

Determination of molybdenum (VI) with 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone using direct and derivative spectrophotometry

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ABSTRACT

Highly sensitive and selective direct spectrophotometric method is proposed for the determination of molybdenum in various real samples. 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone reacts with Mo(VI) forming an orange red coloured soluble complex in aqueous dimethyl formamide which has a λ_{\max} at 450 nm in the pH range 2-3. The system obeyed Beer's law in the range 0.959-9.59 μ g/ml of Mo (VI). The molar absorptivity is $0.65 \pm 0.002 \times 10^4$ l mol⁻¹ cm⁻¹ and the Sandell's sensitivity is 0.0147 μ g/cm². The standard deviation of the method for ten determinations of 9.59 μ g/ml of Mo (VI) is 0.008. The correlation coefficient (γ) of the calibration equation for the experimental data is 0.9995. Studies on effect of diverse ions showed almost all the anions, except Tartrate, Fluoride and Ascorbate and a majority of the cations do not interfere. The interference from Fe(III), Ti(IV), Zr(IV), Th(IV) and Cu(II) was eliminated using suitable masking agents. The direct method was applied for the determination of molybdenum in steel and alloy samples.

Key words: Mo(VI), direct spectrophotometric determination, 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone.

1.Introduction

The agriculture and metallurgy applications of molybdenum are quite abundant. About 85 percent molybdenum that is being produced is used in manufacture of iron based alloys. Benzoic hydrozones of carbonyl compounds has been used extensively for the spectrophotometric determination of metal ions in our laboratories. Although several methods have been reported for the spectrophotometric determination of Mo(VI), but they suffer from some drawbacks. 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone is used for the determination of molybdenum(VI). Derivative spectrophotometry is a very useful approach for determination of the concentration of simple components in mixtures with overlapping spectra as it eliminates much of the interference. 2-HNHBH reacts with molybdenum(VI) in aqueous DMF forming a highly sensitive and stable orange red coloured complex. This has been systematically studied both by direct and first derivative spectrophotometrically and the results are presented in this paper.

2.MATERIALS AND METHODS

2.1. The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively. Suitable settings for first order derivative are as follows: spectra, band width 5 nm; wavelength readability 0.1 nm increment, scan speed fast (nearly 2200 nm min⁻¹); wave length accuracy ± 0.5 cm with automatic wavelength correction and with 9 degrees of freedom.

2.2. **2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrozone:** This reagent was prepared by condensing 2-hydroxy-1-naphthaldehyde and p-hydroxy benzoic hydrazide in methanol using a general procedure. A freshly prepared solution in dimethylformamide is used in the studies.

2.3 .Molybdenum solution (0.01M): A solution of molybdenum(VI) (0.01M) was prepared by dissolving the 0.2419 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (E.Merck) in 100 ml distilled water. The resulting molybdenum(VI) solution was standardized gravimetrically¹. The stock solution is diluted as required.

2.4 Direct spectrophotometry: In each set of different 10 ml standard flasks, 5 ml of buffer solution (pH 2.0), 3 ml of DMF and 0.5 ml of 2-HNHBH (1×10^{-3} M) were taken. Various amounts of molybdenum(VI) were added to these flasks and made up to the mark with DMF. The absorbance was measured at 450 nm against the reagent blank²⁻⁵. The calibration curve was prepared by plotting the absorbance against the amount of molybdenum.

2.5. First order derivative spectrophotometry: For the above solutions, first order derivative spectra were recorded with degrees of freedom 9 in the wavelength range from 400-600 nm. The derivative peak height was measured by peak-zero method at 510 nm. The calibration equations were calculated as $A_{450} = 0.0657C + 0.0016$ for zero order and $A_{510} = 0.00938C + 0.000289$ for the first order derivative data by fitting experimental data⁷⁻⁸. The amount of molybdenum present in the alloy sample was determined by the zero order, first order derivative method and compared with the certified values.

3 RESULTS AND DISCUSSION

3.1. The absorption spectra of the reagent and the complex were recorded in wavelength region 405-500 nm at pH 2.0 (fig.1). The complex shows absorbance maximum at 450 nm where reagent has a negligible absorbance. Hence analytical studies were made at 450 nm against reagent blank⁹. The study of the effect of pH on the colour intensity of the reaction mixture showed that maximum colour was obtained at the pH 2.0. Thus analytical studies were carried out at pH 2.0. A 10 fold molar excess of 2-HNHBH was found necessary for maximum colour development. The yellow colour of Mo^{VI} -2-HNHBH complex was stable for more than 24 hours. Beer's law is obeyed in the range of 0.959-9.59 $\mu\text{g/ml}$. The molar absorptivity and Sandell's sensitivity are $0.65 \pm 0.002 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and 0.0147 $\mu\text{g/cm}^2$ respectively. The standard deviation of the method for ten determinations of 9.59 $\mu\text{g/ml}$ of Mo (VI) is 0.008. The correlation coefficient (γ) of the calibration equation for the experimental data is 0.9995.

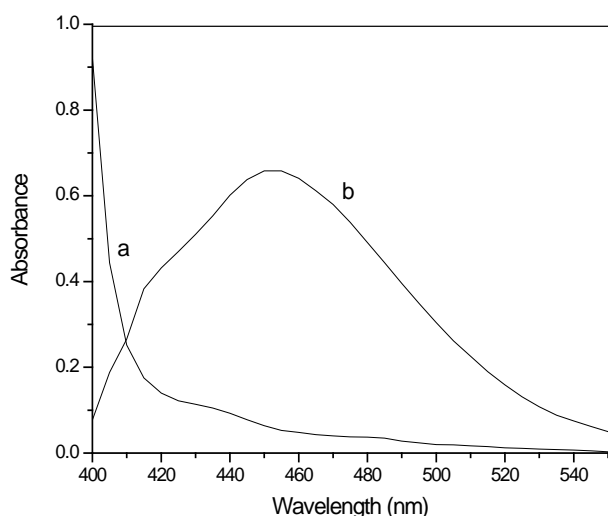


Fig.1. Absorption spectra of

- a) 2-HNHBH Vs buffer blank b) [Mo (VI)] – 2-HNHBH Vs reagent blank
 [Mo (VI)] = 1.0×10^{-3} M; [2-HNHBH] = 1.0×10^{-2} M pH = 2.0

3.2. Effect of foreign ions: The effect of various cations and anions on the determination of Mo(VI) under optimal conditions developed was studied to find out the tolerance limits of these ions in the present method. The results are presented in Table 1. Large amounts of commonly associated cations and anions do not interfere in the present method. 10 fold excess of Cu(II) is masked with thiosulphate and 100 fold excess of Fe(III) and 10 fold excess of Ti(IV) are masked with citrate¹⁰. The composition of the complex was determined using Job's method as 1:1 and confirmed by mole-ratio method. The stability constant of the complex was calculated from Job's method and was obtained as 4.51×10^5 .

3.3. Determination of molybdenum(VI) by first order derivative spectrophotometry: In the zero-order spectrophotometric determination of molybdenum with 2-HNHBH, the commonly associated metal ions such as Ti^{IV} , Cu^{II} and Fe^{III} interferes and were masked by using masking agents. The first derivative spectrophotometric method allows selective determination of Mo^{VI} in presence of these interfering ions without using masking agents. The first derivative spectra of Mo^{VI} -2-HNHBH complex with different concentrations of molybdenum are as shown in fig 2. The peak zero method was followed for peak height measurements and preparation of calibration plot. The maximum peak amplitude was observed at 510 nm where many foreign ions do not interfere. Hence Mo^{VI} is determined by measuring the peak zero amplitude at 510 nm. Beer's law was obeyed in the range 0.959-9.59 μ g/ml. Other statistical data for the present method are the standard deviation of the method for ten determinations of 9.59 μ g/ml of Mo (VI) is 0.008 and the correlation coefficient of the equation is 0.9995.

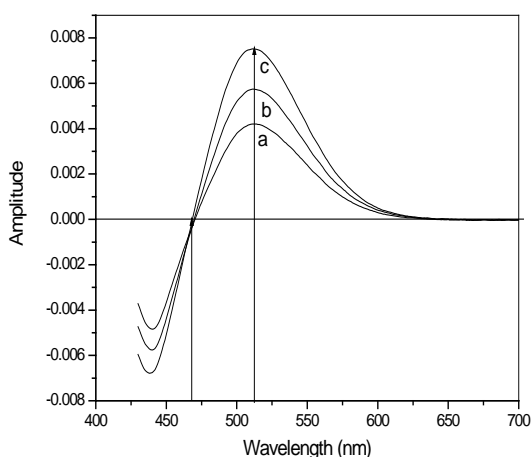


Fig. 2. First derivative spectra of Mo (VI)-2-HNHBH Vs reagent blank

Mo (VI) = a) 5.754 μ g/ml; b) 7.672 μ g/ml; c) 9.59 μ g/ml; pH = 2.0

The effect of various cations and anions on the derivative amplitude was studied. It was noticed that all the ions that do not interfere in the zero order determination of Zr VI (Table 1) did not interfere in the first derivative method also. Further, their limits were in general higher than those of the zero order determination.

4. APPLICATIONS

The present method was employed for the determination of Udimet – 500^a. The amount of zirconium present in alloy sample was determined by the following procedure. A known aliquot of the sample solution is taken in a 10 ml of volumetric flask containing 5 ml of buffer solution of pH 2.0, 0.5 ml of 0.5 M citrate solution (to mask Fe and Ti), 2.5 ml of DMF and 1 ml of (1.0×10⁻² M) reagent solution. The contents of the flask are diluted to 10 ml. The contents, if necessary, are filtered and the absorbance of the filtrate is measured at 450 nm against the reagent blank and the amount of molybdenum is calculated from the predetermined calibration plot. The derivative amplitude of the solution is measured at 510 nm.

5. CONCLUSIONS

The first derivative spectrophotometric method was found to be more sensitive and selective than the zero order method for the determination of molybdenum(VI).

Table 1

Ion	Tolerance Limit (µg/ml)	Ion	Tolerance Limit (µg/ml)
Thiocyanate	3050	Mg (II)	6200
Nitrate	2000	Ca (II)	5800
Thiosulphate	2000	Na (I)	6000
Citrate	2000	K (I)	5200
Chloride	1920	Ba (II)	4650
Bromide	1500	Cd (II)	2500
Iodide	1000	W (VI)	810
Thiourea	650	Hg (II)	512
Sulphate	500	Te (IV)	200
Carbonate	500	Al(III)	200
Oxalate	200	Se (IV)	120
Phosphate	100	Mn (II)	110
EDTA	20	Co (II)	100
Tartrate	Interferes	Pb (II)	76
Fluoride	Interferes	Zn(II)	50

Ascorbate	Interferes	Cr (VI)	46
		Bi (III)	20
		Pd (II)	10
		U (VI)	10
		Ni (II)	10
		V(V)	5
		Fe(III) [#]	Interferes
		Ti(IV) [#]	Interferes
		Zr(IV)	Interferes
		Th(IV)	Interferes
		Cu(II)*	Interferes

*Masked with thiosulphate

#Masked with citrate

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