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Spectrophotometric Determination of Trace amounts of Molybdenum(VI) Using 4-Hydroxybenzaldehydethiosemicarbazone

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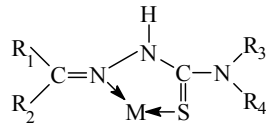
Abstract: The reagent 4-hydroxybenzaldehyde thiosemicarbazone (**4-HBTS**) has been used for the determination of Mo(VI) by spectrophotometric method. The reagent 4-HBTS gives green colour with Mo(VI) solution of weak acidic medium and the maximum absorbance was observed at 365nm, in acidic buffer p ^{H} 6.0. The molar absorptivity and Sandell's sensitivity of Mo(VI)- 4-HBTS complex are 1.25 x 10^4 L mol^{-1} cm^{-1} and 0.00109 µg/cm^2 respectively. The stability constant of 1:1 Mo(VI)-4-HBTS complex is 2.76x10^5. The effect of various diverse ions is also studied. The method was successfully applied for the determination of molybdenum in alloys containing molybdenum. The influence of interferences on the proposed method was studied and presented. The method was successfully applied for the determination of molybdenum in different alloy samples. A detailed report on comparison of spectrophotometric methods for the determination of Mo (VI) using various organic reagents also summarized.
Keywords: Molybdenum(VI), 4-hydroxybenzaldehydethiosemicarbazone,spectrophotometry.

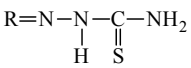
Introduction

Scheela in 1778, distinguished native molybdenum from Galena. In 1782, Hjehn obtained the metal from its sulphide ore. The name molybdenum was given from molybdena, used by dioscorides and pliny to designate galena and other lead compounds. The human body contains 0.07mg of molybdenum per kilogram weight. It occurs in higher concentration in the liver and kidneys. Significant dietary sources of molybdenum include green beans, eggs, sunflower seeds, wheat flour and cucumber. Dietary molybdenum deficiency causes diarrhea, infertility, low birth weight and gout. In view of the complex nature of metal ion species in solution, direct methods for the analytical determination of molybdenum are not many. A number of spectrophotometric methods have been developed for the determination of molybdenum [1-4]. Thiosemicarbazones are known as good analytical reagents [5-9]. These reagents are formed by the condensation of thiosemicarbazide and a carbonyl compound. These compounds contain an azomethine nitrogen atom and this is responsible for their reactivity with a number of trasition metal ions, which form coloured complexes.

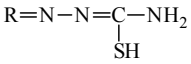


Bonding in thiosemicarbazone complexes

In solution state, thiosemicarbazones probably exist as an equilibrium mixture of thione(II) and thiol(III) tautomers.

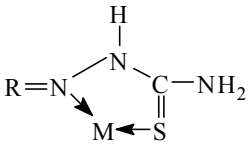


(II)

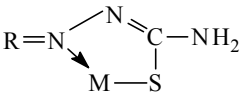


(III)

Thione form acts as a neutral bidentate ligand (IV), while the loss of the thio-proton from thiol yields a singly charged bidentate ligand (V).



IV

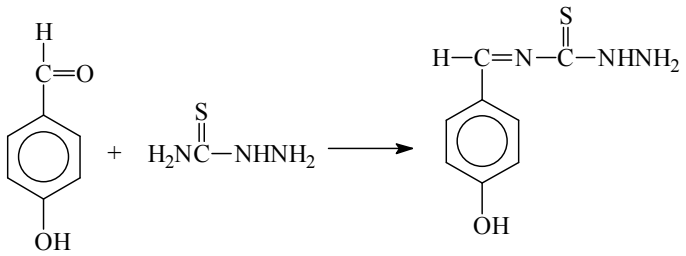


V

Although, several methods have been reported for the spectrophotometric determination of molybdenum (VI) [10-12]. They suffer from drawbacks such as lack of reproducibility, stability, interferences and requirements of prior extraction requirement of heating. In the present paper, a simple, rapid, selective, sensitive direct spectrophotometric method is reported for the determination of micro amounts of molybdenum. It describes very selective and simple spectrophotometric determination of molybdenum by complexing with **4-HBTS.**

Experimental

The reagent 4-hydroxybenzaldehydethio semicarbazone was prepared by simple condensation of 4-hydroxybenzaldehyde with thiosemicarbazide by adopting the standard procedures.



4-hydroxy benzaldehyde (122 M.W)

Thiosemicarbazide (91 M.W)

4-HBTS (195 M.W.)

1.22 g of 4-hydroxy benzaldehyde + 0.919 of thiosemicarbazide

Yield = 1.6392 g

$$\% \text{ of yield} = \frac{1.6392}{2.13} \times 100$$

$$= 76.92\%$$

The structure has been established based on IR and NMR spectra. The M.P. of 4-HBTS is 208 - 210°.

Solutions preparation

Buffer solutions are prepared using HCl,CH_3COOH and NaoAc in acidic medium and NH_4OH, NH_4Cl in basic medium.

Preparation of metal solution and reagent solutions

The stock solution of Mo(VI) was prepared by dissolving 3.0898 g Ammonium molybdate (AR, BDH) in a 250 ml volumetric flask using doubly distilled water in hot condition to get 1 x 10^{-2} M solution. The stock solution was diluted to get the required concentration.

0.195 g of recrystalised sample of the reagent 4-hydroxy benzaldehyde thiosemicarbazone was dissolved in DMF in a 100 ml volumetric flask to obtain the stock solution (0.1 M), and it was suitably diluted to get the required concentration. Fresh reagent solutions were prepared as and when required.

Experimental procedure

An aliquot of the solution containing 0.3837 to 3.837 µg/ml of Mo(VI),10ml of acidic buffer solution of p^H 6 and 1ml of 1x10 $^{-2}$M 4-HBTS were taken in a 25ml volumetric flask and the contents of the flask were made up to the mark with distilled water. The absorbance of this solution was measured at 365nm against reagent blank.

Schimadzu 160A UV-visible spectrophotometer (Japan) equipped with 1cm quartz cell was used in these investigations for making absorbance measurements. A pH meter ELICO L-120 (ELICO - Hyderabad) is used to make pH measurement.

Results and Discussions

Mo(VI) reacts with 4-Hydroxybenzaldehyde thiosemicarbazone in weak acidic medium pH-6 to give green coloured species. The colour reaction of Mo(VI) with the reagent is instantaneous even at room temperature. The absorbance of green coloured species at a wavelength corresponding to maximum absorbance λ_{max} is 365 nm. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH-6. A ten fold excess of the reagent is adequate for the complete colour development. Addition of excess of reagent has no adverse effect on absorbance. The order of addition of various component shows no effect on absorbance values.

Effect of metal ion concentration

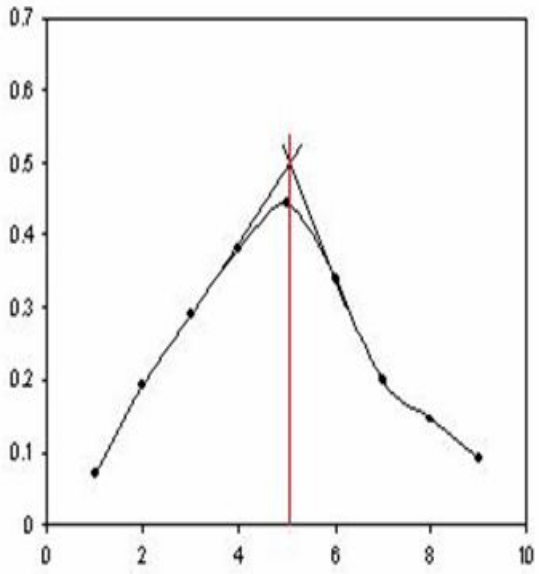
The studies relating to the effect of Mo(VI) revealed that a linear relationship exists between the metal ion concentration and absorbance is in the range 0.03837 to 0.3837 µg/ml. The linear graph can be fitted into the equation $A_{365} = 0.014\ C + 0.0962$. The molar absorptivity and Sandell's sensitivity are 1.25 x 10^4 L mol^{-1} cm^{-1} and 0.00109 respectively.

Effect of the reagent concentration

Keeping the metal ion concentration constant, the reagent concentration is varied from 4 x 10^{-5} to 40 x 10^{-5} M. A linear relationship is obtained between the two parameters upto 3.2 x 10^{-4} M, thereafter the reagent has no influence on the absorbance. This may be attributed that at 3.2 x 10^{-4} M concentration of the reagent the formation of complex is complete and thereafter the addition of excess of reagent has no effect on the absorbance values.

Determination of composition and stability constant of the complex

As the metal ion Mo(VI) forms coloured complex with the reagent, an attempt is made to determine the composition and stability constant of the complex. Job's method and mole ratio method are conducted to make these determinations. It is noticed Mo(VI) forms a stable green colored 1:1 complex with 4-Hydroxybenzaldehydethiosemicarbazone. The stability constant of the complex is calculated and is found to be 2.76 x 10^5.



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Job's continuous varition method

[Mo(VI)]=2 x 10^{-4} M ; [4-HBTS]=2 x 10^{-4} M

pH=6 ; λ_{max} =365 nm

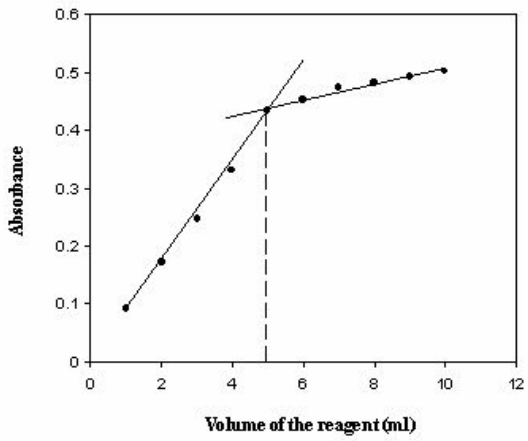

Fig. 3.7.16. Mole ratio method

[Mo(VI)] = 2 x 10^{-4} M
[4-HBTS] = 2 x 10^{-4} M
pH = 6
λ_{max} = 365 nm

Data relating to various parameters of Mo(VI) – 4-HBTS complex presented in table 1. It is noticed from the data that molybdenum forms a stable complex with the reagent.

Table 1: physico-chemical and analytical characterstics of Mo(VI)- 4-HBTS

Characteristics	**Results**
Λ_{max} (nm)	365
p^H range (optimum)	5.5-6.5
Moles of the reagent required per mole of metal ion for complete colour development	10 folds
Molar absoptivity (Lmole $^{-1}$cm $^{-1}$)	1.25x10 ^{4}
Sandell's sensitivity(µg/cm^2)	0.00767
Beer's law validity range(µg/ml)	0.03837 to 0.3837
Composition of the complex (M:L) obtained in job's and mole ratio method.	1:1
Stability constant	2.76 x 10^5.
Standard deviation in the determination of 1.91 µg/ml of Mo (VI) for ten determinations.	0.0036478
RSD	0.19%
Regression equation	Linear equation A_{365} = 0.014C + 0.0962

Interference of diverse ions

The effect of some diverse ions which often accompany molybdenum has been studied. The data is presented in table 2.

Table 2: Tolerance limit of foreign ions in the determination of molybdenum

Ion added (Anions)	Tolerance limit (µg/ml)	Ion added (Cations)	Tolerancelimit (µg/ml)
Chloride	141.8	Chromium(VI)	1.039
Bromide	479	Vanadium(V)	32.6
Iodide	761	Tungsten(VI)	5.8
Nitrate	590	Manganese(II)	3.29
Acetate	472	Cobalt(II)	4.74
Urea	600	Nickel(II)	4.69
Tartarate	736	Silver(I)	5.17
		Cadmium(II)	13.4

Tolerance limit of foreign ions were made in the determination of 0.3876 µg/ml of molybdenum. From the data it is observed that anions do not show much interference. It is also observed that all metal ions except vanadium and cadmium interfere in the determination.

Effect of organic solvents

Effect of organic solvents (50% by volume) on absorbance values of the solution containing fixed concentrations of the metal ion and reagent is studied. The respective data is presented in the **Table 3**.

Table 3: Effect of organic solvent

Solvent (50% V/V)	Absorbance
None	0.578
DMF	0.542
Methanol	0.467
Dioxane	0.316
Acetonitrile	0.186

[Mo(VI)] = 4 x 10-^{5} M; [4-HBTS] = 8 x 10^{-4} M ; pH = 6 ; λ_{max} = 365 nm

It is seen from the data that DMF has little influence on the absorbance value, while in presence of other solvents the absorbance values are low. This may be because of unfavorable condition.

Applications

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, 1:1sulphuric acid was added and was evaporated to dryness. The residue extracted with 15ml of water was transferred in to a 100ml 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. The utility of the proposed method was tested by determining the metal ion content in various alloy samples.

The procedure mentioned is followed for the analytical determination of Mo (VI). Citrate solution is added where ever necessary to mask the excess iron and copper. The results are presented in the table 4.

.**Table 4: Determination of molybdenum (VI) in different alloy samples**

Sample	Alloy composition	Mo(VI)% certified	Calculated	Error%
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	5.71	0.09
Udimet-500	Cr-18.00%;Co-18.50% Al-2.90%;Mo-4.80%; C-0.08%;B-0.06%; 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	5.18	0.03

*Average of five determinations

Table 5: Comparison of spectrophotometric methods for the determination of Mo (VI) using various organic reagents under different experimental conditions.

Reagent	λmax	pH	Molar absoptivity ($Lmole^{-1}cm^{-1}$)	Extraction/heating	Beer's law range	Ref
2-Hydroxy 4-ydroxy valerophenone	420	--	$1.5x10^{-3}$	Heated at 30 ^0C	--	13
O,O'-Bis (2ethyl)dithiophosporic acid	503	Acid medium	$9.6x10^{3}$	Heated at 45 ^0C	0.5-4,0µg	14
3-hydroxy-2-(4-methoxyphenyl)-6-propionyl-4H-chromen-4-one	416	-	$5.5x10^{4}$	Extraction - C_2H_4Cl	0-2.5µg	15
Isomethylxanthane	470	5-5.8	$1.13x10^{4}$	Extraction - $CHCl_3$	0.5-0.8ppm	16
Pipazathatehydrochloride	461	H_3PO_4	$4X10^{4}$	-	0.5-6.9 µg/ml	17
2,4-dihydroxybenzaldehyde isonicotinoylhydrazone	445	-	$2.59x\ 10^{4}$	-	0.1-3.0ppm	18
2-hydroxyacetophenone benzoylhydrazone	443	-	$2.5x10^{4}$	-	0.1-3.0ppm	19
3-methoxysalicialdehyde 4-hydroxybenzoylhydrazide	374	2.5	$7.4x10^{4}$	-	0.096-0.96 µg/ml	20
Cinnamaldyde4-hydroxybenzoylhyrazone (CMBH)	404	3.0	$6.829x10^{4}$	-	0.047-0.5227 µg/ml	21
4-Hydroxy benzaldehyde thiosemicarbazone	365	6.0	$1.25x10^{4}$	-	0.03837 to 0.3837 µg/ml	Present method

The present method is superior on comparing to other methods. Because it does not required any kind of extraction or heating. It has higher molar absorptivity and also appreciable Beer's law range.

Conclusions

A new spectrophotometric method is reported for the determination of micro gram levels of Mo(VI). Mo(VI) forms a 1:1 stable green coloured complex with 4-Hydroxy benzaldehydethiosemicarbazone. The stability constant of the complex is 2.76×10^5. The molar absorptivity and Sandell's sensitivity are 1.25×10^4 L mol^{-1} cm^{-1} and 0.00767µg/cm^2 respectively. In comparison with many expensive instrumental techniques and the procedures which usually require prior separation and pre concentration process and time sensitive procedures, the present method is a new, rapid, simple, sensitive and selective method for the micro determination of molybdenum(VI) in the range of 0.03837 to 0.3837 µg/ml. The method has been applied for the analysis of Mo (VI) in alloys. A detailed report on comparison of spectrophotometric methods for the determination of Mo (VI) using various organic reagents also summarized.

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