A Rapid Spectrophotometric Determination of Molybdenum(VI) Using 2′-Hydroxyacetophenone Benzoylhydrazone

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2′-Hydroxyacetophenone benzoylhydrazone (HABH) has been used for the first time as an analytical reagent for determination of molybdenum spectrophotometrically. Molybdenum (VI) in presence of large number of cations, anions, and complexing agents except oxalate and borate, forms a yellow complex with HABH extractable into carbon tetrachloride from weakly acidic solution. As many as 31 cations, 15 anions, and complexing agents were studied. The absorbance of the complex was measured at 390 nm. The color was stable for more than 18 h. The system conformed to Beer's law over the concentration range of 1.28 to 13.8 μg of molybdenum per cm^3. The procedure is simple, selective, reproducible and takes <10 min in a single determination of molybdenum in large number of synthetic samples.

Gossypol isonicotinoylhydrazone[1] and other hydrazone derivatives[1—3] have been used for spectrophotometric determination of molybdenum (VI) in acidic media. In most of the cases, the sensitivity and Beer's law range are low and the methods are less selective while in one, the stable complex is formed either slowly or on heating for a long time at a fixed acidity and the absorbance measurements are made in aqueous phase. The proposed method using 2′-Hydroxyacetophenone benzoylhydrazone (HABH) as a reagent is more convenient as it is carried out at room temperature, improves Beer's law range, decreases the interferences from many common elements and complexing agents, is rapid and can be successfully applied in the analysis of complex samples in the diversified matrix after extracting the colored complex into carbon tetrachloride, with a better accuracy.

Experimental

Apparatus and Reagents. UV-vis (Shimadzu-140-02) spectrophotometer with 10-mm matched cells was used for absorbance measurements.

A stock solution of molybdenum was prepared by dissolving sodium molybdate dihydrate (E. Merck) in deionized water to give 10 mg-Mo cm^{-3} and standardized by oxine method.[4a] Aliquots were suitably diluted to give solutions with lower concentrations of the metal ion at the $\mu g\,cm^{-3}$ level.

The solutions of the other ions were prepared by dissolving their commonly available salts of C. P. or A. R. quality in water or dilute hydrochloric or sulphuric acid to give ≤ 10 $mg\,cm^{-3}$ concentration of the ions and standardized by conventional methods.[4]

2′-Hydroxyacetophenone benzoylhydrazone (HABH) was synthesized by the reported method[5] and dissolved in ethanol to give 0.3% (w/v) solution.

Procedure. A sample solution containing ≤ 138 μg molybdenum and other ions was taken in a 100-cm^3 pear shaped separatory funnel with standard joint stopper. To this 0.5 cm^3 of 1 mol dm^{-3} HCl and enough water were added to make the volume of aqueous phase 9.0 cm^3. Then 10 cm^3 carbon tetrachloride followed by 1.0 cm^3 of 2′-hydroxyacetophenone benzoylhydrazone were added and the content was shaken without delay for one min. The lower yellow organic layer was passed through a Whatman No.41 filter paper and collected into a 10 cm^3 measuring flask. The volume was made up to the mark with carbon tetrachloride, if necessary and absorbance of the organic extract was measured at 390 nm using 10-mm cells against a similarly prepared reagent blank.

Vanadium(V), copper(II), iron(III), and chromium(VI) when present in the sample were completely masked with ascorbic acid and/or disodium dihydrogen ethylenediaminetetraacetate added to the aqueous phase before the addition of solvent and the reagent.

Molybdenum contents in the samples were obtained from a calibration curve plotted under identical conditions of the procedure.

Results and Discussion

Absorption Spectra, Beer's Law and Sensitivity. The absorption spectrum of yellow colored Mo–HABH complex in carbon tetrachloride against reagent blank shows an absorption maximum at 390 nm as shown in Fig. 1, Curve A. The absorption spectrum of the reagent blank against carbon tetrachloride is also

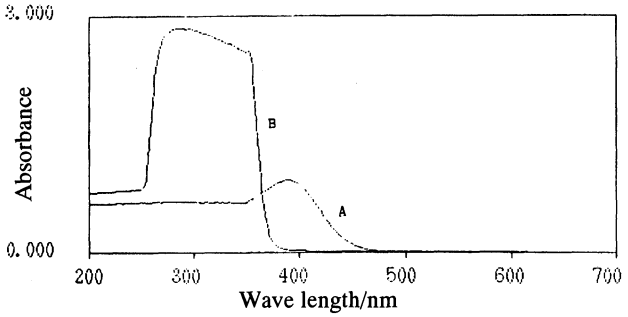

Fig. 1. Absorption spectra of Mo(VI)–HABH Complex. (A) Complex against reagent blank, (B) Reagent blank against pure solvent. Conditions: Mo(VI) = 100 μg; HABH [0.3%(w/v)] = 1 cm^3; 1 mol dm^{-3} HCl = 0.5 cm^3; aqueous volume = solvent volume = 10 cm^3; solvent = carbon tetrachloride; equilibration time = 1 min; number of extractions = 1.

shown in Fig. 1, Curve B. The reagent blank absorbs strongly below 365 nm, above which the absorbance decreases and becomes insignificant in the wavelength region above 380 nm. Therefore, all the measurements are carried out at 390 nm. The absorbance of the yellow complex in carbon tetrachloride shows linear response up to 14.5 $\mu g\,cm^{-3}$ of molybdenum and obeys the Beer's law, with the molar absorptivity of 8.53×10^3 $dm^3\,mol^{-1}\,cm^{-1}$. The optimum range as obtained from Ringbom diagram[6] is 1.28 to 13.8 $\mu g\,cm^{-3}$ of molybdenum at 390 nm. Sandell's sensitivity of the method is 0.0112 μg-Mo cm^{-2}.

Choice of the Solvent and Color Stability. The colored complex is quantitatively extracted into carbon tetrachloride, benzene, diethyl ether, carbon disulfide, chloroform, butyl acetate, isopentyl acetate, isobutyl methyl ketone, isopentyl alcohol, and ethyl acetate as indicated by the complete absence of Mo in the raffinate tested by thiocyanate method[7] and shows maximum molar absorptivity in carbon tetrachloride (Table 1). The λ_{max} is independent of the nature of the solvent used. Other solvents such as cyclohexane, 1,2-dichloroethane, dichloromethane, and 1-butanol extract the colored complex partially. The color intensity of the complex remains constant for more than 18 h in carbon tetrachloride. Single extraction with equal volumes (10 cm^3) of carbon tetrachloride is sufficient to give quantitative extraction of the colored species.

Effect of Acidity. Effect of acidity on the system is examined in terms of absorbance of the complex in the organic phase. Maximum absorbance is obtained when extractions are carried out from 0.01 to 0.15 $mol\,dm^{-3}$ HCl and 0.02 to 0.05 $mol\,dm^{-3}$ H_2SO_4 media (Table 2). The absorbance in H_2SO_4 medium is slightly higher than that in HCl but the latter gives a much wider acidity range for constant absorbance and hence preferred for further investigations. In each case, the aqueous phase after heating to boil for 2—3 min and cooling when tested by the thiocynate method,[7] is void of molybdenum. Thus quantitative extraction of molybdenum occurs in the entire acidity range. In neutral medium, molybdenum shows no color reaction with the reagent. Phosphoric and acetic acids are also tried but not found suitable as the absorbances are much lower in these cases.

Table 1. Effect of Solvent on Mo(VI)–HABH Absorbance

Solvent	λ_{max} nm	Molar absorptivity 10^3 $dm^3\,mol^{-1}\,cm^{-1}$
Carbon tetrachloride	390	8.53
Benzene	389	8.39
Diethyl ether	390	8.25
Carbon disulfide	390	8.06
Chloroform	389	6.91
Isopentyl acetate	390	5.75
Isobutyl methyl ketone	390	5.61
Isopentyl alcohol	390	5.56
Ethyl acetate	390	5.37
Butyl acetate	390	5.23
Cyclohexane	390	1.92
1,2-Dichloroethane	390	1.05
Dichloromethane	390	0.81
1-Butanol	390	0.59

Conditions: Mo(VI) = 100 μg; 1 $mol\,dm^{-3}$ HCl = 0.5 cm^3; HABH [0.3%(w/v) in ethanol] = 1 cm^3; aqueous volume = solvent volume = 10 cm^3, equilibration time = 1 min; number of extractions = 1.

Time of Equilibration. The development of maximum absorbance in carbon tetrachloride takes just 30 s and attains constancy hereafter up to 5 min equilibration time. This shows that time is not a critical factor in the determination (Table 2).

Effect of Concentration and Order of Addition of Reagent. With the variation of the reagent concentration, it is found that 0.5 to 1.2 cm^3 of HABH (0.3% w/v in ethanol) are sufficient to extract 100 μg of molybdenum in a single operation and to give maximum and constant absorbance (Table 2). Increased concentration of the reagent causes turbidity in the solvent phase. Hence, extractions are carried out using 1.0 cm^3 of the reagent. The sequence of adding water and acid to the molybdenum solution is not important in the procedure, provided that the reagent is added after addition of the solvent and the mixture solution is immediately shaken without delay. If the reagent is added prior to the solvent and waited for sometime before shaking, low absorbance is obtained. This is due to the lower stability of the complex in aqueous phase.

Composition of the Complex. In the extracted species, the ratio of Mo(VI)–HABH is found to be 1 : 2 as determined by Job's method of continuous variations[8] at two different concentrations 1.04×10^{-4} M and 2.08×10^{-4} M (1 M = 1 $mol\,dm^{-3}$) showing a sharp peak at 0.67 mole fraction of the ligand (Fig. 2) which is also confirmed by mole-ratio method[9] at two different wavelengths 390 and 410 nm showing a clear break at 1 : 2 metal–HABH ratio and by slope-ratio method[10] showing ratio of slopes as 2 and 1.95 at wavelengths 390 and 410 nm respectively.

Effect of Diverse Ions. Under the optimum conditions as given in the procedure Zn(II), Cd(II), Zr(IV), Fe(II), Ni(II), Al(III), Hg(II), U(VI), Ce(IV), Cr(III), Mn(II), Co(II), Ag(I), Mg(II), Th(IV) up to 1 $mg\,cm^{-3}$ amounts; each of As(V) and Pb(II) 0.5 $mg\,cm^{-3}$; Se(IV) 0.1 $mg\,cm^{-3}$; each of Pt(IV), Au(III), and Rh(III) 0.02 $mg\,cm^{-3}$ and each of Re(VII) and Ru(III) 0.01 $mg\,cm^{-3}$ amounts do not show any absorbance and hence are noninterfering.

Vanadium(V), Cu(II), Fe(III), Cr(VI), and Sn(II) can be masked with suitable masking agents. Each mg of V(V) requires 10 mg ascorbic acid and 15 mg disodium dihydrogen ethylenediaminetetraacetate together for complete masking. The excess amount (5 mg) over the tolerance level (10 mg) of the latter com-

Table 2. Effect of Various Parameters on the Absorbance of Mo(VI)–HABH Complex

$HCl^{a)}$/mol dm^{-3}	0.00	0.01—0.15	0.2	0.25	0.3	0.5			
Absorbance	0.008	0.890	0.885	0.875	0.860	0.790			
$H_2SO_4^{a)}$/mol dm^{-3}	0.00	0.005	0.01	0.015	0.02—0.05	0.075	0.1—0.125	0.15—0.2	0.25
Absorbance	0.008	0.860	0.880	0.895	0.900	0.890	0.885	0.880	0.870
$CH_3COOH^{a)}$/mol dm^{-3}	0.00	0.01	0.02	0.03	0.04—0.15	0.2—0.25	0.3	0.4	0.5
Absorbance	0.008	0.745	0.830	0.845	0.850	0.835	0.820	0.800	0.780
$H_3PO_4^{a)}$/mol dm^{-3}	0.00	0.003	0.006	0.009—0.03	0.05	0.06	0.083	0.1	
Absorbance	0.008	0.870	0.840	0.820	0.815	0.800	0.805	0.800	
2′-Hydroxyacetophenone benzoylhydrazone (0.3% w/v)$^{b)}$/cm^3			0.1	0.2	0.3	0.4	0.5—1.2	1.5	2.0
Absorbance			0.560	0.770	0.865	0.885	0.890	0.905	0.940
Equilibration time$^{c)}$/s			2	15	30—300				
Absorbance			0.270	0.860	0.890				

a) Conditions: Mo(VI) = 100 μg; HABH [0.3%(w/v) in ethanol] = 1 cm^3; aqueous volume = solvent volume = 10 cm^3; solvent = carbon tetrachloride; equilibration time = 1 min; number of extractions = 1; molarity = variable. b) Conditions: 1 mol dm^{-3} HCl = 0.5 cm^3; other conditions are the same as in (a) excepting variation in HABH content. c) Conditions: HABH [0.3%(w/v) in ethanol] = 1 cm^3; other conditions are the same as in (b) excepting variation in equilibration time.

plexing agent does not affect the absorbance of Mo complex in presence of V(V). Each mg of Cu(II) and Sn(II) requires 10 mg disodium dihydrogen ethylenediaminetetraacetate and each mg of Fe(III) requires 4 mg ascorbic acid. For each mg of Cr(VI) 8 mg ascorbic acid and 7 mg disodium dihydrogen ethylenediaminetetraacetate are added together to suppress the extraction completely. Tungsten(VI) can not be suppressed completely by any of the complexing agents studied within the conditions of the proposed method and hence is interfering. Presence of Sn(II) resulted low recovery of molybdenum. Antimony(III) and Bi(III) get hydrolyzed under the proposed conditions of the method. In case of Bi(III) up to 0.2 mg cm^{-3}, the extraction is performed as such. There is no adsorption of the metal ion on the precipitate and the absorbance of Mo complex remains unchanged.

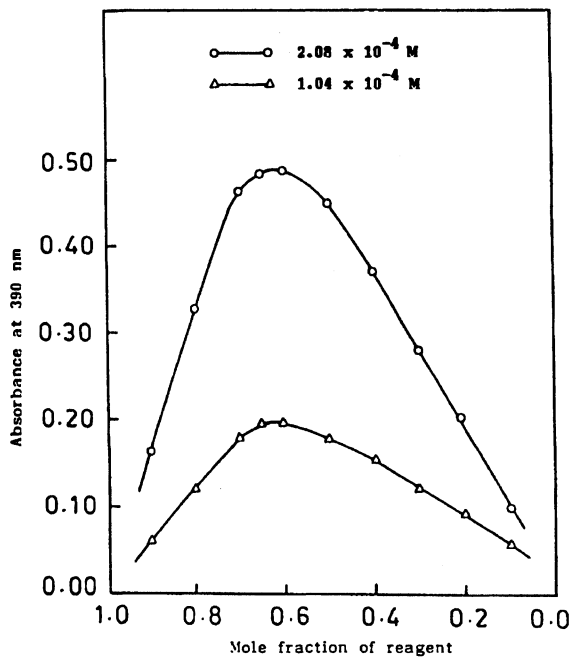

Fig. 2. Job's Continuous variation method. Conditions: 1 mol dm^{-3} HCl = 0.5 cm^3; aqueous volume = solvent volume = 10 cm^3; solvent = carbon tetrachloride; equilibration time = 1 min; number of extractions = 1.

The tolerance limits for many anions and complexing agents have been worked out (Table 3). It is found that ≤50 mg each of thiourea and ascorbic acid, ≤10 mg each of acetate, chloride, sulfate, nitrate, thiocyanate, and disodium dihydrogen ethylenediaminetetraacetate added initially to the aqueous phase (10 cm^3) do not affect the absorbance of Mo(VI)–HABH complex. For phosphate, tartrate and citrate the tolerance limits are 4.0, 1.0 and 0.5 mg respectively. Glycerol has no effect on absorbance if present in less than 0.5 cm^3. Oxalate, fluoride and borate interfere even in small amounts.

Precision and Accuracy. A standard solution containing 50 μg of molybdenum(VI) is estimated 8 times by the recommended procedure. The average absorbance is 0.446 with a standard deviation of 0.004 absorbance unit and a relative mean error of ±0.224%.

Applications. The wide applicability of the method is tested by the satisfactory analysis of a variety of synthetic samples containing molybdenum up to 100 μg in the aliquot (Table 4). This method is quite

Table 3. Effect of Anions and Complexing Agents on Mo(VI)–HABH Absorbance

Salt added	Amount mg/10 cm^3	Absorbance
None	—	0.890
Thiourea	50	0.890
Ascorbic acid	50	0.890
Sodium chloride	10	0.890
Sodium acetate	10	0.890
Sodium sulfate	10	0.890
Sodium nitrate	10	0.890
Potassium thiocyanate	10	0.890
Sodium phosphate	4	0.890
Sodium citrate	0.5	0.890
Glycerol[a)]	0.5, 1	0.890, 0.875
Disodium dihydrogen ethylenediamine tetraacetate	10	0.885
Sodium potassium tartrate	1	0.880
Sodium fluoride	0.5	0.840
Sodium oxalate	1	0.145
Sodium borate	1	0.120

Conditions: Mo(VI)=100μg; HCl (1 mol dm^{-3})=0.5 cm^3; HABH [0.3%(w/v) in ethanol]=1 cm^3, aqueous volume=solvent volume=10 cm^3; solvent=carbon tetrachloride, equilibration time=1 min; number of extractions=1. a) Added in cm^3.

Table 4. Analysis of Different Samples by the Proposed Method

Sr. No.	Composition of sample		Mo(VI) found[c)]
	Matrix[a)]	Mo(VI) added/μg	μg
1.	Fe(2), Co(5), Cu(1.5)	50	50.3
2.	Fe(0.5), V(1), Cr(0.8), Cu(0.8)	100	99.2
3.	Re(0.1), Mn(2)	40	39.7
4.	V(0.5), Cu(1), Ni(0.8)	50	50.6
5.	Mn(1), Al(0.5), Th(2)	80	80.8
6.	Pb(1), Zn(2), Cd(1.5)	70	70.0
7.	Fe(1.5), Cu(0.5), Re(0.1)	10	10.7
8.	Al(0.5), Zn(2), U(1)	10	9.9
9.	Pb(1), Cd(2), Th(1)	40	39.8
10.	U(0.5), Pt(0.2)	25	25.0
11.	Rh(0.2), Ru(0.1)	25	24.7
12.	Zn(3), Se(1)	25	25.4
13.	[Fe(1.75), Cu(0.025), Ni(0.228), Cr(0.475)][b)]	25	24.7
14.	[Fe(0.87), Ni(0.224), Cr(0.3), Cu(0.015), Mn(0.03)][b)]	60	59.8

a) Figure in bracket indicates the amount of the metal ion added in mg/10 cm^3 aqueous phase. b) Sample Nos. 13 and 14 are analogous to stainless-U and stainless steel, respectively. c) Average of triplicate analyses.

selective for molybdenum determination in the presence of large number of elements especially vanadium, chromium, manganese, iron, cobalt, uranium, platinum, rhodium, ruthenium, selenium, arsenic, nickel, copper, rhenium, thorium, gold, bismuth, and aluminium which seriously interfere in most of the existing methods of molybdenum determination.[11)] The present method is found to be simple, rapid, precise and accurate. The total operation for each run requires not more than 10 min. The method can be used satisfactorily in the analysis of commercial samples especially molybdenum steels. Also the reagent 2'-hydroxyacetophenone benzoylhydrazone has been used for the first time for molybdenum determination.

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