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Development of a Sorption-spectroscopic Method for the Determination of Lead Ions by Immobilized Sulfarsarsen

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ABSTRACT

This article defines the optimal conditions for the detection of a heavy metal ion of lead (II) using a newly synthesized PPA 1 sorbent immobilized with a sulfarsazene reagent; PPA 1 and SMA 1 sorbents are selected as sorbents.
The maximum reflectance spectrum of the reagent is 480 nm the maximum light reflectance of the complex is 580 nm (for SMA 1), 570 nm (for PPA 1). The sorption rate of lead exceeds 90% on average.

KEYWORDS

Sulfarsazen, Immobilization, Polymer Carrier, Sorption Photometry.

Introduction

Currently, the identification of foreign substances in water and food products resulting from environmental pollution is becoming increasingly relevant. In the latest resolutions of the government of our country, in the Republic of Belarus, aimed at improving the quality of products and measures to protect the environment, the need to control the chemical composition of raw materials and products used for the content of heavy and toxic metals is indicated [1].

In this regard, the first priority is to identify toxic metals, including mercury, lead, cadmium and other heavy metals due to the established toxic effect of these elements on the human body. To obtain reliable information, it is necessary to carry out constant analytical monitoring of the content of toxic metals in environmental objects and food products.

A number of recent publications [2-4] are devoted to the problems environmental pollution of environmental pollution [5-7]. Various aspects related to the ingress ions of lead ions into the environment, as wellas its effects on the human body, were studied in [5-7]it. Heavy metals (HMS) occupy the second place in terms of danger, behind pesticides and significantly ahead of such well-known pollutants as carbon dioxide and sulfur, while in the forecast they should become the most dangerous, more dangerous than nuclear power plant waste and solid waste [8]. Heavy metal pollution is associated with their widespread use in industrial production, coupled with weak purification systems, as a result of which heavy metals enter the environment, including the aquatic environment, polluting and poisoning it. The main sources of anthropogenic HM input into the environment are various industrial enterprises, incineration of oil and various waste products, production of glass, fertilizers, cement, etc. The most powerful TM occur around ferrous and especially non-ferrous metallurgy enterprises as a result of atmospheric emissions. The effect of pollutants extends for tens of kilometers from the source of elements entering the atmosphere. Thus, metals in the amount of 10 to 30 % of the total emission into the atmosphere are distributed at a distance of 10 km or more from an industrial enterprise. At the same time, combined plant contamination is observed, consisting of direct deposition of aerosols and dust on the surface of leaves and root assimilation of HMS accumulated in the soil during a long time of atmospheric pollution [9-11]. The largest amount of air pollutants is emitted from the exhaust gases of cars. The most dangerous pollutants include mercury, lead, and cadmium [12].

Modern requirements for the analysis of environmental objects and food products provide for the development of new highly sensitive and rapid methods for the determination of toxic metals. The multicomponent nature of the objects of analysis, low concentrations of metal pollutants for solving such problems, make it necessary to use combined analysis methods that include the concentration stage. One of the most promising methods for determining metals in complex objects is spectrophotometric analysis methods [13]. Many photometric and electrochemical methods have been proposed [14-16] for determining lead, but the disadvantage of these methods is their low sensitivity and selectivity, so the development of simple highly sensitive methods for analytical control of lead content in various objects is relevant, since lead is one of the most toxic and dangerous environmental pollutants.

The aim of this work is to develop sorption-spectro photo metric methods definitions for the determination of lead ions, which are one of the new approaches based on the use of immobilized organic reagents and meet the requirements for sensitivity and reliability [19-24].

The Experimental Part

Reagents and equipment: A standard lead solution with a concentration of 1 mg / ml was prepared by dissolving a high-purity metal in HCl and $HNO3_3$ "OC.h." [25, 26]. Buffer solutions with pH from 1 to 10 were prepared from salts and acids "CH. CH." according to the procedure [25].

The organic reagent sulfarsazene with a concentration of 0.01 M was prepared by dissolving 0.0572 g of the reagent in a 10.0 ml volumetric flask0 мл.

We used freshly distilled and purified [26]solvents and bidistillate, deionized water, and previously checked for the absence of luminescence according to [26].

Other assets used marks HH grades. and h. e. a. Solutions of metal salts (1.0 mg / ml) were prepared by dissolving the corresponding nitrates or chlorides according to the methods.

Various fibrous materials (polyacrylonitrile type) containing various functional groups were tested as the solid phase. The sorbent was used in the form of disks with a diameter of 20 mm and a mass of 30-40 mg in the wet state, for which the disks were kept in 0.1 M hydrochloric acid solution, washed with distilled water and then stored in Petri dishes.

IR spectra were recorded on an UR-10 spectrophotometer (Karl Zeiss, Jena), "Analitrsystem 360 FT-IR" by Nikolet Justrument Corporation(USA) in the range of 500-4000 cm^1.

To measure pH, a pH meter from «A METTLER TOLEDO pH meter», calibrated for standard buffer solutions and an I-130 iono meter were used to measure pH ionomer I-130.

To take diffuse reflection spectra from a solid surface and study the dependence of the reflection coefficient (R) and the function of the reflection coefficient F(R) on various factors spectro photo colori meter “, an X-Rite recording spectro photo colorimeter and a UV–ViS SPECORD M -40 two-beam recording spectro photo meter were used SPECORD M.

The difference in diffuse reflection coefficients (ΔR) measured at 5757.0 nm after sorption of the element from the control and analyzed solutions and reaction with the reagent in the solid phase was taken as the analytical signal.

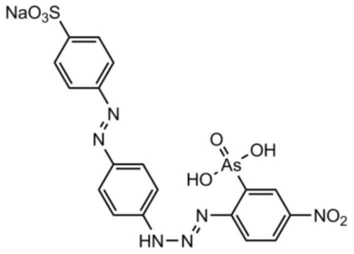
Method of Determination

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

The degree of retention of sulforsazene (R%) on the support was calculated by the formula: $R=100^{\cdot}A/A_{A0,}$ where A is the optical density of the reagent after immobilization, and$_0$ is the optical density before immobilization [22-7].

Results and Discussion

Reagent sulfarsazene (CC) a representativeдиof the diazo dye classкрасителей, characterized by a low sensitivity of the reaction with lead. The dye has a complex structure and the reaction mechanism of sulfarsazene with metal ions to be investigated. It is believed that the interaction of the dye with metals can lead to the formation of an ionic chemical bond and physical adsorption.



Sulfarsazen (4-((4-(3(2-arseno 4-nitrophenyl) tRiaz-2 (enyl) (phenyl)have diazenyl) bansilalsfat sodium.
Mr=572.32 g/mol

Fig. 1. The structural formula of a reagent of sulfarsazene

The determination of lead is strongly hindered 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.

As a carrier for the immobilization of sulfarsazene Fibrous materials modified with various anion-exchange groups SMA-1, SMA-2, SMA-3, and SMA-2 were tested as a carrier for the immobilization of Sul-farsazene. PPA-1 VA PPM-1.

Sorption of the reagent on various types of carriers was studied (table 1).

Table 1. The degree of retention of selfandRazina (R%) for different nositels

Carrier	R_1	R_2	R_3	R_4	R_{cf}
SMA-1	98,9	99,0	100,0	98,0	99,0
SMA-2	51,5	50,5	51,0	51,0	51,0
SMA-3	41,0	43.0	42.5	42.5	42.3
PPA-1	79,5	79,5	79,5	79,5	79,5
PPM-1	69,0	70,5	68,0	69,5	69,0

When studying the degree of retention of reagenta, in the pH range 3-of 3-5, its yield on the SMA-1 sorbent is 98-998-9 9 %.

The greatest analytical effect was achieved by sorption on a fibrous support modified with hexamethylenediamine (SMA-1) and on the sorbent PPA-1 with subsequent complexation on the solid phase and it was found that on ettheir type is Ah theeй Sul-farsazen carrier is sufficiently strongly held, and therefore the SMA-1 system was chosen for further research: SS (NAMESS) and PPA-1-SS (figs. 2 and 3).

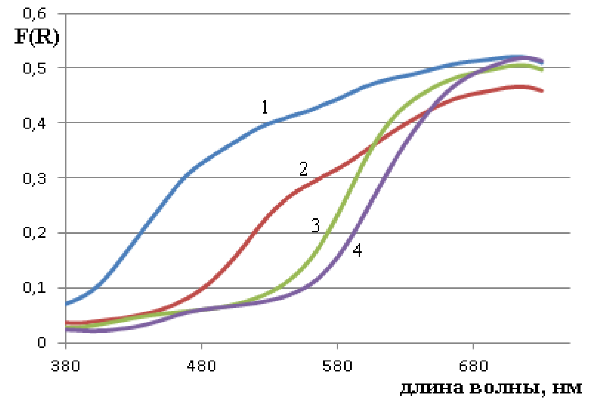


Fig. 2. Reflection Spectra of the polymer support PPA-1 (1) and the sulforsazene reagent immobilized on it sulforsazena (2), a complex with lead at pH 5 (3) and pH 4 (4).

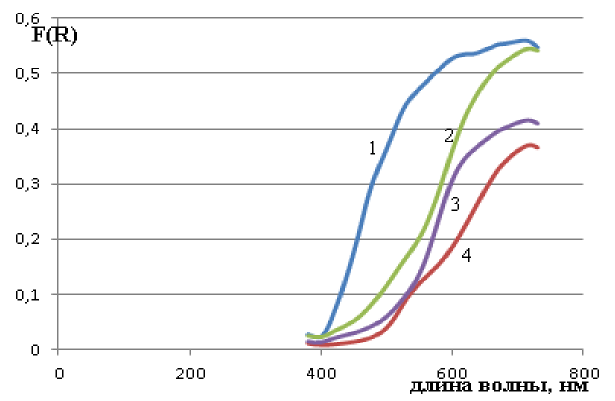


Fig. 3. Reflection Spectra of the polymer carrier SMA-1 (1) and the sulforsazene reagent sulforsazena (2) immobilized on it, a complex with lead at pH 5 (3) and pH 4(4).

Effect of concentrationSS and immobilization time were studied in the range of $1\cdot10^{-6} – 1\cdot 10^{-3}$ M of Sulfarsazen solution and 3-30 minutes, respectively (table 2).

Table 2. Spectrophotometric characteristics Sulsof farcasanu, fixed on the sorbent of the AGR-1 and PPA-1

Carrier	λ_R,nm	λ_{MeR}, nm	$\Delta\lambda$	pH	Time, Min	The concentration of the reactant on the media M
AGR-1	480	580	100	4,0	6	$0,9\cdot10^{-4}$
PPA-1	480	570	90	9,0	30	$4,2\cdot10^{-5}$

The reaction of lead with sulforsarsen on a solid SMA-1 sorbent is more contrasting than with PPA-1 (Δλ=100 nm), so the SMA-1 sorbent was used for further studies.

The dependence of the analytical signal of the immobilized sulforsarsena complex with lead on pH, time, and lead concentration was studied in static and dynamic modes. The effect of acidity was studied in the pH range from 2 to 10. It is found that the maxima in the spectra of complexes shift by 100 nm, and the diffuse reflection coefficient is minimal at pH-3 -5, i.e., immobilization leads to a shift in the pH of complex formation by two units to a more acidic region.

The absorption spectra were recorded under optimized conditions at room temperature (Fig. 4, 5).

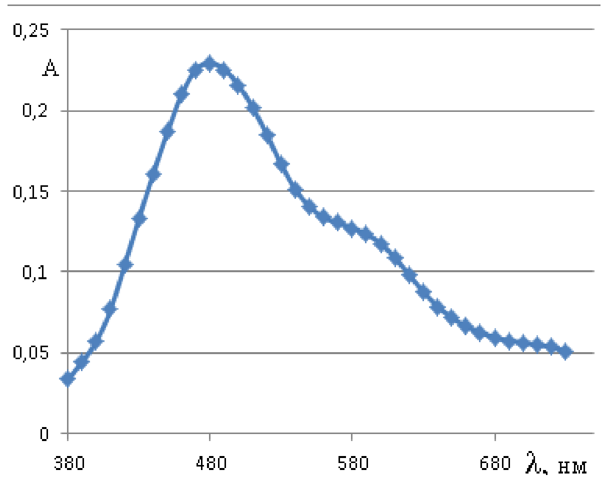


Fig. 4. Absorption Spectrum of sulforsazene reagent sulforsazene, PPA-1 support (l=2, C$_R$CR = 0.0001 M,$_{max}$= 480 nm)

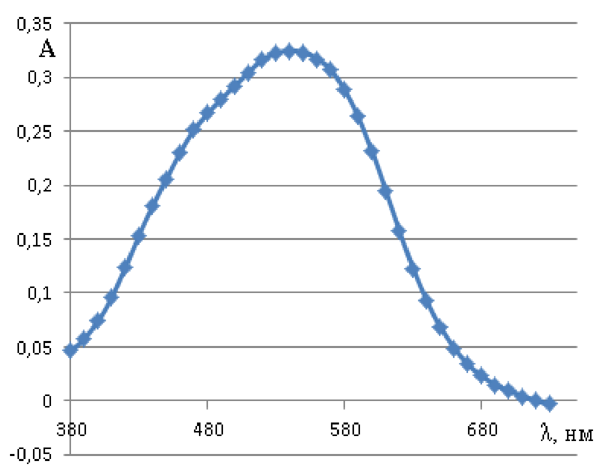


Fig. 5. Absorption spectrum of the lead complex with sulforsazene reagent sulforsazene, PPA-1 carrier (l=2, C$_R$CR = 0.0001 M,$_{max}$=570 nm)

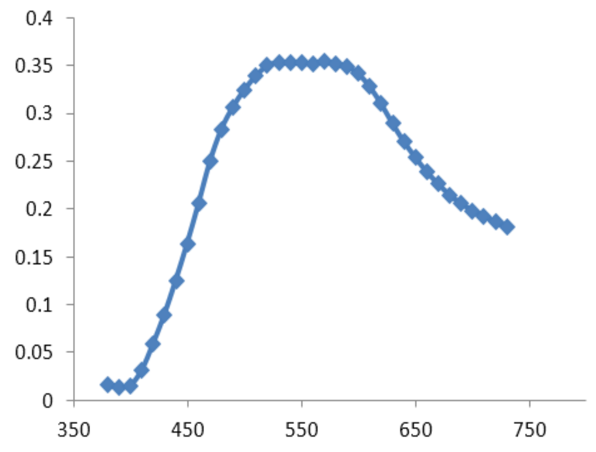


Fig. 6. absorption Spectrum of the sulforsazene reagent sulforsazene, SMA 1 carrier (l=2,C$_R$CR = 0.0001 M,$_{max}$= 520-580 nm)

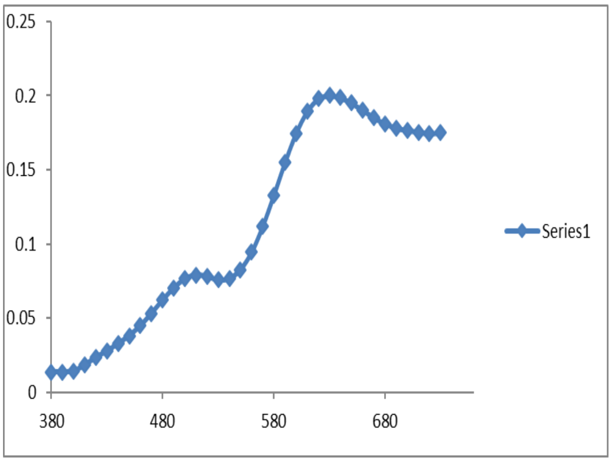


Fig. 7. Absorption spectrum of the complex, sma1 lead carrier with sulforsazene reagent sulforsazene (l=2,C$_R$CR = 0.0001 M,$_{max}$=630 nm hm)

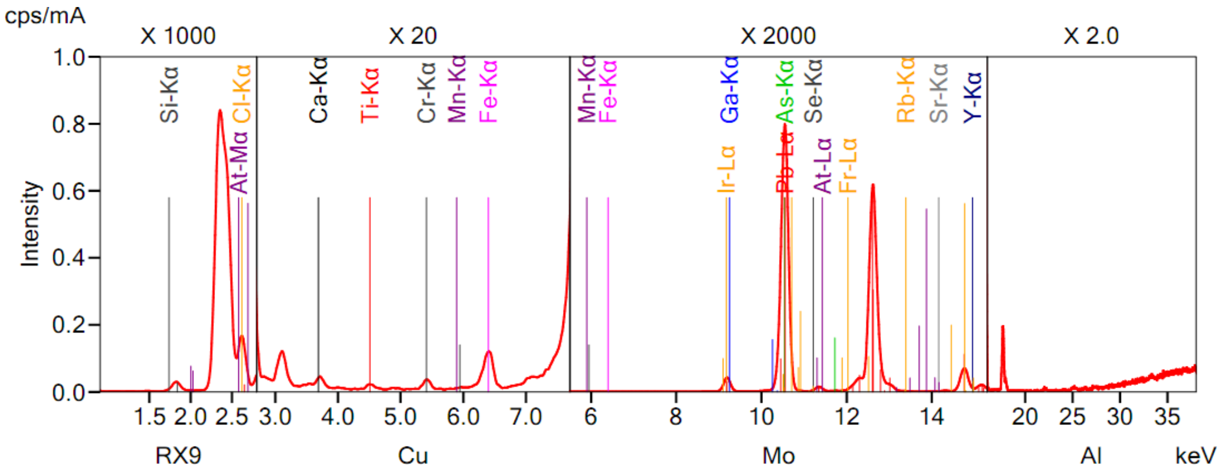


Fig. 8. X-ray fluorescence spectrum of the complex lead sulfarsazene

According to the results of x-ray fluorescence analysis, it was found that the lead content on the carrier is 89.4 %.

When immobilized sulforsazene solutions lead solutions with different volumes were passed through immobilized sulfarsazene, similar results were obtained (table 1).3).

Table 3. Results of determination of Cof wine from various volumes (n=3; P=,0.95; C_{Pb}=50mkg)

The size of the samples, ml	50,0	100,0	200,0	to 500,0	800,0	1000
Found lead, mcg	49,8	49,6	49,7	49,6	49,1	48,7
Coefficient Concentration coefficient	99,6	99,2	99,4	99,2	98,2	97,4

It is shown that the volume of the analyzed solution in certain quantities does not significantly affect the degree and amount retrieving of metal recovery and its concentration coefficient.

When comparing the results of the analysis obtained in solution and on an immobilized sorbent, it is shown that during immobilization, the pH of complexation of sulfarsazene with lead shifts to a more acidic region and the detection limit decreases by an order of magnitude (tab.4).

To assess the selectivity of reactions, numerous experiments were conducted to determine the effect of foreign ions on the results of lead ion determination. According to the obtained data, the maximum permissible ratios of the foreign element to the determined ion were found, which were taken as the selectivity factor (table 4).

Table 4. Comparative characteristics of some analytical parameters of the immobilized sulfarsazene reagent sulfarsazene obtained in solution and on a support

System	λ_{max}, HR, nm	λ_{max}, MeR, Nm	pH	The limit of detection, mkg/ml	Concentration of interfering cations, Mkg
Solution	415	390	9,8-10	0,02	Zn (10), Cd (20), Co (40), Al (80), Zn (50), Cu (2), Ni (50), etc.

Carrier	520	620	3-4	0,008	Ca, Mg (1000), Cd (500), Co, Ni(350), Al(300), Cr(250), Hg (70), Pb(50) Cu(20), Zn (100)

As can be seen from table 4, sulfarsazene can detect lead in the presence of copper (1:20), iron, and mercury (1: 50) and other cations.

One of the most common ways to increase the specificity of detection is to use masking organic and inorganic compounds. However, in some cases, this approach is associated with certain difficulties associated with the need to accurately maintain the optimal ratios between the masking substance and the detected or interfering ion. Nevertheless, the use of various masking agents allowed us to increase the selectivity of certain reactions to some extent. The interfering influence of copper and iron in the determination of lead was eliminated by introducing thiourea into the analyzed solution thiourea, and mercury was masked with triethanolamine.

Method of Determination of Lead

A sample solution containing 2-50 micrograms of lead is introduced into a measuring flask (50 ml), a buffer mixture with a pH of 4.0 and 5 ml of the masking mixture is added and passed through the immobilized reagent on a carrier at a rate of 10 ml / min. The lead content is determined by a calibration graph plotted in coordinates F=f(C). The relative standard deviation (Sr) does not exceed 0.013 (table 5).

Table 5. Results of lead determination using immobilized sulfarsazene by diffuse reflection (n=5, P=0.95, $m_{sorbent\ m}$=0.2 g)

Lead introduced, mcg	Found lead, mcg	S	Sr
2,50	2,48±0,26	1,97	0,008
10,0	3,07±0,06	5,11	0,019
15,0	4,11±0,09	7,57	0,029
20,0	5,10±0,04	2,99	0,023

Conclusion

The results of the study made it possible to propose the SMA-1 - sulfarsazene system for use as a sensitive layer of a sensor sensor for lead ions, which was used to detect industrial wastewater samples.

Determination of lead using immobilized sulfarsazene on fibrous materials makes it possible to selectively determine it without elution, which significantly increases the speed of analysis with a decrease in the detection limit by an order of magnitude.

References

[1] Rulingse President of the Republic of Uzbekistan PP-3983 of October 25, 2018 "on measures to accelerate the development of the chemical industry of the Republic of Uzbekistan».

[2] Medvedev, I.F., & Derevyagin, S.S. (2017). *Heavy metals in ecosystems.* Saratov: "RAKURS", 178.

[3] Ruschenko, N.A., Zhuravskaya, N.S., Okun, B.V., Sheparev, A.A., Titova Yu. V., & Vladimir, S. (2015). Toxic the microelementoses in the clinic of occupational diseases. *Modern problems of science and education,* 3, 133-137.

[4] Mendiola, J., Moreno, J.M., Roca, M., Vergara-Juárez, N., Martínez-García, M.J., García-Sánchez, A., & Torres-Cantero, A.M. (2011). Relationships between heavy metal concentrations in three different body fluids and male reproductive parameters: a pilot study. *Environmental Health, 10*(1), 1-7.

[5] Cinderela, A.V. (2018). Maydanyuk City Environmental assessment of lead action in the soil-plant-animal system and development of scientifically based methods for its de-saccharification. *Bulletin of KRASGAU,* 6(141), 244-249.

[6] Shestova, G.V., Livanov, G.A., Yu. N.O., Ivanova T.M. & Sizov, K.V. (2012). Risk of chronic lead poisoning for the health of the population. *Medicine of extreme situations, 4*(42), 65-76.

[7] Khamidulina Kh. Kh., & Davydova Yu. O. (2013). International regulation of lead and its compounds. *Hygiene and Sanitation, 6,* 57-59.

[8] Selwyn, L. (2005). Health and safety concerns relating to lead and lead compounds in conservation. *J. Canadian Association Conservation (J. CAC),* 30, 18-37.

[9] Grooms, N.A. (2017). D.G. Dianova Metals in the environment and their impact on human health. *Actual problems of the Humanities and natural Sciences, 1*(4), 72-74.

[10] Pohl, H.R., Roney, N., & Abadin, H.G. (2011). Metal ions affecting the neurological system. Met Ions Life Sci, 8(247), 62.

[11] Shachneva M. (2012). Impact of heavy toxic metals on the environment. *Scientific potential of regions for the modernization service, 2*(3), 127-134.

[12] Filov, V.A. (2004). Chemical pollutants of the environment, zakariaou and information. *ROS. xthem. Magazine,* 48(2), 4-8.

[13] Teplaya, G.A. (2013). Heavy metals as a factor of environmental pollution. *Astrakhanskii vestnik ekologicheskogo obrazovaniya, 23*(1), 182-192.

[14] Korenman, I.M. (1980). *Organic reagents in inorganic analysis.* M: Chemistry, 448.

[15] Degtev, M.I. (2009). Organic reagents and their complex compounds. Study. The manual. (Permstate University UN-t) 2nd ed. pererab. Perm.: PSU, 269.

[16] Pochinok, T.B., & Temerdashev, Z.A. (2016). Molecular absorption spectroscopy. Krasnodar: KubSU, 157.

[17] Chernyaeva B. (2013). Actual problems of the impact of waste production and consumption on the environment and the health status of populations (a review). *Hygiene and sanitation.* 3, 32-35.

[18] Zaporozhets, O.A., Gaver O.M., & Sukhan, V.V. (1997). Immobilization of analytical reagents on the surface of carriers. *USP. Chem.* 66(7), 702-712.

[19] *Immobilized cells and enzymes.* (1988). Methods. Ed. J.R. R. Tolkien Inudvorda. M: “Mir”, 215.

[20] Zolotov Yu. A., Ivanov V.M. & Amelin V.G. (2002). *Chemical test methods of analysis.* Editorial URSS, 304.

[21] Yu. S.D., Murav'ev, A.G., & Rodin, A.A. (2010). ExprpESS-analysis of ecological

samples. Practical guide. Moscow: BINOM. *Laboratory of knowledge, CP*. 111-135. (424b).

[22] Savvin, S.B., Kuznetzov, V.V., Sheremet'ev, S.V., & Mikhailova, A.V. (2008). Optical chemical sensors (Micro-and Nanosystems) for analysis of liquids. *Russian journal of general chemistry, 78*(12), 2418-2429.

[23] Shtokolo, M.I., & Kostenko, E.E. (1992). Determination of microquantities lead analysis by solid-phase spectrophotometry. *Chemistry, 47*(10), 1887-1890.

[24] Chemical sensors. (2011). Ed. Vlasova Yu. G. M.: Nauka, 398.

[25] Korostylev, P.P. (1981). *Preparation of solutions for chemical and analytical works.* M: Science, 202.

[26] Weisberg, M., Proskauer, E., & Rydberg J. (1958). *TPPs 3. Organic solvents*. -M.: INR. Letter, 120-145.

[27] Savvin, S.B., Dedkova, V.P., & Shvoeva, O.P. (2000). Sorption-spectroscopic and test methods for determination of metal ions on the solid phase of ion exchangers. *USP. chem, 69*(3), 203-217.