Liquid-Liquid Extraction and Spectrophotometric Determination of Cromium (VI) with o-Hydroxythiophenols In The Presence of Hydrophobic Amines

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Abstract

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 (HITP)] 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 amins aniline (An), N-metilaniline (mAn) and N, N-dimetilaniline (dAn) 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 1.12·10-3M, respectively. Maksimum of light absorption observed at 475-488 nm. The calculated molar absorptivities (emax) belong to the interval (2.7 – 3.02)× 10^4 dm^3 $\cdot mol^{-1}\cdot$ 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 μg 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.

KEY WORDS: chromium, o-hydroxythiophenols, 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol, and 2-hydroxy-5-iodothiophenol, mixed-ligand complexes, extraction-photometric method, determination

I. Introduction

Chromium (VI) is known to be a highly toxic metal and one of sources that drives to many cancer diseases namely, cancer of lung, oesophagus, and liver [1]. Due to sever toxicity of Cr (VI), WHO and USEPA have set the guideline for drinking water with upper limit of 50 μg L^{-1} [2], whereas the Agency for Toxic Substances and Diseases Registry (ATSDR) classifies
Cr (VI) as the top eighteenth hazardous substance and the Minimal National Standards (MINAS) upper limit of Chromium in industrial wastewater is of 100 μg L^{-1} [3]. Consequently, the determination of Cr (VI) in an industrial effluent is necessary to control the level of Cr species in waste water, natural water, and drinking water. The determination of Cr (VI) in other environmental samples such as soils, plants and vegetables is also of prime importance to realize its concentration levels and extent of its impact on human health.

Very few methods for chromium determination are based on the complex formation with Cr(VI) in aqueous solution. However spectrophometric determination of chromium(VI) invariably involves heating the reactants with reflux. This is probably due to the slow reactions of chromium (VI) aquocomplexes. The time required for heating the reactants varies from 5 to 130 min, depending on the reagent employed. Characteristics of previously spectrophotometric methods for chromium determinations are summarized in Table 1. [4]

Table 1. Characteristics of previously spectrophotometric methods for chromium determination

Reagent*[4]	Linear range, mgL^{-1}	Molar absorptivity ($\varepsilon \times 10^{-4}$), $molL^{-1}cm^{-1}$	Relative standard deviation, %	Hetingtime, min
EDTA	6.0 – 160	–	0.6	30
5-Br-DMPAP	0.02 – 0.56	7.8	2	5
PAR	–	4.7	–	135
PAN	0.3 – 2.0	1.28	1.25	25
Br-PADAP	–	1.93	–	40

**Note: EDTA – Ethylene diamine tetraacetat; 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*

In the present paper was studied the complex formation in a liquid-liquid extraction system containing Cr(VI), o-hydroxythiophenols (HTPD) [2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)], and hydrophobic amins (Am), and show the potential of this system for determination of Cr(VI) in real samples. o-Hydroxythiophenolate complexes of metalls are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [5-9].

In this respect, a very promising reagent is 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol, and 2-hydroxy-5-iodothiophenol, which contains one hydroxyl and one sulfohydryl group and is a sulfur-containing analogue of mononuclear polyphenols with two oxygen atoms replaced with sulfur atoms.

The real work is devoted to studying of reaction of a complex formation of chromium (VI) with o-hydroxythiophenols and hydrophobic amines (Aм). As hydrophobic amine aniline (An), N-methylaniline (mAn) and N, N-dimetilaniline (dAn) were used.

2. Materials and Methods

2.1. Reagents and solutions.

A solution of Chromium (VI) (1 mg . ml^{-1} was made by dissolving (0.1935) gm of $K_2Cr_2O_7$ p. f. a." (pure for analysis) in 1000 ml of water. Concentration of solution of Chromium was established gravimetric [10]. Working solution with concentration of 0,1 mg/ml was prepared by dilution of stock with deionized water.

Solutions of HTPD and Am in chloroform (0.01M) were used. HTPD their purity was verified by paper chromatography and melting point determination. An, mAn and dAn is also given used in a freshly distilled look. As an ekstragent the cleared chloroform was applied.

The ionic force of solutions was supported a constant (μ = 0.1) introduction of the calculated quantity of KCl. To create the optimal acidity, 1M solutions of KOH and HCl were used.

2.2. Instruments

The absorbance of the extracts was measured using a KFK-2 photocolorimeter 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±5° C.

2.3. General procedure

2.3. 1. General procedure for the determination of Chromium

Portions of stock solutions of Chromium (VI) 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 HTPD, and a 2.0 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 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 (ℓ=0.5cm).

2.3. 2. Determination of Chromium(III) in Alloys

A 0.5-0.6 g sample of alloys was carefully dissolved in 10 ml of H_2SO_4 (1:4). 2 ml of mix (1:3) conc. HCl and HNO_3 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 HTPD and 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 ℓ=490 nm against chloroform. The Chromium content was found from a calibration graph.

2.3.3. Determination of Chromium 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. HNO_3, and 15 mL of conc. HCl at 50-60^{0}C. to remove excess hydrogen fluoride, a 8 mL portion of conc. HNO_3 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.

3. Results and discussion

3.1. Studies on the oxidation state of Chromium

It is known that HTPD have reducing properties in acidic medium [7]. Previous investigations with Cr(VI)-HCTP and Cr(III)-HCTP suggested that only Cr(III) forms stable complexes with this reagent. To elucidate the oxidation state of chromium in the presence of other HTPDs (HBTP and HITP), 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 $\lambda_{max\ Cr(VI)-\ HTPD}=\lambda_{max\ Cr(III)-\ HTPD}$. This fact can be regarded as an indication [7] that Cr(VI) is reduced to Cr(III) by the reagent itself during the complex formation.

3.2. Charge of the complexes

Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE-ethylenediamine, epichlorohydrin ; 10- serial number of the brand: P- means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the red binary o-hydroxythiophenolate complexes of Chromium (VI) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When hidrophobic amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. Among hydrophobic amins, aniline, N-methylaniline and N, N-dimetilaniline were used. On the basis of the obtained data new selective and highly sensitive prosedures were developed for the extraction-spectrophotometric determination of small amount of Chromium in the alloys various brands and in soils.

3.3.The choice of the extractant

For the extraction of complexes we used chloroform, 1, 2-dichloroethane, tetrachloro-methane, benzene, chlorobenzene, toluene, xylol, isobutanol, isopentanol, ethyl oxide, N-butanol and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Chloroform, dichloroethane, and chlorobenzene appeared to be the best extractants. 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 chloroform, 97.7-98.7% of chromium was extracted as an ion associate. Further researches were conducted with chloroform. The concentration of chromium in the organic phase was determined with diphenylcarbazide [10] 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.

3.4. Influence of the pH of the aqueous phase

Studying of dependence of a complex formation from pH showed that, the exit of complexes of Chromium is maximum at pH 3.0 – 5.0. Extraction of Cr (III) enhanced with the increase in the acidity of the initial solution; the further increase in acidity lead to the gradual decrase of recovery, which was obviously associated with a decrease in the concentration of the ionized form of HTPD. Probably, it is present in the solution in the non-dissociated state. At pH≥7, 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. 1. 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 HTPD and Am.

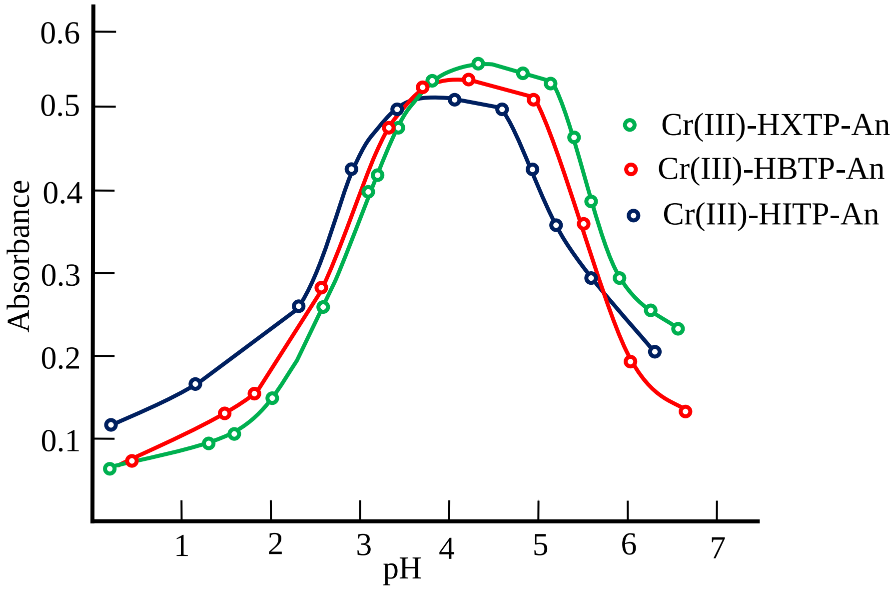

Fig.1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. C_{Cr}=3.84×10^{-5} M. C_{HTPD} =1.0×10^{-3} M, C_{Am}=1.12×10^{-3} M, KFK-2, λ = 490nm, ℓ=0.5 cm.

3.5. Electronic absorption spectra

The absorption maxima (λ_{max}) of the ternary Cr(III)- HTPD-Am complexes lie in the range of 475-488 nm (Table 1, fig. 2)). All colour reactions were very contrast since the initial solutions are colourless (λ_{max} (HTPD)= 270-280 nm). Thus, batochromic shift makes 205-208 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 (2.7 – 3.02)×10^4 dm^3·mol^{-1}· cm^{-1} .

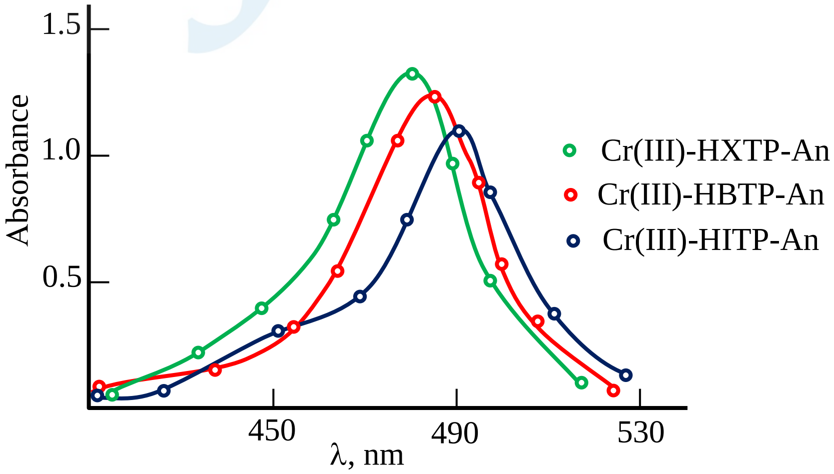

Fig. 2. Absorption of mixed-ligand complexes
C_{Cr}=3.84×10^{-5} M, C_{HTPD} =1.0×10^{-3} M, C_{Am}=1.12×10^{-3} M, SF-26, ℓ=1.0 cm.

3.6. Influence of reagent concentration and incubation time

The studies of the effect of concentration of the reagent revealed that a reagent excess of

26-fold was optimum for the complex formation. Hence, a 29-fold reagent excess was adopted for further investigations. However, the presence of excess of the reagent solution does not interfere with the color reaction. The optimal concentration of o-hydroxythiophenols and Am for formation of the complex was found to be $1.0\cdot10^{-3}$ M and $1.12\cdot10^{-3}$M, respectively.

We investigated dependence of absorbance of extracts on time at excess of reagents and at an optimum pH. MLC of Chromium with o-hydroxythiophenols and Am were stable in aqueous and organic solvents and did not decompose for three days, and after extraction, more than a month. The maximum absorbance is reached within 5-10 minutes.

3.7. Stoichiometry of the complexes

The stoichiometric coefficients of the reaction were determined by the Asmus method, by the relative yield method and by the equilibrium shift method [11]. The results show a complex composition of 1:3:3 (Cr(III):HTPD:Am). Hence, the complexes can be regarded as ion associates between three charged anionic chelates $[Cr(HTPD^{3-})_3]^{3-}$ and three protonated Am species: $(AmH^+)_3[Cr(HTPD)_3]$.

Structure extractable complexes can be represented as in Figure 3.

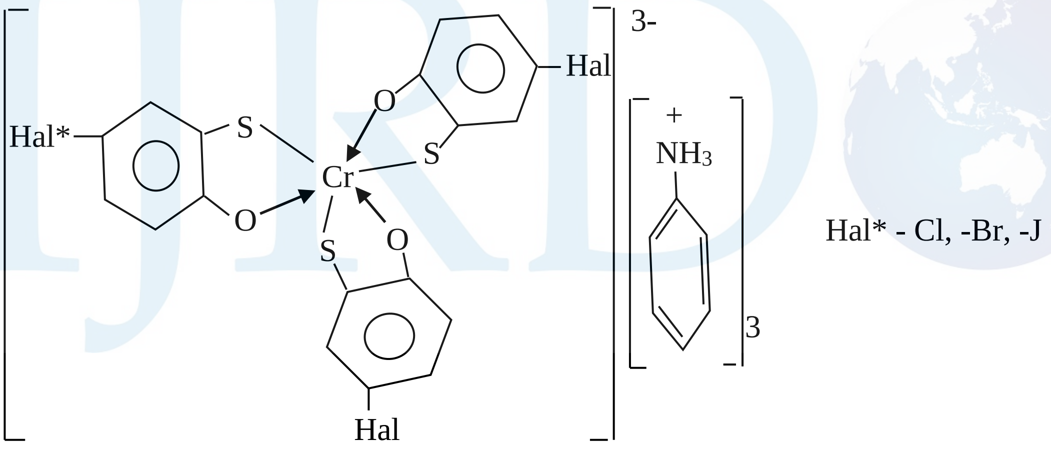

Fig. 3. Structure of complex $(AnH^+)_3[Cr(HTPD)_3]$.

3.8.The mechanism of formation of MLC can be presented as follows

Ions of chromium at interaction with three molecules of HTPD (HTPD = H_2R) 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 $(AnH^+)_3[Cr(HTPD)_3]$. It is assumed that at a complex formation there are processes

$$Cr^{3+} + 3H_2R \leftrightarrow [Cr(HTPD^{3-})_3]^{3-} + 6H^+$$

$$[Cr(HTPD^{3-})_3]^{3-} + 3AmH^+ \leftrightarrow (AmH^+)_3[Cr(HTPD)_3]$$

The sizes of equilibrium constant K_e calculated on a formula

$$\lg K_e = \lg D - 2\lg\left[AmH^+\right]$$

were presented in table 1. Calculation of extent of polymerization of complexes was carried out on the equation [12]. The limit of photometric determination of chromium in the form of ionic associates was counted on the equation [13]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (γ=1.02-1.08). In conclusion the analytical parameters pertaining to the proposed method are given in the Table 2.

Table 2. Optimum conditions of education and analytical the characteristic of MLC of chromium with HTPD and Am.

Compound	Optimum pH interval	Degree of extraction / %	λ_{max} / nm	$\varepsilon\times10^{-4}$ / $dm^3\ mol^{-1}\cdot cm^{-1}$	Working range / $\mu g\cdot cm^{-3}$	Equilibrium constant
Cr-HCTP-An	3.5-4.8	98.4	475	5.1	0.5-16	6.5
Cr-HCTP-mAn	3.7-5.0	98.5	479	5.2	0.5-16	6.8
Cr-HCTP-dAn	3.8-5.2	98.7	484	5.3	0.6-18	7.2
Cr-HBTP-An	3.3-4.6	98.0	480	4.8	0.5-16	6.4
Cr-HBTP-mAn	3.5-4.8	98.1	485	5.0	0.6-18	6.6
Cr-HBTP-dAn	3.6-5.0	98.4	492	5.2	0.6-18	7.0
Cr-HITP-An	3.1-4.5	97.8	488	4.7	0.5-14	6.2
Cr-HITP-mAn	3.2-4.7	97.9	492	4.8	0.5-14	6.4
Cr-HITP-dAn	3.4-4.9	98.2	495	5.0	0.5-16	6.7

3.9.Effect of diverse ions

In order to assess the possible application of this method, the effect of some ions on the determinations were studied. In this study, various amounts of ionic species were added to 50 µg of chromium(III) in buffer solution taken in a 25-mL standard flask and color was developed as outlined for general procedure. The tolerance limits are shown in Table 3. The tolerance was taken as the amount of foreign ions required to cause a ± 2% error in absorbance. The main interference was shown by iron(III), which was effectively masked with sodium fluoride (5 mL, 1% w/v) solution. The results on closer examination show that all the studied anions and most of the cations do not interfere with the determination of chromium(III).

Table 3. Influence of interfering ions on the determination of Cr(III) as MLC with HCTP and An(50.0 mg Cr added) *n*=5, *P*=0,95.

Diverse ions	Tolerance limit (µg)	RSD
Sodium(I) , nitrate, phosphate, chloride, molybdate and barium(II)	300	5
Acetate and hydroxide	200	6
Bromide, bicarbonate, thiosulphate, nickel(II), magnesium(II), calcium(II) and zinc(II)	150	4
EDTA,vanadate, oxychloride, carbonate, zirconium(II), ammonium(I) and iron(III)*	100	5
Iodide, tartarate, citrate, nitrite, sulphate, manganese(II), potassium(I), mercury(II) and bismuth(II)	75	3
Tetraborate, thiocyanate, borate, oxalate, tin(II), cadmium(II), lead(II), cobalt(II) and strontium(III)	50	6

Aluminium(III), titanium(IV), lithium(I) and copper(II)	40	2

*Masked with NaF (5 mL, 1%)

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of cromium with the earlier known procedures [10,14,15].

Table 4. Comparative characteristics of the procedures for determining chromium

Reagent	pH (solvent)	λ, nм	$\varepsilon \cdot 10^{-4}$	Beer's law range, μg	[ref.]
2- [benzene thiazolylazo] - 4-benzenenaphthol	0.1–10 M HCl ($CHCl_3$)	5.46	4.17	1-10	*14*
Diphenylcarbazide	4	540	0.52	3-13	10
Hydroxyamidines	0.2–0.8 M HCl (aseton)	390-400	1.3-1.52	0.2-3.6	15
Proposed method					
HCTP-An	3.5–4.8 ($CHCl_3$)	475	5.1	0.5-16	
HBTP-An	3.3–4.6 ($CHCl_3$)	480	4.8	0.5-16	
HITP-An	3.1–4.5 ($CHCl_3$)	488	4.7	0.5-14	

3.10. 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 0.5-16 μg ml^{-1}. Table 5 summarizes the calibration characteristics obtained with HCTP-An, HBTP-An and HITP-An. The pertaining calibration graph is shown in the Fig. 4.

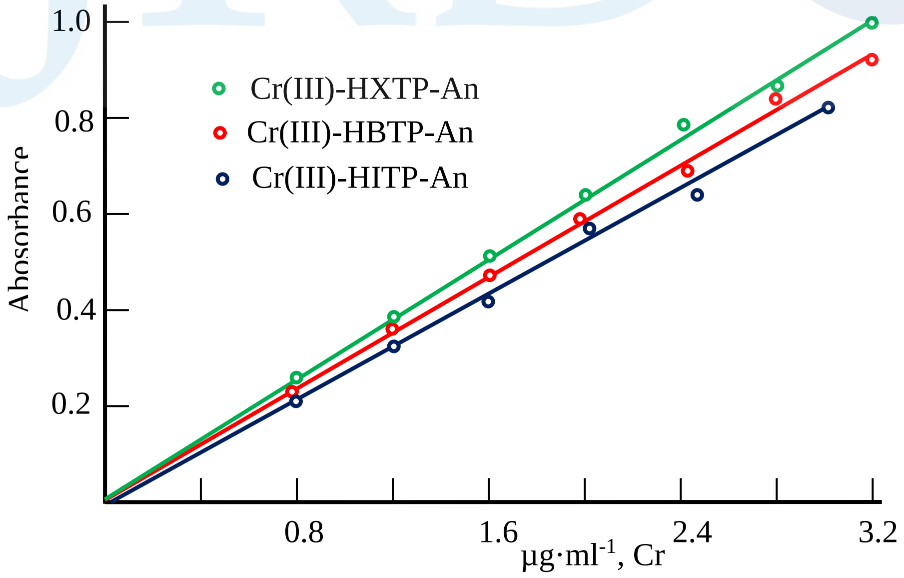

Fig. 4. Analytical determination of Cr (III) with HTPD and hydrophobic amines $C_{HTPD} = 1.0\times10^{-3}$ M, $C_{Am} = 1.12\times10^{-3}$ M, KFK-2, 490 nm, $\ell = 0.5$ cm.

Table 5. Analytical characteristics of some ternary complexes of Cr with HTPD and An

Parameter*	HCTP-An	HBTP-An	HITP-An

ECC	$y = 0.013 + 0.241x$	$y = 0.015 + 0.250\,x$	$y = 0.020 + 0.260x$
CC	0.9981	0.9986	0.9984
LCR / μg· cm^{-3}	0.5-16	0.5-16	0.5-14
LOD / ng ·cm^{-3}	11	12	10
LOQ / ng· cm^{-3}	36	34	32
SS / ng ·cm^{-2}	2.1	2.0	1.8

Note: ECC – The equation of calibration curves; CC – Correlation coefficient (9 standards used); LCR – Linear calibration range; LOD – Limit of detection; LOQ – Limit of quantification; SS – Sandell's sensitivity.*

4. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Cr (III) in alloys and in soils.

4.1. Determination of Chromium(III) in Alloys

The method was applied to the determination of chromium(III) in two alloys, stainless steel and ferrochrome type steel. In both cases, iron is masked by using sodium fluoride solution. The results are summarized in Table 6. 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.

Table 6. Determination of chromium(III) in alloys as MLC with HCTP and An (n=6, P=0,95).

Sample composition (%)	Sl. №.	Alloy taken (μg/mL)	Amount of Cr(III) found (μg/mL)	Amount of Cr(III) found (%)	Average of Cr(III) found (%)	S.D C.V (%)
Stainless Steel (Cr-11-13, Ni-10, C-0.1–0.4, Fe-77)	1.	40.0	4.33	10.91	11.01±0.084	0.767
	2.	80.0	8.79	10.95		
	3.	120.0	13.28	11.06		
	4.	160.0	17.78	11.13		
	5.	200.0	21.85	10.90		
	6.	240.0	26.61	11.11		
Ferrochrome (Cr – 65, Fe – 35)	1.	4.00	2.41	60.47	63.34 ± 2.35	3.72
	2.	5. 60	3.46	61.64		
	3.	7.20	4.36	60.91		
	4.	8.80	5.86	66.31		
	5.	10.40	6.75	65.20		
	6.	12.00	7.88	65.52		

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 7 indicate the successful applicability of the proposed method to real sample analysis.

Table 7. Correctness and reproducibility of Determination of chromium in soil (n=5, P=0.95).

Method	X^{-}, % $\times 10^{-4}$	SD $\times 10^{-4}$	RSD, %	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Standard method				

Diphenylcarbazide	2.95	0.148	5	(2.95±0.18)
	Proposed method			
HCTP-An	2.85	0.114	4	(2.85±0.14)
HBTP-An	2.87	0.087	3	(2.87±0.11)
HITP-An	2.85	0.114	4	(2.85±0.14)

5. Conclusions

Mixed-ligand complexes of chromium (V) with o-hydroxythiophenols (HTPD) and its derivatives [2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)] in the presence of hydrophobic amines have been investigated by spectrophotometric method. Extraction of mixed ligand complexes is maximal at pH 3.0-5.0. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components I the complexes have been determined. The Beer’s law was applicable in the range of 0.5-16μg mL^{-1}. A simple, rapid and sensitive methods proposed for the determination of trace amounts of chromium.

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