

INVERSION CHRONOPOTENTIOMETER OF MERCURY ON THE GRAPHITE ELECTRODE

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Abstract. *Mercury has a carcinogenic effect with a pronounced cumulative action on humans and animals and belongs to the most dangerous water pollutants, as a result of which it is classified as a nutrient that must be controlled. Electrochemical methods of analysis are the simplest ones to operate, and highly sensitive and accessible for ecological control and measurement of mercury ions in water. A method for measuring microconcentrations of mercury in natural drinking water from water supplies, in surface water from lakes and wells, and in aqueous solutions by inverse chronopotentiometry (ICP) with high repeatability and accuracy in accordance with the criteria of metrological certification is developed in this study. The essence of the ICP method is the electrochemical concentration of the element from the sample solution on the indicator electrode with subsequent measurement of its dissolution potentials in time (inversion) at a given resistance in the oxidation circuit. The mercury content in the samples is determined by the method of addition of a standard sample with a known weight of*

mercury ions. It is established that the limit of absolute error in the measurement of mercury concentrations C does not exceed $\pm 0.2C$, and the relative error of measurements ranges from 1.54 to 15.2% depending on the concentration. According to the developed method, the lower limit of determination of is set at $0.1 \mu\text{g}/\text{dm}^3$. The appropriate level of proximity of the results of mercury concentration determinations by the developed electrochemical method of analysis and the atomic absorption spectrometry (AAS) method with electrothermal atomization is found in different samples of drinking water and aqueous solutions. The correctness of determination of mercury is evaluated by the dilution ratio method and the method of additions of certain amounts of a standard mercury salt solution sample. The results of measurements of content in drinking water from wells and surface water samples of lakes of the Kyiv oblast indicate an appropriate level of coincidence of concentration values, as well as suitability of the sample preparation and electrochemical parameters for determining the content of metal ions. The developed method of determination of mercury by the method of inversion chronopotentiometry allows one to maintain reliable ecological control of its content in water samples of different natural origin in the range from 0.1 to $100 \mu\text{g}/\text{dm}^3$, which corresponds to the regulated concentrations for water sources.

Keywords: *determination, electrochemical methods, atomic absorption spectrometry, a standard mercury salt solution, ecological control.*

Introduction. Mercury compounds which are dispersed (fumes or vapors, water-soluble salts, organic compounds) differ with geochemical mobile in comparison with natural mercury (most sulfide, slightly soluble, slightly volatile) mercury compounds and that's why more they jeopardize threatening ecological environment.

From water environment the soluble forms of mercury decay in the ground deposits and with the way of concentration in not biogenic clay mules with the period of complete decay of $n \cdot 10^4$ years. Mercury is firmly fixed with soil due to formation of complex compounds with gumin acids. Period of mercury half decay from the soil is 250 years. Mercury differs high toxicity for any vital form and it is cumulative poison (there is information data on its mutagens action) [1-3].

For drinking-water the possible limited concentrations (PLK) of mercury are set maximum in the interval of 0,001-0,01 g/dm³. The purpose of work is the development of determination method of mercury in drinking-water and any water ecosystems. For this purpose it is necessary to develop the electrochemical parameters of mercury with the method of inversion chronopotentiometer on the graphite electrode.

Analytical function of ICP method - transitional time of electro-oxidization of metal (τ_i) - the concentration of metal ions in solution (C_{me}) is formed in accordance with criterion equation:

$$\tau_i = \frac{KRC_{Me}\tau_{en}\eta_{\tau/2}}{\eta_{\tau/2}},$$

where K is constant; R-resistance into the chain of mercury electro-oxidization; τ_{en} - time of metal concentration; $-\eta_{\tau/2}$ value of potential of indicator electrode in the process of Me inversion. At the standardized terms of electrochemical inversion (value of C_{me} , τ_{en} , R const) and equalization (I) transforms in

$$\tau_i \eta_{\tau/2} = K_i$$

where K_j - constant of inversion. Experimental verification of equalization made by the authors of this article.

Experimental. To determine mercury mostly is utilized graphite electrodes of different modifications [4-7], because graphite is inert during his positive polarization and does not influence on analytical signal at the inversion of electropositive metals. Electrochemical selection of mercury on the mechanically polished graphite needs certain overload for embryo education. This overload is more than lest graphite roughnesses, because defects of surface stimulate embryo education. It is determined [8, 9] that is less number of embryos, which arises up at electro-besieging on the inert electrode, grows linearly in some time after certain induction period.

To remove overload of recovery of mercury on a graphite cooper graphite electrode was applied. The electrode appears during the simultaneous concentration of mercury (potential of mercury is recovers sufficient to renew copper). In the work graphite electrodes Radelkis' firm were utilized. Working surface of such electrode (wooden paving-block with a diameter ~ 3 cm was to mechanically and must be polished with a filtration paper and must be cleaned polished to the glitter condition with a tracing paper).

Preparation of basic background electrolyte: 9,7 g of KSCN are dissolved in 2 cm³ of water, it is added 2 cm³ of concentrated HCl and 0,2 cm³ of standard solution of copper with the concentration of 100 mkg/cm³ and added it to 1000 cm³. In the device M-XA1000-5 it is foreseen the measurement system of with two electrodes: indicator electrode and auxiliary, if this simultaneously devises functions as comparative electrode. A management work of electrodes is executed with the program.

The electrochemical inversion of mercury was conducted in the automatic mode with the program created for the operation system Windows XP. Prototypes for the choice of electrochemical parameters of inversion were the article [10-12].

Results and Discussion. The program has several features (table 1):

- in the program is foreseen the possibility of reversible polarization of indicator electrode;
- chronopotentiogram is registered in differential type $d\varphi/d\tau$ -C and after the proper mathematical treatment information results are added to the database;
- treatment of chronopotentiogram gets better due to set of different mathematical methods of filtration of analytical signals;
- interactive treatment of graphic chronopotentiogram is completed together with the parameters of electrochemical inversion and digital results can be printed;
- the program foresees the usage of 5 additions. Results are approximated with the least squares method and in the graph are for the usage suitable (fig. 1);

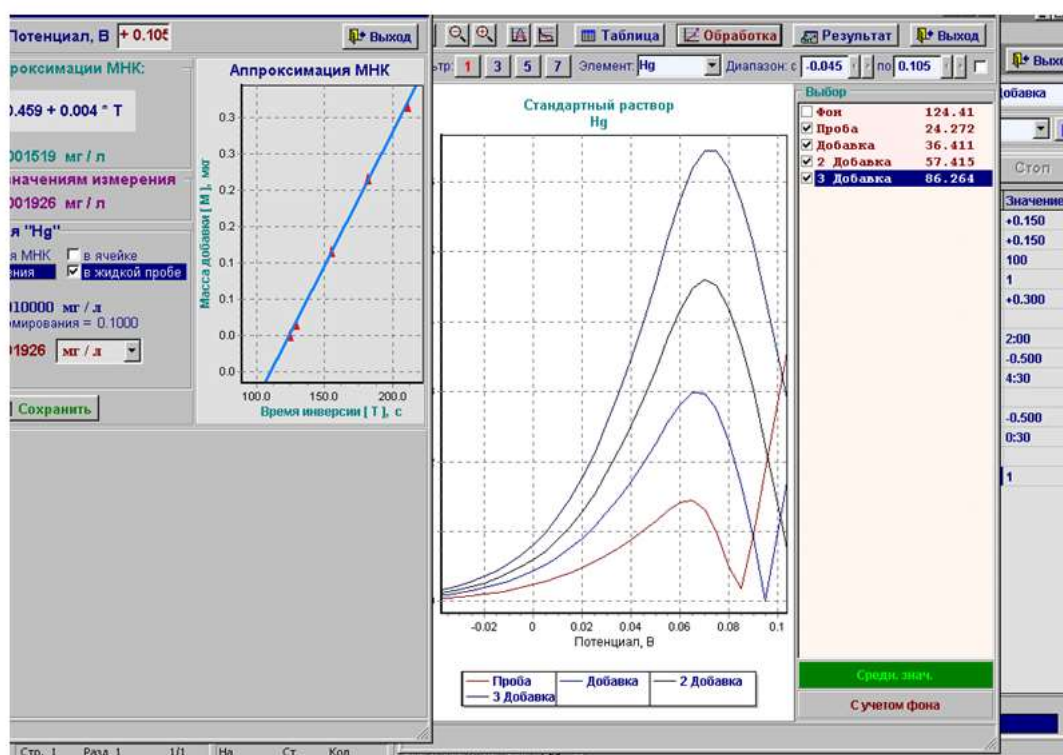


Fig. 1. Chronopotentiogram of mercury on a copper graphite electrode in standard solutions

Mercury contamination is one of the most serious environmental issues worldwide. Long-term accumulation of heavy metals in the body may results in neurological degenerative processes. Repeated long-term contact with certain heavy metals or their compounds may even damage nucleic acids, cause mutation, and eventually lead to cancer. Among the various analytical methods [10-13], electrochemical methods have been widely used because of their advantages such as apparatus low cost, sensitivity and simplicity. The promising area in electrochemistry is development and improvement of electrodes. To address various challenges, metal electrodes, metal-oxide electrodes and ion-selective electrodes are used. Chemical, mechanical, and electrochemical modification of electrode surfaces leads to electrochemical characteristics improving response time reduction, reproducibility and selectivity enhancement, as well as detection limit lowering. However, the development of multifunctional electrodes designed for the analysis of multicomponent systems remains a challenging task. New carbon composite electrodes (CCEs) have many attractive properties that make them a suitable alternative to other electrodes [14]. In this work, CCEs were examined because of their advantages and possible application in various electrochemical techniques. Additionally, the authors have studied the conditions for Hg (II) determination and the effect of interfering ions.

On fig. 1 it is given the chronopotentiograms of mercury in standard solutions, obtained with the method of additions with data approximation after three additions. Linear graph in coordinates mass of addition - inversion time is the basis to apply of ICP method for mercury determination in different objects (table 1).

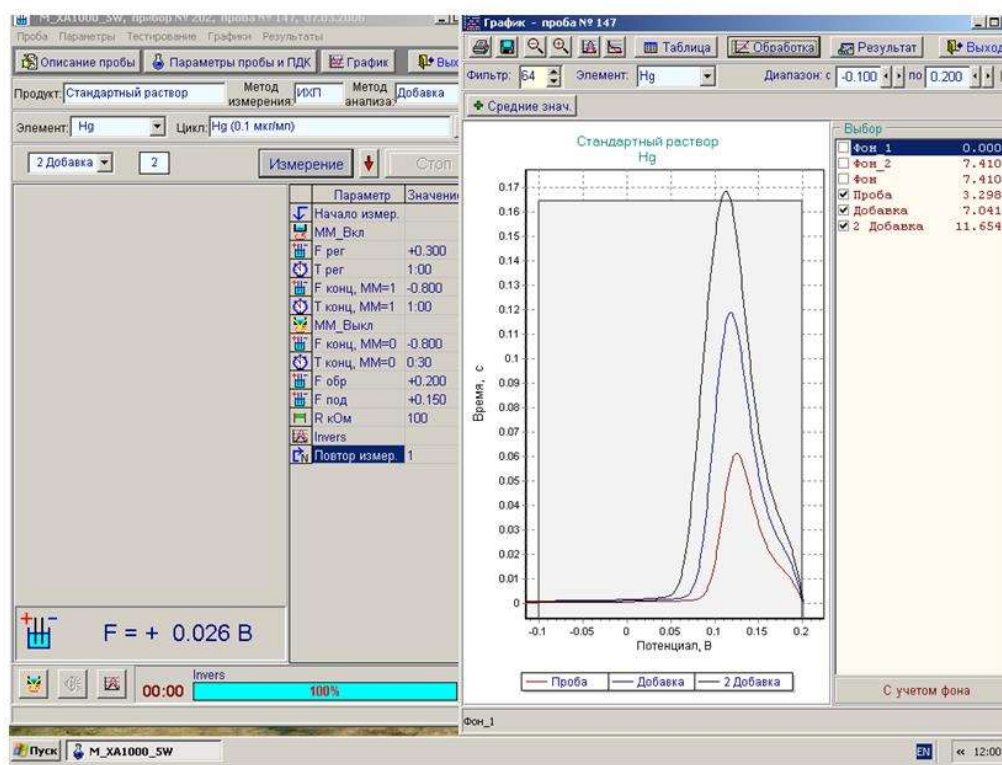


Fig. 2. Chronopotentiogram of mercury on a copper graphite electrode in standard solutions (the method of additions is used)

Table 1. Preparation of the attested mixtures (AC) of mercury

Initial solution for preparation AC (mg/dm ³)	Volume of solution for preparation AC (cm ³)	Volume of the volumetric glassware (cm ³)	Concentration of prepared AC (cm ³)	Code
100	5	50	1,0	AC-1
10	5	50	1,0	AC-2
10	1,25	25	0,50	AC-3
1,00	1,00	10	0,100	AC-4
1,00	0,50	10	0,05	AC-5

AC-1 - stable during 30 days; AC-2 and AC-3 - during 14 days; AC during 5 days; AC-5 - during one day.

As a result of the limited storage terms of standard solutions at while preparing and storage of standard solutions and their little lose in the most cases t

is necessary no to prepare 100 cm³ of standard solutions. It is necessary to estimate the supposed amount of analyses and in accordance with it to choose volume of basic standard solution for its preparation (50 cm³ is recommend). During storage of standard solutions with low concentration we must take account the following circumstances:

- possibilities of solutions contamination from material of glassware, intended for storage;
- ions adsorption on the surface of sides, as a result the concentration of standard solutions diminishes in course of time, work with standard solution in new glassware must be done within three days, after that it is to pour it out and not rinse glassware. It is recommended to made fresh pour standard solution. After three-times of carrying out this operation standard solution can be saved during one month.

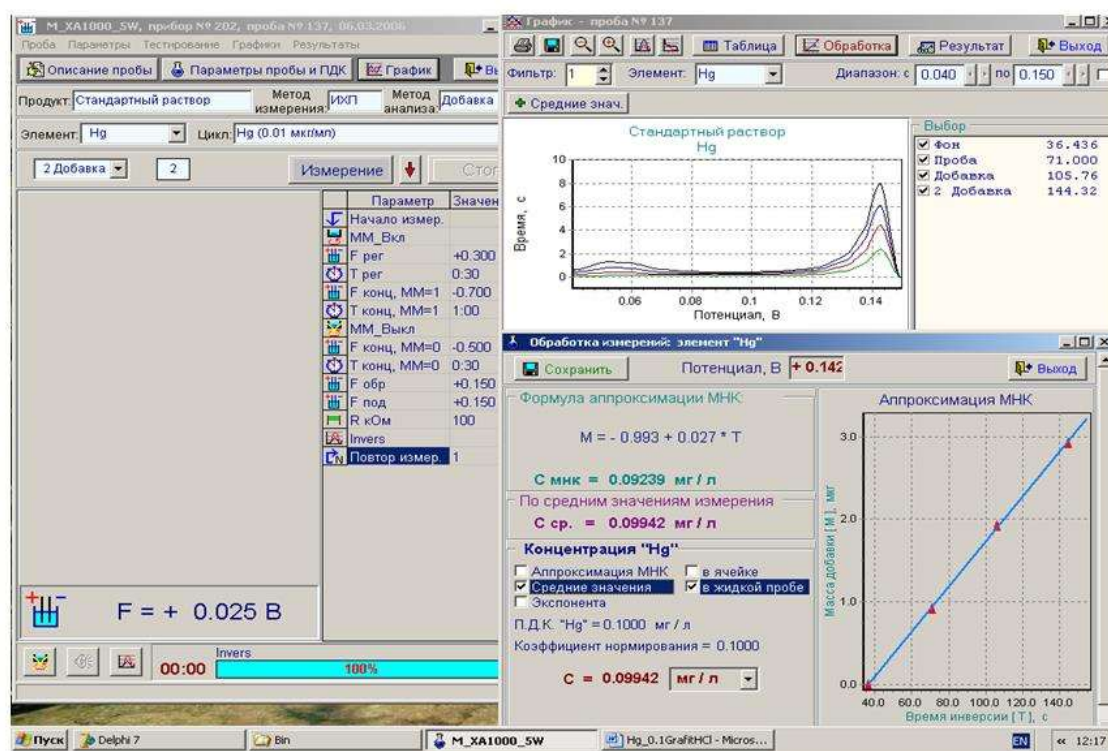


Fig. 3. Indicator electrode for determination of mercury (a)

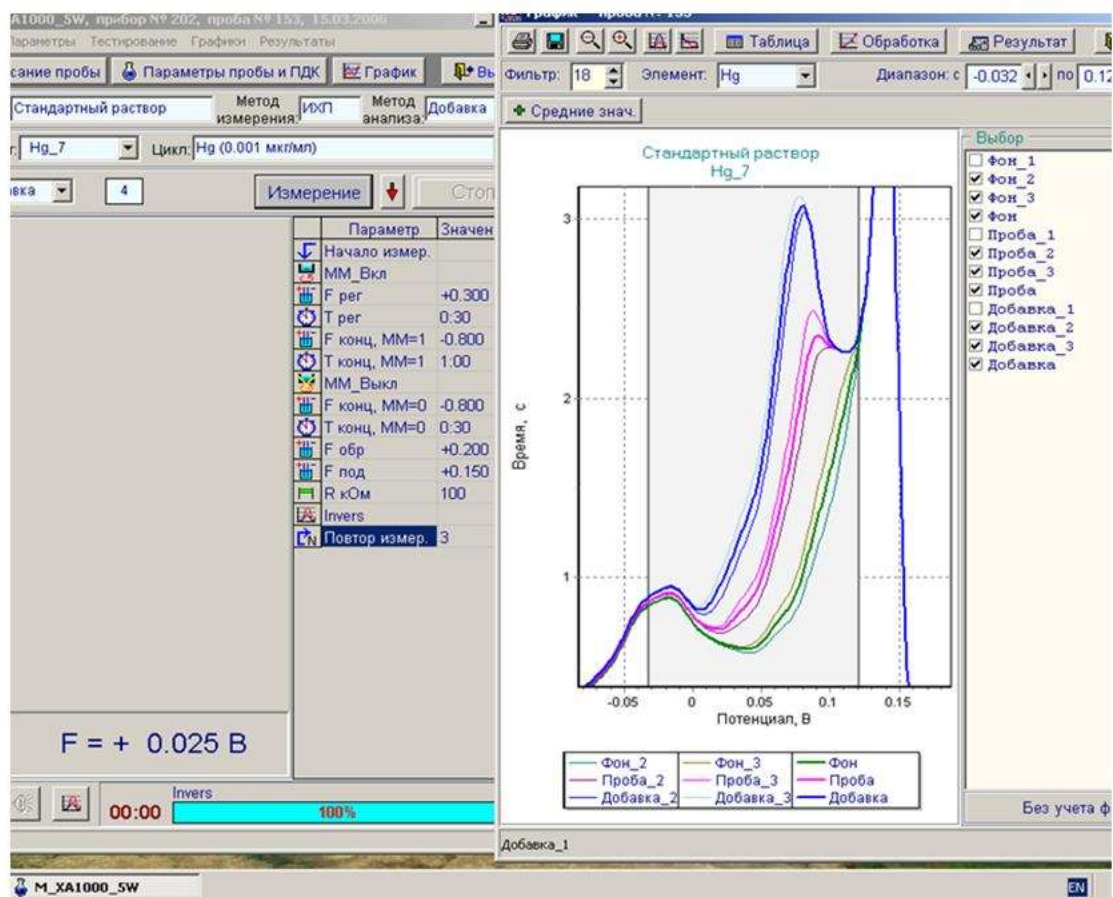


Fig. 3. Indicator electrode for determination of mercury (b).

On Fig. 3 (a, b) it is resulte chronopotentiogram of mercury and inversion program on GGE - indicator electrode. The linear chart of the approximated data is obtained for the interval of mercury concentrations of 0-0,001 mkg/cm³ is the basis for analytical determination of mercury in this interval of concentrations. On the basis of ICP method the methods of mercury determination in drinking - water, and also in any water ecosystems with the use of GGE are developed. For subsequent mineralization of dissolved organic matters i in water we add 1 cm³ HNO₃ (solidity of 1,40 g/cm³) and 2 cm³ of H₂O₂ 30%. The mixture remains on 15-20 minutes,

and then it is evaporated to the dry state. After cooling the dry residue is dissolved in 15-20 cm³ 2M HCl and must be put in a volumetric flask of 25 cm³. Solution is added to the mark of 2M HCl.

Depending on the expected concentration of mercury in electrolyzer wet should put exactly measured volume (1-5 cm³) of tests if necessary to volume 5 cm³ with the bidistilled water. The tested solution prepared in such way must be analyzed during one hour. The yellow color of the tested solution means that this solution can't be used for analysis (insufficient mineralization).

“Single” control test is prepared with the method of preparation of tested solutions for every series of analyses and for every new portion of reagents. Water mineralization can be conducted with ultraviolet irradiation (length of wave is 200 nm and more) with adding peroxide hydrogen by the mercury lamp of DRT-230 during 30-60 minutes at interfusion of solution. The mass concentration of mercury in a test is determined with method of portions.

Developed method is applied for the analysis of drinking-water in Khust, Zacarpathian area and for determination of mercury in water of the river Tissa (table 2).

Table 2. Mercury content in water objects mg/dm³

Object of researches	Tests		
	1	2	3
	IXM M-XA 1000-5	ДІБА РС-ЕТР	-
Khust, drink-water	0,0022/0,0030	0,092/0,0006	0,0014/0,0015
river Tissa	0,0051/0,0058	0,038/0,040	0,0063/0,0055

Conclusion. For comparison mercury content was determined mentioned in objects by the method of inversion chronopotentiometry (ICP) on a graphite electrode at the device M-XA 1000-5 and method of differential impulsive voltamperimeter on a gold disk electrode by RS-ETR. It is made with POLARO-

SENSORS company on the basis of theoretical principles, which have been created during many years by Czech and Ukrainian (NAU) electro-chemists. This device is widely used for modern determination (patents in 30 countries all over the world, gilded youth on the International industrial fair in Brno).

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