



CODEN [USA]: IAJ PBB

ISSN: 2349-7750

**INDO AMERICAN JOURNAL OF
PHARMACEUTICAL SCIENCES**<http://doi.org/10.5281/zenodo.1490077>Available online at: <http://www.iajps.com>

Research Article

**EXTRACTION AND SPECTROPHOTOMETRIC
DETERMINATION OF COBALT (II) WITH 3-PHENYL-2, 4-
THIAZOLIDINEDIONE**A. N. A. Verdizade¹, K. A. Kuliev¹, K. A. Alieva¹, R. A. Ismailova²¹Department of Analytical Chemistry, Azerbaijan State Pedagogical University²Department of Chemical Technology and Technology of Inorganic Substances, Azerbaijan State Oil and Industry University, Azerbaija**Abstract:**

3-Phenyl-2,4- thiazolidinedione (PhTAD) is proposed as an analytical reagent for the extractive spectrophotometric determination of cobalt(II). PhTAD forms blue colored complex with cobalt(II) in the pH range 4.0–5.9. Beer's law is obeyed in the concentration range up to 16 $\mu\text{g mL}^{-1}$. The yellowish Co(II)-PhTAD complex shows a maximum absorbance at 495 nm, with molar absorptivity of $2.62 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of the complex obtained from Beer's data is 1.48 ng cm^{-2} . The composition of the Co(II)-PhTAD complex is found to be 1:2 (Co:PhTAD). The interference of various cations and anions in the method were studied. Thus the method can be employed for the determination of trace amount of cobalt(II) in pharmaceutical, food and plant sample.

Keywords: Cobalt, 3-Phenyl -2,4-thiazolidinedione, determination, chromogenic reagent**Corresponding author:****K. A. Kuliev,**

Department of Analytical Chemistry,
Azerbaijan State Pedagogical University,
E-Mail:kerim.kuliev.69@mail.ru

QR code



Please cite this article in press K. A. Kuliev et al., *Extraction and Spectrophotometric Determination of Cobalt (II) With 3-Phenyl-2, 4-Thiazolidinedione.*, Indo Am. J. P. Sci, 2018; 05(11).

INTRODUCTION:

Cobalt is a transition element of high industrial importance because of its valuable alloying, dyeing, magnetic, catalytic and plating properties. Cobalt widely used in industry, being part of the heavy metal alloys, used for polishing diamonds, in the production of drying agents, pigments and catalysts. Radioactive isotopes of cobalt are used in industry, medicine, nuclear research. Cobalt is essential to the metabolism of all animals. It is a key constituent of cobalamin, also known as vitamin B₁₂, the primary biological reservoir of cobalt as an ultratrace element [1, 2]. In humans and animals, he is a coenzyme of a number of vital enzymes. Deficiency of vitamin B₁₂ results in malignant (pernicious) anemia in humans. Small cobalt additives lead to a significant increase in yield and improve its quality (cereals, potatoes, beans). For foods with a high content of cobalt are: beets (especially greens), bread, buckwheat, cabbage, figs, green onions, mushrooms, pears, radishes, tomatoes. Cobalt refers to the group microelements, i.e. it is vital to the functioning of living organisms [3]. Excess salts of cobalt causes morphological changes in the cell and thus has a carcinogenic effect on it. It plays a big role in the biological processes occurring in the body, and is an indicator of some diseases. For example, the absence of cobalt in the body causes an acobaltosis [4]. It is suggested that cobalt causes Graves's disease. This element is dangerous for the life of organisms because of its extremely high reactivity and belongs to the second class of danger. At the same time, cobalt is a toxic element and its presence in air and natural waters is regulated at the MPC level.

Several spectrophotometric chelating reagents are available for the determination of the cobalt in trace amounts. 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 [5].

For spectrophotometric determination of cobalt in various samples suggested 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 [6], 4-(2-thiazolylazo)resorcinol and 2,3,5-triphenyl-2H-tetrazolium chloride [7], 4-(2-pyridylazo)resorcinol and 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazol [8, 9, 10], 3-hydroxy-3-m-tolyl-1-mhydroxyphenyltriazene [11].

Oxyphenolate and dithiophenolate complexes of

some elements are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [12-15].

In this respect, a very promising reagent is dithiolphenols, which contains one hydroxyl and two sulphohydryl groups and is a sulfur-containing analogue of mononuclear poly-phenols with two oxygen atoms replaced with sulfur atoms. We spectrophotometrically investigated complexes of cobalt(II) with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines. As hydrophobic amine aniline and N-methylaniline were used [16-18].

Cobalt (II) which forms an intense blue coloured complex with PhTAD, which is completely extracted into chloroform. This forms the basis of the proposed extractive spectrophotometric method for determination of cobalt after its extraction in the form of Co(II)- PhTAD complex. The method has been successfully applied to the analysis of a large variety of samples with diverse matrices such as pharmaceutical, food and plant samples.

2. MATERIALS AND METHODS:**2.1. Reagents and Apparatus**

A stock solution (1mg / mL) of cobalt (II) was prepared by dissolving in water an exact linkage CoSO₄ • 7H₂O in water containing 2 ml conc. H₂SO₄, and diluted with water to 1 liter [20]. The concentration of the cobalt solution was adjusted gravimetrically [18]. More dilute standard solutions were prepared from this stock solution as and when required.

Solutions of PhTAD in chloroform (0.01M) were used.

To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 mol x L⁻¹ aqueous solutions of CH₃COOH and NH₄OH.

The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume. The extractant was purified chloroform.

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer 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. Muffle furnace was used for dissolution of the samples. The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H». IR spectra were recorded on a spectrophotometer "Specord M80" (Germany).

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, and a 2.0 mL portion of a 0.01 M solution of PhTAD 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 (or by using buffers). The volume of the aqueous phase was increased to 20 mL using distilled water. In 15 minute 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 490 nm ($l=0.5\text{cm}$).

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 to 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 cobalt using the proposed procedures. The Co(II) content of the sample solution was determined from the calibration curve.

2.2.3. Determination of cobalt in sewage water and bottom sediments

1/ 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. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

2. 2. 4. Determination of cobalt in plant samples

A wet ash method was employed in the preparation of the sample solution. An air-dried food sample (25-50 g) was dissolved in a 1 : 1 mixture of nitric acid and perchloric acid. The solution was evaporated to dryness, and the residue was ashed at 300 °C. The ash was dissolved in 5 mL of 1M sulphuric acid and made up to the volume in a 100

mL standard flask with distilled water. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

2. 2. 5. Determination of cobalt in soils

The proposed procedures for the determination of cobalt were applied to its determination in different soil samples. A 0.5-1.0 g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. After cooling, the sample was treated and dissolved in a graphite cup in a mixture of 16 mL of HF (conc.), 5 mL of HNO_3 (conc.), and 15 mL of HCl (conc.) at 50-60 °C to remove excess hydrogen fluoride. A further 8 mL portion of HNO_3 (conc.) was added triply to the solution that was each time evaporated to 5-6 mL. After that, the solution was transferred into a 100 mL volumetric flask and its volume was brought to the mark with distilled water. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

3. RESULTS AND DISCUSSION:

The reagent solution in chloroform has a yellowish color. The maximum light absorption is observed at 370 nm. Structure of ligand was confirmed by using IR spectra [18, 19, 20].

IR (KBr cm^{-1}): 3210 cm^{-1} (NH), 1650, 1725 cm^{-1} (C=O), 1254 cm^{-1} (C-N), 1495 cm^{-1} (-CH₂), 2345 (C-S), 1612 (C=C Ar), 1570 cm^{-1} (C₆H₅). The chemical structure of the reagent is shown in Fig.1.

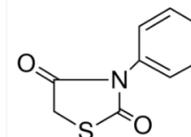


Figure 1. The chemical structure of PhTAD
Co(II) reacts with PhTAD and gives a blue colored complexes. These complexes are soluble in non-polar solvents.

3.1. The choice of the extractant

The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, dichloromethane, benzene, chlorobenzene, toluene, xylol, butanol, isoamyl alcohol, cyclohexane, ethyl acetate, isobutanol, isoamyl acetate and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform, 97,5% of copper was extracted as an colored complex (in a case the dichloroethane and

carbontetrachloride was removed 95.8 % of cobalt). Further researches were conducted with chloroform. The concentration of cobalt in the organic phase was determined with rubeanic acid [21, 22] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

3.2. Extraction as a function of pH

Change in pH affected the complexation of Co(II)– PhTAD. Therefore, the absorbance of complex was studied between pH 1 to 10 by using dilute HCl and NaOH solutions. The absorbance values of extracted complex were measured. The maximum absorbance was obtained in the pH range 4.0 to 5.9 (fig. 2). Beyond this pH range, the observed absorbance values were lower. Thus further extraction and determination carried out at 5.

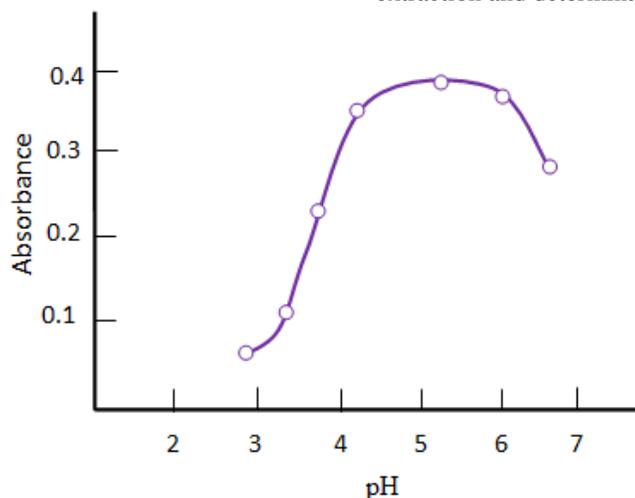


Figure 2. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase $C_{\text{Co(II)}} = 2.035 \times 10^{-5} \text{ M}$; $C_{\text{PhTAD}} = 5.0 \times 10^{-4} \text{ M}$, KФК-2, $\lambda = 490 \text{ nm}$, $l = 0.5 \text{ cm}$.

3.3. Absorption spectrum

Thiazolidinedione-2,4 forms a sparingly soluble complex with cobalt(II). The complex can readily be extracted quantitatively into chloroform in the pH range 4.0–5.9 absorption maximum in the visible region at 495 nm (fig. 3). The reagent has a negligibly small It is evident from the spectrum that the blue solution of the complex in chloroform shows an absorbance at the λ_{max} of the complex and, hence, does not interfere with the determination of cobalt. Thus, further absorbance measurements of the complex were made at 490 nm. The molar coefficient of light absorption is $2.62 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

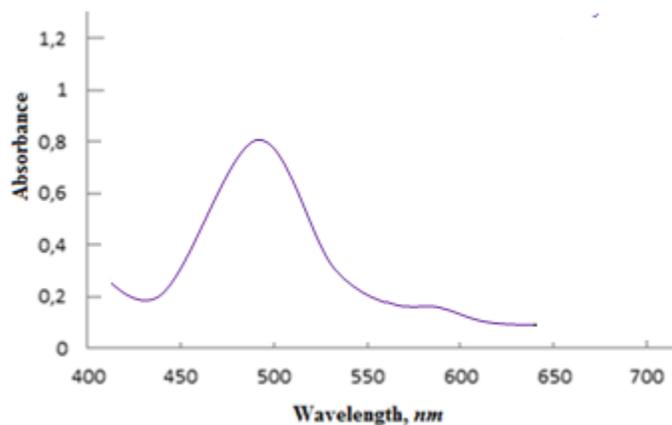


Figure 3. Absorption of complex Co - TAD $C_{\text{Cu}} = 2.035 \times 10^{-5} \text{ M}$; $C_{\text{PhTAD}} = 5.0 \times 10^{-4} \text{ M}$, Shimadzu UV1240, $l = 1 \text{ cm}$.

3.4. Effect of reagent concentration and of shaking time

For the formation and extraction of complex, a 10-15-fold excess of complexing reagent is required; for example, the optimal conditions for formation and extraction of these compounds are provided by 5.0×10^{-4} M PhTAD. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. Under optimum conditions the absorbance of the complex formed in the aqueous phase after equilibration with toluene increased initially and then achieved a constant and maximum value for 10–180 s. Therefore, 30 s was selected as the optimum equilibration time for each extraction during further studies and has been used in the proposed procedure. Based upon the above study optimum conditions providing maximum, stable and reproducible

absorbance values were selected and incorporated in the proposed procedure. The equilibration time of 3.0 minute is sufficient for the quantitative extraction of cobalt. The stability of colour of the Co(II)-PhTAD complex with respect to time shows that the absorbance due to extracted species is stable up to 36 hours, after which slight decrease in absorbance is observed.

3.5. Stoichiometry of the complexes and the mechanism of complexation

The stoichiometry of the Co(II): PhTAD complex was determined by Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods [22]. It shows that the composition of Co(II): PhTAD complex is 1:2 (Fig 4).

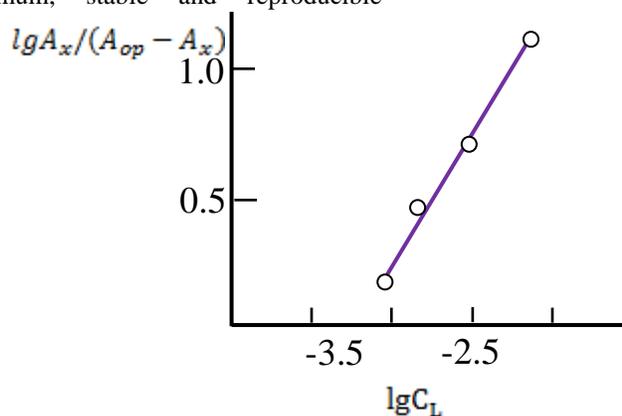


Figure 4. Determination of the ratio of components by equilibrium shift method for Cu -PhTAD $C_{Cu} = 2.035 \times 10^{-5}$ M; $C_{TAD} = 5.0 \times 10^{-4}$ M, pH=6, $\lambda = 590$ nm, KFK-2. $l = 1$ sm.

New bands were observed between 400 - 600 cm^{-1} region in the complex, which were absent in the spectrum of ligand. The bands between 455 cm^{-1} were assigned to stretching frequencies of $\nu(\text{Cu-S})$ and the band between 575 cm^{-1} have been assigned to the stretching frequencies $\nu(\text{Cu-N})$ respectively.

Thermogravimetric study of the complex Cu- PhTAD shown that thermal decomposition of the complex takes place in two stages: at 60-110°C water evaporates, at 430-500°C-decomposed PhTAD. The final product of the termolysis of the complex is CoO.

The stability constant of complex Co(II)-PhTAD was calculated and found to be $\lg \beta = 12.84$ at room temperature. The sizes of equilibrium constant K calculated on a formula $\lg K_e = \lg D - \lg [\text{Am}]$ were presented in Table 4.

Additional experiments by the Akhmedly's method [23] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.08).

In conclusion the analytical parameters pertaining to the proposed method are given in Table 4.

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 PhTAD molecule appeared to be one [24, 25].

3.6. Influence of foreign ions

To evaluate the complex applicability for photometric determination of copper, we examined the influence of foreign ions and reagents. The tolerance limit of the ions shows minimum deviation ($\pm 2\%$) in absorbance. Influence of a number of cations and anions on the accuracy of determination of Co(II) was studied.

Experiments were performed according to the recipe, by which established Calibration curves, with the only difference that a solution other than Co(II) injected a certain amount of the corresponding ions.

The interference of various cations was removed by using suitable masking agents. The ions which show interference in the spectrophotometric determination of cobalt were overcome by using appropriate masking agents. The effect of various ions and reagents on the extraction-spectrophotometric determination of 30 mg copper (II) is summarised in Table 1. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} , NO_2^- , NO_3^- and $\text{C}_2\text{O}_4^{2-}$. Tartrate, citrate, F^- , J^- , CN^- , thiourea interfere deter-

mination of Co(II). Cu(II), Ni(II), Fe(II, III), V(IV,V), W(VI), Mo(VI), Ti(IV) and Mn(II) interfere determination of Co(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA.

Interference of Fe(III) eliminated oxalic acid; Ti(IV) - tiron or sodium fluoride; Hg (II) ion -sulfite; Nb(V) and Ta (V) - oxalic acid, and Mo(VI) and W(VI) - sodium fluoride and oxalic acid. When using a 1% solution of ascorbic acid does not interfere with determination Mn(VII), V(IV), Nb(V), Cr(VI), Mo(VI) и Fe(III). When using 0.01M oxalic acid definition not interfere V(IV), Nb(V), Ta(V), Cr(III), Mo(VI), W(VI) и Fe(III).

Table 1. Influence of interfering ions on the determination of cobalt(II) with (30.0 μg Co added)

<i>Ion</i>	<i>Molar Excess of the Ion</i>	<i>Masking agent</i>	<i>Found Co, μg (S_r)</i>
Ni(II)	30	EDTA	29.7(0.05)
Fe(II)	90		29.8(0.04)
Cd(II)	100		30.4(0.03)
Al(III)	180		29.6(0.03)
Fe(III)	60	Ascorbic acid	30.2(0.05)
Zn(II)	25		29.3(0.04)
Zr(IV)	50		29.8(0.03)
Cu(II)	20	Thiourea	29.5(0.05)
Hg(II)	30		30.2(0.04)
Ag(I)	25		30.5(0.05)
Ti(IV)	30	Ascorbic acid	29.8(0.04)
V(IV)	20		29.7(0.03)
Mo(VI)	45	EDTA	30.4(0.05)
W(VI)	50		29.8(0.03)
Cr(III)	120		29.8(0.03)
Nb(V)	50	$\text{C}_2\text{O}_4^{2-}$	30.5(0.06)
Ta(V)	50	Ascorbic acid	29.7(0.04)
UO_2^{2+}	50		30.2(0.04)
Salicylic acid	25		30.4(0.03)
Sulfosalicylic acid	30		29.6(0.06)
Ascorbic acid	120		30.0(0.05)
<u>Tartaric Acid</u>	120		30.5(0.05)
Oxalate	30		30.7(0.04)
Fluoride	15		29.6(0.04)
H_3PO_4	50		30.3(0.03)

The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

3.7. Beer's law and analytical characteristics

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 0.5-16

$\mu\text{g/ml}$ [26]. The equations of the obtained straight lines and some important characteristics concerning the application of the ternary complexes for extractive-spectrophotometric determination of Co(II) are listed in Table 2.

The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [26].

In conclusion the analytical parameters pertaining to the proposed method are given in Table 2.

Table 2. Optical characteristics, precision and accuracy of the spectrophotometric determination of Co(II) with TAD

Parameter	Value
Color	red
The pH range of education and extraction	2.8-9.2
The pH range of maximum extraction	4.0-5.9
λ_{max} (nm)	495
Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1}$)	$2.62 \cdot 10^4$
Sandell's sensitivity ($\text{ng} \cdot \text{cm}^{-2}$)	2.21
R, %	97.5
The equation of calibration curves	$0.025+0.041x$
Correlation coefficient	0.9975
$\lg k_e$	5.82
Stability constant (β)	14.85
Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)	0.5-16
Limit of detection (LOD): $\text{ng} \cdot \text{mL}$	12
Limit of quantification (LOQ): $\text{ng} \cdot \text{mL}^{-1}$	40

The sensitivities expressed as molar absorptivity, of the proposed method are compared in Table 3 with those of published spectrophotometric methods.

Table 3. Comparison of selected reagents for the spectrophotometric determination of cobalt

Reagent	pH (solvent)	λ , nm	$\epsilon \times 10^{-4}$	Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)	References
2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8	525	4.26	0.2 - 1.5	[7]
1-nitroso-2-naphtol	≥ 3	415	2.9		[3, 27]
2-nitroso-1-naphtol	≥ 4	365	3.7		[3, 27]
Nitroso-R-salt	weakly acidic medium	415	3.5		[3, 27]
Bromopyrogallol red	2.0	575	1.08	0.25-110	[5, 27]
PhTAD	4.0-5.9 (CHCl_3)	495	2.62	0.5-16	This method

4. Analytical applications

The proposed method under the already established optimum conditions was applied for the determination of cobalt in various objects. The results presented in Table 4, Table 5, Table 6 and Table 7 indicate the successful applicability of the proposed method to real sample analysis.

Table 4. Determination of cobalt in steel (n=5, P=0.95)

Reagent	\bar{X}	S_x	ϵ	S_r	μ
<i>Steel M 441(0.012% Co)</i>					
1-nitroso-2-naphtol	0.0125	0.000315	0.00035	0.025	0.0125±0.00035
PhTAD	0.0123	0.000270	0.00029	0.022	0.0123±0.00029
<i>Steel №156(0.56% Co)</i>					
1-nitroso-2-naphtol	0.579	0.021	0.023	0.033	0.579±0.023
PhTAD	0.570	0.020	0.022	0.037	0.570±0.022

Table 5. Determination results of cobalt(II) in the sewage water and bottom sediments (n = 6, P = 0.95)

Analysis object	Added, mg/kg	Found, mg/kg	Found in the sample, mg/kg $\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$	S_r
Sewage water				
Sample 1	2.0	2.48	0.48±0.05	0.06
Sample 2	5.0	6.12	1.12±0.11	0.07
Bottom sediments				
Sample 1	5	6.23	1.23±0.05	0.07
Sample 2	5	6.89	1.89±0.04	0.06

Table 6. Determination results of cobalt(II) in food samples

Analysis object	Reagent	Found, mg/kg	S	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Beans	2-nitroso-1-naphtol	0.22	0.0048	0.024	0.22±0.005
	PhTAD	0,18	0.0034	0.019	0.18±0.004
Bird-Cherry Tree	2-nitroso-1-naphtol	6.72	0.2077	0.031	6.72±0.220
	PhTAD	6.81	0.1292	0.019	6.81±0.136
Peas	2-nitroso-1-naphtol	0.11	0.0038	0.035	0.11±0.0038
	PhTAD	0.12	0.0031	0.026	0.12±0.0037

Table 7. Determination results of cobalt (II) in soil samples

Soil	Метод	\bar{X} , %	S	RSD(%)	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Sod-podzolic sandy and sandy loamy soils	2-nitroso-1-naphtol	3.20	0.157	4.9	3.20±0.164
	PhTAD	3.32	0.140	4.3	3.32±0.145
Sod-podzolic loam and clay soils	2-nitroso-1-naphtol	9.89	0.445	4.4	9.89±0.464
	PhTAD	9.85	0.418	4.2	9.85±0.438
Gray forest soils	2-nitroso-1-naphtol	13.20	0.394	3.1	13.20±0.414
	PhTAD	12.96	0.375	2.9	12.96±0.394
Black earth	2-nitroso-1-naphtol	15.75	0.583	3.7	15.75±0.612
	PhTAD	15.68	0.548	3.5	15.68±0.576
Chestnut soils	2-nitroso-1-naphtol	11.60	0.545	4.7	11.60±0.572
	PhTAD	11.55	0.521	4.9	11.55±0.547

5. CONCLUSION:

The proposed method has been applied to determine cobalt in natural waters, soil and food samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

1. The results obtained show that the newly developed method in which the reagent PhTAD was used, can be effectively used for quantitative extraction and estimation of Co(II) from aqueous media. PhTAD have been investigated by spectrophotometric method.
2. Extraction of mixed ligand complexes is maximal at pH 4.0-5.9. The proposed method is quick and requires less volume of organic solvent.
3. 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.
4. The Beer's law was applicable in the range of 0.5-16 µg/ml.
5. A simple, rapid and sensitive methods proposed for the determination of trace amounts of Co(II). The method is very precise, faster and simpler than other methods.

REFERENCES:

1. Oh R. C., Brown D. L. Vitamin B12 deficiency. *American Family Physician*, 2003, V. 67, No. 5, pp. 979-986.
2. Pyatnitskiy I. V. *Analiticheskaya khimiya kobal'ta*. M: Nauka, 1965.
3. Avtsyn A. P., Zhavoronkov A. A., Rish M. A., Strochkova L.S. *Mikroelementozy cheloveka*. M.: Meditsina, 1991. 496 s.
4. Sadovnikova L. K., Orlov D. S., Lozanovskaya I. N. Ecology and environmental protection in chemical contamination. M.: Higher School., 2006. 334 p. (In Russian).
5. Umland F. et al. *Kompleksnye soedineniya v analiticheskoi khimii: teoriya i praktika primeneniya* [Complex compounds in analytical chemistry: theory and practice of application]. M., Mir, 1975. 531 p.
6. Divarova V. V., Gavazov K. B., Lekova V. D., Dimitrov A. N. Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts *chemija*. 2013. V. 24. No. 2. P. 81-87
7. Divarova V. V., Racheva P.V., Lekova V., Gavazov K. B., Dimitrov A.N. Spectrophotometric determination of cobalt(II) in a liquid-liquid extraction system containing 4-(2-thiazolylazo) resorcinol and 2,3,5-triphenyl-2H-tetrazolium chloride/ *Journal of Chemical Technology and Metallurgy*, 2013, 48, 6, pp. 623-630.
8. Racheva P. V., Gavazov K. B., Lekova V. D., Dimitrov A. N. Complex formation in a liquid-liquid extraction system containing cobalt(II), 4-(2-pyridylazo)resorcinol, and nitron. Hindawi Publishing Corporation. *Journal of Materials V*. 2013, Article ID 897343, 7 pages.
9. Divarova V. V., Stojnova K. T., Racheva P. V. et al. Liquid-liquid extraction of ion-association complexes of cobalt(II)-4-(2-pyridylazo)resorcinol with ditetrazolium salts. *J. Serb. Chem. Soc.* 2014, 79, pp. 1-12
10. Ram G., Chauhan R. S., Goswami A. K., Purohit D. N. Review of spectrophotometric methods for determination of cobalt(II). *Reviews in Analytical Chemistry*, 2003.V. 22, No.4, pp. 255-317.
11. Ombaka O., Gichumbi J. M. Spectrophotometric determination of cobalt(II) in low concentrations using hydroxytriazene as selective chelating agents. *African Journal of Pure and Applied Chemistry*, 2011, V. 5, No 15, pp. 494-502
12. Kuliyev K. A., Verdizadeh N. A. Spectroscopic Investigation of the Complex Formation of Niobium Using 2,6-Dithiophenol and Aminophenols. *American Journal of Analytical Chemistry*, 2015, 6, pp.746-756.
13. Kuliev K. A., Verdizadeh N. A., Gadjieva A. B. Liquid-Liquid extraction and spectrophotometric determination of molybdenum with 2, 6-dithiophenol and its derivatives in the presence of hydrophobic amines // *Chemistry Journal*, 2015, V. 5, № 3, pp. 45-53
14. Kuliyev K. A. Verdizadeh N. A., Gadjieva A. B., Mamedova S. A. Spectroscopic investigation complex formation of molybdenum with 2, 6-dithiophenol and its derivatives in the presence of hydrophobic amines. *International Journal of Chemical Studies* 2016; V.4, No 3: pp. 42-48
15. Kuliev K. A. Spectroscopic investigation complex formation of cobalt using 2,6-dithiol-4-methylphenol and hydrophob amines // *Journal of Advances in Chemistry*, V. 11, № 4, pp. 3487-3497.
16. Kuliyev K. A., Verdizade N. A. Spectroscopic investigation complex formation of cobalt using 2,6-dithiophenol and hydrofob amines // *American Journal of Chemistry*, 2015, V. 5, №1, pp. 10-18.
17. Zalov A. Z., Amanullayeva G. I.

- Spectrophotometric determination of cobalt(II) in a liquid-liquid extraction system containing 2-hydroxy-5-iodothiophenol and diphenylguanidine. *IJRDO-Journal Of Applied Science*. 2016, V.2, 7, 217-225
18. Kuliyev K. A., Verdizadeh N. A., Suleymanova G. S. Spectrophotometric determination of cobalt(II) with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines // *American Journal of Chemistry. USA*. 2016, V. 6. No 4, pp.95-103
 19. Shrayner R., F'yuzon R., Kortin D., Morrill T. *Identifikatsiya organicheskikh soyedineniy: Per. s angl. M.: Mir, 1983. (In Russian)*
 20. Nakamoto K. *IK-spectr KR neorganicheskikh i koordinatsionnykh soedineniy (Infrared and Raman Spectra of Inorganic and Coordination Compounds)*. Moscow: Mir. 1991, 536.
 21. Bellami L. *Infrakrasnie spectra slojnykh molekul (The infrared spectra of complex molecules)*. Moscow: Mir. 1991, 592.
 22. Bulatov M. I., Kalinkin I. P. *Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza (Practical Guide on Photocolorimetric and Spectrophotometric Methods of Analysis)*, Moscow: Khimiya. 1972.
 23. Akhmedly M. K., Kly'gin A.E., Ivanova L. I., Bashirov E. A. On the chemistry of interaction of gallium ions with a number of sulphophthaleins. *Zhurnal Neorganicheskoi Khimii*. 1974, 19(8), pp. 2007-2012.
 24. Nazarenko V.A., Biriuk E.A. *Issledovanie khimizma reaktsii ionov mnogovalentnykh elementov s organicheskimi reagentami [Research of chemism of reactions of ions of multivalent elements with organic reagents]*. *Zhurn. analit. khimii*. 1967, V. 22, N 1, pp. 57. (In Russian)
 25. Nazarenko V. A. *Vzaimodeistvie ionov mnogovalentnykh elementov s organicheskimi reagentami [Interaction of ions of multivalent elements with organic reagents]*. *Trudy komis. Po analit. khimii AN SSSR [Proc. of the Commission on analytical chemistry of Academy of Sciences of the USSR]*. Moscow, Nauka, 1969, V. 17, pp.22. (In Russian)].
 26. Dorokhova E.N., Prokhorova G.V. *Analytical chemistry (physical-chemical methods of analysis)*. M: Higher School, 1991.
 27. Marczenko, Z., Baltsejak, M. K. *Metodi Spectrophotometrii v UF i vidimoy oblasti (Spectrophotometrically in the UV and visible regions in inorganic analysis)*. M. Binom. *Laboratoriya znaniy*. 2007.