

# Spectrophotometric Determination of Trace Amounts of Molybdenum(VI) Using Salicylaldehyde Acetoacetic Acid Hydrazone

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**Abstract:** A simple, sensitive and accurate spectrophotometric method was proposed for the micro determination of molybdenum(VI) using salicylaldehyde acetoacetic acid hydrazone (SAAH) as a reagent. The method was based on the formation of 1:2 complex between the molybdenum(VI) and SAAH. The optimum conditions for the determination were established. The Beer's law was applicable in the range 0.097 to 0.968  $\mu\text{g/mL}$ . The molar absorption coefficient, Sandell's sensitivity and stability constant ( $\beta$ ) of the complex were found to be  $160.00 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ,  $5.998 \times 10^{-4} \mu\text{g cm}^{-2}$  and  $1.425 \times 10^{10}$  respectively. The influence of interferences on the proposed method was studied and presented. The method was successfully applied for the determination of synthetic mixtures and alloys containing molybdenum(VI).

**Keywords:** Molybdenum(VI); salicylaldehyde acetoacetic acid hydrazone; spectrophotometric method; alloys.

## 1. Introduction

Molybdenum finds extensive applications in different fields. 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 [1]. In view of crucial role of molybdenum in different fields, it is necessary to develop sensitive analytical procedures for its determination in trace amounts.

A variety of methods were reported for the analytical determination of molybdenum. The procedures include inductively coupled plasma atomic emission spectrometry [2], neutron activation analysis [3], atomic absorption spectrometry [4-6], spectrophotometry [7-12], spectrofluorimetry [13], electrochemical methods [14,15], flow-injection chemiluminescence [16] etc. Many of these procedures suffer from disadvantages such as they involve complicated procedures, require preconcentration step and/or an extraction step, hence the analyst should always bear in mind that all manipulations at any stage may result either in contamination and/or the loss of the analyte. In some cases the analysis requires costly equipment which may be out of the reach of a common laboratory. In the present communication, simple, rapid, selective and sensitive spectrophotometric method is reported for the micro determination of molybdenum(VI) by complexing with SAAH. The reagent gave an orange colored solution

with molybdenum(VI) in a medium of pH 1. The color reaction was instantaneous and the color intensity of the complex solution was found to remain constant for at least five hours.

## 2. Experimental

### 2.1. Apparatus

The absorbance measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A). pH measurements were made using ELICO pH meter Model L1-10, ELICO Private Limited, Hyderabad, India.

### 2.2. Reagents and chemicals

All the chemicals and reagents used were of analytical grade.

The buffer solutions were prepared by mixing 1M hydrochloric acid and 1M sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0).

0.01M solution of SAAH in dimethyl formamide (DMF) was employed in the present studies.

0.01M solutions of molybdenum(VI) were prepared by dissolving requisite amount of sodium molybdate in distilled water and was standardized [17] by using standard procedure. The working solutions were prepared by diluting the required volume of stock solution to appropriate volume.

### 2.3. Synthesis and characterization of SAAH

Equimolar solutions of acetoacetic acid hydrazide and salicylaldehyde prepared in aqueous methanol were refluxed for two hours. The contents were allowed to cool to the room temperature and the product was separated by filtration. The crude product (yield - 86.2 %) obtained was filtered, washed with water and dried. The dried product was recrystallised from hot aqueous methanol to get pure light yellowish crystals of salicylaldehyde acetoacetic acid hydrazone (Melting point - 220 °C). The compound was characterized by elemental analysis, IR and NMR spectral studies.

The elemental analysis data of the ligand (SAAH) presented in Table 1 reveals that the experimental values are in good agreement with the theoretically calculated values.

TABLE 1. Elemental analysis data of the SAAH

	Percentage of		
	C	H	N
Found	60.81	5.05	13.02
Calculated	60.00	5.45	12.73

The IR spectral peaks at  $3350\text{ cm}^{-1}$  ( $\nu_{\text{N-H}}$ ),  $3178\text{ cm}^{-1}$  (intramolecular hydrogen bonded phenolic -OH),  $3032\text{ cm}^{-1}$  (Ar-H stretching frequency),  $2960\text{ cm}^{-1}$

( $=\text{C}-\text{H}$  group),  $2879\text{ cm}^{-1}$  (methyl group),  $2940\text{ cm}^{-1}$  (methylene group),  $1702\text{ cm}^{-1}$  (carbonyl group),  $1663\text{ cm}^{-1}$  (amide carbonyl group),  $1628\text{ cm}^{-1}$  (azomethine group),  $980\text{ cm}^{-1}$  (N-N group) and the peaks in  $^1\text{H}$  NMR spectrum recorded in dimethyl sulphoxide using tetramethylsilane as internal reference at  $\delta$  1.30 ppm (methyl proton),  $\delta$  3.23 ppm (methylene proton [18]),  $\delta$  4.50 ppm (-OH proton),

$\delta$  10.90 ppm ( $-\text{N}-\text{H}$  group in  $-\text{C}(=\text{O})-\text{NH}-$ ),

$\delta$  9.70 ppm ( $=\text{C}-\text{H}$  of azomethine group [19]),  $\delta$  6.80 ppm as singlet,  $\delta$  7.10 ppm as doublet and  $\delta$  7.40 ppm as doublet (aromatic protons [20]  $\text{H}_a$ ,  $\text{H}_b$  and  $\text{H}_c$  respectively) confirm the following structure for the ligand.

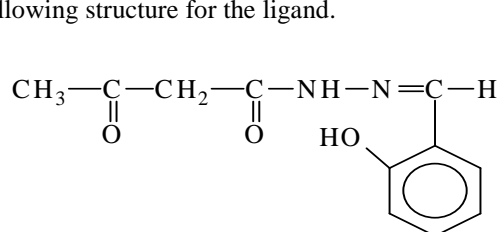


Figure 1. Structural formula of Salicylaldehyde acetoacetic acid hydrazone

### 2.4. General experimental procedure

Aliquots of solution containing different amounts of molybdenum (VI) (0.097 to 0.968  $\mu\text{g/mL}$ ) were transferred into a series of 10 mL standard flasks. 5 mL of buffer

solution required pH, required volume of the SAAH solution of concentration  $4 \times 10^{-4}\text{ M}$  and 1 mL of dimethylformamide were added to the flask and the contents were made up to the mark with distilled water. The absorbance of the solutions was measured at 470 nm against the reagent blank solution.

### 2.5. Preparation of sample solutions

An accurately weighed amount of the alloy sample was dissolved in a mixture of 2 mL of concentrated hydrochloric acid and 10 mL of concentrated nitric acid. The solution was evaporated to a small volume, 1:1 sulphuric acid was added and was evaporated to dryness. The residue extracted with 15 mL of water was transferred into a 100 mL standard flask and was made up to the mark with distilled water. This serves as a stock solution. The stock solution was appropriately diluted to obtain the concentration in the required range. Suitable aliquots were taken and analyzed for the metal by the proposed general procedure.

## 3. Results and Discussion

In order to optimize the experimental variables, the authors conducted following studies.

### 3.1. Effect of pH on the absorbance of the complex

Figure 2 shows the effect of pH on the intensity of the color reaction. Mo(VI)-SAAH complex solution showed maximum absorbance in a medium of pH 1. Hence further analytical investigations were carried out in buffer media of pH 1.

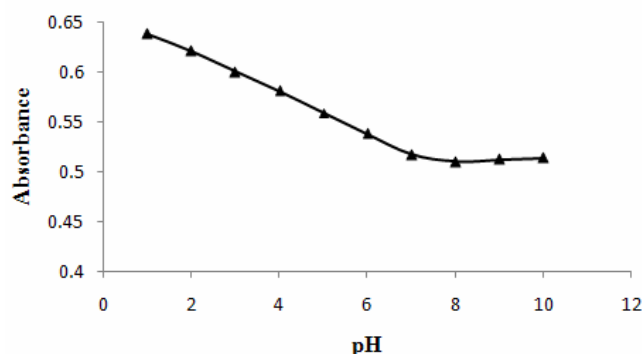


Figure 2. Effect of pH on absorbance.  $[\text{Mo(VI)}] = 4 \times 10^{-6}\text{ M}$ ;  $[\text{SAAH}] = 4 \times 10^{-5}\text{ M}$

The absorption spectra of solution containing Mo(VI)-SAAH complex against the reagent blank, that of SAAH solution against corresponding buffer solution blank and that of metal solution against the respective buffer solution as blank is shown in the Figure 3. The figure reveals that Mo(VI)-SAAH complex has maximum absorbance at 470 nm. Further neither the metal ion nor the reagent has appreciable absorbance at specified wavelength. Hence further investigation was carried out at 470 nm.

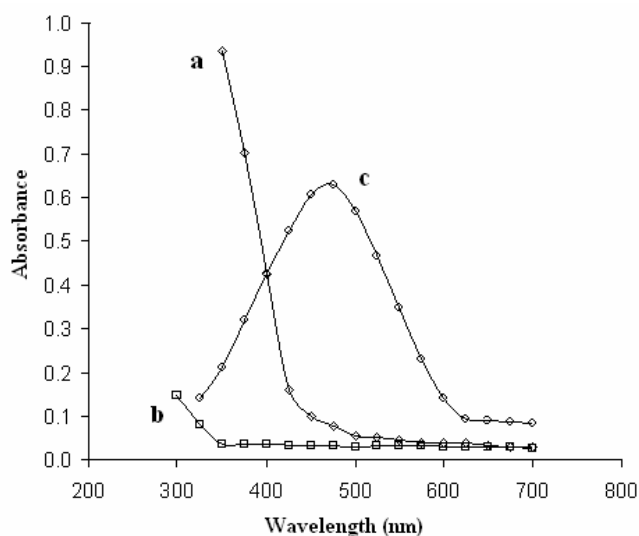


Figure 3: Absorption spectra of  
 a) SAAH against buffer blank, [SAAH] =  $4 \times 10^{-5}$  M  
 b) Mo(VI) against buffer blank, [Mo(VI)] =  $4 \times 10^{-6}$  M  
 c) Mo(VI)-SAAH complex against reagent blank,  
 Mo(VI) =  $4 \times 10^{-6}$  M, [SAAH] =  $4 \times 10^{-5}$  M

### 3.2. Effect of reagent (SAAH) concentration

A series of solutions containing different amounts of reagent, fixed amount of molybdenum (VI) were taken in appropriate buffer media. The absorbance of the solutions was recorded at 470 nm using respective reagent solution as blank. The studies reveal that, a reagent excess of 5 fold was sufficient for the Mo(VI)-SAAH color reaction. However the addition of excess of the reagent solution does not alter the intensity of the color reaction.

### 3.3. Analytical determination of metal ion

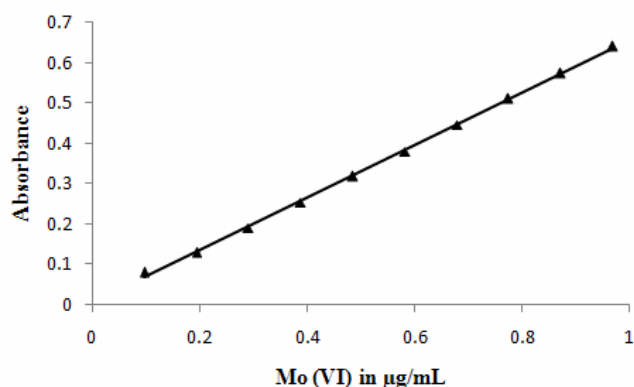


Figure 4. Analytical determination of Mo (VI) [SAAH] =  $4 \times 10^{-5}$  M;  
 pH = 1;  $\lambda_{\text{max}} = 470$  nm

The absorbance of the series of solutions containing different concentrations of the metal ion is determined. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that Mo(VI) can be determined in the range of 0.097 to 0.968  $\mu\text{g/mL}$ . The pertaining calibration graph is shown in the Figure 4. The

regression equation is  $A = 0.650 C + 0.005$  (A is absorbance and C is the concentration Mo(VI) in  $\mu\text{g/mL}$ ) with a correlation coefficient 0.999.

### 3.4. Stoichiometry of the Mo(VI)-SAAH complex

The stoichiometry of the complex determined by Job's method of continuous variation and mole ratio method was found to be 1:2 (Metal : Ligand). The corresponding data is shown in the Figure 5 and 6 respectively. The stability constant determined by Job's method was found to be  $1.425 \times 10^{10}$ .

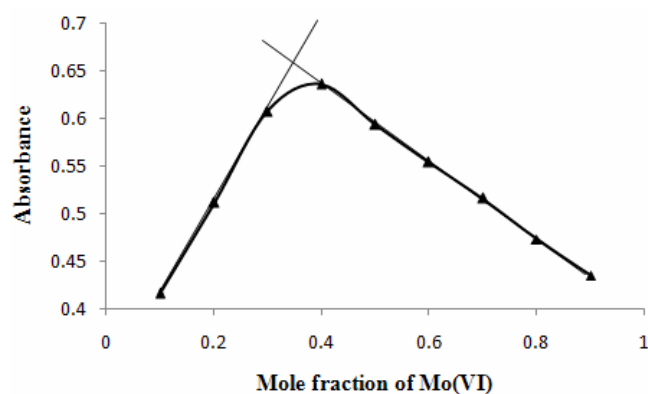


Figure 5. Job's method of continuous variation, Concentration of different aliquots of and Mo(VI) solution and SAAH solution =  $5 \times 10^{-4}$  M; pH = 1;  $\lambda_{\text{max}} = 470$  nm

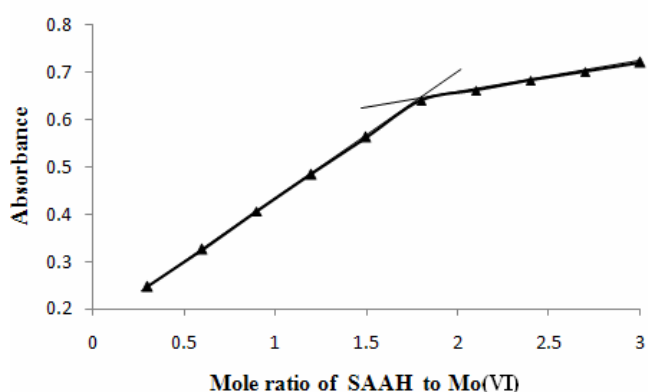


Figure 6. Mole ratio method; [Mo(VI)] =  $5 \times 10^{-5}$  M; Concentration of different aliquots of SAAH solution =  $5 \times 10^{-4}$  M; pH = 1;  $\lambda_{\text{max}} = 470$  nm

### 3.5. Effect of diverse 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 tolerance limit was considered to be the amount that caused a  $\pm 1\%$  deviation in the absorbance value. The tolerance limits of various diverse ions are given in Table 2.

TABLE 2. Tolerance limit of diverse ions,  $[Mo(VI)] = 0.1919$  ppm

Anion added	Tolerance limit (g/L)	Cation added	Tolerance limit (g/L)
Citrate	1.51	Bi(III)	0.251
Tartrate	2.07	W(VI)	0.0735
Iodide	1.52	Fe(III)	0.0782
Thiosulphate	1.49	Mn(II)	0.0330
Oxalate	0.880	Ag(I)	0.0647
Bromide	0.479	Al(III)	0.0648
Thiourea	0.609	Cu(II)	0.0190
Nitrate	0.620	Pb(II)	0.0829
Urea	0.480	Hg(II)	0.0802
Acetate	0.354	Zn(II)	0.0392
Thiocyanate	0.580	Fe(II)	0.0223
Chloride	0.213		
Phosphate	0.380		
Fluoride	0.114		

### 3.6. Determination of molybdenum (VI) in synthetic mixtures

Satisfactory results were obtained when the method was applied for the determination of molybdenum in synthetic mixtures. The results are shown in the Table 3. The analytical parameter pertaining to the proposed method is shown in the Table 4.

TABLE 5. Determination of molybdenum(VI) in different alloy samples

Sample name / number	Alloy Composition	Molybdenum(VI) %		Error %
		Certified	Calculated	
BCS-CRM 387	Ni = 41.90%; Fe = 36.00%; Cr = 12.50%; Mo = 5.80%; Ti = 2.95%; Al = 0.24%; Co = 0.20%; Cu = 0.30%.	5.80	5.72	0.08
Udimet-500	Cr = 18.00%; Co = 18.50%; Al = 2.90%; Mo = 4.80%; C = 0.08%; B = 0.006%; Zr = 0.05%; Ti = 2.90%.	4.80	4.74	0.06
Udimet-700	Cr = 15.00%; Co = 18.00%; Al = 4.30%; Mo = 5.21%; C = 0.08%; B = 0.003%; Ti = 3.50%.	5.21	5.15	0.06

## 4. Conclusions

A new spectrophotometric method is reported for the determination of microgram levels of molybdenum(VI). In comparison with many expensive instrumental techniques and the procedures which usually require prior separation and preconcentration process and time sensitive procedures, the present method is a new, rapid, simple, sensitive and selective method for the micro determination of molybdenum(VI) especially in alloy samples.

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TABLE 3. Determination of Mo (VI) in synthetic mixtures

Mo (VI) $\mu\text{g/mL}$		Recovery*	RSD
Added	Found		
0.20	0.209	105	0.085
0.70	0.716	102	0.037

TABLE 4. Analytical parameters of the proposed method

Parameter	Mo (VI)
Beer's law range	0.097 to 0.968 $\mu\text{g/mL}$
Method detection limit	0.054 $\mu\text{g/mL}$
Limit of quantification	0.107 $\mu\text{g/mL}$
Molar absorption coefficient	$160.000 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity	$5.998 \times 10^{-4} \mu\text{g cm}^{-2}$
Stability constant	$1.425 \times 10^{10}$
Regression equation	$A = 0.650 C + 0.005$
Correlation coefficient	0.999

### 3.7. Determination of molybdenum (VI) in alloys

The utility of the proposed method was tested by determining the metal ion content in various alloy samples. The procedure mentioned in 2.5 and 2.4 was followed for the analytical determination of molybdenum(VI). Citrate solution is added wherever necessary to mask the excess iron and copper. The results are presented in the Table 5.

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