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# Composite Electrode on the Basis of Spectral Coal Modified by Nanoparticles of Manganese Dioxide and its Application for Determination of Hydrogen Peroxide

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**ABSTRACT:** A procedure is described for manufacturing a composite electrode based on carbon graphite powder and manganese dioxide nanoparticles deposited on its surface, obtained during the reduction reaction of potassium permanganate with manganese (II) ions from aqueous solutions. Using the methods of scanning electron microscopy and X-ray diffraction analysis, the success of the modification of carbon powder with nanoparticles of manganese dioxide with sizes of 20-55 nm was proved. For bulk modification of the electrode, paraffin was used as a binder. Design features and a method for manufacturing an electrode for determination hydrogen peroxide are described. Electrochemical studies of the behavior of the composite  $MnO_2 / C$  electrode were carried out using cyclic and differential-pulse voltammetry methods. The  $MnO_2 / C$  electrode showed electrocatalytic activity in the anode region of potentials in the presence of  $H_2O_2$  with a maximum peak of the anode current at pH 7.2–7.4. The optimal scanning speed of potentials in the range of -0.1 -1.0 V is 0.05-0.1 V / s. In this case, the anode peak appears at 0.72 V and the cathode peak at 0.68 V. The linear response of the electrode signal is observed in the concentration range of hydrogen peroxide of 0.1 - 3.0 mM. The detection limit of  $H_2O_2$  calculated by the 3  $\sigma$ -method taking into account the slope of the graph is 0.03 mM. The composite  $MnO_2 / C$  electrode was tested in determining the actual content of hydrogen peroxide in a 3% aqueous solution of hydrogen peroxide, may be found at any pharmacy shop. The results of determining the content of hydrogen peroxide in the samples by permanganometric titration and voltammetry with a  $MnO_2 / C$  composite electrode are compared. Good convergence and reproducibility of the analysis results obtained by these two independent methods are shown. The simplicity of manufacturing composite electrodes volume-modified with manganese dioxide, their excellent performance, low cost, and the results of the determination of hydrogen peroxide, allow their use in the design of various biosensor systems.

**KEYWORDS:** composite electrodes, carbon paste electrodes, modification, manganese dioxide, hydrogen peroxide, voltammetric determination.

## I. INTRODUCTION

Carbon-containing paste electrodes are widely used in the electroanalytical determination of a number of inorganic and organic analytes. Moreover, modification of their surface or volume opens up new prospects for voltammetric

analysis and biosensorics. Researchers are particularly interested in the possibility of such a modification of carbon-containing electrodes, which allows one to obtain a catalytic response in the presence of organic substances. In this regard, metal oxide electrodes have a unique property compared to metal or carbon electrodes, since they are often able to exhibit catalytic activity due to redox processes due to various redox pairs of the metal state in the oxide, as well as practically absent hydrogen adsorption on their surface.

Among these metal oxides exhibiting catalytic activity, manganese oxides are of particular interest, in particular manganese dioxide, which has found its application as a selective heterogeneous catalyst [11,15,29,34,37], adsorbent [41,44], and electrode materials for highly efficient capacitors [9,12,20,35,39] galvanic and fuel cells [32,40].

It is fair to say that the very idea of modifying carbon-containing electrodes with manganese dioxide is not the first time. At various times, various researchers modified the surface or volume of carbon-containing electrodes with a film or MnO<sub>2</sub> micro / nanoparticles. At the same time, each of the authors applied their modification techniques, which were not simple and achieved positive reproducible results.

For example, Taba and Wang [31] deposited a MnO<sub>2</sub> film from a MnCl<sub>2</sub> / NaOH solution on the surface of a glassy carbon electrode. Such an electrode demonstrated a fairly stable and effective oxidation of a number of substances, such as hydrogen peroxide, hydrazine in basic analytes.

Since the electrocatalytic properties of carbon-modified electrodes depend on the physical and chemical state of the electrode surface, it is obvious that such a modification requires a careful choice of the method of film preparation [7,13]. Various approaches are usually used for this, including physical sorption of manganese-containing electrolytes followed by hardening of the film on the surface of the modified electrode by electrochemical methods, in particular, cyclic voltammetry [8,27]. However, such modification methods are considered rather complex, time-consuming and do not guarantee long-term operation of the modified electrode, since the manganese dioxide film in contact with the electrolyte undergoes cracks and thinning during electrochemical processes.

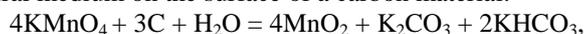
This problem was partially solved by bulk modification of the carbon paste electrode with micro / nano particles of manganese dioxide.

Bai et al. [6] manufactured modified MnO<sub>2</sub> nanoparticles exhibiting catalytic activity with respect to hydrogen peroxide.

Mehmeti E. and colleagues made a carbon paste electrode, volume-modified with 5% microparticles (5 μm) of manganese dioxide, which was successfully used in the voltammetric determination of riboflavin (vitamin B<sub>2</sub>) in some model and real objects [23]. The authors of this article also produced an electrode that was bulk-modified with 10% finely divided MnO<sub>2</sub> and validated the voltammetric method for determining vitamin B<sub>2</sub> in pharmaceuticals. [1].

One cannot ignore the work [21] in which the procedure for volumetric modification of the carbon paste electrode MnO<sub>2</sub> is described. This modification consisted in impregnating the coal powder with a 5 M solution of manganese nitrate, followed by a long (at least 8-10 hours) calcination of the composite mass at a temperature of 520 °C. During this, thermal decomposition of manganese nitrate to its dioxide was expected. Then, an indicator electrode was formed from the obtained composite mass using epoxy resin, which was used in the voltammetric determination of hydrogen peroxide, ascorbic acid and nitrite ions. The disadvantages of manufacturing an MnO<sub>2</sub> / C electrode by this method include the complexity and duration of the preparation of a composite electrode suitable for voltammetric and chrono-amperometric measurements.

In articles [30,38] described a method for producing manganese dioxide nanoparticles by direct reduction of potassium permanganate in a neutral medium on the surface of a carbon material:



where the reaction time is 8 hours or more. Such a slow reaction can become a serious obstacle to the scaling and commercialization of this technology, which is noted in an article by D. G. Gromadsky [17], who improved the hydrothermal synthesis technology by accelerating the formation of manganese dioxide by introducing an additional reagent, a reducing agent, into the reaction mixture, which would be easily removed at the end of the synthesis without contaminating the finished composite. Isopropyl alcohol (IPA) could play the role of such a reducing agent.

A paste carbon electrode was formed from MnO<sub>2</sub> washed with distilled water and dried precipitate by mixing with paraffin oil. Despite the fact that this method is also not without drawbacks, it raises the idea that it is possible to obtain the MnO<sub>2</sub> / C composite by chemical methods using the appropriate red-ox reactions, which are so diverse for manganese compounds in various oxidation states.

The purpose of this work is to obtain a composite MnO<sub>2</sub> / C electrode based on carbon graphite powder and manganese dioxide nanoparticles deposited on its surface, obtained during the reduction reaction of potassium permanganate with manganese (II) ions from aqueous solutions, and its testing in the determination of hydrogen peroxide.

## II. EXPERIMENTAL

As precursors for the production of MnO<sub>2</sub> nanoparticles, the reaction was used



All reagents KMnO<sub>4</sub>, MnCl<sub>2</sub> • 4H<sub>2</sub>O, KCl, Na<sub>2</sub>HPO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> (30%), etc., were purchased by the Shanghai Chemical Reagent Company (China) and were qualified as “chemically pure” and “pure for analysis”. A phosphate buffered saline (PBS) with the required pH value was obtained by mixing different volumes of Na<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> solutions in accordance with the reference manual [18]. The desired pH value was achieved by adding 0.2 M HCl or 0.2 M NaOH to the buffer solution. The pH was measured using an I-130M ionomer (Russia) with a glass pH sensitive electrode ESL-63-07. The concentration of hydrogen peroxide was established weekly by the permanganate method [16]. The concentration of the obtained solutions was also controlled spectrophotometrically taking into account the molar absorption coefficient  $\epsilon_{230\text{ nm}} = 72.7\text{ M}^{-1} \cdot \text{cm}^{-1}$  [24] using an SF-2000 UV-Vis spectrophotometer (LOMO, Saint-Petersburg.) The concentration was calculated by the formula:  $C = \frac{A}{\epsilon}$ , where A is the optical density of the solution, and  $\epsilon$  is the molar absorption (extinction) coefficient [28].

### 2.1. APPARATUS

Voltammetric measurements were carried out on a computerized voltammetric complex based on the PU-1 polarograph (ZIP Gomel, Belarus) using a three-electrode cell from spare parts and accessories of the device [2].

The working electrode was made of carbon-graphite powder modified with manganese dioxide obtained from carbon-graphite rods for spectral analysis of SU-3 and paraffin. A platinum wire with a diameter of 0.4 mm was used as an auxiliary electrode. The EVL-1M3 chloride – silver electrode saturated with KCl served as the reference electrode. Before starting the experiments, the analyzed solution was purged with air freed from oxygen and carbon dioxide by sparging through a strongly alkaline pyrogallol solution.

The work also used special and general laboratory equipment.

Micrographs of the modified carbon powder were obtained on a scanning electron microscope of the brand Shimadzu SSX-550 (Japan). X-ray diffraction patterns were recorded on a Shimadzu XRD-7000 diffractometer (Japan), CuK $\alpha$  radiation, a graphite monochromator. The analysis was carried out using the computer database ICDD (International Center for Diffraction Data) PDF-2.

Of the general-purpose equipment, a UN30 drying oven (Memmert, Germany), magnetic and electromechanical mixers MR25 (Germany) with an adjustable mixing speed, and chemical dishes were used.

The selection of small volumes of liquid (10–200  $\mu\text{L}$ ) was carried out using the Varipipette automatic microdosers (Poland) and Thermo Scientific with an error of no more than 2%.

### 2.2. COAL POWDER MODIFICATION

Modification of carbon powder with manganese dioxide was carried out by the "wet" method. For this, solutions were prepared containing 0.1 M potassium permanganate and manganese chloride. Carbon-graphite powder obtained by grinding carbon electrodes from spectral coal in a mill and sieved through a nylon sieve with a mesh diameter of 0.08-0.05 mm. 4.570  $\pm$  0.010 g of powder was placed in a 150 ml glass, where 20 ml of the prepared KMnO<sub>4</sub> solution and 30 ml of MnCl<sub>2</sub> were simultaneously poured (this ratio of ingredients theoretically allows to obtain 0.435 g of manganese dioxide, which is ~ 10% of the total mass of the MnO<sub>2</sub> / C composite). The resulting mixture was stirred at a speed of > 600 rpm for 1.5 hours, then the precipitate was separated by filtration in vacuo, washing the precipitate with filtrate and then with double distilled water, according to the rate of decomposition of hydrogen peroxide. In all cases: in the colloidal solution of MnO<sub>2</sub>, in the MnO<sub>2</sub> / C precipitate, high catalytic activity was observed on the filter. The washed precipitate and the filter were placed in an oven and dried at a temperature of 110 °C for 2 hours. MnO<sub>2</sub> / C was transferred to a porcelain dish and ground using a glass rod. The precipitate was fairly crumbly, and this procedure was not difficult.

Samples of the obtained MnO<sub>2</sub> / C composite were subjected to microphotographic and X-ray phase studies.

### 2.3. WORKING ELECTRODE PREPARATION

Indicator working electrodes were manufactured in accordance with the patent of the Republic of Uzbekistan No. 01505 [3,4]. For this, the blanks of electrodes made of spectral graphite grade SU-3 with a diameter of 6 mm and a length of 70 mm were impregnated with molten paraffin in a vacuum until the air bubbles completely disappeared. Then the ends of the blanks were leveled with sandpaper, and a cavity 3-5 mm deep was drilled from one of the ends. The workpiece was inserted into an ISKE2- (3X) G: 6.4 / 2.1 heat-shrinkable tube with an adhesive layer (shrinkage

ratio 3: 1) so that 10-15 mm remained from the end opposite to the cavity to connect the contacts of the electrolytic cell. After shrinkage, the film was cut along the edge of the cavity end.

This cavity was filled with a molten mass consisting of equal parts of paraffin and  $\text{MnO}_2 / \text{C}$  composite. The electrodes were left for 1-2 days to solidify the paste on the surface of the carbon graphite rod. Then, the layer protruding beyond the heat shrink tube was removed by sanding with sandpaper, and the surface was sanded with filter paper and a glass plate. An unmodified carbon-graphite electrode was prepared in a similar manner.

### III. RESULTS AND DISCUSSION

Figure 1 shows a micrograph of the  $\text{MnO}_2 / \text{C}$  composite made using a scanning electron microscope.

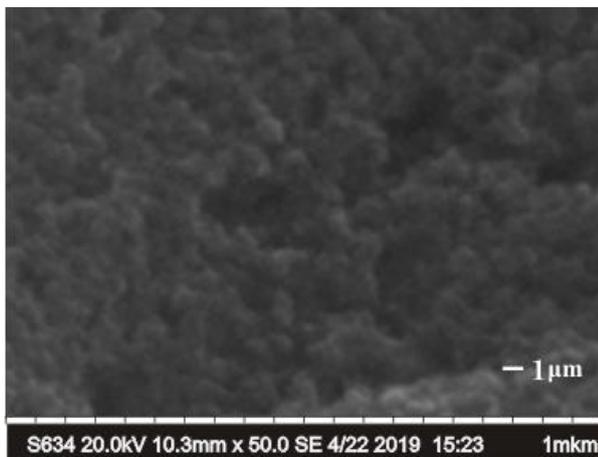


Fig.1. SEM image of the  $\text{MnO}_2 / \text{C}$  composite.

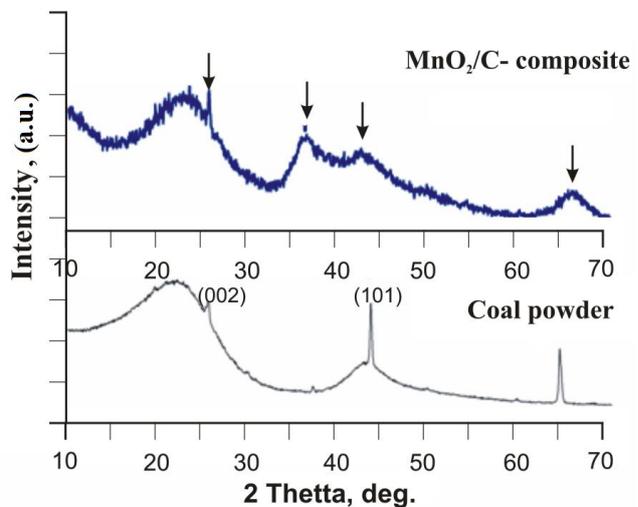


Fig. 2. X-ray diffraction patterns of coal powder and  $\text{MnO}_2 / \text{C}$  composite.

Manganese dioxide nanoparticles with a size of 20 to 55 nm are concentrated on the surface of the coal. Following from the practice of producing nanoparticles by precipitation from solutions, it can be assumed that the nanoparticle sizes will be smaller when using more dilute solutions and high mixing speeds [24]. This means that researchers have the opportunity to vary the particle size of manganese dioxide, if necessary.

Elemental analysis showed that the  $\text{MnO}_2 / \text{C}$  nanocomposite consists of 91.5% C, 5.4% Mn, and 3.1% O, which is close to the calculated data. This also indicates the stoichiometric occurrence of the redox reaction to obtain synthetic manganese dioxide.

It is known that manganese dioxide, depending on the method of its preparation, can have different morphology corresponding to crystallographic forms, such as  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -,  $\epsilon$ -types. [42]. Obviously, each of these forms may have different catalytic activity. So, R.B. Valim et al. studying the oxygen reduction reaction on epsilon-manganese dioxide on a carbon substrate ( $\epsilon$ - $\text{MnO}_2 / \text{C}$ ) showed its greater catalytic activity compared to  $\alpha$ - $\text{MnO}_2$  [14,30].

It may follow from this that the electrochemical characteristics of the electrode modified with manganese dioxide should be associated both with crystallographic forms and with morphologies. Most researchers involved in the problem of chemical modification of carbon paste electrodes note that this modification is mainly carried out with  $\delta$ - $\text{MnO}_2$ , which has hexagonal syngony. Thus, the authors performed sonochemical synthesis of  $\text{MnO}_2 / \text{C}$  nanocomposites, which consisted in the reduction of potassium permanganate on coal under the influence of ultrasonic treatment of the suspension [25,45].

The resulting nanocomposite contained manganese (IV) oxide corresponding to the  $\delta$  modification having hexagonal syngony. The sizes for the  $\text{MnO}_2$  phase was 4–5 nm [25].

On the figure 2 shows X-ray diffraction patterns of a coal powder and a  $\text{MnO}_2 / \text{C}$  composite.

The X-ray diffraction pattern shows that the diffraction peaks for the  $\text{MnO}_2 / \text{C}$  composite are different from those for spectral coal. The observation of peaks at  $2\theta = 37.50; 43.20; 66.40$  may indicate a modification [25].

On the prepared  $\text{MnO}_2 / \text{C}$  composite electrode, its electrochemical behavior in the presence of hydrogen peroxide was studied. Cyclic voltammograms were taken in the range of -0.1 - +1.0 V in buffer solutions with different pH at different scanning speeds of the potential.

On the figure 3 cyclic voltammograms on a composite electrode in phosphate buffer with a pH of 6.86 is shown.

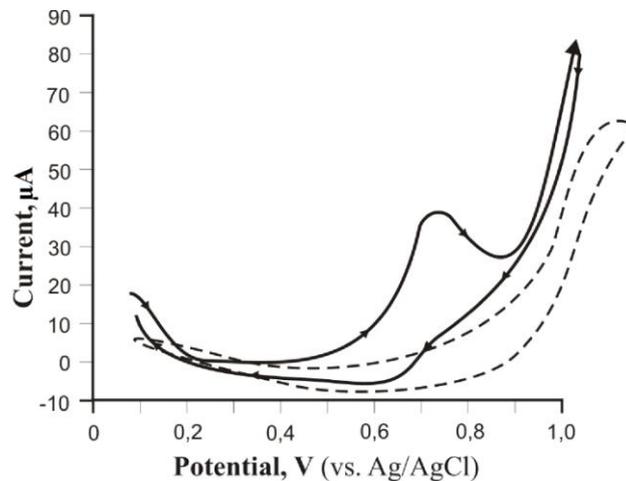
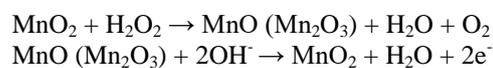


Fig. 3. Cyclic voltammograms on a  $\text{MnO}_2 / \text{C}$  composite electrode in a background solution (0.25 M phosphate buffer with a pH of 6.86) are a dashed curve and in a 0.5 mM hydrogen peroxide solution (solid curve). Scanning speed 50 mV / s.

The peak on the anode branch of the cyclic VA was observed at 0.72 V rel. Ag / AgCl electrode. The cathode peak at 0.68 V. For the unmodified carbon graphite electrode, fuzzy peaks were also observed at almost the same potentials. In this case, the cathode peak was significantly smaller than the anode one.

A possible electrocatalytic mechanism of this process can be described by the following steps: adsorption of hydrogen peroxide on a composite electrode; catalytic decomposition of hydrogen peroxide on the surface of  $\text{MnO}_2$ , leading to a decrease in the oxidation state of Mn (IV) to Mn (II) or Mn (III); subsequent oxidation of Mn (II) or Mn (III) to  $\text{MnO}_2$ :



Since the above reactions are fast, the parallel current is much higher than the oxidation current  $\text{MnO} (\text{Mn}_2\text{O}_3)$  on the electrode surface in the absence of  $\text{H}_2\text{O}_2$ . Therefore, manganese dioxide nanoparticles act as mediators of electron transfer between hydrogen peroxide and the working electrode [5,8].

Based on the above assumptions, it can be assumed that upon anodic polarization of  $\text{MnO} (\text{Mn}_2\text{O}_3)$ , a new phase of manganese dioxide is reprecipitated on its surface, leading to densification of the working layer of the electrode and, as a result, to an increase in the resistance of the modified electrode [36]. This assumption was confirmed during the experiment. The resistance of the  $\text{MnO}_2 / \text{C}$  composite electrode increased from 0.670 k $\Omega$  to 0.960 k $\Omega$  during 1000-1200 potential scan cycles.

Moreover, as shown by microscopic studies, there is a smoothing of the surface of the electrode. The figure 4 shows comparative micrographs of the electrode surface at the beginning and after its operation. A comparative characteristic of surface irregularities showed that during operation, a decrease in the size of the bulges on the electrode surface occurs. This can also be explained by reprecipitation of manganese dioxide and compaction of the working surface of the electrode.

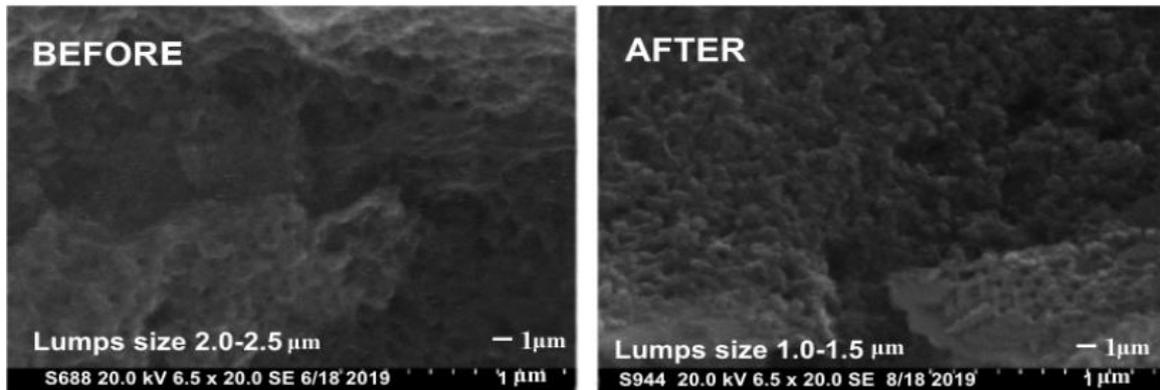


Fig.4. SEM micrographs of the working surface of the MnO<sub>2</sub> / C electrode before (left) and after (right) prolonged use.

The relationship between the oxidation peak current and the scanning speed of the potential of the MnO<sub>2</sub> / C - electrode was investigated. The results are presented on the fig.5.

As shown, the peak oxidation currents were proportional to the square root of the scan rate in the range of 10 -100 mV s<sup>-1</sup>. This dependence is described by a linear equation.  $I = 5,406 + 5,102 \cdot \sqrt{v}$  The correlation coefficient was 0.992 which indicates that the process is controlled by diffusion, as expected for the catalytic system. Moreover, the best forms of anode voltammograms were at a potential scanning speed of at least 50 mV / s.

To optimize the catalytic response of the MnO<sub>2</sub> / C electrode in the presence of hydrogen peroxide, we studied the effect of pH of the electrolyte on the value of the analytical signal. Anodic voltammograms of the MnO<sub>2</sub> / C electrode were recorded in the presence of 50 μmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at different pH values (Fig. 6).

The MnO<sub>2</sub> / C electrode showed electrocatalytic activity in various electrolytes (pH 4.01–9.18), but a higher peak current was observed at pH 7.2–7.4., which corresponded to the results obtained by other authors [6,22,43]. Peak currents and potentials change with changing pH values. With decreasing pH, the peak potential shifted to the positive potential region. Since the MnO<sub>2</sub> / C electrode showed an adequate response to indicate relatively low H<sub>2</sub>O<sub>2</sub> contents at almost physiological pH values of 7.0 ~ 8.0, it can be used to detect hydrogen peroxide, which is a substrate or a reaction product of a number of enzymes.

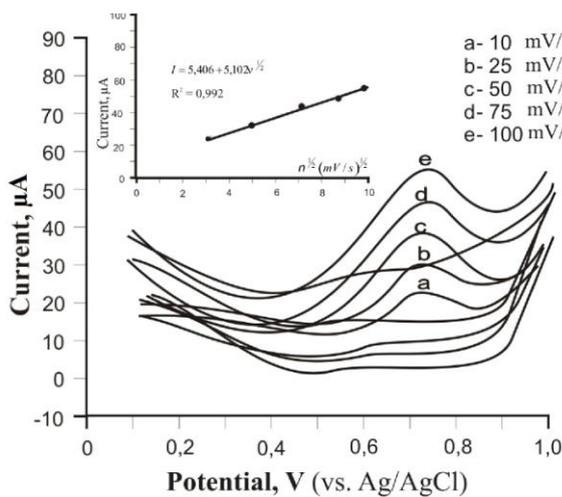


Fig. 5. Cyclic voltammograms of MnO<sub>2</sub> / C, a composite electrode in a 0.5 mM solution of hydrogen peroxide in phosphate buffer (pH 6.86) at various scanning speeds of the potential. Inset: dependence of the analytical signal (Pi current) on the square root of the scanning speed.

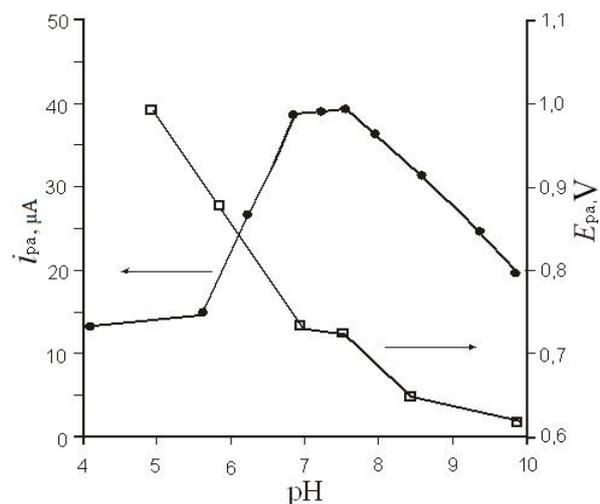


Fig.6. The dependence of the anode peak  $I_{pa}$  and the oxidation potential of E on pH.

In this regard, in further studies, 0.25 M phosphate buffer with a pH of 7.4 was used, containing 0.15 M NaCl, which most fully meets the physiological standards of blood serum.

The figure 7 shows the differential-pulse voltammograms of the MnO<sub>2</sub> / C electrode for various concentrations of hydrogen peroxide.

Composite MnO<sub>2</sub> / C electrode was used for determination of hydrogen peroxide by chronoamperometry, when the potential of the electrode is maintained + 0.72V relatively saturated Ag / AgCl electrode.

Figure 8 shows the dependence of the amperometric signal of the electrode with sequential addition of 0.25 mM hydrogen peroxide at intervals 40 seconds.

The linear response of the electrode signal is observed in the range of hydrogen peroxide concentrations 0.1 -3.0 mM. Detection limit calculated from 3 σ-method taking into account the slope of the graph is 0.03 mM.

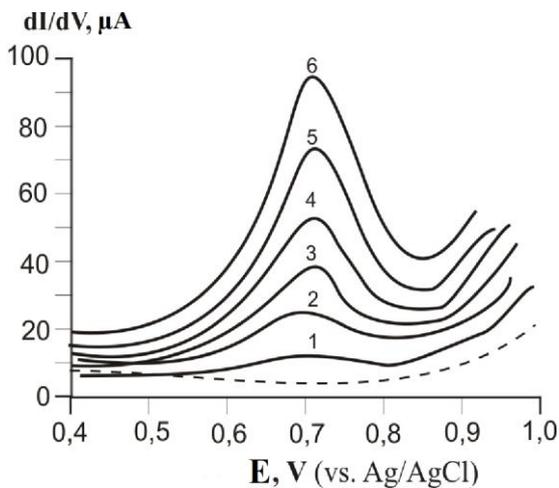


Fig.7. Differential-pulse voltammograms on a composite MnO<sub>2</sub> / C electrode in the presence of increasing amounts of hydrogen peroxide.

1 - 0.010 mM H<sub>2</sub>O<sub>2</sub>; 2 - 0.025 mM H<sub>2</sub>O<sub>2</sub>; 3 - 0.050 mM H<sub>2</sub>O<sub>2</sub>; 4 - 0.10 mM H<sub>2</sub>O<sub>2</sub>; 5 - 0.25 mM H<sub>2</sub>O<sub>2</sub>; 6 - 0.50 mM H<sub>2</sub>O<sub>2</sub>; The dashed line indicates the voltammogram of the electrode in a buffer electrolyte - 0.25 M phosphate buffer with a pH of 7.4, containing 0.15 M NaCl.

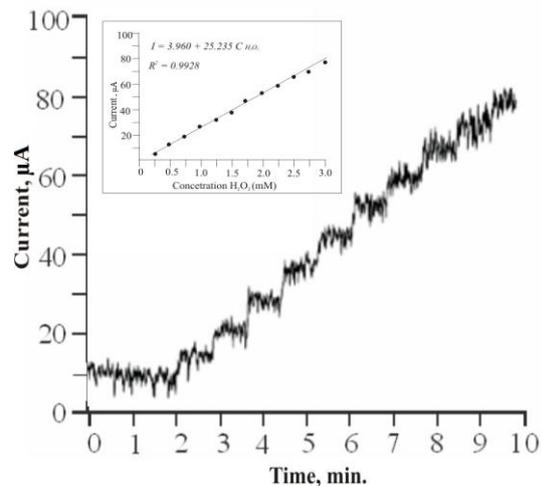


Fig.8. The dependence of the amperometric signal of the electrode with the sequential addition of 0.25 mM hydrogen peroxide.

The composite MnO<sub>2</sub> / C electrode was tested under conditions of the actual content of hydrogen peroxide in a 3% aqueous solution of hydrogen peroxide related to pharmaceuticals that have access to the population everywhere. As is known, pharmaceutical hydrogen peroxide is an antiseptic, deodorizing and hemostatic drug [19]. They are used to treat wounds, abrasion, scratch, stop nasal and other small capillary bleeding, as they are well tolerated by the skin and mucous membranes, do not accumulate in the body with prolonged use. Hydrogen peroxide containing 3% H<sub>2</sub>O<sub>2</sub> belongs to pharmaceutical preparations so that H<sub>2</sub>O<sub>2</sub> is actively oxidized in substances present in water and decomposes under the influence of sunlight [26]. Periodically, the concentration of hydrogen peroxide must be controlled.

A comparison of classical permanganometric titration [16] and voltammetric determination of hydrogen content using the developed MnO<sub>2</sub> / C electrode is of practical interest.

To conduct a titrimetric analysis, 10 ml of the initial sample of a pharmaceutical preparation is placed in a 100 ml volumetric flask and the volume of the solution is adjusted to the mark. To 10 ml of the resulting solution was added 5 ml of 2 N. H<sub>2</sub>SO<sub>4</sub> and titrated with a 0.1M KMnO<sub>4</sub> solution until a faint pink color appears.

The percentage of hydrogen peroxide in the sample is determined by the formula:

$$w_{H_2O_2} = \frac{T \cdot V_T \cdot k \cdot V_1}{V_2 \cdot V_a} \cdot 100\%$$

where:

V<sub>T</sub> is the titrant volume (0.1 M solution of potassium permanganate, which went for titration), ml;

T - titer of potassium permanganate solution for hydrogen peroxide, g / ml

k is the correction coefficient of the titration solution;

V<sub>1</sub> is the volume of the volumetric flask (dilution), ml (in our case, 100 ml);

V<sub>2</sub> is the volume of the sample taken for dilution, ml (in our case, 10 ml)



$V_a$  is an aliquot of the analyzed solution, ml because the accuracy of the diluted hydrogen peroxide solution is  $\sim 1 \text{ g / cm}^3$ )

For voltammetric determination of hydrogen content, the drug was diluted 100 times with distilled water. An aliquot of the resulting 0.1 ml solution was placed in an electrochemical cell with a 20 ml buffer solution of 0.25 M phosphate buffer pH 7.4 and the analytical signal was measured at 0.72 V relative to the Ag / AgCl electrode. Method for determining the added, marked peak height after each addition of 0.25 mM  $\text{H}_2\text{O}_2$ . The table shows the results of the determination of hydrogen peroxide in pharmaceutical preparations, titrimetric and voltammetric methods.

Table 1  
Comparison of the results of determination of hydrogen peroxide from pharmaceutical samples using permanganatometric titration and voltammetric methods  
(n = 5; P = 0.95)

Sample	Permanganatometric method			Voltammetric method			Fisher F-test Ftab. = 6.61
	C ± ΔC, %	s	s <sub>r</sub> , %	C ± ΔC, %	s	s <sub>r</sub> , %	
1.	2.944±0.048	0.038	1.307	2.914±0.030	0.024	0.826	1.58
2.	2.902±0.035	0.027	0.987	2.892±0.028	0.023	0.788	1.17
3.	3.002±0.018	0.015	0.494	2.994±0.024	0.019	0.651	1.27
4.	2.822±0.035	0.029	1.015	2.836±0.054	0.043	1.529	1.48
5.	3.122±0.072	0.057	1.845	3.104±0.054	0.043	1.396	1.33

In accordance with pharmaceutical article FS.2.2.0005.15, the redistribution of hydrogen should be  $3.0 \pm 0.3\%$ , i.e. is in the range of  $2.7 \div 3.3\%$  [19]. Thus, the results of experimental data showed that the hydrogen content in all samples corresponded to the declared and indicated on the label 3%.

Comparison of the analysis results obtained using two independent methods show their identity, which allows us to combine these results into one statistical sample [10].

#### IV. CONCLUSION

A simple design of a carbon-graphite electrode, volume-modified with manganese dioxide nanoparticles obtained during the reduction of potassium permanganate by manganese (II) salts in a neutral medium, is proposed.

Using scanning electron microscopy and an X-ray phase study, it was shown that during this reaction,  $\text{MnO}_2$  nanoparticles with sizes of 20-55 nm are deposited on the surface of the coal powder.

The design features of the electrode is that its body is made of a spectral coal rod placed in a heat-shrink tube, which acts as an insulation and a reinforcing element that imparts mechanical strength to the electrode. At one end of the electrode there is a hole whose surface is electrolytically coated with a metal film of copper or silver. An electroactive mass of manganese dioxide-modified carbon powder and paraffin was placed in a well.

Using cyclic and differential-pulse voltammetry, the behavior of the composite  $\text{MnO}_2 / \text{C}$  electrode in the presence of hydrogen peroxide was studied. It was found that the electrode gives a catalytic response in the presence of hydrogen peroxide at an oxidation potential of 0.72 V relative to a saturated silver chloride electrode and a pH of 7.2 - 7.4 and a scanning speed of 0.05 -0.1 V / sec. Chronoamperometric studies have shown that a linear dependence of the analytical signal of the electrode is observed in the concentration range of hydrogen peroxide from 0.1 to 3.0 mM. The detection limit of  $\text{H}_2\text{O}_2$  calculated by the 3  $\sigma$ -method taking into account the slope of the graph is 0.03 mM.

Composite  $\text{MnO}_2 / \text{C}$  electrode was tested in determining the actual content of hydrogen peroxide in pharmacy products. Comparison of the results of determining the hydrogen peroxide content in the samples by permanganometric titration and voltammetry methods with the  $\text{MnO}_2 / \text{C}$  composite electrode showed good convergence and reproducibility of the analysis results obtained by these two independent methods. The simplicity of manufacturing composite electrodes volume-modified with manganese dioxide, their excellent performance, low cost, and the results of the determination of hydrogen peroxide, allow their use in the design of various biosensor systems.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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