

Spectrophotometric Determination of Vanadium(V) Using Metanil Yellow Dye as an Analytical Reagent†

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A simple, rapid, selective and sensitive method for the spectrophotometric determination of microgram amount of Vanadium(V) utilizing the reaction between metanil yellow dye in 40 % ethyl alcohol medium. Metanil yellow reacts with vanadium (V) instantaneously at room temperature in slightly acidic medium. The complex exhibits an absorption maximum at 512 nm with a molar absorptivity $2.21 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The sensitivity is 4.52 ng of vanadium mL^{-1} and the optimum range for the effective spectrophotometric determination is 0.05-0.41 $\mu\text{g mL}^{-1}$. A five fold molar excess of the dye is necessary for the full development of the colour intensity. The influence of some common ions is reported.

Key Words: Vanadium, Metanil yellow, Spectrophotometry.

INTRODUCTION

Vanadium has abundance in the earth's crust of about 0.02 %. Vanadium is found in about 65 different minerals among which carnotite, roscoelite, vanadinite and patronite are the important sources of the metal¹. Vanadium is also found in phosphate rock and certain iron ores and is present in some crude oils in the form of organic complexes.

Major sources for the emission of vanadium in the environment include combustion of fuel oils, dyeing, ceramics, ink, catalyst and steel manufacturing. Vanadium in trace amounts represents an essential element for normal cell growth, but it can be toxic when present in higher concentrations. It plays an important role in physiological systems including normalization of sugar levels and participation in various enzyme systems as an inhibitor and cofactor of the oxidation of amines². In spite of being a nutritional element, vanadium is not accumulated by the biota; the only organisms known to bio-accumulate it to any significant degree are some mushrooms, tunicates and sea squirts.

Vanadium poisoning is an industrial hazard³. Environmental scientists have declared vanadium as a potentially dangerous chemical pollutant that can play havoc with the productivity of plants, crops and the entire agricultural system.

Thus, highly and selective methods are still required for trace vanadium determination in different kinds of samples.

EXPERIMENTAL

An UV-visible spectrophotometer (ELICO, Model SL-159) with quartz cells of 1 cm path length was used for absorbance measurement. An ELICO digital pH (Model LI-120) with combined glass calomel electrode was used for pH measurements. All chemicals used were of AR grade (Merck). A $1.0 \times 10^{-2} \text{ M}$ solution was prepared by dissolving requisite amount of NH_4VO_3 in double distilled water and then diluting to 1000 mL with distilled water and the solution was standardized by known methods reported in the literature⁴. The standard stock solution of metanil yellow of $1.0 \times 10^{-2} \text{ M}$ concentration was prepared in aqueous alcohol (40 % v/v). The standard stock solutions of various salts (as the source of diverse ions) each of $1.0 \times 10^{-2} \text{ M}$, were prepared in doubly distilled water.

An aliquot of solution containing $0.5094 \mu\text{g/mL}^{-1}$ vanadium(V) was taken in a 10 mL measuring flask and 5 mL of $1.0 \times 10^{-5} \text{ M}$ of the reagent was added to it. The contents were diluted to the mark with aqueous alcohol (40 % v/v), keeping the pH constant, the absorption spectrum of the resultant orange red coloured vanadium(V)-metanil yellow complex was recorded against blank from which the value of λ_{max} was obtained.

The optimum experimental conditions in regard to (1); the concentration of the reagent (Metanil Yellow); (2) the

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concentration of the vanadium(V); (3) the pH of the medium; and (4) ascertaining the λ_{\max} of the vanadium(V)-metanil yellow complex were established.

RESULTS AND DISCUSSION

The absorption spectrum of the vanadium(V)-metanil yellow complex in aqueous alcohol was studied over the wavelength range 420-620 nm. Orange red coloured complex exhibited absorption maximum at 512 nm, where reagents shows negligible absorption at this wavelength. The effect of the quantity of the reagent on the intensity of colour was also studied. It was found that minimum 5- fold excess of the reagent was required for full colour development. The colour develops instantaneously on mixing the two solutions and remains stable for 24 h. The optimum pH for the formation of this complex is 4.5.

The system adheres to Beer's law in the range 0.05094-0.4075 $\mu\text{g mL}^{-1}$ of the vanadium(V) (Fig. 1). The molar absorptivity calculated over the range studied was $2.21 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$, while sensitivity was 4.52 ng mL^{-1} . The standard deviation and coefficient of variance as determined of a series of measurements made according to the optimum conditions were 0.0007 and 0.32 respectively. This speaks the volume for the precision for the present spectrophotometric method for the determination of vanadium(V) using metanil yellow as the analytical reagents as compare to some other recent spectrophotometric method (Table-2).

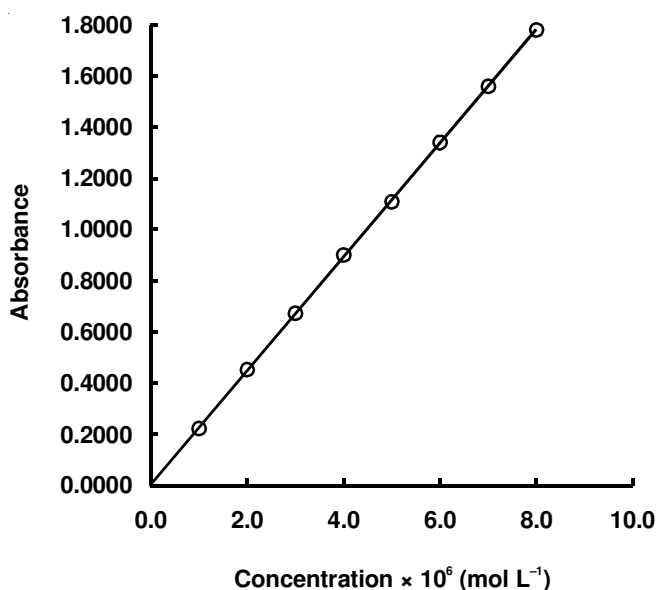


Fig. 1. Plot of absorbance vs. concentration of vanadium(V) in vanadium(V)-metanil yellow complex system at $\lambda_{\max} = 512 \text{ nm}$

The composition of vanadium(V)-metanil yellow complex has been ascertained as 1:5 by mole ratio method.

The effect of diverse ions on the spectrophotometric determination of vanadium(V), using metanil yellow as the reagent has been studied in the terms of tolerance limit which was set as the amount ($\mu\text{g mL}^{-1}$) of the diverse ions causing an error of $\pm 1 \%$ (refer to Table-1). It has been concluded that the following cations and anions do not interfere in the spectrophotometric determination of the vanadium(V).

TABLE-1
EFFECT OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (V) USING METANIL YELLOW AS THE REAGENT VANADIUM (V) = 0.255 $\mu\text{g mL}^{-1}$

S. No.	Diverse ions	Added as	Amount of adverse ion added ($\mu\text{g mL}^{-1}$)	V (V) found ($\mu\text{g mL}^{-1}$)	Relative error (%)
1	NO_2^-	NaNO_2	115.70	0.2489	0.25
2	NO_3^-	NaNO_3	155.05	0.2535	0.45
3	CH_3COO^-	CH_3COONa	590.40	0.2559	-0.46
4	Cl^-	KCl	17.81	0.2570	-0.90
5	Br^-	KBr	409.35	0.2582	-1.35
6	I^-	KI	15.86	0.2489	0.25
7	CO_3^{2-}	CaCO_3	150.49	0.2559	-0.46
8	SO_4^{2-}	K_2SO_4	239.69	0.2489	0.25
9	PO_4^{3-}	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	11.89	0.2512	1.36
10	NH_4^+	NH_4NO_3	449.20	0.2559	-0.46
11	Na^+	NaNO_3	573.48	0.2535	0.45
12	Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	25.90	0.2524	0.90
13	Hg^{2+}	HgCl_2	200.89	0.2512	1.36
14	Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	158.55	0.2570	-0.90
15	Cd^{2+}	$\text{Cd}(\text{NO}_3)_2$	563.00	0.2559	-0.46
16	Al^{3+}	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	135.53	0.2582	-1.35
17	Fe^{3+}	FeCl_3	783.05	0.2489	-0.25
18	Cr^{3+}	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	104.00	0.2558	-0.43
19	Zn^{2+}	$\text{Zn}(\text{NO}_3)_2$	980.40	0.2581	-1.33
20	Mn^{2+}	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	275.00	0.2489	0.25
21	Ni^{2+}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	147.00	0.2570	-0.90
22	Co^{2+}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	736.22	0.2559	-0.46
23	Ba^{2+}	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	343.00	0.2535	0.45
24	Sr^{2+}	$\text{Sr}(\text{NO}_3)_2$	440.83	0.2489	0.25
25	Ca^{2+}	$\text{Ca}(\text{NO}_3)_2$	999.00	0.2524	0.90
26	Mg^{2+}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	180.00	0.2559	-0.46
27	K^+	KCl	498.24	0.2570	-0.90

Conclusion

The proposed method for the determination of vanadium(V) offers advantage of simplicity rapidity, sensitivity and reasonable selectivity over the other methods. The developed colour is stable for 24 h. The major advantage of the proposed method is that the maximum colour intensity is obtained instantaneously at room temperature without the need for heating and also a high tolerance limit for the interfering ions in vanadium(V) determination. Because no extraction step is required, the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed method does not involve any stringent reaction conditions and can be favourably compared with other methods. The sensitivity in terms of the molar absorptivity and precision in terms of the standard deviation of the present method are very reliable for the determination of vanadium(V).

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TABLE-2
COMPARISON OF THE PRESENT METHOD WITH SOME RECENT SPECTROPHOTOMETRIC
METHODS FOR THE DETERMINATION OF VANADIUM(V)

Reagent	Sensitivity ($\mu\text{g mL}^{-1}$)	Linear range ($\mu\text{g mL}^{-1}$)	Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	Ref. no.
<i>N</i> -Hydroxy- <i>N</i> - <i>p</i> -tolyl- <i>N'</i> -(4-chloro-2-methyl phenyl) benzamididine hydrochloride and azide and thiocyanate	0.0152 $\mu\text{g cm}^2$	0.8-7.8 (Thiocyanate) 1.0-9.0 (Azide)	6000	5
Phenothiazine	1.7 ng/cm^2	0.1-8	3.056×10^4	6
<i>N</i> -Hydroxy- <i>N</i> - <i>p</i> -tolyl- <i>N'</i> -(2-methyl) phenyl- <i>p</i> -Toluamididine hydrochloride	-	-	6900	7
8-Hydroxyquinoline and naphthalene	0.0074 $\mu\text{g cm}^2$	3.5-8.9 $\mu\text{g}/10 \text{ mL}$	1.7×10^4	8
Desferrioxamine B	0.016 $\mu\text{g cm}^2$	0.5-50.0	3.15×10^3	9
<i>N</i> - <i>p</i> -Aminophenyl-2-thenylacrylo-hydroxamic acid, 3-(<i>O</i> -carboxyphenyl)-1-phenyltriazine- <i>N</i> -oxide	-	0.2-1.5	9.1×10^3	10
<i>N</i> -Hydroxy- <i>N,N'</i> -diarylbenzamididine and <i>p</i> -Hydroxybenzaldehyde	-	0.8-6.4	7900	11
<i>O</i> -Dianisidine	0.00156 $\mu\text{g cm}^2$	0.05-2	3.01×10^3	12
<i>N</i> - <i>p</i> -Octyloxybenzoyl- <i>N</i> -phenylhydroxyl amine	-	0.2-15	6.1×10^3	13
Benzoyl acetone and dithionite	-	0.2-15	5.73×10^3	14
2-Hydroxyacetophenone oxime	-	1-10	3.6×10^3	15
Thenoyltrifluoroacetone	0.006 $\mu\text{g cm}^2$	0-10	-	16
5,7-Dibromo-8- hydroxyquinoline	-	0.1-20	6.1×10^3	17
Cinnamohydroxamic acid	-	0.2-15	6.0×10^3	18
<i>N</i> -Phenylbenzo- hydroxamic acid	0.1	0.0-8	4400	19
2-(Salicyladene)-Pyridine and Polurethane foam	0.040 $\mu\text{g cm}^2$	1-20	1.09×10^4	20
2'-Hydroxyaceto-phenone benzoylhydrazone	0.0057 μgcm^2	0.0-3.5	8.93×10^3	21
2'-Hydroxyaceto-phenone benzoylhydrazone	0.0049 $\mu\text{g cm}^2$	0.0-1.5	1.05×10^4	22
4-(2-Pyridylazo)-resorcinol	-	0.0-3.0	1.85×10^4	23
4-(2-Pyridylazo)-resorcinol and tetra butylammonium perchlorate	-	5-350 ng mL^{-1}	1.3×10^5	24
Natural Red with K bromate	0.007 ng mL^{-1}	0.0-0.60 ng mL^{-1}	-	25
Metanil Yellow	4.52 ng mL^{-1}	0.0-0.40	2.21×10^5	Present method

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