Liquid-Liquid Extraction and Spectrophotometric Characterization of A New Ternary Ion-Association Complex of Cobalt(Ii)

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ABSTRACT

Complex formation and liquid-liquid extraction were studied in systems containing Co(II), 2-hydroxy-5-thiophenols (HTP)-2 hydroxy-5-aminothiophenol (HATP) and 2-hydroxy-5-nitrothiophenol (HATP) , hydrophobic amines (Am) {2- (N, N-dimethylaminomethyl) -4-bromophenol (AP$_1$) and 2-(N, N-diethylaminomethyl) -4-methylphenol (AP$_2$)}, water and chloroform. The optimum conditions for the extraction of Co were found: pH, extraction time, concentration of the reagents HTP and Am. The results show that the extracted species could be represented with the general formula $(AmH^+)[Co(HTP)_2]$, where Co is in its +2 oxidation state and HTP is in a deprotonated form. The following key constants and characteristics were established for both systems: constants of extraction (K_{ex}), constants of association (β), constants of equilibrium (K_{eq}), recovery factors (R%), wavelengths of maximum absorption (λmax), molar absorptivities, Sandell's sensitivities, intervals of adherence to Beer's Law, limits of detection and limits of quantification. The ion-associate with Am is more stable and extractable (lgK_{ex} =12.84-13.68, lgβ = 10.57-10.94, lgK_{eq} = 5.3-5.9, R = 97.3-98.2 %). Beer's law for the system with this reagent is observed in a wider concentration interval (0.5-100 μg ×5 cm^{-3} Co) with a higher molar absorptivity coefficient (ε' = 2.62-3.01 × 104 L mol^{-1} cm^{-1} at λ$_{max}$ = 540-565 nm).

Keywords: cobalt, 2-hydroxy-5-thiophenols, 2 hydroxy-5-aminothiophenol , 2-hydroxy-5-nitrothiophenol, hydrophobic amines

1. INTRODUCTION

Changes in the degree of oxidation of cobalt contribute to the affinity of the ions of this element to various donor atoms and, as a result, to the diversity of its complexes. Co (II) ions form strong complexes with ligands containing donor oxygen atoms, whereas Co (III) ions show an affinity for nitrogen [1]. The complexing ability of Co (II) and Co (III) ions is more pronounced than that of ions of other transition elements.

The value of Co (II) and Co (III) complexes for analytical chemistry is high due to their kinetic inertness. When complexing reactions are carried out under conditions of low acidity with subsequent increase in the acid concentration to 2-5 M, metal complexes, other than cobalt, are destroyed [2].

The multiligand complexes of cobalt (II) with heterocyclic diamines and azoxy derivatives of salicylic acid have been studied by spectrophotometry [3].

It was proved that 2-hydroxy-5-thiophenols (HTP) is one of the most important reagents for cobalt separation, pre-concentration and determination [4,5]. PAR with intensely stained Co (II) anionic chelates $[Co^{2+}(HTP]_2)^{2-}$ or $[Co^{3+}(HTP]_2)^-$ that can easily react with bulk organic compounds [4-8] to obtain ternary complexes with good extraction behavior and analytical potential. In the present study, we investigated the formation of a complex in a liquid-liquid extraction system containing Co (II), 2-hydroxy-5-thiophenols (HTP) -2 hydroxy-5-aminothiophenol (HATP) and 2-hydroxy-5-nitrothiophenol (HATP)) and hydrophobic amines (Am) - 2- (N, N-dimethylaminomethyl) -4-bromophenol (AP_1) and 2- (N, N-diethylaminomethyl) -4-methylphenol (AP_2).

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2. Experimental
2.1. Reagents and Apparatus

Cobalt standard solution (1000 mgL^{-1}; $Co(NO_3)_2$) was purchased from Merck Darmstadt (Germany). Working solutions ($C_{Co} = 3.38\times10^{-5}$ mol L^{-1}) were prepared by diluting appropriate volumes of the stock solution. The concentration of the cobalt solution was adjusted gravimetrically [9].
0.01 M solutions of HTP and amines (Am) - 2- (N, N-dimethylaminomethyl) -4-bromophenol (AP_1) and 2- (N, N-diethylaminomethyl) -4-methylphenol(AP_2) in chloroform. Hydroxythiophenols were purified by reprecipitation from ethanol solutions by addition of water followed by distillation. As an extractant, purified chloroform was used.
The ionic strength of the solutions, equal to μ = 0.1, was maintained by continuously introducing the calculated amount of KCl. To create the necessary acidity of the solutions, 1 M HCl solution was used.
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.

2.2. 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 HTP, 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 =0.5 cm).

3. Results and Discussion

HTP was synthesized by the procedure of [10] by reacting 5-amino or 5-nitrophenol with sulfur dichloride taken at a molar ratio of n+2 / n+1 (n≥1) and further reducing the resulting polysulfide of 5-amino or nitrophenol with hydrogen at the time of isolation.
Element analysis, NMR and IR spectroscopy were used to identify the synthesized reagents. The absorption spectra of the reagents were studied at different pH values of the medium.
HTP with cobalt (II) forms a colored complex, insoluble in non-polar organic solvents. The charge of the complex was established by the method of electromigration of ions and anion exchange on the anion exchanger EDE-10 P. When

studying the electromigration of this complex, motion of the violet-colored ions to the positive pole was observed, on the basis of which it was concluded that the colored complex is an anion. The transfer of ions was studied in a conventional U-tube with two taps at a voltage of 180 V and a current strength of 0.5-0.8 mA. Electrolysis was carried out for 3 hours. When determining the charge sign of homogeneous ligand complexes by the ion-exchange chromatography method, the EDE-10 P anion exchanger completely absorbs the colored part of the solution. When a hydrophobic Am is introduced into the system, an anionic complex is extracted into the organic phase in the form of a mixed-ligand complex (MLC).

3.1. Selection of extractant

To elucidate the possibility of extracting MLC, aqueous solvents: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, xylene, *iso*-butanol and *iso*-pentanol. The extractability of the complexes was evaluated by the distribution coefficient and the degree of extraction. The best extractants were chloroforms, dichloroethane and carbon tetrachloride. With a single extraction of chlorophore, 97.3-98.2% (Table 1) of cobalt is extracted as a MLC. Further studies were carried out with chloroform. The cobalt content in the organic phase was determined by photometric – phenanthroline [2] after stripping, and in water - by difference.

3.2. Effect of pH

The cobalt (II) complex is extracted into chloroform in the pH range 3.6-6.3 (Fig.1). As the pH of the aqueous phase decreases, the Co (II) extraction gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of HTP and, most likely, in solution, they are in undissociated form. At pH 7.5, MLCs are not practically extracted, which is apparently due to a decrease in the protonation degree of Am. The presence of the second ligand led to a shift in the optimum acidity of the complexation to the more acidic region, pH_{opt} is wider than in the case of the two-component compound.
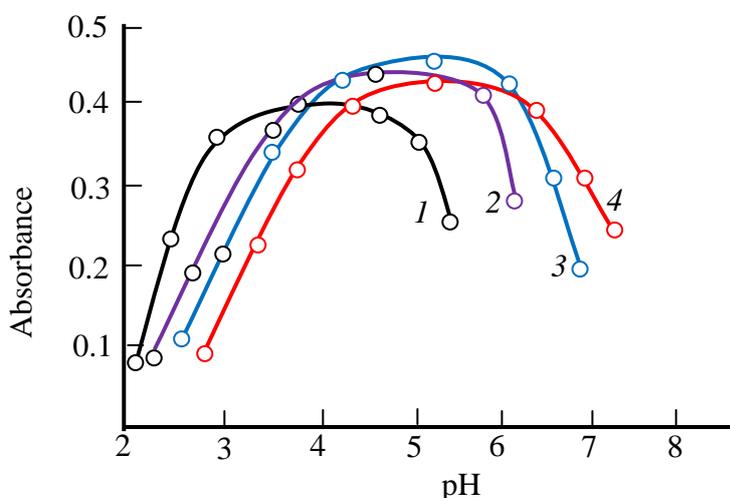

Fig.1. Dependence of the optical density of the complex on the pH of the aqueous phase.

1- Co-HNTP-AP$_1$, 2-Co-HATP-AP$_1$,3- Co-HNTP-AP$_2$, 4- Co-HATP-AP$_2$

$C_{Co (II)} = 3.38 \times 10^{-5}$ M; $C_{HTP} = 7.2 \times 10^{-4}$ M; $C_{Am} = 1.04 \times 10^{-3}$ M; KFK-2, $\lambda = 540$ nm, $\ell = 0.5$ cm

Table 1. Characteristics of the Co(II)-HTP-Am-H$_2$O- CHCl$_3$ extraction-chromogenic systems

Compound	pH^1	pH^2	λ_{max} nm	$\varepsilon \times 10^{-4}$	lgK$_{eq}$	lgK$_{ex}$	lgβ	R%
Co-HATP-AP $_1$	3.5–7.2	4.8–6.2	540	2.62	5.3	12.84	10.57	97.5
Co-HATP-AP $_2$	3.6–7.3	4.9–6.3	542	2.68	5.6	13.02	10.78	98.2
Co-HNTP-AP$_1$	2.3–6.1	3.6–4.9	562	2.96	5.8	13.68	10.94	97.3
Co-HNTP-Ap $_2$	2.5–6.2	3.8–5.0	565	3.01	5.9	12.92	10.61	97.5

Note: 1- pH range complexation;2- The pH range of maximum extraction

3.3. Effect of ligand concentration and aging time

For the selection of optimal conditions, the effect of the concentration of reacting substances, temperature and time on the formation of MLC was studied. The yield of the complexes is maximal at a concentration of 7.2×10^{-4} mol / l HTP and 1.04×10^{-3} mol / l Am.

MLC with HTP and Am are stable in aqueous and organic solvents and do not decompose for three days, and after extraction more than a month. The maximum optical density is reached within 3 minutes. MLC are stable when heated to 700ºC.

The degree of extraction in the form of MLC does not depend on the ratio of volumes of water and organic phases in a wide range (from 5: 5 to 100: 5), which allows simultaneous concentration and photometric determination of cobalt. The value of the concentration factor reaches 20.

3.4. Absorption spectra

The maximum analytical signal for complexed cobalt with HTP and Am is observed at 540-565 nm (Fig. 2). HTP is maximally absorbed at 276-280 nm. The bathochromic shift is 264-285 nm. The contrast of the reactions is high: the initial reagents are almost colorless, and the complexes are red-violet. The molar absorption coefficients are $\varepsilon = (2.62-3.01) \times 10^4$.
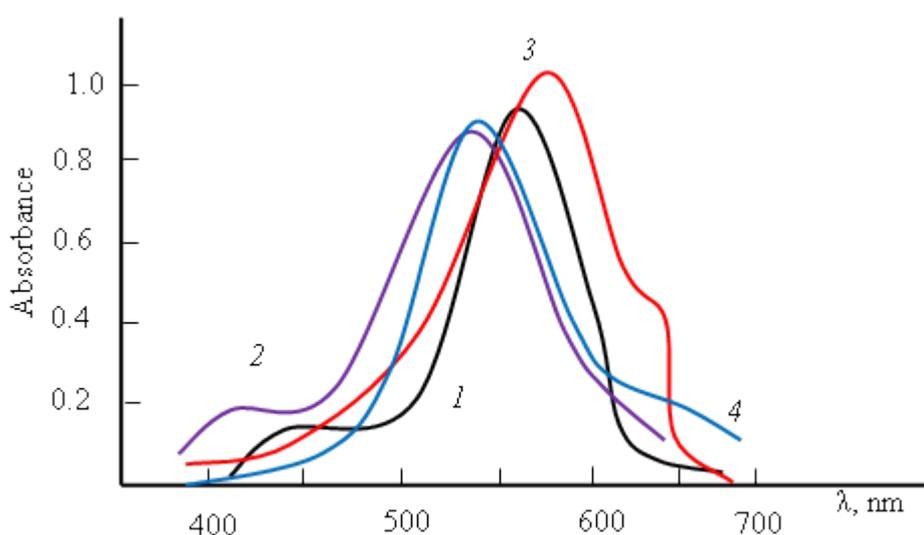
Fig.2. Absorption spectra of the complexes: 1- Co-HNTP-AP$_1$, 2-Co-HATP-AP$_1$,3- Co-HNTP-AP$_2$, 4- Co-HATP-AP$_2$

$C_{Co (II)} = 3.38 \times 10^{-5}$ M; $C_{HTP} = 7.2 \times 10^{-4}$ M; $C_{Am} = 1.04 \times 10^{-3}$ M; SF-26, $\ell = 1$ cm

3.5. Composition of complexes and mechanism of complex formation

The ratio of components in the complex corresponds to Co (II):HTP:AP=1:2:2; it was determined by the methods of straight line, equilibrium shift, and the relative yield [11] (Fig.3,4). By the method of Nazarenko, it was established that the complexing form of cobalt is Co^{2+} [12]. At the same time, the number of hydrogen atoms displaced from one molecule of HTP turned out to be equal to 1. Hence, the complexes can be regarded as ion associates between doubly charged anionic chelates $[Co(HTP^{2-})_2]^{2-}$ and two protonated Am species: $(AmH^+)_2[Co(HTP)_2]$. The stability constant of Co(II)-HTP-Am complexes was calculated and found to be lgβ = 10.57-10.94 (table 1) at room temperature.
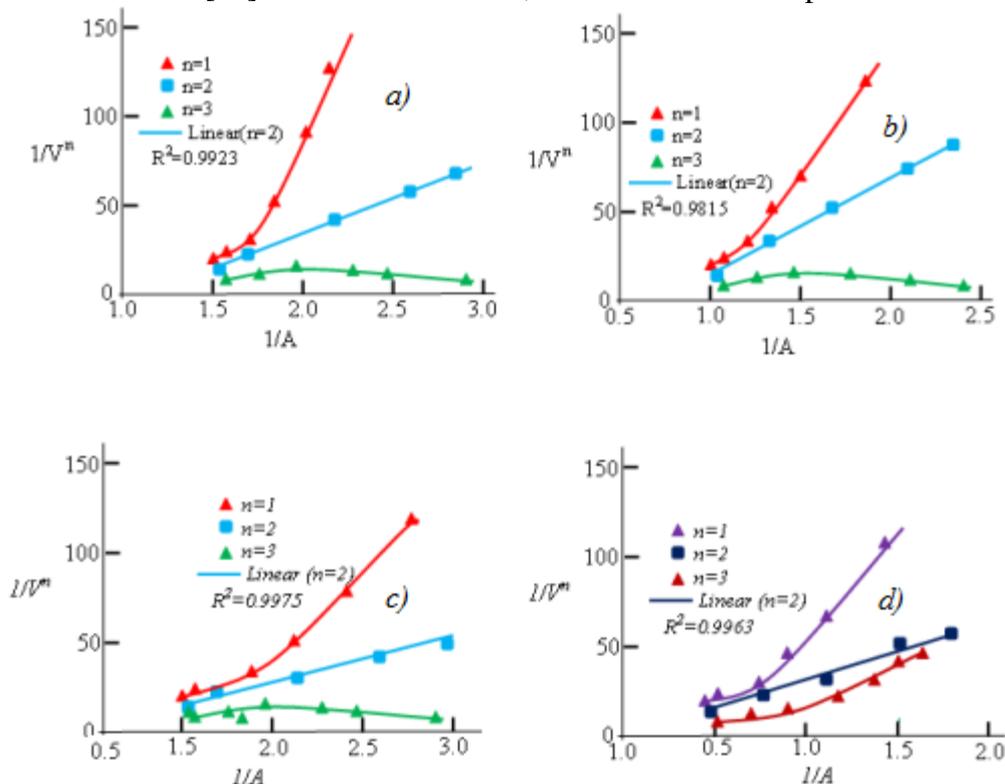

Fig.3. Determination of the *a*) Co:HATP and *b*) Co: AP$_1$; *c*) Co:HNTP and *d*) Co: AP$_1$ molar ratio by the method of Asmus. $C_{Co (II)} = 3.38 \times 10^{-5}$ M; $C_{HTP} = 7.2 \times 10^{-4}$ M; $C_{Am} = 1.0^4 \times 10^{-3}$ M; SF-26, $\ell = 1$ cm, pH 3.6-6.3.
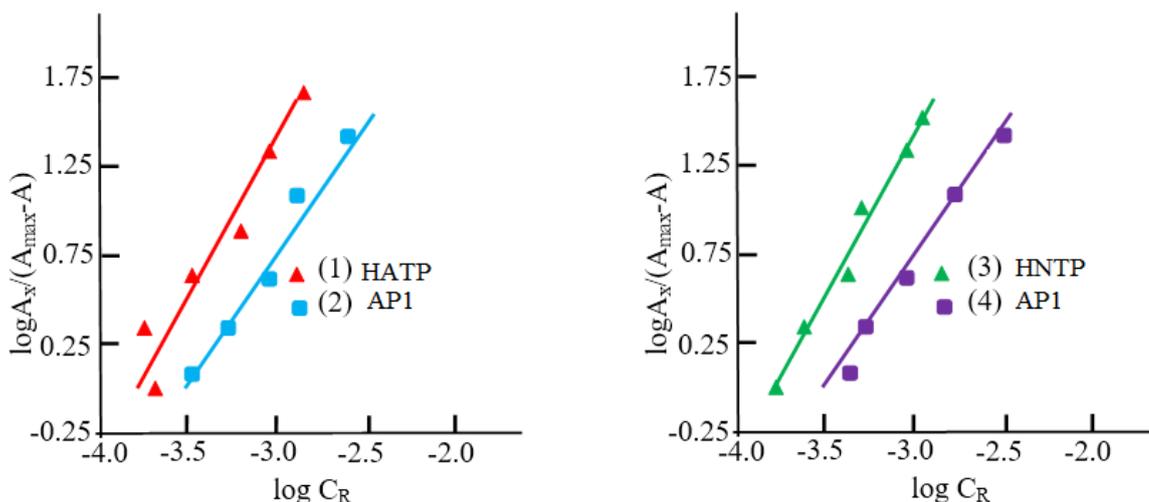
Fig.4. Determination of the ratio of components by the equilibrium shift method for Co (II)-HATP-AP_1 and Co(II)-HNTP-AP_1. 1- Co(II):HATP; 2- Co(II):Am.
$C_{Co\,(II)} = 3.38 \times 10^{-5}$ M; $C_{HTP} = 7.2 \times 10^{-4}$ M; $C_{Am} = 1.04 \times 10^{-3}$ M; SF-26, $\ell = 1$ cm, pH 3.6-5.3.

Taking into account the found ratio of the components in the complex and the ionic state of cobalt, it was assumed that the following reactions occur in the complexation (scheme):
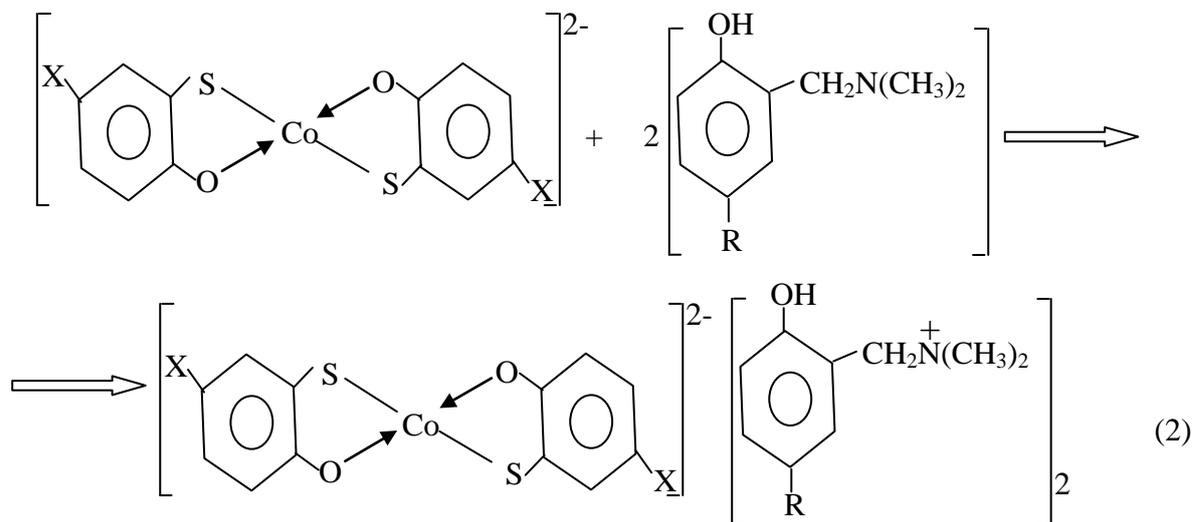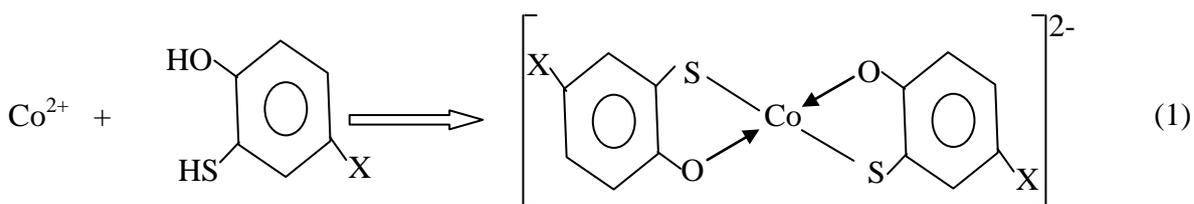
Whereas: X = -NH_2; -NO_2 and R = -CH_3, -Br

Scheme. Chemical mechanism of the process

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The disappearance of the pronounced absorption bands in the 3600-3200 cm-1 with a maximum at 3451 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 2587 cm^{-1} shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1385 cm^{-1} indicates the presence of a protonated diphenylamine (Fig. 5) [13].
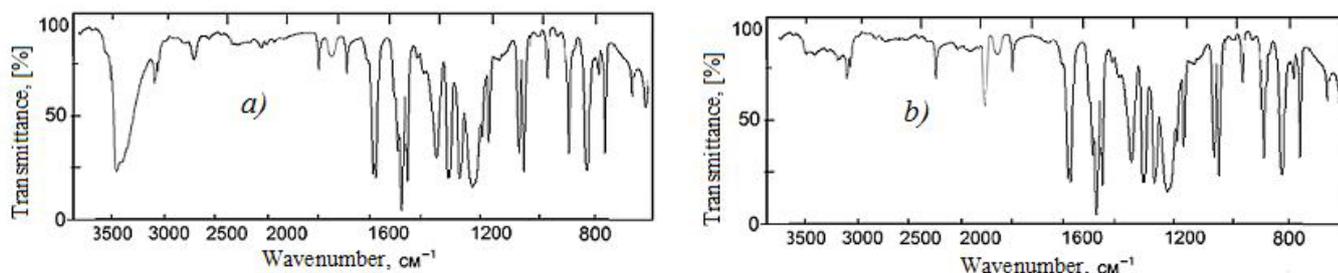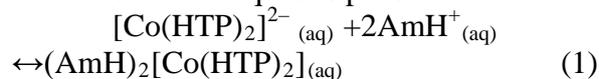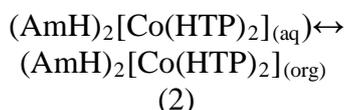

Fig. 5. IR spectrums of HNTP (a) and the Co (II)-HNTP-AP$_1$ (b).

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

Formation in the aqueous phase:
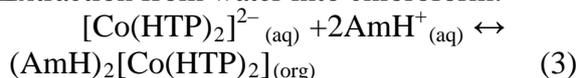
$$[Co(HTP)_2]^{2-}_{(aq)} + 2AmH^+_{(aq)}$$
$$\leftrightarrow (AmH)_2[Co(HTP)_2]_{(aq)} \quad (1)$$

Distribution:

$$(AmH)_2[Co(HTP)_2]_{(aq)} \leftrightarrow$$
$$(AmH)_2[Co(HTP)_2]_{(org)}$$
$$(2)$$

Extraction from water into chloroform:

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

The equilibrium constants describing these processes are shown in Table 1.

The sizes of equilibrium constant K_{eq} calculated on a formula $lgK_{eq} = lgD - 2lg[AmH^+]$ were presented in table 1.

Calculation of extent of polymerization of complexes was carried out on the equation [14]. The made calculations showed that ternary Co(II)-HTP-Am complexes in an organic phase won't be polymerized and are in a monomeric form (γ =1.13-1.22).

3.6. Influence of Interfering Ions

The effect of various ions and reagents on the extraction spectrophotometric determination of 30 µg cobalt (II) is summarised in Table 2. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^+, W^{6+}, Mo^{6+}, Cl^-, $S_2O_3^{2-}$, F^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, tartrate, citrate, oxalate and tiron; moderate amounts of Cr^{6+}, Cr^{3+}, Zn^{2+} and Cd^{2+}; and small amounts of Mn^{2+}, Sn^{2+}, Cu^{2+}, Al^{3+}, ascorbic acid and SCN^- are tolerable. Ni^{2+}, Fe^{2+}, Fe^{3+}, V^{4+}, V^{5+}, Ga^{3+}, In^{3+}, and Tl^{3+} interfere seriously at a ratio of 1:1 with respect to Co^{2+}. However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 2). Co-HTP-An-water-chloroform system are given in Table 2.

Table1 2. Influence of interfering ions on the determination of cobalt(II) as MLC with HTP and Am (30.0 µg Co added)

Foreign ions (FI)	Molar exsess of the ion	Masking agent	Co found (S_r)	
			HATP	HNTP
Mo^{6+}	60	EDTA	29.85 (7)	29.04 (6)
W^{6+}	55		29.88 (5)	92.77 (6)

Cr^{6+}	110		29.91 (4)	28.25 (7)
Cr^{3+}	65		29.80 (3)	29.08 (4)
Cu^{2+}	58	Thiourea	30.17 (7)	31.45 (2)
Al^{3+}	100		30.08 (4)	31.63 (7)
Zn^{2+}	70		30.04 (6)	30.82 (3)
Ni^{2+}	70		29.82 (4)	30.07 (6)
Fe^{2+}	80		29.25 (6)	31.01 (2)
Fe^{3+}	50	Ascorbic acid	30.90 (2)	31.04 (5)
Cd^{2+}	110		29.86 (6)	30.22 (6)
V^{5+}	75		29.25 (3)	29.09 (4)
V^{4+}	92		30.55 (5)	31.02 (3)
Zr^{4+}	45		30.18 (5)	30.51 (5)
Ti^{4+}	85	Ascorbic acid	30.17 (7)	31.34 (4)
Nb^{5+}	72		29.91 (5)	29.27 (7)
Ta^{5+}	88		29.25 (3)	30.06 (6)

3.7. Effect of Cobalt (II) Concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) may be determined in the range 0.5-100 μg/ml. Table 3 summarizes the calibration characteristics obtained with HTP+AP.

Table 3. Analytical characteristics of some ternary complexes of Co with o-hydroxythiophenol derivatives in the presence of Am

Compound	LOD*: ng ×mL^{-1}	LOQ*: ng ×mL^{-1}	SS*: μg× cm^{-2}	Beer's law range (μg ×5cm^{-3})	The equation of calibration curves
Co-HATP-AP$_1$	12	50	2.30	0.5-100	0.043+0.112x
Co-HATP-AP$_2$	13	44	2.22	0.5-80	0.059+0.113x
Co-HNTP-AP$_1$	14	42	2.17	0.8-90	0.071+0.119x
Co-HNTP-Ap$_2$	15	49	1.95	0.6-95	0.068+0.130x

Note: LOD- Limit of detection; LOQ - Limit of quantification; SS-Sandell's sensitivity.

The proposed method compares favourably with the existing ones (Table 4) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [15-19].

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

Reagent	pH (solvent)	λ, nm	$\varepsilon \cdot 10^{-4}$	Beer's law range ($\mu g \times 5cm^{-3}$)	[Ref.]
Nitroso-R-salt	weakly acidic medium	415	3.5	0.7-29	[15]
1-nitroso-2-naphtol	$\geq$3 (*iso*-butanol – chloroform (1:1))	415	2.9	0.8-56	[15, 16]
2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8($CHCl_3$)	525	4.26	0.2 - 75	[17-19]
2-nitroso-1-naphtol	$\geq$4 (*iso*-butanol – chloroform (1:1))	365	3.7	0.1-60	[15]
Co-HATP-AP $_1$	4.8–6.2 ($CHCl_3$)	540	2.62	0.5-100	Proposed method
Co-HATP-AP $_2$	4.9–6.3 ($CHCl_3$)	542	2.68	0.5-80	
Co-HNTP-AP$_1$	3.6–4.9 ($CHCl_3$)	562	2.96	0.8-90	
Co-HNTP-Ap $_2$	3.8–5.0 ($CHCl_3$)	565	3.01	0.6-95	

4. Conclusions

1. Complex formation and liquid-liquid extraction were studied in systems containing Co(II), 2-hydroxy-5-thiophenols (HTP)-2 hydroxy-5-aminothiophenol (HATP) and 2-hydroxy-5-nitrothiophenol (HATP), hydrophobic amines (Am) {2- (N, N-dimethylaminomethyl) -4-bromophenol (AP$_1$) and 2- (N, N-diethylaminomethyl) -4-methylphenol (AP$_2$)}, water and chloroform.

2. For the selection of optimal conditions, the effect of the concentration of reacting substances, temperature and time on the formation of MLC was studied. The yield of the complexes is maximal at a concentration of 7.2×10^{-4} mol / l HTP and 1.04×10^{-3} mol / l Am.

3. The degree of extraction in the form of MLC does not depend on the ratio of volumes of water and organic phases in a wide range (from 5: 5 to 100: 5), which allows simultaneous concentration and photometric determination of cobalt. The value of the concentration factor reaches 20.

4. The maximum analytical signal for complexed cobalt with HTP and Am is observed at 540-565 nm. The contrast of the reactions is high: the initial reagents are almost colorless, and the complexes are red-violet. The molar absorption coefficients are $\varepsilon = (2.62-3.01) \times 10^4$.

5. The ratio of components in the complex corresponds to Co (II):HTP:AP=1:2:2; it was determined by the methods of straight line, equilibrium shift, and the relative yield. By the method of Nazarenko, it was established that the complexing form of cobalt is Co^{2+}.

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