IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 4 Ver. I. (Apr. 2015), PP 60-64
www.iosrjournals.org

Direct Spectrophotometric determination of Vanadiu (V) using 5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl] methyl] sulfinyl]-1H-Benzimidazole [ESMPZL]

B. Ranganath, L.K. Ravindranath and P. Venkataramana.
Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003 (A.P), India

Abstract: *Highly sensitive and selective direct spectrophotometric method is proposed for the determination of aluminium in various real samples. 5- methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl] methyl] sulfinyl]-1H-Benzimidazole reacts with V(V) forming greenish yellow coloured soluble complex in aqueous dimethyl formamide which has a λmax at 410 nm in the pH range 4.0-7.0. The system obeyed Beer's law in the range 0.508 – 0.854 μg mL-1 of V (V). The molar absorptivity is 2.65 x 10^4 L mol^{-1} cm^{-1} and The Sandell's sensitivity is 0.0825 μg/cm2. The standard deviation of the method for ten determinations of 0.579 μg/ml of V (V) is 0.0086. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9897.Studies on effect of diverse ions showed almost all the anions a majority of the cations do not interfere in more than 30 fold excess. The direct method was applied for the determination of vanadium biological samples like cabbage leaves and Goat leaves, blood and urine samples Tap water and plant materials.*

Key words: *V (V), Direct spectrophotometric determination, ESMPZL.*

I. Introduction

Vanadium is very widely distributed in nature. It occurs in nature as a stable element at ordinary temperature. Vanadium is an important constituent of many industrially important alloys. It is widely distributed in various minerals and is a common constituent of coals, asphalts, bitumen's and oil. Vanadium occurs in +2, +3, +4 and +5 oxidation states in its compounds, vanadium (V) compounds being the most stable.

Vanadium is essential for the growth of certain bacteria and algae. It is essential to ascidians (Sea squirts). Vanadium has long been recognized as an essential element in biological systems. It is apparently essential for chlorophyll and porphyrin biosynthesis in some higher plants. The presence of 30 to 40% vanadium in ferrovanadium steels imparts tensile strength, elasticity and toughness. Vanadium is an important component of ferrous alloys used in jet-aircraft engines and in turbine blades where high temperature creep resistance is a basic requirement. Vanadium compounds are used as catalysts in colouring glass and ceramics and as driers in paints and inks.

Vanadium compounds are toxic to human beings and animals. They inhibit biosynthesis of cholesterol in mammals. It is found to be present in many tissues and the concentrations in human blood and plasma are reported[1] to be in the range 0.005-8.4 μm. Vanadium poisoning is an industrial hazard.[2] Vanadium has also been reported as the index element in urban environmental pollution, especially air pollution.[3] Fossil fuels such as crude petroleum, fuels, oils, some coals and lignite contain high amounts of vanadium. Burning of these fuels releases vanadium into the air which then settles on the soil. There are cases of vanadium poisoning, the symptoms of which are nervous depression, vomiting, coughing, anemia, diarrhea and increased risk of lung cancer, that are sometimes fatal.[4]

Though several organic reagents are used for the determination of trace amounts of vanadium, only a few of these reagents are useful for the spectrophotometric determination of the metal ion in aqueous medium. Most of the reagents, however, are utilized for the extraction spectrophotometric determination of vanadium using non-polar solvents. Kinetic spectrophotometric methods based on the catalytic action of vanadium (V) on the oxidation of organic compounds with inorganic reactant (eg. Bromate or periodate) are highly sensitive but are generally lacking simplicity or a long time is necessary to complete the reaction.[5-7] The most widely used reagent for vanadium (V) determination is pyridyl resorcinol (PAR). Most of the reported methods suffer from limitations such as serious interference from U (VI), Ti (IV), Zr (IV) and Nb (V) ions, the delay in colour development and also significant absorbance for the reagent blank solution[8-10]. The analytical results obtained in some of the reported spectrophotometric methods for vanadium are reviewed and presented in table 4.6.0. Some of them are less sensitive and some are less selective. Majority of the reported methods are extraction methods using harmful organic solvents.

Spectrophotometric determination of vanadium using salicyladehyde Acetic acid hydrazone [11]. Spectrophotometric determination of vanadium using 4-(2-pyridylazo)-resorcinol and tetrazolium [12]. Simple and sensitive determination of vanadium using biological and environmental studies [13]. The first two methods are

disadvantageous in terms of cost and instruments. AAS is often lacking in sensitivity and affected by matrix conditions of samples such as salinity. Catalytic solvent extractive methods are highly sensitive but are generally lacking simplicity. Hence its accurate determination at trace levels using simple and rapid methods is of paramount importance. The aim of this study is to develop a simple direct spectrophotometric method for the trace determination of vanadium. Pyridine and chloroform have been used as solvents for the extraction of V (V) which can be classified as toxic and as environmental pollutants and have been listed as carcinogens by the Environmental Protection Agency (EPA). Theodosioss and I.Karaganns et al [14] developed a spectrophtomertic determination Vanadium based on its catalytic effect on the reaction of Diphenyl amine and hydrogen peroxide. A. Abbaspour and S.M.M. Mosavi et al [15] developed a spectrophotmetric determination of vanadium based on the oxidation of alkali blue. Pratap Singh Kadyn and Sonia verma et al [16] developed a spectrophotometric determination of vanadium using 3-(2-Quinonylazo)-2, 4, 5-trihydroxy benzene as an analytical agent.

II. Experimental

Reagent:

ESOMEPRAZOLE SOLUTION:

Esomeprazole is 5-methoxy-2-[[(4-methoxy-3,5-dimethyl-2-pyridinyl]methyl]sulfinyl]-1H-benzimidazole. It is white crystalline powder freely soluble in water and its molecular formula is $C_{17}H_{19}N_3O_3S$. (M.Wt:345.11). The structure of esomeprazole is given in Fig. 1.

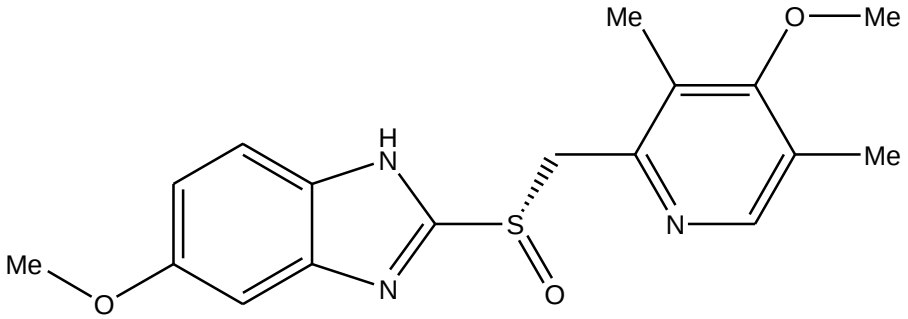

Fig. 1 (S)-5-methoxy-2-[[(4-methoxy-3, 5-dimethyl-2-pyridinyl)-methyl]sulfinyl]-1H benzimidazole (ESOMEPRAZOLE)

Esomeprazole was characterized by IR, ^{1}H-NMR and Mass spectral data.
IR (KBr) ν_{max}: 3346, 3168, 2961, 2928, 2683, 1657, 1597, 1449, 1255, 1218,1092, 876, 710 cm^{-1}
^{1}H NMR (DMSO-d_6, 500 MHz) :δ 2.20 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.60 (d, 1H), 4.77(d, 1H), 6.97, 6.99 (m, 2H, Ar-H), 7.65 (m, 1H, Ar-H), 8.25 (s, 1H, Pyridine ring), 9.57 (s, 1H, NH) ppm.
MS m/z: found 345.11 [M^+]; calcd. 345. Anal $C_{17}H_{19}N_3O_3S$.

Stock Solution:

0.01M stock solution of V(V) was prepared by dissolving requisite amount of nickel ammonium sulphate in distilled water and standardized gravimetrically [17]. The working solutions were prepared by diluting the stock solutions with distilled water.

Buffer solution of pH 7.5 was prepared by mixing 0.2M sodium acetate and 0.2M acetic acid in suitable proportion and the pH was adjusted by a pH meter.

Instrument:

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 pH meter of (Model LI 613) respectively.

III. Procedure:

To 5 ml of buffer solution (pH 7.5), 0.5 ml of ESMPZL (1 x 10^{-2}M) in DMF,1.5 ml of DMF taken in each of a set of 10 ml volumetric flasks, varying amounts of V(V) were added and diluted to 10 ml in a volumetric flask with distilled water. The absorbance of these solutions was measured at 410 nm against reagent blank and plotted against the mount of vanadium. A straight line is obtained which corresponded to the equation A410= 0.1704 C – 0.00704. (C is the amount of vanadium in µg/ml).

IV. Results and Discussion

The absorption spectrum [V(V) –ESMPZL] complex showed maximum absorbance at 410 nm where the reagent showed negligible absorbance. The absorbance was found to be maximum and constant in the pH range 3.0-7.0. Therefore, the analytical studies were carried out at pH 7.5. A 5 fold molar excess of the reagent is sufficient to obtain maximum colour intensity for a given amount of metal ion.

Analytical characteristics of [V (V) –ESMPZL]

The molar absorptivity Beer's law ranges, detection limit, determination limit shown in the Table.2 indicate the high sensitivity of the method. The effect of diverse ions on the absorbance of the experimental solution showed that all do not interfere in more than 30 fold excesses. All the ions do not interfere Al(III), Pb(II), W(VI), Co(II), Se(IV), Mn(II), Cd(II), Zn(II), Ru(III), Ni(II), Th(IV), Cr(VI), U(VI), Ti(IV), Zr(IV), In(III), Sn(II), Sr(II), Ir(III) and Fe(II). The results are presented in Table 1.

Applications:

Preparation of biological samples

Determination of vanadium in Cabbage leaves and Goat liver

The cabbage leaves and goat liver were washed with distilled water thoroughly to remove the adhered impurities. They were dried with filter paper and suitable amount of the sample was weighed. Known amounts of vanadium were added as the real samples do not contain any measurable amounts of vanadium. The samples were dried, ashed and brought into solution by acid treatment as per the recommended procedures [18, 19]. The contents were neutralized with dilute NH_4OH solution and diluted to known volume with distilled water. The amounts of vanadium present in biological samples were determined by the proposed method and the results obtained are presented in the Table 3.

Determination of vanadium in Human blood, urine 40

Human blood or urine (50 ml) samples were taken into 100 ml micro Kjeldhal flask. 5 ml concentrated HNO_3 were added and gently heated. When the initial brief reaction was over, the solution was removed and cooled. 1 ml of concentrated H_2SO_4 was added followed by 1 ml of 70% $HClO_4$. The solution was again heated to dense white fumes, repeating HNO_3 addition. The heating was continued for 30 minutes and then cooled. The contents were filtered and neutralized with dilute NH_4OH in the presence of 1-2 ml of 0.01% sodium tartrate solution. The solution was transferred into 10 ml volumetric flask and diluted to the volume with distilled water. Suitable aliquots were taken and analyzed for vanadium and the results are presented in Table.4

Analytical Applications

Determination of vanadium in tap water, plant tissues and alloys

The proposed method under the already established optimum conditions was applied for the determination of (V) in tap water, plant tissues and alloys. The results presented in Table.5 indicate the successful applicability of the proposed method to real sample analysis.

V. Conclusions:

The present method is a new, simple, sensitive, selective and less expensive method with V(V) –ESMPZL complex was developed for the determination of avanadium in some Cabbage leaves, Goat leaves, Blood and Urine samples, tap water and plant materials. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, ICP-MS, etc. are available for the determination of vanadium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories of developing countries with limited budget. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for the determination of vanadium in real samples.

Acknowledgements

The authors thank the department of Chemistry of S.K.University Anantapur,for providing the necessary facilities. One of authors (B.Ranganath) thanks for my research supervisor.

Table 1
Tolerance limit of foreign ions
Tolerance limit of foreign ions in the determination of 2.486 µg/ml of V (V)
pH = 7.0; λ_{max} = 410 nm

Foreign ion	Tolerance limit (µg/ml)	Foreign ion	Tolerance limit (µg/ml)
Fluoride	35.35	Al (III)	12.01
Chloride	35.00	Pb (II)	19.27
Iodide	203.05	W (VI)	21.63
Nitrate	32.42	Co (II)	3.93
Acetate	248.42	Se (IV)	10.19
Oxalate	42.50	Mn (II)	8.89
EDTA	78.0	Cd (II)	8.56
Thiosulphate	36.13	Zn (II)	10.23
		Ru (III)	26.85
		Ni (II)	10.57
		Th (IV)	16.57
		Cr (VI)	0.315
		U (VI)	15.48
		Ti (IV)	6.08
		Zr (IV)	9.73
		In (III)	2.69
		Sn (II)	4.87
		Sr (II)	17.1
		Ir (III)	32.04
		Fe (II)	8.87

Table 2
Statistical analysis of the data

[V (V)] = 4×10^{5}M
[ESMPZL] = 2.873×10^{-4}M
λ_{max} = 410nm
pH = 7.0

S.No.	Volume of metal ion (1ml)	Volume of reagent (1 ml)	Absorbance (x)	d (X – M)	d^2 $(X - M)^2$
1	1	1	0.452	-0.0037	0.00001369
2	1	1	0.453	-0.0027	0.00000729
3	1	1	0.453	-0.0027	0.00000729
4	1	1	0.456	+0.0003	0.00000009
5	1	1	0.456	+0.0003	0.00000009
6	1	1	0.455	-0.0007	0.00000049
7	1	1	0.457	+0.0013	0.00000169
8	1	1	0.455	-0.0007	0.00000049
9	1	1	0.459	+0.0033	0.00001089
10	1	1	0.461	+0.0053	0.00002809

Standard Deviation (S.D.) = 0.002649 for ten determinations
R.S.D. = 0.579 %

Table 3
Determination of vanadium in cabbage and goat liver

Sample	V(V) added (µg mL-1)	Amount of vanadium found(µg mL-1)					
		Proposed method*	RSD (%)	Recovery (%)	Reference Method*75	RSD (%)	Recovery (%)
Cabbage (5g)	6.0	6.03 ± 0.04	1.02	100.5	5.98 ± 0.02	0.46	99.6
	12.0	11.54 ± 0.08	1.15	96.2	12.2 ± 0.04	0.66	101.6
Goat liver	4.0	3.98 ± 0.03	0.90	99.5	4.02 ± 0.02	0.46	100.5
	7.0	7.42 ± 0.06	1.18	106.07	7.12 ± 0.02	0.69	101.7

*Average of five determinations ± SD

Table 4
Determination of vanadium in blood and urine

Sample	Vanadium(µg.ml-1) *		Sample source
	Present method	Reference method75	
Blood Urine	10.5 ± 0.9 2.8 ± 0.5	12.0 ± 1.4 2.5 ± 0.6	Normal adult(male)
Blood Urine	428 ± 1.8 120 ± 1.2	421 ± 2.1 125 ± 1.5	Lung cancer patient(male)

*Average of five determinations ± SD
a= samples collected from Anantapuramu Medical College (AMC), Anantapuramu, A.P., India.

Table 5
Determination of vanadium in various samples

Sample	Vanadium added	Vanadium found				
	(µg/ml)	Standard Method	Proposed Method	Recovery (%)	SD (%)	RSD (%)
a) Tap water	1.0 2.0	1.06 2.10	1.065±0.019 2.17±0.05	106.5 105.7	2.37 4.15	2.24 1.98
b) plant material	1.0 2.0	1.09 2.11	1.09±0.04 2.12±0.036	109 107	2.76 4.77	2.59 2.29

References

[1]. J.Versieck, and R.Cornelis, Anal. Chim. Acta**,** 1980, **116,** 217.
[2]. G.D. Clayton and F.E.Calyton, Patty's Industrial Hygiene and Toxicology, vol. 2A, 3rd Ed., Wiley New York, 1981, P. 2013.
[3]. S.Langard, T. Norseth, L. Friberg, G.R.Nerberg, and V.B. Vouk, (Eds.), Hand Book on toxicology of metals**,** Elsevier, Amserdam, 1986.
[4]. B.Venugopal and T.D Luckey, Metal Toxicity in Mammals 2**,** plenum press, New York, 1979, P. 220.
[5]. A.Safavi, M.R. Hormozi Nezhad, and E.Shams, Anal Chim. Acta**,** 2000, **409**, 283.
[6]. A.Ali Ensafi, M.K. Amini, and M. Mazloum, Anal. Lett**,** 1999, **32,** 1927.
[7]. H.Wang and A.Zhang, Microchem. J**,** 1997, **57,** 218.
[8]. K.Gavazov and A.Alexandrov, Talanta**,** 2000, **52,** 539.
[9]. M.N.Abbas, A.M. Homoda and C.A. E.Mostafa, Anal. Chim. Acta**,** 2001, **436,** 223.
[10]. G.Chakrapani, D.S.R.Murthy, B.K. Balaji and R. Rangaswamy, Talanta**,** 1993, **40,** 541.
[11]. Shirani Bidabadi, M.; Dadfarnia, S.; Haji Shabani, A. M. J. Hazard. Mater. 2009, 166, 291.B.Cherian, Tom, Narayana, ulletin of the Chem. Soc. of Ethiopia, 2005, **19(7),** 155 -161.
[12]. S.A.Abbasi, Anal.lett, 1987, **20**, 1347.
[13]. D.Glick(Ed), Methods of biochemical analysis, Johnwiley, 1973,**21**, 39.
[14]. Theodosiosss , I.Karayann's Micro clinic Act 135,197-201, **2000**.
[15]. A.Abbas Pour, S.M.M.Mosavi, Iranic Journal of Science and Technology Vol.31. No. A3, **2007**.
[16]. Pratap Singh Kadyn, Sonia Verma, Scholars Research Library, ISSN, 975-413, **2012**.
[17]. Vogel, A.I. A Text book of Quantitative Chemical Analysis, Longman, group pub. London, U.K, **1989.**
[18]. S.A.Abbasi, Anal.lett, **1987**, 20, 1347.
[19]. D.Glick(Ed), Methods of biochemical analysis, Johnwiley, **1973**, 21, 39.