



## SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF VANADIUM (V) USING SALICYLALDEHYDE ACETOACETIC ACID HYDRAZONE. APPLICATIONS

V. Srilalitha \*, A. Raghavendra Guru Prasad \*\* V. Seshagiri \*\*\*  
and L. K. Ravindranath \*\*\*

**abstract:** Simple, sensitive and accurate spectrophotometric method was proposed for the micro determination of vanadium (V) using salicylaldehyde acetoacetic acid hydrazone (SAAH) as a reagent. The method was based on the formation of 1:2 complex between the metal and SAAH. The optimum conditions for the determination were established. The Beer's law was applicable in the range of 0.243-2.438  $\mu\text{g/ml}$ . The method detection limit, limit of quantification, molar absorptivity, Sandell's sensitivity and stability constant ( $\beta$ ) were reported. The method is free from common interferences. The method was successfully applied for the determination of vanadium (V) in tap water samples, plant tissues and alloys.

**key words:** spectrophotometric; vanadium (V); salicylaldehyde acetoacetic acid hydrazone; tap water; plant material; alloys.

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### 1. Introduction

Vanadium is a trace element and is of great industrial, ecological, biological and pharmacological importance. Vanadium metal is present in different alloys and is an important element present in steels. In view of crucial role in different fields, it is necessary to develop sensitive analytical procedures for the determination of trace amounts of vanadium.

Survey of literature reveals that several procedures have been reported for the determination of vanadium. The procedures include high performance liquid chromatography (HPLC) [1], electrochemical [2, 3], spectrofluorimetry [3], neutron activation analysis [4], AAS [5], ICP-AES [6], ICP-MS [7, 8], ion chromatography inductively coupled plasma optical emission spectrometry [9], spectrophotometry [10, 11],

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\* C.M.R. Institute of Technology, Hyderabad, A.P., India

\*\* ICFAI Foundation for Higher Education, Hyderabad, A.P., India

*corresponding author e-mail:* guruprasadar@yahoo.co.in, Phone: 91 9849694428

\*\*\* Sri Krishnadevaraya University, Anantapur, A.P., India.

chemiluminescence [12] etc. Although these techniques are sensitive, inconvenient, expensive and time consuming. Many of these procedures are complicated [13] and involve preliminary isolation and pre-concentration procedures. Especially for vanadium, the technique of atomic absorption has drawbacks [14]. However ICP-MS cannot be used for the determination of low concentrations of vanadium because of spectral and non-spectral interferences [15]. Several kinetic methods based on its catalytic action on the oxidation of organic compounds have been reported in literature [16÷18]. The bromates have been extensively used as the oxidizing agents [17, 18], although hydrogen peroxide and potassium chlorate have also been used for the same purpose [19]. Many of these procedures are time sensitive procedures. In the present work, simple, rapid, selective and sensitive spectrophotometric method is reported for the micro determination of vanadium (v) by complexing with SAAH.

## 2. Experimental

### 2.1. Instrumentation

The absorbance measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A). pH measurements were made using ELICO pH meter Model L1-10, ELICO Private Limited, Hyderabad, India.

### 2.2. Reagents and chemicals

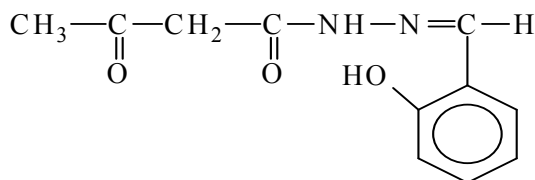
All the chemicals and reagents used were of analytical grade. A 0.01M solution of SAAH in dimethyl formamide was employed for the studies.

Vanadium (V) solution of concentration 0.01M was prepared by dissolving requisite amount of sodium metavanadate in distilled water. Working solutions of vanadium were prepared before use by diluting appropriate volumes of stock solution with distilled water.

The buffer solutions were prepared by mixing 1M hydrochloric acid and 1M sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0).

### 2.3. Synthesis of SAAH

Equimolar solutions of acetoacetic acid hydrazone and salicylaldehyde prepared in aqueous methanol were refluxed for two hours. The contents were allowed to cool to the room temperature and the product was separated by filtration. The crude product obtained was filtered, washed with water, dried and recrystallised from hot aqueous methanol to get pure light yellowish crystals of salicylaldehyde acetoacetic acid hydrazone (SAAH).



**Fig 1** Structural formula of Salicylaldehyde acetoacetic acid hydrazone.

## **2.4. Procedure**

### **2.4.1. General procedure for the determination of vanadium (V)**

Required aliquots of solution containing different amounts (0.243-2.438 µg/ml) of vanadium (V) were transferred into a series of 10 ml standard flasks. 5 ml of buffer solution of required pH, required volume of the SAAH solution of concentration  $1 \times 10^{-3}$  M, 1 ml of dimethylformamide were added to the flask and the contents were made up to the mark with distilled water. The absorbance of the solutions was measured at 460 nm against the reagent blank and the calibration graph was constructed.

### **2.4.2. Determination of vanadium (V) in tap water**

Tap water samples were spiked with known amounts of vanadium (V) and analyzed by the proposed general procedure.

### **2.4.3. Preparation of sample solutions of plant tissue**

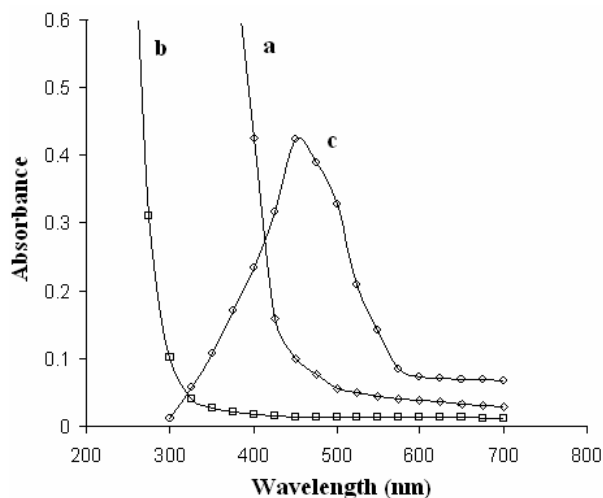
The samples of plants tissue were washed with distilled water. The wet weight was taken after they were wiped with filter paper. The samples were then dried and brought into solution by acid treatment [20, 21], neutralized with dilute  $\text{NH}_4\text{OH}$  and diluted to a known volume with distilled water. Since the vanadium (V) content in samples used was negligible, synthetic samples were prepared by the addition of known amounts of vanadium (V) and analyzed according to the general procedure.

### **2.4.4. Preparation of alloy sample solutions**

Accurately weighted amount of the alloy sample was dissolved in a mixture of 2 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. The solution was evaporated to a small volume, 1:1 sulphuric acid was added and the solution was then evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered. The filtrate was transferred into a 100 ml standard flask and diluted to the mark with distilled water. This serves as stock solution. The stock solution was appropriately diluted to obtain the metal ion solution in the required concentration range.

## **3. Results and Discussion**

The proposed method involved the formation of a brownish yellow color between vanadium (V) and SAAH in a medium of pH 2. The absorption spectra of solution containing V(V)-SAAH complex against the reagent blank, that of SAAH solution against corresponding buffer blank and that of metal solution against the respective buffer blank is shown in the Fig. 2. The figure revealed that V(V)-SAAH complex has maximum absorbance at 460 nm. Neither the metal ion nor the reagent has appreciable absorbance at specified wavelengths. Hence further studies were carried out at 460 nm. The color reaction was instantaneous and the absorbance of the complex solution was found to remain constant for at least five hours.

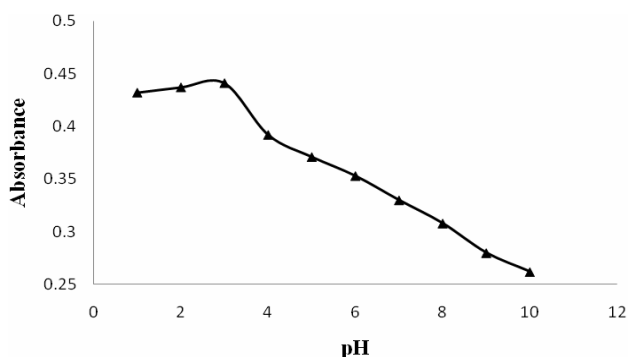


**Fig. 2** Absorption spectra of a) SAAH against buffer blank,  $[SAAH] = 2 \times 10^{-4} M$ ; b)  $V(V)$  against buffer blank,  $[V(V)] = 2 \times 10^{-5} M$ ; c)  $V(V)$ -SAAH complex against reagent blank,  $[V(V)] = 2 \times 10^{-5} M$ ,  $[SAAH] = 2 \times 10^{-4} M$ .

The authors conducted following studies in order to optimize the experimental variables.

### **3.1. Effect of pH**

The effect of  $pH$  on the intensity of the color reaction is shown in the Fig. 3. The absorbance was found to be maximum in the  $pH$  range 1-3. Hence further analytical investigations were carried out in media of  $pH$  2.



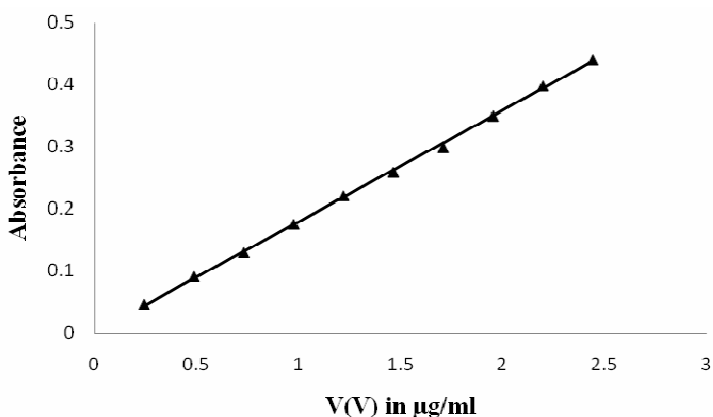
**Fig. 3** Effect of  $pH$  on absorbance.  $[V(V)] = 2 \times 10^{-5} M$ ;  $[SAAH] = 2 \times 10^{-4} M$ .

### **3.2. Effect of reagent (SAAH) concentration**

The studies on effect of various concentrations of the reagent on the color reaction reveal that, a reagent excess of 5 fold was required for the  $V(V)$ -SAAH color reaction. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

### 3.3. Effect of vanadium (V) concentration

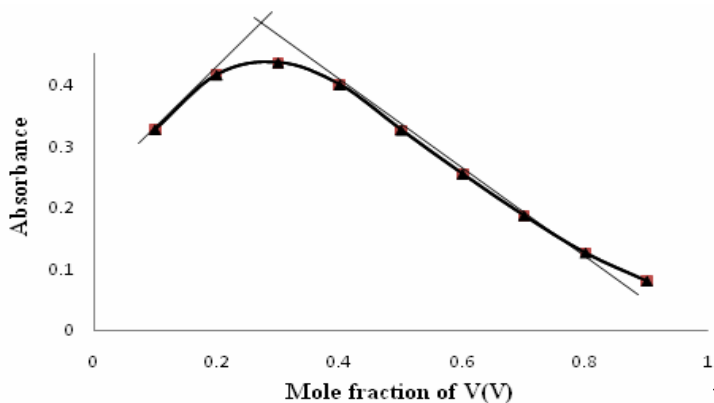
The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that V(V) may be determined in the range 0.243-2.438  $\mu\text{g/ml}$ . The pertaining calibration graph is shown in the Fig. 4.



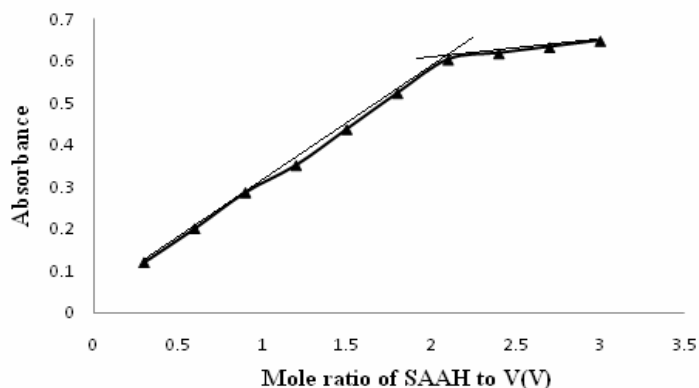
**Fig. 4** Analytical determination of V (V);  $[\text{SAAH}] = 1 \times 10^{-4} \text{ M}$ ;  $\text{pH} = 2$ ;  $\lambda_{\text{max}} = 460 \text{ nm}$

### 3.4. Stoichiometry of the V(V)-SAAH complex

The stoichiometry of the complex was determined by Job's method of continuous variation and by mole ratio method. It was found to be 1:2 (Metal : Ligand). The stability constant determined by Job's method was found to be  $1.683 \times 10^{10}$ . The corresponding plots are shown in the Figs. 5 and 6 respectively.



**Fig. 5** Job's method of continuous variation, Concentration of V (V) solution and SAAH solution taken in different aliquots =  $2 \times 10^{-4} \text{ M}$ ;  $\text{pH} = 2$ ;  $\lambda_{\text{max}} = 460 \text{ nm}$ .



**Fig. 6** Molar ratio method;  $[V(V)] = 2 \times 10^{-4} M$ ; Concentration of SAAH solution taken in different aliquots =  $2 \times 10^{-3} M$ ; pH = 2;  $\lambda_{max} = 460 \text{ nm}$ .

In conclusion the analytical parameters pertaining to the proposed method are given in the Table 1.

**Table 1** Analytical parameters pertaining to the proposed method.

Parameter	Value
Method detection limit	0.053
Limit of quantification	0.107
Molar absorptivity	$22.000 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity	$0.002315 \mu\text{g cm}^{-2}$
Stability constant ( $\beta$ )	$1.683 \times 10^{10}$
Beer's law range	0.243 – 2.438 $\mu\text{g/ml}$
Regression equation	$Y = 0.1788X + 0.0013$
Correlation coefficient	0.9993

### 3.5. Effect of diverse ions

The effect of interfering ions on the proposed method was investigated. The tolerance limit was considered to be the amount that caused a  $\pm 1\%$  deviation in the absorbance value. The results are summarized in Table 2. These results reveal that various cations and anions can be tolerated at satisfactory levels.

**Table 2** Tolerance limit of diverse ions,  $[V(V)] = 0.408 \text{ ppm}$

Anion added	Tolerance limit (ppm)	Cation added	Tolerance limit (ppm)
Citrate	756.00	Bi(III)	125.39
Tartrate	740.00	W(VI)	3.68
Iodide	571.05	Mo(VI)	5.76
Hypo	744.54	Fe(III)	4.47

Oxalate	484.00	Mn(II)	1.10
Bromide	175.80	Ag(I)	43.15
Thiourea	190.30	Al(III)	53.96
Nitrate	279.00	Cu(II)	2.54
Urea	150.00	Pb(II)	4.14
Acetate	147.50	Hg(II)	4.01
Thiocyanate	290.00	Zn(II)	1.27
Chloride	70.90	Fe(II)	0.45
Phosphate	47.49		
Fluoride	47.50		

### 3.6. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of V(V) in tap water, plant tissues and alloys. The results presented in Table 3 indicate the successful applicability of the proposed method to real sample analysis.

**Table 3** Determination of vanadium in various samples  
a) Tap water and plant material

Sample	Vanadium added ( $\mu\text{g/ml}$ )	Vanadium found ( $\mu\text{g/ml}$ )		Recovery (%)	SD (%)	RSD (%)
		Standard Method <sup>22</sup>	Proposed method <sup>a</sup>			
Tap water	1.0	1.04	1.063 $\pm$ 0.017	106.3	2.35	2.22
	2.0	2.08	2.11 $\pm$ 0.03	105.5	4.13	1.96
Plant material Cabbage (5g)	1.0	1.07	1.07 $\pm$ 0.02	107	2.74	2.57
	2.0	2.09	2.10 $\pm$ 0.034	105	4.77	2.27

a: *t* value at 95% confidence level is 2.26.

#### b) Alloy sample

Sample name/number	Composition	Vanadium (V)%		Error (%)
		Certified	Found	
Oakay alloy	Ni = 60.00%; Pt = 20.00%; V = 9.50%; Pd = 10.50%.	9.50	9.39	0.11
7110	C = 0.18%; Si = 0.34%; Mn = 0.33%; Ni = 0.12%; Cr = 1.08%; Mn = 0.85%; V = 0.87%; Cu = 0.22%; P = 0.018%; S = 0.012%; Ti = 0.11%; Al = 0.042%; B = 0.0009%.	0.87	0.86	0.01
T032	C = 0.056%; Si = 0.24%; Mn = 0.91%; Ni = 0.23%; Cr = 1.03%; Mo = 0.04%; V = 0.12%; Cu = 0.19%; P = 0.002%; S = 0.018%.	0.12	0.11	0.01

## 4. Conclusion

A simple, rapid and sensitive method is reported for the determination of trace amounts of vanadium (V). The described method was successfully applied for the determination of V(V) in tap water, plant tissues and alloys.

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