SPECTROPHOTOMETRIC DETERMINATION OF COBALT (II) IN A LIQUID-LIQUID EXTRACTION SYSTEM CONTAINING 2-HYDROXY-5-IODOTHIOPHENOL AND DIPHENYLGUANIDINE

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The complex formation and a liquid-liquid extraction in the cobalt(II) - 2-hydroxy-5-iodothiophenol (HITP) - diphenylguanidine (DPG) - water - chloroform system was studied. The optimum extraction-spectrophotometric conditions were found. The molar ratio of the reacting species was determined to be 1:2:2 (Co:HITP:DPG). The following equilibrium processes were quantitatively examined: the association between the anionic chelate, $[Co(HITP)_2]^{2-}$, and the diphenylguanidine ($lg\beta = 8.7$); the distribution of the ternary complex between the aqueous and organic phases ($logK_D = 1.86$); and the extraction from water to chloroform ($lgK_{ex} = lg\beta + lgK_D = 10.56$). The effect of foreign ions and reagents on the extraction was studied. A sensitive (ε_{590} = 3.3×104 L mol^{-1} cm^{-1}) and simple extraction-spectrophotometric procedure for cobalt determination was developed.

Keywords: cobalt(II), 2-hydroxy-5-iodothiophenol, ternary complex, solvent extraction.

Many metal ions form coloured binary species with 2,6-dithiolphenol (DTP), 2-hydroxythiophenol (HTP) and its derivatives[1-7]. Besides, the colour and extraction properties of these species can be improved by adding auxiliary compounds[2-4,8-11]. The following ion-association reagents were used for liquidliquid extraction of $[Me(DTP)_n]^{z-}$ or $[Me(HTP)_n]^{z-}$ (z = 2 or 3; n= 1 or 2; Me=Mo[3,8-9,11,12], W[14,18,19], Fe[21], Ni[7,17,18], V[2,4,5], Nb[1,6,10], Cu [16,20], Hg[20], Ti[13], Mn[15,19]): aniline, N-methylaniline, N, N-dimetilaniline, o-, m-, p-toluidine, dipyridyl, pyridine.

Spectral and chemical methods are being constantly used for cobalt determination. Therefore, new organic reagents for a selective and sensitive photometric determination of cobalt are of particular interest. Many methods of photometric determination of cobalt with use of the reagents belonging to various classes of organic compounds are offered.

In this respect, a very promising reagent is 2-hydroxy-5-iodothiophenol (HITP), which contains one hydroxyl and one sulfohydryl group and is a sulfur-containing analogue of mononuclear polyphenols with one oxygen atom replaced with sulfur atom.

The real work is devoted to studying of reaction of a complex formation of cobalt (VI) with 2-hydroxy-5-iodothiophenol and diphenylguanidine (DPG).

EXPERIMENTAL SECTION

Reagents and apparatus

Standard cobalt (II) solution

Cobalt standard solution (1000 mg l^{-1}; $Co(NO_3)_2$) was purchased from Merck Darmstadt (Germany). Working solutions ($C_{Co} = 1.7x10^{-4}$ mol L^{-1}) were prepared by diluting appropriate volumes of the stock solution. The concentration of the cobalt solution was adjusted gravimetrically[22].

Reagent solutions

HITP was synthesized according to the procedure[23]. 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.

Apparatus

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

Procedure for determining the optimum extraction-spectrophotometric conditions

Aliquots of Co(II) solution, HITP solution (up to 1.6 ml), DPG solution (up to 1.2 ml) and buffer solution (5 ml; pH ranging from 5.5-7.9) were introduced into 100 ml separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 25 ml. Then 2.2 ml of chloroform were added and the funnels were shaken for a fixed time (up to 5.0 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was recorded against a blank sample.

Procedure for extraction-spectrophotometric determination of cobalt

An aliquot of cobalt solution (0.8-20 mg ml^{-1}) was placed in a separatory funnel. Then 0.8 ml HITP solution, 0.6 ml DPG solution, and 5 ml of acetate buffer with pH 5.5 were added. The resulting solution was diluted with distilled water to a total volume of 25 ml, 3.6 ml of chloroform were added and the funnel was shaken for 1 min. A portion of the organic extract was filtered through a filter paper into a cell and the light absorbance at λ_{max} 598 nm was recorded against a blank sample. The cobalt content was found from a calibration graph.

Procedure for determining the distribution constant

The distribution constant K_D was found from the ratio $K_D = A_1/(A_3-A_1)$ where A1 is the light absorbance measured after a single extraction at the optimum operating conditions (Table 1, 25 ml final volume) and A_3 is the absorbance measured after a triple extraction under the same conditions[10].

Table 1. Optimum conditions and analytical characteristics of the Co(II)-HITP-DPG-water-chloroform system

Optimum conditions	**Parameter**	**Value**
Wavelength: 598 nm	Apparent molar absorptivity:	$\varepsilon=(3.30\pm0.07)\times10^4$ L mol^{-1} cm^{-1}
C_{HITP}: 2.0×10^{-3} mol L^{-1}	True molar absorptivity:	$\varepsilon'=(3.39\pm0.6)\times10^4$ L mol^{-1} cm^{-1}
C_{DPG}: 2.5×10^{-3} mol L^{-1}	Adherence to Beer's law:	0.8-20 mg ml^{-1}
Shaking time: 1 min	Limit of detection:	5 ng ml^{-1}
The pH range of education and extraction: 2.0-10.2	Limit of quantification:	18 ng ml^{-1}
The pH range of maximum extraction: 5.5-7.9	Sandell's sensitivity:	1.38 ng cm^{-2}
	Relative standard deviation:	1.7 %

Results and Discussion

Influence of the pH of the Aqueous Phase

The effect of pH on the intensity of the color reaction is shown in the Fig. 1. The absorbance was found to be maximum in the pH range 2.0-10.2. Hence further analytical investigations were carried out in media of *p*H 5.5-7.9. Extraction of Co (II) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrase 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 pH ≥ 10.3, the complexes were hardly extracted, obviously because of the decrease in the degree of DPG protonation.

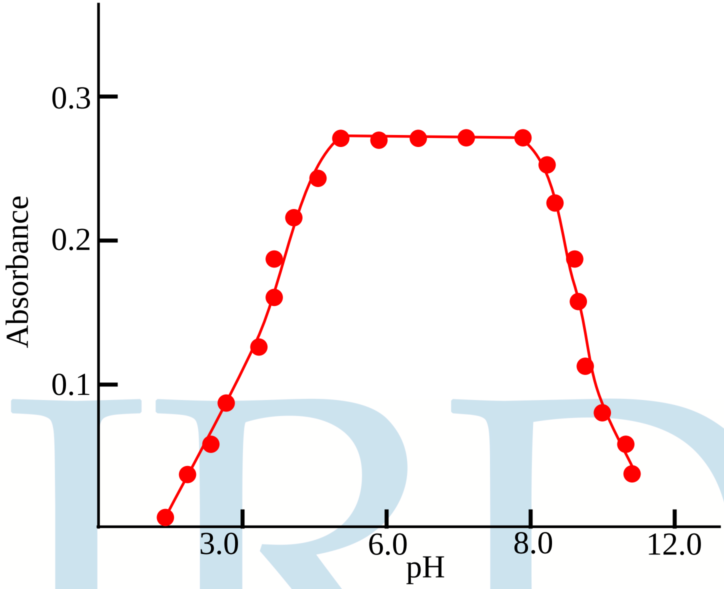

Fig. 1. Absorbance of Co-HITP-DPG extracts function of the pH of the aqueous phase. $C_{Co(II)} = 1.7\times10^{-5}$mol L^{-1}, $C_{HITP} = 2.0\times10^{-3}$mol L^{-1}, $C_{DPG} = 2.5\times10^{-3}$ mol L^{-1}, KFK-2, ℓ=0.5 cm.

Electronic Absorption Spectra

The figure revealed that Co(II)-HITP-DPG complex has maximum absorbance at 598 nm. Neither the metal ion nor the reagent has appreciable absorbance at specified wavelengths. Hence further studies were carried out at 590 nm (Fig.2). The Komar method[24] also allows to calculate the true molar absorptivity of the complex: ε= 3.3 x10^4 L mol^{-1} cm^{-1}.

Effect of the shaking time

The extraction equilibrium is reached for ca. 0.5 min. A longer shaking time (up to 5 min) did not affect the absorbance values. In order to avoid accidental errors, caused by the combination of short shaking times and different shaking rates, the further experiments were carried out with time of shaking 1 min.

Effect of reagents concentration

The effect of HITP and DPG concentrations on the absorbance is shown in Fig. 3. It could be accepted that 115-fold HITP excess and 150-fold DPG excess are sufficient for maximum Co extraction. The optimum reagents concentrations deduced from the mentioned figure are shown in Table 1.

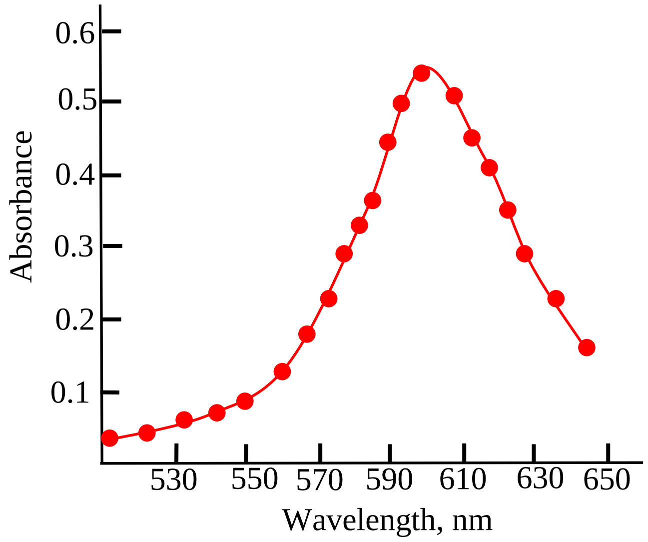

Fig. 2. Absorption spectra of the ternary Co-HITP-DPG complex in chloroform. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{HITP} = 2.0×10^{-3} mol L^{-1}, C_{DPG} = 2.5×10^{-3} mol L^{-1}, SF-26, ℓ=1.0 cm, pH 5.5-7.9.

Composition of the complex and suggested formula

The molar ratios in the ternary compound, Co:HITP:DPG= 1:2:2, were determined by the mobile equilibrium method[24] (Fig. 4) and the straight-line method of Asmus[24] (Figs. 5 and 6). The obtained results, some conclusions[1-6, 8-14,18,19,21], and our previous experience with similar systems[2,5,11,18,21] 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: $[Co(HITP)_2]$ $(DPGH)_2$; in this formula DPG is in its protonated form $(DPGH)^+$.

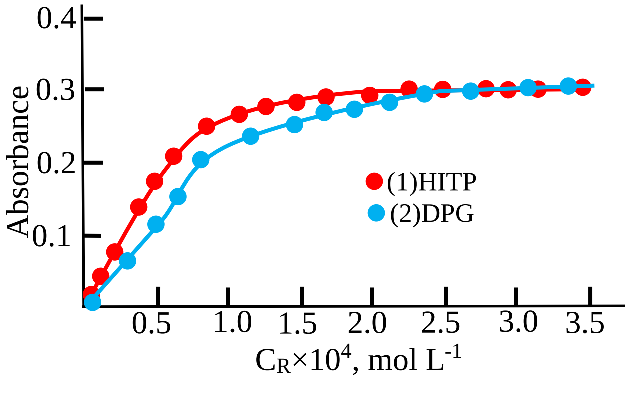

Fig. 3. Absorbance of the extracted ternary complex vs. concentration of the HITP (curve 1) and DPG (curve 2) plots. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, λ=590 nm, KFK-2, ℓ=0.5 cm.

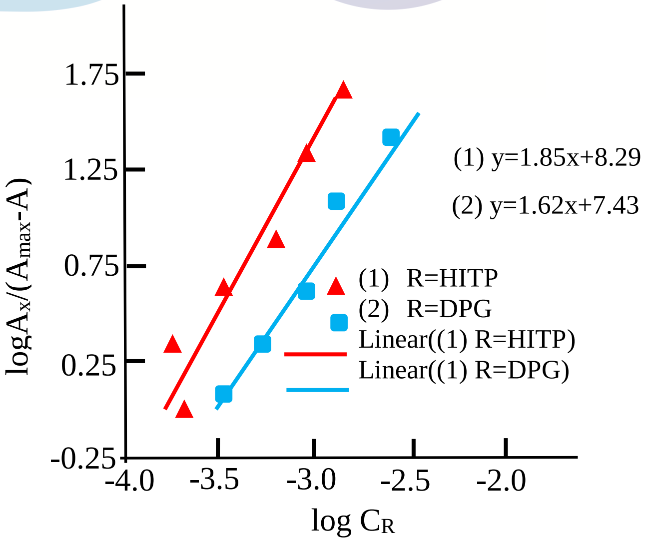

Fig. 4. Determination of the HITP-to-Co (straight line 1) and the DPG-to-Co (straight line 2) molar ratios by the mobile equilibrium method. 1- $C_{Co(II)}$ = 1.7×10^{-5}mol

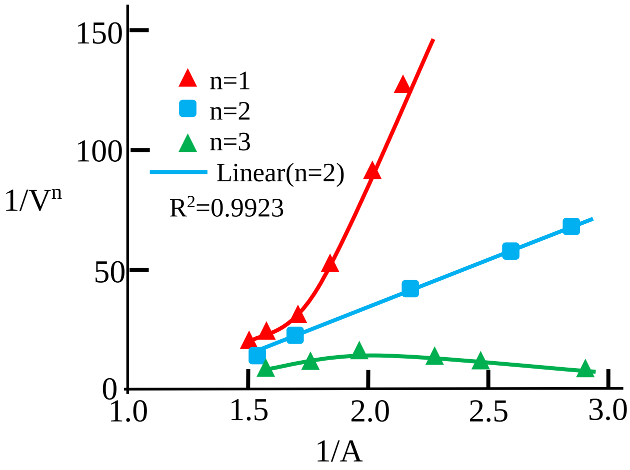

Fig. 5. Determination of the HITP-to-Co molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{HITP} = 2.0×10^{-3}mol L^{-1}, λ=590 nm, KFK-2, ℓ = 0.5 cm.

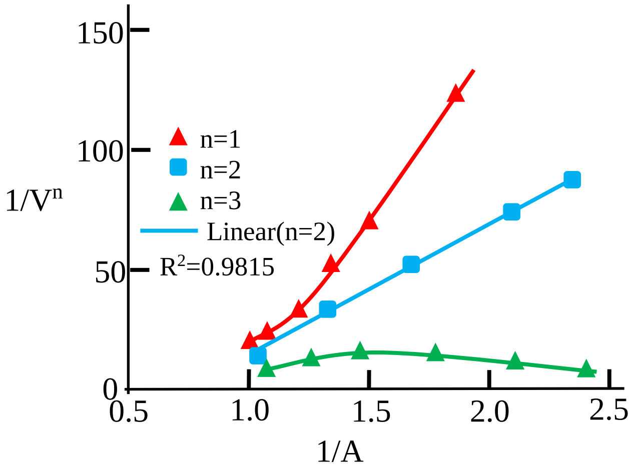

Fig. 6. Determination of the DPG-to-Co molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol L^{-1}, C_{DPG} = 2.5×10^{-3}mol L^{-1}, λ=590 nm, KFK-2, ℓ = 0.5 cm.

Structure extractable complexes can be represented as in Figure 6.

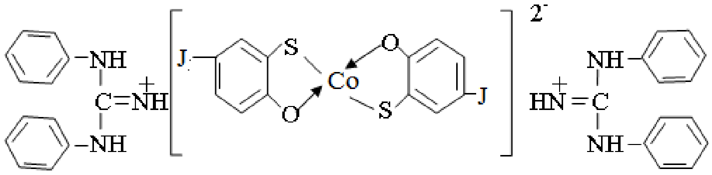

Fig. 6. Structure of complex

Equilibria and equilibrium constants

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $[Co(HITP)_2](DPGH)_2$.

Formation in the aqueous phase:

$$[Co(HITP)_2]^{2-}_{aq} + 2DPGH^{+}_{aq} \leftrightarrow [Co(HITP)_2](DPGH)_{2aq} \qquad (1)$$

Distribution:

$$[Co(HITP)_2](DPGH)_{2\,aq} \leftrightarrow [Co(HITP)_2](DPGH)_{2\,org} \qquad (2)$$

Extraction from water into chloroform:

$$[Co(HITP)_2]^{2-}_{aq} + 2DPGH^{+}_{aq} \leftrightarrow [Co(HITP)_2](DPGH)_{2\,org} \qquad (3)$$

The equilibrium constants describing these processes are shown in Table 2. The association constant b was determined according to a strategy[25] by several independent methods, (Holme-Langmyhr method[26], Harvey-Manning method[27], Komar-Tolmachev method[24], and the mobile equilibrium method[24]), (Fig. 4, straight line 2). 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 $K_{ex} = K_D\times\beta$. All experiments were performed at room temperature of 22±3°C and the calculations were carried out at a probability of 96 %.

Table 2. Calculated values of lg K_{eq}, lg K_D and lg K_{ex}

Equilibrium	Equilibrium constant	Value
1	$K_{eq}=[\,[Co(HITP)_2]\,(DPGH)_2]\,/\,[[Co(HITP)_2]^{2-}]\times[(DPGH^+)_2]$	lg β=8.59±0.2[a] lg β=8.70±0.4[b] lg β=8.46±0.7[c] lg β=8.75±0.3[d]
2	$K_D=[[Co(HITP)_2]\,(DPGH)_2]_{org}\,/\,[[Co(HITP)_2]\,(DPGH)_2]aq$	K_D=1.86±0.01
3	$K_{ex}=[[Co(HITP)_2]\,(DPGH)_2]_{org}\,/\,[[Co(HITP)_2]^{2-}]_{aq}\times[(DPGH^+)_2]_{aq}$	lg K_{ex}=10.56±0.1[e] lg K_{ex}=10.60±0.3[f]

[a]Calculated by the Holme-Langmyhr method; [b]Calculated by the Harvey-Manning method; [c]Calculated by the Komar-Tolmachev method;

[d]Calculated by the mobile equilibrium method; [e]Calculated by the formula $K_{ex} = K_D×β$ where b is determined by the Holme-Langmihr method; [f]Calculated by the formula $K_{ex} = K_D×β$ where b is determined by the Harvey-Manning method.

Effect of foreign ions and reagents

The effect of various ions and reagents on the extraction-spectrophotometric determination of 20 μg cobalt (II) is summarised in Table 3. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^+, W(VI), Mo(VI), $Cl^–$, $S_2O_3^{2–}$, $F^–$, $NO^{3–}$, $SO_4^{2–}$, $PO_4^{3–}$, tartrate, citrate, oxalate and tiron; moderate amounts of Cr(VI), Cr(III), Zn(II) and Cd(II); and small amounts of Mn(II), Sn(II), Cu(II), Al(III), ascorbic acid and $SCN^–$ are tolerable. Ni(II), Fe(II,III), V(IV,V), Ga(III), In(III), and Tl(III) interfere seriously at a ratio of 1:1 with respect to Co(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 3).

Beer's law and analytical characteristics

The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions (Table 1). The following straight line equation was obtained for the concentration interval 0.5 – 12 mg $mL^{–1}$ Co(II): Y=0.1252X+0.054 (R^2=0.9975). The pertaining calibration graph is shown in the Fig. 7.

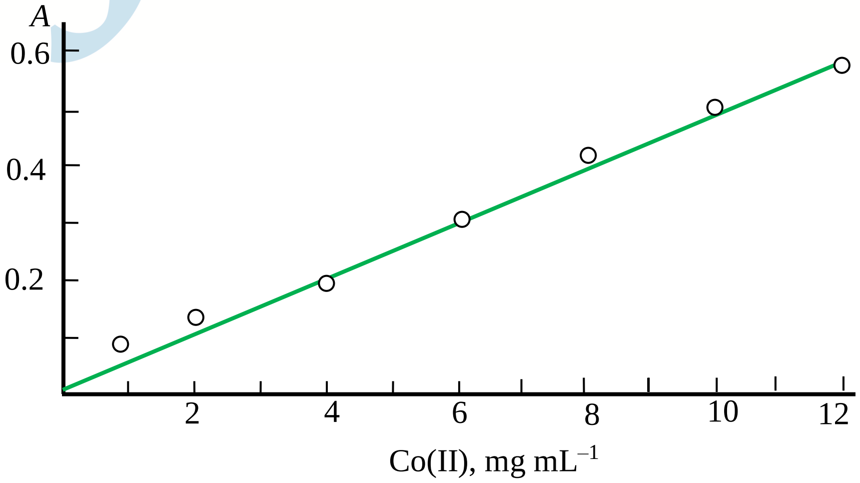

Fig. 7. Analytical determination of Co(II); $C_{HITP} = 2.0×10^{–3}$ mol $L^{–1}$, $C_{DPG} = 2.5×10^{–3}$ mol L^{-1}, pH 5.5-7.9, λ=590 nm, KFK-2, ℓ=0.5 cm.

Calculated apparent molar absorptivity was e = $3.3×10^4$ L $mol^{–1}$ $cm^{–1}$. This value is statistically indistinguishable from that obtained by Komar-Tolmachev method[24]. It could compete successfully with the values reported for many similar Co-containing chromogenic systems[25,28,29]. Some additional characteristics concerning the analytical application of the Co-HITP-DPG-water-chloroform system are given in Table 1.

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
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
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

[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.

Analytical Applications

The relative standard deviation (RSD = 1.7 %) was calculated from the results of four replicate analyses of an artificial mixture containing 5 μg ml^{-1} Co(II) and 10 μg ml^{-1} of each of the following foreign ions: K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cr(IV), W(VI) and Mo(VI).

CONCLUSIONS

1. Cobalt (II) forms well chloroform-extractable ternary ionassociation complex with HITP and DPG. The anionic part of the complexes, $[Co(HITP)_2]^{2-}$, ensures intensive blue coloration, while the cationic part, DPGH$^+$, guarantees their poor solubility in water. The obtained molar ratios, Co :HITP :DPG = 1 : 2 : 2, and literature data about similar extraction-chromogenic systems suggest that during the complex formation Co(II) is no oxidised to Co(III) by the atmospheric oxygen.

2. The following conditional constants are calculated: constant of association (β), constant of distribution (K_D) and constant of extraction (K_{ex}).

3. The apparent molar absorptivitie of the complex are rather high (ε'= 3.3 × 10^4 L mol^{-1} cm^{-1}. In this criterion, they could compete successfully with many complexes used for spectrophotometric determination of cobalt.

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