LIQUID-LIQUID EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM USING o-HYDROXYTHIOPHENOLS

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ABSTRACT

27 liquid-liquid extraction-chromogenic systems containing Mo(VI), o-hydroxythiophenol derivative {HTPDs: 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) or 2-hydroxy-5-iodothiophenol (HITP)} and aromatic amine (AA) were studied. Aniline (An), N-methylaniline (mAn), N,N-dimethylaniline (dAn), o-toluidine (o-Tol), m-toluidine (m-Tol), p-toluidine (p-Tol), 3,4-xylidine (o-Xyl), 2,4-xylidine (m-Xyl), and 2,5-xylidine (p-Xyl) were the examined AAs. Optimization experiments for molybdenum extraction-spectrophotometric determination were performed and the following parameters were found for each of the systems: organic solvent (opt), pH (opt), C_{HTPD} (opt), C_{AA} (opt), shaking time (opt), λ (max) and ε (max). Under the optimum conditions, the molar ratio of the reacting Mo(V), HTPD and AA was 1:2:2 and the degrees of Mo extraction were R≥98.4%. Linear relationships involving the spectral characteristics of the extracted complexes (λ_{max} or ε_{max}) and some fundamental properties of the halogen substituent in the HTPD were discussed. The effect of foreign ions was examined and two sensitive, selective and precise procedures for extraction-spectrophotometric determination of molybdenum were proposed. The relative standard deviations for Mo content of $(3-5)\times10^{-4}$ mass % were 4% (HCTP-An procedure) and 3% (HBTP-An procedure).

Indexing terms/Keywords

Molybdenum(V); solvent extraction; ternary complex; soil analysis; plant analysis; linear relationship

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Analytical chemistry; Inorganic Chemistry; General chemistry

TYPE (METHOD/APPROACH)

Types of research: experiments; Approach: quantitative research

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INTRODUCTION

Molybdenum has been recognized as an essential trace element for plants, animals and humans [1-3]. In plants, it has a key function in the fixation of the atmospheric nitrogen, while in humans, it is important for the activity of the enzymes xantine oxidase, sulphite oxidase, and aldehyde oxidase. It is known that molybdenum has a beneficial effect on patients with sulphite sensitivity and asthma. It has also been stated that it reduces the incidence of dental caries. On the other hand, molybdenum can be toxic at high concentrations [2-4]. In mammals, it increases the lability of blood pressure, disturbs the cholesterol transport and causes bone deformation. Effects of acute molybdenum toxicity include diarrhoea, anaemia and gout. Chronic occupational exposure has been associated with weakness, fatigue, lack of appetite, anorexia, joint pain and tremor [3].

Despite its relative rarity in the Earth's crust (estimated abundance in the range 0.05-40 mg kg^{-1} with a mean value of 1.5 mg kg^{-1}) [5,6], geochemical anomalies leading to molybdenum deficiencies in plants are not common [7,8] and are mostly of concern for leguminous crops. Molybdenum fertilization is often based on visual deficiency symptoms and/or history of crop rotation [8]. However, in order to assess the need for fertilization and the molybdenum dosage it is preferable to use analytical methods [5,6].

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) [9-15]. The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation. In many cases, they are based on ion-association reaction between heavy organic cations and anionic complexes of Mo(V,VI) with thiocyanate or organic reagents containing hydroxyl groups in ortho-position to each other [15-24].

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 [25-29]. In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on 27 different systems, each of which containing Mo(VI), a o-hydroxythiophenol derivative (HTPD) {2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)}, and an aromatic amine (AA) {aniline (An), N-methylaniline (mAn), N,N-dimethylaniline (dAn), o-toluidine (o-Tol), m-toluidine (m-Tol), p-toluidine (p-Tol), 3,4-xylidine (o-Xyl), 2,4-xylidine (m-Xyl), and 2,5-xylidine (p-Xyl)}. We propose new procedures for determining molybdenum in soils and plants, and show that linear relationships exist between the spectral characteristics of the ternary complexes (absorption maximum and molar absorptivity) and some fundamental properties of the halogen atom included in the HTPDs (atomic mass and electronegativity).

EXPERIMENTAL

Reagents and apparatus

A stock solution of Mo(VI) (1 dm^3) was prepared by dissolving 1.8402 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Sigma-Aldrich, 99.98%) in distilled water. The solution was standardized gravimetrically. Working solutions (0.1 mg cm^{-3}) were prepared daily by appropriate dilution of the stock solution.

HTPDs were synthesized according to the procedure [30]; their purity was verified by paper chromatography and melting point determination. AAs were products of Sigma-Aldrich (98-99% purity). Chloroform solutions (0.01 mol dm^{-3}) of HTPDs and AAs were used.

A masking solution (1 dm^3), containing 75 g of citric acid and 150 g of ascorbic acid, was prepared weekly and stored in a refrigerator. A second masking solution was prepared from KI (w=20%).

To create the optimum acidity, 0.1 mol dm^{-3} solutions of HCl or NaOH were used.

The absorbance of the extracts was measured using a KFK-2 photocolorimeter (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.

Procedure for determining the optimum conditions

Aliquots of Mo(VI) solution, HTPD solution (up to 2.5 cm^3) and AA solution (up to 2.5 cm^3) were transferred in a 50 cm^3 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 or NaOH solution. The volume of the aqueous phase was increased with water to 20 cm^3 and the volume of the organic phase was set to be 5 cm^3. 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.

Procedure for molybdenum determination

An aliquot containing molybdenum (no more than 90 μg when HTPD=HCTP or 85 μg when HTPD=HBTP) was placed in a calibrated tube. Chloroform solutions of HTPD (0.7 cm^3) and An (0.7 cm^3) were added and the organic phase was adjusted to 5 cm^3 with chloroform. The volume and pH of the aqueous phase were adjusted to 20 cm^3 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} (535 nm when HTPD=HCTP or 530 nm when HTPD=HBTP) against a simultaneously prepared blank sample. The molybdenum content was found from a calibration graph.

Soil sample preparation for analysis

A soil sample (15 g) collected from depths of 15±5 cm was subjected to available molybdenum extraction procedure [31,32] with an oxalate buffer of pH 3.3. Then the procedure [31] was followed: An aliquot of the obtained soil extract (50-100 cm^3) 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 cm^3 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 cm^3 of 14% hydrochloric acid under heating. Masking solutions were added (4 cm^3 of the citric acid – ascorbic acid solution and 2 cm^3 of the KI solution) and the resulting solution was filtered into a 100-cm^3 separatory funnel. Aliquots of thus obtained filtrate were used to determine the molybdenum content.

Plant sample preparation for analysis

10 g of the powdered plant material (seeds of pea) were soaked in 50 cm^3 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 cm^3 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 cm^3 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 cm^3 [31]. Masking solutions were added (4 cm^3 of the citric acid – ascorbic acid solution and 2 cm^3 of the KI solution) and the flask was filled to the mark with bidistilled water.

RESULTS AND DISCUSSION

Studies on the oxidation state of molybdenum

It is known that HTPDs have reducing properties in acidic medium [26,28,33]. Previous investigations with Mo(VI)-HCTP and Mo(V)-HCTP [26] suggested that only Mo(V) forms stable complexes with this reagent. To elucidate the oxidation state of molybdenum in the presence of other HTPDs (HBTP and HITP), 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). The comparison of the obtained spectra showed that $\lambda_{max\ Mo(VI)-TPHHD}=\lambda_{max\ Mo(V)-TPHHD}$. This fact can be regarded as an indication [26,34] that Mo(VI) is reduced to Mo(V) by the reagent itself during the process of complex formation.

Charge of the complexes

The charge of the Mo(V)-HTPD binary complexes was determined by electromigration and ion-exchange. Experiments on electromigration in a U-shaped tube and sorption on anion exchanger EDE-10P demonstrated the anionic nature of the complexes. Under the experimental conditions, these red binary complexes were insoluble in nonpolar organic solvents. However, when AAs were introduced the formation of electroneutral chloroform extractable ternary complexes was observed.

Choice of organic solvent

The following organic solvents were tested for the extraction of the complexes: chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, diethyl ether and n-butanol. Chloroform was found to be the most effective in terms of degree of extraction (R%) and rapid equilibration. As can be seen from Table 1, chloroform provides R≥98.4%. At that, the nature of AA does not appreciably affect the extraction.

Influence of pH

Figure 1 represents the influence of pH on the absorbance of the Mo(V)-HTPD-An extracts. The optimum pH ranges are wide enough to ensure stable and reproducible results without using buffer solutions. 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 1. At higher pH values, the efficiency of the extraction is impaired, which relates to the lower degree of AA protonation. At lower pH values, the extraction is also impaired most probably due to decrease of the concentration of the anionic HTPDs forms.

Table 1. Characteristics of the Mo(V)-HTPD-AA-water-chloroform extraction-chromogenic systems

| Characteristics	Reagents	An	mAn	dAn	o-Tol	m-Tol	p-Tol	o-Xyl	m-Xyl	p-Xyl
Optimum pH interval	HCTP	4.8-6.3	4.5-5.8	4.2-5.3	5.4-6.3	5.2-6.1	4.7-5.4	5.6-6.4	4.8-5.7	4.3-5.2
	HBTP	4.4-6.1	4.3-6.0	4.0-5.5	5.2-6.1	5.0-6.0	4.5-5.3	5.4-6.2	4.5-5.5	4.2-5.1
	HITP	4.1-5.9	4.1-5.7	3.7-5.5	5.0-5.9	4.8-5.6	4.1-5.2	5.3-6.0	4.2-5.4	4.0-4.9
Degree of extraction / %	HCTP	98.4	98.5	98.7	98.5	98.6	98.4	98.7	98.8	98.4
	HBTP	98.6	98.6	98.7	98.7	98.8	98.5	98.7	98.4	98.4
	HITP	98.8	98.6	98.5	98.8	98.5	98.6	98.5	98.5	98.4
λ_{max} / nm	HCTP	535	537	538	527	530	535	522	525	528
	HBTP	530	533	536	525	526	531	518	520	523
	HITP	527	530	534	523	522	525	515	516	519
$\varepsilon \times 10^{-4}$ / dm^3 mol^{-1} cm^{-1}	HCTP	3.7	3.9	4.2	3.8	4.0	4.3	3.6	3.7	3.9
	HBTP	3.4	3.6	3.8	3.5	3.7	4.0	3.4	3.5	3.6
	HITP	3.2	3.3	3.6	3.3	3.4	3.7	3.1	3.2	3.4
Working range / μg cm^{-3}	HCTP	0.2-18	0.2-19	0.2-20	0.5-19	0.5-20	0.5-20	0.4-22	0.5-23	0.4-24
	HBTP	0.2-17	0.2-18	0.2-19	0.6-18	0.6-18	0.6-18	0.3-20	0.3-21	0.3-22
	HITP	0.2-16	0.2-17	0.2-18	0.6-17	0.4-18	0.5-18	0.2-18	0.2-19	0.2-20
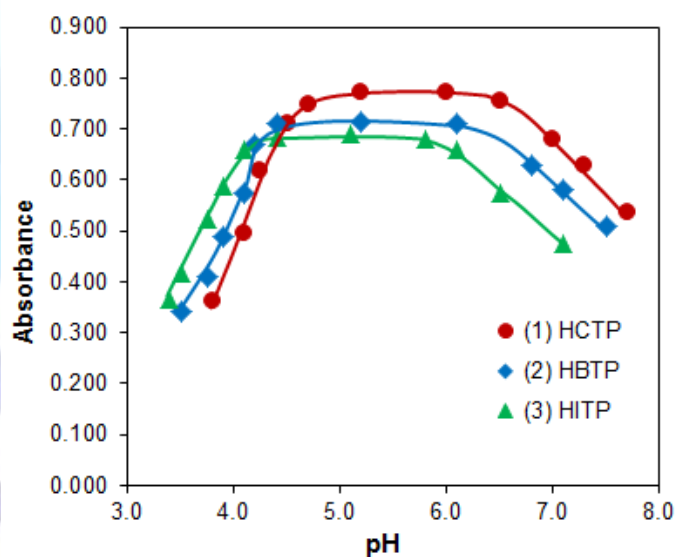
Fig 1: Absorbance of the ternary Mo(V)-HTPD-An complexes vs. pH of the aqueous phase. (1) HTPD=HCTP; (2) HTPD=HBTP; (3) HTPD=HITP. $C_{Mo(V)}$=4.16×10^{-5} mol dm^{-3}, c_{HTPD} = C_{An}=1.4×10^{-3} mol dm^{-3}, ℓ=0.5 cm

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

The absorption maxima (λ_{max}) of the ternary Mo(V)-HTPD-AA complexes lie in the range of 516-538 nm (Table 1). All colour reactions are very contrast since the initial solutions are colourless ($\lambda_{max\ HTPDs}$ = 275-280 nm). Complete extraction is achieved at HTPD and AA concentrations not lower than (1.3-1.5)×10^{-3} mol dm^{-3} and (1.2-1.5)×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 (ε_{max}) belong to the interval (3.1-4.3)×10^4 dm^3 mol^{-1} cm^{-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.

Stoichiometry of the ternary complexes

The molar ratios of the components of the ternary complexes were established by the equilibrium shift method [35] and the method of Asmus [36]. The results show a complex composition of 1:2:2 (Mo(V):HTPD:AA). Using the Nazarenko's

method [37], we found that the molybdenum complexation form is $MoO(OH)^{2+}$. Hence, the complexes can be regarded as ion associates between doubly charged anionic chelates $[Mo^VO(OH)(HTPD^{2-})_2]^{2-}$ and two protonated AA species: $(AAH^+)_2[MoO(OH)(HTPD)_2]$.

Effect of foreign ions and masking reagents

The influence of foreign ions and reagents on the extraction-spectrophotometric determination of molybdenum with HCTP+An and HBTP+An 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 $C_2O_4^{2-}$. 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). For the sake of convenience, we used only two masking solutions in our further analytical work: 1) ascorbic acid + citric acid solution; and 2) KI solution.

Table 2. Influence of foreign ions on the determination of molybdenum (50 μg) with HCTP[a] and An

Foreign ion (FI)	FI-to-Mo ratio	Masking agent	Mo found / μg	RSD[b] / %
Al(III)	100	–	50.0	1.5
Bi(III)	40	–	49.5	4.5
Co(II)	55	–	50.4	4.2
Cr(VI)	70	–	49.6	2.3
Cu(II)	25	KI	50.0	2.1
Fe(III)	50	Ascorbic acid	50.4	4.2
Hg(II)	35	$Na_2S_2O_3$	49.8	2.4
Nb(V)	45	Oxalic acid	50.2	1.5
Ni(II)	50	Citric acid	50.0	1.5
Ta(V)	45	Ascorbic acid	49.7	2.3
Ti(IV)	20	Ascorbic acid	49.6	2.3
V(IV)	40	–	50.0	1.5
W(VI)	40	Citric acid	50.3	4.2
Zr(IV)	70	–	49.6	2.3

[a] Statistically undistinguished results were obtained by using HBTP at the mentioned FI-to-Mo ratios

[b] Relative standard deviation based on three determinations

Calibration graphs, analytical characteristics and application

Table 3 summarizes the calibration characteristics obtained with HCTP+An and HBTP+An. The procedures with these reagents were applied to the determination of molybdenum in samples of soil and pea. The accuracy of the results was checked by two independent methods. The results are listed in Table 4.

Table 3. Analytical characteristics for the Mo-HCTP-An and Mo-HBTP-An extraction-chromogenic systems

Parameter	Mo-HCTP-An	Mo-HBTP-An
Linear calibration range / μg cm^{-3}	up to 4.5	up to 4.3
Slope $\pm$ Standard deviation / A μg^{-1} cm^3	0.383±0.004	0.351±0.03
Intercept $\pm$ Standard deviation / A	0.007±0.011	0.007±0.008
Correlation coefficient (9 standards used)	0.9994	0.9997
Limit of detection (LOD) / ng cm^{-3}	15[a]	12[a]
Limit of quantification (LOQ) / ng cm^{-3}	50[a]	40[a]
Sandell's sensitivity / ng cm^{-2}	2.61	2.85

[a] Defined as 3σ/a (LOD) or 10σ/a (LOQ), where a is the slope of the calibration plot

Table 4. Analytical characteristics for the Mo-HCTP-An and Mo-HBTP-An extraction-chromogenic systems

Method		Molybdenum content in soil		Molybdenum content in pea	
		$\times 10^4$ / %	RSD / %	$\times 10^4$ / %	RSD / %
Present methods	HCTP-An method	2.93	4.0	4.95	4.0
	HBTP-An method	2.86	3.0	5.03	3.0
Dithiol method [31]		2.97	5.0	5.02	5.0
Thiocyanate method [31]		2.96	5.0	5.03	5.0

Some linear relationships involving the spectral characteristics of the complexes

The nature of the substituents and the molecular mass of the associating ions are important factors in the chemistry of ion-association [20,38]. Linear relationships have been described between the molecular mass of a particular class of cationic ion-association reagents [20,38] and some parameters, such as constant of association [38], temperature of decomposition [39], constant of extraction [40], and molar absorptivity [40].

The HTPDs used in this work provided an excellent opportunity to examine the influence of the halogen substituent (Cl, Br, I) on the spectral characteristics of the ternary complexes (molar absorptivity ε_{max} and absorption maximum λ_{max}). The results showed that straight lines can be obtained by plotting the atomic mass of the halogen atom (A_{Hal}) vs. λ_{max} (Figure 2) or ε_{max} (Figure 3). The experimental data plotted in coordinates $\lambda_{max} - \chi_{Hal}$ and $\varepsilon - \chi_{Hal}$ (where χ_{Hal} is the Pauling electronegativity of the halogen atom) also fit linear equations (Table 5) (the squared correlation coefficients R^2 are in the range of 0.9347-1.000). The differences in the slopes (a_i) of the straight-lines $\lambda_{max}=a_1 \times A_{Hal}+b_1$ and $\lambda_{max}=a_2 \times \chi_{Hal}+b_2$ can be attributed to the different nature of the AAs used. However, the slopes were relatively constant for the straight lines $\varepsilon_{max}=a_3 \times A_{Hal}+b_3$ and $\varepsilon_{max}=a_4 \times \chi_{Hal}+b_4$: $a_3=-0.0060 \pm 0.0005$ and $a_4=1.08 \pm 0.09$. This fact can be used for simple prediction of molar absorptivities of still uninvestigated ternary complexes (e.g. Mo-HTPD-AA complexes where AA is 2,3-xylidine, 2,6-xylidine or 3,5-xylidine). For this purpose, only one of the ternary complexes of a given AA (Mo-HCTP-AA, Mo-HBTP-AA or Mo-HITP-AA) must be experimentally examined.

Table 5 shows that the straight-line equations with participation of λ_{max} are characterised by relatively constant ordinate cuts b_i ($b_1=534 \pm 4$ and $b_2=485 \pm 12$). This information can be used for predicting the absorption maxima of new ternary complexes after a single experimental step as outlined above.

Table 5. Equations and squared correlation coefficients (R^2) describing the linear relationships between the atomic mass (A_{Hal}) or Pauling electronegativity (χ_{Hal}) of the halogen atom in the HTPD and the spectral characteristics of the ternary complexes (λ_{max} and ε_{max})

| AA	$\lambda_{max}=f(A_{Hal})$	$\varepsilon_{max} \times 10^{-4}=f(A_{Hal})$	$\lambda_{max}=f(\chi_{Hal})$	$\varepsilon_{max} \times 10^{-4}=f(\chi_{Hal})$
An	y=-0.0873x+537.71 R^2=0.9748	y=-0.0055x+3.8739 R^2=0.9829	y=15.526x+485.23 R^2=0.9347	y=0.9737x+0.5837 R^2=0.9481
mAn	y=-0.0764x+539.5 R^2=0.9904	y=-0.0066x+4.1297 R^2=0.9997	y=13.684x+493.28 R^2=0.9616	y=1.1842+0.1342 R^2=0.9868
dAn	y=-0.0437x+539.53 R^2=0.9997	y=-0.0065x+4.3947 R^2=0.9581	y=7.8947x+512.89 R^2=0.9868	y=1.1579x+0.4779 R^2=0.9098
o-Tol	y=-0.0437x+528.53 R^2=0.9997	y=-0.0055x+3.9739 R^2=0.9829	y=7.8947x+501.89 R^2=0.9868	y=0.9737x+0.6837 R^2=0.9481
m-Tol	y=-0.0875x+533.06 R^2=0.9997	y=-0.0066x+4.2297 R^2=0.9997	y=15.789x+479.79 R^2=0.9868	y=1.1842x+0.2342 R^2=0.9868
p-Tol	y=-0.1095x+539.18 R^2=0.9903	y=-0.0066x+4.5297 R^2=0.9997	y=20x+471.8 R^2=1.000	y=1.1842x+0.5342 R^2=0.9868
o-Xyl	y=-0.07645x+524.5 R^2=0.9904	y=-0.0055x+3.8089 R^2=0.9903	y=13.684x+478.28 R^2=0.9616	y=1.000x+0.44 R^2=1.000
m-Xyl	y=-0.0983x+528.27 R^2=0.9936	y=-0.0055x+3.9089 R^2=0.9903	y=17.632x+468.73 R^2=0.9683	y=1.000x+0.54 R^2=1.000
p-Xyl	y=-0.0983x+531.27 R^2=0.9936	y=-0.0055x+4.0739 R^2=0.9829	y=17.632x+471.73 R^2=0.9683	y=0.9737x+0.7837 R^2=0.9481
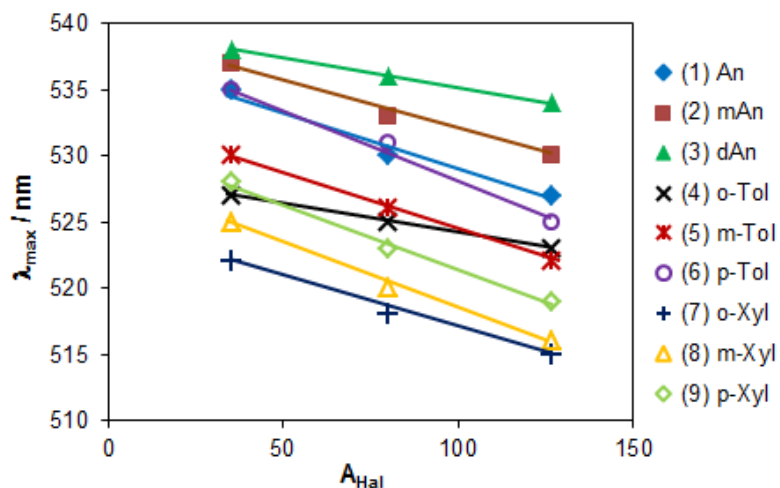
Fig 2: Straight lines obtained by plotting the absorption maxima of the ternary complexes (λ_{max}) vs. the atomic mass of the halogen in HTPDs (A_{Hal}). The corresponding linear equations are included in Table 5.
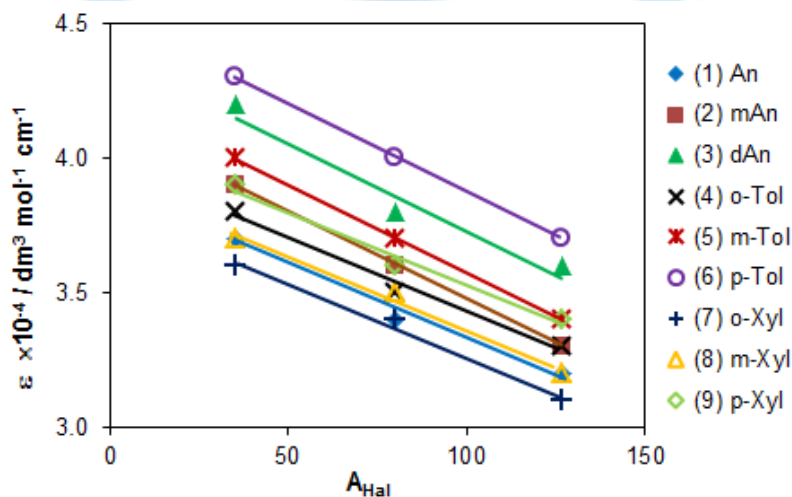

Fig 3: Straight lines obtained by plotting the molar absorptivity coefficients (ε) vs. the atomic mass of the halogen in HTPDs (A_{Hal}). The corresponding linear equations are included in Table 5

CONCLUSIONS

Molybdenum(VI) forms well chloroform-extractable ternary complexes with HTPDs and AAs which can be used for liquid-liquid extraction-spectrophotometric determination of molybdenum. The complexes have a composition of 1:2:2 (Mo:HTPD:AA) and can be regarded as ion associates between doubly charged anionic chelates of Mo(V) and protonated AA species: $(AAH^+)_2[MoO(OH)(HTPD)_2]$. The collected information about the spectral characteristics (absorption maximum λ_{max} and molar absorptivity ε_{max}) of the complexes makes it possible to conclude that linear relationships exist between some fundamental properties of the halogen substituent in the HTPD (atomic mass A_{Hal} and electronegativity χ_{Hal}) and λ_{max} or ε_{max}: (i) The higher the atomic mass, the lower λ_{max} and ε_{max}; (ii) The higher the electronegativity χ_{Hal}, the higher the λ_{max} and ε_{max}. The established constancy of the slopes or ordinate cuts of the obtained straight-line equations can facilitate the prediction of the mentioned spectral characteristics of new complexes of the same class.

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