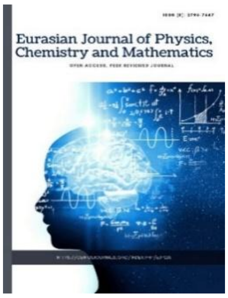

Determination of chromium(III) ion in the soils of Almalyk MMK area of Tashkent region by sorption-spectroscopic methods

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ABSTRACT

The soil of the area of the environmental facility Olmaliq KMK and the areas close to the KMK were analyzed by mass spectrometer method. It was found that the amount of chromium ion in the soil samples exceeded the permissible limit. Analysis of obtained results was compared with sorption-spectroscopic results. The use of organic reagents immobilized on sorbents is of practical importance for the determination of heavy metal ions in environmental objects by sorption-spectroscopic methods.

Keywords: sorption-spectroscopic, immobilized organic reagents, heavy metals, chromium, soil, mass spectrometry (MS) and inductively coupled plasma (ISP).

Today, the state of the environment is the most important factor determining the vital activity and development of a person and the entire society. One of the most common chemical pollutants is heavy metal pollution. The high amount of many chemical elements and their compounds is related to the natural and man-made processes taking place in the world around us. Heavy metals are present in all natural environments, atmosphere, soil, water, plants, and animals. In terms of toxicity, they take the second place in polluting the environment and constitute the most dangerous group of pollutants of the biosphere. [1].

Today, as a result of the development of industrial technologies, production and construction industry, the spread of heavy and toxic, carcinogenic metals into the environment is becoming a global ecological problem. Chromium and lead metals are heavy, toxic and carcinogenic metals. The main sources of chromium metal in the soil are the wastes of enterprises that use the metal and its compounds for mining, processing, as well as for the production of various products. When burning mineral fuel, coal, the substance actively disperses and gradually accumulates on the ground. [2].

Heavy metals include more than 40 elements with an atomic mass of 50 or more: Cr, V, Cu, Mn, Co, Zn, Ni, Fe, Hg, Sn, Mo, Pb, Cd, Bi, and others. Environmental monitoring and environmental pollution studies mainly involve metals with a density of 5 g/cm3 or more. Their high toxicity plays an important role in the classification of heavy metals. Depending on the degree of toxicological effect, according to DavST (GOST) 17.4.1.0283, chemicals are divided into three classes:

- Class I (very dangerous) – As, Cd, Hg, Be, Se, Pb, Zn;
- Class II (moderately dangerous) - B, Co, Ni, Mo, Cu, Sb, Cr;
- Class III (low risk) - Ba, V, W, Mn, Sr.

According to the above classification, Chromium belongs to the II class of moderate danger. The need for new inexpensive, selective, fast, and selective modern methods of determining chromium ion from the composition of environmental objects using organic reagents is increasing.

As a result of the concentration of metals in environmental objects, the excess of the permissible limit has a negative effect on the ecosystem, and it is urgent to control their amount.

In the study, heavy metals in the soil taken from the territory of Almalyk MMK and nearby areas were determined by mass-spectroscopic (ICP-MS) UzOU 0677:2015 (MVI #499-AEM/MS) analysis. It is an analytical method consisting of a combination of inductively coupled plasma (ICP) and mass spectrometry (MS) designed for the analysis of inorganic elements. An ICP uses a high-temperature ion source and fragments to separate and ionize the sample. A mass spectrometer is a mass analyzer and separates all elements simultaneously. The amount of heavy metals in soil is measured in parts per million (ppm). Ions are measured with a mass detector and analyzed from low ppm to high ppm levels. In the analysis, the elements in the sample are ionized in the ICP and sent to the MS, separated according to mass and charge ratios, and measured. [3].

The soil sample from the territory of Almalyk MMK was taken from the following areas and monitored from the outer territory of MMK and from the distance of 1 km, 3 km, 5 km, 10 km, 20 km. The soil sample was found to contain 61 elements. The amounts of some metals present in the data (ppm, µg/g, g/t) are listed in table 1 below.

Table 1

ICP-MS analysis of elements in soil samples of Almalyk MMK region, mkg / g

№	The name of the metal	External territory of MMK	from MMK 1 km	from MMK 3 km	from MMK 5 km	from MMK 10 km	from MMK 20 km
1	Cr	85,7	76,8	75,7	74,9	73,8	64,7
2	Sc	7,48	6,41	13,4	7,10	10,4	14,1
3	Cu	69,5	241	82,2	51,5	35,7	53,0
4	Se	1,38	7,59	<0,50	<0,50	0,505	<0,50
5	Rb	72,1	127	220	62,1	148	111
6	In	0,301	0,202	0,098	0,047	0,019	0,049
7	Ce	42,2	52,7	79,9	40,8	61,7	59,3
8	Pb	104,3	98,7	88,9	78,3	63,9	57,3

Chromium ion distribution diagram in Almalyk MMK soil samples is presented in Figure 1.

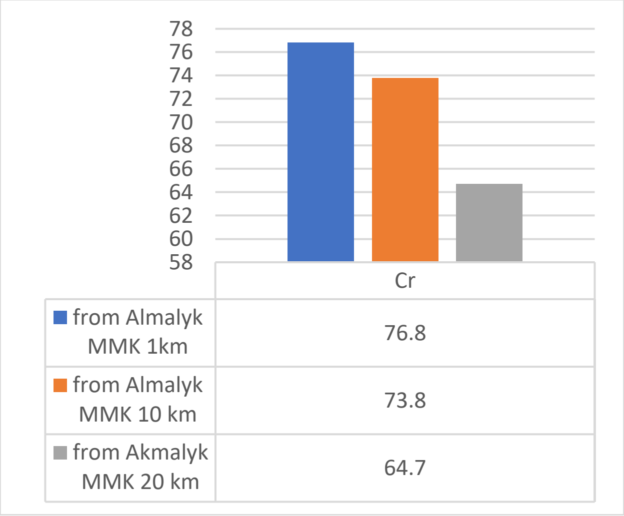

Figure 1. Distribution diagram of chromium metal

When the results are analyzed, it is observed that the content of chromium metal in the soil migration decreases with distance from the MMK. It was observed that the amount of chromium metal increases when approaching MMK. The fixed limit for chromium is equal to 6.0 μg/g, according to the results of the analysis of the soil of the Almalyk KMK area, it can be observed that the amount of chromium metal exceeds the FLA.

Soil samples were taken and analyzed from a depth of 20 cm. Transfer of metal ions from soil to solution was carried out according to SST [4]. After transferring the metals into solution, sorption was carried out on silk fibroin fiber polymer sorbents with the help of an immobilized organic reagent. In order to improve the sorption exchange capacity of sorbents, immobilization of organic reagents was carried out, as well as GNGS and other organic reagents were used. Standard and working solutions of reagents were prepared according to the method indicated in the literature.

Research methods

Before sorption of metals, sorbents are converted to Cl^- form with HCl solution. Then, solutions of organic reagents, their specific concentrations, are prepared for each metal. The sorbents are immersed in the reagent solutions and mixed on a magnetic stirrer. After immobilization, sorbents are washed with bidistilled water and sorption of metals from sample solutions is carried out. [5]. The sorption exchangeability of sorbents with respect to metals is calculated according to SST (23) by the following formula:

$$\text{COE} = \frac{(\text{V x K1} - \text{K x V1 x K2}) \text{ x } 100}{\text{m}(100 - \text{W})}\ x\ c\ ;$$

where: V - is the volume of the working solution, sm^3;

K - is a coefficient equal to the ratio of the volume of the working solution to the volume of the solution taken for titration;

V_1 - is the volume of the solution used for titration of the solution sample after interaction with the ion exchanger, sm^3;

m is the mass of the ion exchanger, g;

W – mass fraction of moisture, %;

c – fixed concentration of working solution and titration solution mol/ dm^3; (N);

K_1 and K_2 are correction factors for working solution and titration solution, respectively [6].

When chromium metals are analyzed by sorption-spectroscopic method, the amount of elements in the soil is determined by (μg/g) [7]. Chromium metal ion was selected for the experiment from the results of ISP-MS mass spectrometric analysis. Organic reagents compatible with the formation of complexes with metal ions were selected.

Determination method: 2.0 ml of (-4-)-4-[(1-hydroxy-naphthalen-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt solution, 5.0 ml of universal solution (pH=8), 1 ml of Cr(III) solution with 50 μg/ml, distilled water up to the mark of the flask are added to 25 ml measuring flasks mixed with [8].

The absorption spectrum of the newly formed complex compound was measured in a spectrophotometer "UV-1800 spectrophotometer" using standard quartz and glass cuvettes with a thickness of l=1.0 cm compared to the comparison solution. The absorption spectrum of the reagent is taken against distilled water.

The results are presented in Figure 2. According to the given absorption spectrum, the maximum optical density absorption region of the (-4-)-4-[(1-hydroxy-naphthalene-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt reagent chromium (III) complex is located at λ_{komp}=618 nm, the maximum optical density absorption region of the GNGS reagent is at a lower wavelength region, i.e. at λ_R=508 nm observed ($\Delta\lambda$=110 nm).Using the highest optical density value of the compound, the result is shown in Fig. 3.

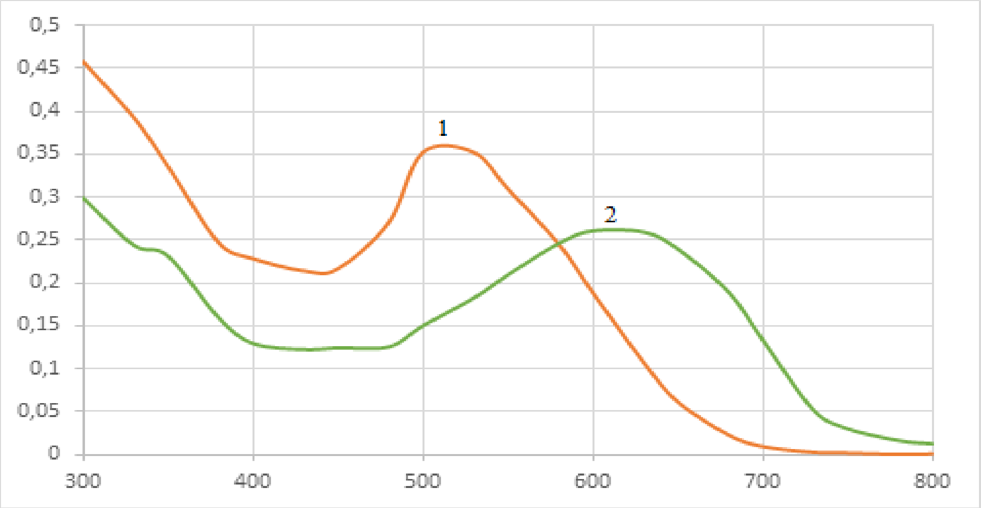

Figure 2. Spectrum of (-4-)-4-[(1-hydroxy-naphthalene-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt reagent (1) and its complex with chromium(III) (2)

It can be concluded from Fig. 2 that (-4-)-4-[(1-hydroxy-naphthalene-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt reagent at λ_R=508 nm nm, the complex formed with Cr(III) showed a bathochromic shift in the region λ_{komp}=618 nm and showed an analytical signal.

When choosing the optimal conditions for the immobilization of Cr(III) ion on fibrous carrier sorbents with organic reagents, different sorbents were weighed on an analytical balance with 0.2 g of four zero accuracy, and the optimal carrier was selected. [9].

The selected sorbents were activated using a standard solution of 0.1 M hydrochloric acid, then the fibers were washed, dried and stored in Petri dishes.

Determination method: the carriers were placed in a glass, 10 ml of 0.02% solution of the selected reagents was added to it and stirred for 10-12 minutes using a magnetic stirrer, then the optical density of the solutions before and after immobilization was measured in the spectrophotometer "UVS-755 B Spectrophotometer". In the analysis, it is observed that the silk fibroin fiber showed the highest analytical signal. The results are presented in Figure 3.

In the study, for the preparation of carrier sorbents, silk fibroin carrier fiber is weighed on an analytical balance with an accuracy of 0.2 g. In order to activate the sorbents, they are immersed in a standard solution of 0.1 molar HCl hydrochloric acid for 24 hours and transferred to the chlorinated form. The fibers are then washed until neutral with distilled water and kept moist.

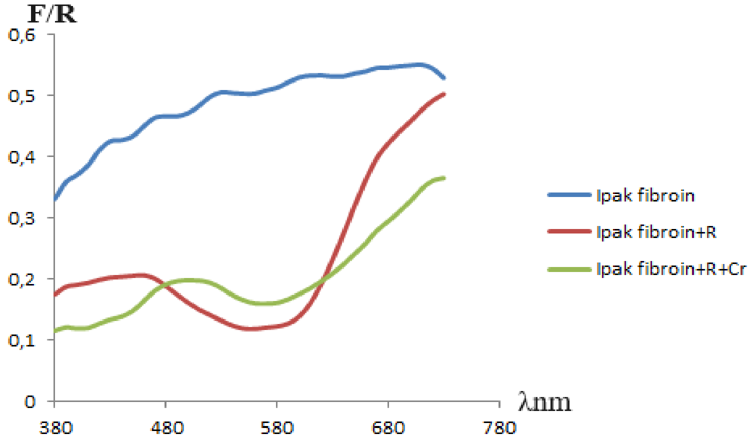

Figure 3. Representation of reflectance spectra of (-4-)-4-[(1-hydroxy-naphthalene-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt reagent) immobilization with silk fibroin fiber

Silk fibroin waste fiber was selected as a polymeric sorbent for the complex formed by the chromium (III) ion with (-4-)-4-[(1-hydroxy-naphthalene-2-yl-hydrazinylidene]-7-nitro-3-oxo-naphthalene-1-sulfo sodium salt reagent) [10].

In order to prove the correctness of the results, the received light absorption spectrum was compared with the light reflection, the maximum of the light absorption was observed as the minimum in the light reflection spectrum.

When the results of the reflection spectrum are transferred to the Kubelki-Munka function, the minimum turns into a maximum and it is found that the maximum area of the light absorption spectrum is observed. After immobilization of the selected activated carrier organic reagents under optimal conditions, their spectra were measured in X-rite Eye-one-pro reflectance spectrophotometer and the results are presented (Figure 3.16).

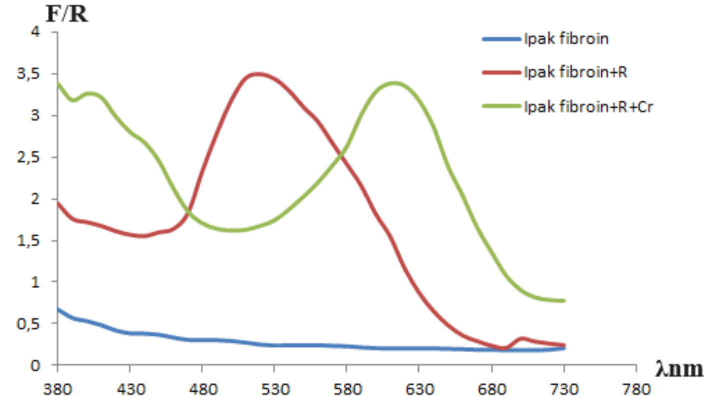

Figure 3.18. The function of dependence on the reflection coefficient (Kubelki-Munka function) of the complex formed by silk fibroin fiber, fiber and GNGS salt, immobilized fiber and Cr(III) ion

When comparing the absorption and reflection spectra of organic reagents in solution and immobilization on a solid fibrous sorbent, the results are the same, that is, it indicates that the metals form a complex compound through the same functional active groups.

Summary

The use of organic reagents immobilized on sorbents is of practical importance for the determination of Cr(III) ions in environmental objects by sorption-spectroscopic methods. Newness, sensitivity, and accuracy of sorption-spectrophotometric methods are considered high, and in these methods they are mainly determined at the level of permissible limit amount (RECHM). Using spectroscopic methods, it is possible to determine 10-3% of elements without separating the main components, up to 10-4% using a simple separation scheme, and the detected the element can be determined by concentrating it up to 10-7%. Determination of heavy metal ions by sorption-spectroscopic method with immobilized organic reagents allows solving many environmental problems.

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