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HIGHLY SENSITIVE METHODS FOR DETERMINING TRACE AMOUNTS OF MERCURY IN THE ENVIRONMENTAL OBJECTS

Abstract. The studies for the development of highly sensitive methods for determining heavy metals in the environmental objects have been carried out, using the example of determining mercury by the inversion voltammetry method, based on the investigation of the regularities of mercury electro-deposition and electro-oxidation on a solid electrode.

Key words: toxic substances, mercury, indicating electrodes, inversion voltammetry, environment.

An increased interest to the problem of determining mercury in the environmental objects is caused by the wide occurrence of this element, its greater toxicity in comparison with the other heavy metals, and its ability to bioconcentration [1]. The major part of mercury, reaching the environment, is of a technology-related character [2]. Maximum permissible concentrations (MPC) of elemental mercury in the atmospheric air are standardized at the level of $0.3 \mu\text{g}/\text{m}^3$, in water bodies – at the level of $0.0005 \text{ mg}/\text{l}$, and in soils – at the level of $2.1 \text{ mg}/\text{kg}$, and MPC of the alkyl derivatives of mercury, most dangerous by their physiological effect, make up $0.1 \mu\text{g}/\text{l}$ in water bodies [3].

The issues of global environmental monitoring include monitoring the pollution levels not only in the industrial, but also in the relatively environmentally clean areas for detecting the so-called natural background [4]. The concentration of mercury in the atmosphere varies from 0.005 to $50 \text{ ng}/\text{m}^3$, and in waters from 2 ng to $2\text{--}3 \mu\text{g}/\text{l}$. In the contaminated rocks, sand and soil an average content of mercury is $0.1\text{--}0.5 \text{ mg}/\text{kg}$ [5].

The data of analytical control alone may offer people a thread to managing the environmental purity and indicate the moment of the required intervention to protect it from the accumulation of toxic substances and environmental poisons, whereto heavy metals and mercury, in particular, are directly related.

Procedure for carrying out an electrochemical analysis. Voltammetric measurements were carried out on a PI-50.1.1 potentiostat, which made it possible to work in the mode of cyclic and inversion voltammetry with different potential sweep rates [6]. An analysis was carried out in a three-electrode cell upon stirring the solution ($V = 25 \text{ ml}$) due to the electrode rotation at the rate of $900\text{--}960 \text{ rpm}$. Nickel electrode and mercury-film, nickel-based electrode, with a visible surface area from 0.03 to 0.013 cm^2 , served as working electrodes.

Voltammograms were recorded on a two-coordinate self-recording potentiometer UI-21 with a potential sweep rate of $100\text{--}200 \text{ mV}/\text{s}$. A silver-chloride electrode EVL-1M3.1, the potential of which in relation to the saturated hydrogen electrode in a saturated solution of KCl at 20°C was equal to 0.237 V . Pt - wire was used as an auxiliary electrode. Removal of oxygen from the solution was achieved by purging with argon for 15 min . The studied solutions were prepared from the salts of CP and AR grades. The solutions of lower concentrations were obtained by diluting the initial solutions with the background electrolytes.

For increasing the efficiency of the study and optimizing the process through the implementation of the step-by-step principle, moving towards the optimum, the Box-Wilson mathematical planning method (the steepest ascent method) was applied [7].

Experimental. Mercury is one of the most toxic elements, widely used in various fields of science and technology. A great interest in the issue of determining mercury is caused by its wide occurrence in the environmental objects, its greater toxicity in comparison with the other metals, its ability to accumulate in living organisms and migration in the environmental objects.

High toxicity of mercury stipulates its low MPC value, which requires using the sensitive methods of analytical chemistry. One of the methods, meeting the requirements for determining the detection limit and concentration range is inversion voltammetry. A large number of works are devoted to mercury determination by the inversion voltammetry method.

Most of the published works are mainly related to the development of procedures for quantitative determination of mercury on various electrodes. The physical and chemical regularities of the process of mercury electro-deposition are insufficiently studied, and the results of the conducted studies do not provide a complete picture of the initial stages of electrochemical isolation of mercury on the electrode. The most promising and modern methods of analysis are electrochemical ones (inversion voltammetry), the value and significance of which are characterized by rapidity of chemical analysis, high sensitivity and good reproducibility of the results, which is determined by the quality of the indicating microelectrodes used.

With the purpose of further developing mercury inversion voltammetry, a more detailed study of the regularities of the electro-deposition and electro-oxidation of mercury is required.

The developed indicating microelectrodes, which may be safely attributed to the new means for controlling toxic substances, were proposed as means for controlling heavy metals [8].

The physical and chemical characteristics of these electrodes and the mechanism of the processes, taking place at the electrode-solution interface at the stages of preparing their surface and subsequent amalgamation, were studied. The optimal parameters of their functioning were determined. The factors influencing the sensitivity and resolution of the film microelectrode were studied. As noted in [9], when carrying out an electrochemical analysis of the compounds of toxic metals, the nature of the indicating electrode matrix, the background composition and the presence of other components produce a great influence upon the cathode-anodic processes. The factors influencing the sensitivity and resolution of the film electrode were studied. The prospects of using new electrodes, made of refractory materials, in an electrochemical analysis for controlling toxic and heavy metals in the technology-related and mineral raw materials of Kazakhstan were shown.

The indicated circumstances determine the necessity to solve a complex problem - the development of highly sensitive methods for the determination of heavy metals, using inexpensive and available materials with the valuable physical, chemical and electrochemical properties. Metals of iron series may be related to such materials.

We studied the processes of Hg reduction and oxidation on the nickel electrode, determined the clear maxima of the cathodic ($E_{\text{Hg}} = +0.29$ V) and anodic ($E_{\text{Hg}} = +0.76$ V) peaks. As it can be seen from Figure 1, the recovery of Hg (II) on the nickel electrode begins at a potential of -0.25 V with the formation of a single cathode wave, reaching a value of the limiting current of 0.925, 0.65 and 0.35 for the concentrations of 10^{-4} , 10^{-5} and 10^{-6} mol/l, respectively.

At the polarization curves of mercury oxidation two waves are expressed: at $E = +0.60$ V and $E = +0.85$ V. This testifies to the complex character of the process of mercury oxidation. In our opinion, the effect of a possible formation in the process of cathodic reduction of mercury of oversaturated amalgams, containing cluster forms of nickel compounds with mercury of non-equilibrium composition, with an increased electrochemical activity, upon the course of the anodic polarization curves, is not excluded. It is also seen from the curves of figure 1, that a concentration dependence of the cathode waves is observed, which may be used for the quantitative determination of bivalent mercury in the solution.

As for the anodic curves, in view of their complex nature, for quantitative accurate analysis it is better to use the cathodic reduction waves (figure 2). However, in case of a less accurate analysis and with the very low mercury content in the analyzed objects, the anode currents may be also used, since they surpass by their value the cathode currents.

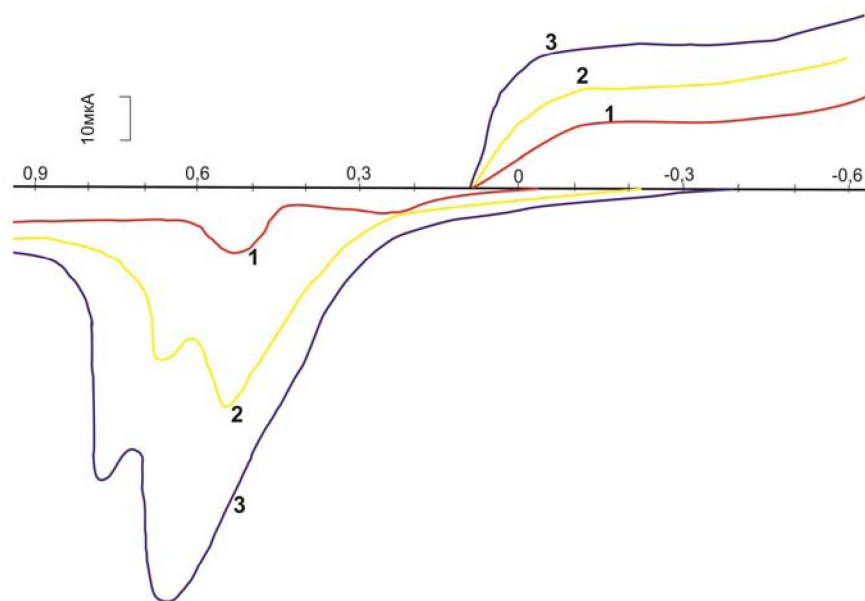


Figure 1 – Cathode-anodic voltammograms of mercury on a nickel electrode horizontal axis: potential (E), V; vertical axis: current strength (I), μA ; $C_{\text{Hg(II)}}$, mol/l: $1 - 10^{-6}$; $2 - 10^{-5}$; $3 - 10^{-4}$

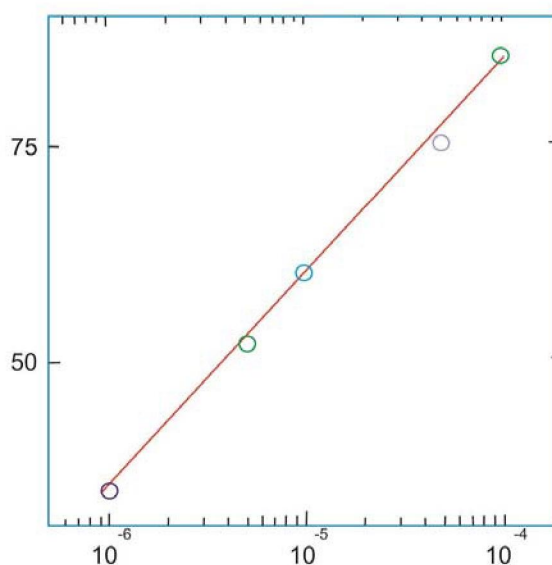


Figure 2 – Calibration chart for determining mercury on a nickel electrode horizontal axis: concentration (C), mol/l; vertical axis: current strength (I), μA

With the purpose of finding the optimal conditions for the determination of low mercury contents by the method of inversion voltammetry, the method of mathematical planning of the experiment (the Box – Wilson method) was used [7].

The study of the single-factor dependencies of the completeness of mercury isolation upon a number of factors (the concentration of ME, the nature and concentration of the background electrolyte, the surface area of the film and solid electrodes, the solution volume and rate of mixing) showed, that the most significant factors were the concentrations of Me and the background electrolyte, the surface area of the indicating electrode, and the remaining factors were insignificant and stabilized subsequently.

Therefore, when determining mercury by the inversion voltammetry method, the planning matrix 2^3 was used. The results of the experiment, related to choosing the optimal conditions for mercury determination by the inversion voltammetry method are presented in table.

Experiment planning matrix 2^3 for mercury determination

Factors	$C_M(\text{Hg}^{2+})$	$C_M(\text{H}_2\text{SO}_4)$	$S_{\text{electr.}}$					
Dimension	mol/l	mol/l	cm^2					
Basic level	10^{-5}	0.75	0.09					
Varying interval	10^{-1}	0.25	0.04					
Upper level	10^{-4}	1.0	0.13					
Lower level	10^{-6}	0.5	0.05					
Code	X_1	X_2	X_3	Y	Y	S^2	y	y^2
Experiment 1	10^{-6}	0.5	0.05	80.7 82.0 81.5	81.4	0.43	80.5	0.80
Experiment 2	10^{-4}	0.5	0.05	83.4 87.0 88.0	83.5	0.43	82.65	0.72
Experiment 3	10^{-6}	1.0	0.05	83.4 83.7 84.4	83.5	0.43	82.65	0.72
Experiment 4	10^{-4}	1.0	0.05	90.2 91.0 89.5	90.2	0.56	91.2	1.00
Experiment 5	10^{-6}	0.5	0.13	83.6 84.8 83.5	84.0	0.52	84.4	0.16
Experiment 6	10^{-4}	0.5	0.13	93.5 93.0 93.1	93.2	0.37	92.95	0.06
Experiment 7	10^{-6}	1.0	0.13	85.3 85.0 85.2	85.1	0.03	86.55	2.10
Experiment 8	10^{-4}	1.0	0.13	97.0 96.8 96.0	96.6	0.28	95.1	1.21
Step		0.09	0.03					
Supposed experiments 1	10^{-6}	0.84	0.12					
Implemented experiments 2	10^{-6}	0.93	0.15		85.3			
Supposed experiments 3	10^{-6}	1.02	0.18					
Implemented experiments 4	10^{-6}	1.11	0.21		97.7			
Implemented experiments 5	10^{-6}	1.20	0.24		98.8			
Implemented experiments 6	10^{-6}	1.029	0.27		97.2			
Supposed experiments 7	10^{-6}	1.38	0.30					
Optimum	10^{-6}	1.2	0.29					

The calculated regression coefficients for mercury determination have the following values:

$$b_0 = 87.8$$

$$b_1 = 4.275$$

$$b_2 = 1.075$$

$$b_3 = 1.95$$

The regression equation is as follows:

$$Y = 87.8 + 4.275X_1 + 1.075X_2 + 1.95X_3$$

Checking:

1. reproducibility of the experiment

$$S^2 \{y\} = \sum S^2 / N = 2.75 / 8 + 0.34$$

2. dispersion homogeneity

$$G = S^2_{\max} \sum S^2 = 0.565 / 2.75 = 0.205$$

$$G_{\text{table}} = 0.51 \text{ at } f_1 = 2 \text{ and } f_2 = 8$$

$G_{\text{table}} > G_{\text{exp.}}$ - dispersion is homogeneous

3. the values of the regression coefficients:

$$S^2 \{bj\} = S^2 \{y\} / N = 0.34 / 8 = 0.0425$$

$$bj\} = \sqrt{S^2 \{bj\}} = \sqrt{0.0425} = 0.206$$

$$\Delta bj = \pm t \cdot \{bj\} = 2.12 \cdot 0.206 = 0.44$$

$$\Delta bj = 0.44$$

$0.44 < 3.26$ (1.53; 2.76) – all coefficients are valuable.

4. adequacy of the model:

$$S^2_{\text{ad.}} = \sum y^2 / f_1$$

$$\Delta y = y_i - y_1$$

$$f_1 = N - (k + 1) = 8 - (3 + 1) = 4$$

$$S^2_{\text{ad.}} = 1.695 / 4 = 0.42$$

$$F(f_1; f_2) = S^2_{\text{ad.}} / S^2 \{y\} = 0.42 / 0.34 + 1.25$$

$$F_{\text{table}} = 3.0 \text{ at } f_1 = 4 \text{ and } f_2 = 16,$$

where $f_2 = N(n-1) = 8(3-1) = 16$.

$F_{\text{exp.}} < F_{\text{table}}$ – the model is adequate

The calculations testify to the fact, that the dispersion of the optimization parameter is homogeneous, the model is adequate, i.e. the steepest ascent method can be applied. The component gradients were calculated by regression. Moving to the optimum was performed by adding the factors, constituting the gradient, to the basic level. Since the determination of small mercury quantities of the order of 10^{-6} – 10^{-7} mol/l on the surface of the film and solid electrodes is of a practical interest, so while calculating the step-by-step procedure, moving to the optimum, we stabilized the mercury concentration by the lower level of the factor (10^{-6} M), and we carried out the step-by-step procedure by only two factors: the concentration of the background solution and the electrode surface area.

From the implemented experiments of the step-by-step procedure the optimal conditions were established for the quantitative determination of low mercury concentrations on the film electrode:

1 – the concentration of mercury at 10^{-6} mol/l;

2 – the concentration of the background solution – 1.2 M;

3 – the electrode surface – 0.24 cm^2 .

Thus, as a result of the conducted studies, the methods for analytical control of mercury in the technology-related raw materials were developed by the inversion voltammetry method on the nickel indicating microelectrode in the concentration range of 10^{-5} – 10^{-6} mol/l, ensuring the selectivity of metal determination.

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ҚОРШАҒАН ОРТА ОБЪЕКТІЛЕРІНДЕГІ СЫНАП ҚАЛДЫҚТАРЫН АНЫҚТАУДЫҢ ЖОҒАРЫ СЕЗІМТАЛ ӘДІСТЕРІ

Аннотация. Сынапты инверсионды вольтамперметрия әдісімен оның қатты электродта тұнбаға түсу және тотығу заңдылықтарын зерттеу негізінде қоршаған ортадағы объектілердегі ауыр металдарды анықтаудың жоғары сезімтал әдістерін анықтауға арналған зерттеулер жүргізілген.

Түйін сөздер: уытты заттар, сынап, индикаторлық электродтар, инверсия вольтаметр, қоршаған орта.

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**ВЫСОКОЧУВСТВИТЕЛЬНЫЕ МЕТОДЫ
ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОЛИЧЕСТВ РТУТИ
В ОБЪЕКТАХ ОКРУЖАЮЩЕЙ СРЕДЫ**

Аннотация. Проведены исследования по разработке высокочувствительных методов определения тяжелых металлов в объектах окружающей среды на примере определения ртути методом инверсионной вольтамперометрии на основании изучения закономерностей её электроосаждения и электроокисления на твердом электроде.

Ключевые слова: токсичные вещества, ртуть, индикаторные электроды, инверсионные вольтамперометрия, окружающая среда.

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