

P-ISSN 2349-8528

E-ISSN 2321-4902

IJCS 2015; 3(2): 88-94

© 2015 JEZS

Received: 23-06-2015

Accepted: 25-07-2015

Abel M Maharramov

Department of Chemistry, Baku
State University, Z. Khalilov
Street 23, Baku, AZ 1148,
Azerbaijan.

Ali Z Zalov

Department of Chemistry,
Azerbaijan State Pedagogical
University, U. Gadjibekov Street
68, Baku, AZ 1000, Azerbaijan.

Naila A Verdizadeh

Department of Chemistry,
Azerbaijan State Pedagogical
University, U. Gadjibekov Street
68, Baku, AZ 1000, Azerbaijan.

Afet B Hajieva

Department of Chemistry,
Azerbaijan State Pedagogical
University, U. Gadjibekov Street
68, Baku, AZ 1000, Azerbaijan.

Spectrophotometric determination of trace Amounts of molybdenum after extraction of its complexes with 2-hydroxythiophenol and its derivatives in the presence of hydrophobic amines into chloroform

Abel M Maharramov, Ali Z Zalov, Naila A Verdizadeh, Afet B Hajieva

Abstract

The mixed-ligand complexes (MLC) of molybdenum (VI) with 2-hydroxythiophenol (HTP) and its derivatives (HTPDs) {(2, 5-dihydroxythiophenol (DHTP) and 2-hydroxy-5-chlorothiophenol (HCTP))} in the presence of hydrophobic amines have been investigated by spectrophotometric method. As hydrophobic amines (HAs) 3, 4-xylidine (o-Xyl), 2, 4-xylidine (m-Xyl), and 2,5-xylidine (p-Xyl) were used. The condition of complexing and extraction, physical-chemical and analytical characteristics of this complex have been found. The obtained mixed-ligand complexes have a composition of 1:2:2 {Mo (V): HTPDs: AA}. Optimal conditions for their liquid-liquid extraction were found: organic solvent (chloroform), pH, concentration of the reagents and extraction time. Under the optimal conditions, the complexes have absorption maxima (λ_{max}) at 522-545 nm and molar absorptivities (ϵ_{max}) between $3.6 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (HCTP+o-Xyl) and $4.7 \cdot 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (DHTP+o-Xyl). The degrees of extraction were $R=98.4-98.9\%$. 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, samples of soil and pea.

Keywords: Molybdenum (V), solvent extraction, mixed-ligand complexes, steel analysis, soil analysis, plant analysis

1. Introduction

Molybdenum has been recognized as an essential trace element for plants, animals and humans. In plants, molybdenum has a key function in the fixation of the atmospheric nitrogen [1]. In mammals, it is important for the activity of the enzymes xantine oxidase, sulphite oxidase, and aldehyde oxidase. Despite its relative rarity in the Earth's crust (estimated abundance in the range $0.05-40 \text{ mg kg}^{-1}$ with a mean value of 1.5 mg kg^{-1}) [2, 3], geochemical anomalies leading to molybdenum deficiencies in plants are not common [4, 5] and are mostly of concern for leguminous crops. Molybdenum fertilization is often based on visual deficiency symptoms and/or history of crop rotation [5]. However, in order to assess the need for fertilization and the molybdenum dosage it is preferable to use analytical methods [2, 3].

Recently, several techniques have been used for molybdenum determination: UV-Vis spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrophotometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), adsorptive anodic stripping voltammetry, and inductively coupled plasma optical emission spectrophotometry (ICP-OES) [6-12].

1154tral and chemical methods are being constantly used for molybdenum determination. Therefore, new organic reagents for a selective and sensitive photometric determination of molybdenum are of particular interest [6]. 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 [13].

Correspondence

Ali Z Zalov

Department of Chemistry,
Azerbaijan State Pedagogical
University, U. Gadjibekov Street
68, Baku, AZ 1000, Azerbaijan.

The reagents containing gidroks- and karboks, or two gidroksi-groups in orto situation to each other, interact with molybdenum mainly in sub-acidic and neutral environments with formation of the painted complex connections [14].

The interaction of Mo (VI) and tetrazolium violet has been examined. A sensitive and selective method for determination of molybdenum (VI) micro-quantities in soils has been developed [15]. Numerous reagents have been suggested for the determination of this element: salicylaldehyde hydrazone acetoacetic acid [16], 4-(2-pyridylazo)-resorcinol [17], pyrogallol [18], mercaptopropionic acid [19], pyrocatechine violet [20], 2, 4-diaminophenol [21], 2, 4-dihydroxyacetophenone [22], 8-hydroxyquinoline [23], capheic acid [24].

In the present paper the complex formation in a liquid-liquid extraction system containing molybdenum, hydroxythiophenols, its derivatives and hydrophobic amines were studied and shown the potential of this system for determination of molybdenum in real samples. Hydroxythiophenolate complexes of metals are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines easily dissolve in various organic solvents [25-30].

In this respect, a very promising reagent is 2-hydroxythiophenol and its derivatives, which contains one hydroxyl and one group sulfohydriyl is sulfur analogue mononuclear polyphenols with one oxygen atom is replaced with sulfur atoms. Sulfur-containing analogues of the aforementioned catecholic reagents have been in our research interests for a long time because of their analytical potential and possibilities of obtaining new ternary complexes with desired properties [25-32].

In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on 9 different systems, each of which containing Mo(VI), a 2-hydroxythiophenol (HTP) and its derivatives (HTPDs) [2,5-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP)], and an hydrophobic amine (HA) [3,4-xylylidine (o-Xyl), 2,4-xylylidine (m-Xyl), 2,5-xylylidine (p-Xyl)]. We propose new procedures for determining molybdenum in steel, soils and plants.

2. Experimental

2.1. Reagents and instrumentation

A stock solution of molybdenum (VI) (1dm³) was prepared by dissolving 1.8402 g of (NH₄)₆Mo₇O₂₄·4H₂O "p. f. a." in distilled water [33]. The solution was standardized gravimetrically [14]. Working solutions (0.1 mg cm⁻³) were prepared daily by appropriate dilution of the stock solution.

HTPDs were synthesized according to the procedure [34]; their purity was verified by paper chromatography and melting point determination. HAs were products of Sigma-Aldrich (98-99% purity). Chloroform solutions (0.01 mol dm⁻³) of HTPDs and AAs were used.

To create the optimum acidity, 0.1 mol dm⁻³ solutions of HCl were used.

The absorbance of the extracts was measured using a KFK-2 photocolorimeter (USSR), a SF-26 spectrophotometer (USSR), equipped with 5 and 10 mm path-length cells. pH of aqueous phase was measured using an I-120.2 potentiometer (USSR) with a glass electrode. IR spectra were recorded on a spectrophotometer; Model «Bruker» (FRG). Muffle furnace was used for dissolution of the samples.

2.2. Procedure for determining the optimum conditions

Aliquots of Mo (VI) solution, HTPD solution (up to 2.5 cm³) and HA solution (up to 2.5 cm³) were transferred in a 100 cm³

calibrated tube with ground-glass stopper. pH of the aqueous phase was adjusted in the interval 3.5-7.9 by adding a small amount of HCl solution. The volume of the aqueous phase was increased with water to 20 cm³ and the volume of the organic phase was set to be 5 cm³. The tube was closed with the stopper and shaken for a fixed time (up to 15 min). After separation of the layers, a portion of the organic extract was transferred into a cell and the absorbance was read against organic solvent or simultaneously prepared blank sample.

2.3. Procedure for molybdenum determination

An aliquot containing molybdenum (no more than 120 µg) was placed in a calibrated tube. Chloroform solutions of HTPD (0.7 cm³) and HA (0.7 cm³) were added and the organic phase was adjusted to 5 cm³ with chloroform. The volume and pH of the aqueous phase were adjusted to 20 cm³ and 5.3-5.8, respectively. The tube was closed with a stopper and after 10 minutes of shaking a portion of the organic extract was transferred through a filter paper into a cell. The absorbance was read at λ_{max} = 540 against a simultaneously prepared blank sample. The molybdenum content was found from a calibration graph.

2.4. Determination of molybdenum in different objects

2.4.1. 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 soil sample (15 g) collected from depths of 15±5 cm was subjected to available molybdenum extraction procedure [35] with an oxalate buffer of pH 3.3. Then the procedure [35] was followed: An aliquot of the obtained soil extract (50-100 cm³) was placed in a quartz beaker and evaporated to dryness on a hot plate. For dehydration of the residue and partial sublimation of the oxalates, the beaker was left on the plate for 30 more minutes. The beaker was transferred in a cold muffle furnace. The temperature was raised to 500 °C and held for 1 hour. After cooling 2 cm³ of perchloric acid were added for complete destruction of the organic matter. The content was heated to near dryness on a hot plate and the beaker was placed again in the muffle furnace. The temperature was raised to 500 °C and held for 15-20 minutes. The residue was cooled and then dissolved in 25 cm³ of 14% hydrochloric acid under heating. Masking solutions were added (4 cm³ of the citric acid – ascorbic acid solution and 2 cm³ of the KI solution) and the resulting solution was filtered into a 100 cm³ separatory funnel. Aliquots of thus obtained filtrate were used to determine the molybdenum content.

Molybdenum was determined in aliquot portions of the solution using the proposed procedures.

2.4.2. Determination of molybdenum in plants

10 g of the powdered plant material (seeds of pea) were soaked in 50 cm³ of 96 % ethanol for 24 h. The sample was dried and carefully carbonized in a quartz beaker on a hot plate. The beaker was placed into a cold muffle furnace and its temperature was slowly increased (at a rate of 100 °C per hour) up to 450°C. The sample was dry-ashed for 10-15 h. The obtained gray ash was cooled and moistened with a few drops of nitric acid (1:1). Then the ash was heated to dryness on a water bath and placed into the muffle furnace. The temperature was raised to 300°C and held for 30 minutes. This cycle was repeated several times until white ash was obtained. Then, several drops of bidistilled water and 2 cm³ of perchloric acid were added. The beaker was heated on a hot plate until

smoking ceased and transferred in a cold muffle furnace. The temperature was raised to 500 °C and held for 15 minutes. After cooling, 25 cm³ of 14% hydrochloric acid were added and the beaker was kept in a boiling water bath for 10-20 min. The obtained solution was quantitatively transferred to a volumetric flask of 50 cm³ [35]. Masking solutions were added (4 cm³ of the citric acid – ascorbic acid solution and 2 cm³ of the KI solution) and the flask was filled to the mark with bidistilled water.

Molybdenum was determined in aliquot portions of the solution using the proposed procedures.

2.4.3. Determination of molybdenum in the steel

A 0.5-0.6 g sample of steel was carefully dissolved in 10 ml of H₂SO₄ (1:4). 2 cm³ of mix (1:3) conc. HCl and HNO₃ was added and heated to release nitrogen oxides. Filtered insoluble precipitate and a filtrate transferred into a 50 cm³ volumetric flask. After cooling, molybdenum was determined in aliquot portions of the solution using the proposed procedures.

2.5. Studies on the oxidation state of molybdenum

It is known that HTPDs have reducing properties in acidic medium [25, 27]. Previous investigations with Mo (VI)-HCTP and Mo (V)-HCTP [25] suggested that only Mo (V) forms stable complexes with this reagent. To elucidate the oxidation state of molybdenum in the presence of other HTPDs (HTP and DHTP), 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 (SnCl₂ or KI). It was found that the spectrophotometric characteristics of the MLC of Mo(VI) and Mo(V) were identical i.e. in the interaction with HTPDs Mo(VI) was reduced to Mo(V).

2.6. Charge of the complexes

The present study is concerned with the investigation of Mo (VI) interaction with DTPs, resulting in the formation of coloured complexes insoluble in nonpolar solvents. Experiments onelectromigration in a U-shaped tube and sorption on EDE-10P 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 HTPDs complexes of molybdenum (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 coloured 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.

3. Results and Discussion

3.1. Choice of organic solvent

Extractability of complexes was estimated in coefficient of distribution (*D*) and extent of extraction (*R* %). The following organic solvents were tested for the extraction of the ternary complexes: chloroform, 1, 2-dichloroethane, tetrachloromethane, benzene, chlorobenzene, toluene, xylol, isobutanol, isopentanol, n-butanol and their mixes. Chloroform was found to be the most effective in terms of degree of extraction and rapid equilibration. The concentration of molybdenum in the organic phase was determined with 8-hydroxyquinoline by photometric [14] measurements after back extraction, while in the aqueous phase it was determined by the difference. As can be seen from Table 1, chloroform provides *R*=98.4-98.9%. At

that, the nature of HA does not appreciably affect the extraction.

3.2. Influence of pH

The optimum pH (pH=2.7-5.2) ranges are wide enough to ensure stable and reproducible results without using buffer solutions. The effect of pH on the intensity of the colour reaction is shown in the Figure 1. The course of all pH curves supports the assumption that only one complex is formed in each of the extraction systems. The optimum pH intervals are listed in Table I. At higher pH values, the efficiency of the extraction is impaired, which relates to the lower degree of HA protonation. At lower pH values, the extraction is also impaired most probably due to decrease of the concentration of the anionic HTPDs forms.

The nature of acids (HCl, H₂SO₄) almost does not influence a complex formation of molybdenum with HTPDs and HA.

3.3. Absorption maxima, reagents concentrations, molar absorptivities and effect of time

The absorption maxima (λ_{\max}) of the ternary Mo (V)-HTPDs-HA complexes lie in the range of 522-545 nm (Table 1). All colour reactions are very contrast since the initial solutions are colourless (λ_{\max} HTPDs = 278-283 nm). Thus, bathochromic shift makes 254-262 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 i.e. initial reagents are colourless while complexes are intensively painted.

Complete extraction is achieved at HTPDs and HA concentrations not lower than $(1.3-1.5) \cdot 10^{-3}$ mol dm⁻³ and $(1.2-1.5) \cdot 10^{-3}$ mol dm⁻³, respectively. Mo (V) concentration ranges in which the Beer's law is obeyed are listed in Table 1. The calculated molar absorptivities (λ_{\max}) belong to the interval $(3.6-4.7) \cdot 10^4$ dm³ mol⁻¹ cm⁻¹ (Table 1). Colour develops almost immediately after the reagents addition. The absorbance of the extracts is stable for at least 48 hours. The optimum shaking time is 10 min.

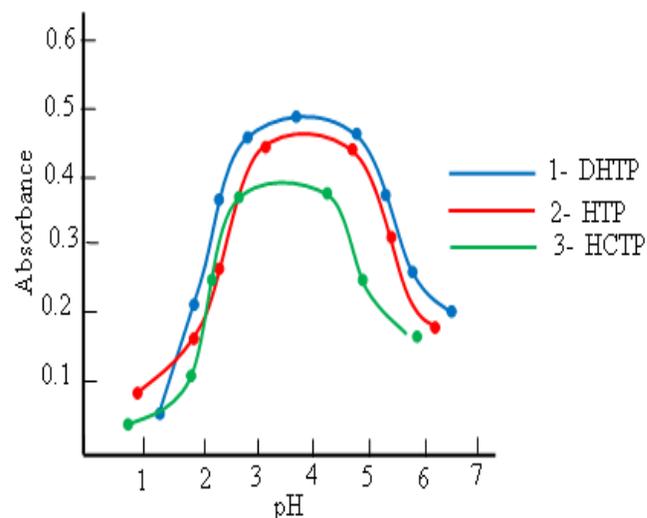


Fig 1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.

1. Mo (V)-DHTP- *o*-Xyl; 2. Mo (V)-HTP- *o*-Xyl; 3. Mo (V)-HCTP- *o*-Xyl.

$C_{\text{Mo (V)}}=2.08 \cdot 10^{-5}$ mol dm⁻³, $C_{\text{HTPD}} = C_{\text{HA}}=1.4 \cdot 10^{-3}$ mol dm⁻³, $\ell=0.5$ cm, $\lambda=540$ nm, KFK-2

Table 1: Characteristics of the extraction-chromogenic systems Mo (V)-HTPDs-HA-water-chloroform

Analytical characteristics	DHTP- <i>o</i> -Xyl	DHTP- <i>m</i> -Xyl	DHTP- <i>p</i> -Xyl	HTP- <i>o</i> -Xyl	HTP- <i>m</i> -Xyl	HTP- <i>p</i> -Xyl	HCTP- <i>o</i> -Xyl	HCTP- <i>m</i> -Xyl	HCTP- <i>p</i> -Xyl
complex formation, pH	1.3-6.5	1.8-6.6	2.3-6.3	1.0-6.2	1.5-6.3	2.1-6.9	0.8-5.9	1.4-6.3	1.9-6.8
Optimum pH interval	3.1-4.7	3.2-5.4	3.6-5.7	2.9-4.5	3.1-5.0	3.4-5.5	2.6-4.2	2.8-4.7	3.3-5.2
Degree of extraction (R) / %	98.4	98.5	98.6	98.5	98.6	98.7	98.7	98.8	98.9
Coefficient of distribution (D)	246.0	262.7	281.7	262.7	281.7	211.4	211.4	329.3	425.7
λ_{\max} / nm	538	542	545	528	530	535	522	525	528
$\varepsilon \times 10^{-4} / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	4.7	4.5	4.3	4.5	4.0	4.1	3.6	3.7	3.9
Working range / $\mu\text{g cm}^{-3}$	0.4-26	0.5-23	0.5-22	0.4-24	0.5-23	0.5-25	0.4-22	0.5-23	0.4-24

3.4. Stoichiometry of the Complexes and the Mechanism of Complexation

The stoichiometric coefficients of the reaction were determined by the Asmus method (Figure 2), the relative yield method and the equilibrium shift method [36]. The results show a complex composition of 1:2:2 (Mo (V):HTPDs:HA).

It was found, using the Nazarenko method, that Mo (V) in the complexes was present in the double charging cation $\text{MoO}(\text{OH})^{2+}$. The number of protons replaced by molybdenum in one HTPDs molecule appeared to be two [37].

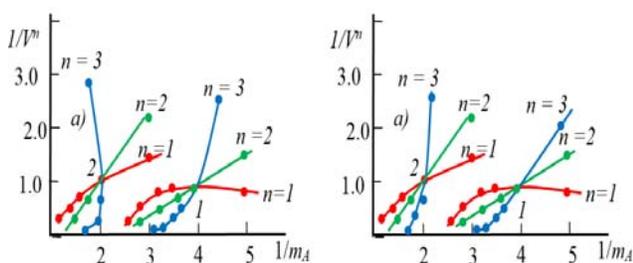


Fig 2: Determination of the ratio of components by the Asmus method for (a) Mo(V)- HTP- *o*-Xyl and (b) Mo(V)-DHTP- *o*-Xyl. $C_{\text{Mo(V)}} = 2.08 \cdot 10^{-5} \text{ mol dm}^{-3}$. SF-26, $\lambda = 540 \text{ nm}$, $\ell = 1.0 \text{ cm}$

The IR spectra of the complexes Mo-HTP- *o*-Xyl, in the field of 780-810 cm^{-1} , there is an intensive strip of absorption caused by valent vibration of group $\text{MoO}(\text{OH})^{2+}$. The disappearance of a distinct strip at 2580 cm^{-1} , observed in ranges HTP and shows that sulfhydryl groups participates in formation of a complex. Observed reduction of intensity of a strip of absorption in area of 3200-3600 cm^{-1} , with a maximum at 3455 cm^{-1} , emergence of a wide strip in area 3050-3150 cm^{-1} shows that the hydroxyl group takes part in formation of coordination communication in the ionized state. Detection of strips of absorption at 1385 cm^{-1} indicates availability of the protonated *o*-Xyl [38, 39].

Structure extractable complexes can be represented as in Figure 3.

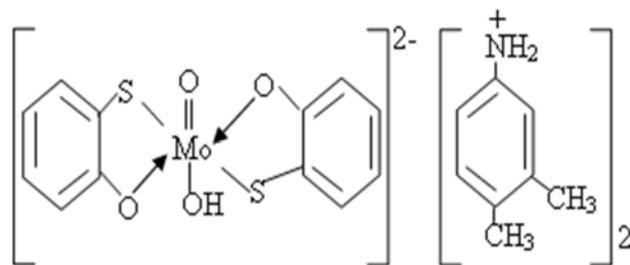
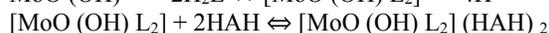
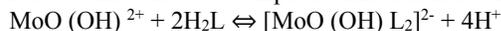


Fig 3: Structure of Complex $[\text{MoO}(\text{OH})(\text{HTP})_2](\text{o-Xyl})_2$

Ions of Molybdenum at interaction with two molecules of HTPDs (H_2L) form doubly charged anionic complexes, which

were extracted with two molecules of protonated HAH. The composition of the extractable complexes can be represented by the formula $\text{MoO}(\text{OH})\text{L}_2(\text{HAH})_2$.

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



The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 0.97-1.04$).

3.5. Effect of foreign ions and masking reagents

The influence of foreign ions and reagents on the extraction-spectrophotometric determination of molybdenum with HTP+ *o*-Xyl and DHTP+ *o*-Xyl was examined in details. It was found that great excesses of alkali, alkali earth, and rare earth cations do not interfere with determination. The same was valid for anions, such as F^- , Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$. Serious interferences were observed from small amounts (less than 200 μg) of Fe (III), Ti (IV), Cu (II), Nb (V), Ta(V), Hg(II) and W(VI). The interfering influence of these ions can be eliminated by using various masking agents (Table 2).

Table 2. Influence of foreign ions on the determination of molybdenum (30 μg) with HTP and *o*-Xyl ($n=5$, $p=0$, 95).

Foreign ion (FI)	FI-to-Mo ratio	Masking agent	Mo found / μg	RSD / %
Al(III)	120	–	30.2	1.6
Bi(III)	50	–	29.5	4.2
Co(II)	55	–	30.2	4.5
Cr(VI)	75	–	29.5	2.0
Cu(II)	25	KI	30.0	2.1
Fe(III)	50	Ascorbic acid	30.4	4.2
Hg(II)	35	$\text{Na}_2\text{S}_2\text{O}_3$	29.8	2.6
Nb(V)	45	Oxalic acid	30.2	1.5
Ni(II)	50	Citric acid	30.2	1.5
Ta(V)	45	Ascorbic acid	29.7	2.7
Ti(IV)	20	Ascorbic acid	29.8	2.3
V(IV)	40	–	30.0	1.8
W(VI)	40	Citric acid	30.3	4.0
Zr(IV)	70	–	29.6	2.3

Table 3 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of molybdenum with the earlier known procedures [13, 14, 40-46].

3.6. Calibration graphs 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 Mo (V). A linear calibration graph drawn

between absorbance and the metal ion concentration indicates that Mo (V) may be determined in the range of 0.4-26 $\mu\text{g/ml}$. The pertaining calibration graph is shown in the Fig. 5.

Table 4 summarises analytical characteristics for the extraction-chromogenic systems Mo- HTPDs - p-Xyl-water-chloroform.

Table 3. Comparative Characteristics of the Procedures for Determining Molybdenum

Reagent	pH (Solvent)	λ , nm	$\epsilon \times 10^{-4}$	Beer's Law Range, μg	[Ref.]
Standard Method					
Ksilonol orange	3.6	-	0.519	-	[14]
8-Hydroxyquinoline-5 sulfonic acid	3.0-4.5	540	0.52	3-13	[13,14]
Rezorsan	0.5 M HCl	460	2.34	0.14-3.8	[40]
Thiocyanat	0.75-1.5M HCl	460	3.86	-	[13,14]
8-Hydroxyquinoline	3.2-4.2 (acetone)	530	-	<20	[13]
Chlorosulphenol S	0.5-3.6 (CHCl_3)	-	1.3	-	[41]
Pyrohallol red +P-polibenzilpiridinxlorid	0.5M H_3PO_4	590	9.5	0.011-0.096	[42]
4-(6-brom-2-benzothiazolilazo) pyrohallol+setiltrimetilammoniumbromid	3.2	585	5.76	-	[14]
Toluene-3,4-dithiol	4-12M HCl (benzene, CCl_4 , CHCl_3)	680	1.8	-	[14, 43]
2-Amino-4-xlorben zenthioi	(CHCl_3)	-	3.6	-	[44,45]
2, 6-dithiol-4-tert-buthylphenol +aminophenol	3.5-5.2 (CHCl_3)	525-530	4.8-5.2	0.04-3.6	[46]
Proposed Method					
DHTP- <i>p</i> -Xyl	3.6-5.7(CHCl_3)	545	4.3	0.5-22	
HTP- <i>p</i> -Xyl	3.4-5.5(CHCl_3)	535	4.1	0.5-25	
HCTP- <i>p</i> -Xyl	3.3-5.2(CHCl_3)	528	3.9	0.4-24	

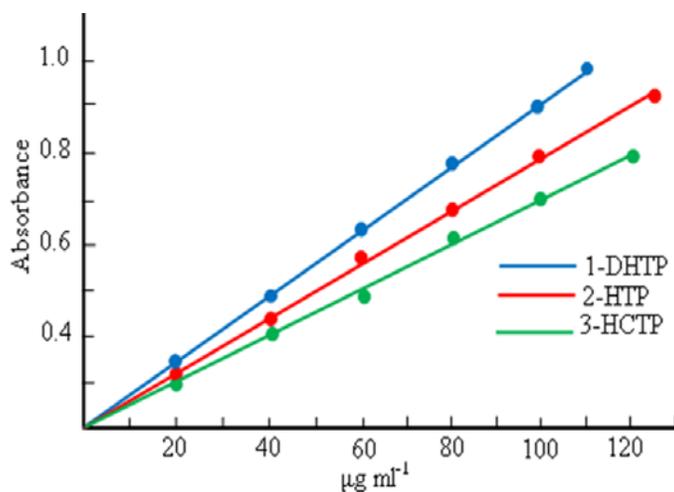


Fig 5: Analytical Determination of Mo (V) with HTPDs and Has.

1- Mo (V)-DHTP+ *p*-Xyl; Mo(V)-HTP+ *p*-Xyl; 3- Mo(V)-HCTP+ *p*-Xyl. $C_{\text{HTPDs}} = C_{\text{HA}} = 1.4 \cdot 10^{-3} \text{ mol dm}^{-3}$, $\ell = 0.5 \text{ cm}$, $\lambda = 540 \text{ nm}$, KFK-2.

Table 4: Analytical characteristics for the extraction-chromogenic systems Mo-HTPDs-*p*-Xyl - H_2O - CHCl_3 .

Parameter	DHTP+ <i>p</i> -Xyl	HTP+ <i>p</i> -Xyl	HCTP+ <i>p</i> -Xyl
The equation of calibration curves	$y=0.019+0.259x$	$y=0.015+0.247x$	$y=0.023x+0.236$
Correlation coefficient (9 standards used)	0.9987	0.9992	0.9989
Linear calibration range / $\mu\text{g cm}^{-3}$	0.5-22	0.5-25	0.4-24
Slope \pm Standard deviation / $A \mu\text{g}^{-1} \text{ cm}^3$	0.347 ± 0.008	0.362 ± 0.091	0.355 ± 0.061
Intercept \pm Standard deviation / A	0.007 ± 0.014	0.007 ± 0.006	0.007 ± 0.008
Limit of detection (LOD) / ng cm^{-3}	11	12	14
Limit of quantification (LOQ) / ng cm^{-3}	31	39	47
Sandell's sensitivity / ng cm^{-2}	2.56	2.63	2.71

3.7. Analytical Applications

The proposed method were applied to the determination of molybdenum in steel, samples of soil and pea. The accuracy of

the results was checked by three independent methods. The results are listed in Table 4.

Table 4: Molybdenum content in steel, soil and pea samples determined by different methods (n=5, P=95%).

Method		Molybdenum content in steel ^a		Molybdenum content in soil		Molybdenum content in pea	
		X, %	RSD, %	× 10 ⁴ , %	RSD, %	× 10 ⁴ , %	RSD, %
Present methods	DHTP+ p-Xyl	0.20	3.0	2.90	4.0	4.95	3.0
	HTP+ p-Xyl	0.22	5.0	2.88	3.0	4.96	3.0
	HCTP+ p-Xyl	0.21	4.0	2.95	5.0	5.06	4.0
Toluene-3,4-dithiol		-	-	2.97	3.0	5.02	5.0
Thiocyanate		-	-	2.96	5.0	5.03	4.0
8-Hydroxyquinoline		-	-	2.94	3.0	4.99	4.0

^a The composition of the sample steel - 22-11-2.5 –(0.25C; 1.0 Mn; 1.5 Si; 25 Cr; 10.0 Ni; 3.5W; 0.2 Mo; 0.2 % V; 56.55. Fe),

4. Conclusions

Mixed-ligand complexes of molybdenum (V) with HTPDs in the presence of hydrophobic amines have been investigated by spectrophotometric method. The complexes have a composition of 1:2:2 (Mo:HTPD:HA) and can be regarded as ion associates between doubly charged anionic chelates of Mo(V) and protonated HA species: [MoO(OH)(HTPD)₂](HAH⁺)₂. Extraction of mixed ligand complexes is maximal at pH 2.9-5.5. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components in the complexes have been determined. The Beer's law was applicable in the range of 0.4-26 µg/ml. Simple, rapid and sensitive methods were proposed for the determination of trace amounts of molybdenum.

5. Acknowledgement

The authors thank the staff of Baku State University academician Abel. M. Maharramov and Professor Famil M. Chyragov for providing research facilities to carryout present work.

6. References

- Gupta UC. Molybdenum in agriculture. Cambridge University Press, Cambridge, UK, 1997, 276.
- Das AK, Chakraborty R, Cervera ML, Guardia MA. review on molybdenum determination in solid geological samples. *Talanta* 2007; 71:987-1000.
- Kabata-Pendias A. Trace elements in soils and plants (4th edition), CRC press, Boca Raton, USA, 2011, 190-198.
- Kaiser BN, Gridley KL, Brady JN, Phillips T, Tyerman SD. The role of molybdenum in agricultural plant production. *Ann. Bot* 2005; 96:745-754.
- Gupta UC, Hettiarachchi GM, Boron, Molybdenum, Selenium. in *Soil sampling and methods of analysis* (2nd edition), Carter M. R., Gregorich E. G. (Eds.) Boca Raton, USA, 2007, 99.
- Kostova D. Triphenyltetrazolium Chloride as a New Analytical Reagent for Molybdenum (VI): Application to Plant Analysis. *J Anal. Chem.* 2011, 66(4):384-388.
- Deng P, Fei J, Zhang J, Feng Y. Food Chem. Determination of molybdenum by adsorptive anodic stripping voltammetry of molybdenum-alizarin violet complex at an acetylene black paste electrode 2011; 124:1231-1237.
- Khan N, Jeong IS, Hwang IM, Kim JS, Choi SH, Nho EY *et al.* Method validation for simultaneous determination of chromium, molybdenum and selenium in infant formulas by ICP-OES and ICP-MS. *Food Chem* 2013; 141:3566-3570.
- Gurkan R, Aksoy U, Ulusoy HI, Akay M. Determination of low levels of molybdenum (VI) in food samples and beverages by cloud point extraction coupled with flame atomic absorption spectrometry. *J Food Compos. Anal.* 2013; 32:74-82.
- Mansouri AI, Afzali D, Ganjavi F. Dispersive liquid-liquid microextraction of trace amounts of molybdenum prior to electro-thermal atomic absorption spectrometry determination *Int. J Environ. Anal. Chem.* 2013; 94:247-254
- Bazán C, Gil R, Smichowski P, Pacheco P. Multivariate optimization of a solid phase extraction system employing l-tyrosine immobilized on carbon nanotubes applied to molybdenum analysis by inductively coupled plasma optical emission spectrometry with ultrasound nebulization *Microchem. J.* 2014; 117:40-45.
- Dass R, Kapoor JK, Gambhir S. Spectrophotometric determination of molybdenum using surfactant-mediated liquid-liquid extraction. *Turk. J Chem.* 2014; 38:328-337.
- Marczenko Z, Balcerzak M. Metod'y spektrofotometrii v UF I vidimoy oblastiakh vneorganicheskoy analize. Moscow, Binom. Laboratoriya znaniy, 2007, 711.
- Busev AI. *Analitiche Chemistry of Molybdenum.* M. Publishing house, Akad. Nauk, 1962, 205.
- Kamburova M, Kostova D. Tetrazolium violet – a new spectrophotometric reagent for molybdenum determination. *Chemija* 2008; 19(2):13-18.
- Srilalitha V, Raghavendra GPA, Raman KK, Seshagiri V, Ravindranath LK. Spectrophotometric Determination of Trace Amounts of Molybdenum (VI) Using Salicylaldehyde Acetoacetic Acid Hydrzone. *Chem. Bull. Politehnica Univ. (Timisoara)* 2010; 559(69):110-115.
- Reddy M, Kumar P, Shyamasundar J, Anjaneylu A. Extractive spectrophotometric determination of Molybdenum in steels and nickel base high temperature alloys with hydroxylamine hydrochloride and 4-(2-Pyridylazo) resorcinol. *Proc. Indian Nat. Sci. Acad* 1990; 56(3):255-261.
- Barrera B, Gonzalez F, Martinez B. Spectrophotometric determination of Molybdenum with thiocyanate and pyrogallol. *Mikrochem. J.* 1987; 35(1):1-6.
- Chandrima R, Swapan M, Jyotirmoy D. Extractive spectrophotometric determination of molybdenum (VI) with anilides of mercaptoacids. *Chem. Anal* 1988; 33(6):917-928.
- Ivanov V, Kochelaeva G. Pyrocatechol violet in new optical methods for determining Molybdenum (VI). *J Anal. Chem.* 2003; 58:38-43.
- Papadopoulos G, Zoton C. Kinetic-Spectrophotometric Determination of Molybdenum (VI) and Tungsten (VI) in Mixtures. *Microchim. Acta* 1992; 106(22):203-210.
- Rao C, Reddy V, Reddy T. Selective spectrophotometric determination of molybdenum(VI) and vanadium(V) with resacetophenone benzoic hydrazone in steels and alloys. *Proc. Indian Nat. Sci. Acad* 1993; 59(5):449-454.
- Burns D, Harriott M, Pornsinlapatip P. Flow-injection spectrophotometric determination of molybdenum (VI) by

- extraction with quinolin-8-ol. *Anal. Chim. Acta* 1993; 281(3):607-610.
24. Shah I, Menon S, Desai W, Agrawal Y. Extraction-spectrophotometric and atomic absorption spectrophotometric determination of molybdenum with caffeic acid and appli-cation in high purity grade steel and environmental samples. *Anal. Lett* 1989; 22:1807-1817.
 25. Verdizade NA, Zalov AZ, Kuliev KA, Amrakhov TA, Samedova VM. Extraction-photometric determination of molybdenum as a mixed-ligand complex with 2-hydroxy-5-chlorothiophenol and diphenylguanidine. *J Anal. Chem.* 2000; 55(4):331-334.
 26. Zalov AZ, Verdizade NA, Abaskulieva UB. Ekstraksionno-fotometricheskoye opredeleniye titana (IV) gidroksigalogenproizvodnymi tiofenola i aminofenolami. *Izv. Vyssh.Uchebn. Zaved. Ser. Khim. Khim. Tekhnol* 2012; 55(10):23-29.
 27. Zalov AZ, Verdizade NA. Extraction-spectrophotometry determination of tungsten with 2-hydroxy-5-chlorothiophenol and hydrophobic amines *J Anal. Chem.* 2013; 68:212-217.
 28. Zalov AZ, Gavazov KB. Extractive spectrophotometric determination of nickel with 2-hydroxy-5-iodothiophenol and diphenylguanidine. *Chem. J.* 2014; 4(5):20-25.
 29. Zalov AZ. Extraction-photometric determination of manganese (II) 2 - hydroxy-5-chlorothiophenol and amino phenols in industrial facilities and prodnyh. *Zavodskaya laboratoriya (Factory laboratory)* 2015; 81(4):17-21.
 30. Zalov AZ. Ekstraksionno-fotometricheskoye opredeleniye margantsa (II) o-gidroksitiofenolom i aminofenolami. *Bulletin of St. Petersburg State University. Ser* 2015; 42(60-1):61-71.
 31. Zalov AZ, Gavazov KB. Liquid-liquid extraction-spectrophotometric determination of molybdenum using o-hydroxythiophenols. *J of Advances in Chemistry.* 2014; 10(8):3003-30011.
 32. Zalov AZ, Verdizade NA, Jamalova RI. Extraction-photometric determination of niobium (V) with 2-hydroxy-5-bromthiophenol and hydrophob amines. *Az. Chim. Journal.* 2011; 1:79-84.
 33. Korostelev PP. Preparation of solutions for chemical analysis works. M. Publishing house of Academy of Sciences of the USSR, 1964, 401.
 34. Kuliev AM, Aliev ShR., Mamedov FN, Movsumzade M. Synthesis of the aminometilic derivatives 2-oxi-5-rubs-alkiltiophenols and their splitting of a tioles. *Zhurn. organ. khimii* 1976; 12(2):426-430.
 35. Mineev VG. *Praktikum po agrokhimii* (2nd ed.), Izd. Mosk. Gos. Univ., Moskow, Russia, 2001.
 36. Bulatov MI, Kalinkin IP. *Prakticheskoe rukovodstvo po fotokolorimetricheskimi spektrofotometricheskimi metodam analiza.* Khimiya, Leningrad, USSR, 1986.
 37. Nazarenko VA, Biryuk EA. A study of the chemistry of reactions of multivalent element ions with organic reagents. *Zh. Anal. Khim* 1967; 22(1):57-64.
 38. Bellami L. *Infra-Red Spectra of Complex Molecules* (The Infra-Red Spectra of Complex Molecules). Moscow, Mir, 1991, 592.
 39. Nakamoto K. *IK-spectr KR neorqaniceskikh I koordinatsionnikh soedineniy* (Infrared and Raman Spectra of Inorganic and Coordination Compounds). Moscow: Mir, 1991, 536.
 40. Lukin AM, Petrov GS. Rezorsan reactant molybdenum. *J Anal. Chem.* 1969; 24(1):39-43.
 41. Zaijun Li, Jiaomai Pan, Tang Jan. Spectrophotometric determination of trace molybdenum in plants and seeds with 3,5-dibromo-4-hydroxyphenylflurone. *Analyst* 2001; 126:1154-1159.
 42. Nagiyev Kh D, Chyragov FM, Gambarov DG, Mugalova GR. Fotofotometricheskoye opredeleniye Mo (VI) proizvodnymi pirogallola v prisut stvii tret'yego komponenta. *Zavodskaya laboratoriya (Factory Laboratory)* 2003; 69(10):15-19.
 43. Umland F, Janssen A, Thierig D, Wünsch G. *Theorie und praktische anwen-dung von complexbildnern.* Frankfurt am Main, Akademische Verlagsgesellschaft, 1975, 531.
 44. Gavazov K, Lekova V, Boyanov B, Dimitrov A. Some tetrazolium salts and their ion-association complexes with the molybdenum (VI) - 4-nitrocatechol anionic chelate. DTA and TGA study. *//J Therm. Anal. Cal.* 2009; 96(1):249-254.
 45. Gavazov KB. Nitroderivatives of catechol: from synthesis to application. *// Acta Chim. Alov* 2012; 59:1-17.
 46. Kuliev KA, Verdizade NA. Liquid-liquid extr action and spectrophotometric determination of molybdenum with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines. *Chemistry Journal.* 2015; 5(3):46-50.