

UDC: 543.4:542.58:546.882:546.883

## EXTRACTION-SPECTROPHOTOMETRIC STUDY OF THE SYSTEM NICKEL(II) – HALOGENASEMERCAPTOPHENOL - AMINOPHENOL - WATER - CHLOROFORM

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> Received 03.05.2024 Accepted 05.07.2024

Abstract: Reaction of nickel with halogenazomercaptophenol (HAMP) {1-(5-fluoro-2-pyridylazo)-2-hydroxy-4-mercaptophenol, 1-(5-chloro-2-pyridylazo)-2-hydroxy-4-mercaptophenol} in the presence aminophenols (AP): 2-(N,N-dimethylaminomethyl)-4-methylphenol, 2-(N,N-dimethylaminomethyl)-4-ethylphenol studied by the Extraction-Photometric method. A single extraction with chloroform yields 97.1–98.9% nickel (II) in the form of a mixed-ligand complex (MLC). The optimal acidity range, at which the optical density is maximum and constant, is at  $pH_{op}$ , 3.3 – 7.8 (pH 2.0 – 9.8). Maximum optical density is achieved within 5-10 minutes. The optimal condition for the formation and extraction of these compounds is  $(1.10-2.35)\times10^{-3}$  mol/l concentration of HAMP and (6.31-8.42) ×10<sup>-4</sup> mol/l - AP. The molar absorption coefficients of Ni (II) complexes at  $\lambda_{max}$  were calculated by the saturation method and amount to  $\varepsilon_{610-650} = (1.3-1.7) \times 10^4$ . MLC in the organic phase are in monomeric form ( $\gamma = 0.91$ -1.09). Newly developed methods for extractionphotometric determination of Ni (II) for use in the analysis of oil and petroleum products Baku.

Key words: nickel, halogenazomercaptophenol, oil, fuel oil, hydron, aminophenol

DOI: 10.32737/2221-8688-2024-4-436-446

## Introduction

The determination of heavy metals in natural objects is relevant due to the toxicity of their compounds [1-16]. Heavy metals enter water and soil from polymetallic and iron ores, as well as from industrial waste: heavy industry, oil refining, etc. [4, 9, 10]. Heavy metals remain in the soil for a long time [1-3, 5, 6, 15, 16]. Due to the high toxicity of heavy metal compounds, reliable control over their content in the environment, industrial waste, biological objects, etc. is necessary. This is especially important due to the rapid growth in production and widespread consumption of oil with high cobalt content[1-14]. The toxicity of nickel compounds necessitates control of sometimes very low levels. To determine low nickel(II) contents, a number of reagents [1, 2, 5, 6, 7, 13] corresponding extraction-photometric techniques [1, 2] have been proposed. However, even the best of them are characterized by multi-operational nature [10, 13], labor intensity [11, 13] and duration [13, 14-16].

Here, the results of study the interaction of nickel(II) halogenazomercaptophenol with  $(HAMP, H_2L)$ {1-(5-fluoro-2-pyridylazo)-2-(FPHMP), 1-(5hydroxy-4-mercaptophenol

chloro-2-pyridylazo) -2-hydroxy-4-mercaptophenol (CPHMP)} in the presence of aminophenols (AP): 2-(N,N-

dimethylaminomethyl)-4-methylphenol ( $AP_1$ ), 2-(N,N-dimethylaminomethyl)-4-ethylphenol ( $AP_2$ ) were represented.

## **Experimental part**

**Reagents and solutions.** The initial solution (1 mg/ml) of Ni(II) was prepared by dissolving an accurately weighed portion of NiCl<sub>2</sub>×6H<sub>2</sub>O in water containing 2 ml of conc.  $H_2SO_4$  [5].

We used 0.01 M solutions of HAMP and AP in chloroform. Purified chloroform was used as an extractant.

The ionic strength of the solutions, equal to  $\mu=0.1$ , was maintained constant by introducing a calculated amount of KCl. To create the required acidity of the solutions, a 1 M HCl solution was used.

**Apparatus.** The optical density of the organic phase was measured on KFK-2 and SF-26. The pH value of the aqueous phase was controlled using an I-120.2 device. with glass electrode. IR spectra were obtained on a Specord-80 instrument, NMR spectra were obtained on a BRUKER-300 spectrometer.

**Method of synthesis of HAMP** [1,5,12]. The synthesis consists of two stages. I-stage of diazolation of 3-halopyridine, II-stage of interaction of diazonium salt with thiophenol.

At stage I, a solution of 2.4 ml (0.025 mol)

of halopyridine and 1.4 g of NaOH in 20 ml of water is added to a three-neck flask with a volume of 0.5 l. The mixture is heated until dissolved. The dissolved mixture was cooled to 0°C with ice. A solution of 1.725 g (0.025 mol) NaNO2 in 8 ml of water is added to the mixture and stirred with a mechanical stirrer. 5 ml of HCl solution is added dropwise to the mixture, controlling the temperature of the system (0°C). If the temperature rises above 0°C when adding HCl solution, add ice cubes from distilled water to the mixture. The reaction was carried out at 0°C for 30 min.

At stage II, 4.05 g (0.025 mol) of 2-hydroxy-4-mercaptophenol, 11.972 g (0.146 mol) CH<sub>3</sub>COONa and 10 ml of C<sub>2</sub>H<sub>5</sub>OH are added to a 0.5 ml three-neck flask. The resulting mixture is cooled to 0°C and the diazonium salt of halopyridine is added dropwise, stirring with a mechanical stirrer. The synthesis reaction of the azo compound is carried out for an hour at 0°C. The resulting yellow reaction product is filtered through filter paper and recrystallized from ethanol. Product yield was 52%.

$$X$$
 $N=N$ 
 $N=SH$ 
 $X = Cl, Br$ 

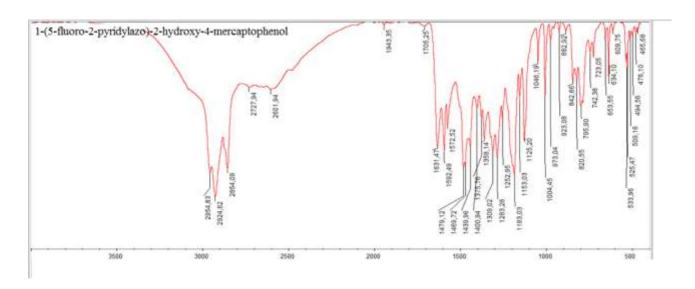
HAMP were characterized by IR (Fig.1) and NMR spectroscopy [17].

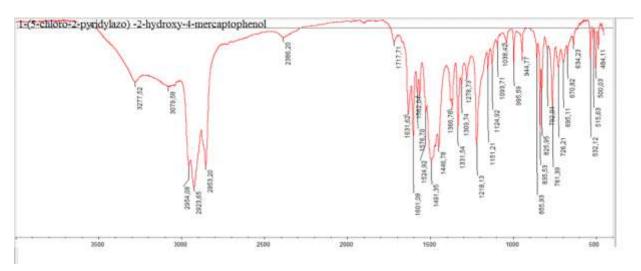
FPHMP - IR (KBr, cm<sup>-1</sup>): -3460 v (OH), 2570 v (SH), 1290 and 1170 v(C-N), 1395 v (N=N), 1250  $\delta$ (C-O).

 $^{1}$ H NMR (300,18 MHz, C<sub>6</sub>D<sub>6</sub>): δ 14.1 (s, 1H– OH), δ 2.562 (s, 1H – SH), δ 6.308 (s,1H Ar–H), δ 6.563 (s,1H Ar–H), δ 7.613 (s,1H Ar–H), δ 7.836 (s,1H Pr–H), δ 7.814 (s,1H Pr–H), δ 7.988 (s,1H Pr–H).

CPHMP - IR (KBr,  $cm^{-1}$ ) – 3460 v (OH), 2573 v (SH), 1294 and 1171 v(C-N), 395 v (N=N), 1250  $\delta$ (C-O).

<sup>1</sup>H NMR (300,18 MΓ<sub>II</sub>, C<sub>6</sub>D6):  $\delta$  14 (s, 1H– OH),  $\delta$  2.560 (s, 1H – SH),  $\delta$  6.304 (s,1H Ar–H),  $\delta$  6.560 (s,1H Ar–H),  $\delta$  7.616 (s,1H Ar–H),  $\delta$  7.812 (s,1H Pr–H),  $\delta$  7.993 (s,1H Pr–H),  $\delta$  8.621 (s,1H Pr–H).





**Fig. 1.** IR spectra of 1-(5-fluoro-2-pyridylazo)-2-hydroxy-4-mercaptophenol and 1-(5-chloro-2-pyridylazo)-2-hydroxy-4-mercaptophenol.

Depending on the acidity of the environment, HAMP can exist in three forms: H<sub>2</sub>L, HL<sup>-</sup>, HL<sup>2</sup>. The first proton of the -SH is eliminated at pH>3; the second proton of the -OH – at pH>6.

Methods. 0.1-0.8 ml, at intervals of 0.1 ml of the original nickel(II) solution, 2.5 ml of a 0.01 M HAMP solution, and 0.8-1.0 ml of AP were introduced into graduated test tubes with ground-in stoppers. The required pH value was adjusted by adding a 1 M HCl solution. The volume of the organic phase was brought to 5 ml with chloroform, and the aqueous phase was brought to 20 ml with distilled water. After 5 minutes, the organic layer was separated from the aqueous layer and its optical density was

measured at room temperature on KFK-2 at 600 nm.

**Selecting an extractant**. The degree of extraction increases in the order  $C_6H_{14} < C_6H_{12}$   $< CCl_4 = C_6H_6 < C_6H_5$  — $CH_3 < C_2H_4Cl_2 < C_6H_5Cl < CHCl_3$ . Rapid separation of layers and the maximum value of the molar absorption coefficient were obtained by extracting the complexes with chloroform (R = 98.2-99.5%).

The nickel content in the organic phase was determined photometrically using 1-dimethylglyoxime [6] after strip extraction, and in the aqueous phase - by the difference. Based on the extracted complexes, the distribution coefficient (D) and the degree of extraction (R,%) were assessed [3]:

$$D = \frac{[Ni]_{org}}{[Ni]_{aq}}; \qquad R = \frac{100 \times D}{(D + \frac{V_{aq}}{V_{org}})}$$

**Equilibrium and extraction constants.** the following processes occur: Let us assume that during complex formation

$$Ni^{2+} + 2H_2L \Leftrightarrow [NiL_2]^{2-} + 4H^+,$$
  

$$[NiL_2]^{2-} + 2APH^+ \Leftrightarrow [NiL_2](APH)_2$$
(1)

Equilibrium constant  $(K_{eq})$  of the reaction

$$K_{eq} = \frac{\{[NiL_2](APH)_2\}_{org}}{\{[NiL_2]^{2-}\}_{aq}\{[APH)^+]^2\}_{aq}} = \lg \frac{A_x}{A_0 - A_x} = D$$
(2)

$$K_{p} = \frac{D}{[(APH)^{+}]^{2}}$$

$$\tag{3}$$

Where,  $A_x$  is the optical density for this experiment;  $A_o$  – optical density at complete binding of cobalt ion into a colored complex; D – distribution coefficient.

Taking logarithm of the last expression, we get

$$lgK_{eq} = lgD-2lg[APH+]$$
 (4)

The value of the extraction constant  $(K_{eq})$  can be calculated from equation (5):

$$K_{ex} = \frac{\{[NiL_2](APH)\}_{org}}{\{[Ni]^{2+}aq\{[H_2L]^2\}_{org}\{(APH)^2\}_{org}} = \frac{D}{\{[H_2L]^2\}_{org}\{[APH]^2\}_{org}}$$
(5)

Taking the logarithm of expression (5), we get:

$$\lg K_{ex} = \lg D - 2\lg [H_2 L^{2-}] - 2\lg [APH^+]$$
(6)

The values of  $K_{eq}$  and  $K_{ex}$ , calculated using formulas (4) and (6), respectively, are given in Table 1.

Table 1. Basic chemical and analytical characteristics of Ni(II) complexes with L and AP

Compound	pН		λ, nm	ε×10 <sup>-4</sup>	$lgK_{eq}$	$lg_{Kex}$
	Form.	Opt.				
Ni- FPHMP -AP <sub>1</sub>	2.0-9.8	3.3-6.2	610	1.7	8.51	14.35
Ni- FPHMP -AP <sub>2</sub>	2.2-9.6	4.1-7.0	638	1.5	8.67	14.46
Ni- CPHMP -AP <sub>1</sub>	3.0-9.7	4.9-7.8	569	1.4	8.49	13.99
Ni- CPHMP -AP <sub>2</sub>	2.3-8.2	4.2-7.0	590	1.3	8.81	13.72

#### **Results and discussion**

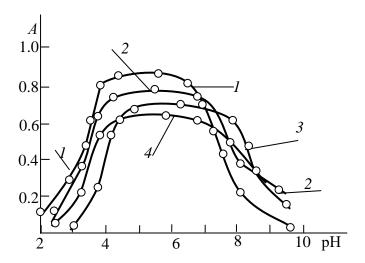
Effect of pH of the aqueous phase. The dependence of optical density on pH is shown in Fig. 2. The optimal acidity range, at which the optical density is maximum and constant, is at  $pH_{opt.}$  3.3 – 7.8 (pH 2.0 – 9.8). At pH > 9.8 of the solution, the extraction of mixsed ligand

complexes (MLC) is practically not observed, which is apparently due to an increase in free AP molecules and the formation of hydrolyzed forms of nickel (II).

Influence of holding time, ligand concentration and phase volume ratios. Ni(II)

MLC with L and AP are stable in aqueous and organic solvents and do not decompose within three days, and after extraction - for more than a

month. Maximum optical density is achieved within 5-10 minutes.



**Fig.2.** Effect of pH of the aqueous phase on the formation and extraction of Ni(II) MLC with L and AP.

1– Ni- FPHMP -AP<sub>1</sub>; 2– Ni- FPHMP -AP<sub>2</sub>; 3–Ni- CPHMP -AP<sub>1</sub>; 4 –Ni- CPHMP -AP<sub>2</sub> 
$$C_{Ni(II)} = 3.4 \times 10^{-5} \text{ M}, C_{H2L} = (1.10-2.35) \times 10^{-3} \text{ M}, C_{AP} = (6.31-8.42) \times 10^{-4} \text{ M}; KFK-2, \ell=0.5 \text{ cm}.$$

The optimal condition for the formation and extraction of MLC is  $(1.10\text{-}2.35)\times10^{-3}$  mol/l concentration L and  $(6.31\text{-}8.42)\times10^{-4}$  mol/l – AP.

The degree of extraction of Ni(II) in the form of MLC does not depend on the ratio of the volumes of aqueous and organic phases in a wide range (from 5:5 to 110:5), which allows for simultaneous concentration and photometric determination of Ni(II). Thus, an increase in the aqueous phase by 20 times relative to the organic phase does not affect the completeness of extraction.

Electronic absorption spectra. The maximum analytical signal during complexation of nickel with H<sub>2</sub>L and AP is noticeable at 590-638 nm. H<sub>2</sub>L absorbs maximum at 510-520 nm. During complex formation, a bathochromic shift of the light absorption maximum by 80-118 nm is observed.

The molar absorption coefficients or extinction coefficients of Ni(II) complexes with

L and AP at  $\lambda$ max were calculated by the saturation method and amount to  $\epsilon = (1.3-1.7)\times 10^4$ .

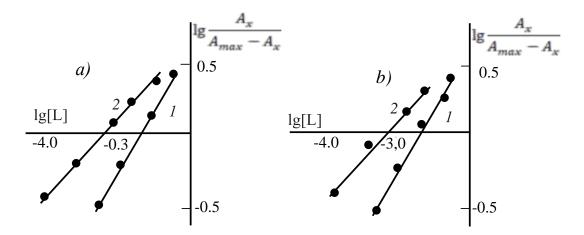
Ni(II) MLC extracts obey the basic law of light absorption at concentrations of 0.15-21 µg/ml. The equation of the calibration graphs are given in Table. 2. Based on the equations of the calibration graphs, the photometric detection limit (PDL) and the detection quantitation limit (DQL) of Ni(II) were calculated in the form of MLC [18].

Composition and structure of complexes. During the formation of complexes, the coordinating ion is  $Ni^{2+}$ . The stoichiometry of the studied complexes (Ni:L:AP=1:2:2) was determined by the methods of equilibrium shift and relative yield [19] (Fig. 3). In this case, the number of protons displaced by it from one  $H_2L$  molecule turned out to be equal to 2. Calculations showed that MLC in the organic phase does not polymerize and is in a monomeric form ( $\gamma = 0.94-1.07$ ).

**Table 2.** Analytical characteristics of MLC of Ni(II) with L and AP

				\-() \	
Compound	PDL	DQL	Sensitivit	Linear	Equation
	ng/cm <sup>3</sup>	ng/cm <sup>3</sup>	y, ng/cm <sup>2</sup>	range of	of
				calibratio	calibration

				n graphs,, mg/5 ml	graphs y=ax+b
Ni- FPHMP -AP <sub>1</sub>	12	35	1.49	0.20-18	0.295x + 0.039
Ni- FPHMP -AP <sub>2</sub>	13	34	1.66	0.15-20	0.286x + 0.037
Ni- CPHMP -AP <sub>1</sub>	8	29	1.69	0.15–19	0.253x + 0.035
Ni- CPHMP -AP <sub>2</sub>	11	35	1.78	0.25-21	0.217x + 0.028



**Fig. 3.** Determination of the composition of the MLC by the equilibrium shift method for Ni-FPHMP-AP<sub>1</sub> (*a*) and Ni-CPHMP-AP<sub>1</sub> (*b*): 1 - Ni: L; 2 - Ni: AP;  $C_{\text{Ni(II)}} = 3.4 \times 10^{-5} \text{ M}$ ; SF-26, 1 = 1.0 cm

IR spectra of Ni(II)-L-AP complexes were recorded and compared with the IR spectra of L [13]. The difference in the spectra of L and the

Ni-L-AP system indicates a strong interaction (Table 3).

<b>Table 3.</b> Comparison of IR spectra of Ni(II)-L-AP complexes with IR spectra of	Table 3. Co	omparison	of IR spect	ra of Ni(II)-L-Al	P complexes with	i IR spectra of L
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Compound	Groups, cm <sup>-1</sup>						
	v <sub>O-H</sub>	v <sub>S-H</sub>	v <sub>C-N</sub>	$\delta_{\text{C-O}}$	v <sub>-N=N-</sub>	$v_{APH}^{+}$	
FPHMP	3600-3200	2600	1290	1250	1394	1370	
СРНМР	3610-3208	2601	1170	1258	1395	1372	
Ni- FPHMP - AP <sub>1</sub>	-	2589	1283	1249	1318	1680	
Ni- FPHMP - AP <sub>2</sub>	-	2592	1279	1261	1320	1373	
Ni- CPHMP - AP <sub>1</sub>	-	2585	1275	1263	1316	1371	
Ni- CPHMP - AP <sub>2</sub>	-	2581	1286	1255	1312	1369	

Based on the data obtained, the represented by the formula  $[NiL_2](APH^+)_2$ : composition of the extracted complexes can be

$$\begin{array}{c|c}
S & -N = N - X \\
O & Ni \\
X & -N = N - S
\end{array}$$

$$\begin{array}{c|c}
CH_2 - NH - (CH_3)_2 \\
R
\end{array}$$

 $X = -Cl, -Br; R = -CH_3, -C_2H_5$ 

Thermogravimetric study of NiC<sub>23</sub>H<sub>14</sub>S<sub>2</sub>O<sub>2</sub>F and NiC<sub>23</sub>H<sub>14</sub>S<sub>2</sub>O<sub>2</sub>Cl {[NiL<sub>2</sub>](AP<sub>1</sub>H)<sub>2</sub>} complexes: showed that their thermal decomposition occurs in three stages: at  $60-120^{\circ}\text{C}$  water evaporates (mass loss -3.79%; in the case of FPHMP 3.62%), at 340  $-390^{\circ}\text{C}$  AP<sub>1</sub> decomposes (weight loss 22.57%; in the case of CPHMP 21.51%), and at 490–510°C - FPHMP (weight loss 67.51%; in the case of CPHMP 69.04%). The final product of thermolysis of the complex is NiO.

Influence of foreign ions. To evaluate the applicability of MLC extracts for the separation and determination of Ni(II), the interfering influence of foreign ions was studied. The determination of Ni (II) with H2L and AP is not interfered with by ions of alkali, alkaline earth elements and rare earth elements. The interfering influence of ions is eliminated by changing the pH of the medium using masking substances and using extraction. The interfering

influence of Nb(V), Ta(V), Ti(IV) is eliminated by increasing the pH and using fluoride ion. The interfering influence of Ti(IV) is ascorbic acid, Cu(II) is thiourea, Mo(VI) and Nb(V) is oxalate ion. When using a 0.01 M EDTA solution, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI) do not interfere with the determination.

Comparison of methods for determination of Ni(II) with known reagents and L in the presence of AP. In Table 4 provides data that allows us to compare various methods for determining nickel. It can be seen that L has advantages over other reagents: the light absorption maximum is shifted to the longwavelength region of the spectrum [20-25], the molar light absorption coefficient is much higher than the molar light absorption coefficients of other complexes [20, 21, 24], the pH of the reaction shifts to a more acidic region [20, 21], which increased selectivity.

**Table 4.** Comparative characteristics of methods for the determination of nickel(II)

Reagent*	pH (solvent)	λ, nm	ε×10 <sup>-4</sup>	Linear range of	Reference
				calibration curves,	S
				μg/ml	
Dimethylglyoxime	8-12 (CHCl <sub>3</sub> )	470	1.56	0.26-2.10	[20]
N - ECCATSC*	$6.0 (C_6H_6)$	400	1.40	0.4-10	[21]
MCCTC*	$6.0 (C_6 H_6)$	410	1.67	0.1-12	[22]
TCAH*	$8.7 - 9.5 (C_6H_6)$	522	3.17	0.02-0.70	[23]
PPTSC*	$4-6(C_6H_6)$	430	1.92	0.5-50	[24]
HBABPH*	$4(C_6H_6)$	497	2.85	0.01-0.10	[25]
FPHM -AP <sub>1</sub>	1.2-8.4 (CHCl <sub>3</sub> )	635	4.60	0.20-18	
CPHM -AP <sub>1</sub>	2.3-8.4 (CHCl <sub>3</sub> )	650	4.40	0.15-20	

Note: N - ECCATSC — N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone, MCCTC-7—Methyl-2-chloroquinoline-3- carbaldehydethiose-mycarbazone, TCAH — Thiazol-2-carbaldehyde-2-quinolylhydrazone, PPTSC —Pyridoxal-4-phenyl-3-thiosemi-carbazone, HBABPH — 4-4-Hydroxybenzaldehyde-4- bromophenylhydrazine

The proposed method, under already established optimal conditions, was used to determine Ni(II) in oil and oil products.

**Determination of nickel(II) in oil and oil products of Baku (Table 5).** For analysis, 40 g of the test fuel was placed in a porcelain cup and burned. Then a porcelain cup with ash was placed in a muffle at a temperature of  $550 \pm 20^{\circ}$  C and kept at a temperature of 1 hour. After cooling, 5 ml of HCl (1:1) was added to the cup, boiled to dryness and 0.5 g of anhydrous Na<sub>2</sub>CO<sub>3</sub> was added to it. Then the cup was

placed for 2-3 minutes in a muffle heated to 800°C. After cooling, the alloy in the cup was dissolved in distilled water and filtered into a capacitance flask. 50 ml and diluted with water to the mark. An aliquot of the resulting solution was taken, transferred to a separatory funnel, the pH was created at 2.8-6.0, and 2.0-2.5 ml of 0.01 M L and AP were added. The volume of the organic phase was brought to 5 ml with chloroform, and the total volume was brought to 25 ml with distilled water. The mixture was shaken for 5 minutes. After phase separation,

the light absorption of the extracts was measured on KFK-2 at 540 nm in a cuvette with an absorbing layer thickness of 0.5 cm. The

Ni(II) content was found using a calibration graph.

<b>Table 5.</b> Results of determination	on of nickel(II) in o	oil and oil products Bak	a (n = 6, P = 0.95)

		Found, mg/L		Relative
Analysis object	Introduced	With	$\overline{X} + \frac{t_p \cdot S}{}$	standard
	mg/l	additive	$x \pm \frac{1}{\sqrt{n}}$	deviation
Oil	10	16.16	$(6.16\pm0.19)\cdot10^{-5}$	0.07
Fuel oil	10	12.64	$(2.64\pm0.31)\cdot10^{-3}$	0.05
Hydron	10	14.28	$(4.28\pm0.19)\cdot10^{-3}$	0.08

#### Conclusion

- 1. Reaction nickel with of halogenazomercaptophenol (HAMP) {1-(5fluoro-2-pyridylazo)-2-hydroxy-4mercaptophenol, 1-(5-chloro-2-pyridylazo)-2-hydroxy-4-mercaptophenol} in the presence aminophenols (AP): 2-(N,Ndimethylaminomethyl)-4-methylphenol, (N,N-dimethylaminomethyl)-4-ethylphenol was studied.
- 2. A single extraction with chloroform yields 97.1–98.9% nickel (II) in the form of a mixed-ligand complex. The optimal acidity
- range, at which the optical density is maximum and constant, is at pH<sub>op.</sub> 3.3 7.8 (pH 2.0 9.8). Maximum optical density is achieved within 5-10 minutes. The molar absorption coefficients of Ni(II) complexes at  $\lambda_{max}$  were calculated by the saturation method and amount to  $\epsilon_{610-650} = (1.3-1.7)\times10^4$ .
- 3. Newly developed methods for extractionphotometric determination of Ni (II) for use in the analysis of oil and petroleum products Baku.

### References

- Zalov A.Z., Isgenderova K.O., Askerova Z.G. Spectrophotometric research into interaction nickel (II) with 1- (2- pyridylazo) -2- hydroxy -4-mercaptofenol and aminophenols // Chemical Problems, 2021, № 3 (19), pp. 150-160.
- Shabani A.M., Dadfarnia S., Shahbazi Z., Jafari A.A. Extraction-spectrophotometric determination of nickel at microgram level in water and wastewater using 2-[(2-mercaptophenylimino)methyl]phenol // Bulletin of Chemical Society of Ethiopia, 2008, V. 22, No.3, pp. 323-329.
- 3. Ravichandran C., Benzil D., Ramachandraiah C., Chandrasekhar K.B. Extraction and spectrophotometric determination of nickel in water, alloys and edible oil samples // *International Journal of Bioassays*, 2015, V. 4, No. 11, pp. 4468-4472.
- 4. Rasulov Ch.K., Zalov A.Z., Ibrahimov H.I., Mammadova Sh.A. Selective and sensitive

- extraction-photometric method for determining cobalt (II) in oil and petroleum products // *Processes of Petrochemistry and oil Refining*, 2023, V. 24, No. 4, pp. 743-753.
- 5. Lokhande P. Solvent Extraction and Spectrophotometric Determination of Nickel (II) using 2 Hydroxy 1- Naphthaldehyde Thiosemicarbazone (HNT) as an Analytical Reagent // International journal of trend in scientific research and development, 2019, V. 3, No 3, pp. 694-697. DOI: https://doi.org/10.31142/ijtsrd22964.
- 6. Zalov A.Z., Novruzova N.A., Aliyev S.G. Extraction-spectrophotometric study on the chromium (VI)- 2-hydroxy-5-nitrothiophenol-hydrophobic amines-water-chloroform system // Вестник Башкирского Государственного Педагогического Университета Им. М. Акмуллы. 2023, V. 69, No. 1, pp.4-13.

- 7. Javadzade T.A., Mardanova V.I., Sudzhaev A.R. Nagiev Kh.D., Chiragov F.M. Determination of trace amounts of nickel(II) after preliminary extraction of complexes with 1-(2-allylamino-1-methylethyl)thiourea // Journal of Analytical Chemistry, 2023, V. 8, No. 11, pp. 1014-1018
- 8. Mammadova Sh.A., Abasqulieva U.B., Zalov A.Z., Novruzova N.A. Spectrophotometric research into complexation of tungsten(VI) with o-hydroxythiophenol derivatives in the presence of hydrophobic amines // Chemical Problems, 2022, No. 2 (20), pp.164-174.
- Asgarova Z.G., Zalov A.Z., Rasulov Ch.K. Highly selective and sensitive extractionphotometric method for the determination of nickel (II) in water, oil and petroleum products of Baku // Processes of Petrochemistry and oil Refining, 2022, V. 23, No 4. pp. 544-555.
- 10. Rasulov C.G., Zalov A.Z., Mammadova S.A., Huseynova G.A. Spectroscopic studies of complexation cu, co, ni using aminophenols. determination of Cu(II), Co(II) and Ni(II) in wastewater, bottom sediments, oil and oil products Baku // Processes of Petrochemistry and oil Refining, 2022, V. 23, No 2, pp. 163-174.
- 11. Muthuselvi R. Determination of nickel (II) by spectrophotometry in micellar media. *Pharmaceutical Analytical Chemistry: Open Access.* 2017, V. 3, No. 3, pp. 129-133. doi: 10.4172/2471-2698.1000129.
- 12. Mambetkaziev E.A. Electrochemistry of dipyridyl complexes of metals. M.: Nauka, 1986. 156 p.
- 13. Marczenko Z. Baltsejak M.K. Metodi Spectrophotometrii v UF I vidimoy oblastyax M: Binom, Laboratoriya znaniy. 2007. P. 711 (in Russian).
- 14. Dospatliev L., Georgieva N.V., Pavlov A.I., Yaneva Z. Extraction-spectrophotometric determination of cobalt in soils by the application of iodine nitrotetrazole chloride (INT) // Trakia Journal of Sciences, 2010, V. 8, No. 2, pp. 16-19.
- 15. Safavi A., Mir M., Abdollahi H. Simultaneous spectrophotometric determination of iron, titanium and aluminium by partial least-squares

- calibration method in micellar medium // *Journal Anal. Lett.* 2003, V. 36, No. 3, pp. 699 –717.
- Nagiyev Kh.D., Alieva A.A., Chiragov F.M. Determination of trace amounts of iron in fruits // Analytics and control. 2013.
   V. 17. No 1. p. 107–111.
- 17. Anisimova N.A. Identification of organic compounds. *Gorno-Altaisk: RIO Gorno.-Alt. gosunta*, 2009. 118 p. (in Russian).
- 18. Dorohova E.N., Prokhorova G.V. Analytical chemistry (physical and chemical methods of analysis). M: Higher school. 1991. 250 p. (in Russian).
- 19. Bulatov M.I., Kalinkin I.P. A practical guide to photocolorimetric and spectrophotometric methods of analysis. Ed. Chemistry. Moscow. 1972. 426 p. (in Russian).
- 20. Yoshikuni N., Baba T., Tsunoda N. et al. Oguma K. Aqueous two-phase extraction of nickel dimethyl-glyoximato complex and its application to spectrophotometric determination of nickel in stainless steel // *Talanta*, 2005, V. 66, № 1, pp. 40–44
- 21. Ramachandraiah C., Kumar J.R., Reddy K.J. Development of a highly sensitive extractive spectrophotometric method for the determination of nickel(II) from environ- mental matrices using N-ethyl-3-carbazolecarboxalde-hyde-3-thiosemicarbazone // Journal Environ Management, 2008, V. 88, № 4, pp. 729–736
- 22. Jadhav V.A., Kulkarni M.U. 7-Methl-2-chloroquin- oline-3-carbaldehyde thiosemicarbazoneas analytical reagentfor copper, cobalt and nickel(II) // Journal of the Indian Chemical Society, 1992, V. 69, № 5, pp. 287–288
- 23. Otomo M., Watanabe T., Moriya M. Solvent Extraction and Spectrophotometric Determination of Nickel (II) with Thiazole-2-carbaldehyde 2-Quinolylhydrazone. *Analytical Sciences*, 1986, Vol. 2, № 6, pp. 549–552
- 24. Sarma L.S., Kumar J.R., Reddy K.J.

  Development of highly sensitive extractive spectro-photometric determination of nickel(II) in medicinal leaves, soil, industrial effluentsand

standard alloy samples using pyridoxal-4-phenyl-3-thiosemicarbazone // Journal of Trace Elements in Med. and Biol., 2008, V. 22, № 4, pp. 285–295

25. Rekha D., Kumar J.D., Jayaraj B.

Nickel(II) Determination by Spectrophotometry Coupled with Preconcentration Technique in Water and Alloy Samples // Bull. Korean Chem. Soc., 2007, V. 28, №. 3, pp. 373–378.

# NİKEL(II) – HALOGENAZOMERKAPTOFENOL - AMİNOFENOL - SU – XLOROFORM SİSTEMİNİN EKSTRAKSİYON-SPEKTROFOTOMETRİK TƏDQİQİ

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**Xülasə:** Nikelin (II) halogenazomerkaptofenol (HAMF) {1-(5-fluor-2-piridilazo)-2-hidroksi-4-nmerkaptofenol, 1-(5-xlor) -2-piridilazo)-2-hidroksi-4-merkaptofenol və aminofenol (AP) {2-(N,N-dimetilaminometil)-4 – etilfenol} iştirakı ilə qarşılıqlı təsiri ekstraksiyalı-fotometrik üsulu ilə tədqiq edilmişdir. Xloroform ilə birdəfəlik ekstraksiya ilə nikelin (II) 97.1-98.9%-i müxtəlif liqandlı kompleks (MLK) birləşmə şəklində ekstraksiya olunur. Optik sıxlığın maksimum və sabit olduğu optimal turşuluq pH<sub>op</sub> 3.3-7.8 (pH 2.0-9.8) uyğun gəlir. Maksimum optik sıxlıq 5-10 dəqiqə ərzində yaranır. Bu birləşmələrin əmələ gəlməsi və ekstraksiyası üçün optimal şərait (1.10-2.35)×10<sup>-3</sup> mol/l HAMF konsentrasiyası və (6.31-8.42)×10<sup>-4</sup> mol/l – AF-dir. Ni(II) komplekslərinin molyar udma əmsalları  $\lambda_{max}$ -da doyma üsulu ilə hesablanmış və ε<sub>610-650</sub> = (1.3-1.7)×10<sup>4</sup> olmuşdur. Üzvi fazada MLK monomer formadadır (γ = 0.91-1.09). Yeni işlənmiş üsullar Bakı neft və neft məhsullarının analizində Ni(II)-nin ekstraksiya-fotometrik təyini üçün istifadə edilmişdir.

Açar sözlər: nikel, halogenazomerkaptofenol, neft, mazut, qudron, aminofenol.

## ЭКСТРАКЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ СИСТЕМЫ НИКЕЛЬ(II) – ГАЛОГЕНАЗОМЕРКАПТОФЕНОЛ - АМИНОФЕНОЛ - ВОДА – ХЛОРОФОРМ

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Резюме: Экстракционно-фотометрическим методом изучены взаимодействия никеля (II) с {1-(5-фтор-2-пиридилазо)-2-гидрокси-4галогеназомеркаптофенолами  $(\Gamma AM\Phi)$ меркаптофенолом, 1-(5-хлор-2-пиридилазо)-2-гидрокси-4- меркаптофенол в присутствии аминофенолов (AP): 2-(N,N-диметиламинометил)-4-метилфенол, 2-(N,N-диметиламинометил)-4-этилфенол. При однократной экстракции хлороформом извлекается 97.1-98.9% никеля(II) в виде разнолигандного комплекса (РЛК). Оптимальный интервал кислотности, при котором оптическая плотность максимальна и постоянна, находится при  $pH_{on}$  3.3-7.8 ( $pH_{of}$  2.0-9.8). Максимальная оптическая плотность достигается в течение 5-10 мин. Оптимальным условием образования и экстракции этих соединений является (1.10- $(6.31-8.42)\times 10^{-3}$  моль/л концентрация ГАМФ и  $(6.31-8.42)\times 10^{-4}$  моль/л – АФ. Молярные коэффициенты поглощения комплексов Ni(II) при  $\lambda_{\text{макс}}$  вычислены методом насыщения и составляют  $\varepsilon_{610-650} = (1.3-1.7) \times 10^4$ . РЛК в органической фазе находятся в мономерной форме (у=0.91-1.09). Новые разработанные методы экстракционно-фотометрического определения Ni(II) использованы при анализе нефти и нефтепродуктов Баку.

Ключевые слова: никель, галогеназомеркаптофенол, нефть, мазут, гудрон, аминофенол.