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Ali Z Zalov
Department of Analytical
Chemistry, Azerbaijan State
Pedagogical University, 68
Gadzhibekova St, Baku 1000,
Azerbaijan.

Nazani A Novruzova
Department of Analytical
Chemistry, Azerbaijan State
Pedagogical University, 68
Gadzhibekova St, Baku 1000,
Azerbaijan.

Gulnare V Babayeva
Department of Analytical
Chemistry, Azerbaijan State
Pedagogical University, 68
Gadzhibekova St, Baku 1000,
Azerbaijan.

Correspondence
Ali Z Zalov
Department of Analytical
Chemistry, Azerbaijan State
Pedagogical University, 68
Gadzhibekova St, Baku 1000,
Azerbaijan.

Extraction studies on the system nickel (ii) – 2-hydroxy-5-iodothiophenol: Water: Chloroform

Ali Z Zalov, Nazani A Novruzova, Gulnare V Babayeva

Abstract

Nickel (II) forms well chloroform-extractable ternary complex with 2-hydroxyl-5-iodothiophenol (HITP) and diphenylguanidine (DPG). The wavelength of maximum absorption, molar absorptivity, Sandell's sensitivity, optimum pH interval, limit of detection, range of linearity, and relative standard deviation of the developed procedure were 480 nm, $2.64 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, 2.23 ng cm^{-2} , 4.5-6.8, $0.02 \mu\text{g mL}^{-1}$, $0.07\text{-}3.6 \mu\text{g mL}^{-1}$, and $\leq 1.8\%$, respectively. The molar ratio of components in the complex is 1 : 2 : 2. It was applied for nickel determination in metallic magnesium and a geological sample – carnallite.

Keywords: Nickel (II), 2-Hydroxy-5-Iodothiophenol, Ternary complex, Liquid-liquid extraction

1. Introduction

Nickel is a transition metal with wide application in industry and important roles in the biology of microorganisms and plants. Most of the produced nickel is applied for production of stainless steels, alloys, and nickel plating. Over 3000 alloys containing nickel are known [1], including these with Mg, which are considered promising materials for optical switching [2], gaseous hydrogen storage [3] and production [4].

In the Earth's crust, nickel occurs most often in combination with sulfur (pentlandite, millerite), iron (pentlandite, kamacite, taenite), arsenic (nickelite, nickel galena), and magnesium (garnierite). It is present in all types of soils, in fossil fuels, volcanic emissions, and iron meteorites.

Several analytical methods have been used for nickel determination, including flame atomic absorption spectrophotometry [7], graphite furnace atomic absorption spectrometry [8], electrothermal atomic absorption spectrometry [9], atomic fluorescence spectrometry [10], inductively coupled plasma-optical emission spectrometry [11], and spectrophotometry [12-18].

The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation. They are often based on ion-association complexes composed of intensively coloured anionic chelate and bulky organic cation which makes the complex hydrophobic and easily extractable into organic solvents [19-22].

In the present paper we study the complex formation in a liquid-liquid extraction system containing Ni (II), 2-hydroxy-5-iodothiophenol (HITP) and diphenylguanidine (DPG), and show the potential of this system for Ni (II) determination in real samples. HITP, an iodine-containing analogue of the known analytical reagents 2-hydroxy-5-chlorothiophenol [23-30] and 2-hydroxy-5-bromothiophenol [26-28, 30], has –OH and –SH groups in ortho-position. Hence, we expected that this reagent would form stable chelate structures with metal ions, like Ni(II), which have ionic radii close to 0.07-0.08 nm.

2. Materials and methods

2.1 Reagents and instruments

Stock solution of Ni (II) was prepared by dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, puriss. p.a.) in distilled water; it was standardized gravimetrically with dimethylglyoxime. Working Ni (II) solutions (0.1 mg mL^{-1}) were prepared by appropriate dilution of the stock solution [22]. HITP was synthesized according to the procedure [31]. DPG was a Sigma-Aldrich product (97%). Chloroform solutions of HITP (0.01 mol L^{-1}) and DPG (0.025 mol L^{-1}) were used. To create the optimum acidity, 0.1 mol L^{-1} solutions of HCl, NaOH, or ammonium acetate buffers were applied. The organic solvent was alcohol-free chloroform. The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR) and KFK 2 photocolorimeter (USSR). (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.

2.2 Procedure

An aliquot containing no more than 90 μg of nickel was placed in a calibrated tube with ground-glass stopper. Then chloroform solutions of HITP (0.6 mL) and DPG (0.4 mL) were added and the chloroform phase was adjusted to 5 mL; the volume of the aqueous phase and pH were adjusted to 25 mL and 5.0, respectively. After 10 min of shaking, a portion of the organic extract was transferred through a filter paper into a cell and the absorbance was read at $\lambda=480$ nm against chloroform. The nickel content was found from a calibration graph.

2.3 Preparation of a solid complex

Solutions of Ni (II), HITP and DPG were mixed in a 1:2:2 molar ratio and the extraction was performed at the optimum pH. The procedure was carried out several times and the extracts were collected in a beaker. Then the beaker was carefully heated up to 70-85°C for complete evaporation of the solvent [32].

2.4 Dissolution of carnallite

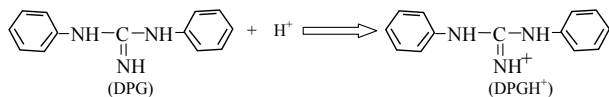
A *ca.* 2.0 g sample of carnallite was placed in a 50-mL beaker. 0.5 mL of a 3% NaF solution and 5 mL of HNO_3 (1:20) were added and the beaker was heated on an electric heater. After cooling, the obtained solution was neutralised with ammonia to pH 6 (universal paper indicator); then it was transferred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

2.5 Dissolution of magnesium

A 0.5-0.6 g sample of magnesium was carefully dissolved in 10 mL of HNO_3 (1:2) and the solution was evaporated to moist salts on an electric heater. After cooling, 3 mL of water were added to dissolve the salts and pH was adjusted to *ca.* 6 with NaOH. The solution was quantitatively transferred into a 25-mL calibrated flask; then distilled water was added to the mark.

2.6 Charge of the complex nickel

At pH 1.6–7.8, the complex of nickel (II) is not extracted by inert organic solvents. To determine the sign of the complex charge, ion exchange chromatography was used: AV-17 anion exchanger in chloroform absorbs a part of solution; the chromatographic column is colored in orange, and nickel is not detected in the filtrate. The anion complex is extracted in the presence of a DPG, wherein the complex stability increases, and the color becomes more saturated. To neutralize the charge of the anion complex, diphenylguanidine is used as a hydrophobic amine, which transforms into a diphenylguanidine ion in acidic medium, that is (scheme 1):



Scheme 1: Protonation molecule of diphenylguanidine.

3. Results and Discussion

3.1. Choice of organic solvent

In a slightly acidic medium, HITP reacts with nickel(II) to produce a coloured anionic complex. In the presence of the cationic ion-association reagent DPG a ternary complex is formed; it is sparingly soluble in water but is easily soluble in organic solvents. The following organic solvents were tested in our experiments: chloroform, 1,2-dichloroethane, carbon

tetrachloride, benzene, chlorobenzene, toluene, xylene, isobutanol, isopentanol, and diethyl ether. The distribution coefficients and extraction rates with these solvents were evaluated. The best ones were chloroform, 1,2-dichloroethane, and carbon tetrachloride. All further investigations were performed with chloroform.

The concentration of nickel(II) in the organic phase was determined photometrically by using dimethylglyoxime after reextraction, and in the aqueous phase, its concentration was found by the difference.

Extractable complexes evaluated coefficient distribution (D) and the extraction ratio (R , %) [30]:

$$D = \frac{[Ni]_{org}}{[Ni]_{aq}} ; \quad R = \frac{100 \times D}{D + \frac{V_{aq}}{V_{org}}}$$

At the optimum conditions this solvent provides degrees of extraction $R=97.6\%$.

3.2 Effect of solution pH

The effect of pH on the intensity of the color reaction is shown in the Fig. 1. The optimum pH for complex formation and extraction is 4.5-6.8. Hence further analytical investigations were carried out in media of pH 5. 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 HITP. Probably, it is present in the solution in the non-dissociated state. At $\text{pH} \geq 7.6$, the complexes were hardly extracted, obviously because of the decrease in the degree of DPG protonation.

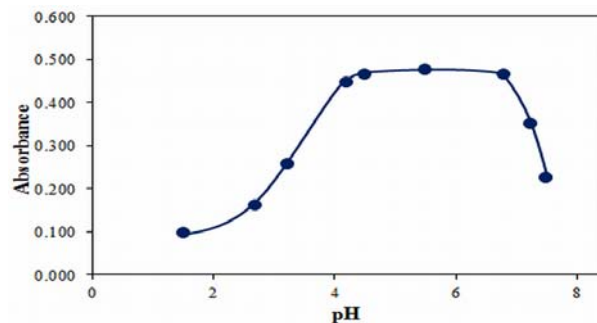


Fig 1: Absorbance of ternary complex vs. pH of the aqueous phase. $C_{Ni}=3.5 \times 10^{-5}$ mol L^{-1} , $C_{HITP}=1.2 \times 10^{-3}$ mol L^{-1} , $C_{DPG}=2.0 \times 10^{-3}$ mol L^{-1} , $l=0.5$ cm

3.3 Effect of the concentrations of reagents and incubation time

The optimum concentrations of the reagents in the organic phase are 1.2×10^{-3} mol L^{-1} (HITP) and 2.0×10^{-3} mol L^{-1} (DPG) (Fig. 2). The extraction equilibrium with this solvent is achieved for *ca.* 6-7 min, but we carried out the extraction for 10 min.

3.4 Optimum operating conditions

The absorption bands in the visible range of the ternary Ni (II)-HITP-DPG complexes are symmetrical and relatively narrow (Fig. 3). The absorption maximum of the ternary complex lies at $\lambda=480$ nm, while the maximum of HITP is at $\lambda=288$ nm. Therefore the colour reaction is very contrast ($\Delta\lambda=192$ nm). The molar coefficient of light absorption is 2.64×10^4 .

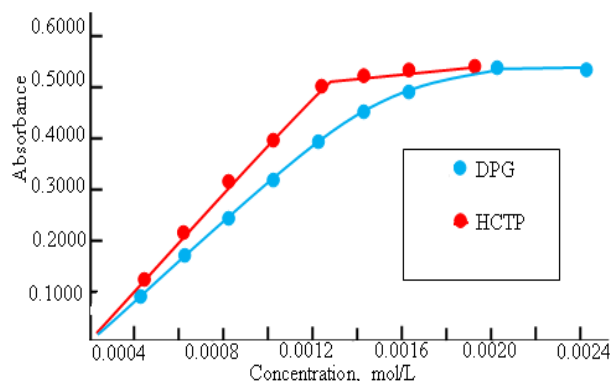


Fig 2: Absorbance of Ni(II) extracts with HITP and DPG concentration of the reagent plots. $C_{Ni(II)} = 1.08 \times 10^{-5} \text{ mol L}^{-1}$, pH 4-6, KFK-2, 440nm, $\ell=0.5 \text{ cm}$.

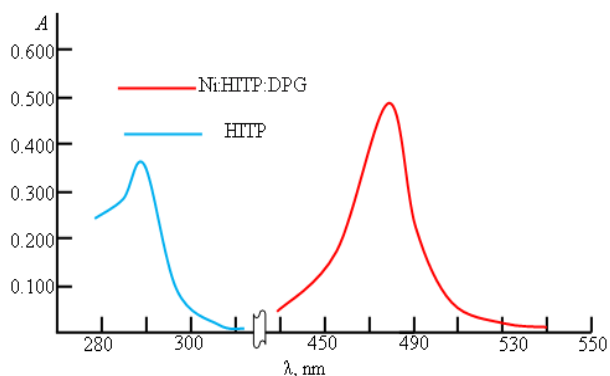


Fig 3: Absorption of mixed-ligand complex. $C_{Ni(II)} = 1.08 \times 10^{-5} \text{ mol L}^{-1}$, pH 4-6, KFK-2, $\ell=0.5 \text{ cm}$.

3.5 Composition, structure and stability

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 (Fig.4) and crossed lines method [33]. The results suggest the complex composition of 1:2:2 (Ni:HITP:DPG).

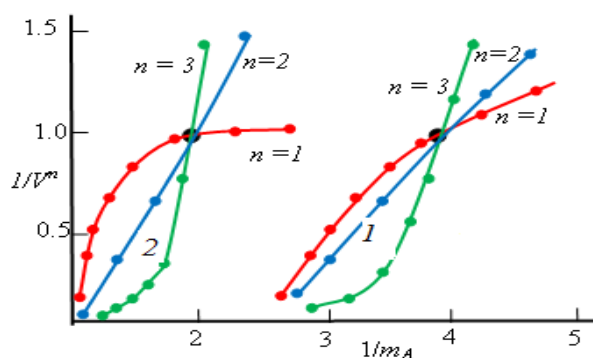


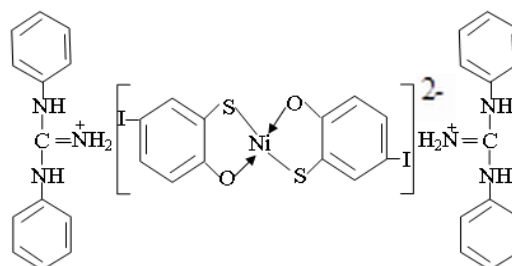
Fig. 4: Determination of complex composition by Asmus: 1-HITP; 2-DPG; $C_{Ni(II)} = 1.08 \times 10^{-5} \text{ mol L}^{-1}$, pH 4-6, SF-26, $\ell=1.0 \text{ cm}$.

In order to establish the degree of aggregation of the complex into the organic phase calculating the degree of polymerization in the equation derived in [34]:

$$\gamma = \frac{\lg \frac{A_i}{A_k}}{(q+1) \lg \frac{C_i \ell - A_i}{C_k \ell - A_k}}$$

where γ is the degree of polymerization, A_i and A_k are the absorbances of the extracts of the compounds in experiments i and k , ε is the molar absorptance, l is the optical path length (in cm), q is the number of molecules of the reagent and C_i and C_k are concentrations of tungsten in experiments i and k . The calculation show that complex are in monomer form ($\gamma=1.0$)

The existence of clearly defined absorption bands at 2410 - 2415 cm^{-1} in the IR-spectrum of the complex indicates the coordination of the DFG in the protonated form [35]. The disappearance of the band at 2580 cm^{-1} , characteristic for the spectrum of HITP, and appearance of corresponding bands in the spectrum of the complex, which are shifted toward lower frequency, suggests that the sulphur atoms are involved in complex formation. 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 broad band in the region of 3050-3150 cm^{-1} shows that the hydroxyl group participates in the formation of a coordination bond [35, 36]. Proceeding from the obtained data, we propose the following structure for the extracted ternary complex (Scheme 2).



Scheme 2: Suggested structure of the ternary complex

For evaluation of the stability of the complex we used the method of crossed lines [41]. The experiments were performed with constant Ni (II) and DPG concentrations and two different HITP concentrations. The calculated value of the two-phase stability constant was $\text{Log } \beta = 6.62 \pm 0.01$.

3.6 Calibration graph and analytical characteristics

In conclusion the analytical parameters pertaining to the proposed method are given in (Table 1). The Ni(II) extracts conform to the Beer's law in the range of 0.07-3.6 $\mu\text{g mL}^{-1}$ with a correlation coefficient of 0.9993 (10 standards used). The limit of detection, calculated according to [34] was 0.02 $\mu\text{g mL}^{-1}$. The straight-line equation was $A=0.449C_{Ni}+0.02$, where A is the absorbance and C_{Ni} is the nickel(II) concentration in $\mu\text{g mL}^{-1}$. The corresponding molar absorptivity was $\varepsilon_{480}=2.64 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; it is higher than the molar absorptivities reported for similar liquid-liquid extraction-spectrophotometric procedures involving pyridoxal-4-phenyl-3-thiosemicarbazone ($\varepsilon_{430}=1.92 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [37], N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone ($\varepsilon_{400}=1.114 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [38], α -furildioxime ($\varepsilon_{435}=2.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [22], sodium isoamyl xantene ($\varepsilon_{360}=1.20 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [17], 1-hydroxy-2-acetonaphtoneoxime ($\varepsilon_{396}=5.7 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [39], 2-hydroxy-1-naphthaldoxime ($\varepsilon_{396}=8.1 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [40], dimethylglyoxime ($\varepsilon_{380}=1.9 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [41], etc.

Table 1: Optical characteristics, precision and accuracy of the spectrophotometric determination of Ni (II) with HITP and DPG.

Parameter	Value
Color	orange
The pH range of education and extraction	4.5 – 6.8
The pH range of maximum extraction	1.7 - 7.6
Concentration of HCTP: mol· L ⁻¹	1.2×10 ⁻³
Concentration of DPG: mol· L ⁻¹	2.0×10 ⁻³
Organic solvent	CHCl ₃
Extraction time	10 min
λ _{max} (nm)	480
Molar absorptivity (L· mol ⁻¹ mL ⁻¹)	2.64 × 10 ⁴
Sandell's sensitivity (μg mL ⁻¹)	0.02
R, %	97.6
Two-phase stability constant (Log β)	6.62±0.01
The equation of calibration curves	0.449C _{Ni} +0.02
Correlation coefficient	0.9993
Beer's law range (μg· mL ⁻¹)	0.07-3.6

3.7 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⁻, SO₃²⁻, SO₄²⁻ and C₂O₄²⁻ 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 (Table 2). 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.

Table 2: Influence of foreign ions on the determination of nickel (30 μg) with HITP and DPG

Ion	Molar ratio to nickel	Masking agent	Found (μg)	RSD (%)
Co(II)	50		30.0	2
W(VI)	50		29.8	2
Fe(II)	200		29.8	3
Cd(II)	200		29.6	4
Al(III)	180		30.0	2
Fe(III)	60	Thioglycolic acid	30.2	4
Zr(IV)	50		29.8	3
Cu(II)	25	Thiourea	29.6	5
Hg(II)	40		30.2	5
Ti(IV)	30		29.6	3
V(IV)	20		29.6	3
Mo(VI)	10	EDTA	30.4	4
Cr(III)	120		29.8	4
Nb(V)	50	C ₂ O ₄ ²⁻	30.1	5
Ta(V)	50	Ascorbic acid	30.1	5
UO ₂ ²⁺	50		29.2	4

3.8 Determination of nickel in magnesium and carnallite

The developed analytical procedure was applied for the analysis of real samples. Four replicates of metallic magnesium and four samples of carnallite were subjected to analysis. The results are shown in Table 3; their reliability was verified by the added–recovered method.

Table 3: Determination of nickel in metallic magnesium and carnallite

Method	Reagent	Sample	Found (%) ×10 ⁻⁴	Added-recovered method		
				Added (%) ×10 ⁻³	Recovered (%) ×10 ⁻³	RSD (%)
Standard	Dimethylglyoxime	1 ^a	7.72±0.03	1.0	1.772	1.6
	α-furildioxime	2 ^a	7.65±0.01	1.0	1.765	1.3
Proposed	HITP + DPG	3 ^a	7.65±0.01	1.0	1.765	1.4
	HITP + DPG	4 ^a	7.64±0.02	1.0	1.764	1.5
	HITP + DPG	5 ^a	7.70±0.02	1.0	1.770	1.2
	HITP + DPG	6 ^a	7.63±0.02	1.0	1.763	1.3
Standard	Dimethylglyoxime	1 ^b	8.85±0.01	1.0	1.885	1.7
	α-furildioxime	2 ^b	8.70±0.01	1.0	1.870	1.4
Proposed	HITP + DPG	3 ^b	8.71±0.01	1.0	1.871	1.3
	HITP + DPG	4 ^b	8.69±0.02	1.0	1.869	1.8
	HITP + DPG	5 ^b	8.90±0.01	1.0	1.890	1.2
	HITP + DPG	6 ^b	8.81±0.01	1.0	1.881	1.5

Note: a – Metallic magnesium; n=6; P=0.95; b – Carnallite; n=5; P=0.95

4. Conclusion

In the present work we developed a selective, sensitive, reliable and inexpensive liquid-liquid extraction-spectrophotometric method for Ni(II) determination based on a ternary complex with a new analytical reagent - 2-hydroxyl-5-iodothiophenol. The method was applied for nickel determination in real industrial and geological samples (metallic magnesium and carnallite) and satisfactory results were obtained.

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