LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC CHARACTERIZATION OF SOME NEW TERNARY ION-ASSOCIATION COMPLEXES OF COBALT (II) AND NICKEL (II)

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ABSTRACT

Complex formation and liquid-liquid extraction were studied in systems containing M(II) (M = cobalt or nickel), 2-hydroxy-5-iodothiophenol (HITP), hydrophobic amines (Am), water and chloroform. Two different Am were used: diphenylguanidine (DPG) and triphenylguanidine (TPG).The optimum conditions for extraction of Co(II) and Ni(II) as ternary complexes with the general formula $[M(HITP)_2](AmH^+)_2$ were found: pH, shaking time, concentration of HITP and concentration of Am. Some key constants (constants of extraction – K_{ex}, constants of association – β, constants of distribution – K_D) and analytical characteristics (molar absorptivities – εmax, Sandell's sensitivities – SS, limits of detection – LOD, limits of quantification – LOQ, etc.) were determined.

Key words: cobalt, nickel, 2-hydroxy-5-iodothiophenol, diphenylguanidin triphenylguanidin, solvent extraction

1. INTRODUCTION

One of the important problems of modern analytical chemistry is the determination of microgram amounts of elements in natural and synthetic materials. Along with the creation of new electoral physical and physico-chemical methods, leading the trend of development of analytical chemistry is to reduce the limit of detection of the element. Among physico-chemical methods for the analysis of availability, ease of performance, reliability, and low values of the limit of detection is beneficial you fissile-photometric methods [1].

Cobalt (II) and nickel (II), are biologically active metals. It was found that excessive "manmade" data flow of metal compounds in the body has a toxic effect on the metabolism. An excess of salts cobalt and nickel causes morphological changes in the cell and, thus, has a carcinogenic effect on him [2].

Cobalt and nickel (M) are the two post-transition metals of the highest industrial interest. Cobalt and Nickel is a transition metal with wide application in industry and important roles in the biology of microorganisms and plants. They is used in many recognizable products, such as stainless steels, alloys, coins, rechargeable batteries, permanent magnets, magnetic shields, superconductors, electric guitar strings, microphone capsules, green tint in glass, and catalysts for various industrial processes, such as hydrogenation of vegetable oils, cracking of petroleum, purification of coal gas, synthesis of organic and inorganic compounds, etc. Most of the produced cobalt and nickel is applied for production of stainless steels and alloys. The chief criteria of use are nickel's resistance to alkalis, acids, and air oxygen, malleability, attractive finish and appearance, and excellent ability to alloy with both ferrous and nonferrous metals [3,4].

Several analytical methods have been used for determination cobalt and nickel, including flame atomic absorption spectrophotometry [1,3-5], graphite furnace atomic absorption spectrometry [1,3,4,6], electro-thermal atomic absorption spectrometry [1,3,4,7], atomic fluorescence spectrometry [1,3,4,8], inductively coupled plasma-optical emission spectrometry [1,3,4,9], and spectrophotometry [1,3,4,10].

2. MATERIALS AND METHODS

2.1. Reagents and instruments

Stock solution of Ni(II) was prepared by dissolving $NiCl_2 \cdot 6H_2O$ (Sigma-Aldrich, puriss. p.a.) in distilled water. Working Ni(II) solutions (0.1 mg mL^{-1}) were prepared by appropriate dilution of the stock solution [11].

Cobalt standard solution (1000 mg L^{-1}; $Co(NO_3)_2$) was purchased from Merck Darmstadt (Germany). Working solutions ($C_{Co} = 1.7 \times 10^{-4}$ mol L^{-1}) were prepared by diluting appropriate volumes of the stock solution [11].

The concentration of the cobalt and nickel solution was adjusted gravimetrically [1].

HITP was synthesized according to the procedure [12]. Am was a Sigma-Aldrich product (97%). Chloroform solutions of HITP (0.01 mol L^{-1}) and Am (0.025 mol L^{-1}) were used.

To create the optimum acidity, 0.1 mol L^{-1} solutions of HCl, NaOH, or ammonium acetate (CH_3COOH+CH_3COONa) buffers were applied.

The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR), KFK 2 photocolorimeter (USSR), and a Camspec M508 spectrophotometer (UK). 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 *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.

2.3. 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.

2.4. Procedure for establishing the optimum operating conditions

Aliquots of M(II) solution, HİTP solution (up to 2.0 mL), AM solution (up to 2.0 mL) and buffer solution (pH ranging from 3.2 to 10) were introduced into 100-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 25 mL. Then 1.0 mL of chloroform was added and the funnels were shaken for a defined period of time (up to 8 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.

2.5. Procedure for determination of the distribution constants

The distribution constants K_D were found from the ratio $K_D = A_1/(A_3–A_1)$ where A_1 is the light absorbance obtained after a single extraction (at the optimum operating conditions – see Table 1) and A_3 is the absorbance obtained after a triple extraction under the same conditions [13,14]. The single extraction and the first stage of the triple extraction were performed with 10 mL chloroform. The organic layers were transferred into 25-mL calibrated flasks and the flask for the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding a 7-mL portion of chloroform to the aqueous phase which remained after the first stage. The third stage was performed in the same manner. The two successive organic layers were transferred to the flask containing the organic layer obtained after the first stage. The volume was brought to the mark with chloroform and shaken for homogenization. Absorbances A_1 and A_3 were measured against a blank.

3. RESULTS AND DISCUSSION

3.1.Absorption spectra

Spectra of the extracted in chloroform ternary M(II)-HİTP-Am complexes are shown in Fig. 1. Maxima are recorded at 598-608 nm for the compounds of Co(II) (curves 1 and 2) and at 480-483 nm for the compounds of Ni(II) (curves 3 and 4). These maxima are shifted to 6-10 nm as compared to the maxima of the binary M(II)-HİTP chelates $[ML_2]^{2-}$ existing in aqueous solutions with similar pH [λ_{max}Co(II)-HİTP=592 nm (curve 3); λ_{max} Ni(II)-HİTP=470 nm (curve 6)]. The observed bathochromic effects are small and suggest the formation of ternary compounds of the ion-association type.

All colour reactions were very contrast since the initial solutions are colourless (λ_{max} (HITP) = 280 nm). Thus, bathochromic shift makes 280-408 nm. Contrast of reactions was high i.e. initial reagents are colourless while complexes are intensively painted.

Table 1 . Optimum operating conditions

Extraction system	Extraction time, s	pH	C_{HITP}, mol L^{-1}	C_{Am}, mol L^{-1}	λ_{max}, nm	$\Delta\lambda_{max}$, nm
Co(II)-HITP-DPG-H_2O-$CHCl_3$	240	5.5-7.9	2.0×10^{-3}	2.5×10^{-3}	598	398
Co(II)-HITP-TPG-H_2O-$CHCl_3$	180	5.5-7.8	2.0×10^{-3}	2.5×10^{-3}	608	408
Ni(II)-HITP-DPG-H_2O-$CHCl_3$	120	4.5-6.8	1.2×10^{-3}	2.0×10^{-3}	480	280
Ni(II)-HITP-TPG-H_2O-$CHCl_3$	40	4.4-6.7	1.2×10^{-3}	2.0×10^{-3}	483	283

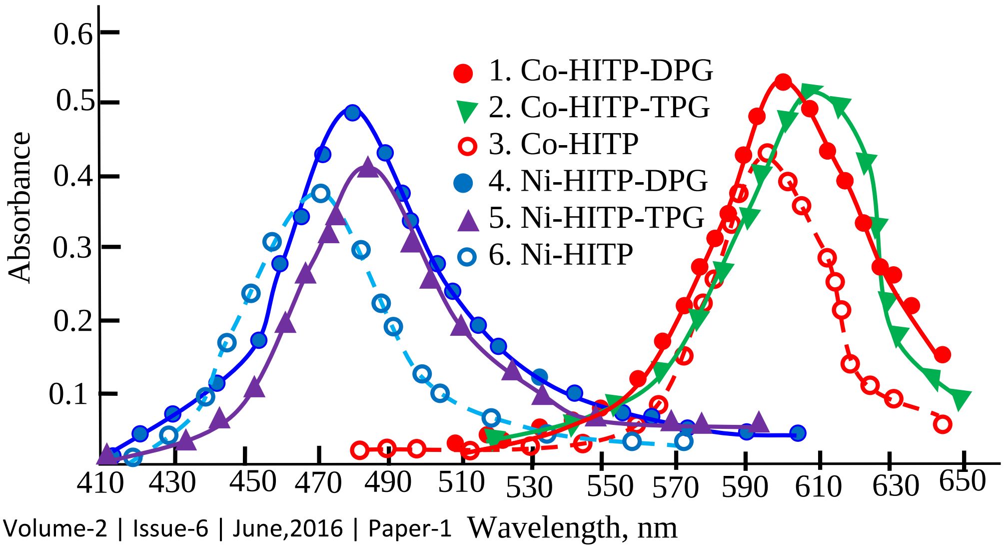

Fig. 1. Absorption spectra of the complexes
$C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{Ni}=3.5 × 10^{-5} mol L^{-1},
1, 2, 3 – C_{HITP} = 2.0×10^{-3}mol L^{-1}, C_{Am} = 2.5×10^{-3} mol L^{-1}, pH 5.5-7.9;
4, 5, 6 – C_{HITP}= 1.2 × 10^{-3} mol L^{-1}, C_{Am}=2.0 × 10^{-3} mol L^{-1}, pH 4.5-6.8.

The following other comments can be made regarding the spectra shown in Fig. 1:
a) The absorbances of both cobalt complexes (Co-HITP-DPG and Co-HITP-TPG; curves 1 and 2) are higher than those of the nickel complexes (Ni-HITP-DPG and Ni-HITP-TPG; curves 4 and 5).
b) The absorbances of both DPG-containing complexes (Co-HITP-DPG and Ni-HITP-DPG; curves 1 and 4) are higher than those of the corresponding TPG-containing complexes (curves 2 and 5).
c) The absorbance of the nickel complex with participation of TPG (curve 5) is significantly lower than that of the corresponding cobalt complex (curve 2).

3.2. Effect of pH

The effect of pH on the extraction of the ternary species is represented on Fig. 2. It could be seen that Co(II)- HITP species are extracted in a great extent at pH values in the range 5.5–7.8 (with TPG) or 5.5–7.9 (with DPG). Ni(II) complexes are extracted at lower pH: 4.4–6.7 (with TPG) or 4.5–6.8 (with DPG). Ni(II) complexes are extracted at lower pH: 4.4–6.7 (with TPG) or 4.5–6.8 (with DPG). DPG appears to be a suitable reagent for simultaneous extraction of Co(II) and Ni(II) (curves 1 and 3; pH = 5.6).

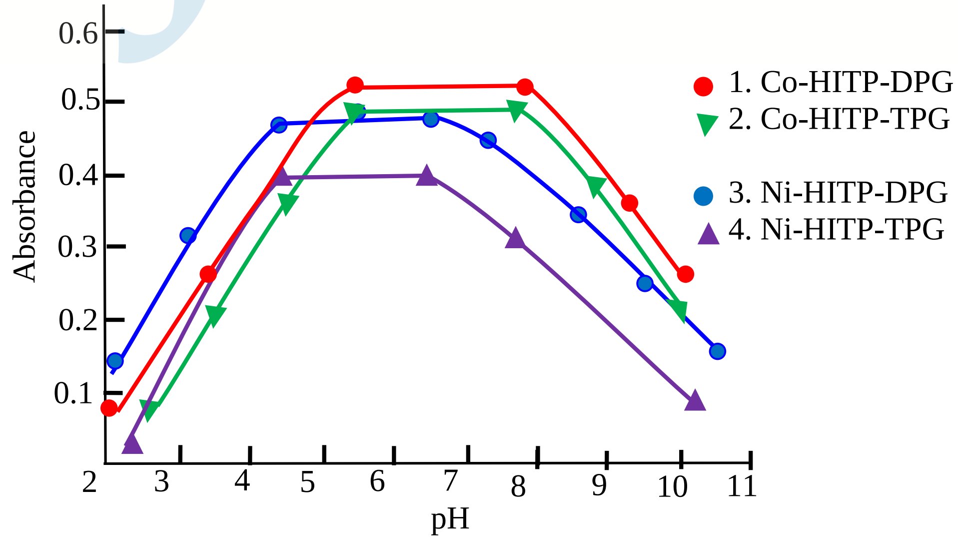

Fig. 2. Absorbance of M(III)-HITP-Am complexes in chloroform vs. pH of the aqueous phase plots
1, 2 – $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{HITP} = 2.0×10^{-3}mol L^{-1}, C_{Am} = 2.5×10^{-3} mol L^{-1}, λ = 590 nm;
3, 4 – C_{Ni}=3.5 × 10^{-5} mol L^{-1}, C_{HITP}= 1.2 × 10^{-3} mol L^{-1}, C_{Am}=2.0 × 10^{-3} mol L^{-1}, λ = 490 nm.

3.3. Effect of reagent concentration

The optimum concentrations of HITP and Am are shown in Table 1. Large excesses of the reagents have no effect on the absorbance, but could make the reproducibility worse. Under the optimum conditions the colouration of the organic extracts remains constant for at least an hour at room temperature.

3.4. Effect of shaking time

Unlike single-ligand complexes, mixed-ligand complexes of M(II) with HITP and Am were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction.The effect of shaking time on the extraction is shown in Fig. 3. The extraction equilibria for Co-containing systems (curves 1 and 2) are reached for about a 4-8 minutes and longer shaking time does not affect the absorbance. However, in the case of Ni(II) extraction, the experimental curves have a different character showing maxima at about 40 seconds (curve 3) or 2 minutes (curve 4). The maximum for the Ni- HITP-TPG system is fairly sharp. This information could be helpful for development of a procedure for Co(II)/Ni(II) separation or elimination of Co(II) interference during TPG-based extraction-spectrophotometric determination of Ni(II).

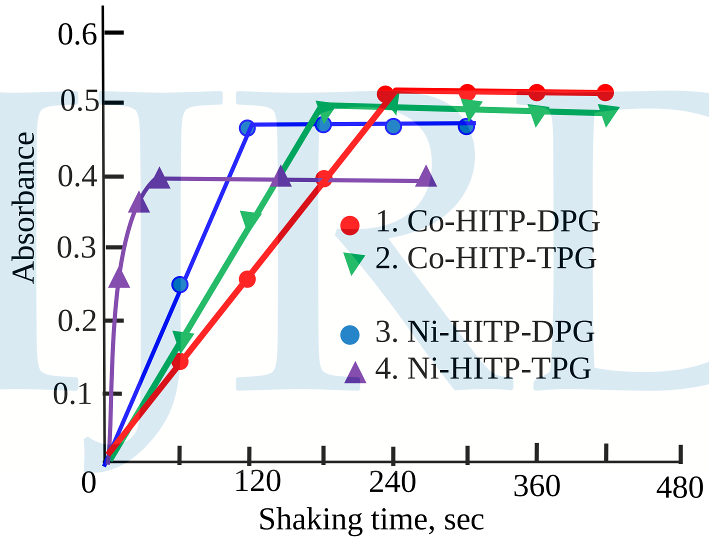

Fig. 3. Effect of shaking time on the absorbance

1, 2 – $C_{Co(II)} = 1.7 \times 10^{-5}$mol L^{-1}, $C_{HITP} = 2.0 \times 10^{-3}$ mol L^{-1}, $C_{Am} = 2.5 \times 10^{-3}$ mol L^{-1}, pH 5.5-7.9, λ = 590 nm;
3, 4 – C_{Ni}=3.5×10^{-5} mol L^{-1}, C_{HITP}= 1.2×10^{-3} mol L^{-1}, C_{Am}=2.0×10^{-3} mol L^{-1}, pH 4.4-6.8, λ = 490 nm.

3.5. Composition of the complexes and suggested formulae

The molar ratios between the components of the ternary complex were found by several methods: Starik–Barbanel relative yield method, straight line method (Figure 4 and 5), equilibrium shift method [15] (Figure 6) and crossed lines method [16]. The results suggest the complex composition of 1:2:2 (M : HITP : Am).

Additional experiments by the Akhmedly’s method [17] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.0-1.23).

The obtained results, some conclusions [13,18] and our previous experience with similar systems [19,20] suggest that cobalt(II) no oxidised to cobalt(III) by the atmospheric oxygen during the complex formation. İn acidic medium, HCTP exhibit reducing properties. Hence, we propose the following formula of the ternary compound: [M(HITP)$_2$] (AmH)$_2$; in this formula Am is in its protonated form (AmH)+.

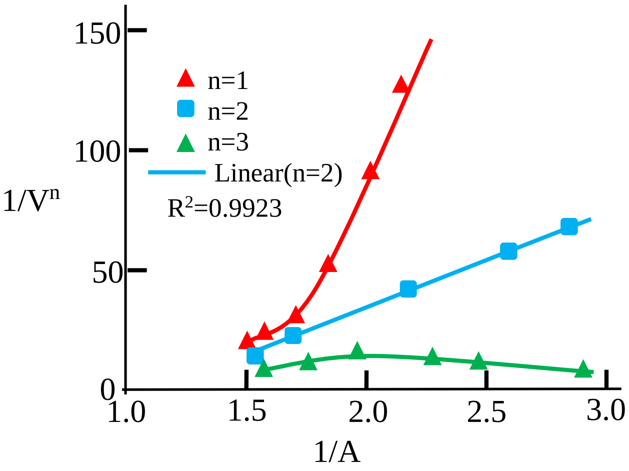

Fig. 4. Determination of the HITP-to-Co molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{HITP} = 2.0×10^{-3}mol L^{-1}, λ=590 nm, KFK-2, ℓ = 0.5 cm.

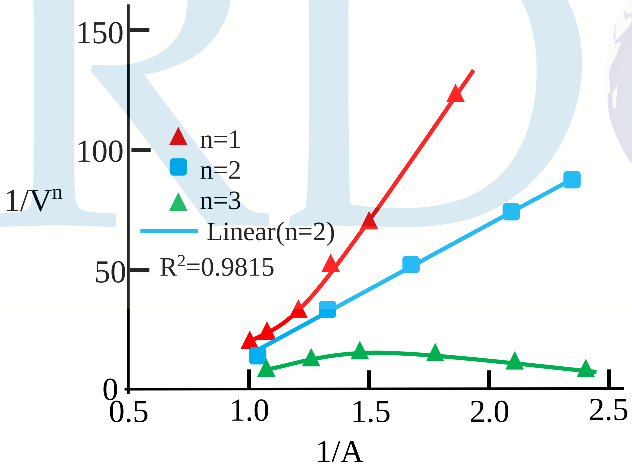

Fig. 5. Determination of the DPG-to-Co molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{DPG} = 2.5×10^{-3}mol L^{-1}, λ=590 nm, KFK-2, ℓ = 0.5 cm.

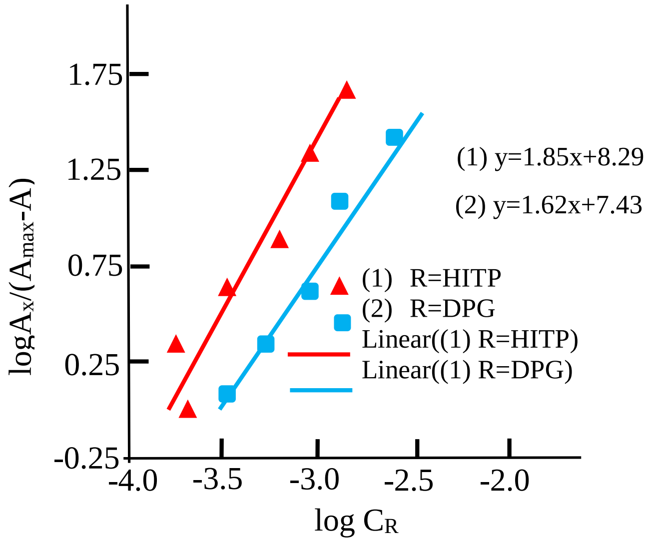

Fig.6. Determination of the HITP-to-Co (straight line 1) and the DPG-to-Co (straight line 2) molar ratios by the mobile equilibrium method. 1- $C_{Co(II)} = 1.7\times10^{-5}$mol L^{-1}, $C_{HITP} = 2.0\times10^{-3}$ mol L^{-1}, $C_{DPG} = 2.5\times10^{-3}$ mol L^{-1},λ=590 nm, KFK-2 ℓ=0.5 cm.

The existence of clearly defined absorption bands at 2410 - 2415 cm^{-1} in the IR-spectrum of the complex indicates the coordination of the Am in the protonated form [21]. 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. Proceeding from the obtained data, we propose the following structure for the extracted ternary complex (Figure 7).

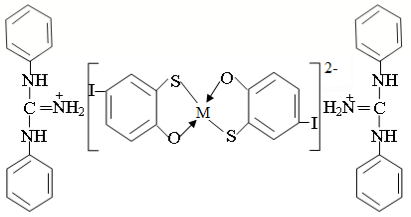

Fig. 7. Suggested structure of the ternary complex

3.6. Equilibrium constants

Several processes should be taken into account for the system of $[M(HITP)_2]^{2-}$, $(AmH^+)_2$, water and chloroform:

I) Association in the aqueous phase between anionic chelate, $[M(HITP)_2]^{2-}$, and the hydrophobic amines cation, $(AmH^+)_2$, with the equilibrium constants

$$\beta = \frac{[M(HITP)_2](AmH)}{[M(HITP)_2]^{2-} \times [(AmH^+)_2]}$$

II) Distribution of the complexes between the aqueous and the organic phase

$$\{[M(HITP)_2](AmH)_2\}_{aq} \leftrightarrow \{[M(HITP)_2](AmH)_2\}_{org}$$

with the distribution constants

$$K_D = \frac{[M(HITP)_2](AmH)_{org}}{[[M(HITP)_2](AmH)_2]_{aq}}$$

III) Extraction of the ternary complexes from water into chloroform

$$[M(HITP)_2]^{2-}{}_{aq} + (AmH^{+})_{2\ aq} \leftrightarrow \{[M(HITP)_2](AmH)_2\}_{org}$$

org with the extraction constants

$$K_{ex} = K_D + \beta = \frac{[[M(HITP)_2](AmH)]_{org}}{[[M(HITP)_2]^{2-}]_{aq} \times [(AmH^{+})_2]_{aq}}$$

The constants of the association β were determined by several independent methods: Mobile equilibrium method [22], Holme-Langmihr method [23], Komar-Tolomachev Method [15] and Harvey-Manning method [24].

The constants of the distribution K_D were determined by comparison of the absorbance values obtained after single extraction at the optimum conditions (A_1) and triple extraction (A_3): $K_D = A_1/(A_3–A_1)$. The extraction constants were calculated by the equation $K_{ex} = \beta + K_D$ [25]. All calculations were carried out at a probability of 95%. The obtained values are presented in Table 2.

Table 2. Values of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recoveries (R%) for the M(II)-HITP-Am-water-chloroform systems

Extraction system	lg β	lgK_D	lg K_{ex}	R%
Co(II)-HIPT-DPG-H_2O-$CHCl_3$	8.59±0.2[a]	1.86±0.01	10.56±0.21[e]	98
	8.70±0.4[b]		10.60±0.43[f]	
	8.46±0.7[c]			
	8.75±0.3[d]			
Co(II)-HIPT-TPG-H_2O-$CHCl_3$	9.87±0.3[a]	2.79±0.04	12.66±0.34[e]	88
	10.65±0.4[b]			
	9.69±0.3[c]			
	10.75±0.2[d]			
Ni(II)-HIPT-DPG-H_2O-$CHCl_3$	6.62±0.01[a]	0.92±0.02	7.64±0.03[e]	95
	6.45±0.04[b]			
	6.34±0.03[c]			
Ni(II)-HIPT-TPG-H_2O-$CHCl_3$	7.55±0.02[a]	0.88±0.04	8.43±0.03[e]	95
	7.14±0.02[b]			

Note: [a]Calculated by the Holme-Langmyhr method [23]; [b]Calculated by the Harvey-Manning method [24]; [c]Calculated by the Komar-Tolmachev method [15]; [d]Calculated by the mobile equilibrium method [22]; [e]Calculated by the formula $K_{ex} = K_D+\beta$ where b is determined by the Holme-Langmihr method [23]; [f]Calculated by the formula $K_{ex} = K_D+\beta$ where b is determined by the Harvey-Manning method [24].

3.7. Influence of Interfering Ions

To evaluate the complex applicability for photometric determination of cobalt and 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 cobalt and nickel with HITP and Am. 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 3 and 4.

Table 3. Effect of foreign ions on the extraction of 20 µg cobalt (II)

Foreign ions and reagents (FI)	mg	FI-to-Co ratio	Co found	R,%
Citrate^{3-}	5	250	20.03	100.5
Oxalate^{2-}	10	200	20.13	102.6
Tartrate^{2-}	2.5	250	5.05	101.0
Ascorbic acid	0.5	25	5.15	103.1
EDTA	0.5	25	5.10	102.0
CDTA	0.005	0.25	19.73	94.6
Tiron	2.5	125	20.11	102.5
SCN^-	0.025	10	20.13	102.6
Cl^-	20	100	20.20	104.0
$S_2O_3^{2-}$	10	200	19.92	98.5
F^-	10	500	20.20	104.0
NO_3^-	20	1000	20.02	100.3
SO_4^{2-}	20	500	20.03	100.5
PO_4^{3-}	7	225	20.10	102.0
ClO_4^-	0.1	0.5	20.73	94.6
NH_4^+	20	500	20.02	100.3
Na^+	30	1500	20.13	100.4
K^+	30	1500	20.11	102.2
Ca^{2+}	15	500	20.01	100.2
Ba^{2+}	5	250	20.15	103.1
Sr^{2+}	20	100	20.11	102.2
Mg^{2+}	30	1500	20.18	103.5
Mo(VI)	5	250	19.85	97.0
W(VI)	5	250	19.88	97.7
Cr(VI)	2.5	125	19.91	98.2
Cr(III)	1.5	75	19.80	96.0
Fe(II)	0.5	2.5	19.25	85.0
Fe(III)	0.5	2.5	20.90	118.0
	1.0^{a}	20	20.05	101.0
V(IV)	0.05	2.5	20.55	111.0
V(V)	0.05	2.5	19.25	85.0
Cd^{2+}	0.2	10	19.86	97.2
Cu^{2+}	0.06	3	20.17	103.4
	1.2^{b}	6	20.04	100.8
Al^{3+}	5	250	20.08	101.6
	10^{c}	500	20.02	100.3
	10^{d}	500	20.13	100.4
Zn^{2+}	0.5	25	20.04	100.8
	1.0^{e}	50	20.18	103.5
Zr(IV)	3.0	150	20.18	103.5
	15^{f}	500	20.01	100.2
Nb(V)	0.5	2.5	19.25	85.0
	10^{f}	500	20.04	100.8
Ti(IV)	2.5	125	20.17	103.4
	5^{i}	250	19.88	97.7
Ni^{2+}	2.5	125	19.91	98.2

Note: [a] in the presence of 2.5 mg oxalate; [b] in the presence of 0.75 mg $SC(NH_2)_2$; 10 min extraction time; [c] in the presence of 2.5 mg oxalate; [d] in the presence of 3.0 mg citrate; [e] in the presence of 0.75 mg EDTA; 15 min extraction time; [f] in the presence of 3.0 mg NaF; [i] in the presence of 3.0 mg Ascorbic acid.

Table 4. Effect of foreign ions on the extraction of 20 μg nickel (II)

Foreign ions and reagents (FI)	mg	FI-to-Ni ratio	Ni found	R,%
Citrate^{3-}	5	250	19.91	98.2
Oxalate^{2-}	10	200	20.17	103.4
Tartrate^{2-}	2.5	250	19.88	97.7
Ascorbic acid	0.5	25	19.25	85.0
EDTA	0.5	25	20.04	100.8
CDTA	0.005	0.25	20.18	103.5
Tiron	2.5	125	20.18	103.5
SCN^-	0.025	10	20.10	102.0
Cl^-	20	100	20.73	94.6
$S_2O_3^{2-}$	10	200	20.02	100.3
F^-	10	500	20.13	100.4
NO_3^-	20	1000	20.11	102.2
SO_4^{2-}	20	500	20.03	100.5
PO_4^{3-}	7	225	19.85	97.0
ClO_4^-	0.1	0.5	19.88	97.7
NH_4^+	20	500	19.86	97.2
Na^+	30	1500	20.17	103.4
K^+	30	1500	20.04	100.8
Ca^{2+}	15	500	20.11	102.2
Ba^{2+}	5	250	20.20	104.0
Sr^{2+}	20	100	19.92	98.5
Mg^{2+}	30	1500	20.20	104.0
Mo(VI)	5	250	20.08	101.6
W(VI)	5	250	20.02	100.3
Cr(VI)	2.5	125	20.13	100.4
Cr(III)	1.5	75	20.20	104.0
Fe(II)	0.5	2.5	19.92	98.5
Fe(III)	0.5	2.5	20.90	118.0
	1.0[a]	20	20.05	101.0
V(IV)	0.05	2.5	20.55	111.0
V(V)	0.05	2.5	19.25	85.0
Cd^{2+}	0.2	10	19.91	98.2
Cu^{2+}	0.06	3	19.80	96.0
	1.2[b]	6	19.25	85.0
Al^{3+}	5	250	20.01	100.2
	10[c]	500	20.15	103.1
	10[d]	500	20.11	102.2
Zn^{2+}	0.5	25	20.18	103.5
	1.0[e]	50	20.02	100.3
Zr(IV)	3.0	150	20.20	104.0
	15[f]	500	20.01	100.2
Nb(V)	0.5	2.5	19.73	94.6
	10[f]	500	20.11	102.5

Ti(IV)	2.5	125	20.13	102.6
	5[i]	250	5.05	101.0
Co^{2+}	2.5	125	20.03	100.5

Note: [a] in the presence of 2.5 mg oxalate; [b] in the presence of 0.75 mg $SC(NH_2)_2$; 10 min extraction time; [c] in the presence of 2.5 mg oxalate; [d] in the presence of 3.0 mg citrate; [e] in the presence of 0.75 mg EDTA; 15 min extraction time; [f] in the presence of 3.0 mg NaF; [i] in the presence of 3.0 mg Ascorbic acid.

3.7. Beer's law and analytical characteristics

The validity of the Beer's law was checked at optimum conditions (Table 2). The equations of the obtained straight lines and some important characteristics concerning the application of the ternary complexes for extractive-spectrophotometric determination of Ga(III) and In(III) are listed in Table 5.

Table 5 . Analytical characteristics

Characteristic	Extraction system			
	Co-HIPT-DPG	Co-HIPT-TPG	Ni-HIPT-DPG	Ni-HIPT-TPG
Apparent molar absorptivity (ε), L mol^{-1} cm^{-1}	3.30×10^4	3.10×10^4	2.64×10^4	2.56×10^4
Adherence to Beer's law, μg mL^{-1}	0.8-20	0.6-12	0.7-18	0.4-15
Equation of the straight line	0.1252X+0.054	0.1255X+0.049	0.149x+0.02	0.145X+0.038
Coefficient of correlation	0.9992	0.9992	0.9904	0.9995
Sandell's sensitivity, ng cm^{-2}	0.00854	0.00725	0.00941	0.00968
Limit of detection (LOD), μg mL^{-1}	14	13	11	10
Limit of quantification (LOQ), μg mL^{-1}	45	42	36	33

4. 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 6; their reliability was verified by the added–recovered method.

Table 6. Determination of cobalt and nickel in metallic magnesium and carnallite

Sample	Found (%) $\times10^{-4}$		Added-recovered method					
	Ni	Co	Added (%) $\times10^{-3}$		Recovered (%) $\times10^{-3}$		RSD (%)	
			Ni	Co	Ni	Co	Ni	Co
1[a]	7.65±0.01	5.12±0.03	1	1	1.765	6.123	1.4	1.3
2[a]	7.64±0.02	5.09±0.01	1	1	1.764	6.094	1.5	1.2
3[a]	7.70±0.02	5.13±0.02	1	1	1.770	6.135	1.2	1.7
4[a]	7.63±0.02	5.09±0.01	1	1	1.763	6.091	1.3	1.5

1^b	8.71±0.01	5.81±0.04	1	1	1.871	6.812	1.3	1.4
2^b	8.69±0.02	5.35±0.02	1	1	1.869	6.351	1.8	1.5
3^b	8.90±0.01	5.74±0.05	1	1	1.890	6.746	1.2	1.4
4^b	8.81±0.01	5.67±0.02	1	1	1.881	6.674	1.5	1.6

Note: ^{a} – Metallic magnesium; n=6; P=95%; ^{b} – Carnallite; n=5; P=95%

5. CONCLUSIONS

1. Gallium(III) and indium(III) form well chloroform extractable ternary ion-association complexes with HITP and DPG. The anionic part of these complexes, $[M(HITP)_2]^{2-}$, ensures intense colouration (λ_{max} = 480-483 nm when M = Ni(II) and λ_{max} = 598-608 nm when M = Co(II)), and the bulkiness of the cationic part (AmH^+: $DPGH^+$ or TPG^+), in its turn, guarantees poor solubility in water.

2. The following equilibrium constants and analytical parameters are calculated: constants of extraction, constants of association, constants of distribution, recovery factors, molar absorptivities, Sandell's sensitivities, limits of detection and limits of quantification. The obtained by independent methods similar values of some of the mentioned above characteristics are the evidence for the correctness of the performed experiments.

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