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Extraction-photometric determination of cobalt (II) with *o*-Hydroxythiophenol derivatives and hydrophobic amines

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Abstract
Mixed-ligand complexes of Cobalt (II) with *o*-hydroxythiophenol derivatives (HTPD) {2-hydroxythiophenol (HTP) (DTP) and its derivatives (2-hydroxy-5-chlorothiophenol (HCTP), 4-hydroxy-3-thiolsulfonic acid (HTSA), 4-hydroxy-3-thiolbenzoic acid (HTBA), 4-Nitro-2-hydroxythiophenol (HNTP)} in the presence of hydrophobic amines (Am) have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 1, 9-5, 1. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components in the complexes have been determined. The Beer's law was applicable in the range of 0.05-3,2μg/ml. The effect of foreign ions and reagents on the extraction was studied. The method is free from common interferences. A procedure has been developed for extraction – spectrophotometric determination Cobalt in different objects.

Keywords: Cobalt, o-hydroxythiophenol derivatives, solvent extraction, spectrophotometry, ion-associate

1. Introduction
Cobalt is a transition element of high industrial importance because of its valuable alloying, dyeing, magnetic, catalytic and plating properties. It is also of biological significance thanks to its ability to be an active center of coenzymes, e. g. vitamin B12. [1, 2] A great variety of photometric reagents is known for the determination of cobalt. For photometric determination of cobalt are quite selective reagents o-nitrozofenole group or a similar structure with the oxime group [3]. Complex formation and liquid-liquid extraction were studied in systems containing Co(II), 4-(2-pyridylazo) resorcinol, tetrazolium salt {2, 3, 5-triphenyl-2H-tetrazolium chloride (TTC) or 2-(4-iodophenyl)-3-(4-nitrophenyl) -5-phenyl-2H-tetrazolium chloride (INT)}, water and chloroform [4]. The complex formation and a liquid-liquid extraction in the cobalt (II) - 4-(2- thiazolylazo) resorcinol (TAR) - 2, 3, 5-triphenyl-2H-tetrazolium chloride (TTC)-water–chloroform system was studied [5]. Complex formation and liquid-liquid extraction were studied in a system containing cobalt(II), 4-(2-pyridylazo) resorcinol (PAR), 1, 4-diphenyl-3-(phenylamino)-1H-1, 2, 4- triazol [6, 7]. A new solid-phase extraction method was developed for trace analysis of cobalt on Duolite XAD-761 resin by using flame atomic absorption spectrometry [8]. Complex formation and liquid-liquid extraction were studied in a system containing cobalt (II), 4-(2-pyridylazo) resorcinol (PAR), 1, 4-diphenyl-3-(phenylamino)-1H-1, 2, 4- triazole (Nitron, Nt), water, and chloroform. The effect of some experimental parameters (pH, shaking time, concentration of PAR, and concentration of Nt) was systematically investigated, and the optimum conditions for cobalt extraction as an ion-association complex, (NtH$^+$) [Co^{3+} (PAR)$_2$], were found [9].
Oxyphenolate and dithiophenolate complexes of cobalt are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [10-12]. In this respect, a very promising reagent is o-hydroxythiolphenols (HTPD), which contains one hydroxyl and one sulphohydryl groups and is a sulfur-containing analogue of mononuclear poly-phenols with two oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Cobalt (II) with o-hydroxythiolphenols (o-HP) in the presence of hydrophobic amines (Am). From o-hydroxythiolphenols {2-hydroxythiophenol (HTP) and its derivatives

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(2-hydroxy-5-chlorothiophenol (HCTP), 4-hydroxy-3-thiolsulfonic acid (HTSA), 4-hydroxy-3-thiolbenzoic acid (HTBA), 4-Nitro-2-hydroxythiophenol (HNTP)} in the presence of hydrophobic amines (Am were used. in the presence of hydrophobic amines (Am). As hydrophobic amine aniline (An) and N-methylaniline (mAn) were used.

2. Experimental
2.1 Reagents and Instruments
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 [13]. The concentration of the cobalt solution was adjusted gravimetrically [3]. Solutions of HTPD and Am in chloroform (0.01M) were used. HTPD were synthesized according to the procedure [14]. Their purity was verified by melting point determination and paper chromatography. To create the optimal acidity, 0.1M solutions of KOH and HCl or $CH_3COOH+CH_3COONH_4$ buffers were applied. The extractant was purified chloroform. The absorbance was recorded with a KFK-2 photocolorimeter and a SF 26 spectrophotometer (USSR), equipped with 5 and 10 mm pathlength cells. pH was measured using an I-120.2 potentiometer with a glass electrode.

2.2 General Procedure
2.2.1 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 HTPD, 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 8 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 540 nm (ℓ=0.5cm).

2.2.2 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.

2.3.3 Determination of Co (II) in Sewage Water and Bottom Sediments
1l 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.

3. Results and Discussion
3.1 Charge of the complexes and Choice of organic solvent
The binary complexes Co(II)-HTPD, cannot be extracted in chloroform or other slightly polar organic solvents. Experiments with KU-2 and AV-17 ion-exchangers showed that these species are charged negatively. Electroneutral ternary complexes can be formed in the presence of Am.

The following organic solvents were tested for the extraction of these complexes: chloroform, 1, 2-dichloroethane, carbon tetrachloride, benzene, toluene, xylene, *iso*-butanol, and *iso*-pentanol. Chloroform was found to be the most effective. At the optimum conditions this solvent provides degrees of extraction R=95.9–99.1 % (Table 1).

Table 1: Optical characteristics, precision and accuracy of the spectrophotometric determination of Co(II) with HTPD and Am

Compound	The pH range of maximum extraction	R,%	λ_{max} (nm)	Molar absorptivity (L· mol^{-1} cm^{-1}) $\varepsilon \cdot 10^{-4}$	lgK$_{eq}$	lgβ	lgK$_{ex}$	Working range / μg 5cm^{-3}
Co-HTP-An	3.5-5.8	98.4	545	2.58	8.46	13.67	10.56	0.5-70
Co-HTP-mAn	3.6-5.9	98.5	550	2.71	8.49	13.62	10.58	0.5-80
Co-HXTP-An	3.0-5.1	96.9	552	2.89	7.96	12.85	10.61	0.5-85
Co-HXTP-mAn	3.1-5.2	97.4	560	2.97	7.98	12.83	10.65	0.6-80
Co- HTSA -An	2.5-4.1	95.9	540	3.12	7.78	12.55	10.72	0.5-100
Co- HTSA -mAn	2.3-3.8	97.8	548	3.38	7.81	12.64	10.77	0.6-95
Co- HTBA -An	2.4-3.5	96.7	556	3.49	7.41	11.94	10.83	0.5-80
Co- HTBA -mAn	2.2-3.4	98.3	552	3.55	7.58	12.20	10.85	0.5-85
Co- HNTP -An	1.9-3.1	99.1	558	3.69	6.38	10.24	10.89	0.6-80
Co- HNTP -mAn	1.8-2.9	98.5	560	3.72	6.65	10.17	10.92	0.5-80

3.2. Influence of the pH of the Aqueous Phase
The effect of pH on the formation of Co(II)- HTPD -Am complex was studied, in order to find a suitable pH that can be adopted in the determination of cobalt(II) (Fig. 1). The absorbance was found to be maximum in the pH range 1.8-5.8. Extraction of Co(II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrase of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HTPD. Probably, it is present in the solution in the nondissociated state. At pH $\geq$ 7.6, the complexes were hardly extracted, obviously because of the decrease in the degree of Am protonation.

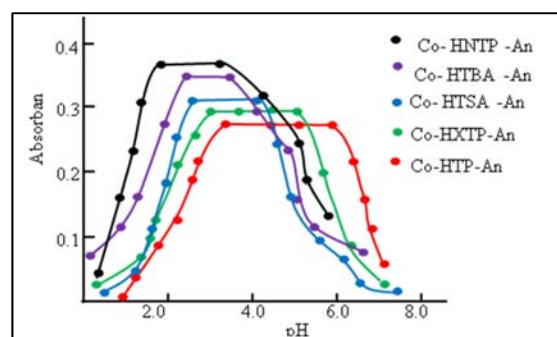**Fig 1:** Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. C_{Co}=2.035×10^{-5} M; C_{HTPD} = C_{Am}=1.0·10^{-3} M, λ=540 nm, ℓ=0.5 cm

3.3 Absorption maxima, reagents concentrations, molar absorptivities and effect of time

The absorption maxima (λ_{max}) of the ternary Co(II)-HTPD-Am complexes lie in the range of 540-560 nm (Table I). All colour reactions are very contrast since the initial solutions are colourless ($\lambda_{max\ HTPD}$ = 275-280 nm). Complete extraction is achieved at reagent concentrations not lower than (1.3-1.5)×10^{-3} mol mL$^-$ (HTPD) and (1.2-1.5)×10^{-3} mol mL$^-$ (Am). Co(II) concentration ranges in which the Beer's law is obeyed are listed in Table 1. The calculated molar absorptivities (ε_{max}) belong to the interval (2, 58-3, 71)×10^4 mL mol^{-1} cm^{-1}. Colour develops almost immediately after the reagents addition. The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 10 min.
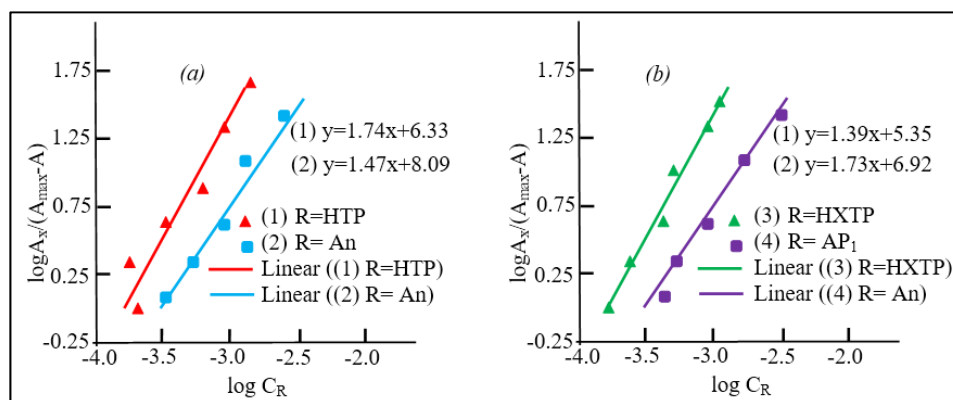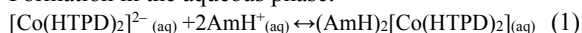
3.4 Stoichiometry of the Complexes and the Mechanism of Complexation

The molar ratios of the components of the ternary complexes were established by the equilibrium shift method and the method of Asmus [15]. The results show a complex composition of 1:2:2 (Co(II):HTPD:Am). The formation of ternary complexes can be presented in the following way. When cobalt interact with two molecules of HTPD, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am. (Fig. 2). Using the Nazarenko's method [16], we found that the cobalt complexation form is Co^{2+}. Hence, the complexes can be regarded as ion associates between doubly charged anionic chelates $[Co(HTPD^{2-})_2]^{2-}$ and two protonated Am species: $(AmH^+)_2[Co(HTPD)_2]$. The stability constant of Co(II)-HTPD-Am complexes was calculated and found to be lgβ = 10.17-13.67 at room temperature.

Fig 2: Determination of the HTPD-to-Co (straight line 1) and the Am-to-Co (straight line 2) molar ratios by the mobile equilibrium method. C_{Co} = 1.7×10^{-5}mol L^{-1}, C_{HITP} = 2.0×10^{-3} mol L^{-1}, C_{AP1} = 2.5×10^{-3} mol L^{-1}, λ=540 nm, KFK-2 ℓ=0.5 cm.
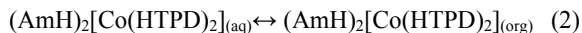
The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3460 sm^{-1} observed in the spectrum of HTPD, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2580 sm^{-1} shows that -SH group involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 2380 cm^{-1} indicates the presence of a protonated aniline [17].

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $(AmH^+)_2[Co(HTPD)_2]$.
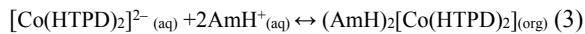
Formation in the aqueous phase:

$[Co(HTPD)_2]^{2-}$ $_{(aq)}$ +2AmH$^+_{(aq)}$ $\leftrightarrow$(AmH)$_2$[Co(HTPD)$_2$]$_{(aq)}$ (1)

Distribution:

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

Extraction from water into chloroform:

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

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

The stability constant determined by crossed lines method. The sizes of equilibrium cons-tant K_e calculated on a formula lg K_e = lgD − 2lg[AmH$^+$] were presented in table 1. Calculation of extent of polymerization of complexes was carried out on the equation [18]. The made calculations showed that ternary Co(II)-HTPD-Am complexes in an organic phase won't be polymerized and are in a monomeric form (γ =1,08-1,31).

3.5 Effect of foreign ions and reagents

The effect of various ions and reagents on the extraction-spectrophotometric determination of 20 μg cobalt (II) is summarised in Table 2. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH$_4^+$, W(VI), Mo(VI), Cl$^-$, S$_2$O$_3^{2-}$, F$^-$, NO$_3^-$, SO$_4^{2-}$, 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), Ga(III), In(III), and Tl(III) interfere seriously at a ratio of 1:1 with respect to Co(II). 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.

Table 2: Effect of foreign ions on the extraction of 20 μg cobalt (II)

Foreign ions and reagents (FI)	mg	FI-to-Co ratio	Co found	R, %	Foreign ions and reagents (FI)	mg	FI-to-Co ratio	Co found	R, %
Citrate^{3-}	5	250	20.03	100.5	Fe(II)	0.5	2.5	19.25	85.0
Oxalate^{2-}	10	200	20.13	102.6	Fe(III)	0.5	2.5	20.90	118.0
Tartrate^{2-}	2.5	250	5.05	101.0		1.0^a	20	20.05	101.0
Ascorbic acid	0.5	25	5.15	103.1	V(IV)	0.05	2.5	20.55	111.0
EDTA	0.5	25	5.10	102.0	V(V)	0.05	2.5	19.25	85.0

CDTA	0.005	0.25	19.73	94.6	Cd^{2+}	0.2	10	19.86	97.2
Tiron	2.5	125	20.11	102.5	Cu^{2+}	0.06	3	20.17	103.4
SCN^-	0.025	10	20.13	102.6		1.2[b]	6	20.04	100.8
Cl^-	20	100	20.20	104.0	Al^{3+}	5	250	20.08	101.6
$S_2O_3^{2-}$	10	200	19.92	98.5		10[c]	500	20.02	100.3
F^-	10	500	20.20	104.0		10[d]	500	20.13	100.4
NO_3^-	20	1000	20.02	100.3	Zn^{2+}	0.5	25	20.04	100.8
SO_4^{2-}	20	500	20.03	100.5		1.0[e]	50	20.18	103.5
PO_4^{3-}	7	225	20.10	102.0	Zr(IV)	3.0	150	20.18	103.5
ClO_4^-	0.1	0.5	20.73	94.6		15[f]	500	20.01	100.2
NH_4^+	20	500	20.02	100.3	Nb(V)	0.5	2.5	19.25	85.0
Na^+	30	1500	20.13	100.4		10[f]	500	20.04	100.8
K^+	30	1500	20.11	102.2	Ti(IV)	2.5	125	20.17	103.4
Ca^{2+}	15	500	20.01	100.2		5[i]	250	19.88	97.7
Ba^{2+}	5	250	20.15	103.1	Ni^{2+}	2.5	125	19.91	98.2
Sr^{2+}	20	100	20.11	102.2	Cr(VI)	2.5	125	19.91	98.2
Mg^{2+}	30	1500	20.18	103.5	Cr(III)	1.5	75	19.80	96.0
Mo(VI)	5	250	19.85	97.0	W(VI)	5	250	19.88	97.7

[a] in the presence of 2.5 mg oxalate;
[b] in the presence of 0.75 mg $SC(NH_2)_2$; 10 min extraction time;
[c] in the presence of 2.5 mg oxalate;
[d] in the presence of 3.0 mg citrate;
[e] in the presence of 0.75 mg EDTA; 15 min extraction time;
[f] in the presence of 3.0 mg NaF;
[i] in the presence of 3.0 mg Ascorbic acid.

3.6 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 $\mu\mu$g/ml (table 1). Table 3 summarizes the calibration characteristics obtained with HTPD+An. With the increase of the basic amine (pKa) complexes improved analytical parameters (pKa(An)=4.58, pKa(mAn) = 4.85.

Table 3: Analytical characteristics of some ternary complexes of Co with *o*-hydroxythiophenol derivatives in the Presence of aniline

Compound	LOD*:ng ·mL⁻¹	LOQ*:ng ·mL⁻¹	SS*:µg· cm⁻²	Beer's law range (µg· mL⁻¹)	The equation of calibration curves
Co-HTP-An	15	53	2.30	0.05-2.8	0.045+0.110x
Co-HXTP-An	14	46	2.22	0.05-2.8	0.056+0.107x
Co- HTSA -An	13	42	2.17	0.05-2.8	0.069+0.103x
Co- HTBA -An	13	42	1.95	0.05-3.0	0.045+0.131x
Co- HNTP -An	12	39	1.87	0.05-3.2	0.054+0.133x

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 [2-6].

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

Reagent [Ref.]	pH (solvent)	λ, nm	ε·10⁻⁴	Beer's law range (µg ×5cm⁻³)
Nitroso-R-salt [2]	weakly acidic medium	415	3.5	0.7-29
1-nitroso-2-naphtol [2, 3]	≥3	415	2.9	0.8-56
2,3,5-triphenyl-2H-tetrazolium chloride [4-6]	5.2-5.8	525	4.26	0.2 - 75
2-nitroso-1-naphtol [2]	≥4	365	3.7	0.1-60
HTSA –An	2.3-3.8($CHCl_3$)	540	3.12	0.6-95
HTBA -An	2.4-3.5 ($CHCl_3$)	556	3.49	0.5-80
HNTP -An	1.9-3.1 ($CHCl_3$)	558	3.72	0.6-80

3.7. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Co(II) in various objects. The results presented in Table 5 and Table 6 indicate the successful applicability of the proposed method to real sample analysis.

Table 5: Determination of Cobalt in steel (*n*=6, *P*=0.95)

Compound	Steel	X	S_x	ε	S_r	µ
Co-HTP-An		0.0124	3.12×10⁻⁴	3.28×10⁻⁴	0.025	(1.24±0.0328) ×10⁻²
Co-HXTP-An	M 441 (0.012 %Co)	0.0129	3.27 ×10⁻⁴	3.31×10⁻⁴	0.022	(1.29±0.0331) ×10⁻²
Co- HTSA -An		0.0118	3.16 ×10⁻⁴	3.45×10⁻⁴	0.017	(1.18±0.0345) ×10⁻²
Co- HTSA -An		0.520	0.026	0.021	0.037	0.520±0.0210
Co- HTBA -An	№156 (0.56 % Co)	0.569	0.020	0.027	0.033	0.569±0.027
Co- HNTP -An		0.552	0.029	0.021	0.049	0.552±0.021

Table 6: Determination results of cobalt (II) in the Sewage water and Bottom sediments ($n = 6$, $P = 0.95$)

Compound	Analysis object	Added, µg	Found, µg	Found in the sample, µg / kg $\bar{X} = \pm \dfrac{t_p S}{\sqrt{n}}$	S$_r$
			Sewage water		
Co- HTBA -An	Sample 1	2.0	2.45	0.45±0.05	0.06
Co- HNTP -An	Sample 2	5.0	6.14	1.14±0.11	0.07
			Bottom sediments		
Co- HTBA -An	Sample 1	5	6.26	1.26±0.05	0.05
Co- HNTP -An	Sample 2	5	6.92	1.92±0.04	0.08

4. Conclusions

1. Mixed-ligand complexes of Cobalt (II) with HTPD and Am have been studied by spectrophotometry. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found: The absorbance was found to be maximum in the pH range 1.8-5.8. Complete extraction is achieved at reagent concentrations not lower than $(1.3\text{-}1.5)\times10^{-3}$ mol mL$^-$ (HTPD) and $(1.2\text{-}1.5)\times10^{-3}$ mol mL$^-$ (Am). Colour develops almost immediately after the reagents addition. The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 10 min. The absorption maxima (λ_{max}) of the ternary Co(II)-HTPD-Am complexes lie in the range of 540-560 nm. The calculated molar absorptivities (ε_{max}) belong to the interval $(2, 58\text{-}3, 71)\times10^4$ mL mol^{-1} cm^{-1}.

2. The molar ratio of the reacting Co(II), HTPD and Am species is 1:2:2. The general formula of the ternary complexes is $[Co(HTPD)_2](AmH)_2$. They can be regarded as ion-associates between doubly chargedanionic chelates $[Co(HTPD)_2]^{2-}$ and protonated Am species.

3. The developed method retains specific interaction of cobalt (II) with HTPD and Am to form a colored complex and has good sensitivity at room temperature. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity. This proposed method has good precision and accuracy. A procedure has been developed for extraction-spectrophotometric determination Cobalt in various objects.

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