Study of New Selective Reagent Acetophenone 2', 4'-Dihydroxy Semicarbazone for Extractive Spectrophotometric Determination of Vanadium

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Abstract Acetophenone 2', 4'- dihydroxy semicarbazone [A24DHS], a new analytical reagent is proposed as a sensitive and selective spectrophotometric reagent for Vanadium (V). The reagent A24DHS is synthesized in the laboratory and characterized by NMR, IR and elemental analysis. A selective spectrophotometric method is presented for the trace determination of Vanadium using A24DHS as spectrophotometric reagent ($\lambda_{\max} = 380$ nm) in basic aqueous solution (pH = 8.2). The Beer's law is obeyed in the concentration range from 1 to 5 ppm. The A24DHS forms a 1:2 yellow colored complex. The Sandell's Sensitivity is $0.0288 \mu\text{g cm}^{-2}$ with molar absorptivity $3899.2 \text{ L mol}^{-1} \text{ cm}^{-1}$. The proposed method has been successfully applied to the determination of Vanadium alloys and synthetic samples. The precision and the accuracy obtained were satisfactory for its use in the concerned industry.

Keywords: vanadium, spectrophotometry, *n*-Butanol, Acetophenone 2', 4'-dihydroxy, semicarbazone derivative

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1. Introduction

Vanadium is a chemical element with the symbol V and atomic number 23. It is a hard, silvery gray, ductile and malleable transition metal. Vanadium was discovered by Andreas M. del Rio in 1801 [1,2,3]. Although vanadium is an essential trace element for some creatures, a number of its compounds are toxic. Generally, higher toxicity is associated with higher oxidation state [4]. Vanadium is resistant to attack by alkalis, HCl, H₂SO₄ and salt water. The metal oxidizes in air at around 660°C to the pentoxide (V₂O₅) [5]. The main use of vanadium is in alloys. Vanadium in small amount gives strength, toughness and heat resistance to the alloys. Ferrovandium is the most used vanadium alloy in the industry [6]. Vanadium steel used in gears. TAV (Ti-Al-V) alloy is used in jet engines and for high speed aircraft. V₂O₅ is used in ceramics and as a catalyst for the production of H₂SO₄. Vanadium plays a very limited role in biology, and is more important in ocean environments than on land. Organobromine compounds in a number of species of marine algae are generated by the action of a vanadium dependent bromoperoxidase. This is a haloperoxidase in algae which requires bromide and is an absolutely vanadium-dependent enzyme. Most organobromine compounds in

the sea ultimately arise via the action of this vanadium bromoperoxidase.

Many methods have been reported for the determination of vanadium such as inductively coupled plasma atomic emission or neutron activation analysis which requires expensive instruments and well-trained operators. Some of the reagents used for the spectrophotometric determination of vanadium are Formaldehyde oxime [7], 8-Quinolinol [8]. However, most of these methods suffer from certain limitation, such as interference by number of ions, of low sensitivity. The purpose of this work is to find selective, sensitive, simple method for exact determination of vanadium by using new analytical reagent. In this paper a new method has been developed using Acetophenone 2', 4'- dihydroxy semicarbazone [A24DHS] for extraction and spectrophotometric determination of vanadium, which is simple, selective and sensitive.

2. Material and Methods

The pH measurements were made using a pH meter Elico, Model LI-129, India in conjugation with a combined glass and calomel electrode. Shimadzu UV-Visible 2100 spectrophotometer with 1.0 cm matched quartz cells were used for all absorbance measurements.

2.1. Reagent and Chemicals

0.1% Acetophenone 2', 4'- dihydroxy semicarbazone is prepared by dissolving the requisite amount of it in a known volume of methanol. All chemicals used were of analytical-reagent grade or the highest purity available in market (MERCK). Doubly distilled de-ionized water and analytical-reagent grade methanol, which is used throughout. Solvents are purified by methods given by Wilfred L. E Armarego, et.al. [9].

2.2. Synthesis of the Reagent

Acetophenone 2', 4' - dihydroxy semicarbazone (A24DHS)

Synthesis of A24DHS involves two steps.

- Conversion of Resorcinol to 2', 4'-Dihydroxy acetophenone [10].
- Synthesis of semicarbazone derivative of 2',4'-dihydroxy acetophenone [11].

a) Conversion of Resorcinol to 2, 4-Dihydroxy acetophenone

Freshly fused and powdered Zinc chloride (0.24 mol ZnCl_2) is dissolved in glacial acetic acid (32 mL) by heating in a beaker on a sand bath. Dry Resorcinol (0.2 mol) is added with stirring to the mixture at 140°C . The solution is heated until it just begins to boil and then kept for 20 min. at 150°C . Dilute hydrochloric acid (1:1) is added to the hot mixture and solution cooled (5°C). The separate product is filtered and washed with dilute hydrochloric acid (1:3). It is recrystallize from hot water containing little hydrochloric acid. Melting point is 142°C . Yield is 84.45 %. (Scheme 1)

Scheme 1. Conversion of Resorcinol to 2', 4'-Dihydroxy acetophenone

Scheme 2. Synthesis of semicarbazone derivative of 2', 4'- dihydroxy acetophenone

b) Synthesis of semicarbazone derivative of 2', 5'-dihydroxy acetophenone

Equimolar mixture of sodium acetate and semicarbazide hydrochloride is dissolved in minimum quantity of water and then it is added to methanolic solution of 2', 4'-Dihydroxy acetophenone. After addition solution was warmed and stir about one hour. The pink colored compound is precipitated, washed and then recrystallized using 50% ethyl alcohol as solvent. (Scheme 2)

2.3. V (V) Standard Solutions

The stock solution of pentavalent vanadium was prepared by dissolving weighed amount of ammonium metavanadate in doubly distilled de-ionized water containing 1–2 mL of ammonia. More dilute standard solutions were prepared from this stock solution as and when required.

2.4. Procedure for the Extraction

1 mL of aqueous solution containing $5\text{ }\mu\text{g}$ of Vanadium metal and 2 mL of Acetophenone 2', 4'- dihydroxy semicarbazone was mixed in a 50 mL beaker. The pH of the solution was adjusted to 8.2. It must be noted that the total volume should not exceed 10 mL. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with n-Butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was passed through anhydrous sodium sulphate in order to absorb trace amount of water from organic phase and then collected in 10 mL measuring flask and made up to the mark with organic solvent if required. The amount of vanadium present in the organic phase was determined quantitatively by spectrophotometric method at wavelength 380 nm. In the aqueous phase vanadium concentration was determined by phosphotungstovanadate method [12].

Figure 1. effect of ph on the extraction of v (v)-a24dhs complex

3. Results and Discussion

A. Extraction as a function of pH

The extraction of vanadium with Acetophenone 2', 4'-dihydroxy semicarbazone has been studied in the pH

range 1-10 and it was observed that maximum percentage extraction of vanadium (V) is obtained at pH range 7.8-8.6 (Figure 1).

B. Absorption spectrum

The absorption spectrum of V (V): A24DHS in n-Butanol shows the maximum absorption at 380 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 380 nm (Figure 2).

Figure 2. absorption spectrum for v - a24dhs complex

C. Influence of diluents

The suitability of solvent was investigated using various organic solvents and the extraction of V (V): A24DHS was quantitative in n-Butanol. Hence, n-Butanol was used for further extraction studies as it gave better and quicker phase separation.

Table 1. Observation table for effect of various solvents on v (v)-a24dhs complex

Solvent	% Extraction
Nitro benzene	55.00
Diethyl ether	59.00
Cyclohexanone	51.29
Chloroform	68.23
Hexane	80.00
n-Butanol	99.96
Ethyl acetate	77.56
Toluene	65.45
CCl ₄	63.22
Xylene	48.31
Isoamyl alcohol	30.23

D. Effect of reagent concentration

It was found that 2 mL of 0.1% reagent is sufficient for the color development of the metal V (V) in 10 mL of aqueous solution at pH 8.2

E. Effect of equilibration time and stability of the complex

The equilibration time of 1 minute is sufficient for the quantitative extraction of vanadium. The stability of color of the V (V): A24DHS complex with respect to time shows that the absorbance due to extracted species is stable up to 35 hours, after which slight decrease in absorbance is observed.

F. Calibration plot

The Beer's law is obeyed from 1 to 5 ppm. The molar absorptivity and sandell's sensitivity were calculated as 0.0288 $\mu\text{g cm}^{-2}$ with molar absorptivity 3899.2 $\text{L mol}^{-1} \text{cm}^{-1}$. (Figure 3)

Figure 3. Calibration Plot Of V (V) – A24dhs Complex

G. Limit Of Detection

The detection limit is the smallest concentration that can be reported with a certain level of confidence. Every analytical technique has a detection limit. For methods that employ a calibration curve, the detection limit is defined as the analyte concentration yielding a response of a confidence factor k higher than the standard deviation of the blank (S_b), as given by equation,

$$LOD = \frac{kS_b}{m}$$

Where, m is the calibration sensitivity. Usually, the factor k chosen to be 2 or 3. A k value of 2 corresponds to a confidence level of 92.1 %. While, a k value of 3 corresponds to a 98.3% confidence level [13]. Limit Of Detection of the present method was calculating at 98.3 % confidence level, it was 0.455 $\mu\text{g/mL}$.

Table 2. observation table for interference of some ions

Sr. No.	Ions	Tolerance ratio
1	Cl^{-1}	1:41
2	ClO_3^{-1}	1:21
3	IO_3^{-1}	1:24
4	NO_2^{-1}	1:25
5	NO_3^{-1}	1:16
6	Oxalate	1:14
7	SO_4^{-2}	1:33
8	Tartrate	1:23
9	Al^{+3}	1:16
10	Pb^{+2}	1:27
11	Bi^{+3}	1:25
12	As^{+3}	1:27
13	W^{+2}	1:35
14	Th^{+4}	1:37
15	Zn^{+2}	1:25
16	Ag^{+1}	1:27
17	Ni^{+2}	1:38
18	Al^{+3}	1:16
19	Pb^{+2}	1:27
20	CN^{-1}	Masked
21	EDTA	Masked
22	Fe^{+3}	Masked
23	Mo^{6+}	Masked
24	Ti^{4+}	Masked
25	Cu^{+2}	Masked
26	U^{+6}	Masked
27	Li^{+1}	1:33
28	Na^{+1}	1:35
29	K^{+1}	1:36
30	Mg^{+2}	1:13
31	Ca^{+2}	1:23

H. Effect of divalent ions and foreign ions

The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 5ppm of vanadium. The ions which show interference in the spectrophotometric determination of vanadium were overcome by using appropriate masking agents. (Table 2 and Table 3)

Table 3. Observation Table For Masking Agents Used

Interfering Ion	Masking agent
Ti (IV)	Ascorbic acid
Fe (III)	Sodium flouride
Cu (II)	Sodium thiasulphate
U (VI)	Oxine
Mo (VI)	Citrate
EDTA	Boiled with concentrated HNO ₃
CN ⁻	Boiled with concentrated HNO ₃ and formaldehyde

I. Precision and accuracy

The precision and accuracy of the developed spectrophotometric method have been studied by analyzing ten solutions each containing 4 µg of vanadium in the aqueous phase. The average of ten determinations was 4.002 and variation from mean at 95% confidence limit was ± 0.0123 .

J. Nature of extracted species

The composition of extracted V (V): A24DHS complex has been determined by Job's continuous variation method. A Job plot is used to determine the stoichiometry of a binding event. In this method, the total molar concentration of metal ion and ligand are held constant, but their mole fractions are varied. A measurable parameter that is proportional to complex formation (such as absorption signal) is plotted against the mole fractions of these two components.

The maximum on the plot corresponds to the stoichiometry of the two species. This method is named after P. Job, who first introduced this methodology in 1928 [14]. It shows that the composition of V (V): A24DHS complex is 1:2 (Figure 4).

Figure 4. job's continuous variation curve

4. Applications

The proposed method was successfully applied for the determination of Vanadium in various alloys and synthetic samples. The results are found to be in good agreement with those obtained by the standard known method. (Table 4).

4.1. Determination of V (V) in Alloys

An accurately weighed amount of 0.3 / 0.5 g of alloy sample were dissolve in 25 mL of 1:4 sulphuric acid. When solution was completed, 5 mL of conc. HNO₃ was introduced and boiled until nitrous fumes no longer evolved. The solution was diluted in 50 mL of hot water and then sat. potassium permanganate solution added until a pink color persists. Boiled for 5 minute. Add slight excess of sulphurous acid and boil off the excess. The solution was cooled. 5 mL orthophosphoric acid and 5 mL of 10 volume hydrogen peroxide were added. Dilute the content to 100 mL and aliquot is used for the determination of Vanadium.

4.2. Synthetic Mixtures

The separation of Vanadium from synthetic mixture of associated metals containing Copper (II), zirconium (II), Cadmium (II), tungsten (II), zinc (II) and Molybdenum (VI) with varying combination was carried out. A definite aliquot of this solution was taken and after the adjustment of basicity of the aqueous solution to pH 8.2 and addition of 2 mL of 0.1% A24DHS solution, formed vanadium complex was extracted into 10 mL of n-Butanol. Molybdenum was mask by using sodium citrate and copper by sodium thiasulphate. The amount vanadium was calculated using the calibration curve method. The result obtained is compared with those obtained by phosphotungstovanadate method.

Table 4. Determination of v (v) using a24dhs from different samples

Sr. No.	Sample	Certified value	Present method
ALLOYS			
1	Ferrovandium	0.250 µg	0.248 µg
2	(V+Cr+Ti) alloy	0.240 µg	0.235 µg
SYNTHETIC MIXTURE			
1	V (100) + Cu (100) + Zn (100)	99.99 ppm	99.98 ppm
2	V (5) + Zr (5) + W (5)	5.0 ppm	4.495 ppm
3	Mo (10) + Cd (30) + V (20)	20 ppm	19.97 ppm

1) Each result is average of three independent determinations.
2) Compared with Phosphotungstovanadate method.

5. Conclusion

Obtained results show that the newly developed method in which the reagent A24DHS was used, can be effectively used for quantitative extraction and estimation of V (V) from aqueous media. The result show good agreement with the standard method.

The developed method is compared with result obtained with the phosphotungstovanadate method for the estimation Vanadium and observed to be comparable. The method can be used even in small laboratories as it requires only UV – VISIBLE spectrophotometer and not much sophisticated and costly measurement devices or instrumentation.

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