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A simple and sensitive spectrophotometric method for vanadium(V) through a nucleophilic coupling of catechol with p-tolidine / o-tolidine

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ABSTRACT

A simple and sensitive spectrophotometric method is developed for the determination of vanadium and used for its determination in water samples of certain lakes that are situated in and around Mysore city and a pharmaceutical sample. The method is based on the catechol oxidation by vanadium(V) followed by its nucleophilic coupling with p-tolidine system 1 or o-tolidine system 2 producing a dye with λ_{max} 540nm/520nm in 0.1M hydrochloric acid. The system is obeying the Beer's law in the range 1-20 $\mu\text{g ml}^{-1}$ of vanadium. The molar absorptivity Sandell sensitivity and regression coefficient values are found to be $1.733 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$, $0.0294 \mu\text{g cm}^{-2}$ and 0.9901 for p-tolidine system, and the corresponding values for the o-tolidine system are $1.84 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$, $0.0276 \mu\text{g cm}^{-2}$ and 0.9673. The optimum reaction conditions and other analytical parameters are investigated to enhance the sensitivity of the method. The compositions of the dye product of both systems are determined by Job's method of continuous variation as well as mole ratio method and are found to be 1:1 and 2:1 for the system 1 and 2 respectively. The method is working successfully for the analysis of vanadium present in water and pharmaceutical samples. The results of vanadium obtained from both the systems are found to be reproducible and also agreeing with the results determined from an official method.

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KEYWORDS

Vanadium(V);
Nucleophilic coupling
reactions;
Catechol;
p-tolidine;
o-tolidine;
Spectrophotometry.

INTRODUCTION

Vanadium is an element of industrial, physiological and environmental importance^[1]. Although vanadium can exist in oxidation states from II to V in aqueous solution but most of its methods are concentrated on its determination in the pentavalent and tetravalent states, as these are the most common forms in which it is found in inorganic and biological systems^[2]. Its industrial applications are including dyeing ceramics, ink and catalyst

manufacturing. A substantial amount of vanadium is released to the environment during the burning of crude petroleum, coal, lignite and it is known to settle on the soil. Vanadium and its compounds are extensively used in steel and petrochemical industries^[3] Vanadium compounds are perhaps better called insulin enhancing drugs, since they do not work in the absence of insulin. The major accumulation of vanadium in the body is in the bones and kidneys.^[4] Vanadium acts as a growth promoting factor and participates in fixation and accumu-

lation of nitrogen in plants, but when it is in high concentration it may reduce the growth of plants. Therefore the determination of vanadium in environmental and biological samples is finding importance. Literature on its determination is revealing several analytical techniques that are being used for its determination, for example, high performance liquid chromatography^[5], anodic stripping voltammetry^[6], volumetry^[7], atomic absorption spectrometry^[8], spectrofluorimetry^[9], and inductively coupled plasma atomic emission spectrometry^[10]. There are several spectrophotometric methods available for the determination of vanadium in environmental and biological samples and those methods are involving various reagents such as 4-(2-pyridylazo) resorcinol (1), 2-(2-quinolyazo)-5-diethylaminophenol^[11], pyrogallol^[12], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol^[13], 2-(8-quinolyazo)-5-(dimethylamino)phenol^[14], 4-(2-thiazolylazo)-resorcinol^[15] and calyx^[4] pyrrole hydroxamic acid^[16]. It is in this background and in continuation of the previous work^[17] an alternate sensitive spectrophotometric method is developed here for the determination of vanadium(V) through a nucleophilic coupling reaction between catechol and p-tolidine, λ_{\max} , 540 nm system 1 or catechol and o-tolidine, λ_{\max} , 520, system 2 in 0.1M hydrochloric acid.

EXPERIMENTAL

Apparatus

Elico spectrophotometer, model SL - 27 (Hyderabad - India) and Acculab Digital balance readable 0.0001g were used.

Reagents

All chemicals used in the experiments were of analytical reagent grade and the water used was distilled water.

Stock solution 255 μgml^{-1} vanadium(V)^[18]: An accurately weighed amount, 1.462g ammonium metavanadate was transferred into a beaker. It was dissolved in warm water and the resulting solution was transferred into a 250ml volumetric flask and diluted to the mark with water.

Catechol, 0.005M: An accurately weighed amount 0.1375g of catechol was transferred to a beaker. It

was dissolved in water and transferred the resulting solution into a 250ml volumetric flask and diluted to the mark with water.

o-Tolidine / p-Tolidine 100 μgml^{-1} : An accurately weighed amount, 0.1g of o-tolidine / p-tolidine was transferred to a beaker. It was dissolved in alcohol and transferred the resulting solution into a 100ml volumetric flask and diluted to the mark with water.

Hydrochloric acid 0.1M: It was prepared by a suitable dilution of concentrated hydrochloric acid (35% 1.18g cm^{-3}) with water.

Recommended procedure

A series of 25ml volumetric flasks were arranged. To each flask 2 ml of 0.005M catechol, 0.5 ml of 0.1M hydrochloric acid and 2 ml of 100 μgml^{-1} p-tolidine/o-tolidine and aliquots of ammonium metavanadate corresponding to 1 - 20 μgml^{-1} (0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.5 and 2 ml) were added. Then, each solution was diluted to the volume with water. The absorbance of each solution was measured at 540nm/520 nm against water.

Procedure for the determination of vanadium in water samples

Water samples of the lakes of Kukkarahalli, Karanji and Lingabudi which are located in Mysore city were collected. The water samples were filtered and analyzed for vanadium through its standard addition.

Procedure for the determination of vanadium present in a pharmaceutical sample.^[19]

A known volume, 10ml of elixir sample was taken in a beaker and it was treated with 7ml concentrated nitric acid, and the solution was evaporated to dryness on a hot plate. The residue produced was taken in a crucible and ashed it by igniting the crucible in an electric burner. The crucible along with its contents was cooled and the ash obtained was dissolved in concentrated hydrochloric acid. The solution was transferred into a volumetric flask and diluted to the volume with water. An aliquot of the made up solution was analyzed for vanadium following the general procedure described for the vanadium determination.

RESULTS AND DISCUSSION

The developed method is based on catechol oxi-

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duction by vanadium(V) followed by its nucleophilic coupling with p-tolidine, system 1 / o-tolidine, system – 2 at λ_{\max} 540/520 in hydrochloric acid medium and the corresponding spectra are shown in the Figure 1 and 2. The reaction conditions as well as the various experimental parameters affecting the development and stability of the dye products were carefully investigated and optimized for the quantitative determination of vanadium(V). The experimental variables such as concentration of catechol, concentration of p-tolidine, types of acids, concentration of hydrochloric acid and order of reagents addition, and also colour stability of the complex were optimized for the effective determination of vanadium. The proposed method was successfully applied for the analysis of vanadium in water samples and a pharmaceutical sample. The results obtained were reproducible and also comparable with the results determined from an official method^[20].

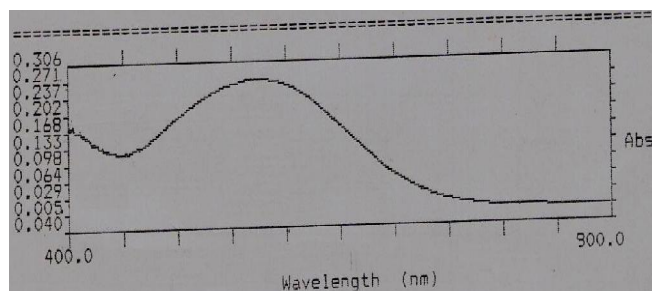


Figure 1 : Absorption spectrum of the solution with 1ml of 255µg/ml vanadium(V) + 2ml of 0.005 M catechol + 0.5ml of 0.1 M HCl + 2ml of 100µg/ml p-tolidine.

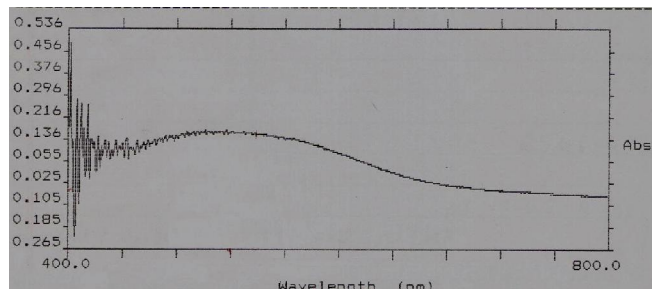


Figure 2 : Absorption spectrum of the solution containing 1ml of 255µg/ml vanadium (V) + 2ml of 0.005 M catechol + 0.5ml of 0.1 M HCl + 2ml of 100µg/ml o-tolidine.

Optimization

Effect of different volumes of catechol

The effect of concentration of catechol on absorbance was investigated to achieve high absorbance via taking various volumes (0.5-3.5ml) of 0.005M catechol, 0.5ml of 0.1ml hydrochloric acid, 1ml of vanadium(V)

and 2ml of 100µgml⁻¹ p-tolidine were added. The absorbance values were found to be 0.26, 0.30, 0.33, 0.34, 0.30 and 0.29 respectively. This indicates that the solution containing 2ml of 0.005M catechol appeared to be more sensitive and hence selected as an optimized volume for the construction of the calibration graph for the determination of vanadium(V).

Effect of different volumes of 0.1 M hydrochloric acid

The effect of concentration of hydrochloric acid was studied as above with different volumes (0.2, 0.5, 1ml) of 0.1M hydrochloric acid. The absorbance values were found to be 0.24, 0.31 and 0.30, respectively for 0.1M hydrochloric acid. Based on these results, 0.5ml of this solution was selected for the construction of calibration graph.

Effect of different volumes of 100 µgml⁻¹ p-tolidine

The concentration influence of p-tolidine was studied as above with different volumes of (0.5, 1, 2, 3 ml) of 100µgml⁻¹ p-tolidine. The absorbance values were found to be 0.18, 0.25, 0.32 and 0.31. 2ml of the 100µgml⁻¹ p-tolidine showed maximum absorbance hence selected throughout the experiment for the determination of vanadium(V).

Effect of order of addition of the reagents

Different orders of the reagent addition were studied using optimized amounts of reagents following the recommended procedure. The results obtained have shown that the orders of reagents addition are not affecting the absorbance values. But for maintaining the uniformity, the order of addition shown in serial No. 1, TABLE 1 was followed throughout the work.

TABLE 1 : Effect of order of reagents addition for the determination of vanadium(V)

Sl. No.	Order of addition	Absorbance
1.	A + B + C + D	0.2464
2.	B + C + D + A	0.2182
3.	C + D + A + B	0.2298
4.	D + A + B + C	0.2898
5.	D + C + B + A	0.225
6.	A + C + B + D	0.2313

A = 1 ml 255 µgml⁻¹ vanadium(V), B = 2ml 0.005 M catechol, C = 0.5ml of 0.1M hydrochloric acid, D = 2ml 100 µgml⁻¹ p-tolidine.

Colour stability of the complex with time

The stability of the colour complex was studied according to the recommended procedure using 10 µg/ml vanadium(V). The absorbance was measured at various intervals of time. The results obtained are shown in Figure 3 : It indicates the instantaneous formation of colour and stable for almost one hour, after which color is decreasing gradually with time.

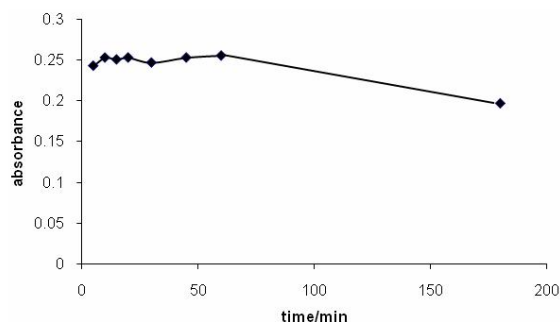


Figure 3 : Effect of time on the stability of the complex.

Calibration graph

The summary of the analytical parameters established for the optimized method of vanadium(V) is given a TABLE 2.

TABLE 2 : The analytical parameters for the determination of vanadium(V).

Parameter	System 1	System 2
Wavelength (nm)	540	520
Linear range (µgml ⁻¹)	1 – 20	1 – 20
Molar absorptivity (l mol ⁻¹ cm ⁻¹)	1.733x10 ³	1.84x10 ³
Sandell sensitivity (µg cm ⁻²)	0.0294	0.0276
Regression equation (Y)		
Slope (b)	0.0220	0.0146
Intercept (a)	0.0498	0.0899
Correlation coefficient (R ²)	0.9901	0.9673

Y = a+bx, where x is the concentration of vanadium(V).

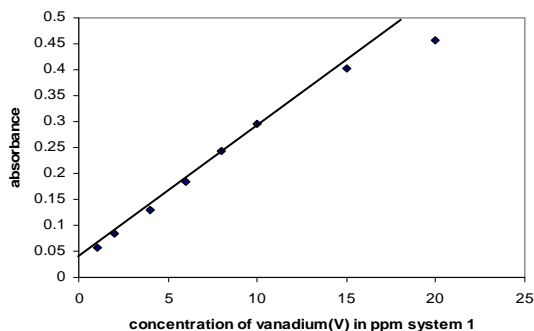


Figure 4 : Calibration graph for the system 1 involving vanadium(V), catechol - p-tolidine.

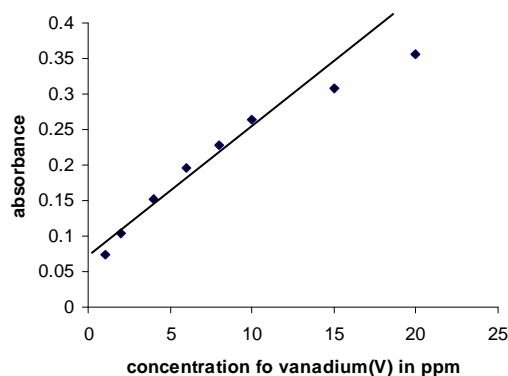


Figure 5 : Calibration graph for the system 2 involving vanadium(V), catechol - o-tolidine

Precision and accuracy

The precision and accuracy of the system 1 were calculated by performing five replicate determinations of vanadium(V) at three different concentrations (2, 6, and 10 µgml⁻¹) following the recommended procedure. The precision of the method as expressed by relative standard deviation was less than 1.4% whereas accuracy expressed by the calculated relative error was less than 2.9%.

Interference studies

In order to evaluate the selectivity of the proposed method for the determination of vanadium, the effect of common foreign substances accompanying vanadium was tested in the determination of 10 µgml⁻¹ of vanadium under the optimum conditions given in the recommended procedure. The tolerance limit was taken as the maximum concentration of the foreign ion causing an error of less than 3%. The results obtained are summarized in TABLE 3, nitrite and iron are seriously interfering even at 1.28 ppm and 0.8 ppm. How-

TABLE 3 : Interference of foreign ions in the determination of 10 µgml⁻¹ of vanadium(V)

Ion added	Tolerance limit (mgml ⁻¹)
Cu ²⁺	101.6 ppm
Zn ²⁺	90.8 ppm
Mg ²⁺	161.2 ppm
K ⁺	419.2 ppm
Fe ³⁺	0.8 ppm
Cl ⁻	375.2 ppm
SO ₄ ²⁻	638.4 ppm
NO ₃ ⁻	74.4 ppm
NO ₂ ⁻	1.288 ppm

These ions concentration were examined only upto 638.4 ppm

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ever iron interference can be eliminated by the addition of EDTA.

Stoichiometry of the dye product of the system 1

Job's method of continuous variation

The experiment was carried out using a series of solutions of 0.002M catechol 0.002M p-tolidine/o-tolidine. The solutions were prepared by mixing complementary proportions of a fixed total volume of 5 ml involving various volumes (0 – 5)ml of 0.001M mixture, (p-tolidine and catechol) or (o-tolidine and catechol) and 0.5ml of 0.1M hydrochloric acid and various volumes (5–0)ml of 0.001 M vanadium were transferred into a series of labelled 25 ml volumetric flasks. Then the solution of each flask was diluted and absorbance was measured. The results obtained were used in plotting the graph, shown in Figure 6 and 7 that are accounting for 1:1 stoichiometry between vanadium (V) and mixture(system1) and 1:2 stoichiometry between mixture and vanadium (V) for the system 2.

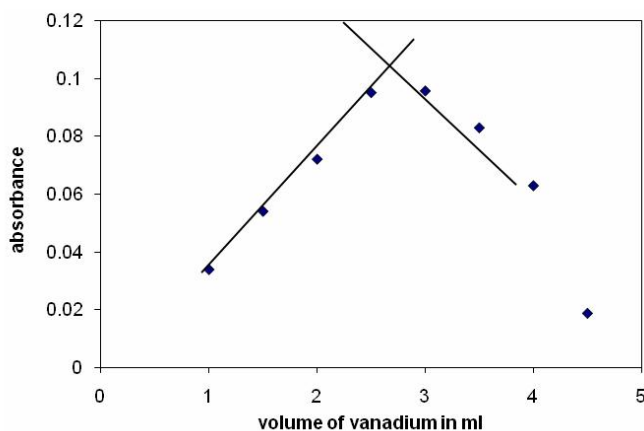


Figure 6 : Composition of vanadium and mixture (system 1)

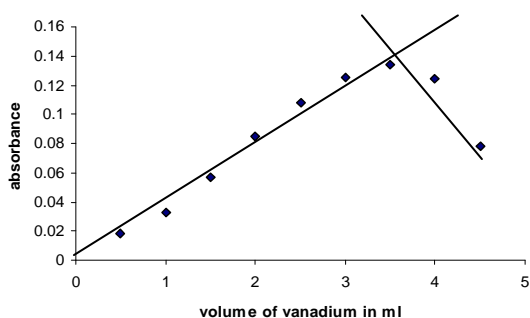


Figure 7 : Composition of vanadium(V) and mixture (system 2)

Molar ratio method

Equimolar solutions of 0.001M catechol and

0.001M p-tolidine were used. A series of solutions were prepared keeping the constant volume, 2.5ml of catechol with various volumes of (0-5ml) of p-tolidine. The procedure followed was involving constant volume, 2.5ml of 0.001m catechol, 0.5ml of 0.01M hydrochloric acid, and 3ml of 0.001M vanadium of various volumes (0-5 ml) of 0.001M p-tolidine, and were transferred into 25ml volumetric flasks and diluted the solutions to the mark with water. The absorbance of each solution was measured at 540nm. The results obtained were used to construct the graph shown above and is accounting for 1:1 stoichiometry between catechol and p-tolidine.

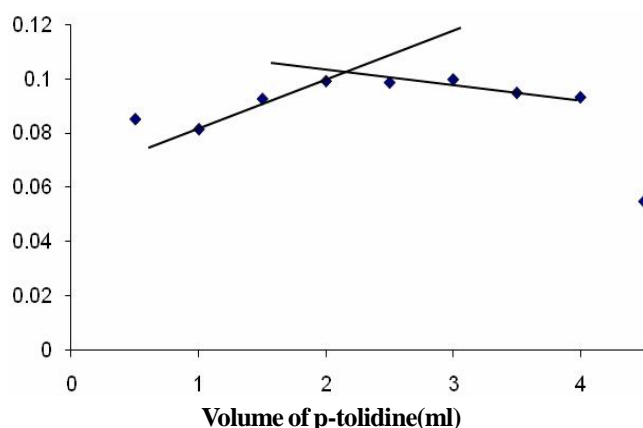


Figure 8 : Molar ratio method for the study of stoichiometry between p-tolidine and catechol.

CONCLUSION

The developed method, involving the two systems, is simple and rapid, as it neither requires solvent extraction^[21,22] nor separation before the analysis. The chemical used in this work are cheap and are available in common chemical laboratory. Both systems developed are successfully employed for the determination of vanadium(V) in the water samples of selected lakes of Mysore city and also a pharmaceutical sample. The values obtained are agreeing with those obtained by and official method^[20].

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Sr. No	Vanadium added (ppm)	New method						Official method(18)			t-test		F-test	
		^a vanadium found(ppm)		RSD%		Recovery%		vanadium found(ppm)	RSD %	Recovery %	System		System	
		System		System		System					1	2	1	2
		1	2	1	2	1	2							
1	10.2	10.09 ± 0.05	10.1 ± 0.07	0.50	0.7	98.9	99.0	10.8 ± 0.06	0.6	98.8	0.287	0.48	1.44	1.36
2	5.0	6.00 ± 0.03	6.01 ± 0.05	0.5	0.83	120	120	5.99 ± 0.04	0.7	119	0.45	0.70	1.77	1.5
3	6.12	6.63 ± 0.06	6.69 ± 0.07	0.9	1.16	108	109.3	6.65 ± 0.05	0.83	108.6	0.57	1.05	1.44	1.96
4	4.10	4.00 ± 0.04	4.07 ± 0.03	1.0	0.75	97.5	99.2	4.02 ± 0.05	1.25	98.0	0.70	1.97	1.56	2.7
5	2.2	2.04 ± 0.06	2.07 ± 0.02	3	0.96	92.7	94.0	2.05 ± 0.03	1.5	93.1	1.7	1.2	4.0	2.25

^aMean ± standard deviation (n = 5) Tabulated t – value at the 95% confidence level is 2.77. Tabulated F – value at the 95% confidence level is 6.39. 1. Tap water, 2. Kukkarhalli Lake water, 3. Lingabudi lake water, 4. Karanji Lake water, 5. Pharmaceutical preparation bNegodine Elixir ®, Raptakos Breet & Co. Ltd India (Each 15 ml contains Iodised peptone 29 mg, magnesium chloride 20 mg, magnesium sulfate 4 mg, sodium metavanadate 0.66, mg. zinc sulfate 6 mg, pyriodamine HCl 0.75 mg, cyanocobalamin 0.5 µg, nicotinamide 10 mg, alcohol (95%) 0.95 ml, Total alcohol 6% (v/v)

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