

# Making And Evaluation Of Preparedness Of Solid Mercury-Graphite Electrodes For The Stripping Voltammetric Determination Of Trace Concentrations Of Heavy Metals

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**Abstract:** The article presents the results of a study on the manufacture of solid mercury-film graphite electrodes for stripping voltammetry and the selection of criteria for evaluating their suitability in the analysis of trace heavy metal contents. The ergonomic design of an indicator carbon-paste electrode made of a high purity graphite rod, coated with an insulating sheath made of a heat shrink tube and having a cavity for filling the electroactive mass from a mixture of graphite powder and paraffin is proposed. The relationship of such physical and mechanical parameters as the size and shape of graphite particles, the ratio of the ingredients of the electroactive mixture, the ohmic resistance of the manufactured electrodes with the range of working potentials and the residual current was studied. The choice of the criterion for determining the readiness of a mercury-film graphite electrode for voltammetric measurements is substantiated. The results of the stripping voltammetric determination of cadmium, lead and copper ions in environmental objects, food and drinks using the developed electrode are presented.

**Keywords:** Stripping Voltammetry, Solid Electrodes, Suitability Criterion, Heavy Metals, Determination.

## 1. INTRODUCTION

To successfully solve the problem of analyzing trace amounts of substances, three problems must be solved [1]:

- 1) sufficiently reduce the detection limit, i.e., increase the signal-to-noise ratio (for example, the magnitude of the ratio of electric current to residual);
- 2) to achieve the required selectivity, i.e., the ability to determine the trace amounts of elements against the background of others present in concentrations several orders of magnitude higher; this problem is usually impossible to solve without the use of preliminary separation;
- 3) to prepare chemical reagents of the required degree of purity and to improve the technique of working with very dilute solutions, the content of the solute in which decreases due to adsorption on the walls of the electrochemical cell, hydrolysis and more.

From a wide range of tools, not all analysis methods meet these requirements. At the same time, the choice of one or another analysis method is determined not only by its potential capabilities but also by specific technical performance, the convenience of working with the device and the presence of a certain technical service during its operation. In this regard, the voltammetric analysis method,

especially the differential-pulse version of stripping voltammetry (ISDIV) [2], can successfully compete with such highly sensitive methods as radiochemical (activation) and atomic absorption methods. The ISV method is based on the idea of the preliminary electrochemical concentration of a substance from a dilute solution on an electrode at a constant potential, which is chosen so that the required electrode reaction proceeds at a sufficient rate [3,4,5]. In this regard, the electrodes in the ISV play a special role, since ideally they should not contain toxic substances, require a complex surface regeneration procedure, and create the ability to determine the concentration of substances at the MPC level and lower [6,7,8]. In this regard, the use of solid-phase, in particular, carbon graphite electrodes, despite the persistence of several problems associated with their preparation for the operation and further operation, remains preferred [9,10]. This work aims to study the conditions for the production of mercury-film carbon-graphite electrodes and to select a criterion for evaluating their suitability in an ISV for determining low concentrations of toxic heavy metal ions  $Cd^{+2}$ ,  $Pb^{+2}$ ,  $Cu^{+2}$ .

## 2. EXPERIMENTAL

### 2.1 Materials and methods

The work uses a computerized analytical complex for IVA based on the modernized universal polarograph PU-1 (Belarus) [11]. The modernization of the polarograph consisted of pairing it with a personal computer (PC) and converting the output analogue signal to digital using a 16-bit multimedia card. Out of a wide variety of sound cards, the most suitable, practically requiring no alteration, turned out to be a multimedia card with a SOLO 9000 processor. A linear card input was used to connect the polarograph sensor unit. As the control program used the program "Electronic recorder" PowerGraph of the second or third version [12]. We experimentally optimized the tuning conditions for displaying the received analytical signal on the display. The advantage in such an analytical complex, while retaining the advantages of the multifunctionality of the PU-1 polarograph

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itself, is the ability to almost instantly evaluate the nature and magnitude of the analytical signal, write it to memory to create an analysis database, and quickly print it out in any of the Microsoft Office editor programs in a convenient form. Self-made thin-film mercury-graphite electrodes with the production of a mercury film by in situ method were also used as a working electrode in the ISV determination of  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$  ions. The object of the study was the fabricated electrodes and their metrological characteristics in the determination of these heavy metal ions in model solutions and environmental objects.

## 2.2 The method of manufacturing working electrodes.

Working indicator electrodes were made of spectral coal of the SU-3 grade, with a diameter of 6 mm and a length of 70 mm. The preforms were impregnated with molten paraffin under vacuum, until the complete removal of air bubbles. A hole was drilled at one of the ends of the billet with a diameter of a slightly smaller diameter of the billet itself and a depth of 3-5 mm. The preform was inserted into a heat shrink tube, for example, ISKE2- (3X) G: 6.4 / 2.1 with an adhesive layer (shrinkage coefficient 3: 1) so that 10-15 mm remained from the end of the hole to connect the contacts of the electrolytic cell. The blank with a heat shrink tube was heated to  $125^{\circ}\text{C}$  with a stream of hot air or a soldering iron [13]. After shrinkage, the film was cut along the edge of the end with the hole. The electrode well was electrolytically coated with a thin layer of copper at a current density of  $\sim 10 \text{ mA} \cdot \text{cm}^{-2}$  for 10 minutes. Then the electrodes were dried at room temperature for 8-10 hours. The procedure for applying a layer of electrolytically deposited copper reduces the ohmic resistance of the electrode and favours the adhesion of the carbon-containing paste to the coal billet. An electroactive carbon-containing paste was prepared by mixing finely dispersed powder of spectral-grade graphite with molten paraffin in various proportions — graphite powder: paraffin 20:80; 30:70; 40:60; 50:50; 60:40; 70:30; 80:20, respectively.

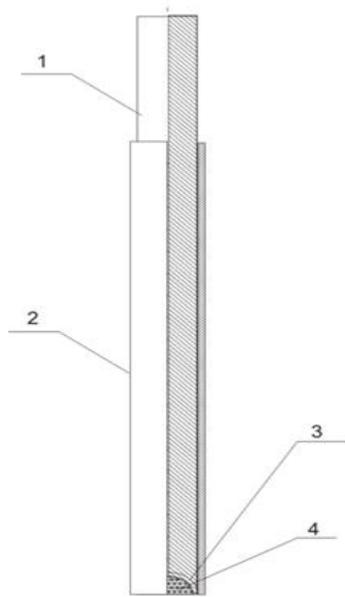


Fig. 1. Coal paste electrode for voltammetric analysis. 1 - Graphite rod electrode housing. 2 - Insulating sheath from heat shrink tube. 3 - Metal film electrolytically deposited on the surface of the hole. 4 - Electroactive carbon-containing composition.

A molten carbon-containing mass was filled with a glass or wooden stick into the hole of the electrode blank fixed vertically. The volume of the paste, which was placed in the hole, is only 0.05 - 0.1 ml. The electrode was left for 1-2 days to completely solidify the paste and set it with the surface of the carbon-graphite rod. Then, the layer protruding beyond the shrink tube was removed by grinding on sandpaper and the surface was polished on filter paper and a glass plate. On figure 1 coal paste electrode for voltammetric analysis is shown.

The features of such an electrode that distinguish it from the known carbon graphite electrodes used in the voltammetric analysis are as follows:

- the electrode is made so that the rod of spectral carbon graphite itself acts as a body and an electrical contact at the same time;
- the heat shrink tube fits snugly to the surface of the rod and protects it from mechanical damage and contact with the analyte.
- electrolytic coating of the cavity surface with a thin layer of metal ensures good conductivity of the electrode and adhesion of the electroactive material from carbon-graphite powder and paraffin to the electrode body.

## 2.3 Modification of a carbon-graphite electrode with a mercury film

The electrode was placed in a measuring cell with 20 ml of background electrolyte 0.2 N. HCl, 0.2 ml of a  $10^{-4}$  M Hg  $(\text{NO}_3)_2$  solution was added and a mercury film was formed on the electrode surface at  $-0.2 \text{ V}$  vis. Ag / AgCl electrode for 5 minutes. From time to time, a potential scan was performed in the range  $-1.2 \text{ V} \div +0.3 \text{ V}$ . The electrode was considered prepared if it responded to mercury ions in the range corresponding to the dissolution of mercury on the carbon-graphite substrate  $-0.05 \div +0.2 \text{ V}$ . In this case, the shape and reproducibility of the anode peak were taken into account.

## 3. RESULTS AND DISCUSSION

The method of stripping voltammetry is one of the few methods that allow determining the group of heavy metal ions, such as cadmium, lead, copper from one volume of the analyzed solution [14]. It is these advantages of ISV that led to the testing of electrodes manufactured by us according to the above procedure. The most significant parameter affecting the performance of impregnated electrodes is the qualitative and quantitative composition of the impregnating mixture. We used food paraffin as a binder. Under certain conditions, it is possible to improve the performance of carbon-graphite materials: expand the range of working potentials, reduce residual current, and reduce resistance. All of the above is achieved by ordering the structure of the carbon-graphite electrode [15,16]. For this purpose, we propose the use of graphite powder with particle sizes of 0.3 mm or less, obtained by thoroughly grinding carbon graphite electrodes for spectral analysis. Research under a microscope showed that as a result of mechanical grinding and sifting of coal powder, the particles have a globular and

lamellar shape. By additional grinding of the sieved particles, it was possible to reduce their size to 0.08 mm.

We linked such physical and mechanical parameters as the size and shape of the coal particles, the ratio of the binder (paraffin) and the electrochemically active (coal) components, the ohmic resistance of the manufactured electrodes with a range of working potentials and residual current. The metrological indicators for the determination of cadmium and copper in a model solution served as a criterion for assessing the quality of the electrode. The research results are summarized in Table 1.

TABLE 1

THE RESULTS OF A COMPARATIVE STUDY OF THE CHARACTERISTICS OF ELECTRODES WITH DIFFERENT CONTENTS OF GRAPHITE POWDER (T=30 S; N=50 MV·S-1; N=3, P 95%)

The size and particle shape mm	composition w graphite / w paraffin	R, kOhm	Working potential range, V	Found Cd (II), * $\mu\text{g} \cdot \text{ml}^{-1}$	Sr/Cd	Found Cu (II), * $\mu\text{g} \cdot \text{ml}^{-1}$	Sr/Cu
0.3 globular	20 : 80	4.2	-1.10 - + 0.40	0.42±0.09	0.12	0.56±0.07	0.10
0.3 globular	30 : 70	2.6	-1.10 - + 0.46	0.48±0.08	0.13	0.54±0.07	0.10
0.3 globular	40 : 60	1.7	-1.00 - + 0.50	0.52±0.08	0.13	0.52±0.06	0.09
0.3 globular	50 : 50	0.9	-1.10 - + 0.42	0.50±0.04	0.10	0.50±0.02	0.08
0.3 globular	60 : 40	0.4	-1.08 - + 0.45	0.51±0.04	0.09	0.50±0.03	0.08
0.3 globular	70 : 30	0.3	-0.92 - + 0.50	0.50±0.05	0.12	0.51±0.05	0.13
0.3 lamellar	80 : 20	5.2	-0.80 - + 0.60	0.60±0.09	0.16	0.56±0.05	0.16
0.08 globul.	40 : 60	3.9	-0.80 - + 0.50	0.48±0.09	0.14	0.59±0.05	0.16
0.08 globul.	50 : 50	2.5	-0.75 - + 0.40	0.53±0.06	0.11	0.54±0.04	0.14
0.08 lamel.	60 : 40	2.1	-0.80 - + 0.45	0.51±0.11	0.21	0.51±0.04	0.24
0.08 lamel.	70 : 30	1.9	-0.70 - + 0.50	0.55±0.12	0.19	0.50±0.02	0.17

As shown by microscopic studies, the surface microrelief of solid film mercury-graphite electrodes of graphite particles of globular shape and size <0.3 mm is less pronounced and homogeneous compared to electrodes of other graphite powders and is a more or less ordered alternation of protrusions of graphite microparticles and troughs from dielectric-binder. As one would expect electrodes with a high content of carbon-graphite powder and with larger particles had less resistance and a wider range of working potentials. Introduction to the composition of a solid graphite electrode more than 60% of the mass a binder causes a deterioration in the considered electrochemical parameters. In the case of a decrease in the binder fraction of less than 30% the electroactive carbon-containing mass crumbles, it is difficult to polish the working surface of the electrode and the working range is reduced. Thus the most optimal proportion is graphite powder: paraffin is in the range 50:50 ÷ 60:40. This ratio was taken by us as the basis for the manufacture of a mercury-graphite electrode. The modification of a solid graphite electrode with mercury can be carried out by several methods. The first one is to obtain a mercury film on the surface of a graphite electrode in advance the other is to obtain one during analysis. The second method is called in situ modification with mercury and it seems to us more preferable. However despite the outward simplicity of the procedure for forming a mercury film on the surface of a carbon electrode, obtaining stable and reproducible readings of the discharge of mercury ions which in essence makes it possible to use a mercury-graphite electrode as an indicator in stripping voltammetry turned out to be a difficult engineering task involving some ideas guesses and know-how [15,17,18,19]. To comprehend the "discharge – ionization" process of mercury we studied the behaviour of

fabricated film mercury – graphite electrodes which differ in the way of surface treatment. The controllable factor was the mercury ionization half-wave potential. In this case, the potential and time of the pre-electrolysis were taken into account. The results of this study are shown in Table 2 from which it can be seen that the method of surface treatment of electrode has a significant effect on the value of the half-wave potential of mercury and the level of the analytical signal. An increase in electrolysis time leads to the accumulation of mercury on the surface of thermoelectric elements. To assess the readiness of the indicator electrode for operation it is advisable to use the parameter  $I/Q$  (Hg), where I is the level of the analytical signal in  $\mu\text{A}$  and Q is the calculated value of the amount of electricity that passed through the electrode during the pre-electrolysis. It is this assessment that was proposed by N. Stozhko [15].

TABLE 2

Electrochemical characteristics of the ionization process of mercury recovered from a solution of 0.2 M HCl +  $10^{-4}$  M Hg (II) on HMGE at a potential of  $-1.1$  V for 180 s.

Electrode surface treatment method	Graphite particle size, mm	Graphite : binder, % mass	$E_p$ (Hg), V	$Q$ (Hg) $10^{-2}$ , $\mu\text{C}$	$I/Q$ (Hg), $\text{s}^{-1}$
1	2	3	4	5	6
1	0.3	60:40	0.05	0.14	1.40
2	0.3	60:40	0.20	1.11	0.75
3	0.3	60:40	0.28	2.53	0.30
1	0.3	50:50	0.06	0.23	1.25
1	0.08	50:50	0.05	0.46	1.30
2	0.08	50:50	0.22	1.58	0.60
3	0.08	50:50	0.30	1.92	0.35

depending on the method of treating the electrode surface the size of graphite particles in graphite-containing composite and its composition

As can be seen (Table 2, column 6) the smallest values of this parameter were obtained on electrodes with a level surface and the highest - on electrodes with a native untreated surface. The highest shear potential for half-waves of mercury is also observed for electrodes subjected to additional grinding and polishing. Thus it can be assumed that as a result of additional surface machining the characteristic parameters of the electrodes approach those of pyrolytic graphite and glassy carbon electrodes. Also with a decrease in the analytical signal the residual current decreases. It would seem that the effect of modifying the electrode surface is obvious. However, for electrodes with a smooth surface, it is difficult to plant a mercury film. In [15, 20] observations were made under a microscope during the electrolysis of a solution containing mercury (II) ions. By extrapolating these results to the behaviour of the electrodes that we noticed we came to the following conclusion: on the native (untreated) surface of a HMGE reduced mercury is localized mainly at the vertices of graphite particles (active centres). First, two-dimensional mercury nuclei are formed which during electrolysis turn into three-dimensional formations and then into drops of 1-2 microns in size located at far distances from each other. Mercury drops fill the smoothed surface more densely. Having reached a critical size ( $\geq 1 \mu\text{m}$ ) the droplets move and coalesce with the formation of larger droplets (7–8  $\mu\text{m}$ ) [20].

The  $I/Q$  (Hg) parameter is significantly affected by the dispersion of graphite particles and the graphite content in a graphite-containing paste.  $I/Q$  (Hg) tends to increase with the increasing particle size of graphite and its content in the graphite-containing paste for electrodes with a native surface. An increase in the particle size of graphite from 0.08 to 0.3 mm leads to a change in  $I/Q$  (Hg) from 0.3 to 1.4. When the graphite content is 50-60% of the mass in the graphite-paraffin matrix  $I/Q$  (Hg) takes maximum values. Due to the large particles of graphite, a more prominent surface is formed with many protruding tops of graphite particles. To some approximation, the structure of such an electrode can be considered as a combination of graphite ultramicroelectrodes providing quasispherical diffusion of an electroactive substance. This assumption is supported by the fact that an electrode with a native surface makes it possible to obtain an analytical cadmium signal in a non-mixed solution of a diluted electrolyte, but an electrode with a cleaned surface does not.

Fig. 2. The relationship of the parameter  $I/Q$  (Hg) with the amount of mercury (a) recovered from a solution of 0.2 M HCl +  $10^{-4}$  M Hg (II) on a HMGE with a potential of  $-1.1$  V for 180 s and ionization potential mercury (b).

The relationship between the  $I/Q$  (Hg) parameter and the amount of reduced mercury and its ionization potential is shown in Fig. 2. With an increase in the amount of mercury on the surface and a shift in its ionization potential to the positive region the parameter,  $I/Q$  (Hg) decreases. Therefore the parameter  $I/Q$  (Hg) can serve as a measure of the electrochemical activity of a mercury-modified electrode.

As a result of research we came to the following seemingly paradoxical conclusion:

- to obtain a larger analytical signal and hence greater sensitivity the electrode does not need to be thoroughly cleaned mechanically;
- to shift the ionization potential of mercury to the positive region necessary to expand the working range of potentials electrodes made of fine-grained coal powder with globular particles should be used;
- before work, it is necessary to conduct a "training" of the electrode in the background electrolyte with the addition of  $10^{-4}$  M mercury (II). The training consists of conducting multiple cyclic potential sweeps from  $-1.1$  to  $+0.4$  V vs. Ag/AgCl.

Figure 3 shows a typical voltammogram of a model mixture of cadmium, lead and copper ions on a film mercury-graphite electrode according to the in situ method.

The developed mercury-graphite electrodes were used in the methods for determining the number of heavy metals in environmental objects and food products.

On the table 3 some results of the determination of Cd, Pb, Cu in food, soil and natural waters by stripping voltammetry are presented.

Fig. 3. Voltammogram of a model mixture of ions  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+2}$  ( $0.5 \mu\text{g} \cdot \text{ml}^{-1}$ , each) on a film mercury-graphite electrode according to the in situ method.

As can be seen from the results presented in table 3 manufactured under laboratory conditions working mercury-graphite electrodes give adequate characteristics depending on the composition and can be used in routine inversion-

voltammetric measurements.

TABLE 3

The results of the determination of Cd, Pb, Cu in food, soil and natural waters by stripping voltammetry ( $n = 3$ ;  $P = 0.95$ ; Background 0.2 M HCl +  $10^{-4}$  M  $\text{Hg}^{+2}$ .  $E_{\text{Accumulation}} -1.1$  V.  $\tau = 20$  s,  $v = 50 \text{ mV} \cdot \text{s}^{-1}$ )

Analyzed object	Found Me, mg·kg								
	MPC*	Cd	Sr	MPC*	Pb	Sr	MPC*	Cu	Sr
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	-	-	0.25	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	0.03	0.008	0.5	0.73	0.04	5	2.12	0.04
Rye bread	0.02	-	-	0.03	-	-	5	0.49	0.03
Premium Flour Bread	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 (Urgut)	0.20	следы	-	0.5	0.21	0.03	0.5	0.18	0.014
Soil ("Geophysics" vilage)	0.20	-	-	0.5	0.32	0.03	0.5	0.11	0.010
Soil ("Geology" vilage)	0.20	-	-	0.5	0.49	0.04	0.5	0.14	0.011
Soil "Airport"	0.20	0.16	0.021	0.5	0.62	0.05	0.5	0.18	0.009

\* MPC - maximum permissible concentration

#### 4. CONCLUSIONS

1. A method for manufacturing mercury-graphite electrodes for voltammetric measurements has been developed.
2. A substantiated criterion for assessing the suitability and availability of mercury-graphite electrodes for stripping voltammetric analysis.
3. The working electrodes were tested for the determination of cadmium, lead and copper ions in environmental objects, food and drinks by stripping voltammetry.

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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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