IJPSR (2017), Volume 8, Issue 9 **(Research Article)**

INTERNATIONAL JOURNAL OF PHARMACEUTICAL SCIENCES AND RESEARCH

Received on 15 February, 2017; received in revised form, 14 April, 2017; accepted, 26 April, 2017; published 01 September, 2017

SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM IN ENVIRONMENTAL AND FOOD SAMPLES USING SOLVENT EXTRACTION

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Keywords:

Molybdenum determination,
Solvent extraction,
Spectrophotometry,
2,6-dithiol-4-methylphenol,
Environmental analysis

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ABSTRACT: 2, 6-dithiol-4-methylphenol (DTMP) is proposed as an analytical reagent for the extractive spectrophotometric determination of molybdenum (V). DTMP in the presence 2, 6- bis (N, N-dimethylaminomethyl)-4-methylphenol (AP) forms red colored complex with molybdenum (V) in the pH range 4.8 - 5.8. The Beer's law was applicable in the range 0.4-22μg mL^{-1}. The dark red Mo-DTMP-AP complex shows a maximum absorbance at 525 nm, with molar absorptivity of 5.21×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity of the complex obtained from Beer's data is 1.84 ng cm^{-2}. The composition of the Mo (V)-DTMP-AP complex is found to be 1:2:1 (Mo: DTMP: AP). The interference of various cations and anions in the method were studied. The results of the prescribed procedure applied for the determination of the micro amounts of Mo (V) in plant, water and soil samples are presented.

INTRODUCTION: Molybdenum is the one utmost important element for many organisms and has a wide distribution throughout nature [1]. Molybdenum is a bio-essential element and its occurrence in water samples is of interest from both environmental and chemical points of view [2].

Molybdenum is commercially important in metallurgical and agricultural laboratories. Besides its widespread industrial uses, molybdenum is an essential trace element required by both plants and animals[3]. Molybdenum finds extensive applications in different fields.

QUICK RESPONSE CODE

DOI:
10.13040/IJPSR.0975-8232.8(9).3709-18

Article can be accessed online on:
www.ijpsr.com

DOI link: http://dx.doi.org/10.13040/IJPSR.0975-8232.8 (9).3709-18

The alloys of molybdenum are extensively used in integrated circuits, anti-friction coatings, catalysts, aircraft parts, missile parts, high temperature vacuum components, furnace components, silicon power devices etc. Molybdenum is also an essential trace element in animal physiology. Molybdenum is essential to humans [4]. Molybdenum is an essential trace element for several enzymes important to animal and plant metabolism: mammalian xanthine oxidase / xanthine dehydrogenase, aldehyde oxidase, sulfite oxidase, formate dehydrogenase, nitrate reductase and nitrogennase. In view of crucial role of molybdenum in different fields, it is necessary to develop sensitive analytical procedures for its determination in trace amounts.

Therefore, it is important to develop simple, rapid, and efficient methods for monitoring molybdenum in the environment. For the determination of molybdenum at trace amount levels, there are several frequently adopted methods using analytical techniques such as atomic absorption spectrometer (AAS), ICP-AES, ICP-MS, X-ray fluorescence spectroscopy, neutron activation analysis], spectrophotometry, spectrofluorimetry, and other techniques [5-8]. Among these, spectrophotometric methods are preferred because they are cheaper and easier to handle, with comparable sensitivity and accuracy. Therefore, a sample separation / pre-concentration step prior to analysis are usually necessary.

For spectrophotometric determination of molybdenum in different oxidation states suggested: 4-(2-pyridylazo)-resorcinol [9], pyrogallol [10], lignocaine [11], mercaptopropionic acid [12], 8-mercaptoquinoline [13], isonicotinoylhydrazone salicylic aldehyde [14], malachite green [15], 1,5-diphenylcarbazone [16], alpha-benzoinoxime [17], 2,4-diaminophenol [18], 2,4-dihydroxyacetophenone [19], 8-hydroxyquinoline [20], capheic acid [21], N-benzoylphenyl-hydroxylamine [22], pyrocatechine violet [23]. 3-hydroxy-2-(4-methoxyphenyl)-6-propionyl-4H-chromen-4-one [24], N, N^1-bis(2-hydroxy-5-bromobenzyl)-1,2diaminopropane [25]. 5-Bromosalicylaldehyde isonicotinoyl hydrazone [26], 6-chloro-3-hydroxy-2-(3^1-hydroxyphenyl)-4-oxo-4H-1-benzopyran [27],1-methyl-3-octadecyl-imidazolium bromide [28], $N^/$-(2-hydroxebenzyliden)-3-(4-o-tolylpiperazin-1-il) [29], salicylaldehydeacetoacetic acid hydrezone [30], tetrazolium violet [31], triphenyltetrazolium chloride [32].

For highly sensitive methods for determination of Molybdenum belong methods using dithiol, thioglycolic acid, 8-hydroxyquinoline, 8-mercaptoquinoline, fluorone etc [33]. Most of these methods, however, suffer from a large number of interferences and low sensitivity due to which they are unsuitable for the routine determination of molybdenum in the samples with diverse matrices.

Reagents, containing hydroxy and carboxy, or two hydroxy groups in ortho - position to each other, interact with molybdenum preferably in weakly acidic and neutral media to form a colored complex compounds [34, 35].

The sulphur-containing organic substances having the following groups represent in most cases valuable analytical reagents on molybdenum:

$$\underset{-C-}{=C-SH} \quad \text{or} \quad \underset{-A}{=C-SH}$$

Whereas: A=-COOH, -SH, -OH

Dithiolphenolate complexes of metalls are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and amino phenols easily dissolve in various organic solvents [36-40]. In the present communication, simple, rapid, selective and sensitive spectrophotometric method is reported for the micro determination of Mo (VI) complexing with 2,6-dithiol-4-methylpenol (DTMP) and 2,6-bis(N, N-dimethylaminomethyl)-4-methylphenol (AP).

MATERIALS AND METHODS:

Reagents and Solutions: Stock solution (1 mg/mL) of Mo (VI) was prepared by dissolving 1.8402 g $(NH_4)_6Mo_7O_{24}$×4 H_2O p. f. a." (Pure for analysis) in hot water. On cooling; solution was diluted with water in a measured flask to 1 L. The concentration of the solution was adjusted gravimetrically [41]. Working solution with concentration of 0.1 mg/ml was prepared by dilution of stock with deionised water. Solutions of DTMP and AP in chloroform (0.01 M) were used. DTMP purified by recrystallization from CCl_4. The extractant was purified chloroform. Chloroform was purified by washing with conc. H_2SO_4 and shaking with distilled water followed by washing with a 5% solution of NaOH. The ionic force of solutions was supported a constant (μ = 0.1) by introduction of the calculated quantity of KCl. To create the optimal acidity, 1 M solutions of KOH and HCl were used.

A buffer solution of pH 5.0 was prepared by mixing proper proportions of acetic acid (0.2 M) and sodium acetate solutions (0.2 M). The stock solution of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

Characterization of the Reagent: DTMP were synthesized according to the procedure [42]. The reagent was characterized by taking the elemental analysis, NMR and IR spectra [43-45].

IR (KBr): 3460 см$^{-1}$ ν (OH), 3050 см$^{-1}$ ν(CH), 2570см$^{-1}$ ν(SH), 2962 и 2872 см$^{-1}$ ν(-CH_3), 1555см$^{-1}$ δ(C_6H_5), 1390 см$^{-1}$ δ_{as} (-CH_3).

^1H NMR (300,18MHz, C_6D_6): δ 5.24 (s, 1H- OH), δ 3.32(s, 2H - 2SH), δ 7.11 (s, 2H Ar-H), δ 2.38 (s, 3H $–CH_3$).

The results of the elemental analysis (C - 48.92%, N - 9.35%, H - 37.13%) of the reagent are in good agreement with the calculated values (C - 48.84 %, O - 9.30%, S - 37.21%).

Apparatus: The absorbance of the extracts was measured using a Shimadzu UV1240 spectrophotometer and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. 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. The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H». IR spectra were recorded on a spectrophotometer "Bruker" (Germany). ^1H-NMR spectra were recorded on "Bruker" Fourier Transform (300.18 MHz) in C_6D_6.

General Procedure for the Determination of Molybdenum: To an aliquot containing 50 µg of molybdenum, add 1.8 mL 0.01 M DTMP, and a 1.3 mL 0.01M AP 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 0.1 M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. After the complete separation of the phases, the organic phase was separated from the aqueous phase in 10 minutes and the absorbance of the extracts was measured on KFK-2 photo colorimeter using 540 nm (l=0.5 cm) and at room temperature.

Determination of Molybdenum in Soils: A 0.5-1.0 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 a graphite cup in a mixture of 16 mL of HF (conc.), 5 mL of HNO_3 (conc.), and 15 mL of HCl (conc.) at 50-60 °C to remove excess hydrogen fluoride.

A further 8 mL portion of HNO_3 (conc.) was added triply to the solution that was each time evaporated to 5-6 mL. 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 aliquots of the solution using the procedure proposed by us.

Preparation of Environmental Water Samples: The water samples were filtered through Whatman No. 40 filter paper then 100 mL of each filtered water sample was accurately transferred into a 250 mL round bottom flask, and 10 mL of a mixture consisting of HNO_3 and H_2O_2 (1:9, v/v) were added. These samples were digested by heating under reflux for 1.5 h. The cooled samples were transferred into 100 mL volumetric flask and made up to the mark. With deionized distilled water, mixed well, then subsequently analysed by the proposed spectrophotometric methods.

Preparation of Food Samples: A wet ash method was employed in the preparation of the sample solution. 0.5 g of the sample was dissolved in a 1:1 mixture of nitric acid and perchloric acid. The solution was evaporated to dryness, and the residue was ashed at 300 °C. The ash was dissolved in 2mL of 1M sulphuric acid and made up to the volume in a 25mL standard flask with distilled water.

RESULTS AND DISCUSSION: It is known that DTMP 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 ($SnCI_2$ or KI). It was found that the spectrophotometric characteristics of the MLC of Mo (VI) and Mo (V) were identica, *i.e.* in the interaction with DTMP; Mo (VI) was reduced to Mo (V).

Absorption Spectra: Under the experimental conditions, the absorption spectrum of the Mo (V)-DTMP-AP complex was recorded against the blank solution. The absorption spectrums of the complexin are shown in **Fig. 1.** The obtained spectra reveal that the Mo (V)–DTMP-AP complex and reagent have the maximum absorbance of 524 nm and 274 nm, respectively. The reagent DTMP and AP does not absorb at the maximum absorbance of the complex, and hence does not interfere with the determination of molybdenum. Hence, all the spectral measurements of the complex were carried out at 540 nm against a blank solution.

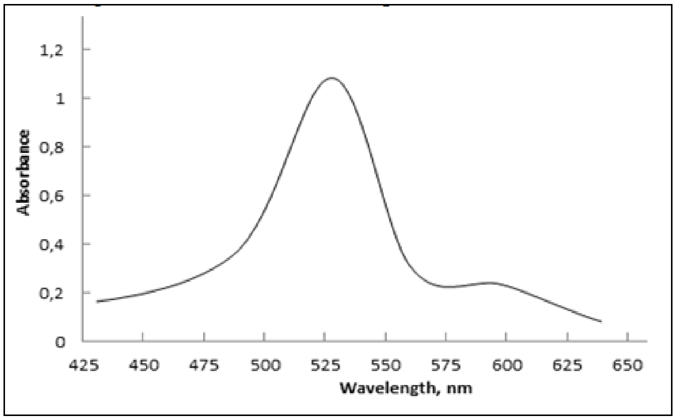

FIG. 1: ABSORPTION SPECTRA OF THE Mo (V)-DTMP-AP SYSTEM IN CHLOROFORM SOLUTIONS

CMo = 2.08 ×10-5 M, CDTMP = 7.2×10-4 M, CAP = 5.2×10-4 M, pH = 5, Shimadzu UV1240, l=1 cm

Effect of pH: To study the effect of pH on maximum color development and also on quantitative extraction of the colored complex into chloroform, the color reaction and the extraction were carried out at different pH values. A series of buffer solutions, each differing by 0.2 pH units were prepared and in the presence of these buffers, the color was developed and then the complex was extracted into chloroform layer as per the procedure. The absorbance values of each of the extracted solutions were measured. It is seen from that the extraction of the complex into chloroform is quantitative and the complex shows maximum absorbance in the pH range 4.8–5.8 (**Fig. 2**).

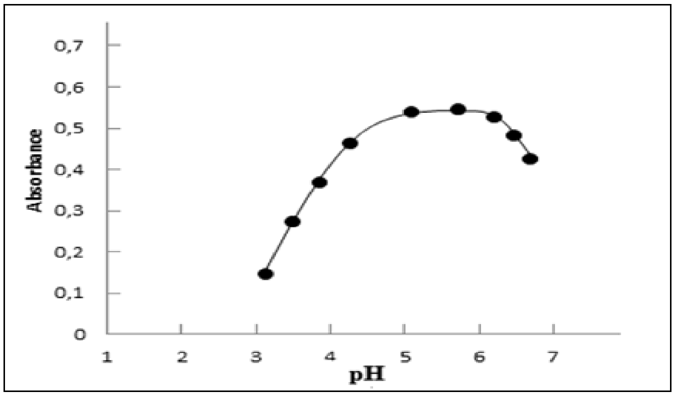

FIG. 2: ABSORBANCE OF MIXED-LIGAND COMPLEXES AS A FUNCTION OF THE pH OF THE AQUEOUS PHASE

C_{Mo} = 2.08×10^{-5} M. C_{DTMP} = 7.2×10^{-4} M, C_{AP} = 5.2×10^{-4} M, KFK-2, 590 nm, l = 0.5 cm

The complete extraction of the complex into chloroform is confirmed by the fact that the aqueous phase does not show any absorbance. However, outside this pH range, it is observed that either the extraction of the complex into chloroform is incomplete or the solution does not attain the maximum color. For all subsequent studies, therefore, the pH is maintained at an optimum level of 5.0. Thus further extraction and determination carried out at pH 5.0.

Effect of Temperature: The Mo (V)–DTMP-AP system attained maximum and constant absorbance at 15–50 °C. All subsequent measurements were done at room temperature (25 ± 1°C).

Effect of Reagent Concentration: The studies of the effect of concentration of the reagent revealed that a reagent excess of 30 fold was optimum for the complex formation. Hence, a 30-fold reagent excess was adopted for further investigations. However, the presence of excess of the reagent solution does not interfere with the colour reaction. The optimal concentration of DTMP and AP for formation of the complex was found to be 7.2× 10^{-4} and 5.2×10^{-4} M, respectively.

Effect of Extractants: Mo (V) reacts with DTMP and gives red colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins (AP) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. The extraction of the complex has been tried with several solvents: chloroform, 1, 2-dichloroethane, tetrachloromethane, benzene, dichloromethane, 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. 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. Organic solvents used for extraction of Mo (V) can be arranged on the basis of their extraction coefficient values as chloroform > carbon tetrachloride > dichlorethane > xylene > toluene > benzene > ethyl acetate > n-butanol > isoamyl alcohol > benzyl alcohol > nitrobenzene. Chloroform was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. After a single extraction with chloroform, 98.5 % of molybdenum was extracted as an ion associate (in a case the dichloroethane and carbontetrachloride was removed 96.5 – 97.7% of molybdenum).

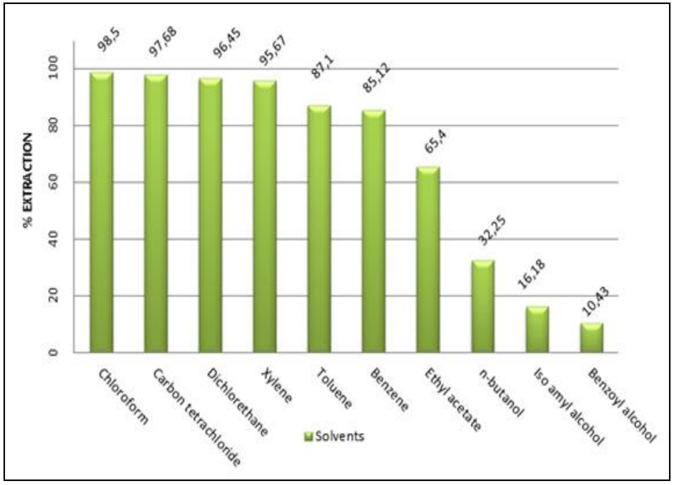

FIG. 3: EFFECT OF SOLVENTS ON EXTRACTION OF Mo (V)

Effect of Shaking Time: The results from the optimization experiments showed that an incubation time of 20 min was adequate for quantitative complexation. The sample solution was examined with a Mo (V) standard solution (1.04×10^{-3} M) and no change in absorbance was observed up to 72 h. The stability of these solutions provides an indication of the method robustness.

Order of Additions: The order of mixing DP seriously affects the absorbance value of complex. However, addition in the order (molybdenum (V)-DTMP- buffer of pH 5.0 - AP) gives the best results in all complexes formed.

Composition of the Complex: The stoichiometric coefficients of the reaction were determined by the Asmus method, by the relative yield method and by the equilibrium shift method [46]. The formation of MLC can be presented in the following way. When Molybdenum ion interacts with two molecules of DTMP, they form doubly-charged anionic complexes, which were extracted with one molecules of twice protonated AP. 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 one [47, 48].

The IR spectra of the complexes Mo-DTMP-AP in the field of 880-920 cm^{-1} there is an intensive strip of absorption caused by valent vibration of group $MoO(OH)^{2+}$. The disappearance of the pronounced absorption bands in the 3620-3250cm^{-1} with a maximum at 3475 sm^{-1} observed in the spectrum of DTMP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2570 sm^{-1} shows that one of the - SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 2380 cm^{-1} indicates the presence of a coordinated amino-phenole [43-45].

Thermogravimetric study of the complex Mo-DTMP-AP shown that thermal decomposition of the complex takes place in three stages: at 50-80 °C water evaporates (weight loss - 4.95%), at 420-490 °C-decomposed AP (weight loss -30.56%), and at 490-530 °C- DTMP (weight loss - 46.75%). The final product of the termolysis of the complex is MoO_3.

Additional experiments by the Akhmedly's method [49] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.05).

Characteristics of the Analytical Method: A series of solutions containing different amounts of the metal ion were prepared as per the general experimental procedure. The absorbance of the solutions was measured at 500 nm. A calibration graph drawn between absorbance and the metal ion concentration indicates that Ti (IV) can be determined in the concentration range 0.4 to 22.0μg mL^{-1}. The molar absorptivity of the extracted complex on the basis of Mo (V) content was calculated to be 5.21×10^{4} L mol^{-1} cm^{-1}.

Detection limit estimated from the standard deviation (SD) of the blank and calibration sensitivity (slope of calibration line), (LOD = 3 SD/sensitivity [50] amounted to 9 ng·$mL^{-1}$of Mo (V) (**Table 1**). Limit of quantication (LOQ) is 29 ng.mL^{-1} of Mo (V), and the LOD/LOQ ratio is 3.2.

The sensitivities expressed as molar absorptivity, of the proposed method are compared in **Table 2** with those of published spectrophotometric methods.

TABLE 1: ANALYTICAL FEATURES OF THE PROPOSED METHOD FOR DETERMINATION OF MOLYBDENUM WITH DTMP AND AP

Parameter	Value
Color	dark red
The pH range of education and extraction	2.5-8.8
The ph range of Maximum extraction	4.8-5.8
λmax (nm)	525
Molar absorptivity (L· mol^{-1} cm^{-1})	5.21×10^4
Sandell's sensitivity (μg·cm^{-2})	1.8
R %	98.5
The equation of calibration curves	0.062+0.0473x
Correlation coefficient	0.9963
Detection limits (ng mL^{-1}	9
Quantification limits (ngmL^{-1}	29
lg k_e	5.65
Stability constant (β)	9.32
Beer's law range (μg·ml^{-1})	0.4-22
Sandell sensitivity (ng cm^2)	1.84

Effect of Foreign Ions: To assess the expediency of the proposed method, the effect of several diverse ions was examined under already established optimum conditions. The interference of various ions was determined by measuring the absorbance of solutions containing a constant amount of Mo (VI) and varying amounts of diverse ions. The tolerances limit was considered to be the amount that caused a ± 1% deviation in the absorbance value. The tolerance limits of various diverse ions are given in **Table 3.**

Ba(II), Mg(II), Ca(II), Sr(II), Cr(III), Zn(II), Cd(II), Hg(II), Al(III) and Bi(III) did not affect the absorbance of Mo(V)-DTMP-AP complex when present in 10 mL of the aqueous phase and were found to cause < 1% error. However, Hg(II), Pb(II), U(VI), Mn(II), V(IV), Fe(II), Fe(III), Cr(VI), Pd(II), Pt(IV), V(V), Zr(IV), Ti(IV), Ta(V), Co(II), Cu(II), Nb(V), Ni(II) and W(VI) required masking agents, as mentioned under the procedure.

TABLE 2: COMPARISON OF SELECTED REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM

Reagent	pH	λ_{max} (nm)	$\varepsilon\times10^4$ (L $mol^{-1}cm^{-1}$)	Line arrange ($ngmL^{-1}$)
Toluene-3,4-dithiol [33]	4-12M HCl	675	2.1	
2-Hydroxy-5-methylacetophenoneisonicotinoylhydrazone [51]	0.015M-0.018MHCl	410	5.643	3 - 16
6-chloro-3-hydroxy-2-(3^1-hydroxyphenyl)-4-oxo-4H-1-benzopyran [27]	1M H_2SO_4	404	5.62	to 2.31
4-hydroxybenzaldehyde thiosemicarbazone [52]	6.0	365	1.25	0.03837 - 0.3837
Cinnamaldehyde-4-hydroxybenzoylhydrazone [53]	3.0-4.0	404	6.82	0.047 - 0.479
Acetophenone 2',4'-dihydroxy semicarbazone [54]	1.6-2.4.	370	0.26	1 - 8
8-Hydroxyquinoline-5 sulfonic acid [33]	3.0-4.5	540	0.52	3 - 13
O,O'-Bis(2-ethyl)dithiophosphoric acid [55]	Acid medium	503	9.6	0.5 - 4,0
DTMP + AP	4.8–5.8	525	5.21	0.4 - 22

TABLE 3: TOLERANCE LIMIT OF FOREIGN IONS IN THE DETERMINATION OF MOLYBDENUM

Ion	Molar Excess of the Ion	Found Mo, μg	Ion	Molar Excess of the Ion	Found Mo, μg
Co(II)	40	30.0	UO_2^{2+}	55	29.3
Ni(II)	40	29.8	Wine acid	200	30.4
Fe(II)	180	30.7	Citric acid	215	30.0
Cd(II)	200	29.9	Complex one III	10	29.7
Al(III)	180	30.0	Thiocyanate	300	30.2
Fe(III)	50	30.2	Thiourea	250	29.8
Zr(IV)	45	29.8	Thiosulfate	300	29.6
Cu(II)	25	29.6	Sulfate	400	30.3
Hg(II)	40	30.3	Ascorbic acid	100	30.5
Ti(IV)	35	29.6	Carbonate	200	29.8
V(IV)	20	29.3	Fluoride	230	29.6
W(VI)	10	29.0	Iodide	320	30.1
Cr(III)	130	29.8	Chloride	150	30.2
Nb(V)	60	30.1	Phosphate	210	29.8
Ta(V)	60	30.2	Acetate	350	30.5

The interference of Cu(II) can be eliminated by using 1.0 mL 0.2% EDTA as a masking agent. Fe(II) and Fe(III) are masked with 1.0 mL of 3% sodium fluoride. The interference of Zn(II), Cd(II) can be eliminated by using 1.0 mL of 0.5% thiosulphate solution. The interference of Ti(IV) can be eliminated by using 1.0 mL 0.2% ascorbic acid as a masking agent. The interfering influence of Nb(V), Ta(V), Mn(II) and Hg(II) removed by Controlling pH .

Analytical Applications: The proposed method has been applied for the determination of molybdenum (V) in plants, water and soil samples. The data presented in the **Table 4, 5** and **6** indicate the accuracy and precision of the proposed method.

TABLE 4: DETERMINATION OF MOLYBDENUM IN PLANTS, n = 5, p = 0.95

Sample	Method	Found Mo, mg kg^{-1}	S	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Barley	Toluene-3,4-dithiol	0.139	0.0061	0.044	0.139 ± 0.007
	8 Mercaptoquinoline	0.141	0.0068	0.048	0.141 ± 0.008
	DTMP + AP	0.140	0.0046	0.033	0.140 ± 0.005
Wheat	Toluene-3,4-dithiol	0.238	0.0067	0.028	0.238 ± 0.008
	8 Mercaptoquinoline	0.239	0.0108	0.045	0.239 ± 0.012
	DTMP + AP	0.238	0.0078	0.033	0.238 ± 0.009
Peas	Toluene-3,4-dithiol	0.842	0.0243	0.029	0.842 ± 0.028
	8 Mercaptoquinoline	0.850	0.0306	0.036	0.850 ± 0.035
	DTMP + AP	0.864	0.0301	0.035	0.864 ± 0.035
Ris	Toluene-3,4-dithiol	0.263	0.0080	0.031	0.263 ± 0.009
	8 Mercaptoquinoline	0.280	0.0073	0.026	0.280 ± 0.008
	DTMP + AP	0.295	0.0122	0.042	0.295 ± 0.014
Beans	Toluene-3,4-dithiol	0.398	0.0104	0.026	0.398 ± 0.012
	DTMP + AP	0.373	0.0103	0.028	0.373 ± 0.012

TABLE 5: CORRECTNESS AND REPRODUCIBILITY OF DETERMINATION OF MOLYBDENUM LEVELS IN SURFACE SOIL SAMPLES (n=5, p=0.95)

Soil sample	Methods	x , mg kg-1	S	RSD (%)	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Agricultures oil	Toluene-3,4-dithiol	1.69	0.066	3.9	1.69 ± 0.069
	DTMP + AP	1.73	0.055	3.2	1.73 ± 0.058
Marines oil	Toluene-3,4-dithiol	1.13	0.039	3.5	1.13 ± 0.042
	DTMP + AP	1.09	0.035	3.2	1.09 ± 0.038
Gray forest	Toluene-3,4-dithiol	2.62	0.394	3.0	2.62 ± 0.041
	DTMP + AP	2.70	0.078	2.9	2.70 ± 0.082
Industrial soil	Toluene-3,4-dithiol	1.71	0.061	3.7	1.71 ± 0.067
	DTMP + AP	1.64	0.057	3.5	1.64 ± 0.060
Road sides oil	Toluene-3,4-dithiol	1.25	0.036	2.9	1.25 ± 0.038
	DTMP + AP	1.32	0.037	2.8	1.32 ± 0.039

TABLE 6: DETERMINATION OF MOLYBDENUM LEVELS IN ENVIRONMENTAL WATER SAMPLES (n = 5, p = 0.95)

Sample	Molybdenum(mg L^{-1})		Recovery± s (%)	RSD (%)	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
	Added	Found			
Tap water	50	57.50	101.7±1.20	2.2	7.50 ± 0.173
	100	108.42	99.0±1.32	3.5	8.42 ± 0.309
	100	107.93	100.8±0.81	2.3	7.93 ± 0.191
Well water	50	54.60	99.2±1.03	3.3	4.60 ± 0.159
	100	104.65	100.5±0.91	3.1	4.65 ± 0.151
	100	104.58	100.6±1.54	2.4	4.58 ± 0.115
River water	50	65.36	101.2±0.83	2.5	15.36 ± 0.403
	100	115.00	99.2±1.05	3.8	15.00 ± 0.599
Sea water	50	63.05	98.7±0.84	2.1	13.05 ± 0.288
	100	112.86	99.1±1.24	2.5	12.86 ± 0.338
Drain water	50	57.20	100.6±1.43	3.4	7.20 ± 0.257
	100	107.53	98.9±1.14	3.5	7.53 ± 0.277

CONCLUSION: The proposed method has been applied to determine molybdenum in natural waters, soil and food samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

The results obtained show that the newly developed method in which the reagent 2, 6-dithiol-4-methylphenol (DTMP) was used, can be effectively used for quantitative extraction and estimation of Mo (V) from aqueous media.

Mixed-ligand complexes of molybdenum (V) with DTMP in the presence of AP have been investigated by spectrophotometric method.

Extraction of mixed ligand complexes is maximal at pH 4.8 - 5.8. The proposed method is quick and requires less volume of organic solvent.

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 0.4-22µg/ml.

A simple, rapid and sensitive method proposed for the determination of trace amounts of molybdenum. The method is very precise, faster and simpler than other methods.

ACKNOWLEDGEMENT: Nil.

CONFLICTS OF INTEREST: Nil.

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How to cite this article:
Kuliev KA, Verdizadeh NA, Suleymanova GS, Mamedova RA and Mamedova SA: Spectrophotometric determination of molybdenum in environmental and food samples using solvent extraction. Int J Pharm Sci Res 2017; 8(9): 3709-18.doi: 10.13040/IJPSR.0975-8232. 8(9). 3709-18.