

Complex Formation in a Liquid-Liquid Extraction System Containing Nickel (II), 2-hydroxy-5-nitrothiophenol and Hydrophobic amines

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ABSTRACT

The conditions for the complexation of nickel (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time (300 minutes), pH of the medium (pH_{op} 3.6-5.2), the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law (0.06-22 µg / 5 ml). The spectral characteristics of the complex ($\lambda = 460-465$ nm) and the HNTPh reagent ($\lambda = 195$ nm) were studied which showed high sensitivity and contrast ($\lambda = 265-270$ nm) and the true molar coefficient ($\epsilon = (3.34-3.53) \times 10^4$) of light absorption was determined. The mole ratio of nickel: re: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition. The interval of obedience to the Bouguer-Lambert-Beer law (0.06-22 µg / 5 ml) and the Sendel sensitivity of 0.0109 - 0.0172 µg / cm² are shown. Based on the achieved results and revealed regularities, a photometric technique for determining nickel (II) with HNTPh and Am.

KEYWORDS: Nickel, 2-hydroxy-5-nitrothiophenol, diphenylamine, triphenylamine, chloroform.

1. INTRODUCTION

Nickel-containing sewage is harmful after ingress into water. This fact explained the importance of the monitoring of nickel concentration in natural and waste water samples. Spectrophotometric method provides accurate and rapid determination of nickel in natural and waste waters [1]. However, very frequently a direct determination cannot be applied due to low concentration of analyte or matrix interferences.

Nickel (II) chelates of several ligands like diphenylcarbazone, diphenylthiocarbazone, 8-quinolinol and its substituted analogues produce intense absorption in the optical spectra, in the visible range, which is characteristic of the ligand itself. Structural changes occurred in the nickel (II) chelates on addition of nitrogen bases forms adduct which gives rise to profound spectral changes. Such bathochromic and hypsochromic shifts observed in the visible region of the spectra of nickel (II) chelates of dithizone, diphenylcarbazone, 8-quinolinol, methylsubstituted 8-quinolinols, substituted diphenylcarbazones and dithizones on addition of nitrogen bases [2]. These were employed for the determination of adduct formation constants. Oxyphenolate and dithiophenolate complexes of nickel are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [3-5].

A spectrophotometric method for determining trace amounts of cobalt, nickel, and copper ions was developed [6] after the adsorption of their 2-aminocyclopentene-2-dithiocarboxylate complexes

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

Sorption of Cu^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} sorbent POLIORGS was studied [7] and concentrating conditions were chosen for the analysis of small volumes of natural waters. The behavior of these metals has been studied and the atomic absorption regimes have been established in the aqueous suspension of the sorbent. A sorption-atom-absorption method for determining Cu^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} in seawater has been developed. The limits of detection of elements are 0.4 $\mu\text{g L}^{-1}$ for Cu^{2+} and Ni^{2+} , 0.05 $\mu\text{g L}^{-1}$ for Co^{2+} , 0.2 $\mu\text{g L}^{-1}$ for Pb^{2+} and 0.1 $\mu\text{g L}^{-1}$ for Cd^{2+} .

The authors of Ref. [8] found the optimum conditions for the concentration of Ni^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} on silica by C-120 siloxane modified with 4- (2-tialylazo) resorcinol, and the colorimetric characteristics of the complexes were determined. It is shown that the separation criterion is satisfied by complexes of nickel and zinc. A colorimetric method for the separate determination of 0.05-1.00 $\mu\text{g L}^{-1}$ was developed of nickel and 0.15-5.0 $\mu\text{g mL}^{-1}$ of zinc.

A technique was developed [9] for the spectrophotometric determination of the Co^{2+} , Ni^{2+} , Cu^{2+} , Pd^{2+} , Ru^{2+} and Mo^{6+} macroquantities after extraction of their isoamylxanthogenates with molten naphthalene. The optimum condition for determining Co^{2+} at pH 3.0-8.0 is selected, the complex is formed by the ratio 1: 2; The molar coefficient of light absorption is equal to 2.06×10^4 at 360 nm, the Sendel sensitivity is 0.0052 $\mu\text{g cm}^3$, $\text{Sr} = 0.0081$.

The possibility of direct determination of Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} and Ni^{2+} in concentrated solutions of calcium chloride by the method of electrothermal atomic absorption spectrometry was shown in [10]. As chemical modifiers, ascorbic and oxalic acids, as well as magnesium nitrate, have been studied. The best modifier was oxalic acid. Despite the use of an atomic absorption spectrometer with a relatively ineffective background correction system (with a deuterium lamp) in the presence of oxalic acid, it is possible to confidently determine the studied elements to a concentration of calcium chloride in a solution of 6%. Due to the fact that cadmium evaporates before the main part of this matrix, it can be determined without a modifier.

The method [11] of the sorption concentration of Fe^{3+} , Co^{2+} , Pb^{2+} , Cd^{2+} and Cr^{3+} was developed on a column with an Ambersorb 563 sorbent from the sample solution and the eluent was set by a peristaltic pump. In $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution (pH = 9.0), these ions were quantitatively retained by the sorbent. Then they were eluted with 5 ml of 0.25 M HNO_3 at a rate of 5 ml min^{-1} . The detection limits of Cd^{2+} and Pb^{2+} are 0.33 and 72 $\mu\text{g L}^{-1}$, respectively. The relative standard deviation is less than 0.10. The method is used to determine the ions Fe^{3+} , Co^{2+} , Pb^{2+} , Cd^{2+} and Cr^{3+} in drinking and sea water samples (recovery > 95%).

Oxyphenolate and hydroxthiophenolate complexes of cobalt are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [12-13]. In this respect, a very promising reagent is hydroxthiophenols, which contains one hydroxyl and one sulphohydril groups and is a sulfur-containing analogue of mononuclear poly-phenols with one oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Cobalt (II) with hydroxthiophenols in the presence of hydrophobic amines (Am). From hydroxthiophenol 2-hydroxy-5-nitrothiophenol (HNTPh) were used in the presence of hydrophobic amines (Am). As hydrophobic amine diphenylamine (DPhA) and triphenylamine (TPhA) were used.

2. Experimental

2.1. Reagents and Apparatus

HNTPh were synthesized according to the procedure [14]. The purity was checked by determining the melting point and chromatography on paper. The HNTPh was identified by IR and NMR spectroscopy: IR (KBr): 3462 cm^{-1} $\nu(\text{OH})$, 2564 cm^{-1} $\nu(\text{SH})$, 3045 cm^{-1} $\nu(\text{CH})$, 1700 cm^{-1}

$\nu(\text{NO}_2)$, 1535 cm^{-1} $\nu(\text{C}_6\text{H}_5)$]; $^1\text{H NMR}$ (300,18 MHz, C_6D_6); [δ 5.16 (s, 1H- OH), δ 3.25(s, 1H - SH), δ 7.18 (s, 2H Ar-H), δ 7.41 (s, 1H - Ar-H)].

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

Stock solution of Ni(II) was prepared by dissolving $\text{NiCl}_2 \times 6\text{H}_2\text{O}$ (Sigma-Aldrich, puriss. p.a.) in distilled water; it was standardized gravimetrically with dimethylglyoxime [15]. Working Ni(II) solutions (0.1 mg mL^{-1}) were prepared by appropriate dilution of the stock solution.

To create the necessary pH, fixated HCl (pH 0-3) and $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONH}_4$ buffer solutions (pH 4-12) were used. The ionic strength of the solutions was kept constant ($\mu = 0.1$) by introducing the calculated amount of 1M KNO_3 .

The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer and KFK 2 photocolormeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. The process of thermolysis of the compounds was studied using derivatograph system «Shimadzu TGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany). $^1\text{H-NMR}$ spectra were recorded on "Bruker" Fourier Transform (300.18 MHz) in C_6D_6 .

2.2. General Procedure

2.2.1 General Procedure for the Determination of nickel (II)

Portions of stock solutions of nickel(II) varying from 0.1 to 1.0 mL with a 0.1 mL step, a 2.2 – 2.5 mL portion of a 0.01 M solution of HNTPh, and a 2.5 – 3.0 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with groundglass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONH}_4$ buffer solutions (pH 4-12). The volume of the aqueous phase was increased to 20 mL using distilled water. In 6 - 12 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 480 nm ($\ell=0.5\text{cm}$).

2.2.2. Dissolution of Carnallite

A ca. 2.0 g sample of carnallite was placed in a 50 mL beaker. 0.5 mL of a 3% NaF solution and 5 mL of HNO_3 (1:20) were added and the beaker was heated on an electric heater. After cooling, the obtained solution was neutralized with ammonia to pH 6 (universal paper indicator); then it was transferred through a filter paper into a 50 mL calibrated flask and diluted to the mark with distilled water and was determined nickel using the proposed procedures.

2.3.3. Determination of nickel (II) in tap water

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

3. Results and Discussion

Ni (II) reacts with 2-hydroxy-5-nitrothiophenol and gives complexes that are insoluble in non-polar solvents. When diphenylamine and triphenylamine were introduced into the system, extraction of these compounds in the organic phase as a complex of mixed ligands (MLC) was observed.

3.1. Effect of the pH of the aqueous phase and selection of extractant.

Light absorption spectra of nickel complexes (II) with HNTPh and Am were studied in a wide range of pH of the medium. The maximum yield of complexes is observed at pH 1.4-8.2. Hence further analytical investigations were carried out in media of pH 3.6-5.2 (Fig. 1). Extraction of Ni(II) enhanced with the increase in the acidity of the initial solution. The further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HNTPh. $\text{pH} \geq 8.2$ complexes are not practically extracted, which, apparently, is associated with a decrease in the Am protonation degree.

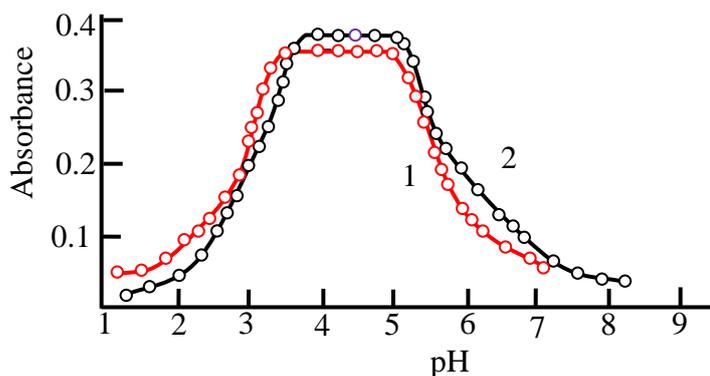


Fig. 1. Absorbance of Ni- HNTPh -Am extracts function of the pH of the aqueous phase.

1. Ni–HNTPh–DPhA, 2. Ni–HNTPh–TPhA

$C_{Ni(II)} = 2.035 \times 10^{-5}$ M, $C_{HNTPh} = (1.12-1.25) \times 10^{-3}$ M, $C_{Am} = (0.90-1.30) \times 10^{-3}$ M, $\lambda = 480$ nm, KFK-2, $\ell = 0.5$ cm

To extract the complexes, $CHCl_3$, CCl_4 , C_6H_5Cl , C_6H_6 , $C_6H_5-CH_3$, $C_6H_4(CH_3)_2$, *iso*- C_4H_9OH , C_4H_9OH , *iso*- $C_5H_{11}OH$, $C_2H_4Cl_2$ were used. The extractability of the complexes was evaluated by the distribution coefficient and the degree of extraction. The best extractants were $CHCl_3$, $C_2H_4Cl_2$ and C_6H_5Cl . All further studies were carried out with $CHCl_3$. The content of cobalt in the organic phase was determined photometrically by dimethylglyoxime [3] after stripping, and in the aqueous phase by the difference.

Extractable complexes evaluated coefficient distribution (D) and the extraction ratio

$$(R, \%) [16]: \quad D = \frac{[Ni]_{aq}}{[Ni]_{org}}, \quad R = \frac{100 \times D}{D + \frac{V_{aq}}{V_{org}}}$$

At the optimum conditions this solvent provides degrees of extraction $R = 98.3-98.6\%$.

3.2. The study of the ordering of the components of the reaction, Reagents Concentrations and Effect of Time.

From the experimental data obtained, it can be seen that the maximum optical density is observed at the order of the discharge of the components: nickel (II) + HNTPh + Am + $CHCl_3$ + CH_3COOH + CH_3COONH_4 + water. In further studies, this order of draining the components was used as the optimal one.

For the formation and extraction of MLC, a 20-25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by $(1.11-1.24) \times 10^{-3}$ M HNTPh and $(0.89-1.32) \times 10^{-3}$ M Am. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

To determine the stability of the color of the nickel complex in time, the optical density of the solutions was measured at definite intervals of time. The optical density of the complex does not change for 300 minutes, which is enough to obtain reproducible results.

3.3. Spectral characteristics of nickel (II) complexes with HNTPh and Am.

The spectra of HNTPh and its complex with nickel (II) are shown in Fig. 2. It can be seen from the figure that in the light absorption spectrum of the cobalt (II) complex there is one expressed maximum at 460-465 nm, and the maximum light absorption of the HNTPh reagent is observed in the shorter-wave region of the spectrum, at 295 nm, which characterizes the contrast between the color of the complex and the reagent, is 165-170 nm, which contributes to the sensitivity of the method.

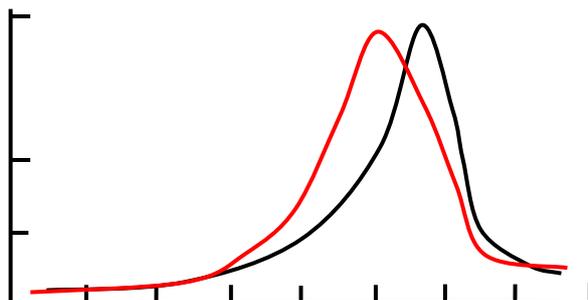


Fig. 2. Absorption of mixed-ligand complexes. 1. Ni–HNTPh – DPhA, 2. Ni–HNTPh–TPhA
 $C_{Ni(II)} = 2.035 \times 10^{-5}$ M, $C_{HNTPh} = (1.12-1.25) \times 10^{-3}$ M, $C_{Am} = (0.90-1.30) \times 10^{-3}$ M, pH 3.6-5.2, Shimadzu UV1240, $\ell=1.0$

The molar absorptivity of the complex was calculated with Komar method [16] to be $\epsilon = (3.34-3.53) \times 10^4$ L mol⁻¹ cm⁻¹.

3.4. Stoichiometry of the Complexes and the Mechanism of Complexation

The stoichiometric reaction coefficients were established by the methods of the Asmus straight (Fig. 3) line and the equilibrium shift (Fig. 4). [16]. The formation of MLC can be represented as follows. Nickel ions interacting with two molecules of HNTPh form a doubly charged anionic complex, which is extracted with two molecules of protonated Am.

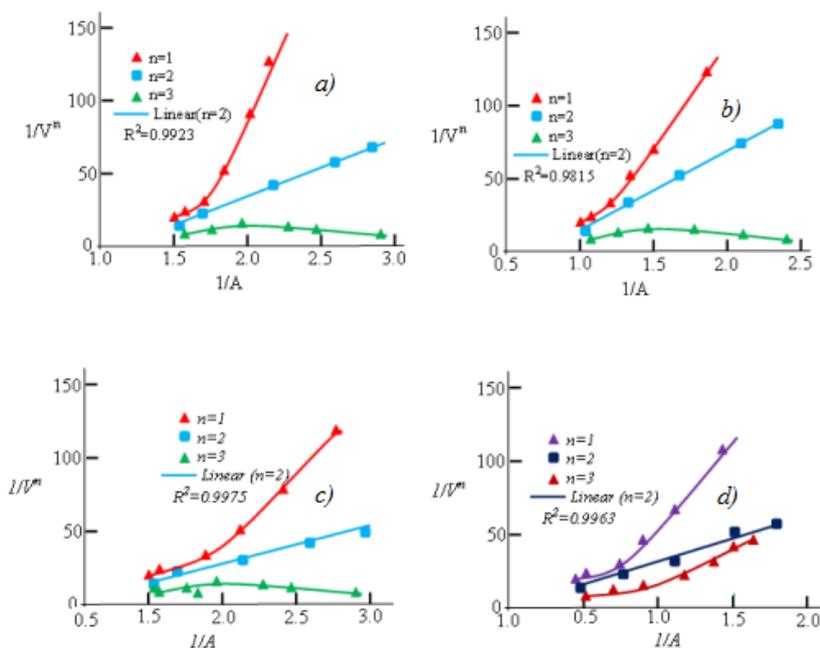


Fig.3. Determination of the *a,c*)HNTPh-to-Ni molar ratio; *b*) DPhA-to-Ni; *c*) TPhA-to-Ni molar ratio by the method of Asmus. $C_{Ni(II)} = 2.035 \times 10^{-5}$ M, $C_{HNTPh} = (1.12-1.25) \times 10^{-3}$ M, $C_{Am} = (0.90-1.30) \times 10^{-3}$ M, $\lambda=540$ nm, Shimadzu UV1240, $\ell=1.0$ cm, pH 3.6-5.2.

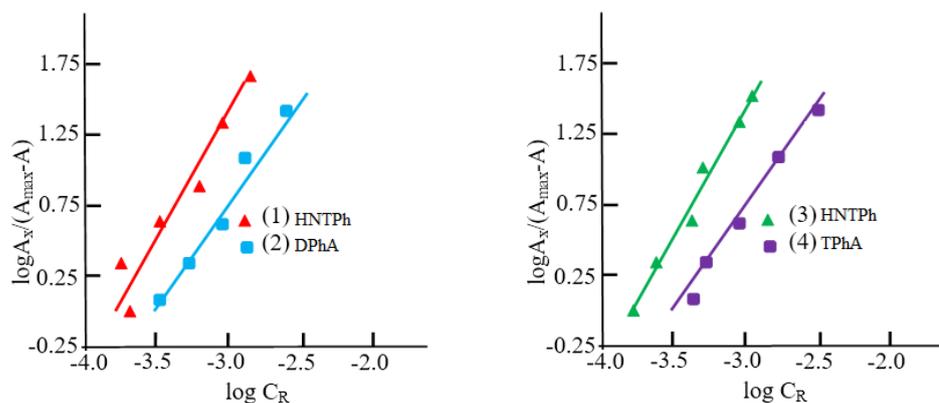


Fig.4. Determination of the ratio of components by the equilibrium shift method for (a) Ni (II)-HNTPh-DPhA and (b) Ni (II)- HNTPh-TPhA. 1- Ni (II) : HNTPh; 2- Ni (II): Am. $C_{Ni(II)} = 2.035 \times 10^{-5} M$, $C_{HNTPh} = (1.12-1.25) \times 10^{-3} M$, $C_{Am} = (0.90-1.30) \times 10^{-3} M$, $\lambda=540 \text{ nm}$, Shimadzu UV1240 , $\ell=1.0 \text{ cm}$, pH pH 3.6-5.2.

The pH of the start of precipitation of $Ni(OH)_2$ is 8.0, and the pH of the total precipitation is - 10.0 [17]. HNTPh is a sufficiently strong reducing agent, so oxidation of Ni (II) is not possible. Thus, Ni(II) in the complexes is in the unhydrolyzed state. The number of protons displaced by nickel from one HNTPh molecule turned out to be 2 [18].

The disappearance of the pronounced absorption bands in the $3200-3600 \text{ cm}^{-1}$ with a maximum at 3451 cm^{-1} observed in the spectrum of HNTPh, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2587 cm^{-1} shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1385 cm^{-1} indicates the presence of a protonated diphenylamine (Fig. 4) [19].

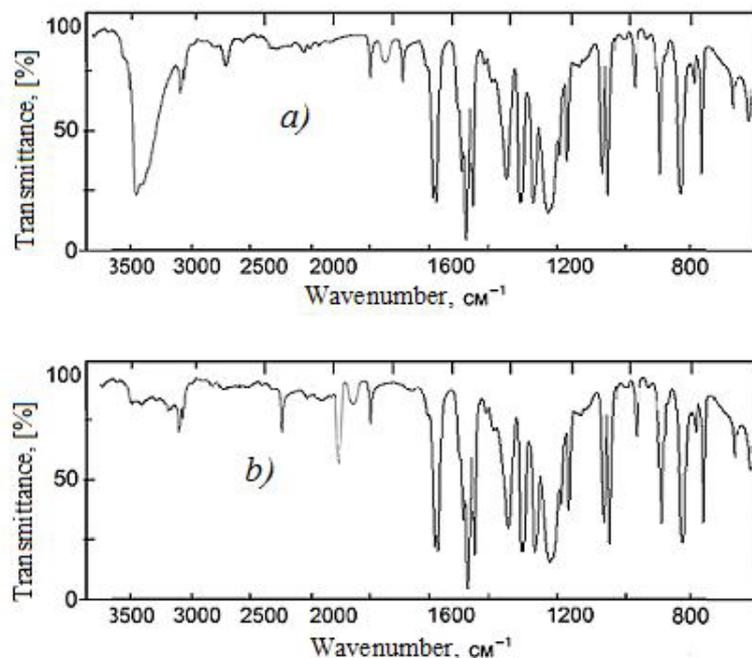
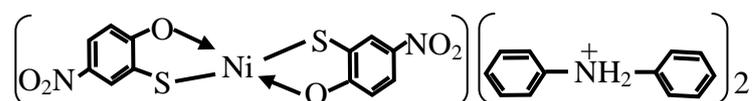


Fig. 4. IR spectrums of HNTPh (a) and the Ni (II)- HNTPh-DPhA (b).

Calculation of extent of polymerization of complexes was carried out on the equation [20]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1.06-1.10$).

Thermogravimetric study of the complex $[\text{Ni}(\text{H}_2\text{O})(\text{C}_6\text{H}_5\text{O}_3\text{SN})_2(\text{C}_{12}\text{H}_{11}\text{N})_2]$ Ni(II)-HNTPh-DPhA shown that thermal decomposition of the complex takes place in three stages: at 80-120°C water evaporates (weight loss - 4.90%) , at 430-495°C-decomposed DPhA (weight loss -44.13 %), and at 495-540°C- HNTPh (weight loss - 43.61%). The final product of the termolysis of the complex is NiO.

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

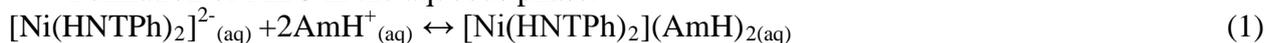


Scheme. Structure of complex $[\text{Ni}(\text{HNTPh})_2](\text{DPhAH})_2$

Equilibria and equilibrium constants

Several equilibrium processes should be taken into account for the system of Ni – HNTPh – AmH^+ – H_2O – CHCl_3 .

Formation of MLC in the aqueous phase:



Distribution:



Extraction from water into chloroform:



The association constant β was determined according to a strategy [21] by several independent methods. The constant of distribution K_D was calculated from the absorption values obtained after single and triple extraction as described above. The constant of extraction K_{ex} was calculated by the formula $K_{\text{ex}} = K_D \times \beta$.

Calculated values of $\lg\beta$, $\lg K_D$ and $\lg K_{\text{ex}}$:

$$\begin{aligned} \beta &= \frac{[\text{Ni}(\text{HNTPh})_2](\text{DPhAH})_2}{[\text{Ni}(\text{HNTPh})_2]^{2-} \times [\text{DPhAH}^+]_2} & \lg\beta &= 4.8 \pm 0.1 \\ K_D &= \frac{[\text{Ni}(\text{HNTPh})_2](\text{DPhAH})_2_{(\text{org})}}{[\text{Ni}(\text{HNTPh})_2](\text{DPhAH})_2_{(\text{aq})}} & \lg K_D &= 0.88 \pm 0.01 \\ K_{\text{ex}} &= \frac{[\text{Ni}(\text{HNTPh})_2](\text{DPhAH})_2_{(\text{org})}}{[\text{Ni}(\text{HNTPh})_2]^{2-}_{\text{aq}} \times [\text{DPhAH}^+]_{2(\text{aq})}} & \lg K_{\text{ex}} &= 5.6 \pm 0.1 \end{aligned}$$

3.5. Influence of interfering ions

To evaluate the complex applicability for photometric determination of nickel, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as NO_3^- , ClO_4^- , SO_4^{2-} and CH_3COO^- do not interfere determination of nickel with HNTPh and DPhA. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in Table 1.

Table 1. Influence of interfering ions on the determination of nickel(II) as MLC with HNTPh and Am (30.0 μg Ni added)

Foreign ions (FI)	Molar excess of the ion	Masking agent	Co found (S_r)	
			DPhA	HNTPh
Mo^{6+}	50	EDTA	29.85 (7)	29.04 (6)
W^{6+}	50		29.88 (5)	92.77 (6)
Cr^{6+}	170		29.91 (4)	28.25 (7)
Cr^{3+}	60		29.80 (3)	29.08 (4)

Co ²⁺	75		29.82 (4)	30.07 (6)
Fe ²⁺	83		29.25 (6)	31.01 (2)
Fe ³⁺	49	Ascorbic acid	30.90 (2)	31.04 (5)
V ⁴⁺	90		30.55 (5)	31.02 (3)
V ⁵⁺	78		29.25 (3)	29.09 (4)
Cd ²⁺	120		29.86 (6)	30.22 (6)
Cu ²⁺	52	Thiourea	30.17 (7)	31.45 (2)
Al ³⁺	120		30.08 (4)	31.63 (7)
Zn ²⁺	79		30.04 (6)	30.82 (3)
Zr ⁴⁺	40		30.18 (5)	30.51 (5)
Nb ⁵⁺	80		29.25 (3)	30.06 (6)
Ti ⁴⁺	80	Ascorbic acid	30.17 (7)	31.34 (4)
Nb ⁵⁺	70		29.91 (5)	29.27 (7)

In conclusion the analytical parameters pertaining to the proposed method are given in Table 2.

Table 2. Optical characteristics, precision and accuracy of the spectrophotometric determination of Ni(II) with HNTPh and Am

Parameter	[Ni(HNTPh) ₂](DPhAH) ₂	[Ni(HNTPh) ₂](TPhAH) ₂
The pH range of education and extraction	1.4-7.2	1.4-8.2
The pH range of maximum extraction	3.6-5.0	3.7-5.2
λ_{\max} (nm)	460	465
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	3.34×10^4	3.53×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0172	0.0109
R,%	98.3	98.6
The equation of calibration curves	0.022+0.091x	0.016+0.112x
Beer's law range ($\mu\text{g ml}^{-1}$)	0.06-18	0.06-22
Correlation coefficient	0.9986	0.9989

3.6. Effect of nickel (II) concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Ni(II) may be determined in the range 0.06-22 $\mu\text{g/ml}$ (table 2).

Table 3 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of nickel with the earlier known procedures [22-27, 4].

Table 3. Comparative characteristics of the procedures for determining of nickel

Reagent	pH (solvent)	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range ($\mu\text{g} \cdot \text{mL}^{-1}$)	Ref.
Dimethylglyoxime	12 (CHCl ₃)	470	2.18	0.26 - 2.1	[35]
N-ethyl-3-carbazo- lecarboxaldehyde-3- thiosemicarbazone	6 (C ₆ H ₅ CH ₃)	400	1.11		[36]
7-Methyl-2-chloroquinoli- ne-3-carbaldehyde thio- semicarbazone	6 (CHCl ₃)	410	1.67		[37]
Thiazole-2-carbaldehyde 2-Quinolylylhydrazone	8.7-9.5	522	7.17	0.4-0.7	[38]

pyridoxal-4-phenyl-3-thiosemicarbazone	4-6 (C ₆ H ₅ Cl)	430	1.92	0.5-5	[39]
4-gidroksibenzal'degid-4-bromfenilgidrazin	4	497	1.2	0.01-0.1	[40]
2,6-Ditiol-4-metylphenol + Diphenilquanidine	6.5-7.5 (CHCl ₃)	527	3.24	0.05-3.2	[4]
HNTPh - DPhA	3.6-5.0 (CHCl ₃)	460	3.34	0.06-18	
HNTPh - TPhA	3.7-5.2 (CHCl ₃)	465	3.53	0.06-22	

3.7. Analytical Applications

The developed analytical procedure (as mentioned in Section 2.2.2 and 2.2.3) was used to analyze real samples. Wastewater, Bottom sediments and Carnallite were analyzed. The results are shown in Table 4. Their reliability was verified using the added recovery method.

Table 4. Determination of nickel in Sewage water, Bottom sediments and carnallite

Sample*	Found (%) × 10 ⁻³	Added-recovered method		
		Added (%) × 10 ⁻²	Recovered (%) × 10 ⁻²	RSD (%)
1 ^a	5.65±0.02	1	1.565	1.2
2 ^a	5.64±0.03	1	1.564	1.4
3 ^a	5.70±0.01	1	1.570	1.1
4 ^a	5.63±0.02	1	1.563	1.5
1 ^b	4.14±0.01	1	1.414	1.5
2 ^b	4.29±0.02	1	1.429	1.3
3 ^b	4.70±0.02	1	1.470	1.7
4 ^b	4.63±0.02	1	1.463	1.3
1 ^c	8.74±0.01	1	1.874	1.5
2 ^c	8.63±0.02	1	1.863	1.7
3 ^c	8.92±0.01	1	1.892	1.4
4 ^c	8.80±0.01	1	1.880	1.3

Note: Sample*: a – Sewage water; n=6; P=95%; b – Bottom sediments; n=6; P=95%; c – Carnallite; n=5; P=95%

4. CONCLUSIONS

1. The conditions for the complexation of nickel (II) with HNTPh and Am (DPhA and TPhA) are optimized, such as the formation of the complex in time, pH of the medium, the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law.
2. The spectral characteristics of the complex and the HNTPh reagent were studied which showed high sensitivity and contrast ($\lambda = 165-170$ nm) and the true molar coefficient of light absorption was determined.
3. The mole ratio of nickel: re: agent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Co: HNTPh: Am = 1: 2: 2 composition.

4. The interval of obedience to the Bouguer-Lambert-Beer law ($0.06-22 \mu\text{g} / 5 \text{ ml}$) and the Sendel sensitivity of $0.0109 - 0.0172 \mu\text{g} / \text{cm}^2$ are shown. Based on the achieved results and revealed regularities, a photometric technique for determining nickel (II) with HNTPh and Am.
5. The selectivity of the developed methodology was studied. The developed technique is applied to the analysis of various objects.

REFERENCES

1. Perelman F.M., Zvorykin A.Ya. Cobalt and nickel. Moscow, 1975.
2. Pyatnitsky I.V. Analytical chemistry of elements. Cobalt. Moscow, 1965.
3. Marczenko Z. and Balcerzak M. Metod'y spektrofotometrii v UF I vidimoy oblasti v neorganicheskom analize. Moscow, Binom. Laboratoriya znanij. 2007.
4. Kuliev K.A., Mamedova R.A., Ismailova Sh.Y. Complex Formation in a Liquid-Liquid Extraction System Containing Nickel (II), 2,6-Dithiol-4-methylphenol, and Diphenylguanidine. Journal of Multidisciplinary Engineering Science and Technology. 2016, V. 3, No. 9, pp. 5510-5517.
5. Zalov A.Z., Gavazov K.B. Extractive Spectrophotometric Determination of Nickel with 2-hydroxy-5-iodothiophenol and Diphenylguanidine. Chemistry Journal. 2014, V.4, No. 5, pp. 20-25.
6. Golivand M.V., Mozaffari Yu., Sobhani Sh., Gazemi J. Simultaneous spectrophotometric determination of trace amounts of cobalt, nickel and copper after their concentration in the form of 2-aminocyclopentene-1-dithiocarbonylate complexes on microcrystalline naphthalene using the partial least squares. Jour. analyte. chemistry. 2008, V.63, No. 3, pp. 258-264.
7. Immiyarova G.R., Shcherbinina N.I., Sedykh E.M., Myasoedova G.V., Wolfson E.K. Sorption concentration of copper, lead, cobalt, nickel and cadmium from sea water and their electrothermal atomic-absorption determinations in the sorbent suspension. Jour. analyte. chemistry. 1988, V.43, No. 11, pp. 1981-1983.
8. Ivanov V.M., Kuznetsova O.V. Separate determination of 4- (2-tialylazo) -resorcinates of nickel, zinc and cobalt in the sorbent phase by the method of light metry. Jour. analyte. chemistry. 2000, V.55, No. 9, pp. 998-103.
9. Malik K.A., Rao D.L. Spectrophotometric determination of Co (II), Ni (II), Cu (II), Cd (II), Pd (II), Ru (II), Mo (VI) after their isoamyloxanthogenate extraction in molten naphthalene. Jour. analyte. chemistry. 2000, V.55, No. 8, pp. 830-833.
10. Ignatova S.N., Bolynsky A.B. Determinations of cadmium, cobalt, manganese, copper, nickel and chromium in concentrated solutions of calcium chloride by electrothermal atomic absorption spectrometry. Jour. analyte. chemistry. 2001, V.56, No. 11, p. 1158-1162.
11. Sarakoglu S., Soylak M., Elsie L. Preliminary concentration and separation of iron, cobalt, lead, cadmium and chromium on the Ambersorb 563 sorbent before determination by a flame atomic absorption method. Jour. analyte. chemistry. 2003, V.58, No. 12, pp. 1259-1263.
12. Kuliyevev K.A., Verdizadeh N.A., Suleymanova G.S. Spectrophotometric Determination of Cobalt (II) with 2, 6-Dithiolphenol and Its Derivatives in the Presence of Hydrophobic Amines American Journal of Chemistry 2016, V.6, No. 4, pp. 95-103.
13. Zalov A. Z., Amanullayeva G. I. Spectrophotometric determination of cobalt (II) in a liquid-liquid extraction system containing 2- hydroxy-5-iodothiophenol and diphenylguanidine. IJRDO-Journal Of Applied Science. 2016, V.2, No. 7, pp. 17-25.
14. Kuliev A. M., Aliev S. R., Mamedov F. N., Movsumzade M. Synthesis of 2-aminomethyl- 5-hydroxy alkyl phenols, thiols and their cleavage, Zhurnal organicheskoi khimii.1976. 12. P. 426 Korostelev P.P. Preparation of solutions for chemical analysis works. M.: Publishing house of Academy of Sciences of the USSR. 1964.
15. Bulatov M.I., Kalinkin I.P., Practicheskoe rukovodstvo po photocolorimetriceskim i spectrophotometriceskim metodam analiza, Leningrad, 1976.
16. Pyatnitsky I.V. Analytical chemistry. M., 1990.
17. Nazarenko V. A., Biryuk E. A. A study of the chemistry of reactions of multivalent element ions with organic reagents. Zh. Anal. Khim., 1967. V.22 № 13, pp.57-64.

18. Bellami, L. The infra-red spectra of complex molecules. Moscow: Mir, 1991. P. 592.
19. Akhmedly M. K., Kly'gin A. E., Ivanova L. I., and Bashirov E. A. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. Zhurnal Neorganicheskoi Khimii, 1974. V.19.№8. pp. 2007-2012.
20. Divarova V.V., Racheva P.V., Lekova V., Gavazov K.B., Dimitrov A.N. Spectrophotometric determination of cobalt (II) in a liquid-liquid extraction system containing 4-(2-thiazolylazo) resorcinol and 2,3,5-triphenyl-2H -tetrazolium chloride. Journal of Chemical Technology and Metallurgy, 48, 6, 2013, 623-630.
21. Yoshikuni N., Baba T., Tsunoda N., Oguma K.. Aqueous twophase extraction of nickel dimethylglyoximato complex and its application to spectrophotometric determination of nickel in stainless steel. Talanta. 2005,V. 66, No 1, pp. 40–44.
22. Ramachandraiah C., Kumar J. R., Reddy K. J. et.al.. Development of a highly sensitive extractive spectrophotometric method for the determination of nickel(II) from environmental matrices using N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone. J Environ Manage. 2008 V. 88, №4, pp.729-736.
23. Jadhav V.A., Kulkarni M.U. 7-Methyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone as analytical reagent for copper, cobalt and nickel (II). J. Indian Chem Soc 1992, V. 69, pp.287–288.
24. Otomo M., Watanabe T. and Moriya M.. Solvent Extraction and Spectrophotometric Determination of Nickel (II) with Thiazole-2-carbaldehyde 2-Quinolylyhydrazone Analytical Sciences. 1986, V. 2, No. 6, pp. 549-552.
25. Sarma L. S., Kumar J. R., Reddy K. J. et al. Development of highly sensitive extractive spectrophotometric determination of nickel (II) in medicinal leaves, soil, industrial effluents and standard alloy samples using pyridoxal-4-phenyl-3- thiosemicarbazone. Journal of Trace Elements in Medicine and Biology. 2008, V. 22, pp.285–295
26. Rekha D., Kumar J. D., Jayaraj B. et al. Nickel (II) Determination by Spectrophotometry Coupled with Preconcentration Technique in Water and Alloy Samples Bull. Korean Chem. Soc. 2007, Vol. 28, No. 3 pp. 373-378.