

## Inversion-Chronopotentiometric Analysis of Mercury in Water

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**Abstract**—We have developed a technique for determination of mercury in drinking and natural waters ( $0.5 \mu\text{g}/\text{dm}^3$ ) based on the improved method of inverse chronopotentiometry using an M-XA1000-5 analyzer. The article has discussed the expediency of using this method for monitoring the state of the environment.

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### INTRODUCTION

At present, the issue of providing the population with quality drinking water is rather important. The necessity to control the content of mercury in water as one of the most dangerous toxicants is declared by the documents of the World Health Organization and national norms according to which mercury MAC in drinking water constitutes  $0.1\text{--}0.5 \mu\text{g}/\text{dm}^3$  [1–3].

Mercury features high toxicity for any form of life and is a cumulative poison and produces a mutagenic effect. When mercury gets into a human organism it is actively accumulates there and causes chronic poisoning—micromercurialism [4].

From anthropogenic sources into aqueous systems mercury gets predominantly in the form of metallic mercury, Hg(II) ions, and phenylmercury acetate. In aqueous media mercury forms metalorganic compounds like R–Hg–X and R–Hg–R, where R is methyl- or ethyl radical. For instance, according to [4] organisms of fish and crustaceans contain methylmercury, which is formed biologically under the effects of enzymes of microorganisms. This neurotoxin is especially hazardous for children and pregnant women.

Mercury compounds, which disperse in nature technogenically (vapors, water-soluble salts, organic compounds) present the greatest ecological hazard since they are distinguished by substantial geochemical mobility compared with natural compounds (mainly, sulfide ones, hardly soluble) [15]. Therefore it is very important to find mercury contamination and monitor its content in the water at the level of trace quantities.

Most of analytical methods by means of which the concentration of mercury in water is determined, call for complex and expensive analytical equipment. Producers of laboratory analytical equipment, such as Analytical Jena AG (Germany), Aurora Instruments Ltd. (Canada), Brooks Rand Labs LLC (USA), are specialized in the output of atomic fluorescent spectrometers for highly sensitive determination of mercury by the method of atomic fluorescence of cold vapor (determination limit— $0.1 \text{ ppt Hg}$ ). Electrochemical methods of analysis, which use the principle of inversion voltamperometry (devices TA, AVC, IVA-5, Russia) are simpler and less sensitive.

Recently, new methods of inversion chronopotentiometry (ICP) [6, 7] have been developed and has a number of advantages: they are convenient in servicing; have a better sensitivity; the change of the concentration takes place automatically for several minutes without the account of sample preparation; experiments may be carried out in laboratory and field conditions. An M-XA 1000-5 analyzer [8] has been developed. Computer software has been developed too by means of which all measuring and computing operations are performed as well as a number of techniques for determination of heavy metals in natural and waste waters, soils, plants, and foodstuffs [6–10].

Many of these studies have been performed by using mercury film electrodes. However, the possibilities of mercury electrodes are limited in the case of electrochemical inversion of electropositive metals (Au, Ag, and Hg) and some anions since their electric solubility occurs within the interval of positive values of potentials.

Difficulties of the inversion-chronopotentiometric method of determination of electropositive metals are determined by the necessity of reverse polarization of an indicator electrode since the reduction of ions of

metal being determined takes place during its cathode polarization, while in inversion electrosolubility—during anodic polarization.

For further perfection of the ICP method it was proposed to use pulse methods and histogram digital filtration chronopotentiometric data, which were used in a new modification of an M-XA1000-5 analyzer. Thus, the range of inversion potentials expanded into the positive region (from 0 to 0.35 mV) and the sensitivity of the method increased from 10 to  $0.5 \mu\text{g}/\text{dm}^3$  [11–13].

The objective of the present paper is the development of the technique of measuring trace concentration Hg(II) ions in drinking water and other aqueous solutions.

## EXPERIMENTAL

Laboratory utensils for its purification were treated by a chromium mixture and nitric acid, washed with distilled water and then with bidistillator and dried out

Selection and storage of water samples were made according to DSTU ISO 5667-3-2001—DSTU ISO 5667-19: 2007. These samples were selected into polyethylene or glass bottles of  $0.10.5 \text{ dm}^3$  and were preserved with hydrochloric acid ( $0.5 \text{ cm}^3$  of concentrated HCl per  $0.1 \text{ dm}^3$  of the sample), stored at  $4^\circ\text{C}$  for not more than a month.

The water sample ( $0.1 \text{ dm}^3$ ) was transferred to a conic flask of  $250 \text{ cm}^3$ ,  $1-3 \text{ cm}^3$  of concentrated  $\text{HNO}_3$ ,  $1-3 \text{ cm}^3$  of 33%  $\text{H}_2\text{O}_2$  were added and left for one hour. The flask with the solution was fixed in a stand and was placed above a water bath so that between the water and the flask there a distance was of 2–3 cm. The solution was heated at a gradual increase of the temperature to  $70^\circ\text{C}$  and was evaporated to  $2 \text{ cm}^3$ . After cooling the content of the flask was added with  $5 \text{ cm}^3$  of bidistillate and again evaporated over the water bath until the state of humid salts. Then the flask was taken off and cooled; the remainder was dissolved in 2M of HCl and quantitatively transferred to a measuring flask of  $25 \text{ cm}^3$  [14].

Graduation solutions of Hg(II) with the concentration of 10.0; 1.0 and  $0.1 \mu\text{g}/\text{cm}^3$  was prepared by dissolving the standard solution MSO 0345:2002, DSZU 022.6-96 with the concentration  $100 \mu\text{g}/\text{cm}^3$ . The background solution was prepared directly before measurement:  $1 \text{ cm}^3$  of the solution (0.2 M by KI and 1.6% by  $\text{Na}_2\text{EDTA}$ ) and  $0.1 \text{ cm}^3$  1 M of  $\text{Na}_2\text{S}_2\text{O}_3$  was added to  $9 \text{ cm}^3$  1 M HCl.

For conducting research on an M-XA1000-5 analyzer (Fig. 1) a unit consisting of a stand, measuring and auxiliary electrodes and a comparison electrode, a magnetic stirrer, an electrolyzer (a chemical glass containing  $10-25 \text{ cm}^3$ ) and a mixing element.

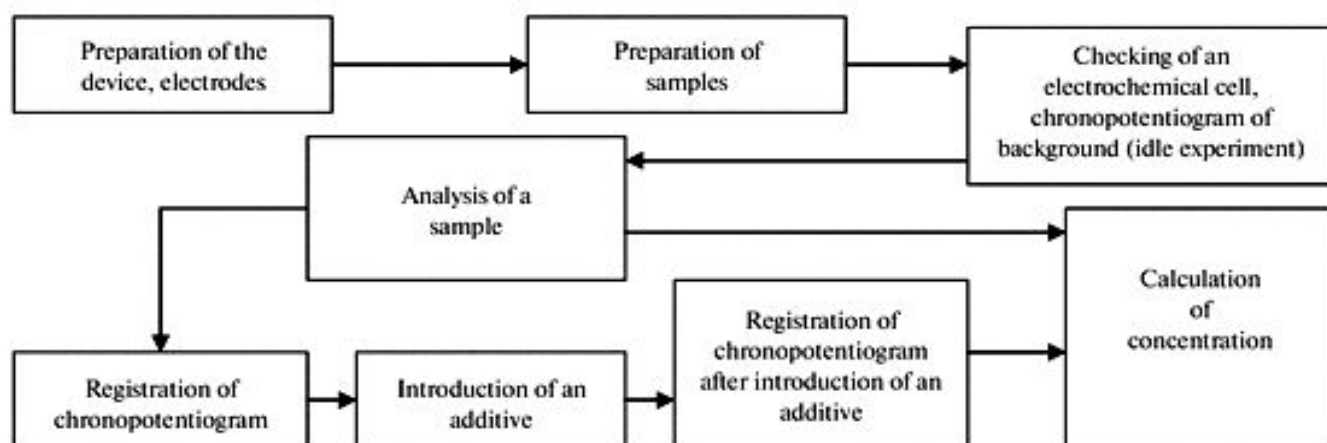


Fig. 1. General schematic of the analysis by the method of inversion chronopotentiometry on an M-XA1000-5.

Prior to the operation of the measuring electrode (golden solid-state) was ground by chemically precipitated calcium carbonate, rinsed by bidistillate, immersed in the solution of 1M hydrochloric acid; the comparison electrode (silver-chlorine) was filled with a 2 M HCl solution. Electrodes were dipped in the background solution of the electrolyzer, which was installed on the magnetic stirrer.

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