды фонового электролита от 0,80 до 7,17 высота пика восстановления KHSO₅ уменьшается, а потенциал пика восстановления сдвигается в сторону более электротрицательных значений, причем при рН около 5 аналитический сигнал практически исчезает. Максимальный пик (Iₚ) наблюдался при рН 0,8-2, а также в этих условиях потенциал пика практически не изменяется. Экспериментально установлено, что NaДБС, который входит в состав исследуемого средства, приводит к увеличению силы тока в максимуме пика и сдвигает потенциал пика в более электроположительную сторону (+0,25→+0,3 B). Изучение влияния концентрации NaДБС на высоту пика восстановления KHSO₅ показало, что при увеличении концентрации NaДБС до 1,2·10⁻³ моль/л высота пика стремительно увеличивается, а при достижении 3,0·10⁻³ моль/л остается практически неизменной. Линейная зависимость наблюдалась в диапазоне концентраций KHSO₅ (1,8-9,0)·10⁻⁵ моль/л, уравнение градуировочного графика: Iₚ = (4,3±1,1)·10⁴ с (r = 0,998). При определении KHSO₅ в растворах дезинфирующего средства «Экоцинд С» с концентрациями 4,65·10⁻⁵, 6,20·10⁻⁵ и 7,75·10⁻⁵ моль/л относительное стандартное отклонение (RSD) составило 0,025, 0,023 и 0,021 соответственно (δ = –0,64…+0,16 %); LOD = 6,50·10⁻⁶ моль/л, LOQ = 2,17·10⁻⁵ моль/л.