

SENSITIVE LAYERS FOR OPTICAL SENSORY DEVICES FOR ALUMINUM

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ABSTRACT--The possibility and optimal conditions for immobilization by eriochrome blue SE, eriochrome gray SQL on polymeric carriers were studied. The positive effect of immobilization of the investigated oxyazocompounds on their chemical-analytical properties is shown. The optimum conditions for the complexation of the reagents with aluminum are established. New systems of organic carrier reagent for solid-phase luminescent determination of aluminum are proposed.

Key words--aluminum, sensitive layers, immobilization, solid phase-luminescent determination.

I. INTRODUCTION

With the increasing human impact on the environment and the intensification of agricultural production methods, the involvement of toxic elements in the biogeochemical circuit has increased. This, ultimately, leads to increased pollution of the final product - human food, which cannot but have a negative impact on human health. In this regard, there is a need to expand the circle of defined elements in environmental objects and food products. So, previously assumed minor toxicity of aluminum. However, since the late 70s of the last century, evidence has emerged that aluminum is the cause of Alzheimer's syndrome [1]. In addition, aluminum is an immunotoxic element. In this aspect, the development of rapid and sensitive methods for the determination of Al in environmental objects promising. Monitoring the state of environmental objects involves the presence of simple, selective and sensitive methods of analysis. Recently, chemical analysis methods of analysis have been widely used for these purposes [2, 3]. Chemical sensors constitute a separate group among the express methods of analytical chemistry, which provide rapid determination of substances with minimal sample preparation, accurate and reproducible measurement under various conditions of analysis [4, 5].

Organic reagents immobilized onto solid matrices are used as sensitive layers of optical sensors. The role of organic reagents is reduced to the concentration and determination of inorganic and organic molecules. Detection is usually carried out by solid-phase spectroscopic or luminescent method [6,7].

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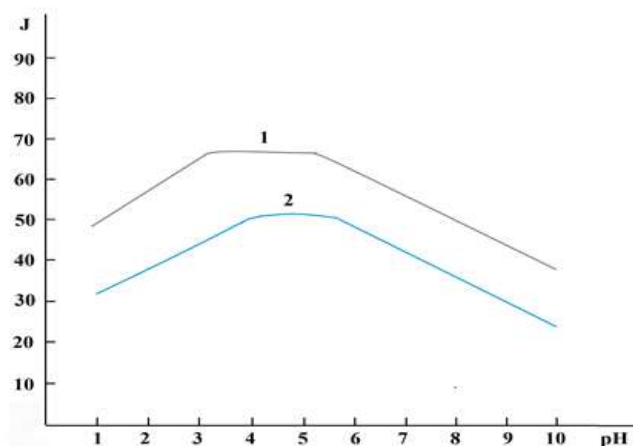


Figure 1: Dependence of the fluorescence intensity of the complex on the acidity of the medium upon immobilization: 1 - Eriochrome blue SE on Molselect 72 G-10; 2 - eriochrome gray SGL on Molselect 72 G-25;

According to the detection limit of a number of substances, luminescent analysis methods worthily compete with chromatographic and mass spectrometric methods that are most often used in the determination of organic and inorganic substances, differing from them in the simplicity of equipment operation. The advantages of luminescent analysis methods are minimal sample preparation, the test substances are not destroyed during the analysis, flow analysis is possible. These advantages significantly reduce the duration of the analysis and reduce the cost of analytical control. Luminescent analysis allows the use of screening methodology and can be used as a test method [8, 9]. Information on the working methods and competitive such devices, on the technical design and their functions, as well as on the terminology in this area, which provides an unambiguous understanding of the subject, can be found in [10-13]. The universality of luminescent analysis methods makes it possible to use them to determine not only substances with their own luminescence, but also forming luminescent products of various chemical reactions [14-16].

Among the new approaches to improving the analytical characteristics of luminescent reagents, it should be noted the immobilization of organic reagents on solid carriers, which allows combining concentration with simultaneous determination directly on the sorbent. Using immobilized reagents, effective, reliable and rapid methods for determining micro- and trace amounts of metals in various environmental objects (natural, waste and drinking water, soil, biological products, air, etc.) have been proposed [17-21]. Exact, express, sensitive, and highly selective sorption-luminescent methods have been developed that allow the determination of the studied metals in objects of various nature [22-24].

The optimal conditions for the reaction of complexation of aluminum with immobilized calconcarboxylic and carminic acids were selected, the possibility of sorption-luminescent determination of a metal ion was shown, while the dependence of the obtained data on various factors (reagent concentration, immobilization time, pH of the medium and others) was established, at the same time, Some physicochemical characteristics of the obtained complexes are calculated. The luminescence intensity does not depend on temperature changes over a wide range.

The aim of this work was to study the carrier-phosphor system to create a sensitive layer of a luminescent sensor on aluminum.

In this work, we studied the possibility of immobilizing *Eriochrome Blue SE* and *Eriochrome Gray SQL* on carriers of various nature: gels, inorganic silicas, fibrous sorbents, silica gels, etc. Studies have shown that the greatest effect is achieved when immobilizing *Eriochrome Gray SGL* on *Molselect 72 G-25*, *Eriochrome Blue SE* on *Molselect 72 G-10*. The optimal conditions for the immobilization of the studied reagents were established (table 1). The immobilization conditions were optimized by determining the maximum analytical signal with varying acidity, concentration of the reagent in solution, and contact time of the reagent-carrier.

To select the optimal concentration of reagents during immobilization, the «load» of the carrier was determined. The «load» of the support was determined by the residual concentration of reagents over the precipitate by spectrophotometric method. The research results are shown in table 1.

Table 1 : Optimal conditions for the immobilization of the studied reagents

$m_H=0,4$ gr

Reagent	Carrier	pH environment	The volume of the buffer mixture, ml	“Load” to carriers kg / gr	Contact time min.
Eriochrome gray SGL	Molselect 72 G-25	2.5-3.5	3.00	116.0	5
Eriochrome blue SE	Molselect 72 G-10	3.0-5.0	3.00	158.7	5

The conditions for the complexation of immobilized reagents with the studied ions were studied. The results are shown in table 3. The analytical parameters of the complexation of the studied ions were compared with immobilized reagents and with reagents in solution.

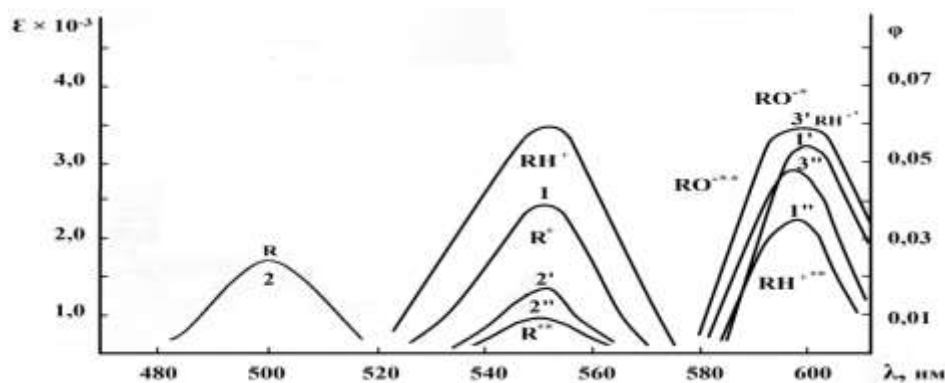


Figure 2: Absorption (1-3) and luminescence spectra in solution (1'-3 ') and in the immobilized state (1''-3'') of Eriochrome blue-black R at various acidity values

- 1 – pH = 1,0 2 – pH = 2,0 3 – pH = 8,0
 1' – pH = 2,0 2' – pH = 5,0 3' – pH = 5,5
 1'' – pH = 2,0 2'' – pH = 5,0 3'' – pH = 4,3

Comparison of the spectral and fluorescence characteristics of the complexation of metals with the studied reagents in solution and in the immobilized state showed that for complex compounds of immobilized reagents, Stokes shift decreases compared with complexes in solution. This indicates that the magnitude of the quantum of absorbed energy and the quantum of energies converted to luminescent began to differ less. Consequently, the structures of metal complexes with the studied reagents became more rigid, as evidenced by an increase in the quantum number of the yield of complex compounds with an immobilized reagent compared with complexes in solution. This is associated with a decrease in the detection limit of aluminum using the proposed new analytical systems.

Table 2: Comparison of optimal conditions for ion complexation aluminum with eriochrome gray SGL (R1) and eriochrom blue SE (R2) in solution in an immobilized state

Options	Eriochrome gray SGL		Eriochrome blue SE	
	R ₁ -Me	R ₂ -Me	R ₁ -Me	R ₂ -Me
λ fl., nm	545	525	550	515
Interval pH	5,0-7,5	2,0-4,0	5,5-7,5	3,0-5,0
about. % org solvent	30 (DMF)	15 (DMF)	30 (ethanol)	15 (ethanol)
Fluorescence development time, min	8	5	40	15
C _H , ng	10	2	4	0,1

Based on the studied complexation reactions, methods are proposed for the quantitative sorption-fluorimetric determination of aluminum in environmental objects.

The proposed new rapid technique includes pre concentration of aluminum, allows the quantitative separation of aluminum from a large sample volume with a complex background composition, and ensures reliable and correct determination. rotation of the ligands and, due to this, an increase in the fluorescence intensity of the complexes.

Thus, the studies showed a positive effect of immobilization of the studied reagents for the determination of aluminum, which consists in increasing the luminescence intensity, lowering the detection limit of metals, increasing the selectivity of reactions on solid carriers due to a shift of pH to the acidic region. The proposed systems *eriochrome blue SE - Molselect 72 G-10*, *eriochrome gray SQL - Molselect 72 G-25* can be offered as sensitive layers of sensor devices.

REFERENCES

1. I.V. Shugaley, A.V. Garabadzhiu, M.A. Ilyushin, A.M. Sudarikov. Some aspects of the influence of aluminum and its compounds on living organisms // *Ecological chemistry*. T. 21. - No. 3.– 2012.– P.172-186.
2. O.M. Petrukhin, O.O. Maksimenko. Sensors in analytical chemistry. // *Ros.chem. g. (J. Ros. Chemical. About. Va. D.I. Mendeleev)*. - 2008 .-- T. LII. - No. 2. - C.3-7.
3. Zolotov Yu.A., Ivanov V.M., Amelin V.G. Chemical test methods of analysis. M.: URSS editorial, 2002.
4. Cattrall R.V. Chemical sensors. M. : Scientific world. -2000. - from. 144.
5. Smanova Z.A. Monitoring of natural waters using immobilized reagents for the determination of heavy and toxic metals Reports of the Academy of Sciences of the Republic of Uzbekistan. 2011. No. 5, S.58-60.
6. AgnieszkaZuber, Malcolm Purdey, Erik Schartner, Caroline Forbes Benjaminvan der Hoek and etc.
7. Detection of gold nanoparticles with different sizes using absorption and fluorescence based method //
8. *Sensors and Actuators B: Chemical*. – May 2016. – Vol. 227. – P.117-127.
9. Gavrilenko N. A., Saranchina N. V., Gavrilenko M. A. Solid-phase spectrophotometric determination of selenium (IV) using dithizone immobilized in a polymethacrylate matrix // *Analytics and Control*. - 2014 .-- T.18. - No. 4. - C.424-429.
10. Romanovskaya G. I. Development of luminescent analysis methods in Russia over twenty years // *Zh. analit. chemistry*. 2011, Volume 66, No. 11, p. 1157-1163 No. 3, p. 72-76.
11. Ostrovskaya V.M., Zaporozhets O.P. Indicator systems. Moscow: FSUE VTIII 2002.266 p.
12. Otto M. Modern methods of analytical chemistry (in 2 volumes). M. : Technosphere, 2004, 416 p. (v. 1), 288 s. (v. 2).
13. Markhol M. Ion exchangers in analytical chemistry. M.: Mir, 1985, v. 2, 280 p.
14. Myasoedova G.V., Shvoeva O.P., Savvin S.B. Chelating sorbents. The science. Moscow 1984.239 p.
15. Zeltser L.E., Arkhipova A.A., Bychenko A.V. Immobilized 8-hydroxyquinoline as a sensitive sensor layer on aluminum // *Zh. analyte. Chemistry*. - 1995.-T.50.-No. 7.- S. 725-728.
16. Golovina A.P., Levshin L.V. Chemical luminescent analysis of inorganic substances. - M.: Chemistry, 1978.- 245 p.

17. Smanova ZA Immobilization as a way to improve the analytical characteristics of organic reagents Uzb. chemical journal 2009. No4. S.72-76.
18. Zeltser L.E., Vereshchagina N.V., Arkhipova A.A. Improvement of chemical-analytical parameters of some oxyazo compounds as reagents on aluminum during immobilization on some carriers // Dokl. An RUz. -1994.- No. 7.-S. 26-28.
19. Yagov V.V., Zuev B.K., Kovarsky I.I., Kovalenko V.V. Sensor, 2001, No. 2, p. 46-50.
20. Swan N.B., Planck A.B. Rapid test for the detection and semi-quantitative determination of the amount of heavy metals in waters // J. Analytical Chemistry. - 1997. - T.52. - No. 6.- P.643-646.
21. Zaporozhets O.A., Haver O.M., Sukhan V.V. Immobilization of analytical reagents on the surface of carriers // Advances in Chemistry. - 1997. - T.66.- No. 7.
22. 20. Smanova Z.A., Gevorgyan A.M., Mamazhanova G.A. Sorption-photometric determination of aluminum on the surface of a polymer carrier // Uzbek Chemical Journal.-Tashkent, 2010. No. 2.-S.38-41.
23. Reshetov V. Around the World, 2007, No. 4, p. 84-92. M.: Nauka, 1984, 171 p.
24. Brykina G.D., Smirnova I.P. "Optics and spectroscopy." Determination of trace amounts of aluminum in wastewater by solid-phase spectrophotometry. 1991, Vol. 70, issue 4, - 270 s.
25. Carrol M.K., BringtF.V., HiftyeG.M. Fiber-optic fluorescent sensor with a time resolution for simultaneous determination and / or // - 1989. - 61, - 15. P. 1768-1772.
26. Smanova Z.A., Gafurova D.A., Savchikov A.V. 1- (2-pyridyl-azo) -2-oxynaphthalene-3,6-disulfonic sodium immobilized reagent for the determination of iron LC. St. Petersburg, 2011.-No 4.-S.648-651.
27. Smanova ZA Development of sorption-spectroscopic analysis methods using immobilized organic reagents Vestnik NUUz, 2010. No. 3, S.156-161.