



P-ISSN: 2349-8528
 E-ISSN: 2321-4902
 IJCS 2017; 5(4): 1255-1262
 © 2017 IJCS
 Received: 03-05-2017
 Accepted: 04-06-2017

Rafiga K Mamedova
 Azerbaijan State Pedagogical
 University, Department of
 Organic Chemistry, U.
 Gadjiybekov Street 68. Baku, AZ
 1000, Azerbaijan

Sultan G Aliyev
 Azerbaijan State University of
 Oil and Industrial, Department
 of Chemistry and Technology
 inorganic substances, Azadlg
 Street 34, Baku, 1000 Azerbaijan

Novrasta S Hasanova
 Azerbaijan State University of
 Oil and Industrial, Department
 of Chemistry and Technology
 inorganic substances, Azadlg
 Street 34, Baku, 1000 Azerbaijan

Mahendra Choudhary
 Department of Agronomy, JAU,
 Junagadh, Gujarat, India

Nailya A Verdizadeh
 Azerbaijan State Pedagogical
 University, Department of
 Analytical Chemistry, U.
 Gadjiybekov Street 68. Baku, AZ
 1000, Azerbaijan

Ali Z Zalov
 Azerbaijan State Pedagogical
 University, Department of
 Analytical Chemistry, U.
 Gadjiybekov Street 68. Baku, AZ
 1000, Azerbaijan

Correspondence

Ali Z Zalov
 Azerbaijan State Pedagogical
 University, Department of
 Analytical Chemistry, U.
 Gadjiybekov Street 68. Baku, AZ
 1000, Azerbaijan

Extraction-spectrophotometric study of ternary complexes of Cr (VI) using O-Hydroxythiophenols and Aminophenol

Rafiga K Mamedova, Sultan G Aliyev, Novrasta S Hasanova, Nailya A Verdizadeh and Ali Z Zalov

Abstract

The o-hydroxythiophenols was synthesized and an extractive spectrophotometric method was developed for determination of Cr (III) at microgram level by using 0.1M HCl solution. Mixed-ligand complexes of Cr (III) with HTPD and Am have been studied by spectrophotometry. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found. Extraction of mixed ligand complexes is maximal at pH 3.0-5.0. The molar ratio of the reacting Cr (III), HTPD and Am species is 1:3:3. For the formation and extraction of MLC, a 26-30-fold excess of complexing reagents is required $\{1.0 \times 10^{-3}$ M HTPD and $(1.12-1.16) \times 10^{-3}$ M Am $\}$. A large excess of hydrophob amin interferers with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. Unlike single-ligand complexes, mixed-ligand complexes of Cr (III) with HTPD and Am were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 15 min. The molar absorptivity of the complex was calculated with Komar method to be $\epsilon = (3.1-3.3) \times 10^4$ L mol⁻¹ cm⁻¹. The general formula of the ternary complexes is They can be regarded as ion-associates between three charged anionic chelates $[Cr(HTPD)_3]^{3-}$ and protonated Am species. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1.09-1.15$). 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 0.5-20.0 μ g/ml. Method is rapid, selective, reproducible and reliable. The method is applicable for determination of Cr (III) in the steel and soil samples. The results obtained are in good agreement with the certified values and comparable to those obtained by known methods. The method is eco-friendly, as extraction is carried out in pH medium and has good potential for its use in the determination of Cr (III) after extraction in organic phase at microgram level.

Keyword: chromium, o-hydroxythiopheno, 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol, tolydine

1. Introduction

Chromium occurs in elemental form in natural samples in two relatively stable valence states, i.e. in the form of Cr (III) and Cr (VI) species, which exert quite different effects on biological systems. In fact, while Cr (III) is an essential component having an important role in the glucose, lipid and protein metabolism, Cr (VI) has a definitely adverse impact on living organisms. Cr (VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases ^[1, 2], since one of the routes of Cr incorporation into the human body is by ingestion ^[3,4]. Levitskaia *et al* ^[5] reported a direct spectrophotometric analysis of Cr (VI) using a liquid waveguide capillary cell. A novel spectrophotometric determination of chromium as the chromium- peroxy-4-(2-pyridylazo) resorcinol complex has been investigated ^[6]. Revanasiddappa *et al* ^[7] reported a sensitive spectrophotometric method for the determination of trace amounts of chromium (VI). The method is based on the oxidation of trifluoperazine hydrochloride (TFPH) by chromium (VI) in the presence of orthophosphoric acid. Aydin and Soylok ^[8] developed a coprecipitation procedure for chromium speciation in natural water samples. The procedure is based on the coprecipitation of Cr (III) on thulium hydroxide precipitate. After reduction of Cr (VI) to Cr (III) by using potassium iodide, the method was applied to the determination of the total chromium.

A simple extractive separation method has been developed for the determination of chromium based on the extraction of Cr (VI) as its ion-pair with tribenzylamine [9]. Tuzen and Soylak [10] developed a solid phase extraction procedure for chromium speciation in natural water samples. The procedure is based on the solid phase extraction of the Cr (VI)-ammonium pyrrolidine dithiocarbamate (APDC) chelate on multiwalled carbon nanotubes (MWNTs). Spectrophotometric determination of chromium in steel samples was investigated [11] with 4-(2-thiazolylazo)-resorcinol (TAR) using microwave radiation. Boef *et al* [12] developed a novel spectrophotometric determination of chromium in environmental samples using EDTA. 5-Br-DMPAP, a novel spectrophotometric reagent has been reported [13] for the determination of chromium. Yotsuyanagi *et al* [14] reported a novel method using PAR for the determination of chromium species in natural water samples. Subrahmanyam and Eshwar [15] studied the complexation of PAN with that of chromium species. A novel spectrophotometric reagent Br-PADAP for chromium species determination in various samples has been studied by Sheng *et al* [16]. Spectrophotometric determination of chromium in ores, steels and pure nickel samples using phenothiazines was reported by Mohamed [17]. Many authors reported chromium determination in various samples using FAAS [18-22].

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) and 2-hydroxy-5-bromothiophenol (HBTP)], and hydrophobic amins (Am) { o-tolydine (o-Tol), m-tolydine (m-Tol) and p-tolydine (p-Tol) }, and show the potential of this system for determination of Cr(VI) in real samples.

2. Materials and Methods

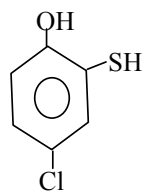
2.1. Reagents and solutions.

A solution of Chromium (VI) (1 mg ml^{-1}) was made by dissolving (0.1935) gm of $\text{K}_2\text{Cr}_2\text{O}_7$ p. f. a. (pure for analysis) in 1000 ml of water. Concentration of solution of Chromium was established gravimetric [23]. Working solution with concentration of 0,1 mg/ml was prepared by dilution of stock with deionized water.

HTPD were synthesized according to the procedure [24]. HTPD their purity was verified by paper chromatography and melting point determination. Solutions of HTPD and Am in chloroform (0.01M) were used. o-tol, m-tol and p-tol 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 ($\mu = 0.1$) introduction of the calculated quantity of KCl. To create the optimal acidity, 1M solutions of KOH and HCl were used. Complexing agents may be a dibasic (HCTP, HBTP) 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 1.

Table 1: Some characteristics of the studied reagents

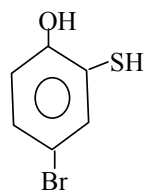


HCTP

$pK_1=5.05$; $pK_2=10.4$

pH neutral form of existence:

0-3.5 ($\lambda=283 \text{ nm}$);



HBTP

$pK_1=5.10$; $pK_2=10.6$

0-3.3 ($\lambda=286 \text{ nm}$);

The synthesized compounds were characterized by physicochemical methods: IR [16] and NMR spectroscopy (Table 2).

2.2. Instruments

The absorbance of the extracts was measured using a KFK-2 photocolimeter (USSR) and a Camspec M508 spectrophotometer (UK), equipped with 5 and 10 mm path-

length cells. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples.

Table 2: Results of studies of IR and NMR spectroscopy HTPD

Reagent	IR (KBr) [16]	¹ H NMR (300.18 MHz, C ₆ D ₆)
HCTP	3460 cm^{-1} v(OH), 2570 cm^{-1} v(SH), 1580 cm^{-1} v(C6H5) (Fig.3)	δ 5.70 (s, 1H- OH), δ 3.40(s, 1H - SH), δ 7.05 (s, 2H Ar-H), δ 6.25 (s, 2H Ar-H).
HBTP	3458 cm^{-1} v(OH), 2568 cm^{-1} v(SH), 1550 cm^{-1} v(C6H5)	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)

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 ($\ell=0.5\text{cm}$).

2.3.2. 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) anionexchangers have demonstrated the anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the orange dithiophenolate complexes of chromium 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 hydrophobic amines were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. Based on these data, new selective and highly sensitive procedures were developed for the extraction-spectrophotometric determination of trace chromium in steel and soils.

2.3.3. Studies on the oxidation state of Chromium

It is known that o-hydroxythiophenols have reducing properties in acidic medium. To elucidate the oxidation state of chromium in MLC, we conducted two series of experiments. In the first series we had used Cr (VI), while in the second series we had used Cr (III) obtained by addition of a supplementary reducing agent (SnCl₂ or KI). It was found that the spectrophotometric characteristics of the MLC of Cr (VI) and Cr (III) were identical i.e. in the interaction with HTPD, Cr (VI) was reduced to Cr (III).

2.3.4. Analysis of chromium (VI) in steel

Steel sample (0.5g) was dissolved in aqua regia and evaporated nearly to dryness. Sulphuric acid (2 ml, 1:1) was added and evaporated to white fumes. Cooled and diluted using distilled water. Ammonium persulphate (0.5g) and silver nitrate solution (2 drops, 2%) were added and heated for about 10 min. The excess of persulphate was removed by boiling the solution for 5 min. The permanganate and manganese dioxide present in small amounts were destroyed with sodium azide in regulated excess. The solution was cooled and diluted to 100 ml with distilled water. An aliquot of the solution was transferred into a separatory funnel and traces of vanadium (V) and iron (III) were separated by extracting their complexes into chloroform with 8-hydroxy quinolone at pH 4. The amount of chromium (VI) was determined using the standard procedure.

2.3.5. Analysis of soil samples

To an accurately weighed soil sample (about 2 g) was added sulphuric acid (4M, 5 ml). The mixture was stirred well and filtered through a Whatman filter paper 41. The residue was washed thoroughly with distilled water and the filtrate was collected into a 250, ml beaker. The filtrate was evaporated to about 10 ml, added potassium permanganate solution (0.5 M) dropwise till the solution attained pink colour and boiled for five minutes (a few more drops of potassium permanganate solution were added if the colour was discharged). The excess permanganate was removed by adding sodium azide (0.1 %) dropwise with constant stirring. Ammonium phosphate solution (10 ml, 5 %) was added and then pH of the solution was maintained to 7-8 using ammonia solution. The precipitates of iron and aluminium were removed by filtration. The precipitate was washed with dilute ammonia solution (1%) and the washings were collected into a 100 ml standard flask, acidified it with phosphoric acid (2 M) and diluted up to

the mark with distilled water. Suitable aliquot of the solution was transferred into a 25 ml standard flask and the amount of chromium present was investigated using the procedure as outlined earlier.

3. Results and Discussion

3.1. The Choice of the Extractant

For the extraction of complexes we used CHCl₃, CCl₄, C₆H₆, C₆H₅CH₃, C₆H₄(CH₃)₂, C₂H₄Cl₂, isobutanol and isopentanol. The extractivity of the complexes was estimated by the distribution coefficient and recovery. CHCl₃, CCl₄ and C₂H₄Cl₂ appeared to be the best extractants. All the further investigations were carried out with chloroform. The concentration of chromium in the organic phase was determined with diphenylcarbazide [3] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference. The basicity of Am hardly influences the recovery of niobium. After a single extraction with chloroform, 98.2-98.8% of niobium was extracted as an ion associate.

3.2. 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 decrease 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 and table 3. 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, H₂SO₄) almost does not influence a complex formation of chromium with HTPD and Am.

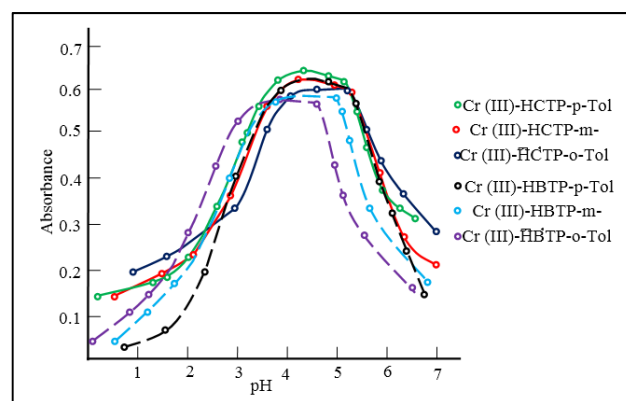


Fig 1: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. $C_{Cr}=3.84 \times 10^{-5}$ M, $C_{HTPD}=1.0 \times 10^{-3}$ M, $C_{Am}=(1.12-1.16) \times 10^{-3}$ M, KFK-2, $\lambda=490$ nm, $\ell=0.5$ cm.

3.3. Influence of Reagent Concentration and Incubation Time

For the formation and extraction of MLC, a 26-30-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by 1.0×10^{-3} M HTPD and $(1.12-1.16) \times 10^{-3}$ M Am. A large excess of hydrophob amin interferers with the determination. However it was found that the presence of

excess of the reagent solution does not alter the absorbance of the color reaction.

Unlike single-ligand complexes, mixed-ligand complexes of Cr (III) with HTPD and Am were stable in aqueous and

organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 15 min.

Table 3: Optimum conditions of education and analytical the characteristic of MLC of chromium with HTPD and Am.

Compound	Optimum pH interval	λ_{\max} / nm	$\epsilon \times 10^{-4} / \text{L mol}^{-1} \cdot \text{cm}^{-1}$	Working range / $\mu\text{g/ml}$
Cr-HCTP- o-Tol	3.6-4.9	475	3.1	0.5-18
Cr-HCTP- m-Tol	3.7-5.1	479	3.2	0.5-18
Cr-HCTP- p-Tol	3.9-5.3	484	3.3	0.6-18
Cr-HBTP- o-Tol	3.4-4.7	480	3.0	0.5-20
Cr-HBTP- m-Tol	3.5-4.9	485	3.1	0.6-20
Cr-HBTP- p-Tol	3.7-5.2	492	3.2	0.6-20

3.4. Electronic Absorption Spectra

Neither the metal ion nor the reagent has appreciable absorbance at specified wavelengths. Hence further studies were carried out at 475-492 nm (Fig.2 and table 3). The reagent has minimum absorbance at the maximum absorbance

of the complex. Hence further absorbance measurements were made at 490 nm. The molar absorptivity of the complex was calculated with Komar method [26] to be $\epsilon = (3.1-3.3) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

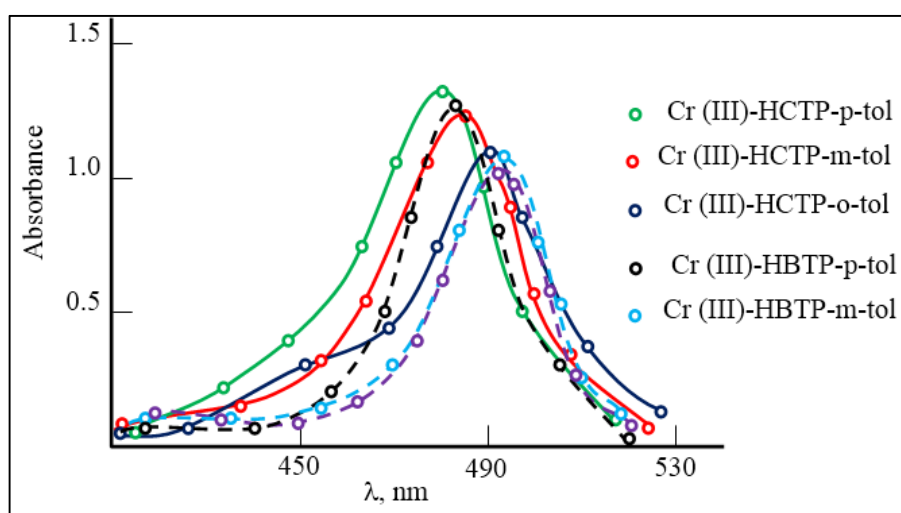


Fig 2: Absorption of mixed-ligand complexes. $C_{\text{Cr}} = 3.84 \times 10^{-5} \text{ M}$, $C_{\text{HTPD}} = 1.0 \times 10^{-3} \text{ M}$, $C_{\text{Am}} = (1.12 - 1.16) \times 10^{-3} \text{ M}$, SF-26, $\ell = 1.0 \text{ cm}$.

3.5. Stoichiometry of the Complexes and the Mechanism of Complexation

The stoichiometric coefficients of the reaction were determined by the Asmus method, the relative yield method and the equilibrium shift method [25]. The formation of MLC can be presented in the following way. When chromium ion interacts with three molecules of o-hydroxythiophenols, they form three-charged anionic complexes, which were extracted with three molecules of protonated Am.

It was found, using the Nazarenko Method, that Cr(III) in the complexes was present in the Three charging cation Cr^{3+} . The

number of protons replaced by chromium in one HTPD molecule appeared to be two [26].

The disappearance of the pronounced absorption bands in the $3200-3600 \text{ cm}^{-1}$ with a maximum at 3452 cm^{-1} observed in the spectrum of HTPD, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2585 cm^{-1} shows that the -SH group involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1387 cm^{-1} indicates the presence of a protonated o-tolydine (Fig. 3) [27].

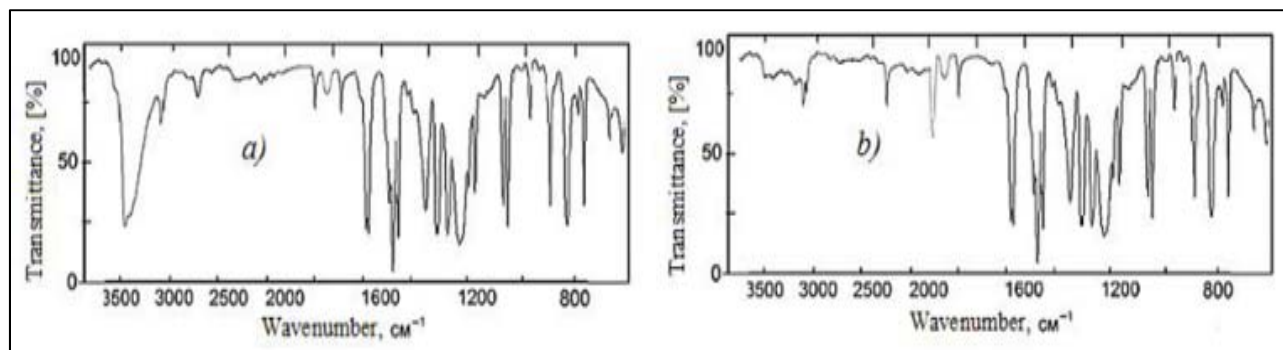


Fig 3: IR spectrums of HCTP (a) and the Cr (III)- HCTP -o-Tol (b).

Structure extractable complexes can be represented as in Fig.

4.

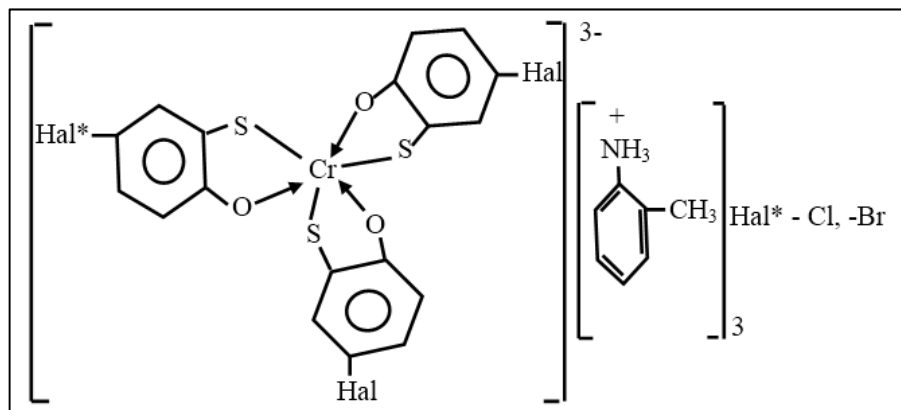
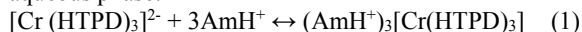
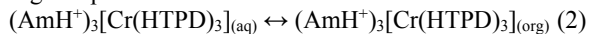


Fig 4: Structure of complex $(o\text{-TolH}^+)_3[\text{Cr}(\text{HTPD})_3]$.

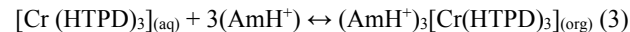
Several equilibrium processes should be taken into account for the system of $[\text{Cr}(\text{HTPD})_3]^{2-} - o\text{-TolH}^+ - \text{water} - \text{chloroform}$. Formation of ion-association complex in the aqueous phase:



Distribution of the complex between the aqueous and the organic phase:



Extraction from water into chloroform:



Based on the equation:

$$\beta = \frac{\{[\text{Cr}(\text{HTPD})_3](\text{AmH})_3\}}{[\text{Cr}(\text{HTPD})_3]^{3-}][\text{AmH}^+]^3} \quad (4)$$

$$K = \frac{\{[\text{Cr}(\text{HTPD})_3](\text{AmH})_3\}_{\text{org}}}{\{[\text{Cr}(\text{HTPD})_3](\text{AmH})_3\}_{\text{aq}}} \quad (5)$$

$$K_{\text{ex}} = K_D + \beta = \frac{\{[\text{Cr}(\text{HTPD})_3](\text{AmH})_3\}_{\text{org}}}{\{[\text{Cr}(\text{HTPD})_3]^{3-}\}_{\text{aq}}\{(\text{AmH}^+)\}_3}_{\text{aq}} \quad (6)$$

The constants of the association β were determined by several independent methods: Mobile equilibrium method [28], Holme-Langmyhr method [29], Komar-Tolomachev Method [25] and Harvey-Manning method [30].

The constants of the distribution K_D were determined by comparison of the absorbance values obtained after single extraction at the optimum conditions (A_1) and triple extraction (A_3): $K_D = A_1/(A_3 - A_1)$. The extraction constants were calculated by the equation $K_{\text{ex}} = \beta + K_D$ [31]. All calculations were carried out at a probability of 95%. The obtained values are presented in Table 4.

Table 4: Values of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β) and recoveries (R%) for the Cr(III)-HTPD -Am-water-chloroform systems

Extraction system	$\lg \beta$	$\lg K_D$	$\lg K_{\text{ex}}$	R%
Cr(III)-HCTP- o-tol -H ₂ O-CHCl ₃	8.59±0.2 ^a 8.70±0.4 ^b	1.86±0.01	10.56±0.21 ^e 10.60±0.43 ^f	98
	8.46±0.7 ^c			
	8.75±0.3 ^d			
Cr(III)-HCTP- m-tol -H ₂ O-CHCl ₃	8.11±0.3 ^b	1.42±0.08	9.53±0.11 ^e	97
	8.32±0.5 ^c			
Cr(III)-HCTP- p-tol -H ₂ O-CHCl ₃	7.09±0.3 ^a 7.11±0.2 ^b	1.15±0.02	8.24±0.32 ^f	98
Cr(III)-HBTP- o-tol -H ₂ O-CHCl ₃	6.87±0.3 ^a 6.65±0.4 ^b	1.79±0.04	8.66±0.34 ^e	88
	6.69±0.3 ^c			
	6.75±0.2 ^d			
Cr(III)-HBTP- m-tol -H ₂ O-CHCl ₃	6.62±0.01 ^a 6.45±0.04 ^b	0.92±0.02	7.54±0.03 ^e	95
	6.34±0.03 ^c			
Cr(III)-HBTP- p-tol -H ₂ O-CHCl ₃	6.55±0.02 ^a 6.14±0.02 ^b	0.88±0.04	7.43±0.42 ^e	95

Note: ^aCalculated by the Holme-Langmyhr method [29]; ^bCalculated by the Harvey-Manning method [30]; ^cCalculated by the Komar-Tolomachev method [25]; ^dCalculated by the mobile equilibrium method [28]; ^eCalculated by the formula $K_{\text{ex}} = K_D + \beta$ where b is determined by the Holme-Langmyhr method [29]; ^fCalculated by the formula $K_{\text{ex}} = K_D + \beta$ where b is determined by the Harvey-Manning method [30].

Calculation of extent of polymerization of complexes was carried out on the equation [32]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1.09-1.15$).

3.6. Influence of Interfering Ions

To evaluate the complex applicability for photometric determination of chromium, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as NO_3^- , ClO_4^- , SO_4^{2-} and CH_3COO^- do not interfere

determination of chromium with HTPD and Am. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in Table 5.

Table 5: Influence of interfering ions on the determination of niobium (III) as MLC with HCTP and o-Tol (30,0 µg Cr added)

Ion	Molar excess of the ion	Masking agent	Found Nb,µg	RSD,%
Zr(IV)	60	NaF	30.4	4
Cu(II)	35	SC(NH ₂) ₂	29.9	3
Ti(IV)	50	Ascorbic acid	29.0	3
Mn(II)	50		29.8	5
W(VI)	80		29.3	6
Mo(VI)	15		29.4	4
Cd(II)	150		30.0	6
Nb(V)	30		30.5	3
V(IV)	10		30.0	2
Ta(V)	50	Na ₂ C ₄ H ₄ O ₆	30.0	4
Pt(II)	40		29.3	3
Pd(II)	40		30.4	5
Co(II)	100		29.9	4
Ni(II)	100		30.2	6
Al(III)	190		29.8	5
Fe(II)	80		29.9	3
Fe(III)	80		30.3	5
Ascorbic acid	20		31.0	4
Tartaric acid	20		29.2	3
Oxalate	80		30.5	5
Fluoride	45		30.6	6
Phosphoric acid	45		30.3	3
Thiourea	60		31.2	6

3.7. Beer's law and analytical characteristics

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 0.5-20.0 µg/ml.

The equations of the obtained straight lines and some important characteristics concerning the application of the ternary complexes for extractive-spectrophotometric determination of Cr (III) are listed in Table 6.

Table 6: Analytical characteristics

Characteristic*	Extraction system			
	Co-HCPT- o-tol	Co-HCPT- m-tol	Co-HBTP- o-tol	Co-HBTP- m-tol
AMA (ε), L mol ⁻¹ cm ⁻¹	3.1×10 ⁴	3.2×10 ⁴	3.0×10 ⁴	3.1×10 ⁴
ABL, µg mL ⁻¹	0.5-18	0.5-18	0.5-20	0.6-20
ESL	0.1252x+0.054	0.1255x+0.049	0.149x+0.02	0.145x+0.038
CC	0.9996	0.9994	0.9902	0.9997
SS, ng cm ⁻²	0.00854	0.00725	0.00941	0.00968
LOD, µg mL ⁻¹	12	14	11	11
LOQ, µg mL ⁻¹	41	44	38	30

*Note: AMA – Apparent molar absorptivity, ABL – Adherence to Beer's law, ESL – Equation of the straight line, CC – Coefficient of correlation, SS – Sandell's sensitivity, LOD – Limit of detection, LOQ – Limit of quantification.

Table 7 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of chromium with the earlier known procedures [13-16].

4. Determination of chromium (VI) in steel and soil samples

The developed analytical procedure was applied for the analysis of real samples. Steel and soil samples were analyzed. The results presented in Table 8-9 are in good agreement with the certified values. When analyzing the soil,

the results were compared with the spectrophotometric method of atomic absorption obtained according to the standard. The performance of the proposed method was judged by calculating the students t- and F- values. At 95% confidence level, the calculated t- and F- values do not exceed the theoretical values as represented in table 9. Therefore, there is no significant difference between the proposed method and the standard (AAS) method, indicating that the proposed method is as accurate and precise as the standard (AAS) method.

Table 7: Comparative characteristics of the procedures for determining chromium

Reagent	pH (solvent)	λ, nm	ε·10 ⁻⁴	Beer's law range, µg	[Ref.]
5-Br-DMPAP	0.1–10 M HCl (CHCl ₃)	546	7.8	0.02 – 0.56	13
PAR	4-5	540	4.7	3.2-13.0	14
PAN	0.2–0.8 M HCl (aseton)	390-400	1.28	0.3 – 2.0	15
Br-PADAP	4.7	600	7.93	0.6 – 15.0	16
<i>Proposed method</i>					
Cr-HCTP- o-Tol	3.6-4.9(CHCl ₃)	475	3.1	0.5-18	
Cr-HBTP- o-Tol	3.4-4.7(CHCl ₃)	480	3.0	0.5-20	

Table 8: Determination of chromium (VI) in steels.

Steel samples. Comp.,%	Chromium (VI), %		RSD
	Certified	Found*	
Cr 1.19; Mo 0.48; Ni 1.71; V 0.08; C 0.54; S 0.09; Mn 0.76; Al 0.016; Cu 0.01; Ti 0.001	1.19	1.18	1.55
Cr 0.8; Mo 0.8; Ni 1.65; V 0.07; C 0.54; S 0.09; Mn 0.8; Al 0.016; Cu 0.01; Ti 0.01	0.80	0.78	1.34
Mn 0.45; Ni 1.65; Cr 0.4; Mo 0.2	0.40	0.41	1.75

Table 9: Determination of chromium (VI) in soil samples.

Soil samples	Chromium(VI), mg/ml		Std. Dev.	F	t
	AAS	Present method*			
S1	3.61	3.68	0.007	1.55	1.72
S2	3.25	3.19	0.009	1.66	1.48
S3	4.58	4.37	0.004	1.91	2.33
S4	2.36	2.29	0.005	1.18	1.09

Conclusion

The o-hydroxythiophenols was synthesized and an extractive spectrophotometric method was developed for determination of Cr (III) at microgram level by using 0.1M HCl solution. Mixed-ligand complexes of Cr (III) with HTPD and Am have been studied by spectrophotometry. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found. Extraction of mixed ligand complexes is maximal at pH 3.0-5.0. The molar ratio of the reacting Cr (III), HTPD and Am species is 1:3:3. The general formula of the ternary complexes is They can be regarded as ion-associates between three charged anionic chelates [Cr (HTPD)₃]³⁻ and protonated Am species. Method is rapid, selective, reproducible and reliable. The method is applicable for determination of Cr (III) in the steel and soil samples. The results obtained are in good agreement with the certified values and comparable to those obtained by known methods. The method is eco-friendly, as extraction is carried out in pH medium and has good potential for its use in the determination of Cr (III) after extraction in organic phase at microgram level.

References

- Environmental Protection Agency. Toxicological review of trivalent chromium (CAS no. 16065-83-1) in support of summary information on the integrated risk information system (IRIS), US Environmental Protection Agency, Washington, DC, 1998.
- Nriagu JO, Nieboer E. Chromium in Natural and Human Environment, Wiley, New York, 1988-94.
- Lavrukina A, Yukina LV. Analytical Chemistry of Chromium, Nauka, Moscow, 1979, 217.
- Matuoka S, Tennichi Y, Takehara K, Yoshimura K. Flow analysis of micro amounts of chromium(III) and (VI) in natural water by solid phase absorptiometry using diphenylcarbazide. *Analyst*. 1999; 124:787-792.
- Levitskaia TG, Ohara MJ, Sinkov SI, Egorov OB. Direct Spectrophotometric Analysis of Cr (VI) Using a Liquid Waveguide Capillary Cell. *Applied Spectroscopy*. 2008; 62(1):107-113.
- Valencia WW, Mudasar, Roto. Extraction and speciation of chromium(vi) and chromium(III) as ionassociation complexes of tetramethylammonium-chromate. *Indo. J Chem*. 2006; 6(2):150-154
- Revanasiddappa HD, Kiran Kumar TN. Rapid Spectrophotometric Determination of Chromium with Trifluoperazine Hydrochloride. *Chemia analityczna (Warsaw)*. 2002; 47:311-316.
- Aydin FA, Soy lak M. Thulium hydroxide: A new coprecipitant for speciation of chromium in natural water samples. *Journal of Hazardous Materials*. 2009; 162(2-3):1228-1231.
- Kalidhasan S, Ganesh M, Sricharan S, Rajesh N. Extractive separation and determination of chromium in tannery effluents and electroplating waste water using tribenzylamine as the extractant. *Journal of Hazardous Materials*. 2009; 165:886-891.
- Tuzen M, Soy lak M. Multiwalled carbon nanotubes for speciation of chromium in environmental samples. *Journal of Hazardous Materials*. 2007; 147(1-2):219-224.
- Luciene S de Carvalho, Antônio Celso S Costa, Sérgio LC Ferreira, Leonardo SG. Teixeira. Spectrophotometric determination of chromium in steel with 4-(2-thiazolylazo)-resorcinol (TAR) using microwave radiation. *Journal of the Brazilian Chemical Society*. 2004; 15(1):153-157.
- Boef G, Jong WJ, Krijn GC, Poppe H. Spectrophotometric determination of chromium (III) with EDTA. *Anal. Chim. Acta*. 1960; 23:557-564.
- Zhao Y, Han G. Rapid spectrophotometric determination of chromium (III). *Talanta*. 1994; 41(10):1247-1251.
- 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.
- 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.
- 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.
- Mohamed AA. Spectrophotometric Determination of Chromium in Ores, Steels and Pure Nickel Samples using Phenothiazine. *Bull. Chem. Soc. Jpn*. 2001; 74(12):2373-2379.
- Sun M, Wu Q. Cloud point extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr(III) in human serum samples. *J Pharm Biomed Anal*. 2012; 60(1):14-18.
- Henriquez C, Hostkotte B, Solich P, Cerda V. In-syringe magnetic-stirring-assisted liquid-liquid microextraction for the spectrophotometric determination of Cr(VI) in waters. *Analytical and Bioanalytical Chemistry*. 2013; 405(21):6761-6769.
- Lutfullah, Khan F, Rahman N. Solid phase extraction and determination of Cr(III) by spectrophotometry using cefaclor as a complexing reagent and FAAS. *Environ Monit Assess*. 2013; 185(6):4959-4967.

21. Amin AS, Kassem MA. Chromium speciation in environmental samples using a solid phase spectrophotometric method. *Spectrochim Acta A Mol Biomol Spectrosc.* 2012; 96(5):541-547.
22. Kiran K. Spectrophotometric determination of chromium in various environmental samples using p-dimethylaminobenzylethylenediamine, *Journal of International Academic Research for Multidisciplinary.* 2014; 2(4):180-186.
23. Korostelev PP. Preparation of solutions for chemical analysis works. M.: Publishing house of Academy of Sciences of the USSR, 1964.
24. Kuliev AM, Aliev SR, Mamedov FN, Movsumzade M. Synthesis of 2-aminomethyl- 5-hydroxy alkyl phenols, thiols and their cleavage. *Zhurnal organicheskoi khimii.* 1976; 12(2):426-430
25. Bulatov MI, Kalinkin IP. Practical Guide on Photocolorimetric and Spectrophotometric Methods of Analysis. Moscow, Khimiya, 1972.
26. Nazarenko VA, Biryuk EA. A study of the chemistry of reactions of multi-valent element ions with organic reagents. *Zh. Anal. Khim.* 1967; 22(1):57-64.
27. Fritz JS, Schenk GH. Quantitative analytical chemistry. Boston, Allyn and Bacon, 1974.
28. Zhiming Z, Dongsten M, Cunxiao Y. Mobile equilibrium method for determining composition and stability constant of coordination compounds of the form M_nR_n . *Journal Rare Earth.* 1997; 15(2):216-220.
29. Holme A, Langmyhr FJ. A modified and a new straight-line method for determining the composition of weak complexes of the form A_mB_n . *Anal. Chim. Acta,* 1966; 36(3):383-387.
30. Harvey AE, Manning DL. Spectrophotometric Methods of establishing empirical formulas of colored complexes in solution. *Journal Amer. Chem. Soc.* 1950; 72(8):4488-4453.
31. Alexandrov A, Budevski O, Dimitrov A. Investigation of the extraction equilibrium of ternary ion-association complex of thallium(III) with iodo-nitro-tetrazolium chlorid // *Journal of Radioanalytical Chemistry.* 1976; 29(2):243-250.
32. Akhmedly MK, Kly'gin AE, Ivanova LI, Bashirov EA. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. *Zhurnal Neorganicheskoi Khimii.* 1974; 19(8):2007-2012.