

Research Article

**Immobilized Oxyazo Compounds as Analytical Reagents for the Sorption-Luminescent Determination of Certain Metals**

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**Abstract**

New luminescent reagents for the determination of aluminium, beryllium, zinc and lead have been proposed. The positive effect of immobilization of the studied oxyazo compounds on their chemical-analytical properties is shown. Highly sensitive and selective methods for the sorption-luminescent determination of aluminium, beryllium, lead and zinc in environmental objects have been developed.

**Keywords:** *Immobilization, toxic metals, oxyazocompounds, sorption-luminescent determination.*

**Introduction**

Modern tasks of monitoring the environment, sources of its pollution, as well as problems of environmental analytical chemistry of low concentrations of heavy and toxic elements, determine the development and improvement of methods of physical and chemical analysis [1-4].

The Republic of Uzbekistan is a rich resource base for the extraction and processing of polymetallic, ferrous and non-ferrous ores. In this aspect, the development of highly sensitive and selective methods for the determination of several toxic elements such as aluminium, beryllium, lead and zinc is an urgent task [5].

To solve this problem, one of the promising methods of analysis is fluorescence, due to its high sensitivity and relatively inexpensive hardware design [6-10].

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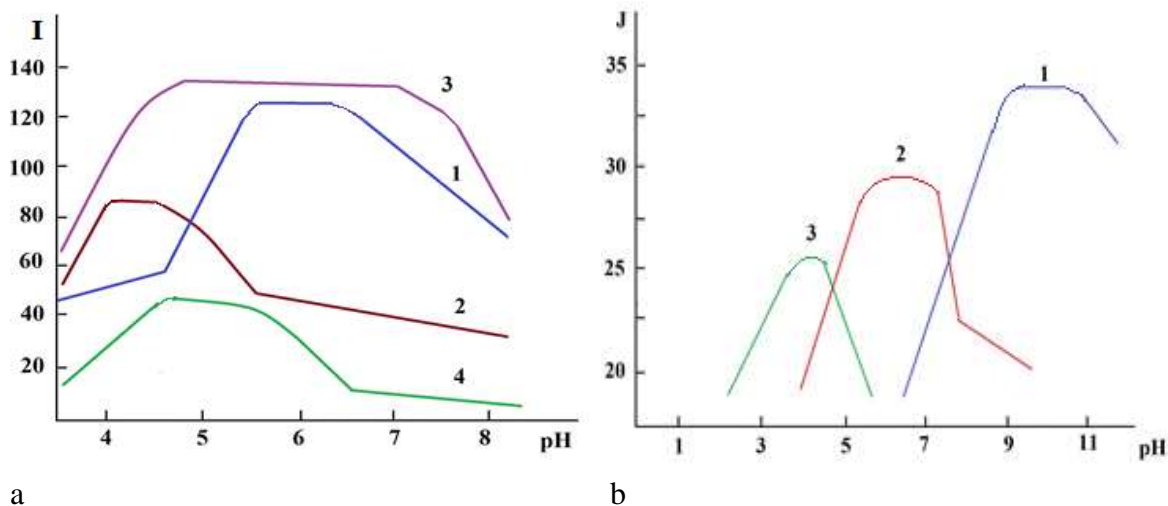
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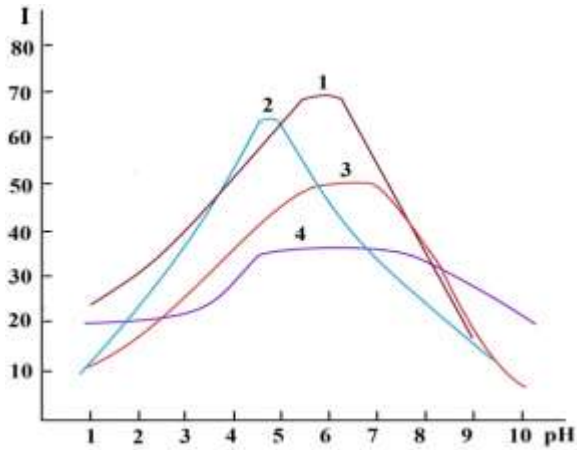
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The efficiency of the use of luminescent methods depends on the search for new fluorescent reagents that provide high selectivity and sensitivity, as well as on the search for methodological techniques that allow improving the metrological characteristics of organic luminescent reagents. In recent works, the promising application for these purposes of the method of immobilization of organic reagents on solid matrices, the specific effect of which has a positive effect on the chemical and analytical characteristics of organic reagents and their complex compounds with metal ions [11-18].

### Methodology

This work aimed to establish the effect of immobilization on the chemical and analytical properties of oxyazo compounds and to develop, on their basis, sorption-luminescent methods for the determination of aluminium, beryllium, zinc and lead in natural and wastewaters, soils and food products. The complexation of aluminium with calconcarboxylic and carminic acids, eriochrome grey SQL, eriochrome blue SE, beryllium with calconcarboxylic acid, eriochrome red B, lead with eriochrome red B and eriochrome blue-black R, zinc with eriochrome red B and eriochrome blue-black B. Complexation in each metal-reagent system was studied by plotting curves: luminescence intensity - pH, the composition of the buffer mixture, the content of organic solvent, concentration of organic reagent, order of decantation, and time (Fig. 1). To improve the chemical-analytical properties using preliminary sorption concentration, the possibility of immobilizing the reagents under study on sorbents of various types was studied [19].





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Fig. 1. Dependence of the Intensity of Fluorescence of the Complexes on the pH of the Medium:

- a) 1 - Al with calconcarboxylic acid (blue); 2 - Al with calconcarboxylic acid (red);  
3 - Al with eriochrome gray SGL; 4 - Al with carminic acid;  
b) 1 - Be- with calconcarboxylic acid; 2 - Be with eriochrome red B; 3 - Be with carminic acid;  
c) 1 - Pb with eriochrome red B; 2 - Pb with eriochrome blue-black R; 3 - Zn- with eriochrome red B; 4 - Zn with eriochrome blue-black B  
CR1C = CR1K = CR3 = CR7 =  $1 \times 10^{-3}$ ; CMe =  $5 \mu\text{g}$

The immobilization conditions were optimized by determining the maximum analytical signal with varying acidity, reagent concentration in solution, and reagent-carrier contact time.

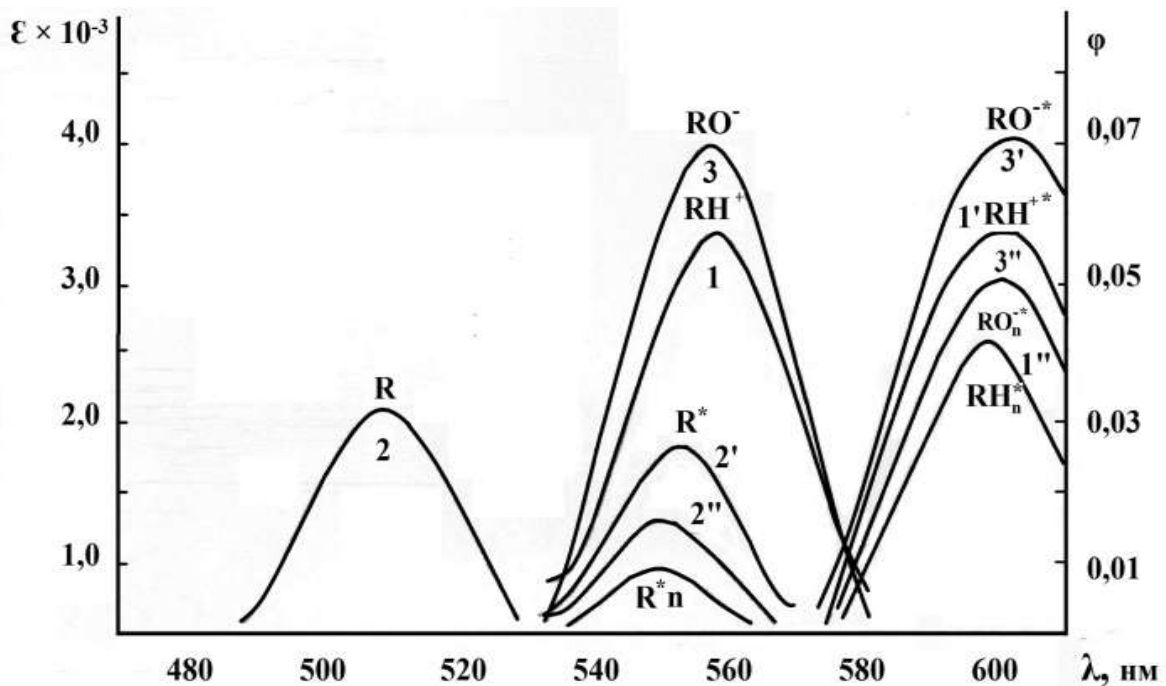


Fig. 2. Absorption (1-3) and luminescence spectra in solution (1''-3'') and in the immobilized state (1'''-3''') calconcarboxylic acid at different acidity values:

1 – pH = 0      1'' – pH = 2,0    1''' – pH = 2,0  
 2 – pH = 2,0    2'' – pH = 5,0    2''' – pH = 5,0  
 3 – pH = 3,5    3'' – pH = 5,5    3''' – pH = 4,5

To select the optimal concentration of reagents during immobilization, the "load" of the carrier was determined. The "load" of the carrier was determined by the residual concentration of the reagents over the sediment by the spectrophotometric method. The research results are shown in Table 1.

Table 1.  
*Optimal Conditions for Immobilization of the Studied Reagents  $mH = 0.4g$*

Reagent	Carrier	pH of the medium	Buffer volume, ml	"Load" of the carrier $\mu g/g$	Contact time min.
Calconcarboxylic acid	Amberlit XAD-2	1.0-3.0	3.0	19.72	10
Eriochorus red B	Molselect 72 G-15	3.5-5.0	4.00	636.00	5
Eriochrome blue-black R	Sephadex G-25	3.0-4.0	3.00	226.38	5
Eriochrome gray SGL	Molselect 72 G-25	2.5-3.5	3.00	116.0	5
Eriochrome blue-black B	Molselect 72 G-50	3.5-5.5	3.00	589.5	5
Eriochrome blue SE	Molselect 72 G-10	3.0-5.0	3.00	158.7	5

To assess the change in the donor-protolytic characteristics of the reagents in the immobilized state, the absorption and luminescence spectra were studied at different pH (Fig. 2). The results showed that the electron-donating properties of oxyazo compounds increase by 2-3 orders of magnitude in comparison with the ground state, and in the excited state by 0.81-0.83 orders of magnitude compared to the immobilized excited state (Table 2). Thus, the immobilization process makes a significant contribution to the change in protolytic properties, which significantly determines the acidity of the formation of luminescent complexes of the studied metals with immobilized reagents.

Table 2.

*Donor-acceptor Properties of Singly-ionized forms of Reagents in various States*

Reagent	Ground state	Excited-state	Excited immobilized state	Modifying properties	
				Excited Immobilized	Basic-excited-immobilized
	$pK_1 + 0,2$	$pK_1 + 0,2$	$pK_1 + 0,2$	$\Delta pK + 0,2$	$\Delta pK + 0,2$
Calcon carboxylic acid	4,00	2,10	1,31	0,79	2,69
Eriochrome blue-black R	8,7	5,7	4,6	1,1	4,1

The conditions for the complexation of immobilized reagents with the ions under study were studied (Fig. 3). The analytical parameters of the complexation of the ions under study are compared with immobilized reagents and with reagents in solution.

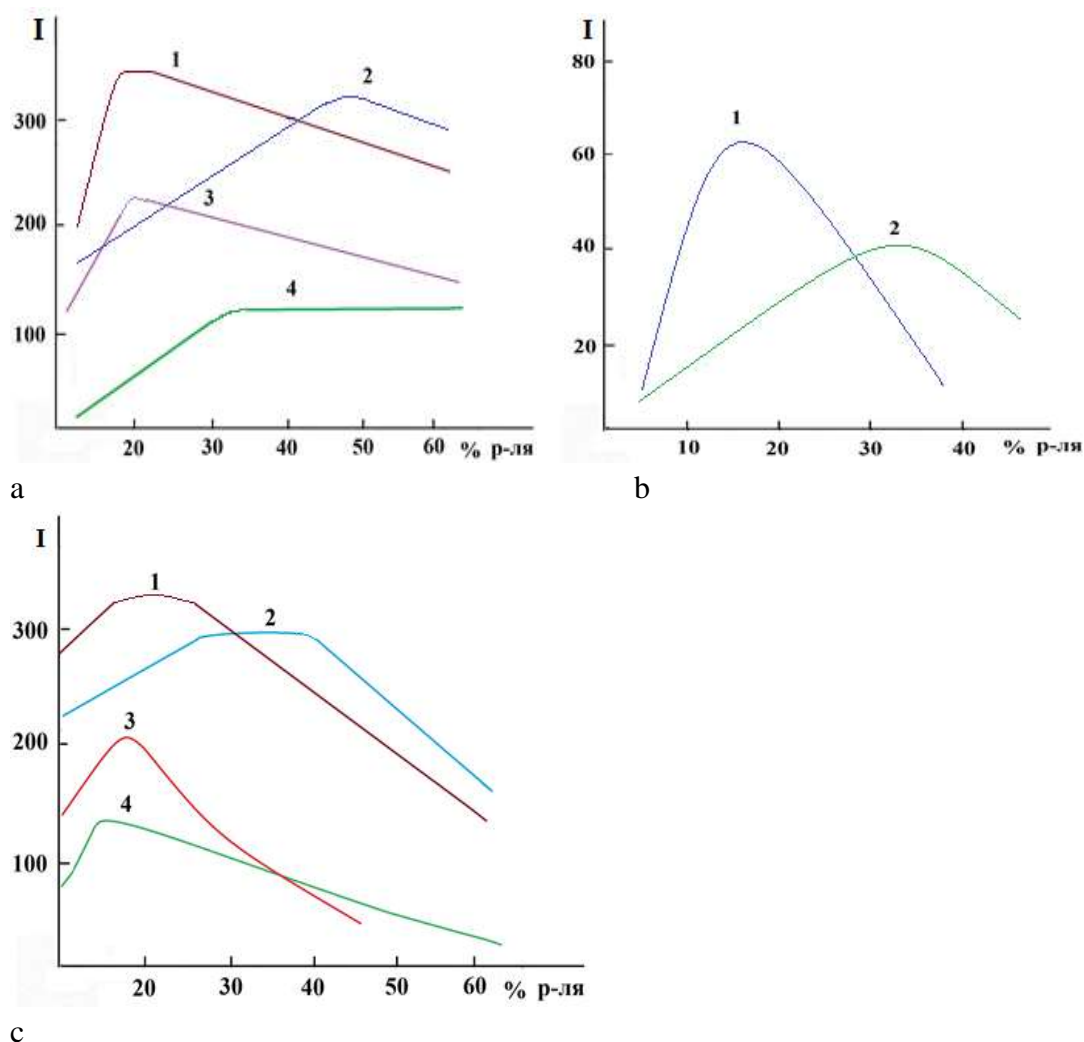


Fig. 3. Dependence of the fluorescence intensity on the amount of solvent for complexes with immobilized reagents:

- a) 1 - Al with eriochrome blue; 2 - Al with calconcarboxylic acid); 3 - Al with eriochrome gray SGL); 4 - Al with carminic acid.  
 b) 1 - Be with calconcarboxylic acid; 2 - Weight with carminic acid.  
 c) 1 - Pb with eriochrome red B; 2 - Pb with eriochrome blue-black R; 3 - Zn with eriochrome red B; 4 - Zn with eriochrome blue-black B.

Comparison of the optimal acidity values for the complexation of aluminium, beryllium, lead, zinc with the test reagents in solution and with immobilized reagents shows that the optimal pH value shifts by 1-3 units to the acidic region for all complexes with immobilized reagents as compared to complexation in solution. This explains the significant improvement in the selectivity of the determination of metals by immobilized reagents in comparison with reagents in solution. It is important to note that the fraction of the organic phase as a result of immobilization of the reagents decreased 60 times for the complex of beryllium with eriochrome red B; 2-3 times for complexes of beryllium with calconcarboxylic acid, lead with eriochrome red B and eriochrome blue-black R; for the zinc complex with eriochrome red B, the proportion of the organic phase decreased by 1.5 times, and for the zinc complex with eriochrome blue-black B, by 4 times. The fluorescence development time was reduced by 2-10 times; the expressiveness of the developed techniques has increased.

### Discussion and Conclusion

Taking into account the above data, it can be concluded that the immobilization of calconcarboxylic acid, eriochrome red B, eriochrome blue-black R, eriochrome blue-black B, eriochrome grey SGL, eriochrome blue SE led to an improvement in the metrological characteristics of complex compounds of reagents with aluminium, beryllium, and lead ions, zinc in comparison with complexes in solution. On the basis of the studied complexation reactions, express, sensitive and selective methods for the quantitative sorption-luminescent determination of aluminium, beryllium, zinc and lead by immobilized reagents in environmental objects and food products have been proposed (Table 3).

Table 3  
*Results of determination of beryllium in samples of natural and wastewaters of industrial zones by immobilized reagents.  $n = 5P = 0.95 V_{\text{tot}} = 100 \text{ cm}^3$*

Analyzed sample	Reagent metal	Found metal ( $x+\Delta x$ ), g/l according to the calibration graph	Sr	Found metal by the control method $**x$ , g/l
Mineral water				
sample No. 1	Be-R* <sub>1</sub>	$(2,33+0,11) \times 10^{-7}$	0,04	$2,15 \times 10^{-7}$
	Be-R* <sub>2</sub>	$(2,36+0,16) \times 10^{-7}$	0,06	
sample No. 2	Be-R* <sub>1</sub>	$(0,87+0,20) \times 10^{-7}$	0,12	$0,79 \times 10^{-7}$
	Be-R* <sub>2</sub>	$(0,84+0,08) \times 10^{-7}$	0,03	
Potato	Al-R* <sub>1</sub>	$(1,96+0,07) 10^{-3}$	0,03	$2,01 \times 10^{-3}$

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$(2,04+0,03) 10^{-3}$	0,01
$(2,20+0,02) 10^{-3}$	0,01

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The advantage of the proposed sorption-luminescent methods for the determination of metals is the possibility of their determination directly from the surface of immobilized reagents after sorption concentration.

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**Conflict of Interest:** The authors report no conflicts of interest. Source of funding is nil.

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