

## 2,4-Diphenyl-3-azabicyclo[3.3.1]nonan-9-one Semicarbazone as a Chromogenic Reagent for Vanadium(V)

V. THANIKACHALAM\*, S. MANIVARMAN and J. JAYABHARATHI

*Department of Chemistry, Annamalai University, Annamalainagar-608 002, India*

Spectrophotometric determination of vanadium(V) was carried out using 2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one semicarbazone in aqueous acetic acid medium at  $30 \pm 0.1^\circ\text{C}$ . Beer's law is obeyed in the concentration ranging from 10–52 ppm and molar absorptivity is  $747 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  with sensitivity  $0.068 \mu\text{g cm}^{-2}$  at 910 nm. Most of the anions and cations did not interfere except copper and tartrate. The composition of the complex is found to be 1 : 1 (metal : ligand) and stability of the complex is determined to be  $2.4 \times 10^3$ .

**Key Words:** Spectrophotometric determination, Chromogenic reagent, Vanadium(V).

### INTRODUCTION

Many reagents<sup>1–7</sup> have been adopted for spectrophotometric determination of vanadium(V). It suffers from deficiencies such as narrow ranges of determination, extraction, tedious procedures and interference by common ions. The method described herein overcomes some of the difficulties for spectrophotometric determination of vanadium. Present investigation was undertaken to study the use of 2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one semicarbazone (DPABS), a selective reagent for spectrophotometric determination of vanadium(V).

### EXPERIMENTAL

All the chemicals were of AnalaR grade (BDH, E.Merck). Dimethylformamide, acetic acid and ethanol were used as such.

A stock solution of 0.01 M vanadium(V) was prepared by dissolving ammonium metavanadate made up to 250 mL in a standard flask; the contents were estimated according to the standard procedure<sup>8</sup>. Desired strengths were obtained by dilution with deionized water.

2,4-Diphenyl-3-azabicyclo[3.3.1]nonan-9-one<sup>9</sup> (m.p.  $183^\circ\text{C}$ ) and the reagent DPABS (m.p.  $225^\circ\text{C}$ ), were prepared by literature method<sup>10</sup>. A stock solution of DPABS was prepared in dimethylformamide; lower concentrations were obtained by dilution with DMF and the solution was stable for at least three months at room temperature.

**Instruments:** Spectrophotometric measurements were made with a UV-Visible spectrophotometer model JASCO 7800 using 1 cm glass transmission cells operating at the maximum sensitivity of the instrument with variable temperature accessory.

**Recommended analytical procedure:** 5 mL of (30 ppm) standard vanadium solution, 5 mL of acetic acid (0.1 M) and 10 mL of (0.01 M) reagent solution were mixed in a 50 mL conical flask, heated on a steam bath for 20 min, cooled and transferred into 25 mL standard measuring flask and made up to the mark with deionized water. The absorbance of the blue coloured solution was measured at 910 nm against reagent blank. A plot of absorbance vs. amount of V(V) was linear ( $r = 0.990$ ).

## RESULTS AND DISCUSSION

**Absorption spectra:** The vanadium(V)-DPABS complex shows a broad peak at 910 nm, whereas reagent blank showed negligible absorbance at this wavelength. Hence, all the absorbance measurements were carried out at 910 nm.

**Choice of solvent:** Various water soluble and insoluble organic solvents were attempted. Dimethylformamide was provided (40% v/v) to be the most satisfactory medium.

**Effect of acid:** It was observed that strength of acetic acid plays an important role in the variation of absorbance. After taking a series of readings, it was found that 4 to 6 mL of 0.1 M acetic acid gives almost constant values. Therefore, 5 mL of 0.1 M acetic acid was used throughout the study.

**Effect of reagent:** The effect of reagent concentration was studied by varying the amount of reagent and maintaining the other conditions constant. Maximum and almost constant absorbance values were observed with 7–12.5 mL of 0.01 M reagent solution. 10 mL of 0.01 M reagent solution was considered to be most suitable for absorbance studies. No adverse effect was noticed on changing the order of addition of reagents.

**Beer's law, stability and statistical parameters:** The absorbance of V-DPABS complex was stable for 12 h. Eight replicate determinations gave a final mean measured absorbance of 0.441, with a standard deviation of 0.0016. Beer's law was obeyed in the concentration range 10–52 ppm. The effective working range from the Ringbom's plot was found to be 20–52 ppm of vanadium. The sensitivity of colour reaction is  $0.068 \mu\text{g V cm}^{-1}$  at 910 nm with molar absorptivity  $747 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

**Composition of the complex:** The composition of the complex was determined by Job's method of continuous variation<sup>11</sup>, mole ratio<sup>12</sup> and slope-ratio methods<sup>13</sup> and was found to be 1 : 1 (metal : ligand). The stability constant of the V-DPABS complex was determined to be  $2.4 \times 10^3$ .

**Study of interference of foreign ions:** The recommended analytical procedure was used to analyze standard vanadium solution in the presence of constituent of associated anions and cations, under the optimum condition as given in the procedure. Copper can be masked with suitable masking reagent; each microgram of copper required 5  $\mu\text{g}$  of disodium salt of EDTA. Fe(III) was masked by adding ascorbic acid (0.2 g). The tolerance limits for many anions and complexing agents have been worked out in Table-1. It is found that less than or equal to 250  $\mu\text{g}$  of each of arsenate, oxalate, iodate and EDTA added initially to the aqueous solution do not affect the absorbance of vanadium(V). Tolerance limits of foreign ions are reported in Table-1.

TABLE-1  
STUDY OF INTERFERENCE OF FOREIGN IONS (765 µg OF VANADIUM IN 25 mL)

Cations	Tolerance limit (µg in 25 mL)	Anions	Tolerance limit (µg in 25 mL)
K <sup>+</sup>	7500	Cl <sup>-</sup>	7500
Na <sup>+</sup>	2500	Br <sup>-</sup>	2500
Ba <sup>2+</sup>	250	I <sup>-</sup>	1000
Mg <sup>2+</sup>	5000	NO <sub>3</sub> <sup>-</sup>	7500
Ca <sup>2+</sup>	190	SO <sub>4</sub> <sup>2-</sup>	3750
Sr <sup>2+</sup>	500	HSO <sub>4</sub> <sup>2-</sup>	1250
Al <sup>3+</sup>	25	IO <sub>3</sub> <sup>-</sup>	250
Hg <sup>2+</sup>	625	arsenate	250
Mn <sup>2+</sup>	75	oxalate	250
Mo <sup>6+</sup>	50	bromate	250
Ni <sup>2+</sup>	250	EDTA	250
Co <sup>2+</sup>	50	thiosulphate	1000
Zn <sup>2+</sup>	7.5	tartrate	seriously interferes
Fe <sup>2+</sup>	75		
Cd <sup>2+</sup>	275		
Pb <sup>2+</sup>	50		
U <sup>6+</sup>	5		
Cu <sup>2+</sup>	seriously interferes		

**Application of the method:** The proposed method for the determination of vanadium is a sensitive and effective method. The method is quite simple and no extraction is required and the reagent is easily prepared. Application of the method has been tested by the satisfactory analysis of synthetic samples (Table-2).

TABLE-2  
ANALYSIS OF DIFFERENT SYNTHETIC MIXTURES BY THE PROPOSED METHOD  
(765 µg OF VANADIUM IN 25 mL)

Matrix <sup>a</sup>	Vanadium (V) added (µg in 25 mL)	Vanadium (V) found (µg in 25 mL) <sup>b</sup>
Ni(250), Co(50), Cd(275)	765	770
Mg(125), Ba(250), Hg(625)	765	765
Fe(75), Sr(1500), Mo(50)	765	765
Pb(50), Mn(75), Co(50)	765	775
Mg(125), As(150), Hg(625)	765	780
Mn(75), Zn(7.5)	765	780
U(5.0), Mo(50), Zn(7.5)	765	775
Ce(190), U(5.0), Zn(7.5)	765	750
Al(5), Co(50), Mn(75)	765	765

(a) Figures in parentheses indicate the amount of metal ion added in µg/25 mL

(b) Average of triplicate analyses

## REFERENCES

1. K. Satyanarayanan and R.K. Mishtar, *Anal. Chem.*, **46**, 1609 (1974).
2. L.P. Pandey, *NML Technical J.*, **19**, 45 (1977).
3. K.S. Patel and R.K. Mishra, *Bull. Chem. Soc., Japan*, **52**, 595 (1979).
4. H. Mohabey and R.K. Mishra, *J. Indian Chem. Soc.*, **57**, 142 (1980).
5. A.R.S. Chauhan and L.R. Kakkar, *Chem. Anal. (Warsaw)*, **39**, 585 (1994).
6. P. Chandak, S. Singhal, N. Mathur and S.P. Mathur, *Indian J. Chem.*, **36A**, 455 (1997).
7. N. Agnihotri, R. Dass and J.R. Mehta *J. Indian Chem. Soc.*, **75**, 514 (1998); **77**, 264 (2000).
8. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th Edn., Longman p. 390 (1978).
9. P. Usha, Ph.D. Thesis, Annamalai University (India) (1972).
10. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longmans, 4th Edn., p. 1074 (1978).
11. P. Job, *Ann. Chim. (Paris)*, **9**, 113 (1928).
12. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
13. A.E. Harvey and D.L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

(Received: 14 May 2003; Accepted: 27 November 2003)

AJC-3249

**INTERNATIONAL SYMPOSIUM ON ADVANCES IN  
SYNTHETIC, COMBINATORIAL AND MEDICINAL  
CHEMISTRY (ASCMC)**

**MOSCOW, RUSSIA**

**MAY 5-8, 2004**

**Contact:**

ASCMC Secretariat

LD Organization sprl, Route de Blocry 55

B-1348 Louvain-la-Neuve, Belgium

Tel: +32 1045 47 77 Fax: +32 1045 97 19

E-mail: [ASCMC@LDOrganisation.com](mailto:ASCMC@LDOrganisation.com)

<http://www.efmc.ch/pagcs/confrencs/ASCMC/1st%20announcement.htm>