

## Extraction Study on the Colour Reaction for Cobalt (II) with the 2-hydroxy-5-nitrothiophenol - Di-, triphenylamine - Water - Chloroform System

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### ABSTRACT

The conditions for the complexation of cobalt (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time (300 minutes), pH of the medium (pH<sub>op</sub> 3.6-5.2), the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law (0.06-20 µg / 5 ml). The spectral characteristics of the complex ( $\lambda = 560-565$  nm) and the HNTPh reagent ( $\lambda = 295$  nm) were studied which showed high sensitivity and contrast ( $\lambda = 265-270$  nm) and the true molar coefficient ( $\epsilon = (3.4-3.6) \times 10^4$ ) of light absorption was determined. The mole ratio of cobalt: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition. The interval of obedience to the Bouguer-Lambert-Beer law (0.06-20 µg / 5 ml) and the Sendel sensitivity of 0.0111 - 0.0175 µg / cm<sup>2</sup> are shown. Based on the achieved results and revealed regularities, a photometric technique for determining cobalt (II) with HNTPh and Am. The selectivity of the developed methodology was studied. The developed technique is applied to the analysis of various objects, the results obtained are processed by the method of mathematical statistics.

**KEYWORDS:** Cobalt, 2-hydroxy-5-nitrothiophenol, hydrophobic amines, diphenylamine, triphenylamine, chloroform.

### 1. Introduction

The urgency of the development of simple, rapid and sensitive techniques for determining cobalt is due to the extensive use of this metal in industry, on the one hand, and its toxicity on the other [1]. Despite the development of atomic-spectral methods for determining cobalt, the extraction-photometric method, which does not require an expensive equipment, is simple in execution and is available for small production and agrochemical laboratory.

In connection with these circumstances, it is very attractive to extract cobalt

in the form of thiocyanate complexes, which have a characteristic absorption spectrum and are well extracted from the aqueous phase by various extractants [2]. Although the thiocyanate method for determining cobalt is known more than a hundred years and finds so wide practical application that it stands out as an independent direction in the analytical chemistry of cobalt [3], its capabilities are constantly expanding by using new extractants.

As a reagent for cobalt, a number of reagents belonging to the class of o, o-hydroxyaminazo compounds are proposed [4]. For cobalt complexes with them, the conventional molar light absorption coefficients are calculated. They are  $4.37 \times 10^4$  for nitrazone F,  $3.75 \times 10^4$  for chloroxaminase F. The ratio of complexes is studied by saturation, isomolar series and Asmus, it is 1: 1 and 1: 3. It has been established that alkali and alkaline-earth metals,  $W^{4+}$ ,  $Mo^{4+}$ ,  $Mn^{2+}$ ,  $Pb^{2+}$ ,  $V^{5+}$ ,  $Cr^{3+}$ , and others practically do not interfere with the determination of cobalt with nitrosan.  $Al^{3+}$  and  $Cd^{2+}$  interfere in large quantities due to hydrolysis. In their presence, the determination is carried out at  $pH > 10.0$ . Under optimal conditions of complexation,  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Fe^{3+}$  strongly interfere.

A spectrophotometric method for determining trace amounts of cobalt, nickel, and copper ions was developed [5] after the adsorption of their 2-aminocyclopentene-2-dithiocarboxylate complexes on microcrystalline naphthalene. These complexes are adsorbed on microcrystalline naphthalene at  $pH = 4.5$  after shaking for 5 minutes. The resulting solid mass is separated by filtration and is dissolved in dimethylformamide. For the analysis of the three-component mixture  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , the absorption spectra were processed using a calibration multiparameter method of partial least squares. The detection limits for  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  were 3.3; 10.0 and 0.8  $\mu g / ml$ . The proposed method has also been successfully applied to determine the content of  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  in alloys.

Sorption of  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$  sorbent POLIORGS was studied [6] and concentrating conditions were chosen for the analysis of small volumes of natural waters. The behavior of these metals has been studied and the atomic absorption regimes have been established in the aqueous suspension of the sorbent. A sorption-atom-absorption method for determining  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$  in seawater has been developed. The limits of detection of elements are 0.4  $\mu g L^{-1}$  for  $Cu^{2+}$  and  $Ni^{2+}$ , 0.05  $\mu g L^{-1}$  for  $Co^{2+}$ , 0.2  $\mu g L^{-1}$  for  $Pb^{2+}$  and 0.1  $\mu g L^{-1}$  for  $Cd^{2+}$ .

The authors of Ref. [7] found the optimum conditions for the concentration of  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$  on silica by C-120 siloxane modified with 4- (2-tialylazo) resorcinol, and the colorimetric characteristics of the complexes were determined. It is shown that the separation criterion is satisfied by complexes of nickel and zinc. A colorimetric method for the separate determination of 0.05-1.00  $\mu g L^{-1}$  was developed of nickel and 0.15-5.0  $\mu g mL^{-1}$  of zinc.

A technique was developed [8] for the spectrophotometric determination of the  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Pd^{2+}$ ,  $Ru^{2+}$  and  $Mo^{6+}$  macroquantities after extraction of their isoamylxanthogenates with molten naphthalene. The optimum condition for determining  $Co^{2+}$  at  $pH 3.0-8.0$  is selected, the complex is formed by the ratio 1: 2; The molar coefficient of light absorption is equal to  $2.06 \times 10^4$  at 360 nm, the Sendel sensitivity is 0.0052  $\mu g cm^3$ ,  $Sr = 0.0081$ .

The possibility of direct determination of  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$  and  $Ni^{2+}$  in concentrated solutions of calcium chloride by the method of electrothermal atomic absorption spectrometry was shown in [9]. As chemical modifiers, ascorbic and oxalic acids, as well as magnesium nitrate, have been studied. The best modifier was oxalic acid. Despite the use of an atomic absorption spectrometer with a relatively ineffective background correction system (with a deuterium lamp) in the presence of oxalic acid, it is possible to confidently determine the

studied elements to a concentration of calcium chloride in a solution of 6%. Due to the fact that cadmium evaporates before the main part of this matrix, it can be determined without a modifier.

The method [10] of the sorption concentration of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$  was developed on a column with an Ambersorb 563 sorbent from the sample solution and the eluent was set by a peristaltic pump. In  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution ( $\text{pH} = 9.0$ ), these ions were quantitatively retained by the sorbent. Then they were eluted with 5 ml of 0.25 M  $\text{HNO}_3$  at a rate of  $5 \text{ ml min}^{-1}$ . The detection limits of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are 0.33 and  $72 \mu\text{g L}^{-1}$ , respectively. The relative standard deviation is less than 0.10. The method is used to determine the ions  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$  in drinking and sea water samples (recovery > 95%).

The optimum conditions for the complexation of cobalt with nitroso-P-salt (HPC) in the presence and absence of ascorbic acid were found in [11]. The molar coefficients of the colorimetric functions of the complexes were calculated and it was shown that only the colorimetric functions make it possible to distinguish the complexes of cobalt (II) and cobalt (III), while the optical characteristics are practically identical. For practical purposes, it is better not to inject ascorbic acid and obtain a kinetically inert cobalt (III) complex with a nitroso-P salt. Under optimum complexation conditions, the maximum light absorption of the reagent is at 360-380 nm from the obtained data [12], 430, 490 and 710 nm are chosen as the characteristic wavelengths. At 710 nm, only the iron (III) complex with HPS is absorbed to the maximum and a potential for separate determination of cobalt and iron appears in a joint presence by the method of two-wave spectrophotometry.

Oxyphenolate and hydroxthiophenolate complexes of cobalt are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [13-14]. In this respect, a very promising reagent is hydroxthiophenols, which contains one hydroxyl and one sulphohydril groups and is a sulfur-containing analogue of mononuclear poly-phenols with one oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Cobalt (II) with hydroxthiophenols in the presence of hydrophobic amines (Am). From hydroxthiophenol 2-hydroxy-5-nitrothiophenol (HNTPh) were used in the presence of hydrophobic amines (Am). As hydrophobic amine diphenylamine (DPhA) and triphenylamine (TPhA) were used.

## 2. Experimental

### 2.1. Reagents and Apparatus

Cobalt standard solution ( $1000 \text{ mgL}^{-1}$ ;  $\text{Co}(\text{NO}_3)_2$ ) was purchased from Merck Darmstadt (Germany). Working solutions ( $C_{\text{Co}} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$ ) were prepared by diluting appropriate volumes of the stock solution. The concentration of the cobalt solution was adjusted gravimetrically [15].

HNTPh were synthesized according to the procedure [16]. The purity was checked by determining the melting point and chromatography on paper. The HNTPh was identified by IR and NMR spectroscopy: IR (KBr): [ $3462 \text{ cm}^{-1} \nu(\text{OH})$ ,  $2564 \text{ cm}^{-1} \nu(\text{SH})$ ,  $3045 \text{ cm}^{-1} \nu(\text{CH})$ ,  $1700 \text{ cm}^{-1} \nu(\text{NO}_2)$ ,  $1535 \text{ cm}^{-1} \nu(\text{C}_6\text{H}_5)$ ];  $^1\text{H NMR}$  (300,18 MHz,  $\text{C}_6\text{D}_6$ ): [ $\delta$  5.16 (s, 1H- OH),  $\delta$  3.25 (s, 1H - SH),  $\delta$  7.18 (s, 2H Ar-H),  $\delta$  7.41 (s, 1H - Ar-H)].

0.01M solutions of HNTPh and Am in chloroform were used in the work. The HNTPh was purified by reprecipitation from ethanol solutions by addition of water and then by distillation.

To create the necessary pH, fixated HCl (pH 0-3) and  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONH}_4$  buffer solutions (pH 4-12) were used. The ionic strength of the solutions was kept constant ( $\mu = 0.1$ ) by introducing the calculated amount of  $1\text{M KNO}_3$ .

The optical density of the solutions was measured on a SF-26 spectrophotometer and on a KFK-2 photoelectric colorimeter in a cuvette with a layer thickness of  $\ell = 1\text{ cm}$  and  $0.5\text{ cm}$ , respectively. The pH of the solutions was monitored with an I-120 ionomer with a glass electrode. IR spectra were recorded on a UR-20 spectrophotometer in the  $400\text{-}4000\text{ cm}^{-1}$  region. All of these devices were tested by the state.

## **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  $1.0\text{ mL}$  with a  $0.1\text{ mL}$  step, a  $2.2 - 2.5\text{ mL}$  portion of a  $0.01\text{ M}$  solution of HNTPh, and a  $2.5 - 3.0\text{ mL}$  portion of a  $0.01\text{M}$  solution of Am were placed in to calibrated test tubes with groundglass stoppers (the volume of the organic phase was  $5\text{ mL}$ ). The required value of pH was adjusted by adding  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONH}_4$  buffer solutions (pH 4-12). The volume of the aqueous phase was increased to  $20\text{ mL}$  using distilled water. In  $8 - 10$  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  $540\text{ nm}$  ( $\ell=0.5\text{cm}$ ).

#### **2.2.2. Determination of Cobalt in metallic nickel**

A sample weighing ( $8\text{ g}$ ) is dissolved in  $30\text{ ml}$  of a mixture (3: 1) of HCl and  $\text{HNO}_3$ . The solution is evaporated to a syrupy state, the salts are dissolved in water and the solution is transferred to a volumetric flask.  $25\text{ ml}$ . An aliquot ( $10\text{ ml}$ ) was taken, a certain amount of cobalt ( $30\text{ }\mu\text{g}$ ) was added thereto and cobalt with HNTPh and Am was extracted and photometrically determined under optimal conditions.

#### **2.2.2. Determination of Cobalt (II) in Steel**

A weighed sample of  $0.2\text{ g}$  was dissolved in  $20\text{ ml}$  of  $\text{H}_2\text{SO}_4$  (1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice lo vapor  $\text{SO}_3$ . The precipitated salt was dissolved in  $20\text{ ml}$  of  $15\%$  tartaric acid under heating, the solution was cooled, adjusted with water to  $100\text{ ml}$  in a volumetric flask, stirred and filtered. An aliquot of  $5\text{ ml}$  was put into a separatory funnel, was added  $1\text{ ml}$  of  $10\%$  hydroxylamine solution,  $1\text{ ml}$  of  $3\%$  ascorbic acid and was determined cobalt using the proposed procedures.

#### **2.3.3. Determination of cobalt (II) in tap water.**

Pour  $2$  liters of water into a flask and evaporate to dryness. The dry residue is dissolved in a buffer solution of pH 4 and transferred to a  $50\text{ ml}$  flask by filtration. In an aliquot ( $3\text{ ml}$ ), photometric determination of cobalt.

## **3. Results and Discussion**

Co (II) reacts with 2-hydroxy-5-nitrothiophenol and gives complexes that are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Cobalt(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 diphenylamine and triphenylamine were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

**3.1. Selection of extractant.** To extract the complexes,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_6\text{H}_5\text{Cl}$ ,  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{-CH}_3$ ,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , *iso*- $\text{C}_4\text{H}_9\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OH}$ , *iso*- $\text{C}_5\text{H}_{11}\text{OH}$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$  were used. The extractability of the complexes was evaluated by the distribution coefficient and the degree of extraction. The best extractants were  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{C}_6\text{H}_5\text{Cl}$ . All further studies were carried out with  $\text{CHCl}_3$ . The content of cobalt in the organic phase was determined photometrically by 2-nitroso-1-naphtol [3] after stripping, and in the aqueous phase by the difference. With a one-time extraction (R,%) by chloroform, 96.0 - 97.0% of cobalt is extracted as a MLC.

**3.2. Effect of the pH of the aqueous phase.** Light absorption spectra of cobalt (II) complexes with HNTPh and Am were studied in a wide range of pH of the medium. The maximum yield of complexes is observed at pH 1.4-8.2. Hence further analytical investigations were carried out in media of pH 3.6-5.2 (Fig. 1). 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 HNTPh.  $\text{pH} \geq 8.2$  complexes are not practically extracted, which, apparently, is associated with a decrease in the Am protonation degree.

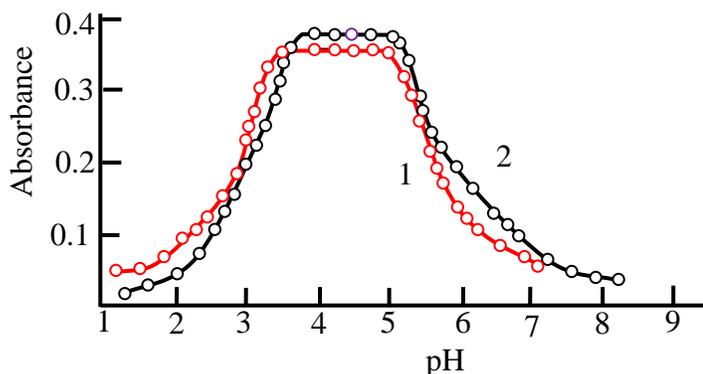


Fig. 1. Absorbance of Co- HNTPh -Am extracts function of the pH of the aqueous phase.  
1. Co- HNTPh – DPhA, 2. Co- HNTPh – TPhA

$C_{\text{Co(II)}} = 1.7 \times 10^{-5}$  M,  $C_{\text{HNTPh}} = (1.12-1.25) \times 10^{-3}$  M,  $C_{\text{Am}} = (0.90-1.30) \times 10^{-3}$  M,  $\lambda = 540$  nm, KFK-2,  $\ell = 0.5$  cm

### 3.3. Influence of Reagent Concentration

For the formation and extraction of MLC, a 20-25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by  $(1.12-1.25) \times 10^{-3}$  M HNTPh and  $(0.90-1.30) \times 10^{-3}$  M Am. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

### 3.4. A study of the stability of the optical density of the cobalt (II) complex with HNTPh and Am in time.

To determine the stability of the color of the cobalt complex in time, the optical density of the solutions was measured at definite intervals of time.

Method of work: 1.0 ml of cobalt (II) solution, ( $\text{Co}^{2+} = 10 \mu\text{g} / \text{mL}$ ), 1.0 mL of 0.01M reagent solution, 5.0 ml of sodium acetate buffer solution were added to 25 ml volumetric flasks with a pH of 3.6-5.2 and the volume was adjusted to the mark with distilled water. The optical

density of the complex was measured on KFK-2,  $\ell = 0.5$  cm. The results of the measurements are shown in Table 1.

**Table 1. A study of the stability of the optical density of the cobalt (II) complex with HNTPh and DPhA in time.**

|              |       |       |       |       |       |       |       |       |       |       |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Time minutes | 3     | 5     | 10    | 20    | 30    | 40    | 50    | 60    | 80    | 100   |
| A            | 0.180 | 0.285 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 |
| Time minutes | 140   | 180   | 200   | 220   | 240   | 260   | 300   | 320   | 340   | 380   |
| A            | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.340 | 0.288 | 0.250 | 0.170 |

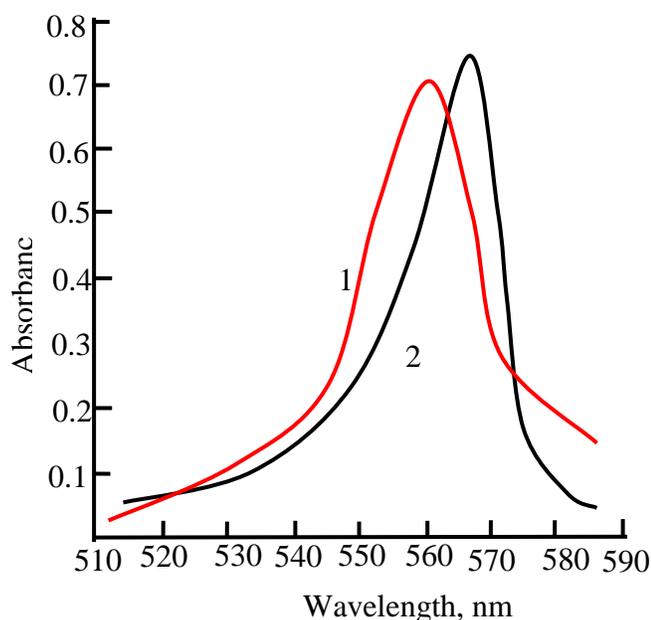
It can be seen from the table data that the optical density of the complex does not change for 300 minutes, which is full enough to produce reproducible results.

### 3.5. The study of the ordering of the components of the reaction

From the experimental data obtained, it can be seen that the maximum optical density is observed at the order of the discharge of the components: cobalt (II) + HNTPh + Am +  $\text{CHCl}_3$  +  $\text{CH}_3\text{COOH}$  +  $\text{CH}_3\text{COONH}_4$  + water. In further studies, this order of draining the components was used as the optimal one.

### 3.6. Spectral characteristics of cobalt (II) complexes with HNTPh and Am.

The spectra of HNTPh and its complex with cobalt (II) are shown in Fig. 2. It can be seen from the figure that in the light absorption spectrum of the cobalt (II) complex there is one expressed maximum at 560-565 nm, and the maximum light absorption of the HNTPh reagent is observed in the shorter-wave region of the spectrum, at 295 nm, which characterizes the contrast between the color of the complex and the reagent, is 265-270 nm, which contributes to the sensitivity of the method.



**Fig. 2.** Absorption of mixed-ligand complexes

1. Co– HNTPh – DPhA, 2. Co– HNTPh – TPhA

$C_{Co(II)} = 1.7 \times 10^{-5}$  M,  $C_{HNTPh} = (1.12-1.25) \times 10^{-3}$  M,  $C_{Am} = (0.90-1.30) \times 10^{-3}$  M, pH 3.6-5.2, SF-26,  $\ell=1.0$

Sensitivity of the method was calculated by the Sendel method in  $\mu\text{g}/\text{cm}^2$  per 0.001 light absorption unit according to the formula:

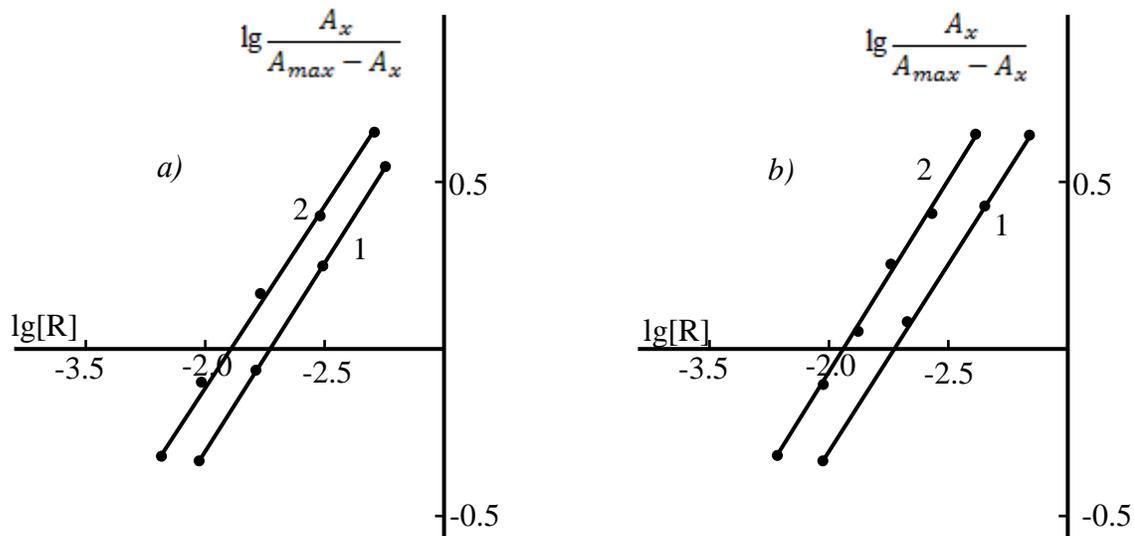
$$S_s = \frac{G \times \lambda \times 0.001}{A \times 25} = \frac{20.0 \times 1.0 \times 0.001}{0.34 \times 5} = 0.0175 \mu\text{g} / \text{cm}^2$$

where  $G$  is the amount of cobalt, in  $\mu\text{g}$ ;  $A$ -optical density.

According to the calculated value of Sendel, it can be concluded that the technique for determining cobalt (II) is quite sensitive. The molar absorptivity of the complex was calculated with Komar method [17] to be  $\varepsilon = (3.4-3.6) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

**3.7. Stoichiometry of the Complexes and the Mechanism of Complexation**

The stoichiometric reaction coefficients were established by the methods of the Asmus straight line and the equilibrium shift [17]. The formation of MLC can be represented as follows. Cobalt ions interacting with two molecules of HNTPh form a doubly charged anionic complex, which is extracted with two molecules of protonated Am (Fig. 3).



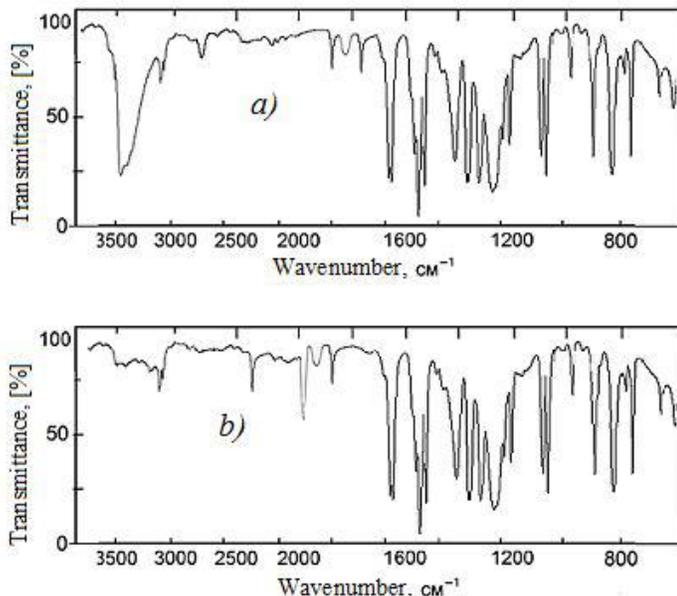
**Fig.3.** Determination of the ratio of components by the equilibrium shift method for (a) Co (II)-HNTPh-DPhA and (b) Co (II)- HNTPh-TPhA. 1- Co (II) : HNTPh; 2- Co (II): Am.

$C_{Co(II)} = 1.7 \times 10^{-5}$  M, SF-26,  $\lambda=540$  nm,  $\ell=1.0$  cm.

The pH of the start of precipitation of  $\text{Co}(\text{OH})_2$  is 8.0, and the pH of the total precipitation is -10.0 [18]. HNTPh is a sufficiently strong reducing agent, so oxidation of Co (II) is not possible. Thus, Co(II) in the complexes is in the unhydrolyzed state. The number of protons displaced by cobalt from one HNTPh molecule turned out to be 2 [19].

The disappearance of the pronounced absorption bands in the  $3200-3600 \text{ cm}^{-1}$  with a

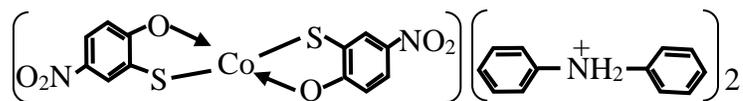
maximum at  $3451\text{ cm}^{-1}$  observed in the spectrum of HNTPh, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area  $2587\text{ cm}^{-1}$  shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at  $1385\text{ cm}^{-1}$  indicates the presence of a protonated diphenylamine (Fig. 4) [20].



**Fig. 4.** IR spectrums of HNTPh (a) and the Co (II)- HNTPh-DPhA (b).

Calculation of extent of polymerization of complexes was carried out on the equation [21]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ( $\gamma = 1.06-1.10$ ).

Proceeding from the obtained data, we propose the following structure for the extracted ternary complex (scheme).



Scheme. Structure of complex  $[\text{Co}(\text{HNTPh})_2](\text{DPhAH})_2$

### 3.8. 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  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$  and  $\text{CH}_3\text{COO}^-$  do not interfere determination of cobalt with HNTPh and DPhA. 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 2.

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

| Foreign ions (FI) | µg   | FI-to-Co ratio | Co found | R,%   |
|-------------------|------|----------------|----------|-------|
| 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 <sup>2+</sup>  | 0.2  | 10             | 19.86    | 97.2  |
| Cu <sup>2+</sup>  | 0.06 | 3              | 20.17    | 103.4 |
| Al <sup>3+</sup>  | 5    | 250            | 20.08    | 101.6 |
| Zn <sup>2+</sup>  | 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 <sup>2+</sup>  | 2.5  | 125            | 19.91    | 98.2  |

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

**Table 3. Optical characteristics, precision and accuracy of the spectrophotometric determination of Co(II) with HNTPh and Am**

| Parameter  | [Co(HNTPh) <sub>2</sub> ](DPhAH) <sub>2</sub> | [Co(HNTPh) <sub>2</sub> ](TPhAH) <sub>2</sub> |
|--|---|---|
| The pH range of education and extraction                   | 1.4-7.2                                       | 1.4-8.2                                       |
| The pH range of maximum extraction                         | 3.6-5.0                                       | 3.7-5.2                                       |
| λ <sub>max</sub> (nm)                                      | 560   | 565   |
| Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> ) | 3.4× 10 <sup>4</sup>                          | 3.6× 10 <sup>4</sup>                          |
| Sandell's sensitivity (µg cm <sup>-2</sup> )               | 0.0175  | 0.0111  |
| R,%  | 96.0  | 97.0  |
| The equation of calibration curves                         | 0.020+0.098x                                  | 0.018+0.102x                                  |
| Beer's law range (µg ml <sup>-1</sup> )                    | 0.06-18                                       | 0.06-20                                       |
| Correlation coefficient                                    | 0.9988  | 0.9985  |

**3.9. Effect of Cobalt(II) Concentration** The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Co(II) may be determined in the range 0.06-20 µg/ml (table 3).

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of cobalt with the earlier known procedures [2,3, 11, 22, 23].

**Table 4. Comparative characteristics of the procedures for determining of cobalt**

| Reagent                                 | pH (solvent)                | $\lambda$ , nm | $\epsilon \cdot 10^{-4}$ | Beer's law range ( $\mu\text{g} \cdot \text{mL}^{-1}$ ) | Ref.          |
|---|-----------------------------|----------------|--------------------------|---|---------------|
| 2,3,5-triphenyl-2H-tetrazolium chloride | 5.2-5.8                     | 525            | 4.26                     | 0.2 - 1.5   | [ 22]         |
| 1-nitroso-2-naphtol                     | $\geq 3$                    | 415            | 2.9                      |   | [2,3,11, 23]  |
| 2-nitroso-1-naphtol                     | $\geq 4$                    | 365            | 3.7                      |   | [2,3, 11, 23] |
| Nitroso-R-salt                          | weakly acidic medium        | 415            | 3.5                      |   | [2,3, 23]     |
| HNTPh - DPhA                            | 3.6-5.0 ( $\text{CHCl}_3$ ) | 560            | 3.4                      | 0.06-18   |               |
| HNTPh -TPhA                             | 3.7-5.2 ( $\text{CHCl}_3$ ) | 565            | 3.6                      | 0.06-20   |               |

**3.10. Analytical Applications**

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

**Table 5. Results of spectrophotometric determination of cobalt in metallic nickel ( $n = 6, P = 0.95$ ).**

| Method              | Found Co, % $10^{-5}$<br>$\bar{x}$ | $S \times 10^{-5}$ | $S_r$ | $\bar{x} \pm \frac{t_p \cdot S}{\sqrt{n}}$ |
|---------------------|------------------------------------|--------------------|-------|--|
| Known methods       |                                    |                    |       |  |
| 1-nitroso-2-naphtol | 7.92                               | 0.316              | 0.040 | $(7.92 \pm 0.33) \cdot 10^{-5}$            |
| 2-nitroso-1-naphtol | 7.90                               | 0.395              | 0.050 | $(7.90 \pm 0.44) \cdot 10^{-5}$            |
| Proposed method     |                                    |                    |       |  |
| HNTPh - DPhA        | 7.8                                | 0.195              | 0.025 | $(7.8 \pm 0.20) \cdot 10^{-5}$             |
| HNTPh -TPhA         | 7.8                                | 0.218              | 0.028 | $(7.8 \pm 0.23) \cdot 10^{-5}$             |

**Table 6. Determination of Cobalt in steel ( $n=3, P=0.95$ )**

| Compound                       | X      | Sx                     | $\epsilon$            | $S_r$ | $\mu$                |
|--------------------------------|--------|------------------------|-----------------------|-------|----------------------|
| <i>Steel M 441 (0.012% Co)</i> |        |                        |                       |       |                      |
| Co-HNTPh-DPhA                  | 0.0124 | $0.311 \times 10^{-3}$ | $0.33 \times 10^{-3}$ | 0.026 | $0.0124 \pm 0.00033$ |
| Co-HNTPh-TPhA                  | 0.0123 | $0.267 \times 10^{-3}$ | $0.29 \times 10^{-3}$ | 0.023 | $0.0123 \pm 0.00029$ |
| <i>Steel №156 (0.56% Co)</i>   |        |                        |                       |       |                      |
| Co-HNTPh-DPhA                  | 0.582  | 0.021                  | 0.020                 | 0.033 | $0.582 \pm 0.02$     |
| Co-HNTPh-TPhA                  | 0.573  | 0.022                  | 0.024                 | 0.038 | $0.573 \pm 0.024$    |

**Table 6. Results of the determination of cobalt (II) in drinking water ( $n = 6, P = 0.95$ )**

| Method              | Found in the sample, mg / L | S       | S <sub>r</sub> | $\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$ |
|---------------------|-----------------------------|---------|----------------|--|
| Known methods       |                             |         |                |  |
| 1-nitroso-2-naphtol | 0.0205                      | 0.00044 | 0,022          | 0.0205±0,0005                              |
| 2-nitroso-1-naphtol | 0.0219                      | 0.00040 | 0,018          | 0.0219±0,0004                              |
| Proposed method     |                             |         |                |  |
| HNTPh - DPhA        | 0.0182                      | 0.00022 | 0,012          | 0.0182±0,0002                              |
| HNTPh -TPhA         | 0.0179                      | 0.00027 | 0,015          | 0.0179±0.0003                              |

#### 4. CONCLUSIONS

1. The conditions for the complexation of cobalt (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time, pH of the medium, the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law.
2. The spectral characteristics of the complex and the HNTPh reagent were studied which showed high sensitivity and contrast ( $\lambda = 265-270$  nm) and the true molar coefficient of light absorption was determined.
3. The mole ratio of cobalt: re: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition.
4. The interval of obedience to the Bouguer-Lambert-Beer law (0.06-20  $\mu\text{g} / 5$  ml) and the Sendel sensitivity of 0.0111 - 0.0175  $\mu\text{g} / \text{cm}^2$  are shown. Based on the achieved results and revealed regularities, a photometric technique for determining cobalt (II) with HNTPh and Am.
5. The selectivity of the developed methodology was studied. The developed technique is applied to the analysis of various objects, the results obtained are processed by the method of mathematical statistics.

#### REFERENCES

1. Kogan V.Yu., Petukhova N.E. Cobalt. United Nations Environment Program. Moscow, 1986.
2. Perelman F.M., Zvorykin A.Ya. Cobalt and nickel. Moscow, 1975.
3. Pyatnitsky I.V. Analytical chemistry of elements. Cobalt. Moscow, 1965.
4. Kelina S.Yu. Hydroxyaminoazo compound as photometric reagents for cobalt. Jour. Analyte. Chemistry. 1991, T.46, No. 5, p. 858-862.
5. Golivand M.V., Mozaffari Yu., Sobhani Sh., Gazemi J. Simultaneous spectrophotometric determination of trace amounts of cobalt, nickel and copper after their concentration in the form of 2-aminocyclopentene-1-dithiocarbonylate complexes on microcrystalline

- naphthalene using the partial least squares. *Jour. analyte. chemistry.* 2008, V.63, No. 3, pp. 258-264.
6. Immiyarova G.R., Shcherbinina N.I., Sedykh E.M., Myasoedova G.V., Wolfson E.K. Sorption concentration of copper, lead, cobalt, nickel and cadmium from sea water and their electrothermal atomic-absorption determinations in the sorbent suspension. *Jour. analyte. chemistry.* 1988, V.43, No. 11, pp. 1981-1983.
  7. Ivanov V.M., Kuznetsova O.V. Separate determination of 4- (2-tialylazo) -resorcinates of nickel, zinc and cobalt in the sorbent phase by the method of light metry. *Jour. analyte. chemistry.* 2000, V.55, No. 9, pp. 998-103.
  8. Malik K.A., Rao D.L. Spectrophotometric determination of Co (II), Ni (II), Cu (II), Cd (II), Pd (II), Ru (II), Mo (VI) after their isoamyloxanthogenate extraction in molten naphthalene. *Jour. analyte. chemistry.* 2000, V.55, No. 8, pp. 830-833.
  9. Ignatova S.N., Bolynsky A.B. Determinations of cadmium, cobalt, manganese, copper, nickel and chromium in concentrated solutions of calcium chloride by electrothermal atomic absorption spectrometry. *Jour. analyte. chemistry.* 2001, V.56, No. 11, p. 1158-1162.
  10. Sarakoglu S., Soylak M., Elsie L. Preliminary concentration and separation of iron, cobalt, lead, cadmium and chromium on the Amborsorb 563 sorbent before determination by a flame atomic absorption method. . *Jour. analyte. chemistry.* 2003, V.58, No. 12, pp. 1259-1263.
  11. Ivanov V.M., Figurovskaya V.N., Ershova N.I., Mamedova A.M., Chin Thi My Tuyu. Optical and colorimetric characteristics of cobalt 1-nitroso2-naphthol-3,6-disulfonates. . *Jour. analyte. chemistry.* 2007, T.62, No. 4, pp. 364-368.
  12. Ivanov V.M., Mamedova A.M., Figurovskaya V.N., Ershova N.I., Barbalat Yu.A., Chin Thi My Tuyet. *Jour. analyte. chemistry.* 2006, V.61, No. 6, pp. 620-623.
  13. Kuliyevev 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* 2016, V.6, No. 4, pp. 95-103.
  14. 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, No. 7, pp. 17-25.
  15. Korostelev P.P. Preparation of solutions for chemical analysis works. M.: Publishing house of Academy of Sciences of the USSR. 1964.
  16. Kuliev A. M., Aliev S. R., Mamedov F. N., Movsumzade M. Synthesis of 2-aminomethyl - 5-hydroxy alkyl phenols, thiols and their cleavage, *Zhurnal organicheskoi khimii.*1976. 12. P. 426.
  17. Bulatov M.I., Kalinkin I.P., *Practicheskoe rukovodstvo po photocolorimetriceskim i spectrophotometriceskim metodam analiza,* Leningrad, 1976.
  18. Pyatnitsky I.V. *Analytical chemistry.* M., 1990.
  19. Nazarenko V. A., Biryuk E. A. A study of the chemistry of reactions of multivalent element ions with organic reagents. *Zh. Anal. Khim.,* 1967. V.22 № 13, pp.57-64.
  20. Bellami, L. *The infra-red spectra of complex molecules.* Moscov: Mir, 1991. P. 592.
  21. Akhmedly M. K., Kly'gin A. E., Ivanova L. I., and Bashirov E. A. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. *Zhurnal Neorganicheskoi Khimii,* 1974. V.19.№8. pp. 2007-2012.

22. 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*, 48, 6, 2013, 623-630.
23. Marczenko Z., Baltsejak, M. K. Spectrophotometrically in the UV and visible regions in inorganic analysis. *Binom*. 2007. P. 711 p.