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Micro-determination of Vanadium using 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene as an Analytical Reagent

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ABSTRACT

A sensitive and selective spectrophotometric method is proposed for the rapid determination of vanadium using 1-(2-quinolylazo)-2,4,5-trihydroxybenzene(QATB). Alcoholic solution of QATB form a 1:2 dark brown complex with vanadium(V) ions at pH ranges 6.0-7.5, absorbing maximum at 590 nm. The molar absorptivity and the Sandell's sensitivity of the complex are 2.55 X10^4 L mol^{-1}cm^{-1} and 0.002 µg cm^{-2} respectively. Beer's law was followed up to 2.4 ppm with the optimum concentration range of 0.32- 2.0 ppm. The tolerance limits for interfering ions are discussed. All variable were studied in order to optimize the reaction conditions. The efficiency of the proposed method is shown by the successful determination of traces of vanadium in some synthetic mixture of minerals and alloys.

Keywords: 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene, Vanadium(V), micro-determination.

INTRODUCTION

Vanadium and its compounds used extensively in the steal and petrochemical industries. Vanadium species are most stable and toxic. Vanadium affects the numerous physiological processes and biochemical reactions. Vanadium remains a relatively unknown trace element as its uses are still being targeted in various clinical applications worldwide. Its content in food is directly dependent upon the concentrations present in the soil. Once consumed, vanadium is stored primarily in fatty tissues, with the remaining amounts stored in the kidney, liver, spleen or bone. However, vanadium deficiency is also known to consistently impair biological function. Vanadium is a trace element of highly critical role in biochemical processes and of significant importance in environmental, biological and industrial analysis due to its toxicity. Vanadium in trace amounts is an essential element for cell growth at µg l^{-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. The amount of vanadium in blood and urine depends upon intensity and duration of its exposure.

Scrutiny of literature reveals that several spectrophotometric methods have been reported for the determination of vanadium in environmental and biological samples. Recently, few authors introduced various reagents for spectrophotometric determination of vanadium in various samples[1-11]. Many reported reagents suffer from poor selectivity, interference of large number of metal ions require specific solvent for the extraction of colored species and few other require activators for catalytic photometric determination of vanadium. These deficiencies have encouraged the authors to develop novel reactions for facile, sensitive, accurate and reliable method for the determination of trace amounts of vanadium in environmental and biological samples. These types of reactions for the determination of vanadium(V) have not been reported yet.

This paper reports 1-(2-quinolylazo)-2, 4, 5-trihydroxybenzene as an analytical reagent for the micro-determination of vanadium(V) spectrophotometrically, whereas a limited number of heterocyclic azo dyes find their use for the determination of vanadium(V). Comparatively this reagent has been found a potential reagent for vanadium(V).

MATERIALS AND METHODS

2.1 Reagents and Chemicals

2.1.1 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene (QATB) Solution

QATB as synthesized as described by Singh and Poonam[12] was used as a 1 X 10^{-3} M solution prepared by dissolving 0.281 g in 1 L of pure ethanol. Solutions more than a week old were discarded.

2.1.2 Standard Vanadium(V) Solution

A stock solution of vanadium(V) was prepared by dissolving appropriate amounts of sodium vanadate (Anala R) in acidulated double distilled water. The solution was standardized gravimetrically as silver vanadate[13].

2.1.3 Sodium acetate solution

0.1 M sodium acetate solution was prepared and was used during the studies. Dilute solutions of sodium hydroxide and hydrochloric acid were used for pH adjustment during preliminary investigations.
All other reagents were of analytical grade and doubly distilled water was used throughout**.**

2.2 Determination of Vanadium(V)

To a suitable aliquot of sample containing 3.20-20.0 µg of vanadium(V), add 4 mL of $1X10^{-3}$ M QATB solution in ethanol followed by 1 mL of 0.1 M sodium acetate to maintain pH ~ 7.0 and make up the volume to 10 mL maintaining 50% (v/v) ethanol concentration. Measure the absorbance at 590 nm against a corresponding reagent blank prepared under identical conditions.

2.3 Apparatus

A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and Beckman pH meter was used for pH measurements.

RESULTS AND DISCUSSION

Ethanolic solution of QATB formed a dark brown color complex with vanadium(V) ions at neutral pH. The complex was soluble if ethanolic concentration was maintained above 40% (v/v). The absorption spectra of the V-QATB complex solution maintaining 50% ethanolic concentration recorded against corresponding reagent blank (QATB solution without metal ions) are shown in Fig. 1. The complex had constant and maximum absorbance in the pH range 6.0-7.5. For maintaining an appropriate pH of complex solution 1mL of 0.1 M sodium acetate was sufficient. It was observed that a minimum of two minutes time is needed for full color development. The complex was found to be stable for more than 24 hours. For attaining maximum sensitivity, at least 6-times molar excess of reagent was required and hence in subsequent studies, 10-times molar excess of reagent was used.

Under these optimum conditions, various Physico-chemical constants were established and are given in Table 1. A comparative study of the sensitivities of various spectrophotometric reagents known for vanadium is given in Table 2, shows that the present reagent has a good sensitivity for the micro determination of vanadium.

3.1 Effect of diverse ions

In the determination of vanadium(V) at 1.04 µg/mL level; fluoride, chloride, bromide, iodide, nitrate, nitrite, sulphate, sulphite, thiosulphate, alkaline earths, lanthanides, Al(III), In(III), Sb(III), Bi(III), Cr(III), platinum metals [except palladium(II)] and Th(IV) ions did not interfere at all. However, cyanide and zinc (II) interfered in the determination.

Under the appropriate conditions found for vanadium(V), ~40 molar excess of EDTA could be tolerated, which was used to mask most of the interfering cations. The method is quite simple. Furthermore, the importance of the method is that vanadium determination can be carried out even in the presence of large amounts of thorium, zirconium, tantalum and titanium which generally interfere in most of the methods reported.

Table 3 represents the tolerance limits in ppm of various ions in solution that caused a deviation smaller than ± 2% in absorbance for the determination of vanadium(V).

3.2 Applications for Determining vanadium(V) in synthetic mixtures of alloys and minerals:

Appropriate compositions of the minerals and alloys were prepared by mixing the metal salts in exact proportions (percentages given in table 4) and treated them as follows: 0.2 g of the mixture was treated with 10 mL of 6N sulphuric acid and heated gently with the addition of 5 mL concentrated HNO_3. Then 2 mL of 1:1 (v/v) H_2SO_4 was added and evaporated gently until the dense white fumes subsided to remove oxides of nitrogen. The residue was dissolved in doubly distilled water to 50 mL. Appropriate dilutions were made in subsequent studies and the samples were analyzed according to the recommended procedure. The results of the analysis obtained are given in Table 4.

Table 1: Physico-chemical characteristics of the vanadium(V)-QATB complex

Characteristics	Vanadium(V)-QATB complex
λ max.(nm)	590
pH range	6.0 - 7.5
Reagent required for full complexation (mol)	6
Beer's law range (ppm)	0.0 - 2.4
Optimum concentration range (ppm)	0.32 - 2.0
Sandell's sensitivity (µg cm^{-2})	0.002
Molar absorptivity (Є) (l. mol^{-1}.cm^{-1})	2.55 X 10^4
Composition (M:L) by Job's method	1:2

Table 2: Comparison of sensitivities of various spectrophotometric reagents for vanadium(V)

Reagent	λ_{max} (nm)	Molar absorptivity (L mol^{-1} cm^{-1})	References
Variamine blue	570	1.65 X 10^4	2
Pyrogallol	580	7.75 X 10^3	5
N-(1-Naphthalene-1-yl)ethane-1,2-diaminedihydrochloride	525	1.93 X 10^4	14
2,4 – Dinitrophenyl hydrazine	495	2.22 X 10^4	14
2, 2'-Iminodibenzoic acid	610	1.2 X 10^4	15
5,7-Dibromo-8- hydroxyquinoline	400	6.1 X 10^3	16
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	596	8.45 X 10^4	17
4-(2-pyridylazo)-resorcinol/tetrazolium violet	550	3.05 X 10^4	18
Acetoacetanilide salicyloylhydrazone	405	1.20 X 10^4	19
3,3', 5,5'-Tetramethylbenzidine-N-propanesulfonic acid	450	2.74 X 10^4	20
4-Nitrocatechol/thiazolyl blue tetrazolium	400	3.13 X 10^4	21
1-(2- Quinolylazo)-2,4,5-trihydroxybenzene	590	2.55 X 10^4	This work

Table 3: Tolerance limits of diverse ions on the determination of 1.04 µg mL^{-1} of vanadium(V)

Foreign ions	Tolerance limits (ppm)	Masking agents
CNS^-	50	------
S^{2-}	40	------
$S_2O_3^{2-}$	500	------
Oxalate	40	------
Citrate	50	------
Tartrate	50	------
EDTA	40	------
BO_3^{3-}	40	------
PO_4^{3-}	200	------
Mo(VI)	40	------
W(VI)	40	------
UO_2(II)	5	Masked by EDTA
Cd(II)	5	------
Hg(II)	5	------
Pb(II)	5	------
Mn(II)	3	-----
Fe(II)	10	Masked by EDTA
Pd(II)	10	Masked by Iodide
Ag(I)	10	” ” ” ” ”

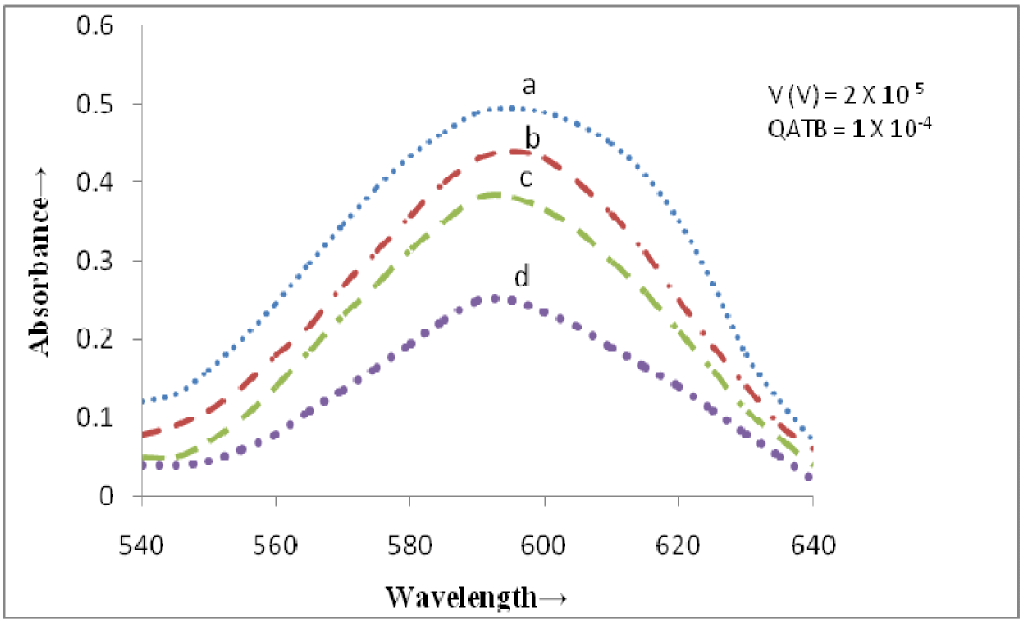

Fig. 1: Absorption Spectra of Vanadium (V) – QATB complex at various pH.
(pH values for series : a= 6.0-7.5, b=5.0, c=8.5, d=4.5)

Table 4: Estimation of vanadium (V) in synthetic mixture of minerals and alloys

Sample	Chemical composition (%) /formula	Chemical composition taken (ppm)	V(V) present (ppm)	V(V) found (ppm)	Mean value	% recovery	Standard deviation (σ)
Alloys							
VAlFe	V 69, Al 19, Fe 12	V 6.9, Al 1.9, Fe 1.2	6.9	6.8, 7.0, 6.8, 6.9, 7.1, 7.0	6.93	100.48	0.1212
VAlSn	V 43, Al 43, Sn 14	V 4.3, Al 4.3, Sn 1.4	4.3	4.1, 4.4, 4.3, 4.2, 4.1, 4.2	4.22	98.05	0.1169
VNi	V 65, Ni 35	V 6.5, Ni 3.5	6.5	6.6, 6.4, 6.3, 6.7, 6.3, 6.4	6.45	99.23	0.15
VMoAl	V 52, Mo, 26, Al 22	V 5.2, Mo 2.6, Al 2.2	5.2	5.1, 5.0, 5.3, 5.4, 5.0, 5.1	5.183	99.7	0.14697
FeV40	V 40, C 0.5, Si 20, Al 0.5	V 4.0, Fe 5.7	4.0	3.98, 3.99, 4.2, 4.1, 4.2, 3.9	4.075	101.875	0.00 0.1988
FeV50	V 50, C 0.5, Si 2, Al 0.3	V 5.0, Fe 4.7	5.0	5.2, 5.3, 5.1, 4.98, 4.99, 5.1	5.11	102.2	0.1230
FeV60	V 60, C<0.15, Si 1.5, Al 2	V 6.0, Fe 3.7	6.0	5.99, 5.98, 6.2, 5.99, 6.1, 6.2	6.077	101.28	0.1052
FeV80	V 80, C 0.15, Si 1.5, Al 1.5	V 8.0, Fe 1.7	8.0	8.2, 8.1, 8.2, 7.8, 7.9, 8.1	8.05	100.625	0.1643
Minerals							
Vanadinite	$Pb_5(VO_4)_3Cl$	Pb^{2+} 103.5, V^{5+} 15.3	15.3	15.5, 15.4, 15.2, 15.1, 15.2, 15.1	15.25	99.673	0.1643
Carnotite	$K_2O.2U_2O_3.V_2O_5.3H_2O$	K^+ 7.8, U^{6+} 95.2, V^{5+} 10.2	10.2	10.0, 10.3, 10.1, 10.4, 10.1, 10.0	10.15	99.51	0.1643
Roscoelite	$2K_2O.2Al_2O_3(Mg,Fe)O\text{-}3V_2O_5.10SiO_2.4H_2O$	K^+ 7.8 Al^{3+} 5.4, Mg^{2+} 1.2, Fe^{2+} 2.8, V^{5+} 15.3	15.3	15.4, 15.1, 15.5, 15.2, 15.4, 15.2	15.3	100	0.1549
Sulvanite	$3Cu_2S.V_2S_6$	Cu^{2+} 38.1, V^{5+} 10.2, S^{2-} 28.8	10.2	10.1, 10.4, 10.3, 10.4, 10.1, 10.0	10.216	100.156	0.1722

REFERENCES

[1] Hu. Qiufen, G. Yang and J. Yin, *Bull. Korean Chem. Soc.*, **2004**, 25, 263.
[2] T. N. Kiran Kumar and H.D. Revanasiddappa, *J. Iran. Chem. Soc.*, **2005**, 2(2), 161.
[3] J. M. Bosque-Sendra, L.C. Valencia and S. Boudra, *Fresenius' J. Anal. Chem.*, **1998**, 360, 31.
[4] R. S. Chauhan and L. R. Kakkar, *Bull. Chem. Soc. Japan*, **1992**, 65, 1033.
[5] N. Iranpoor, N. Maleki, S. Razi and A. Safavi, *Talanta*, **1992**, 39(3), 281.

[6] J. H. Miura, *Anal. Chim.*, **1990**, 62, 1424.
[7] G. V. R. Murthy, T. S. Reddy and S. B. Rao, *Analyst*, **1989**, 114, 493.
[8] M. J. C. Taylor, G. D. Marshall, S. J. S. Williams, J. F. Vanstaden and C. Sailing, *Anal. Chim. Acta*, **1996**, 329, 275.
[9] F.B. Serrat and G.B. Morell, *Fresenius' J. Anal. Chem.*, **1994**, 349, 717.
[10] C. Zucchi, M. Forneris, L. Martizez, R. Oisina and E. Marchevsky, *Fresenius' J. Anal. Chem.*, **1998**, 360, 128.
[11] N. Shigenori, E. Tanaka and Y. Mizutani , *Talanta*, **2003**, 61, 203.
[12] I. Singh and Poonam, *Talanta*, **1984**, 31, 109.
[13] A.I. Vogel, "A Text Book of Quantitative Inorganic analysis" 3rd ed., **1975**, Longman, London.
[14] P. B. Krishna, P. Subrahmanyam, J.D. Kumar and P. Chiranjeevi, *E- Journal of Chemistry*, **2006**, 3(13), 286.
[15] N. Zhou, C.X. He, N.L. Gu and P.G. Chen, *Analyst*, **1994**, 119, 2105.
[16] M.J. Ahmed and A.K. Banerjee, *Analyst*, **1995**, 120, 2019.
[17] C. Xianzhong and K. Yun, *Geostandars and Geoanalytical Research*, **2007**, 31(4), 353.
[18] K. Gavazov, V. Lekova, G. Patronov and M. Turkyilmaz, *Chem. Anal. (Warsaw)*, **2006**, 51, 221.
[19] A. Varghese and A.M.A. Khadar, Mapana J. Sci. , **2008**, 7(1), 13.
[20] D. Jw, T. YF, F. Wu and L. DQ, *Pu xue Guang Yu Guang Pu Fenxi*, **2002**, 22 (5), 800.
[21] P.V. Rcheva, K.B. Gavazov, V.D. Lekova and A.N. Dimitrov, *J. Anal. Chem.*, **2010**, 65(1), 21.