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Research Article

**EXTRACTION-SPECTROPHOTOMETRIC STUDY ON THE
COMPLEX FORMATION IN THE NICKEL (II) - 4-HYDROXY-
3-THIOLBENZOIC ACID - DIPHENYLGUANIDINE SYSTEM**

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Abstract

The conditions for the complexation of nickel (II) with 4-hydroxy-3-thiolbenzoic acid (HTBA) and diphenylguanidine (DPG) are optimized, such as the formation of the complex in time (8 minutes), pH of the medium (pH_{op} 4.2-5.8), the excess of the reagent, and the conditions for obeying the Bouguer-Lambert-Beer law. The spectral characteristics of the complex ($\lambda = 510$ nm) and the HTBA reagent ($\lambda = 195$ nm) were studied which showed high sensitivity and contrast ($\lambda = 315$ nm) and the true molar coefficient ($\epsilon = (3.35 \times 10^4)$) of light absorption was determined. The mole ratio of nickel: reagent is determined by two methods; the equilibrium shift method and the Asmus straight line method, and in both cases the Ni: HTBA: DPG = 1: 2: 2 composition. The interval of obedience to the Bouguer-Lambert-Beer law ($0.5-12 \mu\text{g} / 5 \text{ ml}$) and the Sendel sensitivity of $5.34 \times 10^{-3} \mu\text{g} / \text{cm}^2$ are shown. Based on the achieved results and revealed regularities, a photometric technique for determining nickel (II) with HTBA and DPG.

Key Words: Nickel (II), 4-Hydroxy-3-Thiolbenzoic Acid, Diphenylguanidine, Mixed-Ligand Complexes, Extraction-Photometric Method, Determination

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INTRODUCTION:

Nickel is one of the common components that are constantly present in natural waters. Nickel can get into the water from the soil, as well as as a result of decomposition of plant and animal organisms present in water bodies. Nickel compounds are transferred to tanks with wastewater from nickel workshops, synthetic rubber plants and nickel plants. In rivers of unpolluted and slightly polluted waters, nickel concentrations usually range from 0.8 to 10 $\mu\text{g} / \text{l}$, in polluted waters - several tens of micrograms per liter.

Nickel compounds play an important role in the formation of blood, are oxidative catalysts in the form of organometallic complexes in animals and humans. Increased nickel content has a specific effect on the vascular endothelium (especially the brain and adrenal glands), where multiple hemorrhages occur.

Industrial and waste waters of many industrial enterprises contain high concentrations of heavy and non-ferrous metals, including nickel (II), therefore the determination of nickel content in industrial waters is an actual problem.

Atomic absorption spectrometry of a flame and graphite furnace and spectrophotometric methods provide accurate and rapid determination of nickel in natural and waste waters [1]. However, very often a direct definition cannot be used, since a low concentration of the analyzed or matrix noise.

The most widely used methods for separation and pre-concentration of nickel are liquid-liquid extraction [2], precipitation [3] and chelate resin [4]. Many classical ligands, such as dimethylglyoxime, dithizone and sodium diethyldithiocarbamate, are known as the definition of an extraction / spectrophotometric extractant of nickel [5-7].

Oxyphenolate and hydroxythiophenol nickel complexes are insoluble in chloroform, whereas complexes of a mixed ligand with hydrophobic amines and aminophenols dissolve easily in various organic solvents [8-12]. In this regard, very important reagents are hydroxythiophenols, which contain one hydroxyl and one sulfhydryl groups and are a sulfur-containing analogue of mononuclear polyphenols with one oxygen atom replaced by sulfur atoms.

In the present communication, we describe the extractive spectrophotometric determination of nickel (II) with 4-hydroxy-3-thiolbenzoic acid (HTBA) in presence diphenylguanidine (DPG).

II. EXPERIMENTAL:

A. Reagents and Apparatus

Reagents. All reagents and solvents had an analytical class of reagents. 4-hydroxy-3-thiol-benzoic acid was synthesized and purified as described below, where [13]. Their purity was verified by melting point determination and paper chromatography. Structure of HTBA was confirmed by using NMR and IR spectra {NMR: [^1H NMR (300,18 MHz, C_6D_6); 5.24 (s, 1H- OH), δ 3.32(s, 1H - 1SH), δ 7.11 (s, 3H Ar-H), δ 12.38 (s, 1H - COOH)], IR: [IR (KBr); 3470 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2580 cm^{-1} ν (SH), 1580 cm^{-1} ν (C_6H_5), 1380 cm^{-1} ν (COOH)]}[14]. Solutions of HTBA and DPG in chloroform (0.01M) were used. The extractant was purified chloroform.

To create the optimal pH, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 $\text{mol} \times \text{L}^{-1}$ aqueous solutions of CH_3COOH and NH_4OH . The ionic force of solutions was supported a constant ($\mu = 0.1$) by introduction of the calculated quantity of KCl.

Nickel stock solution (1mg/ml) was prepared by dissolving an appropriate amount of $\text{Ni}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ in 1 ml of nitric acid in a 100 ml volumetric flask and diluted to the mark with water. Nickel standard solutions were prepared by appropriate dilution of the stock solution [15]. The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

Apparatus. 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. Muffle furnace was used for dissolution of the samples. The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany). ^1H -NMR spectra were recorded on "Bruker" Fourier Transform (300.18 MHz) in C_6D_6 .

B. General Procedure

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 HTBA, and a 2.5 –

3.0 mL portion of a 0.01M solution of DPG 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 min 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 ($l=0.5\text{cm}$).

2. 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.

C. RESULTS AND DISCUSSION:

Nickel (II) reacts with HTBA and gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Nickel (II) moved to the

cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When DPG were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

1. Effect of pH

The effect of pH on the formation of the Ni (II) - HTBA - DPG complex was studied in order to find a suitable pH that can be adopted in the determination of nickel (II) (Fig. 1). Extraction of nickel HTBA was performed in the pH range of 2-10. It was found that the absorption was maximum in the pH range of 4.2-5.8. Nickel extraction from the aqueous phase decreases gradually with a lower pH. This is probably due to a decrease in the concentration of the ionized form of HTBA, which causes a decrease in the stability of its complex with Ni^{2+} ions.. It is probably present in the solution in the undissociated state. At $\text{pH} \geq 10$, the complexes were practically not removed, apparently due to a decrease in the degree of protonation of DPG. Although nickel can precipitate in aqueous phase at high pH, but it will dissolve in the presence of the complexing agent HTBA and no precipitate was observed in this experiment.

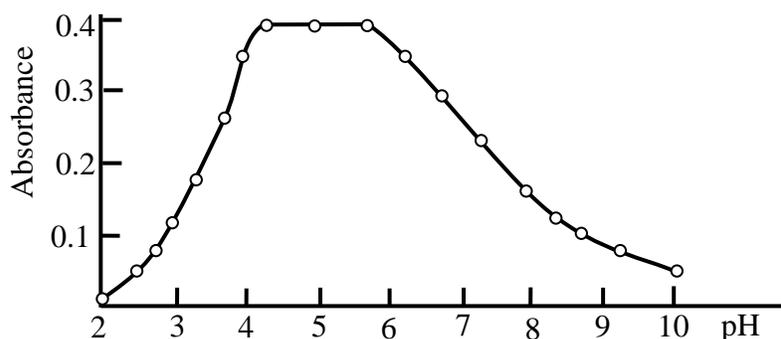


Fig. 1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.
 $C_{\text{Ni}} = 2.035 \times 10^{-5} \text{ M}$, $C_{\text{HTBA}} = 1.25 \times 10^{-3} \text{ M}$, $C_{\text{DPG}} = 2.60 \times 10^{-3} \text{ M}$, $\lambda = 540 \text{ nm}$, $l = 0.5 \text{ cm}$.

2. The choice of extractant

To determine the possible extraction of the tested non-aqueous MLC solvents: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, chlorobenzene, toluene, xylene, *iso*-butanol, and *iso*-pentanol and organic solvent mixtures The most effective for the extraction of Ni (II) in the form of

MLC and equilibrium speeds are chloroform, dichloroethane and carbon tetrachloride. During one extraction, Ni (II) is extracted with 98.4% chloroform as MLC. The extraction ability decreases with increasing number of carbon atoms in the solvent molecule: chloroform > carbontetrachloride > 1,2-dichloroethane > *iso*-butanol > *iso*-pentanol >

chlorobenzene > benzene > toluene > xylene. Depending on the nature of the solvents, the maximum absorption of MLC varies. The rapid separation of the layers and the maximum value of the molar absorption coefficient obtained during the extraction of the complexes with chloroform.

$$D = \frac{[Ni]_{aq}}{[Ni]_{org}},$$

$$R = \frac{100 \times D}{D + \frac{V_{aq}}{V_{org}}} \quad (1)$$

3. Absorption Spectra

Spectra of the extracted ternary Ni - HTBA - DPG complex and the blank are shown in Figure 2. A maximum is recorded at 510 nm, where the blank absorbs insignificantly. It is shifted to 20 nm as compared to the maximum of the binary Ni - HTBA chelate existing in aqueous medium in the pH interval

The concentration of nickel in the organic phase was determined with dimethylglyoxime [7] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference. Extractable complexes evaluated coefficient distribution (D) and the extraction ratio (R,%) [16]:

from 1.2 to 9.3): 490 nm. The observed bathochromic effect is small and gives us grounds to suggest the formation of a ternary compound of the ion-association type. The molar absorptivity was calculated to be $3.35 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

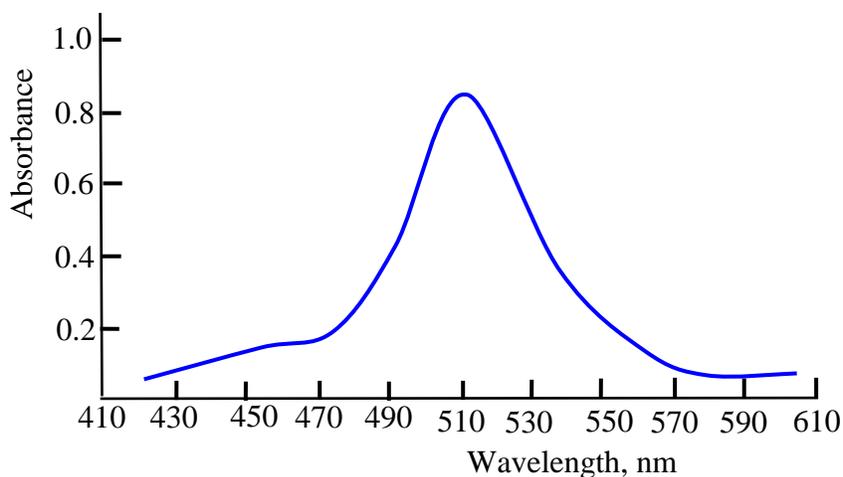


Fig.2. Absorption of mixed-ligand complexes

$C_{Ni} = 2.035 \times 10^{-5} \text{ M}$, $C_{HTBA} = 1.25 \times 10^{-3} \text{ M}$, $C_{DPG} = 2.60 \times 10^{-3} \text{ M}$, pH 4.2-5.8, Shimadzu UV1240, $\ell = 1.0$

4. Effect of reagent concentration and of shaking time

It was also found that there was no adverse effect of excess reagent concentration. Therefore 60-100 fold excess of reagent was suggested in general procedure to ensure complete complexation of Ni (II). The optimum concentrations of the reagents in the organic phase are $1.25 \times 10^{-3} \text{ M}$ (HTBA) and $2.60 \times 10^{-3} \text{ M}$ (DPG).

In present investigation 8 minute shaking time was recommended for quantitative extraction of Ni(II) in

organic phase. The colour of the chloroform extract was found to be stable at least 72 hrs at room temperature.

5. Composition of the complexes and structure formulae

The molar ratios between the components of the ternary complex were found by several methods: straight line method and equilibrium shift method [17] (Figure 3). The results suggest the complex composition of 1:2:2 (Ni: HTBA:DPG).

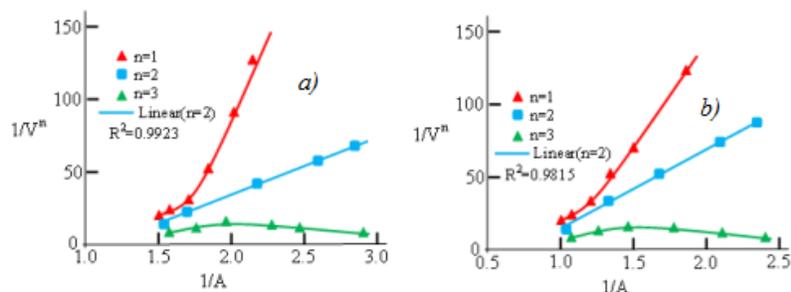


Fig.3. Determination of the *a)* HTBA -to-Ni molar ratio; *b)* DPG-to-Ni; molar ratio by the method of Asmus. $C_{Ni} = 2.035 \times 10^{-5} M$, $C_{HTBA} = 1.25 \times 10^{-3} M$, $C_{DPG} = 2.60 \times 10^{-3} M$, pH 4.2-5.8, $\lambda = 540 \text{ nm}$, Shimadzu UV1240, $\ell = 1.0 \text{ cm}$

The observed decrease in the intensity of the absorption bands at 3200-3600 cm^{-1} with a maximum at 3460 cm^{-1} and the appearance of a wide band in the region of 3050-3150 cm^{-1} shows that the hydroxyl group is involved in the formation of a coordination bond (Figure 4). The disappearance of the band at 2580 cm^{-1} , characteristic of the HTBA spectrum, and the appearance of the corresponding

bands in the spectrum of the complex, which are shifted to a lower frequency, show that sulfur atoms are involved in the formation of the complex. The existence of well-defined absorption bands at 2410 - 2415 cm^{-1} in the IR spectrum of the complex indicates the coordination of DFG in the protonated form [14].

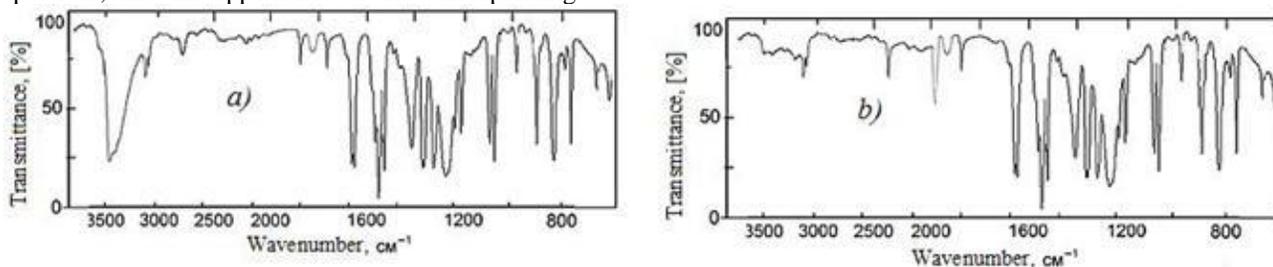


Fig. 5. IR spectra of HTBA (a) and the Ni(II)- HTBA-DPG(b).

Using the Nazarenko method, it was found that Ni (II) in the complexes is present as Ni^{2+} . The number of protons substituted by Ni(II) in one HTBA molecule turned out to be one [18]. Additional experiments according to the Ahmedli method [19] showed that the complex exists in monomeric form in the organic phase (the resulting polymerization

coefficient γ is equal to 1.07). Therefore, we propose the following ternary compound formula: $[\text{Ni}(\text{HTBA})_2](\text{DPGH})_2$; in this formula, DPG is in the protonated form (DPGH^+). Based on the data obtained, we propose the following structure for the selected MLC (Figure 5).

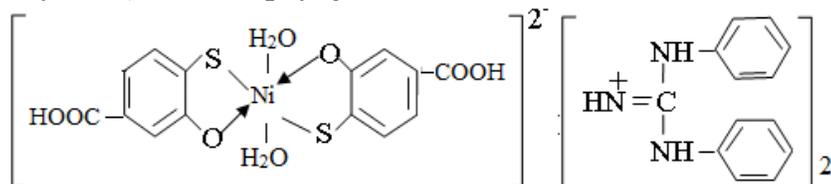


Fig. 5. Suggested structure of the MLC

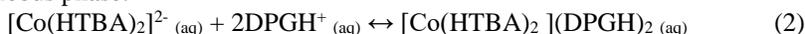
Thermogravimetric study of the complex $Ni(C_7H_3O_3S)_2(C_{13}H_{14}N_3)_2(H_2O)_2$ shown that thermal decomposition of the complex takes place in three

stages: at 60 -124° C water evaporates (weight loss - 4.42 %), at 433 - 500° C-decomposed DPG (weight loss - 49.31%), and at 525 - 530° C - HTBA (weight loss - 41.17 %). The final product of the termolysis of the complex is NiO.

6. Equilibria and equilibrium constants

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of nickel (II) - 4-hydroxy-3-thiolbenzoic acid – diphenylguanidine- water- chloroform system.

Formation in the aqueous phase:



Distribution:



Extraction from water into chloroform:



The equilibrium constants describing these processes are shown in Table 1. The constant of distribution K_D was calculated from the absorption values obtained after single and triple extraction as described above. The association constant β was determined according to a strategy [20] by several independent methods. The constant of extraction K_{ex} was calculated by the formula $K_{ex} = K_D \times \beta$. The recovery factor R was estimated by the dependence (1) and the following value was obtained $R=98.4\%$. All experiments were performed at room temperature of 20-25°C and the calculations were carried out at a probability of 95 %.

Table 1. Calculated values of $\lg\beta$, $\lg K_D$ and $\lg K_{ex}$

Equilibrium	Equilibrium constant	Value
Distribution	$K_D = \frac{[Ni(HTBA)_2](DPGH)_{(org)}}{[Ni(HTBA)_2](DPGH^+)_{2(aq)}}$	$\lg K_D = 0.93 \pm 0.04$
Formation in the aqueous phase	$\beta = \frac{[Ni(HTBA)_2](DPGH)_{(aq)}}{[Ni(HTBA)_2]^{2-}_{(aq)} \times [DPGH^+]_{2(aq)}}$	$\lg \beta = 7.34 \pm 0.11$
Extraction from water into chloroform	$K_{ex} = \frac{[Ni(HTBA)_2](DPGH)_{(org)}}{[Ni(HTBA)_2]^{2-}_{(aq)} \times [DPGH^+]_{2(aq)}}$	$\lg K_{ex} = 6.83 \pm 0.14$

7. Effect of the foreign 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 F^- , Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with determination. The influence of Fe(III) was eliminated by thioglycolic acid; Ti(VI), by ascorbic acid; Cu(II), by thiourea; and Mo(VI) and Nb(V), by oxalate. If a 0.01 mol L⁻¹ solution of EDTA was used, Ti(IV), V(IV), Nb(V), Ta(V), Mo(VI) and Fe(III) exhibited no interference.

8. Beer's law and analytical characteristics

The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions (Table 2). The following straight line equation was obtained for the concentration interval 0.5 – 12 mg mL⁻¹ Ni(II): $y=0.136x+0.062$ ($R^2 = 0.9982$). This value could compete successfully with the ones obtained for similar HBTP-containing complexes (Table 3). The limit of detection and limit of quantification were estimated at 3 times and 10 times standard deviation of the intercept divided by the slope. Sandell's sensitivity was calculated as well. The values of the abovementioned characteristics are included in Table 2. Sandell's sensitivity ($\mu g \cdot cm^{-2}$) 5.34×10^{-4} [21].

Table 2. Analytical characteristics for the extraction-chromogenic system Ni-HBTP-DPG-H₂O-CHCl₃

Parameter	Value
Color	red
The pH range of education and extraction	2.0-10.0
The pH range of maximum extraction	4.2-5.8
Organic solvent	CHCl ₃
R,%	98.4
λ_{\max} (nm)	510
$\Delta\lambda$ (nm)	20
Molar absorptivity (L mol ⁻¹ cm ⁻¹)	3.35×10^4
Concentration of DHTP: M	1.25×10^{-3}
Concentration of Am: M	2.60×10^{-3}
Extraction time (min)	8
Stability constant (lg β)	7.34
Constant of extraction (lgk _{ex})	6.83
Constant of distribution (lgK _D)	0.93
Sandell's sensitivity ($\mu\text{g} \cdot \text{cm}^{-2}$)	5.34×10^{-3}
The equation of calibration curves	$0.136x+0.062$
Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)	0.5 – 12
Correlation coefficient	0.9982
Limit of detection : ng · mL ⁻¹	18
Limit of quantification : ng · mL ⁻¹	36

Furthermore, a comparison of analytical parameter obtained by this method and with that reported by several other extraction spectrophotometric methods for determination of nickel is given in Table 3. As

could be seen, the presented method has high molar absorptivity and is more sensitive; thus it is suitable for trace analysis of nickel in the sample type examined.

Table 3. Comparison of the present method with other reported spectrophotometric methods.

Reagent	pH	λ_{\max} (nm)	Molar absorbtivity, Lmol ⁻¹ cm ⁻¹	Linear range ($\mu\text{g mL}^{-1}$)	Ref.
Thiazole-2-carbaldehyde 2-quinolyl hydrazone	8.7 - 9.5	522	7.17×10^4	0.7	[22]
Dimethylglyoxime	12	470		0.26-2.1	[23]
N-Ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	6.0	400	1.114×10^4	1.2-5.6	[24]
2-Hydroxy-4-isopropoxyacetophenone thiosemicarbazone	9.0	400	8.4×10^2	16.44	[25]
7-Methyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	6.0	410	1.67×10^2	4.0	[26]
2,4-Dihydroxy acetophenone thiosmicarbazone	7.0 - 8.0	385	8.2×10^3	1.0-8.0	[27]
4-hydroxy-3-thiolbenzoic + diphenylguanidine	4.2-5.8	510	3.35×10^4	0.5- 12	This work

9. Analytical applications

As mentioned in section B; 2. the developed analytical procedure was used to analyze tap water. The results are shown in Table 4. Their reliability was verified using an additional recovery method.

Table 4. Determination of nickel content in tap water

Sample	Found (%) $\times 10^{-3}$	Added-recovered method		
		Added (%) $\times 10^{-2}$	Recovered (%) $\times 10^{-2}$	RSD (%)
1	5.72 \pm 0.04	5	5.572	1.2
2	5.58 \pm 0.05	5	5.558	1.4
3	5.72 \pm 0.02	5	5.572	1.1
4	5.67 \pm 0.03	5	5.567	1.5

CONCLUSIONS:

1. In the present communication, we describe the extractive spectrophotometric determination of nickel (II) with HTBA in presence DPG. Structure of HTBA was confirmed by using NMR and IR spectra {NMR: [1H NMR (300,18 MHz, C₆D₆); 5.24 (s, 1H- OH), δ 3.32(s, 1H - 1SH), δ 7.11 (s, 3H Ar-H), δ 12.38 (s, 1H - COOH)], IR: [IR (KBr); 3470 cm⁻¹ ν (OH), 3050 cm⁻¹ ν (CH), 2580 cm⁻¹ ν (SH), 1580 cm⁻¹ ν (C₆H₅), 1380 cm⁻¹ ν (COOH)]};
2. Extraction of nickel HTBA was performed in the pH range of 2-10. It was found that the absorption was maximum in the pH range of 4.2-5.8. The most effective for the extraction of Ni (II) in the form of MLC and equilibrium speeds are chloroform, dichlorotane and carbon tetrachloride. During one extraction, Ni (II) is extracted with 98.4% chloroform as MLC.
3. A maximum is recorded at 510 nm, where the blank absorbs insignificantly. It is shifted to 20 nm as compared to the maximum of the binary Ni-HTBA chelate existing in aqueous medium in the pH interval from 1.2 to 9.3): 490 nm. The molar absorptivity was calculated to be 3.35 \times 10⁴ L mol⁻¹ cm⁻¹.
4. The optimum concentrations of the reagents in the organic phase are 1.25 \times 10⁻³ M (HTBA) and 2.60 \times 10⁻³ M (DPG).
5. In present investigation 8 minute shaking time was recommended for quantitative extraction of Ni(II) in organic phase. The colour of the chloroform extract was found to be stable at least 72 hrs at room temperature.
6. The molar ratios between the components of the ternary complex were found by several methods: Starik-Barbanel relative yield method, straight line method, equilibrium shift method and crossed

lines method. The results suggest the complex composition of 1:2:2 (Ni: HTBA:DPG).

7. The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions. The following straight line equation was obtained for the concentration interval 0.5-12 mg mL⁻¹ Ni(II): $y=0.136x+0.062$ ($R^2=0.9982$).

The developed analytical procedure was used to analyze tap water. Their reliability was verified using an additional recovery method.

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