

EXPRESS METHOD FOR THE DETERMINATION OF MOLYBDENUM (VI) IONS WITH IMMOBILIZED PHENYLFLUORONE

Bobojonov B.B. - Competitor of the Department of Analytical Chemistry of the Faculty of Chemistry of the National University of Uzbekistan

Madatov O.A. – PhD, Lecturer, Department of Analytical Chemistry, Faculty of Chemistry, National University of Uzbekistan

Rakhimov S. - PhD, Lecturer, Department of Analytical Chemistry, Faculty of Chemistry, National University of Uzbekistan

Abdrakhimova R.A. Prepodavatel'khimii Ferganskogopolytehnicheskogoinstitutu

Smanova, Z.A. Doctor of Medical Sciences, Professor, Department of Analytical Chemistry, Faculty of Chemistry, National University of Uzbekistan

ABSTRACT

Rapid and efficient determination of Mo(VI) ions is an important task in medicine, pharmacology, biology, chemistry, and technology. Existing methods for its determination are expensive, inefficient and time-consuming. This study presents a new, highly effective and selective analytical reagent for molybdenum ions. The analytical properties of immobilized phenylfluorone (FF) in a PPA (polyethylenepolyamine-polyacrylonitrile) matrix were studied by X-ray fluorescence and scanning electron microscopy to determine Mo (VI) ions by the sorption-spectrophotometric method.

Keywords. analytical reagent; phenylfluorone; molybdenum (VI) ions; polyethylenepolyamine, polyacrylonitrile, immobilization, spectrophotometry, X-ray fluorescence analysis, scanning electron microscope.

MANAGEMENT

Studies show that molybdenum may run out in 50-100 years, so the focus should be on increasing molybdenum recycling, since it is almost impossible to replace molybdenum in its main areas. To do this, it is necessary to increase the level of utilization of molybdenum from expired products from the current 20% to 80% [1]. The electrical conductivity of molybdenum is higher than that of iron and lower than that of copper. In terms of mechanical action, molybdenum is slightly inferior to tungsten, but it is easier to process by pressure. The refractory metal molybdenum is widely used in modern industry, both as an additive to various alloys and as a structural material [2]. Molybdenum is a relatively rare metal and it is difficult to obtain it in its pure form [3]. Mixed oxides based on molybdenum are universal catalysts in the chemical industry [4, 5].

The main problem in obtaining molybdenum is that its melting point is very high: 2622 °C. Therefore, known metallurgical methods cannot be used for its production - there is no material to cover such a hot furnace. It seems that it can be made from graphite, but then molten molybdenum absorbs this element, and when cooled, carbides are released from the metal, which makes the material brittle. In addition, molybdenum oxidizes at high temperatures [6]. The structural-phase composition of composite coatings containing molybdenum and titanium of the Co-Mo-TiO₂ galvanic alloy on copper and FeO_x-MO_y (M=Ti, Mo) oxide layer on stainless steel was studied [7]. The redox chemistry of molybdenum in natural waters and its participation in biological evolution show that molybdenum has different valencies (from II to VI) and has been studied for participation in the formation of cofactors for more than 60 enzymes [8].

Molybdenum is a mineral component necessary for the human body. The daily requirement of the body for molybdenum is 45 mcg. However, high concentrations of molybdenum lead to the development of many diseases. The maximum permissible concentration of molybdenum in drinking water is 0.25 mg/l, in packaged drinking water 0.07 mg/l [9].

Molybdenum as a trace element necessary for microorganisms, plants and animals. To date, only 4 molybdenum-requiring enzymes have been identified in humans: sulfite oxidase, xanthioxidase, aldehyde oxidase, and the mitochondrial amidoxime-reducing component (mARC) [10]. Currently, at least 50 molybdenum enzymes of bacteria, plants, and animals are known [11, 12]. In humans, molybdenum is present in tooth enamel and may help prevent decay [13]. According to animal studies, consumption of more than 10 mg of molybdenum ions per day can cause infertility, as well as affect the lungs, kidneys and liver [14, 15].

The determination of molybdenum in biological materials is of great importance. This element plays an important role in human metabolism [16].

The importance of molybdenum compounds in the fight against cancer has been studied. It was analyzed on examples of its role and transition from inorganic molybdenum compounds through organomolybdenum complexes to nanoparticles for the control of esophageal and breast cancer [17].

Recently, the use of organic reagents immobilized on various supports makes it possible to reduce the complexity and time of analysis, for example, preconcentration of sorption with separation, separation of mixtures, and spectrophotometric determination of elements directly on the surface of an immobilized organic reagent [18–19]. Recently, fibrous materials based on polyacrylonitrile have been widely used as matrices for the immobilization of organic reagents [20]. Unlike other sorbents, polymer fibers have a large sorption capacity, the ability to regenerate, and improved kinetic properties [21].

The aim of this work is to study the complex formation of molybdenum ions with phenylfluorone immobilized on a polymeric sorbent in order to develop a solid-phase sorption-spectrophotometric method for the determination of molybdenum ions in natural objects.

EXPERIMENTAL PART

Reagents: to prepare a solution of phenylfluorone, 50 ml of ethanol and 1 ml of concentrated hydrochloric acid were added to 0.16 g of the reagent and diluted with ethanol to a volume of 500 ml.

On fig. Figure 1 shows the molecular structure of phenylfluorone [22, 23].

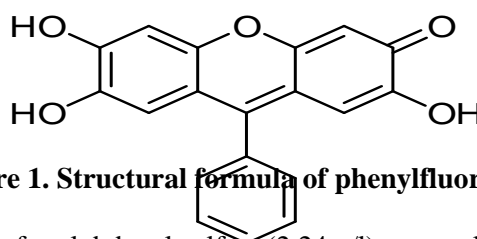


Figure 1. Structural formula of phenylfluorone.

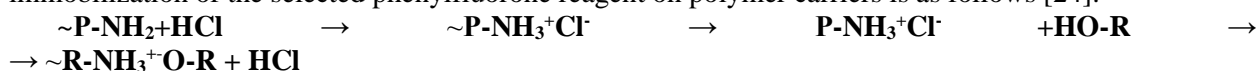
Reagents: To prepare a solution of molybdenyl sulfate (2.24 g/l), a sample of 1.62 g of H_2MoO_4 acid was taken on an analytical balance and mixed with an ammonia solution until molybdic acid was completely dissolved, then 1×10^{-3} M sulfate was added to the resulting ammonium molybdate, with the formation of a saturated solution, another 30 ml of acid was added. The obtained molybdenyl sulfate is placed in a volumetric flask with a capacity of 1 l and topped up to the mark with bidistilled water. In this work, a standard solution of molybdenum was used to determine the metal ion with phenylfluorone. Solutions of magnesium, cadmium, calcium, iron, zinc, and lead salts at a concentration of 1 mg/mL were prepared by dissolving the corresponding chloride and nitrate salts of these metals. All metal salts were purchased from Khimreaktivinvest LLC, Uzbekistan (Tashkent). To study the effect of phenylfluorone on the determination of the molybdenum (VI) ion by the sorption-spectrophotometric method, standard solutions of other metal ions were used.

Buffer solutions. To optimize the solution environment, a universal buffer solution ($H_3PO_4+H_3BO_3+CHCOOH$) was used. This buffer solution was used in the process of reagent

immobilization on a fibrous sorbent and the formation of a metal ion complex with the immobilized reagent.

Used methods and equipment. The medium of the solution was measured using a Mettler-Toledo AG and I-130 potentiometer-ionometer. The reflective and light-absorbing properties of the substances were measured on X-Rite eye-one-pro mini-spectrophotometer, EMC-30PC-UV Spectrophotometer, and UV-5100 UV VIS Spectrophotometer spectrophotometers. IR spectra of the reagent, carrier, immobilized reagent, and complex were obtained on a Bruker Invenio S-2021 IR-Fure IR spectrometer. These devices were used to select the optimal conditions for the formation of the complex, to determine the optical density and reflectance.

Research methodology. Immobilization processes in a polymer matrix: The mechanism of immobilization of the selected phenylfluorone reagent on polymer carriers is as follows [24]:



The first process consists in the transfer of the polymer carrier to the ionized state ($\sim\text{P-NH}_3^+\text{Cl}^-$). To do this, 0.2 g of a polymer carrier was placed in a flask with a capacity of 50 ml, 30 ml (0.1 N) of an HCl solution was added to it, and the resulting solution was kept at room temperature for 24 hours. A day later, the carrier polymers were washed with distilled water until neutral (pH=7). As a result $\sim\text{P-NH}_3^+\text{Cl}^-$ is formed.

RESULTS AND DISCUSSION

Spectrophotometric analysis of the reflection of immobilization: Initially, a polymer carrier was selected for the immobilization of the reagent. To do this, the sorbents were activated with hydrochloric acid fibrous sorbents with different functional groups. To immobilize the chlorinated carrier, 20 ml of a 2×10^{-3} M phenylfluorone solution was added, then the fiber and the immobilized reagent were analyzed on a reflective spectrophotometer.

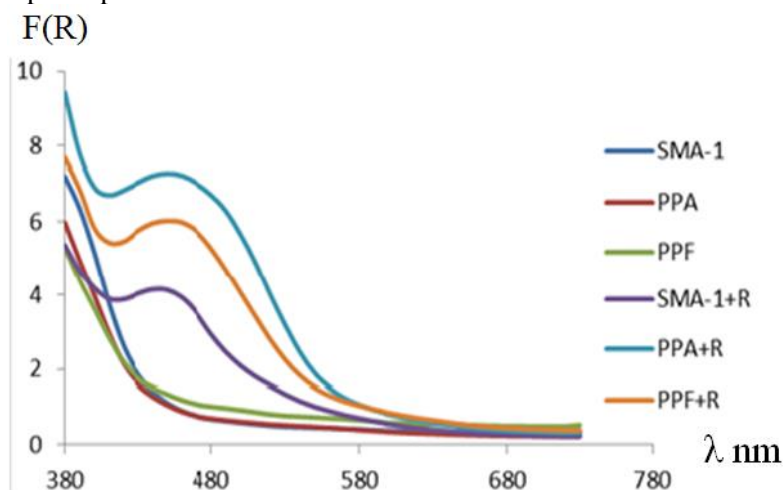


Figure 4. Representation of reflectance spectra in the Kubelka-Munk function.

According to the results obtained, the highest optical density during the immobilization of phenylfluorone is achieved when using the reagent + PPA carrier, and PPA (polyethylene polyamine modified with polyacrylonitrile fiber) was chosen as the best carrier. The optimal conditions for the complexation of phenylfluorone immobilized on PPA fiber with the Mo(VI) ion have been studied. The environment of the solution (pH=2.5), the nature of the buffer solution (universal buffer), the sequential addition of components, and other conditions were investigated, and the results were analyzed.

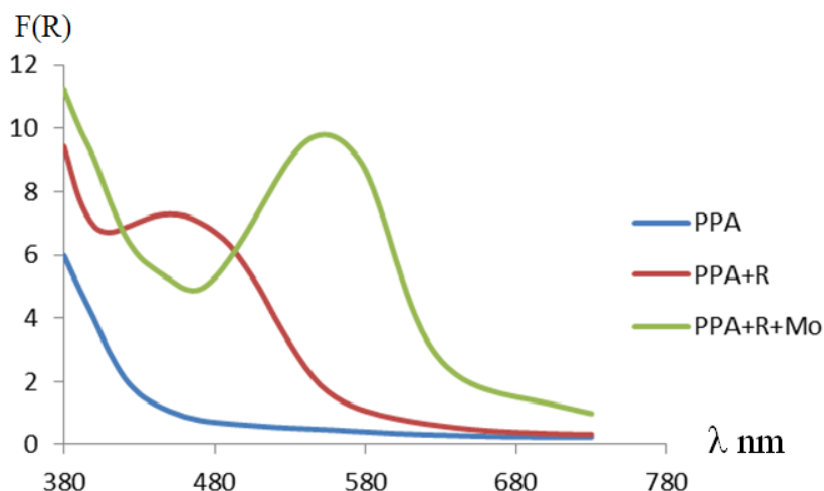


Figure 7. Reflection spectra in the Kubelka-Munk function: 1-PPA polymer, 2-immobilized phenylfluorene, 3-complex formed by the Mo(VI) ion with immobilized phenylfluorene.

It should be noted that the absorption spectra of phenylfluorene (about 440 nm) changed upon binding with the Mo(VI) ion. The adsorption spectra of the complex of phenylfluorene with a molybdenum ion in the solid phase showed a bathochromic shift up to 550 nm. As already mentioned, the reagent molecule contains –OH groups, where oxygen acts as an electron acceptor. As a result, Mo (VI) ions are added to these groups. Subsequently, it forms intensely colored and fairly stable complex compounds with the Mo (VI) ion.

Scanning electron microscope (SEM) analysis. The morphological study and elemental composition of the fibers were performed using a SEM-EVO MA 10 scanning electron microscope (Zeiss, Germany).

Phenylfluorene immobilized in the appropriate medium was added to the sample prepared for analysis and removed after 15 minutes, after which it was examined under a scanning electron microscope. The results are shown in Figures 4-5.

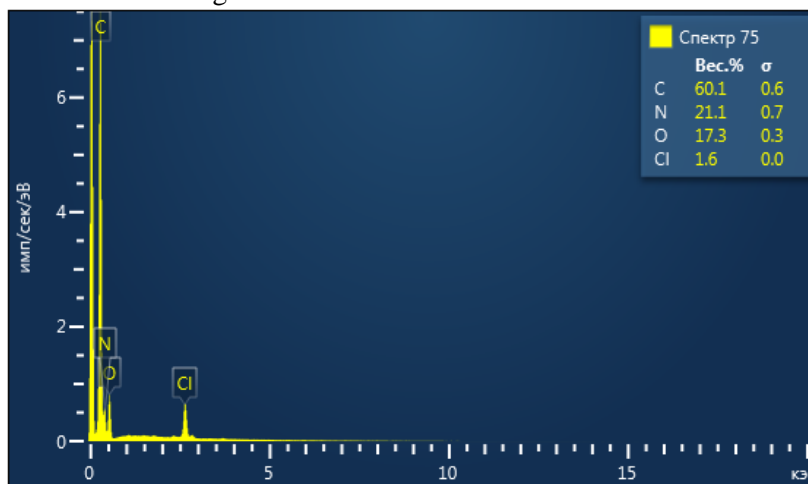


Figure 4. Spectrum of phenylfluorene immobilized on a PPA fiber, taken under a scanning electron microscope.

Table 1

The results of the spectra of phenylfluorene immobilized on a PPA fiber obtained using a scanning electron microscope

Element	Wt.%	Sigma Wt.%
C	60.1	0.6
N	21.1	0.7
O	17.3	0.3
Cl	1.6	0.0

C	60.08	0.60
N	21.11	0.74
O	17.25	0.29
Cl	1.56	0.03
Total:	100.00	

From the results shown in the spectra and the table, we can say that chlorine is being replaced by phenylfluorene on the carrier, since the mass ratio of chlorine ions to the mass of nitrogen atoms is very small. Then, the complex of the immobilized reagent with the molybdenum (VI) ion was analyzed under a scanning electron microscope.

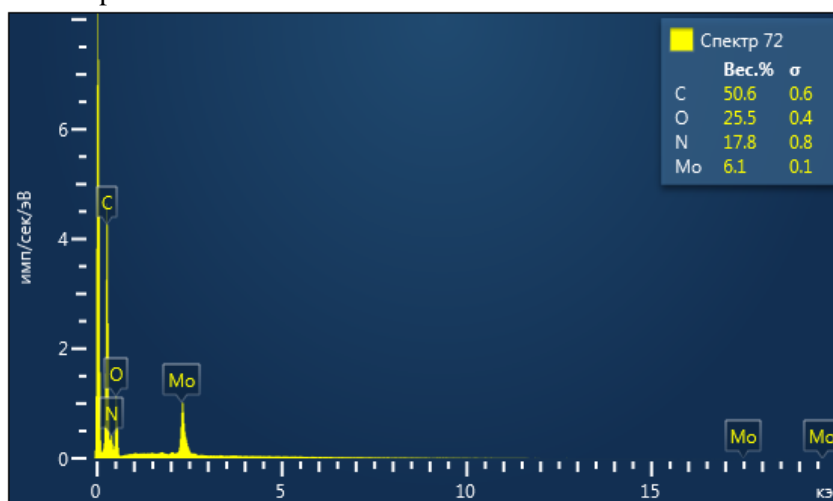


Figure 5. SEM spectrum of the complex formed by the Mo(VI) ion with phenylfluorene immobilized on a PPA fiber.

Table 2
Results of the SEM spectrum of the complex formed by the Mo(VI) ion with phenylfluorene immobilized on the PPA fiber

Element	Wt.%	Sigma Wt.%
C	50.64	0.57
N	17.81	0.81
O	25.46	0.39
Mo	6.09	0.12
Total:	100.00	

As can be seen from the obtained results, it can be concluded that the Mo (VI) ion forms a complex with phenylfluorene immobilized on the fiber, and the developed method can be applied to the analysis of natural objects containing molybdenum ions.

Comparison of analytical properties of complexes in solution and carrier

Comparing the analytical characteristics of the complex formed by the Mo (VI) ion with phenylfluorene in solution and in the solid phase (Table 3), the following conclusions were made:

- 1) The spectrum of absorption in solution and reflection in the carrier of complex formation was in the same region;
- 2) Determination of the Mo(VI) ion using a phenylfluorene reagent immobilized on a PPA polymer support confirms the intensity of the phenylfluorene itself.

3) The time of formation of the specified complex was 2 times faster, PPA gave a better result in the detection of Mo (VI) ions than the immobilized solution of phenylfluorene on a polymer carrier.

4) The sensitivity of the method increased 10 times compared to the solution when using the immobilized reagent.

Table 3
Comparison of optimal conditions for the complex formation of Mo(VI) with FF in solution and on a PPA polymer carrier

Parameter	Difficult educational conditions	
	in solution	PPA is in a polymer carrier
λ , nm	550	550
pH	2,5	2,5
C_n , mkg/ml	0,01	0,002
Complex formation time, min	15	10
Selectivity	Cu (50), Pb (50), Ag (100), Au (100), Fe (25)	Cu (50), Pb (50), Ag (100), Au (100), Fe (25)

Molybdenum (VI) forms a stable complex compound with phenylfluorene at pH=2.5. In this environment, several ions can interfere with the detection of molybdenum(VI). Therefore, when studying the selectivity of the developed method, the influence of foreign ions was studied.

Table 4
Determination of the molybdenum (VI) ion in the presence of foreign ions (CMo=50 μ g)

Mo: scavenger ion μ g/ml [Mo:X]	Found Mo(VI) sum	S_r
Mo :Cu		
1 : 1	0,55 \pm 0,08	0,098
1: 25	0,48 \pm 0,05	0,083
1: 50	0,46 \pm 0,04	0,131
Mo : Pb		
1: 50	0,49 \pm 0,02	0,041
1: 100	0,51 \pm 0,05	0,055
Mo : Ag		
1 : 50	0,52 \pm 0,05	0,038
1 : 100	0,54 \pm 0,17	0,129
Mo :Cd		
1 : 1	0,49 \pm 0,02	0,040
1 : 25	0,53 \pm 0,05	0,075
1 : 100	0,52 \pm 0,08	0,096
Mo : Fe		
1 : 1	0,53 \pm 0,04	0,056
1 : 25	0,52 \pm 0,10	0,115
1 : 100	0,49 \pm 0,06	0,102

As can be seen from Table. 4, the presence of Cu²⁺, Pb²⁺, Ag⁺, Cd²⁺, Fe³⁺ ions in various ratios does not interfere with the determination of 50 μ g of molybdenum (VI).

Determination of Mo (VI) ions from natural objects

To determine the molybdenum (VI) ion from the composition of various river waters, 20–30 ml of the analyzed sample, 5 ml of 10% NH₄OH and 2 ml of 2 N H₂SO₄ are added to a 100 ml volumetric flask and dissolved in distilled water. An aliquot (15 ml) of the solution prepared for analysis is poured into a volumetric flask. When determining molybdenum, immobilized phenylfluorene was added to the sample for 5 min, and then the reflection spectra were measured on a spectrophotometer.

For the quantitative determination of molybdenum ions from different river waters, the amount of analyzed water was increased two or more times from its standard solution and reflection spectra were obtained. The concentration of molybdenum ions is calculated from the analytical signal. The waters of the Chirchik and Angren rivers were taken as a natural object, the results are presented in Table. 5.

Table 5
The results of the determination of molybdenum (VI) ions in river waters by the sorption-spectrophotometric method (P=0.95)

Sampling location	Found Mo, $\mu\text{g}/\text{dm}^3 (\bar{x} \pm \Delta X)$	n	S	S _r
Chirchik	1.21±0.09	5	0.11	0.090
Angren	0.94±0.11	4	0.07	0.074

Based on the results of the analysis of river and drinking water, it can be concluded that the content of molybdenum in them does not exceed the MPC concentration, which indicates the safety of the region's water.

CONCLUSION

In this work, we studied and compared the analytical properties of phenylfluorene immobilized on a PFC matrix for the determination of Mo(VI) ions by spectrophotometric and scanning electron microscopic methods. According to the results obtained, the following can be said:

The optimal conditions for the immobilization of the phenylfluorene reagent on a PPA matrix and the formation of a complex with the phenylfluorene reagent immobilized by the Mo(VI) ion were studied; in particular, the spectroscopic signals of the reagent and the complex give 440 and 550 nm, respectively.

It has been established that the developed method and the recommended analytical reagent have high selectivity, speed and sensitivity for the determination of the Mo (VI) ion in real objects without isolating satellite ions.

REFERENCES

- Henckens M.L., Driessen P.J. Molybdenum resources: Their depletion and safeguarding for future generations.// Resources. Conservation & Recycling journal homepage: www.elsevier.com/locate/resconrec 2018. P 127-128.
- Никонов Н.В. Молибден. Свойства. применение. производство. продукция.// М.:ООО Метотехника. 2014. 34 с.
- Хоут., Samuel Lesli. Metallography.// М.: McGraw-Hill. 1921. 96 с.
- Fierro J.G.L. Metal oxides, chemistry and applications.// CRC Press. 2006. P 414-455.
- Centi G., Kavani F., Trifiro F. Selective oxidation by heterogeneous catalysis. Kluwer Academic.// Plenum Publishing House. 2001. P 363-384.
- МотыляевА. Молибден.// Journal of Biomedical Materials Research A. 2017. С 23-29.
- Штефан В.В., Елифанова А.С. Канунникова Н.А. Структурно-фазовый сос-тавтомолибдени-титан содержащих покрытий.// конф. Минск: БГТУ. 2019. С 287.
- Sergio Sanudo-Wilhelmy. Redox chemistry of molybdenum in natural waters and its involvement in biological evolution.// Aquatic Microbiology December. 2012 V 3. P 427.
- Беспамятное Г.П., Кротов Ю.А. Предельно допустимые концентрации химических веществ в окружающей среде.// Л.: Химия. 1985. 528 с.
- Novotny J.A. Molybdenum nutriture in humans.// Department of Nutrition and Exercise Physiology. 2011. P 164
- Byornsson Ragnar., Niz Frank., Shrok Richard., Eynzl Oliver., DeBeer Serena. Discovery of Mo (III) in Fe Moco: acoupling enzyme and model chemistry.// Journal of Biological Inorganic Chemistry. 2015. P 20.
- Van Stappen Keysi., Davydov Roman; Yang Chji-Yong., Fan Ruixi., Guo Yisong., Bill Ekxard., Zefeldt Lans., Xofman Brayan., De-Beer Serena. [Spectroscopic characterization of the Mo nitrogenase E1](#)

- [state based on Mo and Fe X-ray absorption and Messsbauerstudies.](#)//Inorganic chemistry. 2019. V 58. № 18. P 12365-12376.
13. Curzon M. E. J., Kubota, J., Bibbi, B. G. Environmental Effects of Molybdenum on Caries.// Journal of Dental Research. 1971. V 50 № 1. P 74–77.
14. Coughlan M. P. "The role of molybdenum in human biology.// Journal of Hereditary Metabolic Disease. 1983. V 6. № 1. P 70-77.
15. Barselu Donald G., Barselu Donald. Molybdenum.// Clinical toxicology. 1999. V 37. № 2. P 231–237.
16. Zygmunt Marczenko and Ryszard Lobinski. Determination of molybdenum in biological materials.// Chem. 1991. V 63. № 11. P 1627-1636.
17. Ayodele T., Odularu S., Peter A., Ajibade Johannes Z. Mbese Impact of Molybdenum Compounds as Anticancer Agents.// Hindawi Bioinorganic Chemistry and Applications. 2019. P 420.
18. Басаргин Н.Н., Аникин В.Ю., Салихов В.Д., Розовский Ю.Г. Предварительное концентрирование марганца (II) и висмута при определении их микроколичеств в природных и сточных водах.// Диагностика материалов. 2000. Т 66. № 2. С 14-17.
19. [Madusmanova N.K.](#), [Smanova Z.A.](#), [Zhuraev I.I.](#) Properties of the New Analytical Reagent 2-Hydroxy-3-Nitrosophthaldehyde// [Journal of Analytical Chemistry](#). 2020. T75. № 1. С 135-138.
20. Мусаев У.Н., Мухамедиев М.Г., Икрамова М.Э. Синтез модифицированных сорбентов на основе полиакрилонитрильных волокон.// Научный вестник НамГУ. 2001. № 2. С 117-119.
21. [Nurmukhammadov Z.Sh.](#), [Smanova Z.A.](#), [Tadzhimukhamedov K.S.](#), [Inatova M.S.](#) Synthesis and properties of a new analytical reagent, 2-hydroxy-3-nitrosophthalene-1-carbaldehyde.//[Russian Journal of Organic Chemistry](#). 2014. T50. № 6. С 895–897.
22. Коростылев П.П. Приготовление растворов. 1962. С. 203-206.
23. Лурье Ю.Ю. Справочник по аналитической химии. М. Химия. 1979. 480 с.
24. Smanova Z.A., Gafurova D.A., Savchikov A.V. Disodium 1-(2-pyridylazo)-2-oxynaphthalene-3, 6-disulfonate: An immobilized reagent for iron (III) determination, Russ. J. Gen. Chem. 2011. P 739–742.