CHOOSING THE OPTIMAL CONDITIONS FOR COMPLEX PRODUCTION OF IMMOBILIZATED POLYOXYFLAVONES AND OXYAZOCOMPOUNDS WITH ALUMINUM, GALLIUM, INDIUM AND TIN IONS

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Abstract

The possibility of using immobilized organic reagents oxyazobirims and polyoxyflavones in the determination of aluminum, gallium, indium and tin ions by sorption-fluorescence method was studied. The optimal conditions for complex formation of these reagents with the studied metals were selected. The chemistry and spectral properties of chemical reactions were studied. Detection capabilities in solution and immobilized states were compared.

Keywords: oxyazocompounds, polyoxyflavone, eriochrome red B, morin, quercetin, fluorescent.

INTRODUCTION

In recent years, we can observe the increase in environmental pollution, that is, poisoning of the environment with various heavy and toxic metals. The reason for this is the increase in anthropogenic influence, that is the increase in production and industry. Among the main national threats that threaten the ecological security of our country, it is necessary to highlight the pollution of water resources, natural and man-made disasters, production and household waste, radiation pollution of some areas, and groundwater pollution [1-3].

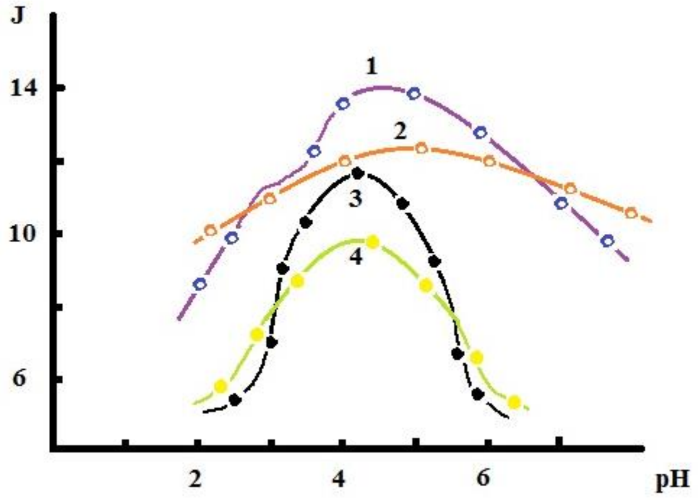
LITERATURE ANALYSIS AND METHODOLOGY

Allowed amounts of gallium and aluminum ions from the environment, food, drinking water and wastewater, if not controlled, pose a threat to public health. Today, the requirements for the metrological and analytical properties of the methods developed for the determination of toxic metals are increasing, which requires the development of modern methods for the determination of these metal ions [4-6].

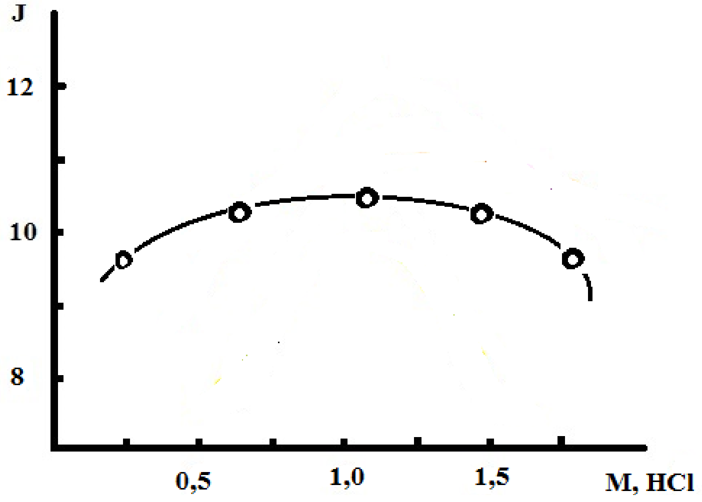
To determine some metals from complex objects - rocks, types of mineral raw materials, especially unenriched ore materials, high selectivity methods are required at a low detection limit [7-10].

It is necessary to use sorption-spectroscopic methods, including sorption-fluorescence method, as an effective method for high sensitivity determination of small amounts of aluminum, gallium, indium and tin ions from environmental objects. By immobilizing the organic reagents used in this method of detection on carriers of various forms (granules and fibers), their chemical-analytical properties are improved. In order to determine aluminum, gallium, indium and tin ions by this method, various oxyazo compounds and polyoxyflavone reagents were immobilized. Immobilized oxyazocompounds (chalcone (R_{kal}) and eriochrome red B (R_E)) and polyoxyflavones (morin (R_M) and quercetin (R_{kv})) were selected as the most suitable reagents for detection.

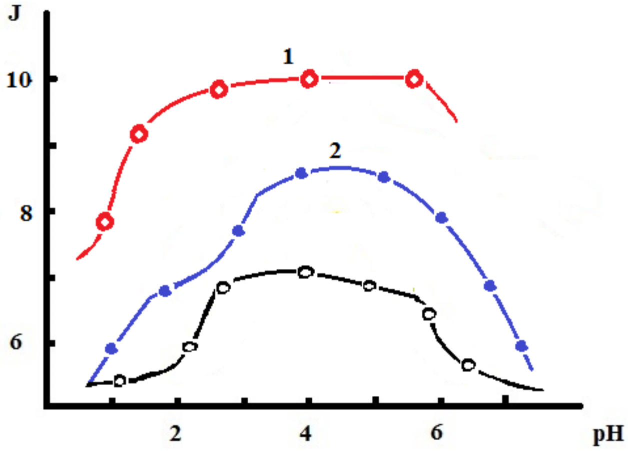
Complex formation in each immobilized reagent-metal system is studied by plotting curves of complex fluorescence intensity as a function of pH, organic solvent nature, dissolution rate, and time (Figures 1-3). Samples of complex compounds were prepared according to the above methodology. The obtained results show that the formation of the complex occurs in a strongly acidic medium for the Sn-R_M complex, 0.5-1.5 M HCl, for the Al-R_E complex, pH 2.0, and for the rest of the systems, in a weak acidic medium (pH 3.0-6, 0) occurs. The luminescence intensities of indium complexes formed with immobilized R_m and R_{kv} are maximum when pH is equal to 1.0. On the contrary, the luminescence intensities of aluminum and gallium complexes do not depend on pH 3-4 and 4-6, the complex of tin with R_M is stable to a wide range of acidity (0.5-1.5 M HCl). When studying the organic solvent nature (Table 1) and its concentration dependence (Fig. 2) of complexation of immobilized polyoxyflavones and oxyazo compounds with aluminum, gallium, indium and tin ions, in the medium with strong basic solvents (DMFA and DMSO) and 10-25% com. If carried out, the luminescence intensity of the complex compound will be maximum. Complex formation of immobilized polyoxyflavones is carried out in ethanol and acetone, but there is almost no change in the luminescence intensity of the complex (Fig. 2 a).



A) 1- P_{M}-Al; 2- P_{M}-Ga; 3- P_{KV}-In; 4- P_{M}-In



B) P_{M}-Sn



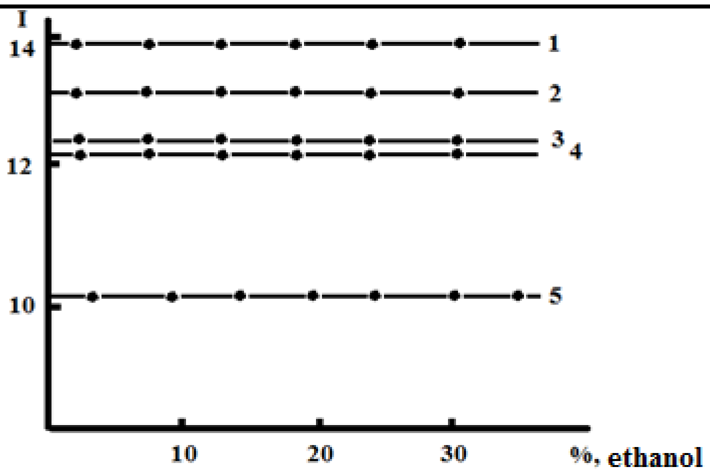
V) 1- P_e-Al; 2- P_{ca}-Al; 3- P_e-Ga;

Figure 1. Dependence of the luminescence intensity of the immobilized reagent complex on the acidity of the environment C_{me}=10 mkg

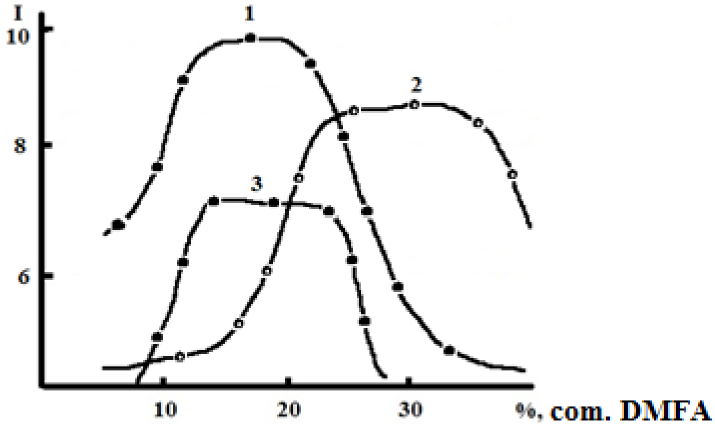
Table 1 The dependence of fluorescence intensity on the nature of the solvent (solvent=40%) of immobilized oxyazocompound and polyoxyflavone complexes formed with aluminum, gallium, indium and tin ions

Complex	**Fluorescence intensity**					
	Ethanol	**Acetone**	**DMFA**	**DMFA +ethanol**	**DMFA +aceton**	**ethanol+acetone**
$P_{\text{м}}$-Al	14,8	14,5	12,3	13,0	12,9	14,6
$P_{\text{м}}$-Ga	13,8	13,3	13,1	12,9	13,0	13,5
$P_{\text{м}}$-In	10,0	9,8	6,9	7,2	7,5	9,8
P_{kv}-In	13,0	12,7	9,0	10,2	10,5	12,9
P_{kal}-Al	5,0	5,1	9,0	7,8	7,7	5,0
P_e-Al	6,2	6,0	10,0	8,7	8,8	6,1
P_e-Ga	3,1	3,0	7,0	6,1	6,3	3,31

A relative decrease in luminescence intensity was observed when DMFA and its mixture with ethanol and acetone were carried out. This may be due to sufficient solubility of the resulting complex in DMFA and adsorption between the solvent and the reagent.



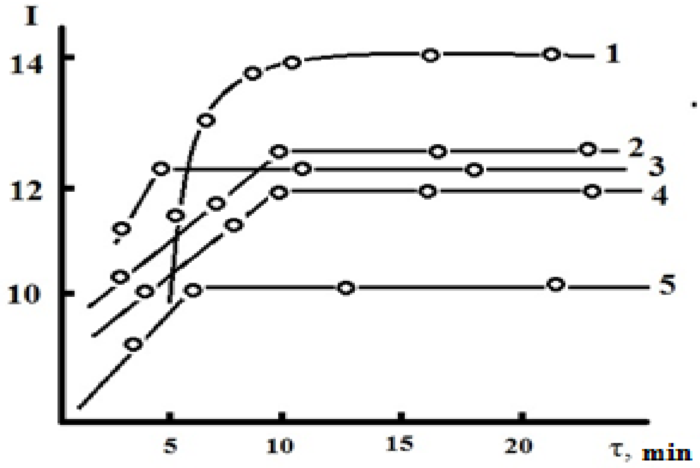
1- $P_{\text{м}}$-Al; 2- $P_{\text{м}}$-Ga; 3- $P_{\text{кv}}$-In; 4- $P_{\text{м}}$-Sn; 5- $P_{\text{м}}$-In



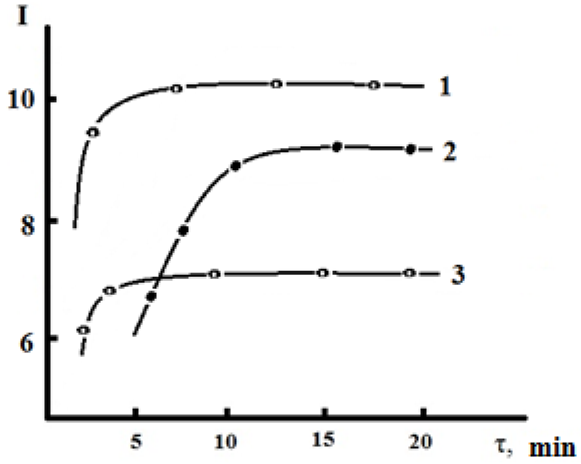
1-P_e-Al; 2-P_{cal}-Al; 3- P_e-Ga

Figure 2. Dependence of the fluorescence intensity of the complex formed by the immobilized reagent on the organic solvent concentration

The rate of transfer of the analyzed solution through the immobilized carrier depends on the reagent-detectable element contact time and its concentration. Figure 3 shows the time dependence of the luminescence intensity of immobilized organic luminophore polyoxyflavones R_m, R_{kv} and oxyazo compounds R_{cal}, R_e reagents complexes with aluminum, gallium, indium and tin ions. It can be seen that 5 minutes of indium with polyoxyflavones, 5 minutes of aluminum and gallium with eriochrome red B, 10 minutes of aluminum, gallium, tin morin, and 10 minutes of aluminum with chalcone are sufficient.



1-$P_{М}$-Al; 2- $P_{М}$-Ga; 3- $P_{КV}$-In; 4- $P_{М}$-Sn; 5- $P_{М}$-In



1- $P_{КV}$-Al; 2- $P_{М}$-Al; 3- P_{e}-Ga; C_{Me}=10 mkg

Figure 3. Time dependence of the luminescence intensity of immobilized reagent complexes

The dependence on the composition of various buffer mixtures (sodium acetate and hydrochloric acid; sodium acetate and acetic acid; acetic acid and ammonia; biphthalate and urotropin) was also studied. The maximum luminescence intensity is: sodium acetate-acetic acid for R_m, R_{cal} and R_e complexes with aluminum; for R_m and R_e with gallium; for R_{cal} complexes with indium was observed in hydrochloric acid-sodium acetate buffers.

The dependence of the fluorescence intensity of the complex compounds on the light filter was studied for the selection of the optimal field of excitation..

Table 2 Optimum conditions for complex formation of immobilized reagents with studied metals

Complex	Carrier "load", mg/g	$\lambda_{\text{instigator}}$, light filter	I_{flu}	Interval pH	% gen, organic solvent	Flow rate (ml/min)
$P_{\text{м}}$-Al	Sephadex-G-25, 1,31	430 (C3C-24-2)	540	4-6		1 (10)
$P_{\text{м}}$-Ga		425 (C3C-24-2)	555	4-6		1 (10)
$P_{\text{м}}$-In		436 (C3C-24-2)	540	4		2 (5)
$P_{\text{м}}$-Sn		430 (C3C-24-2)	500	0,5-1,5 M		2 (5)
P_{kv}-In	Sephadex-G-25, 1,36	436 (C3C-24-2)	526	4		2 (5)
P_{kv}-Al	Silasorb-diol, 20,20	436 (Hg-436)	567	4-4,4	20 DMFA	1 (10)
P_{e}-Al	Silasorb-amine, 1*10^{-3}	546 (Hg-436)	590	2,0-5,5	15 DMFA	2 (5)
P_{e}-Ga		580 (Hg-436)	651	3,0-5,0	15 DMFA	2 (5)

Thus, immobilized polyoxyflavones of aluminum, gallium, indium and tin ions - morin and quercetin; Oxyazobimers - chalcone and eriochrome red B are optimal conditions for formation of a complex with acidic environment pH from 2 to 6, DMFA organic solvent environment and contact time of 5-10 minutes.

Study of spectral-luminescence properties of immobilized reagent complexes:
Absorption and fluorescence spectra of the complexes of aluminum, gallium, indium and tin ions formed under optimal conditions with the researched immobilized polyoxyflavones R_{m}-R_{kv} and oxyazocompounds R_{k}-R_{e} reagents were obtained. The fluorescence emission of the immobilized reagent was used for comparison. Excitation spectra of complexes of polyoxyflavones and oxyazocompounds consist of broad amorphous bands in the region of 410-450 nm and 520-590 nm, respectively. Luminescence electron spectra are amorphous and 480-520 nm for R_{m}-tin, R_{m}-aluminum, gallium, indium, R_{kv} 520-570 nm for indium, R_{cal}-aluminum, 540-620 nm for R_{e}-aluminum and 620 for R_{e}-gallium complex It is equal to - 680 nm. A bathochromic shift of 40-95 nm was observed for polyoxyflavones and R_{e}-gallium complexes when immobilized, and a hypsochromic shift of 20-25 nm for oxyazobirims.

When a complex compound is formed, the absorption and luminescence spectra change compared to the immobilized reagent, that is, the radiation intensity increases sharply. It shows that the functional-analytical reconstruction of the nucleus in the luminophore molecule is observed in the formation of a complex.

Under these conditions, even when changing the amount of immobilized reagent and metal ions to be detected, only the same absorption and luminescence spectra were obtained, which confirms the formation of a complex with only the same composition.

To objectively assess the sensitivity of the studied reaction, the fluorescence quantum yield of the immobilized reagent was calculated. For the purpose of comparison, a 5% solution of fluorescein in sodium hydroxide ($C=1*10^{-5}$ M) was used. Immobilized polyoxyflavones (R_{m}-R_{kv}) and oxyazobirims (R_{cal}-R_{e}) form luminescent complexes with aluminum, gallium, indium and tin ions.

Table 3 Spectral-luminescent properties of complex combinations of immobilized reagents

Complex	**λ_{sw}, см$^{-1}$**	**Λ_{fl}, см$^{-1}$**	**Stokes shift, см$^{-1}$**	**Quantum output**
$P_{м}$-Al	23255	18528	4737	0,65
$P_{м}$-Ga	22222	18018	4204	0,56
$P_{м}$-In	22935	18518	4417	0,48
$P_{м}$-Sn	23255	20000	3255	0,46
P_{kv}-In	22935	19011	3924	0,52
P_{cal}-Al	22935	17635	5300	0,67
P_{e}-Al	18315	171118	1197	0,87
P_{e}-Ga	17271	15361	1910	0,77

Comparison of analytical properties of complexes of aluminum, gallium, indium and tin ions with polyoxyflavones and oxyazobirims in solution and immobilized state:

Optimum conditions for complex formation of immobilized morin (R_{m}), quercetin (R_{kv}), chalcone (R_{cal}) and eriochrome red B (R_{e}) with aluminum, gallium, indium and tin ions were found. The spectroanalytical properties of these complex compounds were studied and compared in solution and immobilized state. It can be seen from the data that the maximum of the excitation spectra of immobilized morin with indium and tin and quercetin with indium complexes does not change. A hypsochromic shift is observed in aluminum and gallium with morin, in aluminum with chalcone, in complexes formed by eriochrome red B with aluminum (121 nm) and with gallium (149 nm). The Stokes shift for the immobilized oxyazocompound complex is reduced, and the immobilized polyoxyflavones are virtually unchanged in solution. In particular, the Stokes shift decreases strongly in R_{e}-Aluminum (103 nm) and R_{e}-

gallium (80 nm), and slightly decreases in R_{cal}-aluminum (33 nm). The Stokes shift shift is reduced by the absorption quantum energy, luminescence spectra, and quantum yields. The structure of R_e-gallium, R_{cal}-aluminum and R_e-aluminum complexes is more rigid, which means that the quantum yield of complex compounds increases compared to that in solution. The interaction of aluminum, gallium, indium and tin with immobilized reagents shifts the pH to the cystolate medium by 1-3 units compared to that in the solution. The optimal value of pH does not change in immobilized morin and indium. In the complex of immobilized morin with aluminum and gallium, pH shifts by 1 unit to alkaline medium.

RESULTS OBTAINED

By immobilization, the fraction of the organic phase for polyoxyflavones was reduced by 40-50 times and for oxyazobirims by 4-5 times, the fluorescence time was reduced by 2-5 times. The influence of various factors on the reaction of organic fluorescent reagents with metals in their immobilized state and the formation of complexes was studied.

From the given data, it can be concluded that by immobilizing polyoxyflavones and oxyazocompounds, metrological properties of aluminum, gallium, indium and tin complexes were improved compared to those in solution.

CONCLUSION

The conditions for complex formation of aluminum, gallium, indium and tin ions with immobilized reagents were established. The results showed that the luminescent complexes of immobilized organic reagents were formed in acidic and weakly acidic environments. Complex compounds of immobilized oxyazo compounds are formed in the absence of an organic phase in the presence of 10-20% DMFA.

Spectral-luminescent properties of immobilized reagent complexes were determined. The fluorescence quantum yields of the immobilized reagent complexes were calculated. The results showed that all complexes have intense fluorescence (φ_{kv}=0.46-0.90), which means that these reagents can be used in the fluorescence analysis of these elements.

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