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Spectroscopic investigation complex formation of molybdenum with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines

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Abstract
The mixed-ligand complexes of Molybdenum (VI) with 2, 6-dithiolphenol (DTP) and its deriva-tives {(2, 6-dithiol-4-methylphenol (DTMP) and 2, 6-dithiol-4-*tert*-buthylphenol (DTBP)} in the presen-ce of hydrophobic amines have been investigated by spectrophotometric method. The condition of comp-lexing and extraction, physical-chemical and analytical characteristics of this complex have been found. As hydrophobic amins *p*-chloraniline (chAn), aniline (An), N-metilaniline (mAn), N, N-dimetilaniline (dAn), *o*-toluidine (*o*-Tol), *m*-toluidine (*m*-Tol) and *p*-toluidine (*p*-Tol) were used. It has been found that mixed-ligand complex were formed in weakly acidic medium (pH 2, 8 – 5, 3). Maksimum of light absorp-tion observed at 520-548 nm. The calculated molar absorptivities (ε_{max}) belong to the interval (4, 3-5, 4)$\bullet$10 [4].

The extraction-photometric methods of Molybdenum determination have been worked out. The influence of diverse ions on determination of Molybdenum has been studied. The proposed method was applied successfully to determine amount of Molybdenum in steel and in soil.

Keywords: Molybdenum, 2, 6-dithiolphenol, 2, 6-dithiol-4-methylfenol, 2, 6-dithiol-4-*tret*-buthyl phenol, mixed-ligand complexes, extraction-photometric method, determination
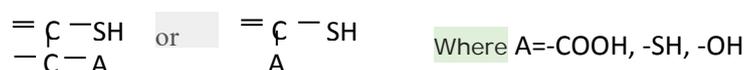
1. Introduction
Molybdenum is one of the microelements which are actively absorbed by plants. Complete information about the molybdenum content in plants is required to establish the need for molybdenum in fertilizers. Molybdenum takes part in a number of important physiological and biological processes in the nitrogen metabolism, photosynthesis, breathing the needed oxidation-reduction conditions in the cell. The formation of plant mass depends on molybdenum supply. Molybdenum is important for the synthesis of the organic substance in plants and the metabolism of a number of nutrient elements in a plant organism.

Spectrophotometric methods are generally preferred for the microdetermination of molybdenum as they are quite convenient and easy to use while analyzing samples of varying complexities. Undoubtedly, a large number of methods based on different reactions of their metal ions with various ligands have already been worked out, but there are still serious limitations in them for want of selectivity and sensitivity, and thus, a continuous search for new or improved methods is necessitated to overcome these problems usually encountered in their use.

Many methods of photometric determination of Molybdenum with use of the reagents belonging to various classes of organic compounds are offered. For highly sensitive methods for determination of Molybdenum belong methods using dithiol, thioglycolic acid, 8-hydroxyquinoline, 8-mercaptoquinoline, fluorone etc. [1].

The reagents containing gidroks - and karboks, or two gidroksi-groups in orto situation to each other, interact with Molybdenum mainly in subacidic and neutral environments with formation of the painted complex connections [2, 3]. The sulfur-containing organic substances having the following groups:

Represent in most cases valuable analytical reagents on Molybdenum and tungsten.

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It is known that Molybdenum forms in the sour environment complexes with o, o^I - dioksiazoconnections, in particular with lyumogalliony and magnezony [4].

Spectrophotometric method defined Molybdenum (VI) in soil and plant samples in the form of thiocyanate complex [5].

Trace amounts of Molybdenum (VI) is determined spectrophotometrically using salicylalde hydehydrazon eacetoacetic acid [6].

The interaction of Mo (VI) and tetrazolium violet (TV) has been examined. A sensitive and selective method for determination of Molybdenum (VI) microquantitiesin soils has been developed [7].

Numerous reagents have been suggested for the determinationof this element: 4-/2-pyridylazo/-resorcin [8], pyrogallol [9], lignocain [10], mercaptopropionic acid [11], 8-mercap-toquinoline [12], isonicotinoyl hydrazine salicylic aldehyde [13], malachite green [14], 1,5-diphenylcarbazone [15], pyrocatechol [16], 2,4-diaminophenol [17], 2,4-dihydroxyaceto-phenone [18], 8-hydroxyquinoline [19], capheic acid [20], N-benzoylphenylhydroxylamine [21], pyrocatechine violet [22].

In the present paper was studied the complex formation in a liquid-liquid extraction system containing Mo (VI), ditiolphenols and hydrophobic amins (Am), and show the potential of this system for determination of Mo(VI) in real samples. Thiophenolate complexes of metals are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [23, 24, 25].

In this respect, a very promising reagent is 2,6-dithiolphenol (DTP)and its derivatives{(2, 6-dithiol-4-methylphenol (DTMP) and 2, 6-dithiol-4-*tert*-buthylphenol (DTBP)}, which contains one hydroxyl and two sulfohydryl groups 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 Molybdenum (VI) with dithiolphenols and hydrophobic amines (Aм). From dithiolphenol it is used 2, 6-dithiolphenol (DTP), 2, 6-ditiol-4-methylphenol (DTMP) and 2, 5-dithiol-4-*tert*-butylphenol (DTBP). As hydrophobic amine *p*-chloraniline (chAn), aniline (An), N-methylaniline (mAn) and N, N-dimetilaniline (dAn), o-toluidine (*o*-tol), m-toluidine (*m*-tol), p-toluidine (*p*-tol) were used.

2. Materials and Methods
2.1. Reagents and solutions
Stock solution (1 mg/ml) of Mo (VI) was prepared dissolution in hot water 1, 8402 g (NH$_4$)$_6$Mo$_7$O$_{24}$ • 4H$_2$O p.f.a." (pure for analysis). On cooling solution was diluted with water in a measured flask to 1 l. Concentration of solution of Molyb-denum was established gravimetric [26]. Working solution with concentration of 0, 1 mg/ml was prepared by dilution of stock with deionized water.

Solutions of dithiolphenols and Am in chloroform (0.01M) were used. Dithiolphenole 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 photocolorimete rand 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 specified devices passed state check. All measurements was carried out at 20±1 ºC.

2.3. General procedure
2.3.1. General procedure for the determination of Molybdenum
Portions of stock solutions of Molybdenum (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 DTP, 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 590 nm (l=0.5cm).

2.3.2. Determination of Molybdenum in the steel
A 0.5-0.6 g sample of steel was carefully dissolvedin 10 ml of H$_2$SO$_4$ (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 dithiolphenol 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 = 540 nm against chloroform. The Molybdenum content was found from a calibration graph.

2.3.3. Determination of Molybdenum in soils
The proposed procedures for the determination of Molybdenum 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. Molybdenum was determined in aliquot portions of the solution using the proposed procedures.

3. Results and discussion
The present study is concerned with the investigation of Mo (VI) interaction with 2, 6-Dithiolphenol (DTP) and its derivatives (DTMP and DTBP), resulting in the formation of colored complexes insoluble in nonpolar 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 colored binary dithiolphenolate complexes of molibdenum (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 hydrophobic 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 *p*-chloraniline (chAn), aniline (An), N-methylaniline (mAn) and N, N-dimetilaniline (dAn), *o*-toluidine (*o*-tol), *m*-toluidine (*m*-tol) and *p*-toluidine (*p*-tol) were used. On the basis of the obtained data new selective and highly sensitive prosedureswere developed for the extraction-spectrophotometric determination of small amount of Molybdenum in the steel of various brands and in soils.

It is known that dithiolphenols have reducing properties in acidic medium. To elucidate the oxidation state of Molybdenum in MLC, we conducted two series of experiments. In the first series we used Mo (VI), while in the second series we used Mo (V) obtained by addition of a supplementary reducing agent ($SnCl_2$ or KI). It was found that the spectrophotometric charac-teristics of the MLC of Mo (VI) and Mo (V) were identica, i.e., in the interaction with DTP, Mo (VI) was reduced to Mo (V).

3.1. The choice of the extractant
The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, dichloromethane, benzene, chlorobenzene, toluene, xylol, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, 1-butanol, isoamyl acetate and their mixes.

Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. The extraction decreases in the order: chloroform > dichloromethane > 1, 2-dichloroethane > chlorobenzene > xylol > toluene > benzene > cyclohexane > carbontet-rachloride > ethyl acetate > isoamyl acetate > butyl acetate >1-butanol > isoamyl alcohol. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes.

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, 5-98, 7% of Molybdenum was extracted as an ion associate (in a case the dichloroethane and carbontetrachloride was removed 95, 0-96, 4% of Molybdenum). Further researches were conducted with chloroform. The concentration of Molybdenum in the organic phase was determined with 8-hydroxyquinoline [1] 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
Studying of dependence of a complex formation from pH showed that, the exit of complexes of Molybdenum is maximum at pH 2, 8 - 5, 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 decrase of recovery, which was obviously associated with a decrease in the concentration of the ionized form of dithiolphenols. 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 absorbancein 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 Molybdenum with dithiophenols and Am.

3.3. Electronic absorption spectra
The absorption maxima (λ_{max}) of the ternary Mo (V)- DTP-Am complexes lie in the range of 520-548 nm (Table 1, fig. 2)). All colour reactions were very contrast since the initial solutions are colourless (λ_{max} (dithiolphenols) = 270-280 nm). Thus, batochromic shift makes 250-278 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 (4, 3-5, 4) • 10^4 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

3.4. Influence of reagent concentration and incubation time
The studies of the effect of concentration of the reagent revealed that a reagent excess of 40-fold was optimum for the complex formation. Hence, a 50-fold reagent excess was adopted for further investigations. However, the presence of excess of the reagent solutiondoes not interfere with the color reaction. The optimal concentration of dithiolphenols and Am for formation of the complex was found to be $1.0 \cdot 10^{-3}$ M and $1.12 \cdot 10^{-3}$ M, respectively.

We investigated dependence of absorbance of extracts on time at excess of reagents and at an optimum pH. MLC of Molybdenum with dithiolphenols 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 minutes. At weak heating (to 30^0 C) coloring develops instantly.

3.5. Stoichiometry of the complexes and the mechanism of complexation
The stoichiometric coefficients of the reaction were determined by the Asmus method, by the relative yield method and by the equilibrium shift method [27]. The formation of MLC can be presented in the following way. When Molybdenum ion interact with two molecules of dithiolpenols, they form doubly-charged anionic complexes, which were extracted with two molecules of protonated Am.

It was found using the Nazarenko method that Mo (V) in the complexes was present in the double charging cation MoO (OH) $^{2+}$. The number of protons replaced by Molybdenum in one dithiolpenols molecule appeared to be two [28, 29].

The IR spectra of the complexes Mo-DTP-An in the field of 780-810 cm^{-1} there is an intensive strip of absorption caused by valent vibration of group $MoO(OH)^{2+}$. The disappearance of a distinct strip at 2580 sm^{-1}, observed in ranges DTP and emergence spectrum of complexes of two strips of absorption one of which is displaced towards smaller frequencies, says that one of the sulfhydryl groups participates in formation of a complex. Observed reduction of intensity of a strip of absorption in area 3200-3600 sm^{-1} with a maximum at 3450 sm^{-1}, emergence of a wide strip in area 3000-3100sm^{-1} shows that the hydroxyl group takes part in formation of coordination communication in the ionized state. Detection of strips of absorption at 1380 cm^{-1} indicates availability of the protonated anyline [30, 31].

Structure extractable complexes can be represented as in Figure 4.

Ions of Molybdenum at interaction with two molecules of dithiophenol form doubly charged anionic complexes, which were extracted with two molecules of protonated Am. The composition of the extractable complexes can be represented by the formula $[MoO(OH)(HR)_2](AmH)_2$.

It is assumed that at a complex formation there are processes:

$$MoO(OH)^{2+} + 2H_3R \Leftrightarrow [MoO(OH)(HR)_2]^{2-} + 4H^+$$

$$[MoO(OH)(HR)_2]^{2-} + 2AmH^+ \Leftrightarrow [MoO(OH)(HR)_2](AmH)_2$$
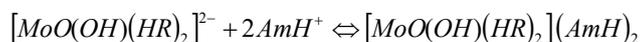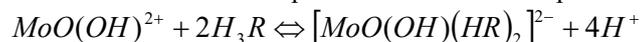
The sizes of equilibrium constant K_e calculated on a formula $\lg K_e = \lg D - 2\lg[AmH^+]$ were presented in table 1.

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 (γ =1, 01-1, 08).

The limit of photometric determination of Molybdenum in the form of ionic associates was counted on the equation [33].

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

Table 1: Optimum conditions of education and analytical the characteristic of MLC of Molybdenum with dithiolphenols and Am.

	Optimum pH interval	Degreeof Extraction, %	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, $dm^3\,mol^{-1}\cdot cm^{-1}$	Workingrange, $\mu g \cdot cm^{-3}$	Equilibrium constant
DTP- chAn	2.8-4.2	97.5	535	4.3	0.5-14	
DTP- An	3.1-4.5	97.8	538	4.7	0.5-14	
DTP- mAn	3.2-4.7	97.9	543	4.8	0.5-14	
DTP- dAn	3.4-4.9	98.2	548	5.0	0.5-16	
DTP- o-Tol	3.0-4.4	97.7	535	4.6	0.5-14	
DTP- m-Tol	3.3-4.6	97.8	540	4.7	0.5-16	
DTP- p-Tol	3.6-4.8	98.2	542	5.1	0.5-16	
DTMP- chAn	3.1-4.3	97.7	530	4,4	0.5-16	
DTMP- An	3.3-4.6	98.0	535	4,8	0.5-16	
DTMP- mAn	3.5-4.8	98.1	540	5,0	0.6-18	
DTMP- dAn	3.6-5.0	98.4	542	5,2	0.6-18	
DTMP- o-Tol	3.2-4.5	97.8	530	4.8	0.5-16	
DTMP- m-Tol	3.4-4.8	98.1	534	4.9	0.6-18	
DTMP- p-Tol	3.7-4.9	98.3	536	5,3	0.6-18	
DTBP- chAn	3.3-4.6	98.2	520	4,7	0.5-16	6.2
DTBP- An	3.5-4.8	98.4	525	5,1	0.5-16	6.5
DTBP- mAn	3.7-5.0	98.5	530	5,2	0.5-18	6.8
DTBP- dAn	3.8-5.2	98.7	534	5,3	0.6-18	7.2
DTBP- o-Tol	3.5-4.4	98.3	528	5.0	0.4-16	6.3
DTBP- m-Tol	3.4-4.9	98.4	533	5.1	0.5-18	6.5
DTBP- p-Tol	3.8-5.3	98.5	535	5.4	0.5-18	6.6

3.6. Influence of foreign ions

Influence of a number of cations and anions on the accuracy of determination of Mo (V) was studied. Experiments were performed according to the recipe, by which established calibration curves, with the only difference that a solution other than Mo (V) injected a certain amount of the corresponding ions. The selectivity of the photometric determination of Mo with dithiophenols and Am is demonstrated in Table 2.

Table 2: Influence of interfering ions on the determination of Mo (V) as MLC with DTBP and An (50, 0 µg Mo added)n=5, p=0,95.

Ion	Molar excess of the ion	Masking agent	FoundMo,µg	RSD
Oxalate	200		30.1	4
Bromide	250		29.5	3
Nitrate	300		29.7	4
Urea	220		29.9	5
Thiourea	300		30.0	2
Acetate	350		30.1	4
Thiocyanate	325		29.8	3
Chloride	200		29.5	3
Phosphate	100		29.9	4
Fluoride	100		30.0	3
Citrate	100		30.1	6
Tartrate	200		29.8	3
Iodide	220		29.8	3
Sulphate	200		29.9	5
Co (II)	40		30.1	4
Ni (II)	40		29.8	3
Fe (II)	180		29.7	3
Cd (II)	200		29.9	4
Al (III)	180		30.0	2
Fe (III)	50	Ascorbic acid ($C_6H_8O_6$)	30.2	4
Zr (IV)	45		29.8	3

Cu (II)	25	Thiourea	29.6	5
Hg (II)	40	$Na_2S_2O_3$	30.4	5
Ti (IV)	35	Ascorbic acid ($C_6H_8O_6$)	29.6	3
V (IV)	20		29.6	5
W (VI)	10	Tartaric acid	29.4	6
Cr (III)	130		29.8	4
Nb (V)	60	$C_2O_4^{2-}$	30.1	5
Ta(V)	60	Ascorbic acid ($C_6H_8O_6$)	30.2	3
UO_2^{2+}	55	CH_3COO^-	29.3	4

Large amounts of alkali and alkaline-earth metals and REE, F⁻, CI⁻, Br^-, SO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, F⁻ and CI⁻ 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, do not interfere with the determination Ti (IV), V (IV), Nb (V), Ta (V) and Fe (III).

Table 3 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of Molibdenum with the earlier known procedures [1, 2, 34].

Table 3: Comparative characteristics of the procedures for determining molybdenum

Reagent	pH (solvent)	λ, нм	ε·10⁻⁴	Beer's law range, µg
Standard method				
Toluene-3,4-dithiol	4-12 M HCl (benzene, CCl₄)	675	2.10	
8 - Hydroxyquinoline-5 sulfonicacid	3,0-4,5	540	0.52	3-13
8 - Hydroxyquinoline	3,2-4,2 (aseton)	530		<20
Proposed method				
DTMP+mAn	3,5-4,8 (chloroform)	540	5,00	0,04-3.6
DTBP+mAn	3,7-5,0 (chloroform)	530	5,20	0.05-3.6
DTBP+dAn	3,8-5,2 (chloroform)	534	5,3	0.05-3.6

3.7. Effect of Molybdenum (V) 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 Mo(V) may be determined in the range 0.04-3.6 μg/ml. Table 4 summarizes the calibration characteristics obta-ined with DTMP+ chAn, DTMP+An, DTMP+mAn and DTMP+dAn. The pertaining calibration graph is shown in the Fig. 5.

Table 4: Analytical characteristics of some ternary complexes of Mo with DTMF and Am

Parameter	chAn	An	mAn	dAn
The equation of calibration curves	0.014 +0.25x	0.015 + 0.242x	0.014 + 0.255x	0.018 + 0.262x
Correlation coefficient (9 standards used)	0.9875	0.9982	0.9985	0.9983
Linear calibration range / µg· cm⁻³	0.04-3.2	0.04-3.2	0.04-3.6	0.04-3.6
Limit of detection (LOD) / ng·cm⁻³	12	11	10	9
Limit of quantification (LOQ) / ng· cm⁻³	40	36	34	32
Sandell's sensitivity / ng ·cm⁻²	2.2	2.1	2.0	1.8
Stability constant (lgβ)	7.42	7.85	7.87	8.05

3.8. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Mo (V) in steel and in soils. The usefulness of the method is tested by quite simple, rapid, and takes less than 15 minutes for a single determination, and also has an edge over some of the existing methods of molybdenum determination in trace amounts.

The proposed procedures for determining Molybdenum in analyzing satisfactorily a wide variety of samples. In addition, the methods has a wider Beer's law range, better precision and accuracy, and free from the interference of a large number of metal ions of great analytical importance. It is Soils and in in steel were verified by 8-hydroxyquinoline and dithiole methods [34]. The results of the analysis are listed in Table 5 and 6 indicate the successful applicability of the proposed method to real sample analysis.

Table 5: Correctness and reproducibility of Determination of Molybdenum in steel. n=5, P=0, 95.

Method		X^-, %	SD	RSD,%	$\overline{X} \pm \dfrac{t_P \cdot S}{\sqrt{n}}$
EI-69(45X14H14B2M) (Mo-0, 40 of %)					
Standardmethod	Toluene-3,4-dithiol	0.41	0.0164	4	0.41±0.020
	8 - Hydroxyquinoline	0.42	0.0210	5	0.42±0.026
Proposedmethod	DTP+An	0.40	0.0120	3	0.40±0.014
	DTMP+An	0.40	0.0120	3	0.40±0.014
	DTBP +мAn	0.39	0.0117	3	0.39±0.015
	DTBP +dAn	0.41	0.0205	5	0.41±0.025

8XF (C16[b]) (Mo-0.193 of %)					
Standard method	Toluene-3,4-dithiol	0.200	0.006	3	0.200±0.007
	8 - Hydroxyquinoline	0.198	0.010	5	0.198±0.012
Proposed method	DTP+An	0.192	0.0038	2	0.192±0.004
	DTMP+An	0.192	0.0038	3	0.192±0.004

Table 6: Correctness and reproducibility of Determination of Molybdenum in soil. n=5, P=0.95.

Method	$\overline{X}, \%$ 10^{-4}	SD 10^{-4}	RSD,%	$\overline{X} \pm \dfrac{t_P \cdot S}{\sqrt{n}}$
Standard method				
Toluene-3,4-dithiol	2.95	0.148	5	(2.95±0.18)
8 - Hydroxyquinoline	3.02	0.151	5	(3.02±0.19)
Proposed method				
DTP+An	2.85	0.114	4	(2.85±0.14)
DTMP+An	2.87	0.087	3	(2.87±0.11)
DTMP+ p-Cl-An	2.88	0.086	3	(2.86±0.10)
DTBP +мAn	2.85	0.114	4	(2.85±0.14)
DTBP +dAn	2.92	0.145	5	(2.92±0.18)

4. Conclusions

1. Mixed-ligand complexes of Molibdenum (V) with 2, 6-dithiolphenol (DTP) and its derivatives {(2, 6-dithiol-4-methylphenol (DTMP) and 2, 6-dithiol-4-*tert*-butylphenol (DTBP)} in the presence of hydrophobic amines have been investigated by spectrophotometric method.
2. Extraction of mixed ligand complexes is maximal at pH 2.8-5.3.
3. 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.
4. The Beer's law was applicable in the range of 0.04-3.6μg/ml.
5. A simple, rapid and sensitive methods proposed for the determination of trace amounts of Molybdenum.

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