EXTRACTION OF COBALT (II) IN THE PRESENCE OF RHODANIDE IONS AND DIMETHYLFORMAMIDE AND COMPLEXATION WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOLH IN THE ORGANIC PHASE

[1]A.Sh. Giyasov, [2]Rakhmatullaeva N.T., [3]A.A. Shokhakimova, [4]Rakhmatov U.N., [5]Otayuziea V.U

[1,2,3,4,5]Tashkent State Technical University named after Islam Karimov

Abstract. Low selectivity for the determination of metal ions using azo dyes, as well as when using other organic reagents, during complex formation in the aqueous phase is the main disadvantage of existing methods. We have studied the conditions for selective extraction of the thiocyanate complex cobalt (II) in the presence of thiocyanate dimethylformamide (DMF) with inert organic solvents and its determination with 1-(2-pyridylazo)-2-naphthol (PAN) directly in the organic phase without separating accompanying elements.

Experiments have shown that cobalt (II) from a strongly acidic medium in the presence of thiocyanate ions and DMF is selectively extracted with chloroform at 10-15 sec. shaking the cobalt (II) phases by 99.9% without changing to a phase volume ratio of 40:1.

After extraction of cobalt (II) under optimal conditions, add to the extract the PAN reagent, a buffer solution pH = 3-5.5 containing 0.2% sodium nitrite and shaking the phases for 10-15 seconds. Interacting with a 1:2 ratio, a colored complex compound is formed. The rhodanide complex of cobalt (III) in the extract is stable for more than 3 days. The maximum absorption spectrum of cobalt with PAN is at 640 nm. The apparent molar absorption coefficient at 640 nm is $2 \cdot \llbracket 10 \rrbracket^4$, obeying Beer's law over a wide concentration range.

Under optimal conditions, together with cobalt (II), ions of copper, iron (III), bismuth (III), tungsten (VI) are partially extracted and interfere with the determination of cobalt (III) with PAN. The interfering influences of iron (III) and bismuth (III) are eliminated by adding sodium fluoride and thiourea, copper (II) and tungsten (VI) to the buffer solution by adding thiourea and tartaric acid, respectively. It has been established that the thiocyanate complex of cobalt (II) is selectively extracted from a strongly acidic medium in the presence of DMF by the hydrate-solvate mechanism.

The developed method for the extraction-spectrophotometric determination of cobalt with PAN was tested in model solutions composed according to the type of rocks and ores, as well as salts and ores, and is recommended for the analysis of ores, concentrates, steel and other materials with complex compositions without preliminary separation of associated elements.

Keywords: extraction, spectrophotometry, selectivity, sensitivity, inert organic solvents, azoreagents.

INTRODUCTION

Known photometric and extraction-photometric methods for the determination of cobalt (II) using organic dyes [1-14] are highly sensitive, but at the same time they are poorly selective.

To increase the selectivity of methods for determining elements, extraction of colorless complexes of elements with inert organic solvents is used, followed by the addition of organic

dyes to the extract, and it is determined as a result of interaction with organic dyes directly in the organic phase [15-19].

This work discusses a new, selective, simple method based on the extraction of cobalt thiocyanate complex with inert organic solvents and its complexation with PAN directly in the organic phase.

EXPERIMENTAL PART

The initial solution of cobalt (II) with a concentration of 2 mg/ml was prepared from the salt $CoCl_2*6H_2O$ of the chemical grade, weighed. The titer of the solution was established potentiometrically by titration with potassium bromate. [20]. A chloroform solution of PAN (Reanal, Hungary) was used. The spectra of cobalt (III) complexes with PAN and the reagent were recorded on an SF-26 spectrophotometer, $\ell=1$ cm. The optical densities of the complexes were measured on a KFK-2 photoelectrocolorimeter. The pH of solutions was concentrated using an EV-74 ion meter.

Method for determining cobalt in pure solutions. The test solution containing 2-200 μg of cobalt is added to a measuring cylinder with a capacity of 25 ml with a ground stopper, 3 ml of 5 M H_2SO_4, 1 ml of 10 M potassium thiocyanate are added and the volume of the solution is adjusted to 8.5 ml with distilled water, 1.5 ml of DMF is added, 5 ml of chloroform and shake for 5-10 seconds. The mixture is transferred into a separating funnel, the extract is separated into another separating funnel, 5 ml of 0.06% chloroform solution of PAN, 2 ml of acetate-ammonium buffer solution with pH = 4 containing 0.2% sodium nitrite and shake for 10-15 seconds. The resulting colored extract is filtered through thick filter paper and photometered relative to the blank solution.

Method for determining cobalt in salts. A sample (0.1-0.3 g) is placed in a conical flask (250 ml), 10 ml of hydrochloric acid ($\rho = 1.19$) and 3 ml of nitric acid ($\rho = 1.4$) are added and evaporated to wet salts. Add 30-40 ml of 4M sulfuric acid and mix, and then transfer to a volumetric flask (100 ml). The solution is diluted with 4M sulfuric acid to the mark. An aliquot of the solution is taken into a measuring cylinder (25 ml) with a ground-in stopper; 1 ml of 10 M potassium thiocyanate is added and then determined using the method for determining cobalt with PAN in pure solutions.

Methodology for determining cobalt in ores. Weigh (0.5-1.0 g) a platinum cup, add 1-2 ml of 70% per chloric acid, 3-5 ml of water and 5-10 ml of hydrofluoric acid (35%). I heat it on a hotplate and evaporate twice to wet salts; add 10-15 ml of 2M hydrochloric acid to the residue and heat if necessary to dissolve all substances. The solution is filtered through a paper filter into a volumetric flask (50-100 ml). The filtrate is diluted with distilled water to the mark and the cobalt content is determined from an aliquot of the solution using the method for determining cobalt with PAN in pure solutions, adding masking agents to the solution.

RESULTS AND ITS DISCUSSION

Cobalt (II) from a solution containing H_2SO_4, thiocyanate ions and DMF showed that the optimal conditions for extraction of cobalt (II) are: 1.25–3.5 mol/l H_2SO_4, 0.5–3.0 mol/l potassium thiocyanate , 13-30 vol.% (by volume) DMF and shook the phases for 3-5 sec. With equal volumes of aqueous and organic phases, the recovery of cobalt (II) during a single extraction is 99.9% and does not change until the phase volume ratio is 40:1.

The composition of the extracted cobalt (II) thiocyanate complex was determined by the equilibrium shift method [21]. For this purpose, the dependence of the extraction distribution

coefficient of cobalt (II) on the concentration was studied: 1) H2SO4 (from 0.05-1.5 mol/l) at a constant DMF concentration (20 vol.%) and ionic strength ($\mu = 1.3$) , which was provided by adding the required amount of KCNS; 2) thiocyanate ions (from 0.05-0.7 g-ion/l) at a constant concentration of H2SO4 (2mol/l), DMF (20 vol.%) and ionic strength ($\mu=1.3$); 3) DMF from (2 to 15 vol.%), KCNS (1 mol/l) and ionic strength ($\mu=1.3$): the concentration of cobalt (II) in the extract was determined by the photo calorimetric method with the PAN reagent. To do this, 5 ml of a 0.03% chloroform solution of PAN and 2 ml of an acetate buffer solution with pH = 4 containing 0.2% sodium nitrite were added to the cobalt (II) extract, shaken for 5-10 sec and the resulting colored complex cobalt(III) with PAN photometers.
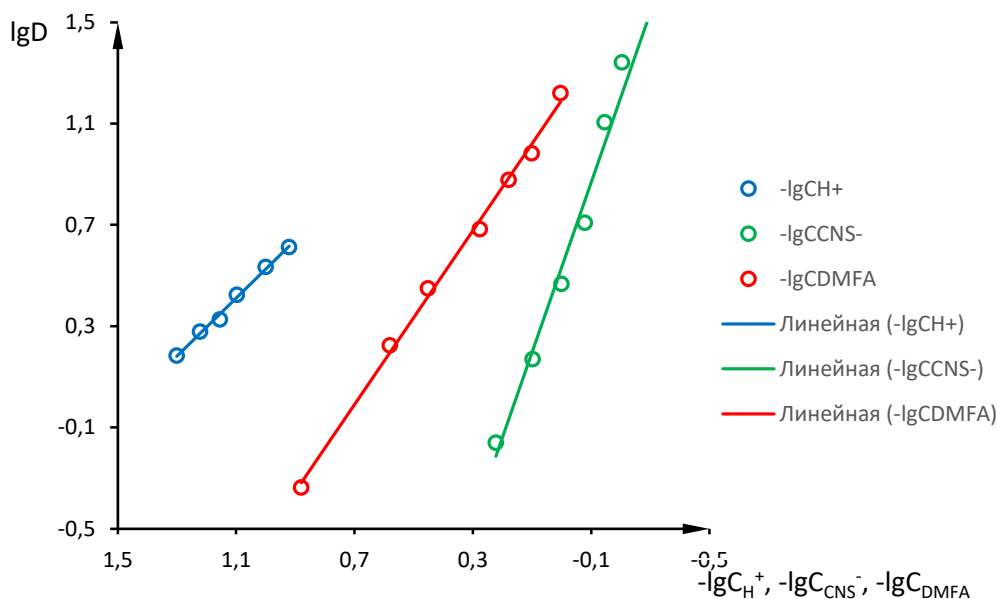

Fig.1. Determination of the molar ratios of cobalt and hydrogen ions (3), thiocyanate ions (1), DMF (2) by the equilibrium shift method during extraction with chloroform. SSO=1.695·10-4m; Apr=0.53

The obtained data shown in Fig. 1 show that in logarithmic coordinates

$$lgD_{(Co2+)}-lgC_{(H+)}, lgD_{(Co2+)}-lgC_{(CNS-)}, lgD_{(Co2+)}-lgC_{DMF}$$

(Where D is the distribution coefficient, C is the concentration), a linear relationship is observed with the tangents of the slope of the straight lines equal to 2.4 and 4, respectively.

Consequently, cobalt (II) is extracted by chloroform in the form of $H_2[Co(CNS)_4]$; the solvate number of $H_2[Co(CNS)_4]$ in the extract is 3. The number of water molecules associated with $H_2[Co(CNS)_4]$ in the extract determined by the Fischer method [22] is 5. Based on experimental data on the apparent thiocyanate complex of cobalt (II) from acidic solutions in the presence of DMF is extracted with chloroform according to the hydrate-solvate mechanism [20]:

$$〚Co〛^{2+}+4CNS^-+2H^++3DMF+5H_2O \leftrightarrow [H_2(H_2O)_5·(DMF)_3^{2+}]·[Co(CNS)_4^{2-}]_o$$
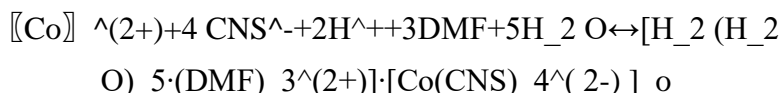
After extraction of cobalt (II) under optimal conditions, separation of the aqueous phase by adding to the extract a chloroform solution of PAN, an acetate-ammonia buffer solution with pH = 4, containing 0.2% sodium nitrite and shaking the phases for 10-15 seconds, interaction of cobalt (III) with PAN occurs in the organic phase.

A study of the dependence of optical density on pH of an ammonium acetate buffer solution showed that almost complete complexation of cobalt (III) with PAN in chloroform

occurs in the pH range = 3-5.5. Using the equilibrium shift method, it was established that cobalt (III) interacts with PAN in a molar ratio of 1:2 (Fig. 2).
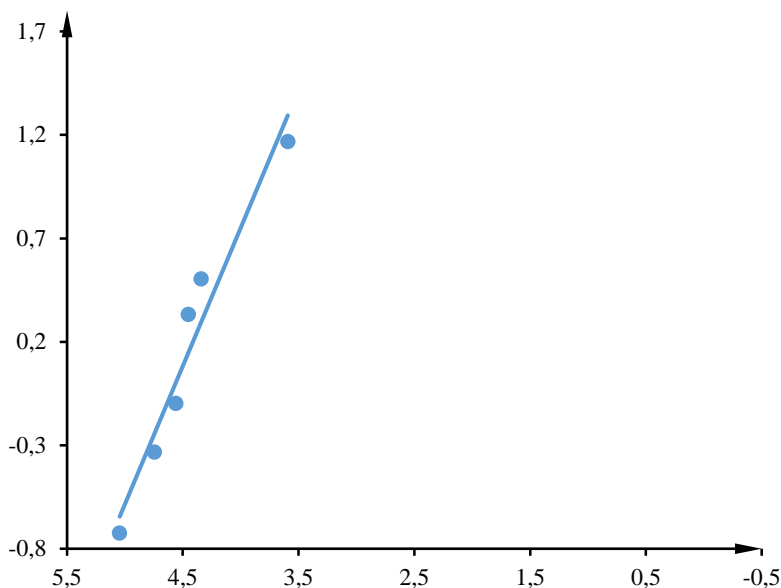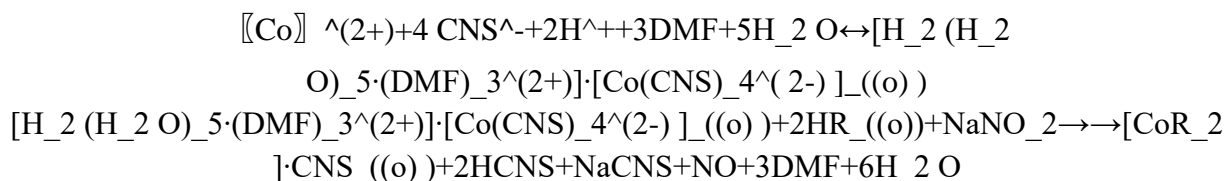

Fig.2. Determination of the composition of the cobalt complex with PAN by the equilibrium shift method. SSO=1.77·10-5m; lp=1 cm

Consequently, the reaction of complexation of cobalt (III) with PAN in the organic phase can be briefly represented by the following scheme:

$$〚Co〛^{(2+)} + 4 CNS^- + 2H^+ + 3DMF + 5H_2O ↔ [H_2(H_2O)_5·(DMF)_3^{(2+)}]·[Co(CNS)_4^{(2-)}]_{((o))}$$

$$[H_2(H_2O)_5·(DMF)_3^{(2+)}]·[Co(CNS)_4^{(2-)}]_{((o))} + 2HR_{((o))} + NaNO_2 → → [CoR_2]·CNS_{((o))} + 2HCNS + NaCNS + NO + 3DMF + 6H_2O$$

The cobalt (III) complex with PAN in the extract is stable for more than three days. The maximum absorption spectrum of the cobalt (III) complex with PAN is at 640 nm (Fig. 3), and that of the reagent at 470 nm.
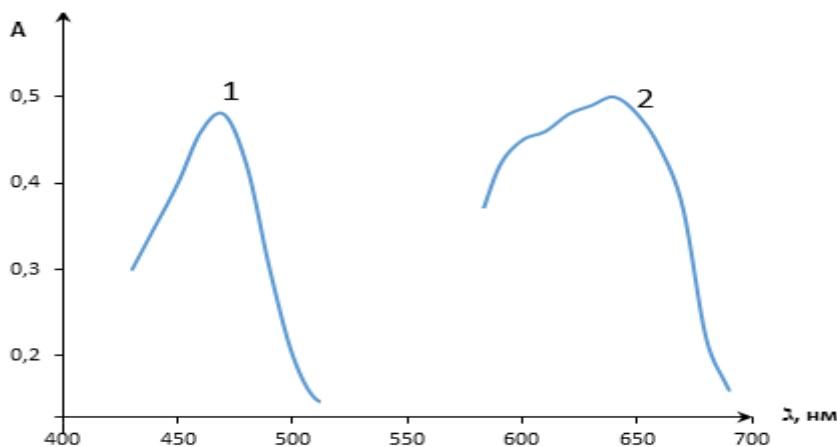

Fig. 3. Absorption spectrum of chloroform extracts of PAN and cobalt (III) complex with PAN. 〚C〛_Co=0.24· 〚10〛^(-4) m; V_o=V_в=10ml; l=1 cm.

The apparent molar absorption coefficient is $2 \cdot 10^4$. Beer's law is observed in the range of 2-200 μg of cobalt (III) in 10 ml of extract. The reproducibility of the determination is within 2-4%. Three calibration graphs were constructed, covering the limits of 2-10, 10-100, and 100-200 μg per μg of cobalt. The optical densities of the complexes were measured in cuvettes with absorbing layer thicknesses of 2, 1, and 0.3 cm, respectively. Under optimal cobalt (II) extraction conditions, the effects of foreign ions were studied. Experiments have shown that under optimal conditions for the extraction of cobalt (II), ions of copper (II), iron (III), bismuth (III), tungsten (VI) are partially extracted and interfere with the determination of cobalt (II). The interfering influences of iron (III), bismuth (III) are eliminated by adding sodium fluoride and thiourea to the buffer solution, copper (II) and tungsten (VI) by adding tartaric acid to the extraction mixture. The influence of many foreign ions on the determination of cobalt with PAN has also been studied and is shown in Table 1.

Table 1

Determination of cobalt with PAN in the presence of foreign ions (25 mcg cobalt taken)

M	M/Co	M	M/Co	M	M/Co
Ag (I)	4000	Au (III)	400	Cr (VI)	2000
Zn (II)	20	Rh (III)	400	W (VI)	200
Pb (II)	20000	Ru (III)	400	W (VI)	1000[3]
Cu (II)	4000[1]	In (III)	4000	Te (VI)	4000
Mn (II)	20000	Ga (III)	20000	Mn(VII)	4000
Cd (II)	40000	Cr (III)	1000	Os (VIII)	400
Hg (II)	8000	La (III)	4000	F$^-$	Doesn't interfere
Ca (II)	20000	Ti (IV)	2000	Cl$^-$	Doesn't interfere
Ba (II)	20000	Ti (IV)	8000[2]	J-	Doesn't interfere
Mg (II)	40000	Zr (IV)	20000	NO_3^-	Doesn't interfere
Pd (II)	400	Se(IV)	2000	PO_4^{-3}	Doesn't interfere
Be (II)	2000	Th (IV)	2000	$C_2O_4^{-2}$	Doesn't interfere
Ni (II)	20000	Pt(IV)	2000	CH$_3$COO$^-$	5000
Al (III)	40000	As (V)	1000	$O_2S_3^{-2}$	Doesn't interfere
Fe(III)	4	Sb (V)	1000	EDTA	Doesn't interfere
Fe(III)	400[2]	V(V)	200	Thiourea	Doesn't interfere
Tl(III)	2000	Nb (V)	1000	Wine acid	Doesn't interfere

Bi(III)	40	U (VI)	400	Lemon acid	Doesn't interfere
Bi (III)	8000[1]	Mo (VI)	2000	Ascorbic acid	Doesn't interfere

Where M is an ion or compound; M/Co – permissible mass ratio to cobalt by mass; 1 – in the presence of 200 mg of thiourea; 2 – in the presence of 150 mg NaF in buffer; 3 – in the presence of 200 mg of tartaric acid.

The developed method for the extraction-spectrophotometric determination of cobalt (III) with PAN was tested in the analysis of model solutions compiled according to the type of rocks and ores of the Almalyk MMC (Table 2), in salts and ores (Table 3).

To determine cobalt with PAN in model solutions, aliquots (1-4 ml) of the model solution are taken into a 25 ml measuring cylinder with a ground stopper and then proceed according to the method for determining cobalt in pure solutions.

Table 2

Results of determination of cobalt (II) in model solutions compiled according to the type of rocks and ores of the AGMK (n=4; α=0.95)

Name and number of the standard sample	Certified chemical composition of the standard sample, %	Cobalt found, %	$S \cdot 10^2$	Relative error, %
Cobalt-nickel ore No. 1347-18	SiO_2 – 31; TiO-0,192; Al_2O_3-7,1; Fe_2O_3-6,03; MnO – 0,25; CaO-18,7; MgO-4,24; Zn-0,039; Ni-1,57; Cu-0.39; As-5,77; S-0,4; Co-1,13.	1,12	1,51	2,14
Skarn copper ore #4818	SiO_2 – 33,77; Ti-0,882; Al_2O_3-5,47; Fe – 15,9; MnO – 0,36; CaO-29,75; MgO-0,66; P_2O_5 – 0,11; K_2O – 0,13; Na_2O – 0,01; CO_2 – 2,73; Cu-1,98; Mo- 0,02; Co- 0,43.	0,45	1,01	3,55
Breed No. 519	SiO_2 – 49,1; Ti-1,11; Al_2O_3-7,1; FeO-10,26; Mn – 0,21; CaO-10,2; MgO-5,74; Na_2O – 2,49; P_2O_5 – 0,21; K_2O – 0,7; W – 0,0007; Nd – 0,0015; Zn-0,015; F – 0,023; Co-0,046.	0,05	0,19	6,00
Breed No. 521	SiO_2 – 46,4; Ti-1,026; Al_2O_3-14,88; Fe_2O_3-11,66; MnO – 7,0; Na_2O – 2,82; K_2O – 2,96; P_2O_5 – 1,01; W – 0,0001; Nd – 0,007; Zn-0,012; As – 0,001; Co-0,046.	0,026	0,10	6,15

Table 3

Results of determination of cobalt in salts and ores (n=4; α=0.95)

Name and number of the standard sample		Certified cobalt content, %	Cobalt found, %	$S \cdot 10^2$	Relative error, %
Steel	156	10,50	10,52	8,800	1,33
	157	5,47	5,48	6,920	2,01
	158	1,35	10,34	9,750	1,49
	164 [a]	4,36	4,38	6,600	1,14
Ore	1347-18	1,130	1,150	1,735	2,40
	3032-18	0,200	0,220	0,389	2,80
	606-18	0,094	0,091	0,188	3,30
	3597-18	0,170	0,156	0,372	3,70
	9013-18	0,025	0,030	0,117	6,20

CONCLUSIONS

Thus, the developed method is recommended for the analysis of ores, concentrates, rocks, steel and other materials with complex compositions without preliminary separation of associated elements.

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