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# SPECTROPHOTOMETRIC STUDY OF TERNARY COMPLEXES OF Cr (VI) and Co (II)

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*The following reagents were used: thiocatechols (TCs, $H_2L$):2-hydroxy-5-iodthiophenol (HBTP), and 2-hydroxy-5-nitrothiophenol (HNTP); and aminophenols (HAs): -2(N, N-dimethylaminomethyl)phenol - ($AP_1$) and 2(N, N-dimethylaminomethyl) -4- methylphenol ($AP_2$). The TCs were characterized by physicochemical methods: IR and NMR spectroscopy. Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation. After a single extraction with chloroform, 98.4-98.7% of chromium and cobalt was extracted as an ion associate. For the formation and extraction of chromium (III) and cobalt (II) complexes, pH 1.3-5.8 and 1.0-7.2, respectively, are optimal. The optimal condition for the formation and extraction of these codents is concentration (1.3-1.5) × $10^{-3}$ M TCs and (1.2-1.5) × $10^{-3}$ M AP. For $Cr^{3+}$ and $Co^{2+}$ ions, the Beer law is valid in the ranges 0.2-19 and 0.2-20 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) - HITP-AP triple complexes lie in the range 438-442 nm (in the case of cobalt 540-555 nm). The molar absorption coefficients for chromium complexes (3.57 – 3.73 4) × $10^4$ (in the case of cobalt (2.43 - 2.94) × $10^4$). The molar relationships between the components of the ternary complex were found by several methods (Cr:TCs:AP=1:3:3 and Co:TCs:AP=1:2:2). 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). 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, extraction, spectrophotometry, thiocatechols, aminophenols*
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## Introduction

According to the analogy hypothesis, reactions with reagents of the R-SH type are possible for ions of elements forming sulfides that are poorly soluble in water [1]. Chromium and cobalt are some of the metals that have chromophore properties, so among many photometric methods for their determination there are both methods based on the use of color reagents with chromophore groups and methods that use colorless reagents. Most methods are very selective.

Numerous methods are known for the photometric determination of chromium and cobalt using reagents belonging to various classes of organic compounds [2-8]. Methods have been developed for determining elements in the form of multiligand complexes (MLC) with 2-hydroxy-5-nitrrothiophenol [5] and 2,6-dithiol-4-alkiylphenols in the presence of hydrophobic amines [6]. However, research aimed at finding and researching new spectrophotometric reagents with various functional groups is still ongoing.

The following reagents were used in this work: thiocatechols (TCs, $H_2L$): 2-hydroxy-5-iodothiophenol (HITP) and 2-hydroxy-5-

nitrothiophenol (HNTP); and aminophenols (AP): -2- (N,N-dimethylaminomethyl) phenol ($AP_1$) and 2- (N,N-dimethylaminomethyl)-4-methylphenol ($AP_2$).

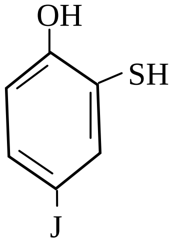
## Materials and methods

**Reagents.** 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 [9].

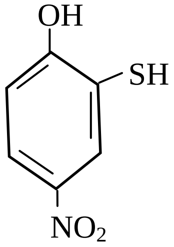
TCs was synthesized according to the procedure [10]. Chloroform solutions of TCs (0.01 mol/l) and AP (0.02 mol/l) were used.

To create the optimum acidity, 0.1 mol/l solutions of HCl, NaOH, or ammonium acetate {$CH_3COOH+CH_3COONH_4$ (pH 4-12)} buffers were applied.

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



HITP



HNTP

$pK_1$=5.0; $pK_2$=10.2

$pK_1$=3.52; pK=9.72

pH neutral form of existence:

0 – 3.4 (λ=280 nm);

0 – 2.6 (λ=295 nm)

The synthesized compounds were characterized by physicochemical methods: IR and NMR spectroscopy: IR (KBr) [1] - { HITP [3458 см$^{-1}$ ν(OH), 2568 см$^{-1}$ ν(SH), 1550 см$^{-1}$ ν($C_6H_5$)]; HNTP [3462 см$^{-1}$ ν (OH), 2571см$^{-1}$ ν(SH), 1579 см$^{-1}$ ν($C_6H_5$) (Fig.2)]}and 1H NMR (300.18 MHz, $C_6D_6$) - {HITP [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)]; HNTP [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)].

**Apparatus.** The absorbance of the extracts was measured using a SP 26 spectrophotometer and KPK 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.

**Studies on the oxidation state of Chromium.** It is known that TCs have reducing properties in acidic medium [12]. 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 (HITP and HNTP), 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 $\lambda_{max}$ Cr(VI)-HITP =$\lambda_{max}$ Cr(III)- HITP. This fact can be regarded as an indication [12] that Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation.

**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 0.1ml 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 AP 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 KPK-2 at room temperature and 490 nm (in case of cobalt 540 nm) (ℓ=0.5cm).

**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 AP 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.

**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.

## Results and discussion

**The 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. Extractability of complexes was estimated in coefficient of distribution (*D*) and extent of extraction (*R*%) [12]:

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

The extractivity of the complexes was estimated by the distribution coefficient and recovery. $CHCl_3$ and $CCl_4$ appeared to be the best extractants. All the further investigations were carried out with chloroform. After a single extraction with chloroform, 98.4-98.7% 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 [3] and α-nitros-β-naphthol [2], after stripping respectively, and in the aqueous phase by the difference.

**Effect of pH of the aqueous phase.** For the formation and extraction of Cr (III) and Co (II) complexes, pH 1.3-5.8 and 1.0-7.2, 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> 7.2, the formation of 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 1.

**Effect of reagent concentration and aging time.** The optimal condition for the formation andexpression of these codents is concentration $(1.3\text{-}1.5)\times10^{-3}$ M TCs and $(1.2\text{-}1.5)\times 10^{-3}$ M AP. Extracts of $Cr^{3+}$ and $Co^{2+}$ ions 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 Cr (III) complexes and Co (II) is reached within 8 and 12 minutes, respectively.

**Table 1.** Optimal formation conditions and analytical characteristics of MLC of chromium (III) and cobalt (II) with TCs and AP

| Compound | pH range complexation | The pH range of maximum extraction | $\lambda_{max}$, nm | $\varepsilon \times 10^{-4}$ | $lgK_{eq}$ | $lgK_{ex}$ | R,% | Working range / μg $ml^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Cr-HITP-$AP_1$ | 1.3-5.4 | 2.5-4.1 | 438 | 3.73 | 4.27 | 10.4 | 98.4 | 0.2-18 |
| Cr-HITP-$AP_2$ | 1.5-5.8 | 2.2-3.9 | 442 | 3.57 | 4.74 | 10.6 | 98.5 | 0.2-19 |
| Co- HNTP -$AP_1$ | 1.0-7.2 | 3.3-5.2 | 540 | 2.94 | 5.68 | 12.8 | 98.7 | 0.2-20 |
| Co- HNTP -$AP_2$ | 1.5-6.6 | 3.5-4.8 | 555 | 2.43 | 5.83 | 12.7 | 98.6 | 0.2-16 |

**Electronic absorption spectra.** The absorption maxima ($\lambda_{max}$) of the Cr (III) - HITP-AP triple complexes lie in the range 438-442 nm (in the case of cobalt 540-555 nm) (Table 1, Fig. 1). The molar absorption coefficients for chromium complexes (3.73 – 3.57) × $10^4$ (in the case of cobalt (2.94 – 2.43) × $10^4$).

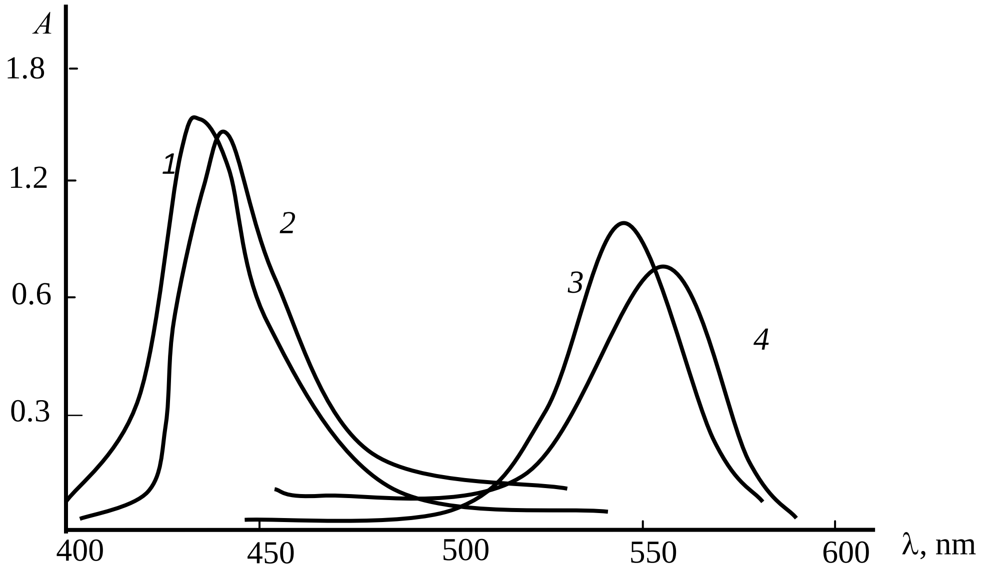


**Fig 1.** Absorption of mixed-ligand complexes

*1*- Cr-HITP-$AP_1$; *2*- Cr-HITP-$AP_2$; *3*- Co-HNTP-$AP_1$; *4*- Co-HNTP-$AP_2$

$C_{Cr\ (VI)} = 3.84 \times 10^{-5}$ M; $C_{Co(II)} = 2.035 \times 10^{-5}$ M; $C_{TCs} = (1.3\text{-}1.5) \times 10^{-3}$ M; $C_{HAP} = (1.2\text{-}1.5)\ ) \times 10^{-3}$ M; SP-26, ℓ=1.0 см

**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 HITP molecules, they form triple-charged anionic complexes that are extracted by three protonated AP molecules (Cr:HITP:AP=1:3:3). In the case of cobalt the results suggest the complex composition of Co:HNTP:AP= 1:2:2. These AP are included into the complex as double charged molecules.

The existence of clearly defined absorption bands at 2410 - 2415 $cm^{-1}$ in the IR-spectrum of the complex indicates the coordination of the AP in the protonated form [11]. 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 2.).

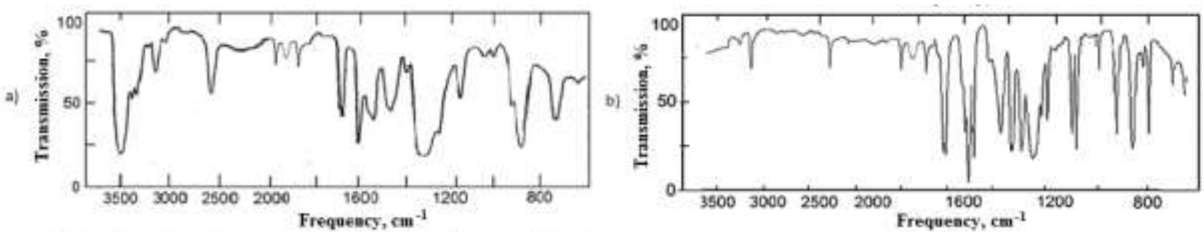
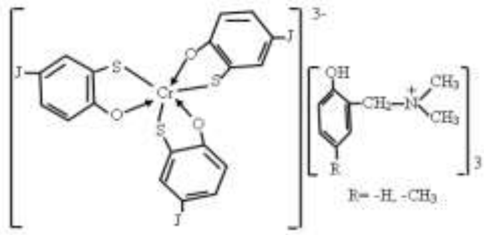
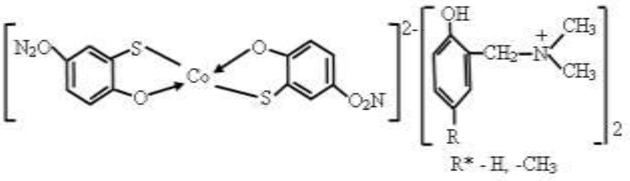


**Fig 2.** IR spectrums of HNTP(*a*) and the Co(II)-HNTP-AP$_1$ (*b*).

It was established by Nazarenko's method that the complexing form of chromium (III) and cobalt (II) is Cr$^{3+}$ and Co$^{2+}$, respectively [14]. The calculations showed that the MLC in the organic phase does not polymerize and is in monomeric form ($\gamma$ = 1.01-1.05). The degree of polymerization of the complexes was calculated from the equation given in [15]. Proceeding from the obtained data, we propose the following structure for the extracted ternary complex:





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

$$Cr^{3+} + 3H_2L \Leftrightarrow [Cr(HL)_3]^{3-} + 3H+ \qquad (1)$$

$$Co^{2+} + 2H_2L \Leftrightarrow [Co(HL)_2]^{2-} + 2H+ \qquad (1")$$

$$[Cr(HL)_3]^{3-} + 3HAP^{+} \Leftrightarrow (HAP)_3[Cr(HL)_3] \qquad (2)$$

$$[Co(HL)_2]^{2-} + 2HAP^{+} \Leftrightarrow (HAP)_2[Co(HL)_2] \qquad (2")$$

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

$\lg K_{eq} = \lg D - 3\lg[HAP^{+}]$ and $\lg K_{ex} = \lg D - 3\lg[TCs] - 3\lg[HAP]$ (in the case of cobalt, $\lg K_{eq} = \lg D - \lg[HAP^{+}]$ and $\lg K_{ex} = \lg D - 2\lg[TCs] - 2\lg[HAP]$) are respectively shown in Table 3. In Table 3 the main spectrophotometric characteristics of the procedure for determining chromium and cobalt are presented.

**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 2. 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 2.** Effect of foreign ions (FI) on the extraction of chromium (III) (30 μg) and cobalt (II) (20 μg) ($n = 5$, $P = 0.95$).

| FI | Molar excess of the ion | | Masking agent | Found Cr, μg; ($S_r$) | | Found Co, μg; ($S_r$) | |
|---|---|---|---|---|---|---|---|
| | Cr | Co | | HITP-$AP_1$ | HITP-$AP_2$ | HNTP-$AP_1$ | HNTP-$AP_2$ |
| Co(II) | 60 | - | $NaNO_2$ | 30.4 (0.06) | 30.7(0.02) | 20.3 (0.04) | 19.56 (0.04) |
| Ni(II) | 40 | 50 | | 29.6 (0.03) | 29.2(0.03) | 19.9 (0.04) | 19.7 (0.04) |
| Fe(II) | 10 | 200 | $PO_4^{3-}$ | 30.2 (0.05) | 29.3(0.03) | 19.9 (0.05) | 20.3 (0.05) |
| Fe(III) | 10 | 60 | Ascorbic acid | 30.3 (0.02) | 30.3(0.03) | 20.2 (0.02) | 19.7 (0.04) |
| Cd(II) | 70 | 20 | NaI | 30.4 (0.05) | 29.8(0.02) | 19.6 (0.05) | 19.8 (0.04) |
| Al(III) | 15 | 20 | NaF | 29.8 (0.03) | 29.7(0.05) | 19.6 (0.04) | 19.8 (0.04) |
| Bi(III) | 20 | 112 | $CS(NH)_2$ | 29.7 (0.06) | 30.3(0.03) | 20.1 (0.04) | 20.0 (0.04) |
| Nb(V) | 20 | 40 | Wine acid | 30.2 (0.02) | 29.5(0.01) | 19.6 (0.02) | 19.8 (0.05) |
| Zr(IV) | 45 | 40 | | 29.6 (0.03) | 29.6(0.05) | 19.4 (0.02) | 19.6 (0.02) |
| Cu(II) | 50 | 25 | $CS(NH)_2$ | 30.5 (0.03) | 30.4(0.01) | 19.3 (0.02) | 20.3 (0.06) |
| Hg(II) | 30 | 50 | | 30.0 (0.0) | 20.3(0.01) | 19.7 (0.02) | 20.6 (0.02) |
| Ti(IV) | 20 | 30 | Wine acid | 29.6 (0.01) | 19.7(0.02) | 19.8 (0.02) | 19.8 (0.04) |
| V(V) | 70 | 50 | EDTA | 29.8 (0.06) | 19.8(0.06) | 20.4 (0.02) | 20.0 (0.07) |
| W(VI) | 40 | 50 | $NaNO_2$ | 29.7 (0.03) | 20.6(0.03) | 19.4 (0.01) | 19.2 (0.02) |
| Mo( VI) | 140 | 10 | | 30.0 (0.0) | 20.0(0.0) | 20.2 (0.04) | 19.2 (0.04) |
| Ta(V) | 45 | 45 | Wine acid | 29.5 (0.03) | 20.3(0.01) | 20.3 (0.04) | 19.8 (0.02) |
| $UO_2^{2+}$ | 50 | 40 | Wine acid | 30.7 (0.05) | 20.5(0.06) | 19.4 (0.04) | 19.1 (0.02) |
| Cr(VI) | - | 60 | $CS(NH)_2$ | 30.6 (0.05) | 20.0(0.05) | 19.1 (0.02) | 20.1 (0.02) |
| Mn(II) | 50 | 40 | | 29.7 (0.01) | 20.0(0.05) | 20.3 (0.04) | 19.56 (0.04) |

**Analytical Characteristics.** In table 3 shows the analytical characteristics of certain chromium and cobalt complexes with TCs and AP.

**Table 3.** Analytical characteristics of some ternary complexes of chromium and cobalt with TCs and HAP

| 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-HITP-$AP_1$ | 0.0037 | 13 | 37 | $0.035+0.27x$ | 0.9986 |
| Cr-HITP-$AP_2$ | 0.0035 | 14 | 43 | $0.029+0.26x$ | 0.9975 |
| Co-HNP-$AP_1$ | 0.0043 | 16 | 52 | $0.017+0.23x$ | 0.9890 |
| Co-HNTP-$AP_2$ | 0.0047 | 15 | 48 | $0.015+0.22x$ | 0.9958 |

Table 4 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 [2-4, 7].

**Table 4.** Comparative characteristics of the procedures for determining chromium and cobalt

| Reagent* | pH ( solvent) | λ, пм | $\varepsilon \cdot 10^{-4}$ | Beer's law range, μg | [Ref.] |
|---|---|---|---|---|---|
| Cr–5-Br–DMPAP | 0.1–10 M HCl ($CHCl_3$) | 546 | 7.8 | 0.02 – 0.56 | [7] |
| Cr–PAR | 4-5 | 540 | 4.7 | 3.2-13.0 | [2,3,7] |
| Cr–PAN | 0.2–0.8 M HCl (aseton) | 400 | 1.28 | 0.3 – 2.0 | [2,3,7] |
| Cr–Br–PADAP | 4.7 | 600 | 7.93 | 0.6 – 15.0 | [7] |
| Cr – diphenylcarbazide | 1N HCl (aseton) | 540 | 2.7 | 0.25-1.0 | [3] |
| Co–PAR–TTC | 5.2-5.8($CHCl_3$) | 525 | 4.26 | 0.2 - 1.5 | [4] |
| Co–Nitroso-R-salt | weakly acidic medium | 415 | 3.5 | | [2] |
| Co–1-nitroso-2-naphtol | 3.4-6.9 ($CHCl_3$) | 415 | 2.9 | | [2] |
| Co– 2-nitroso-1-naphtol | 3.0-7.2 ($CHCl_3$) | 365 | 3.7 | | [2] |
| Cr–HBTP–$AP_1$ | 2.5-4.1 ($CHCl_3$) | 438 | 3.73 | 0.2-18 | Proposed method |
| Cr–HBTP–$AP_2$ | 2.2-3.9 ($CHCl_3$) | 442 | 3.57 | 0.2-19 | |
| Co-HNTP-$AP_1$ | 3.3-5.2($CHCl_3$) | 540 | 2.94 | 0.2-20 | |
| Co-HNTP-$AP_2$ | 3.5-4.8($CHCl_3$) | 555 | 2.43 | 0.2-16 | |

*Note: 5–Br-DMPAP – 2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol); PAR – 4-(2-pyridylazo)resorcinol; PAN – 1-(2-Pyridylazo)-2-naphthol; 5-Br-PADAP – 2-(5-brorno-2-pyridylazo)-5-diethylaminophenol; ; TTC – 2,3,5-triphenyl-2H-tetrazolium chloride.

**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 7 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 5.** 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 | 5.2 | 5.21 | 0.37 | 5.21±0.040 | 5.0 | 6.92 | 0.29 | 6.92±0.030 |
| | 5.3 | 5.43 | 0.50 | 5.43±0.030 | 5.0 | 5.96 | 0.46 | 5.96±0.041 |
| Sour Cream | 5.1 | 5.23 | 0.50 | 5.23±0.030 | 5.2 | 5.52 | 0.52 | 5.52±0.023 |
| | 10.0 | 10.10 | 0.90 | 10.10±0.015 | 10.0 | 10.41 | 0.88 | 10.41±0.029 |
| Cottage Cheese | 5.0 | 5.92 | 0.81 | 5.92±0.042 | 5.4 | 5.43 | 0.73 | 5.43±0.035 |
| | 10.0 | 10.94 | 0.41 | 10.94±0.043 | 10.0 | 10.24 | 0.28 | 10.24±0.044 |

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## *Cr (VI) VƏ Co (II)-IN MÜXTƏLİFLİQANDLI KOMPLEKSLƏRİNİN SPEKTROFOTOMETRİK TƏDQİQİ*

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*Aşağıdakı reagentlərdən istifadə edilmişdir: tiopiropkatexin (TP): 2-hidroksi-5-yodotiofenol (NITF) və 2-hidroksi-5-nitrotiofenol (HNTF); və aminofenollar (AF): -2 (N,N-dimetilaminometil) fenol - ($AF_1$) və 2 (N,N-dimetilaminometil)-4-metilfenol ($AF_2$). TP fizik-kimyəvi metodlarla - İQ və NMR spektroskopiyası ilə tədqiq edilmişdir. Kompleks əmələ gələn zaman HİTF Cr (VI) -dan Cr (III)-ə qədər reduksiya edir. Xrom və kobalt müxtəlifligandlı kompleksi (MLK) şəklində xloroformla 98.4-98.7% ekstraksiya olunur. Xrom (III) və kobalt (II) komplekslərinin əmələ gəlməsi və ekstraksiyası üçün uyğun olaraq optimal pH 1.3-5.8 və 1.0-7.2-dır. Reagentlərin optimal qatılığı müəyyən edilmişdir: (1.3-1.5)×$10^{-3}$ M TP və (1.2-1.5)×$10^{-3}$ M AF. Ber qanunu $Cr^{3+}$ və $Co^{2+}$ ionları üçün müvafiq olaraq 0.2-19 və 0.2-20 mkq/ml intervalında özünü doğruldur. Xrom (III) və kobalt (II) komplekslərinin maksimum optik sıxlığı müvafiq olaraq 12 və 10 dəqiqə ərzində əldə edilir. Cr (III) - HITP-AF MLK maksimum işıqudması 438-442 nm dalğa uzunluğunda (kobalt 540-555 nm) baş verir. Xrom kompleksləri üçün molar udma əmsalı (3.57 - 3.73 4) × $10^4$ (kobalt olduqda (2.43 - 2.94) × $10^4$) bərabərdir. Komplekslərdəki komponentlərin molar nisbəti bir neçə üsulla müəyyən edilmişdir (Cr: TP: AF = 1: 3: 3 və Co: TP: AF = 1: 2: 2). Nazarenko metodundan istifadə edərək xrom (III) və kobaltın (II) kompleks əmələ gətirən ion formasının müvafiq olaraq $Cr^{3+}$ və $Co^{2+}$ olduğu müəyyən edilmişdir. MLK üzvi fazada polimerləşmir və monomer formadadır ($\gamma$ = 1.01-1.05). İşlənilmiş yeni metodika süd, xama və kəsmikdə xrom və kobaltı təyin etmək üçün istifadə edilmişdir.*

***Açar sözlər:*** *xrom, kobalt, ekstraksiya, spektrofotometriya, tiopirokatexinlər, aminofenollar*

## *СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ РАЗНОЛИГАНДНЫХ КОМПЛЕКСОВ Cr (VI) И Co (II)*

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*Были использованы следующие реагенты: тиопирокатехины (ТП): 2-гидрокси-5-йодтиофенол (НИТФ) и 2-гидрокси-5-нитротиофенол (ГНТФ); и аминофенолы (АФ): -2 (N, N-диметиламинометил) фенол - ($АФ_1$) и 2 (N, N-диметиламинометил) -4-метилфенол ($АФ_2$). ТП были охарактеризованы с помощью физико-химических методов: ИК и ЯМР спектроскопия. Cr (VI) восстанавливается до Cr (III) самим реагентом во время образования комплекса. После однократной экстракции хлороформом 98.4-98.7% хрома и кобальта экстрагировали в виде разнолигандных комплексов (РЛК). Для образования и экстракции комплексов хрома (III) и кобальта (II) оптимальными являются pH 1.3-5.8 и 1.0-7.2 соответственно. Оптимальным условием для формирования и извлечения этих комплексов является концентрация (1.3-1.5) × $10^{-3}$ M ТП и (1.2-1.5) × $10^{-3}$ M АФ. Для $Cr^{3+}$ и $Co^{2+}$ закон Бера выполняется в интервалах 0.2-19 и 0.2-20 мкг/мл соответственно. Максимальная оптическая плотность комплексов хрома (III) и кобальта (II)* *достигается в течение 12 и 10 минут соответственно. Максимумы поглощения тройных комплексов Cr (III) - ГИТФ-АФ лежат в диапазоне 438-442 нм (в случае кобальта 540-555 нм). Молярные коэффициенты поглощения для комплексов хрома (3.57 – 3.73 4)×10$^4$ (в случае кобальта (2.43 – 2.94) ×10$^4$). Молярные соотношениz компонентов в комплексах определены несколькими методами (Cr:ТП:АФ = 1:3:3 и Co:ТП:АФ = 1: 2: 2). Методом Назаренко было установлено, что комплексообразующая форма хрома (III) и кобальта (II) представляет собой $Cr^{3+}$ и $Co^{2+}$ соответственно. Расчеты показали, что РЛК в органической фазе не полимеризуется и находится в мономерной форме (γ = 1.01-1.05). Предлагаемая методика используется для определения хрома и кобальта в молоке, сметане и твороге.*

***Ключевые слова:*** *хром, кобальт, экстракция, спектрофотометрия, тиопирокатехины, аминофенолы*