International Journal of Chemistry Studies
ISSN: 2581-348X
Impact Factor: RJIF 5.44
www.chemistryjournal.in
Volume 2; Issue 3; May 2018; Page No. 17-24

Extraction-spectrophotometric study of ternary complexes of Cr (VI) and Co (II) Using *o*-Hydroxythiophenols and Aminophenol

Shahla A Ibrahimova[1], Ali Z Zalov[2*], Novrasta S Hasanova[3]
[1] Department of Organic Chemistry, Baku State University, Baku, Azerbaijan
[2] Department of Analytical Chemistry, Azerbaijan State Pedagogical University, Baku, Azerbaijan
[3] Department of Chemistry and Technology Inorganic Substances, Azerbaijan State University of Oil and Industrial, Baku, Azerbaijan

Abstract

The following reagents were used: thiocatechols (TCs, H_2L):2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-3-thiolsulphonic asid (HTSA); and hydrophobic amines (HAs): -2,6-bis (N, N-dimethylaminomethyl) -4-methylphenol (AP_1) and 2,6-bis (N, N-dimethylaminomethyl) -4-chlorophenol (AP_2). The TCs were characterized by physicochemical methods: IR and NMR spectroscopy. To elucidate the oxidation state of chromium in the presence of TCs, we conducted two series of experiments. In the first series we used Cr(VI), while in the second series we used Cr(III) obtained by addition of a supplementary reducing agent (SnCI2 or KI). The comparison of the obtained spectra showed that λ_{max} Cr(VI) - TCs = λ_{max} Cr(III) - TCs. This fact can be regarded as an indication that Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation.After a single extraction with chloroform, 97.4-98.8% of chromium and cobalt was extracted as an ion associate. For the formation and extraction of chromium (III) and cobalt (II) complexes, pH 2.9-4.9 and 3.3-6.8, respectively, are optimal. The optimal condition for the formation andexpression of these codents is concentration (1.3-1.5) × 10^{-3} M TCs and (1.2-1.5) × 10^{-3} M HAs. Extracts of Cr^{3+} and Co^{2+} radionuclides obey the basic law of light absorption at concentrations of 0.2-20 and 0.2-22 μg / ml, respectively. The maximum optical density of chromium (III) complexes and cobalt (II) is reached within 12 and 10 minutes, respectively. The absorption maxima of the Cr (III) - HBTP-HAs triple complexes lie in the range 437-440 nm (in the case of cobalt 545-560 nm). The molar absorption coefficients for chromium complexes (2.70 - 2.74) × 10^4 L×mol^{-1} × cm^{-1} (in the case of cobalt (3.43 - 4.14) × 10^4 L × mol^{-1} × cm^{-1}). The molar relationships between the components of the ternary complex were found by several methods: the method of relative profitability of the old Barbanel, the linear method, and the equilibrium shift method (Cr:TCs:Has = 1:3:3 and Co:TCs:Has = 1:2:1). It was established by Nazarenko's method that the complexing form of chromium (III) and cobalt (II) is Cr^{3+} and Co^{2+}, respectively. The calculations showed that the MLC in the organic phase does not polymerize and is in monomeric form (γ = 1.01-1.05). It has been established that large amounts of alkali, alkaline earth elements, rare earth elements, F^-, CI^-, Br^-, SO_3^{2-}, SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with the determination of chromium and cobalt. The selectivity of the determination is significantly increased in the presence of masking agents. The proposed method, within the established optimal conditions, was used to determine Cr (III) and Co(II) in milk, sour cream and cottage cheese.

Keywords: chromium, cobalt, solvent extraction, spectrophotometry, thiocatechols, hydrophobic amines

Introduction

The most important application of chromium in the metallurgic industry is its use as an alloying element in steels. In these materials, chromium contributes to increase the hardness, tempering and oxidation resistance [1].

Cobalt is a transition element of high industrial importance because of its valuable alloying, dyeing, magnetic, catalytic and plating properties. It is also of biological significance thanks to its ability to be an active center of coenzymes, e. g. vitamin B12 [2, 3].

A great variety of spectrophotometric reagents is known for the determination of chromium and cobalt. Characteristics of previously spectrophotometric methods for chromium and cobalt determinations are summarized in Table 1 [3-7].

Table 1: Characteristics of previously spectrophotometric methods for chromium determination

Reagent*	Linear range/ mg L^{-1}	Molar absorptivity/ L mol^{-1}cm^{-1}	Relative standard deviation/ %	Heating time/ min	Ref.
Co-PAR-TTC	0.8-1.8	5.0 × 10^4	1.31	1.5	[3]
Co-PAR-INT	0.5-2.6	5.2 × 10^4	1.34	1.0	[3]
Co-DTP-An	0.5-14	3.45× 10^4	2.65	15	[5]
Co - DTP-мАн	0.5-85	3.68× 10^4	1.67	20	[5]
Co - DTMP -Ан	0.5-80	3.72× 10^4	2.71	20	[5]
Co - DTPP -An	0.6-80	3.97× 10^4	1.02	20	[5]
Co -DTBP-An	0.5-100	4.12× 10^4	1.15	30	[5]
Cr-EDTA	6.0-160	2.1× 10^3	0.6	30	[4,6,7]

Cr-5-Br-DMPAP	0.02- 0.56	7.8 × 10^4	2	5	[6,7]
Cr-PAR	_	4.7 ×10^4	-	135	[6,7]
Cr-PAN	0.3-2.0	1.28 × 10^4	1.25	35	[4,6,7]
Cr-Br-PADAP	_	7.93× 10^4	-	40	[6,7]
Cr-TAR	3.4-79	4.51×10^4	0.95	45	[4,6,7]

*Note: EDTA – ethylenediamine tetraacetic acid; TAR – 4-(2- Thiazolylazo)-resorcinol; PAR – 4-(2-pyridylazo)resorcinol; PAN – 1-(2-Pyridylazo)-2-naphthol; TTC – 2,3,5-triphenyl-2H-tetrazolium chloride; INT – 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride; DTP – 2, 6-dithiolphenol; DTMP – 2, 6-dithiol-4- methyl-phenol; DTPP – 2,6-dithiol-4-propylphenol; DTBP –2, 6-dithiol-4-tert-buthylphenol ; An – aniline; mAn – N-methylaniline; 5-Br-PADAP – 2-(5-brorno-2-pyridylazo)-5-diethylaminophenol; 5–Br-DMPAP – 2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol).

However, the studies aiming to find and investigate new spectrophotometric reagents with different functional groups are still going on. In the present work we use conventional spectrophotometry to investigate the formation and liquid-liquid extraction of series of Cr(VI) and Co(II) ternary complexes which seems to be prospective for the spectrophotometric determination of these elements. The following reagents were used: thiocatechols (TCs, H_2L):2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-3-thiolsulphonic asid (HTSA); and hydrophobic amines (HAs): -2,6-bis (N, N-dimethylaminomethyl) -4-methylphenol (AP_1)
and 2,6-bis (N, N-dimethylaminomethyl) -4-chlorophenol (AP_2).

2. Experimental

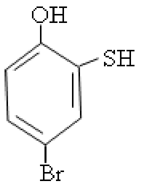
2.1 Reagents and Instruments

The initial solution of Cr (VI) and Co (II) was prepared by dissolving $K_2Cr_2O_7$ and $Co(NO_3)_2 \times 6H_2O$, respectively, in distilled water. Working solutions of Cr (VI) and Co (II) (0.1 mgL^{-1}) were prepared by appropriate dilution of the stock solution. The concentration of the chromium and cobalt solution was adjusted gravimetrically [8].

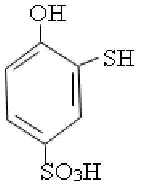
TCs was synthesized according to the procedure [9]. Chloroform solutions of TCs (0.01 mol L^{-1}) and HAs (0.02 mol L^{-1}) were used. To create the optimum acidity, 0.1 mol L^{-1} solutions of HCl, NaOH, or ammonium acetate {$CH_3COOH+CH_3COONH_4$ (pH 4-12)} buffers were applied.

Complexing agents may be a dibasic (HBTP, HTSA) weak acid, and depending on pH of the medium may be in molecular and anionic forms. Some characteristics of the reagents studied are presented in Table 2.

Table 2: Some characteristics of the studied reagents



HBTP



HTSA

$pK_1=5.10$; $pK_2=10.6$ $pK_1=4.80$; $pK=8.73$

pH neutral form of existence:

0 – 3.5 (λ=283 nm); 0 – 3.1 (λ=297 nm)

The synthesized compounds were characterized by physicochemical methods: IR [10] and NMR spectroscopy (Table 3).

Table 3: Results of studies of IR and NMR spectroscopy TCs

Reagent	IR (KBr) [10]	1H NMR (300.18 MHz, C_6D_6)
HBTP	3458 см$^{-1}$ ν(OH), 2568 см$^{-1}$ ν(SH), 1550 см$^{-1}$ ν(C_6H_5)	δ 5.60 (s, 1H- OH), δ 3.35(s, 1H- 1SH), δ 6.85 (s, 1H Ar-H), δ 7.15 (s, 2H Ar-H)
HTSA	3462 см$^{-1}$ ν (OH), 2571см$^{-1}$ ν(SH), 1579 см$^{-1}$ ν(C_6H_5) (Fig.4)	δ 5.72 (s, 1H- OH), δ 3.41(s, 1H - SH), δ 7.06 (s, 1H Ar-H), δ 6.25 (s, 2H Ar-H), δ 1.42 (s, 1H SO_3H).

The absorbance of the extracts was measured using a SF 26 spectrophotometer and KFK 2 photocolorimeter. 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 General procedure for the determination of chromium (VI) and cobalt (II)

Portions of stock solutions of chromium (VI) and cobalt (II) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.5 mL portion of a 0.01 M solution of TCs, and a 2.0 mL portion of a 0.01M solution of HAs were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 0.1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 10 minnute 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 490 nm (in case of cobalt 540 nm) (ℓ=0.5cm).

2.3 Determination of chromium and cobalt content in milk

A sample of milk (10 ml) is evaporated in a water bath in a porcelain dish to dryness, charred and 1 ml of conc. HNO_3, evaporated, then calcined in a muffle furnace at 450-500°C. 5-7 ml of a 1 M solution of KOH, 0.4-0.5 ml of a 3% solution of H_2O_2 are added to the dry residues, the solution is heated to 70-80°C for 5-10 minutes, evaporated to dryness, poured 5-7 ml of the pod, again evaporated to dryness. Then 1 M HCl is added, heated to 60-70°C, and filtered in a 25 ml flask with a capacity of 1 M HCl. A portion of aliquot of the resulting solution is selected, transferred to a in a separatory funnel, the desired pH is adjusted by the addition of 0.1 M HCl. 2.2 ml of 0.01 M TCs and 0.01 M HAs were added. The volume of the organic phase was adjusted to 5 ml of chloroform and a total of up to 25 ml of distilled water. 10 minutes after shaking, a portion of the organic extract was transferred through filter paper to the well and the absorbance was read at ℓ = 440 nm (in the case of cobalt = 540 nm) against chloroform. The content of chromium and cobalt was found on the calibration graph.

2.4 Determination of chromium content in sour cream and cottage cheese

A portion of sour cream (10 g) or cottage cheese (10 g) in a porcelain crucible is charred on a plate, 1 ml of conc. HNO_3, evaporated and then calcined in a muffle furnace at 450-500°C. The determination of chromium and cobalt continues in accordance with the above described procedure for determining the chromium and cobalt content of the milk.

2.5 Studies on the oxidation state of Chromium

It is known that TCs have reducing properties in acidic medium [10, 11]. Previous investigations with Cr (VI)-TCs and Cr(III)-TCs suggested that only Cr(III) forms stable complexes with this reagent. To elucidate the oxidation state of chromium in the presence of other TCs (HBTP and HTSA), we conducted two series of experiments. In the first series we used Cr(VI), while in the second series we used Cr(III) obtained by addition of a supplementary reducing agent ($SnCI_2$ or KI). The comparison of the obtained spectra showed that λ_{max} Cr(VI)-TCs=λ_{max} Cr(III)-TCs. This fact can be regarded as an indication [10, 11] that Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation.

3. Results and Discussion

3.1 Choice of solvent

As TCs is insoluble in water, an organic solvent was used for the system. For the extraction of complexes we used $CHCl_3$, CCl_4, C_6H_6, $C_6H_5CH_3$, $C_6H_4(CH_3)_2$, $C_2H_4Cl_2$, *iso*-butanol and *iso*-pentanol. The extractivity of the complexes was estimated by the distribution coefficient and recovery. Chloroform, dichloroethane and chlorobenzene appeared to be the best extractants. All the further investigations were carried out with chloroform. After a single extraction with chloroform, 97.4-98.8% of chromium and cobalt was extracted as an ion associate. The content of chromium and cobalt in the organic phase was determined photometrically by diphenylcarbazide [12] and α-nitros-β-naphthol [4, 12], after stripping respectively, and in the aqueous phase by the difference. The basis of HAs does not significantly affect the degree of chromium and cobalt extraction.

3.2 Effect of pH of the aqueous phase

For the formation and extraction of chromium (III) and cobalt (II) complexes, pH 2.9-4.9 and 3.3-6.8, respectively, are optimal. At the beginning, with increasing acidity of the initial solution, the extraction of Cr (III) and Co (II) increases, and with further increase - gradually decreases, which is obviously associated with a decrease in the concentration of the ionized form of H_2L, and is most likely in solution in undissociated form. With an increase in pH> 8.1, the formation of mixed-ligand complex (MLC) is practically not observed, which is apparently due to a decrease in the degree of protonation of amines.

The dependence of the optical density on pH is shown in Table 4.

3.3 Effect of reagent concentration and aging time

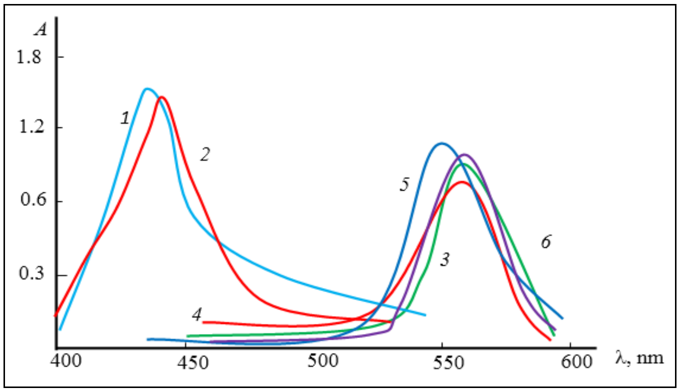
The optimal condition for the formation and expression of these codents is concentration (1.3-1.5) × 10^{-3} M TCs and (1.2 1.5) × 10^{-3} M HAs. Extracts of Cr^{3+} and Co^{2+} radionuclides obey the basic law of light absorption at concentrations of 0.2-20 and 0.2-22 μg / ml, respectively. MLC are resistant to water and organic waste, and they are not diluted for three days, and after extraction more than a month. The maximum optical density of chromium (III) complexes and cobalt (II) is reached within 12 and 10 minutes, respectively.

Table 4: Optimal formation conditions and analytical characteristics of MLC of chromium (III) and cobalt (II) with TCs and Has

Compound	pH		λ_{max}, нм	ε×10^{-4}	lgK_{eq}	lgK_{ex}	R,%	Working range / μg mL^{-1}
	pH range complexation	The pH range of Maximum extraction						
Cr-HBTP-AP_1	1.5-5.6	2.9-4.4	437	3.73	2.27	10.4	98.4	0.2-18
Cr-HBTP-AP_2	1.7-6.0	2.9-4.9	440	3.57	2.74	10.6	98.5	0.2-19
Co- HBTP -AP_1	1.0-7.2	3.3-5.2	560	3.94	2.68	12.8	98.7	0.2-20
Co- HBTP -AP_2	1.5-6.6	3.5-4.8	555	3.43	2.83	12.7	98.6	0.2-17
Co-HTSA-AP_1	2.0-8.1	5.3-6.4	545	4.14	2.93	13.4	98.1	0.2-20
Cr-HTSA-AP_2	2.5-7.6	5.5-6.8	560	4.09	2.97	13. 8	98.8	0.2-22

3.4 Electronic absorption spectra

The absorption maxima (λ_{max}) of the Cr (III) - HBTP-HAs triple complexes lie in the range 437-440 nm (in the case of cobalt 545-560 nm) (Table 1, Fig. 1). The contrast of the reactions was high: the initial reagents were colorless (λ_{max} (TCs) = 270-280 nm), and the complexes intensively stained. The molar absorption coefficients for chromium complexes (2.70 - 2.74) × 10^4 L mol^{-1} cm^{-1} (in the case of cobalt (3.43 - 4.14) × 10^4 L mol^{-1} cm^{-1}).



1- Cr-HBTP-AP_2; *2*- Cr-HBTP-AP_1; *3*- Co-HTSA-AP_1; *4*- Co-HTSA-AP_2; 5- Co-HBTP-AP_1; 6- Co-HBTP-AP_2
$C_{Cr\,(III)}$ =3.84×10^{-5} M; $C_{Co(II)}$ = 2.035×10^{-5} M; C_{TCs}=(1.3-1.5)×10^{-3} M; C_{HAs}=(1.2-1.5))×10^{-3} M; CF-26, ℓ=1.0 см

Fig 1: Absorption of mixed-ligand complexes

3.5 Composition, structure and stability

The molar relationships between the components of the ternary complex were found by several methods: the method of relative profitability of the old Barbanel, the linear method, and the equilibrium shift method [13]. When three chromium ions interact with three HBTP molecules, they form triple-charged anionic complexes that are extracted by three protonated HAs molecules. (Fig. 2 and 3). İn the case of cobalt the results suggest the complex composition of Co:TCs:HAs= 1:2:1. These HAs are included into the complex as double charged molecules.

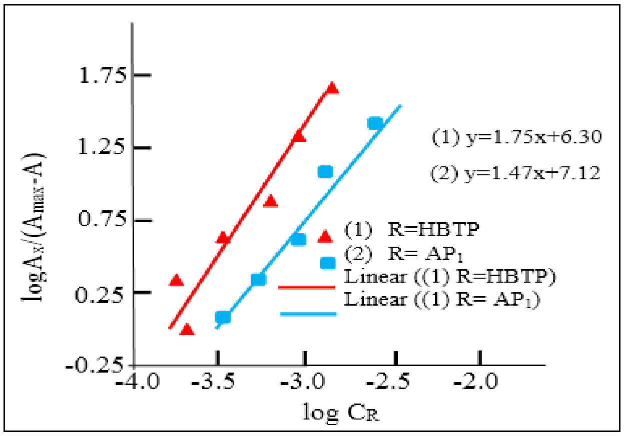


Fig 2: Determination of the HITP-to-Cr (straight line 1) and the AP_1-to-Cr (straight line 2) molar ratios by the mobile equilibrium method. C_{Cr} = 3.84×10^{-5} M , C_{HBTP} = 1.5×10^{-3} M, C_{AP1} = 1.2×10^{-3} M, λ=440 nm, KFK-2, ℓ=0.5 cm.

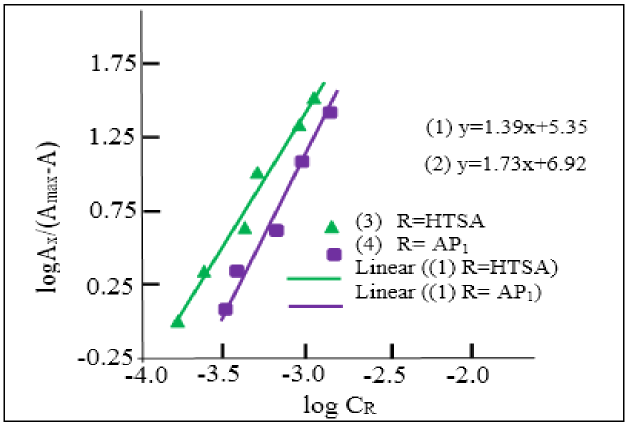


Fig 3: Determination of the HITP-to-Co (straight line 1) and the AP_1-to-Co (straight line 2) molar ratios by the mobile equilibrium method. C_{Co} = 2.035×10^{-5} M, C_{HTSA} = 1.5×10^{-3} M, C_{AP1} = 1.2×10^{-3} M, λ=560 nm, KFK-2, ℓ=0.5 cm.

The existence of clearly defined absorption bands at 2410 - 2415 cm^{-1} in the IR-spectrum of the complex indicates the coordination of the HAs in the protonated form [14]. The disappearance of the band at 2580 cm^{-1}, characteristic for the spectrum of TCs, 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.

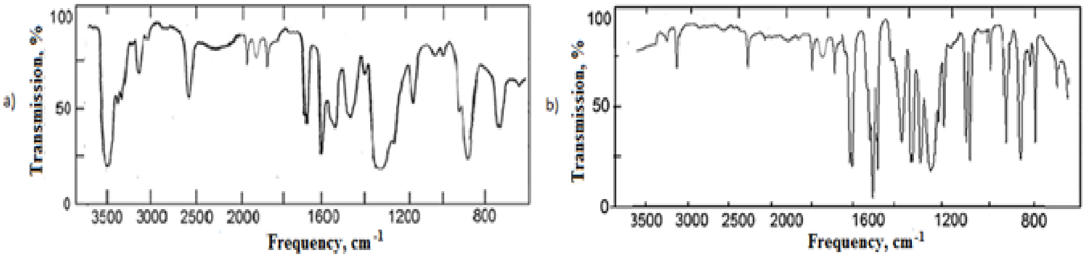


Fig 4: IR spectrums of HTSA (*a*) and the Co(II)-HTSA-AP1 (*b*).

It was established by Nazarenko's method that the complexing form of chromium (III) and cobalt (II) is Cr^{3+} and Co^{2+}, respectively [15]. The calculations showed that the MLC in the organic phase does not polymerize and is in monomeric form (γ = 1.01-1.05). The degree of polymerization of the complexes was calculated from the equation given in [16]. Proceeding from the obtained data, we propose the following structure for the extracted ternary complex (Fig 1 and 2).

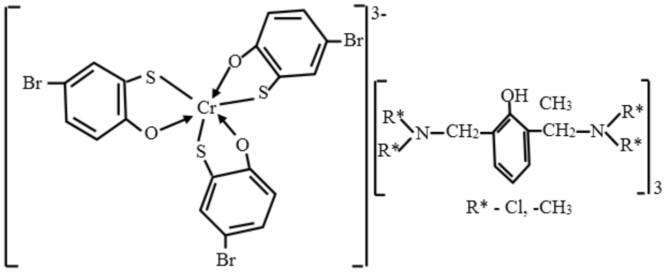


Fig 5: Structure of complexes Cr-HTBP-HAs.

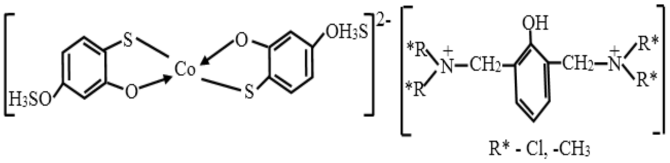


Fig 6: Structure of complexes Co-HTSA-HAs

The mechanism of RLK formation can be represented as follows: Ions Cr^{3+} and Co^{2+} interact with H_2L molecules to form anionic complexes that are extracted from protonated HAs. The composition of the extractable complexes can be represented by the formula $(HAs)_3\,[Cr(HL)_3]$ and $(HAs)[Co(HL)_2]$. Suppose that complexation processes occur:

$$Cr^{3+} + 3H_2L \Leftrightarrow [Cr(HL)_3]^{3-} + 3H+ \quad (1)$$
$$Co^{2+} + 2H_2L \Leftrightarrow [Co(HL)_2]^{2-} + 2H+ \quad (1”)$$
$$[Cr(HL)_3]^{3-} + 3HAs+ \Leftrightarrow (HAs)_3[Cr(HL)_3] \quad (2)$$
$$[Co(HL)_2]^{2-} + HAs+ \Leftrightarrow (HAa)[Co(HL)_2] \quad (2”)$$

After solving equation (1) and (2), the values of the equilibrium constant (lgK_{eq}) and the extraction constant (lgK_{ex}) calculated by equationsl

$$lgK_{eq} = lgD - 3lg[HAs^+] \text{ и } lgK_{ex} = lgD - 3lg[TCs] - 3lg[HAs]$$

(in the case of cobalt, $lgK_{eq} = lgD - lg[HAs^+]$ and $lgK_{ex} = lgD - lg[TCs] - lg\,[HAs]$) are respectively shown in Table 4.
In Table 4. The main spectrophotometric characteristics of the procedure for determining chromium and cobalt are presented.

3.6. Influence of foreign ions

The effect of a number of cations and anions on the accuracy of the determination of chromium and cobalt was studied. The experiments were carried out according to the recipe on which the calibration curves were plotted, with the only difference being that a certain amount of the corresponding ions was introduced into the solution of chromium and cobalt. The selectivity of the spectrophotometric determination of chromium and cobalt in the form of the studied complexes is shown in Table 5 and 6. It has been established that large amounts of alkali, alkaline earth elements, rare earth elements, F^-, CI^-, Br^-, SO_3^{2-}, SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with the determination of chromium and cobalt. The selectivity of the determination is significantly increased in the presence of masking agents.

Table 5: Effect of foreign ions on the extraction of 20 μg chromium (III) (*n* = 5, *P* = 0,95).

Foreign ions	Molar excess of the ion	Masking agent	Found Cr, μg; (S_r)	
			HBTP-AP₁	**HBTP-AP₂**
Co(II)	70	$NaNO_2$	20.2 (0.06)	19.7(0.02)
Ni(II)	25		19.9 (0.03)	20.2(0.03)
Fe(II)	120	PO_2^{3-}	20.0 (0.05)	20.3(0.03)
Fe(III)	10	Ascorbic acid	20.2 (0.02)	20.3(0.03)
Cd(II)	60	NaI	20.2 (0.05)	19.8(0.02)
Al(III)	10	NaF	19.9 (0.03)	20.7(0.05)
Bi(III)	1:1	$CS(NH)_2$	19.5 (0.06)	20.3(0.03)
Nb(V)	20	Wine acid	20.2 (0.02)	19.5(0.01)
Zr(IV)	40		19.6 (0.03)	19.6(0.05)
Cu(II)	55	$CS(NH)_2$	20.5 (0.03)	20.4(0.01)
Hg(II)	35		20.0 (0.0)	20.3(0.01)
Ti(IV)	20	Wine acid	19.6 (0.01)	19.7(0.02)
V(V)	70	ЭДТА	19.8 (0.06)	19.8(0.06)
W(VI)	40		19.7 (0.03)	20.6(0.03)
Mo(VI)	140		20.0 (0.0)	20.0(0.0)
Ta(V)	45	Wine acid	19.5 (0.03)	20.3(0.01)
UO_2^{2+}	50	Wine acid	19.7 (0.05)	20.5(0.06)
Cr(VI)	50	$CS(NH)_2$	19.6 (0.05)	20.0(0.0)
Mn(II)	50		19.7 (0.01)	20.0(0.0)

Table 6: Effect of foreign ions on the extraction of 20 μg cobalt (II) (*n* = 5, *P* = 0,95).

Foreign ions	Molar excess of the ion	Masking agent	Found Co, μg; (S_r)			
			HBTP-AP$_1$	HBTP-AP$_2$	HTSA-AP$_1$	HTSA-AP$_2$
W(V)	50	$NaNO_2$	20.1 (0.03)	19.6 (0.03)	20.2 (0.01)	19.8 (0.02)
Ni(II)	50		19.9 (0.04)	19.8 (0.04)	19.8 (0.05)	20.2 (0.05)
Fe(II)	200	PO_4^{3-}	19.8 (0.05)	20.2 (0.05)	19.9 (0.03)	20.2(0.03)
Fe(III)	60	Thioglycolic acid	20.2 (0.02)	19.7 (0.03)	20.2 (0.02)	20.3(0.03)
Cd(II)	200	NaI	19.6 (0.05)	19.8 (0.04)	19.7 (0.05)	20.5(0.06)
Bi(III)	1:12	$CS(NH)_2$	19.6 (0.03)	19.8 (0.03)	19.8 (0.06)	19.8(0.06)
Nb(V)	50	$C_2O_4^{2-}$	20.1 (0.04)	20.0 (0.04)	19.5 (0.02)	19.6 (0.02)
Zr(IV)	50		19.5 (0.02)	19.8 (0.02)	19.6 (0.03)	19.5 (0.02)
Cu(II)	25	$CS(NH)_2$	19.5 (0.02)	19.6 (0.02)		
Hg(II)	40		19.2 (0.02)	20.3 (0.02)	19.2 (0.04)	19.1 (0.02)
Ti(IV)	40	Ascorbic acid	19.6 (0.02)	20.6 (0.02)	19.2 (0.04)	19.1 (0.02)
V(V)	50	EDTA	19.9 (0.02)	19.8 (0.04)	19.2 (0.04)	19.6 (0.03)
Mo(VI)	10	EDTA	20.4 (0.02)	20.0 (0.02)	19.5 (0.02)	19.6 (0.02)
Cr(III)	120		19.5 (0.01)	19.2 (0.02)		
Ta(V)	45	Ascorbic acid	20.0 (0.03)	19.2 (0.03)	19.5 (0.02)	19.6 (0.03)
UO_2^{2+}	50		20.2 (0.01)	19.8 (0.02)	20.0 (0.0)	20.3(0.01)
Cr(VI)	50	$CS(NH)_2$	19.2 (0.04)	19.1 (0.02)	19.5 (0.02)	19.5 (0.02)
Mn(VII)	50	$CS(NH)_2$	19.1 (0.03)	19.4 (0.04)	19.9 (0.04)	19.8 (0.04)
Mn(II)	50		19.1 (0.02)	20.1 (0.02)	20.2 (0.02)	19.5(0.01)

3.6 Analytical Characteristics

In Table 7 shows the analytical characteristics of certain chromium and cobalt complexes with TCs and HAs.

Table 7: Analytical characteristics of some ternary complexes of chromium and cobalt with TCs and Has

Compound	Sandell's sensitivity, μg cm^{-2}	Limit of detection , ng mL^{-1}	Limit of quantificat ion, ng mL^{-1}	The equation of calibration curves	Correlation coefficient
Cr-HBTP-AP$_1$	0.0033	11	36	0.032+0.25x	0.9987
Cr-HBTP-AP$_2$	0.0034	12	40	0.027+0.24x	0.9974
Co-HBTP-AP$_1$	0.0035	11	36	0.045+0.22x	0.9931
Co-HBTP-AP$_2$	0.0038	12	40	0.039+0.21x	0.9981
Co-HTSA-AP$_1$	0.0040	15	50	0.015+0.20x	0.9891
Co-HTSA-AP$_2$	0.0040	14	45	0.014+0.20x	0.9956

Table 8 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of chromium and cobalt with the earlier known procedures [3, 4, 6, 12, 17-20].

Table 8: Comparative characteristics of the procedures for determining chromium and cobalt

Reagent	pH (solvent)	λ, nм	ε·10^{-4}	Beer's law range, μg	[Ref.]
Cr–5-Br–DMPAP	0.1–10 M HCl ($CHCl_3$)	546	7.8	0.02 – 0.56	[17]
Cr–PAR	4-5	540	4.7	3.2-13.0	[18]
Cr–PAN	0.2–0.8 M HCl (aseton)	390-400	1.28	0.3 – 2.0	[4,6,19]
Cr–Br–PADAP	4.7	600	7.93	0.6 – 15.0	[20]
Cr – diphenylcarbazide	1N HCl (aseton)	540	2.7	0.25-1.0	[12]
Co–PAR–TTC	5.2-5.8($CHCl_3$)	525	4.26	0.2 - 1.5	[3]
Co–Nitroso-R-salt	weakly acidic medium	415	3.5		[4,12]
Co–1-nitroso-2-naphtol	3.4-6.9 ($CHCl_3$)	415	2.9		[4,12]
Co– 2-nitroso-1-naphtol	3.0-7.2 ($CHCl_3$)	365	3.7		[4,12]
Cr–HBTP–AP$_1$	2.9-4.4 ($CHCl_3$)	437	3.73	0.2-18	Proposed method
Cr–HBTP–AP$_2$	2.9-4.9 ($CHCl_3$)	440	3.57	0.2-19	
Co–HBTP–AP$_1$	3.3-5.2 ($CHCl_3$)	560	3.94	0.2-20	
Co– HBTP –AP$_2$	3.5-4.8 ($CHCl_3$)	555	3.43	0.2-17	
Co–HTSA–AP$_1$	5.3-6.4 ($CHCl_3$)	545	4.14	0.2-20	
Cr–HTSA–AP$_2$	5.5-6.8 ($CHCl_3$)	560	4.09	0.2-22	

4. Analytical Applications

The proposed method, within the established optimal conditions, was used to determine Cr (III) and Co(II) in milk, sour cream and cottage cheese. The results presented in Table 9 show successful applicability of the proposed method to real analysis of samples. The correctness of the results of the analysis is verified by the method of additives.

Table 9: Determination of chromium and cobalt in milk, sour cream and cottage cheese. The correctness of the results is proved by the method of additives (*n*=6, *P*=0,95).

An object	Chromium, μg				Cobalt, μg			
	Introduced	Found	S_r	$\Delta\bar{G} \pm t_\alpha \times \frac{S}{\sqrt{n}}, \mu g$	Introduced	Found	S_r	$\Delta\bar{G} \pm t_\alpha \times \frac{S}{\sqrt{n}}, \mu g$
Milk	-	-	-	-	-	-	-	-
	5	5.10	0.37	5.10±0.040	5.0	6.02	0.29	6.02±0.030
	5	5.13	0.50	5.13±0.030	5.0	5.96	0.46	5.96±0.041
Sour Cream	-	-	-	-	-	-	-	-
	5	5.13	0.50	5.13±0.030	5.0	5.32	0.52	5.32±0.023
	10	10.10	0.90	10.10±0.015	10.0	10.41	0.88	10.41±0.029
Cottage Cheese	-	-	-	-	-	-	-	-
	5	4.42	0.81	4.92±0.042	5.0	5.03	0.73	5.03±0.035
	10	9.94	0.41	9.94±0.043	10.0	10.04	0.28	10.04±0.044

Concisions

1. The following reagents were used: thiocatechols (TCs, H_2L):2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-3-thiolsulphonic asid (HTSA); and hydrophobic amines (HAs): -2,6-bis (N, N-dimethylaminomethyl) -4-methylphenol (AP_1) and 2,6-bis (N, N-dimethylaminomethyl) -4-chlorophenol (AP_2). TCs are determined by physicochemical methods: IR spectroscopy and NMR spectroscopy: IR (KBr, ν, см$^{-1}$): HBTP { 3458 см$^{-1}$ ν(OH), 2568 см$^{-1}$ ν(SH), 1550 см$^{-1}$ ν(C_6H_5)}; HTSA { 3462 см$^{-1}$ ν (OH), 2571см$^{-1}$ ν(SH), 1579 см$^{-1}$ ν(C_6H_5)}. 1H NMR (300.18 MHz, C_6D_6, δ, ppm): HBTP {δ 5.60 (s, 1H-OH), δ 3.35(s, 1H- 1SH), δ 6.85 (s, 1H Ar-H), δ 7.15 (s, 2H Ar-H) }; HTSA{δ 5.72 (s, 1H- OH), δ 3.41(s, 1H -SH), δ 7.06 (s, 1H Ar-H), δ 6.25 (s, 2H Ar-H), δ 1.42 (s, 1H SO_3H)}.
2. To elucidate the oxidation state of chromium in the presence of TCs, we conducted two series of experiments. In the first series we used Cr(VI), while in the second series we used Cr(III) obtained by addition of a supplementary reducing agent (SnCI2 or KI). The comparison of the obtained spectra showed that λ_{max} Cr(VI)- TCs= λ_{max} Cr(III)- TCs. This fact can be regarded as an indication that Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation.
3. After a single extraction with chloroform, 97.4-98.8% of chromium and cobalt was extracted as an ion associate. For the formation and extraction of chromium (III) and cobalt (II) complexes, pH 2.9-4.9 and 3.3-6.8, respectively, are optimal. The optimal condition for the formation andexpression of these codents is concentration (1.3-1.5) × 10^{-3} M TCs and (1.2 1.5) × 10^{-3} M HAs. Extracts of Cr^{3+} and Co^{2+} radionuclides obey the basic law of light absorption at concentrations of 0.2-20 and 0.2-22 μg / ml, respectively. The maximum optical density of chromium (III) complexes and cobalt (II) is reached within 12 and 10 minutes, respectively.
4. The absorption maxima of the Cr (III) - HBTP-HAs triple complexes lie in the range 437-440 nm (in the case of cobalt 545-560 nm). The molar absorption coefficients for chromium complexes (2.70 - 2.74) × 10^4 L×mol^{-1} × cm^{-1} (in the case of cobalt (3.43 - 4.14) × 10^4 L × mol^{-1} × cm^{-1}).
5. The molar relationships between the components of the ternary complex were found by several methods: the method of relative profitability of the old Barbanel, the linear method, and the equilibrium shift method (Cr:TCs:Has = 1:3:3 and Co:TCs:Has = 1:2:1). It was established by Nazarenko's method that the complexing form of chromium (III) and cobalt (II) is Cr^{3+} and Co^{2+}, respectively. The calculations showed that the MLC in the organic phase does not polymerize and is in monomeric form (γ = 1.01-1.05).
6. It has been established that large amounts of alkali, alkaline earth elements, rare earth elements, F-, CI-, Br-, SO_3^{2-}, SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with the determination of chromium and cobalt. The selectivity of the determination is significantly increased in the presence of masking agents.
7. The proposed method, within the established optimal conditions, was used to determine Cr (III) and Co(II) in milk, sour cream and cottage cheese.

References

1. Othmer K, Encyclopedia of Chemical Technology, John Wiley & Sons: New York. 1981.
2. Oh RC, Brown DL. Vitamin B12 deficiency, American Family Physician. 2003; 67(5):979-986.
3. Divarova VV, Gavazov KB, Lekova VD, Dimitrov AN. Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts chemija. 2013; 24(2):81-87.
4. Pyatnitskiy IV. Analiticheskaya khimiya kobal'ta. 1965(In Russian).
5. Kuliyev KA, Verdizadeh NA, Suleymanova GS. Spectrophotometric Determination of Cobalt (II) with 2, 6-Dithiolphenol and Its Derivatives in the Presence of Hydrophobic Amines American Journal of Chemistry. 2016; 6(4):95-103.
6. Luciene SC, Antonio CS, Sérgio LC, Leonardo SG. Spectrophotometric Determination of Chromium in Steel with 4-(2- thiazolylazo)-resorcinol using microwave radiation J. Braz. Chem. Soc. 2004; 15(1):153-157.
7. Mamedova RK, Aliyev SG, Hasanova NS, Verdizadeh

NA, Zalov AZ. International Journal of Chemical Studies. Extraction-spectrophotometric study of ternary complexes of Cr (VI) using O-Hydroxythiophenols and Aminophenol. 2017; 5(4):1255-1262.

8. Korostelev PP. Preparation of solutions for chemical analysis works. Publishing house of Academy of Sciences of the USSR, 1964.
9. Kuliev AM, Aliev SR, Mamedov FN, Movsumzade M. Synthesis of aminomethyl derivatives of 2-hydroxy-5-tert-alkylthiophenols and their cleavage by thiols Zhurnal Organicheskoi Khimii. 1976; 12(2):426-430.
10. Verdizadeh NA, Zalov AZ, Kuliev KA, Amrakhov TA, Samedova VM. Extraction-photometric determination of molybdenum as a mixed ligand complex with 2-hydroxy-5- chlorothiophenol and diphenylguanidine. Journal of Analytical Chemistry. 2000; 55(4):331-334.
11. Zalov AZ, Verdizade NA. Extraction-spectrophotometry determination of tungsten with 2-hydroxy-5-chlorothiophenol and hydrophobic amines. Journal of Analytical Chemistry. 2013; 68 (2):212-217.
12. Marczenko Z, Baltsejak MK. Metodı Spectrophotometrii v UF I vidimoy oblastyax(Spectrophotometrically in the UV and visible regions in inorganic analysis). M. Binom. Laboratoriya znaniy, 2007, 711.
13. Bulatov MI, Kalinkin IP. Prakticheskoe rukovodstvo po fotokolorimetricheskim I spektrofotometri Cheskim metodam analiza (Practical Guide on Photocolorimetric and Spectropho-tometric Methods of Analysis). Moscow, Khimiya, 1972.
14. Bellami L. Infrakrasnie spectri slojnikh molecul (The Infra-Red Spectra of Complex Molecules). Moscow, Mir, (In Russian), 1991, 592.
15. Nazarenko VA, Biryuk EA. A study of the chemistry of reactions of multivalent element ions with organic reagents. Zh. Anal. Khim. 1967; 22(13):57-64.
16. Akhmedly MK, Kly'gin AE, Ivanova LI, *et al.* On the chemistry of interaction of gallium ions with a number of sulphophtaleins. Zhurnal Neorganicheskoi Khimii. 1974; 9(8):2007-2012.
17. Zhao Y, Han G. Rapid spectrophotometric determination of chromium (III). Talanta. 1994; 419(10):1247-1251.
18. Yotsuyanagi T, Takeda Y, Yamashita R, Aomura K. The extraction-spectrophotometric determination of chromium (III) with 4-(2-pyridylazo)-resorcinol. Anal. Chim. Acta. 1973; 67(3):297-302.
19. Subrahmanyam B, Eshwar MC. Extractive Spectrophotometric Determination of chromium (iii) with 1-(2-pyridylazo)-2-naphthol. Bull. Chem. Soc. Jpn. 1976; 49(4):347-350.
20. Sheng WF, Rui ZY, Hua QP, Fang Y, Kui SN. Spectrophotometric determination of microgram amounts of chromium (VI) and total chromium in waste water. Mikrochim. Acta. 1982; 77(2):67-72.