

Ecological Monitoring of the Content of Heavy Metal Ions in the Aquatic Environment

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ABSTRACT

Solid-phase spectrophotometry is one of the effective methods for detecting heavy metals in water. Environmental monitoring of the content of heavy metal ions in the aquatic environment is an urgent task for controlling the quality of wastewater from enterprises, as well as studying their impact on natural water bodies. In this study, an rapid and easy-to-use method for the determination of a number of heavy metals by solid-phase spectrophotometry was developed.

Keywords: environmental monitoring of water bodies, solid-phase spectrophotometry, heavy metals, sorption, test method.

INTRODUCTION

Heavy metals (hereinafter HMs) are of particular interest for research and various services involved in the control as well as monitoring of environmental components and ecosystems. The term “heavy metals” refers to the elements of the periodic system of Mendeleev, a group of metals the atomic weight of which is more than 40. The importance of their study is associated with the fact that most of them have biological activity, that is, they are able to affect the normal functioning of living organisms, infiltrating them, accumulating, being passed along the trophic chain, etc. Depending on the type of compound, nature of the metal and concentration. Heavy metals have different physiological effects on humans and animals. Some metals are vital (essential), while the presence of others (xenobiotics) leads to negative consequences, up to the death of the organism. Among metals-toxicants, a group of that is especially dangerous for human and animal health is distinguished, namely Cd, Cu, As, Ni, Pb, Hg, Zn, and Cr.

A large number of HMs are capable of exhibiting complexing properties. For example, in an

aqueous medium, ions of such metals are hydrated and capable of forming hydroxo complexes. The composition of these complexes depends on the acidity of the solution, and, if organic compounds or anions are found in a given solution, HM ions are capable of forming complexes of various stability and different structures.

Due to anthropogenic impact, HMs enter the environment mainly through the operation of non-ferrous and ferrous metallurgy enterprises, mechanical engineering, processing industry, as well as components of emissions from vehicles.

MATERIAL AND METHODS

The object of this work involves heavy metals (I, Fe²⁺, Fe³⁺), the content of which was determined on silica gel modified in various ways. To prepare for the sorption of silica powder, its surface was activated and a reagent was applied. Further, the sorption method was used to concentrate HM on the surface of the obtained sorbents. To obtain an analytical signal, the method of solid-phase spectrophotometry was chosen, and MS Office products (MS Excel and MS Word) were

used to process and structure the obtained data and build calibration graphs (Losev et al. 2010).

The measurements were performed on a device that fixed the luminous flux. The physical parameter of the study is the reflection coefficient R . The reciprocal of R serves as an analytical signal. The process of synthesis of sorbents included several stages. A sample of SiO_2 , weighing 20 g, was placed in a slightly alkaline medium (NaOH solution with $\text{pH} = 9$) for 1 hour. Within 1 hour, the pH should not fall below 8. This is necessary in order to activate the surface of the SiO_2 molecules. Then the silica gel was washed with distilled water until $\text{pH} = 6-7$.

The SiO_2 surface is negatively charged and repels negatively charged groups of organic substances. To avoid this, it is necessary to deposit a layer of positively charged polymers on the silica gel. With constant stirring, a solution of polyhexomethylene guanidine (PHMG) was added at the rate of 50% by weight of silica. Accordingly, in this case, a sample of 10 g of PHMG was taken. A 10% solution of PHMG was prepared and added to the silica gel, with constant stirring, at a speed of 1 ml/min. After adding the entire mass of the solution, it is necessary to additionally mix the sorbent for 30 minutes.

Next, the settled solution was drained and 100 ml of 1% NaCl solution was added to silica gel and stir for another 5 minutes and rinse the sorbent with distilled water until $\text{pH} = 6$. The silica gel was transferred to a Petri dish and dried in an oven at $t = 50^\circ\text{C}$. A ready-made sorbent was obtained, on which it is only required to apply the necessary reagent to concentrate the substance on the surface of the sorbent. In these cases, the following reagents were used:

- For concentration I – 8-hydroxyquinoline;
- For the concentration of Fe^{2+} – bathophenanthroline;
- For the concentration of Fe^{3+} – nitroso-P-salt.

Concentration of Fe^{2+} , Fe^{3+} , I on the sorbent surface

Stock solutions of heavy metals were prepared by diluting a concentrated solution of iron and iodine to a concentration of $2.16 \mu\text{g/mL}$. Three experiments were carried out to concentrate iron on the sorbent. In each case out of three, only the weight of the sorbent was changed. Used sample $m = 0.1 \text{ g}$ in the amount of 6 pieces for each metal. A 0.05% solution of the corresponding reagent was

added to these weighed portions and stirred for 15 min. Then, the solution was merged; the Fe^{2+} solution adjusted to $\text{pH} = 4.5-6$ and Fe^{3+} solution adjusted to $\text{pH} = 3.5-4$ were added to different test tubes with weighed portions. The initial data are given in Tables 1–3. Afterwards, 1 ml of hydroxylamine is added to each tube (Lurie, 1984).

As a result, HM complexes of different colors were obtained: the complex with Fe(II) became pink, with Fe(III) it became orange, and with I2 it turned from yellow to green. As the HM concentration increases, the color becomes brighter (Nikiforova et al. 2009).

Obtaining an analytical signal and its processing

The principle of measuring the concentration of a specific heavy metal component is based on

Table 1. Obtaining the complex 7-Iodine-8-Oxyquinoline

Tube number	Concentration on the surface, mg/0.1 g of sorbent
11	0
12	0.1
13	0.25
14	0.5
15	1
16	2

Table 2. Preparation of the Fe(II) -Bathophenanthroline complex

Tube number	Concentration on the surface, mg/0.1 g of sorbent
1	0
2	0.25
3	0.5
4	1.25
5	2.5
6	5

Table 3. Preparation of Fe(III) -nitroso-P-salt complex

Tube number	Concentration on the surface, mg/0.1 g of sorbent
21	0
22	0.25
23	0.5
24	1.0
25	2.5
26	5

its selective chemical reaction with a specially selected component. This selective chemical reaction leads to the formation of a colored stable complex compound with characteristic minima and maxima in the absorption and reflection spectra. Thus, the analytical signal is related to the reflectance R at a certain wavelength: for example, when iron ions react with sulfosalicylic acid in an ammonium hydroxide medium, a brightly colored yellow complex is formed. This complex, adsorbed on silica, gives a minimum reflectivity in the wavelength range of 420–490 nm.

Light-emitting diodes and photodiodes were used for optical measurements. The photodiode converts the light flux focused by an optical lens on a single crystal of silicon into an electric current, which is further converted by an operational amplifier into a voltage, which is measured by an analog-to-digital converter.

SFH229 was used as a photodiode in a package that is transparent in the visible wavelength range. The current-to-voltage converter is based on a high-quality AD8606 dual rail-to-rail operational amplifier. The current-to-voltage conversion factor is set by a 100 k Ω feedback resistor (100 mV per 1 μ A). The circuit uses an ADS1115 modern 16-bit analog-to-digital converter, which has four measuring channels. This converter transmits data to the microcontroller through the I2C communication interface.

A high-performance 32-bit microcontroller from the STM32F0 series was used as a microcontroller. In digital form, the data came from the microcontroller to the computer for further processing. Communication with the computer was

carried out through the USB-UART converter on the CP2102. The commercially available LEDs of the FYL3014 series were selected with the following wavelengths: 470, 525, 590 and 660 nm, which corresponds to blue, green, yellow and red glow colors. These LEDs are characterized by a high luminous efficiency up to 1000 mCd at a current of 20 mA, as well as a narrow spectrum, the spectral width at half maximum does not exceed 5–15 nm. Structurally, the LED and the photodiode are made in the same housing with a transparent converging lens and have a diameter of 3 mm (Caletka. et al. 1990). The circuit diagram is shown in Figure 1. Figure 2 and 4 shows R versus gray intensity. Figure 3 shows the dependence of R on the intensity of the blue color. Figure 5 shows the dependence of R on the intensity of the yellow color. Tables 4–7 show results of the experiment.

The linear dependences of the reflection coefficient on the color intensity indicate that the device is working correctly. With all this, it distinguishes color differences almost invisible to the eye, which can be seen from the color scales. Accordingly, the next stage of the work can be the measurement of real prepared sorbents with the concentration of heavy metals carried out on them.

RESULTS

As a result of the measurements, an analytical signal was obtained, equal to the reciprocal of the reflection coefficient R . The data obtained for all determined HMs are summarized in Table 8–10.

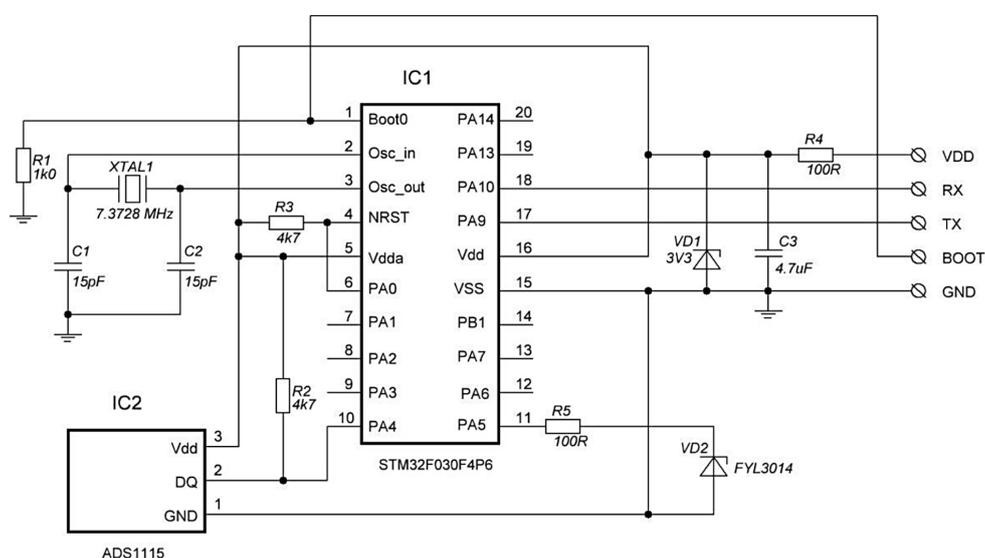


Fig. 1. Schematic diagram of the device

Table 4. Results of measuring the intensity of gray color

Colour	R	G	B	Instrument readings	Reflected luminous flux	R
	255	255	255	15355	4645	1
	127	127	127	15786	4214	0.90721
	63	63	63	16247	3753	0.80797
	31	31	31	16823	3177	0.68396

Table 5. Blue intensity measurement results

Colour	R	G	B	Instrument readings	Reflected luminous flux	R
	255	255	255	15595	4405	1
	200	200	255	15958	4042	0.91759
	150	150	255	16188	3812	0.86538
	120	120	255	16287	3713	0.84291

Table 6. Red Intensity Measurement Results

Colour	R	G	B	Instrument readings	Reflected luminous flux	R
	255	255	255	15657	4343	1
	255	220	220	15843	4157	0.95717
	255	200	200	15933	4067	0.93645
	255	150	150	16302	3698	0.85149

Table 7. Yellow color intensity measurement results

Colour	R	G	B	Instrument readings	Reflected luminous flux	R
	255	255	255	15745	4255	1
	200	255	200	15991	4009	0.94219
	150	255	150	16253	3747	0.88061
	120	255	120	16358	3642	0.85593

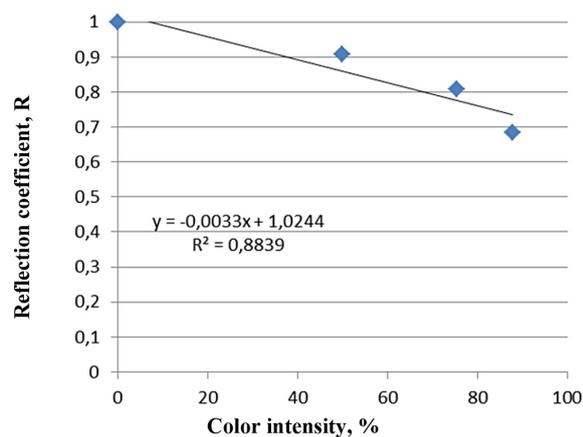


Fig. 2. Graph of R versus gray intensity

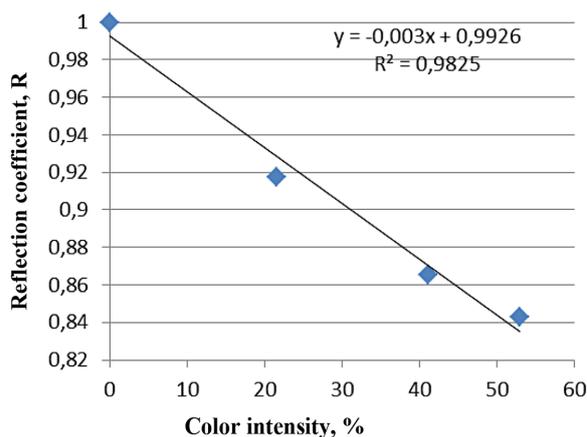


Fig. 3. Graph of the dependence of R on the intensity of the blue color

Accordingly, in line with the tables obtained, graphs of the dependence of concentration on the analytical signal were plotted (Fig. 6–8). The brighter the sample is colored, the less reflective it is and the more light is absorbed.

When constructing calibration graphs with the reciprocal of R, a linear relationship should be observed. It can be seen that in all three cases this dependence is observed. This indicates that the Bouguer-Lambert-Beer law is observed (a beam

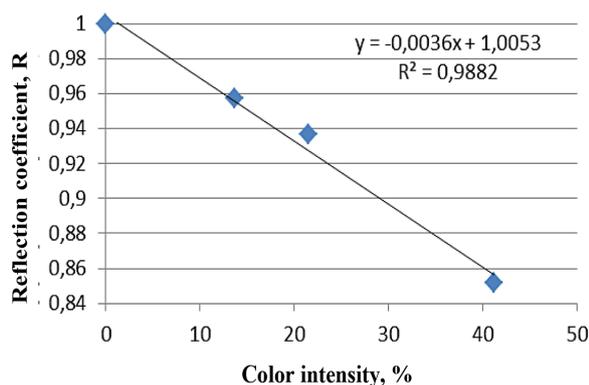


Fig. 4. Graph of R versus red intensity

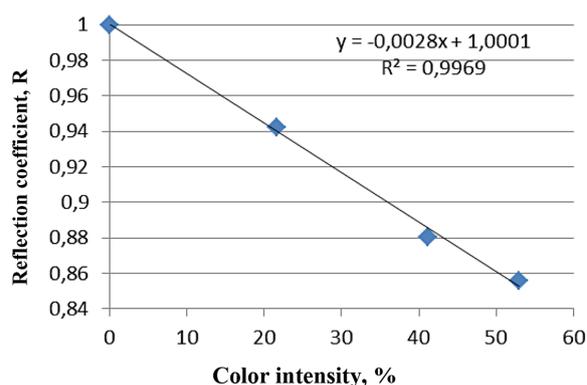


Fig. 5. Graph of the dependence of R on the intensity of the yellow color

Table 8. Measurement result I

C(I) on the surface, $\mu\text{g}/0.1$ g of sorbent	Luminous flux that does not take into account background illumination	Luminous flux that does not take into account background illumination	Analytical signal
0	15683	1617	0
0.1	16305	995	0.625126
0.25	16599	701	1.306705
0.5	16880	420	2.85
1	17020	280	4.775
2	17130	170	8.511765

*Measurements were carried out at $\lambda = 470$ nm, taking into account background illumination

Table 9. Fe(II) measurement result

C (Fe ²⁺) on the surface, $\mu\text{g}/0.1$ g of sorbent	Luminous flux that does not take into account background illumination	Luminous flux that does not take into account background illumination	Analytical signal
0	16360	681	0
0.25	16434	607	0.121911
0.5	16532	509	0.337917
1.25	16673	368	0.850543
2.5	16750	291	1.340206
5	16854	187	2.641711

* The measurements were carried out at $\lambda = 520$ nm, taking into account the background illumination

Table 10. Fe(III) measurement result

C (Fe ³⁺) on the surface, $\mu\text{g}/0.1$ g of sorbent	Luminous flux that does not take into account background illumination	Luminous flux that does not take into account background illumination	Analytical signal
0	14700	2293	0
0.25	14839	2154	0.064531
0.5	14980	2013	0.139096
1.25	15189	1804	0.271064
2.5	15827	1166	0.966552
5	16167	826	1.776029

* Measurements were carried out at $\lambda = 595$ nm, taking into account background illumination

of monochromatic light, having passed through a layer of an absorbing substance, exits weakened). However, it is worth noting that when carrying

out such measurements, it is very important to choose the optimal wavelength of the light flux. For example, when making measurements in this

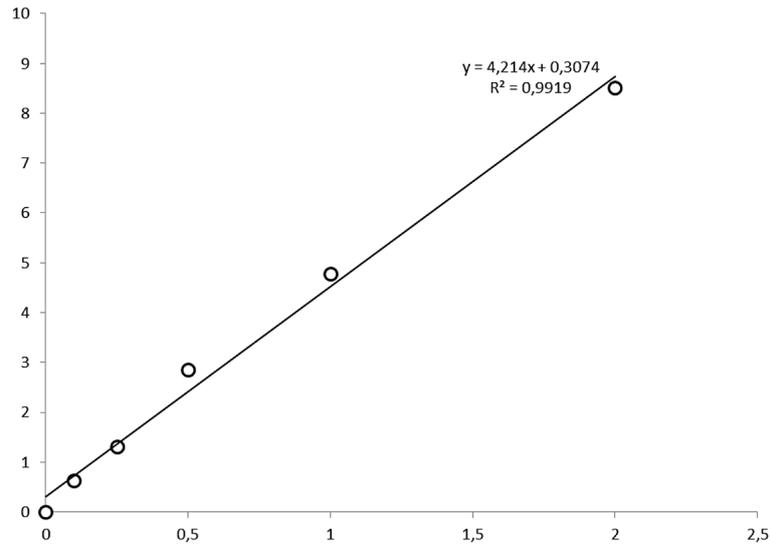


Fig. 6. Dependence of the analytical signal on C(I)

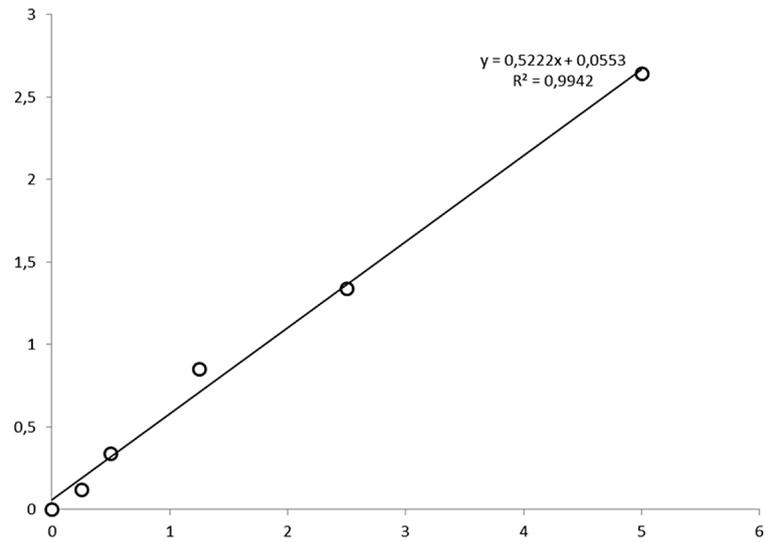


Fig. 7. Dependence of the analytical signal on C(Fe²⁺)

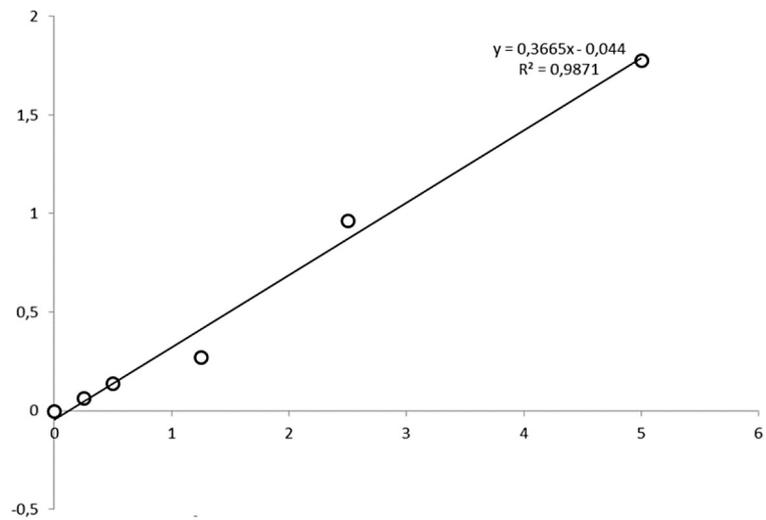


Fig. 8. Dependence of the analytical signal on C(Fe³⁺)

work, blue light was applied to yellow-colored iodine complexes, and green light was applied to pink-colored Fe(II) complexes.

CONCLUSIONS

The development of test methods for the determination of HMs in the aquatic environment, and, as a result, in its other components, is indeed an urgent task of our time. Taking into account the long-term performance of certain types of analyses, as well as the laborious painstaking process of sampling and sample preparation, the emergence of a light compact mobile device for the determination of heavy metals that does not impose special requirements for sampling and sample preparation is a real breakthrough in the field of environmental monitoring, as well as the implementation of production control at enterprises..

To perform real measurements on real samples of the sorbent on which heavy metals were concentrated, work was carried out to create ready-made working sorbents. The above-mentioned description of the operation of the device is easy to understand. Accordingly, highly qualified personnel are not required to work with it. The measurements of model and real samples showed that the device is able to distinguish between

minor changes in the color intensity of the sample, which indicates its high sensitivity.

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