



SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF Mo(VI) BY USING ACETOPHENONE 2',4'-DIHYDROXY SEMICARBAZONE AS AN ANALYTICAL REAGENT

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ABSTRACT

Acetophenone 2',4'-dihydroxy semicarbazone (A24DHS) as a photometric reagent for the extractive spectrophotometric determination of Molybdenum (VI) is presented in this paper. The reagent A24DHS gave instantaneous and stable yellow colour with Molybdenum (VI) in the pH range 1.6 to 2.4. The system obeys Beer's law in the concentration range of 1.0 µg/mL to 8.0 µg/mL at 370 nm. The Limit of Detection (LOD) is calculated by using standard deviation of blank solution at confidence limit 98.3%, which is found to be 0.315 µg / mL. The stoichiometry of the complex is established as 1:3 (M:L) by Job's method of continuous variation and confirmed by mole ratio method. The standard deviation and the coefficient of variance are presented. The results of the prescribed procedure applied for the determination of the micro amounts of Mo (VI) in standard steel samples, alloys, pharmaceutical and synthetic samples are presented.

KEY WORDS: Molybdenum, Spectrophotometric determination, n-Butanol, Acetophenone 2', 4'-dihydroxy, semicarbazone derivative.



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INTRODUCTION

Molybdenum is a Group 6 element with the symbol Mo and atomic number 42. Molybdenum is the 54th most abundant element in the Earth's crust and the 25th most abundant element in the oceans, with an average of 10 parts per billion; it is the 42nd most abundant element in the Universe^{1,2}. The amount of molybdenum in soils and plants has been found to be a critical factor in recent years. The metal is an important alloying element and is present as minor constituent in many industrially important materials. Even small amounts cause tremendous increase in hardness and strength. The increasing use of the metal necessitates development of rapid and sensitive methods for the determination of minute quantities of the metal. Colorimetric and Atomic Emission or Atomic Absorption methods are most commonly used for the determination of Mo (VI). However, colorimetric methods are generally preferred, as they involve less expensive instrumentation and afford better sensitivity when appropriate photometric reagents and solvent extraction pre-concentration steps are employed. Most of the extractive spectrophotometric methods developed for Mo(VI) are based on reactions with suitable colour producing reagents such as 2-(2'-furyl)-3-hydroxychromone³, quinolin-8-ol⁴, thiocyanate and pyrogallol⁵, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone⁶. However, most of the existing methods suffer from limitations such as longer periods of time for phase separations, weak stability of coloured complexes and interferences from metal ions like tungsten, tin, antimony and anions⁷. In the present paper, extractive spectrophotometric determination of Molybdenum (VI) with Acetophenone 2', 4'-dihydroxy semicarbazone (A24DHS) is presented.

EXPERIMENTAL

The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode. Shimadzu UV-Visible

2100 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements.

Reagent and chemicals

0.1% A24DHS reagent is prepared by dissolving the requisite amount of A24DHS in a known volume of methanol. All chemicals used were of analytical-reagent grade or the highest purity available. Doubly distilled de-ionized water and A.R. grade methanol, which is were used throughout.

Mo (VI) standard solutions

The stock solution of Molybdenum was prepared by dissolving weighed amount of Ammonium molybdate in doubly distilled de-ionized water. More dilute standard solutions were prepared from this stock solution as and when required.

PROCEDURE FOR THE EXTRACTION

1 mL of aqueous solution containing 2.0 µg of Molybdenum metal and 1 mL of reagent was mixed in a 50 mL beaker. The pH of the solution adjusted to 1.8, it must be noted that the total volume should not exceed 10 mL. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with n-Butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was passed through anhydrous sodium sulphate in order to absorb trace amount of water from organic phase and then collected in 10 mL measuring flask and made up to the mark with organic solvent if required. The amount of Molybdenum present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 370 nm and that in the aqueous phase was determined by dithiol method.

RESULTS AND DISCUSSION

The results of various studies are discussed below.

Extraction as a function of pH

The extraction of Molybdenum with Acetophenone 2',4'-dihydroxy semicarbazone has been studied over the

pH range 1-10 and was observed that percentage extraction of Mo(VI) is maximum at pH range 1.6 to 2.4. Thus further extraction and determination carried out at pH 1.8 (Fig. 1).

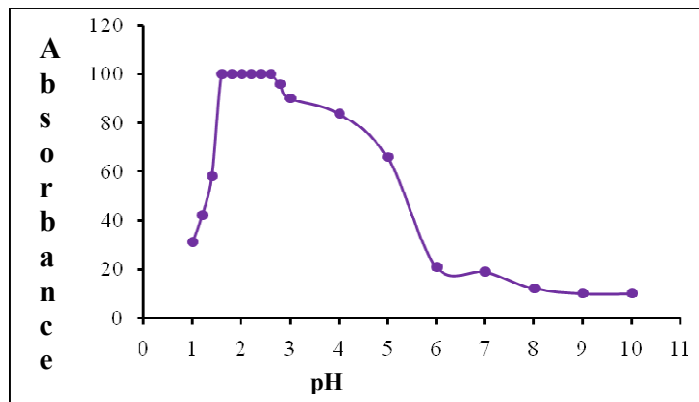


Figure 1
Extraction as a function of pH

Absorption spectrum

The absorption spectrum of Mo(VI): A24DHS in n- Butanol shows the maximum absorption at 370 nm. The absorption due to

reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 370 nm (Fig. 2).

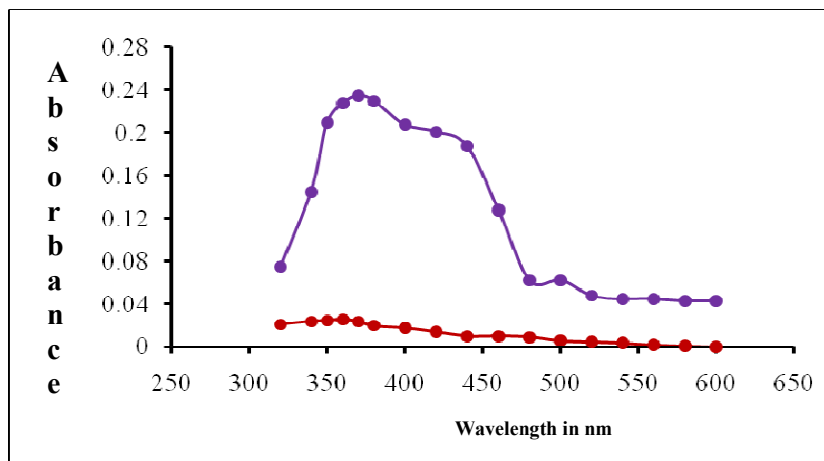


Figure 2
Absorption spectrum

Influence of diluents

The suitability of solvent was investigated using various organic solvents and the extraction of Mo(VI): A24DHS was quantitative in n-Butanol. Hence, n-Butanol was used for further extraction studies as it gave better and quicker phase separation.

Effect of reagent concentration

It was found that 1.0 mL of 0.1% reagent is sufficient for the colour development of the metal Mo(VI) in 10 mL of aqueous solution at pH 1.8.

Effect of equilibration time and stability of the complex

The equilibration time of 2.0 minute is sufficient for the quantitative extraction of Molybdenum. The stability of colour of the Mo(VI): A24DHS complex with respect to time shows that the absorbance due to extracted species is stable up to 30 hours, after which slight decrease in absorbance is observed.

Calibration plot

A linear plot was obtained when the measured absorbance values are plotted against the amount of Mo(VI) in the concentration range of 1.0 – 8.0 µg/mL at 370 nm. The Molar Absorptivity and Sandell's sensitivity were calculated and found to be 2628.82 L mol⁻¹cm⁻¹ and 0.0366 µg cm⁻² at 370 nm respectively (Fig 3).

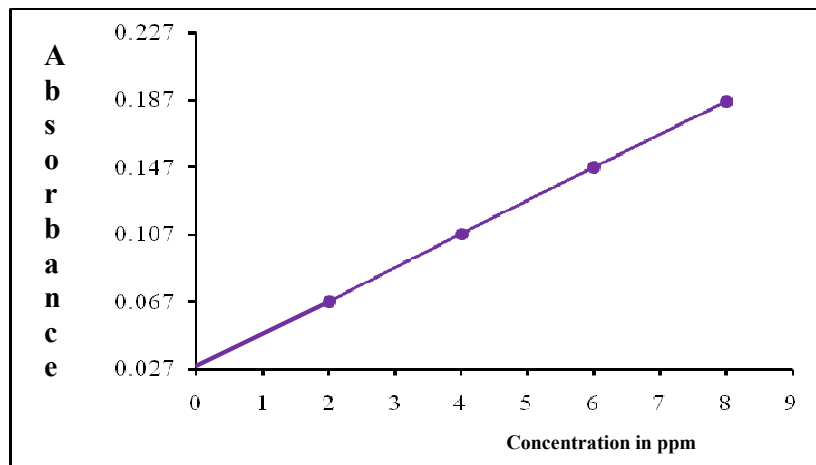


Figure 3
Calibration curve

Limit of detection (LOD)

LOD¹⁰ (Limit Of detection) of the present method was calculate at 98.3 % confidence level by analyzing blank solution with reference to solvent. Standard deviation of blank solution and slope of calibration curve use for calculating limit of detection is found to be 0.315 µg / mL.

Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of Molybdenum. The ions which show interference in the spectrophotometric determination of Molybdenum were overcome by using appropriate masking agents (Table 1).

Table 1
Use of masking agent

Sr. No.	Interfering Ion	Masking agent
1	V(V)	Controlling pH
2	Fe(III)	Sodium flouride
3	U (VI)	8-Hydroxy quinoline
4	Cu (II)	Thiasulphate
5	Ti (IV)	Ascorbic acid

Precision and accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 6.0 µg of Molybdenum in the aqueous phase. The average of ten determinations was 5.975 and variation from mean at 95% confidence limit was ± 0.0944.

Nature of extracted species

The composition of extracted Mo(VI): A24DHS complex has been determined by Job's continuous variation method, Slope ratio method and Mole ratio method. It shows that the composition of Mo(VI): A24DHS complex is 1:3. (Fig 4).

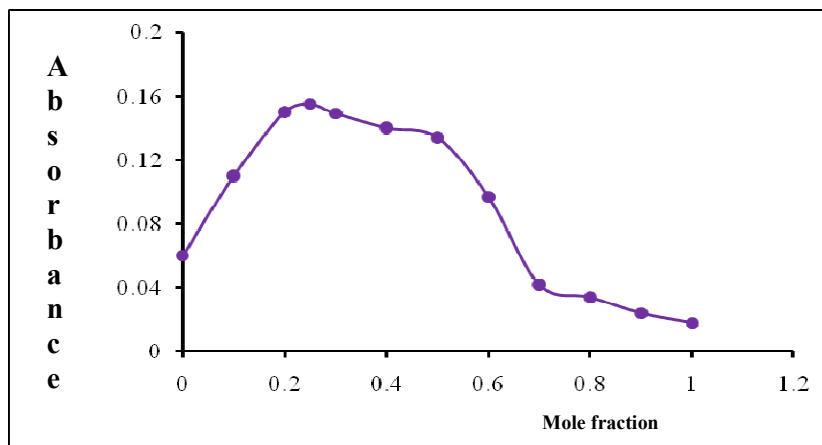


Figure 4
Job continuous variation

Application

The proposed method was successfully applied for the determination of Molybdenum from various alloys, pharmaceutical and

synthetic samples. The results found to be in good agreement with those obtained by the standard known method (Table 2).

Table 2
Applications

Sr.No.	Sample	Standard Method	Present method
Alloys			
1	Plain carbon steel(BCS320)	0.22 µg	0.219 µg
2	TZM alloy (0.3 g)	0.297 g	0.295 g
3	Mo-W steel (0.5 g)	0.350 g	0.349 g
Pharmaceutical sample			
1	Molyphen injection (USP)	25.0 µg	25.0 µg
Synthetic mixture:			
1	Mo (5) + Cr (5) + Pb (10)	4.98 ppm	4.98 ppm
2	Mo (10) + Cd (30) + V (20)	10.0 ppm	9.97 ppm

1) Each result is average of three independent determinations.
2) Compared with dithiol method

CONCLUSION

The results obtained show that the newly developed method in which the reagent A24DHS was used, can be effectively used for quantitative extraction and estimation of Mo (VI) from aqueous media. The proposed method is quick and requires less volume of organic solvent. The result show good agreement with the standard method. The method is very precise, faster and simpler than other methods. The developed method

is compared with result obtained with the dithiol method for the estimation Mo (VI) and observed to be comparable. The method is precise, accurate, less time consuming and easily employed anywhere, even in small laboratories as it requires only uv – visible spectrophotometer and not much sophisticated and costly measurement devices or instrumentation.

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