Eurasian Journal of Analytical Chemistry

Eurasian J. Anal. Chem. 4(2): 141-151, 2009

Facile and Sensitive Spectrophotometric Method for the Determination of Vanadium

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Received: *14 February 2009;* ***Accepted:*** *17 May 2009*

Abstract

Highly sensitive and simple spectrophotometric method is described for the determination of vanadium(V) using a new reagent Azure B. The method is based on the reaction of vanadium(V) with potassium iodide in an acidic condition to liberate iodine, the liberated iodine bleaches the blue color of Azure B and is measured at 636 nm. The decrease in absorbance is directly proportional to vanadium concentration. The method obeys Beer's law over a concentration range of 0.02–9.0 μg mL^{-1} vanadium. The molar absorptivity, Sandell's sensitivity, detection limit and quantification limit of the reaction system were found to be 4.33×10^4 L mol^{-1} cm^{-1}, 0.0011 μg cm^{-2}, 0.75 μg mL^{-1} and 2.27 μg mL^{-1} respectively. The optimum reaction conditions and other analytical parameters have been evaluated. The proposed procedure has been successfully applied to the determination of vanadium in water, soil, plant material, urine, pharmaceutical preparations and steel samples. The results were compared to those obtained with the reference method.

Keywords:

Spectrophotometry; Vanadium; Azure B

1. Introduction

Vanadium is an important element frequently present in steels. Vanadium is an element of great industrial, ecological, biological and pharmacological importance, and investigations on its compounds as well as on systems allowing for its quantitative determination are attracting increasing interest. Spectrophotometry is the most common technique used for vanadium determinations [1–3] owing to the high sensitivity and selectivity achieved in these reactions.

Vanadium is an essential trace element for plants and animals which acts in the synthesis of chlorophyll and promotes the growth of young animals. Vanadium compounds are toxic in high concentrations or after long periods of exposure [4, 5]. There are also vanadium compounds that exhibit chemotherapeutic effects in the treatment of leukemia1 and recent studies showed promising application in management of diabetes [6-9]. Vanadium in trace amounts is an essential element for cell growth at μg mL^{-1} levels, also has been shown to inhibit cholesterol synthesis and to increase the oxidation of fatty acids of higher concentrations. It is excreted through urine.

Several analytical techniques have been reported for the determination of vanadium, such as high performance liquid chromatography [10-12], voltammetry [13, 14], atomic

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ISSN: 1306-3057 Moment Publication ©2009

absorption spectrometry [15, 16], spectrofluorimetry [17], atomic emission spectrometry [18], and ion chromatography inductively coupled plasma optical emission spectrometry [19, 20]. These techniques suffer from several disadvantages such as high expensive instruments (i.e., ICP-AES and IC-ICP-OES) or poor sensitivity. Several spectrophotometric methods have been reported for the determination of vanadium in environmental and biological samples. Recently, a few authors introduced various reagents for spectrophotometric determination of vanadium in various samples such as 2-(2-quinolylazo)-5-diethylaminophenol [21], Variamine blue [22], Eriochrome cyanine R [23], Benzylacetate [24], Pyrogallol [25], 2-hydroxyacetophenone [26], 4-(2-pyridylazo) resorcinol [27], 4-(2-thiazolylazo)resorcinol [28] Tannic acid [29], 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol [30], *N*,*N*-bis(2-hydroxyl-3-sulfopropyl)-tolidine [31] and Pyridylazoresorcinol [32]. Some of the above reported reagents are suffers from poor selectivity [24, 27], large number of metal ions are interfere [23, 24] few other are required specific solvent for the extraction of color species[23,30] and few others are required activators [30] for catalytic photometric determination of vanadium. These deficiencies have encouraged us to develop a facile, sensitive, accurate and reliable method for the determination of trace amounts of vanadium using Azure B as a chromogenic reagent. The method has been successfully applied to the determination of vanadium in water, soil, plant material, urine, pharmaceutical preparations and steel samples.

2 Experimental

2.1 Apparatus

A SHIMADZU Deutschland GmbH (Model No: UV-2550) UV-Visible spectrophotometer with 1 cm matching quartz cells were used for the absorbance measurements and a WTW pH 330, pH meter was used.

2.2. Reagents

All chemicals and solvents used were of analytical reagent grade, and doubly distilled water was used in the preparation of all solutions in the experiment. Standard stock solution containing 1000 μg mL^{-1} of vanadium(V) was prepared by dissolving 0.2393 g of Ammonium vanadate in 100 mL volumetric flask and diluted up to the mark using doubly distilled water. Working solutions were prepared by appropriate dilution of the standard solution. 0.05 % solution of Azure B reagent and sodium acetate buffer were used.

2.3 General procedure for determination of vanadium

An aliquots of stock solution containing 0.02-9.0 μg mL^{-1} of vanadium(V) was pipetted out in to a series of 10 mL standard flasks. To each of this was added 1.0 mL potassium iodide followed by 1.0 mL of 2 M hydrochloric acid. The mixture was gently shaken until the appearance of yellow color, indicating the liberation of iodine. Then 0.5 mL of 0.05 % Azure B reagent was added, followed by 2.0 mL of 2 M sodium acetate solution. The contents were made up to the mark by using distilled water and mixed well. Absorbance was measured at 636 nm and the calibration graph was constructed.

2.4 Determination of vanadium in water

Each filtered environmental water sample (100 mL) was analyzed for vanadium. They tested negative. To these samples known amount of vanadium(V) was added and then analyzed by the proposed procedure.

2.5 Determination of vanadium in soil

An air-dried homogenized soil sample (1 g) was weighed accurately and placed in a 100 mL Kjeldahl flask. The sample was digested in the presence of an oxidizing agent following the method recommended by Murthy et al., [26]. The content of flask was filtered through a Whatman no. 40 filter paper, into a 25 mL calibrated flask and neutralized with dilute ammonia in the presence of 1–2 mL of 0.01% tartrate solution. It was then diluted to the mark with water. Appropriate aliquots of 1–2 mL of the solution was transferred into a 25 mL calibrated flask and analyzed for vanadium content according to the general procedure, after adding 1–2 mL of 0.01% fluoride solution as masking agent [33]. They tested negative. To these samples known amount of vanadium(V) was added and then analyzed by the proposed procedure.

2.6 Determination of vanadium in urine

About 50 mL of the urine sample was concentrated to 5 mL by evaporation. To this solution was spiked a known amount of vanadium and mixed with 5 mL of conc. HNO_3 and 5 g of potassium sulfate and heated to dryness. The process was repeated 2–3 times and then HNO_3 (1:3, 25 mL) was added to the residue and digested on a water bath for 30 min [33]. The contents were again evaporated to dryness, cooled and the residue was dissolved in water, filtered, and neutralized with dilute ammonia. The mixture was diluted to a known volume with water. Appropriate aliquots of this solution were taken and the proposed general procedure was followed for the vanadium determination. They tested negative. To these samples known amount of vanadium(V) was added and then analyzed by the proposed procedure.

2.7 Determination of vanadium in biological samples

The samples of plant tissues were collected from Hassan region (Karanataka state, India). These plant tissues were washed with distilled water to get them free from adhering soil. They were carefully wiped with filter paper before taking their wet weight. The sample was then dried and brought into solution by acid treatment as per standard procedure [32] and neutralized with dilute NH_4OH and then diluted to a known volume with water. An appropriate aliquot of this solution was finally analyzed according to the general procedure for vanadium. They tested negative. To these samples known amount of vanadium(V) was added and then analyzed by the proposed procedure.

2.8 Determination of vanadium in pharmaceutical samples

A volume of 10 mL of neogadine elixir sample was treated with 10 mL of conc. HNO_3, the mixture was then evaporated to dryness. The residue was leached with 5 mL of 0.5 M H_2SO_4. The solution was diluted to a known volume with water, after neutralizing with dilute ammonia. An aliquot of the made up solution was analyzed by the present method for vanadium determination.

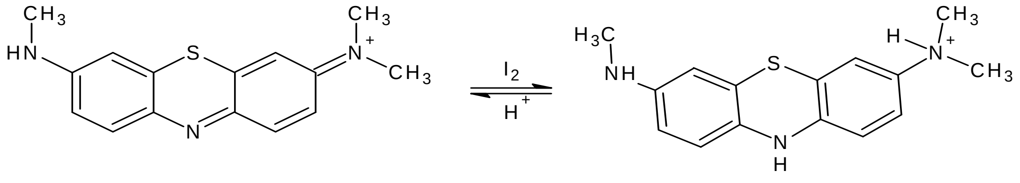
2.9 Determination of vanadium in alloy steels

About 0.1 g of a steel sample containing 0.13% of vanadium was weighed accurately and placed in a 50-mL beaker. To it, was added 10 mL of 20% H_2SO_4 and carefully covered with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5 mL of conc. HNO_3 until all carbides were decomposed. Then, 2mL of a 1:1 H_2SO_4 solution was added and the mixture was evaporated carefully until the dense white fumes derived off the oxides of nitrogen, and then cooled to room temperature. After appropriate dilution with water, the contents of the beaker were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH solution in the presence of 1–2 mL of 0.01% tartrate. The resulting solution was filtered, if necessary, through a Whatman no. 40 filter paper into a calibrated flask of known volume. The residue was washed with a small volume of hot 1% H_2SO_4 followed by water and the volume was made up to the mark with water. A suitable aliquot of the above solution was taken into a 10 mL calibrated flask and the vanadium content was determined by the general procedures using 1–2 mL of saturated fluoride solution as masking agent. Iron(III) can be effectively removed from the solution by precipitation with saturated flouride solution The precipitates were filtered off before the addition of Azure B reagent. Higher concentrations of iron(III) were removed by adding 5–10 mL of saturated ammonium thiocyanate solution to the test solution and the resulting Fe(III) and Fe(II) complexes with thiocyanate were extracted into methyl isobutyl ketone (MIBK) in an aqueous acidic medium prior to the determination of vanadium.

3. Results and discussion

Vanadium(V) reacts with potassium iodide in presence of dilute hydrochloric acid to liberate iodine quantitatively. The liberated iodine bleaches the blue color of Azure B and is measured at 636 nm (Fig. 1). The decrease in absorbance is directly proportional to vanadium concentration. The probable reaction pathway is presented in Scheme 1.

$$2\,VO_4^{3-} + 2\,I^- + 12\,H^+ \longrightarrow 2\,VO^{2+} + I_2 + 6\,H_2O$$



Scheme 1. Proposed reaction pathway

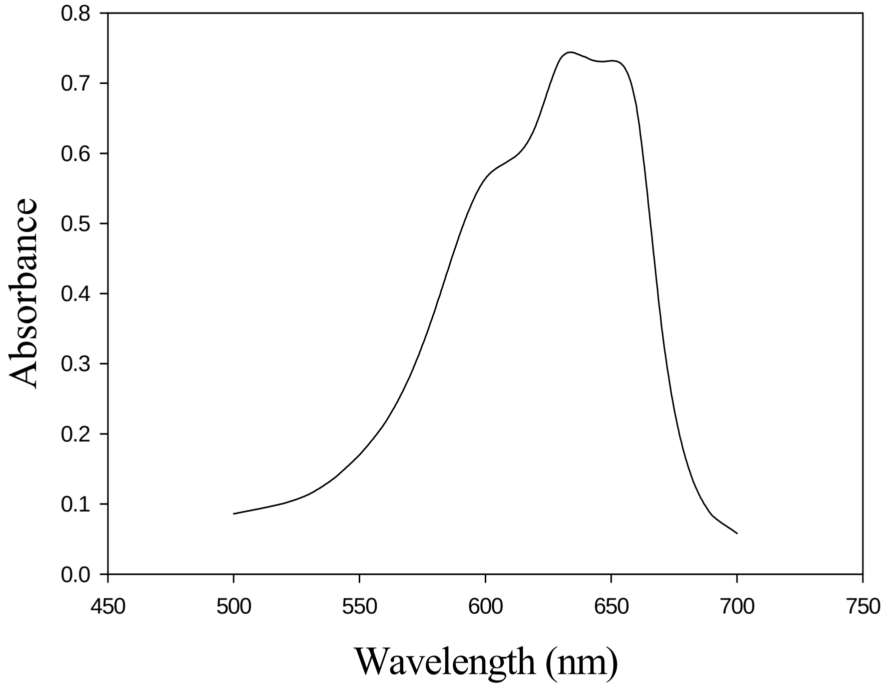


Fig 1. Absorption Spectrum

3.1 Effect of iodide concentration, acidity, temperature and time

The effect of iodide concentration and acidity on the reaction of Azure B was studied with 2 µg mL^{-1} of vanadium. The oxidation of iodide to iodine by vanadium is effective in acidic medium which could be maintained by adding 1 mL of 2 M HCl in the final volume of 10 mL. The liberation of iodine from potassium iodide in an acidic medium is quantitative. The appearance of yellow color indicated the liberation of iodine. It was found that 1 mL of 2 % potassium iodide and 1 mL of 2 M HCl are sufficient for the liberation of iodine from iodide by vanadium. Normal room temperature is sufficient for this reaction and also 10 min time was needed for completion of the reaction after dilution to 10 mL. The reaction is stable up to 5 days.

3.2 Effect of non-target species

The effect of various foreign ions at µg mL^{-1} levels on the determination of V(V) was studied. Tolerance limits of interfering species were established at those concentrations that do not cause more than ± 2% error in the absorbance values of V(V) at 2 µg mL$^{-1.}$ The studies revealed that Pb(II), Sn(II), Fe(III), Cr(III), Mo(VI) and Ce(IV) showed severe interference. However, the interference of these ions could be masked by using EDTA (1000 µg mL^{-1}) up to 25 µg mL^{-1}. The tolerance limits of the foreign species examined are listed in Table 1.

Table 1. Effect of non-target species in the determination of vanadium(V) 5 µgml^{-1}

Non-target species	Tolerance limit (µg mL^{-1})	Effect
Na^+, $Mg^{2+,}$ Cl^-, NO_3^-, F^-, $CHCOO^-$, K^+,Ca^{2+}, SO_4^{2-}, citrate, oxalate, tartarate	2500	No interference
Al^{3+}, Cd^{2+}, Ba^{2+}, Te^{4+}, interference	500	No interfere
Ni^{2+}, Co^{2+}, Zn^{2+} interference	100	No interfere
Ce^{4+}, Fe^{3+}, Cr^{3+}, Sn^{2+}, Pb^{2+}, Mo^{6+}	25^a	Positive

^{a} Masked by masking agents

3.3 Analytical data

The adherence to Beer's law was studied by measuring the absorbance value of solutions by varying vanadium concentration. A straight line graph was obtained by plotting absorbance against the concentration of vanadium. Beer's law is obeyed for the determination of vanadium, by using Azure B with vanadium in the range of 0.02-9.0 µg mL^{-1}. Adherence to Beer's law graph for the determination of vanadium using Azure B is presented in Fig. 2. The molar absorptivity, Sandell's sensitivity detection limit and quantification limit were found to be 4.33×10^4 L mol^{-1} cm^{-1}, 0.0011 µg cm^{-2}, 0.75 µg mL^{-1} and 2.27 µg mL^{-1} respectively. Beer's law range, correlation coefficient and other parameters are given in Table 2.

3.4 Application

The proposed procedure is applied to the determination of trace amounts of vanadium in real matrixes of water, soil, plant material, urine, pharmaceutical preparations and steel samples. A parallel determination was carried out with a reference method [22]. The proposed method has significant advantages over other reported methods [21, 22. 27, 31] in terms of its simplicity and free from most interfering substances. Accurate and reproducible results were obtained with permissible standard deviations.

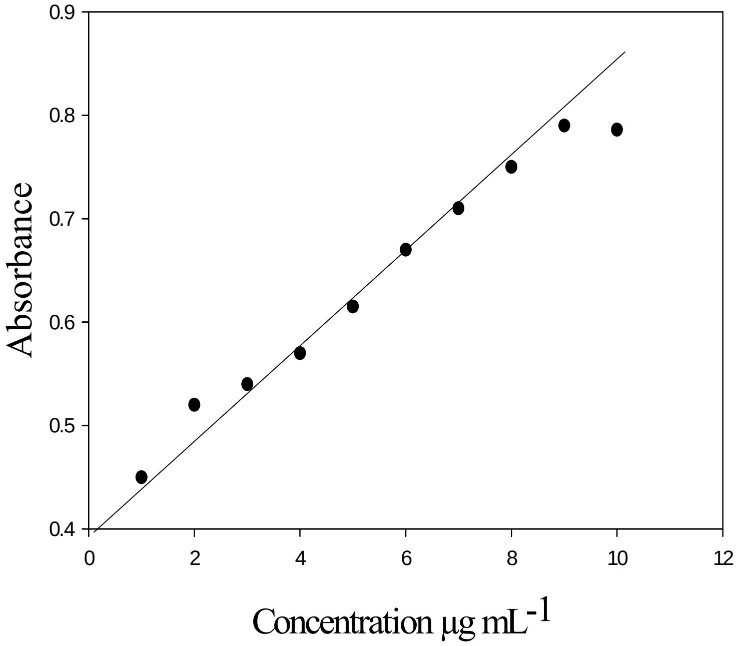


Fig 2. Adherence to Beer's law

Table 2. Optical characteristics, precision and accuracy of the proposed method

Concentration range (µg mL^{-1})	0.02–9.0
Color change	Blue to colorless
λmax (nm)	636
Stability	5 days
Molar absorptivity ($\times 10^4$ L mol^{-1} cm^{-1})	4.33
Sandell's sensitivity (µg cm^{-2})	0.0011
Limit of detection (µg mL^{-1})	0.75
Limit of quantification (µg mL^{-1})	2.27
Correlation coefficient r	0.9927
Range of error (95% confidence level)	± 1.0

It is evident from the data that the proposed method is simple, highly sensitive and rapid than the reported method in literature as shown in Table 3. The results of the method are favorably compared with the method reported by Kiran Kumar and Revanasiddappa [22] and results were summarized in Table 4. Statistical analysis of the results by use of t- and F-tests showed no significant difference between the accuracy and precision of the proposed and reference method. Also, the reliability was checked by standard addition and recovery method.

Table 3. Comparison of the present method with reported methods for the determination of vanadium(V)

Reagent	Molar absorptivity (L mol^{-1} cm^{-1})	λmax (nm)	Beer's law range (µg mL^{-1})	Remarks
Pyrogallol [25]	0.775 x 10^4	580	0-14	Low sensitive
2-HAPO [26]	---	400	1.0–6.0	Less detection limit and extraction needed
Varamine blue [22]	1.650 x 10^4	570	0.1–2.0	Less sensitive and less stable
Eriochrom cyanine R [23]	---	585	0.001 –0.15	Large number of metal ions are interfere
5-Cl DMPAP [29]	6.570 x 10^4	588	0.09-1.2	Solvents required for the extraction of color derivatives
MBTH–NEDA [34]	3.126 x 10^4	595	0.05–6.0	Low sensitive and less detection limit
DPH–MBTH [34]	2.921 x 10^4	526	0.06–7.0	Reducing species expected to interfere
3,4-DHBINH [35]	1.290 x 10^4	360	0.5-5.3	Low sensitive
2,2'-Iminodibenzoic acid [36]	1.200 x 10^4	610	0.4-2.0	Low sensitive
3,5-DNC & Rhodamine [37]	2.100 x 10^5	555	0.03-0.3	Flotation step required, time consuming and not selective
Azure B [present work]	4.330 x 10^4	636	0.02-9.0	Facile, Sensitive, rapid, non-extractive stable color derivati ves and less interference

HAPO - Hydroxyacetophenone oxime; Cl DMPAP - 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol; MBTH -3-methyl-2-benzothiazolinone hydrazone hydrochloride; NEDA *N*-(1-naphthyl)ethylenediamine dihydrochloride; DPH – dopamine Hydrochloride; DBIH -3, 4-dihydroxybenzaldehydeisonicotinoylhydrazone; DNC–3,5-Dinitrocatechol; N-PCHA-N-phenyl cinnamohydroxamic acid; DBHQ-5,7-Dibromo-8-hydroxyquinoline

Table 4: Determination of vanadium(V) in various samples

Sample	Vanadium Added µg mL^{-1}	Proposed method			Reference method [22]			t-test[b]	F-test[b]
		found[a]	Recovery	RSD (%)	Found[a]	Recovery	RSD (%)		
Natural water[c]	2.0	1.98 ± 0.01	99.00	0.50	1.98 ± 0.01	99.00	99.00	0.44	1.62
	4.0	3.98 ± 0.03	99.60	0.75	3.98 ± 0.02	99.50	99.50	0.66	2.25
	6.0	5.97 ± 0.02	99.50	0.33	5.96 ± 0.02	99.33	99.33	1.12	1.23
Soil[c]	2.0	1.99 ± 0.02	99.30	1.20	1.98 ± 0.03	99.30	99.30	0.37	1.08
	4.0	3.99 ± 0.03	99.75	0.70	3.98 ± 0.03	99.45	99.45	0.95	1.25
	6.0	5.99 ± 0.03	99.93	0.55	5.98 ± 0.03	99.76	99.76	0.67	1.06
Urine[c]	2.0	1.97 ± 0.02	98.70	1.16	1.97 ± 0.02	98.50	98.50	0.38	1.32
	4.0	3.99 ± 0.03	99.70	0.82	3.98 ± 0.03	99.60	99.60	0.41	1.13
Plant material	2.0	1.96 ± 0.04	98.00	1.83	1.95 ± 0.04	97.70	97.70	0.37	1.06
(Cabbage)[c]	4.0	3.99 ± 0.03	99.80	0.72	3.98 ± 0.03	99.40	99.40	1.08	1.29
pharmaceutical	---	4.39 ± 0.02	99.70	0.45	4.38 ± 0.02	99.59	99.59	0.52	1.17
preparations[d]	3.0	7.39 ± 0.04	99.86	0.50	7.38 ± 0.03	99.70	99.70	0.60	1.34
Steel[e] *	---	5.19 ± 0.03	99.73	0.63	5.18 ± 0.03	99.57	99.57	0.27	1.49
**	1.5	6.69 ± 0.03	99.82	0.41	6.68 ± 0.02	99.73	99.73	0.48	1.48

a Mean ± S.D. (*n* = 5). b Tabulated *t*-value for 8 degrees of freedom at *P*(0.95) is 2.65 and tabulated *F*-value for (4, 4) degrees of freedom at *P*(0.95) is 5.72. c Gave no test for vanadium.

d Neogadine Elixir®, Raptakos Brett&Co. Ltd., India (each 10 ml contains Iodised peptone 19.33 mg, magnesium chloride 13.33 mg, magnesium sulfate 2.66 mg, sodium metavanadate 0.44 mg, zinc sulfate 4 mg, pyridomine HCl 0. 5 mg, cyanocobalamin 0.33 µg, nicotinamide 6.66 mg, alcohol (95%) 0.63 ml, total alcohol 6%), vanadium taken 4.4µg.

e GKW Steel Ltd., India (C, 0.54%; Mn, 0.89%; S, 0.018%; P, 0.034%; Si, 0.33%; Cr, 1.02%; V, 0.13%), vanadium taken 5.2 µg

4 Conclusions

The proposed method for the determination of vanadium is simple, rapid, sensitive and has the advantage of enabling a wide range of determination without the need for extraction or heating. The satisfactory applicability of the proposed procedure to the determination of vanadium in various samples shows the utility of the method. The proposed method has an advantage of high sensitivity ($\varepsilon = 4.33 \times 10^4$ L mol^{-1} cm^{-1}and Sandell’s sensitivity is 0.0011 µg cm^{-2}) over the reference method [22] ($\varepsilon = 1.65 \times 10^4$ L mol^{-1} cm^{-1}and Sandell’s sensitivity is 0.003 µg cm^{-2}). Although many sophisticated techniques; ICP-MS, AAS, etc. are available for the determination of vanadium at trace levels, the factors such as the low cost of the instrument, ease of handling, lack of need for consumables, and almost no maintenance have caused spectrophotometry to remain a popular and inevitable technique, particularly in the laboratories of developing countries with a limited budget.

Acknowledgement

The authors are thanking full to DST and UGC for financial assistance through FIST and SAP programmes respectively.

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