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Extraction-spectrophotometric study on the chromium (VI)-2-hydroxy-5-bromothiophenol-hydrophobic amines-water-chloroform system and its analytical application

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Abstract

The present work is devoted to the study of the conditions for the interaction of chromium (VI) with 2-hydroxy-5-bromothiophenol (HBTP). In the presence of hydrophobic amines (Am), these compounds are extracted into the organic phase in the form of a Mixed-ligand complexes (MLC). Of the hydrophobic amines (Am), N, N-dimethylaminomethyl -4-methylphenol (Ap1) and N, N-dimethylaminomethyl -4-chlorophenol (Ap2) were used. To determine the state of chromium oxidation in MLC, two series of experiments were carried out. In the first series, Cr (VI) was used, and in the second series, Cr (III) was used, obtained by adding an additional reducing agent (SnCl₂ or KI). It was found that the spectrophotometric characteristics of MLC Cr (VI) and Cr (III) are identical, that is, in interaction with HBTP, Cr (VI) were reduced to Cr (III). Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. After a single extraction with CH₃Cl 98.5% of chromium was extracted as an ion associate. The absorption maxima of the ternary Cr (III)-HBTP-Am complexes lie in the range of 465-470 nm. Molar coefficients of absorption make $(2.92-3.28) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Optimum conditions for the formation and extraction of MLC were found: {The maximum absorption of the extracted complex (in 5 ml of chloroform) is achieved when the pH of the aqueous phase is in the range 4.0-5.3, and the reagent concentrations $(1.2-4.0) \times 10^{-3} \text{ mol / ml}$ of HBTP and $(0.92 - 4.0) \times 10^{-3} \text{ moles / ml}$ Am. Our experiments are performed at pH = 4.5 in the presence of $1.6 \times 10^{-3} \text{ mol / ml}$ HBTP and $1.5 \times 10^{-3} \text{ mol / ml}$ at. The volume of the aqueous phase is 20 ml and contains 20 µg of Cr (III). Phase equilibrium is achieved after 90 s, but the extraction is carried out for 3 min in all experiments. Absorption of the work piece remains constant for 15 minutes}. It was found using the Nazarenko method that Cr (III) in the complexes was present in the form of Cr³⁺. The number of protons replaced by chromium in one HBTP molecule appeared to be one. Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex. The results show that the molar ratio of Cr: HBTP: Am is 1: 3: 3. The effect of a diverse set of ions on the determination of chromium (III) with HBTP and Am is studied at pH 4.5 in the presence of 15 µg Cr (III) in 20 mL of an aqueous solution. The following ions (in n-fold excess) do not interfere: Cd (II) (435), Cu (II) (80), Ce (III) (125), Zn (II), Co (II) and HPO₄²⁻ 1200, V (IV,V) and Ni (II) (130), Mo (VI) (10), Fe (II) (40), W (VI) (13), Mn (II) (30), Al (III), (120). A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cr (III) may be determined in the range 0.5-18 µg mL⁻¹. Table 2 summarizes the calibration characteristics obtained with Cr (III)-HBTP-Ap1 and Cr (III)-HBTP-Ap2. The proposed method under the already established optimum conditions was applied for the determination of Cr (III) in alloys, in sewage water and Bottom sediments and in soils.

Keywords: Chromium, 2-hydroxy-5-bromothiophenol, mixed-ligand complexes, extraction-photometric method, determination

1. Introduction

Chromium is one of the toxic metals. Chromium (VI) compounds, which are among the most dangerous pollutants of natural objects, have the most carcinogenic effect [1]. In this connection, in modern practical chemical analysis, there is a need to determine this pollutant element. Special control is required by drinking, natural and industrial waters, the chromium content in which is strictly regulated. For this purpose, it was suggested to use a selective and sensitive reaction with 1,5-diphenylcarbazide [2]. To assess the content of toxic components in various environmental objects, methods based on the determination of elements with

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organic reagents are promising and actively developing.

The interaction of chromium(VI) with 1,5-diphenylcarbazine immobilized in transparent polymethacrylate matrix was studied. The optimal conditions were found for interaction metal with reagent in solid phase. The solid-phase spectrophotometric procedure was proposed for determination of chromium(VI) with the range of determined concentrations 0.05...1.0 mg/L and the detection limit 0.014 mg/L. The possibility of using thermal lens spectrometry as a more sensitive method of molecular absorption spectroscopy for lowering the limit of detection of chromium(VI) was studied. The thermal lens spectrometer with the modulated excitation beam at 514.5 nm was used for measurement thermal lens signal. Changes in the preparation of transparent polymethacrylate matrix and analytical procedures for photothermal measurements compared with spectrophotometry not required. The using of thermal lens spectrometry allowed decreasing of the detection limit to the value 0.002 mg /L. The range of determined concentrations was 0.005...0.05 mg/L [3].

The method of photometric determination in solutions of Cr(III) and Fe(III) in a simultaneous presence has been developed. The method is intended for the analysis of iron and chromium-containing technical products. The method is based on differences in the electronic spectra of Cr(III) and Fe(III) complexes with Na₂EDTA. The electronic spectra of complexes with Cr (III) have absorption maxima at 394 and 584 nm. The electronic spectra of complexes with Fe(III) have an absorption maximum at 470 and a shoulders at 540-560 nm and at 240-280 nm. The wavelength of 315 nm was chosen to determine Fe(III), since chromium cations do not interfere. The wavelength of 660 nm was used to determine Cr(III), since iron cations do not interfere. The optimal conditions for the reaction and the metrological characteristics of the method are determined. The complex of the iron cation is formed at the moment of mixing the solutions. The complexation of the Cr (III) cation occurs slowly at room temperature. Therefore, a photometric reaction with Na₂EDTA is carried out in a boiling water bath for 5 minutes. The reaction mixture is then basified with ammonia water. Alkalinization allows 2-3 times increase in absorption. The calibration dependence for the determination of Cr(III) ions is direct (pair correlation 0.9999). To determine of Fe(III), the calibration curve is parabole. The accuracy of determining of Cr (III) and Fe (III) ions is 99-104%. The results of the reaction are well repeated, the coefficient of variation does not exceed 1.4% [4].

The mixed-ligand complexes of chromium (VI) with *o*-hydroxythiophenols (HTPD) and its derivatives [2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol in the presence of hydrophobic amines have been investigated by spectrophotometric method. The condition of complexing and extraction, physical-chemical and analytical characteristics of this complex have been found. As hydrophobic amines (Am) aniline, *N*-metilaniline and *N,N*-dimetilaniline were used. It has been found that mixed-ligand complex were formed in weakly acidic medium (pH 3.0 – 5.0). The optimal concentration of *o*-hydroxythiophenols (HTPD) and Am for formation of the complex was found to be 1.0×10^{-3} M and 1.12×10^{-3} M, respectively. Maximum of light absorption observed at 475-488 nm. The calculated molar absorptivities (ϵ_{\max}) belong to the interval $(2.70 - 3.02) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The stoichiometric coefficients of the reaction were determined by the Asmus method, by the relative yield

method and by the equilibrium shift method. The results show a complex composition of 1:3:3 (Cr(III):HTPD: Am).

A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Cr(III) may be determined in the range 0.5-16 $\mu\text{g mL}^{-1}$. The extraction-photometric methods of chromium determination have been worked out. The proposed method was applied successfully to determine amount of chromium in alloys and in soil [5].

The present work is devoted to the study of the conditions for the interaction of chromium (VI) with 2-hydroxy-5-bromothiophenol (HBTP)]. In the presence of hydrophobic amines (Am), these compounds are extracted into the organic phase in the form of a Mixed-ligand complexes (MLC). Of the hydrophobic amines (Am), *N,N*-dimethylaminomethyl -4-methylphenol (Ap1) and *N,N*-dimethylaminomethyl -4-chlorophenol (Ap2) were used.

2. Experimental

2.1 Reagents and Apparatus

A solution of Chromium (VI) ($1 \mu\text{g mL}^{-1}$) was made by dissolving (0.1935) gm of K₂Cr₂O₇ p. f. a. (pure for analysis) in 1000 ml of water. Concentration of solution of Chromium was established gravimetric [6]. Working solution with concentration of 0,1 mg/ml was prepared by dilution of stock with deionized water.

HBTP were synthesized according to the procedure [7]. HTPD their purity was verified by paper chromatography and melting point determination. Solutions of HBTP and Am in chloroform (0.01M) were used. As an ekstragent the cleared chloroform was applied.

The ionic force of solutions was supported a constant ($\mu = 0.1$) introduction of the calculated quantity of KCl. To create the optimal acidity, 1M solutions of KOH and HCl were used. The absorbance of the extracts was measured using a KFK-2 photo colorimeter and an SF-26 spectrophotometer; the equilibrium value of the pH of aqueous phase was measured using a I-120.2 potentiometer with a glass electrode. IR - spectra were recorded on a spectrophotometer UR-20. All measurements was carried out at $20 \pm 5^\circ \text{C}$.

2.2 General Procedure for the Determination of cobalt (II)

Portions of stock solutions of chromium (III) varying from 0.1 to 1.0 mL with a 0.1-mL step, a

2.2 mL portion of a 0.01 M solution of HBTP, and a 2.5 mL portion of a 0.01M solution of Am 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 1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 15 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 440 nm ($l=0.5\text{cm}$).

2.3 Studies on the oxidation state of Chromium (VI)

It is known that *o*-hydroxythiophenols have reducing properties in an acidic environment [8-12]. To determine the oxidation state chromium in MLC, we conducted two series experiments. In the first series, we used Cr (VI), and in In the second series we used Cr (III), obtained by adding an additional reducing agent (SnCl₂ or KI). Was found that the spectrophotometric characteristics of MLC Cr (VI) and Cr (III) were identical, that is, in interaction with HBTP, Cr (VI) were reduced to Cr (III).

2.4 Charge of complexes

Experiments on electro migration in a U-tube and sorption on EDE-10P, anion exchangers demonstrated anionic character of single use, ligands, at studying the electro migration of complexes, it was found that the complexes of chromium (VI) red binary *o*-hydroxythiophenolate are transferred to the cathode. When the charge sign of complexes with one ligand was determined by ion chromatography, the anion exchange EDE-10P completely absorbed the colored component of the solution. When hydrophobic amines (Am) were introduced into the system, extraction of these compounds in the organic phase as a complex of mixed ligands (MLC) was observed. Among the hydrophobic amines (Am), *N,N*-dimethylaminomethyl -4-methylphenol (Ap1) and *N,N*-dimethylaminomethyl -4-chlorophenol (Ap2) were used. On the basis of the data obtained, new selective and highly sensitive prospectuses were developed for extraction-spectrophotometric determination of a small amount of chromium in alloys of different varieties, soils and water.

2.5 Determination of Chromium (III) in Alloys

A 0.4-0.7 g sample of alloys was carefully dissolved in 12 mL of H₂SO₄ (1:3). 2 mL of mix (1:3) conc. HCl and HNO₃ was added and heated to release of nitrogen oxides. Filtered insoluble precipitate and a filtrate transferred into a 50 mL volumetric flask. After cooling solution was diluted with water to a tag. Select aliquot portions of the received solution, transfer to a in a separatory funnel, the required value of pH was adjusted by adding 0.1M HCl. 2,2 mL 0,01 M of HBTP and 2.5 mL 0.01M Am was added. The volume of an organic phase adjusted to 5 mL chloroform, and total amount - to 25 mL the distilled water. After 10 min of shaking, a portion of the organic extract was transferred through a filter paper into a cell and the absorbance was read at $\lambda=490$ nm against chloroform. The Chromium content was found from a calibration graph.

2.6 Determination of Chromium (III) in soils

The proposed procedures for the determination of Chromium were applied to its determination in light-chestnut soil from

the Caspian zone. A 0.5-g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. after cooling, the sample was treated and dissolved in an graphite cup in a mixture of 16 mL of conc. HF, 5mL of conc. HNO₃, and 15 mL of conc. HCl at 50-60°C. to remove excess hydrogen fluoride, a 8 mL portion of conc. HNO₃ was added triply to the solution that was each time evaporated to 5-6mL. After that, the solution was transferred into a 100 mL volumetric flask and its volume was brought to the mark with distilled water. Chromium was determined in aliquot portions of the solution using the proposed procedures.

2.7 Determination of Chromium (III) in sewage water and Bottom sediments

1/ taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 mL of HNO₃, was transferred to a 50 mL flask and diluted to the mark with water. Chromium was determined in aliquot portions of the solution using the proposed procedures.

3. Results and Discussion

3.1 The choice of the extractant

For the extraction of complexes we used CH₃Cl, C₂H₄Cl₂, CCl₄, C₆H₆, C₆H₅Cl, C₆H₅-CH₃, xylol, *iso*-butanol, *iso*-pentanol, ethyl oxide, *n*-butanol and their mixes (Fig. 1). Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. CH₃Cl, C₂H₄Cl₂ and CCl₄ appeared to be the best extractants (96.45-98.50%). Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with CH₃Cl 98.5% of chromium was extracted as an ion associate. Further researches were conducted with CH₃Cl. The concentration of chromium in the organic phase was determined with diphenylcarbazide [13] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes.

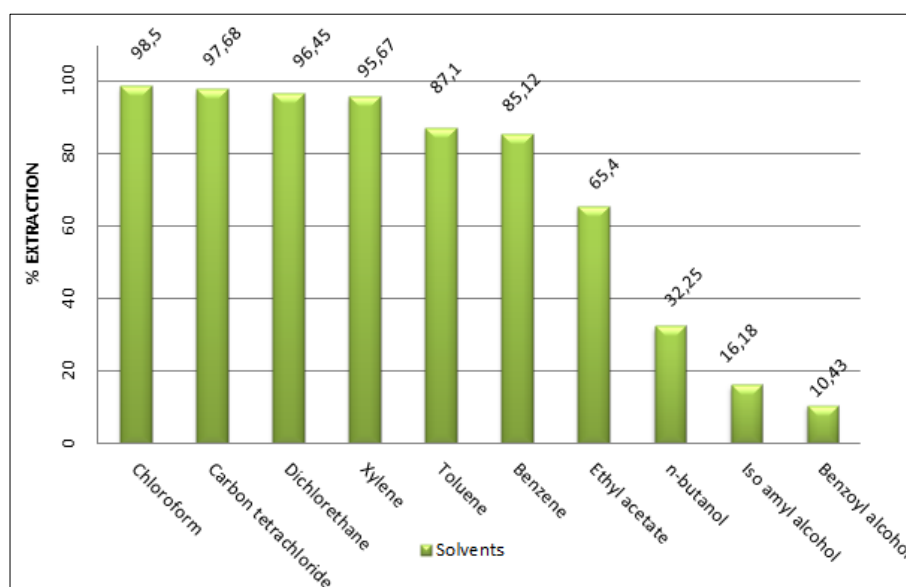


Fig 1: Effect of solvents on extraction of Cr(III) with HBTP and AP1

3.2 Influence of the pH of the Aqueous Phase

The effect of pH on the formation of Co(II)-HBTP-Am complex was studied, in order to find a suitable pH that can

be adopted in the determination of cobalt(II) (Table 1, Fig. 2). The absorbance was found to be maximum in the pH range 4.0-5.3. Hence further analytical investigations were carried

out in media of pH 4.5. Extraction of Cr(III) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HBTP. Probably, it is present in the solution in the non-dissociated state. At $\text{pH} \geq 8.6$, the complexes were hardly extracted, obviously because of the decrease in the degree of Am protonation. The effect of pH on the intensity of the color reaction is shown in the Fig. 2. Existence of one maximum of absorbance in the specified limits pH confirms the assumption of formation of one complex connection. The nature of acids (HCl, H_2SO_4) almost does not influence a complex formation of Chromium with HBTP and Am.

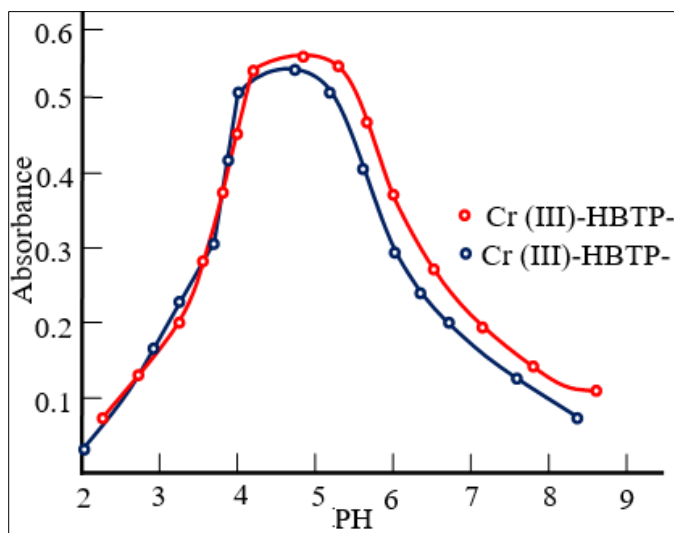


Fig 2: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. $C_{\text{Cr}}=3.84 \times 10^{-5}$ M, $C_{\text{HBTP}}=1.6 \times 10^{-3}$ M, $C_{\text{Am}}=1.5 \times 10^{-3}$ M, KFK-2, $\lambda = 440$ nm, $\ell=0.5$ cm.

3.3 Electronic absorption spectra

The absorption maxima (λ_{max}) of the ternary Cr(III)- HBTP-Am complexes lie in the range of 465-470 nm (Table 1, Fig. 3)). All colour reactions were very contrast since the initial solutions are colourless (λ_{max} (HBTP) = 280 nm). Thus, bathochromic shift makes 185-190 nm. Close values of maxima of light absorption allow to draw a conclusion that the formed complexes were ionic associates. Contrast of reactions was high: initial reagents - are colourless, and complexes - are intensively painted. Molar coefficients of absorption make $(2.92-3.28) \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

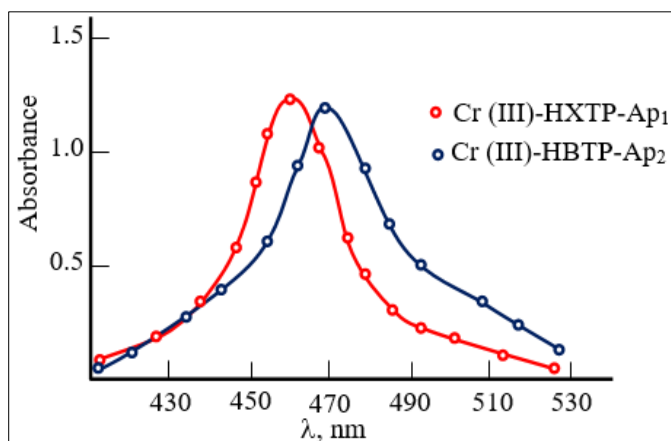


Fig 3: Absorption of mixed-ligand complexes $C_{\text{Cr}}=3.84 \times 10^{-5}$ M, $C_{\text{HBTP}}=1.6 \times 10^{-3}$ M, $C_{\text{Am}}=1.5 \times 10^{-3}$ M, SF-26, $\ell=1.0$ cm.

3.4 Optimal operating conditions

In a weakly acidic medium, HBTP reacts with chromium (III) to form a color anionic complex. In the presence of hydrophobic amines, a compound is formed which readily dissolves in chloroform. The maximum absorption of the extracted complex (in 5 mL of chloroform) is achieved when the pH of the aqueous phase is in the range of 4.0-5.3 and the reagent concentrations are $(1.2 - 4.0) \times 10^{-3}$ mol / mL HBTP and $(0.92 - 4.0) \times 10^{-3}$ mol / mL Am. Our experiments are carried out at $\text{pH} = 4.5$ in the presence of 1.6×10^{-3} mol / mL HBTP and 1.5×10^{-3} mol / mL Am. The volume of the aqueous phase is 20 mL and contains 20 μg of Cr (III). Phase equilibrium is achieved after 90 s, but the extraction is carried out for 3 min in all experiments. Absorption of the work piece remains constant for 15 minutes.

3.5 Stoichiometry of the Complexes and the Mechanism of Complexation

It was found using the Nazarenko method that Cr(III) in the complexes was present in the form of Cr^{3+} . The number of protons replaced by chromium in one HBTP molecule appeared to be one [14]. Starik-Barbanel relative yield method, equilibrium shift method (Fig. 4), crossed lines method and Asmus' methods were employed to elucidate the composition of the complex [15]. The results show that the molar ratio of Cr: HBTP: Am is 1: 3: 3.

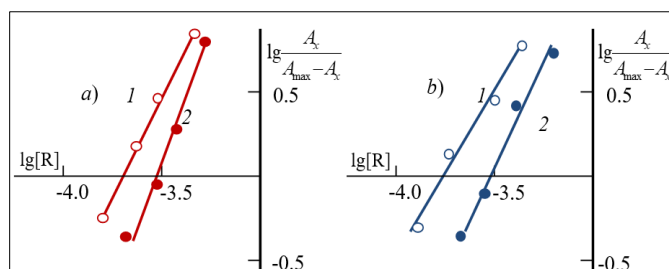
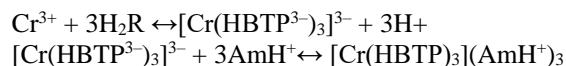


Fig 4: Determination of the ratio of components by the equilibrium shift method for (a) Cr(III)- HBTP-Ap1 and (b) Cr(III)-HBTP-Ap2.

1. Cr: HBTP; 2.Cr: Am.

Ions of chromium at interaction with three molecules of HBTP ($\text{HBTP} = \text{H}_2\text{R}$) form three charged anionic complexes, which were extracted with three molecules of protonated Am. The composition of the extractable complexes can be represented by the formula $[\text{Cr}(\text{HBTP})_3] (\text{AmH}^+)_3$. It is assumed that at a complex formation there are processes



The stability constant determined by crossed lines method. The sizes of equilibrium constant K_e calculated on a formula $\lg K_e = \lg D - 2 \lg [\text{AmH}^+]$ were presented in table 1.

Calculation of extent of polymerization of complexes was carried out on the equation [16]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1.05-1.12$).

Formed ion-association complex between anionic chelates of chromium (III) with HBTP and Am. The stability constant of Cr(III)-HBTP-Am complexes was calculated and found to be $\lg \beta = 8.13-10.34$ at room temperature [17].

3.6 Influence of various ions

The effect of a diverse set of ions on the determination of chromium (III) with HBTP and Am is studied at pH 4.5 in the

presence of 15 μg Cr(III) in 20 mL of an aqueous solution. The following ions (in n -fold excess) do not interfere: Cd (II) (435), Cu (II) (80), Ce (III) (125), Zn (II), Co (II) and HPO_4^{2-} 1200, V (IV,V) and Ni (II) (130), Mo (VI) (10), Fe (II) (40), W (VI) (13), Mn (II) (30), Al (III), (120). The interference in the determination of chromium is caused by U (VI), Nb (V), Re (VII), Ti (IV), NO_3^- , SCN^- , tartrate and urea. Using 1.5 mg F- and 2×10^{-3} mol / dm³ sulfosalicylic acid as masking agents, let us assume a 125-fold excess of Al and a 10-fold

excess of Nb (V). A solution containing 2×10^{-5} mole / mL α , α' -dipyridyl, will mask a 250-fold excess of Cu (II), and 10 mg of HPO_4^{2-} will mask a 30-fold excess of Fe (III) and a 60-fold excess Mg (II). Elements of W, Nb and Si are separated as the corresponding insoluble acids during the dissolution of the sample.

In conclusion the analytical parameters pertaining to the proposed method are given in Table 1.

Table 1: Optical characteristics, precision and accuracy of the spectrophotometric determination of Cr(III) with HBTP and Am

Compound	The pH range of maximum extraction	R, %	λ_{max} (nm)	Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1}$) $\epsilon \cdot 10^{-4}$	$\lg K_e$	$\lg \beta$	Working range / $\mu\text{g mL}^{-1}$
Cr- HBTP- Ap1	4.1-5.3	98.5	470	2.92	5.40	8.13	0.5-16
Cr- HBTP- Ap2	4.0-5.2	98.2	465	3.28	5.69	10.34	0.5-18

3.7 Effect of chromium (III) concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion

concentration indicates that Cr(III) may be determined in the range 0.5-18 $\mu\text{g mL}^{-1}$. Table 2 summarizes the calibration characteristics obtained with Cr (III)-HBTP-Ap1 and Cr(III)-HBTP-Ap2. The pertaining calibration graph is shown in the Fig. 5.

Table 2: Analytical characteristics of some ternary complexes of Cr with HBTP and Am

Parameter	Cr(III)-HBTP-Ap1	Cr(III)-HBTP-Ap2
The equation of calibration curves	$y = 0.012 + 0.253x$	$y = 0.016 + 0.257x$
Correlation coefficient (8 standards used);	0.9983	0.9989
Linear calibration range / $\mu\text{g mL}^{-1}$	0.5-16	0.5-18
Limit of detection / ng mL	10	13
Limit of quantification / ng mL	33	32
Sandell's sensitivity / ng mL	1.9	2.0

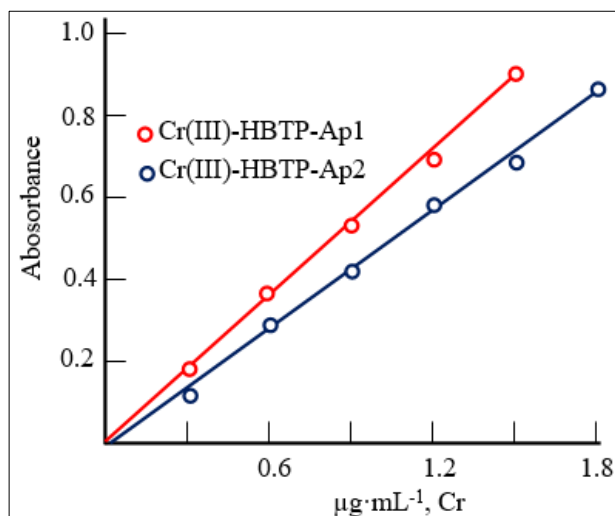


Fig 5: Analytical determination of Cr (III)
 $C_{\text{HBTP}} = 1.6 \times 10^{-3}$ M, $C_{\text{Am}} = 1.5 \times 10^{-3}$ M, KFK-2, 440 nm, $\ell = 1.0$ cm.

Table 3 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the

determination of chromium with the earlier known procedures [13, 18-21].

Table 3: Comparative characteristics of the procedures for determining chromium

Reagent	pH (solvent)	λ , nm	$\epsilon \times 10^{-4}$	Beer's law range, $\mu\text{g mL}^{-1}$	[Ref.]
PAN	0.2–0.8 M HCl (CH_3COCH_3)	390-400	1.28	0.3 – 2.0	[18]
5-Br-DMPAP	0.1–10 M HCl (CHCl_3)	546	7.8	0.02 – 0.56	[19]
Br-PADAP	4.7	600	7.93	0.6 – 15.0	[20]
PAR	4.0-5.0	540	4.7	3.2-13.0	[21]
Cr- HBTP- Ap1	4.1-5.3 (CHCl_3)	470	2.92	0.5-16	Proposed method
Cr- HBTP- Ap2	4.0-5.2 (CHCl_3)	465	3.28	0.5-18	

4. Analytical Applications

The proposed method under the already established optimum

conditions was applied for the determination of Cr (III) in alloys, in sewage water and Bottom sediments and in soils.

4.1 Determination of Chromium (III) in Alloys

The method was applied to the determination of chromium (III) in two alloys. In both cases, iron is masked by using sodium fluoride solution. The results are in good agreement

with the certified values, and, hence, the presently developed method is effective in the determination of chromium in alloy samples. The results are summarized in Table 4.

Table 4: Determination of chromium (III) content in alloys ($n = 5, P = 0.95$).

Sample composition (%)	Sl. №.	Alloy taken ($\mu\text{g/mL}$)	Amount of Cr(III) found ($\mu\text{g/mL}$)	Amount of Cr(III) found (%)	Average of Cr (III) found (%)	S.D C.V (%)
Stainless Steel, (%) (Cr-11-13, C-0.1-0.4, Ni-10, Fe-77)	1	30.0	2.95	10.88	10.99±0.062	0.681
	2	60.0	7.63	10.92		
	3	90.0	12.06	11.12		
	4	120.0	16.59	10.94		
	5	150.0	20.91	11.09		
Ferrochrome, (%) (Cr – 65, Fe – 35)	1	14.10	2.34	64.95	65.12 ± 0.045	0.793
	2	25.50	3.52	64.82		
	3	37.10	4.61	66.01		
	4	48.90	5.94	65.89		
	5	50.00	6.14	63.93		

4.2 Determination of Chromium in soils

The proposed procedures for determining chromium in soils were verified by Diphenylcarbazide methods. The results of the analysis are listed in Table 5 indicate the successful applicability of the proposed method to real sample analysis.

Table 5: Correctness and reproducibility of Determination of chromium in soil ($n=5, P=0.95$).

Method	$X^-, \% \times 10^{-4}$	$SD \times 10^{-4}$	RSD, %	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
<i>Standard method</i>				
Diphenylcarbazide	2.89	0.156	6	(2.89±0.027)
<i>Proposed method</i>				
HBTP-Ap1	2.80	0.123	7	(2.80±0.013)

4.3 Determination of Chromium (III) in sewage water and Bottom sediments

The results of the analysis are shown in Table 6, which indicates the successful applicability of the proposed method to the actual analysis of the samples.

Table 6: Determination of Chromium (III) in sewage water and Bottom sediments ($n=5, P=0.95$).

Analysis object	Added, μg	Found, μg	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}, \mu\text{g} / \text{kg}$	S_r
Sewage water				
Sample 1	3.0	3.47	0.47±0.045	0.13
Sample 2	7.0	7.73	0.73±0.013	0.18
Bottom sediments				
Sample 1	3.0	4.60	1.60±0.028	0.29
Sample 2	5.0	6.25	2.25±0.033	0.30

5. Conclusions

1. Mixed-ligand chromium (III) complexes with HBTP and Am were studied by spectrophotometry. Optimum conditions for the formation and extraction of MLC were found: {The maximum absorption of the extracted complex (in 5 ml of chloroform) is achieved when the pH of the aqueous phase is in the range 4.0-5.3, and the reagent concentrations $(1.2-4.0) \times 10^{-3}$ mol / mL of HBTP and $(0.92-4.0) \times 10^{-3}$ moles / mL Am. Our experiments are performed at pH = 4.5 in the presence of 1.6×10^{-3} mol / ml HBTP and 1.5×10^{-3} mol / mL at. The volume of the aqueous phase is 20 ml and contains 20 μg of Cr (III). Phase equilibrium is achieved after 90 s, but the extraction is carried out for 3 min in all experiments.

Absorption of the workpiece remains constant for 15 minutes}.

- The molar ratio of the reacting compounds Cr (III), HBTP and Am is 1: 3: 3. The general formula for ternary complexes is $[\text{Cr}(\text{HBTP})_3](\text{AmH})_3$. They can be considered as ion associates between triply charged chelates $[\text{Co}(\text{HBTP})_3]^{3-}$ and protonated species of Am. Calculations made showed that MLC in the organic phase will not polymerize and is in monomeric form ($\gamma = 1.05-1.12$). The stability constant of Cr (III) -HBTP-Am complexes was calculated and was found to be equal to $\lg \beta = 8.13-10.34$ at room temperature.
- The developed method preserves the specific interaction of chromium (III) with HBTP and Am to form a color complex and has a good sensitivity at room temperature. The proposed method has a significant advantage in comparison with other spectrophotometric methods in terms of simplicity and sensitivity. The technique of extraction-spectrophotometric determination of chromium in various objects has been developed.

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