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# DESIGN AND APPLICATION OF NITROSONAPHTHOL-BASED SELECTIVE REAGENTS FOR THE DETERMINATION OF METAL IONS

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*Immobilization, nitrosonaphthol derivatives, heavy and toxic metals*

**ANNOTATSIYA:**

*New organic reagents based on nitrosonaphthols were synthesized and proposed as analytical reagents for cobalt(II) ions. The immobilization of the reagents was conducted, their kinetics studied, and optimal conditions for both immobilization and cobalt ion complexation were determined*

In the mid-20th century, problems related to chemical pollution of the biosphere sharply intensified, often leading to acute toxic-ecological situations. Pollution of the biosphere by heavy metals has become particularly significant. The set of heavy metals largely coincides with the list of "trace elements" essential for plant and animal organisms. Nevertheless, exceeding certain concentration thresholds transforms them into potent poisons. One such heavy metal is cobalt.

One of the existing methods meeting these requirements is spectrophotometry using immobilized organic reagents (OR). Their application allows for lowering the lower detection limits of elements and improving the metrological characteristics of the developed techniques.

Currently, methods utilizing immobilized organic reagents on various types of carriers for the determination of heavy and toxic metals are intensively developing. The rapid development of sorption-spectroscopic analysis is driven by the simplicity of instrumental setup, rapidity, and the possibility of using immobilized organic reagents in field conditions outside the laboratory [1].

Many spectrophotometric methods for cobalt determination using various reagents have been proposed [2-5], but each method has its limitations regarding metrological and analytical characteristics, such as low selectivity, low sensitivity, lengthy sample preparation, etc.

For many years, Ilinsky's reagent (α-nitroso-β-naphthol) has been used for the qualitative determination of iron, chromium, nickel, and cobalt [6].

The aim of this work is to develop sorption-spectroscopic methods for cobalt determination by immobilizing newly synthesized organic reagents based on nitrosonaphthol derivatives on fibrous carriers, and to improve the metrological characteristics of these cobalt determination methods in the analysis of environmental objects and industrial materials.

Analysis of literature data [7-10] shows that the new scientific direction associated with the use of reagents immobilized on the surface of various carriers in chemical analysis is highly promising. Such reagents increase the sensitivity and selectivity of determining many elements.

Lowering the detection limit is achieved by concentrating the target analytes from a relatively large solution volume into the sorbent phase. Unlike extraction concentration, sorption methods do not require the use of organic solvents and are therefore safer for health [11]. The sorbents themselves are non-toxic and are easily separated from the solution by filtration, making the analysis more rapid.

## Experimental Section

Solutions, Reagents, Sorbents. Standard metal solutions were prepared by dissolving high-purity metals in diluted (1:1) acids, followed by dilution with distilled water. A series of buffer solutions were prepared from 1M HAc, HCl, NaOH, $NH_4OH$, NaAc [12].

Immobilization Procedure. Immobilization was performed by stirring 50-100 mg of sorbent with 5-10 ml of a reagent solution at a concentration of $1 \cdot 10^{-4}$ M for 1-10 minutes, followed by washing the carriers with distilled water. The immobilized carrier was stored in Petri dishes in a moist state. The influence of pH, metal concentration, buffer composition, and reagent content in the solid phase was studied at a flow rate of 5 ml/min.

Methodology for Conducting Immobilization. Carriers were used in the form of disks with a diameter of 2 cm and a mass of 20-50 mg. The obtained carriers were washed with

50 ml of 0.1 M HCl, then with 10 ml of acetone, after which they were immersed for 4-10 minutes in beakers containing 10 ml of organic reagent solution with a concentration of $1.0 \cdot 10^{-5} – 1.0 \cdot 10^{-2}$ M, washed with 50 ml of distilled water, and stored in a moist state in Petri dishes. The influence of pH, metal concentration, buffer mixture, and reagent content in the solid phase was studied at a solution flow rate of 10 ml/min. The reagent concentration on the carrier was determined spectrophotometrically by the change in absorption of the solutions at the optimal wavelength for each reagent before and after immobilization.

Trosonaphthol interacts with many metals to form complexes, making this reagent one of the less selective ones. However, to increase selectivity, new reagents based on nitrosonaphthol were synthesized: 2-hydroxy-3-nitroso-1-naphthaldehyde, 4-bromo-2-nitroso-1-naphthol, 4-hydroxy-3-nitronaphthalene-1-sulfonic acid, by introducing bromine atoms, sulfonic groups, and others into the reagent molecule [13-15]. For example, when transitioning from nitrosonaphthol to halogen-substituted derivatives (e.g., 4-bromo-2-nitroso-1-naphthol), the new reagents become more specific, their selectivity improves, as they gain the ability to interact in more acidic media and with a smaller number of ions.

Thus, introducing a sulfonic group into the nitrosonaphthol molecule increases the reagent's solubility in water. For instance, the reagent 4-hydroxy-3-nitronaphthalene-1-sulfonic acid [13] was synthesized, which forms an intense blue soluble complex with cobalt(II) ions. Some cations with this reagent form insoluble compounds due to salt formation occurring at the sulfonic group.

The increase in selectivity upon modifying the reagent is associated with changes in steric factors in the nitrosonaphthol molecule. At pH 4-5, nitrosonaphthol reacts with many elements, including cobalt, nickel, iron, copper, and zinc ions, whereas the 2-hydroxy-3-nitroso-1-naphthaldehyde synthesized by us does not interact with copper and zinc. At the same time, the new reagent 2-nitroso-4-isoamylnaphthol-1 does interact with both copper and zinc. The isoamyl group creates spatial hindrances for accommodating an ion with a larger radius in the chelate ring. However, copper and zinc, which exhibit stronger affinity for nitrogen, react with 2-nitroso-4-isoamylnaphthol-1 [14]. The assumption that spatial hindrances play a role here, not merely the introduction of an isoamyl group, is confirmed by studying the properties of 2-nitroso-4-isoamylnaphthol-1. This reagent interacts with metals similarly to unsubstituted nitrosonaphthol, as the isoamyl group in this case is located quite far from the heterocyclic nitrogen.

The improvement in selectivity is due to the fact that upon immobilization, organic reagents, thanks to the geometric features of ligand fixation on the carrier surface, can change their complex-forming properties, such as denticity. It can be assumed that modified sorbents most effectively extract metal ions that form ionic associates or complexes with an immobilized reagent having a metal:ligand ratio of 1:1. In this case, steric difficulties caused by ligand fixation on the sorbent surface are minimized.

Complexes of metals with immobilized 2-hydroxy-3-nitroso-1-naphthaldehyde and 2-nitroso-4-isoamylnaphthol-1, unlike their reactions in solution, are also more stable.

**Selection of the Optimal pH Value for Cobalt(II) Ion Sorption**. Since the ligands are weak anions, the complexing ability of nitrosonaphthol strongly depends on the pH of the medium. This is very important for the selective precipitation of nitrosonaphthol complexes of cobalt because the lower the stability constant of the complex, the higher the pH of the solution must be for its satisfactory precipitation. Furthermore, selectivity achieved by pH regulation can be further increased by using suitable masking reagents.

The results of the influence of solution pH on the degree of cobalt sorption on the anion exchanger SMA-1, immobilized with 2-hydroxy-3-nitroso-1-naphthaldehyde (HNNA) and 2-nitroso-4-isoamylnaphthol-1 (NIAN), are shown in Fig.1.

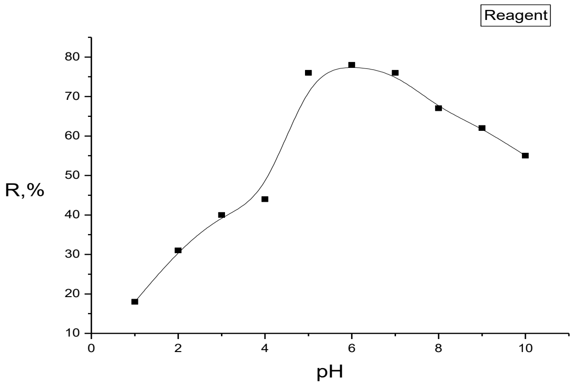

**Fig.1.** Dependence of the analytical signal on the pH of the medium for HNNA.

At low pH values (in an acidic medium), cobalt(II) ions are in a hydrated form. This ensures a high sorption rate but a low degree of extraction on unmodified carriers. On modified carriers, the cobalt(II) sorption process proceeds as follows. As the pH value increases, cobalt(II) hydroxide forms in the solution. In this case, the sorption rate increases. Apparently, under these conditions, nucleation, for example of cobalt(II) hydroxide, is facilitated, leading to the formation of a more finely dispersed system. The globular sorption mechanism becomes more efficient, which is proven by the maximum degree of cobalt ion extraction in a more alkaline medium on unmodified carriers.

The sorbent obtained by immobilizing 2-nitroso-4-isoamylnaphthol-1 on the anion exchanger SMA-1 acquires a green color after contact with a cobalt solution. The filtrate is transparent. However, starting from pH 8.5, the filtrate color becomes pale yellow. At the same time, the color intensity of the sorbent significantly decreases.

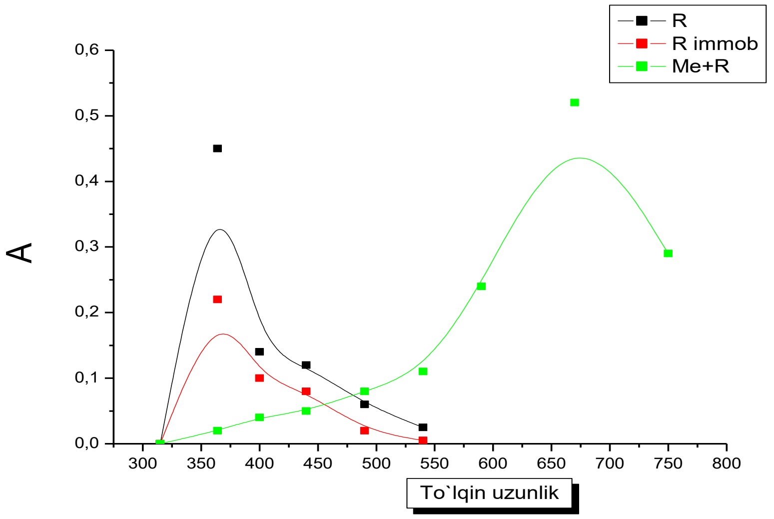

**Fig.2.** Absorption spectra of the reagent HNNA, the immobilized reagent, and its complex with the cobalt ion.

**Dynamics of Cobalt Ion Sorption on Anion Exchanger SMA-1 Immobilized with 2-Nitroso-4-isoamylnaphthol-1 and 2-Hydroxy-3-nitroso-1-naphthaldehyde**

The sorption rate of cobalt ions was studied using the limited solution volume method. For this, 10 ml of a model solution with a specific concentration was added to a series of test tubes containing 0.1 g sorbent aliquots and kept from 2 minutes to 1 hour with constant stirring. At specific time intervals, the liquid phases were analyzed photometrically as described earlier. Sorption kinetics were studied at the selected optimal pH value. The pH in the solutions was adjusted using 0.1 N hydrochloric acid, acetic acid, and a dilute ammonia solution.

Table 1.

| Time, min. | 2 | 4 | 6 | 8 | 10 | 15 | 25 | 30 | 45 | 60 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ΔA(НИАН) | 0,12 | 0,18 | 0,20 | 0,22 | 0,225 | 0,225 | 0,22 | 0,225 | 0.22 | 0,22 | 0,22 |
| ΔA(ГННА) | 0,18 | 0,21 | 0,30 | 0,32 | 0,32 | 0,32 | 0,32 | 0,32 | - | 0,32 | - |

The experimental results (Table 1) showed that to achieve maximum cobalt extraction at the optimal pH, 10-15 minutes are required, regardless of the initial concentration of cobalt ions in the liquid phase. With longer contact time, the extraction degree remains constant, indicating the establishment of sorption equilibrium.

River, sea, mineral waters, brines, and wastewater are multicomponent systems where the macrocomponents are potassium and sodium ions, and the anionic composition of macrocomponents consists of chlorides, sulfates, and to a lesser extent, nitrates. Therefore, it is important to know the influence of the matrix of the analyzed object on the sorption pattern of microgram quantities of cobalt.

We studied the influence of sodium chloride, sodium nitrate, and sodium sulfate. The methodology for determining cobalt distribution was the same as in all previous experiments. The research results showed that sodium chloride and sodium nitrate practically do not affect cobalt sorption up to a concentration of 7.5 mg/ml. For sodium sulfate, a decrease in the degree of cobalt sorption is observed already at concentrations of 4.5 mg/ml. Such behavior can be explained by the possibility of cobalt ion forming anionic sulfate complexes in a sulfate medium.

Thus, lowering the detection limit is achieved by sorption concentration of the target metal from a relatively large solution volume into the sorbent phase. Unlike extraction concentration, sorption methods do not require the use of organic solvents and are therefore safer for health. The sorbents themselves are non-toxic and are easily separated from the solution by filtration, making the analysis more rapid.

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