

Determination of Arsenic in the Water Using the Method of Inversion Chronopotentiometry

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Abstract—The technique has been developed for determination of arsenic in drinking and natural waters ($\geq 0.5 \mu\text{g}/\text{dm}^3$) based on the improved method of inversion 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

Among numerous contaminating components of the water one of the most hazardous is arsenic; its MAC in drinking water constitutes $1\text{--}50 \mu\text{g}/\text{dm}^3$ [1, 2]. Increased concentrations of arsenic are detected in some underground waters, where it is a natural component of mountainous rocks. Arsenic compounds are incorporated by the compositions on pesticides, contained in wastewaters of enterprises of nonferrous metallurgy, production of pharmaceutical industry and substances of special purity.

In natural waters arsenic is mainly in the form of arsenate and arsenite [3]. The As (V) compounds are stable in oxidizing condition, while in weakly-reducing media As (III) prevails. At the pH values, which are characteristic of natural waters, oxidation of arsenite takes place slowly. In water basins subjected to a substantial load, the arsenic concentration varies within the range $1\text{--}50 \mu\text{g}/\text{dm}^3$, while in fresh unpolluted water basins its content mainly does not exceed $1 \mu\text{g}/\text{dm}^3$. The waters of the open ocean are characterized by the content of arsenic in the amounts $2\text{--}3 \mu\text{g}/\text{dm}^3$ [4]. Arsenic toxicity depends on the form of its existence: inorganic compounds are more toxic than organic ones [5], while As (II) is more toxic than As (V) [6].

As is known arsenic is a metabolite of phosphorus, selenium, and iodine. It is capable of being built up in a thyroid gland causing an endemic goiter. Penetrating a human organism arsenates compete with phosphates having a similar structure, which negatively affects the reaction of the formation of adenosine triphosphate and causes the destruction of the cells of an organism. Some authors refer As (V) to genotoxic substances, which directly affect a DNA molecule and given the content of arsenic in the water in an amount of $4 \mu\text{g}/\text{dm}^3$ one may observe its stimulating influence on the growth of an oncological tumor [7]. A lethal dose of arsenic for a human constitutes $0.1\text{--}0.3 \text{ g}$ [8].

It should also be noted that active regulatory documents regulate only the general content of arsenic, while the toxicity of the element depends on the form of its occurrence in the water [9, 10]. Therefore it is necessary to monitor the content of arsenic in drinking water at a level of $0.5 \mu\text{g}/\text{dm}^3$, which is declared by the documents of the World Health Organization and national regulatory documents [1, 2, 11].

For determination of traces of arsenic in water and biological objects many methods are used, the most sensitive among them are presented in Table 1.

The main restriction for a wide-spread use of spectral and combined methods for ecological monitoring is a high cost of the equipment itself and its maintenance [6].

The use of electrochemical methods, especially of inversion chronopotentiometry (ICP) with calibrated resistance in the oxidation circuit is more preferential. Theoretical principles of this variant of ICP are discussed in [17]. The given method due to the presence of resistance in the oxidation circuit have high protection against interferences and for all intents and purposes is not sensitive to capacitive currents. It makes possible to use various modifications of indicator electrodes of noble metals, for instance, solid-state golden ones [16]. The M-XA10000-5 analyzer has been developed based on the ICP method, which was tested in laboratories of sanitary-epidemiological monitoring, the system of water-piping supply, veterinary service, etc [16, 18].

However, its application for determination of low concentrations of toxicants turned out to be limited due to insufficient sensitivity (10 mg/dm^3) and the absence of using a positive area of potentials, which is necessary when determining As (III).

Table 1. Methods of arsenic determination in solutions

| Method | Detection limit, $\mu\text{g/dm}^3$ | Source |
|---|-------------------------------------|---------|
| Spectrophotometry | 4–30 | [12] |
| Ionic chromatography in combination with induction-bound plasma | 0.3–0.4 | [13–15] |
| Atomic absorption with the AsH_3 trap | 0.05 | |
| Atomic absorption with preliminary solid-phase extraction | 0.05 | |
| Induction-bound plasma with generation arsenic hydrates | 0.02 | |
| Gas-phase chemiluminescence | 0.05 | |
| Inversion voltammetry | 1.0 | [16] |
| Inversion chronopotentiometry | 0.5 | |

For improving the ICP method we have studied the influence of the composition and concentration of electrolytes, the type of indicator electrodes, parameters and cycles of inversion to electrochemical behavior of As (III) during measurement of its trace amounts. The device for the measurement of the concentration of heavy metals with the use of pulse methods of chronopotentiometry and the histogram of digital filtration of chronopotentiometric data has been modernized [19, 20]. The range of potentials of inversion to the positive area (0 to +0.35 mV), where the inversion of As (III) takes place with the application of a gold solid-state electrode has been extended. The measurement time of the content of the element depends on its concentration in the solution of a sample and constitutes not more than 3 min. Other important features of the method have been described in [21].

EXPERIMENTAL

The research was carried out according to the developed technique [22]. The laboratory glassware was cleaned by a chromium mixture and nitric acid, rinsed with distilled water and then by a distillate and dried out. The selection and storage of the water samples were carried out according to DSTU ISO 5667-3-2001, DSTU ISO 5667-19:2007. In this case they were placed in polyethylene or glass bottles of $0.1\text{--}0.5 \text{ dm}^3$ and preserved with hypochloric acid (0.5 cm^3 conc. HCL per 0.1 dm^3 of a sample), stored at 4°C not more than one month.

The water sample (0.1 dm^3) was transferred to a conic flask of 250 cm^3 , added $1\text{--}3 \text{ cm}^3$ of conc. HNO_3 , $1\text{--}3 \text{ cm}^3$ of 33% of H_2O_2 and left it for one hour. The flask with the solution was fixed on a tripod and was placed above the water bath so that the distance between the water and the flask be $2\text{--}3 \text{ cm}$. The solution was heated at gradual increase of the temperature to 70°C and was evaporated to 2 cm^3 . After cooling the content of the flask was added with 5 cm^3 of the bidistillate and again was evaporated above the water bath to the state of humid salts. Then the flask was removed and cooled, the remnant was dissolved in 2M of HCl and quantitatively was transferred to a measuring flask of 25 cm^3 .

For preparing other solutions the bidistillate was used. Graduation solutions with the As (III) concentration 10.0; 1.0, and $0.1 \mu\text{g/cm}^3$ were prepared by diluting its standard solution (GSO 022.49-96, MSO 0031:1998) at the concentration $100 \mu\text{g/cm}^3$. The background solution was prepared directly before the use. 9 cm^3 of 2M of HCl was added with 1 cm^3 of 0.1 M of EDTA and 0.01 cm^3 of the solution of copper salt with the concentration $100 \mu\text{g/cm}^3$. 9 cm^3 of the solution of the sample mineralizate was added with 1 cm^3 of 0.1 M of EDTA and 0.01 cm^3 of the solution of copper ions.

When conducting measurements of As (III) concentrations in water samples on an M-XA1000-5 analyzer an electrochemical cell, consisting of a tripod, a golden measurement electrode and a silver chloride comparison electrode, a magnetic stirrer, an electrolyzer (a chemical glass, capacity $10\text{--}25 \text{ cm}^3$) and an intermixing element were used.

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