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Indicator Carbon-Paste Electrode for Voltammetric Analysis

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Abstract: The design of an indicator electrode made of carbon paste of ergonomic design for the voltammetric determination of a number of substances of inorganic and organic origin is described. The electrode is made of a graphite rod with a diameter of 6 mm and a length of 70 mm, covered with insulation and having a cavity filled with an electroactive carbon-containing material at the end of the rod. The characteristic features of the proposed electrode - the insulating shell of the housing made of shrink tubing and the electrolytic coating of the cavity surface with a conductive metal film - make it possible to simplify the design of the electrode and increase mechanical strength, extend the service life of the electrode, and also provide the possibility of volumetric and surface modifications with an economical consumption of modifying reagents.

Examples of the use of an indicator electrode modified with mercury and bismuth films and volumetrically modified with manganese dioxide nanoparticles in the analysis of food, beverages, natural objects for the content of heavy metal ions and pharmaceuticals for the content of hydrogen peroxide, vitamins of groups B and C are given.

The simplicity of making the developed indicator electrode from carbon paste, mechanical strength and cost-effectiveness when using expensive and scarce modifiers allow us to recommend it for use in voltammetric analysis and the creation of various biosensor systems.

Keywords: carbon-paste electrode; modified carbon-containing electrodes; voltammetric analysis; cyclic and differential-pulse voltammetry; heavy metals; hydrogen peroxide; vitamin B2; determination

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1. Introduction

Voltammetry as a method of analysis over the years of its existence has passed a long evolutionary path full of hopes, disappointments, and triumph. Conceived at the beginning by J. Geyrovsky as a polarographic method for the determination of heavy metals using a mercury dripping electrode, by now voltammetry has acquired modern features and has taken its place among the physico-chemical methods of analysis, making them a strong competition [1,2].

This was facilitated not only by the expansion of the theoretical foundations of the method, but also by original engineering and technical solutions. So, the dripping mercury electrode was replaced by solid electrodes, first mercury-film, and then modified electrodes [3,4]. The application design of voltammetric analysis has also changed, devices have appeared that provide various modes of potential scanning: linear, square-wave, differential-pulse, cyclic, which has significantly expanded the scope of the method, including the determination of microconcentrations of substances of inorganic and organic origin.

At the same time, the main problem of electroanalytics remains the possibility of obtaining a stable and reproducible under the selected conditions of removing the voltammogram of the analytical signal

Considering the fact that the formation of the electrode response in the electrochemical system occurs at the interface of the electrode-solution phases, the success of measuring the analytical signal, which is determined by its magnitude and reproducibility, will depend on the correct choice of the electrode, i.e. the nature of the material, the state of its surface, the presence of modifying substances, etc. As a result, considerable attention should be paid to the material of the electrodes, methods of their chemical and physical modification, methods of regeneration and expansion of the working area of potentials.

From this point of view, carbon-containing materials, for example, graphite and glass carbon, are an excellent material for the construction of electrodes for voltammetric analysis. It is the combination of mechanical, chemical and electrical properties of these materials that makes it possible to create electrodes with specified sensitivity and selectivity parameters [3].

The 60 – 70 years of the last century were the time of the creation and widespread use of carbon paste electrodes. The main idea in creating carbon-paste electrodes was to produce an electroactive paste consisting of a mixture of graphite powder and binder [5], which, as a rule, uses non-drying oils [6]. This paste was filled with a glass or teflon tube, inside of which there was a metal piston that simultaneously acted as a piston for pushing a portion of carbon-containing paste out of the tube and an electrical contact for connection to the measuring device.

Modification of the surface of the carbon-paste electrodes with a mercury film obtained by the ex- or in situ method made it possible to abandon the dripping mercury electrode.

Since then, many designs of carbon paste electrodes have been proposed for various variants of voltammetric analysis [7]. These electrodes have found their application in the analysis of a number of inorganic and organic substances. An example is a recent review [8].

However, most of these devices, despite satisfactory metrological parameters of analytical signal measurements, had a limited service life, and the electroactive paste was prepared almost daily. This, especially in cases of manufacturing and using modified electrodes, leads to overspending of scarce and expensive modifiers that are part of carbon-containing pastes.

The aim of this work is to present a new ergonomic design of a carbon-paste electrode for voltammetric analysis and to demonstrate its capabilities.

2. Experimental

The main task that the authors of this article faced was to simplify the design of solid electrodes designed for voltammetric measurements, increase the reliability of their operation and expand the range of carbon-containing composite materials with economical consumption of the modifier included in their composition.

An electrode was manufactured, the design features of which are described in detail in our previous works [9,10]. As a prototype, when applying for a patent, we used the patent No. 1315884 USSR [11] in particular, the second option for manufacturing an indicator electrode.

The carbon-containing paste was prepared by mixing fine graphite powder obtained by grinding the same material as the blanks themselves with molten paraffin in a ratio of 50:50% (wt.) [12].

Volumetric modification of the composite mixture, in accordance with the task, was carried out by introducing a modifier reagent into the molten carbon–containing paste with thorough mixing.

The molten modified carbon-containing mass was placed in the hole of the electrode blank. At the same time, the volume of paste placed in the well is only 0.05 – 0.1 cm^3. The electrochemical behavior of the manufactured electrodes in the presence of the analyzed substances was studied by removing voltamperometric curves in a glass 3-electrode cell using a universal polarograph PU-1 [13] and a potentiostat- galvanostat P-40X.

3. Results and discussion

Figure 1 shows the proposed electrode.

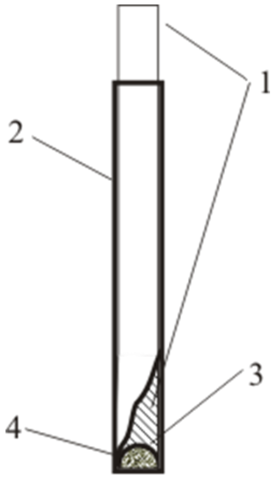

Figure 1. Coal paste electrode for voltammetric analysis. 1 - Graphite rod electrode housing; 2 - Insulating sheath from heat shrink tube; 3 - Metal film electrolytically deposited on the surface of the hole; 4 - Electroactive carbon-containing composition.

A distinctive feature of the voltammetric sensor proposed by us is the absence of moving parts in the form of a piston pushing out the paste, constriction rings, gaskets, which are present in the prototype [11]. This clearly indicates a simplification of the design. The mechanical strength of the electrode is provided by a reinforcing shrink tube, which is also an insulating material. The presence of a hole for the carbon paste at the end of the electrode with a volume of only 0.05 ml makes it possible to economically consume the modified carbon-containing composite material, which is especially valuable when choosing and optimizing the method of modifying the surface or volume of the carbon paste electrode. At the same time, the electrical resistance of such an electrode is significantly less than that of others used in voltammetry, which makes it possible to broadly the current range of the measuring device. These facts determine the ergonomics of the proposed electrode.

The efficiency of the electrode and the possibility of its use in the analysis of inorganic and organic substances is illustrated by the following examples.

Example 1. Determination of a group of heavy metals by the inversion stripping voltammetry method from a carbon paste electrode modified with a mercury film.

The developed mercury-film graphite electrode was used to determine cadmium, lead and copper ions in environmental objects, beverages and food products using the additive method. Preparation for the analysis of samples was carried out in accordance with GOST 33824-2016 and GOST 31866-2012.

Table 1 shows some of the results of the analysis

Table 1. The results of the determination of Cd, Pb, Cu in food, soil and natural waters by inversion stripping voltammetry (n = 3; P = 0.95; Background 0.2 M HCl + 10^{-4}M Hg^{+2}, $E_{accum.}$ -1.1 V, τ = 20 sec, sweep speed 50 mv / s).

Analyzed Object	Found Me, mg/kg								
	Permissible Concentration, mg/kg	**Cd**	**s^***	**Permissible Concentration, mg/kg**	**Pb**	**s^***	**Permissible Concentration, mg/kg**	**Cu**	**s^***
Drinking water	0.001	-	-	0.03	-	-	1	0.08	0,01
"Pulsar" beer 12%	0.003	0.002	0.001	0.03	0.006	0.001	1	0.41	0.007
Apple juice	0.003	0.027	0.008	0.25	0.17	0.003	5	0.97	0.007
Canned "Sardines in oil"	0.20	0.11	0.012	1.5	0.15	0.008	10	6.94	0.032
Vegetable oil	0.04	-	-	0.08	0.07	0.01	0.5	0.41	0.03
Beans	0.02	0.11	0.008	0.5	0.73	0.04	5	2.12	0.04
Rye bread	0.02	-	-	0.03	-	-	5	0.49	0.03
Bread from flour (top grade)	0.02	-	-	0.03	<0.02	-	5	2.18	0.04
Water of the Zeravshan river	0.02	0.002	0.001	0.06	0.035	0.009	0.1	0.06	0.008
Soil of municipality Urgut	0.20	traces	-	0,5	0.21	0.03	0.5	0.18	0.014
Soil of village. "Geophysics"	0.20	-	-	0,5	0.32	0.03	0.5	0.11	0.010
Soil of village "Geology"	0,20	-	-	0,5	0.49	0.04	0.5	0.14	0.011
Soil of village "Airport"	0.20	0.16	0.021	0.5	0.62	0.05	0.5	0.18	0.009

s^* - the mean quadratic error.

The detection limit for these heavy metals, as for most inversion stripping voltammetry methods, is n·10^{-8} – n·10^{-9} mol/dm^3 [14]. With an increase in the accumulation time and the scanning speed of the potential, the detection limit will decrease [15]. As can be seen from the Table 1, only in a few cases there is an excess of permissible standards for cadmium and lead, which is most likely due to anthropogenic impact on the environment in these provinces.

Example 2. Making of an electrode made of carbon paste modified with a bismuth film.

The electrode is made similarly to the one described above, except that the coating of the surface of the well was carried out by applying a silver film by electrolysis [16].

Modification by bismut was carried out by ex-situ method from 0.001 m bismuth (III) nitrate solution in 0.2 M hydrochloric acid at -0.5 V relative to the silver chloride electrode for 5 minutes (300 sec.). The resulting electrode was washed three times with bidistilled water. In this case, the bi-modified electrode was coated with a dark matte film.

Figure 2 shows a voltammogram of a modified electrode in a solution containing cadmium and lead ions/

The results of the study are shown in Table 2.

The conducted studies have shown the fundamental possibility of using the proposed carbon-paste electrode, the surface of which is modified with a bismuth film, in the analysis of real objects.

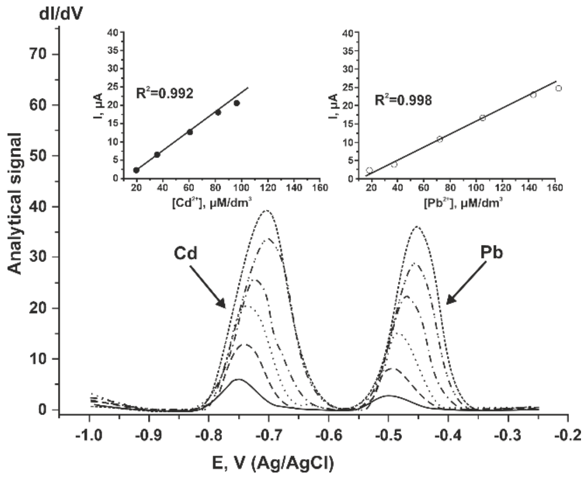

Figure 2. Voltammograms showing the dependence of the analytical signal on the increasing contents of Cd^{2+} and Pb^{2+} in model solutions with concentrations of 25, 50, 75, 100, 125 and 150 μg / dm^3. Conditions*:* E elect.= -1.2 B; accumulation time 60 sec; potential sweep rate ν = 50 mV / s.

Table 2. Evaluation of the accuracy of determining the concentration of Cd^{2+} and Pb^{2+} ions in model solutions.

Metal - Ion	Entered, μg/dm³	Found, μg/dm³
Cd	25.0	21.3 ± 1.6
	50.0	44.1 ± 1.4
	100.0	105.4 ± 5.2
Pb	20.0	18.2 ± 1.8
	40.0	36.1 ± 1.6
	80.0	86.8 ± 5.4

Example 3. Determination of vitamin B_2 using a carbon paste electrode modified by a bismuth film.

The same Bi-modified electrode was used to determine vitamin B_2 using the cyclic voltammetry technique [17]. To confirm the practical application of the developed method, a comparison was made of the correspondence of the experimental results obtained with the declared vitamin B_2 content given in the description of the pharmaceutical. Three samples of vitamin B_2 were examined:

Sample A: Multivitamin syrup for children PIKOVIT ® , LLC "KRKA PHARMA",containing 1 mg B_2 in 5 ml.

Sample B: Riboflavin-mononucleotide solution for injection 1% 1ml, Pharmstandard-Ufa Vita, Russia.

Sample C: Bentavit Valenta Pharmaceuticals JSC (Russia) in tablets of 100 mg vitamin B_2.

The control method was the fluorescent method for determining B_2.

Table 3 shows the results of the determination of vitamin B_2 in these samples.

Table 3. The results of the determination of vitamin B_2 in the pharmaceutical products of a voltammetric with Bi-modified electrode and fluorometric methods*.

Probe	Indicated, mg	voltammetric with Bi-modified electrode					fluorometric					
		$\bar{X}$, mg	s	s_r %	t [4,3]	R %	$\bar{X}$, mg	s	s_r %	t [4,3]	R %	*F[19]
A	1	1.01 ± 0.08	0.247	6.0	0.85	101	0.98±0.02	0.145	2.1	1.12	98	2,.93
B	10	9.97 ± 0.18	0.384	1.48	0.89	99.7	9.94±0.15	0.348	1.22	0.85	99.4	1.21
C	100	99.40±0.86	0.833	0.7	1.45	99.4	99.96±1.42	1.07	1.14	0.06	100	1.64

* s - the mean quadratic error; s_r – relative error; t- Student 's criterion; F- Fischer's criterion; critical values at a significance level of 0.05 reference values are given in square brackets; R% - percentage of substance discovery in the analyzed sample.

As can be seen, both methods have shown reliable results for analytical parameters. The values of the relative standard deviation s for the mean value of the three measurements ranged from 0.247 to 0.833 when quantifying riboflavin using the proposed sensor and from 0.145 to 1.07 using the fluorescence method, demonstrating good accuracy of these methods.

Example 4. The use of a carbon paste electrode, volumetrically modified with manganese dioxide in the determination of riboflavin (vitamin B_2). In the work, methodological approaches and modes of voltammogram removal were used, indicated in [18].

The electrode was prepared as described above. Volumetric modification of the electrode with manganese dioxide was carried out by introducing 10% of the total mass of a mixture of finely ground MnO_2 into a molten mixture of graphite powder and paraffin [19]. Cyclic voltammograms were taken without mixing the solution at a potential scan rate of 0.01 – 0.5 V/s. To do this, voltammograms of the background electrolyte with a certain pH value were first taken. Then a standard sample with a known riboflavin content or an analyzed sample was introduced into the electrochemical cell. Voltammograms were recorded in the scanning range of potentials -0.5 - +0.5 V. Differential pulse voltammetry with optimized parameters in the potential range from -0.5 V to +0.3 V was used for quantitative evaluation.

Figures 3 and 4 show cyclic and differential pulse voltammograms in the presence of increasing amounts of vitamin B_2

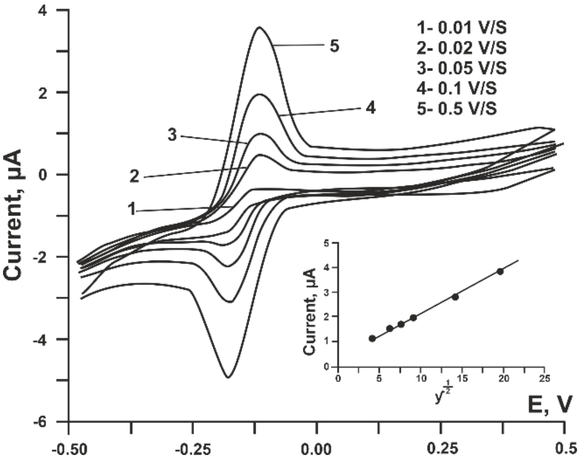

Figure 3. Cyclic voltammograms of 0.1 mM riboflavin in a Britton-Robins buffer solution with pH 2 on a carbon-containing electrode modified with manganese dioxide at different scanning speeds. Inset: dependence of the magnitude of the peak current of oxidation of vitamin B_2 as a function of $v^{1/2}$

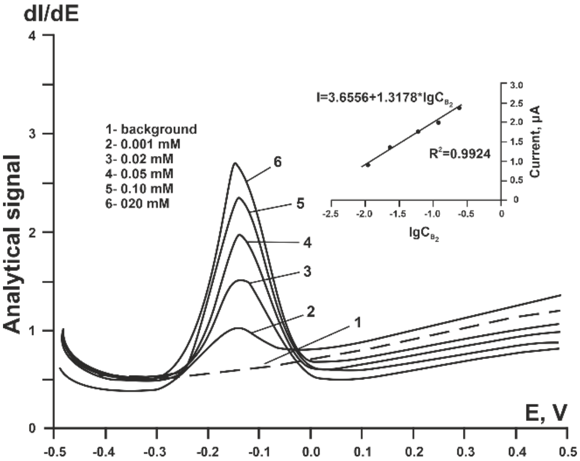

Figure 4. Differential-pulse voltammograms of vitamin B2 of various concentrations on a carbon-containing electrode modified with manganese dioxide. Conditions: background electrolyte - Britton-Robins buffer with pH 2; differential pulse mode, potential sweep speed of 100 mV/s. Inset: dependence of the analytical signal I, μA on the logarithm of the concentration of vitamin B2, mmol/L

Example 5. Determination of hydrogen peroxide using a carbon paste electrode volumetrically modified with manganese dioxide nanoparticles.

The paper [20] describes the process of synthesis of manganese dioxide nanoparticles and their modification of the volume of coal paste. The reaction was used as precursors for the production of MnO_2 nanoparticles

$$3MnCl_2 + 2KMnO_4 + 2H_2O = 5MnO_2 + 2KCl + 4HCl$$

The proof of successful modification was microscopic and X-ray dispersion studies, which showed the production of MnO_2 nanoparticles with sizes of 20-55 nm.

Its electrochemical behavior in the presence of hydrogen peroxide was studied on a manufactured MnO_2/C composite electrode. Cyclic voltammograms were taken in the range of -0.1 - +1.0 V in buffer solutions with different pH at different potential scanning speeds.

The results of the experiment are illustrated in Figures 5 and 6, which show cyclic voltammograms on a MnO_2/C composite electrode and testing of this electrode in the amperometric mode for determining hydrogen peroxide [21].

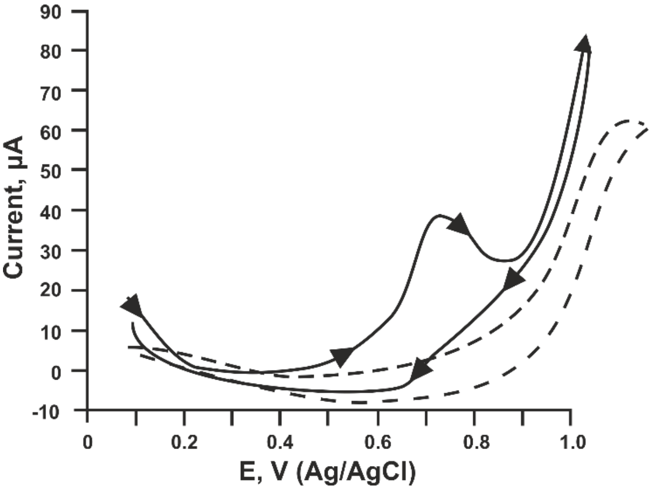

Figure 5. Cyclic voltammograms on a MnO_2 / C composite electrode in a background solution (0.25 M phosphate buffer with a pH of 7,0) are a dashed curve in a 0.5 mM hydrogen peroxide solution. Scanning speed 50 mV / s.

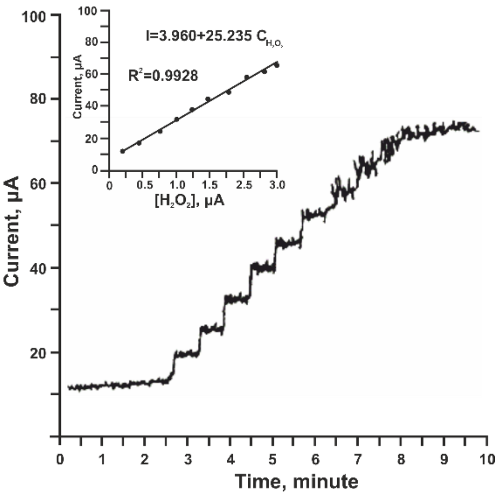

Figure 6. Amperometric response observed on the MnO_2 / C composite electrode with the sequential introduction of 0.25 mM H_2O_2 additives into the background electrolyte at a holding working potential of +0.72 V relative to the saturated Ag / AgCl electrode.

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

Thus, the examples given prove the operability of the proposed electrode for the determination of inorganic and organic substances in a wide range of detectable contents using various voltammetry techniques. At the same time, the electrode has a simple design, is reliable in operation and economical when using modifying agents.

3. Conclusions

A carbon-paste electrode of ergonomic design has been developed for conducting voltammetric measurements. The characteristic features of the manufactured electrode is that its body is made of a graphite rod of spectral purity and is covered with an insulating shell made of a shrink tube. At the end of the rod there is a cavity of a hemispherical or conical shape, the surface of which is electrolytically coated with a copper or silver film that improves the conductive properties of the electrode and the adhesion of the electroactive carbon-containing paste filling it with the electrode body.

The positive effect is achieved by simplifying the design of the electrode, improving mechanical strength, extending service life, the possibility of volumetric and surface modification with economical consumption of reagents-modifiers.

The electrode has been tested in various versions of voltammetry to determine a number of substances of inorganic and organic origin, which have shown that the metrological parameters of measurements in sensitivity and reproducibility of results are not inferior to those described in the literature, or are in agreement with it.

Institutional Review Board Statement: Not applicable.

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