

Extraction-Spectrophotometric Study on the Complex Formation in the Cobalt (II) - 4-Hydroxy-3-Thiolbenzoic Acid - Diphenylguanidine System

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ABSTRACT

A simple, rapid and sensitive spectrophotometric method has been developed for the determination of Co(II) by using 4-hydroxy-3-thiolbenzoic acid (HTBA) as an analytical reagent. HTBA has been synthesized and characterized by elemental and spectral analysis. HTBA in the presence of diphenylguanidine (DPG) extracts Co(II) quantitatively (97.6 %) into chloroform from an aqueous solution of pH range 5.1-6.9. The chloroform extract shows an intense peak at 542 nm. Beer's law is obeyed over the Co(II) concentration range of 0.5-12.0 $\mu\text{g}/\text{cm}^3$. The composition of extracted species is found to be 1:2:2 [Co : HTBA : DPG]. Thermogravimetric study of the complex $\text{Co}(\text{C}_7\text{H}_3\text{O}_3\text{S})_2(\text{C}_{13}\text{H}_{14}\text{N}_3)_2(\text{H}_2\text{O})_2$ shown that thermal decomposition of the complex takes place in three stages: at 65-120° C water evaporates, at 430 - 498° C-decomposed DPG and at 510-520° C - HTBA. The final product of the termolysis of the complex is Co_2O_3 . The proposed method is rapid, sensitive, reproducible and has been successfully applied for determination of Co(II) in the Sewage water, Bottom sediments and plants. The method is eco-friendly, as extraction is carried out in pH medium and has good potential for its use in the determination of Co(II) after extraction in organic phase at microgram level.

KEYWORDS: Cobalt, 4-hydroxy-3-thiolbenzoic acid, diphenylguanidin, chloroform, solvent extraction.

1. INTRODUCTION

Modern requirements to the objects of the analysis of the environment and food products include the development of new highly sensitive and rapid methods for the determination of toxic metals. One of the promising methods for the determination of metals in complex objects are spectrophotometric methods of analysis. Multicomponent analysis of objects, low concentrations of metal contaminants to solve such problems, necessitate the use of combined methods of analysis, including the concentration step. Cobalt (II) are biologically active metal. It is found that excessive "technogenic" flow of data in the body of metal compounds has a toxic effect on the metabolism. An excess of cobalt salts causes morphological changes in the cell and thereby renders it carcinogen. They play an important role in the biological processes occurring in the body, and are an indicator of certain diseases [1]. Therefore, the analytical control of their content should be carried out sufficiently reliable methods.

A great variety of photometric reagents is known for the determination of cobalt. However, the studies aiming to find and investigate new photometric reagents with different functional groups are still going on. For photometric determination of cobalt are quite selective reagents o-nitrozofenole group or a similar structure with the oxime group [2].

The synthesis and characterization of mixed ligand complexes of Cobalt (II) with phthalic and heterocyclic amines were synthesized and characterized on the basis of elemental analysis, conductometric, magnetic measurements, UV-vis and IR spectral studies [3].

Complex formation and liquid-liquid extraction were studied in a system containing cobalt(II), 4-(2-pyridylazo) resorcinol, 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazol (Nt) [4]. 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, $(\text{NtH}^+)[\text{Co}^{3+}(\text{PAR})_2]$, were found. The complex formation and a liquid-liquid extraction in the cobalt (II) - 4-(2-thiazolylazo) resorcinol - 2,3,5-triphenyl-2H-tetrazolium chloride - water - chloroform system was studied [5].

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 or 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride, water and chloroform [6-8]. Several analytical methods have been used for determination cobalt, including flame atomic absorption spectrophotometry, graphite furnace atomic absorption spectrometry, electrothermal atomic absorption spectrometry, atomic fluorescence spectrometry, inductively coupled plasma-optical emission spectrometry, and spectrophotometry [2-15].

Dithiolphenols and hydroxithiophenols [TPh] has been proved to be one of the most important reagents for cobalt separation, preconcentration and determination [10-13]. TPh forms with Co(II) intensively colored anionic chelates, $[\text{Co}^{2+}(\text{TPh})_2]^{2-}$, which can readily react with bulky organic compounds [10-13] to give ternary complexes with good extraction behavior and analytical potential.

Application of MLC in many cases leads to increase in selectivity, contrast of reactions, improvement of extraction and other properties. Introduction of the second reagent often leads to improvement of extraction properties of complexes and decrease in a limit of detection.

In the present communication, we describe the extractive spectrophotometric determination of Co(II) with 4-hydroxy-3-thiolbenzoic acid (HTBA) in presence diphenylguanidine (DPG).

2. MATERIALS AND METHODS

2.1. Reagents and instruments

A stock solution ($1\mu\text{g} / \text{mL}$) of cobalt (II) was purchased from Merck Darmstadt (Germany) $\text{Co}(\text{NO}_3)_2$ [14]. The concentration of the cobalt and nickel solution was adjusted gravimetrically. Working solutions of Co(II) were made by diluting the stock solution to an appropriate volume. HTBA were synthesized according to the procedure [15]. HTBA was recrystallised using aqueous ethanol. Its solution (0.01 M) was prepared in chloroform. Structure of ligand was confirmed by using NMR and IR spectra {NMR: [^1H NMR (300,18 MHz, C_6D_6); 5.24 (s, 1H - OH), δ 3.32(s, 1H - 1SH), δ 7.11 (s, 3H Ar-H), δ 12.38 (s, 1H -COOH)], IR: [IR (KBr); 3470 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2580 cm^{-1} ν (SH), 1580 cm^{-1} ν (C_6H_5), 1380 cm^{-1} ν (COOH)]} [16].

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer (Japan) and KFK 2 photocolormeter (USSR). Glass cells with optical path of 10 or 5 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples. IR spectra were recorded on a spectrophotometer "Specord M80" (Germany). ^1H -NMR spectra were recorded on "Bruker" Fourier Transform (300,18 MHz) in C_6D_6 .

2.2. Procedure for establishing the optimum operating conditions

An aliquot containing no more than $90\mu\text{g}$ of cobalt was placed in a calibrated tube with ground-glass stopper. Then chloroform solutions of HTBA (0.8 mL) and DPG (0.6 mL) were added and the chloroform phase was adjusted to 5 mL; the volume of the aqueous phase and pH were adjusted to 25 mL and 5.0, respectively. After 10 min of shaking, a portion of the organic

extract was transferred through a filter paper into a cell and the absorbance was read at $\lambda=540$ nm against chloroform. The cobalt content was found from a calibration graph.

2.3. 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.

2.4. 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 HTBA and DPG.

3. RESULTS AND DISCUSSION

3.1 Charge of the complexes

Cobalt(II) reacts with 4-hydroxy-3-thiolbenzoic acid and gives a purple colored complex. These complex are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE-ethylenediamine, epichlorohydrin; 10- serial number of the brand: P- means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single-ligand complex, in the electromigration study of the complexes, it was found that the purple 4-hydroxy-3-thiolbenzoic acid complex of Co(II) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-

10P anion exchanger completely absorbed the colored component of the solution. When DPG were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

3.2. Choice of Solvent

The following organic solvents were tested in our experiments: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, xylene, isobutanol, isopentanol, and diethyl ether. The distribution coefficients and extraction rates with these solvents were evaluated. The best ones were chloroform (extraction rate of 97.6%), 1,2-dichloroethane, and carbon tetrachloride. All further investigations were performed with chloroform. The extraction equilibrium with this solvent is achieved for ca. 6-7 min, but we carried out the extraction for 10 min.

3.3. Effect of pH

The effect of pH on the extraction of the ternary species is represented on Figure 1. Studying of dependence of a complex formation from pH showed that, the exit of complexes of cobalt is maximum at pH 5.1 – 6.9. Extraction of Co(II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HTBA. Probably, it is present in the solution in the non-dissociated state. At $\text{pH} \geq 10$, the complexes were hardly extracted, obviously because of the decrease in the degree of DPG protonation. The effect of pH on the intensity of the color reaction is shown in the Fig. 1. Existence of one maximum of absorbance in the specified limits pH confirms the assumption of formation of one complex connection.

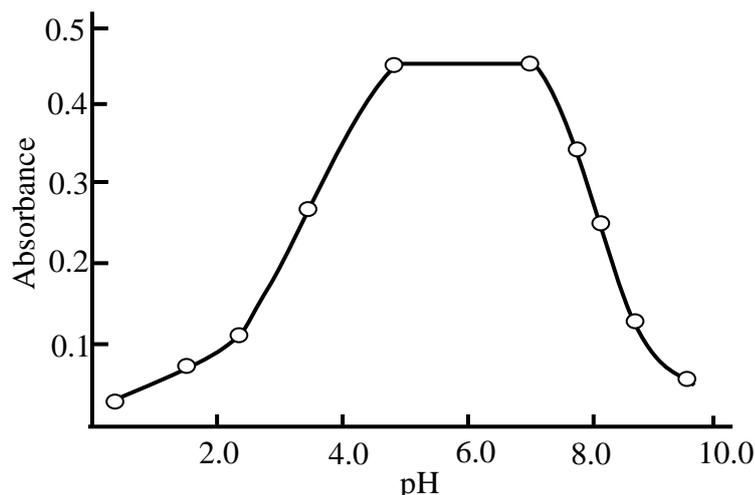


Figure 1: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. $C_{Co}=2.035 \times 10^{-5}$ M; $C_{HTBA} = C_{DPG}=1.0 \cdot 10^{-3}$ M, $\lambda=540$ nm, $\ell=0.5$ cm

3.4. Absorption spectra

Spectra of the extracted in chloroform ternary Co(II)-HTBA-DPG complex are shown in Figure 2. The absorption measurements were made in the spectral range 360–750 nm. The absorption maximum of the ternary complex lies at $\lambda=542$ nm, while the maximum of HTP is at $\lambda=296$ nm. Therefore the colour reaction is very contrast (bathochromic shift of 246 nm). It is

shifted to 15 nm as compared to the maximum of the binary Co(II)-HTBA chelate existing in aqueous medium (in the pH interval from 3.0 to 9.8). Close values of maxima of light absorption allow to draw a conclusion that the formed complexes were ionic associates. The corresponding molar absorptivity was $\epsilon_{542}=3.8 \times 10^4$ L mol⁻¹ cm⁻¹.

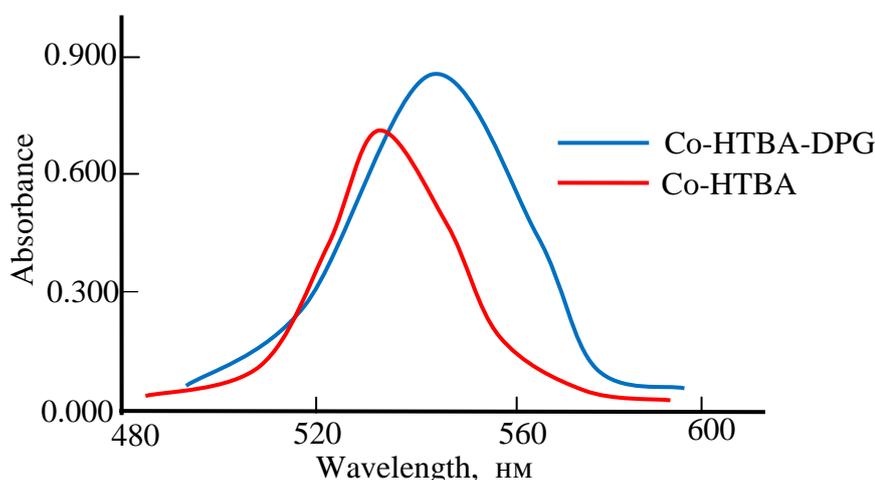


Figure 2: Absorption spectra of the complexes Co(II)-HTBA-DPG and Co-HTBA $C_{Co}=2.035 \times 10^{-5}$ M; $C_{HTBA} = C_{DPG}=1.0 \cdot 10^{-3}$ M, pH 5.5, Shimadzu UV1240, $\ell= 1.0$ cm

3.5. Effect of reagent concentration and of shaking time

It was also found that there was no adverse effect of excess reagent concentration. Therefore 60-

100 fold excess of reagent was suggested in general procedure to ensure complete complexation of Co (II).

The optimum concentrations of the reagents in the organic phase are $1.2 \times 10^{-3} \text{ mol L}^{-1}$ (HTBA). In present investigation 5 minute shaking time was recommended for quantitative extraction of Co(II) in organic phase. The colour of the chloroform extract was found to be stable at least 48 hrs at room temperature.

3.6. Composition of the complexes and structure formulae

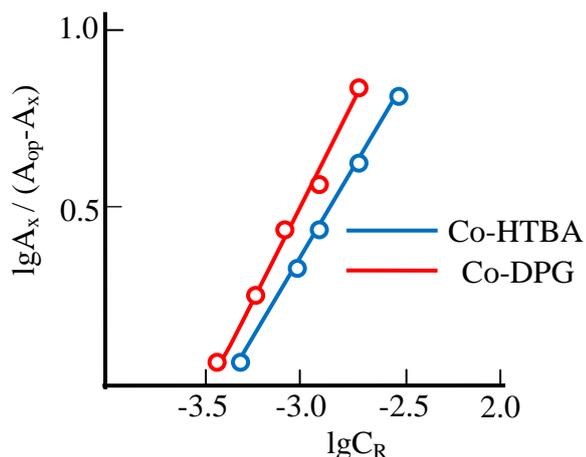


Figure 3: Determination of the ratio of components by equilibrium shift method.

$C_{\text{Co}} = 2.035 \times 10^{-5} \text{ M}$; $C_{\text{HTBA}} = C_{\text{DPG}} = 1.0 \cdot 10^{-3} \text{ M}$, pH 5.5, $\lambda = 540 \text{ nm}$, KFK-2. $l = 0.5 \text{ cm}$.

The existence of clearly defined absorption bands at $2410 - 2415 \text{ cm}^{-1}$ in the IR-spectrum of the complex indicates the coordination of the DFG in the protonated form. The disappearance of the band at 2580 cm^{-1} , characteristic for the spectrum of HTBA, 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 $3200 - 3600 \text{ cm}^{-1}$ with a maximum at 3460 cm^{-1} and the appearance of a broad band in the region of $3050 - 3150 \text{ cm}^{-1}$ shows that the hydroxyl group participates in the formation of a coordination bond [16].

Thermogravimetric study of the complex $\text{Co}(\text{C}_7\text{H}_3\text{O}_3\text{S})_2(\text{C}_{13}\text{H}_{14}\text{N}_3)_2(\text{H}_2\text{O})_2$ shown that thermal decomposition of the complex takes place in three stages: at $65 - 120^\circ \text{ C}$ water evaporates (weight loss - 4.33 %), at $430 - 498^\circ \text{ C}$ decomposed DPG (weight loss - 48.55%), and

and $2.0 \times 10^{-3} \text{ mol L}^{-1}$ (DPG).

The molar ratios between the components of the ternary complex were found by several methods: Starik-Barbanel relative yield method, straight line method, equilibrium shift method and crossed lines method [17] (Figure 3). The results suggest the complex composition of 1:2:2 (Co:HTBA:DPG).

at $510 - 520^\circ \text{ C}$ - HTBA (weight loss -40.14 %). The final product of the termolysis of the complex is Co_2O_3 .

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 Co(II) in one HTBA molecule appeared to be one [18]. Additional experiments by the Akhmedly's method [19] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.12).

The obtained results, some conclusions and our previous experience with similar systems [20] suggest that Co(II) no oxidised to Co(III) by the atmospheric oxygen during the complex formation. In acidic medium, HTBA exhibit reducing properties. Hence, we propose the following formula of the ternary compound: $[\text{Co}(\text{HTBA})_2](\text{DPGH})_2$; in this formula DPG is in its protonated form (DPGH)⁺. Proceeding from the obtained data, we propose the following

structure for the extracted ternary complex (Figure 4).

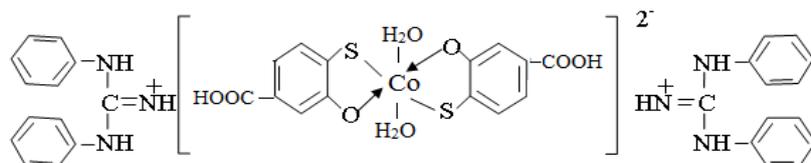


Figure 4: Suggested structure of the ternary complex

3.7. Influence of interfering ions

To evaluate the complex applicability for photometric determination of cobalt, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as

well as NO_3^- , ClO_4^- , SO_4^{2-} and CH_3COO^- do not interfere determination of cobalt with HTBA and DPG. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in Table 1.

Table 1: 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,%
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
Tiron	2.5	125	20.11	102.5
SCN ⁻	0.025	10	20.13	102.6
Cl ⁻	20	100	20.20	104.0
S ₂ O ₃ ²⁻	10	200	19.92	98.5
F ⁻	10	500	20.20	104.0
PO ₄ ³⁻	7	225	20.10	102.0
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
Sr ²⁺	20	100	20.11	102.2
Mg ²⁺	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
Cr(III)	1.5	75	19.80	96.0
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
Cd ²⁺	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

3.8. Beer's law and analytical characteristics

The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions (Table 2). The

following straight line equation was obtained for the concentration interval 0.5 – 12 mg mL⁻¹ Co(II): $y=0.1252x+0.054$ ($R^2=0.9975$). The pertaining calibration graph is shown in the Fig. 5.

Table 2: Optimum conditions and analytical characteristics of the Co(II)-HBTA-DPG-water-chloroform system

Optimum conditions	Parameter	Value
Wavelength: 542 nm	Apparent molar absorptivity:	$\epsilon=3.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
$C_{\text{HBTA}}: 1.0 \times 10^{-3} \text{ mol L}^{-1}$	True molar absorptivity:	$\epsilon'=3.846 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
$C_{\text{DPG}}: 1.0 \times 10^{-3} \text{ mol L}^{-1}$	Adherence to Beer's law:	0.8-20 mg ml ⁻¹
Shaking time: 1 min	Limit of detection:	8 ng ml ⁻¹
The pH range of education and extraction: 0.4-9.8	Limit of quantification:	15 ng ml ⁻¹
The pH range of maximum extraction: 5.1-6.9	Sandell's sensitivity:	1.42 ng cm ⁻²
	Relative standard deviation:	1.7 %

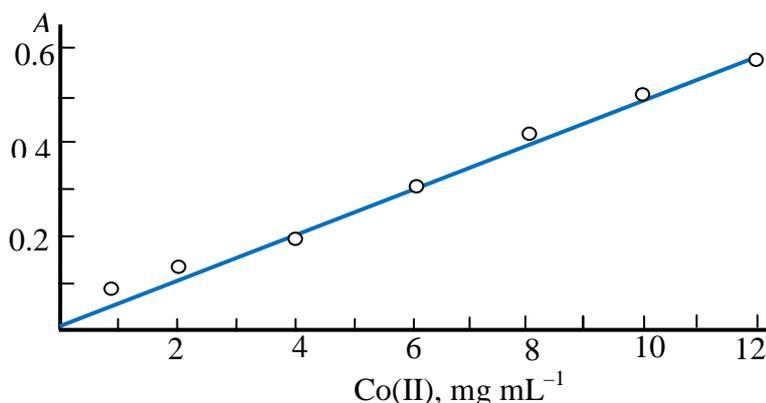


Figure 5: Analytical determination of Co(II); $C_{\text{HBTA}} = C_{\text{DPG}} = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, pH 5.5, $\lambda=540 \text{ nm}$, KFK-2, $\ell=0.5 \text{ cm}$.

Calculated apparent molar absorptivity was $\epsilon = 3.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. This value is statistically indistinguishable from that obtained by Komar-Tolmachev method [17]. The proposed method compares favourably with the existing ones (Table

3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

Table 3: Comparative characteristics of the procedures for determining of cobalt

Reagent	pH (solvent)	λ , nm	$\epsilon \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)	Ref.
Nitroso-R-salt	weakly acidic medium	415	3.5		[2]

2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8	525	4.26	0.2 - 1.5	[4]
1-nitroso-2-naphtol	415	2.9			[2,9]
2-nitroso-1-naphtol	365	3.7			[2,9]
HBTA - DPG	5.1-6.9 (CHCl ₃)	542	3.8	0.5-12.0	

The proposed method was successfully applied for the determination of Co(II) in the sewage water, Bottom sediments and plants.. The results found to be in good agreement with those obtained by the standard known method (Table 4 and 5).

4. APPLICATION

Table 4: Determination results of cobalt (II) in the Sewage water and Bottom sediments ($n = 6, P = 0.95$)

Analysis object	Added, μg	Found, μg	Found in the sample, $\mu\text{g} / \text{kg}$	$\bar{X} + \frac{t_p \times S}{\sqrt{n}}$	RSD(%)
Sewage water					
Sample 1	3.0	3.46	0.46±0.05		6
Sample 2	4.0	4.15	0.15±0.11		7
Bottom sediments					
Sample 1	4	5.27	1.27±0.05		6
Sample 2	4	5.92	1.92±0.04		5

Table 5: The results of the cobalt (II) in plants ($n = 6, P = 0.95$)

Sample	Method	Found in the sample, mg / kg	Recovered (%)	RSD, %	$\bar{X} + \frac{t_p \times S}{\sqrt{n}}$
<i>Beans</i>	Formaldoksim	0.25	0.52	2.9	0.25±0.005
	8- Mercaptoquinoline	0.34	0.39	2.3	0.34 ±0.005
	HBTA+DPG	0.28	0.43	1.9	0.28±0.004
<i>Peas</i>	Formaldoksim	0.16	0.41	3.5	0.16±0.0041
	8- Mercaptoquinoline	0.19	0.25	3.8	0.19±0.0052
	HBTA + DPG	0.13	0.31	2.6	0.13±0.0033

CONCLUSION

The 4-hydroxy-3-thiolbenzoic acid was synthesized and an extractive spectrophotometric method was de-veloped for determination of Co(II) at microgram level by using acetate buffer solution. Mixed-ligand complex of Co(II) with HBTA and DPG have been studied by spectrophotometry. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found. Extraction of mixed ligand complexes is maximal at pH 5.1-

6.9. The molar ratio of the reacting Co(II), HBTA and DPG species is 1:2:2. The general formula of the ternary complexes is They can be regarded as ion-associates between doubly charged anionic chelates $[\text{Co}(\text{HBTA})_2]^{2-}$ and protonated DPG species. Method is rapid, selective, reproducible and reliable. The method is applicable for determination of Co(II) in the Sewage water, Bottom sediments and plants. The results obtained are in good agreement with the certified values and comparable to those obtained by known methods. The method is eco-

friendly, as extraction is carried out in pH medium and has good potential for its use in the determination of Co(II) after extraction in organic phase at microgram level.

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