



INVESTIGATION OF COBALT(II) COMPLEXING WITH 2-HYDROXY-5-NITROTHIOPHENOL AND AMINOPHENOLS

Shahla Adalat Ibrahimova

Baku State University

E-mail: zalov1966@mail.ru

The complex formation of cobalt(II) with 2-hydroxy-5-nitrothiophenol (HNTP) and aminophenols (AP) was studied by physicochemical methods. Of the aminophenols, 2(N, N-dimethylaminomethyl)-4-ethylphenol (AP₁) and 2(N, N-dimethylaminomethyl)-4-iodophenol (AP₂) were used. Mixed-ligand complexes are formed in a slightly acidic medium (pH_{opt} 5.5–6.4). For one extraction, Co(II) is extracted with chloroform by 98.8–99.3% in the form of a mixed ligand complex (MLC). The optimal condition for the formation and extraction of these compounds is $(1.2-2.0) \times 10^{-3}$ mol/l HNTP concentration and $(2.0-2.5) \times 10^{-3}$ mol/l AP. The ratio of the reacting components in the MLC corresponds to Co(II) : HNTP : AP = 1:2:2. The maximum light absorption is observed at $\lambda = 520-530$ nm. The molar light absorption coefficients are $(3.78-3.95) \times 10^4$. Based on the obtained data, photometric methods for the determination of cobalt in various industrial and natural objects have been developed.

Keywords: cobalt, 2-hydroxy-5-nitrothiophenol, aminophenol, mixed ligand complexes, chloroform

INTRODUCTION

Cobalt (II) is a biologically active metal. This requires constant monitoring of technogenic pollutants and migration of toxic substances in the environment and creates the need for prompt and reliable control of the content of heavy metals with toxic properties.

For the photometric determination of cobalt, reagents with an o-nitrosophenol group or a similar structure with an oxime group are quite selective [1]. The most widespread are methods that use organic reagents - nitrosonaphthol derivatives, pyridine azo compounds, of which 4-(2-pyridylazo)-resorcinol is widely used [2].

For the extraction-photometric determination of cobalt in various natural and industrial objects, mixed-ligand complexes (MLC) of cobalt with 4-(2-pyridylazo) resorcinol and 1,4-diphenyl-3-(phenyl-amino)-1H-1,2,4-triazole [3], with 4-(2-pyridylazo)resorcinol and tetrazolium salts [4].

The present work is devoted to the spectrophotometric study of mixed-ligand complexes (MLC) of Co(II) with 2-hydroxy-5-nitrothiophenols (HNTP, H₂R) and aminophenols. Of the aminophenols (AP), we used 2 (N,N-dimethylaminomethyl)-4-ethylphenol (AP₁), 2(N,N-dimethylaminomethyl)-4-iodophenol (AP₂).

MATERIAL AND METHODS

Reagents and instruments. The stock solution (1 mg/mL) of Co(II) was prepared by dissolving an accurate weight of CoSO₄ · xH₂O in water containing 2 mL of conc. H₂SO₄, and dilute with water to 1L [5].

We used a 0.01 M solution of HNTP and AP in chloroform. Purified chloroform was used as an extractant.

An acetate buffer solution was used to create the required acidity of the solutions. All reagents used were analytical grade.

The optical density of the organic phase was measured on KFK-2. Spectrophotometric measurements in the UV and visible regions were carried out on an SF-26 spectrophotometer. The pH value of the solutions was controlled using an I-130 ion meter with a glass electrode. IR spectra were taken on a Specord-M80 spectrophotometer.

The process of thermolysis of the compounds was studied using a Shimadzu TGA-50H derivatograph in air in the range of 20–1000°C, the heating rate was 10 deg/min. The test substances and the standard were heated in platinum crucibles.

Methods. In graduated test tubes with ground stoppers, from 0.1 to 1.0 ml, with an interval of 0.1 ml of the initial nickel(II) solution, 2.8 ml of a 0.01 M HNTP solution, and 2.2 ml of a 0.01 M solution of AP were introduced (the volume of the organic phase was 5 ml). The required pH value was adjusted by adding 1 M HCl solution or buffer solution. The volume of the aqueous phase was adjusted to 20 ml with distilled water. After complete phase separation, the organic layer was separated and its optical density was measured at room temperature on KFK-2 at 540 nm ($l = 0.5$ cm).

Determination of Co (II) in sewage water and Bottom sediments. 1 l taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of HNO_3 , was transferred to a 50 ml flask and diluted to the mark with water.

Determination of Co (II) in plants. A portion of beans (10 g) was crushed and dried in a porcelain dish at 120°C. The dry residue is heated in a muffle furnace at 500°C. The ash was dissolved in diluted (1:1) HNO_3 and evaporate to moist salts, which are then dissolved in water, filtered into a volumetric flask of 100 ml. The cobalt content is determined with HNTP and AP.

RESULTS AND DISCUSSION

Influence of the pH of the aqueous phase. The extraction efficiency strongly depends on the pH of the solution, and the quantitative extraction of MLC is maximum at pH 5.5–6.4. The presence of the second ligand led to a shift in the optimal acidity of the complex formation to a more acidic region, the pH_{opt} range being wider than in the case of a two-component compound.

As the pH of the solution decreases, the extraction gradually decreases, which is apparently associated with a decrease in the concentration of the ionized form of GNTP and, most likely, it is present in the solution in the undissociated form.

At high pH values, the complex formation process is complicated by the hydrolysis of the cobalt ion.

The dependence of optical density on pH is shown in fig. 1. The presence of one maximum of optical density within the indicated pH limits confirms the assumption of the formation of one complex compound.

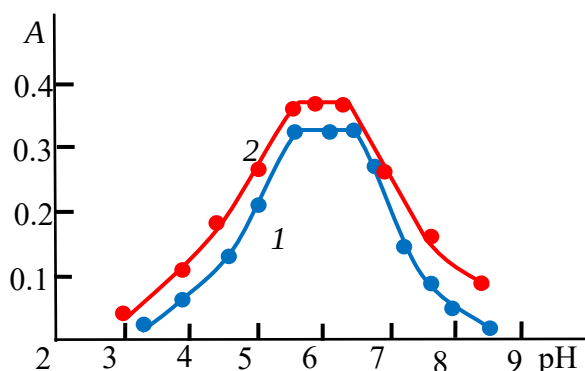


Figure 1. Absorbance of mixedligand complexes as a function of the pH of the aqueous phase: Co- HNTP- AP_1 (curve 1) and Co- HNTP- AP_2 (curve 2).

$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{HNTP}} = (1.2 - 2.0) \times 10^{-3} \text{ mol L}^{-1}$, $C_{\text{AP}} = (2.0 - 2.5) \times 10^{-3} \text{ mol L}^{-1}$, KFK-2, $l = 0.5$ cm, $\lambda = 540$ nm

MLC Co(II) with HNTP and AP are stable in aqueous and organic solvents and do not decompose for three days, and after extraction for more than a month. The maximum optical density is reached within 8-10 minutes.

Absorption spectra. The maximum analytical signal upon complex formation of MLC and Co(II) is observed at 520–530 nm (Fig. 2), where the complexing agent does not absorb (HNTTP absorbs maximum at 274 nm). Thus, the bathochromic shift is 246–256 nm. The close values of the light absorption maxima allow us to conclude that the resulting complexes are ion associates. The reaction contrast is high: the initial reagents are colorless, and the complexes are red-violet.

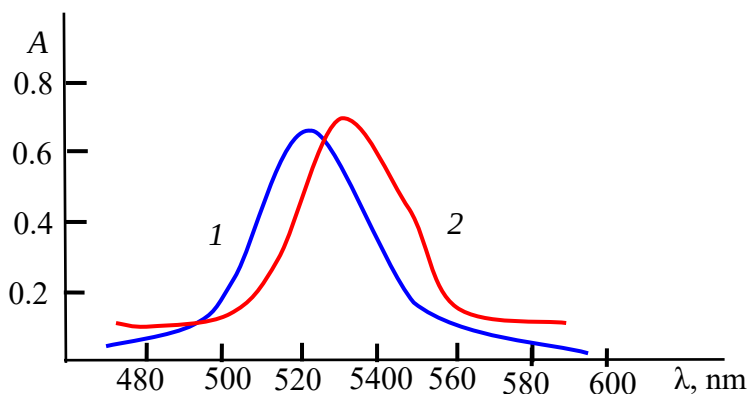


Figure 2. Absorption spectra of the complexes: Co- HNTTP-AP₁ (curve 1) and Co- HNTTP-AP₂ (curve2)

$C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{HNTTP}} = (1.2 - 2.0) \times 10^{-3} \text{ mol L}^{-1}$, $C_{\text{AP}} = (2.0 - 2.5) \times 10^{-3} \text{ mol L}^{-1}$, pH 5.5-6.4, CΦ-26, $l = 1 \text{ cm}$

Influence of phase volume ratios. The degree of extraction of Co(II) in the form of MLC does not depend on the ratio of the volumes of the aqueous and organic phases in a wide range (from 5:5 to 120:5), which allows simultaneous concentration and photometric determination of Co(II). Thus, an increase in the aqueous phase by 25 times relative to the organic phase does not affect the completeness of the extraction.

Determination of the composition and IR-spectroscopic study of the complexes. The stoichiometry of the studied complexes was established by the straight line method and confirmed by the methods of equilibrium shift and relative yield [6]. The data shown in fig. 3 show that the ratio of Co(II):HNTTP:AP = 1:2:2 in the composition of the MLC.

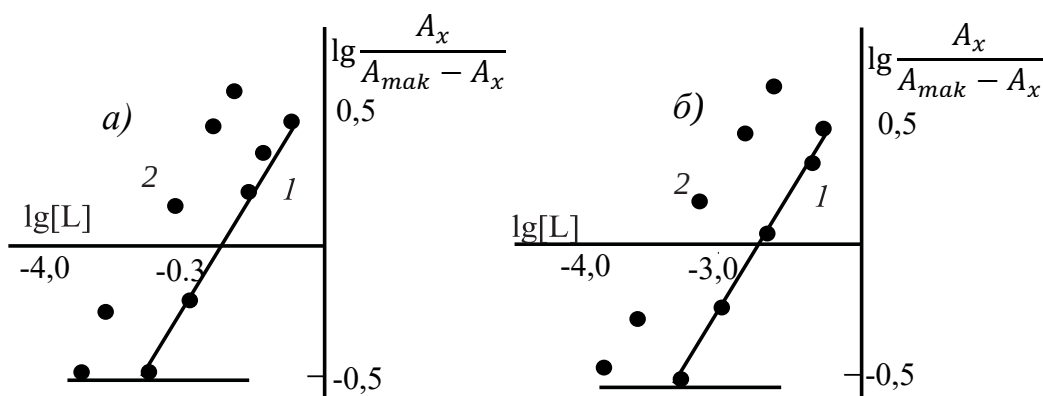


Figure 3. Determination of the composition of complexes using the straight line method for:
1. Co- HNTTP; 2. Co - AP a)Co- HNTTP -AP₁; b) Co- HNTTP-AP₂. $C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, ;
pH = 5; CP-26, $l = 1 \text{ sm}$

The nature of the bond in the Co(II) complexes was refined by IR spectroscopic analysis of the isolated complex, HNTP and AP₁. IR spectra were taken on a Specord M 80 spectrophotometer in the spectral range 400–4000 cm⁻¹ at 300 K.

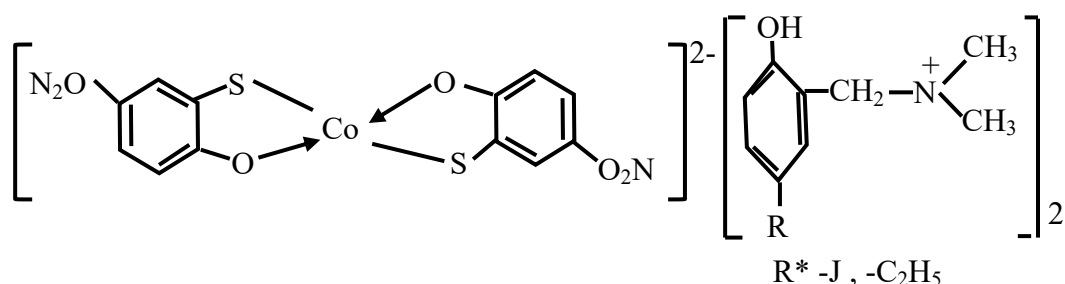
The disappearance of the band at 2580 cm⁻¹, characteristic for the spectrum of HNTP, and appearance of corresponding bands in the spectrum of the complex, which are shifted toward lower frequency, suggests that the sulphur atoms are involved in complex formation. The observed decrease in the intensity of the absorption bands at 3200–3600 cm⁻¹ with a maximum at 3460 cm⁻¹ and the appearance of a broad band in the region of 3050–3150 cm⁻¹ shows that the hydroxyl group participates in the formation of a coordination bond [7].

Thermogravimetric study of complexes. The thermogravimetric analysis of Co-HNTP-AP shows that the DTA curve of the complex in the temperature range 440–580°C has one exothermic peak, which is accompanied, judging by the weight loss, by the elimination of AP. At temperatures above 580°C, thermolysis of HNTP occurs. The final product of the thermolysis of the complex is Co₂O₃.

Chemistry of formation of MLCs of Co(II) with HNTP and AP. To elucidate the chemistry of the complex formation process, it is necessary to know the number of protons displaced from the FAG reagent, as well as to establish the form of the Co(II) cation that interacts with the reagent. The reaction form of Co(II) and the number of displaced protons were determined using the Nazarenko method [8]. The constructed dependence of –lgB on pH with an integer value of the slope tangent is observed for Co²⁺ ions. Thus, during the formation of MLC, the Co²⁺ ion is the coordinating one. Since the tangent of the angle in this case is equal to 2, the complexation proceeds with the displacement of one proton from one molecule of HNTP.

To determine the actual composition of the complexes, the polymerization coefficients of the complexes (γ) were preliminarily estimated according to the procedure [10]. For all the systems studied, the γ values are close to 1 ($\gamma = 1.02$ – 1.08), i.e., the studied reagents form mononuclear complexes with Co(II) ions.

Taking into account the ratios of the reacting components, the state of the resulting complexes in the organic phase, IR spectroscopic and thermogravimetric studies, as well as literature data, we can assume the following probable formula for the formed extractable outer-sphere MLCs:



During the formation of complexes, five-membered chelate cycles are formed.

The apparent molar absorption coefficients for the complexes at $\lambda_{\max}$ were calculated from the absorption spectra. The true values of the molar absorption coefficients were calculated by the Komar method. The molar absorption coefficients of the complexes are $\varepsilon = (3.78$ – $3.95) \times 10^4$.

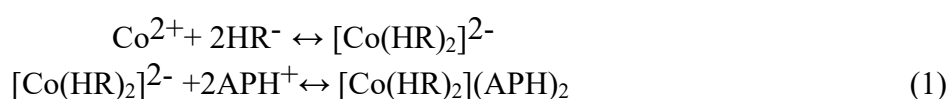
The two-phase stability constants of the complexes were calculated by the curve-crossing method [6]. The calculation results are presented in Table 1.

Table 1.

Optimal conditions for the formation and analytical characteristics of cobalt(II)
MLCs with HNTp and AP

Compound	pH		λ , nm	$\Delta\lambda$, nm	$\varepsilon \times 10^{-4}$	$\lg\beta$	R	D	$\lg K_{\text{ex}}$	$\lg K_{\text{eq}}$
	Education and extraction	Optimal								
$[\text{Co}(\text{HNTp})_2](\text{AP}_1\text{H})_2$	3.2–8.3	5.5–6.4	520	246	3.78	9.57	98.60	281.7	14.8	7.85
$[\text{Co}(\text{HNTp})_2](\text{AP}_2\text{H})_2$	3.0–8.2	5.5–6.3	530	256	3.95	9.96	98.75	315.5	14.6	7.70

It can be assumed that during complexation with the formation of associates, the following processes occur:



The equilibrium constant of the reaction is

$$K_{\text{eq}} = \frac{\{[\text{Co}(\text{HR})_2](\text{APH})_2\}_o}{\{[\text{Co}(\text{HR})_2]^{2-}\}_{\text{aq}}\{[\text{APH}^+]\}_{\text{aq}}} \quad (2)$$

Since the distribution coefficient (D) is

$$D = \frac{\{[\text{Co}(\text{HR})_2](\text{APH})_2\}_o}{\{[\text{Co}(\text{HR})_2]^{2-}\}_{\text{aq}}} \quad (3)$$

then

$$K = \frac{D}{[\text{APH}^+]^2} \quad (4)$$

Taking the logarithm of the last expression, we get

$$\lg K_{\text{eq}} = \lg D - 2 \lg [\text{APH}^+] \quad (5)$$

The K_{eq} values calculated by formula (5) are 7.85–7.70.

The reaction equation for the extraction of compounds can be written:



The expression for the extraction constant is:

$$\lg K_{\text{eq}} = \lg D - 2 \lg [\text{HR}^{2-}] - 2 \lg [\text{APH}^+] \quad (7)$$

The MLC extraction constants calculated by formula (7) are 14.6–14.8.

In table 1 shows the main spectrophotometric characteristics of the procedure for the determination of Co(II).

Spectrophotometric determination of cobalt (II). The use of MLC in many cases leads to an increase in selectivity, reaction contrast, improvement in extraction and other properties. The introduction of the second reagent leads to an improvement in the extraction properties of the complexes and a decrease in the detection limit.

Cobalt MLC extracts obey the basic law of light absorption at concentrations of 0.4 - 16 $\mu\text{g/ml}$. The equations of the calibration curves are given in Table. 2. Based on the equations of the calibration graphs, the limit of photometric detection and the limit of quantitative determination of cobalt in the form of MLC were calculated.



Table 2.

Analytical characteristics of Co(II)-HNTP-AP complexes

Parameters	Complexes	
	[Co(HNTP) ₂](AP ₁ H) ₂	[Co(HNTP) ₂](AP ₂ H) ₂
Limit of photometric detection, ng/cm ³	14	15
Limit of Quantitation, ng/cm ³	44	36
Sensitivity, according to Sendall, ng/cm ²	1.51	1.47
Linear range of calibration curves, µg/ml	0.5–15	0.4–16
Correlation coefficient	0.9645	0.9589
Equation of calibration curves	0.052+0.609x	0.046+0.624x

Influence of foreign ions. To assess the applicability of MLC extracts for the separation and determination of Co(II), the interfering effect of foreign ions was studied. The determination of Co(II) with HNTP and AF is not interfered with by ions of alkali, alkaline earth elements, and rare earth elements. The interfering effect of ions is eliminated by changing the pH of the medium, using masking agents and using extraction. The interfering effect of Nb (V), Ta (V), Ti (IV) was eliminated by increasing the pH, as well as using fluoride ion.

The interfering effect of Fe(III) was eliminated with orthophosphate ion, Ti(IV) with ascorbic acid, Cu(II) with thiourea, and Mo(VI) and Nb(V) and Ta(V) with oxalate ion. When using a 0.01 M EDTA solution, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI), and Fe(III) do not interfere with the determination.

In table 3 shows the data that make it possible to compare the analytical characteristics of the photometric methods developed by us for the determination of cobalt(II) with some already known [1, 10, 11] methods. As can be seen from the table, the methods proposed by us are quite selective, sensitive, fast, and make it possible to determine even small amounts of cobalt(II) and obtain reproducible results.

Table 3.

Comparative characteristics of methods for the determination of cobalt

Reagent	pH	Solvent	λ , nm	$\epsilon \times 10^{-4}$	Beer's law range (µg/ mL)
1-nitrosonaphthol-2 [1]	pH $\geq$ 3	CHCl ₃	415	2.9	0.2-20
Nitroso R-salt [1]	weakly acidic	C ₆ H ₆	500	1.5	0.8-13
Bromopirogall red [10]	2.0	-	575	1.08	0.25-110
PAR + chloride 2- (4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium [11]	4.7	-	515	1.4	
HNTP-AP ₁	3.2–8.3	CHCl ₃	520	3.78	0.5-15
HNTP-AP ₂	3.0–8.2	CHCl ₃	530	3.95	0.4-16

Based on the results of a spectrophotometric study of cobalt(II) with HNTP and AP, methods have been developed for the determination of cobalt in plants (Table 4), wastewater, and bottom sediments (Table 5).

Table 4.

The results of the determination of cobalt (II) in plants ($n = 6, P = 0.95$)

Plant	Methods	Found in sample, mg/kg	Convergence, %	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Beans	1-nitrosonaphthol-2	1.67	101	0.036	1.67±0.062
	HNT-AP ₁	1.71	103	0.029	1.71±0.050
	HNT-AP ₂	1.66	99	0.026	1.66±0.045
Peas	1-nitrosonaphthol-2	2.46	102	0.043	2.46±0.116
	HNT-AP ₁	2.28	98	0.037	2.28±0.093
	HNT-AP ₂	2.39	102	0.035	2.39±0.085
Oats	1-nitrosonaphthol-2	0.43	99	0.041	0.43±0.021
	HNT-AP ₁	0.43	96	0.041	0.43±0.018
	HNT-AP ₂	0.47	103	0.028	0.47±0.014
Rye	1-nitrosonaphthol-2	3.05	102	0.039	3.05±0.118
	HNT-AP ₁	3.11	99	0.029	3.11±0.095
	HNT-AP ₂	2.97	98	0.046	2.97±0.139

Table 5.

The results of the determination of nickel in wastewater ($n = 6, P = 0.95$)

Room sample	Methods	Photometric method			Additive method		
		$\bar{X}, \text{mg/l}$	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$	$\bar{X}, \text{mg/l}$	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
1	HNT-AP ₁	0.086	0.053	0.086±0.0048	0.093	0.045	0.093±0.0044
	HNT-AP ₂	0.088	0.045	0.088±0.0042	0.088	0.039	0.088±0.0036
2	HNT-AP ₁	0.094	0.051	0.094±0.0050	0.096	0.042	0.096±0.0042
	HNT-AP ₂	0.097	0.053	0.097±0.0054	0.098	0.0048	0.098±0.0049

CONCLUSION

The extraction efficiency strongly depends on the pH of the solution, and the quantitative extraction of MLC is maximum at pH 5.5–6.4. The presence of the second ligand led to a shift in the optimal acidity of the complex formation to a more acidic region, the pH opt. range being wider than in the case of a two-component compound.

As the pH of the solution decreases, the extraction gradually decreases, which is apparently associated with a decrease in the concentration of the ionized form of GNTP and, most likely, it is present in the solution in the undissociated form. At high pH values, the complex formation process is complicated by the hydrolysis of the cobalt ion.



LITERATURE

1. Умланд, Ф. Комплексные соединения в аналитической химии. Теория и практика применения / Ф. Умланд, А. Янсен, Д. Тириг. - Москва: Мир, -1975. -531 с.
2. Banu, L. A. Studies on synthesis and characterization with antimicrobial activity of mixed ligand coordinating Co (II) Complexes with phthalic acid and heterocyclic amines // IJCS, -2015, 2, № 6, -p. 38-41.
3. Кулиев, К.А., Вердизаде, Н.А. Спектрофотометрическое определение тяжелых металлов в почвах // Заводская лаборатория. Диагностика материалов, -2019, 85, № 5, -p. 18-27.
4. Zalov, A.Z., Amanullayeva, G. I. Spectrophotometric determination of cobalt (II) in a liquid-liquid extraction system containing 2- hydroxy-5-iodothiophenol and diphenylguanidine // Journal of Applied Science, -2016, 2, № 7, -p. 17-25.
5. Коростелев, П.П. Приготовление растворов для химико-аналитических работ / П.П. Коростелев. -Москва: Изд-во АН СССР, -1964. -401 с.
6. Булатов, М.И. Практическое руководство по фотоколориметрическим и спектрофотометрическим методам анализа / М.И. Булатов, И.П.Калинкин. -Химия: -1986, -432 с.
7. Беллами, Л. Инфракрасные спектры сложных молекул / Л.Беллами. -Москва: Изд-во иностранной литературы, -1963, -592 с.
8. Назаренко, В.А. Взаимодействие ионов многовалентных элементов с органическими реагентами //- Москва: Наука, -1969, 17, -с. 22-27.
9. Sharp, G.A. Spectrophotometric determination of cobalt (II) as complexes with brompirogallol red in micellar media // Journal of The Chemical Society of Pakistan, -2006. № 5, -p. 444-447.
10. Divarova, V.V. Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts / V.V.Divarova, K.B. Gavazov, V.D.Lekova [et al.] // Chemija, -2013. № 2, -p. 81-87.

KOBALTIN (II) 2-HİDROKSİ-5-NİTROTIÖFENOL VƏ AMİNOFENOLLAR İLƏ KOMPLEKSƏMƏLƏGƏLMƏSİNİN TƏDQİQİ

Ş.Ə. İbrahimova

Kobaltın(II) 2-hidroksi-5-nitrotiofenol (HNTP) və aminofenollarla (AF) kompleks əmələ gəlməsi fiziki-kimyəvi üsullarla tədqiq edilmişdir. Aminofenollardan 2(N, N-dimetilaminometil)-4-etilfenol (AF1) və 2(N, N-dimetilaminometil)-4-yodfenol (AF2) istifadə edilmişdir. Müxtəlifliqanlı komplekslər (MLK) turşu mühitdə əmələ gəlir (pH_{opt} 5.5-6.4). Kobaltın MLK şəklində xloroformla ekstraksiya dərəcəsi 98.6-99.5% olmuşdur. Bu birləşmələrin əmələ gəlməsi və ekstraksiyası üçün optimal şərait $(1.2-2.0) \times 10^{-3}$ mol/l HNTP konsentrasiyası və $(2.0-2.5) \times 10^{-3}$ mol/l AF-dir. MLK tərkibində komponentlərin molyar nisbəti Co(II) : HNTP : AF = 1:2:2 uyğun gəlir. Maksimum işığın udulması $\lambda = 520-530$ nm-də müşahidə olunur. Molar işığın udma əmsalı $(3.78-3.95) \times 10^4$. Əldə edilmiş məlumatlar əsasında müxtəlif təbii obyektlərdə kobaltın təyini üçün fotometrik üsullar işlənilib hazırlanmışdır.

Açar sözlər: kobalt, 2-hidroksi-5-nitrotiofenol, aminofenol, qarışıq liqand kompleksləri, xloroform



ИССЛЕДОВАНИЕ КОМПЛЕКСООБРАЗОВАНИЯ КОБАЛЬТА(II) С 2-ГИДРОКСИ-5-НИТРОТИОФЕНОЛОМ И АМИНОФЕНОЛАМИ

Ш.А. Ибрагимова

Физико-химическими методами исследовано комплексообразование кобальта(II) с 2-гидрокси-5-нитротиофенолом (ГНТФ) и аминифенолами (АФ). Из аминифенолов использован 2(N, N-диметиламинометил)-4-этилфенол (АФ1) и 2(N, N-диметиламинометил)-4-иодфенол (АФ2). Разнолигандные комплексы образуются в слабокислой среде ($pH_{\text{опт}}$ 5.5–6.4). За одну экстракцию Co(II) извлекается хлороформом на 98.6–99.5% в виде разнолигандного комплекса (РЛК). Оптимальным условием образования и экстракции этих соединений является $(1.2-2.0) \times 10^{-3}$ моль/л концентрация ГНТФ и $(2.0-2.5) \times 10^{-3}$ моль/л – АФ. Соотношение реагирующих компонентов в РЛК соответствует Co(II) : ГНТФ : АФ = 1:2:2. При образовании РЛК координирующим является ион Co^{2+} . Максимальное светопоглощение наблюдается при $\lambda = 520-530$ нм. Молярные коэффициенты светопоглощения равны $(3.78-3.95) \times 10^4$. На основании полученных данных разработаны фотометрические методики определения кобальта в различных природных объектах.

Ключевые слова: 2-гидрокси-5-нитротиофенол кобальта, аминифенол, разнолигандные комплексы, хлороформ