

## DETERMINATION OF SMALL AMOUNTS OF ELEMENTS BY THE ATOMIC EMISSION METHOD WITH PRELIMINARY CONCENTRATION OF A SAMPLE

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*The results of ICP spectrometer measurements of low concentrations of lead and copper in aqueous solutions with preliminary concentration of a sample by means of a flow-injection system are presented. A significant decrease in the detection limits of the indicated elements has been obtained. The influence of different methods used for mathematical processing of the results of measurements on the error in determining elements in aqueous solutions has been investigated.*

**Keywords:** *atomic emission spectral analysis, inductively coupled plasma spectrometer, flow-injection system, low concentrations of atoms, mathematical processing of data, measurement error.*

**Introduction.** Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a highly informative and very sensitive method for analyzing aqueous solutions of different samples. The sensitivity of the method gives the possibility of estimating the content of about seventy elements in samples of foodstuffs or environmental objects at the level of maximum permissible concentrations [1]. However, there are a number of problems which cannot be solved by the ICP-AES method. Among them are determination of heavy metals in natural waters at the level of background contents and determination of metals in sea, hydrothermal, and other waters with high mineralization. Because of the high salt background, there arise considerable spectral superpositions of the spectra from the elements whose concentration is high. Moreover, a high concentration of salts in an aqueous solution introduced into an apparatus contaminates its sprayer and burner. Similar problems arise in analysis of highly toxic elements in foodstuffs, food raw materials, forage, and other samples containing a large amount of various organic substances.

Combination of sorption concentration onto a special sorbent placed in a column with subsequent determination of the elements by the ICP-AES method or other methods of atomic analysis substantially raises their potentialities [2–4]. In [5], for simultaneous sorption concentration of Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn, and Y from sea water a dynamic variant of sorption concentration was used as the most technological one and the one which makes it possible to automate the entire cycle of determination of elements. The dynamic variant of concentration provides for both "off-line" and "on-line" determinations. In the first case, the concentrate from the column is collected into a separate container, and the solution obtained is analyzed by the ICP-AES method; in the second case, the concentrate in a flow of a desorbing solution is fed directly into a spectrometer. As a result of the investigations carried out in [6], a sorption atomic-emission method of determining heavy metals in natural waters upon atomization of a sample in an inductively coupled plasma has been developed.

The deficiencies of the proposed "off-line" method are the necessity of using large amounts of solutions for concentration, carrying out measurements separately from the process of concentration, and, as a consequence, a low productivity of the analysis. Increase in the productivity of the analysis is attained by combining the flow-sorption con-

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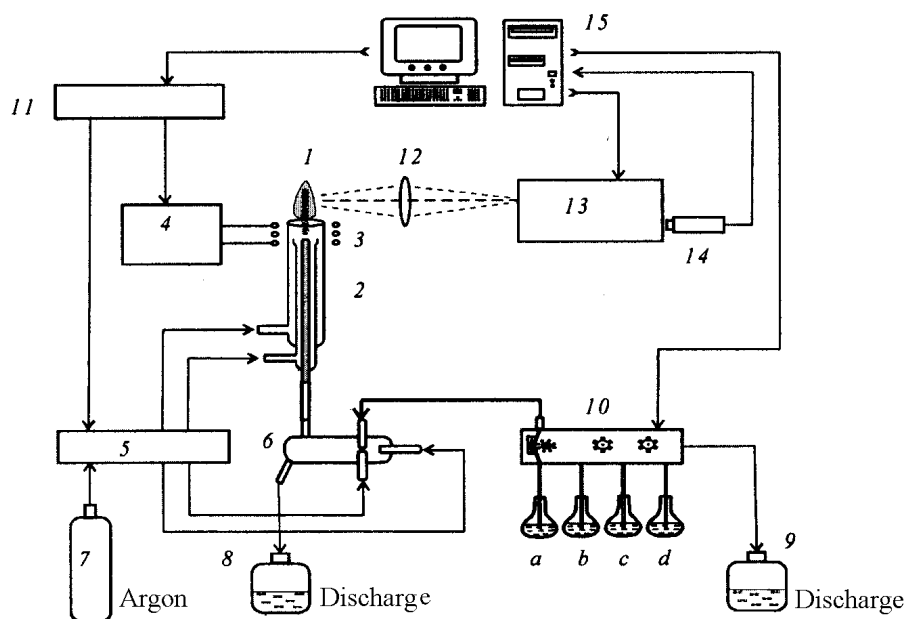


Fig. 1. Functional scheme of the ICP spectrometer with the flow-injection system: 1) plasma flare; 2) burner; 3) inductor; 4) matcher; 5) relay-regulators of argon flows; 6) sprayer of solutions; 7) cylinder with argon; 8, 9) vessels for discharging a waste solution; 10) flow-injection system; 11) controller; 12) moving mirrors focusing the image of a plasma flare onto the monochromator slit; 13) monochromator; 14) photomultiplier; 15) computer.

centration and ICP-AES determination of elements when an eluate-concentrate is introduced from a column into a plasma in an "on-line" regime [7, 8].

Flow-through concentration imposes higher requirements on the sorbents used. Sorption of the microcomponent must be carried out rapidly and reversibly. To attain a substantial increase in an analytical signal it is necessary that extraction of metals could be brought about at a high velocity of passing a solution through a column. The capacity of the sorbent must be high, since, when extracting metals from a solution, large amounts of macrocomponents remain in the column because of the insufficient selectivity of the sorbent. The dimensions of the column with a sorbent must be minimal in this case; otherwise the zone of the concentrate in the eluate flow is blurred. In [9], in an "on-line" regime low concentrations of rare-earth elements were analyzed with application of the DETATA, HMDATA, and Chelex 100 sorbents.

**Experimental.** In the present work, testing of an inductively coupled plasma atomic emission spectrometer with preliminary concentration of a sample in a flow-injection system has been carried out. The spectrometer was devised at the Institute of Molecular and Atomic Physics of the National Academy of Sciences of Belarus. Different methods of mathematical processing of the results of measurements have been applied. As the objects of investigation we selected aqueous solutions containing low concentrations of copper and lead.

Figure 1 presents a functional scheme of the ICP spectrometer in a set with a flow-injection system (the arrangement and operation of the ICP spectrometer are described in detail in [10]). The flow-injection system consists of an eight-channel peristaltic pump, two valve-injectors, and power and monitor units. The valve-injectors have two fixed positions. By switching them into one or the other position, it is possible to control the flows of four solutions (of a sample, acetate buffer, distilled water, and a 2-M solution of nitric acid). The process of concentration consists of five regimes effected in a certain sequence and synchronized with the operation of the analytic device. Control of the flow-injection system operation and synchronization with the ICP spectrometer were done with the aid of a computer using a specially developed program. The concentration was made with the aid of a DETATA-type sorbent.

We will consider in succession each of the regimes of the process of concentration [11].

1. *Washing with acid.* This regime is needed to remove remnants of the elements that contaminate a sorbent and to wash pipelines before carrying out measurements. The washing is done by a 2-M solution of nitric acid.

2. *The first washing with a buffer.* After the washing with a solution of nitric acid, the sorbent is placed in a very acidic medium. For sorption to be carried out with maximum efficiency, the pH of the solution of the sample must lie within 4–6. The acid is neutralized by an acetate buffer whose solution is pumped through the sorbent for ~15 sec. After washing with the buffer, the sorbent is prepared for sorption of metal atoms from the solution with the sample.

3. *Concentration.* At the stage of concentration the solution with a test sample is passed through the column with a sorbent. Usually, the time of sorption is 60 sec or more.

4. *The second washing with a buffer.* The arrangement of valves-injectors and directions of the flows are the same as in the first washing with a buffer. This regime is needed to remove the substances remaining when metals were sorbed from the complex matrix. The sorbed ions of the metals after the second washing with the buffer remain on the surface of the sorbent.

5. *Measurement.* As concerns the arrangement of the valve-injectors and direction of flows, the stage of measurement coincides with stage 1 (washing with an acid). A solution of nitric acid, while passing through a column with a sorbent, washes out metal ions accumulated in the sorbent in the previous stage. Thus, some time after the switching-in of the stage of measurement (in about 10–15 sec) atoms of the sample appear in the plasma of the measuring device. They are excited in the plasma and begin to emit spectral lines characteristic of them. By recording the dependence of the radiation intensity of the brightest analytical lines on time, it is possible to measure the concentrations of atoms in a sample.

Thus, implementing the above-indicated cycle of the flow-injection system in a set with an emission spectrometer with an inductively coupled plasma, we carry out measurement of the concentration of investigated atoms in a sample. Repeating this cycle several times, it is possible to obtain several values of the concentration and calculate its average value, standard deviation, etc.

In the present work, an analysis of low concentrations of copper and lead was carried out in aqueous solutions with preliminary concentration of a sample. The following sets of calibrating solutions were prepared: 1, 5, 10, 20, and 50  $\mu\text{g/liter}$  for copper and 20, 50, 100, 200, and 500  $\mu\text{g/liter}$  for lead.

The time dependence of the radiation intensity of the analytical line of the element investigated  $I(t)$  represents a curve consisting of increasing and decreasing components of exponential character. It should be noted that the noises imposed on  $I(t)$  have the greatest value at the least concentration of a sample and they decrease when this concentration is increased. In our case, the smallest noise was at the maximum concentration of copper in the series of solutions of 50  $\mu\text{g/liter}$  used for calibration.

To find the detection limit of copper, we used a solution with a concentration close to the detection limit (1  $\mu\text{g/liter}$ ). Twenty measurements were carried out under the same conditions, and the standard deviation of the random component of the error of observation  $\sigma$  was calculated. The quantity  $C_{d,l} = 3\sigma$  was taken as the detection limit of the spectrometer. According to calculation, the detection limit is 0.2  $\mu\text{g/liter}$ . The detection limit measured earlier without a flow-injection system was equal to 7  $\mu\text{g/liter}$ . An almost 35-fold decrease in the detection limit was obtained. The detection limits of lead obtained similarly were equal to: 500  $\mu\text{g/liter}$  without preliminary concentration and 40  $\mu\text{g/liter}$  with preliminary concentration (there is an almost 13-fold reduction). The time of concentration in these experiments is 120 sec.

In practice, the unknown concentration of atoms in a solution is determined with the aid of a calibration curve, which represents the dependence of some parameter of the spectrum on the concentration of the measured element in a calibrating solution. The maximum of the intensity  $I_m$  in the function  $I(t)$  and the area  $S$  restricted by the line of the background and by the curve of the function  $I(t)$  were selected as the parameters depending on the concentration. Figure 2 presents the dependences of  $I_m$  and  $S$  on the time of sorption in a flow-injection system. For measurements we used a calibrating solution containing copper with a concentration of 50  $\mu\text{g/liter}$ . It is seen that with increase in the time of sorption the maximum of the intensity gradually stops growing and attains saturation (curve 1). This seems to be due to the limited possibilities of the reaction of copper elution from a sorbent, i.e., at the given volume of the sorbent and fixed speed of pumping of the eluent, no more than a certain quantity of the atoms of the

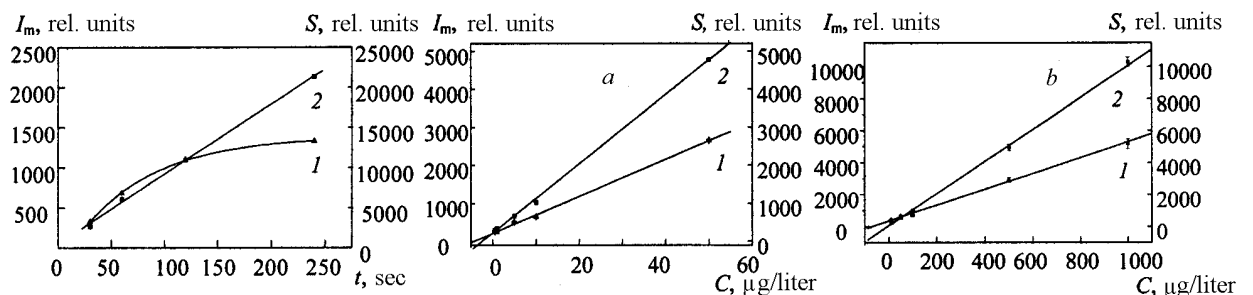


Fig. 2. Dependence of the maximum of the emission signal intensity  $I_m$  (1) and of the area of its contour  $S$  (2) at the analytical line of copper  $\lambda = 324.754$  nm on the time of sample sorption in the flow-injection system.

Fig. 3. Dependence of the intensity maximum  $I_m$  (1) and area  $S$  (2) of the time dependence of the luminescence line of copper  $\lambda = 324.754$  nm (a) and lead  $\lambda = 220,353$  nm (b) on the concentration of copper in a calibrating solution (regime of preliminary concentration).

sorbed element can be washed out from the sorbent. If many atoms are sorbed, their washing-out is extended in time without an increase in the maximum. This inference is confirmed by the linear behavior of the function  $S(t)$  (curve 2). Figure 3 presents the dependences of  $I_m$  and  $S$  on the concentration of copper and lead in calibrating solutions.

In the present work, we applied different methods of processing the results of measurements to search for the most optimal ones that will make it possible to decrease the value of the relative standard deviation of the results of observations in order to decrease the detection limits of the elements cited above [12].

The main negative factors that hinder the process of processing the functions  $I_m(t)$  and  $S(t)$  obtained on the ICP spectrometer are the noises of the system of registration, drift of the background intensity, and error in the determination of the wavelength of the analyzed spectral lines. It has been established experimentally that the overall noise has a distribution of the probability density close to the normal one.

To eliminate noises, low-frequency digital filtration was used. Several digital filters (Butterworth, elliptical, and Chebyshev filters) were considered, but none gave satisfactory results in correction of the dependences  $I_m(t)$  and  $S(t)$ . Therefore, filtration was carried out in the following way. A Fourier transform of the corrected graph of the dependence  $I_m(t)$  or  $S(t)$  was found. Its real and imaginary parts were convoluted with a window of special shape, and the inverse Fourier transformation was carried out. The process of the processing is described in more detail in [12]. It should be noted that the values of the errors in operation with preliminary concentration are smaller than without concentration. Mathematical processing of the time dependences gave a nearly 20% decrease in the detection limit.

**Conclusions.** A measuring complex which involves an ICP spectrometer and a flow-injection system can be used for rapid concentration of samples with a further measurement in them of supersmall concentrations of atoms of different elements. The detection limit of the overwhelming majority of atoms with application of the given complex is below the maximum permissible concentration. Moreover, with the aid of a flow-injection system it is also possible to carry out modification of the sample matrix of its dissolution.

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