



Determination of Ni (II) Ions in Natural Objects and Industrial Alloys via a Spectrophotometric method with 4,5-dihydroxy-3,6-dinitrosonaphthalene-2,7-disulfoxic acid

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ARTICLE INFO

Article history:

Received 08 August 2024

Received in revised form 16 October 2024

Accepted 17 October 2024

Available online 28 October 2024

Keywords:

Chromogenic reagents,
 Heavy and toxic metals,
 Equilibrium shift method,
 Isomolar series method,
 Asmus' correct linear method,
 Calibration graph.

ABSTRACT

The development of a simple, fast, sensitive, and accurate spectrophotometric method for determining nickel (II) ions is one of the most urgent issues today. In this study, a spectrophotometric method for complexing nickel (II) ions with 4,5-dihydroxy-3,6-dinitrosonaphthalene-2,7-disulfoxic acid (HR) as an organic analytical reagent was developed. The optimal conditions were determined as follows: $\lambda_{\max} = 575$ nm, pH = 9.15, universal buffer, HR concentration = 0.05% relative to $T_{\text{Ni}^{2+}} = 50.0$ $\mu\text{g}/25$ ml and HR volume = 1.2 ml. The area of adherence to the Bouguer–Lambert–Beer law was found to be 5.0–55.0 $\mu\text{g}/25$ ml. Absorption spectra were studied, showing Sandell's sensitivity (S) as 0.009174 $\mu\text{g}/\text{cm}^2$, and the contrast $\Delta\lambda = 65$ nm (HR = 510 nm). The composition of the complex and the mechanism of its formation were examined using the equilibrium shift method, the isomolar series method, and Asmus' straight-line method. The molar ratio of the complex was determined to be $\text{Ni}^{2+} : \text{HR} = 1:2$. The molar absorptivity coefficient ($\epsilon_{\text{real}} = 23585$), the formation equilibrium constant ($K_{\text{eq}} = 1.6200 \cdot 10^{-8}$) for the complex formed by nickel (II) with HR, the stability constant ($\beta = 1.30 \cdot 10^{23}$, $\lg\beta = 23.11$) using Babko's dilution method, the confidence interval of the deviation from the mean value ($\Delta X = 0.2270$), and the lower limit of detection ($Q_{\min} = 0.6004$ $\mu\text{g}/25$ ml) were determined. The results from the graduated graph were processed using the method of least squares, leading to a linear mathematical equation: $Y_i = 0.0014 + 0.0041X_i$. The effects of side ions on the determination of nickel ions were studied. The suggested spectrophotometric method was applied to the analysis of model mixtures, industrial alloys based on aluminum, natural waters (Omonkhon spring water) and polymetallic ore from the Khandiza mine with the results metrologically evaluated. The relative standard deviation (S_r) did not exceed 0.0461.

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<https://doi.org/10.22034/crl.2024.472110.1397>



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1. Introduction

The progression of the science, medicine, agriculture, manufacturing and chemical industries and the integration of novel technological processes has heightened concerns about environmental pollution [1]. The potential consequences of these activities include air and water contamination, soil degradation, and disruptions to ecosystems. To prevent ecological catastrophes stemming from these issues, there is an urgent need to establish comprehensive environmental monitoring systems. These systems play pivotal roles in the systematic collection, analysis, and interpretation of data related to air and natural water quality, soil health, biodiversity, and other environmental parameters.

Currently, advancements in science and technology emphasize the need to develop and enhance analytical methods with improved metrological characteristics. These methods should be applicable across a wide range of metal concentrations in natural, industrial, and biological materials. With the significant increase in substances emitted into the environment, maintaining and monitoring the purity of the atmosphere, soil, and water has become a critical issue.

Spectrophotometric determination of transition metals via chromomeric reagents has long been a time-tested and basic analytical method [2]. The beauty of this technique lies in its sensitivity, selectivity and high economy. The branch of analytical chemistry has evolved leaps and bounds for better methods, yet spectrophotometric methods have not lost their place, as these methods offer simplicity with accuracy and are relevant even today. Organic reagents, on the other hand, are still the basis for determining chemical reactions, and they are currently the most widely used quantitative analysis methods in chemical, pharmaceutical, industrial, forensic, environmental and clinical research worldwide. Absolute leaders in the number of methods used to analyze substances in environmental objects (35–50%) at present. The sensitivity of the method is 10^{-7} M (10^{-2} $\mu\text{g/ml}$ or mg/l).

Nickel is present in various organs and tissues in amounts of several micrograms per 100 grams of tissue. According to medical and sanitary data, the liver contains the highest concentration of nickel in the human body, as do some parts of the brain. The primary source of nickel entering the body is food. Additionally, nickel is widely used in industry, technology, mechanical engineering, science, and medicine [3].

Nickel resists corrosion and is commonly used to plate other metals for protection. However, it is primarily used in making alloys, such as stainless steel. Nichrome, an alloy of nickel and chromium with small amounts of

silicon, manganese, and iron, resists corrosion even when red heats and is thus used in toasters and electric ovens. A copper–nickel alloy, which converts seawater into fresh water, is frequently used in desalination plants. Other nickel alloys are utilized in boat propeller shafts and turbine blades. Nickel is also used in batteries, including rechargeable nickel–cadmium batteries and nickel–metal hydride batteries found in hybrid vehicles. Finely divided nickel serves as a catalyst for hydrogenating vegetable oils [4].

Biological role of nickel: Nickel can influence plant growth and is essential for certain species. However, some nickel compounds can cause cancer if inhaled as dust, and some individuals may be allergic to direct contact with the metal. **Natural Abundance:** Most nickel is extracted from iron–nickel sulfide minerals, such as pentlandite. Nickel is also found in other minerals, including garnierite [4].

The maximum permissible concentration (MPC) of nickel in industrial premises is 0.003 mg/m^3 . For metallic nickel, the MPC was 0.05 mg/m^3 , which was measured as a pure substance. Nickel can enter the human body through the respiratory system, skin, and digestive tract. Excessive nickel in the body can cause vitiligo and poisoning symptoms. In unpolluted and slightly polluted river water, nickel concentrations typically range from 0.80 to $10.0 \text{ }\mu\text{g/dm}^3$. In more polluted waters, concentrations can reach several tens of micrograms per dm^3 . The average concentration of nickel in seawater is $2.0 \text{ }\mu\text{g/dm}^3$, and in groundwater, it is approximately $0.103 \text{ }\mu\text{g/dm}^3$. However, when groundwater washes nickel-containing rocks, concentrations can sometimes increase to 20.0 mg/dm^3 . The nickel content in water bodies is regulated: the MPC for general sanitary purposes is 0.10 mg/dm^3 , whereas for toxicological purposes, it is 0.01 mg/dm^3 [5-7].

Nickel ions are nutritionally essential trace metals for at least several animal species [8], microorganisms and plants; therefore, either deficiency or toxicity symptoms can occur when too few or too many Ni ions are taken up, respectively. Although a number of cellular effects of nickel ions have been documented, a deficiency state in humans has not been described. Nickel ions are very important both industrially and biologically. Nickel ions are among the essential trace elements, along with cobalt, copper, zinc and manganese ions, in the human diet. Heavy metals such as nickel (II) ions have long been regarded as highly hazardous forms of pollution that are poisonous to humans even at low doses. Pb, Cu, Cr, Cd, Hg, Zn, Ni, As, and other heavy metals can be refractory and accumulate in organisms. The concentrations of heavy metals such as nickel (II)

ions in aquatic systems, as well as their accumulation through the food chain, may pose health risks and cause environmental problems [9]. After optimizing the preparation conditions, including the reaction solution pH, the optimal reagent concentration, and the reaction duration, the nickel (II) ions in the aqueous solution were determined via a spectrophotometric method using the reagent 1-(4-(((4,5-dimethyl-1H-imidazol-2-yl)diazanyl)methyl)phenyl)-N-(4-nitrobenzyl)ethan-1-imine [10]. The spectrophotometric detection method for complexing nickel (II) ions with 7-bromo-2-nitroso-1-oxynaphthalene-3,6-disulfoacid with organic analytical reagents involves the following optimal conditions: λ_{\max} =6.40, pH=6.5, universal buffer and a Bouguer–Lambert–Behr law area of 1.0–17.5 $\mu\text{g}/25\text{ ml}$ [11]. The optimal conditions for the spectrophotometric determination of nickel (II) ions via D-penicillamine have been investigated [12]. This study outlines simultaneous spectrophotometric techniques for quantifying Ni^{2+} ions via 1-(2-pyridylazo)-2-naphthol (PAN) in micellar media. The ligand and its metal complexes, namely, Ni^{2+} -PAN, were rendered water soluble with the neutral surfactant Triton X-100, eliminating the need for organic solvent extraction [13]. The spectrophotometric technique was employed to investigate the interaction between nickel (II) and copper (II) ions with three different ligands: ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate, 4-(1H-benzimidazol-2-yl)phenol, and 2-(3-phenylamino-4,5-dihydro-1,2-oxazol-5-yl)phenol [14]. The compound 2-(2-thiazolylazo)-p-cresol (TAC) reacts with nickel (II) ions within the pH range of 6.0–10.0, resulting in the formation of a blue complex at a ratio of 1:2. The stability constant of this complex was determined to be 5.0 ± 0.3 [15]. A method was developed for the extraction and concentration of nickel ions in the form of a dimethylglyoxime complex by using triethylamine. The nickel-enriched triethylamine extract was then separated and evaporated. The resulting residue was dissolved in chloroform (50 μL), and the absorbance at 380 nm was measured. A spectrophotometric procedure for the determination of nickel was established, with a limit of detection of 0.020 $\mu\text{g}/\text{mL}$ ($n = 10$; $P = 0.95$) [16].

Some spectrophotometric determinations of the investigated nickel ions include pyridoxal-3-thiosemicarbazone [17], 1-(2-pyridylazo)-2-hydroxy-4-mercaptophenol and aminophenols [18], 2-hydroxythiophenol [19], 2-hydroxy-5-iodothiophenol and biphenyldiamidine [20], 2-hydroxy-1-naphthaldehyde thiosemicarbazone [21], 2-aminoacetophenone isonicotinoylhydrazone [22],

esomeprazole [23], 1-[(5-benzyl-1,3-thiazol-2-yl)diazanyl]-naphthalene-2-ol [24], 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone [25] and 5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione [26]. Some preconcentration and separation approaches have been utilized for the determination [27] of nickel (II) ions. A literature survey indicated that several spectrophotometric methods [28–29] have been used for the determination of nickel (II) ions by using various chromogenic reagents. Many reagents have been used in spectrophotometric methods for the determination of heavy and toxic metal ions such as nickel (II) ions, but most of them have various disadvantages, such as selectivity and detection limits, long-term color changes, and the overheating or interference of many ions [30–32].

On the basis of the literature sources analyzed above, the current study aims to develop rapid, simple, selective, highly sensitive spectrophotometric methods for quantifying low levels of nickel (II) ions in various samples, such as individual solutions, ore samples, alloys, natural water and real objects. The principle of this method is based on allowing nickel (II) ions to react with the reagent 4,5-dihydroxy-3,6-dinitro-naphthalene-2,7-disulfoic acid (HR) as a newly prepared reagent at a selected pH. We have also encouraged this research to produce microscopic amounts of nickel (II) ions in real samples.

2. Experimental part

Methodology. Spectrophotometric, colorimetric, potentiometric, Asmus straight line and equilibrium shift methods, the isomolar series method, the Tolmachev and Babko methods, the least squares method and the additive method were used in this investigation.

Devices. Spectrophotometric studies of the colored solutions were carried out on a KFK-3 concentration photocolimeter in glass cuvettes with a layer thickness of 1.0 cm. The pH of the solutions was monitored with a pH meter (pH Mettler-Toledo AG 8603; Made in China, №-B507604800).

Solutions and reagents. Standard solutions of nickel (II) ion salts with a titer of $T_{\text{Ni}^{2+}} = 1000\text{ mg/ml}$ were prepared using accurately weighed portions of analytical grade metallic mineral salts. “Clean” and “Chemically clean” brand reagents were used in the experiment. An accurately weighed portion of nickel (II) ion salt was placed in a 1000 mL volumetric flask and dissolved in distilled water. Small-concentration solutions were prepared by serial dilution of the prepared standard solution [33]. HR solutions are prepared by dissolving 0.0500 g of reagent with distilled water in a 100 mL

volumetric flask. For preparation of a 0.05% solution of HR, 0.1000 g of its exact weight was dissolved in a 200 ml volumetric flask, added to the mark with distilled water and stirred [33].

Buffer solutions. A universal buffer solution [34] was prepared by mixing H_3BO_3 , CH_3COOH and H_3PO_4 (0.04 M each) and adding 0.2 M NaOH to obtain the corresponding pH. The Na tetraborate buffer solution was prepared by mixing 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and adding 0.1 N HCl to obtain a pH of 9.15, the glycine buffer solution was prepared by mixing 0.1 M NaOH and adding 0.1 M $\text{NH}_2\text{CH}_2\text{COOH}$ to obtain a pH of 9.18, and the phosphate-borate buffer solution was prepared by mixing 0.1 M KH_2PO_4 and adding 0.05 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to obtain a pH of 9.20. All reagents were of analytical grade and chemical grade. Distilled water was used in this study.

3. Results and Discussion

HR was identified via spectrophotometry. HR was identified on the basis of its electronic spectrum. Spectrophotometric studies (400 to 770 nm) revealed that the HR used in this work as an organic reagent is characterized by one light absorption maximum located in the region of 440–540 nm. To determine the state of the reagent in solution, its absorption spectra were studied depending on the pH of the medium. The results obtained are presented in Fig. 1. The data obtained show that HR in the pH range of 1.68–2.80 has a light absorption maximum at 440–470 nm, in the pH range of

3.0–4.80 at 450–470 nm, in the pH range of 5.0–6.75 at 450–480 nm, in the pH range of 6.80–7.00 at 480–540 nm and in the pH range of 7.25–13.05 at 510–540 nm. As shown in Fig. 1, the light absorption spectra of HR depending on pH are symmetrical curves, with a maximum at 440–540 nm [35, 36].

Determination of the optimal pH. One of the main conditions of the complex formation reaction is the medium of the solution [35]. Therefore, buffer solutions with different pH values were used to obtain reproducible results. For this 5.0 ml of universal buffer solution with a pH of 6.73–11.50, 0.05% HR was added to a 25.0 ml measuring flask reagent solution, and 1.0 ml of 50.0 $\mu\text{g}/\text{ml}$ nickel (II) solution was added and diluted by adding distilled water to the mark of the flask. The optical density (A) of the complex solution was measured on a KFK-3 concentration photocolorimeter at a wavelength of $\lambda_{\text{max}}=575$ nm in cuvettes with an absorption thickness of $\ell=1.0$ cm. The obtained results are presented in Fig. 2.

According to the results presented in Fig. 2, the highest optical density (A) of the complex compound was observed in the range of pH 9.02–9.30. The highest optical density (A) was chosen at pH=9.15.

Determination of the optimal buffer solution. The effects of buffer solutions of different compositions (for example, universal, Na-tetraborate, glycine and phosphate-borate) with the same pH of 9.10–9.20 on the light absorption of the color complex have been studied [34, 28]. The results are presented in Fig. 3.

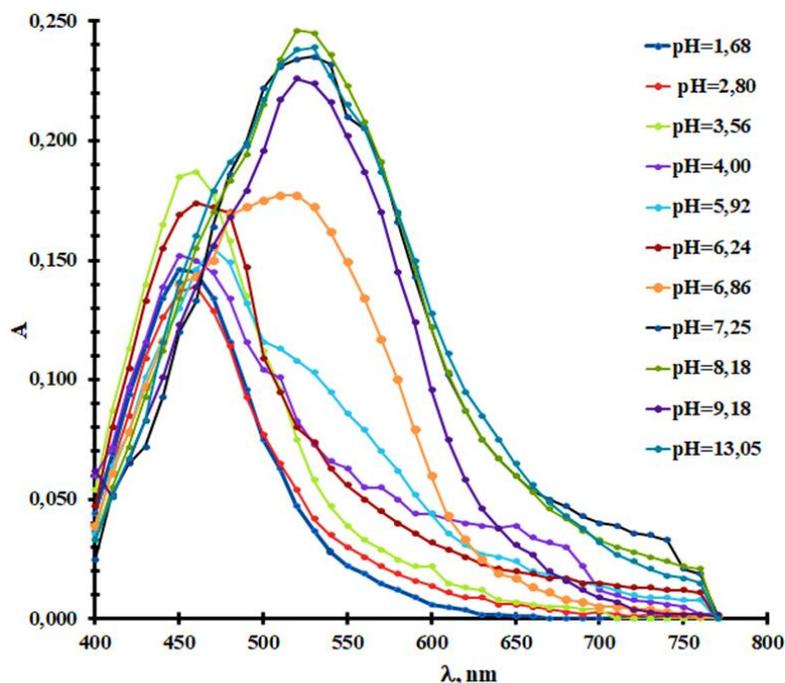


Fig. 1. Electronic spectra of HR at different pH values.

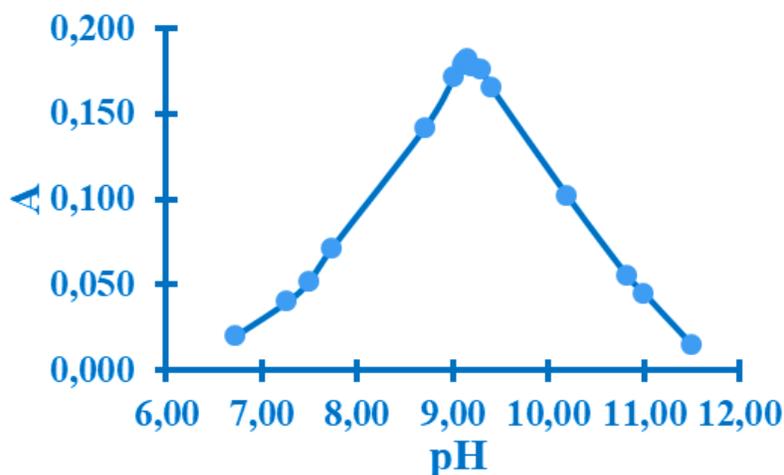


Fig. 2. Dependence of the optical density on the solution environment ($\lambda_{\max}=575$ nm, $\ell=1.0$ cm, $n=5$).

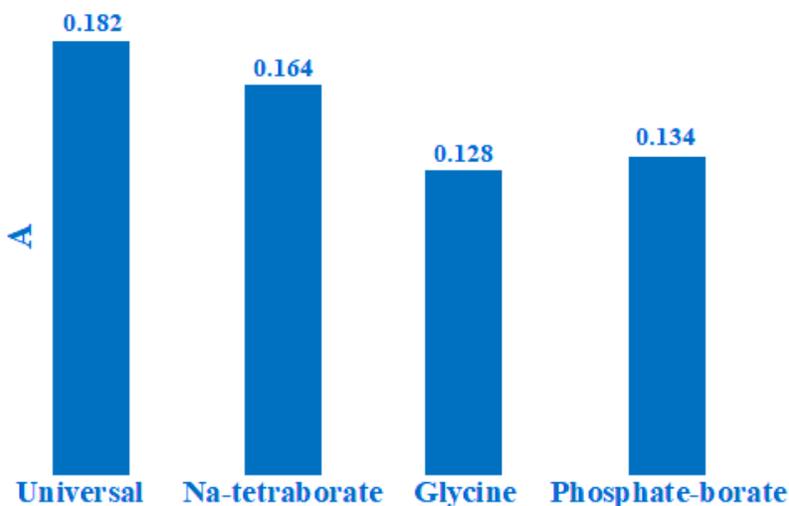


Fig. 3. Dependence of the optical density on the buffer solution content ($\lambda_{\max}=575$ nm, $\ell=1.0$ cm, $\text{pH}=9.15$, $n=5$).

According to the presented results (Fig. 3), the color complex presented the highest optical density under the influence of the universal buffer solution.

During this research, the time dependence of the formation of colored complexes was studied [35]. According to the obtained results, the fact that the optical density of the formed colored complex did not change for 3.5 hours indicates that there was enough time for analysis. When the order of addition was studied, buffer–nickel (II)–reagent–distilled water produced the highest optical density.

Effect of the reagent concentration on the nickel (II) complex. In complexation reactions, the amount of added reagent plays a key role in the complete binding of the metal to HR. To find the necessary amounts of reagents to ensure the complete binding of metals into a complex, a series of experiments were carried out in which the

concentration of metal ions was maintained constant, but the amount of reagents was gradually increased. To determine the dependence of the optical density of the solutions of the complexes on the amount of added HR, solutions were prepared by adding 5.0 ml of a universal buffer solution at pH 9.15, containing 50.0 μg of nickel (II) ions, increasing amounts of a 0.05% HR solution, and the volume was brought to the mark with distilled water. The solutions were mixed, and their optical density (A) was measured on a KFK-3 photocolormeter, with an absorption maximum at 575 nm at $\ell=1.0$ cm relative to the blank experimental solution (Fig. 4). A complete consistency of the optical density (A) was observed in the presence of 1.1–1.4 ml ($V_{\text{opt}} = 1.2$) of 0.05% HR solution. This amount of reagent is considered sufficient for connecting complexes with added amounts of metal ions [28].

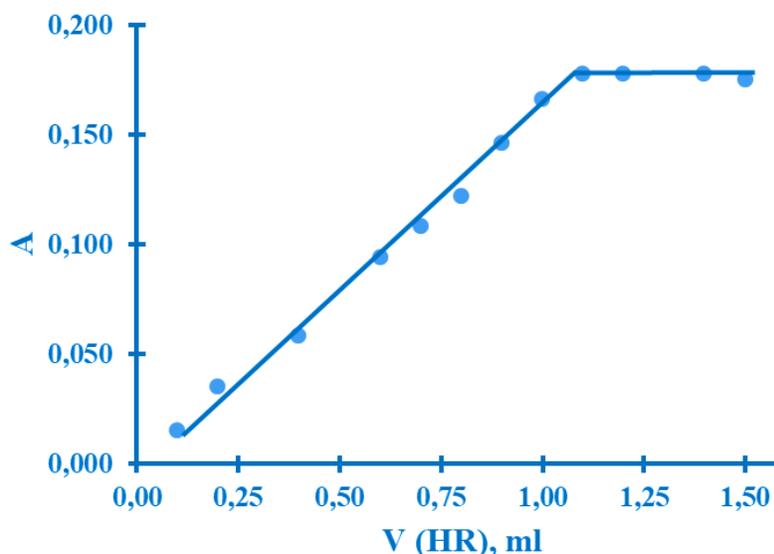


Fig. 4. The dependence of the optical density (A) of the complex on the amount of added reagent ($\lambda_{\max}=575$ nm, $\ell=1.0$ cm, pH=9.15, n=5).

The area of submission to the Bouguer–Lambert–Beer law for the nickel (II) complex. A total of 1.2 ml of 0.05% HR aqueous solution, 5.0 ml of universal buffer solution (pH=9.15), and a variable amount of 50 $\mu\text{g}/\text{ml}$ nickel (II) standard solution were diluted to the mark of the flask by adding distilled water. After the optical densities of the solutions were mixed, they were measured and compared with those of the reference solution. The obtained results are presented in Fig. 5.

According to the obtained results, compliance with the Bouguer–Lambert–Beer law was observed in the range of 5.0–55.0 $\mu\text{g}/25$ ml. At higher concentrations, deviation from the linear relationship [35] was observed.

Determination of the absorption spectrum of the reagent (HR) and its complex with nickel (II). UV-visible spectra were obtained (Table 1) under optimal conditions using the HR reagent, and the complex formed with nickel (II). In accordance with the method's sensitivity by Sendel, the light absorption per unit area (0.001 of mkg/sm^2) was calculated via the following formula:

$$S = \frac{Q \cdot \ell \cdot 0.001}{A \cdot 25} = \frac{50.0 \cdot 1.0 \cdot 0.001}{0.218 \cdot 25.0} = 0.009174 \mu\text{g}/\text{sm}^2$$

where S is the sensitivity of Sendel, Q is the concentration of the absorbed metal ion, ℓ is the path length of the cuvette, and A is the optical density.

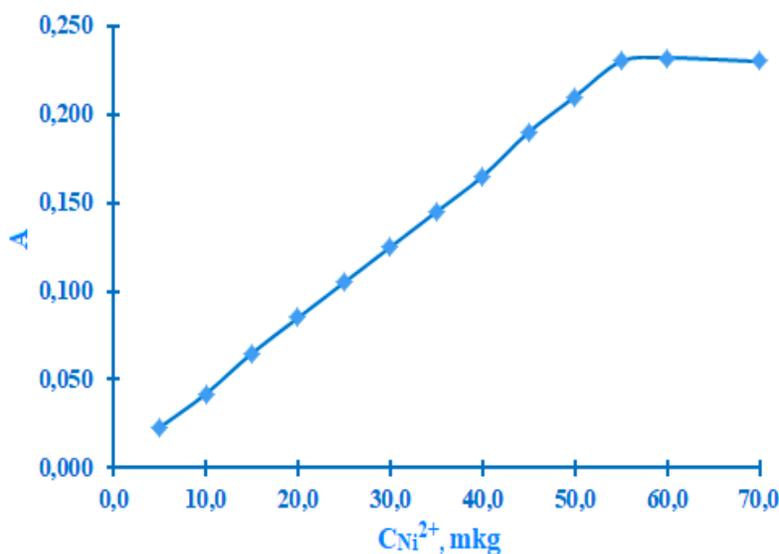


Fig. 5. Graph of the dependence of the optical density (A) on the amount of added nickel (II) ($\lambda_{\max}=575$ nm, $\ell=1.0$ sm, pH=9.15, n=5).

The obtained results clearly indicate that the reaction has both considerable contrast ($\Delta\lambda=65$ nm) and high sensitivity ($S=0.009174$ $\mu\text{g}/\text{cm}^2$).

Determination of the composition of the Ni (II)-HR complex. The composition and mechanism of complex formation were determined. By utilizing the Nazarenko method (equilibrium shift method), it was established

that the shape of the complex involving nickel (II) is Ni^{2+} (Fig. 6) [35, 36]. The stoichiometry of the complex was determined via the Isomolar series method (Fig. 7) and Asmus' correct linear method (Fig. 8). All the methods employed confirmed that the molar ratio of the components in the complex was $\text{Ni}:\text{HR}=1:2$.

Table 1. Spectral characterization of HR and its complex with nickel (II)
($C_{\text{Ni}^{2+}}=50$ mkg, $\lambda_{\text{max}}=575$ nm, $\ell=1.0$ cm, $\text{pH}=9.15$, $n=5$).

Color of the complex	pH	λ_{NiR_2}	λ_{HR}	$\Delta\lambda$, nm	ε (NiR_2)	$C_{\text{Ni}^{2+}}$, mkg/25 ml	$C_{\text{Ni}^{2+}}$, mol/l	\bar{A}	Sendel sensitivity $\mu\text{g}/\text{cm}^2$
Light purple	9.15	575	510	65	23585	50	$3.4075 \cdot 10^{-5}$	0.218	0.009174

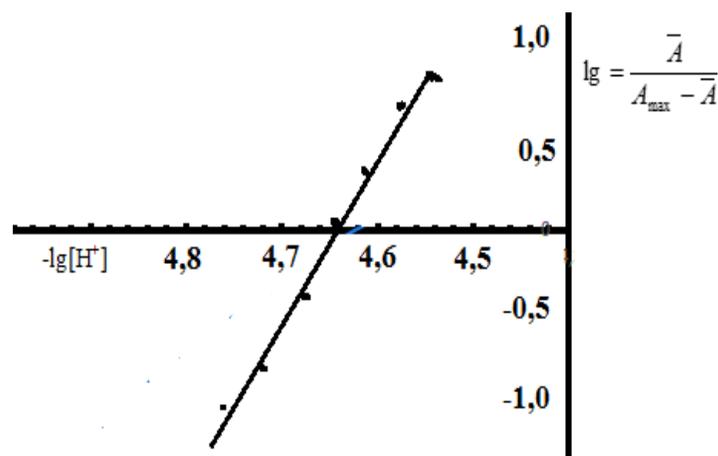


Fig. 6. The ratios of the components in a complex were determined via the equilibrium shift method ($\lambda_{\text{max}}=575$ nm, $\ell=1.0$ cm, $\text{pH}=9.15$, $n=5$).

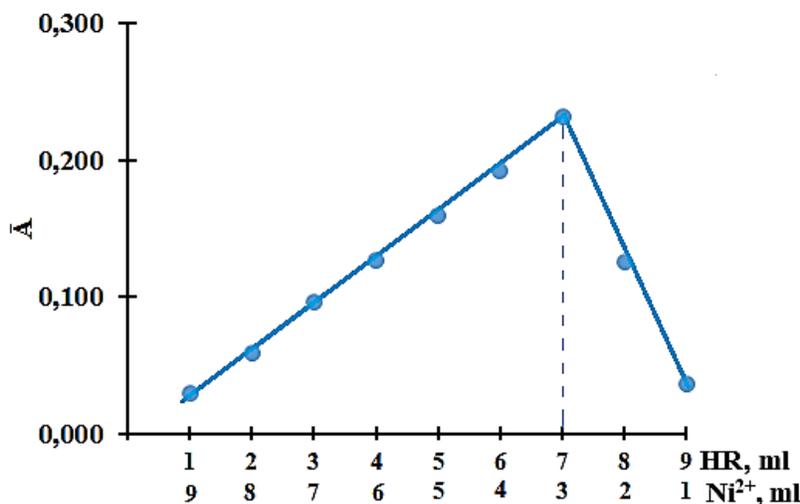


Fig. 7. Isomolar series method graph of the composition of the complex formed by nickel (II) with HR ($\lambda_{\text{max}}=575$ nm, $\ell=1.0$ cm, $\text{pH}=9.15$, $n=5$).

Method for determining the charge of the nickel (II) complex: To determine the charge of the complex, the solution was passed through columns containing the cation KU-2 and the anion AB-16-GS.

a) First, 1.0 g of cationite KU-2 was transferred to a column with a 1.0 cm diameter, treated 3 times with 10 ml of 0.1 N hydrochloric acid and then washed with 50 ml of distilled water. Then, under optimal conditions, 1.2

ml of a 0.05% HR reagent solution, 1.0 ml (50 µg/ml) of nickel (II) solution, and 5 ml of universal buffer solution were poured into a volumetric flask with a volume of 25 ml, the volume was adjusted to the mark with distilled water, and 10.0 ml of the complex solution was passed through cation KU-2. The red solution of the complex was not retained on cationite KU-2.

b) One gram of anionic AB-16-GS was transferred to a column with a diameter of 1.0 cm and treated 3.0 times with 10 ml of 0.1 N NaOH solution. The column was subsequently washed with 50 ml of distilled water, after which 10 ml of the complex solution was passed. In this case, the complex was retained on the upper layers of anionite. The solution that passed through the anionite was discolored. The complex has a negative charge. This can be explained by the fact that the sulfone groups present in the reagent (HR) at the optimum pH (pH=9.15) are in a dissociated state, and owing to steric

factors, they do not participate in complexation. On the basis of data obtained by determining the charge and composition, the expected structure of the complex can be represented as follows: $2[\text{HR}]^{2-} + \text{Ni}^{2+} = [\text{ZnR}_2]^{2-} + 2\text{H}^+$.

Determination of the molar absorption coefficient, equilibrium and stability constants. To thoroughly investigate the complex formation reaction of nickel (II) with the HR reagent, the main characteristics of the complex, namely, the true molar extinction coefficient and the formation equilibrium constant, were determined via the graphical method of Tolmachev (Fig. 9). Additionally, the stability constant of the complex was determined via Babko's dilution method (Table 2):

$$\varepsilon_{\text{true}} = \frac{1}{1/\varepsilon \cdot 10^n} = \frac{1}{4.24 \cdot 10^{-5}} = 23585$$

$$\text{tg} \alpha = \frac{b}{a} = \frac{2.0}{1.3800 \cdot 10^{-5}} = 6.9 \cdot 10^{-6}$$

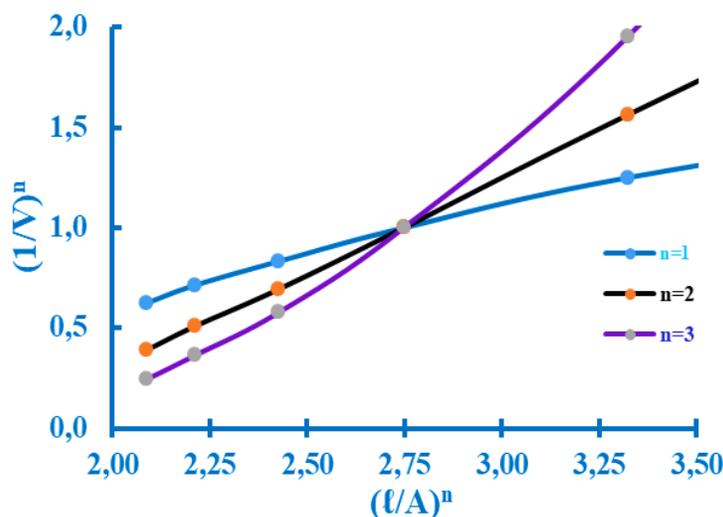


Fig. 8. Graph of the composition of the complex formed by nickel (II) with HR via Asmus' correct linear method ($\lambda_{\text{max}}=575$ nm, $\ell=1.0$ cm, pH=9.15, $n=5$).

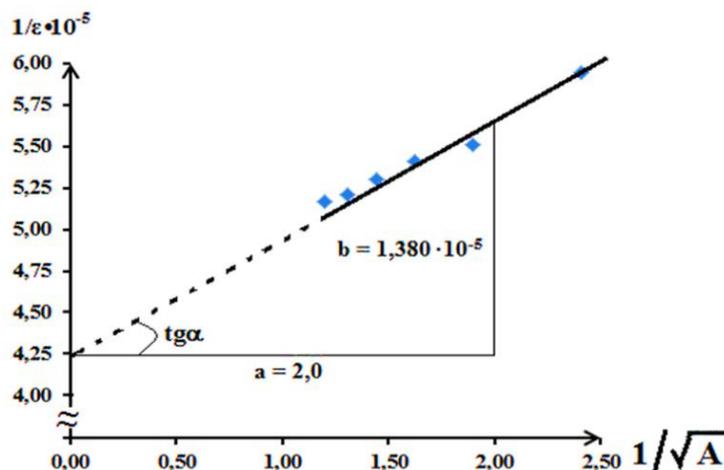


Fig. 9. Graph for determination of the molar extinction coefficient ($\lambda_{\text{max}}=575$ nm, $\ell=1.0$ cm, pH=9.15, $n=5$).

$$K_{\text{equil.}} \frac{C_H^n \cdot l^n}{n^n \cdot \varepsilon_{\text{true}} \cdot b^{n+1}} = \frac{(7.079 \cdot 10^{-10})^2 \cdot 1^2}{2^2 \cdot 23585 \cdot (6.9 \cdot 10^{-6})^3} = 1.6200 \cdot 10^{-8}$$

where C_H is the concentration of hydrogen ions at the optimal pH, l is the thickness of the absorbing layer, and n is the stoichiometric coefficient $\varepsilon_{\text{true}}$ - true molar extinction coefficient of the complex, b - tangent of the slope angle found from the graph.

$$K_{\text{unstable. (NiR}_2)} = \frac{[H^+] \cdot (A_1 \cdot C_2 - A_2 \cdot C_1)^{q+1}}{(C_1 \cdot \sqrt[3]{A_2} - C_2 \cdot \sqrt[3]{A_1}) \cdot (A_1 \cdot \sqrt[3]{A_2} - A_2 \cdot \sqrt[3]{A_1})^q}$$

$$K_{\text{stable}} = \frac{1}{K_{\text{unstable. (NiR}_2)}}$$

where $[H^+]$ is the concentration of hydrogen ions in the solution; A_1 and A_2 are the optical densities of the solutions of the nickel (II) complex before and after dilution, respectively; C_1 and C_2 are the concentrations of nickel (II) ions before and after dilution of the solution, respectively; and the degree of dilution is $q=2$.

On the basis of the calculated values of $\varepsilon_{\text{true}}=23585$, $K_{\text{equil.}}=1.6200 \cdot 10^{-8}$ and $\lg\beta=23.11$, the developed method has high sensitivity, whereas the complex has average stability.

Calculation of the equation of the calibration graph via the least squares method. The results obtained from the graph with calibration were mathematically reprocessed via the least squares method, and a linear mathematical equation was constructed. For the analytical application of the nickel (II) complex with HR, a graph was used to determine the amount of metal ions via spectrophotometric measurements. This graph links the measured value "Y", optical density "A", and the desired content of the analyte "Xi" (Table 3 and Fig. 10).

From the obtained results, the calibration graph (calibrated graph) equation was $Y_i = a + bX_i$, which is $Y_i = 0.0014 + 0.0041X_i$ ($\lambda_{\text{max}}=575$ nm, $l=1.0$ cm, $\text{pH}=9.15$, $n=5$, $P=0.95$). The accuracy and repeatability of the determination were calculated via the "Entered-found" method. The relative standard deviation value (S_r) did not exceed 0.0293, the confidence interval relative to the average value (ΔX) was 0.2270, and the lower limit of determination (Q_{min}) did not exceed 0.6004 $\mu\text{g}/25$ ml.

Table 2. Determination of the stability constant of the complex via Babko's dilution method ($\lambda_{\text{max}}=575$ nm, $l=1.0$ cm, $\text{pH}=9.15$, $n=5$)

No	$V_{\text{Ni}^{2+}}$, ml	V_R , ml	$C_1 \cdot 10^{-5}$	A_1	$C_2 \cdot 10^{-5}$	A_2	$K_{\text{unstable}}(\text{NiR}_2)$	$K_{\text{stable}}(\text{NiR}_2)$ (β_k)	$\lg K_{\text{stable}}(\text{NiR}_2)$ ($\lg\beta_k$)
1	0.50	1.0	1.02	0.162	0.511	0.079	$5.21 \cdot 10^{-24}$	$1.92 \cdot 10^{23}$	23.28
2	0.75	1.5	1.53	0.268	0.767	0.131	$6.11 \cdot 10^{-24}$	$1.64 \cdot 10^{23}$	23.21
3	1.00	2.0	2.04	0.37	1.02	0.181	$1.09 \cdot 10^{-23}$	$9.17 \cdot 10^{22}$	22.96
4	1.25	2.5	2.56	0.472	1.28	0.231	$1.70 \cdot 10^{-23}$	$5.88 \cdot 10^{22}$	22.77
5	1.50	3.0	3.07	0.578	1.53	0.283	$2.44 \cdot 10^{-23}$	$4.10 \cdot 10^{22}$	22.61
6	1.75	3.5	3.58	0.662	1.79	0.328	$4.31 \cdot 10^{-24}$	$2.32 \cdot 10^{23}$	23.37
Mean							$1.13 \cdot 10^{-23}$	$1.30 \cdot 10^{23}$	23.11

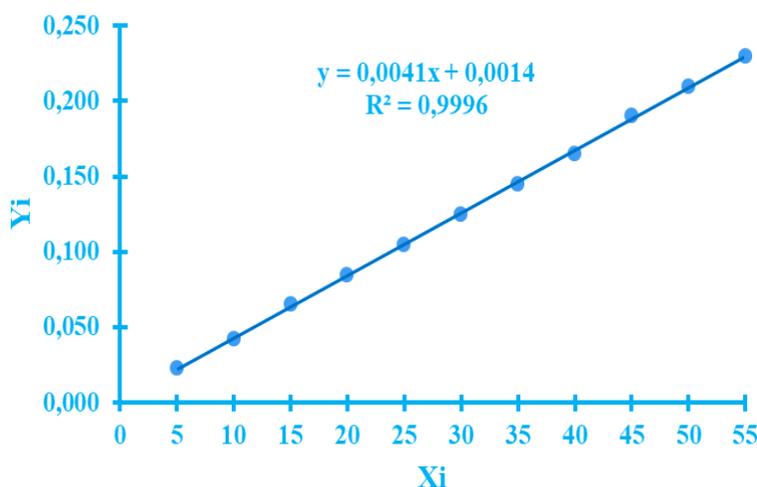


Fig. 10. Calibration graph for the determination of nickel (II) ions.

$$Q_{\min} = \frac{5 \cdot Sa \cdot M \cdot V \cdot B \cdot 1000}{\varepsilon_{\text{true}} \cdot l}$$

$$Q = \frac{5 \cdot 0.00193 \cdot 1 \cdot 25 \cdot 58.6934 \cdot 1000}{23585 \cdot 1} = 0.6004 \text{ mkg}$$

where Q_{\min} where Sa is the mean standard deviation of the optical density suitable for each

concentration, M is the number of nickel atoms contained in the complex ($M=1$), V is the volume of the spectrophotometric solution, B is the atomic mass of the determined component, $\varepsilon_{\text{true}}$ is the true molar absorption coefficient of the complex, and l is the thickness of the absorbing layer

Table 3. Results of constructing and reprocessing the calibration graph ($\lambda_{\text{max}} = 575 \text{ nm}$, $\text{pH} = 9.15$, $n = 5$)

No	$X_i, \mu\text{g}$	\bar{A}, Y_i	X_i^2	$X_i \cdot Y_i$	$Y_{i\text{calculated}}$	$Y_i - Y_{i\text{calculated}}$	$(Y_i - Y_{i\text{calculated}})^2 \cdot 10^{-7}$
1	5	0.023	25	0.115	0.0222	0.00080	6.400
2	10	0.042	100	0.420	0.0429	-0.00090	8.100
3	15	0.065	225	0.975	0.0637	0.00130	16.90
4	20	0.085	400	1.700	0.0844	0.00060	3.600
5	25	0.105	625	2.625	0.1052	-0.00020	0.400
6	30	0.125	900	3.750	0.1259	-0.00090	8.10
7	35	0.145	1225	5.075	0.1467	-0.00170	28.90
8	40	0.165	1600	6.600	0.1674	-0.00240	57.60
9	45	0.190	2025	8.550	0.1881	0.00190	36.10
10	50	0.210	2500	10.500	0.2089	0.00110	1.210
11	55	0.230	3025	12.650	0.2296	0.00040	1.600
Σ	330	1.385	12650	52.960	1.3850		179.8

Effect of different ions (selectivity). The effects of various foreign ions on the spectrophotometric determination of nickel (II) with HR were studied, except that they were introduced before the HR solution. The experimental data are presented as the selectivity factor ($F = \frac{C_{Me^{n+}}}{C_{Ni^{2+}}}$, which is the maximum permissible mass excess. The relative error in the determination was $\pm 5\%$. For the spectrophotometric analysis of nickel (II) ions (50 μg) with the HR reagent, the influence of foreign ions was investigated. The following ions did not interfere with the detection of nickel (II) ions at the specified ratios: Al^{3+} , NH_4^+ , Mn^{2+} , Sn^{2+} , Ba^{2+} , I^- , F^- , Cl^- , Br^- , PO_4^{3-} , NO_2^- (1:1000), Sn^{2+} , ClO_4^- , SO_4^{2-} (1:100), Fe^{2+} , and Fe^{3+} (1:10). The interfering ions used were as follows: Zn^{2+} , Co^{2+} (1:10), Cd^{2+} , Pb^{2+} , Cu^{2+} (1:1), citrate, SCN^- and EDTA (1:0.5). The interfering ions are neutralized [35] via the precipitation method. A comparison of the selectivities of reagents known from the literature [37, 38] for the determination of nickel (II) revealed that the synthesized reagents are more selective.

4. Analytical applications

The selectivity data make it possible to apply the developed technique for the spectrophotometric determination of nickel (II) ions in complex objects.

Determination of nickel (II) ions by HR in model mixtures. To verify the accuracy and repeatability of the method, the "Entered-found" method was employed

with artificial mixtures. To neutralize interfering foreign ions in the determination of nickel (II) ions, $\text{S}_2\text{O}_3^{2-}$, F^- and NO_2^- ions were added at a ratio of 1:5. According to the obtained results, it is possible to detect nickel (II) in such naturally occurring samples. The measurement results and their metrological data are presented in Table 4, which shows that the spectrophotometric determination of nickel (II) ions in complex model mixtures imitating real objects is quite possible, and the relative standard deviation (S_r) does not exceed 0.0237, which indicates good accuracy and reproducibility of the developed method.

Determination of nickel (II) ions in industrial samples. An elaborate sensitive and selective spectrophotometric method for the determination of nickel (II) ions with the HR reagent was applied to analyze standard samples of industrial alloys. The AK12MK 203-5 samples, which have polymetallic and elemental compositions, were used.

To prepare the samples for analysis, a 1.1111 g sample of alloy was dissolved in heat-resistant glass with a capacity of 50.0 ml, and a minimal volume (10.0–12.0 ml) of the tsar vodka was added. The mixture was heated with gentle boiling on an electric stove until complete dissolution, and nitrogen oxides were removed. After cooling, the solution was quantitatively transferred to a 500 ml volumetric flask, diluted with distilled water to the mark and stirred. The contents of nickel (II) ions were determined from aliquots of this solution [35, 36].

The methods for determining nickel (II) ions were as follows: a certain amount of sample mixture was placed in a 25 ml volumetric flask, 5 ml of universal buffer solution with a pH of 9.15, 1.2 ml of 0.05% HR solution, masking agents (KJ for Cu²⁺ ions; NH₄F for Fe²⁺, Fe³⁺, Al³⁺ and Sn²⁺; NH₄OH for Zn²⁺), and the

volume was adjusted to the mark with distilled water. The optical density (A) of KFK-3 was measured at an ℓ of 1.0 cm relative to that of the blank solution. The obtained data and their mathematical processing are presented in Table 5, with a relative standard deviation (S_r) not exceeding 0.0187.

Table 4. The results of the determination of nickel (II) ions in artificial mixtures ($\lambda_{\max}=575$ nm, $\ell=1.0$ cm, pH=9.15, n=5, P=0.95, $Y_i=0.0014+0.0041X_i$).

The composition of artificial mixtures (ratio)	Introduced Ni ²⁺ , μg	\bar{A}_{575}	Found Ni ²⁺ , μg	S	S_r	$\bar{X} \pm \Delta X$
K ⁺ , Na ⁺ , I ⁻ (1:1000) Al ³⁺ , Co ²⁺ , Fe ²⁺ (1:10) Mn ²⁺ , F ⁻ , S ₂ O ₃ ²⁻ , NO ₂ ⁻ (1:5), Cu ²⁺ (1:1)	50.0	0.213	51.61	1.20	0.0237	50.73 \pm 1.49
		0.208	50.39			
		0.210	50.88			
		0.212	51.37			
		0.204	49.41			

Table 5. Spectrophotometric determination of nickel (II) ions in standard samples of industrial aluminum and copper alloys (pH=9.15, $\ell=1.0$, n=3, P=95, $Y_i=0.0014+0.0041X_i$).

Sample, Ni, %	V _{sample} , (aliquot), ml	Contined Ni (II) in solution, μg	\bar{A}_{575} , Y_i	Found Cu ²⁺ , μg , X_i	$\bar{X}_i \pm \Delta x$	S	S_r
AK12MK -203-5, 0.45	3.0	30.0	0.125	30.15	29.82 \pm 0.94	0.3764	0.0126
			0.122	29.41			
			0.124	29.90			
	3.5	35.0	0.143	34.54	34.86 \pm 0.92	0.3721	0.0107
			0.144	34.78			
			0.146	35.27			
	4.0	40.0	0.162	39.17	39.5 \pm 1.41	0.5658	0.0143
			0.166	40.15			
			0.162	39.17			
	4.5	45.0	0.185	44.78	44.86 \pm 2.08	0.8368	0.0187
			0.188	45.51			
			0.183	44.29			
5.0	50.0	0.204	49.41	49.30 \pm 0.93	0.3732	0.0076	
		0.202	48.93				
		0.205	49.66				

Thus, (Table 5), the developed spectrophotometric method for the determination of nickel (II) ions in standard samples by the HR reagent is characterized by high sensitivity, selectivity and reproducibility, with a relative standard deviation (S_r) not exceeding 0.0187.

The nickel (II) ion concentrations in natural waters were determined via the addition of additives. Spectrophotometric determination of the concentrations of nickel (II) ions via the sample method, known as the "Method of additives" in the literature and widely used in chemical analysis, has been used, which requires the observance of the basic law of light absorption [35]. On the basis of studies to optimize direct spectrophotometric conditions for the determination of nickel (II) ions in real

objects and to obtain optimal estimates of the selectivity of its determination in individual and complex mixtures, an expressive spectrophotometric method for analyzing natural waters to determine the content of nickel (II) ions was developed. Water samples taken for analysis from Omonkhona Spring (Surkhandarya region, Omonkhon village) are complex systems containing, in addition to mineral macrocomponents, cations of various heavy metals.

The content of water taken from Omonkhona according to the passport date (the results were determined via atomic absorption spectroscopy) was as follows: elemental composition (mg/l): Al-0.007, As-0.0013, Sr-6.6, Mo-0.0016, Mn-0.0005, Cu-0.004, Zn-

0.008, Ni-0.0069, Hg-0.00006; mineral composition (mg-eq/l): K-11.99, Na-11.99, Ca-8.0, Mg-11.39, HCO_3^- -6.59, SO_4^{2-} -23.19, Cl^- -1.9. A 2.0 L sample taken from the Omonkhon spring was placed in heat-resistant glass with a capacity of 2000 ml, 20.0 ml of a 1.0 N HNO_3 solution was added, and the sample was heated in a sand bath and evaporated to form wet salts. The precipitate was dissolved in 10 ml of distilled water and filtered through glass to a volume of 50 ml [39-41].

Method for determination of nickel (II) ions in natural waters. The solution was quantitatively transferred into a flask with a volume of 25 ml, various amounts (5.0–40.0 μg) of standard nickel (II) solution

(50.0 $\mu\text{g}/\text{ml}$), 5 ml of universal buffer solution at pH 9.15, and 1.20 ml of 0.05% HR solution, and the volume was adjusted to the mark with distilled water with subsequent stirring. To improve the selectivity of the method, the following masking agents were added: $\text{S}_2\text{O}_3^{2-}$, F^- and NO_2^- ions were added at a ratio of 1:1 [35] at calculated concentrations for the binding of aluminum, manganese, copper, zinc and arsenic ions. The optical density of KFK-3 was measured at $\ell=1.0$ cm relative to that of a blank test solution. The experimental results obtained via the determination of nickel (II) ions in the samples from the Omonkhon spring and their mathematical processing are presented in Table 6.

Table 6. The results of the determination of the microconcentration of nickel (II) ions with HR in Omonkhon spring water by the “Method of additive” ($V_{\text{water}}=2.0$ l, $\text{pH}=9.15$, $\ell=1.0$ cm, $n=3$, $P=0.95$, $Y_i=0.0014+0.0041X_i$).

Introduced Ni^{2+} , μg	Continued. Ni^{2+} in solution, μg	\bar{A}_{575}	Found Ni^{2+} , μg	$\bar{X} \pm \Delta X$	Quantity of Ni^{2+} in the sample, μg	S	S_r
-	13.80	0.056	13.32	13.56±0.88	13.56	0.356	0.0263
		0.059	14.05				
		0.056	13.32				
5.00	18.80	0.079	18.93	18.60±0.92	13.60	0.371	0.0199
		0.076	18.20				
		0.078	18.68				
10.00	23.80	0.098	23.56	23.48±0.35	13.48	0.139	0.0059
		0.097	23.32				
		0.098	23.56				
15.00	28.80	0.120	28.93	28.44±1.22	13.44	0.490	0.0172
		0.116	27.95				
		0.118	28.44				
20.00	33.80	0.140	33.80	33.90±1.53	13.90	0.615	0.0181
		0.138	33.32				
		0.143	34.54				
25.00	38.80	0.160	38.68	38.68±1.20	13.68	0.485	0.0125
		0.162	39.17				
		0.158	38.20				
30.00	43.80	0.179	43.32	43.32±0.61	13.32	0.246	0.0057
		0.178	43.07				
		0.180	43.56				
35.00	48.80	0.201	48.68	48.60±1.53	13.60	0.614	0.0126
		0.203	49.17				
		0.198	47.95				
40.00	53.80	0.221	53.56	53.88±0.92	13.88	0.372	0.0069
		0.224	54.29				
		0.222	53.80				

Thus, (Table 6), the developed spectrophotometric method for the determination of nickel (II) ions by HR is characterized by high selectivity, with a relative standard deviation (S_r) not exceeding 0.0263.

Spectrophotometric determination of nickel (II) ions in ore from the Khandizinsky deposit. The

developed method was applied to analyze ore from the Khandizinsky deposit, which is located in the Surkhandarya region of the Republic of Uzbekistan. The ore analysis was performed without separating nickel, copper, and other associated elements.

Composition of the ore, % (the results were determined via atomic absorption spectroscopy): Zn-3.17; Cu-11.45; Ni-12.37; Au-0.001; Ag-0.00131; Mn-0.6; Cd-0.1; Pb-3.32; Fe₂O₃-9.92; S-20.4; SiO₂-38.67.

Sample preparation method: Decomposition of a 0.2000 g ore sample was carried out according to the instructions [42-43]. After evaporation, the salt was leached with water in a heat-resistant beaker by heating. The precipitate was filtered and washed five times with 10 ml of distilled water, filtered each time, and the filtrate was collected in a 100.0 ml measuring flask. After unfolding the filter, the precipitate was washed into another beaker, and 4.0 ml of 5 M HCl was added; the insoluble part of the sample was then filtered. The resulting solutions were quantitatively transferred to a

1000 ml measuring flask and diluted to the mark with distilled water.

Determination method. A certain amount of the solution was placed in a 25 ml volumetric flask. Ascorbic acid was added to reduce the iron, along with masking agents (50.0 µg F⁻ for Fe²⁺ and ³⁺ ions and 5.0 ml of a 0.5 M sodium diethyldithiocarbamate solution for Cu²⁺ ions). Next, 5.0 ml of a universal buffer solution with a pH of 9.15 and 1.2 ml of a 0.05% HR solution were added. The volume was then brought to the mark with distilled water and mixed. The optical density of the solutions was measured via a KFK-3 spectrophotometer at optimal wavelengths in a cuvette with a thickness of $\ell = 1.0$ cm. The results of the analysis of the ores and concentrates are presented in Table 7.

Table 7. Results of the spectrophotometric determination of nickel (II) ions in ores from the Khandizinsky deposit.

($m_{\text{Ore sample}}=0.2000$ g, pH=9.15; $\lambda_{\text{max}}=575$ nm; $\ell=1.0$ cm $n=5$, $P = 0.95$, $Y_i=0.0014+0.0041X_i$)

$V_{\text{ore sample solution, ml}}$	Contined Ni ²⁺ in solution, µg	\bar{A}_{575}	Found Ni ²⁺ , µg	$\bar{X} \pm \Delta X$	S	S _r
0.5	12.37	0.048	11.37	12.05±0.69	0.556	0.0461
		0.052	12.34			
		0.050	11.85			
		0.054	12.83			
		0.050	11.85			
1.0	24.74	0.096	23.07	24.19±0.79	0.634	0.0262
		0.102	24.54			
		0.104	25.02			
		0.099	23.8			
		0.102	24.54			
1.5	37.11	0.148	35.76	36.54±0.81	0.654	0.0179
		0.150	36.24			
		0.154	37.22			
		0.154	37.22			
		0.150	36.24			
2.0	49.48	0.203	49.17	49.22±0.81	0.316	0.0064
		0.202	48.93			
		0.204	49.41			
		0.205	49.66			
		0.202	48.93			

On the basis of the analysis of the ore from the Khandizinsky deposit, the developed spectrophotometric methods are suitable for analyzing various metal-containing materials. The results obtained are reliable and valid, with a S_r value not exceeding 0.0461, indicating the accuracy and reproducibility of the proposed methods (Table 7).

Competitiveness of the developed spectrophotometric method for the determination of nickel (II) ions. To establish the competitiveness of the proposed spectrophotometric method for the

determination of nickel (II) ions and to assess the degree of reliability and accuracy of the obtained results, some metrological characteristics and analytical parameters of the developed methods were compared with those obtained by other researchers via other independent methods of analysis.

As an example, in Tables 8 and 9, comparative results obtained via the developed method for the spectrophotometric determination of nickel (II) ions with HR are presented, as are data obtained via other independent methods and different researchers who analyze objects of different natures and complexities.

Table 8. Results of the competitiveness evaluation of the elaborate spectrophotometric method for Determination of nickel (II) ions with other organic reagents.

Organic reagent	pH _{opt.}	λ_{\max} , $\Delta\lambda$, nm	Molar ratio Me:R	True molar absorption coefficient, ϵ	Interfering influence of foreign components	References
5-(2-bromo-5-methoxybenzylidene)-thiazolidine-2,4-dione	7.1–8.9	482, $\Delta\lambda=146$	1:2	17500	Fe ³⁺ , Cu ²⁺ , Mo ⁶⁺ , Se ⁴⁺ , Pt ²⁺ , Mn ²⁺ , Cd ²⁺ , Zn ²⁺ , Pb ²⁺ (1:1)	[26]
5-bromo-2-hydroxyl -3-methoxybenzal-dehyde-4-hydroxy benzoichydrazone	5.5–7.5	440 $\Delta\lambda=50$	1:1	20130	Cu ²⁺ , Fe ³⁺ , Th ⁴⁺ (1:5), Ti ⁴⁺ (1:4), EDTA (1:1)	[28]
N',N''-((1E,1'E)-(propane-1,3-diylbis (sulfanediy)) bis (1-(4-bromophenyl) ethan-2-yl-1-ylidene)) bis (2-hydroxybenzohydrazide)	4.0–6.0	343 $\Delta\lambda=28$	1:1	72100	Al ³⁺ , Cr ³⁺ (1:4000), Mo ⁴⁺ , W ⁵⁺ (1:2000), Cu ²⁺ , Zn ²⁺ , Pb ²⁺ (1:1), Pd ²⁺ , Cd ²⁺ (1:1)	[30]
2,4-dimethoxybenzal-dehyde isonicotinoyl hydrazone (DMBIH)	8.5–9.5	410 $\Delta\lambda=50$	1:1	59200	Cu ²⁺ (1:1.32), Hg ²⁺ (1:1.67), Fe ³⁺ (1:1.73), Mo ⁶⁺ (1:2.67)	[32]
HR (4,5-dihydroxy-3,6-dinitroso-naphthalene-2,7-disulfoxic acid)	9.0–9.3	575, $\Delta\lambda=65$	1:2	23585	Zn ²⁺ , Co ²⁺ (1:10), Cd ²⁺ , Pb ²⁺ , Cu ²⁺ (1:1), EDTA (1:0.5)	Developed methodology

Table 9. Results of assessing the competitiveness of the developed method a spectrophotometric method for the determination of nickel (II) ions.

Analytical parameters	Direct photometric determination	Extraction spectrophotometry	Developed methodology
Buffer solution (pH value)	Acetate buffer (5.5–7.5)	Basic buffer (pH=8.5–9.5)	Universal buffer (pH=9.02–9.30)
Lower limit of determined contents, $\mu\text{g/ml}$	0.016	0.098	0.6004
Concentration (Beer's law) range, $\mu\text{g/ml}$	0.117–2.64	0.1467–1.7607	5.0–55.0
Relative standard deviation (S_r)	0.00256	1.36	0.0237
Stability constant of the complex, β_k	$2.83 \cdot 10^6$ ($\lg\beta = 6.45$)	$7.12 \cdot 10^7$ ($\lg\beta = 7.85$)	$1.30 \cdot 10^{23}$ ($\lg\beta = 23.11$)
Sensitivity, ϵ	20130	59200	23585
Volume of the analyzed solution, ml	25.0	25.0	25.0
Sandell's sensitivity ($\mu\text{g}\cdot\text{cm}^{-2}$)	0.0029	0.00099	0.009174
References	[28]	[32]	Developed methodology

From the data given in Tables 7 and 8, it is possible to conclude that the developed spectrophotometric method for the determination of nickel (II) ions with 4,5-dihydroxy-3,6-dinitrosonaphthalene-2,7-disulfoxic acid by metrological characteristics (accuracy,

reproducibility, selectivity, contrast, lower limit of determined contents, sensitivity, detection limit, expressiveness, stability constant, relative standard deviation not exceeding 0.0461, etc.) is not inferior to the long-known and widely used analytical methods for the

determination of this element, and the results obtained are characterized by reliability and validity, which indicates the competitiveness of the proposed method of spectrophotometric determination of nickel (II) ions

5. Conclusion

A simple, sensitive and accurate spectrophotometric method has been developed for the determination of nickel (II) ions. The molar ratio of the components in the complex was determined via the equilibrium shift, isomolar series, and Asmus' straight-line methods (Figs. 6-8). Tolmachev's graphical method was used to determine the true molar extinction coefficient and equilibrium constant of the complex (Fig. 9.) The stability constant of the complex was determined via Babko's dilution method (Table 2). The linear equation of the calibration graph for the analytical application of the developed method was calculated via the least squares method (Table 3 and Fig. 10). The results of the analysis of artificial mixtures (Table 4), standard samples of industrial alloys (Table 5), natural waters (Omonkhon spring water) (Table 6), and polymetallic ore from the Khandiza mine (Table 7) demonstrated that the spectrophotometric method for the determination of nickel (II) ions via HR under optimal conditions was consistent with the literature data. The method showed correctness, reproducibility, selectivity, and low limits of detection, with a relative standard deviation not exceeding 0.0461 in all cases. The determination error did not exceed the confidence interval, indicating the accuracy and reproducibility of the proposed spectrophotometric method for nickel (II) ions with the HR reagent. The proposed method is highly sensitive due to the stabilization of the colored complex for more than 3.5 hours formed by interactions of the nickel (II) ions with the new reagent, which results in low reagent consumption, elimination of analytical error, less interference, and statistical analysis, increasing the sensitivity and selectivity of the method.

Acknowledgments

This work was supported by the research program of the National University of Uzbekistan named after Mirzo Ulugbek for 2020-2024 "Monitoring of microquantities of some heavy toxic metals as an environmental factor and development of new spectrophotometric methods for their detection".

References

- [1] N. Rakhmatullaeva, A. Giyasov, S. Aliev, S. Obloberdiev, O. Bakhtiyorov, M. Kholov, Y. Ergashev and S. Turabdjanov, Extracting photometric determination of antimony with 5-pyridylazo-2-monoethylaminoparacresol(PAAC). E3S Web of Conferences. 497 (2024) 03040. <https://doi.org/10.1051/e3sconf/202449703040>
- [2] A.K. Goswami and Sh. Agarwal, Spectrophotometric determination of copper and iron:reagents and methods, De Gruyter. Monograph. 4 (2021) 268. <https://doi.org/10.1515/9781501514999>.
- [3] N. Turabov, Y. Eshmurzayev and J. Todjiev, Photometric methods for the determination of certain metals: Development of new methods with azoreagents based on pyridine. Monograph, LAP Lambert Academic Publishing RU. Moldova (2022).
- [4] John Emsley, Nature's Building Blocks: An A-Z Guide to the Elements, Oxford University Press, New York, 2nd Edition. (2011). https://books.google.co.uz/books?id=Yhi5X7OwuGkC&printsec=frontcover&source=gbg_summary_r&cad=0#v=onepage&q&f=false
- [5] T.I. Suldina, Content of heavy metals in food products and their impact on the body. Rational nutrition, food additives and biostimulants, 1 (2016) 136-140. <https://journal-nutrition.ru/ru/article/view?id=35727>
- [6] K.A. Parsunkova, Analysis for the determination of nickel in hair, Available online in: https://analizy-sochi.ru/analizy/analiz_volos_nickel.html/
- [7] Kh.E. Yunusov, A.A. Sarymsakov, A.I. Shukurov, J.N. Todjiev, A.A. Atakhanov, J. Guohua, and O.S. Sergey, Sodium-Carboxymethylcellulose/Polyphenol-Gossypol-Carboxymethylcellulose Copolymer Films for Ocular Drug Delivery: Preparation and Physico-Chemical Properties. Asian Journal of Chemistry, an International Peer Reviewed Research. 12 (2022) 3087-3092. <https://doi.org/10.14233/ajchem.2022.23912>
- [8] M. Cempel and G. Nickel, Nickel: A Review of Its Sources and Environmental Toxicology. Polish J. of Environ. Stud. 3 (2006) 375-382. https://www.pjoes.com/pdf-87881-21740?file-name=Nickel_%20A%20Review%20of%20Its.pdf
- [9] M. Afzaal, S. Hameed, I. Liaqat, A. Amanat, A. Khan, H.A. Manan, R. Shahid and M. Altaf, Heavy metals contamination in water, sediments and fish of freshwater ecosystems in Pakistan. Water Practice & Technology. 5(2022) 1253-1272. <https://doi.org/10.2166/wpt.2022.039>.
- [10] A.A. Nayif, M.A. Al-Da'amy and S.H. Kadhim. Spectrophotometric determination of Ni (II) ion by using a new azo reagent (DMIPNI). 4th International Scientific Conference of Engineering Sciences and Advances Technologies. AIP Conference Proceedings. 1 (2023)070031. <https://doi.org/10.1063/5.0156800>
- [11] Sh.S. Nazirov, Kh.Kh. Turaev, Sh.A. Kasimov, Kh.R. Tillaev, B.Sh. Alimnazarov and B.B. Abdullaeva, Spectrophotometric Determination of Ni (II) Ion with 7-Bromo-2-Nitroso-1-Oxinaphthalene-3,6-Disulphocid. International Journal of Engineering Trends and

- Technology. 6 (2024) 57-63. <https://doi.org/10.14445/22315381/IJETT-V72I6P106>
- [12] A. Martinović-Bevanda and N. Radić, Spectrophotometric Sequential Injection Determination of D-Penicillamine Based on a Complexation Reaction with Nickel Ion. *Analytical Sciences*. 29 (2013) 669-671. <https://doi.org/10.2116/analsci.29.669>
- [13] A. Afkhami, M. Bahram and A.R. Zarei, Comparison of Partial Least Squares Regression and H-Point Standard Addition Method for Simultaneous Spectrophotometric Determination of Zinc, Cobalt and Nickel by 1-(2-Pyridylazo)-2-Naphthol in Micellar Media. *Microchimica Acta*. 148 (2004) 317-326. <https://doi.org/10.1007/s00604-004-0281-8>
- [14] S. Badhe, P. Tekade, S. Bajaj and Sh. Thakare, Stability constants of Ni (II)- and Cu (II)-N-heterocycle complexes according to spectrophotometric data. *Russian Journal of Physical Chemistry A*. 89 (2015) 2254-2258. <https://doi.org/10.1134/S0036024415120250>
- [15] N. Thang and L. Tan, Comparison of Two Preconcentration Methods for the Determination of Nickel Using a Ni-2-(2-thiazolylazo)-p-Cresol Complex: Extraction and Sorption onto Ion Exchange Resin. *Journal of Analytical Chemistry*. 77 (2022) 1413-1418. <https://doi.org/10.1134/S1061934822110132>
- [16] Y. Bazel', M. Recló and J. Šandrejová, Using a Switchable-Hydrophilicity Solvent for the Extraction-Spectrophotometric Determination of Nickel. *Journal of Analytical Chemistry*. 72 (2017) 1018-1023. <https://doi.org/10.1134/S1061934817080032>
- [17] D. Nagarjuna Reddy, Extractive direct and derivative spectrophotometric determination of Nickel (II) in Medicinal leaves, Soil, and Alloy samples by using Pyridoxal-3-thiosemicarbazone (PDT). *Journal of Materials and Environmental Science*. 4 (2014) 1188-1199. https://www.jmaterenvironsci.com/Document/vol5/vol5_N4/147-JMES-833-2014-Reddy.pdf
- [18] A.Z. Zalov, K.O. İsgenderova and Z.G. Askerova, Spectrophotometric research into interaction nickel (II) with 1-(2-pyridylazo)-2-hydroxy-4-mercaptophenol and aminophenols. *Kimya Problemleri*. 3 (2021) 150-159. <https://doi.org/10.32737/2221-8688-2021-3-150-159>
- [19] A.Z. Zalov, K.O. Iskenderova, Z.G. Askerova and A.B. Hajiyeva, Spectrophotometric study of nickel (II) complexes with 2-hydroxythiolphenol and its derivatives in the presence of hydrophobic amines. *Kimya Problemleri*. 4 (2021) 224-231. <https://doi.org/10.32737/2221-8688-2021-4-224-231>
- [20] A.Z. Zalov and K.B. Cavazov, Extractive spectrophotometric determination of nickel with 2-hydroxy-5-iodothiophenol and biphenyldiamine. *Chemistry Journal*. 5 (2014) 20-25.
- [21] L. Pradnya, Solvent extraction and spectrophotometric determination of nickel (II) using 2-hydroxyl-1-naphthaldehyde thiosemicarbazone as an Analytical Reagent. *International Journal of Trend in Scientific Research and Development (IJTSRD)*. 3 (2019) 694-697. <https://doi.org/doi:10.31142/ijtsrd22964>
- [22] M.R. Sathyanarayana, P. Saifulla Khan and R. Reddy Spectrophotometric determination of nickel (II) with 2-aminoacetophenone isonicotinoylhydrazone. *Der Pharmacia Lettre*. 7 (2015) 281-286.
- [23] B. Ranganath, V. Saleem Rasha, M.R. Jayapal and P.V.Ramana Direct Spectrophotometric Determination of Ni (II) Using Esomeprazole. *International Journal of Pharmacy and Chemistry*. 1 (2015) 7-11. <https://doi.10.11648/j.ijpc.20150101.12>
- [24] Y. Bazel, A. Tupys, Y. Ostapiuk, O. Tymoshuk and V. Matychuk, A green cloud-point microextraction method for spectrophotometric determination of Ni (II) ions with 1-[(5-benzyl-1,3-thiazol-2-yl)-diazenyl]-naphthalene-2-ol. *Journal of Molecular Liquids*. 242 (2017) 471-477. <https://doi.org/10.1016/j.molliq.2017.07.047>
- [25] K. Aruna Bai, G.V.S. Vallinath, K.B. Chandrasekhar and N. Devanna, Derivative spectrophotometric determination of nickel (II) using 3,5-dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazine (DMHBIH). *RASĀYAN J Chemistry*. 3 (2010) 467-472. <https://www.rasayanjournal.co.in/vol-3/issue-3/12.pdf>
- [26] K.A. Kuliyeve, N.A. Verdizade and K.R. Aliyeva, Spectrophotometric Determination of Nickel (II) Using 5-(2-Bromo-5-Methoxybenzylidene)-Thiazolidine-2,4-Dione. *International Journal of Innovative Science, Engineering and Technology*. 10 (2021) 268-276. https://ijiset.com/vol8/v8s10/IJSET_V8_I10_23.pdf
- [27] R. Muthuselvi, Determination of Nickel (II) by Spectrophotometry in Micellar Media. *Pharmaceutical Analytical Chemistry*. 3 (2017) 1-3. <https://doi.org:10.4172/2471-2698.1000129>
- [28] B. Saritha and T. Sreenivasulu Reddy, Direct Spectrophotometric Determination of Ni (II) Using 5-Bromo-2-hydroxyl-3-methoxybenzaldehyde-4-hydroxy benzoic hydrazone. *Journal of Applied Chemistry*. 3 (2014) 22-26. <http://dx.doi.org/doi:10.9790/5736-07312226>
- [29] W. José Barreto, S. Regina Giancoli Barreto, I. Spacino Scarminio, D. Norio Ishikawa M. de Fátima Soares and M. Vinícius Brás de Proença, Determination of Ni (II) in metal alloys by spectrophotometry UV-Vis using dopasemiquinone. *Quim. Nova*. 1 (2010) 109-113. <https://doi.org/10.1590/S0100-40422010000100020>
- [30] N.C. Gangi Reddy, A rapid spectrophotometric determination of Ni (II) in medicinal plant materials and water samples using N',N''-((1E,1'E)-(propane-1,3-diylbis(sulfanediy)) bis(1-(4-bromophenyl)ethan-2-yl-1-ylidene)) bis(2-hydroxybenzohydrazide) as a selective and sensitive analytical reagent. *International Journal of Pharmaceutical Sciences and Research*. 12 (2021) 838-844.
- [31] B. Natesh Kumar, S. Kanchi, M.I. Sabela, K. Bisetty and NVV. Jyothi, Spectrophotometric determination of nickel (II) in waters and soils: Novel chelating agents and

- their biological applications supported by DFT method. *Karbala International Journal of Modern Science*. 2 (2016) 239-250. <https://doi.org/10.1016/j.kijoms.2016.08.003>
- [32] C. Viswanatha, N. Devanna and KB. Chandrasekhar, Direct and Derivative Spectrophotometric Determination of Nickel (II) using 2,4-Dimethoxy Benzaldehyde Isonicotinoyl Hydrazone (DMBIH). *International journal of advances in pharmacy, biology and chemistry*. 2 (2013) 380-384. <https://ijapbc.com/files/20-2231.pdf>
- [33] P.P. Korostelev, Preparation of solutions for chemical-analytical work, M.: Chemistry, (1964).
- [34] Yu.Yu. Lurie, Handbook of analytical chemistry, M.: Chemistry, (1989).
- [35] M.I. Bulatov and I.P. Kalinkin, Practical Handbook of Photometric Methods of Analysis, Khimiya, Leningrad, (2013).
- [36] J.N. Todjiyev, N. Turabov, G.S. Turaeva, B.M. Xusanov, Kh.E. Yunusov, B.A. Tulyev, A.S. Gazieva, G.U. Pulatova and Z.A. Smanova, Spectrophotometric Determination of Microconcentrations of Zinc (II) and Copper (II) in Water and Industrial Alloys Using a New Chromogenic Reagent [4-Amino-5-hydroxy-6-[(5-methyl-2-pyridyl)azo]-3-sulfo-1-naphthyl]sulfonyloxysodium. *Chemical Review and Letters. Review Article*. 3 (2024) 388-403. <https://doi.org/10.22034/CRL.2024.457689.1338>
- [37] A.I. Busev, Synthesis of new organic reagents for inorganic analysis, M.: Moscow State University, (1986).
- [38] S. Razzoqova, B. Torambetov, J. Todjiyev, Sh. Kadirova, A. Ibragimov, A. Ruzmetov and J. Ashurov, 2-Aminobenzoxazole–oxalic acid (2/1). *IUCr Data*. 1 (2024) 263-276. doi.org/10.1107/S2414314624000336.
- [39] N.K. Madusmanova, L.M. Khalilova, E.S. Zhumaeva, D.A. Gafurova, Z.A. Smanova and K.S. Tozhimukhamedov, Nitrosonaphthol Derivatives as Analytical Reagents for Cobalt Ions. *Journal of Analytical Chemistry*. 1 (2022) 26-34. <https://doi.org/10.1134/S1061934822010099>
- [40] J.K. Khaitov, J.N. Todjiyev, Kh.I. Nematov, M.I. Jurayeva, B.M. Muhammedova, I.Q. Bekjanov and Kh.E. Yunusov, Recent progress in cross-dehydrogenative sulfonamidation of (hetero) arenes. *Chemical Review and Letters*. 2 (2024) 263-276. <https://doi.org/10.22034/crl.2024.446350.1302>
- [41] Kh.E. Yunusov, F.M. Turakulov, A.A. Sarymsakov, Sh.A. Yuldoshov, S.Sh. Rashidova and J. Guohua, Physicochemical characteristics of a nanocomposite film based on purified sodium carboxymethylcellulose and selenium nanoparticles. *The Bulletin of the Korean Chemical Society*, 3 (2024) 273-283. doi.org/10.1002/bkcs.12813.
- [42] P.P. Korostelev, Chemical analysis in metallurgy, - M.: Metallurgy, (1988).
- [43] P.P. Korostelev, Laboratory technique of chemical analysis, - M.: Chemistry, (1981).