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Determination of Heavy Metals in Aqueous Ecosystems by the Method of Inversion Chronopotentiometry

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Abstract—We have developed and tested the techniques of measuring heavy metals (lead, cadmium, copper, and zinc) in drinking water and aqueous ecosystems by the method of inversion chronopotentiometry by means of an M-XA1000-5.

INTRODUCTION

The assessment of the state of water resources of surface and underground waters under conditions of constantly active sources of their pollution with heavy metals (HM) is an extremely complicated and important problem and its solution is conducive to the development of a complex of measures for the improvement of drinking water quality and aqueous ecosystems.

From the viewpoint of the fact that water of natural sources is an electrolyte, for determination of its quality the use of electrochemical methods of analysis became the most promising one. These methods are characterized by high sensitivity, selectivity, and the capacity of recording a broad spectrum of chemical elements in various matrices. One of them is the method of inversion chronopotentiometry (ICP), which is widely used in the practice of laboratory measurements in Ukraine.

BASIC PROVISIONS OF THE THEORY OF INVERSION CHRONOPOTENTIOMETRY

The principle of the ICP method consists in measuring the dissolving time of Me^{n+} from the surface of the indicator electrode, which was in advance concentrated on it during electrolysis. In the general form the process of electrochemical inversion is described by the scheme

$$Me^{n+} + ne \overset{\varphi_k}{\underset{\varphi_i}{\leftrightarrow}} Me, \tag{1}$$

where φ_k and φ_i are respectively potentials of concentration and inversion.

Based on the analysis of the Nernst's theory in papers [1, 2] we obtained the equation linking the inversion time τ_i with the concentration of metal ions $C_{Me^{..}}$, which are determined in solution at a set potential of inversion φ_i and the time of electrolytic concentration τ_k:

$$\tau_i = \frac{nFDSRC_{Me}}{\varphi_i \delta} \cdot \tau_k, \tag{2}$$

where n is valence of metal; F is the Faraday constant; D is coefficient of the diffusion of metal ions Me^{n+} in solution; S is surface of the indicator electrode; R is resistance in the electrical scheme of inversion; δ is thickness of a double electric layer.

In identical conditions of conducting the experiment a number of parameters in Eq. (2) is invariable and they can be represented as

$$\frac{nFDSR}{\varphi_i \delta} = const = K. \tag{3}$$

In this case Eq. (2) is simplified:

$$\tau_i = K \cdot C_{Me} \cdot \tau_k. \tag{4}$$

Thus, the inversion time is directly proportional to the concentration of the ions being determined in the solution. For measuring τ_i an electrochemical wiring circuit is made, which provides conditions for conducting electrolysis followed by inversion. The inversion time also depends on the value of calibrated resistance included into the oxidation circuit. If the circuit resistance is small the dissolution process occurs very quickly and the potential instantaneously drops to zero. But if the calibration resistance constitutes 100–150 kΩ, then the potential φ_k decreases to the value φ_i and remains constant within the time at which the indicator electrode contains the accumulated metal. Unlike other electrochemical techniques the ICP method has a high protection against interferences due to large values of resistance. It is virtually insensitive to capacitive currents, which provides a possibility of using various indicator electrodes (mercury film electrodes, silver, gold, etc.) and simplifies the device design.

Upon the completion of the inversion the potential φ_i decreases to zero or to any set potential of dissolving metal φ_τ. The time within which φ_τ retains its constant value proportionally to metal concentration on the indicator electrode and at standardized concentration conditions—directly proportional to the Me^{n+} concentration in the solution.

The possibility of setting φ_τ making possible to decrease the electromotive force of metal dissolution, which results in an increase of the inversion time and an increase of the ICP method sensitivity. As a rule, such value of φ_τ is set when determining low concentrations of metals.

When implementing the ICP method a two-electrode electrochemical cell is used (indicator and comparison electrodes, chemical support for holding the electrode, electrolyzer with a sample and stirring element, magnetic stirrer), a control unit and a computer. By means of a specially developed computer software in the control unit the required potential is formed, which is sent to the electrodes, the operation of the magnetic stirrer is regulated, the data on inversion for the calculation of concentration of elements are read and sent to the computer.

The whole process of measuring the HM concentration is automated on the computer. For measuring the concentration of Pb and Cu a background solution of 2M HCl is used and a 1M ammonium buffer—for Zn and Cd. In the case the content of an element in the electrolyzer is higher than the upper boundary of the determination range then such a sample is diluted with the background solution to the required concentration level.

As a rule, the determination of HM concentration in the sample is carried out for every element separately. This is caused by the different MAC level of the elements in the environmental objects (different value of φ_τ with a change of inversion time) and the use of many background solutions.

Using the resultant values of the potentials a solubility curve or a chronopotentiogram of inversion is built. The chronopotentiogram is a function of the inversion potential over time $\varphi(\tau)$.

If ions of several metals are present in the solution the chronopotentiogram has a general form shown in Fig. 1. As can be seen, at first a more electronegative potential is transferred into the solution and then a more
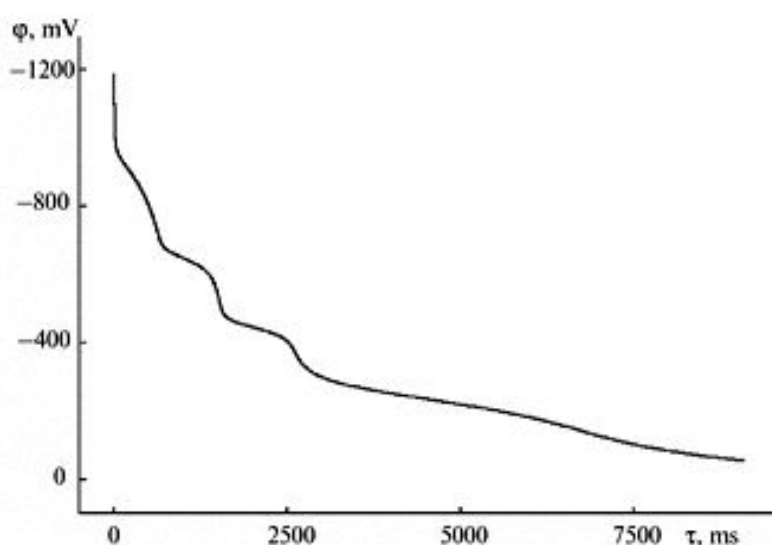
Fig. 1. Chronopotentiogram of successive dissolution of metals over time. Experimental conditions: the measuring electrode—solid body silver, amalgamated with mercury; the comparison electrode—silver chloride; background—2M HCl; $C_{Me+} = 0.5$ µg/cm^3; concentration time—1 min; regeneration potential—$\varphi_p = 20$ mV; electrolysis potential—$\varphi_k = -1500$ mV; treatment potential—$\varphi_{treat} = -100$ mV; resistance—150 kΩ.

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