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# Liquid-liquid extraction of ion-association complexes of cobalt(II)- o-hydroxythiophenols with 2-(N,N-dimethylaminomethyl)-4-bromophenol

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ABSTRACT

The complex formation and liquid–liquid extraction of Co(II) were systematically investigated in aqueous–chloroform systems using 2-hydroxy-5-thiophenol derivatives and a hydrophobic amine. Co(II) was found to form stable mixed-ligand complexes with 2-hydroxy-5-aminothiophenol or 2-hydroxy-5-nitrothiophenol in the presence of 2-(N,N-dimethylaminomethyl)-4-bromophenol, which were efficiently extracted into chloroform. The optimal pH ranges were 4.8–6.2 for the Co(II)–HATP–AP system and 3.6–4.9 for the Co(II)–HNTP–AP system. Single-step extraction achieved cobalt recoveries of 97.5% and 98.6%, with distribution coefficients of approximately 156 and 282, respectively. The molar absorption coefficients were on the order of (4.12–4.26) × $10^4$. Beer's law was obeyed over the range 0.20–22 μg $mL^{-1}$ Co(II), with detection limits of 15–16 ng $mL^{-1}$. Both complexes had a stoichiometry of 1:2:2 and a monomeric structure in chloroform. The method showed high selectivity and was successfully applied to real sample analysis with accurate and reproducible results.

## 1. Introduction

Cobalt is a transition element of considerable industrial and biological importance, and a wide variety of organic reagents has been developed for its photometric determination [1–8]. Owing to its rich coordination chemistry and sensitivity to ligand structure and experimental conditions, cobalt occupies a special position in analytical chemistry.

Despite the availability of numerous extraction-spectrophotometric procedures for cobalt determination, many of them suffer from one or more disadvantages, including narrow pH working ranges, relatively low extraction efficiency, insufficient selectivity, or the use of less stable chromogenic systems. Therefore, the development of new ion-association reagents capable of forming highly stable and intensely colored extractable complexes remains an important task in analytical chemistry.

In the present study, the chemistry of cobalt is considered strictly in its divalent state. Any references to cobalt(III) complexes are limited to general background information and are not used in the interpretation of experimental data. The novelty of this work is associated not with the use of o-hydroxythiophenols per se, but with the introduction of 2-(N,N-dimethylaminomethyl)-4-bromophenol as a new hydrophobic ion-association reagent for Co(II), as well as with a systematic comparison of the effect of electron-donating ($–NH_2$) and electron-withdrawing ($–NO_2$) substituents on the extraction behavior, stability, and spectral properties of the resulting complexes. Organic compounds containing S, N, and O donor atoms are known to exhibit high biological activity,[1] and related compounds have found wide application in materials science, coordination chemistry, medicine, and pharmaceuticals [1,9–19]. At present, the most widely used methods for the spectrophotometric determination of cobalt in solution involve organic complexing reagents, including nitroso oxo compounds (1-nitroso-2-naphthol, nitroso-R-salt), azo compounds (4-(2-pyridylazo)resorcinol, 1-(2-pyridylazo)-2-naphthol), oximes (dimethylglyoxime,

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sodium diethyldithiocarbamate), and sulfur-containing compounds such as rubeanic acid derivatives and ethyl xanthate [1]. Halogenated azomercaptophenols [1-(5-chloro-2-pyridylazo)-2-hydroxy-4-mercaptophenol and 1-(5-bromo-2-pyridylazo)-2-hydroxy-4-mercaptophenol] [3], 2-hydroxy-5-halothiophenols [4], and 2,6-dithiol-4-alkylphenols [11] have also been reported as effective reagents for cobalt determination. Magnetic solid-phase extraction combined with high-resolution detection techniques further offers enhanced preconcentration and selectivity for trace metals in complex matrices [20].

Among these reagents, compounds belonging to the o-nitrosophenol group and structurally related oxime-containing ligands exhibit particularly high selectivity toward cobalt.[1] Considerable progress in extractive–photometric analysis has been achieved through investigations of complex formation and liquid–liquid extraction in systems comprising Co(II), 4-(2-pyridylazo)resorcinol (PAR), tetrazolium salts such as 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) or 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT), water, and chloroform [14,15]. Similar studies have been reported for the Co(II)–4-(2-thiazolylazo)resorcinol (TAR)–TTC–water–chloroform system [15], as well as for systems containing Co(II), PAR, and 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole [14,15].

In addition, a solid-phase extraction method for the trace determination of cobalt using Duolite XAD-761 resin in combination with flame atomic absorption spectrometry has been proposed [8]. In the Co(II)–PAR–nitron (Nt)–water–chloroform system, the influence of experimental parameters such as pH, shaking time, and the concentrations of PAR and Nt was systematically examined, resulting in the establishment of optimal conditions for cobalt extraction in the form of the ion-association complex $(NtH^{+})[Co^{3+}(PAR)_2]$ [14,15,17].

It is well known that cobalt oxyphenolate [20] and dithiophenolate [16] complexes are practically insoluble in chloroform, which significantly limits their applicability in extractive systems. In contrast, mixed-ligand complexes formed with hydrophobic amines and aminophenols exhibit good solubility in a wide range of organic solvents. In this context, o-hydroxythiophenols (HTPDs) are especially promising reagents. These compounds contain one hydroxyl and one sulfhydryl group and represent sulfur-containing analogues of mononuclear polyphenols in which two oxygen atoms are replaced by sulfur atoms.

Cobalt is distinguished by its flexible coordination chemistry arising from the interconversion between the Co(II) and Co(III) oxidation states. Such redox transformations substantially alter the electronic structure and ligand-field environment of the metal ion, thereby affecting its affinity toward specific donor atoms. In its divalent state, Co(II) typically exhibits a high-spin $d^7$ electronic configuration and forms relatively labile complexes with oxygen- and sulfur-donor ligands, adopting octahedral or tetrahedral geometries depending on ligand-field strength and solvent polarity. In contrast, Co(III) usually exists as a low-spin $d^6$ species and forms kinetically inert octahedral complexes, particularly with nitrogen-donor ligands [19]. These differences largely account for the diversity of cobalt coordination compounds and their relevance in analytical chemistry.

One of the most valuable analytical features of cobalt is the resistance of its Co(III) complexes to acid-induced decomposition. When complexes are formed under weakly acidic conditions and the acidity is subsequently increased to 2–5 M, most transition-metal complexes dissociate readily, whereas cobalt chelates remain intact due to slow ligand-exchange kinetics. This inertness is widely exploited for selective separation, controlled masking, and accurate determination of cobalt in complex matrices.

Numerous spectrophotometric and extractive studies involving heterocyclic diamines, salicylic acid derivatives, azoxy compounds, and π-conjugated chelating agents have provided valuable insight into cobalt coordination behavior [21,22]. Within this broad class of ligands, derivatives of o-hydroxythiophenols ($H_2L$, L) are of particular interest because they combine hard (oxygen) and soft (sulfur) donor atoms, enabling mixed O, S-chelation consistent with the intermediate acid–base character of cobalt according to HSAB principles. Electron-donating or electron-withdrawing substituents, such as amino or nitro groups, further modulate ligand acidity and electron density, thereby influencing the stability, geometry, and spectral properties of the resulting metal complexes [23,24].

Cobalt readily forms intensely colored anionic chelates with $H_2L$ ligands, including species such as $[Co^{2+}(L)_2]^{2-}$ and $[Co^{3+}(L)_2]^{-}$. These anionic complexes can undergo ion-association reactions with hydrophobic ammonium-type cations, leading to the formation of ternary species that are highly soluble in low-polarity organic solvents. Such systems are characterized by high molar absorptivities, enhanced extraction efficiencies, and improved selectivity, making them suitable for liquid–liquid extraction combined with spectrophotometric detection [21,22]. The extraction mechanism generally involves the formation of an anionic chelate in a mildly acidic medium followed by its association with a protonated amine ($AmH^{+}$), yielding a neutral, readily extractable ion pair.

In the present study, ternary ion-association complexes formed in systems containing Co(II), two thiophenol-based ligands—2-hydroxy-5-aminothiophenol (HATP, $L_1$) and 2-hydroxy-5-nitrothiophenol (HNTP, $L_2$)—and a hydrophobic amine reagent, 2-(N,N-dimethylaminomethyl)-4-bromophenol

(AP), are investigated. Particular emphasis is placed on elucidating the effects of substituent nature, donor-site protonation, steric factors, and solvent polarity on complex formation, extraction behavior, and spectral characteristics. The ultimate objective of this work is to establish optimal chemical conditions for the formation of these ternary complexes and to evaluate their applicability for the sensitive and selective determination of cobalt using liquid–liquid extraction combined with spectrophotometric analysis.

The novelty of the present work consists in the first use of 2-(N,N-dimethylaminomethyl)-4-bromophenol as a hydrophobic ion-association reagent for cobalt(II), systematic comparison of amino- and nitro-substituted thiophenols, determination of extraction and equilibrium constants, and application of the developed extraction-spectrophotometric system to cobalt determination in plant samples.

## 2. Materials and Methods

### 2.1. Reagents and solutions

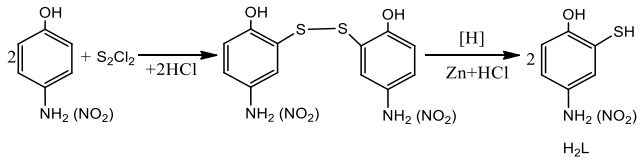
Cobalt(II) nitrate $Co(NO_3)_2 \cdot H_2O$ (≥99%, Merck, Germany) was used to prepare standard Co(II) solutions. $CHCl_3$ (≥99.8%, Sigma-Aldrich, USA) served as an extractant. HCl (37%, Sigma-Aldrich, USA) and $HNO_3$ (≥65%, Merck, Germany) were used for pH adjustment and sample preparation. $KNO_3$ (≥99%, Sigma-Aldrich, USA) was used to maintain the ionic strength of the solutions. The following solvents were used in the ligand synthesis: $S_2Cl_2$, (≥98%, Sigma-Aldrich, USA), formaldehyde (37%, Merck, Germany), dimethylamine (≥99%, Sigma-Aldrich, USA), and 2-hydroxy-5-amine(nitro)thiophenols (≥98%, Sigma-Aldrich, USA). $Na_2SO_4$ (≥99%, Merck, Germany) was used to dry the organic phase, and silica gel (L 100/160, Merck, Germany) was used for chromatographic purification.

$CH_3Cl$ was used as an extractant and 0.01M solutions of $L_{1,2}$ and AP in chloroform were applied. The ionic strength of the solutions (μ = 0.1) was maintained constant by adding $KNO_3$. To create the required pH of the solutions, 1 M HCl was used. A stock cobalt(II) solution (1.0 mg $mL^{-1}$) was prepared by dissolving an accurately weighed amount of analytical-grade cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Merck) in distilled water. The exact cobalt concentration was verified gravimetrically using 1-nitroso-2-naphthol according to a recommended analytical procedure. Fresh working standard solutions were prepared daily by appropriate dilution of the stock solution with distilled water and stored in polyethylene bottles until use.

**Instrumentation.** The optical density of the extract was measured on a KPK-2 and SP-26 (LOMO, Russia) with a cuvette thickness of 0.5 and 1.0 cm, respectively. The pH of the solution was measured on an I-120.2 (Belarus) device. IR spectra of the compounds in thin films were recorded on a Specord 75 IR spectrometer. The $^1H$ and $^{13}C$ NMR spectra of the substances in $CDCl_3$ were recorded on a Bruker SP-300 instrument [300.13 for ($^1H$), 75 MHz for ($^{13}C$)], with HMDS used as the internal standard. Thermogravimetric analysis of the mixture under consideration was performed on a STA 449C Jupiter synchronous thermal analysis device (Netzsch, Germany) combined with a QMS 403C Aeolos mass spectrometer. Samples of the prepared mixtures were placed in a corundum crucible and heated at a rate of 10 deg $min^{-1}$ in an argon flow (40 mL $min^{-1}$). Intermediate products of thermal decomposition for studying their phase and chemical composition were obtained in a flow-through quartz reactor inserted into a tubular furnace in an argon flow at a rate of 40 mL/min at temperatures corresponding to the endo- and exo-effects on the thermograms. Elemental analysis for C, H, O, Br and N atoms was performed on a Carlo Erba 1106 elemental analyzer. Chromatographic separation was carried out on a glass column ($l$ = 20 cm, $d$ = 2 cm) filled with silica gel of grade L 100/160. The eluent was a hexane-ethyl acetate mixture in a 9 : 1 ratio.

### 2.2. Synthesis and characterization of HATP and HNTP

HATP and HNTP were synthesized according to the procedure [25]. The starting 5-amino- or 5-nitrophenol reacted with sulfur dichloride ($S_2Cl_2$) at a molar ratio of (n+2):(n+1) (n ≥ 1) under stirring. During the reaction, polysulfide intermediates were formed. The resulting polysulfides were subjected to reduction in the Zn/HCl system with cleavage of S–S bonds. After completion of the reaction, the mixture was filtered, the product was washed with water until neutral reaction and dried. The solvent was removed under reduced pressure. As a result, the target 2-hydroxy-5-amine(nitro)thiophenols containing $–NH_2$ or $–NO_2$ substituents were obtained. The synthesized compounds were identified using IR and NMR spectroscopy. The reaction schemes for the synthesis of $H_2L$ are given below (Scheme 1).




**Scheme 1.** The synthesis of $H_2L$

**2-Hydroxy-5-aminothiophenol ($L_1$).** Yield 0.84 g (61.9%). IR spectrum, ν, $cm^{-1}$: 3400, 1620, 850. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: δ 4.8–5.0 (s, 1H, –OH), δ 3.5 (s, 2H, $–NH_2$), δ 6.5–7.2 (m, 3H, Ar H). $^{13}C$ NMR spectrum ($CDCl_3$), δC, ppm: 156.9 (C–OH), 131.5 (C–S), 118.7 (Ar CH), 126.3 (Ar CH), 146.8 (Ar $NH_2$), 123.6 (Ar CH). Found, (%): C 52.12; H 5.05; N 11.30; S 18.30. ($C_6H_7NOS$). Calculated, (%): C 52.16; H 5.08; N 11.25;

S 18.36. $pK_1$ (SH)= 7.1; $pK_2$ (OH)= 10.6

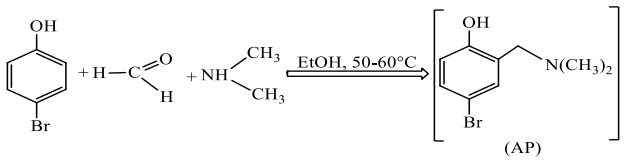
**2-Hydroxy-5-nitrothiophenol ($L_2$).** Yield 0.79 g (59.7%). IR spectrum, ν, $cm^{-1}$: 3450,1520, 1620, 770. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: δ 4.9 (s, 1H, –OH), δ 7.0 –8.2 (m, 3H, Ar H). $^{13}C$ NMR spectrum ($CDCl_3$), δC, ppm: 158.7 (C–OH), 132.9 (C–S), 124.7 (Ar CH), 128.5 (Ar CH), 145.9 (Ar C-$NO_2$), 125.7 (Ar CH). Found, (%): C 39.10; H 2.68; N 8.18; S 14.40. ($C_6H_5N_1O_3S$). C 39.13; H 2.70; N 8.21; S 14.42. $pK_1$ (SH)= 5.2; $pK_2$ (OH)= 7.5

### 2.3. Synthesis and characterization of AP

The target compound was synthesized according to the classical Mannich reaction. *p*-Bromophenol was reacted with formaldehyde and dimethylamine in ethanol as solvent. In a typical procedure, *p*-bromophenol was dissolved in ethanol, followed by the addition of an equimolar amount of dimethylamine. Aqueous formaldehyde was then added dropwise under stirring. The reaction mixture was heated at 50–60 °C for 3–4 h.

After completion of the reaction, the mixture was cooled to room temperature and the solvent was partially evaporated. The residue was diluted with water, and the product was extracted with an organic solvent (chloroform or dichloromethane). The combined organic layers were dried over anhydrous sodium sulfate. After removal of the solvent, the crude product was purified by recrystallization to afford 2-(N,N-dimethylaminomethyl)-4-bromophenol.

The reaction proceeds with ortho-orientation relative to the phenolic hydroxyl group, resulting in selective aminomethylation at the 2-position of the aromatic ring. The synthesized compounds were identified using IR and NMR spectroscopy. The reaction schemes for the synthesis of AP are given below (Scheme 2).




**Scheme 2.** The synthesis of AP

**2-(N,N-dimethylaminomethyl)-4-bromophenol.** Yield 0.92 g (65.8 %). IR spectrum, ν, $cm^{-1}$: 820, 1240, 1398, 1595, 2870, 3390. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: δ 2.26 (s, 6H, $N(CH_3)_2$), 3.68 (s, 2H, $CH_2N$), 6.78 (d, $J$ = 2.2 Hz, 1H, Ar–H), 6.98 (dd, $J$ = 8.4, 2.2 Hz, 1H, Ar–H), 7.28 (d, $J$ = 8.4 Hz, 1H, Ar–H), 9.7 (br s, 1H, OH). $^{13}C$ NMR spectrum ($CDCl_3$), δC, ppm: δ 45.9, 61.5, 114.8, 117.4, 121.2, 128.9, 135.6, 153.8.

### 2.4. General procedure for the synthesis of complexes Co-L-AP

Cobalt(II) nitrate $Co(NO_3)_2 \cdot H_2O$ (0.30 g, 1.03 mmol) was dissolved in 30 mL of distilled water. Separately, an ethanolic solution containing $L_1$ (HATP) or $L_2$ (HNTP) (1.25 g, 8.86 mmol for $L_1$ or 7.30 mmol for $L_2$) and AP (1.40 g, 6.08 mmol) was prepared in 30 mL of ethanol.

The ethanolic ligand solution was added dropwise to the aqueous cobalt(II) nitrate solution under constant stirring. The reaction mixture was heated at 70–80 °C and stirred for 10 min, then a reflux condenser was attached and stirring was continued at the same temperature for an additional 30 min. The reaction was carried out in air at pH ≈ 4**.** After cooling to room temperature, the resulting precipitate was filtered, washed with cold ethanol and distilled water, and left to recrystallize in ethanol. After two days, crystals were obtained, which fully formed within 24 h. The complexes were isolated as red–violet crystals with a yield of 62.4 %. $L^1$, $L^2$ and AP were used in significant molar excess relative to Co(II) (Co:L:AP ≈ 1:7–9:6**)** to ensure complete complexation and stabilization of the formed complexes.

**Co-HATP-AP:** Found, %: C 44.74; H 5.26; N 6.96; O 7.95; S 7.96; Br 19.85; Co 7.32. $C_{30}H_{42}N_4O_6S_2Br_2Co$. Calculated, %: C 44.96; H 5.71; N 6.39; O 7.34; S 7.68; Br 19.63; Co 7.87. VB spectrum ($CHCl_3$), $\lambda_{max}$, nm: 540.

**Co-HNTP-AP:** Found, %: C 42.89; H 4.57; N 6.31; O 11.88; S 8.07; Br 18.68; Co 6.81. $C_{30}H_{40}N_4O_8S_2Br_2Co$. Calculated, %: C 43.23; H 4.60; N 6.72; O 11.52; S 7.69; Br 19.17; Co 7.07. VB spectrum ($CHCl_3$), $\lambda_{max}$, nm: 562.

### 2.5. Procedure for the determination of cobalt(II)

Aliquots of the stock cobalt(II) solution (0.1–1.0 mL, at 0.1 mL intervals), 2.2 mL of 0.01 M $H_2L$ solution and 2.5 mL of 0.01 M AP solution were transferred into calibrated glass-stoppered test tubes. The pH was adjusted with 1 M HCl to the optimum range, namely pH 4.8–6.2 for the Co(II)–HATP–AP system and pH 3.6–4.9 for the Co(II)–HNTP–AP system. The volume of the organic phase was adjusted to 5.0 mL with chloroform, whereas the volume of the aqueous phase was adjusted to 20.0 mL with distilled water, giving a total phase volume of 25.0 mL. The solutions were shaken under the optimum extraction conditions and then allowed to stand for 15 min to ensure complete phase separation. The extracted chloroform phase exhibited an intense red-violet color, whereas the initial extractant was colorless, indicating the formation of the Co(II) mixed-ligand complex. The organic phase was carefully separated, and the absorbance of the chloroform extracts was measured at the respective absorption maxima ($\lambda_{max}$ = 540 nm for complex Co(II)–HATP–AP (**1**) and 554 nm for complex Co(II)–HNTP–AP (**2**)) using a KFK-2 photocolorimeter equipped with a 0.5 cm optical cell at room temperature. All measurements were performed in triplicate, and the results are reported as the mean values of three independent determinations.

### 2.6. Determination of cobalt in plant samples

For the quantitative analysis of cobalt, representative

samples of wheat (*Triticum aestivum* L.), oat (*Avena sativa* L.) and pea (*Pisum sativum* L.) grains were used as plant materials. A representative portion of each sample (2.0 g, weighed to an accuracy of ±0.01 g) was placed in a suitable porcelain crucible.To facilitate preliminary extraction of soluble components, 5 mL of 96% ethanol is added, and the sample is covered with a watch glass and allowed to stand at ambient conditions for 24 h. After the ethanol treatment, the plant material is dried and subjected to controlled charring on an electric hotplate. This is performed carefully to avoid ignition, continuing until smoke emission ceases and a uniform char is obtained. The crucible is then transferred to a cold muffle furnace, which is gradually heated at a rate of 50°C per 30 min until a temperature of 450°C is reached. The mineralization process is maintained for 10–15 h, or until the plant matter is converted into a homogeneous gray ash. The cooled ash (20–25°C) is treated incrementally with concentrated nitric acid ($HNO_3$, 1:1) by adding small aliquots dropwise. The crucible is returned to the furnace, and the temperature is raised to 350°C for 30–35 min. This acid treatment and heating cycle is repeated several times until the ash becomes white or slightly colored, indicating the absence of any carbonized residues. Finally, an aliquot of the prepared ash solution (5 mL) is used for the determination of Co(II). Quantification is achieved by ligand-assisted liquid–liquid extraction followed by photometric measurement under optimal experimental conditions. This procedure ensures high reproducibility and sensitivity, providing reliable data for cobalt content in plant samples.

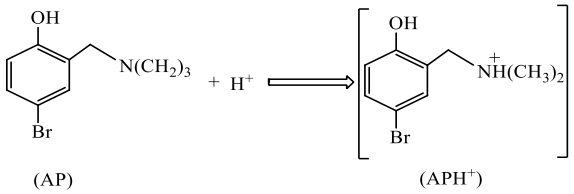
## 3. Results and Discussion

### 3.1. Determining the charge sign of complexes

This study examined the interaction of Co(II) ions with $H_2L$, resulting in the formation of colored complexes that are virtually insoluble in non-polar organic solvents. The charge sign of the resulting complexes was determined using ion electromigration and ion-exchange chromatography.

When using AB-17 anion exchange resin in a chloroform medium, absorption of the colored complex was observed: the chromatographic column acquired a violet-pink color, while no cobalt was detected in the filtrate, indicating the anionic nature of the complex. Similar results were obtained using EDE-10 P anion exchange resin, which completely retained the complex. Electromigration in a U-shaped tube ($R$ = 200-220 V, $I$ = 0.5–0.8 mA, 3 h) revealed the migration of violet-colored ions toward the positive electrode, further confirming the negative charge of the Co(II)–L complex.

The addition of hydrophobic amines facilitates the extraction of the anionic complex into the organic phase by forming a stable mixed-ligand complex (MLC). The amine used is aminephenol, which is protonated in an acidic medium and compensates for the charge of the anionic complex (Scheme 3). The resulting system is characterized by increased stability and intense color, making it promising for the selective and sensitive determination of Co(II) in aqueous media.




**Scheme 3.** The amine used is aminephenol

### 3.2. Selection of extractant, effect of holding time and ligand concentration

The efficiency of solvent extraction strongly depends on the polarity, dielectric constant, and solvating properties of the organic phase, which influence the distribution equilibrium:

$$MLC_{(aq)} \rightleftharpoons MLC_{(org)} \quad (1)$$

To systematically study the possibility of extracting metal-ligand compounds (MLCs), organic solvents of varying polarity and donor-acceptor capacities were investigated: $CHCl_3$, $C_2H_4Cl_2$, $CCl_4$, $C_6H_6$, $C_6H_5$-$CH_3$, $C_6H_5Cl$, $i$-$C_4H_9OH$, $i$-$C_5H_{11}OH$, $n$-$C_4H_9OH$. This selection of solvents allowed us to evaluate the influence of their physicochemical properties – specifically, permittivity, solvation parameters, and dissolving capacity – on the shift in extraction equilibrium.

The extraction capacity of each solvent was determined based on the distribution coefficient ($D$) and the degree of recovery ($R$, %). The distribution coefficient was calculated using the standard expression:

$$D = \frac{c(\mathrm{Co})_{\mathrm{org}}}{c(\mathrm{Co})_{\mathrm{aq}}} \quad (2)$$

$$R = \frac{D}{D + \frac{V_{\mathrm{aq}}}{V_{\mathrm{org}}}} \times 100 \quad (3)$$

The obtained data showed that $CHCl_3$, $C_2H_4Cl_2$, $CCl_4$ were the best extractants, with the highest distribution coefficients observed. This indicates favorable solvation conditions and a high degree of compatibility between the organic phase and the resulting MLC. The superior extraction performance of chloroform can also be attributed to its relatively low dielectric constant (ε = 4.81). The low polarity of chloroform facilitates the transfer of neutral hydrophobic mixed-ligand complexes from the aqueous phase into the organic phase, thereby shifting the extraction equilibrium toward the organic phase. As a result, high distribution coefficients and extraction recoveries were achieved for both Co(II)–HATP–AP and Co(II)–HNTP–AP systems. With a single extraction using chloroform, the cobalt recovery was 97.5% for the Co(II)–HATP–AP system and 98.6% for

the Co(II)–HNTP–AP system, corresponding to distribution coefficients of approximately $D$ = 156 and $D$ = 282, respectively. Thus, the system is characterized by a stable equilibrium shift toward the organic phase. The cobalt concentration in the organic phase was determined photometrically using the phenanthroline method [1] after its reextraction into the aqueous phase. The amount of cobalt in the initial aqueous solution ($c_0$) was calculated using the material balance:

$$c_0 = c_{aq} + c_{org} \quad (4)$$

Cobalt-based MLCs with L and AP are stable in aqueous and organic solvents and do not decompose for three days or more than a month after extraction. Maximum optical density is reached within 5-8 minutes.

For the formation and extraction of MLCs, a 10-15-fold excess of complexing agents is required. As the L and AP concentrations increase, the spectral pattern does not change, but the light absorption intensity increases. Optimal conditions for the formation and extraction of these compounds are L concentrations of (1.0-1.12) × $10^{-3}$ mol $L^{-1}$ and AP concentrations of (0.8-1.0) × $10^{-3}$ mol $L^{-1}$.

### 3.3. Effect of pH of the aqueous phase

The study of the dependence of complexation on pH shows that the extraction efficiency is strongly dependent on the pH of the solution.

The change in pH significantly affects the complexation of Co(II) with L and AP. At low pH values (pH < 2.3), complex formation is not observed since $H_2L$ is not ionized under these conditions and therefore cannot participate in coordination with Co(II). The optimal acidity range for the Co(II)–HATP–AP (1) and Co(II)–HNTP–AP (2) complexes is $pH_{opt}$ 4.8–6.2 ($pH_{form}$ 3.5–7.9) and $pH_{opt}$ 3.6–4.9 ($pH_{form}$ 2.3–6.1), respectively (Figure 1, Table 1).

In these pH intervals, effective ionization of L and favorable coordination conditions lead to the formation of stable MLCs. At solution pH > 8.0, extraction of the complexes is not observed. This is attributed both to the absence of protonation of AP, which reduces its ability to participate in complex formation, and to the hydrolysis of Co(II), resulting in the formation of hydrolyzed cobalt species:

$$Co^{2+} + nH_2O \rightleftharpoons Co(OH)_n^{2-n} + nH^+, \; n = 1,2 \quad (5)$$

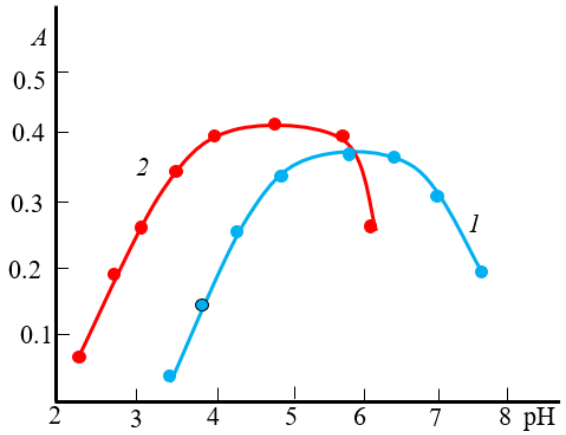



**Fig. 1.** Effect of aqueous phase pH on formation of complexes 1 (1) and 2 (2). ($c_{Co\,(II)} = 1{,}7 \times 10^{-5}\,M$; $c_{H_2L} = (1{,}0 - 1{,}12) \times 10^{-3} M$. $c_{AP} = (0{,}8 - 1{,}0) \times 10^{-3} M$. $\lambda = 540\,nm$. $KFK - 2$. $\ell = 0{,}5\,cm$)

**Table 1.** Analytical characteristics of $[CoL_2](APH)_2$ complexes

| **Parameter** | | **Co(II)–HATP–AP** | **Co(II)–HNTP–AP** |
|---|---|---|---|
| pH | Formation | 3.5-7.9 | 2.3-6.1 |
| | Optimal | 4.8-6.2 | 3.6-4.9 |
| λ, nm | | 540 | 554 |
| ε·$10^{-4}$ | | 4.12 | 4.26 |
| log $K_{eq}$ | | 10.93 | 9.71 |
| log $K_{ex}$ | | 12.49 | 11.68 |
| log β | | 10.30 | 11.71 |
| Beer's law execution interval, μg $mL^{-1}$ | | 0.1-20 | 0.5-22 |
| $y=ax+b$ | | 0.227$x$ + 0.025 | 0.236$x$ + 0.041 |
| LOD (ng $mL^{-1}$) | | 63 | 69 |
| LOQ (ng $mL^{-1}$) | | 191 | 50 |
| Distribution coefficient (D) | | 156 | 208 |
| $R$, % | | 97.5 | 98.6 |

These processes lead to the destabilization and decomposition of the complexes at high pH values. The presence of a single maximum in optical density within the specified pH range confirms the assumption of the formation of only one predominant complex compound.

Absorption spectra and analytical characteristics

The electronic absorption spectra of Co(II) complexes formed with ligands L and AP exhibit well-defined absorption maxima, indicating effective coordination and charge-transfer interactions. Complexes 1 and 2 show maximum absorbance at $\lambda_{max}$ = 540 nm and 554 nm, respectively (Figure 2). In contrast, the free ligands $L_1$ (HATP) and $L_2$ (HNTP) display absorption maxima at 287 nm and 296 nm, respectively. The bathochromic shift ($\Delta\lambda$), reflecting changes in the electronic structure upon complex formation, was calculated according to: $\Delta\lambda = \lambda_{Co(II)\text{-}L} - \lambda_L$ and amounts to 253 nm for complex 1 and 254 nm for complex 2, confirming strong metal–ligand interactions and the formation of stable coordination compounds. Each experiment was performed in six independent replicates. Calibration curves were constructed using eight calibration solutions. Regression equations were obtained by least-squares analysis. Correlation coefficients exceeded 0.999. Confidence intervals were calculated at the 95% confidence level using Student's t-distribution. The molar absorption coefficients were determined using the Beer–Lambert law: ε=A/lC, where *A*- is the absorbance, *ε* is the molar absorptivity, *l* -is the optical path length (1 cm), and *C*- is the molar concentration of Co(II). The 95% confidence interval($P$ = 0.95) for the molar absorption coefficient was evaluated using the Student's *t*-factor. The confidence interval for the molar absorption coefficient was calculated: $\Delta\varepsilon = (t_{0.95}\cdot S)/\sqrt{n} = 2.571\cdot(0.06\cdot10^4)/\sqrt{6} = 0.063\cdot10^4$ and the confidence interval: $\varepsilon_{540} = (4.12\pm0.06)\times10^4$ (for 1); $\Delta\varepsilon=(t_{0.95}\cdot S)/\sqrt{n}= 2.571\cdot(0.08\cdot10^4)/\sqrt{6} = 0.084\cdot10^4$ and the confidence interval: and $\varepsilon_{554}=(4.26\pm0.08)\times10^4$ (for 2).

A linear dependence between absorbance and Co(II) concentration was observed over a wide concentration range (0.20–22.0 μg $mL^{-1}$), confirming compliance with the Beer–Lambert law. The calibration equations were obtained as $A = 0.227C + 0.025$ (system 1) and $A = 0.236C + 0.041$ (system 2), with correlation coefficients of $R^2$ =0.995 and $R^2$ = 0.996, respectively. The high molar absorptivities (Table 1), together with the calculated Sandell sensitivities of 0.00143 μg $cm^{-2}$ (1) and 0.00138 μg $cm^{-2}$ (**2**), demonstrate the high sensitivity of the proposed spectrophotometric systems. The limits of detection (LOD) and limits of quantification (LOQ) were calculated according to the IUPAC recommendations using the expressions LOD = 3.3σ/S and LOQ = 10σ/S, where σ is the standard deviation of the blank response and S is the slope of the calibration curve. The calculated values were 63 ng $mL^{-1}$ and 191 ng $mL^{-1}$ for system 1, and 69 ng $mL^{-1}$ and 208 ng $mL^{-1}$ for system 2, respectively. Each experimental point represents the mean value of repeated measurements, and the precision of the method was evaluated by the relative standard deviation (RSD), which did not exceed 0.2%.

### 3.4. Composition of the complexes

The stoichiometry of the studied complexes was established using the equilibrium shift and relative yield methods.[26] The composition of the complexes per 1 mol of cobalt is 2 mol of $L_{1,2}$ and AP (Figure 3).

To clarify the chemistry of the complexation process, information on the ionic forms of Co(II), as well as the number of protons displaced during the formation of one molecule of the complex, is necessary. For this purpose, a method based on determining the degree of complexation of Co(II) ions with $L_{1,2}$ and AP depending on the pH of the solution was used.

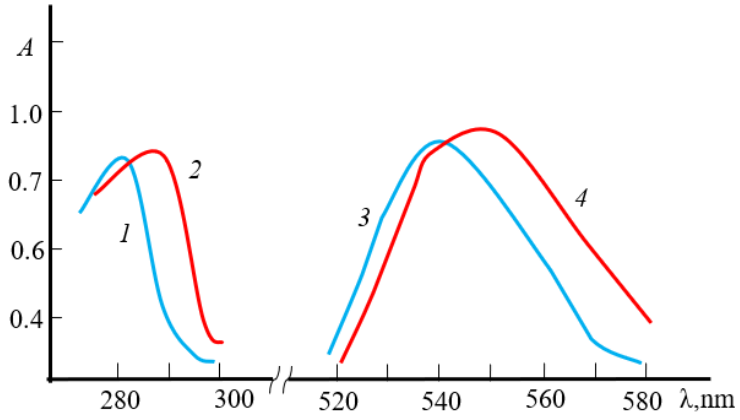



**Fig. 2.** Electronic spectra of the ligands and Co(II)-L-AP complexes in $CHCl_3$: (1) $L^1$, (2) $L^2$, (3) 1, (4) 2. ($c_{Co\ (II)}$ = $1{,}7 \times 10^{-5}\ M.\ c_{H_2L} = (1.0 - 1.12) \times 10^{-3} M\ .\ c_{AP} = (0{,}8 - 1{,}0) \times 10^{-3} M\ C.SF - 26{,}$)

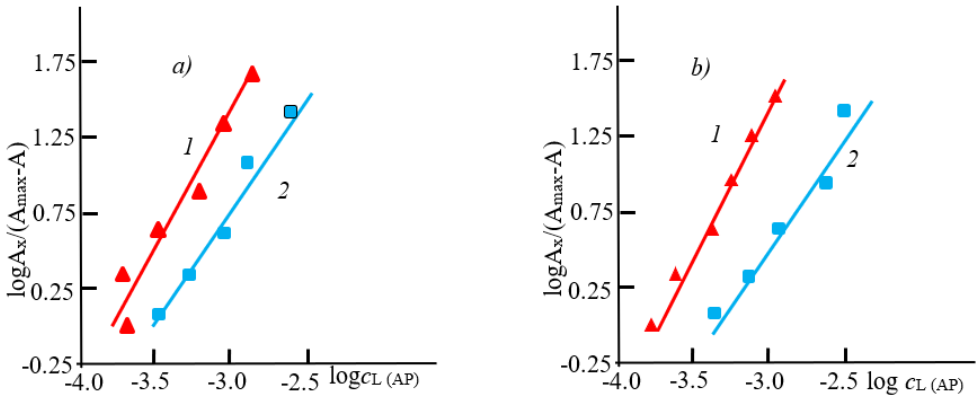



**Fig. 3.** Determination of the molar ratios of components in complex systems by the equilibrium shift method: *a*) Co(II)–HATP–AP (*1*– HATP, *2*–AP); *b*) Co(II)–HNTP–AP(*1*–HNTP, *2*–AP). $c_{Co}$ = 1.7×10$^{-5}$ M, $c_{H2L}$ = (1.0-1.12) × 10$^{-3}$ M, $c_{AP}$ = (0.8-1.0) × 10$^{-3}$ M, λ=540 nm, KFK-2, ℓ=0.5 cm.

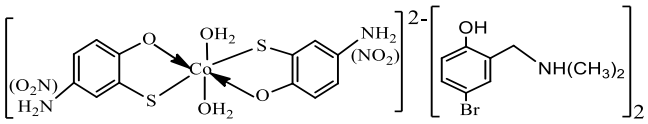
If we represent the graphical dependence of −log B on pH, assuming that two types of ions ($Co^{2+}$ and $CoOH^{+}$) can be present in the solution, then one of the graphs, corresponding to the truth, will be linear, and the slope of the line (qn) will be an integer. The obtained results showed that the complexing ion of cobalt is the divalent cation $Co^{2+}$. In this case, the number of protons displaced from one $H_2L$ molecule is equal to 1. $[Co(L)_2](APH)_2$ does not polymerize in chloroform (γ = 1.13–1.17).

A comparative analysis of the IR spectra of the Co(II)–HATP–AP and Co(II)–HNTP–AP complexes with respect to the corresponding free ligands reveals general patterns of complex formation and the specific effects of substituents. According to the hard-soft acid-base (HSAB) theory, the Co(II) ion is a borderline acid, which determines its ability to effectively interact with both hard donor oxygen atoms and softer donor sulfur and nitrogen centers. In the studied complexes, the thiophenol ligands HATP and HNTP, after deprotonation, act as S, O-donor bases of mixed nature, ensuring thermodynamically favorable binding to the cobalt center. Coordination via the sulfur atom (a soft base) is stabilized by the polarizability of the Co–S bond, while interaction with the phenolate oxygen (a hard base) is compensated by the boundary nature of Co(II), which together leads to the formation of a stable coordination node.

The HSAB concept also justifies the participation of a water molecule in the inner coordination sphere. Water is a typical hard donor, and its coordination to the boundary Co(II) ion is energetically permissible, especially under conditions of incomplete saturation of the coordination number with ligands. Thus, the presence of an aqua ligand facilitates the achievement of an optimal coordination number and additional stabilization of the complex.

Crystal chemical data for related cobalt(II) complexes with S,O-donor ligands suggest that distorted octahedral or square-pyramidal coordination geometries are the most probable structural models for the present complexes. However, since single-crystal X-ray diffraction data are not available, these structural assignments should be regarded as tentative and based on spectroscopic, thermogravimetric, magnetic susceptibility, cryoscopic, and crystal-chemical evidence. The magnetic susceptibility measurements demonstrated the paramagnetic behavior of the extracted complexes, confirming that cobalt remains in the +2 oxidation state. Therefore, the proposed coordination environment should be considered as the most probable structural model rather than an unequivocally established structure.

The composition of the complexes can be represented by the formula $[CoL_2](APH)_2$ (Scheme 4). Some analytical characteristics of $[CoL_2](APH)_2$ complexes are given in Table 1.




**Scheme 4.** The composition of the complexes

Thermogravimetric study of the complexes $C_{30}H_{42}N_4O_6S_2Br_2Co$ and $C_{30}H_{40}N_4O_8S_2Br_2Co$ showed that they are stable up to 170°C. Thermal decomposition of the complexes occurs in three stages. At 174-198°C water evaporates - the total mass loss is 4.5% ($\Delta m_{theor}$ = 4.3%), the mass of the solid residue is 95.5% ($\Delta m_{theor}$ = 95.7%) {for 2 4.1% ($\Delta m_{theor}$ = 4.0%), the mass of the solid residue is 95.9% ($\Delta m_{theor}$ = 96.0%)}, in the second stage at 340-450°C AP decomposes and endoeffects are recorded on the DSC curve, and signals of $H_2O$, $Br_2$, $N_2$ and $CO_2$ are recorded in the mass spectra. The mass loss is 55.3% ($\Delta m_{theor}$ = 55.2%), the mass of the solid residue is 44.72% ($\Delta m_{theor}$ = 44.81%) {for 2 51.3% ($\Delta m_{theor}$ = 51.6%), the mass of the solid residue is 48.66% ($\Delta m_{theor}$ = 48.44%)}. The third stage in the temperature range of 480–520°C decomposition of $H_2L$ is accompanied by endoeffects on the DSC curve. According to mass spectrometry data, signals of $H_2O$,

$Br_2$, $N_2$, $CO_2$ and $SO_2$ are detected in the gas phase in the specified temperature range. The mass loss here is $\Delta m_{exp}$ = 33.9% ($\Delta m_{theor}$ = 33.5%), the mass of the solid residue is 11.1% ($\Delta m_{theor}$ = 10.5%), {for 2 37.3% ($\Delta m_{theor}$ = 37.7%), the mass of the solid residue is 9.9% ($\Delta m_{theor}$ = 9.1%)}, which is in good agreement with the experimental data (Table 2). In both cases, the final product of thermolysis of the complex is CoO. The thermal stability of the complexes in the solid phase changes in the same sequence as their thermodynamic stability in solutions. More stable complexes are destroyed at higher temperatures:

$$C_{30}H_{42}N_4O_6S_2Br_2Co \xrightarrow{174-198} C_{30}H_{36}N_4O_4S_2Br_2Co \xrightarrow{340-450} C_{12}H_{12}N_2O_2S_2Co \xrightarrow{480-520} CoO$$

$$C_{30}H_{40}N_4O_8S_2Br_2Co \xrightarrow{174-198} C_{30}H_{38}N_4O_6S_2Br_2Co \xrightarrow{340-450} C_{12}H_8N_2O_2S_2Co \xrightarrow{480-520} CoO$$

### 3.5. Equilibrium, extraction and stability constants

The complexation reaction can be predicted as follows:

$$Co^{2+}_{(aq)} + 2H_2L_{(aq)} + 2APH^+_{(aq)} \Leftrightarrow \{[Co(HL)_2](APH)_2\}_{(org)} + 2H^+_{(aq)} \quad (6)$$

Equilibrium constant ($K_{eq}$) of the reaction

$$K_{eq} = \frac{\{[Co(HL)_2](APH)_2\}_{(org)} \cdot [H^+]^2_{(aq)}}{[Co]^{2+}_{(aq)} \cdot [H_2L]^2_{(aq)} \cdot [APH^+]^2_{(aq)}} \quad (7)$$

$$\frac{\{[Co(HL)_2](APH)_2\}_{(org)}}{[Co]^{2+}_{(aq)}} = \log \frac{A_x}{A_o - A_x} = D \quad (8)$$

$$K_{eq} = \frac{D \cdot [H^+]^2_{(aq)}}{[HL^-]^2_{(aq)} \cdot [APH^+]^2_{(aq)}} \quad (9)$$

where, $A_x$ – is the optical density for a given experiment; $A_o$ – is the optical density for complete binding of the nickel ion into a complex. Taking the logarithm of equation (9), we obtain

$$\log K_{eq} = \log D - 2pH - 2\log[HL^-] + 2\log[APH^+] \quad (10)$$

To calculate the extraction constant, the reaction equation can be represented as follows:

$$[Co(HL)_2]^{2-}_{(aq)} + 2APH^+_{(aq)} \Leftrightarrow \{[Co(HL)_2](APH)_2\}_{(org)} \quad (11)$$

The value of the extraction constant ($K_{ex}$) can be calculated from equation (12):

$$K_{ex} = \frac{\{[Co(HL)_2](APH)_2\}_{(org)}}{[Co(HL)_2]^{2-}_{(aq)} \cdot (APH^+)^2_{(aq)}} \quad (12)$$

If we substitute the value of equation (8) into equation (12), we get

$$K_{ex} = \frac{D}{(APH^+)^2_{(aq)}} \quad (13)$$

Taking the logarithm of expression (13), we obtain

$$\log K_{ex} = \log D - 2\log[APH] \quad (14)$$

The stability constants are calculated using equation (15): and are 10.30 for 1 and 11.71 for 2.

$$\log\beta_{s,c,} = \frac{C_c}{(C_{Co} - C_c)(C_L - nC_c)^n (C_{AP} - mC_c)^m} \quad (15)$$

where $C_{Co}$, $C_L$ and $C_c$ are the concentrations of cobalt ion, L and complexes, respectively. The values of $\log K_{eq}$, $\log K_{ex}$, and $\log\beta_{s.c.}$ calculated using formulas (10), (14) and (15) respectively, are given in Table 1.

**Table 2.** Thermal and mass spectrometric analysis data for the system of complexes $C_{30}H_{42}N_4O_6S_2Br_2Co$ and $C_{30}H_{40}N_4O_8S_2Br_2Co$ (Co:L:AP = 1:2:2) and the expected gross compositions of the intermediate solid products

| Stage | t,ºC | t-effect, °C | | Δm, % | | m/formula | Gross composition | |
|---|---|---|---|---|---|---|---|---|
| | | DTG* | DSC | exp | theor | | gas phase | solid phase |
| $C_{30}H_{42}N_4O_6S_2Br_2Co$ | | | | | | | | |
| 1 | 174-198 | 192.9 | 195.3 | 4.5 | 4.3 | 18/ $H_2O$ | 2$H_2O$ | $C_{30}H_{36}N_4O_4S_2Br_2Co$ |
| 2 | 340-450 | 395.7 | 447.2 | 55.3 | 55.2 | 44/ $CO_2$ | 18/ $CO_2$ | $C_{12}H_{12}N_2O_2S_2Co$ |
| | | | | | | 18/ $H_2O$ | 12/ $H_2O$ | |
| | | | | | | 28/ $N_2$ | 1/ $N_2$ | |
| 3 | 480-520 | 491.4 | 515.9 | 33.5 | 33.9 | 44/ $CO_2$ | 12/ $CO_2$ | CoO |
| | | | | | | 18/ $H_2O$ | 4/ $H_2O$ | |
| | | | | | | 160/ $Br_2$ | 1/ $Br_2$ | |
| | | | | | | 64/ $SO_2$ | 2/ $SO_2$ | |
| | | | | | | 28/ $N_2$ | 1/ $N_2$ | |
| $C_{30}H_{40}N_4O_8S_2Br_2Co$ | | | | | | | | |
| 1 | 174-198 | 191.4 | 195.3 | 4.1 | 4.0 | 18/ $H_2O$ | 2$H_2O$ | $C_{30}H_{38}N_4O_6S_2Br_2Co$ |
| 2 | 340-450 | 375.9 | 432.6 | 51.3 | 51.6 | 44/ $CO_2$ | 18/ $CO_2$ | $C_{12}H_8N_2O_2S_2Co$ |
| | | | | | | 18/ $H_2O$ | 12/ $H_2O$ | |
| | | | | | | 28/ $N_2$ | 1/ $N_2$ | |
| 3 | 480-520 | 497.3 | 510.0 | 33.5 | 33.5 | 44/ $CO_2$ | 12/ $CO_2$ | CoO |
| | | | | | | 18/ $H_2O$ | 4/ $H_2O$ | |
| | | | | | | 160/ $Br_2$ | 1/ $Br_2$ | |
| | | | | | | 64/ $SO_2$ | 2/ $SO_2$ | |
| | | | | | | 28/ $N_2$ | 1/ $N_2$ | |

### 3.6. Influence of foreign ions

The following ions do not interfere with the determination of cobalt(II) with $L_{1,2}$ and AP: $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$ and rare earth elements. The interference of Nb(V), Ta(V) and Ti(IV) is eliminated by changing the pH, Cu(II)–$NH_2C(S)NH_2$ and Mo(VI) and W(VI)–$C_2O_4^{2-}$ ion. When using 0.01 M EDTA solution, Ti(IV), V(IV), Ni(II), Ta(V) and Mo(VI) do not interfere with the determination. In the $CH_3COOH$–$CH_3COONH_4$ buffer, Mn(II) binds more strongly to EDTA than to $L_{1,2}$, which is used to mask it when determining Co(II).

The proposed Co(II)–L–AP systems demonstrate improved analytical characteristics, including high distribution coefficients, intense absorption bands in the visible region, and low detection limits. Compared with previously reported extractive systems for cobalt, the present complexes exhibit enhanced sensitivity and selectivity, which is attributed to the combined effect of S, O-chelation and hydrophobic ion association (Table 3).

### 3.7. Comparison with previously reported methods

A comparison of the proposed extraction–spectrophotometric procedure with representative methods reported in the literature is presented in Table 3. The comparison demonstrates that the Co(II)–HATP–AP and Co(II)–HNTP–AP systems exhibit several analytical advantages over many previously described cobalt reagents. First, the developed systems possess relatively high molar absorptivities ($\varepsilon = 4.12 \times 10^4$ and $4.26 \times 10^4$ L mol$^{-1}$ cm$^{-1}$), which are among the highest values reported for extractive spectrophotometric determination of cobalt(II). The corresponding Sandell sensitivities of 0.00143 and 0.00138 μg cm$^{-2}$ per 0.001 absorbance unit for the Co(II)–HATP–AP and Co(II)–HNTP–AP systems, respectively, further confirm the excellent analytical sensitivity of the proposed method. The intense coloration of the extracted complexes enables reliable determination of trace amounts of cobalt and compares favorably with many previously reported extractive spectrophotometric procedures. Second, the proposed procedure offers broad linear determination ranges (0.20–22 μg mL$^{-1}$), allowing accurate analysis over a wide concentration interval without the need for repeated dilution of samples. The calculated detection limits (15–16 ng mL$^{-1}$) and quantification limits (45–50 ng mL$^{-1}$) compare favorably with those reported for many conventional extractive spectrophotometric systems. Another important advantage of the present method is the high extraction efficiency achieved in a single extraction step. Under the optimized conditions, extraction recoveries reached 97.5% and 98.6%, corresponding to distribution coefficients of approximately 156 and 282 for the HATP and HNTP systems, respectively. Such high extraction efficiency simplifies the analytical procedure and minimizes analyte losses. The extracted complexes are also characterized by good stability. No significant change in absorbance was observed for at least three days in solution, while the extracted complexes remained stable for more than one month after extraction.

This feature is advantageous for routine analytical laboratories where immediate spectrophotometric measurements are not always possible. In addition, the developed mixed-ligand systems exhibit satisfactory selectivity toward Co(II). The interference from most foreign ions can be effectively eliminated by appropriate pH adjustment or by using suitable masking agents such as EDTA or oxalate. The successful application of the proposed method to plant samples further confirms its practical applicability.

Overall, the combination of high molar absorptivity, low detection limits, wide working concentration range, excellent extraction efficiency, good stability, and satisfactory selectivity demonstrates that the proposed extraction–spectrophotometric procedure represents a competitive alternative to previously reported cobalt determination methods.

### 3.8. Analytical application

The proposed method under the already established optimal conditions has been applied to determine Co(II) in various natural objects (Table 4). The obtained analytical results are in good agreement with those obtained by the reference spectrophotometric methods. Relative standard deviations did not exceed 3%, confirming good repeatability of the proposed procedure.

**Table 3.** Comparative characteristics of the procedures for determining of cobalt

| Reagent[a] | pH | λ, nm | ε×10$^{-4}$ | Beer's law range (μg· ml$^{-1}$) | References |
|---|---|---|---|---|---|
| TRTTC | 5.2– 5.8 | 525 | 4.26 | 0.2 – 1.5 | [15] |
| 1-NN | >3 | 415 | 2.9 | 0.1– 50 | [1, 28] |
| 2-NN | >4 | 365 | 3.7 | 0.05– 75 | [1, 28] |
| NRS | 6.4 – 6.7 | 415 | 3.5 | 0.06– 80 | [1, 28] |
| BSTSC | 5 | 381 | 1.42 | 0.8– 27 | [29] |
| HTAR | 3.4-10 | 553 | 2.63 | 5.4–189 | [30] |
| HATP+AP | 4.8 – 6.2 | 540 | 4.12 | 0.1– 100 | This method |
| HNTP+AP | 3.6 – 4.9 | 554 | 4.26 | 0.5– 110 | This method |

[a]TRTTC—4-(2-thiazolylazo) resorcinol +2,3,5-triphenyl-2H-tetrazolium chloride, 1-NN— 1-nitroso-2-naphtol, 2-NN— 2-nitroso-1-naphtol, NRS— Nitroso-R-salt, BSTSC—5- bromosalicylaldehyde thiosemicarbazone, HTAR—6-hexyl-4-(2-thiazolylazo)resorcinol

**Table 4.** Results of cobalt(II) determination in plants (n = 6, P = 0.95)

| Analyzed object | Reagent | Found in sample, mg/kg | $\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$, % | $S_r$ |
|---|---|---|---|---|
| Wheat (grain) | 1-Nitroso-2-naphthol | 0.31 | 0.31±0.14 | 0.016 |
| (*Triticum aestivum L.*) | 2-Nitroso-1-naphthol | 0.33 | 0.33±0.12 | 0.031 |
| | $L_1$ (HATP) | 0.28 | 0.28±0.12 | 0.024 |
| | $L_2$ (HNTP) | 0.31 | 0.31±0.11 | 0.023 |
| Oats (grain) | 1-Nitroso-2-naphthol | 0.19 | 0.19±0.06 | 0.039 |
| (*Avena sativa L.*) | 2-Nitroso-1-naphthol | 0.17 | 0.17±0.05 | 0.033 |
| | $L_1$ (HATP) | 0.18 | 0.18±0.01 | 0.019 |
| | $L_2$ (HNTP) | 0.19 | 0.19±0.03 | 0.024 |
| Peas (grain) | 1-Nitroso-2-naphthol | 0.28 | 0.28±0.06 | 0.031 |
| (*Pisum sativum L.*) | 2-Nitroso-1-naphthol | 0.27 | 0.27±0.01 | 0.019 |
| | $L_1$ (HATP) | 0.29 | 0.29±0.04 | 0.032 |
| | $L_2$ (HNTP) | 0.27 | 0.27±0.04 | 0.022 |

## 4. Conclusion

Stable mixed-ligand complexes of Co(II) with 2-hydroxy-5-aminothiophenol (L) or 2-hydroxy-5-nitrothiophenol (L) and 2-(N,N-dimethylaminomethyl)-4-bromophenol (AP) were successfully synthesized and applied to the development of a simple and sensitive extraction–spectrophotometric method for cobalt determination. The complexes, having a Co:L:AP stoichiometry of 1:2:2, were quantitatively extracted into chloroform under optimum conditions with recoveries of 97.5–98.6% and high distribution coefficients *(D* = 156–282). The proposed method exhibited high analytical performance, including high molar absorptivities ($\varepsilon = 4.12 \times 10^4$ and $4.26 \times 10^4$ L mol$^{-1}$ cm$^{-1}$), a wide linear range (0.20–22 μg mL$^{-1}$), low detection limits (15–16 ng mL$^{-1}$), good selectivity, and excellent stability of the extracted complexes. Structural characterization based on elemental analysis, extraction stoichiometry, IR spectroscopy, thermogravimetric analysis, magnetic susceptibility measurements, and cryoscopic studies supports the proposed composition of the extracted species. The developed procedure was successfully applied to the determination of cobalt in plant samples, providing accurate, reproducible, and reliable results. Owing to its high sensitivity, single-step extraction, low detection limits, and good analytical characteristics, the proposed method represents a competitive alternative to previously reported extraction–spectrophotometric methods for the determination of trace amounts of Co(II).

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