IMPROVEMENT OF THEIR PHYSICAL-CHEMICAL PROPERTIES BY IMMOBILIZING THE REAGENTS USED IN THE DETERMINATION OF ALUMINUM, LEAD, INDIUM AND GALLIUM IONS BY THE SOLID-PHASE LUMINESCENT METHOD

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Abstract. Optimal conditions for immobilization of chalcone carbonic acid, eriochrome gray SGL, eriochrome blue SE on various types of sorbents were found and the positive effect of immobilization on their analytical parameters (selectivity and sensitivity) was determined. The laws of the effect of electronic excitation on improving the chemical-analytical properties of hydroxyazo compounds in solutions and in the immobilized state have been proven..

Key words: hydroxyazo compounds, morin, chalconic acid, eriochrome gray SGL, eriochrome blue SE, immobilization, solid-phase fluorescence detection, aluminum, lead, indium, gallium, photoprotolytic properties.

Introduction. The protection of environmental objects implies constant analytical control over the state of natural objects. The priority is to control the content of toxic elements in the atmosphere, waters, soils, plants, and biological objects [1–2]. The Republic of Uzbekistan is a rich resource base for the extraction and processing of polymetallic, non-ferrous and ferrous ores. Their intensive processing, as well as the widespread use of these metals, contributes to the pollution of environmental objects, increasing the danger to the population [3-4].

All this stimulates the development and improvement of a number of highly sensitive and selective methods of physicochemical analysis for the determination of toxic elements, including aluminum. In this regard, the luminescent method of analysis is promising due to its high sensitivity and relatively inexpensive hardware design [5-7].

Recent years have been characterized by the development of solid-phase spectroscopy methods, which have a number of advantages, namely, the possibility of combining preconcentration and determination [8–11]. Work in this direction is being intensively developed all over the world and is of great theoretical and practical interest.

In this regard, the aim of our work was to improve the chemical-analytical properties of hydroxyazo compounds by immobilization for the solid-phase luminescent determination of aluminum, lead, indium, and gallium.

To achieve this goal, we studied reagents of various classes. The choice of reagents was guided by synthetic and economic availability, as well as the known advantages of certain classes of organic reagents and their use in analytical chemistry. Oxyazo compounds have shown themselves well as organic reagents. These compounds have the best metrological characteristics, high sensitivity and selectivity. The complex formation of aluminum, lead, gallium, and indium ions with hydroxyazo compounds and polyoxyflavones: calconic acid, eriochrome gray SGL, eriochrome blue SE, and morine was studied [12].

Main part. In the light of the development of solid-phase luminescence spectroscopy, the immobilization of hydroxyazo compounds and polyoxyflavones: calconic acid, eriochrome gray SGL, eriochrome blue SE on sorbents of various types was studied by luminescence, IR spectroscopy, and spectrophotometric methods. The results of studying the conditions of immobilization and the "load" of the carrier with the reagent are summarized in Table 1.

Table 1.

Optimal conditions for immobilization of the studied reagents

Reagent	**Carrier**	**pH of the medium**	**Volume of the buffer mixture, ml**	**“Load” of the carrier mg/g**	**Contact time, min**
Calconcarbon acid	Amberlit XAD-2	1,0- 3,0	3,00	191,72	10
Eriochrome red	Silasoramin	2,0-2,5	3,00	96,84	10
Eriochrome gray SGL	Molselect 72 G-25	2,5-3,5	3,0	116,0	5
Morin	Сефадекс Г-25	1,5- 3,5	3,0	113,34	5
Eriochrome blue SE	Molselect 72 G-10	3,0-5,0	3,0	158,7	5

The properties of organic analytical reagents are known to be determined by the distribution of electron density on donor atoms of functional-analytical groups. A significant redistribution of the electron density in the molecules of immobilized organic reagents, caused by photoexcitation on the one hand and the process of immobilization on the other hand, determines a significant change in the characteristics of the protolytic equilibrium and, consequently, in the reactivity during complex formation.

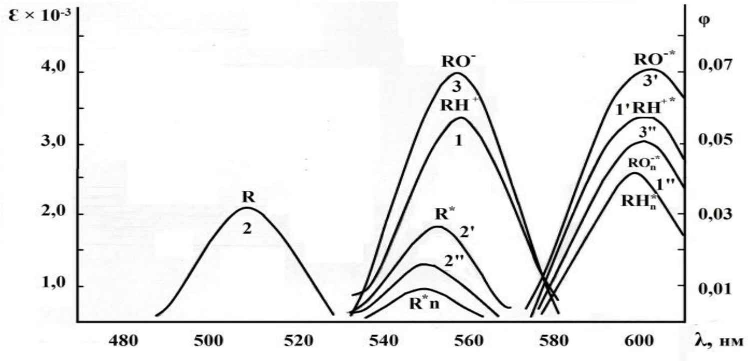

Fig.1. Absorption (1-3) and luminescence spectra in solution (1¢-3¢) and in immobilized state (1^2-3^2) of

calcocarboxylic acid

Study of the acid-base properties of the studied organic reagents in solution and in the immobilized state in the range pH from 0 to 12 showed that in the studied acidity range, the studied reagents are in the form of the following equilibrium forms: molecular, singly ionized and protonated, and with a change in acidity, the spectral characteristics in the ground state differ significantly, in the excited state the difference is insignificant, and in the excited immobilized state practically do not differ (see figure 1). The deprotonation constants of functional-analytical groups are the most important physicochemical characteristics of reagents that determine the optimal conditions and selectivity of their interaction with metal ions, the stability of the resulting complexes, and other analytical properties. The results of the studies carried out to determine the ionization constants of the studied reagents indicate that the electron-donating properties of the reagents increase by 2.69-4.1 orders of magnitude compared to the ground state, and in the excited-immobilized state by 0.74-1.5 orders of magnitude compared to excited.

This fact indicates that, in the process of immobilization of organic reagents, as well as during photoexcitation, the electron density in the phosphor molecule is redistributed, which confirms the proposal on the formation of chemical (hydrogen, etc.) bonds between the polar groups of the reagent and carrier.

Thus, the processes of immobilization and excitation of reagent molecules make a significant contribution to the change in their protolytic properties, which significantly determines the acidity of the formation of luminescent complexes of metal ions with immobilized reagents.

To judge the mechanism of immobilization of organic reagents data of quantum-chemical calculations, IR-spectroscopic and spectral-luminescent studies were used on various carriers. The data obtained indicate the formation of numerous intermolecular hydrogen bonds between the hydroxyl groups of the support and the sulfo groups of the hydroxyazo compounds.

The invariance of the spectral and luminescent characteristics of the immobilized compounds compared to the reagents in solution confirms the assumption about the formation of hydrogen bonds, especially taking into account the established changes in the protolytic properties of the reagents during their immobilization. The results of IR and luminescent spectroscopy, as well as quantum chemical calculations, made it possible to suggest a possible mechanism for the immobilization of oxyazo reagents on polydextran supports due to hydrogen bonds between the hydroxyl groups of the support and the sulfo groups of the reagent.

Thus, the results of the studies performed show that the immobilization of organic reagents can be used to improve the metrological characteristics of the reactions of complex formation of immobilized organic reagents in comparison with similar reactions in solutions.

A change in the acid-base properties of immobilized reagents in an excited state, a change in the rigidity of molecules, and spatial factors determine the peculiarity of chelation of reagents in an excited immobilized state.

The complex formation was studied by IR spectroscopic, spectral luminescence, and other methods. As a result of these studies, the main spectral-luminescent and chemical-analytical characteristics of the formation of luminescent complexes in the immobilized state were established (see Figure 2).

As a result of the analysis of the spectral and luminescent characteristics of the complex compounds of immobilized hydroxyazo compounds with aluminum ions, an increase in the intensity of the luminescence of the complexes, as well as a change in the spectral characteristics of the absorption and luminescence of the complex compounds relative to the immobilized reagents, was noted, which gives reason to conclude that the complexation is accompanied by a significant rearrangement of the functional-analytical core of the fluorophore molecule by fixing the reagent on a solid support, which leads to an increase in the rigidity of the reagent molecule and changes in the electronic structure of the reagent molecule. This is confirmed by an increase in the quantum yield of complex compounds with an immobilized reagent compared to complexes in solution. This is associated with a decrease in the detection limit of the studied metals using the proposed new analytical systems.

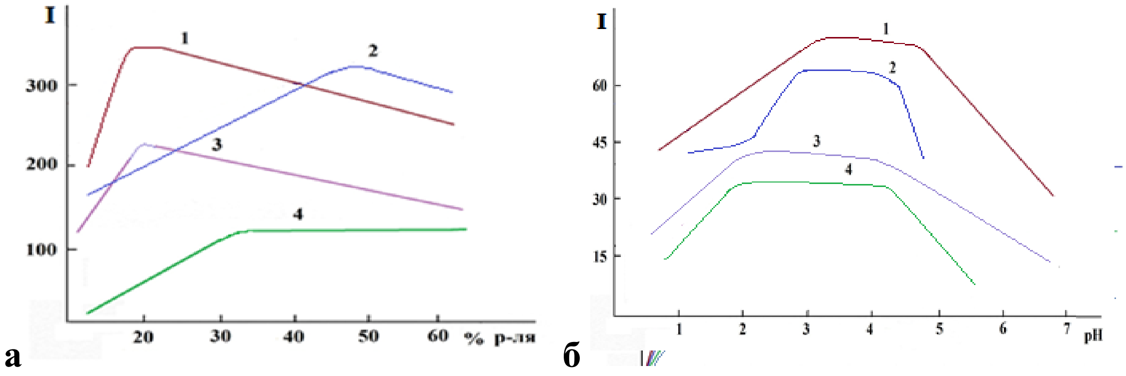

Figure. 2. Dependence of the fluorescence intensity of the complexes on various factors: b) on the pH of the medium; a) on the concentration of the reagent

1 - Al-R$_{3imm}$; 2 - Al-R$_{1imm}$; 3 - Al-R$_{4imm}$; 4 - Al-R$_{7imm}$

The study of the spectral and luminescent characteristics of complex compounds, the establishment of optimal conditions for the complex formation reactions of aluminum, lead, gallium, and indium ions with reagents in solution and in the immobilized state, makes it possible to compare the main analytical parameters for the formation of luminescent complexes in solution and with the use of immobilized organic phosphors.

Comparison of the optimal value of the acidity of the studied metals with immobilized reagents relative to solutions shows the shift of the optimal pH to the acidic region for complexes of immobilized reagents by 1-3 pH units. This is due to the enhancement of the proton-donor properties of the complexing agents under immobilization conditions. It is important to note that the proportion of the organic phase decreased by a factor of 2–4 as a result of immobilization of the reagents. The fluorescence development time decreased for all complexes by a factor of 2–10; the expressness of the developed methods has increased.

Comparison of the spectral and luminescent characteristics of complex compounds of organic reagents with ions of the studied metals in solution and in the immobilized state showed that the quantum yield increased for complexes with immobilized reagents compared to reagents in solution, which is associated with an increase in the rigidity of the structure of the molecule of organic reagents in the immobilized state.

As a result of the correlation analysis performed, correlation relationships were obtained between the acceptor properties of the ligand center of the complexes in the excited state ΔpК, lgβ and the spectral-luminescent characteristics (φ).

A series of increasing values of the luminescence quantum yield (φ) of the complexes of the studied metal ions with reagents depending on ΔpK is given: R1-Al < R4-Al < R3-Al. The given values of φ are in a satisfactory correlation (R^2=0.98) with ΔpК, which confirms their correctness.

The quantum yield increases in sympathy with the change in the acceptor properties in that series of related compounds of various classes, which is in accordance with the well-known position on the decrease in nonradiative transitions with an increase in the strength of chemical bonds. That is, the quantum yield of the luminescence of the complexes increases with increasing stability and acceptor properties of the functional-analytical groups of the complexes in the excited state.

Conclusion. The value of analytical forms in luminescent analysis is determined by the photoinduced change in the donor-acceptor properties of the complexing groups of phosphors, which is a reflection of the redistribution of the electron density in the excited state, changes in the charges on atoms that form chemical bonds with metal ions. Naturally, the greater the value of photoinduced changes, the higher the reactivity, the greater the differences in the strength of the formed metal-chelate bonds in excited complex compounds.

Considering the above data, we can conclude that the effect of excitation leads to a significant improvement in the chemical-analytical parameters of hydroxyazo compounds and polyoxyflavones in the excited state on a solid matrix. The results obtained show that the immobilization of organic reagents can be used to improve the metrological characteristics of reagents in the course of complex formation with metal ions.

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