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EXTRACTIVE SPECTROPHOTOMETERIC STUDIES OF ACETOPHENONE 2', 4'- DIHYDROXY THIOSEMICARBAZONE WITH MOLYBDENUM

P. K. Rana*, R. S. Lokhande[1], S. M. Pitale[2], S.P.Janwadkar[2], P. S. Navarkar[2] and D.K.Yadav[2]

[1]Department of Chemistry, Jaipur National University, Jaipur.
[2,*]S. D. Arts, V. S. Apte Commerce and M. H. Mehta, Science College, Palghar, Thane.
*E-mail: ranaparitosh@gmail.com

ABSTRACT

A highly selective spectrophotometric method for the determination of trace amount of Molybdenum with Acetophenone 2', 4'-dihydroxy thiosemicarbazone [APDHTS] is described[1]. The reagent is synthesized in the laboratory and characterized by IR, NMR and elemental analysis for its purity. The metal Molybdenum[2] is quantitatively extracted in the solvent n-butanol at pH 1.8. The light yellow colour of Mo (VI): APDHTS complex shows maximum absorption at 430nm (λ_{max}). The study of colour change intensity of Mo (VI): APDHTS complex showed that 1cm^3 of 0.1% reagent is sufficient for the colour development with 10 sec as equilibration time. A linear calibration graph over the concentration range 1 ppm to 5 ppm with a 3σ limit of detection of 0.323 ppm was obtained by applying the spectrophotometric method. The composition of extracted species is found to be 1: 3 determined by Jobs continuous variation, Mole ratio and Slope ratio method. The molar absorptivity and Sandell's sensitivity of the complex is 0.2492 x 10^3 L / mol cm and 0.03614 µg /cm respectively. Excellent agreement with the reference method was achieved when the proposed methodology was applied for the determination of Molybdenum various samples of industrial, environmental and biological importance.

Keywords: Extractive Spectrophotometric Determination, Acetophenone 2',4'-dihydroxy thiosemicarbazone (APDHTS), Molybdenum, Beer's Law, Molar Absorptivity, Sandell's Sensitivity.

INTRODUCTION

Molybdenum is a valuable alloying agent, as it contributes to the harden ability and toughness of quenched and tempered steels. It also improves the strength of steel at high temperatures. Animal experiment has shown that too much Molybdenum causes fetal deformities. Fodder with more than 10 ppm of Molybdenum would put most livestock at risk. Molybdenum is an important mineral for human being and study reveals that 75 µg must be taken daily Doses larger than 200 µg may cause kidney problems and Copper deficiency. Some evidence of liver dysfunction with hyperbilirubinemia has been reported in workmen chronically exposed in a Soviet Mo-Cu plant[3]. The main features were joint pains in the knees, hands, feet, articular deformities, erythema, and edema of the joint areas.

It becomes necessary to be detected in such a trace amount. Among the techniques suitable for the quantification of metal ions inductively coupled plasma mass spectrometry and Atomic absorption and Emission spectroscopy are likely to be the most widely employed. However, although these techniques are reliable and sensitive[9], they suffer from the limitation of being rather costly (considering instrument acquisition and maintenance), time-consuming (with respect to sample preparation), and not always readily available[4]. Thus, simple spectrophotometric techniques, which tend to be less costly and labor-intensive, are viable alternatives to those methods requiring more sophisticated instrumentation[8].

EXPERIMENTAL

The reagent Acetophenone 2', 4'- dihydroxy thiosemicarbazone was synthesized by the given procedure. The purity of reagent was checked by TLC, and characterized by IR, NMR-spectra and elemental analysis. The 0.1 % solution of reagent was prepared using methanol. The stock solution of Mo (VI) was prepared by dissolving a weighed amount of Ammonium molybdate in double distilled water and then diluted to the desired volume with double distilled water and standardized by standard

method[1]. Working solutions of Mo (VI) were made by diluting the stock solution to an appropriate volume[5]. All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water Absorbance and pH measurements were carried out on a Shimadzu UV-Visible 2100 spectrophotometer and Elico- LI 127 pH meter respectively.

Procedure for the extraction

1.0 cm^3 of aqueous solution containing 1µg of Molybdenum metal and 1cm^3 of reagent were mixed in a 50 cm^3 beaker. The pH of the solution adjusted to 1.8. It must be noted that the total volume should not exceed 10 cm^3. The solution was transferred to 100 cm^3 separating 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 cm^3 measuring flask and made up to the mark with organic solvent if required[6]. The amount of Molybdenum present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 430 nm and that in the aqueous phase was determined by standard method[7].

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 ,thiosemicarbazone (APDHTS) has been studied over the pH range 1-10 and was observed that percentage extraction of Mo(VI) is more in the range from pH 1.5 to pH 3.0 so for further estimations the pH was adjusted to 1.8 (Fig.1).

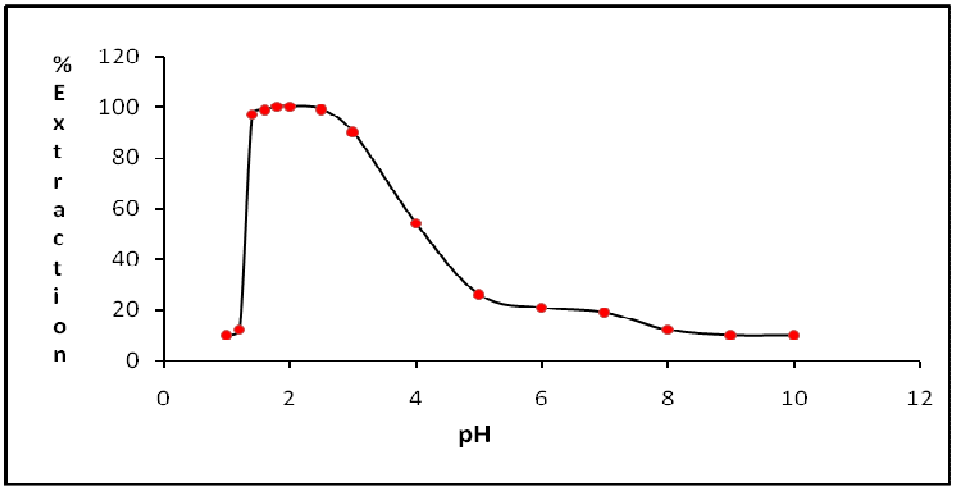

Fig.-1: Extraction as a function of pH

Absorption Spectrum

The absorption spectrum of Mo (VI): APDHTS in n-butanol was studied between the range of 200-800nm and it shows the maximum absorption at 430 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 430 nm (Fig-2).

Influence of Diluents

The suitability of solvent was investigated using various organic solvents and the extraction of Mo (VI): APDHTS 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

The varying amount of reagent was done form 1 cm^3 to 3 cm^3 and it was found that 1 cm^3 of 0.1% reagent is sufficient for the colour development of the metal Mo (VI) in 10 cm^3 of aqueous solution at pH 1.8.

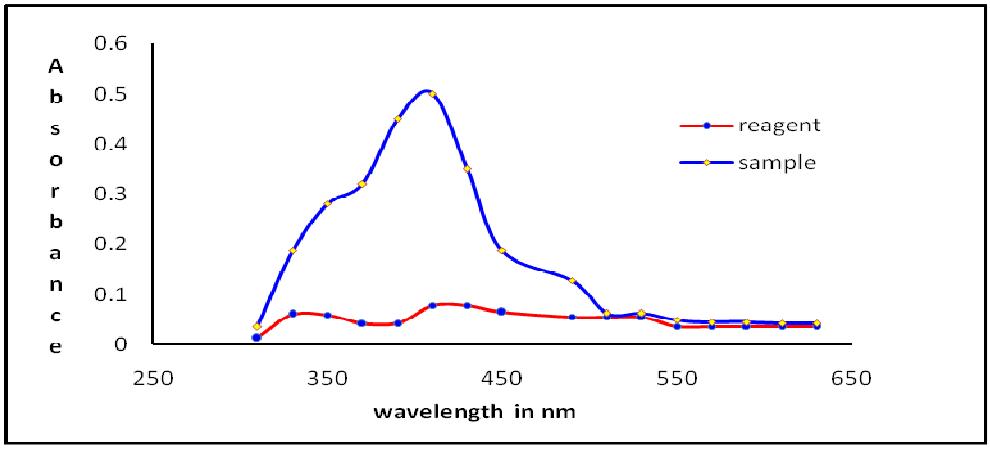

Fig.-2

Effect of Equilibration time and stability of the Complex

The equilibration time of 1 minute is sufficient for the quantitative extraction of Molybdenum. The stability of colour of the Mo (VI): APDHTS complex with respect to time shows that the absorbance due to extracted species is stable up to 46 hours, after which slight decrease in absorbance is observed.

Calibration plot

The Beer's law is obeyed in the range of 1 ppm to 5 ppm. The molar absorptivity and Sandell's sensitivity were calculated to be is 2492 L $mol^{-1}cm^{-1}$ and 0.03614 µg cm^{-2} respectively (Fig.- 3).

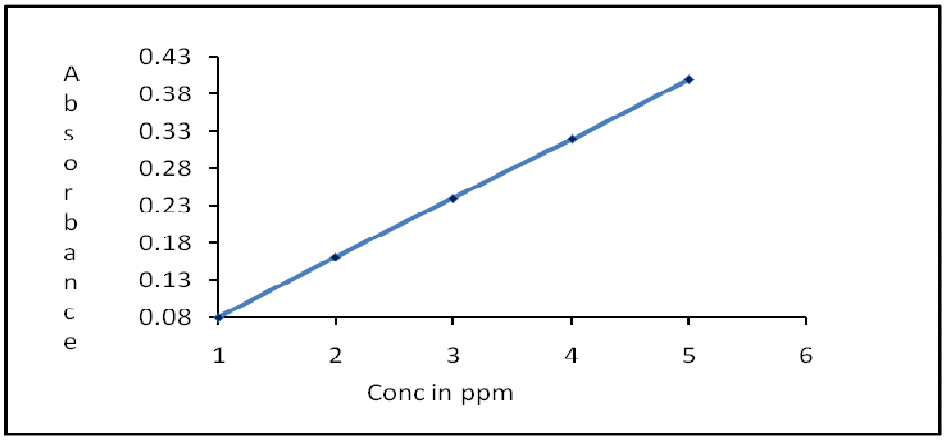

Fig.-3: Calibration Curve

Effect of Divalent ions and Foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 4 ppm of Molybdenum. The ions which show interference in the spectrophotometric determination of Molybdenum were overcome by using appropriate masking agents (Table-1).

Table-1: Masking agents used

S. No.	Interfering Ion	Masking agent
1	Ni (II)	Sodium cyanide
2	Fe(III)	Sodium fluoride
3	Cu (II)	Sodium thiosulphate
4	V (V)	Thiourea
5	Ag (I)	Potassium iodide
6	U (VI)	8-hydroxy quinoline

Accuracy and Precision

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 4 µg of Molybdenum in the aqueous phase. The average of ten determinations was 3.93 and variation from mean at 95 % confidence limit was ± 0.00495.

Nature of Extracted Species

The composition of extracted Mo (VI): APDHTS complex has been determined by Job's Continuous method, Mole ratio method and Slope ratio method. The results from all the three methods show that the composition of Mo (VI): APDHTS complex is 1:3 (Fig.- 4).

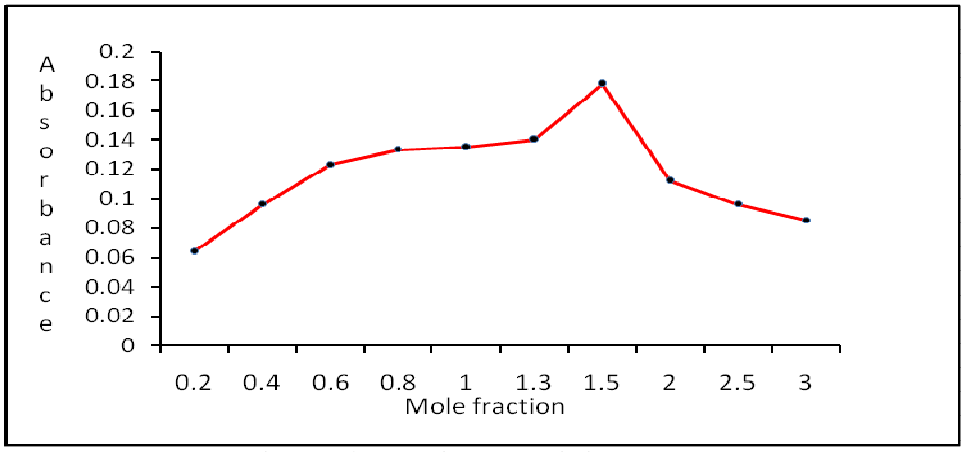

Fig.-4: Job's Continuous Variation

Limit of Detection

1 cm^3 of 0.1 % methanolic APDHTS is diluted with buffer of pH 1.8 which is then extracted with n-butanol as per the procedure and then its absorbance is measured between 430 nm by taking solvent as a blank. The process is repeated for five times separately and five observations are obtained. The limit of detection for Molybdenum for the method was found to be 0.323 ppm.

Applications

The proposed method was successfully applied for the determination of Molybdenum from various alloys, ores and pharmaceutical samples. The results found to be in good agreement with those obtained by the standard known method.

CONCLUSION

The proposed method permits the determination of trace amounts of Molybdenum without any prior separation. The major advantage of the proposed method is that the colour development is instantaneous at room temperature and stable. The proposed method has higher sensitivity and selectivity than that of the methods reported earlier.

Table-2: Determination of Molybdenum

S. No.	Sample	Standard method	Present method
1	Steel	0.19µg	0.188µg
2	Plain steel	0.22µg	0.219µg
3	Mn-Mo steel	0.25µg	0.2489µg
	Pharmaceutical sample		
1	Molypen injection	25.0 µg	24.97 µg
	Synthetic Mixture		
1	Al(55)+Mo(30)	30µg	29.8µg
2	Zr (50)+Mo(20)	20µg	19.7µg
3	Mg(45)+Mo(25)	25µg	24.8µg

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