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A Rapid Spectrophotometric Determination of Vanadium(V) and Molybdenum(VI) Using 2,2′-Dihydroxyazoxybenzenes

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The photometric studies of vanadium(V) and molybdenum(VI) are carried out with 2,2′-dihydroxyazoxybenzenes (DHAB) in 50% ethanol-water medium at pH 2.4 and 1.5, respectively. The maximum absorbance occurred at 405 nm and 625 nm for vanadium-DHAB and molybdenum-DHAB systems. Beer's law is obeyed in the concentration ranging from 0–7 ppm and 0–54 ppm and molar absorptivities of the systems are 5.814×10^3 and 8.90×10^2 dm^3 mol^{-1} cm^{-1} for V-DHAB and Mo-DHAB systems, respectively. The effects of foreign ions are also studied.

Key Words: Spectrophotometric determination, Vanadium(V), Molybdenum(VI), 2,2′-Dihydroxyazoxybenzenes.

INTRODUCTION

Various reagents have been adopted for spectrophotometric determination of vanadium[1–7] and molybdenum[8–15]. We report herein the spectrophotometric determination of vanadium(V) and molybdenum(VI) using 2,2′-dihydroxyazoxybenzenes (DHAB] as a new analytical reagent.

EXPERIMENTAL

All the chemicals were of analytical grade, otherwise it is specified. 2,2′-dihydroxyazoxybenzene (DHAB) was prepared according to literature method[16]. Stock solution of 0.05 mol dm^{-3} of reagent was prepared in absolute ethanol and lower concentrations were obtained by diluting with ethanol. Vanadium and molybdenum 0.01 mol dm^{-3} were prepared from ammonium metavanadate[17] and ammonium heptamolybdate[17] and the contents were estimated by standard procedures[17].

The photometric measurements were recorded on Jasco 7800 using 10 mm glass transmission cells. Elico pH meter combined electrode was used for pH measurements.

Buffer Solutions: These were prepared by mixing an appropriate amount of HCl and KCl for pH 1 to 3 and acetic acid and sodium acetate for pH 3–6.

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Calibration curve for V-DHAB system: 3 mL aliquot of the ammonium metavanadate (3 ppm), 2 mL of buffer of pH 2.4 solution and 5 mL of 0.001 mol dm^{-3} reagent were added in 25 mL of standard measuring flask and made up to the mark with an appropriate volume of ethanol. The red-orange complex of vanadium(V) was measured spectrophotometrically at 405 nm against blank reagent. The amount of vanadium(V) was computed from a calibration curve.

Calibration curve for Mo-DHAB system: To an aliquot of the sample solution containing 9 to 50 ppm of Mo(VI) in a 25 mL standard flask, 2 mL of buffer of pH 1.5, and 5 mL of 0.06 mol dm^{-3} reagent solution were added. The contents were made up to the mark with ethanol and absorbance was measured at 625 nm against a blank prepared identically. The amount of Mo(VI) was determined from the calibration curve.

RESULTS AND DISCUSSION

The maximum absorption occurred at 405 and 625 nm for V-DHAB and Mo-DHAB systems respectively against a reagent blank in ethanol-water (50% v/v) and pH at 2.4 and 1.5 respectively.

Choice of solvent: These complexes were not extracted by most of the organic solvents. Among the water miscible solvents like methanol, ethanol, dimethylformamide and dimethyl sulfoxide, ethanol is most suitable solvent for both the systems.

Effect of pH: On varying the pH and volume of buffer solutions, the maximum absorbance occurred at 2 mL of buffer with pH 2.4 for V-DHAB and pH 1.5 Mo-DHAB system, respectively. No absorbance changes were noted on changing the order of addition of the reagents for both the systems.

Effect of reagent: On examination, the amount of reagent required to bring maximum absorption was found to be two-fold for V-DHAB and four-fold for Mo-DHAB systems.

Beer's law, sensitivity and time stability: The stability of the complexes was found to be more than 12 h. The systems obeyed Beer's law in concentration ranging from 0–7 ppm and 0–52 ppm for V-DHAB and Mo-DHAB systems with molar absorptivity of 5.814×10^3 and 8.90×10^2 dm^3 mol^{-1} cm^{-1}. Sandell's sensitivity of the systems was determined to be 0.009 μg V cm^{-2} and 0.105 μg Mo cm^{-2} respectively. These were tested by ten replicate analyses and standard deviation were found to be 1.68×10^{-3} and 2.0×10^{-3} respectively.

Composition of the complexes: The composition of the complexes was determined by Job's[18], mole-ratio[19] and slope-ratio[20] methods. Both the complexes were found to be 1 : 1 (metal : ligand). The stability constant of the complexes was determined to be 1.5×10^4 and 2.0×10^3 for V-DHAB and Mo-DHAB systems, respectively.

Effect of diverse ions: At constant amount of vanadium (3 ppm) and molybdenum (30 ppm) were carried out with varying concentrations of different anions and cations. The tolerance limits of each ion giving a maximum error of ±2% are summarized in Table-1.

TABLE-1
STUDY OF INTERFERENCE OF FOREIGN IONS (3 PPM OF VANADIUM AND 30 PPM OF MOLYBDENUM(VI) IN 25 mL)

Cations	Tolerance limit (μg in 25 mL) (vanadium system)	Tolerance limit (μg in 25 mL) (Molyhdenum system)	Anions	Tolerance limit (μg in 25 mL) (vanadium system)	Tolerance limit (μg in 25 mL) (molybdenum system)
Na^+	1000	1000	Cl^-	1000	100
K^+	6000	2000	Br^-	500	50
Mg^{2+}, Mn^{2+}, Hg^{2+}	1000	100	I^-	750	15
Al^{3+}	5	10	NO_3^-	35	15
Ba^{2+}	250	10	SO_4^{2-}	3000	50
Ni^{2+}	25	10	BrO_3^{2-}	2000	100
Zn^{2+}, Fe^{2+}, U^{6+}	125	100	IO_3^-	375	50
Sr^{2+}, Co^{2+}	30	5	oxalate	1750	50
Cu^{2+}	35	10	tartrate	250	20
Cd^{2+}	3000		bisulphate	375	20
Ce^{4+}	0.5		acetate	1600	—
			thiosulphate	125	10

Application: The proposed method for determination of vanadium (3 ppm) and molybdenum (30 ppm) was rapid (took < 5 min for single operation), and free from large number of cations and anions, which interfered in most of the methods, are employed for its determination. The applicability of the method was tested by satisfactory analysis of synthetic mixture. The results obtained were highly reproducible (Table-2).

TABLE-2
ANALYSIS OF DIFFERENT SYNTHETIC SAMPLES BY THE PROPOSED METHOD

Matrix[a]	V(V) added (μg in 25 mL)	V(V)[b] found (μg in 25 mL)	Matrix[a]	Mo(VI) added (μg in 25 mL)	Mo(VI)[b] found (μg in 25 mL)
Ce(0.5), Al(5.0), Zn(7.5)	200	198	Mn(100), Mg(100), Hg(100)	600	602
Mg(50), Ni(25), Cd(3000)	180	182	Al(10), Hg(100), Cu(10)	765	760
Cu(35), Ni(25), Ba(250)	200	202	Zn(10), Co(5), Sr(5)	720	720
Mo(30), Sr(125), U(7.5)	190	190	Cu(10), Ni(10), Ba(10)	650	645
Mn(50), Co(125), U(7.5)	200	198	Fe(100), U(100), Al(10)	675	678
Ni(125), Fe(10), U(7.5)	180	185	Sr(5), Ni(10), Mg(100)	680	680

(a) Figure in parentheses indicate the amount of metal ions added in μg/25 mL.
(b) The average of triplicate analyses.

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