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Direct and derivative spectrophotometric determination of Molybdenum (VI) in presence of micellar medium in food stuffs, pharmaceutical samples and in alloys using cinnamaldehyde-4-hydroxy benzoylhydrazone (CHBH)

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ABSTRACT

A rapid, simple, sensitive and selective spectrophotometric method has been developed for the determination of Molybdenum (VI) using newly synthesized reagent cinnamaldehyde-4-hydroxybenzoylhydrazone (CHBH) in neutral surfactant of TritonX-100-5 % (micellar medium). Molybdenum (VI) forms a green coloured water soluble complex with Cinnamaldehyde-4-hydroxy benzoylhydrazone in the pH range 1.0-6.0. The complex shows maximum absorbance at λmax 404 nm and in the pH range 3.0-4.0. However, at this wavelength, the reagent shows considerable absorbance. At λmax 404 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence, analytical studies are carried out at λmax 404 nm and at pH 3.0 (Phosphate buffer) against reagent blank. Beer's law is obeyed in the range 0.047-0.479 µg ml^{-1} and the optimum concentration range from ringbom plot is 0.095-0.863 µg/ml of Molybdenum (VI). The molar absorptivity and Sandell's sensitivity for the coloured solution are found to be 6.82×10^4 L mol^{-1} cm^{-1} and 0.0014-µg. cm^{-2} respectively. The interference effect of various diverse ions has been studied. The complex shows 1:1 [Mo (VI): CHBH] stoichiometry with stability constant 12.29×10^6. The standard deviation of the method in the determination of 0.191-µg ml^{-1} of Molybdenum (VI) is 0.0008 and the Relative standard deviation is 1.0%. First and second order derivative spectroscopic method is developed at λmax 433 nm and λmax 457 nm respectively for the determination of molybdenum (VI), which is more sensitive than the zero order method. The developed method has been employed for the determination of molybdenum (VI) in foodstuffs, pharmaceutical samples and in alloys. The results are in good agreement with the certified values.

Keywords: Determination of Mo (VI), Spectrophotometry, foodstuffs, pharmaceutical sample and in alloys, CHBH.

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INTRODUCTION

Molybdenum has been shown to be essential trace element in animal physiology [1]. Analytical methods have been described for the determination of molybdenum in plant material, but application to the low levels in a range of real foodstuffs for human consumption is rare. The measurement of molybdenum by flame atomic absorption spectrometry (AAS) after chelation and extraction has been described [2], but this technique does not reach at the desired levels, while the use of graphite furnace atomic absorption spectrometry (GFAAS) is susceptible to matrix interferences [3,4]. Molybdenum has been determined spectrophotometrically by its catalytic effect on the liberation of iodine from iodide by hydrogen peroxide using an automated procedure [5,6]. Many spectrophotometric methods for the determination of Molybdenum (VI) based on its reaction with thiocyanate in the presence of a reducing agent [7] and with toluene-3, 4-dithiol [8] are not too selective,as they are subject to interference from many other elements. Some of the recently proposed methods using thiosemicarbazones [9] are found to be less sensitive. The methods employing different organic reagents have also been reported [10]. Although, several methods have been reported for the spectrophotometric determination of Molybdenum (VI) [11-14], 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 and derivative spectrophotometric method are reported for the determination of micro amounts of molybdenum by complexing with Cinnamaldehyde-4-hydroxy benzoylhydrazone (CHBH). Further, the method does not require heating or extraction. In the present studies, Molybdenum (VI) is determined in foodstuffs, Pharmaceutical samples and in alloys with good accuracy.

EXPERIMENTAL PART

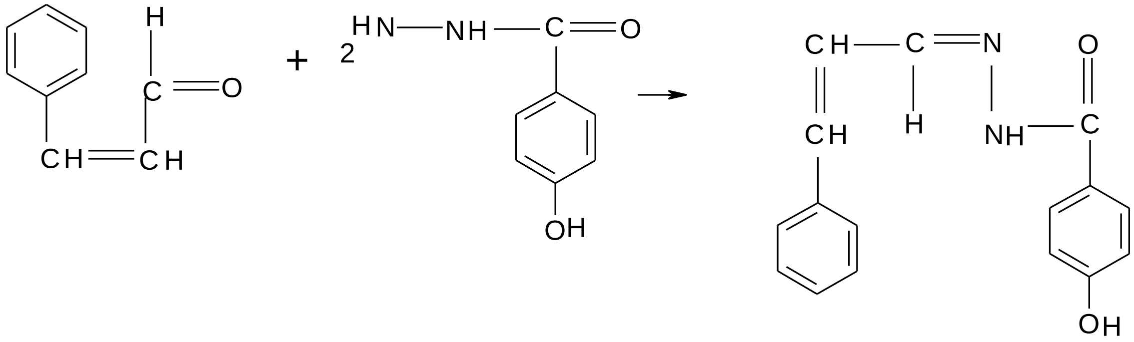
The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was 0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm

Reagents

Preparation of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CHBH)

The reagent (CHBH) is prepared by the Sah and Daniels [15] procedure. 1.32 ml of Cinnamaldehyde (I) and 1.52 g of 4-hydroxy benzhydrazide (II) were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{13}0_2N_2$). The resultant product is recrystallised twice from hot methanol. Pure light yellowish crystals of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CHBH) (III) (m.p. 242-

244°C.) was obtained. IR and NMR spectral studies characterized the compound. The infrared spectrum of the reagent shows bands at v 3452 (NH), 3218-3092 (OH), 1620 (C=O), 1577 (C=N). The 1H NMR (300 MHz) spectrum of the reagent was recorded in DMSO solvent. It shows signals corresponding to δ 11.57 (s, 1H, NH), 10.74 (s, 1H, OH phenolic), 8.19-8.22 (s, 1H, N-CH), 7.77 – 7.80 (d, 2H, ArH), 7.60 – 7.62 (d, 2H, ArH), 7.31 – 7.40 (m, 3H, ArH), 7.03 – 7.05 (d, 2H, ArH). The mass spectrum shows that molecular ion peak at m/z 267 (M+ 1). The structure of CHBH was confirmed based upon above IR, NMR and mass spectral data.



I (Cinnamaldehyde)
II (4-Hydroxy benzoylhydrazine)
III (CHBH)

A 0.01M solution of CHBH in Dimethyl formamide (DMF) was employed in the present studies. The reagent (CHBH) solution (0.01M) was prepared by dissolving suitable quantity (0.316 g) of the compound in 100 ml of dimethylformamide. The reagent solution is stable for 12 hours.

A 0.01 solution of molybdenum (VI) was prepared by dissolving requisite amount of $Na_2MoO_4.2H_2O$ in distilled water and then standardized [16]. The stock solution of Molybdenum (VI) was diluted as required.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

Buffer solutions :(Phosphate)

0.2M KCl and 0.2M HCl (pH-1.0), 0.2M KCl and 0.02M HCl (pH-2.0), 0.1M Potassium Dihydrogen phosphate and 0.1M HCl (pH-3.0 and 4.0), 0.1M Potassium Dihydrogen phosphate and 0.1M Sodium hydroxide (pH-5.0 and 6.0). The pH of these solutions was checked with a digital pH meter

Procedure

Direct spectrophotometry

In each set of different 10ml volumetric flasks, 3.0ml of buffer solution (pH 3.0), 0.5ml of Cinnamaldehyde-4-hydroxy benzoylhydrazone ($1x10^{-3}$ M) and various volumes of ($1x10^{-5}$ M) Molybdenum (VI) solution were taken and made up to the mark with distilled water. The absorbance was measured at λmax 404 nm against the reagent blank. The calibration plot was prepared.

First order derivative spectrophotometry

For the above solutions, first order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees of freedom, in the wavelength range 360 – 600 nm. The First order derivative peak height was measured by the peak-zero method at λmax 433 nm. The peak height was plotted against the amount of Molybdenum (VI) to obtain the calibration plot.

Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}), slit width of 1 nm with nine degrees of freedom, in the wavelength range 360-600nm. The second order derivative peak height was measured by the peak-zero method at λmax 457nm. The peak height was plotted against the amount of Molybdenum (VI) to obtain the calibration plot.

The calibration graph follows the straight-line equation $Y= a\ c + b$; where c is the concentration of the solution, Y is measured absorbance or peak height and a and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as A λmax 404 nm= 0.70559x-0.0208 for zero order data and A λmax 433 nm = $0.120x + 3.3196X10^{-4}$ for first derivative data, A λmax 457nm = 0.31763x-0.02293 for second derivative data which gives the straight lines.

Preparation of sample solutions

Foodstuffs

5g of food or fruit material (dried for about 24hrs at 30°C in an oven) were wet ashed with nitric acid and perchloric acid [17,18]. The ash was dissolved in 5ml of hydrochloric acid and evaporated to dryness. This procedure was repeated and the dried residue was dissolved in water. The solution was filtered into a 25 ml standard flask, one or two drops of concentrated hydrochloric acid was added and made up to the mark with distilled water.

Alloy steels

An accurately weighed amount of steel sample (0.5g) was dissolved completely in minimum amount of aquaregia by slow heating on sand bath and then heated to fumes of oxides of nitrogen. After cooling 5-10ml of 1:1 $H_20:H_2SO_4$ mixture was added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue was dissolved in 20 ml of distilled water and filtered and the filtrate was made up to 100 ml in a calibrated volumetric flask with distilled water. The sample solution was appropriately diluted to obtain the concentration in the required range.

RESULTS AND DISCUSSION

Absorption spectra of CHBH and the molybdenum (VI) complex

The absorption spectra of the solution containing molybdenum (VI) complex against the reagent blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 350-500 nm at pH 3.0. Typical spectra are presented in Fig-1. The spectra show that molybdenum (VI) complex has an absorption maximum at λmax 404 nm. However, at this wavelength, the reagent shows considerable absorbance. At λmax 404 nm, the complex shows maximum absorbance while the reagent blank shows negligible absorbance. Hence the analytical studies were carried out at λmax 404 nm

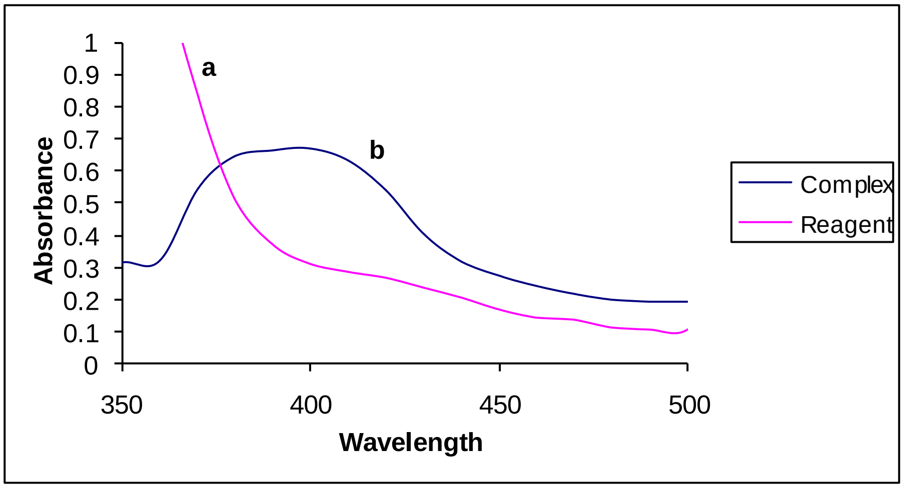


Fig- 1. Absorption spectra of
(a) CHBH Vs Buffer blank, (b) Mo (VI)-CHBH Vs Reagent blank
Mo (VI) - $2x10^{-4}$M (0.5ml), CHBH- $2x10^{-3}$M (0.5ml),
Buffer pH-3.0 (3.0ml), Triton-X-100 (5%)-1.0ml

Effect of pH on the absorbance of the complex

The study of the effect of pH on the colour intensity of the reaction mixture showed that the maximum colour was obtained in the pH range 3.0-4.0. Analytical studies were therefore, carried out at pH 3.0 Fig-2

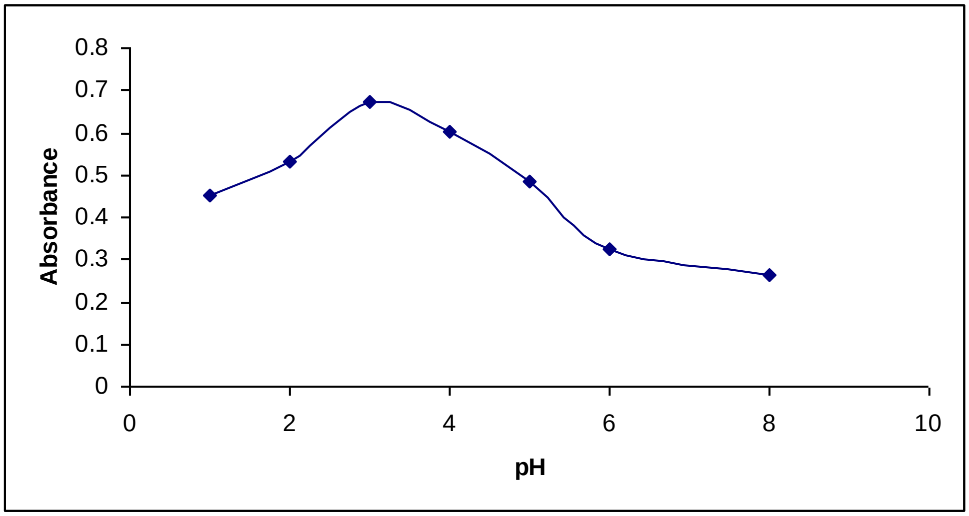


Fig-2- Effect of pH on Absorbance of Mo (VI)-CHBH
Mo (VI)-2x10^{-4} M (0.5ml), CHBH-2x10^{-3} M (0.5ml)
Buffrer pH 3.0 - (3.0ml), Triton-X-100 (5%)-1.0ml
λmax ------------------ 404 nm

Effect of reagent (CHBH) concentration

A 10-fold molar excess of CHBH was necessary for complex and constant colour development. Excess of the reagent has no effect on the absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reactants.

Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex. The colour reaction between Mo (VI) and CHBH was found to be instantaneous at room temperature and the colour remained stable for more than 24 hours.

Applicability of Beer's law

For the possible determination of molybdenum (VI) at micro levels, the absorbance of the solutions containing different amounts of metal ion was measured. Calibration plot drawn between absorbance and amount of Mo (VI) Fig 3 showed that Beer's law was obeyed in the concentration range 0.047-0.479 μg ml^{-1} of Mo (VI). The straight line obeyed the equation A λmax 404 nm =0.70559x-0.02083. The molar absorptivity and Sandall's sensitivity were 6.82x10^4Lmol^{-1}cm^{-1} and 0.0014 ug/cm^2 respectively. The correlation coefficient of the calibration curve for experimental data was 0.9994. The standard deviation of the method for ten determinations of 0.191-µg ml^{-1} of Molybdenum (VI) was 0.0008.

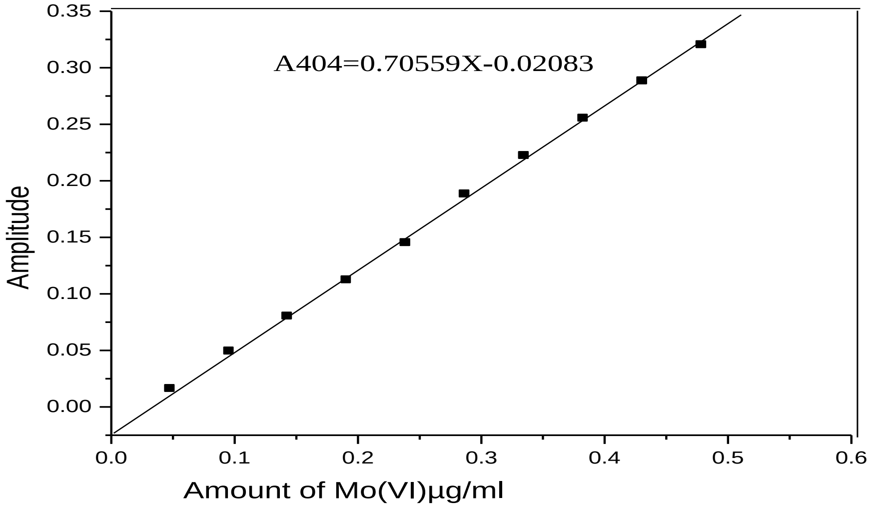


Fig-3: Mo (VI)-CHBH-Zero order Beers law
CHBH-1X10^{-3} M (0.5ml) (Constant), Mo (VI)-1X10^{-5} M
Buffer pH -3.0 (3.0ml), Triton-X-100 (5%)-1.0ml (Constant)
λmax ------------------ 404 nm

Determination of Mo (VI) first order derivative method

The first order derivative method has been employed for the determination of molybdenum (VI) employing CHBH in trace quantities. The second derivative spectra Fig-4 (a) showed maximum amplitude at λmax 433 nm. The derivative amplitudes at λmax 433 nm were proportional to the concentration of Molybdenum (VI). The straight line obeyed the equation A λmax 433 nm =0.120x+3.319X10^{-4}.

Determination of Mo (VI) by second order derivative method

The second order derivative method has been employed for the determination of molybdenum (VI) employing CHBH in trace quantities. The second derivative spectra Fig-5 (a) showed maximum amplitude at λmax 457 nm. The derivative amplitudes at λmax 457 nm were proportional to the concentration of Molybdenum (VI). The straight line obeyed the equation A λmax 457 nm=0.31763x-0.0229.

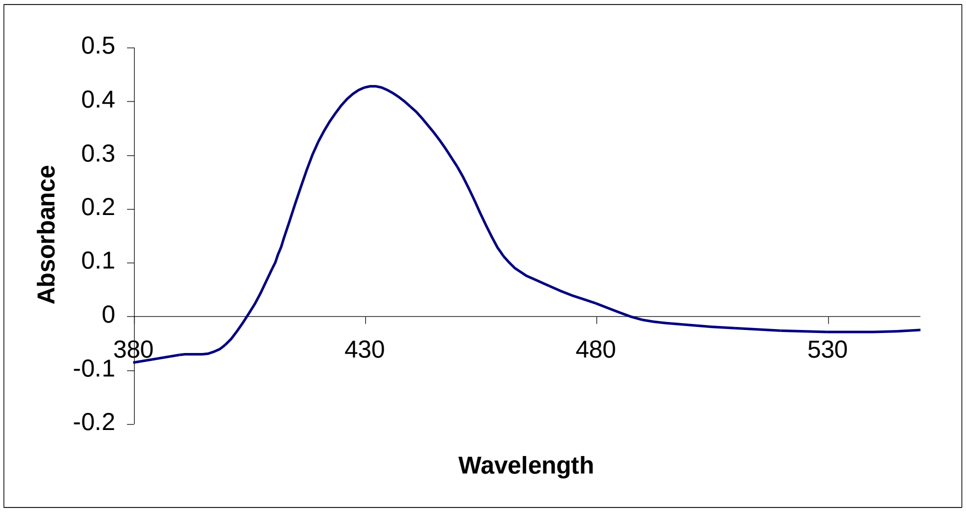


Fig-4 (a) Mo (VI)-CHBH- Fist order derivative spectra
CHBH-2X10^{-3} M (0.5ml), Mo (VI) -2X10^{-4} M (0.5ml)
Buffer pH --3.0 (3.0ml Triton-X-100 (5%)-1.0ml
λmax--------------433 nm

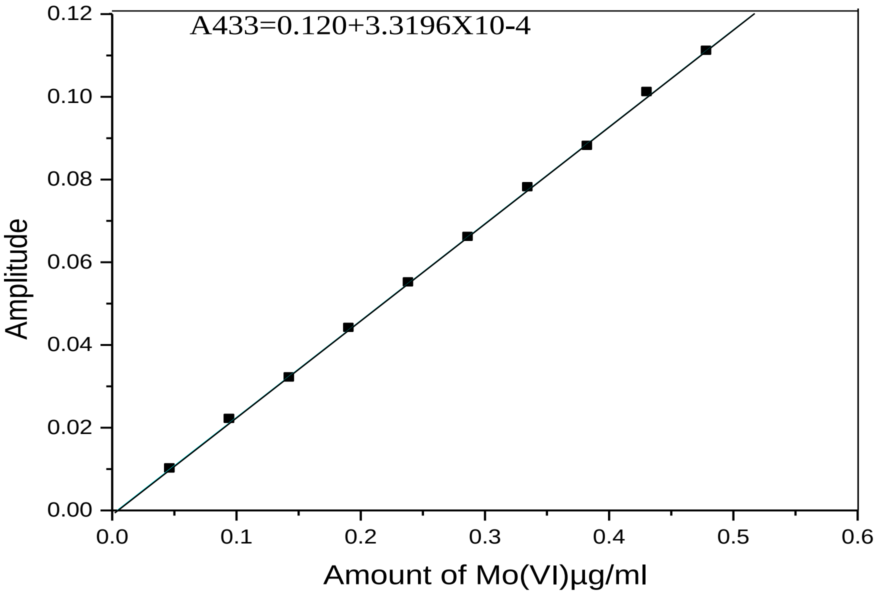


Fig-4 (b): Mo (VI)-CHBH- First order Beers law
CHBH-1X10^{-3} M (0.5 ml) (Constant), Mo (VI) -1X10^{-5} M
Buffer pH-3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax ------------------ 433 nm

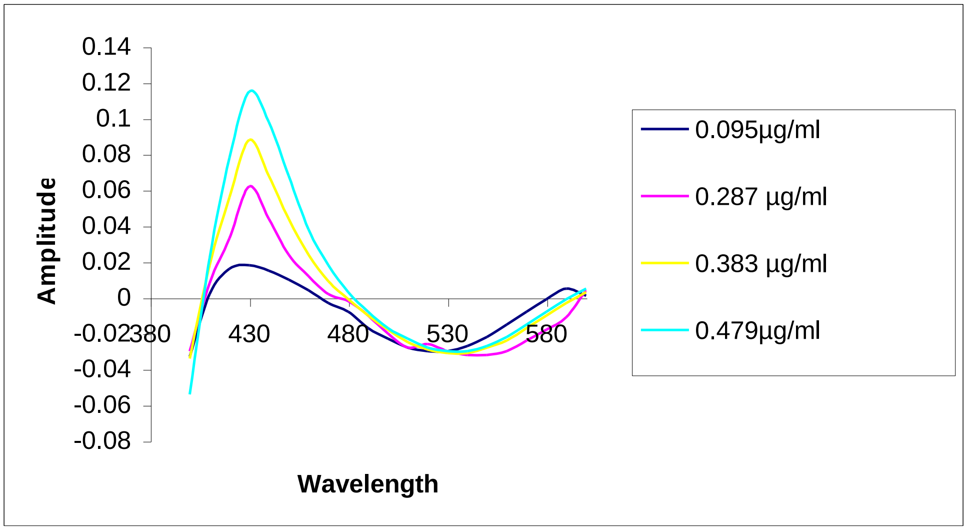


Fig.4 (c) Mo (VI)-CHBH- Beers law first order derivative spectra
CHBH-1X10^{-3} M (0.5ml) (Constant), Mo (VI)-1X10^{-5} M
Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax--------------433 nm

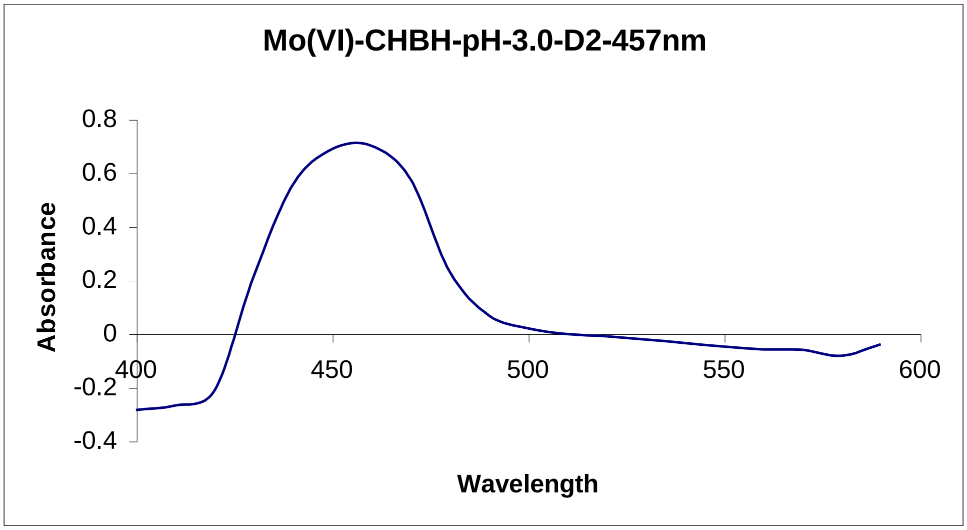
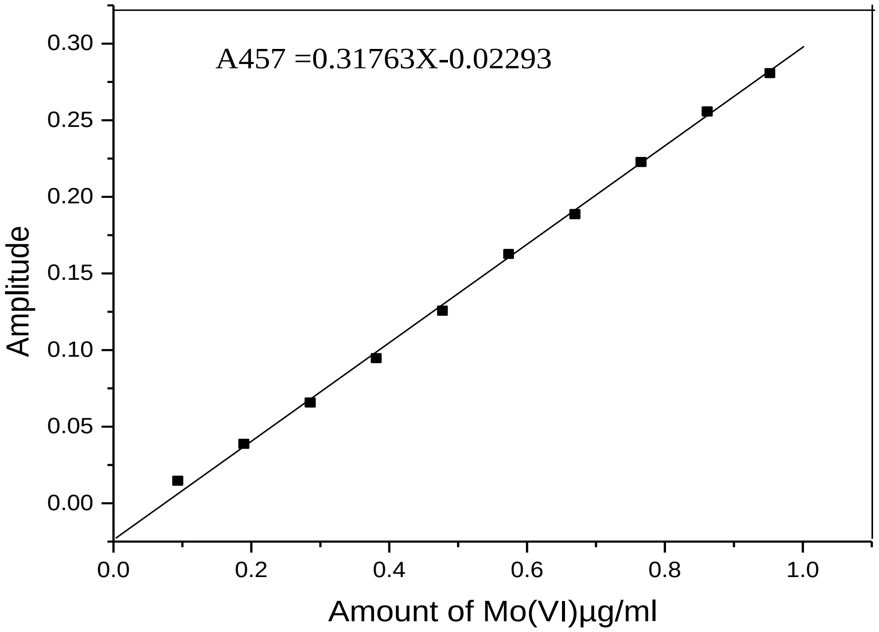


Fig-5 (a) Mo (VI)-CHBH- Second order derivative spectra
CHBH-2X10^{-3} M (0.5 ml), Mo (VI) -2X10^{-4} M (0.5 ml)
Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant)
λmax--------------457 nm



Fig—5(b): Mo (VI)-CHBH-Second order Beers law
CHBH-1X10^{-3} M (0.5 ml) (Constant), Mo (VI) -1X10^{-5} M
Buffer pH-3.0 (3.0 ml) Triton-X-100 (5%)-1.0 ml (Constant)
λmax--------------457nm

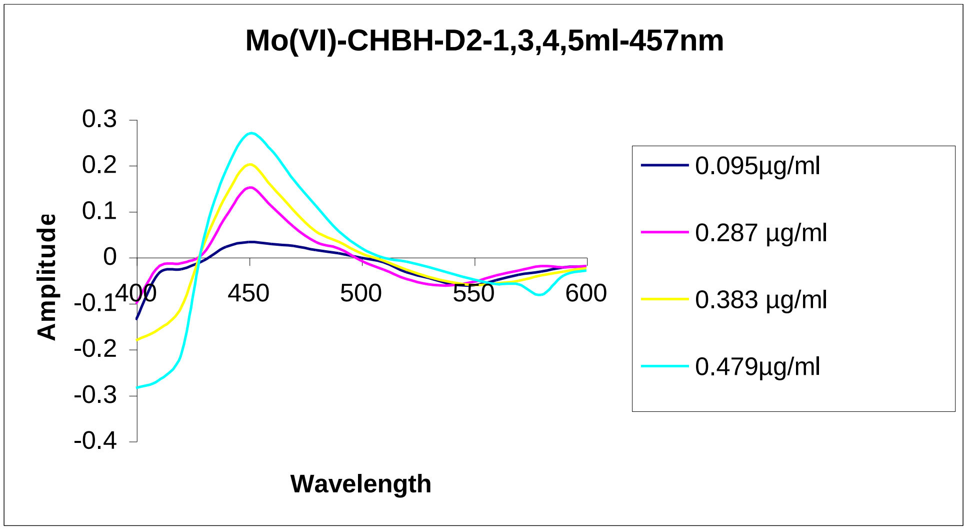


Fig-5 (c): Mo (VI)-CHBH-Second order derivative spectra, CHBH-1X10^{-3} M (0.5 ml) (Constant), Mo (VI)-1X10^{-5} M Buffer pH --3.0 (3.0 ml), Triton-X-100 (5%)-1.0 ml (Constant), λmax ------------------ 457 nm

Composition and stability of the complex

The stoichiometry of the complex was determined by Job's method and molar ratio method and found to be 1:1 (M: L). The stability constant was determined by Job's method as 12.29 x 10^6.

Effect of diverse ions

The tolerance limits (µg ml^{-1}) of various diverse ions in the present method are given in Table1 Tolerance limit was set as the amount of foreign ion that caused an error in the absorbance by ± 2%. The effect of several diverse ions on the determination of Molybdenum (VI) was examined under the optimum conditions. The extent of interference by various anions and cations was determined by measuring the absorbance of solutions containing a constant amount of Molybdenum (VI) and varying amounts of diverse ions.

Table: 1.Tolerance limit of foreign ions in the determination of 0.4797 µg/ml of Molybdenum (VI)

Ion Added	Tolerance Limit (µg/ml) (Zero order) 404 nm	Tolerance Limit (µg/ml) (D1) 433 nm	Tolerance Limit (µg/ml) (D2) 457 nm
Iodide	507	507	507
Sulphate	288	480	480
Ascorbic acid	353	353	353
Urea	180	240	240
Thiocyanide	186	186	186
Bromide	40	64	64
Thiourea	48	76	76
Nitrate	37	112	112
Tetra borate	49	49	49
Acetate	47	47	47
Phosphate	76	94	94
Chlorides	28	28	28
Tartarate	63	63	63
Citrate	19	19	19
Flourude	9.5	9.5	9.5
U^{+6}	120	120	120
Sn^{+2}	60	60	60
La^{+3}	28	28	28
Ba^{+2}	42	42	42
Na^{+}	23	42	42
Hg^{+2}	20	20	20
Pb^{+2}	21	21	21
W^{+6}	6	7	7
Zr^{+4}	3	4	4
Zn^{+2}	2	3	3
Bi^{+3}	3	3	3
Ti^{+4}	5	5	5
Ni^{+2}	1	2	2
Ce^{+4}	3	3	3
$Fe^{+3\,*}$	1.117	1.117	1.117
$Cu^{+2\,**}$	0.127	0.127	0.127
Ru^{+3}	2	3	3
Pd^{+2}	2	3	3
Cd^{+2}	3	5	5
Co^{+2}	1.17	1.76	1.76

***Masked by phosphate 76 µg/ml**

**** Masked by Thiourea 48 µg/ml**

The effect of various diverse ions in the determination of 0.4797µg/ml Molybdenum (VI) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ± 2%

in the absorbance or amplitude. The results are given in Table 1. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess, such as iodide, nitrate, thiosulphate, thiocyanide, bromide, sodium (I), bismuth (III), tungsten (VI) and zirconium (IV). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as iron (III) and copper (II) is decreased by adding masking agents Phosphate and thiourea respectively.

APPLICATIONS

Zero order method: The method proposed in the present studies was applied for the determination of Molybdenum (VI) in foodstuffs Pharmaceutical samples and in some alloys.

Application to foodstuffs

To a 10 ml standard flask containing 3.0 ml of buffer of pH 3.0 and 1ml of ($1x10^{-3}$ M) CHBH solution, a suitable aliquot of the sample solution was added and the contents were diluted to 10 ml with distilled water and its absorbance was measured at λmax 404 nm against the reagent blank. The amount of molybdenum present in these samples was computed from a pre-determined calibration plot and the results are presented in Table.2

Table.2: Determination of Molybdenum (VI) in foodstuffs

Foodstuff	Amount of Molybdenum (µg/ml)						
	Standard Method	Present method*					
		Zero Order	Recovery (%)	D1	Recovery (%)	D2	Recovery (%)
Banana	0.479	0.476	99.37	0.478	97.79	0.478	97.79
Apple	0.239	0.234	97.9	0.238	99.5	0.238	99.5
Cabbage	1.439	1.42	98.67	1.431	99.65	1.431	99.65
Tomato	0.959	0.954	99.47	0.955	99.5	0.955	99.5
Rice	0.718	0.705	98.18	0.711	99.0	0.711	99.0
Potato	0.240	0.238	99.16	0.239	99.58	0.239	99.58

*Average of three determinations

The average daily intake of Molybdenum is 0.3 mg. Daily intake above 0.4mg can be toxic. Molybdenum deficiency less than 0.05 mg/day can cause stunned growth, reduced appetite and impaired reproduction.

Application to alloy steels

A suitable aliquot of the sample solution was taken in a 10 ml standard flask containing 3.0 ml of buffer of pH 3.0, 48 µg of Thiourea (to mask Cu) and 0.5 ml of (1x10^{-3}M) CHBH solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λmax 404 nm against the reagent blank. The absorbance values were referred to the pre-determined calibration plot to compute the amount of Molybdenum present. The results are presented in table 3.

Table3: Determination of Molybdenum (VI) in alloys.

Sample	Compositions (%)	Amount of Mo (VI) %						
		Certified	Found* (Relative error) (%)					
			Zero	R (%)	D1	R (%)	D2	R (%)
BCS 406/1	Ni (0.14); Mo (0.05); Cr (1.06); Co (0.016); Cu (0.09); V (0.19); Mn (0.066);	0.050	0.048	-4.0	0.049	-2.0	0.049	-2.0
BCS 406	Mn (0.53); Ni (1.69); Mo (1.03); Cr (2.12); Cr (2.12); Cu (0.32); V (0.02);	1.030	1.010	-1.92	1.020	-0.97	1.020	-0.97
BCS 219/4	Mn (0.81); Cr (0.66); Ni (1.69); Mo (0.58); Fe (95.0); Cu (0.088); Sn (0.11);	0.580	0.575	-0.86	0.577	-0.17	0.577	-0.17
BCS483	W (10.08); Mo (0.17); Cr (3.21); V (0.54); Mn (0.29); Co (1.94); Rest Fe(0.170);	0.170	0.165	-2.94	0.168	-1.17	0.168	-1.17

NBS 362	Mo (0.068); C (0.16); Mn (1.04); Si (0.39); V (0.04); Ti (0.084); W (0.20); Sn (0.016); Al (0.09); Zr (0.019); Sb (0.013);Cr (0.30): Cu+2(0.050) As(0.09)	0.068	0.066	-2.94	0.067	-1.47	0.067	-1.47
JSS 169-3	Mo (0.064) Ti (0.013); As (0.005) Ni (0.050); Sn (0.011) Al (0.045); Ca (0.0006);	0.064	0.062	-3.12	0.063	-1.56	0.063	-1.56
JSS 171-3	Mo (0.035) Ti (0.036); As (0.045) Ni (0.011); Sn (0.034) Al (0.040) Ca (0.0013); Cr (0.067);	0.035	0.033	-5.71	0.034	-2.85	0.034	-2.85
Die Steel H 13 Grade EA 0958	Mo (1.254);Si (0.974); Mn (0.364) P (0.024); S (0.006) Cr (4.962) Ni (0.318) V (0.994)	1..254	1.250	-0.31	1.252	-0.15	1.252	-0.15

*Average of three determinations

Application to Pharmaceutical sample:

Pharmaceutical sample (2 g) (Pantobionta) was heated after treating it with 15 ml of 1 N $HNO_{3.}$Then 15 ml 1:1 mixture of HNO_3 and $HClO_4$ were added and the solution was heated until dryness. The residue was dissolved in hot distilled water and 15 ml of 2 M HCl were added. The solution was filtered and diluted unto 50 ml with distilled water. To avoid the interference of Fe (III) in the determination of Molybdenum (VI) Fe (III) was precipitated as Fe $(OH)_3$ by adding 2 M NaOH solution. The resulting solution was filtered, neutralized and made upto the mark in a 100 ml volumetric flask. The Molybdenum (VI) in this solution was determined by the recommended procedure from a pre determined calibration plot and the results are presented in the table 4

Table4: Determination of Molybdenum (VI) in Pharmaceutical sample

Sample	Amount of Molybdenum (VI) (µg/ml)						
	Certified	Amount found*					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Bearing metal alloy	2.0	1.94	-3.0	1.96	-2.0	1.96	-2.0

Physico-chemical and analytical characteristics:

The results obtained in zero order and derivative spectrophotometric methods for Molybdenum (VI)-CHBH complex were compared and presented in Table 5. From this it was noticed that in derivative spectra the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

Table 5: Physico-chemical and analytical characteristics of Molybdenum (VI) - CHBH complex

Characteristics	Results
λ_{max}	404 nm
pH range	1.0-6.0
Optimum pH range	3.0-4.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)
Molar absorptivity (L.mol^{-1}cm^{-1})	6.829 x 10^{4}
Sandal's sensitivity (µg/cm^{2})	0.0014
Beer's law validity range (µg/ml)	0.047-0.479
Optimum concentration range (µg/ml)	0.0954-0.863
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1
Stability constant of the complex	12.29 x 10^{6}
Standard deviation in the determination of 0.191 µg/ml of Mo (vi) (III) for ten determinations.	0.0008

Relative standard deviation (%)	1.0
Regression coefficient	0.999
Detection limit (µg/ml)	0.0024
Determination limit (µg/ml)	0.0072

Table 6 Comparison of spectrophotometric methods for the determination of Mo (VI)

Reagent	λmax (nm)	pH	Molar absorptivity (L mol^{-1} cm^{-1})	Extraction/ Heating	Beer's law Range	Ref
2-Hyroxy-4- ethoxyvalerophenone	420	-	1.5×10^3	Heated at 30°C	-	22
O, O' -Bis (2-ethyl) dithiophosphoricacid	503	Acid medium	9.6×10^3	Heated at 45°C	0.5-4.0 µg	23
3-hydroxy- 2-(4-metoxyphenyl) -6-propionyl-4H-chromen-4-one	416	-	5.5×10^4	Extn - C_2H_4Cl	0-2.5µg	24
Isoamylxanthane	470	5.0-5.8	1.13×10^4	Extn. $CHCl_3$	0.5-8.0 ppm	25
pipazathatehydrochloride	461	H_3PO_4 medium	4.0×10^4	-	0.5-6.9 µg/mL	26
2,4-dihydroxy benzaldehyde isonicotinoyl hydrazone	445	1.5	1.02×10^4	-	0.3-0.6 µg/mL	27
2-hydroxy acetophenonebenzoylhydrazone	443	-	2.59×10^4	-	0.1-3.0 ppm	28
3-methoxy saIciladehyde-4-hydroxy benzoylhydrazide	374	2.5	7.4×10^4		0.096 - 0.96 (µg/ml)	29
Cinnamaldehyde 4hydroxybenzoyhydrazone (CHBH)	404	3.0	6.829×10^4		0.047-0.527	Present method

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