Trace level determination of molybdenum in environmental and biological samples using surfactant-mediated liquid–liquid extraction

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ABSTRACT

A novel and sensitive spectrophotometric method for the determination of molybdenum at trace levels in environmental and biological samples is proposed. The method is based on the reaction of Mo (V) with thiocyanate (SCN$^-$) and methyltrioctyl ammonium chloride (MTOAC) in acidic medium. The red colored complex of molybdenum is extracted with N-phenylbenzimidoyl thiourea (PBITU) in 1-pentanol for its determination by spectrophotometry. The sensitivity of the present method is higher than other conventional thiocyanate method, due to the use of MTOAC in liquid–liquid extraction. The value of molar absorptivity of the complex with respect to molybdenum is 7.6×10^4 L mol^{-1} cm^{-1} at 470 nm. The limit of detection of the metal is 5 ng mL^{-1}. The system obeys Beer's law between 20 and 1000 ng mL^{-1} with slope, intercept and correlation coefficient values of 0.81, 2.5×10^{-3} and +0.999, respectively. Most of the metal ions tested did not interfere in the determination of molybdenum. The proposed method has been successfully applied for the determination of the molybdenum in environmental and biological samples.

1. Introduction

Molybdenum is an essential trace element for both animals and plants. In animals, it is a component of xanthine oxidase and other redox enzymes. In plants, this element is necessary for the fixation of atmospheric nitrogen by bacteria to begin the protein synthesis. Deficiency or excess of molybdenum can cause damage to plants, and hence its routine control is highly recommended for healthy plant growth. Molybdenum is added in trace amounts to fertilizers to stimulate the plant growth. Molybdenum is also used as a component in glass, fertilizer, catalyst, lubricant and alloy of steel [1–7]. As a result, industrial effluents contain excess of molybdenum that causes detrimental effects in animals and human beings. Molybdenum poisoning causes severe gastrointestinal irritation with diarrhea, coma ruminants and death from cardiac failure [8]. Thus, monitoring of molybdenum in environmental and biological sample is necessary in order to know the exposure level of this element.

Several techniques such as atomic absorption spectrometry (AAS) [9,10], inductively coupled plasma mass spectrometry (ICP-MS) [11,12], differential pulse anodic stripping voltammetry [13,14], spectrofluorimetry [15], polarography [16] have been reported for the determination of molybdenum. Preconcentration and separation of the molybdenum is necessary in order to detect trace level of analyte and subsequently eliminate the interference present in the sample [17,18]. However, these techniques are quite expensive with high running expenditure and require skilled hands for operation. Various organic and inorganic reagent viz. 4-unsubstituted pyrazoline-5-ones [19], alizarin red S [20], O,O'-bis(2-ethylhexyl)dithiophosphoric acid + TX-100 [21], xylenol orange [22], phenylfluorone [23], 8-hydroxyquinoline [24] have also been reported for the spectrophotometric determination of molybdenum at trace levels. However, these methods are not suitable for routine monitoring as the procedures are complicated, report poor sensitivity and susceptible to pH changes and interferences. In the present work, a new method has been proposed for the extraction and spectrophotometric determination of molybdenum using thiocyanate, methyltrioctyl ammonium chloride (MTOAC) and N-phenylbenzimidoyl thiourea (PBITU). It is applied for the determination of molybdenum in environmental (soil, root nodules and water) and biological (urine) samples.

2. Experimental

2.1. Apparatus

A Systronics VIS-spectrophotometer type-106 with 1-cm quartz cell was used for absorbance measurements. A Varian SpectrAA

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Zeeman 220 atomic absorption spectrometer equipped with transversely heated graphite atomizer (THGA) and hollow cathode lamp source was employed for comparison of the data. A hollow-cathode lamp operated at 7 mA was used and absorbance was measured at 313.3 nm with a slit width of 0.5 nm. The maximum heating power and gas stop flow were applied at the atomization stage.

2.2. Reagents

All the chemicals used were of analytical grade reagents purchased from E. Merck (Darmstadt, Germany). A fresh standard solution of molybdenum, 1000 μg mL^{-1} was prepared by dissolving appropriate amounts of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ in 1 L double distilled water. The working standard solutions were prepared by an appropriate dilution of the stock solution. A 0.56 M fresh solution of ascorbic acid was used for the reduction of metal. Ammonium thiocyanate (5.0 M) was used for the formation of the thiocyanate complex. The acidity of the solution was maintained by using 10.0 M of HCl. A 0.5 M solution of MTOAC was used for increasing the color intensity of molybdenum complex. A 15×10^{-3} M solution of *N*-phenybenzimidoyl thiourea in 1-pentanol was used for the extraction of the molybdenum complex that was synthesized by condensation of *N*-phenylbenzimidoyl chloride with thiourea in equimolar ratio as described in literature [25].

2.3. Sample collection and preparation for the determination of molybdenum

All samples were collected in 100-mL polyethylene bottles during March 2006 from Raipur region, Chhattisgarh, India. The root nodules of leguminous plants were washed with distilled water in order to remove soil matter and dried in oven for 24 h at 100 °C.

A 1.0 g of soil or root nodule samples was ground to 100-mesh size and placed in a 100-mL Teflon beaker. To this, 4 mL of 70% perchloric acid ($HClO_4$) and 10 mL 40% hydrofluoric acid (HF) were added. The sample was made wet with acids by swirling and kept on a hot plate. The dried mass was dissolved in 50 mL of 1.0 M hydrochloric acid (HCl), filtered and 1 mL of sample solution was used for the determination of molybdenum.

A 100 mL aliquot of filtered water sample was evaporated nearly to dryness after adding a mixture of 5 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3, and then cooled to room temperature. The residue was heated further with 10 mL of distilled water in order to dissolve the salts. The resulting solution was filtered with Whatman filter paper into 25-mL volumetric flask and made up to the mark with distilled water. Then, 1 mL of sample solution obtained was used for the analysis of molybdenum.

Urine samples were collected in cleaned polyethylene bottle from age group of 23–50 people and stored in refrigerator until analysis. A 100 mL aliquot of urine sample was treated with 5 mL of sulfuric acid and 10 mL of nitric acid, and then heated nearly to dryness. The residue obtained was dissolved in 10 mL of deionized and filtered with Whatman filter paper. A 1.0 mL sample solution was used for the analysis of molybdenum.

2.4. Procedure for liquid–liquid extraction

An aliquot of the sample solution containing 200–10,000 ng of Mo (VI) was transferred into a 100 mL-separatory funnel, 2 mL ascorbic acid solution was added to reduce Mo (VI) to Mo (V), followed by addition of 3 mL 10 M HCl, 1 mL of ammonium thiocyanate and MTOAC. The aqueous phase was diluted to 10 mL with distilled water maintaining the temperature at 22 ± 2 °C. Then, the colored complex was extracted with 5 mL 1-pentanol (5.0×10^{-3} M) con-

taining PBITU for 5 min. All extracts after drying over anhydrous sodium sulphate ($\approx$2.0 g) were transferred to a 10-mL volumetric flask and filled to the mark with 1-pentanol. The absorbance of the solution was measured at 470 nm by using the reagent blank as reference.

3. Results and discussion

3.1. Optimization of analytical variables for liquid–liquid extraction

3.1.1. Effect of acid

Hydrochloric acid and sulfuric acid were tested as medium for the extraction of the metal complex. Both the acids were found to be suitable for the extraction of thiocyanate complex of molybdenum in 1-pentanol. However, the complex was unstable at room temperature (22 ± 2 °C) when extracted with sulfuric acid. Thus, hydrochloric acid was chosen for the detailed experimental work. The effect of HCl concentration on absorptivity of the complex is shown in Fig. 1. The optimum acidity range was found to be 3.0–5.0 M of HCl at unit volume ratio of both phases.

3.1.2. Effect of reducing agent and ammonium thiocyanate

In the present investigation, different reducing agents including, tin chloride, hydrazine sulfate and ascorbic acid were tested for the reduction of Mo (VI) to Mo (V). Among them, ascorbic acid showed better performance in the reduction of metal. A 0.04 M ascorbic acid was found to be optimum for color development. The effect of ammonium thiocyanate was also studied in the range of 0.03–1.2 M on the formation of colored complex, shown in Fig. 2. At least, 0.5 M of ammonium thiocyanate was necessary to obtain maximum absorbance and further addition up to 1.2 M had no adverse effect.
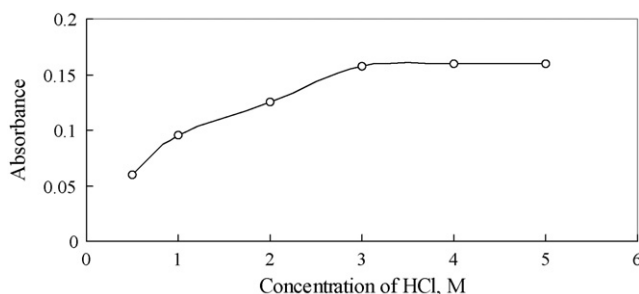

Fig. 1. Effect of HCl concentration on absorptivity of the complex in 1-pentanol. Other experimental conditions: [Mo] = $(2.0) \times 10^{-6}$ M; [NH$_4$SCN] = 0.5 M; [MTOAC] = 0.05 M; [PBITU] = 5.0×10^{-3} M.

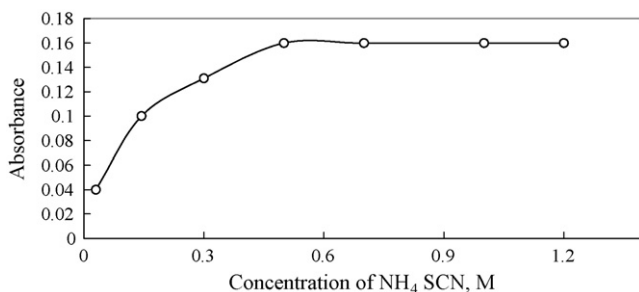**Fig. 2.** Effect of NH$_4$SCN concentration on absorptivity of the complex in 1-pentanol. Other experimental conditions: [Mo] = $(2.0) \times 10^{-6}$ M; [HCl] = 3.0 M; [MTOAC] = 0.05 M; [PBITU] = 5.0×10^{-3} M.
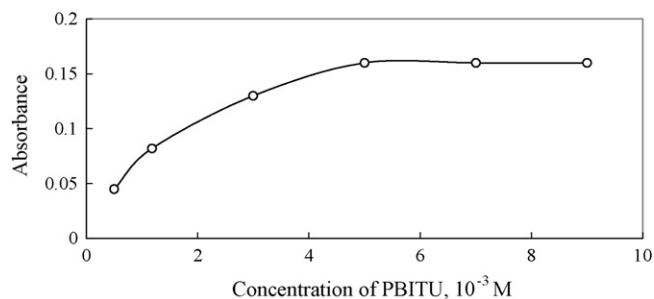
Fig. 3. Effect of PBITU concentration on absorptivity of the complex in 1-pentanol. Other experimental conditions: $[Mo] = (2.0) \times 10^{-6}$ M; $[HCl] = 3.0$ M; $[NH_4SCN] = 0.5$ M; $[MTOAC] = 0.05$ M.

3.1.3. Effect of surfactants

The absorptivity of the thiocyanate complex was increased by the addition of different types of cationic surfactants like, methyl trioctyl ammonium chloride (MTOAC), cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide (CTAB), dodecyltrimethyl ammonium bromide (DTAB). From these, MTOAC was found to yield maximum color intensity of the complex due to the presence of higher number of carbon chain. A 0.05 M MTOAC was sufficient in further enhancement of thiocyanate complex of molybdenum.

3.1.4. Effect of N-phenyl benzimodyl thiourea

Effect of the concentration of PBITU on the extraction of molybdenum from aqueous solution was also studied. As shown in Fig. 3, at least 5×10^{-3} M of PBITU in 1-pentanol was found to be necessary for the complete extraction of the metal. Further addition of the reagent up to 9×10^{-3} M did not cause adverse effect.

3.1.5. Effect of solvents

The effect of various organic solvents on the extraction of the complex was studied using 1-pentanol, methyl isobutyl ketone, benzene and chloroform. The value of molar absorptivity of the complex was greatly affected with respect to the nature of solvent used. The complex was completely extracted into organic solvents tested. Among them, 1-pentanol was chosen as the extracting solvent for further studies, due to highest value of absorptivity of the complex, shown in Fig. 4.

3.1.6. Effect of other conditions

Addition of strong electrolyte such as KCl and NaCl up to 1.0 M in the aqueous solution did not affect the extraction of the molyb-
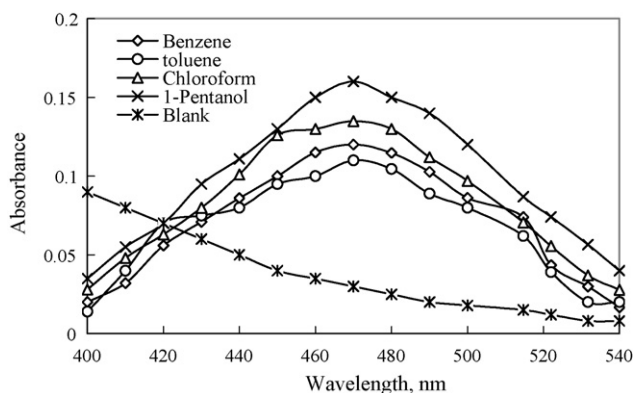

Fig. 4. Effect of various solvents on absorptivity of the complex. Other experimental conditions: $[Mo] = (2.0) \times 10^{-6}$ M; $[HCl] = 3.0$ M; $[NH_4SCN] = 0.5$ M; $[MTOAC] = 0.05$ M; $[PBITU] = 5.0 \times 10^{-3}$ M.

Table 1
Tolerance limit of the diverse ion in the determination of molybdenum ($200\,ng\,mL^{-1}$)

Ion added	Tolerance limit ($\mu g\,mL^{-1}$)[a]
Nb^{5+}	40
Ag^+, Hg^{2+}, Ti^{4+}, V^{3+}, Zn^{2+}	500
Bi^{3+}, W^{6+}, Fe^{3+}, Re^{7+}, Co^{2+}, Cu^{2+}, F^-	800
$C_2O_4{}^{2-}$, $AsO_4{}^{3-}$, tartrate	1000
Cd^{2+}, La^{2+}, Al^{3+}, EDTA, citrate	1300
Ni^{2+}, Cr^{3+}, Mn^{2+}	2000

[a] Causing error of <±2%.

Table 2
Determination of molybdenum in water

Water samples[a]	Molybdenum by present method		Molybdenum by ETAAS method	
	$ng\,mL^{-1}$	R.S.D. ($n=5$), ±%	$ng\,mL^{-1}$	R.S.D. ($n=5$), ±%
River	25.4	1.3	26.0	2.6
Pond	60.0	1.4	61.2	2.5
Municipal	200.4	1.5	202.1	2.9
Industrial	350.3	1.6	348.8	3.1
Rain	30.6	1.3	29.8	2.9
Well	20.5	1.6	21.0	3.8

[a] 1 mL volume of water sample used for analysis.

denum complex. An extraction time of 5 min was sufficient for the complete extraction of the metal and prolonged extraction up to 10 min had no adverse effect. The extract was stable for at least 2 h at room temperature.

3.2. Optimum concentration range, detection limit, precision and sensitivity

The calibration curve was found to be linear up to $1000\,ng\,mL^{-1}$ of molybdenum with slope, intercept and correlation coefficient of 0.81, 2.5×10^{-3} and +0.999, respectively. The detection limit of the method was found to be $5\,ng\,mL^{-1}$. The relative standard deviation (R.S.D.) of the method at $200\,ng\,mL^{-1}$ Mo (V) was found to be ±1.4% ($n=6$). The value of apparent molar absorptivity of the complex was $7.6 \times 10^4\,L\,mol^{-1}\,cm^{-1}$ at 470 nm.

3.3. Reaction mechanism and composition of the complex

The thiocyanate ions spontaneously react with Mo (V) giving red colored complex in acidic aqueous solution depending upon the analytical conditions. Their color intensity is proportional to the number of SCN^- ligands coordinated to the molybdenum. The color intensity of the Mo(V)–thiocynate complex in the presence of MTOAC was further increased. Then, the complex was extracted

Table 3
Determination of molybdenum in soil and root nodule

Samples	Molybdenum by present method		Molybdenum by ETAAS method	
	$ng\,g^{-1}$	R.S.D. ($n=5$), ±%	$ng\,g^{-1}$	R.S.D. ($n=5$), ±%
Soil				
Agricultural	150.5	1.4	151.2	2.8
Industrial	250.6	1.3	249.4	2.3
Forest	200.2	1.4	201.0	2.5
Residential	60.5	1.5	59.2	3.8
Root nodule				
Soybean	55.0	1.6	53.8	2.2
Peanut	15.5	1.4	16.5	3.9
Black gram	21.6	1.3	22.3	3.0
Green gram	25.0	1.7	25.8	2.3

Table 4
Determination and recovery of molybdenum in urine

Samples	Molybdenum ($ng\,mL^{-1}$)					
	Proposed method (a)	Added (b)	Total by proposed method (c)	Difference ($c - a$)	Recovery, % $[(c - a)/b] \times 100$	R.S.D., $\pm$%
1	32.4	20.0	51.9	19.5	97.5	1.2
2	ND	20.0	19.2	19.2	96.0	1.6
3	15.0	20.0	34.6	19.6	98.0	1.8
4	44.6	10.0	54.1	9.5	95.0	1.2
5	ND	10.0	9.8	9.8	98.0	1.0
6	25.0	10.0	34.1	9.1	91.0	1.7

ND = not detected.

Table 5
Comparison of present method with other spectrophotometric methods

Reagent	λ_{max} (nm)	L ($mol^{-1}\,cm^{-1}$)	Linear range ($ng\,mL^{-1}$)	Remarks	Ref.
Alizarin Red S	500	2.1×10^4	50–5500	Cu^{2+}, Al^{3+} and Fe^{3+} interfere	[20]
Thiocyanate + Rhodamine 6G	570	1.1×10^5	90–1100	Pb^+, Fe^{3+}, Co^{2+}, Cu^{2+}, Al^{3+}, Zn^{2+} interfere and masking agent is used	[27]
Thiocyanate + tin cholride	462	2.0×10^4	1000–8000	W^{6+}, Cu^{2+}, Co^{2+}, Fe^{3+} interfere and masked by citric acid	[28]
4-Nitrocatechol + tetrazolium blue chloride	445	2.38×10^4	200–6700	Fe^{3+}, Al^{3+}, and Cr^{3+}	[29]
Thiocyanate + N-octylacetamide	470	3.5×10^4	30–600	–	[18]
3,4,5-Trihydroxy benzoic acid	245	1.67×10^4	150–3000	–	[18]
Thiocyanate + MTOAC + PBITU	470	7.6×10^4	20–1000	None of the metal ions interfere	Present method

with PBITU in 1-pentanol. The composition of the complex was evaluated by the curve-fitting method by plotting the log distribution ratio of the metal vs. log molar concentration of the reagent taken [26]. The ratio of Mo (V), SCN^-, $MTOA^+$, PBITU in the complex was found to be 1:4:1:1. Thus, the probable overall extraction mechanism can be expressed as

$$MoO^{3+} + 4SCN^- + MTOA^+ + PBITU \rightarrow [MoO(SCN)_4]MTOA\,[PBITU]_o$$

where subscript 'o' represents the organic phase.

3.4. Effect of diverse ions

The effect of diverse ions in the determination of $200\,ng\,mL^{-1}$ molybdenum was studied as per the procedure. The tolerance limits of the various diverse ions are summarized in Table 1.

3.5. Application of present method in environmental, biological and reference standard samples

The present method was successfully applied for the determination of molybdenum in environmental, biological samples and reference standard samples. A 1 mL of pretreated sample of water/soil/nodules or urine was added to separatory funnel and followed by the addition of 3 mL 10 M HCl, 1 mL ammonium thiocyanate and MTOAC. The solution was diluted to 10 mL with deionized water, and then the colored complex was extracted with 5 mL 1-pentanol containing PBITU for 5 min. The concentration of molybdenum found in different types of water, soil and root nodule are given in Tables 2 and 3. The results obtained from soil and root nodules by the spectrophotometric method were found to be excellent agreement with those obtained by ETAAS at the optimized conditions. In addition, the present method was further extended for the determination of molybdenum in urine samples. The concentration of molybdenum in urine sample is given in Table 4.

In order to evaluate the practical applicability of the present method, accuracy of method was investigated by performing recovery in urine samples. The urine samples were spiked with 10 and $20\,ng\,mL^{-1}$ of molybdenum. The good recoveries between 91.0 and 98.0%, show the effectiveness for the extraction and determination of molybdenum from complex biological samples. The results of recovery studies obtained in urine samples are given in Table 4. The proposed method was validated by the determination of molybdenum in certified reference materials, light sandy soil (BCR CRM 142R), and calcareous loam soil (BCR CRM 141R). The determination of molybdenum in reference material was performed as similar to the procedure of soil analysis. The concentration of molybdenum in BCR CRM 142R and BCR CRM 141R were 0.40 ± 0.14 and 3.7 ± 0.5, which agreed with the certified value of 0.45 ± 0.10 and 3.5 ± 0.4, respectively.

3.6. Comparison of present method with other spectrophotometric methods

The performance of the method was compared with other spectrophotometric methods with respect to rapidity, selectivity and sensitivity for the determination of molybdenum (Table 5).

4. Conclusions

The proposed method is simple, sensitive and reproducible for the rapid spectrophotometric determination of molybdenum in different types of water, soil, root nodules and urine samples. The selectivity and sensitivity of the present method is better than other reported spectrophotometric methods. The promising features of the proposed method are quantitative surfactant-mediated liquid–liquid extraction and interferences-free measurements from all probable cations and anions. This method could be highly useful for the routine monitoring of molybdenum in environmental and biological samples.

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