

Spectrophotometric Determination of Vanadium (V) using 2-Furohydroxamic Acid as A New Analytical Reagent

Vinita Rajeev^{*1}, Surendra K Rajput^{#2}

¹Professor, Department of Engg. Chemistry, Technocrats Institute of Technology Excellence, Bhopal-462621, India.

²Professor, Department of Chemistry, Govt. College of Science, Raipur – 492010, India,

Abstract: The new reagent FHA gives a purple-colored complex with Vanadium(V) in an acidic medium. The complex exhibits a wavelength of maximum absorption at 475 nm. The colored system obeys Beer's law in the concentration range of 0.2-16 $\mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity were found to be $2.6 \times 10^4 \text{ litre mol}^{-1}\text{cm}^{-1}$ and $0.0136 \mu\text{gcm}^{-2}$. The color reaction has been investigated to develop a spectrophotometric method for the determination of Vanadium (V) in an aqueous medium. The reagent has been used for the determination of vanadium in environmental and biological samples.

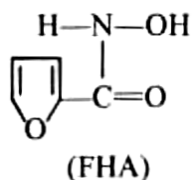
Keywords: FHA, Vanadium.

INTRODUCTION

Vanadium (V) is reported to be a toxic as well as an essential trace element for all living being¹. Several spectrophotometric methods for the determination of vanadium have been reported²⁻⁴, based on the formation of colored complexes with organic reagent hydroxamic acids⁵⁻⁶, such as N-phenyl benzo hydroxamic acid⁷, benzohydroxamic acid, and N-phenylcinnamohydroxamic acid⁹ etc. Here a new heterocyclic hydroxamic acid FHA is used as a complexing agent for the spectrophotometric determination of Vanadium in an aqueous medium.

EXPERIMENTAL

A Systronics spectrophotometer model 106 and Systronics pH meter model 331 were used for spectral and pH measurement, respectively. All chemicals used were of the AR grade. 2-Furohydroxamic acid (FHA), melting point = 115°C was synthesized by the standard method¹¹, which dissolved in distilled water to give 1.6% (w/v) solution. The chemical formula of the compound is $\text{C}_5\text{H}_5\text{NO}_3$, and its structure is



The stock solution of Vanadium 500 ppm was prepared by dissolving 1.1482 gm ammonium metavanadate in double-distilled water. The working standard solutions were prepared by appropriate dilution of the stock solution. Solutions of other metal ions were prepared by dissolving their commonly available chemically pure salts in distilled

water, and a 3M aqueous solution of hydrochloric acid was prepared.

RESULT AND DISCUSSION

In acidic solution, Vanadium (V) forms a purple-colored complex with FHA whose absorbance maximum lies at 475 nm. The absorbance measurements were taken in the aqueous medium as the resulting complex is non-extractable in nature. The absorbance of the purple-colored complex remains stable for 30 minutes. The color system obeys Beer's law in the concentration range $0.2-1.6 \mu\text{g ml}^{-1}$ of vanadium. The molar absorptivity and Sandell's sensitivities are $2.6 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$ and $0.0136 \mu\text{gcm}^{-2}$, respectively.

The influence of various parameters such as temperature, pH, and reagent concentration are shown in Table 1. The absorbance of the complex was insensitive to temperature alteration from $10 - 30^\circ\text{C}$. Various acids, i.e., HCl, H_2SO_4 , CH_3COOH , were tested for the formation of a purple-colored complex in an aqueous solution, but it was found stable with hydrochloric acid. The optimum pH range to study the effect of acidity was 2.0-3.0 pH. Beyond this range, the absorbance of the complex decreased. The effect of variation in concentration of FHA on the color intensity of the complex was studied. 0.12M FHA solution was needed for the maximum color development, and beyond 0.15 M FHA, the complex formed was unstable.

Table 1: Effect of various parameters on the absorbance of Vanadium-FHA complex.

Temp. ($^\circ\text{C}$)	5	10-30	35	40	45			
Absorbance	0.260	0.355	0.320	0.260	0.210			
pH	0.5	1.0	1.5	2.0-3.0	3.2	3.6	4.0	
Absorbance	0.220	0.250	0.280	0.355	0.320	0.260	0.200	
FHA (0.63M) (ml)	0.4	0.5	0.6	0.7	0.8	2.0	2.5-5.5	6.0
Absorbance	0.065	0.103	0.118	0.112	0.160	0.250	0.355	0.299



STOICHIOMETRY OF THE COMPLEX

The ratio of Vanadium (V) to FHA in the complex was determined as 1:1 by curve fitting method¹⁰. FHA forms stable 5-membered chelates (or inner complex compounds) with metal ions.



where R =  ring, R' = H in FHA

EFFECT OF DIVERSE IONS

The effect of diverse ions which often accompany vanadium has been studied. Most of the ions were found not to interfere under the optimum conditions employed; only interference of Fe (III) was noticed in the determination of the analyte, which was successfully masked by using sodium hexametaphosphate. The tolerance limit of various diverse ions in solution containing 15 µg/25ml of vanadium are summarised in Table 2.

Table 2: Effect of diverse / foreign ions concentration of Vanadium = 15 µg / 25 ml.

Ions	Added as	Tolerable Amount µg/25ml
Cu ²⁺	CuSO ₄ ·5H ₂ O	40
Pb ²⁺	Pb(CH ₃ COO) ₂	78
Ni ²⁺	NiSO ₄ ·6H ₂ O	38
Cr ³⁺	K ₂ CrO ₄	25
Mn ⁷⁺	KMnO ₄	100
MO ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	11
Fe ³⁺	Fe ₂ (SO ₄) ₃	15
Al ³⁺	Al(NO ₃) ₃ ·9H ₂ O	20
Ba ²⁺	Ba(NO ₃) ₂	12
Bi ³⁺	Bi(NO ₃) ₂ ·5H ₂ O	12
Cd ²⁺	3CdSO ₄ ·5H ₂ O	25
Co ²⁺	CoSO ₄ ·7H ₂ O	17
SO ₄ ²⁻	Na ₂ SO ₄	25
NO ₃ ⁻	NaNO ₃	25
PO ₄ ³⁻	(NaPO ₃) ₆	15

PROCEDURE

To an aliquot of working standard of 5-40 ppm (0.2-1.6 µgml⁻¹) Vanadium, 0.05 ml of 3M hydrochloric acid was added, followed by 5 ml of FHA. The mixture was shaken for few minutes for maximum color development, and the volume was made up to 25 ml adding distilled water. The absorbance of the complex was measured at 475 nm against the similarly prepared reagent blank.

APPLICATION

The proposed method has been satisfactorily applied to the determination of vanadium in polluted air, water, vanadium in steel and biological samples using calibration graphs.

In polluted air: Air sample was collected from nearby industrial and highway area by Respirable dust sampler. The air was flown at a rate of 1LMP and the collection time was 24 hours. The air sample consisted of two parts - respirable dust and non-respirable dust. The respirable dust was collected on glass microfibre filter paper. The filter paper was cut into small pieces and digested in aqua regia. It was evaporated to dryness, and this process was repeated 2-3 times. The content was dissolved in 1:1 HCl, and the volume was made up to 100 ml. Non-respirable dust was digested in a minimum quantity of aqua regia and filtered by Whatman filter paper no. 42. After that, the volume was made up to 100 ml by 1:1 HCl. Suitable aliquots of these solutions were taken, and vanadium content was determined by the proposed method.

In polluted water:

The polluted effluents from nearby iron and steel industries were collected, and the vanadium content was determined by the proposed method, and synthetic samples were prepared by adding known amounts of vanadium. The total vanadium content was again determined by the proposed method.

In steel:

A weighed quantity of high-speed steel sample (No. A.S. 1239, M-2, A-8) containing about 1mg of vanadium was dissolved in 40% nitric acid. It was slowly evaporated to dryness and then treated with 0.5 ml of concentrated hydrochloric acid. Brown yellow precipitate of hydrated tungstic acid along with other insoluble residue was filtered off. The filtrate was again evaporated to a small volume, and the process repeated 2-3 times by addition of hydrochloric acid and then diluted to 100 ml. Suitable aliquots of this solution were taken, and the vanadium content was determined by the proposed method. The results on the average obtained were 1.96% against the certified value of 2%.

In blood:

About 5gm of the blood sample was spiked with a known quantity of Vanadium and transferred to a 100 ml kjeldahl flask fitted with a loose stopper. 0.5 gm of potassium sulfate and 5 ml of concentrated nitric acid were added to it and heated gently for guarding against too vigorous initial reaction. Digestion was then proceeded moderately rapidly by increasing the temperature without too greater loss of nitric acid. The solution was evaporated to dryness. The process was repeated three times. The content was dissolved in 25 ml of 1:3 nitric acid and kept on the water bath for digestion for 30 minutes. Then the flask was transferred to the hot plate and evaporated to fumes. A light yellow clear solution was obtained after cooling and adding 25 ml of distilled water to it. Suitable aliquots were taken and analyzed.

In Urine:

Urine samples each of 50 ml were concentrated up to 5ml and treated as described above. Vanadium content was then analyzed by the present method.

CONCLUSION

The present method for the determination of vanadium (V) is simple, rapid, and selective. The important feature of this method is that the reagent is water-soluble, and the complex is non-extractable in nature. Hence, the present method does not discharge any chemicals which harm our environment as compared to other solvent extraction methods of hydroxamic acids, where chloroform sink is required.

ACKNOWLEDGEMENT

The authors are thankful to Professor and Head Dr. Piyush Kant Pandey and Reader Dr. Madhurima Pandey,

Department of Engineering Chemistry, BIT, Durg(C.G), for providing laboratory facilities.

REFERENCES

- [1] F.A. Patty, Industrial Hygiene and Toxicology., Interscience Publisher, New York, 3(1174)(1963).
- [2] M. Assefaand, B.S. Chandravanshi, Miko. Chem. Acta,1(1983)(3-4) 255.
- [3] A. K. Shrivastava, Int. J. Environ Anal. Chem.,1(27)(1986).
- [4] C.L. Chakrabarti, R. J. Magee and C.L. Wilson, Talanta, 34(402) (1968).
- [5] U. Priyadarshini and S.G. Tandon, Analyst, 86(1961) 544.
- [6] A. Sao, A. Pillai and V. K. Gupta, J. Indian Chem. Soc., 83(400), (2006).
- [7] D.E. Ryan, Analyst, 85(1960) 569.
- [8] Z. Marczenko, Spectrophotometric Determination of Elements, Wiley New York, (1976).
- [9] Y.K. Agrawal, Anal Lett., 5(1972) 563.
- [10] L.C. Sillen, Acta Chem. Scand., 10(1956) 185.
- [11] (a) U. Priyadarshini and S.G. Tandon, J. Chem. Engg. Data,12(143) (1967).
(b) S. K. Rajput, Ph.D. Thesis, Pt. Ravishankar Shukla University, Raipur, (1984).