

Investigation of the Extraction Equilibrium of Ion-Association Complexes of Molybdenum (VI) With Some O-Hydroxythiophenols and Aromatic Amine Extraction-Spectrophotometric Determination of Molybdenum

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ABSTRACT

The extraction process of ternary mixed-ligand complex of molybdenum (VI) with some o-hydroxythiophenols (2-hydroxythiophenol, 2,4-dihydroxythiophenol, 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol, 2-hydroxy-5-iodothiophenol) and aromatic amine has been investigated by using an extraction-spectrophotometric method. The optimum conditions for their quantitative preparation in aqueous medium and subsequent extraction into an organic solvent have been found. The extraction, distribution and association constants, and the recovery factors have been calculated. The composition of the complexes has been determined. A precise, sensitive and simple extraction-spectrophotometric method for determination of molybdenum in products from ferrous metallurgy has been developed.

1 Introduction

In aqueous solution, Mo(VI) ions react with o-hydroxythiophenols to form chelate complexes. In contact with bulky organic cations, these chelates form ternary ion-association complexes [1–4]. Our investigations carried out with aromatic amine [5–10], showed that mixed-ligand complex (MLC) are readily extracted into organic solvents and could be applied for extraction-spectrophotometric determination of a number of metals. Of interest to us are the negatively charged complex ions of Mo(VI) with o-hydroxythiophenols (o-HTPh, H₂L), which interact with aromatic amine [10,11]. In the present work we have studied the formation and extraction of MLC of Mo(VI) with the following o-HTPh: 2-hydroxythiophenol (HTP), 2,4-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP) on the one hand and the aromatic amine (AA{The aromatic amine used as 2 - (N, N-dimethyl-aminomethyl) -4-methylphenol}) on the other. A detailed study of the extraction equilibrium in the system Mo(VI) - o-HTPh – AA – water – organic solvent will allow the determination of the constants characterizing this equilibrium and for selecting satisfactory conditions for extraction-spectrophotometric determination of molybdenum in suitable samples.

2. EXPERIMENTAL

2.1. Reagents and apparatus

A standard Mo(VI) solution with a concentration of 1×10^{-2} mol/ dm⁻³ was prepared by dissolving (NH₄)₂MoO₄ × 2H₂O. Lower concentrations of the metal ion are obtained by suitable dilution of the stock solution. The concentration of the niobium solution was adjusted gravimetrically [11]. o-

hydroxythiophenols solutions were prepared with concentrations of $1.15 \times 10^{-2} \text{ mol dm}^{-3}$ (2-hydroxythiophenol, HTP), $1.10 \times 10^{-2} \text{ mol dm}^{-3}$ (2,4-dihydroxythiophenol, DHTP), $1.15 \times 10^{-2} \text{ mol dm}^{-3}$ (2-hydroxy-5-chlorothiophenol, HCTP), $1.20 \times 10^{-2} \text{ mol dm}^{-3}$ (2-hydroxy-5-bromothiophenol, HBTP) and $1.30 \times 10^{-2} \text{ mol dm}^{-3}$ (2-hydroxy-5-iodothiophenol, HITP chloroform solution), respectively. o-HTPh were synthesized according to the procedure [12] Their purity was verified by melting point determination and paper chromatography. The concentration of aromatic amine - 2(N, N-dimethylaminomethyl)-4-methylphenol (AA) was $(2.2-2.5) \times 10^{-3} \text{ mol dm}^{-3}$. The other reagents were HCl, H₂SO₄, CHCl₃, C₂H₂Cl₄ and solutions of diverse ions and reagents. All reagents were of analytical grade from Fluka.

The absorbance of the extracts was measured using a KFK-2 photocolormeter 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. ESR spectra of solutions of mixed-ligand complexes were registered on a JEOS-JES-PE-3X spectrometer (Japan) with working a frequency of 9400 MHz.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) (employing a Q Derivatograph, Hungary) were carried out under the following conditions: sensitivity of DTA, 1 mV; DTG, 1 mV; TG, 100 mg; heating rate, $10^\circ \text{ min}^{-1}$; sample mass 50 mg. All the studies were performed in air medium. A platinum crucible was used.

2.2. Procedure for determining the optimum conditions

Portions of a working Mo(VI) solution, 0.1 to 0.8 cm³ with an increment of 0.1 cm³, 1.0-2.0 cm³ of $1 \times 10^{-3} \text{ mol dm}^{-3}$ HCl, and 0.3-0.5 cm³ of a $(1.10-1.30) \times 10^{-3} \text{ mol dm}^{-3}$ o-HTPh solution were placed in calibrated test tubes with ground stoppers. The mixture was stirred thoroughly for 5 min to reduce tungsten, and 2.0-3.0 cm³ of a $2.2 \times 10^{-3} \text{ mol dm}^{-3}$ solution of AA was added. The volume of the organic phase was adjusted to 5 cm³ with chloroform, and the volume of the aqueous phase was brought to 20 cm³ with distilled water. After the formation of the o-hydroxythiophenolate complex of molybdenum (VI), it was extracted, and the absorbance of extracts was measured by a KFK-2 photoelectrocolorimeter at 540 nm.

2.3. Studies on the oxidation state of molybdenum

In acidic medium, o-HTPh exhibit reducing properties [4-6,8]. Hence, in the complex formation with HCTP, molybdenum (VI) is reduced to molybdenum (V) by the reagent itself. This fact was confirmed by ESR spectrometry [8].

2.4. Procedure for the determination of Mo in steels

A steel sample [*Standard steel A* — (12.33 Cr; 7.38 Mn; 6.96 Ni; 1.34 Mo; 1.24 V; 0.66 Si; 0.51 Nb 0.386 C; 0.101 Cu; 0.044 N; 0.036 Ti; 0.012 P; 0.005% S);, *Standard steel B*—(1.03 Cr; 0.64 Mn; 0.36 Si; 0.255 C; 0.25 Mo; 0.013 P; 0.009 %S) and *Ferromolybdenum* — (53.2 Mo; 0.12 S; 0.12% Si)] of 1.0 g (the mass of steel depends on its Mo content) is dissolved into 15 cm³ of H₂SO₄ (1:1). A 2 cm³ aliquot of concentrated HNO₃ is added to dissolve the carbides. The dissolved sample is heated in a sand bath to remove the excess of HNO₃ until white fumes of SO₃ appear. After the excess of HNO₃ is removed, the solution is neutralized with 30 % NaOH until a stable precipitate appears. The latter is dissolved with a minimum amount of H₂SO₄(1:5). After cooling with running water, 15 cm³ of a 20 % solution of ferroammonium sulfate are added and the solution is allowed to

stand for 2 min. Then it is transferred into a 500 cm³ volumetric flask containing 50 cm³ of a hot 20 % solution of NaOH. The flask is shaken and after cooling, the contents are diluted to the mark with distilled water. The solution is filtered through double filter paper. A 15 cm³ aliquot of the filtrate is taken and neutralized with 5M H₂SO₄. The volume of the acid consumed is recorded.

For the analysis of molybdenum a 100 cm³ aliquot of the filtrate is taken and the required volume of 5M H₂SO₄ is added to neutralize the medium. Aliquots (depending on Mo content) of this solution are placed into separating funnels followed by addition of 0.5 cm³ 1 × 10⁻² mol dm⁻³ HCl, 1.5 cm³ 1 × 10⁻² mol dm⁻³ o-HTPh, 1.5 cm³ 2.4 × 10⁻³ mol dm³ AA, 1 cm³ 0.1 % Na - EDTA. The volume of an organic phase adjusted to 5 ml chloroform, and total amount to 25 ml with 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 540 nm against chloroform by KFK-2 photocolimeter. The Molybdenum content was found from a calibration graph.

3. RESULTS AND DISCUSSION

Mo (V) reacts with o-hydroxythiophenols and gives a red colored complexes. These complexes are insoluble in non-polar solvents. 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 o-hydroxythiophenolate complexes of molybdenum (V) 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 aromatic amines were introduced into the system, the extraction of these compounds into the organic phase as a MLC was observed.

3.1. The Choice of the Extractant

For the extraction of complexes, we used CHCl₃, C₂H₄Cl₂, CCl₄, C₆H₆, C₆H₅-CH₃, C₆H₅Cl, *iso*-C₄H₉OH, *iso*-C₅H₁₁OH, *n*-C₄H₉OH and their mixes. Extractability of complexes was estimated in coefficient of distribution (*D*) and extent of extraction (*R*%). CHCl₃, C₂H₄Cl₂ and C₆H₅Cl 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 about 96.2-98.8% of tungsten was extracted as an ion associate. Further researches were conducted with chloroform. The concentration of molybdenum in the organic phase was determined with toluene-3,4-dithiol by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

3.2. Influence of the pH of the Aqueous Phase

The effect of pH on the formation of Mo(V)-o-HTPh-AA complex was studied, in order to find a suitable pH that can be adopted in the determination of molybdenum(V) (Fig. 1). The absorbance was found to be maximum in the pH range 3.0-6.0. Hence further analytical investigations were carried out in media of pH 3. Extraction of Mo(V) 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 o-HTPh. Probably, it

is present in the solution in the non-dissociated state. At $\text{pH} \geq 7.5$, the complexes were hardly extracted, obviously because of the decrease in the degree of AA protonation.

3.3 Optimum extraction-spectrophotometric conditions

The optimum conditions for extraction of Mo with o-HTPh and AA are shown in table 1. The results indicate that the system Mo(V)- o-HTPh -AA is the better one for extraction-spectrophotometric determination of Mo.

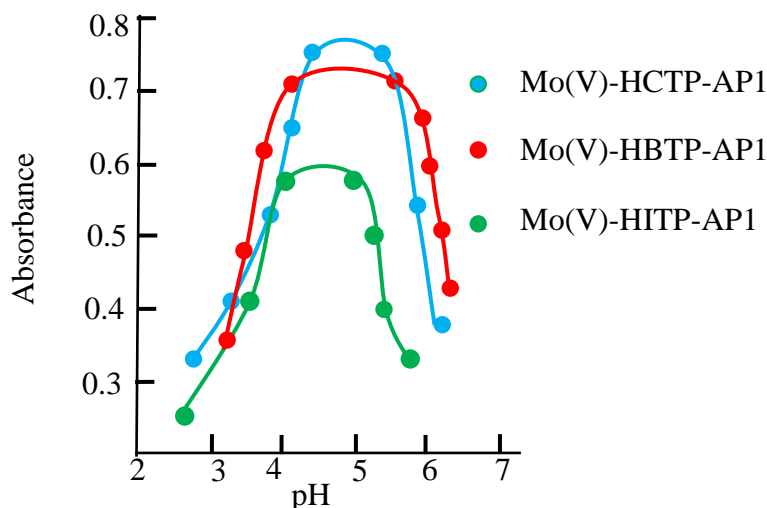


Fig.1. Absorbance of Mo(V)-o-HTPh-Am complexes in chloroform vs. pH of the aqueous phase. $C_{\text{Mo}} = 4.16 \times 10^{-5} \text{ mol dm}^{-3}$, o-HTPh = $(2.2-2.8) \times 10^{-3} \text{ mol dm}^{-3}$, $C_{\text{AA}} = (2.2-2.5) \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 540 \text{ nm}$

Table 1. Optimum extraction-spectrophotometric conditions.

Optimum conditions	HTP	DHTP	HCTP	HBTP	HITP
Absorbance maximum / nm	490	495	496	510	512
Volume of the aqueous phase / cm^3	5	5	5	5	5
Volume of the organic phase / cm^3	20	20	20	20	20
Extraction time / minute	7	7	8	9	10
pH of the aqueous phase	3.1-6.2	3.5-6.6	2.6-5.5	2.3-5.0	2.0-4.8
Concentration of AA / fold excess	53	55	58	58	61
Concentration of o-HTPh / fold excess	36	26	36	29	31
Beer's law / $\mu\text{g}/\text{cm}^3$	0.2-18	0.2-19	0.2-20	0.5-19	0.5-20
Number of samples	10	10	10	10	10
Molar abs.coef. ϵ , $\ell \text{ mol}^{-1} \cdot \text{cm}^{-1}$	3.62	3.53	3.46	3.25	3.11
Determin. limits – absorp.units	0.050	0.060	0.052	0.065	0.051
– $\mu\text{g Mo}/\text{cm}^3$	0.2	0.2	0.2	0.5	0.5

3.4. Composition, stability, distribution

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex [13]. The results suggest the

complex composition of 1:2:2 (Mo : o-HTPh : AA). The formation of MLC can be presented in the following way. When molybdenum ion interact with two molecules of o-HTPh, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated AA. (Fig. 2). Formed MLC between anionic chelates of molybdenum (V) with o-HTPh and AA.

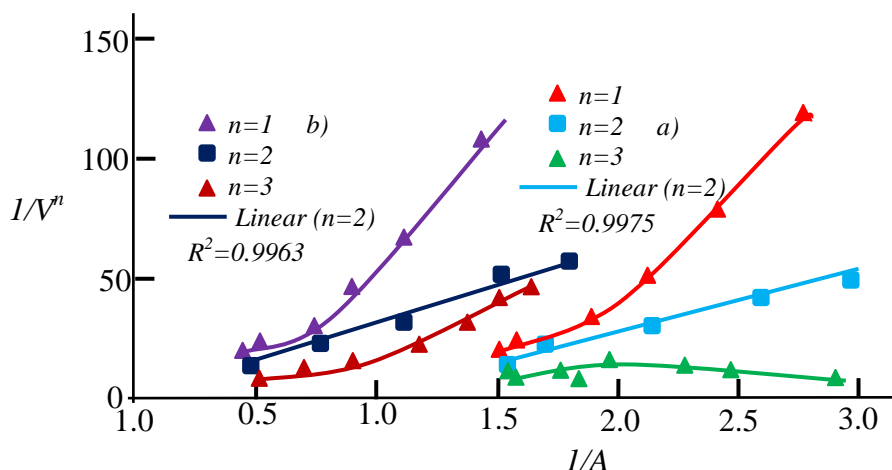
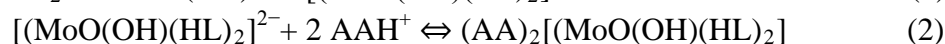


Fig. 2. Determination of the a) HCTP-to-Mo molar ratio; b) AP-to-Mo molar ratio by the method of Asmus. $C_{Mo} = 4.16 \times 10^{-5} \text{ mol dm}^{-3}$, $C_{HCTP, AA} = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda=496 \text{ nm}$, CF-26 $\ell=1.0 \text{ cm}$, pH 2.6-5.5.

The data from DTA and TGA (Fig. 3) proved the established ratios and showed that the complex obtained is stable up to 190°C and can be used for analytical purposes. On the DTA curve three exothermal effects are observed. The first one is very fast and is connected with heat liberation. The next steps of oxidation and mass loss are associated with maxima at 380°C and 450°C. The total mass loss is 75.2 % at 1000°C. On the basis of the obtained results we propose the scheme of interaction (Scheme).



Scheme. Formation and extraction of the MLC of Mo(V) with HTP and AA.

From Eqs (1) and (2), one can judge the reaction mechanism: molybdenum (VI) is reduced by o-hydroxythiophenol derivative in a hydrochloric acid medium to molybdenum (V), and the latter in the form of a complex cation interacts with excess o-HTPh. The resulting anionic complex $[(MoO(OH)(HL)_2]^{2-}$ is reacted with AA, which the acidic solution is in the protonated state (AAH^+). The constants required for the quantitative assessment of the extraction equilibria

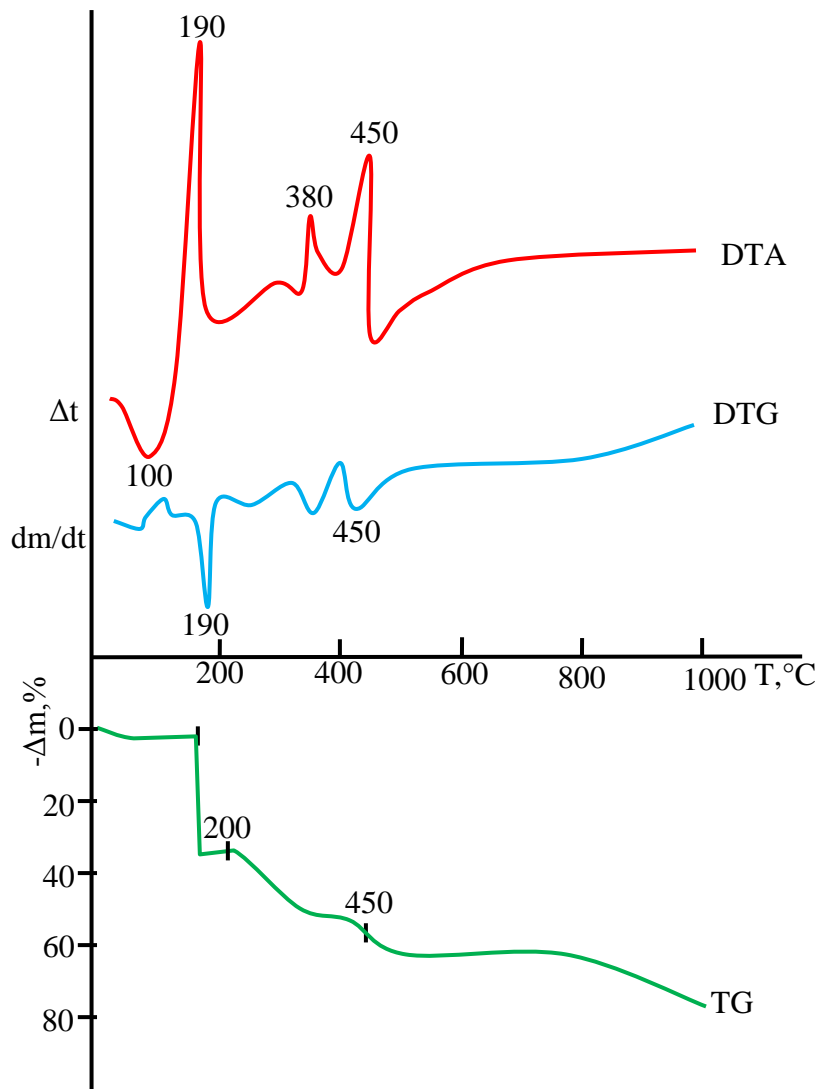


Fig. 3. DTA, TGA and DTG curves of the MLC Mo(V)-HTP-AA.

(Table 2) were calculated as follows: the extraction constant K_{ex} by the method of Likussar and Boltz [14]; the distribution constant K_D and the recovery factor R by comparing the absorption for single extraction (A_1) to that for triple extraction (A_3) in the equal volumes $\{K_D=[Mo]_o/[Mo]_{aq}; K_D=A_1/(A_3 - A_1); R=A_1/A_3\}$; the stability constant from the equation $\beta = K_{ex}/K_D$.

Table 2. Values for the constants characterizing the extraction of molybdenum.

Equilibrium constants	HTP	DHTP	HCTP	HBTP	HITP
Extraction constant K_{ex}	1.34×10^7	2.56×10^7	2.78×10^7	3.12×10^7	3.45×10^7
Association constant β	1.04×10^{15}	2.28×10^{15}	2.16×10^{16}	2.59×10^{16}	2.78×10^{16}
Distribution constant K_D	14.92	13.56	12.11	11.66	11.04
Recovery factor $R\%$	98.7	98.5	96.3	96.8	96.5

3.5. Effect of diverse ions

Influence of a number of cations and anions on the accuracy of determination of Mo(V) was studied. Experiments were performed in accordance with a recipe, which is set via the calibration curves, with the only difference that a solution other than Mo(V) introduced a certain amount of the corresponding ions. Table 3 gives the selectivity of Mo with o-HTPh for the photometric determination. Large amounts of alkali, alkaline-earth metals and rare earth element i.e. F⁻, Cl⁻, Br⁻, SO₃⁻², C₂O₄⁻² do not interfere with the determination of molybdenum. Selectivity of definition significantly increases in the presence of the masking substances. The interference of Fe(III) and Ti(IV) was eliminated with ascorbic acid, Cu (II)-thiourea and Nb(V)-oxalate anion. When using a 0.01M EDTA solution, determining of molybdenum do not interfere ions Ti (IV), V(IV), Nb (V), Ta (V) and Fe (III).

Table 3. Effect of diverse ions and reagents on the determination of 10 µg Mo with HTP and AA.

Ion	C _{ion} [µg/cm ³]	C _{ion} /C _{Mo}	Mo(V)[µg] Found	Mo(V) [%]
EDTA	100	50	10.18	101.80
Ni ²⁺	60	30	9.78	97.80
Cd ²⁺	100	50	10.03	100.30
Al ³⁺	2	1	-	Interferes
Mn ²⁺	20	10	9.87	98.70
Zn ²⁺	200	100	9.82	98.20
Co ²⁺	200	100	9.95	99.50
Complexone IV	100	50	-	Interferes
Cu ²⁺	100	50	9.96	99.60
CH ₃ COO ⁻	100	50	-	Interferes
Mn(VII)	10	5	10.12	101.20
V(V)	20	10	-	Interferes
Cr ³⁺	200	10	10.25	102.50
Cr(VI)	40	20	-	Interferes
W(VI)	20	10	-	Interferes
Fe ³⁺	20	20	10	Interferes
Tartrate	20	10	10.04	100.40
Citrate	30	15	9.80	98.00
SCN ⁻	20	10	-	Interferes
F ⁻	20	10	-	Interferes
I ⁻	30	15	9.76	97.60
Br ⁻	100	50	-	Interferes
Ascorbate	20	10	-	Interferes

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of Molybdenum with the earlier known procedures [1, 15, 16].

Table 3. Comparative characteristics of the procedures for determining molybdenum

Reagent	pH (solvent)	λ , nm	$\varepsilon \cdot 10^{-4}$	Beer's law range, μg
<i>Standard method</i>				
Toluene-3,4-dithiol	4-12 M HCl (C_6H_6), CCl_4)	675	2.10	
8 - Hydroxyquinoline-5 sulfonic acid	3,0-4,5	540	0.52	3-13
8 - Hydroxyquinoline	3,2-4,2(aseton)	530		<20
<i>Proposed method</i>				
HTP+AA	3.1-6.2 (CHCl_3)	490	3.62	0.2-18
HTP+AA	3.5-6.6 (CHCl_3)	495	3.53	0.2-19
HTP+AA	2.6-5.5 (CHCl_3)	496	3.46	0.2-20
HTP+AA	2.3-5.0(CHCl_3)	510	3.25	0.5-19
HTP+AA	2.0-4.8(CHCl_3)	512	3.11	0.5-20

3.6. Application

The proposed method under the already established optimum conditions was applied for the determination of Mo(V) in steel. The proposed procedures for determining molybdenum in steel were verified by 8-hydroxyquinoline and toluene-3,4-dithiol methods. The results of the analysis are listed in table 5 indicate the successful applicability of the proposed method to sample analysis.

Table 5. Determination of molybdenum in steel ($n=5$, $P=0.95$)

Prosedure	\bar{X} , %	RSD,%	\bar{X} , %	RSD,%	\bar{X} , %	RSD,%
	$A^*: \text{Mo} - 1.34\%$		$B^{**}: \text{Mo} - 0.25\%$		$F^{***}: \text{Mo} - 53.2\%$	
<i>Standard method</i>						
8-hydroxyquinoline	1.34±0.022	2.1	0.250±0.0042	2.4	52.9±0.87	2.5
Toluene-3,4-dithiol	1.33±0.031	2.2	0.254±0.0071	2.2	53.7±0.62	2.1
<i>Proposed method</i>						
HTP-AA	1.36±0.021	2.3		2.6	53.3±0.79	2.6
HDTP-AA	1.31±0.036	2.5		2.7	53.4±0.85	2.3
HCTP-AA	1.30±0.031	2.3	0.243±0.0068	2.2	52.8±0.92	2.1
HBTP-AA	1.29±0.030	2.4	0.257±0.0032	2.5		2.4
HITP-AA	1.28±0.029	2.6	0.251±0.0057	2.7		2.7
<i>Note: A* - Standard steel A; B**-Standard steel B; F***-Ferromolybdenum</i>						

4. CONCLUSION

1.Mixed-ligand complexes of molybdenum (V) with o-HTPh and AA have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 2.0-6.6. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.

2.The molar ratio of the reacting Mo(V), o-HTPh and AA species is 1:2:2. The general formula of the ternary complexes is $[\text{MoO}(\text{OH})(\text{o-HTPh})_2](\text{AAH})_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[\text{MoO}(\text{OH})(\text{o-HTPh})_2]^{2-}$ and protonated AA species.

3. The developed method retains specific interaction of molybdenum(V) with o-HTPh and AA to form a colored complex and has good sensitivity at room temperature. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity. This proposed method has good precision and accuracy.
4. A procedure has been developed for extraction-spectrophotometric determination molybdenum steels of different brands.

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