

# Direct and Second Order Derivative Spectrophotometric Determination of Vanadium (IV)

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**Abstract:** A new spectrophotometric method has been developed for the determination of vanadium (IV) in aqueous dimethyl formamide using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATC) as a chromophoric reagent. The vanadium (IV) reacts with HMBATC forming a dark yellowish green colored water soluble complex, [V(IV)-HMBATSC] in the pH range of 4.0-7.0. The yellowish green colored complex shows the absorption maximum at 395 nm. The Beer's law is obeyed in the range of 0.152 to 1.520  $\mu\text{g ml}^{-1}$ . The molar absorptivity and Sandell's sensitivity were  $2.49 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$  and  $0.02 \mu\text{g cm}^{-2}$  respectively. The interference effect of various foreign ions has been studied. The complex has 1:1 [V(IV)-HMBATSC] stoichiometry with a stability constant of  $0.72 \times 10^3$ . A second order derivative spectroscopic method is also developed for the determination of V(IV), which is more sensitive than the zero order method. The developed method has been employed for the determination of V(IV) in water samples.

**Key words:** Spectrophotometry, Determination of Vanadium (IV), HMBATSC.

## INTRODUCTION

Vanadium is one of the most important micro-elements in environmental chemistry because of its toxic nature; therefore, the determination of vanadium in environmental samples, especially in fuel oil, foodstuffs, and coal fly ash, is of great importance. Vanadium compounds are toxic to human beings and animals. It is found to be present in many tissues, and the concentrations in human blood and plasma are reported<sup>1</sup> to be in the range of 0.005-8.4 mM. Vanadium content in food is directly dependent upon the concentrations present in the soil. Once consumed, vanadium is stored primarily in fatty tissues, and the remaining amounts are stored in the kidney, liver, spleen, or bone. Vanadium poisoning is an industrial hazard<sup>2</sup>. Vanadium has also been reported as the index

element in urban environmental pollution, especially air pollution<sup>3</sup>.

The two most common vanadium forms encountered in environmental, biological and industrial systems are vanadium (V) and vanadium (IV). These forms have different toxic, nutritional, catalytic and other properties<sup>4,5</sup>. The V (IV) is less toxic than V (V) in environmental systems and can be produced by various industrial redox processes. The toxicity of vanadium depends on its physico-chemical state; particularly on its valance state and solubility<sup>6,7</sup>. In body, vanadium can undergo changes in oxidation state (V (V) and V (IV) oxidation states) and it can also bind with blood protein. The concentration of vanadium in several environmental, biological and industrial samples is very low, of the order of a few  $\mu\text{g ml}^{-1}$ , hence accurate

and sensitive methods for determination of vanadium are desirable.

In the literature, some spectrophotometric methods have been reported for the determination of V (IV) based on the complex formation<sup>8</sup>, solvent extraction<sup>9</sup>, redox reaction<sup>10</sup>, catalytic<sup>11</sup>, and catalytic-kinetic methods<sup>12,13</sup>. However, some of the methods suffer from a number of limitations such as interference by diverse ions, standing for a long time for color development followed by extraction and lack of sensitivity. The catalytic methods have serious interference from the oxidants and reductants and also required expensive experimental set up.

The present work describes rapid, simple, sensitive, and selective direct and second derivative spectrophotometric methods for the determination of V (IV) using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent. The developed method was applied for the spectrophotometric determination of micro amounts of V (IV) water samples.

## EXPERIMENTAL

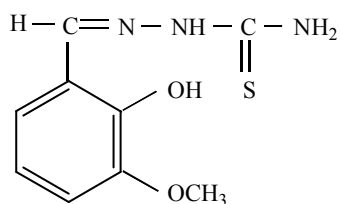
### Apparatus

A Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1 cm quartz cells was used for all spectral measurements. A Philips digital pH meter (model L1 613) was used for pH measurements. The pH meter has temperature compensation arrangement and reproducibility of measurements within  $\pm 0.01$  pH.

### Reagents and Chemicals

The 2-hydroxy-3-methoxy benzaldehyde and thiosemicarbazide were purchased from SD Fine Chemicals, India. Vanadyl sulfate ( $\text{VO}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ ) was obtained from Merck (Darmstadt, Germany). All chemicals and solvents used were of analytical reagent grade. A doubly distilled water was used for preparation of all solutions and experiments.

The preparation and characterization (IR and NMR spectral data) of the reagent, HMBATSC, was done using the reported procedure from Praveen Kumar *et al.*<sup>14</sup> The structural formula of HMBATSC was given below.



A 0.01 M solution of the reagent was prepared by dissolving 0.2250 g of HMBATSC in dimethyl formamide (DMF). Lower concentrations were prepared by diluting the appropriate volume of 0.01 M reagent solution.

### Vanadium (IV) solution

A stock solution vanadium (IV) was prepared by dissolving required amount of  $\text{VO}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  in 0.01 mol L<sup>-1</sup> HCl.

### Buffer solutions

The buffer solutions were prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate for pH 1.0–3.0 and 0.2 M acetic acid and 0.2 M sodium acetate for pH 3.5–7.0. The pH of these solutions was checked with the above mentioned pH meter.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. Solutions of the studied interfering ions of suitable concentrations were prepared using analytical grade reagents.

### Water sample collection and preparation

The water samples (500 mL) collected from Anantapur (Andhra Pradesh, India) were filtered through 0.45  $\mu\text{m}$  pore size membrane filters immediately after sampling, and stored at 4 °C. The filtered water samples were analyzed using the proposed procedure to determine vanadium (IV).

## General procedure

### Direct spectrophotometry

In each of a set of different 10 mL standard flasks, 5 mL buffer solution (pH 6.0), varying volumes of  $1 \times 10^{-4}$  M V (IV) solution and 1 mL of HMBATSC ( $1 \times 10^{-3}$  M) were taken and the remaining volume was made up to the mark with doubly distilled water. The absorbance was measured at 395 nm against the reagent blank. The calibration curve was constructed by plotting the absorbance against the amount of V (IV). The calibration graph follows the straight line equation  $Y = a c + b$ ; where c was the concentration of the solution, Y was measured absorbance or peak height and a and b were constants.

### Second order derivative method

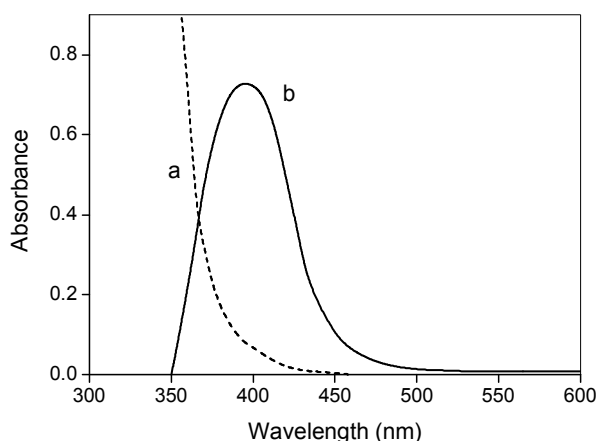
The second order derivative spectra of yellowish green colored vanadium complex solutions were recorded with a scan speed of fast (nearly 2400 nm min<sup>-1</sup>); slit width of 1 nm with one degree of freedom, in the wavelength range 400–550 nm. The derivative peak height was measured by the peak-zero method at 445 nm. The peak height was plotted against the amount of V (IV) to obtain the calibration.

## RESULTS AND DISCUSSION

### Direct spectrophotometry

#### Absorption Spectra

Vanadium (IV) reacts with HMBATSC at pH 6.0 forming dark yellowish green colored solution. The absorption spectra of the solution containing [V (IV)–HMBATSC] complex against the reagent (HMBATSC) blank and that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 300–600 nm (Fig. 1). The V (IV) complex has an absorption maximum at 395 nm where HMBATSC has considerably low absorbance. Hence, further the analytical studies were carried out at 395 nm using the reagent blank.



**Fig. 1.** Absorption spectra of (a) HMBATSC Vs Buffer blank; (b) [V(IV)-HMBATSC] Vs HMBATSC blank; [V(IV)]  $5 \times 10^{-5}$  M; [HMBATSC]  $5 \times 10^{-4}$  M, pH = 6.0.

#### Effect of pH

The effect of pH on the intensity of dark yellowish green color formation was studied to optimize the pH of [V(IV)-HMBATSC] complex. The absorbance measurements were made for the experimental solutions of V(IV) and HMBATSC at different pH values ranging from pH 4.0 to 7.0. The results indicate the absorbance value maximum at pH region 6.0 for the dark yellowish green colored complex. Therefore, further studies therefore, were carried out at pH 6.0.

#### Effect of HMBATSC concentration on the absorbance

The effect of variation in the concentration of HMBATSC on the yellowish green color intensity of the V (IV) complex was studied and the results are presented in Table 1. From the Table 1 can be observed that a minimum of 20 fold excess of reagent was necessary to obtain maximum sensitivity for the

color reaction between V (IV) and HMBATSC. The green color [V(IV)-HMBATSC] complex was instantaneous and stable for more than 48 hours.

**Table 1: Effect of HMBATSC concentration**

V(IV): HMBATSC	Absorbance
1 : 5	0.528
1 : 10	0.655
1 : 15	0.710
1 : 20	0.728
1 : 25	0.725
1 : 30	0.724

#### Determination of V (IV)

To determine of V (IV) at micro levels, the absorbance of the solutions was measured at 395 nm containing variable amounts of V (IV). A straight line was obtained between the absorbance and the amount of V (IV) and indicates the Beer's law obeyed in the concentration range of  $0.152$  to  $1.52 \mu\text{g mL}^{-1}$  of V (IV). The sensitivity of the proposed method has been derived from its molar absorptivity value ( $\epsilon = 2.49 \times 10^4 \text{ lit mol}^{-1} \text{ cm}^{-1}$ ), detection limit ( $0.0093 \mu\text{g mL}^{-1}$ ) and determination limit ( $0.0278 \mu\text{g mL}^{-1}$ ) and correlation coefficient (0.9999). A relative standard deviation of 0.56% confirms the best suitability of the proposed method for the determination of V (IV). The Sandell's sensitivity was found to be  $0.02 \mu\text{g cm}^{-2}$ .

#### Stoichiometry and stability constant

The stoichiometry of [V(IV)-HMBATSC] complex solution was determined by Job's continuous variation method and mole ratio method and obtained as 1:1. The stability constant of the yellowish green soluble complex was calculated from the Job's method as  $0.72 \times 10^3$ .

#### Effect of foreign ions

The effect of various anions and cations normally associated with V (IV) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by  $\pm 2\%$  were calculated and presented in Table 2. Almost all the tested anions possess high tolerance levels ( $>110$  fold excess). Among the metal ions most of them are tolerable is more than 30 fold excess. The metal ions, Ga (III), Cr (VI) and Co (II) were tolerable up to 10-15 fold excess. Co (II) and Cr (VI) were tolerable up to 15 folds excess, and Fe (III) and Co (II) interferes seriously.

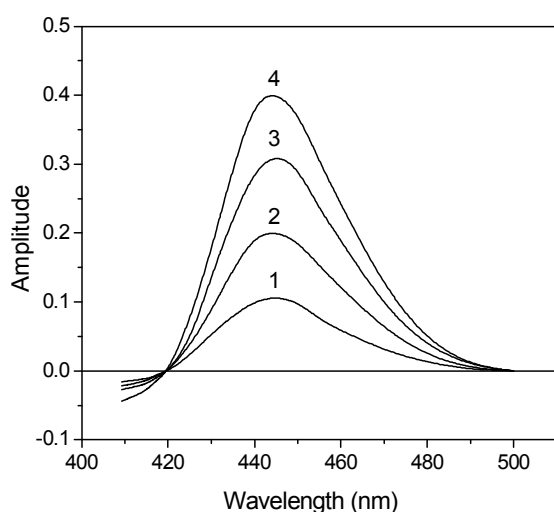
**Table 2. Tolerance limit of diverse ions in the determination of V (IV) ( $0.76 \mu\text{g mL}^{-1}$ )**

Diverse Ion	Tolerance Limit ( $\mu\text{g mL}^{-1}$ )
Chloride, Iodide, Thio sulphate, EDTA, Citrate Tartrate, Pb(II), Th(IV), U(VI), W(VI), Sn(II)	1000-2000
Sulphate, Phosphate, Flouride, Thio Urea, Nitrate, Zr(IV), Ag(I), Y(III), Tl(III), Te(IV)	600-1000
Thio Cyanate, Oxalate, Mo(II), Cd(II), Hg(II)	200-500
Ascarbate, , Al(III), In(III), Ru(III)	100-200
Se(IV), Pd(II), Mn(II), Zn(II)	35-60
Fe(II), Ni(II), Cu(II)	20-30
Ga(III), Cr(VI), V(V)	12-18
Fe(III), Co(II)	3-5

The masking agents like citrate, tartrate and EDTA are not interfering in the recovery of vanadium. Therefore, these masking agents were used to obviate interferents such as Fe (III), and Co (II) and up to a  $20 \mu\text{g}$  level in the determination of vanadium (IV).

### Second order derivative method

In order to improve the sensitivity and selectivity of the direct spectrophotometric method proposed, the absorbance data was derivatized twice and plotted against the wavelength which gave the second order derivative curve. The second derivative spectra of experimental solutions containing different amounts of V (IV) were recorded in the wavelength region 400-550 nm (Fig. 2). The second derivative curve shows a peak at 445 nm. At this wavelength, the derivative amplitudes were proportional to the amount of V (IV) in the range  $0.028 - 2.028 \mu\text{g mL}^{-1}$ .



**Fig. 2. Second derivative spectra of V(IV)-HMBATSC Vs reagent blank; V(IV) ( $\mu\text{g mL}^{-1}$ ) 1) 0.760; 2) 1.145; 3) 2.231**

When compared to the zero order method, the tolerance limits of the ions which were very low in the zero order method are found to be much higher in the derivative method. This shows the greater selectivity of the derivative method when compared to zero order method. The results obtained in these studies are presented in the Table 3.

**Table 3: Tolerance limits of diverse ions**

Diverse Ion	Tolerance limits (in folds)	
	Zero order	Second derivative
Ni(II)	20	40
Cu(II)	24	48
Fe(II)	30	45
Ga(III)	18	36
V(V)	15	30
Cr(VI)	12	25
Fe(III)	03	10
Co(II)	05	15

### Application

#### Determination of V (IV) in water samples

The proposed method was applied for the determination of V (IV) in four different water samples. A known amount of V (IV) was added to the water samples and the recovery was evaluated as an average of five determinations. The results were presented in Table 4 and indicate the recoveries were in the acceptable range of 98.4–101.6%.

**Table 4: Determination of V (IV) in water samples**

Water sample	Amount of V (IV) (		Recovery (%)
	Added	Found <sup>a</sup>	
1	0.253	0.257	101.6
2	0.506	0.498	98.4
3	0.760	0.769	101.2
4	1.012	1.007	99.51

<sup>a</sup> Average of five determinations

## **CONCLUSIONS**

The reagent (HMBATSC) allows a simple method for the spectrophotometric determination of vanadium

(IV). The developed spectrophotometric method does not involve any extraction or heating process and hence the use of the solvents was avoided. A second order derivative spectrometric method for determination of (IV) also developed and was more sensitive than zero order method. The developed method was successfully employed for the determination of vanadium (IV) in the water samples.

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