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Direct, derivative spectrophotometric determination of micro amounts of Vanadium (V) by 5-bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH)

M.Swetha*, P. Raveendra Reddy, V. Krishna Reddy

Department of Chemistry, Sri Krishnadevaraya University, Anantapur, 515003(A.P) India

***Corres.author: swetha.maddike@gmail.com**

Abstract: A simple and highly selective spectrophotometric method has been developed for the determination of trace amounts of V (V) using newly synthesized reagent 5-bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH) in aqueous DMF medium. Vanadium (V) forms a brown colored soluble complex with 5-BrSAINH in the pH range 1.0-5.0. The complex shows maximum absorbance at 400nm in the pH range 4.5-5.5 where the reagent blank shows negligible absorbance. Hence analytical studies were carried out at 400nm and at pH 5.0. Beer's law was obeyed in the range 0.51-5.1µgmL^{-1} of V (V). The molar absorptivity and sandell's sensitivity for the colored solution were found to be 1.25 x 10^{4} L.mol^{-1}cm^{-1} and4.0 X10^{-3}µgcm$^{-2,}$ respectively. The brown colored complex has 1:1 stoichiometry. The interference effect of various diverse ions has been studied .The stability constant of the complex was determined as 2.70 X 10^{8} by Job's method. A second order derivative spectrophotometric method was developed for the determination of vanadium (V) which was found to be more sensitive than zero order method. The developed methods have been employed for the determination of vanadium (V) in water, human hair and rice samples.
Key words: Spectrophotometer, 5-BrSAINH, determination of Vanadium (V), water samples, human hair and rice samples.

Introduction

Vanadium is an important element in environmental and biological components. Vanadium in trace amounts is an essential element for all growth, but can be toxic at higher concentrations [1]. 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 and catalytic and other properties [2].

Vanadium (V) and vanadium (IV) species play an important role in many industrial and environmental processes. Vanadium (V) may be toxic, when it may enter in to the natural environment, in particular in surface waters. Vanadium is also found in phosphate rock and certain iron ores, and is present in some crude oils in the form of organic complexes. It is also found in small percentages in meteorites. Vanadium compounds are used as catalysts in coloring glass and ceramics and as driers in paints and inks.

Vanadium act as a growth promoting factor and participates in fixation and accumulation of nitrogen in plants [3], where as high concentration of vanadium reduces the productivity of the plants. Vanadium poisoning is an industrial hazard [4]. The symptoms of vanadium poisoning are nervous depression, coughing, vomting, diarrhea,

anaemia and increased rise of lung cancer, that are sometimes fatal. Recently vanadium has been noticed as the index element in urban environmental pollution and air pollution.

A wide variety of techniques are available for the determination of vanadium. It's solid phase extraction [5], kinetic spectrophotometric determination[6], ion exchange chromatography and inductively coupled mass spectrophotometry[7], redox reaction[8], catalytic methods[9],and simple spectrophotometry in aqueous solution[10-14]. However, some of the methods suffer from number of limitations such as interference by diverse ions, followed by extraction and lack of sensitivity. The catalytic methods have serious interference from the oxidants and reductants and also require expensive experimental set up.

The present work describes rapid, simple, sensitive, and selective direct and second derivative spectrophoto metric methods for the determination of trace amounts of V (V) by complexing with 5-bromo salicylaldehyde isonicotinoyl hydrazone (5-BrSAINH). The developed methods were applied for the spectrophotometric determination of micro amounts of V (V) in environmental and biological samples.

Experimental procedure

Apparatus

The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital P^H meter of (Model LI 613), respectively.

Reagents

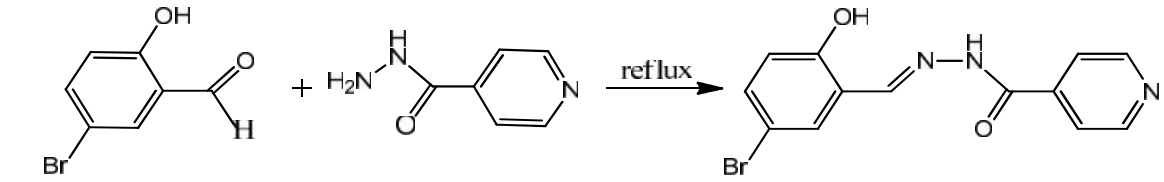
All chemicals used were of analytical grade. 0.01 M vanadium (V) solution was prepared by dissolving 0.1170g of ammonium meta vanadate in hot distilled water. The stock solutions were diluted appropriately as required. Working solutions were prepared by appropriate dilution of the standard solution. Solutions of the studied interfering ions of suitable concentrations were prepared using A.R.grade salts.

Buffer Solutions

The buffer solutions were prepared by mixing 1 M hydrochloric acid and 1 M sodium acetate (p^H 1.0-3.0) and 0.2M acetic acid and 0.2 M sodium acetate (p^H 3.5-7). The p^H of these solutions was checked with a p^H meter.

Preparation Of 5-BrSAINH

Equimolar solutions of 5-bromo salicylaldehyde (I) and isonicotinic acid hydrazide (II) were dissolved in sufficient volume of methanol and the mixture was refluxed for 1 hour. The contents were allowed to cool and the product was separated by filtration. A crude sample (yield 80%) was obtained. The resultant product was recrystallized thrice from hot methanol. Pure light yellowish green colored crystals of 5-bromo salicylaldehyde isonicotinoyl hydrazone (III) were obtained (m.p 238-240^{0}c)



5-bromo salicylaldehyde I

Isonicotinicacidhydrazide II

5-bromosalicylaldehydeisonicotinoylhydrazone III

Reagent Solution

5-BrSAINH (1 x 10^{-2} M) is prepared in dimethyl formamide (DMF). 0.320g of the reagent (5-BrSAINH) is transferred into a 100 ml volumetric flask and made up to the mark with DMF. The stock solution is suitably diluted to get the required concentration wherever necessary. Fresh reagent solution is prepared every day before use.

Procedure

General method

Aliquots of solutions containing 1.0-10.0µg of vanadium (V) were transferred into a series of 10ml volumetric flasks. To these 5-BrSAINH (5×10^{-4}) was added and the contents were diluted to the mark with distilled water and mixed well. The absorbance was measured at 400nm against the reagent blank. The calibration graph was constructed by plotting the absorbance against the concentration of V (V) ions.

Derivative method

For the solutions as prepared above, the second derivative spectra were recorded with reference to the reagent blank in the wavelength range 380-570nm. The derivative amplitudes were measured at 444nm for second order curves. Calibration graphs were constructed by plotting the derivative amplitudes against the concentration of V (V).

Determination of vanadium in water samples

Filtered environmental water samples (100ml) were analyzed for vanadium. To samples, not containing V (V) known amounts of V (V) were added and remaining mixtures were analysed by the proposed procedure.

Determination of vanadium in human hair, rice sample solutions

The human hair were soaked over with 5ml of concentrated nitric acid and 0.5ml of perchloric acid was added. The mixture was heated gently to boiling with the evolution of white fumes. The residue was then dissolved in distilled water and transferred in to 50ml volumetric flask and diluted to the volume with distilled water. Suitable aliquots of this solution were taken and the proposed general procedure was followed for the vanadium determination.

The rice sample was dried at 110^0c until constant weight was obtained. One gram of the sample was heated with 10ml of 5M HNO_3 on a sand bath.5ml of $HClO_4$ (70%w/w) were added and the solution was evaporated to near dryness. The residue was dissolved in 10ml of 0.1M HCl heated to boiling, cooled and filtered. The filtrate obtained was transferred into a 100ml volumetric flask and diluted to the mark with distilled water. Suitable aliquots of this solution were taken and the proposed general procedure was followed for the vanadium determination.

Results and Discussion

Absorption spectra

The reaction of 5-BrSAINH with V (V) at room temperature gives a green colored soluble complex. The V (V) - 5-BrSAINH complex shows maximum absorbance at 400nm where the reagent blank does not absorb appreciably,was shown in fig 1.

Effect of pH on the absorbance of the experimental solution:

The plot between absorbance and of pH reveals that the metal complex shows maximum and constant absorbance in the pH range 4.5-5.5. Therefore, pH 5.0 was selected for further studies.

Effect of reagent concentration on absorbance of the complex solution:

The minimum amount of reagent to acquire maximum color intensity with a given amount of V (V) was evaluated from the absorbance measurements of experimental solution with different amounts of reagents. The results prove that a 15-fold molar excess of the reagent was required for the development of maximum color intensity with a given amount of vanadium (V).

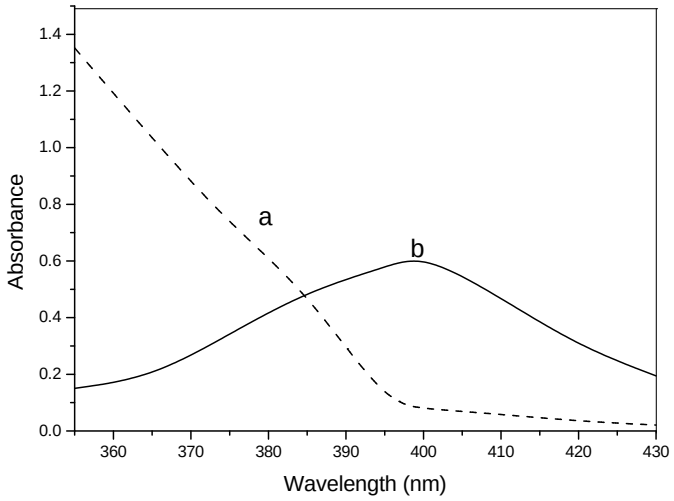


Fig. 1. Absorption spectra of
(a). Br–SAINH Vs Buffer blank
(b). [U(VI)–Br–SAINH] Vs Reagent blank
([U(VI)] = 5 × 10^{-5}M; [Br–SAINH] = 5 × 10^{-4}M; pH = 5.

Composition and stability of the complex:

The composition of the complex was determined using Job's continuous variation method. The results indicate a 1:1 stoichiometry between the metal ion and the reagent. The stability constant of the complex was determined as 2.70 X 10^{8}.

Validity of Beer's law:

The calibration plot between absorbance and concentration of V (V) shows that Beer's law is obeyed by the system in the concentration range 0.51-5.1µgmL^{-1} of V (V). The straight line obeys the equation A_{400}=0.0722C+0.0187. The molar absorptivity and sandell's sensitivity of the method were found as 1.25 x 10^{4} L.$mol^{-1}cm^{-1}$ and 4.0 X10^{-3} µgcm^{-2}, respectively.

Effect of foreign ions:

The effect of various anions and cations normally associated with V (V) 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 +2% were calculated and presented **in table 1.** Almost all the tested anions possess high tolerance levels (>100 fold). The metal ions Zn(II), Pt(IV), Fe(III) were tolerable up 20-40 fold excess respectively and U(VI), Hg(II), Cd(II), Pd(II), Fe(II), Th(IV) were tolerable up to10-20 fold excess. It was noticed that all the ions which did not interfere in the zero order determination of vanadium (V) also did not interfere in the second order derivative method.

Derivative Method

In order to improve the sensitivity and selectivity of the direct spectrophotometric method developed; the absorbance data was derivatised once and twice and plotted against the wavelength(380-570nm) which gave the corresponding second order derivative curves (fig 2). The second derivative curve shows a peak at 444nm. At this wavelength, the derivative amplitudes were proportional to the amount of V (V) in the range 0.052-2.90µg $mL.^{-1}$

Table.1 Tolerance limits of foreign ions
Amount of V (V) taken = 1.25µg mL^{-1}, pH = 5.

Foreign ions	**Tolerance limit (µg mL^{-1})**
Thiosulphate, Ascorbic acid, EDTA, Thiourea, Tatarate, Thio cyanate, Oxalate, Bi(III), Pb(II)	**600-1000**
Phosphate, Citrate, Au(III), Ir(III), W(VI), Te(IV), Sn(II)	**200-600**
Sulphate, Iodide, Carbonate, Zr(IV), Se (IV), Ag(I)	**100-200**
Ce(IV) Ni(II), Al(III), Co(II),Zn(II)	**40-90**
Zn(II), Pt(II) Fe(III)	**20-40**
U(VI), Hg(II), Cd(II), Pd(II), Fe(II), Th(IV)	**10-20**

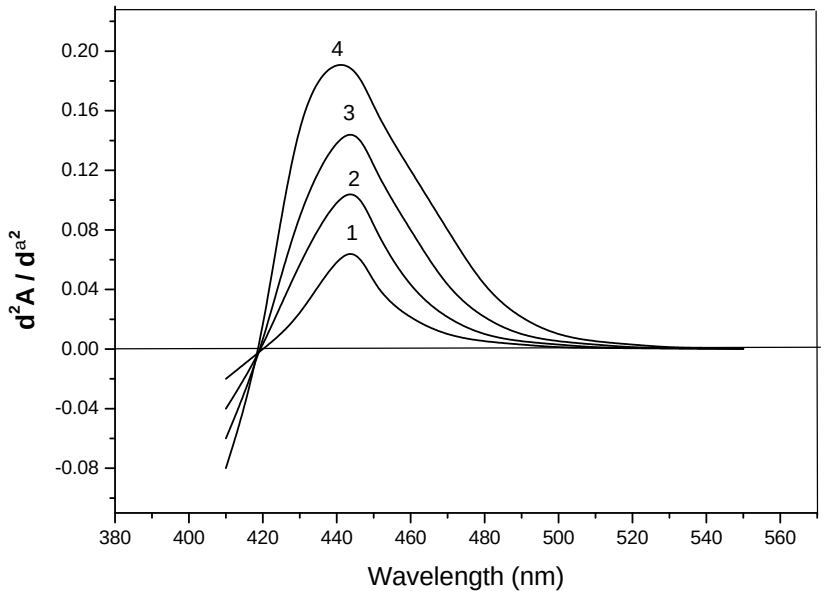


Fig.2: Second order derivative spectra of V (V) -5BrSAINH Vs reagent blank
V (V) (µg mL^{-1}) = (1) 0.51; (2)1.02; (3)2.04; (4) 3.06

The analytical results of both direct and derivative methods were summarized and are presented in Table 2. The tolerance limits of some cations in derivative methods were compared with those in direct method and presented in Table 3.

Applications

Zero order method:

The developed spectrophotometric method was employed for the determination of vanadium (V) in water samples**.**

Three different samples of water were spiked with known amounts of V (V) and the resultant samples were analyzed for their V (V) by the proposed method. The results obtained are presented in table 4.

Derivative method

The second order derivative method was applied for the analysis of vanadium (V) in, human hair, rice samples and are presented in table 5.

Table 2: Analytical characteristics of [V (V)-5 BrSAINH]

Parameter	Zero order	Second derivative
Analytical Wavelength (nm)	400nm	444nm
Molar Absorptivity ($L.mol^{-1}cm^{-1}$)	$1.25X10^4$	-
Compositon (metal: ligand)	1:1	-
Beer's law range ($\mu g\ mL^{-1}$)	0.51-5.10	0.052-2.90
Sandell's sensitivity($\mu g\ cm^{-2}$)	0.0040	-
Angular Co-efficient (m)	0.0722	0.2036
y-intercept(b)	0..0187	0.0131
Correlation co-effiicient(r)	0.9998	0.9997
Standard deviation($\mu g\ mL^{-1}$)	± 0.0113	± 0.0128
Stability constant	$2.70X10^8$	-
Detection limit($\mu g\ mL^{-1}$)	0.06431	0.1253
Determination limit ($\mu g\ mL^{-1}$)	0.2463	0.3956

Table 3: Tolerance limits of foreign ions

Foreign ion	Tolerance limits(in folds)	
	Zero order	Second derivative
Zn(II)	22	46
Pt(II)	25	49
Fe(III)	32	42
U(VI)	18	38
Hg(II)	15	35
Cd(II)	15	34
Fe(II)	13	25
Th(IV)	10	20

Table 4: Determination of Vanadium (V) in water samples

Sample	Amount of vanadium ($\mu g\ mL^{-1}$)		RSD (%)
	Added	Found	
Well water	25	31.15	0.40
	50	70.45	0.91
	100	120.00	1.18
Tap water	25	35.40	0.45
	50	85.65	0.46
	100	140.20	0.96
Drain water [a]	25	50.80	0.64
	50	108.80	1.08
	100	155.50	0.89

*Average of four determinations

a = collected from discharges of J.K.steel Industry , Tadipatri, A.P. India

Table 45 Determination of Vanadium (V) in rice and human hair

Sample	V(V) added ($\mu g\ mL^{-1}$)	V(V) found* (n=4) ($\mu g\ mL^{-1}$)	Recovery (%)
Rice	0.00	0.152 ± 0.002	-
	0.50	0.630 ± 0.005	99.69
	1.00	1.126 ± 0.003	99.47
	1.50	1.640 ± 0.014	100.48
Human hair	0.00	0.175 ± 0.008	-
	0.50	0.680 ± 0.002	100.73
	1.00	1.192±0.010	99.75
	1.50	1.608±0.009	1.1.36

*Average of five determinations ± SD

Conclusions

Rapid color development, simplicity and selectivity are the advantages of the proposed method. The intensity of the colored species will not be affected by slight variation of the experimental parameters such as concentration of the reagent. The proposed method does not involve extraction, heating or any other stringent reaction conditions and offers the advantage of high color stability (24h). The commonly associated metal ions, especially Bi(III), Pb(II), Sn (II) and Te (IV) could be tolerated in considerable excess, which is an advantage over other reported reagents. The proposed method can be used as an alternative method for the determination of trace amounts of vanadium in water, human hair and rice samples.

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