

Spectroscopic Study of Complex Formation of Cobalt (II) with 2,6-Mercapto-4-Sec-Butylphenol and Heterocyclic Amines

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Abstract

Mixed-ligand complexes of cobalt (II) with 2,6-dimercapto-4-sec-butylphenol (DMSBF) in the presence of heterocyclic amines (Am) were studied by spectroscopy methods. Dipyriddy, phenanthroline, and bathophenanthroline were used from the heterocyclic amines. Various factors such as the volume of ligand used, the pH of the solution, the stability of the complex over time and the interference of other metals that affect the formation of the complex have been studied in detail. Extraction of mixed ligand complexes is maximal at pH 5.2-7.9. 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 0.4-18 µg/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 (in steel, sewage water, bottom sediments, food and soil samples).

Keywords: Cobalt, Solvent Extraction, Spectroscopic Method, Mixed-Ligand Complex

1. Introduction

In general, heavy metal ions are toxic, non-biodegradable and tend to accumulate in human vital organs where they can act gradually over a long period through the food chain. Due to its valuable alloying, coloring, magnetic, catalytic and galvanic properties, cobalt is widely used in industry, is a component of heavy metal alloys, is used for polishing diamonds, in the production of desiccants, pigments and catalysts [1]. Radioactive isotopes of cobalt are used in nuclear research, industry and medicine. It is a key component of vitamin B12, the main biological reservoir of cobalt as an ultratrace element [2,3]. Vitamin B12 deficiency leads to pernicious anemia in humans. Food products with high cobalt content include: beets, bread, buckwheat, cabbage, figs, green onions, mushrooms, pears, radishes, tomatoes. Small additions of cobalt lead to a significant increase in crop yields and improvement in their quality (cereals, potatoes, beans). Cobalt belongs to the group of microelements, i.e. it is vital for the functioning of living organisms [4]. Excess cobalt causes morphological changes in the cell and thus has a carcinogenic effect on it. It plays a major role in biological processes occurring in the body and is an indicator of some diseases. For example, the absence of cobalt in the body causes acobaltosis [5]. It is assumed that cobalt causes Graves' disease. This element is dangerous for the vital activity of organisms due to its extremely high reactivity and belongs to the second hazard class. Cobalt is a toxic element and its presence in the air and natural waters is regulated at the MPC level.

Various methods have been proposed for the determination of cobalt, including spectrophotometry atomic absorption spectrophotometry (AAS) flow injection polarography high performance liquid chromatography (HPLC) inductively coupled plasma atomic emission spectrophotometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) [6-22]. Among these methods, the spectrophotometric method is the most common and widely used because the equipment is readily available, the process is simple, and the methodology is inexpensive, rapid, accurate, and precise, all of which contribute to its suitability.

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-nitrozophenole group or a similar structure with the oxime group [23]. Hydroxyphenolate 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 [24-28].

In this respect, a very promising reagent is dimercaptophenols, which contains one -OH and two -SH 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-dimercaptophenol and its derivatives in the pres-

ence of hydrophobic amines. As hydrophobic amine aniline and N-methylaniline were used [29,30].

The real work is devoted to studying of reaction of a complex formation of cobalt (II) with 2, 6-dimercapto-4-sec-butylphenol (DMSBP) in the presence of hydrophobic amines. Heterocyclic diamines – dipyrindyl (Dip), phenanthroline (Phen) and bathophenanthroline (BPhen) - were used as hydrophobic amines. The use of MLC in many cases leads to an increase in the selectivity, the contrast of the reactions, the improvement of extraction and other properties. The introduction of the second reagent often leads to an improvement in the extraction properties of the complexes and a reduction in the detection limit.

1.1. Experimental

Reagents Apparatus: A stock solution (1mg / mL) of cobalt (II) was prepared by dissolving in water an exact linkage $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in water containing 2 ml conc. H_2SO_4 , and diluted with water to 1 liter [31]. The concentration of the cobalt solution was adjusted gravimetrically [31]. Solutions of DMSBP 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.

Apparatus: 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 M 80" (Germany). $^1\text{H-NMR}$ 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 «Shimadzu TGA-50H».

1.2. General Procedure

1.3. General Procedure for the Determination of Cobalt (II)

Portions of the stock cobalt (II) solutions with a volume of 0.1 to 1.0 ml at 0.1 ml intervals, 2.0 ml of a 0.01 M DMSBP solution and 2.0 ml of a 0.01 M Am solution were placed in calibrated test tubes with ground glass stoppers. The required pH value was set by adding 1 M HCl or using buffers. The volume of the aqueous phase was brought to 20 ml with distilled water, and the volume of the organic phase to 5 ml with chloroform. Five minutes after complete separation of the phases, the organic phase was separated from the aqueous one and the optical density of the extracts was measured on KFK-2 at room temperature and 540 nm ($l = 0.5$ cm).

1.4. Determination of Cobalt (II) in Steel

A 0.2 g sample was dissolved in 20 ml of H_2SO_4 (1:1), oxidized with a few drops of concentrated nitric acid and evaporated twice until SO_3 vapor was released. The precipitated

salt was dissolved in 20 ml of 15% tartaric acid with heating, the solution was cooled, brought to 100 ml with water in a measuring flask, stirred and filtered. An aliquot of 5 ml was placed in a separatory funnel, 1 ml of 10% hydroxylamine solution and 1 ml of 3% ascorbic acid were added and cobalt was determined using the methods developed by us. The Co (II) content in the sample solution was determined using a calibration curve.

1.5. 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.

1.6. Determination of Cobalt in Plant Samples

The wet ash method was used to prepare the sample solution. A weighed portion of the air-dried food product (25-50 g) was dissolved in a mixture of nitric and perchloric acids in a 1:1 ratio. The solution was evaporated to dryness and the resulting residue was ashed at 300°C . The ash was dissolved in 5 ml of 1 M sulfuric acid and the volume of the solution was brought to 100 ml with distilled water. Cobalt was determined in aliquot parts of the solution using the method we proposed.

1.7. Determination of Cobalt in Soils

A 0.5-1.0 g sample is finely ground in an agate mortar and calcined in a muffle furnace for 3 hours. After cooling, the sample is processed and dissolved in a graphite cup in a mixture of 15 ml conc. HCl, 5 ml conc. HNO_3 and 16 ml conc. HF at 50-70 oC to remove excess hydrogen fluoride. Another 8 ml of HNO_3 (conc.) are added to the solution three times and evaporated each time to 5-6 ml. After this, the solution is transferred to a 100 ml measuring flask and its volume is brought up to the mark with distilled water. Cobalt is determined in aliquots of the solution using the methods we proposed.

2. Results and Discussion

Co (II) reacts with DMSBP to form yellow-brown complexes. This complex is insoluble in non-polar solvents. When determining the charge sign of the single-ligand complex using ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchangers (EDE - ethylenediamine, epichlorohydrin; 10 - serial number of the brand: P - means that the matrix has a macroporous structure) demonstrated the anionic nature of the single-ligand complex. When studying the electromigration of the complex, it was found that the yellow-brown dimercaptophenolate complex Co (II)-DMSBP moves toward the cathode. When amines (Am) were introduced into the system, extraction of this compound into the organic phase was observed in the form of a mixed-ligand complex (MLC). DMSBP were synthesized according to the procedure [32]. The synthesized compound was identified by IR and NMR spectroscopy (table 1).

Reagent	IR (KBr)	¹ H NMR (300.18 MHz, C ₆ D ₆)
DMSBP	3458 cm ⁻¹ ν(OH), 2568 cm ⁻¹ ν(SH), 3040 cm ⁻¹ ν(CH), 1535 cm ⁻¹ ν(C ₆ H ₅), 1395 cm ⁻¹ δ(-CH(CH ₃)) 1380 cm ⁻¹ (CH ₂ -CH ₃).	δ 5.05 (s, 1H- OH), δ 3.35 (s, 2H- 2SH), δ 7.04 (s, 2H Ar -H), δ 2.51 (s, 1H- -CH), δ 1.56 (s, 2H- (CH ₂), δ 1.18 (s, 3H- CH ₃), δ 0.91 (s, 3H- CH ₃).

Table 1: The Research Results of IR and ¹H NMR Spectroscopy

2.1. Influence of the pH of the Aqueous Phase

The effect of pH on the formation of Co (II)-DMSBP-Am complex was studied, in order to find a suitable pH that can be adopted in the determination of cobalt (II) (Fig. 1). pH is always considered as quite important and critical for complex formation and its stability. It is always inevitable to find the optimum pH at which the complex is most stable. The universal buffer solution used for pH maintenance did not interfere in actual analysis and provided the desired pH for complex formation. The absorbance was found

to be maximum in the pH range 5.2-7.9. Hence further analytical investigations were carried out in media of pH 5.5. 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 DMSBP. It is probably present in the solution in an undissociated state. At pH ≥ 8.5, the complexes are practically not extracted, apparently due to the hydrolysis of the cobalt ion.

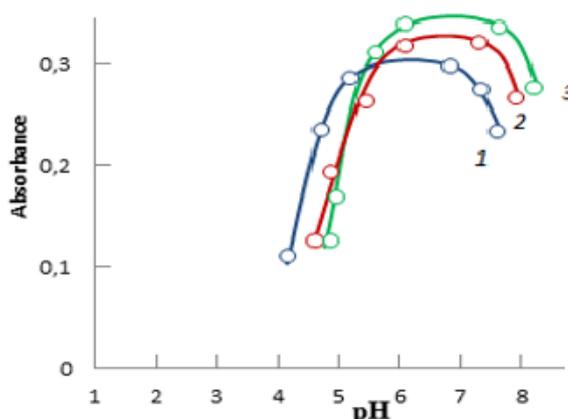


Figure 1: Absorbance of Mixed-Ligand Complexes as a Function of the pH of the Aqueous Phase

Co (II)-DMSBP-Dip; 2. Co (II)-DMSBP-Phen; 3. Co (II)-DMSBP-BPhen
 $C_{Co} = 2.035 \times 10^{-5}$ M, $C_{DMSBP} = 8 \times 10^{-4}$ M, $C_{Am} = 1.0 \times 10^{-3}$ M, 540 nm, $l = 0.5$ cm.

2.2. The Choice of the Extractant

Chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, xylenes, isoamyl and benzoyl alcohols were used for extraction of the complexes. The extraction efficiency of the complexes was estimated by the distribution coefficient and recovery. The best extractants were chloroform, dichloroethane, carbon tetrachloride and chlorobenzene. All further studies were carried out with chloroform. The cobalt concentration in the organic phase was determined using 2-nitroso-1-naphthol by the spectrophotometric method after reextraction, and in the aqueous phase - by difference [23]. The basicity of Am has virtually no effect on cobalt extraction. After a single extraction with chloroform, 99.3–99.5% of cobalt was extracted as MLC (Fig. 1). Apparently, this is due to the fact that the volatility and wetting ability of chloroform are high. Chloroform molecules are not included in the extracted complexes. With a decrease in the dielectric constant of the solvent, the stability constants of the complexes increase. A decrease in the solubility of reagents and complexes in water is usually accompanied by an improvement in their solubility in organic solvents, and the sensitivity of complexation reactions increases.

2.3. Influence of Reagent Concentration and Incubation Time

The concentration of the chelating agent is an important factor to optimize in the preconcentration method. It is very important to establish the minimum concentration of the reagent that results in the formation of a complete complex while achieving the highest extraction. The formation and extraction of MLC requires a 15-20-fold excess of complexing reagents. Optimum conditions for the formation and extraction of these compounds are provided by 8.0×10^{-4} M DMSBP and 1.0×10^{-3} M Am. The presence of excess reagent solution and hydrophobic amine does not change the absorption of the color reaction.

The absorption of the colored [Co-DMSBP-Am] complexes in chloroform was recorded at 540 nm over time intervals. It was noted that the absorption values of the cobalt (II) complex in chloroform remained virtually stable for approximately 72 h. This demonstrates the stability of the extracted cobalt (II) complex, making it suitable for accurate determination for three days. In contrast to single-ligand complexes, the mixed-ligand Co (II) complexes with DMSBP and Am are stable in

aqueous and organic solvents and do not decompose for two days. After extraction in closed vessels, the light absorption of the complexes persisted for more than a month. The required phase contact time was 5 min.

2.4. Effect of Phase Volume Ratio

The degree of Co (II) extraction as MLC does not depend on the volume ratio of the aqueous and organic phases in a wide range (from 5:5 to 100:5), which allows for simultaneous concentration and photometric determination of the specified elements. The concentration factor reaches 20.

Thus, an 18-fold increase in the aqueous phase relative to the organic phase does not affect the completeness of extraction.

2.5. Spectral Characteristics

The complexes have maximum absorption at 520-528 nm (Fig. 2). The reagents have minimum absorption at maximum absorption of the complexes. Therefore, further absorption measurements were carried out at 540 nm. The molar absorption coefficients of the complexes were calculated using the Komar method [33] and were $\epsilon = (3.11-3.45) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

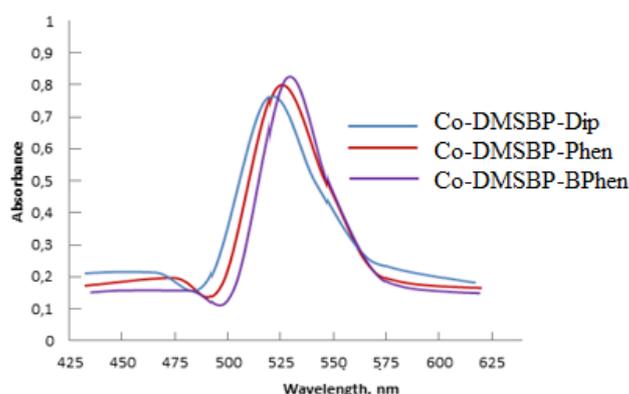


Figure 2: Absorption of Mixed-Ligand Complexes

$C_{\text{Co}} = 2.035 \times 10^{-5} \text{ M}$, $C_{\text{DMSBP}} = 8.0 \times 10^{-4} \text{ M}$, $C_{\text{Am}} = 1.0 \times 10^{-3} \text{ M}$, Shimadzu UV1240, 540 nm, $l = 1.0 \text{ cm}$.

2.6. Stoichiometry of the Complexes and the Mechanism of Complexation

The composition of the complexes was determined by the methods of relative yield, equilibrium shift, intersection of curves and the Asmus method [33]. The results suggest a complex composition of 1:1:2 (Co: DMSBP: Am). The formation of MLC can be represented as follows. The cobalt

ion interacts with two DMSBP molecules, forming a divalent anionic complex, which, when interacting with heterocyclic diamines, is extracted as a mixed-coordination-sphere MLC (Fig. 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 cobalt in one DMSBP molecule appeared to be one [34, 35].

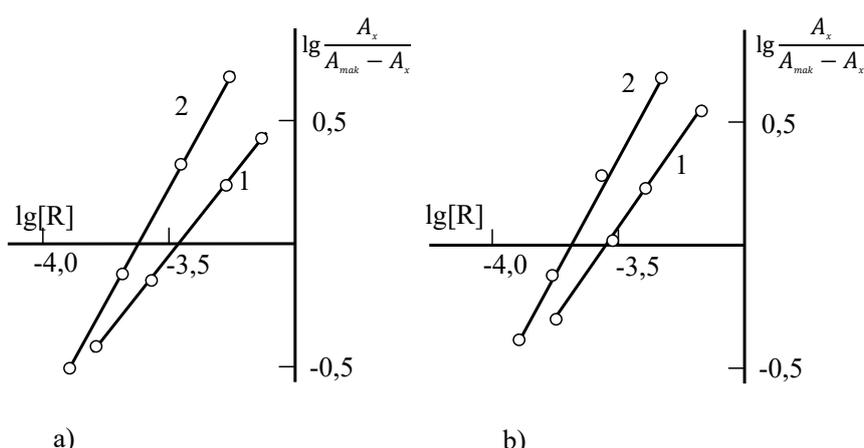


Figure 3: Determination of the Ratio of Components by Equilibrium Shift Method for Co (II)-DMSBP-Phen

(a) and Co (II)-DMSBP-BPhen (b) 1. Co (II): DMSBP; 2. Co (II): Am.

$C_{\text{Co(II)}} = 2.035 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{DMSBP}} = 8.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{Am}} = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, pH 6, 540 nm, $l = 0.5 \text{ cm}$

The disappearance of the pronounced absorption bands in the $3600-3250 \text{ cm}^{-1}$ with a maximum at 3458 cm^{-1} observed in the spectrum of DMSBP, says that the -OH group is involved

in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2568 cm^{-1} shows that one of the -SH groups involved in the formation

of coordination bond in the ionized state. The detection of absorption bands at 1395 cm^{-1} indicates the presence of coordinated phenanthroline [36, 37].

In the region of stretching vibrations of C-N and C-C bonds of the rings, a shift of the bands of 1585 cm^{-1} in the Dip molecule to 1565 cm^{-1} and 1400 to 1385 cm^{-1} in the complex is observed, which indicates a bond between the metal and nitrogen. $\nu(\text{C}=\text{C})$ in the DMSBP spectrum, observed at 1450 cm^{-1} , shifts to 1421 cm^{-1} in the spectrum of the complex. The

weak band in the Phen spectrum observed at 3075 cm^{-1} refers to $\nu(\text{C}-\text{H})$ in the aromatic ring. During complex formation, a shift of this band to 2920 cm^{-1} is observed (fig.4).

New bands were observed between 600 - 400 cm^{-1} region in the complex, which were absent in the spectrum of ligand. Evidence of the formation of a new MLC is provided by three peaks in the low-frequency region: 464 cm^{-1} M-N bond, 535 cm^{-1} M-O bond and 440 cm^{-1} M-S bond [36,37].

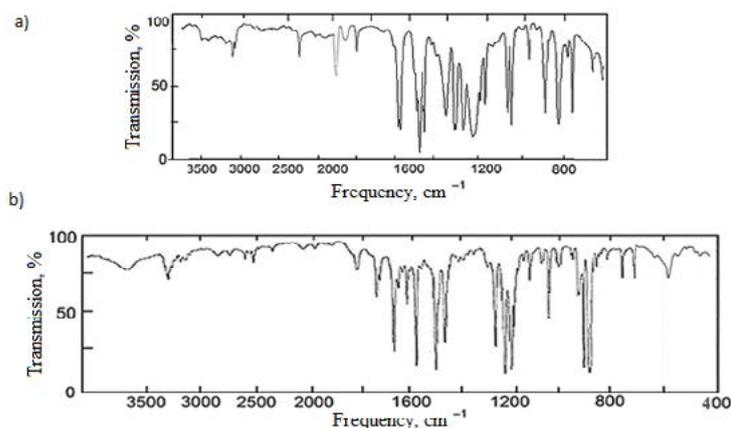


Figure 4: IR Spectrum of the Complex Co (II)-DMSBP-Phen (a) Co (II)-DMSBP-Dip

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

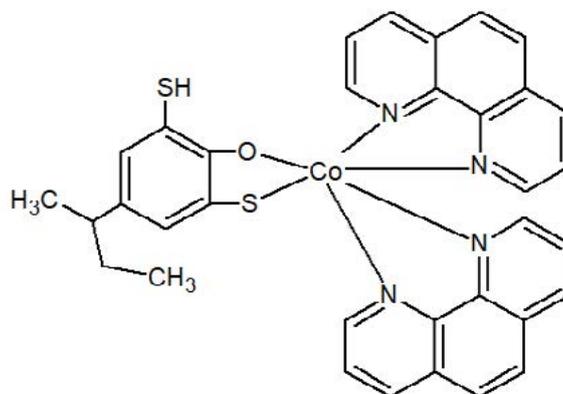
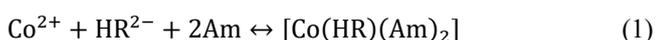


Figure 5: Structure of Complex Co-DMSBP-Phen

Cobalt is found mainly in the +2-oxidation state. As part of some of the systems it is easily oxidized to Co (III). It is known that paramagnetic Co^{2+} and it maintains this property in combination with organic compounds. On the contrary, Co^{3+} is diamagnetic. Therefore, the measurement of the magnetic susceptibility of the complex solutions gives the answer on the valence state of cobalt. The data show that the solution of the complex is paramagnetic, and it confirms the state of divalent cobalt complex.

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $\text{Co}(\text{DMSBP})(\text{Am})_2$.

Formation in the aqueous phase:



Distribution:



Equilibrium and extraction constants in Table 3.

Calculation of extent of polymerization of complexes was carried out on the equation [38]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (=1.08-1.15).

The stability constants of MLC were determined by crossed lines method (Table 3). Higher charges on smaller metals and smaller ligands with higher electron density also impart stability to the complexes. These molecular interactions between electron donors and acceptors are mainly associated with the formation of colored charge-transfer complexes

that absorb in the visible region. Thermogravimetric study of the complex Co-DMSBP-Phen shown that thermal decomposition of the complex takes place in three stages: at 60-90°C water evaporates, at 430-490 °C-decomposed Phen and at 500-530°C - DMSBP. The final product of the thermolysis of the complex is Co_2O_3 .

2.7. Influence of Interfering Ions

To demonstrate the selectivity of the developed extraction system, the influence of coexisting ions in the samples on cobalt recovery was also assessed. A study of potential interferences in the determination of cobalt was performed.

An error of $\pm 5\%$ 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^- , oxalate, 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 (see table 2).

Ion	Molar excess of the ion	Masking agent	Found Co, μg	RSD (%)
Ni(II)	50		29.8	5.2
Fe(II)	200		29.8	4.2
Cd(II)	200		30.3	3.4
Al(III)	200		29.5	3.8
Fe(III)	60	Ascorbic acid	30.2	5.4
Zr(IV)	50		29.6	4.2
Cu(II)	25	Thiourea	30.1	5.5
Hg(II)	40		30.2	4.9
Ti(IV)	30	Ascorbic acid	29.8	4.5
V(IV)	20		29.6	5.3
Mo(VI)	10	EDTA	29.5	4.3
W(VI)			29.8	3.5
Cr(III)	120		29.8	5.2
Nb(V)	50	$\text{C}_2\text{O}_4^{2-}$	29.5	4.5
Ta(V)	50	Ascorbic acid	30.2	4.9
UO_2^{2+}	50		30.4	3.8
Salicylic acid	30		29.7	5.2
Sulphosalicylic acid	30		30.0	3.7
Ascorbic acid	100		30.3	4.3
Tartaric acid	100		30.6	3.9
Oxalate	28		29.6	3.9
Fluoride	35		30.3	3.6
Phosphoric acid	30		31.2	5.6
Thiourea	30		29.8	3.5
Thiosulphate	35		29.5	4.8

Table 2: Influence of Interfering IONS on the Determination of Cobalt (II) AS MLC with DMSBP and DIP (30.0 μg CO Added)

In conclusion the analytical parameters pertaining to the proposed method are given in Table 3.

Compound	The pH range of maximum extraction	R, %	λ_{max} (nm)	Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1}$) $\times 10^{-4}$	$\lg K_e$	$\lg \beta$	$\lg K_{\text{ex}}$
Co(DMSBP)(Dip)_2	5.2-7.5	99.3	520	3.11	5.08	16.64	17.64
Co(DMSBP)(Phen)_2	5.5-7.7	99.4	526	3.23	5.25	17.25	17.75
Co(DMSBP)(BPen)_2	5.6-7.9	99.5	528	3.45	5.26	17.05	17.87

Table 3: Optical Characteristics, Precision and Accuracy of the Spectrophotometric Determination of Co (II) With Dmsbp and Am

2.8. Effect of Cobalt (II) Concentration

Under optimal experimental conditions, a series of experiments were designed to obtain the linear range, accuracy, detection limit, pre-concentration factor and other characteristics of the proposed methods. Three replicate experiments were performed for each concentration level. 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. We observed absorbency to be in accordance with Beer's law for complex extracts with dichloretane in intervals of concentration between 0.4 to 18 mkg/ mL (Table 4). The pertaining calibration graph is shown in the Fig. 7. The correlation coefficient of the calibration curve equation was greater

than 0.995, indicating that a good linear regression was established between absorbance and concentrations. The data obtained for constructing the calibration graphs were processed by the method of least squares [39]. The equation of the calibration graphs is given in Table. 4. On the basis of the equations of the calibration graphs, the LOD and the LOQ of cobalt in the form of MLC were calculated.

$$\text{LOD} = \frac{3\sigma}{S}$$

$$\text{LOQ} = \frac{10\sigma}{S}$$

where σ and S are identified as the standard deviation of the response and slope of the calibration curve, respectively.

Compound	Limit of detection (LOD): ng • mL ⁻¹	Limit of quantification (LOQ): ng • mL ⁻¹	Sandell's sensitivity (μg • cm ⁻²)	Beer's law range (μg • mL ⁻¹)	The equation of calibration curves
Co(DMSBP)(Dip) ₂	10	34	1.68	0.5-16	0.053+0.0278x
Co(DMSBP)(Phen) ₂	10	33	1.71	0.5-16	0.046+0.0301x
Co(DMSBP)(BPhen) ₂	9	31	1.87	0.4-18	0.050+0.0326x

Table 4: Analytical Characteristics of Some Ternary Complexes of Co (II) With Dmsbp and Am

The proposed method compares favourably with the existing ones (Table 5) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

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	[6]
1-nitroso-2-naphtol	≥3	415	2.9		[23]
2-nitroso-1-naphtol	≥4	365	3.7		[23]
Nitroso-R-salt	weakly acidic medium	415	3.5		[23]
DMSBP-Dip	5.2-7.5 (CHCl ₃)	520	3.11	0.5-16	This method
DMSBP -Phen	5.5-7.7 (CHCl ₃)	526	3.23	0.5-16	This method
DMSBP-BPhen	5.6-7.9 (CHCl ₃)	528	3.45	0.4-18	This method

Table 5: Comparative Characteristics of the Procedures for Determining of Cobalt

2.9. Analytical Applications

The methods we proposed were applied under already established optimal conditions to determine cobalt in

various objects: in wastewater and bottom sediments of steel plants, and food samples (Table 6,7,8,9).

Reagent	Content Co, in %	S _x	ε	S _r	μ
<i>Steel M 441 (0.012%Co)</i>					
1-nitroso-2-naphtol	0.0125	0.000308	0.00033	0.025	0,0125±0.00042
Co-DMSBP-Phen	0.0123	0.000270	0.00029	0.022	0.0123±0.00031
<i>Steel №156 (0.56%Co)</i>					
1-nitroso-2-naphtol	0.587	0.023	0.025	0.033	0.587±0.025
Co-DMSBP-BPhen	0.561	0.028	0.030	0.045	0.561±0.030

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

Analysis object	Added, mg/kg	Found, mg/kg	Found in the sample, mg/kg	S_r
			$\bar{x} \pm \frac{t_p \cdot S}{\sqrt{n}}$	
Sewage water				
Sample 1	2.0	2.55	0.55±0.06	0.076
Sample 2	5.0	6.01	1.09±0.12	0.074
Bottom sediments				
Sample 1	5.0	6.25	1.25±0.07	0.065
Sample 2	5.0	6.85	1.85±0.05	0.062

Table 7: Determination Results of Cobalt (Ii) With Dmsbp And Phen In the Sewage Water and Bottom Sediments (N = 6, P = 0.95)

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	0.0047	0.027	0.22±0.0052
	DMSBP+Phen	0.18	0.0034	0.021	0.18±0.0043
	DMSBP+BPhen	0.20	0.0032	0.018	0.20±0.0032
Bird-Cherry Tree	2-nitroso-1-naphtol	6.75	0.2077	0.021	6.75±0.2185
	DMSBP +Phen	6.81	0.1290	0.029	6.81±0.1356
	DMSBP+BPhen	6.94	0.1449	0.021	6.94±0.1536
Peas	2-nitroso-1-naphtol	0.11	0.0033	0.030	0.11±0.0037
	DMSBP +Dip	0.12	0.0036	0.027	0.12±0.0043
	DMSBP +Phen	0.11	0.0053	0.042	0.11±0.0046

Table 8: Determination Results of Cobalt (Ii) In Food Samples

Soil	Method	\bar{x} , mg/kg	S	RSD (%)	$\bar{x} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Sod-podzolic sandy and sandy loamy soils	2-nitroso-1-naphtol	3.19	0.157	5.1	3.19±0.164
	DMSBP+Dip	3.21	0.145	4.2	3.21±0.146
	DMSBP+Phen	3.20	0.128	3.9	3.20±0.124
	DMSBP+BPhen	3.15	0.125	4.5	3.15±0.116
Sod-podzolic loam and clay soils	2-nitroso-1-naphtol	9.89	0.445	4.5	9.89±0.467
	DMSBP+Phen	9.95	0.418	4.2	9.95±0.438
Gray forest soils	2-nitroso-1-naphtol	13.05	0.392	3.0	13.05±0.410
	DMSBP+BPhen	12.96	0.375	3.9	12.96±0.394
	2-nitroso-1-naphtol	15.78	0.583	3.7	15.78±0.612
Black earth	DMSBP+BPhen	15.72	0.548	3.5	15.72±0.576
	2-nitroso-1-naphtol	11.64	0.545	4.7	11.64±0.572
	DMSBP+Phen	11.55	0.521	4.5	11.55±0.547
Chestnut soils	DMSBP+BPhen	11.75	0.530	4.2	11.75±0.553
	DMSBP+Phen	11.55	0.521	4.5	11.55±0.547
	DMSBP+BPhen	11.75	0.530	4.2	11.75±0.553

Table 9: Determination Results of Cobalt (Ii) In Soil Samples

Validation of the results obtained by the proposed methods was carried out on model solutions according to the “introduced-found” method. The test results are given in table 10.

Found	Introduced	Found	S	Sr	$\bar{x} \pm \frac{t_p \cdot S}{\sqrt{n}}$
1.15	3.0	4.17	0.128	0.04	4.17±0.14
2.45	5.0	7.49	0.358	0.05	7.49±0.37

Table 10: The Correctness of the Developed Methods by the Method "Entered-Found"

3. Conclusion

- Mixed-ligand complexes of cobalt (II) with DMSBP and Am have been studied by spectrophotometry.
- Extraction of mixed ligand complexes is maximal at pH 5.2-7.9. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found. Chloroform, dichloroethane and chlorobenzene appeared to be the best extractants. All the further investigations were carried out with chloroform.
- The complexes have maximum absorption at 520-528 nm. The molar absorption coefficients of the complexes are $\epsilon = (3.11-3.45) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.
- The molar ratio of the reacting components Co (II), DMSBP and Am is 1:1:2. The general formula of the ternary complexes is Co (DMSBP)(Am)_2 . First, a divalent anionic complex $[\text{Co (DMSBP)}_2]^{2-}$ is formed, which, upon interaction with Am, is extracted as a mixed-ligand complex with a mixed coordination sphere.
- The developed method retains specific interaction of cobalt (II) with DMSBP 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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