

# Study Of The Complexation Reaction Of Iron, Cobalt And Nickel With Dimercaptophenols And Heterocyclic Diamines

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**Abstract**—Physico-chemical methods investigated complexing Fe(II,III), Co(II) and Ni(II) with dimercaptophenols (2,6-dimercaptophenol, 2,6-dimercapto-4-methylphenol, 2,6-dimercapto-4-ethylphenol, 2,6-dimercapto-4-propylphenol and 2,6-dimercapto-4-tert-butylphenol), and hydrophobic amines. The hydrophobic amine were used as heterocyclic diamine-1,10-phenanthroline, 2,2'-bipyridyl and 4,7-diphenyl-1,10-phenanthroline (batofenanthroline). The optimal conditions for the formation and extraction mixedligand complexes and set the ratio of the components in the complexes. Developed photometric methods for determination Fe (II,III), Co(II) and Ni(II) in various objects. The proposed techniques are characterized by good reproducibility and low detection limits.

**Keywords**—iron, cobalt, nickel, dimercaptophenols, heterocyclic diamines, extraction-spectrophotometric method

## INTRODUCTION

In living organisms, iron is an important trace element that catalyzes oxygen exchange processes. Iron deficiency manifests itself as a disease of the body (chlorosis in plants and anemia in animals). Excess is also harmful: iron compounds are deposited in the tissues of the eyes and lungs, causing siderosis [1]. Cobalt and nickel are biologically active metals. It has been established that excessive "technogenic" intake of these metal compounds into the body has a toxic effect on metabolism. An excess of cobalt and nickel salts causes morphological changes in the cell and thereby has a carcinogenic effect on it [2].

Since Fe<sup>2+</sup> and Fe<sup>3+</sup> ions have chromophore properties, most methods use reagents that do not contain chromophore groups [3].

Iron forms very strong coordination bonds with any donor atoms. Selective reagents for Fe(III) are compounds containing phenolic OH groups. Sensitivity increases with the introduction of another phenolic OH group in the ortho or peri position, but this leads to a significant deterioration in the selectivity of the determination [4]. Reagents containing OH groups and donor nitrogen atoms are considered the most suitable for the determination of Fe(III) [4,5].

Methods for the photometric determination of Fe(III) in the form of mixed-ligand complexes (MLC) with these reagents in the presence of third components of various classes are highly sensitive and selective [6,7,8]. For the photometric determination of iron, ferrioxal chelating reagents are most important. Mainly used are 1,10-phenanthroline, 2,2'-dipyridyl and 2,2',2''-tripirydyl [3]. One of the classical photometric methods for determining Fe(III) is the thiocyanate method [3].

For the photometric determination of cobalt, reagents with an o-nitrosophenol group or a similar structure with an oxime group are quite selective [4]. The most widely used methods are those that use organic reagents derived from nitrosonaphthols and pyridine azo compounds, of which 4-(2-pyridylazo)-resorcinol is widely used [9].

Many chelating reagents belonging to different classes of compounds and containing N, O or S as donor atoms are suitable for the photometric determination of nickel. Dioximes, oxyazo compounds, and thiocarboxylic acids are most often used [4].

The most important photometric methods for determining nickel use reactions with dioximes and dithizones [9].

MLC of Fe(III) with heterocyclic diamines and azo derivatives of salicylic acid were studied using spectrophotometric methods [10]. Methods for the photometric determination of Fe(III) with 1-phenyl-2,3-dimethylpyrazolone-5-azopyrogallol in the presence of 1,10-phenanthroline and  $\alpha,\alpha'$ -dipyridyl have been developed. The developed method was used to determine trace amounts of iron in fruits [11].

Mixed phenanthroline-thiosalicylate complexes of iron, cobalt, nickel and copper in aqueous solutions were studied. The composition of the complexes and the mechanism of complex formation have been determined [12,13].

The equilibrium of complexation reactions of iron(III) ions with 5-nitrosalicylic acid and  $\alpha$ -alanine, serine and valine was studied [14].

Optimal conditions for complex formation of transition metal ions [Cu(II), Ni(II), Co(II, III) and Fe(II,III)] with 1-nitroso-2-naphthol-3,6-disulfonic acid were found using the spectrophotometric method in the presence of cationic (cetylpyridinium and cetyltrimethylammonium bromides) and nonionic (OP-10, neonol) surfactants (surfactants) [15].

The spectrophotometric method was used to study Co(II) MLC with aromatic diamines: 2,2'-dipyridyl, 1,10-phenanthroline, 4,7-diphenylphenanthroline and a chromogenic organic ligand - 2,4-dinitrobenzene-lasopyrocatechin. Methods for the extraction-photometric determination of cobalt in various objects have been developed [16]. The MLC of nickel with 2,2'-dipyridyl and dinitrobenzene azosalicylic acid was studied [17].

To determine trace amounts of nickel, an extraction-spectrophotometric method using 2 - [(2-mercaptophenylimino) methyl] phenol was proposed. The technique was applied to the determination of nickel in wastewater and alloys [18]. The method for determining nickel with 2-hydroxy-5-iodothiophenol and diphenylguanidine was used for metallic magnesium and carnallite [19].

The complexation of nickel with 1-(5-halogen-2-pyridylazo)-2-hydroxy-4-mercaptophenol and aminophenols was studied [20]. The interaction of nickel (II) with 2,2'-dipyridyl in an aqueous solution was studied using absorption spectroscopy. Complexes of various compositions have been established and their stability constants have been determined [21].

Equilibria in binary and ternary systems containing Co(II) and Ni(II) salts, as well as nitrilotriacetic acid and dicarboxylates were studied using the spectrophotometric method [22]. New complexes of Cu(II), Co(II) and Ni(II) nitrates were synthesized. with 1,3-bis(3,5-dimethylpyrazol-1-yl)propane [23].

The processes of complex formation in water-ethanol solutions of s-, p-, d- and f-metal cations with heterocyclic derivatives of azopyrazolone-5 have been studied [24].

According to the pH metric study, the formation of a mixed-ligand complex nickel - citric acid - 2,2'-dipyridyl was established [25].

We have studied MLC of Fe(II,III), Co(II) and Ni(II) with dimercaptophenols (DP) {2,6-dimercaptophenol (DMP), 2,6-dimercapto-4-methylphenol (DMMP), 2,6-dimercapto-4-ethylphenol (DMEP), 2,6-dimercapto-4-propylphenol (DMPP) and 2,6-dithiol-4-tert-butylphenol (DMBP)} and heterocyclic diamines (1,10-phenanthroline (Phen ), 2,2'-dipyridyl(Dip) and 4,7-diphenyl-1,10-phenanthroline (batophenanthroline (BPhen))).

## EXPERIMENTAL

**Reagents and solutions.** A standard solution of iron (III), 1 mg/ml, was prepared by dissolving an

accurately weighed portion of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in water containing 5 ml of concentrated  $\text{H}_2\text{SO}_4$  [3].

A standard solution of Fe(II), 1 mg/ml, was prepared by dissolving a sample of mohr's salt in water and acidifying it with 10 ml of concentrated  $\text{H}_2\text{SO}_4$ . The iron content in the solution was determined titrimetrically [3].

The initial solution (1 mg/ml) of Co(II) was prepared by dissolving an accurately weighed portion of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in water containing 2 ml of conc.  $\text{H}_2\text{SO}_4$ , and diluted with water to 1 liter [3].

A standard solution (1 mg/ml) of Ni(II) was prepared by dissolving an accurately weighed portion of  $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in water containing 2 ml of conc.  $\text{H}_2\text{SO}_4$ [3].

Solutions with lower concentrations were obtained by diluting the original ones with the appropriate acid immediately before the experiment.

In this work, we used 0.01 M solutions of DP and Am in chloroform. DP was purified by reprecipitation from ethanol solutions by adding water and then distillation. Purified chloroform was used as an extractant.

The ionic strength of the solutions, equal to  $\mu = 0.1$ , was maintained constant by introducing the calculated amount of KCl. To create the required acidity of the solutions, a 1 M KOH solution was used. All reagents used were of analytical grade or chemical grade.

**Apparatus.** The optical density of the organic phase was measured on KFK-2. Spectrophotometric studies of colored reagents were carried out on an SF-26 spectrophotometer. The pH value of solutions was controlled using an I-130 ion meter with a glass electrode. IR spectra were recorded on a Bruker spectrophotometer. The process of thermolysis of compounds was studied using a derivatograph of the ShimadzuTGA-50H system in air in the range of 20-1000°C, heating rate 10 degrees/min.

**Procedure.** 0.1-0.8 ml, at intervals of 0.1 ml of the initial M(II) solution, 1.5-2.0 ml of a 0.01 M DP solution, and 2.0-2.5 ml of a 0.01 M Am solution were introduced into graduated test tubes with ground-in stoppers. The required pH value was adjusted by adding a 0.1 M KOH solution. The volume of the organic phase was brought to 5 ml with chloroform, and the aqueous phase was brought to 20 ml with distilled water. After 10 minutes, the organic layer was separated and its optical density was measured at room temperature on KFK-2 at 540 nm (in the case of Ni-DP-Am at 490 nm).

## RESULTS AND DISCUSSION

Fe(II,III), Co(II) and Ni(II) form colored complexes with dimercaptophenols that are insoluble in non-polar organic solvents. The charge of the complexes was established by the method of electromigration of ions and by anion exchange on an EDE-10 P anion

exchanger. When studying the electromigration of these complexes, the movement of red-colored ions to the positive pole was observed, on the basis of which it was concluded that the colored M-DP complexes are anions. Ion transport was studied in a conventional U-shaped tube with two taps, at a voltage of 180 V and a current of 0.5-0.8 mA. Electrolysis was carried out for 3 hours. As one would expect, complexes with heterocyclic amines move into the cathode space. When determining the sign of the charge of homogeneous ligand Me-DP complexes using ion exchange chromatography, the EDE-10 P anion exchanger completely absorbs the colored part of the solution. When hydrophobic amines are introduced into the system, extraction of anionic complexes into the organic phase in the form of MLC is observed. Experiments have shown that MLC of Fe(II) and Fe(III) behave completely similarly during extraction: the absorption spectra and the pH range of optimal extraction are almost the same. This gives

grounds to conclude that Fe(III) is reduced by dimercaptophenols and in both cases the same Fe(II) compound is formed.

Complexing reagents (DMP, DMMP, DMEP, DMPP and DMBP) are a tribasic weak acid ( $H_3R$ ) and, depending on the pH of the environment, can exist in molecular and two anionic forms.

The reagents were synthesized according to a well-known method [26] and characterized by physicochemical methods: IR and NMR spectroscopy [27,28] (Table 1). **Effect of pH of the aqueous phase.** The study of the dependence of complex formation on pH shows that the interaction of M(II) with DP and amines and their extraction (release of MLC) into the organic phase is maximum at pH 5.2–8.6. The presence of the second ligand led to a shift in the optimal acidity of complexation to a more acidic region,  $pH_{opt}$  being wider than in the case of a two-component compound.

**Table 1. Results of IR and NMR spectroscopy studies**

Reagent	IR (KBr)	$^1H$ NMR (300,18 MHz, $C_6D_6$ )
DMP	3470 $cm^{-1}$ v (OH), 3050 $cm^{-1}$ v(CH), 2580 $cm^{-1}$ v(SH), 1580 $cm^{-1}$ v( $C_6H_5$ ).	$\delta$ 5.48 (s, 1H - OH), $\delta$ 3.57 (s, 2H - 2SH), $\delta$ 7.28 (s, 2H Ar-H), $\delta$ 6.95 (s, 1H - Ar-H).
DMMP	3460 $cm^{-1}$ v (OH), 3050 $cm^{-1}$ v(CH), 2570 $cm^{-1}$ v(SH), 2962 and 2872 $cm^{-1}$ v( $-CH_3$ ), 1555 $cm^{-1}$ $\delta$ ( $C_6H_5$ ), 1390 $cm^{-1}$ $\delta_{as}$ ( $-CH_3$ ).	$\delta$ 5.24 (s, 1H- OH), $\delta$ 3.32(s, 2H - 2SH), $\delta$ 7.11 (s, 2H Ar-H), $\delta$ 2.38 (s, 3H $-CH_3$ ).
DMEP	3460 $cm^{-1}$ v (OH), 3050 $cm^{-1}$ v(CH), 2575 $cm^{-1}$ v(SH), 2965 and 2874 $cm^{-1}$ v( $-CH_3$ ), 1555 $cm^{-1}$ $\delta$ ( $C_6H_5$ ), 1460 $cm^{-1}$ $\delta_{as}$ ( $-CH_2-CH_3$ ).	$\delta$ 5.29 (s, 1H- OH), $\delta$ 3.38(s, 2H - 2SH), $\delta$ 7.15 (s, 2H Ar-H), $\delta$ 2.59 (s, 2H $-CH_2-$ ), $\delta$ 1.22 (s, 3H $-CH_3$ ).
DMPP	3465 $cm^{-1}$ v (OH), 3050 $cm^{-1}$ v(CH), 2572 $cm^{-1}$ v(SH), 2950 and 2874 $cm^{-1}$ v( $-CH_3$ ), 1565 $cm^{-1}$ $\delta$ ( $C_6H_5$ ), 1460 $cm^{-1}$ $\delta_{as}$ ( $-CH_2-CH_3$ ).	$\delta$ 5.39 (s, 1H- OH), $\delta$ 3.42 (s, 2H - 2SH), $\delta$ 7.21 (s, 2H Ar-H), $\delta$ 2.59 (s, 2H $-CH_2-$ ), $\delta$ 1.22 (s, 3H $-CH_3$ ).
DMBP	3458 $cm^{-1}$ v(OH), 2568 $cm^{-1}$ v(SH), 3040 $cm^{-1}$ v(CH), 1535 $cm^{-1}$ v( $C_6H_5$ ), 1395 $cm^{-1}$ $\delta$ ( $-C(CH_3)_3$ ).	$\delta$ 5.15 (s, 1H- OH), $\delta$ 3.28 (s, 2H- 2SH), $\delta$ 7.05 (s, 2H Ar-H), $\delta$ 1.42 (s, 9H- $C(CH_3)_3$ ).

At the beginning, with an increase in the acidity of the initial solution, the extraction of Me(II) increases, and with a further increase, it gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of DP and, most likely, they are in the solution in an undissociated form. At pH 9, the complexes are practically not extracted, which is apparently due to an increase in the concentration in the aqueous solution of the non-extractable complexes  $[Me(DP)_2]^{4-}$  and  $[Me(DP)_3]^{7-}$  since the dissociation of DP at the second sulfhydryl group ( $pK_2 = 8.36-8.72$ ) continues to increase.

The dependence of optical density on pH is shown in Fig. 1. The presence of one maximum optical density within the specified pH limits confirms the assumption of the formation of one complex compound.

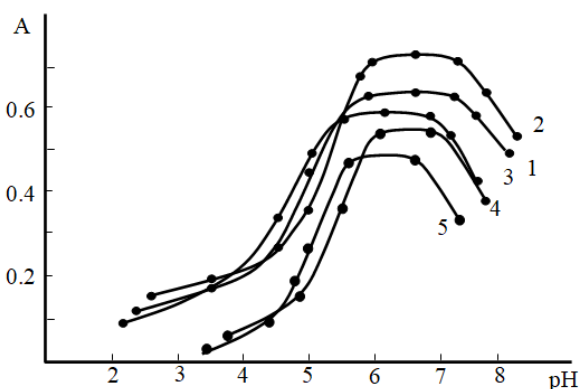


Fig.1. Dependence of the optical density of MLC on the pH of the aqueous phase.

1 - Fe(II)-DMMP-Fen, 2 - Fe(II)-DMMP-BPhen, 3 - Fe(II)-DMMP-Dip, 4-Co-DMPP-Phen, 5-Ni - DTEP-BPhen

$C_{Fe} = 3.57 \times 10^{-5}$  M;  $C_{Co(II)} = 3.38 \times 10^{-5}$  M;  $C_{Ni(II)} = 3.44 \times 10^{-5}$  M;  $C_{DP} = (0,6-0,8) \times 10^{-3}$  M;  $C_{Am} = (0,8-1,2) \times 10^{-3}$  M, KFK-2,  $\lambda = 490$  nm,  $l = 0,5$  cm

**Selecting an extractant.** To determine the possibility of MLC extraction, non-aqueous solvents were tested: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, xylene, isobutanol, isopentanol and diethyl ether and mixtures of organic solvents. The most effective for extracting Me(II) in the form of MLC and quickly achieving equilibrium are chloroform, dichloroethane and carbon tetrachloride. In one extraction, Me(II) is extracted with chloroform by 98.4-99.6% in the form of MLC. Within compounds of the same class, the extraction ability decreases with increasing number of carbon atoms in the solvent molecule. Depending on the nature of organic solvents, the stability and maximum light absorption of the MLC changes. Rapid separation of layers and the maximum value of the molar absorption coefficient were obtained by extracting the complexes with chloroform. In this case, the basicity of amines has a noticeable effect on the conditions and extraction of complexes.

**Effect of ligand concentration and holding time.** MLC of Me(II) are formed in the presence of a large excess of complexing reagents. The optimal condition for the formation and extraction of these compounds is  $(0.6-0.8) \times 10^{-3}$  mol/l concentration of DP and  $(0.8-1.2) \times 10^{-3}$  mol/l - Am. The concentration of DP required for the formation and extraction of MLC does not change depending on the basicity of the amines. Changing the concentration of reagents does not change the composition (at pH 5-9). In the case of heterocyclic diamines, a change in the concentration of Am leads to a change in the composition of the MLC.

MLC is stable in aqueous and organic solvents and does not decompose within three days, and after extraction for more than a month. Maximum optical density is achieved within 5-10 minutes. With low heating (up to  $30^{\circ}$  C), the color develops instantly. We studied the dependence of the optical density of extracts on time with an excess of reagents and at optimal pH.

**Absorption spectra.** The maximum analytical signal during complexation of MLC M(II) is observed at 450 – 586 nm (Fig. 2), where there are no absorption spectra of the reagents, since they do not absorb in the visible part of the spectrum. DP absorbs maximum at 270-280 nm. Thus, the bathochromic shift is 176-306 nm. The contrast of the reactions is high: the initial reagents are colorless, and the complexes are intensely colored.

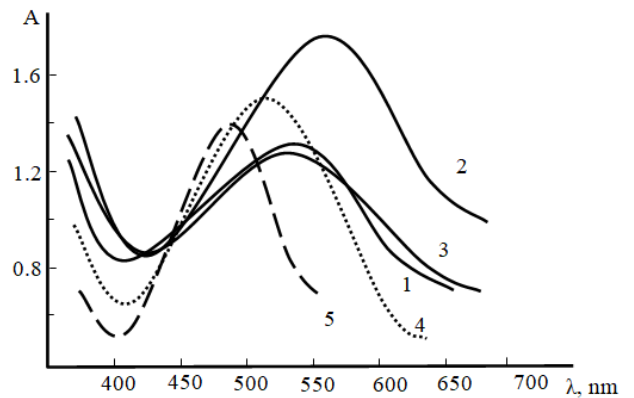


Fig.2. Absorption spectra of MLC  
 1 - Fe(II)-DMEP -Phen, 2 - Fe(II)-DMEP -BPhen, 3- Fe(II)- DMEP -Dip, 4-Co(II)- DMPP -Phen, 5-Ni(II) – DMEP -Phen  
 $C_{Fe} = 3.57 \times 10^{-5}$  M;  $C_{Co(II)} = 3.38 \times 10^{-5}$  M;  $C_{Ni(II)} = 3.44 \times 10^{-5}$  M;  $C_{DP} = (0.6-0.8) \times 10^{-3}$  M;  $C_{Am} = (0.8-1.2) \times 10^{-3}$  M, KФК-2,  $\lambda = 490$  nm,  $l = 1$  sm

**Influence of phase volume ratios.** The degree of extraction of M(II) in the form of MLC does not depend on the ratio of the volumes of aqueous and organic phases in a wide range (from 5:5 to 100:5), which allows for simultaneous concentration and photometric determination of Me(II). Thus, an increase in the volume of aqueous phase 20 times relative to the organic one does not affect the completeness of extraction.

**Composition of M(II) complexes with ditmercaptophenols and hydrophobic amines.** The stoichiometry of the studied complexes was determined by the equilibrium shift method and confirmed by the methods of relative yield, straight Asmus line, and intersection of curves [29]. Data shown in Fig. 3. show that in the composition of the MLC the ratio Me: DP : Am = 1: 1: 2.

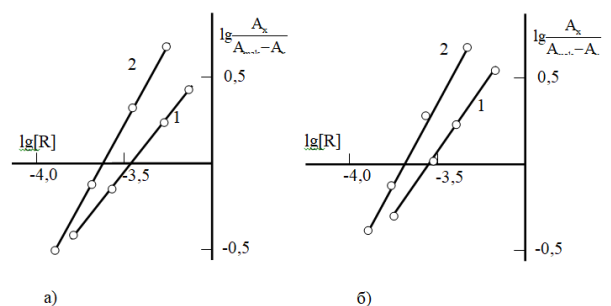


Fig.3. Determination of the composition of the MLC by the equilibrium shift method of Co-DMMP-Phen (a) and Ni-DMMP-Dip (b)  
 1. M : DMMP; 2. M : Dip.  
 $C_{Co(II)} = 2.035 \cdot 10^{-5}$  M;  $C_{Ni(II)} = 3.44 \cdot 10^{-5}$  M; CФ-26,  $l = 1$  sm.



The protonation constant of the studied aromatic diamines (pKa) in the order of 4.4-4.88 shows that under the conditions of formation and extraction of complexes, aromatic diamines are not protonated. Under conditions of formation and extraction of complexes (pH 5-10), DP in solution can exist both in the form of a singly charged and doubly charged anion (pK1 = 6.30-6.98; pK2 = 8.36-8.72).

**IR spectroscopic study of complexes.** To isolate the M-DP-Am complex in solid form, a red ethanol solution of  $[M(\text{Am})_3]\text{Cl}_2$  was added to the previously prepared ethanol solution of DP with stirring. The complex immediately precipitated as a dark red powder, which was filtered, washed successively with water, ethanol and diethyl ether, and dried over silica gel. IR spectra of Fe(II)-DTMP-Phen complexes were recorded; Co(II)-DTMP-Dip and Ni(II)-DTMP-Dip. They are compared with the IR spectra of DTMF, Phe and Dip. In the IR spectra of the complexes, the disappearance of a pronounced band at  $2580\text{ cm}^{-1}$ , observed in the spectrum of DTMP, and the appearance in the spectra of the complexes of two absorption bands, one of which is shifted towards lower frequencies, indicates that one of the sulfhydryl groups is involved in the formation of the complex. The disappearance of the absorption band at  $3460\text{ cm}^{-1}$  indicates that the hydroxyl group is involved in the formation of the bond. The detection of absorption bands at  $1375\text{-}1385\text{ cm}^{-1}$  indicates the presence of a coordinated amine [28, 29]. It is assumed that in the extracted compound the M(II) ions are connected by a main valence bond to the oxygen atom and are coordinately bound to the sulfur atom. In the region of stretching vibrations of the C-N and C-C bonds of the rings, a shift of the bands  $1585\text{ cm}^{-1}$  in the Phen molecule to  $1565\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  in the complexes is observed, which indicates the bond of the metal with nitrogen.

**Thermogravimetric study of M(II)-DMMP-Phen complexes.** Thermogravimetric study of the complexes showed that the complexes are thermally stable up to  $382^\circ\text{C}$ . The thermal decomposition of the complex occurs in two separate stages: at  $405\text{-}560^\circ\text{C}$ , Phen decomposes (61.1-61.4% weight loss), and at  $570\text{-}680^\circ\text{C}$ -DP (28.8-29.0% weight loss). The final product of thermolysis of the complex is  $\text{M}_2\text{O}_3$ .

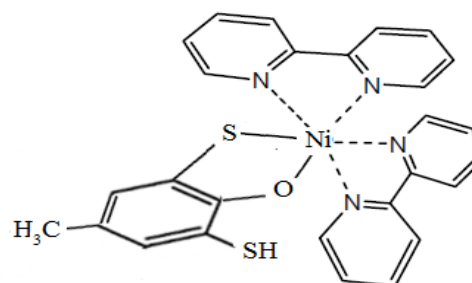
The ability of heterocyclic diamines to form complex compounds with various metals is widely used in many areas of chemistry and technology. The use of these complexes in analysis is due to their specific chemical and analytical properties. Strong ligand fields and the formation of reverse  $\pi$ -bonds with metals contribute to the high thermal and thermodynamic stability of complexes of iron, copper, nickel, cobalt and other metals, and the presence of a system of conjugated bonds in the molecules of 1,10-phenanthroline and 2,2'-dipyridyl causes deep coloring of complex compounds, which allows them to be used in photometric analysis [30].

**Chemistry of formation of MLC of M(II) with dithiolphenols and hydrophobic amines.** To clarify the chemistry of the complexation process, information is needed on the number of protons displaced from the reagent, as well as establishing the form of the M(II) cation that interacts with the reagent. When determining the reaction form M(II) and the number of displaced protons, the Nazarenko method was used [31,32]. The plotted dependence of  $-\lg B$  on pH with an integer value of the slope angle is observed for  $\text{M}^{2+}$  ions. Thus, during the formation of MLC, the  $\text{M}^{2+}$  ion is the coordinating one. Since the tangent of the angle in this case is equal to 1, complexation occurs with the displacement of one proton from one DP molecule.

The calculations showed that MLC in the organic phase do not polymerize and are in monomeric form ( $\gamma = 1.02\text{-}1.18$ ) [33].

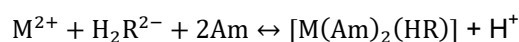
When complexes are formed, five-membered chelate rings are formed. When using an ammonia solution, M(II) and DP quantitatively pass into the aqueous phase, while Am remains at the bottom of the vessel in the form of a sediment.

Based on the establishment of the ratio of the reacting components, the state of the resulting complexes in the organic phase and IR spectroscopic studies, as well as literature data, we can assume the following probable formula of the resulting extractable mixed-ligand MLCs using the example of  $\text{M}(\text{DP})(\text{Am})_2$ . Taking into account that the coordination number of M(II) is 6 and the denticity of the ligands is 2, the proposed structures of octahedral complexes can be represented by the following scheme:



The proposed composition was confirmed by elemental analysis. The content of Fe, Co, and Ni in the complexes was determined photometrically after their decomposition with aqua regia using phenanthroline, 1-nitrosonaphthol-2, and dimethylglyoxime, respectively.

The reactions of formation of mixed-ligand complexes can be represented:



**Chemical and analytical characteristics of MLC of M(II) with DP and hydrophobic amines.** The apparent molar absorption coefficients of M(II)-DP-Am complexes at  $\lambda_{\text{max}}$  were calculated by the saturation method (from absorption spectra). The true values of the molar absorption coefficients were calculated by the Komar method. The molar absorption coefficients of the complexes are  $\epsilon = (2.6\text{-}2.8) \times 10^4$ . For comparison: the molar absorption coefficient of the

nickel complex with the traditionally used reagent for nickel, dimethylglyoxime, is only  $3.5 \times 10^3$ .

Conditional stability constants of the complexes were calculated using the curve intersection method [29]. The calculation results are presented in table. 2. Metal complexes with Phen and BPhen are more durable and intensely colored than complexes with dipyriddy. Apparently, the expansion of conjugation due to the inclusion of another aromatic

ring in the case of Phen and BPhen creates energetically more favorable orbitals for the formation of feedback  $\pi$ -bond. The strongest bonds are in cases where one of the ligands has free or low-occupied orbitals, and the second ligand is an electron donor [34].

In table 2. The main spectrophotometric characteristics of the method for determining M(II) are given.

Table 2. Main chemical and analytical characteristics of MLC M(II) with DP and Am.

Compound	pH		$\lambda$ , nm	$\Delta\lambda$ , nm	$\epsilon \cdot 10^{-4}$	$\lg\beta$	$\lg K_p$	$\lg K_{\text{ок}}$
	Education	Optimal						
Fe-DMP-Phen	3,8-8,0	5,5-6,8	558	288	3.25	14.68		
Fe-DMP-BPhen	3,6-7,9	5,3-6,6	565	295	4.05	15.05		
Fe-DMP-Dip	3,5-7,6	5,3-6,5	552	282	3.08	14.62		
Fe-DMMP-Phen	3,8-8,2	5,9-7,2	565	291	3.42	18.46	5.71	21.2
Fe-DMMP-BPhen	3,6-8,1	5,8-7,0	574	300	4.22	18.45	5.86	21.3
Fe-DMMP-Dip	3,1-7,8	5,7-6,8	562	288	3.15	18.12		
Fe-DMEP-Phen	3,8-7,8	5,8-7,1	572	296	3.60	18.10	5.82	21.1
Fe-DMEP-BPhen	3,5-7,6	5,7-6,8	582	306	4.33	17.23	5.94	21.2
Fe-DMEP-Dip	3,4-7,4	5,6-6,6	568	292	3.26	16.79		20.4
Fe-DMBP-Phen	4,1-8,9	6,0-7,5	580	300	3.91	18.95	5.89	
Fe-DMBP-BPhen	4,0-8,8	5,9-7,4	586	306	4.40	19.28	5.96	21.2
Fe-DMBP-Dip	3,9-8,7	5,8-7,2	578	298	3.55	17.92		
Co-ДМПФ-Phen	3.0-8.3	5.5-7.1	515	237	3.05	16.36		
Co-DMBP-Dip	3.0-8.0	5.2-7.6	520	240	3.17	16.7	6.03	19.9
Co-DMBP-Phen	3.2-8.5	5.6-7.8	525	245	3.25	18.4	6.11	20.5
Co-DMBP-BPhen	3.0-8.6	5.6-7.9	520	240	3.75	19.6	6.15	20.4
Ni-DMMP-Dip	2.5-8.5	5.4-7.8	450	176	1.75	17.20		
Ni-DMMP-Phen	2.8-8.8	5.8-8.5	465	191	1.94	17.65	6.15	19.5
Ni-DMMP-BPhen	3.0-9.0	5.9-8.6	475	201	2.53	17.89		
Ni-DMEP-Phen	4.0-8.0	5.5-6.3	465	189	2.15	18.54		
Ni-DMEP-BPhen	4.0-8.2	5.6-6.5	475	199	2.83	19.08	6.24	21.05

**Spectrophotometric determination of Fe(II), Co(II) and Ni(II).** The use of MLC in many cases leads to increased selectivity, reaction contrast, and improved extraction and other properties. The introduction of a second reagent often leads to an improvement in the extraction properties of complexes and a decrease in the detection limit. Thus, nickel dithizonate is very poorly extracted with non-aqueous solvents. Its complete extraction with carbon tetrachloride requires approximately 24 hours. If a third component, Phen or Dip, is introduced, the complex is extracted very quickly, and the detection limit of nickel is reduced by five times [34].

The ability of heterocyclic diamines to form complex compounds with various metals is widely used in many areas of chemistry and technology. Strong ligand fields and the formation of reverse  $\pi$ -bonds with metals contribute to the high thermal and thermodynamic stability of complexes of iron, copper, nickel, cobalt and other metals, and the presence of a

system of conjugated bonds in the molecules of 1,10-phenanthroline, 4,7-diphenyl- 1,10-phenanthroline and 2,2'-dipyridyl causes deep coloration of complex compounds, which allows them to be used in photometric analysis [30].

MLC of M(II) extracts obey the basic law of light absorption at concentrations of 0.03 – 4.4  $\mu\text{g/ml}$ .

The data obtained to construct calibration graphs were processed using the least squares method [35]. The equation of the calibration graphs are given in table. 3. Based on the equations of the calibration graphs, the photometric detection limit (LOD) and the quantitation limit (LOQ) of M(II) were calculated in the form of MLC. It can be seen that with an increase in the slope angle (a) of the linear equations, the molar absorption coefficients of the complexes increase, and the segment of the ordinate axis (b) increases accordingly, i.e., the detection limit of M(II) for the complexation reaction with DP and Am decreases.

**Table 3.** Analytical characteristics of mixed-ligand complexes M(II) with dimercaptophenols and Am

Complexes	LOD ng/ sm <sup>3</sup>	LOQ ng/ sm <sup>3</sup>	Sensitivity, ng/ sm <sup>2</sup>	Linear range of calibration graphs, µg/ml	The equation calibration graphs
[Fe(DMP)(Phen) <sub>2</sub> ]	11	36	1.72	0.03-3.6	0.049+0.265x
[Fe(DMP)(BPhen) <sub>2</sub> ]	10	33	1.38	0.02-3.8	0.055+0.334x
[Fe(DMP)(Dip) <sub>2</sub> ]	11	36	1.81	0.04-3.6	0.042+0.249x
[Fe(DMMP)(Phen) <sub>2</sub> ]	10	33	1.64	0.03-4.0	0.037+0.286x
[Fe(DMMP)(BPhen) <sub>2</sub> ]	9	30	1.32	0.03-4.2	0.045+0.354x
[Fe(DMMP)(Dip) <sub>2</sub> ]	10	33	1.77	0.05-3.6	0,025+0,315x
[Fe(DMEP)(Phen) <sub>2</sub> ]	10	33	1.55	0.04-3.8	0.045+0.230x
[Fe(DMEP)(BPhen) <sub>2</sub> ]	9	30	1.29	0.03-4.2	0.071+0.351x
[Fe(DMEP)(Dip) <sub>2</sub> ]	10	33	1.72	0.04-4.0	0.063+0.260x
[Fe(DMBP)(Phen) <sub>2</sub> ]	9	30	1.43	0.03-4.2	0.045+0.326x
[Fe(DMBP)(BPhen) <sub>2</sub> ]	8	28	1.27	0.02-4.4	0.059+0.363x
[Fe(DMBP)(Dip) <sub>2</sub> ]	9	31	1.58	0.05-4.0	0.065+0.285x
[Co(DMPP) <sub>2</sub> (Phen) <sub>2</sub> ]	12	39	1.93	0.05-2.8	0.028+0.141x
[Co(DMBP)(Dip) <sub>2</sub> ]	12	39	1.86	0.05-2.8	0.051+0.135x
[Co(DMBP)(Phen) <sub>2</sub> ]	10	33	1.81	0.05-3.0	0.046+0.165x
[Co(DMBP)(BPhen) <sub>2</sub> ]	9	31	1.57	0.04-3.2	0.050+0.166x
[Ni(DMMP)(Dip) <sub>2</sub> ]	13	42	3.31	0.2-2.4	0.047+0.127x
[Ni(DMMP)(Phen) <sub>2</sub> ]	13	45	2.98	0.1-2.8	0.038+0.148x
[Ni(DMMP)(BPhen) <sub>2</sub> ]	10	33	2.92	0.1-2.8	0.078+0.179x
[Ni(DMEP)(Phen) <sub>2</sub> ]	11	36	2.69	0.1-2.8	0.026+0.159x
[Ni(DMEP)(BPhen) <sub>2</sub> ]	10	33	2.05	0.1-3.0	0.037+0.226x

**Influence of foreign ions.** To evaluate the applicability of MLC extracts for the separation and determination of M(II), the interfering influence of foreign ions was studied. The selectivity of the spectrophotometric determination of M(II) in the form of the studied complexes is presented in Table 4-6. The determination of M(II) with DP and Am is not interfered with by ions of alkali, alkaline earth

elements and rare earth elements. The interfering influence of ions is eliminated by changing the pH of the medium, using masking substances and using extraction. The interfering influence of Nb(V), Ta(V), Ti(IV) is eliminated by increasing the pH and using fluoride ion. Interfering influence of Zn(II), Mn(II), Co(II), Ni(II), Cd (II) and Ag(I) during the determination of iron were eliminated by precipitation of Fe(III) with ammonia.

**Table 4.** Effect of foreign ions on the determination of iron with DMBP and Phen. n=6, P=0.95 (50 µg Fe(II) taken)

Ions	Molar excess of ion	Masking reagent	Found, µg (S <sub>r</sub> )
Co(II)	50		50,0(0,04)
Ni(II)	50		49,8(0,02)
Cd(II)	200		49,5(0,04)
Bi(III)	200		50,2(0,02)
Cu(II)	20	Thiourea	49,2(0,04)
Zr(IV)	50		49,8(0,03)
W(VI)	25	Oxalic acid	49,6(0,05)
Hg(II)	40	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	50,3(0,05)
Ti(IV)	30		49,8(0,03)
V(IV)	20		50,6(0,03)
Mo(VI)	15	Sodium fluoride	49,4(0,04)
Cr(III)	120		49,5(0,06)
Nb(V)	50	Sodium fluoride	50,2(0,04)
Ta(V)	50	Sodium fluoride	49,6(0,06)
UO <sub>2</sub> <sup>2+</sup>	50	Acetyl acetone	49,2(0,03)
Salicylic acid	50		50,5(0,03)
Sulfosalicylic acid	45		49,2(0,04)
Thiourea	25		50,8(0,06)

**Table 5.** Effect of foreign ions on the determination of cobalt with DMBP and Dip. (30 µg Co(II) taken, n=3, P=0.95)

Ions	Molar excess of ion	Masking reagent	Found, µg (S <sub>r</sub> )
Ni(II)	50		29,8(0,02)
Fe(II)	200		29,8(0,05)
Cd(II)	200		30,3(0,02)
Al(III)	180		29,6(0,04)
Fe(III)	60	Ascorbic acid	30,2(0,05)
Zr(IV)	50		29,8(0,03)
Cu(II)	25	Thiourea	30,1(0,02)
Hg(II)	40		30,2(0,05)
Ti(IV)	30	Ascorbic acid	29,8(0,02)
V(IV)	20		29,6(0,02)
Mo(VI)	10	EDTA	30,4(0,03)
Cr(III)	120		29,8(0,02)
Nb(V)	50	$C_2O_4^{2-}$	29,8(0,05)
Ta(V)	50	Ascorbic acid	29,7(0,05)
UO <sub>2</sub> <sup>2+</sup>	50		30,2(0,02)
Salicylic acid	75		30,4(0,03)
Sulfosalicylic acid	60		29,8(0,02)
Thiourea	40		29,8(0,05)

**Table 6.** Effect of foreign ions on the determination of nickel(II) with DMEP and BPhen (30 µg Ni(II) taken, n=3, P=0.95)

Ions	Molar excess of ion	Masking reagent	Found, µg(S <sub>r</sub> )
Co(II)	50		30,2(0,02)
Fe(II)	200		29,8(0,03)
Cd(II)	200		30,3(0,04)
Al(III)	180		29,6(0,03)
Fe(III)	60	Ascorbic acid	30,2(0,05)
Zr(IV)	50		29,8(0,03)
Cu(II)	25	Thiourea	30,1(0,05)
Hg(II)	40		30,2(0,05)
Ti(IV)	30	Ascorbic acid	29,8(0,04)
V(IV)	20		29,6(0,03)
Mo(VI)	10	ЭДТА	30,4(0,04)
Cr(III)	120		29,8(0,04)
Nb(V)	50	$C_2O_4^{2-}$	29,8(0,04)
Ta(V)	50	Ascorbic acid	29,7(0,05)
UO <sub>2</sub> <sup>2+</sup>	50		30,2(0,04)
Salicylic acid	70		29,8(0,04)
Sulfosalicylic acid	60		30,1(0,05)
Thiourea	45		29,6(0,03)



The interfering influence of Ti(IV) is ascorbic acid, Cu(II) is thiourea, and Mo(VI) and Nb(V) are oxalate ions. When using a 0.01 M EDTA solution, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI) do not interfere with the determination. In the ammonium acetate buffer,  $Mn^{2+}$  binds more firmly to EDTA than to phenanthroline, which is used to mask it in the determination of Ni and Co.

Oxidizing anions ( $MnO_4^-$ ,  $Cr_2O_7^{2-}$ , etc.) and ligands that form strong complexes with iron ( $F^-$ ,  $Sal^-$ ,  $SalSO_3^-$ ,  $S_2O_3^{2-}$ , complexone III) interfere. It has been established that zinc in tenfold quantities interferes with the determination of iron with DP and 1,10-phenanthroline. The interfering effect of Zn is weakly masked by a small amount of EDTA.

A comparison of the analytical capabilities of the studied reagents and hydrophobic amines shows

that the contrast and sensitivity of the reaction decreases in the series DMBP - DMPF - DMEP - DMMP - DMP.

**Comparison of methods for determining M(II) with known reagents and DP in the presence of amines.** In table 7-9 provide data that allows us to compare the analytical characteristics of the photometric methods we have developed for determining M(II) with some already known methods.

The results of studies of the formation and extraction of MLC M(II) with DP and heterocyclic diamines, the physicochemical and analytical characteristics of these compounds served as the basis for the development of new methods for the extraction-photometric determination of M(II) in various natural and industrial materials.

**Table 7. Comparative characteristics of methods for determining iron**

Reagent	pH (solvent)	$\lambda$ , nm	$\epsilon \cdot 10^{-4}$
Gallic acid+aniline [36]	4-5 (n-amyl alcohol)	560	0,44
Sulfosalicylic acid [3]	1,2	528	0,38
Phenanthroline [25]	2-9 (isoamyl alcohol)	512	1,1
Bathophenanthroline [2]	4-7(chloroform-ethanol)	533	2,24
DMMP+Dip	5,7-6,8 (chloroform)	562	3.15
DMBP+Phen	6,0-7,5 (chloroform)	580	3.91
DMBP +BPhen	5,9-7,4 (chloroform)	586	4.40

**Table 8. Comparative characteristics of methods for determining cobalt**

Reagent	pH	solvent	$\lambda$ , nm	$\epsilon \cdot 10^{-4}$	Linear range of calibration graphs, $\mu\text{g/ml}$
1-nitrosonaphthol-2	$\text{pH} \geq 3$	chloroform	415	2,9	
Nitroso R-salt	slightly acidic		500	1,5	
1-hydroxy-2-naphthoic acid+aniline [37]	6-8	chloroform	575	1.08	0.0125-5.5
Bromopyrogallol red [38]	2.0		575	1.08	0.25-110
DMPP- Phen	5.5-7.1	chloroform	515	3.05	0.05-2.8
DMBP +Dip	5.2-7.6	chloroform	520	3.17	0.05-2.8
DMBP +Phen	5.6-7.8	chloroform	525	3.25	0.05-3.0
DMBP +BPhen	5.6-7.9	chloroform	520	3.75	0.04-3.2

**Table 9. Comparative characteristics of methods for determining nickel(II)**

Reagent	pH	$\lambda_{\text{max}}$	$\epsilon$	Linear range of calibration graphs, $\mu\text{g/ml}$
Dimethylglyoxime [39]	12	470		0.26-2.1
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone [40]	6.0	400	$1.114 \times 10^4$	
7-Methyl-2-chloroquinoline-3-carbaldehyde Thiosemicarbazone [41]	6.0	410	$1.67 \times 10^2$	
Thiazol-2-carbaldehyde-2-quinolyldrazone [42]	8.7-9.5	522	$7.17 \times 10^4$	0-0.7
Pyridoxal-4-phenyl-3-thiosemicarbazone [43]	4-6	430	$1.92 \times 10^4$	0.5-5
4-4-hydroxy benzaldehyde-4-bromophenyl hydrazine [44]	4	497	$12.85 \times 10^4$	0.01-0.1
DMEP-Phen	5.5-6.3	465	$2.15 \times 10^4$	0.1-2.8
DMEP-BPhen	5.6-6.5	475	$2.83 \times 10^4$	0.1-3.0

**Determination of iron in soils.** A sample finely ground in an agate mortar (0.5-1.0 g) was calcined in a muffle furnace for 3 hours. After cooling, the sample was processed and dissolved in a graphite cup at a temperature of 50-60°C with a mixture of 16 ml of conc. HF, 5 ml of conc. HNO<sub>3</sub> and 15 ml of conc. HCl. In order to remove excess hydrogen fluoride, 8 ml of concentrated HNO<sub>3</sub> was added to the solution 3 times and evaporated each time to 5-6 ml. After this, the solution was transferred to a 100 ml volumetric flask and the volume was adjusted to the mark with distilled water. An aliquot of the resulting solution was taken, transferred to a separatory funnel, and 1 M KOH was added to obtain a pH of 6 and 2.0 ml of 0.01

M DMMP. After thorough mixing, 2.5 ml of 0.01 M Am was added. The volume of the organic phase was brought to 5 ml with chloroform, and the total volume was brought to 25 ml with distilled water. The mixture was shaken for 5 minutes. After phase separation, the light absorption of the extracts was measured on KFK-2 at 540 nm in a cuvette with a thickness of 0.5 cm. The iron content was found using a calibration graph.

The results obtained are presented in table 10 and compared with analysis data using widely used photometric methods (rhodanide and sulfosalicylic acid) and the atomic absorption method (AAS). The results of the proposed method and AAS are in good agreement with each other.

**Table 10. Results of determination of iron in soil.** n=6, P=0,95

Method	$\bar{X}\%$	S	S <sub>r</sub>	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
AAS	$2,72 \cdot 10^{-2}$	0,00204	0,075	$(2,72 \pm 0,21) \cdot 10^{-2}$
Rodanide	$2,71 \cdot 10^{-2}$	0,00191	0,070	$(2,71 \pm 0,20) \cdot 10^{-2}$
DMMP+Phen	$2,67 \cdot 10^{-2}$	0,00121	0,045	$(2,67 \pm 0,12) \cdot 10^{-2}$
DMMP+BPhen	$2,70 \cdot 10^{-2}$	0,00112	0.041	$(2,70 \pm 0,12) \cdot 10^{-2}$

**Determination of iron(III) in fruits.** After drying, a weighed sample of fruit weighing 200 g is placed in a graphite cup and burned in a muffle furnace at 550-750°C until the organic substances are completely decomposed. The resulting ash is dissolved in a mixture of 15 ml of HCl and 5 ml of HNO<sub>3</sub> in a glassy carbon cup and treated three times with 4-5 ml of HCl

at 60-70°C until the nitrogen oxides are completely distilled off. Next, the mixture is dissolved in distilled water, filtered in a 100 ml flask and diluted to the mark. The iron content with DP and Am was determined in the aliquot. The results of the determination are presented in Table 11.

**Table 11. Results of determination of iron(II) in fruits (n = 6, P = 0.95)**

object	Methodology	Found in sample, mg/kg	S	S <sub>r</sub>	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Cherry	Sulfosalicylic acid	5.2	0.14	0.024	$5.2 \pm 0.07$
	8-mercaptoquinolin	5.3	0.13	0.023	$5.3 \pm 0.05$
	DMMP+Phen	5,1	0.09	0.014	$5.1 \pm 0.09$
	DMEP + BPhen	5.2	0.10	0.016	$5.2 \pm 0.08$
White Cherry	Sulfosalicylic acid	14.0	0.06	0.031	$1.9 \pm 0.063$
	8-mercaptoquinolin	14.2	0.05	0.025	$2.1 \pm 0.052$
	DMEP + BPhen	13.8	0.03	0.015	$2.2 \pm 0.031$
	DMMP + Dip	13.9	0.03	0.014	$2.1 \pm 0.031$
Red Cherry	Sulfosalicylic acid	20.4	0.714	0.035	$20.4 \pm 0.75$
	8-mercaptoquinolin	19.5	0.565	0.029	$19.5 \pm 0.59$
	DMEP+ BPhen	20.2	0.727	0.036	$20.2 \pm 0.76$
	DMMP + Dip	19.8	0.693	0.035	$19.8 \pm 0.73$
Strawberry	Sulfosalicylic acid	11.6	0.475	0.041	$11.6 \pm 0.50$
	8-mercaptoquinolin	11.4	0.408	0.035	$11.4 \pm 0.42$
	DMEP + BPhen	11.3	0.282	0.025	$11.3 \pm 0.29$
	DMMP +Dip	11.5	0.333	0.029	$11.5 \pm 0.35$
Rose hip	Sulfosalicylic acid	13.0	0.403	0.031	$13.0 \pm 0.42$
	DMEP + BPhen	14.1	0.357	0.025	$14.1 \pm 0.37$
Strawberries	Sulfosalicylic acid	12.0	0.348	0.029	$12.0 \pm 0.37$
	DMEP +BPhen	11.3	0.495	0.045	$11.3 \pm 0.52$

**Determination of cobalt(II) and nickel(II) in wastewater.** For analysis, we took 1 liter of waste water and evaporated it until a precipitate was obtained, without bringing it to a boil. The precipitate was dissolved in 5 ml of HNO<sub>3</sub> and transferred to a

flask with a capacitance. 50 ml and diluted with water to the mark. In the aliquot, the content of Co(II) and Ni(II) was determined with DMBF and Phen. The results of the determination are presented in Table 12.

**Table 12.** Results of determination of cobalt(II) and nickel(II) in wastewater and bottom sediments (n = 6, P = 0.95)

Object of analysis		Introduced mg/l	Found mg/kg		S <sub>r</sub>
			With additive $\bar{X}$	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$	
Determination of cobalt					
Waste water	sample 1	2.0	2.45	0.45±0.05	0.07
	sample 2	5.0	6.14	1.14±0.11	0.08
Bottom sediments	sample 1	5	6.26	1.26±0.05	0.06
	sample 2	5	6.92	1.92±0.04	0.07
Determination of nickel					
Waste water	sample 1	2.0	2.55	0.55±0.05	0.10
	sample 2	5.0	6.64	1.64±0.12	0.07
Bottom sediments	sample 1	2.0	3.46	1.46±0.07	0.08
	sample 2	5.0	6.25	2.25±0.04	0.09

**Determination of cobalt (II) and nickel (II) in plants.** Reliable control of Co(II) and Ni(II) content in biological materials is important due to its high

biological activity. A sample of plants was laid out according to the method [45]. The results of the determination are presented in Table 13.

**Table 13.** Results of determination of cobalt (II) and nickel (II) in plants (n = 6, P = 0.95)

Methodology		Found in sample, mg/kg	S	S <sub>r</sub>	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
<i>determination of cobalt(II)</i>					
<i>beans</i>	1-nitrosophthal-2	0.20	0.0048	0.024	0.20±0.005
	8-mercaptoquinolin	0.19	0.0044	0.023	0.19 ±0.005
	DMMP+Phen	0,18	0.0034	0.019	0.18±0.004
	DMBP+Phen	0.20	0.0032	0.016	0.32±0.003
<i>peas</i>	1-nitrosophthal-2	0.11	0.0038	0.035	0.11±0.0040
	8-mercaptoquinolin	0.12	0.0046	0.038	0.12±0.0048
	DMBP+BPhen	0.12	0.0031	0.026	0.12±0.0033
	DMBP+Dip	0.11	0.0053	0.048	0.11±0.0055
<i>determination of nickel(II)</i>					
<i>beans</i>	Dimethylglyoxime	1.68	0.059	0.035	1.68 ±0.062
	8-mercaptoquinolin	1.65	0.041	0.025	1.65 ±0.043
	DMMP+Dip	1,71	0.048	0.028	1.71±0.050
	DMMP+Phen	1.66	0.043	0.026	1.66±0.045
<i>peas</i>	Dimethylglyoxime	2.46	0.110	0.045	2.46±0.116
	8-mercaptoquinolin	2.35	0.090	0.039	2.35±0.096
	DMMP +Phen	2.28	0.088	0.039	2.28±0.093
	DMBP +BPhen	2.39	0.081	0.034	2.39±0.085
<i>oats</i>	Dimethylglyoxime	0.43	0.0198	0.046	0.43±0.021
	8-mercaptoquinolin	0.46	0.0133	0.029	0.46±0.014
	DMMP+Dip	0.42	0.0172	0.041	0.42±0.018
	DMEP+Phen	0.47	0.0136	0.029	0.47±0.014

### Conclusions

- Complexation of Fe(II,III), Co(II) and Ni(II) with dimercaptophenols (2,6-dimercaptophenol, 2,6-dimercapto-4-methylphenol, 2,6-dimercapto-4-tert-butylphenol) and hydrophobic amines. Heterocyclic diamines-1,10-phenanthroline, 2,2'-dipyridyl were used as a hydrophobic amine and 4,7-diphenyl-1,10-phenanthroline (batophenanthroline).

- The interaction of M(II) with DP and amines and their extraction (release of MLC) into the organic phase is maximum at pH 5.2 – 8.6. In one extraction,

M(II) is extracted with chloroform by 98.4-99.6% in the form of MLC. The optimal condition for the formation and extraction of these compounds is (0.6-0.8)•10<sup>-3</sup> mol/l concentration of DP and (0.8 -1.2)•10<sup>-3</sup> mol/l - Am.

- The maximum analytical signal during the complexation of MLC M(II) is observed at 450 – 586 nm in the composition of MLC the ratio M: DP : Am = 1:1:2.

- The results of studies of the formation and extraction of MLC M(II) with DP and heterocyclic diamines, the physicochemical and analytical characteristics of these compounds served as the

basis for the development of new methods for the extraction-photometric determination of M(II) in various natural and industrial materials.

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