

## Spectrophotometric determination of molybdenum using surfactant-mediated liquid–liquid extraction

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**Abstract:** A new spectrophotometric method has been developed for determination of molybdenum using surfactant-mediated liquid–liquid extraction. Molybdenum(V) obtained by ascorbic acid reduction in 2.5 M H<sub>2</sub>SO<sub>4</sub> reacted spontaneously with thiocyanate and cetyl trimethyl ammonium bromide (CTAB), forming an intense orange yellow complex that was extracted quantitatively into 1,2-dichloroethane and absorbed at 460 nm. The absorbance of the extract was found to be stable for more than 24 h. Beer's law was obeyed over the concentration range 0.1–4.2 μg Mo mL<sup>-1</sup> of the extract. The linear range for an accurate determination was found to be 1.2–2.6 μg Mo mL<sup>-1</sup>. The molar absorptivity and LOD of the procedure were 4.01 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> and 0.00239 μg Mo mL<sup>-1</sup>, respectively. The stoichiometry of the orange yellow complex (Mo:SCN:CTAB) was found to be 1:3:2. The effect of a large number of cations, anions, and complexing agents was studied. For 10 replicate determinations of 1 μg Mo mL<sup>-1</sup>, the standard deviation was 0.014 concentration units with a relative mean error of ±0.38%. The method developed was applied for determination of molybdenum in various alloy steels and a wide variety of biological and environmental samples, including different types of water samples.

**Key words:** Molybdenum, thiocyanate, spectrophotometry, extraction, cetyl trimethyl ammonium bromide, 1,2-dichloroethane

### 1. Introduction

Molybdenum plays an important role as an element of interest in various fields of modern science, engineering, and agriculture.<sup>1–3</sup> Moreover, at trace levels it is a bio-essential nutrient for all living organisms, especially for plants, animals, and microorganisms.<sup>4</sup> Recent studies have shown that molybdenum is an important element in promoting healthy teeth.<sup>5</sup> It is also added in micro amounts to vital supplements and specialized medicines. Its biochemical role is extremely important in the nitrogen metabolism of plants, where it is necessary for the fixing of atmospheric nitrogen by bacteria at the start of protein synthesis. Addition of trace amounts of molybdenum to fertilizers leads to increased crop yields.

On the other hand, prolonged exposure to molybdenum in the environment can cause toxicity to humans, animals, and plants.<sup>6</sup> Molybdenum(VI) raises the lability of blood pressure and reduces cholesterol transportation.<sup>7</sup> These ions also decrease catalase activity, which causes an increase in uric acid concentrations in organisms, leading to podagra. The presence of molybdenum in water samples at about 5 mg L<sup>-1</sup> level in-

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hibits biochemical self-purification processes of water. An even higher content of molybdenum in water prevents the growth of some microorganisms.<sup>4</sup>

Therefore, for a chemist, an accurate and precise determination of molybdenum at trace levels is a prime necessity to know the levels of exposure to this element. Although there are several highly sensitive analytical techniques for determination of molybdenum, such as inductively coupled plasma atomic emission spectrometry,<sup>8</sup> inductively coupled plasma mass spectrometry,<sup>9</sup> flame atomic absorption spectrometry,<sup>10</sup> and neutron activation analysis,<sup>11</sup> these techniques require the use of rather sophisticated and high cost instruments. A literature survey revealed that spectrophotometric methods are most commonly used. Although there are many spectrophotometric methods<sup>12–20</sup> using different reagents, as they are prone to many interferences<sup>17–19</sup> and suffer from low sensitivity<sup>12–20</sup> these are not suitable for routine analysis of the metal.

Our aim in the present study was to develop a simple, sensitive, and highly selective spectrophotometric method for the trace determination of molybdenum. In the present work, a new method has been developed for extraction and spectrophotometric determination of Mo(V) using thiocyanate and cetyl trimethyl ammonium bromide (CTAB) as a surfactant that can be successfully applied for the analysis of varieties of steel, reverberatory flue dust, different type of water samples, including industrial effluents, and a wide variety of synthetic samples of diverse matrix.

## 2. Experimental

### 2.1. Instrument

A double beam UV-VIS spectrophotometer (ELICO SL164) with 10-mm matched cells was used for absorbance measurements.

### 2.2. Reagents and solutions

Molybdenum solution: An accurately weighed amount of sodium molybdate dihydrate (E Merck, A.R.) was dissolved in deionized water to get a stock solution of molybdenum(VI) containing  $10 \text{ mg mL}^{-1}$  and standardized by the oxine method.<sup>21</sup> The working standard solutions at lower concentration levels ( $\mu\text{g mL}^{-1}$ ) were prepared by suitable dilutions of the stock solution.

Solutions of other diverse metal ions were prepared by dissolving their salt (A.R.) in deionized water or dilute acids for the interference studies and for preparation of synthetic samples.

Sulfuric acid (5 M) was prepared by suitable dilution of 17.8 M  $\text{H}_2\text{SO}_4$  (RANBAXY, density  $1.84 \text{ g mL}^{-1}$ , 98%).

Ascorbic acid (S.R.L., A.R.) was used as solid.

A  $10^{-3}$  M solution of cetyl trimethyl ammonium bromide (CTAB, s d Fine Chemicals Ltd, A.R.) was prepared in deionized water.

Ten percent KSCN (s d Fine Chemicals Ltd, A.R.) was prepared by dissolving an accurately weighed amount in water.

### 2.3. Samples

Synthetic and technical samples: Molybdenum solution was mixed with solutions of other diverse metal ions in suitable proportions to get synthetic samples of desired composition. Well water, steels [BCS(261/1),

BCS(406/1), and BCS(219/4)], and reverberatory flue dust samples were prepared as reported earlier<sup>22</sup> and suitable aliquots were subjected to Mo determination by the proposed procedure.

### 2.3.1. Canal water

A known amount of molybdenum (15  $\mu\text{g}$ ) was added to a 10-mL water sample taken from the Western Yamuna Canal at Yamuna Nagar. After adding 1 mL of hydrogen peroxide (6% w/v) and 2 mL of aqueous ammonia, the contents were boiled and evaporated to dryness. The residue was dissolved in 3 mL of 2 M  $\text{H}_2\text{SO}_4$  and subjected to analysis for Mo by the proposed method.

### 2.3.2. Industrial effluent

An industrial effluent sample (1 L) was collected from the main outlet of effluents of metal industries located in twin cities, Yamuna Nagar and Jagadhri, into which a solution of known molybdenum content (2 mg) was mixed. To a 10-mL aliquot of the sample solution were added 1 mL of hydrogen peroxide (6% w/v) and 2 mL of aqueous ammonia. After boiling and evaporating to dryness, the resulting mass was leached with 5 mL of 2 M  $\text{H}_2\text{SO}_4$  and subjected to Mo determination by the proposed procedure.

### 2.3.3. Biological samples

An accurately weighed amount of the dried and powdered sample (1.0 g of agricultural soil or soybean nodules, 100 mesh) was taken in a 100-mL Teflon beaker to which 5 mL of 70%  $\text{HClO}_4$  and 10 mL of 40% HF were added. The contents were homogenized and slowly heated to dryness and the dried mass was leached with 50 mL of 2 M  $\text{H}_2\text{SO}_4$ . After filtration, a 1-mL aliquot was taken each time and subjected to Mo determination by the proposed procedure.

## 2.4. Procedure

An aliquot of the sample solution containing  $\leq 42 \mu\text{g Mo}^{VI}$  and other metal ions was transferred to a 25-mL beaker covered with a watch glass. To this solution were added 2.5 mL of 5 M  $\text{H}_2\text{SO}_4$  and 100 mg of solid ascorbic acid to reduce  $\text{Mo}^{VI}$  to  $\text{Mo}^V$  state. This was followed by addition of 1 mL of 10% KSCN and 3 mL of  $10^{-3}$  M CTAB. Finally the aqueous phase was diluted with deionized water to raise the volume to 10 mL. The contents were heated on a hot plate to 50 °C and allowed to stand for 10 min at room temperature. After transferring to a separatory funnel (100 mL), the contents were equilibrated gently with an equal volume (10 mL) of 1,2-dichloroethane for 2 min. After equilibration the 2 phases were allowed to separate and the organic phase was collected in a 10-mL measuring flask after passing through a piece of Whatman filter paper No. 41 (9-cm size, pretreated with the organic solvent) to remove water droplets. The absorbance of the extract was measured at 460 nm against the pure solvent. The amount of molybdenum was computed from a calibration curve drawn under identical conditions.

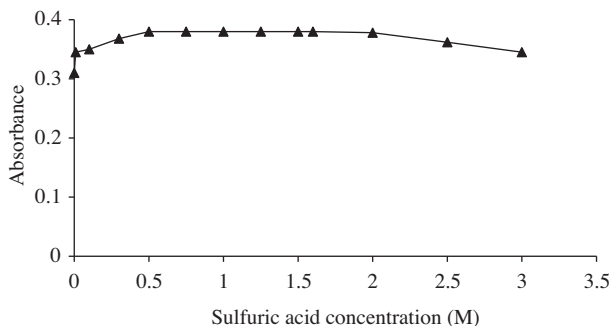
## 3. Results and discussion

In an acidic medium,  $\text{Mo}^{VI}$  reacts with thiocyanate and CTAB imparting a greenish yellow color that is not extracted into 1,2-dichloroethane. However,  $\text{Mo}^V$  obtained by ascorbic acid reduction in  $\text{H}_2\text{SO}_4$  medium also reacted spontaneously with thiocyanate and CTAB forming an intense orange yellow complex that was extracted quantitatively into 1,2-dichloroethane and absorbed at 460 nm. The absorbance of the extract was found to be stable for more than 24 h.

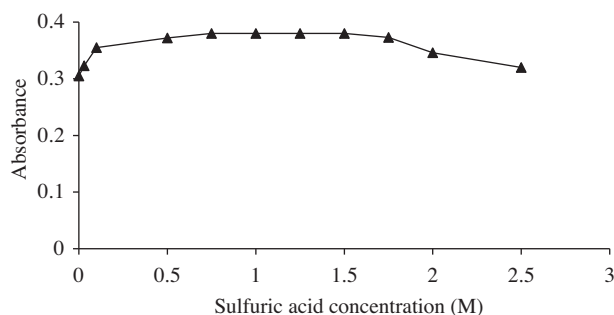
### 3.1. Effect of varying experimental conditions

The influence of experimental conditions on the absorbance of the complex was studied, keeping molybdenum concentration at  $1.0 \times 10^{-5}$  M. Other conditions were kept the same as in the procedure, except where the relevant parameter was varied.

- i) Choice of solvent: The complex was quantitatively extracted in a single contact with an equal volume (10 mL) each of 1,2-dichloroethane, ethyl methyl ketone, ethyl acetate, and *n*-amyl alcohol. However, its absorbance decreases in the above order. The extraction was found to be partial in chloroform, *iso*-amyl alcohol, *iso*-amyl acetate, and *iso*-butyl methyl ketone and the color of the extract diminished with time. The complex was not extracted at all in toluene or cyclohexane. Further, extraction in 1,2-dichloroethane was found to be clear and quantitative with satisfactory sensitivity and stability of the complex for 24 h. Hence, 1,2-dichloroethane was selected as a solvent for further studies.
- ii) Effect of acidity: The metal complex showed maximum and stable absorbance when the reduction and extraction were carried out with ascorbic acid in  $H_2SO_4$  medium. The absorbance was found to be decreasing in the order:  $H_2SO_4 > HCl > CH_3COOH > H_3PO_4$ . Hence, the effect of concentration of  $H_2SO_4$  both on reduction and extraction behavior was studied in terms of the absorbance of the complex in the extract. The maximum and constant absorbance was obtained when the reduction was achieved using solid ascorbic acid in the aqueous phase containing 0.5–2.0 M  $H_2SO_4$  (Figure 1) and the extraction was performed at 0.75–1.75 M  $H_2SO_4$  (Figure 2) acidity range. Therefore, the acid concentration was maintained at 1.25 M  $H_2SO_4$  for further studies.



**Figure 1.** Effect of acid concentration on the absorbance of Mo-SCN-CTAB complex in reduction step.

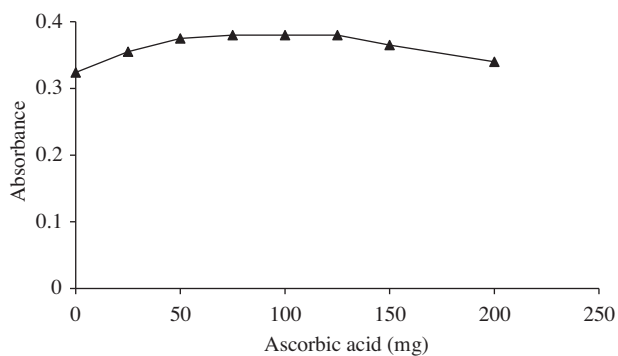


**Figure 2.** Effect of acid concentration on the absorbance of Mo-SCN-CTAB complex in extraction step.

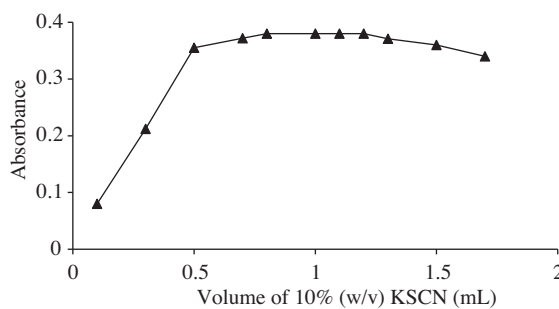
- iii) Effect of nature and concentration of reductant: The pentavalent molybdenum can be obtained by reduction of hexavalent molybdenum with different reducing agents such as ascorbic acid, hydrazine sulfate, Sn(II)-HCl, thiourea, dithionite, and Zn-Hg amalgam. Reduction with hydrazine sulfate in 1 M HCl and  $H_2SO_4$  is not advantageous as it provides low absorbance. Reduction with Sn(II)-HCl is not quantitative and furthermore higher amounts of Sn(II) interfere seriously during determination of molybdenum due to formation of a highly extractable (more than 90%) greenish yellow complex with the reagent. Very low absorption values were obtained when reduction was carried out with thiourea, dithionite, or Zn-Hg amalgam due to reduction of molybdenum to much lower oxidation states. However, a maximum and constant absorbance was obtained only when Mo(VI) was reduced by adding ascorbic

acid to an aqueous phase well before the addition of the reagent. Further, it was observed that varying ascorbic acid concentration in a total 10 mL of aqueous phase gave constant and maximum absorbance for 75–125 mg ascorbic acid, while a higher amount of it decreased the absorbance significantly (Figure 3). Hence, 100 mg of ascorbic acid was used for further studies.

- iv) Effect of KSCN concentration: It was observed that the absorbance of the complex in the extract increased initially with an increase in the concentration of KSCN, attaining a maximum and constant value for 0.8–1.2 mL of 10% (w/v) KSCN solution in a single extraction (Figure 4). The absorbance was found to decrease slightly at higher concentration. Therefore, concentration of KSCN in aqueous phase was fixed at 1.0% (w/v) level for further investigations.

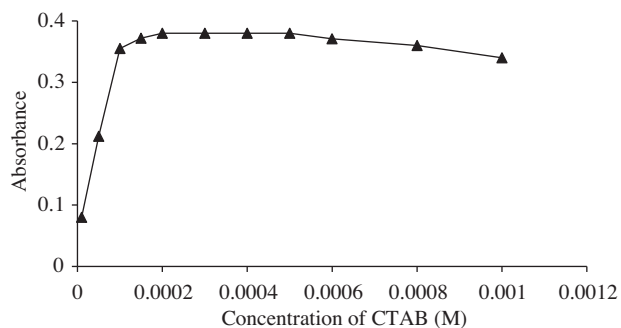


**Figure 3.** Effect of the amount of ascorbic acid on Mo–SCN–CTAB absorbance of the complex.

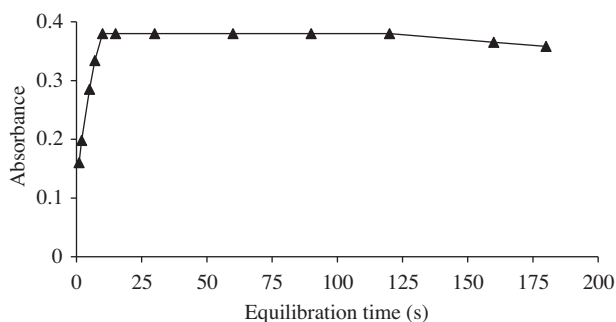


**Figure 4.** Effect of KSCN concentration on the absorbance of MoSCNCTAB complex.

- v) Effect of CTAB concentration: The effect of the nature and concentration of the surfactant on absorbance of the thiocyanate complex was studied. The absorbance of the thiocyanate complex increased in the presence of different types of surfactants such as cetyl trimethyl ammonium bromide (CTAB), tri-*n*-octyl amine (TOA), cetyl pyridinium chloride (CPC), dodecyltrimethyl ammonium bromide (DTAB), and methyl trioctyl ammonium bromide (MTAB). Out of these, CTAB provided maximum absorbance with clear separation of the 2 layers after extraction. The absorbance of the complex reached a maximum and constant value for 2–5 mL of  $10^{-3}$  M CTAB (Figure 5). At higher concentration absorbance decreased significantly due to the appearance of turbidity. Hence,  $3 \times 10^{-4}$  M CTAB was selected for further studies.
- vi) Effect of equilibration time: An extraction time of 2 min was sufficient for complete extraction of the metal complex (Figure 6). The extract was stable for at least 24 h at room temperature.
- vi) Effect of heating temperature: The absorbance of the complex in the extract increases with time. It was found that the color intensity became stable when the aqueous phase was heated at 40–55 °C for 1 min, beyond which the absorbance decreased. Therefore, the aqueous phase was heated for 1 min at 40–55 °C each time before the extraction step. Further, the absorbance values obtained after heating were found to be highly reproducible.



**Figure 5.** Effect of CTAB concentration on the absorbance of Mo-SCN-CTAB complex.

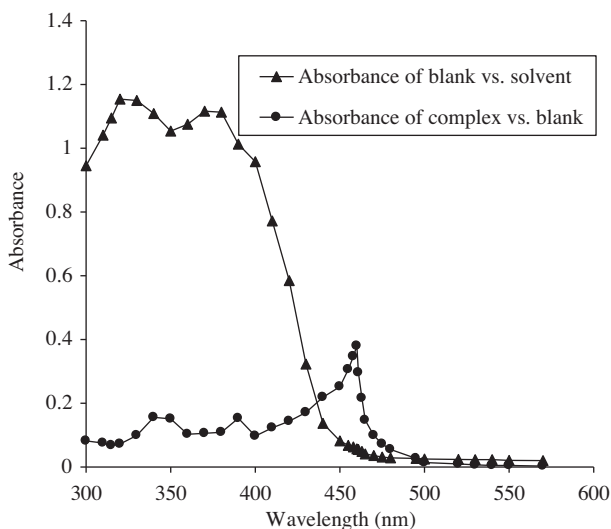


**Figure 6.** Effect of equilibration time on the absorbance of Mo-SCN-CTAB complex.

vii) Effect of color development time: It was found that absorbance attained a constant and maximum value when the solution was kept for 10 min at room temperature and there was no further increase in the intensity when more color development time was allowed. Therefore, a color development time of 10 min was sufficient for maximum and reproducible intensity; however, prolonging the time up to 15 min had no adverse effect. Hence, a minimum 10 min color development time was selected for further studies.

### 3.2. Spectral characteristics and Beer's law range

The absorption spectrum of the orange yellow Mo-SCN-CTAB complex recorded against reagent blank indicated that under optimum conditions the extracted species absorbed maximally at 460 nm where the reagent blank itself absorbed negligibly against the pure solvent (Figure 7). Therefore, all the absorbance measurements were carried out at 460 nm against the pure solvent.



**Figure 7.** Absorption spectra of Mo-SCN-CTAB complex.

Beer's law was obeyed over the concentration range  $0.1\text{--}4.2 \mu\text{g Mo mL}^{-1}$  of the extract. However, the range of an accurate determination was found to be  $1.2\text{--}2.6 \mu\text{g Mo mL}^{-1}$  from a Ringbom plot.<sup>23</sup> The molar absorptivity and LOD of the procedure were  $4.01 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.00239 \mu\text{g Mo mL}^{-1}$ , respectively.

### 3.3. Stoichiometry of the complex

The stoichiometry of the orange yellow complex (Mo:SCN:CTAB) was studied by Job's method of continuous variations<sup>24</sup> as modified by Vosburgh and Cooper<sup>25</sup> for the 2-phase system (Figure 8). The absorbance values were recorded at 2 wavelengths, namely 440 and 460 nm. The curves were indicative of 1:3 stoichiometry for Mo:SCN and 1:2 for Mo:CTAB. This stoichiometric ratio was further confirmed by the mole ratio method<sup>26</sup> at  $1.04 \times 10^{-3}$  M concentration measuring the absorbance at both wavelengths.

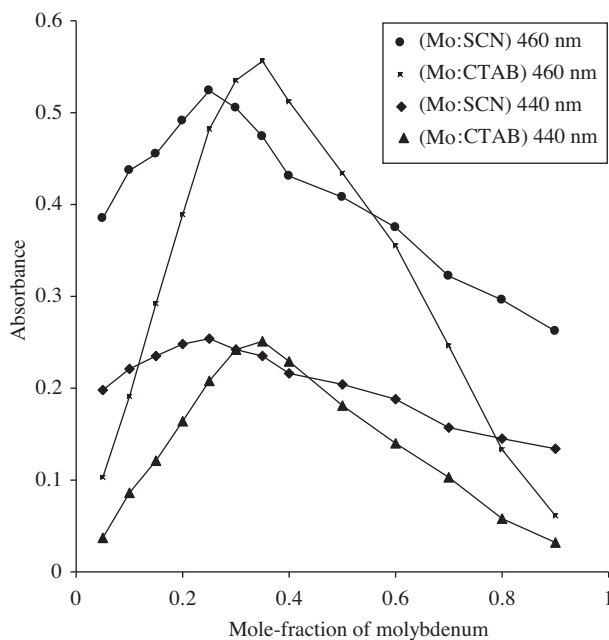


Figure 8. Job's continuous variations method.

### 3.4. Effect of diverse ions

Various cations such as Cu(II), Fe(II and III), V(V), Cr(III), Mn(II), Ni(II), Cd(II), Zn(II), Zr(IV), Se(VI), Ce(IV), Th(IV), Mg(II), Sb(III), Hg(II), Pb(II), Al(III), Co(II), Ca(II), Mg(II), Ba(II), Sr(II), and As(III) (5000 fold each); Re(VII), Pt(IV), Ag(I), and Au(III) (100-fold each, higher amounts were not tested) did not affect the absorbance of Mo(V) complex when present in 10 mL of the aqueous phase. Lower amounts of Ti(IV) (250-fold) and Sn(II) (100-fold) also did not interfere.

Under the optimum conditions, the effect of various anions/complexing agents was studied. Acetate (60,000-fold); carbonate, chloride, bromide, iodide, nitrate, fluoride, citrate, tartrate, tetraborate, and phosphate (50,000-fold each); thiourea and oxalate (1000-fold each); and hydrogen peroxide (0.5 mL of 6%) did not interfere.

### 3.5. Applications

The present procedure was applied for the determination of molybdenum in industrial, environmental, biological, and reference standard samples. The applicability of the method straightaway to a wide variety of synthetic and technical samples is shown in Tables 1 and 2 by the satisfactory accuracy and precision. This procedure has the advantages<sup>27-33</sup> of better sensitivity (Table 3), selectivity, wider Beer's law range, accuracy, and applicability to samples having several interfering elements in concentrations higher than those normally encountered.<sup>34</sup>

**Table 1.** Determination of molybdenum in synthetic (spiked) samples.

Sr. no.	Composition of sample	Mo added/ $\mu\text{g}$	Mo found <sup>b</sup> / $\mu\text{g}$
	Matrix <sup>a</sup>		
1	Zn(0.4), Th(0.1), Cd(1.9)	10	10.20
2	Cr(0.8), Co(2.5), Cu(3)	20	20.05
3	Zn(3.5), Cu(2.0), Mn(3)	25	24.86
4	Ag(1.0), Re(0.1), Ba(2)	25	25.10
5	V(0.5), Cr(0.5), Cu(0.5), Fe(1.5)	15	15.05
6	Pt(0.1), Au(0.1), Mg(3)	20	19.80
7	[Co(0.0004), Cu(0.0075), Mn(0.015), Ni(0.0563), Cr(0.015), Fe(0.2175)] <sup>c</sup>	15	15.15
8	[Cu(0.01), Ni(0.0912), Cr(0.190), Fe(0.70)] <sup>c</sup>	10	10.18
9	[Mn(0.033), Ni(0.33), Cr(0.4665), Fe(2.6655)] <sup>c</sup>	15	15.05
10	Well water	20	19.95 $\pm$ 0.19 <sup>d</sup>
11	Canal water	15	15.10 $\pm$ 0.11 <sup>d</sup>
12	Industrial effluent	20	19.90 $\pm$ 0.17 <sup>d</sup>
13	Reverberatory flue dust	20	20.56 $\pm$ 0.18 <sup>d</sup>

<sup>a</sup> Number in brackets indicates mg amounts of elements in the aliquot for analysis. <sup>b</sup> Average of triplicate analyses.

<sup>c</sup> Sample no. 7, 8, and 9 are analogous to stainless steel, stainless U, and cast steel, respectively. <sup>d</sup> Mean  $\pm$  relative standard deviation (n = 6).

**Table 2.** Determination of molybdenum in real (nonspiked) samples.

Sr. no.	Composition of sample	Mo present/ $\mu\text{g}$	Mo found/ $\mu\text{g}$
1	BCS (406/1)	1.00% <sup>e</sup>	0.915 $\pm$ 0.012% <sup>d</sup>
2	BCS (261/1)	0.11% <sup>e</sup>	0.112 $\pm$ 0.01% <sup>d</sup>
3	BCS (219/4)	0.58% <sup>e</sup>	0.598 $\pm$ 0.004% <sup>d</sup>
4	Agriculture soil	0.156% <sup>f</sup>	0.161 $\pm$ 0.011% <sup>d</sup>
5	Soybean root nodule	0.048% <sup>f</sup>	0.044 $\pm$ 0.02% <sup>d</sup>

<sup>d</sup> Mean  $\pm$  relative standard deviation (n = 6). <sup>e</sup> Certified value. <sup>f</sup> Molybdenum determined by AAS method.

**Table 3.** Comparison of the proposed method with the existing methods of molybdenum determination.

Sr. no.	Initial aqueous conditions	i) Solvent used ii) $\lambda_{\text{max}}$ (nm)	i) Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ ) ii) Sandell's sensitivity ( $\mu\text{g Mo cm}^{-2}$ )	Beer's law range ( $\mu\text{g Mo mL}^{-1}$ )	Reference number
1.	Mo(VI), HCl, $\text{SCN}^-$ , $\text{SnCl}_2$	i) Isopentyl alcohol ii) 467	i) $1.37 \times 10^4$ ii) 0.007	---	27
2.	Mo(VI), $\text{H}_2\text{SO}_4$ , thiourea, KSCN	i) --- ii) 460	i) $1.96 \times 10^4$ ii) ---	0–3.0	30
3.	Mo(V), $\text{SCN}^-$ , 2,2'-dipyridyl	i) Chloroform ii) 505	i) $1.24 \times 10^4$ ii) 0.0075	0–11.0	31
4.	Mo(VI), HCl, $\text{SCN}^-$ , pyridine-thiosemicarbazone	i) $\text{CHCl}_3$ ii) 470	i) $1.7 \times 10^4$ ii) 0.0056	0.1–6.5	32
5.	Mo(V), HCl, $\text{SCN}^-$ , N <sup>1</sup> -OH-N <sup>2</sup> -N <sup>2</sup> -diphenylbenzamidine	i) Amyl alcohol in benzene ii) 470	i) $1.31 \times 10^4$ ii) ---	0.5–9.6	33
6.	Mo(VI), $\text{H}_2\text{SO}_4$ , ascorbic acid, KSCN, CTAB	i) 1,2-Dichloroethane ii) 460	i) $4.01 \times 10^4$ ii) 0.00239	0.1–4.2	Proposed method



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