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COMPLEX FORMATION IN A LIQUID-LIQUID EXTRACTION SYSTEM CONTAINING COBALT (II), 2, 6-DITIOL-4-ETYLPHENOL AND PHENANTROLINE

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Abstract:
 2,6-dithiol-4-ethylphenol (DTEP) has been synthesized and characterized with IR and NMR spectroscopic methods. A simple and spectrophotometric methods has been developed for the determination of trace amounts of cobalt (II). The reagents forms an blue coloured insoluble in water complex with cobalt (II) in acidic medium (pH 2.5-8.5). In the presence of hydrophobic amines form ternary complexes. As hydrophobic amine phenantroline (Phen) were used. The molar absorptivity of coloured species are 3.12×10^4 $L.mol^{-1}$ cm^{-1}. Beer's law is obeyed in the range 0.2– 18 µg/ml of cobalt (II) at λ_{max} 537 nm. Cobalt (II) forms 1 : 1 : 2 complex with DTEP and Phen, stability constant of the complex was found to be 10.55 (pH_{opt} = 5.2-7.3). The proposed methods was successfully applied to the analysis of cobalt in soil, natural water samples and plant material. The results obtainned were agreed with the reported methods at the 99.2 % confidence level. The optimum reaction conditions and other analytical parameters were investigated to enhance the sensitivity of the present method. The detailed study of various interferences made the method more selective.
Key words: *2,6-dithiol-4-ethylphenol, spectrophotometry, cobalt(IV,V), soil, water and biological samples.*

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1. 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 [1]. 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 B_{12}, the primary biological reservoir of cobalt as an ultratrace element [2, 3]. In humans and animals, he is a coenzyme of a number of vital enzymes. Deficiency of vitamin B_{12} 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 [4]. Excess salts of cobaltcauses 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 [5]. 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 [6].

For spectrophotometric determination of cobalt in various samples suggested4-(2-pyridylazo)resorcinol, tetrazolium salt {2,3,5-triphenyl-2H-tetrazolium chloride or 2-(4-iodophenyl) -3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride [7], 4-(2-thiazolyla-zo)resorcinol and 2,3,5-triphenyl-2H-tetrazolium chloride [8], 4-(2-pyridylazo)resorcinol and 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazol [9, 10, 11], 3-hydroxy-3-m-tolyl-1-mhydroxyphenyltriazene [12].

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 [13-18].

In this respect, a very promising reagent is dithiolphenols (DP), 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 [19].

In this respect, a very promising reagent is 2, 6-dithiol-4-ethylphenol (DTEP), which contains one hydroxyl and two sulphohydryl groups and is a sulfur-containing analogue of mononuclear polyphenols 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 2, 6-dithiol-4-ethylphenol in the presence of phenantroline (Phen).

2. EXPERIMENTAL:

2.1. Reagents

A stock solution (1mg / mL) of cobalt (II) was prepared by dissolving in water an exact linkage $CoSO_4 \cdot 7H_2O$ in water containing 2 ml conc. H_2SO_4, and diluted with water to 1 liter [20]. The concentration of the cobalt solution was adjusted gravimetrically [21].

Solutions of DP and Am in chloroform (0.01M) were used. To create the optimal acidity, 1M solutions of KOH and HCl or ammonium acetate buffers were applied. The extractant was purified chloroform. Acetate buffers of pH 4, 5 and 6 were prepared by mixing 0.05 M solutions of CH_3COONa and acetic acid. Phosphate buffers of pH 7 and 8 were prepared by mixing 0.05 M solutions of KH_2PO_4 and 0.01 M NaOH.

DTEP were synthesized according to the procedure [22]. The reagent was characterized by taking the elemental analysis, NMR and IR spectra [23-25].
IR (KBr), см$^{-1}$
3460 ν (OH), 3050 ν(CH), 2575 ν(SH), 2965 и 2874 ν(-CH$_3$), 1555 δ(C$_6$H$_5$), 1460 δ$_{as}$ (-CH$_2$-CH$_3$).
^{1}H NMR (300.18 MHz, C$_6$D$_6$)
 δ 5.29 (s, 1H- OH), δ 3.38(s, 2H - 2SH), δ 7.15 (s, 2H Ar-H), δ 2.59 (s, 2H –CH$_2$-), δ 1.22 (s, 3H –CH$_3$).

2. 2. Apparatus

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer (Japan) and KFK 2 photocolorimeter (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 M 80" (Germany). ^{1}H-NMR spectra were recorded on "Bruker" Fourier Transform (300.18 MHz) in deuterated benzene (C_6D_6). The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H».

2.3. Procedure

2.3.1. 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 2.0 mL portion of a 0.01 M solution of DTEP, 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 (or by using buffers). The volume of the aqueous phase was increased to 20 mL using distilled water. In 10 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).

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

2.3.3. Determination of cobalt 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. Cobalt was determined in aliquots of the solution using the procedure proposed by us.

2. 3. 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. 3. 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:

Co(II) reacts with DTEP gives a bluish red colored complexes. These complexes are insoluble in non-polar solvents. When phenantroline were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. DTEP are weak tribasic acid (H_3R) and depending on the pH of the medium may be in molecular and tree anionic forms.

3.1. Effect of pH

The effect of pH on the intensity of the color reaction is shown in the Fig. 1. The absorbance was found to be maximum in the *p*H range 5.2-7.3. Hence further analytical investigations were carried out in media of *p*H 4. With further increase in the acidity of the aqueous phase, the recovery of cobalt (II) decreases. This is because with increasing acidity, the concentration of the anionic reactive form of Cobalt (II) decreases. At pH ≥ 9, the extraction of the complex is practically not observed, which is probably because a decrease in the degree of protonation of Am.
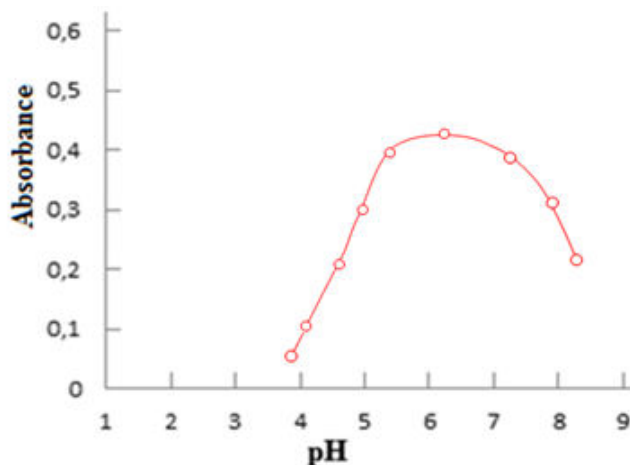
Fig. 1. Absorbance of mixed-ligand complexes as a function of the ph of the aqueous phase;
$C_{Co(II)}$= 2.035×10^{-5} mol L^{-1}, C_{DTEP} =0.92 ×10^{-3} M, C_{Phen}=1.2 ×10^{-3} M, λ = 540 nm, λ=0.5 см.

3.2. Effect of extractants

Co(II) reacts with DTEP and gives a red colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, benzene, chlorobenzene, toluene, o-xylene, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, *n*-butanol, isoamyl acetate,benzoyl alcohol 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. Organic solvents used for extraction of Co(II) can be arranged on the basis of their extraction coefficient values as chloroform > carbon tetrachloride > dichlorethane > chlorbenzene > toluene > benzene > ethyl acetate > n-butanol > iso amyl alcohol> benzoyl alcohol (fig.2). Chloroform was found to be the best extracting solvent hence; it was selected for the ext-raction throughout the work. After a single extraction with chloroform, 98.7 % of cobalt was extracted as MLC (in a case the dichloroethane and carbon tetrachloride was removed 95.8-97.5 % of cobalt). The concentration of cobalt(II) in the organic phase was determined photometrically by using 2-nitroso-1-naphtol [20] after reextraction, and in the aqueous phase, its concentration was found by the differrence.
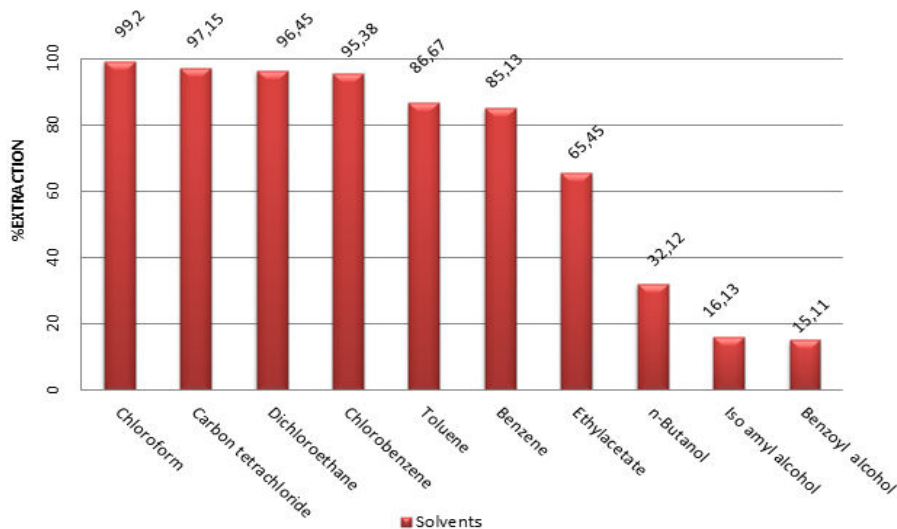

Fig. 2. Effect of solvents on extraction of Co(II) as Co-DTEP-Phen

3.3. Electronic absorption spectra

The proposed method involved the formation of a blue-green color between cobalt(II) and DTEP in a medium of pH 5.2-7.3. The figure revealed that Co(II)-DTEP-Am complex has maximum absorbance at 527 nm (fig 3). Neither the metal ion nor the reagent has appreciable absorbance at specified wavelengths. Hence further studies were carried out at 540 nm. The molar coefficient of light absorption is 3.12×10^4 L mol^{-1} cm^{-1}.

The color reaction was instantaneous and the absorbance of the complex solution was found to remain constant for at least five hours.
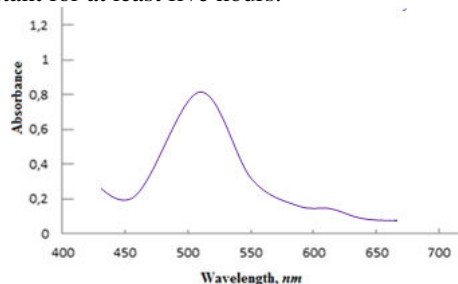

Fig. 3. Absorption of mixed-ligand complexes Co(II)-DTEP-Phen

$C_{Co(II)} = 2.035 \times 10^{-5}$ mol L^{-1}, $C_{DTEP} = 0.92 \times 10^{-3}$ M, $C_{Phen} = 1.2 \times 10^{-3}$ M; Shimadzu 1240, $\lambda = 1$ см.

3.5. Effect of reagent concentration and incubation time

The studies on effect of various concentrations of the reagent on the color reaction reveal that, a reagent excess of 5-10 fold was required for the Co(II)-DTEP-Phen color reaction. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. For the formation of mixed-ligand complex Co(II)-DTEP-Phen, the concentration of 0.92×10^{-3} M of DTEP and 1.2×10^{-3} M of Phen in the solution is required. Unlike single-ligand complexes, mixed-ligand complexes of cobalt (II) with DTEP and Phen were stable in aqueous and organic solvents and did not decompose for 48 hours, or over a month after extraction. After mixing the components, the absorbance reaches its maximum within 10 min at room temperature.

The Co(II)–DTEP-Phen system attained maximum and constant absorbance at 15-60 ^{o}C. All subsequent measurements were done at room temperature (25±1 ^{o}C).

3.6. Stoichiometry of the complexes and the mechanism of complexation

The ratio of components in the complex corresponds to Co(II) : DTEP : Phen = 1 : 1 : 2; it was determined

by the methods of straight line, equilibrium shift, and the relative yield [26]. 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 DTEP molecule appeared to be one [27, 28].
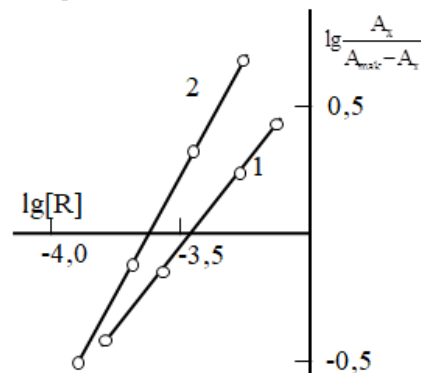

Figure 4. Determination of the ratio of components by equilibrium shift method for Co(II)- DTEP-Phen Co(II):DTEP; 2. Co(II) : Phen

$C_{Co(II)} = 2.035 \times 10^{-5}$ mol L^{-1}, $C_{DTEP} = 0.92 \times 10^{-3}$ mol· L^{-1}, $C_{Phen} = 1.2 \times 10^{-3}$ mol· L^{-1}, pH = 3, 540 nm, l = 0.5 cm

The disappearance of the pronounced absorption bands in the 3250-3620 cm^{-1} with a maximum at 3475 sm^{-1} observed in the spectrum of DTEP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2570 sm^{-1} shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1380 cm^{-1} indicates the presence of a coordinated phenantroline [24, 25].

Thermogravimetric study of the complex Co(II)-DTEP-Phen shows that the rapid expansion of the complex starts at 500 ^{o}C. wherein the mass loss of 49.1% (calculated 49.7%), which corresponds to the removal phenanthroline. At 570-650 °C stands DTEP mass loss of 39.1% (calculated 39.7%). Further, when heated to 670°C formed Co$_2$O$_3$.

The stability constant of Co(II)-DTEP-Phen complexes was calculated by method of crossing of curves [33] and found to be lgβ = 15.34at room temperature. The sizes of equilibrium constant K ecalculated on a formula lgKe= lg D - 2lg [Am] were presented in Table 3.

Additional experiments by the Akhmedly's method [29] showed that the complex exists in monomeric

form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.12).

Cobalt is mainly found in the oxidation state +2. In some complexes it is easily oxidized to Co (III). To determine the valence of the cobalt ion in MLC with DTEP and Phen, the Guy method, based on the measurement of the magnetic susceptibility of the compound, was used. It is known that Co^{2+} is paramagnetic and retains this property in complexes with organic compounds. Conversely, Co^{3+} is diamagnetic. Therefore, the measurement of the magnetic susceptibility of solutions of the complex gives an answer about the valence state of cobalt. The obtained data showed that the solution of the complex is paramagnetic, and this confirms the bivalent state of cobalt in the complex.

The probable structures of the complex under investigation on the basis of the above experimental evidence can be shown as figure 5.
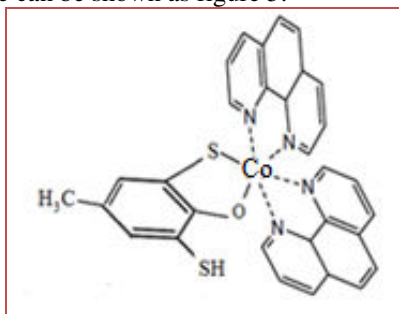

Fig. 5. Structure of complex Co-DTEP-Phen

Chemical-analytical parameters pertaining to the proposed methods are given in Table 3.

3.7. Effect of foreign ions

A study of potential interferences in the determination of cobalt was performed. An error of ±5% in absorbance reading was considered tolerable. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH. The tolerance limits of various foreign ions are given in table 2. These results demonstrate that the effect of Al^{3+}, Ba^{2+}, NH_4^+, Nb(V), Ta(V), Sn(II), NO_3^-, SO_4^{2-}, ClO_4^-, PO_4^{3-}, F^-, I^-, oxalalate , thiosulphate, ascorbic acid and SCN^- are negligible, while the effect of Fe(II). Ni(II), Cu(II), V(IV,V), W(VI), Mo(VI), Ti(IV), Mn(II) are seriously interfere. However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (Table 2).

Table 2. Influence of interfering ions on the determination of cobalt (II) as MLC with DTEP and Phen (30.0 µg Co added)

Ion	Molar Excess of the Ion	Masking agent	Found V, µg (S_r)
Ni(II)	30	EDTA	29.8(0.05)
Fe(II)	90		29.8(0.04)
Cd(II)	100		30.3(0.03)
Al(III)	180		29.6(0.03)
Fe(III)	60	Ascorbic acid	30.2(0.05)
Zn(II)	20		29.3(0.04)
Zr(IV)	50		29.8(0.03)
Cu(II)	20	Thiourea	30.1(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		29.6(003)
Mo(VI)	15	EDTA	30.4(0.05)
W(VI)			29.8(0.03)
Cr(III)	120		29.8(0.03)
Nb(V)	50	$C_2O_4^{2-}$	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		29.8(0.06)
Ascorbic acid	120		30.0(0.03)
Tartaric Acid	120		30.2(0.05)
Oxalate	30		30.7(0.04)
Fluoride	15		29.6(0.04)
H_3PO_4	30		30.3(0.03)
Thiourea	50		31.2(0.06)

3.8. Characteristics of the analytical method

A series of solutions containing different amounts of the metal ion were prepared as per the general experimental procedure. The absorbance of the solutions was measured at 540 nm. A calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) can be determined in the concentration range 0.5 to 14.0 μg mL^{-1}. 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 3.

Table 3. Some chemical-analytical parameters of Co(II)-DTEP- Phen complexes

Parametrs	Value
pH_{opt}	5.2-7.3
R	98.7
D	304
λ, nm	527
Δλ, nm	253
$\varepsilon \cdot 10^{-4}$	3.12
lgK_e	5.11
lgβ	15.34
$lgK_{эк}$	13.54
Beer's law range(μg·ml^{-1})	0.5-14
The equation of calibration curves	0.038+0.0285x
Detection limits (ng mL^{-1})	11
Quantification limits (ng mL^{-1})	34
Sandell sensitivity (ng cm^2)	1.82

The sensitivities expressed as molar absorptivity, of the proposed method are compared in Table 4 with those of published spectrophotometric methods.

Table 4. Comparison of selected reagents for the spectrophotometric determination of cobalt

Reagent	pH (solvent)	λ, nm	ε×10^{-4}	Beer's law range (μg· ml^{-1}	References
2,3,5-triphenyl-2H-tetrazolium chloride	5.2-5.8	525	4.26	0.2 - 1.5	[8]
1-nitroso-2-naphtol	≥ 3	415	2.9		[4, 20]
2-nitroso-1-naphtol	≥ 4	365	3.7		[4, 20]
Nitroso-R-salt	weakly acidic medium	415	3.5		[4, 20]
Bromopyrogallol red	2.0	575	1.08	0.25-110	[20,30]
DTEP-Phen	5.2-7.3 (CHCl$_3$)	527	3.13	0.5-14	This method

3.8. 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 5, Table 6, Table 7 and Table 8 indicate the successful applicability of the proposed method to real sample analysis.

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

Reagent.	$\overline{X}$	S_x	ε	S_r	μ
Steel M 441(0.012%Co)					
1-nitroso-2-naphtol	0.0125	0.000312	0.000328	0.025	0,0125±0.00033
Co - DTBP −AP$_7$	0.0122	0.000268^3	0.000280	0.022	0.0122±0.00028
Steel №156(0.56%Co)					
1-nitroso-2-naphtol	0.583	0.020	0.021	0.033	0.581±0.021
Co - DTEP+Phen	0.570	0.021	0.022	0.038	0.574±0.022

Table 6. 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 $\overline{X} \pm \dfrac{t_p \cdot S}{\sqrt{n}}$	S_r
Sewage water				
Sample 1	2.0	2.45	0.45±0.05	0.07
Sample 2	5.0	6.14	1.14±0.11	0.08
Bottom sediments				
Sample 1	5	6.26	1.26±0.05	0.06
Sample 2	5	6.92	1.92±0.04	0.07

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

Analysis object	Reagent	Found, mg/kg	S	S_r	$\overline{X} \pm \dfrac{t_p \cdot S}{\sqrt{n}}$
Beans	2-nitroso-1-naphtol	0.20	0.0048	0.024	0.20±0.005
	DTEP+Phen	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±0.2180
	DTEP+Phen	6.81	0.1292	0.019	6.81±0.1356
	DTEP+Phen	6.94	0.1449	0.021	6.94±0.1521
Peas	2-nitroso-1-naphtol	0.11	0.0038	0.035	0.11±0.0040
	DTEP+Phen	0.12	0.0031	0.026	0.12±0.0033

Table 8. Determination results of cobalt (II) in soil samples

Soil	Метод	$\overline{X}$, %	S	RSD(%)	$\overline{X} \pm \dfrac{t_p \cdot S}{\sqrt{n}}$
Sod-podzolic sandy and sandy loamy soils	2-nitroso-1-naphtol	3.20	0.157	4.9	3.20±0.164
	DTEP+Phen	3.33	0.140	4.2	3.33±0.146
Sod-podzolic loam and clay soils	2-nitroso-1-naphtol	9.89	0.445	4.5	9.89±0.467
	DTEP+Phen	9.95	0.418	4.2	9.95±0.438
Gray forest soils	2-nitroso-1-naphtol	13.15	0.394	3.0	13.15±0.414
	DTEP+Phen	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
	DTEP+Phen	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
	DTEP+Phen	11.58	0.521	4.5	11.58±0.547

4. 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 DTEP was used, can be effectively used for quantitative extraction and estimation of Co(II) from aqueous media.
2. Mixed-ligand complexes of cobalt(II) with DTEP in the presence of Phen have been investigated by spectrophotometric method.
3. Extraction of mixed ligand complexes is maximal at pH 5.2-7.3. The proposed method is quick and requires less volume of organic solvent.
4. 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.
5. The Beer's law was applicable in the range of 0.5-14 µg/ml.
6. A simple, rapid and sensitive methods proposed for the determination of trace amounts of vanadium. The method is very precise, faster and simpler than other methods.

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