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Extraction-spectrophotometric determination of cobalt (ii) in a liquid-liquid extraction system containing 4-nitro-2-hydroxythiophenol and diphenylguanidine, determination of cobalt (ii) in steel

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Abstract

The complex formation and a liquid-liquid extraction in the cobalt (II) - 4-Nitro-2-hydroxythiophenol (HNTP) - diphenylguanidine (DPG) - water - chloroform system was studied. The optimum extraction-spectrophotometric conditions were found. The molar ratio of the reacting species was determined to be 1:2:2 (Co: HNTP: DPG). The following equilibrium processes were quantitatively examined: the association between the anionic chelate, $[Co^{2+}(HNTP)_2]^{2-}$, and the diphenylguanidine ($\lg\beta = 4.8$); the distribution of the ternary complex between the aqueous and organic phases ($\lg K_D = 0.88$); and the extraction from water to chloroform ($\lg K_{ex} = \lg\beta + \lg K_D = 5.6$). The effect of foreign ions and reagents on the extraction was studied. A sensitive ($\varepsilon_{560} = 4.3 \times 10^4$ L mol^{-1} cm^{-1}) and simple extraction-spectrophotometric procedure for cobalt determination was developed.

Keywords: cobalt (II), nitro-2-hydroxythiophenol, diphenylguanidine, ternary complex, solvent extraction

Introduction

Many metal ions form coloured binary species with azodyes, such as dithiolphenol (DP) {2, 6-dithiolphenol (DTP) and its derivatives (2, 6-dithiol-4-methylphenol (DTMP), 2, 6-dithiol-4-propylphenol (DTPP), 2, 6-dithiol-4-*tert*-buthylphenol (DTBP)}[1, 6] and *o*-hydroxythiophenol (HP) (HTPD) {2-hydroxythiophenol (HTP) and its derivatives (2-hydroxy-5-chlorothiophenol (HCTP), 4-hydroxy-3-thiolsulfonic acid (HTSA), 4-hydroxy-3-thiolbenzoic acid (HTBA)}[7, 13]. The following ion-association reagents were used for liquid-liquid extraction of $[Co\ (DP)_2]^{2-}$ or $[Co(HP)_2]^{2-}$: aniline and N-methylaniline [2, 13], diphenylguanidine and triphenylguanidine [9], diphenylguanidine [12], and aminophenol [10]. In a previous paper the complex formation and extraction in a system containing Co (II), HTBA and diphenylguanidine (DPG) has been described [12]. Here, results of systematic investigations on a similar extraction-chromogenic system, which 4-Nitro-2-hydroxythiophenol (HNTP) involve instead of HTBA, are presented.

Experimental

Reagents and Apparatus

A stock solution (1mg/mL) of cobalt (II) was prepared by dissolving in water an exact linkage $CoSO_4 \times 7H_2O$ in water containing 2 ml conc. H_2SO_4, and diluted with water to 1 liter [14]. The concentration of the cobalt solution was adjusted gravimetrically [15]. Solutions of HNTP and DPG in chloroform (0.01M) were used. HNTP were synthesized according to the procedure [16]. To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. The extractant was purified chloroform. The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR) and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode.

General Procedure

General Procedure for the Determination of Cobalt (II)

Portions of stock solutions of Cobalt (II) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.2 mL portion of a 0.01 M solution of HNTP, and a 2.5 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 15 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 560 nm (l=0.5cm).

Determination of Cobalt (II) in Steel

A weighed sample of 0.2 g was dissolved in 20 ml of H_2SO_4 (1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice lo vapor SO_3. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel, was added 1 ml of 10% hydroxylamine solution, 1 ml of 3% ascorbic acid and was determined cobaltusing the proposed procedures.

3. Results and Discussion

Spectral characteristics and effect of pH

The coloured cobalt (II) - HNTP species which is readily formed in slightly acidic aqueous medium can be efficiently extracted in chloroform in the presence of the cationic ion-pair reagent DPG. The absorption maximum is shifted from 550 nm to 560 nm (Fig. 1). It could be seen on Fig. 2 that the maximum and constant extraction of the ternary compound is achieved in the pH range from 5.2 to 7.0. The molar absorptivity of the complex was calculated with Komar method [17] to be $\varepsilon = 4.3 \times 10^4$

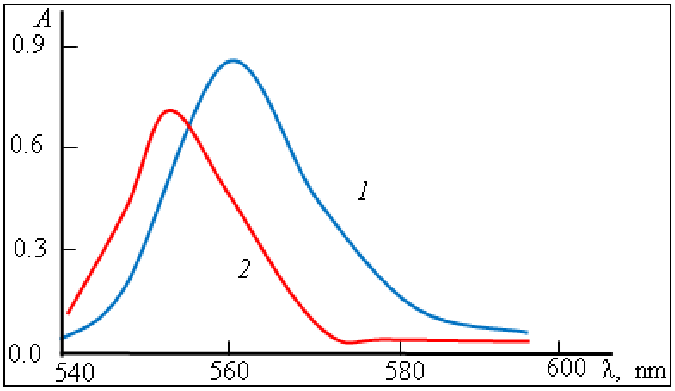

Fig 1: Absorption spectra of the complexes *1*– Co(II)-HTBA-DPG and *2* – Co-HTBA $C_{Co}=2.035\times10^{-5}$ M, $C_{HNTP} = C_{DPG}=1.0\cdot10^{-3}$ M, pH 5.5, SF-26, $\ell = 1.0$ cm.

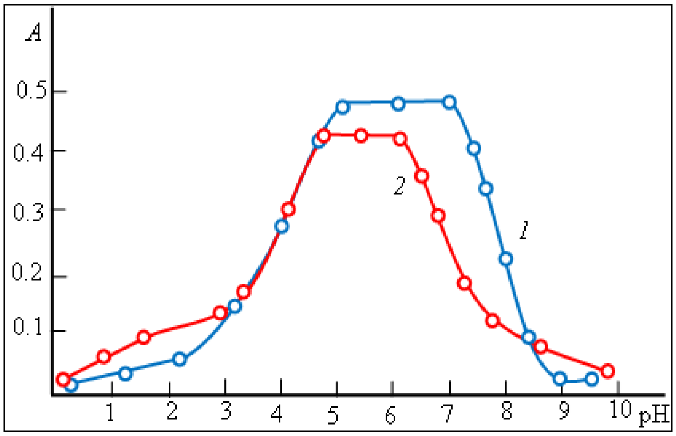

Fig 2: Absorbance of *1* – Co- HNTP-DPG and *2* – Co- HNTP extracts function of the pH of the aqueous phase. $C_{Co(II)} = 2.035\times10^{-5}$mol L^{-1}, $C_{HITP} = 2.0\times10^{-3}$mol L^{-1}, $C_{DPG} = 2.5\times10^{-3}$ mol L^{-1}, KFK-2, $\ell=0.5$ cm.

Effect of the shaking time

The extraction equilibrium is reached for ca. 0.5 min. A longer shaking time (up to 5 min) did not affect the absorbance values. In order to avoid accidental errors, caused by the combination of short shaking times and different shaking rates, the further experiments were carried out with time of shaking 1 min.

Effect of reagents concentration

The effect of HNTP and DPG concentrations on the absorbance is shown in Fig. 3. It could be accepted that 98-fold HNTP excess and 122-fold DPG excess are sufficient for maximum Co extraction. The optimum reagents concentrations deduced from the mentioned figure are shown in Table 1.

Table 1: Optimum conditions and analytical characteristics of the Co (II)- HNTP - DPG -water-chloroform system.

Optimum conditions	**Analytical characteristics**
Wavelength: 560 nm	Apparent molar absorptivity: $\varepsilon=4.3\times10^4$
pH: 5.5 (acetate buffer)	Adherence to Beer's law: up to 1.5 mg ml^{-1}
C_{HNTP}: 2.0×10^{-3}mol L^{-1}	Limit of detection: 0.05 mg ml^{-1}
C_{DPG}: 2.5×10^{-3} mol L^{-1}	Limit of quantification: 0.18 mg ml^{-1}
Shaking time: 1 min	Sandell's sensitivity: 1.38 ng cm^{-2}
	Relative standard deviation: 1.9 %

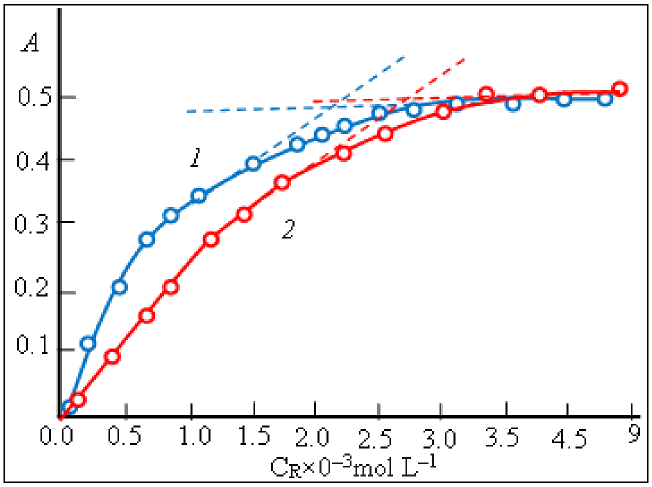

Fig 3: Absorbance of the extracted ternary complex vs. concentration of the HNTP (curve 1) and DPG (curve 2) plots. *1* – $C_{Co(II)} = 2.035\times10^{-5}$mol L^{-1}, $C_{DPG} = 2.5\times10^{-3}$ mol L^{-1}, KFK-2, $\ell=0.5$ cm; *2* – $C_{Co(II)} = 2.035\times10^{-5}$mol L^{-1}, $C_{HITP} = 2.0\times10^{-3}$mol L^{-1}, KFK-2, $\ell=0.5$ cm.

Stoichiometry of the Complexes and the Mechanism of Complexation

Composition of the complex and suggested formula The molar ratios in the ternary compound, HNTP:Co = 2:1 and DPG:Co = 2:1, were determined by the mobile equilibrium method [17] (Fig. 4) and the straight-line method of Asmus [17] (Figs. 5). We propose the following formula of the ternary compound: $[Co^{2+}(HNTP)_2](DPGH)_2$.

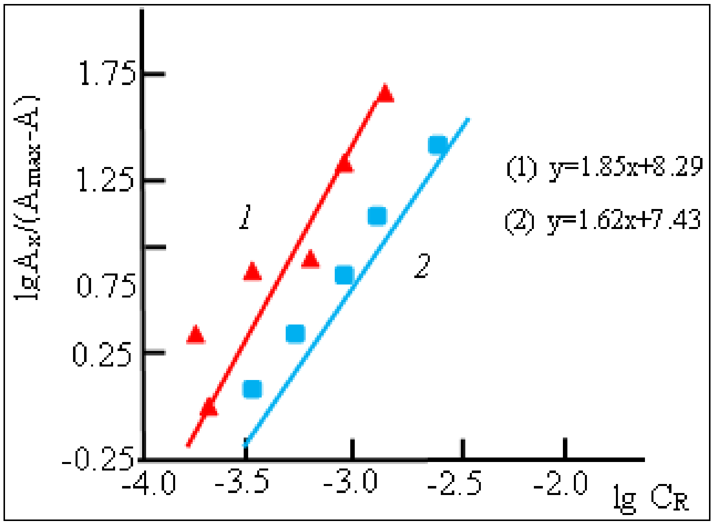

Fig 4: Determination of the HNTP -to-Co (straight line 1) and the DPG-to-Co (straight line 2) molar ratios by the mobile equilibrium method. 1- $C_{Co(II)}$ = 1.7×10^{-5}mol L^{-1}, C_{HNTP} = 2.0×10^{-3} mol L^{-1}, C_{DPG} = 2.5×10^{-3} mol L^{-1},λ=560 nm, SF-62 ℓ=1.0 cm.

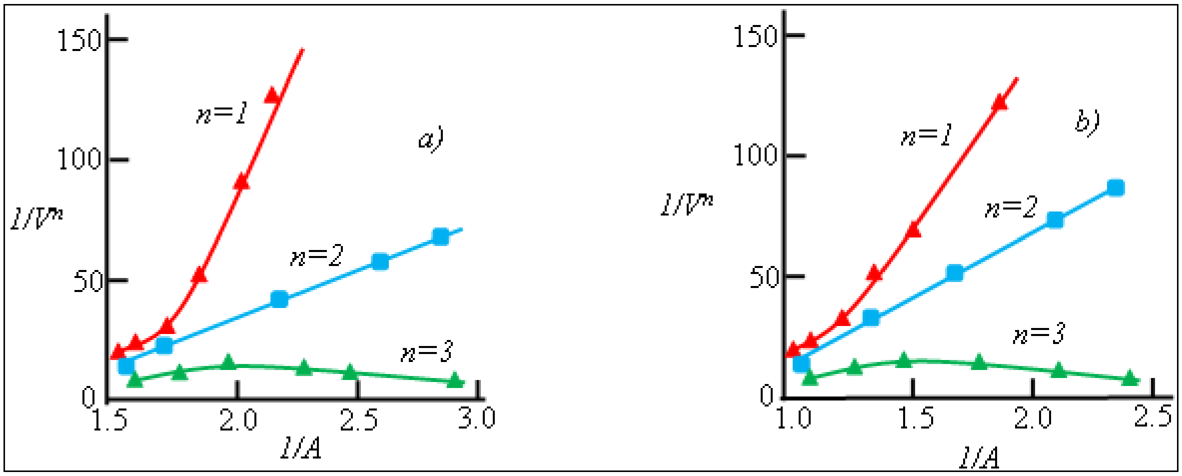

Fig 5: Determination of the *a)* HNTP -to-Co and *b)* molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{HITP} = 2.0×10^{-3}mol L^{-1}, C_{DPG} = 2.5×10^{-3}mol L^{-1}, λ=560 nm, KFK-2, ℓ = 0.5 cm.

It was found using the Nazarenko method that Co (II) in the complexes was present in the form of Co^{2+}. The number of protons replaced by cobalt in one HNTP molecule appeared to be one [18].

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3452 cm^{-1} observed in the spectrum of HNTP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2585cm^{-1} shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1387 cm^{-1} indicates the presence of a protonated diphenylguanidine (Fig. 6) [19].

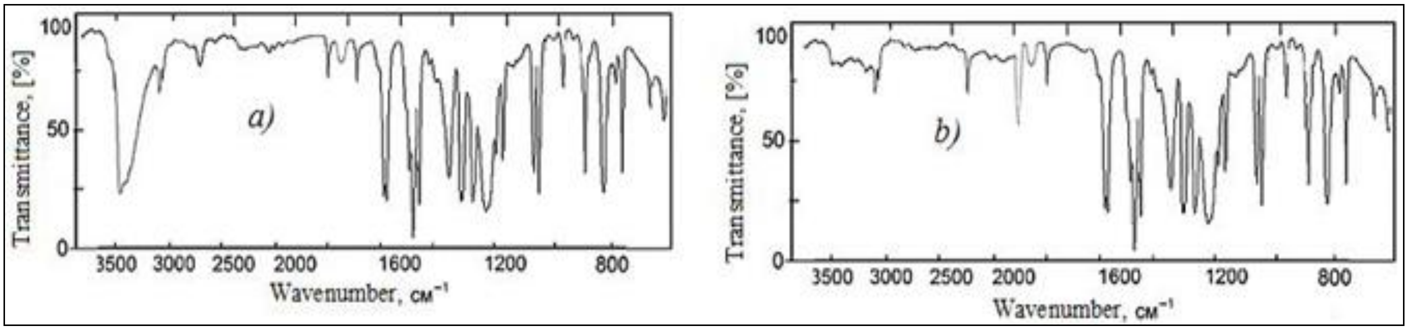

Fig 6: IR spectrums of HNTP (*a*) and the Co(II)- HNTP-DPG(*b*).

Structure extractable complexes can be represented as in Figure 7.

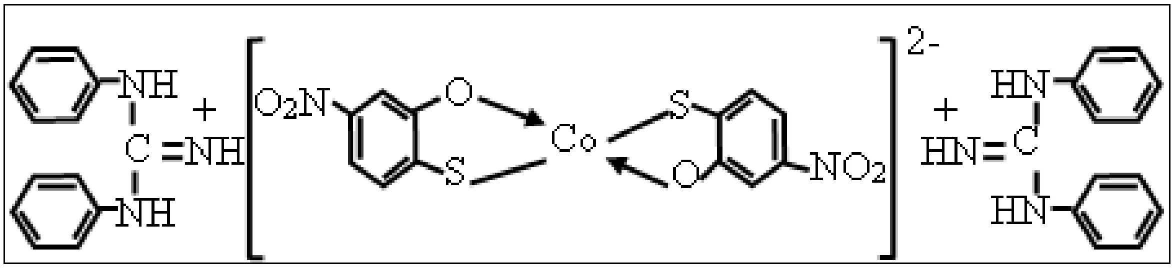

Fig 7: Structure of complex

Equilibria and equilibrium constants

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $[Co(HNTP)_2](AmH)_2$.

Formation in the aqueous phase:

$$[Co(HNTP)_2]^{2-}_{(aq)} + 2DPGH^{+}_{(aq)} \leftrightarrow [Co(HNTP)_2](DPGH)_{2\,(aq)} \quad (1)$$

Distribution:

$$[Co(HNTP)_2](DPGH)_{2\,(aq)} \leftrightarrow [Co(HNTP)_2](DPGH)_{2\,(org)} \quad (2)$$

Extraction from water into chloroform:

$$[Co(HNTP)_2]^{2-}_{(aq)} + 2DPGH^{+}_{(aq)} \leftrightarrow [Co(HNTP)_2](DPGH)_{2\,(org)} \quad (3)$$

The equilibrium constants describing these processes are shown in Table 2. The association constant β was determined according to a strategy [20] by several independent methods. The constant of distribution K_D was calculated from the absorption values obtained after single and triple extraction as described above. The constant of extraction K_{ex} was calculated by the formula $K_{ex} = K_D \times \beta$. All experiments were performed at room temperature of ~ 22°C and the calculations were carried out at a probability of 95 %.

Table 2: Calculated values of lg β, lg K_D and lg K_{ex}.

Equilibrium	Equilibrium constant	Value
1	$\beta=[[Co(HNTP)_2](DPGH)_2] / [[Co(HNTP)_2]^{2-}] \times [DPGH^{+}]^2$	$\lg\beta = 4.8 \pm 0.1$
2	$K_D=[[Co(HNTP)_2](DPGH)_2\,]_{org} / [[Co(HNTP)_2](DPGH)_2\,]_{aq}$	$\lg K_D = 0.88 \pm 0.01$
3	$K_{ex}=[[Co(HNTP)_2](DPGH)_2]_{org} / [[Co(HNTP)_2]^{2-}]_{aq} \times [DPGH^{+}\,]^2_{aq}$	$\lg K_{ex} = 5.6 \pm 0.1$

Influence of Interfering Ions

The effect of various ions and reagents on the extraction-spectrophotometric determination of 5 mg cobalt (II) is summarised in Table 3. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^{+}, Cl^{-}, $S_2O_3^{2-}$, F^{-}, NO_3^{-}, SO_4^{2-}, ClO_4^{-}, PO_4^{3-}, tartrate, citrate, oxalate and tiron; moderate amounts of Cr(VI), Cr(III), Zn(II) and Cd(II); and small amounts of Mn(II), Sn(II), Cu(II), Al(III), ascorbic acid and SCN^{-} are tolerable. Ni(II), Fe(II,III), V(IV,V), W(VI), Mo(VI), Ti(IV) and Nb(V) interfere determination of Co(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 3).

Table 3: Influence of interfering ions on the determination of cobalt (II) as MLC with HNTP and DPG (30,0 µg Co added)

Foreign ions and reagents (FI)	mg	FI-to-Co ratio	Co found	R,%
$Citrate^{3-}$	5	250	20.03	100.5
$Oxalate^{2-}$	10	200	20.13	102.6
$Tartrate^{2-}$	2.5	250	5.05	101.0
Ascorbic acid	0.5	25	5.15	103.1
EDTA	0.5	25	5.10	102.0
CDTA	.005	0.25	19.73	94.6
Tiron	2.5	125	20.11	102.5
SCN^{-}	0.025	10	20.13	102.6
NH_4^{+}	20	500	20.02	100.3
Na^{+}	30	1500	20.13	100.4
K^{+}	30	1500	20.11	102.2
Ca^{2+}	15	500	20.01	100.2
Ba^{2+}	5	250	20.15	103.1
Sr2+	20	100	20.11	102.2
Mg2+	30	1500	20.18	103.5
Mo(VI)	5	250	19.85	97.0
W(VI)	5	250	19.88	97.7
Cr(VI)	2.5	125	19.91	98.2
Fe(II)	0.5	2.5	19.25	85.0
Fe(III)	0.5	2.5	20.90	118.0
V(IV) 0.05 2.5 20.55 111.0				
V(V) 0.05 2.5 19.25 85.0				
Cd2+ 0.2 10 19.86 97.2				

Cu^{2+}	0.06	3	20.17	103.4
Al^{3+}	5	250	20.08	101.6
Zn^{2+}	0.5	25	20.04	100.8
Zr(IV)	3.0	150	20.18	103.5
Nb(V)	0.5	2.5	19.25	85.0
Ti(IV)	2.5	125	20.17	103.4
Ni^{2+}	2.5	125	19.91	98.2

Beer's law and analytical characteristics

The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions (Table 1). The following straight line equation was obtained for the concentration interval 0.2 – 1.5 mg ml^{-1} Co (II):

$$Y=0.7059X+0.0087\ (R^2=0.9988).$$

Some additional characteristics concerning the analytical application of the Co- HNTP- DPG -water-chloroform system are given in Table 1.The proposed method compares favourably with the existing ones (Table 4) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

Table 4: Comparative characteristics of the procedures for determining of cobalt

Reagent	pH (solvent)	λ, nm	ε×10^{-4}	Beer's law range (µg×ml^{-1})	Ref.
2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8	525	4.26	0.2 - 1.5	[20]
1-nitroso-2-naphtol	≥3	415	2.9		[14]
2-nitroso-1-naphtol	≥4	365	3.7		[14]
Nitroso-R-salt	weakly acidic medium	415	3.5		[14]
DTPP- An	4.3-5.2($CHCl_3$)	555	3.02	0.05-3.0	[3]
DTBP -An	4.5-5.6($CHCl_3$)	560	3.15	0.05-3.2	[3]
HNTP- DPG	5.2-7.0 (acetate buffer) ($CHCl_3$)	560	4.3	0.2-1.5	

Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Co (II) in in Steel. The results presented in Table 5.

Table 5: Determination of Cobalt in steel (n=5, P=0.95)

Reagent	*X*	Sx	*ε*	Sr	μ
*Steel:*M 441 (0.012% Co)					
1-nitroso-2-naphtol	0.0125	0.000312	0.0003281	0.025	0,0125±0.00033
Co - HNTP - DPG	0.0122	0.00030268	0.0003028	0.022	0,0122±0,00028
Steel: 156(0.56% Co)					
1-nitroso-2-naphtol	0.574	0.022	0.023	0.038	0.574±0.023
Co - HNTP - DPG	0.558	0.025	0.0263	0.045	0.558±0.0263

Conclusions

This work represents the results of a detailed extraction-spectrophotmetric study on the ion-association system of cobalt- HNTP and DPG. The optimum conditions for ternary complex formation and extraction were found. The constants characterizing the equilibria of ion-association, distribution and extraction were determined. The relatively high sensitivity and selectivity of the colour reaction make the studied system appropriate for analytical applications.

References

1. Kuliyev KA, Verdizade NA. Spectroscopic Investiqation Complex Formation of Vanadium Using 2,6-Dithiolphenol and Hydrofob Amins //American Journal of Chemistry. 2015; 5(1):10-18.
2. Kuliyev KA, Verdizadeh NA, Suleymanova GS. Spectrophotometric Determination of Cobalt (II) with 2, 6-Dithiolphenol and Its Derivatives in the Presence of Hydrophobic Amines. American Journal of Chemistry, 2016; 6(4):95-103.
3. Kuliyev KA, Verdizadeh NA. Spectroscopic Investigation of the Complex Formation of Niobium Using 2,6-Dithiolphenol and Aminophenols. American Journal of Analytical Chemistry. 2015; 6:746-756.
4. Kuliev KA, Verdizadeh NA, Gadjieva AB. Liquid-Liquid Extraction and Spectrophotometric Determination of Molybdenum with 2, 6-Dithiolphenol and its Derivatives in the Presence of Hydrophobic Amines // Chemistry Journal. 2015; 05(3):45-53.
5. Kuliyev KA, Verdizadeh NA, Gadjieva AB, Mamedova SA. Spectroscopic investigation complex formation of molybdenum with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines.International Journal of Chemical Studies. 2016; 4(3):42-48.
6. Kuliyev KA. Spectroscopic Investiqation Complex Formation Of Vanadium Using 2, 6-Dithiol-4-Methylphenol And Hudrophob Amins // Journal of Advan-ces in Chemistry, 11(4):3487-3497.
7. Zalov AZ, Verdizade NA, Jamalova RI. Extraction-photometric determination of niobium (V) with 2-hydroxy-5-bromthiophenol and hydrophob amines // Az. Chim. Journ. 2011; 1:97-102.
8. Zalov AZ, Amanullayeva GI. Spectrophotometric determination of cobalt (II) in a liquid-liquid extraction system containing 2- hydroxy-5-iodothiophenol and diphenylguanidine // IJRDO-Journal Of Applied Science. 2016; 2(7):17-25.
9. Zalov AZ, Gasimova YC, Ibrahimova ShA.
10. Liquid-liquid extraction and spectrophotometric Characterization of some new ternary ion-association

complexes of cobalt (II) and nickel (II) // IJRDO-Journal Of Applied Science. 2016; 2(7):1-10.

11. Zalov AZ, Verdizadeh NA, Agayeva RM. Extraction Spectrophotometric Study of Ternary Complexes of Co(Ii) And Ni(Ii) // Journal of Research Analytica. 2016; 2(3):83-9.
12. Novruzova NA, Mamedova RA, Maharramo AA, Ibrahimova Sh A, Zalov AZ. Extraction-Spectrophotometric Study on the Complex Formation in the Cobalt (Ii) - 4-Hydroxy-3-Thiolbenzoic Acid - Diphenylguanidine System // IJISET - International Journal of Innovative Science, Engineering & Technology. 2017; 4(6):233-242.
13. Extraction-photometric determination of cobalt (II) with *o*-Hydroxythiophenol derivatives and hydrophobic amines Aliyev Sultan Gasham, Zalov Ali Zal, Verdizadeh Nailya Allakhverdi, Geysar Suleyman Suleymanova and Shahla Ibrahimova Adalet International Journal of Chemical Studies. 2017; 5(3):382-386.
14. Marczenko Z, Baltsejak MK. Metodı Spectrophotometrii v UF I vidimoy oblastyax (Spectrophotometrically in the UV and visible regions in inorganic analysis). M. Binom. Laboratoriya znaniy, 2007, 711.
15. Korostelev PP. Preparation of solutions for chemical analysis works. M.: Publishing house of Academy of Sciences of the USSR. 1964.
16. Kuliev AM, Aliev SR, Mamedov FN, Movsumzade M. Zh. Org. Khim. 1976; 12:426.
17. Bulatov MI, Kalinkin IP. Practicheskoe rukovodstvo po photocolorimetricheskimi spectrophotometricheskim metodam analysa, Leningrad, 1976.
18. Nazarenko VA, Biryuk EA. A study of the chemistry of reactions of multivalent element ions with organic reagents. Zh. Anal. Khim. 1967; 22(13):57-64.
19. Bellami L. Infrakrasnie spectri slojnikh molecule (The infra-red spectra of complex molecules). Moscov: Mir, 1991, 592.
20. Gavazov K, Lekova V, Dimitrov A. Extraction studies on the system vanadium(V) – 4-(2-thiazolylazo)- resorcinol – neotetrazolium chloride – water – chloroform, J.Univ. Chem. Technol. Met. (Sofia). 2006; 41:217-220.