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SORPTION-PHOTOMETRIC DETERMINATION OF LEAD (II) IONS BY IMMOBILIZED SODIUM 4-AMINO-5-HYDROXY-3 - ((E) - (4-NITROPHENYL) DIAZENYL) - 6 - ((E) -PHENYLDIAZENYL) NAPHTHALENE-2,7-DISULFONATE

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Аннотация: Мақолада ППД полиакрилонитрил толасида иммобилизация қилинган натрий 4-амино-5-гидрокси-3 - ((е) - (4-нитрофенил) диазенил)-6-((е)-фенилдиазенил) нафталин-2,7-дисульфонатни қўрғошин ионларини аниқлаш учун реагент сифатида ишлатиш мумкинлиги кўрсатилган. Иммобилизация ва комплекс ҳосил қилишни мақбул шароитлари топилган.

Калит сўзлар: иммобилланаган реагент, 4-амино-5-гидрокси-3-((е)-(4-нитрофенил) диазенил)-6-((е)-фенилдиазенил) нафталин-2,7-дисульфонат натрий, сорбцион – спектроскопик анализ усули, қўрғошин, чиқинди сув.

Аннотация: В статье показана возможность использования натрий 4-амино-5-гидрокси-3-((е)-(4-нитрофенил) диазенил)-6-((е)-фенилдиазенил) нафталин-2,7-дисульфонат, иммобилизованного на полиакрилонитрильном волокне ППД, в качестве реагента для определения ионов свинца. Найдены оптимальные условия иммобилизации и комплексообразования.

Ключевые слова: иммобилизованный реагент, 4-амино-5-гидрокси-3-((е)-(4-нитрофенил) диазенил)-6-((е)-фенилдиазенил) нафталин-2,7-дисульфонат натрия, сорбционно-спектрофотометрические методы анализа, свинец, сточные воды.

Abstract: The article shows the possibility of using sodium 4-amino-5-hydroxy-3 - ((e) - (4-nitrophenyl) diazenyl) - 6 - ((e) -phenyldiazenyl) naphthalene-

2,7-disulfonate, immobilized on polyacrylonitrile fiber PPD, as a reagent for the determination of lead ions. The optimal conditions for immobilization and complexation were found.

Keywords: immobilized organic, 4-amino-5-hydroxy-3 - ((e) - (4-nitrophenyl) diazenyl) - 6 - ((e) -phenyldiazenyl) naphthalene-2,7-disulfonate, sorption spectrophotometric methods of analysis, lead, waste water.

Introduction. Nowadays, one of the acute global problems of our era is the uncontrolled pollution of the environment caused by human factor and activities. Among them, contamination of natural waters is especially dangerous. The insufficiency of drinking water is becoming a key problem for the region of Central Asia, owing to its shortage of water resources. Fresh water supplies suitable for drinking in the rivers and lakes of Uzbekistan are very limited. Scientists are put forwarding the idea that ground and glacial waters serve as a global solution to this problem, however, these reserves have a significant tendency to accumulate toxic pollution. Thus, drinking water is becoming a truly “strategic resource of the 21st century”.

The aim of the work was to develop an express and sensitive technique for the sorption-spectrophotometric determination of lead using an organic reagent (OR) immobilized on a fibrous carrier of a series of diazoazo compounds sodium 4-amino-5-hydroxy-3 - ((e) - (4-nitrophenyl) diazenyl) - 6 - ((e) -phenyldiazenyl) naphthalene-2,7-disulfonate (ACh). Due to its selectivity, this reagent has found its application in the analysis of lead in the presence of many other metals.

This article shows the advantage of the sorption-spectrophotometric determination of lead (II) using an organic reagent immobilized on a polymer carrier in comparison with the photometric method.

Literature Review. In the study of which conducted by World Health Organization, the special attention are paid to the heavy toxic metals (cadmium, lead, mercury, arsenic, chromium, copper, zinc, etc.), which are assigned to the group of priority pollutants. Therefore, the problem of detecting and determining heavy metal ions in waters is especially acute. One of the widespread types of anthropogenic pollutants is the entry of HTM into the soil [1-4].

The actuality and importance of the problem raised in the work lies in the intake of ecotoxicants into the human body according to the scheme: soil - plant - man - environment [5]. Control of environmental pollution, which means the ability to reduce the technogenic impact on nature, inevitably sets the task of expanding the means and methods of comprehensive environmental monitoring [6]. In recent years, methods for the determination of elements with organic reagents immobilized on the solid phase have been intensively developed. Compared with photometry in solutions, sorption-spectrophotometric methods of analysis are more sensitive and selective [7, 8]. Lead is widespread in nature. It is found in many ores, galena, anglesite and kerrosite. It is widely used in batteries, cable sheaths, solder and radiation shielding [9]. Lead is widely used and applied in a wide variety of industries. All these are large-scale industries with large volumes of waste and emissions, both into the atmosphere and into water. Due to the low MPC value (MPC

for lead in drinking water is 30 μg/l), constant monitoring of the lead content in various environmental objects and in waters is required [1–2,7].

As analytical methods for the determination of lead in environmental objects, various optical methods are used: atomic absorption, spectrophotometric methods using organic reagents of various classes, among which diazo-reagents are the most famous [3-5]. Sorption-spectrophotometric methods for the determination of lead are few, there are few good organic reagents for lead [6]. Meanwhile, the advantages of specifically sorption-spectrophotometric methods, in terms of high sensitivity for the determination of various toxicants, suggest that the development of these methods for the determination of lead is most urgent. Among the new approaches to improving the analytical characteristics of luminescent reagents, one should note the immobilization of organic reagents on solid carriers, which makes it possible to combine concentration with simultaneous determination directly on a solid matrix [10–12].

Research Methodology. Reagents and equipment. A standard lead solution with a concentration of 1mg/ml was prepared by dissolving a high-purity metal in HCl and HNO_3 with special purity [13]. Buffer solutions with pH from 1 to 10 were prepared from salts and acids of “chemically pure” grade, according to the method presented in this work [14]. Working solutions of the organic reagent amido black were prepared by appropriate dilution of the initial standard metal solutions with bidistillate. We used freshly distilled and purified solvents and bidistillate, deionized water, previously checked for the absence of luminescence.

IR spectra of reagents, carriers, and immobilized ORs were recorded on a UR-10 spectrophotometer (Carl Zeiss, Jena), Analitrsystem 360 FT-IR (USA) in KBr, LiF tablets in the region of 500-4000 cm^{-1}.

To record the diffuse reflectance spectra from a solid surface and study the dependence of the reflectance (R), the function of the reflectance F (R) on various factors, an X-Rite recording spectrophotocolorimeter and a UV-ViS SPECORD 50 double-beam recording spectrophotometer were used.

Absorption spectra were measured on SF-46 and SPECORD 50 spectrophotometers and KFK-3 and KFK-2 photometers.

To measure pH, a METTLER TOLEDO pH meter was used, it was calibrated against standard buffer solutions in the medium of the solvent in which the determination was carried out. The pH values were used for buffer mixtures in an H_2O medium [14]. The solutions were pumped using a PP-2-15 peristaltic pump.

Reagents of chemically pure and pure for the analysis grade were used. Solutions of metal salts (0.1M) were prepared according to known methods by dissolving the corresponding nitrates or chlorides; dilutions were used to obtain solutions of the required concentration.

The organic reagent amido-black was prepared by dissolving 0.06165 g of the reagent in a 100 ml volumetric flask.

Various fibrous materials (polyacrylonitrile type) containing various functional groups have been tested as a solid phase. The sorbent was used in the form of disks with a diameter of 20 mm and weighing 30–40 mg in a wet state, for which the disks

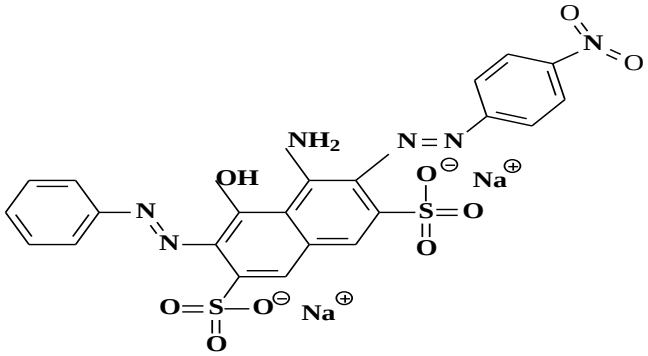
were kept in a 0.1 N solution of hydrochloric acid, washed with distilled water, and then stored in Petri dishes.

The analytical signal was taken as the difference between the diffuse reflectance coefficients (ΔR) measured at 610 nm of the disks after the sorption of the element from the control and analyzed solutions and the reaction with the reagent on the solid phase.

The study was carried out in static and dynamic modes. In a static mode, 10.0 ml of reagent solution was injected into 50.0 ml flasks, and the carrier disk was lowered therein and stirred for 5-8 minutes. Holding the carrier with a glass rod, the reagents were decanted, the immobilized carrier was washed with distilled water, and it was immersed in the analyzed solution. In the dynamic mode, the analyzed solution was passed through the immobilized disk at a rate of 10 ml/min.

The degree of retention of amido-black (R%) on the carrier was calculated by the formula: $R=100 \cdot A/A_0$, where A is the optical density of the reagent after immobilization, A_0 is the optical density before immobilization.

Analysis And Results. The reagent amido-black (AB) is a representative of the class of diazo dyes, characterized by a low sensitivity of reaction with lead. The dye has a complex structure and the mechanism of the reaction of amido-black 10 V with metal ions is not fully understood. It is believed that when the dye interacts with metals, the formation of a mixed type of interaction is possible: ionic chemical bonding and physical adsorption.



Formula $C_{22}H_{14}N_6Na_2O_9S_2$
Molar mass 616,5 g/mol.
Reagent appearance:
dark brown powder.

Figure 1. The structural formula of the amido-black reagent.

The determination of lead is strongly interfered with by iron, aluminum, bismuth, lead and other metals, the interfering effect of which is eliminated by introducing masking substances and varying the acidity of the medium.

Fibrous materials modified with various anion-exchange groups were tested as a carrier for immobilization of amido-black. The greatest analytical effect was achieved during sorption on a fibrous carrier modified with hexamethylenediamine (PPD-1) with subsequent complexation on the solid phase, and it was found that on this type of carrier, AB is sufficiently firmly retained and therefore the PPD-1: AB (IMAB) system was selected for further studies.

The influence of concentration and immobilization time was studied in the range of $1 \cdot 10^{-6}$ – $1 \cdot 10^{-3}$ M solution of amido-black and 3-30 minutes, respectively (Table 1).

Table 1

Spectrophotometric characteristics of amido-black attached to PPD -1 sorbent

λ_R,nm	λ_{MeR}, nm	pH	Time, min	Concentration of the reagent on the carrier, M
490	610	6-7	7	$8{,}2 \cdot 10^{-5}$

The reaction of lead with AB on a solid sorbent is more contrasting than in a solution ($\Delta\lambda$=120 nm).

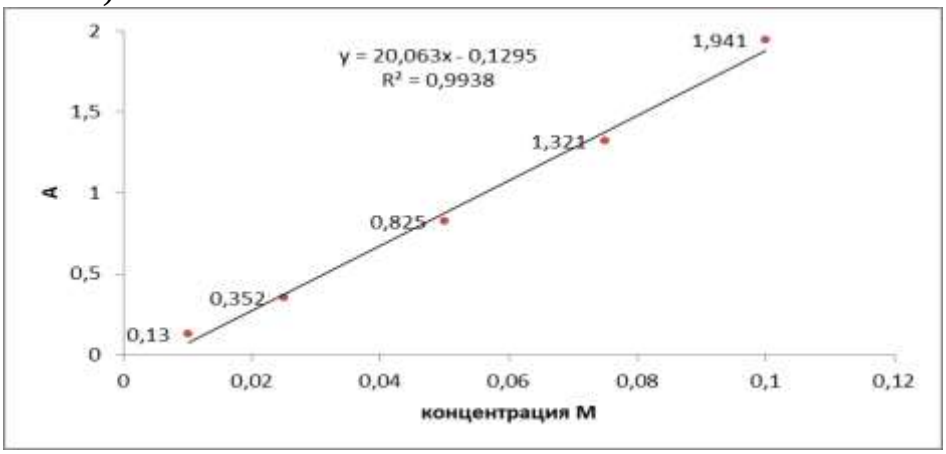


Figure 2. Calibration graph for the determination of lead ions with amido black.

It was found that Cd (II), Mn (II), Ni (II), Co (II), Zn (II), Mg (II) do not interfere with the determination of lead up to concentrations of 100 mg/l. The interfering effect of 50 mg/l on Fe (III), Bi (III), Al (III) is eliminated by introducing 0.1 M citric acid solution into the test solution. A method for the determination of lead in natural waters has been developed. The correctness of the developed technique was checked by the "introduced-found" method (Table 2). The duration of the analysis is 10-15 minutes.

Table 2

Results of determination of lead (II) in waters (n = 3, P = 0.95)

№ samples	Introduced lead, μg / l	Found lead, μg / l	S	Sr
1	2,00	2,71± 0,01	0,07	0,026
2	4,00	4,84±0,16	0,11	0,023
3	6,00	6,90±0,09	0,06	0,009
4	5,00	5,92±0,07	0,05	0,008

The relative standard deviation does not exceed 0.33.

CONCLUSION

Determination of lead using immobilized amido black on fibrous materials makes it possible to selectively determine the element without elution, which increases the rapidity of the analysis and reduces the detection limit by an order of magnitude.

The stability of the analytical signal for a long time, the stability of the dye immobilized on the fiber layer, the mechanical strength of polymer fiber materials, the ease of immobilization of the dye, the contrast of color change, as well as the linearity of metal concentration in solution allow the use of lead in the studied system for sorption-spectroscopic and visual-photometric detection in aqueous media.

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