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Synthesis and use of 3-hydroxy-2-[1'-phenyl-3'-(p-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPB): A novel analytical reagent for trace determination of vanadium (V) in various samples

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ABSTRACT

Vanadium (V) in trace amounts forms an intense green 1:3 (M:L) complex with 3-hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPB) in acetic acid medium (0.2 mol L^{-1}) which is extractable into toluene and is stable for more than 10 h. Beer's law is obeyed in the vanadium concentration range of 0-1.2 μg mL^{-1}. Molar absorptivity, detection limit and Sandell's sensitivity when applying spectrophotometric determination at the wavelength of 415 nm, are 2.496×10^{4} L mol^{-1} cm^{-1}, 7.628×10^{-5} g mL^{-1} and 0.0020 μg V^{V} cm^{-2}, respectively. The correlation coefficient being r = 0.9967. Ascorbic acid, oxalate and hydrogen peroxide interfere in the determination. The method handles has been satisfactorily applied to the analysis of vanadium in various synthetic, technical and natural samples, including reverberatory flue dust and high speed steel with super rapid extra 500.

KEYWORDS

Vanadium;
Pyrazolylchromones;
Spectrophotometric;
Sensitivity.

INTRODUCTION

Humans and other species may be exposed to the vanadium through the atmosphere, polluted from the combustion products of vanadium-bearing fuel oils, fumes and dust generated from metallurgical refining and by food[1]. Foods contain low vanadium concentrations (below 1 ng/g), but the estimated daily intake of the US population ranges from 10 to 60μg[2]. Vanadium enters the organism by inhalation, the gastrointestinal tract and the skin and it is specifically stored in certain organs mainly in the liver, kidney and bones[3-5]. Environmental scientists have declared vanadium as a potentially dangerous chemical pollutant that can play havoc with productivity of plants, crops and the entire agricultural system. The toxicity of vanadium is dependent on its oxidation state, with vanadium (V) being more toxic than vanadium (IV)[6]. Vanadium in trace amounts is an essential element for cell growth; at μg L^{-1} levels, acts as a growth-promoting factor and participates in fixation and accumulation of nitrogen in plants[7]. Vanadium has also been reported as the index element in urban environmental pollution, especially air pollution[8]. Vanadium in environmental samples has been determined by NAA[9], ICP-AES[10] and AAS[11]. The first two methods are disadvantageous in terms of cost and instruments used in routine analysis. AAS is often lacking in sensitivity and is affected by matrix conditions of samples such as salinity. A number of catalytic methods having high sensitivity were reported[12-15]. Catalytic solvent extraction methods are highly sensitive but are generally lacking simplicity. Several spectrophotometric methods using different analytical reagents for the determination of vanadium (V) have been reported, but most of these methods suffer from a number of limitations such as interferences by large number of ions,[16-20] heating and standing for a long time for colour development[21] followed by extraction; reduction to lower oxidation state followed by colour development and extraction[22] or reduction and heating for colour development followed by extraction;[23] or lack of sensitivity[16,18,31,32]. These deficiencies have encouraged the authors to develop a new chromone derivative 3-hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPB) as an analytical reagent for trace determination of vanadium (V). This reagent provide a very facile, simple, selective, sensitive, accurate and reliable method for the determination of trace amounts of vanadium (V).

EXPERIMENTAL

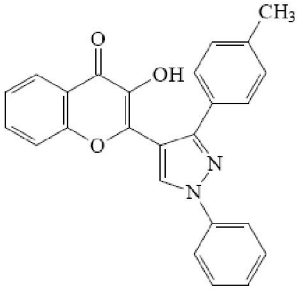
Apparatus

UV-visible (Shimadzu-140-02) spectrophotometer with 10 mm matched quartz cells was used for absorbance measurements and spectral studies.

Reagents and solutions

A stock solution of vanadium (V) containing 1 mg mL^{-1} of metal ion was prepared by dissolving 0.2218 g of sodium metavanadate (A.R.) in deionized water to give 100 mL solution and standardized by ferrous sulphate method[24a] volumetrically. Aliquots were suitably diluted to give 100 and 10 μg mL^{-1} solutions. Solutions of interfering ions were prepared by dissolving their A.R. salts in water or dilute acid to give ≤10 mg mL^{-1} concentrations. Acetic acid (2 mol L^{-1}) was prepared by suitable dilution of glacial acetic acid (17.4 mol L^{-1}).

3-Hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPB) was synthesized by AFO reaction[25] and its structure was confirmed by its spectral (IR, ^{1}HNMR) and analytical data. The structure and spectral analysis of the compound is given as:



(HPMPB)

IR (KBr) : 3284cm^{-1} (-OH str.), 1611 cm^{-1} (C=O str.);

^{1}H NMR (CDCl$_3$, 300MHz, δ): 8.86 (s, 1H); 8.25 (dd, 1H, J=1.5, 8.1Hz); 7.87 (d, 2H, J=7.8Hz); 7.30 (d, 2H, J=7.8Hz); 7.63-7.53 (m, 5H); 7.40-7.36 (m, 2H); 6.97 (d, 1H, J=8.4Hz); 2.49 (s, 3H, CH$_3$);

Anal Calculated for $C_{25}H_{18}N_2O_3$: C, 76.14, H, 4.57, N, 7.11. Found : C, 75.88, H, 4.73, N, 7.24. Yield 58% : M.p. = 221-224^{0}C.

A solution of 0.1% (w/v) of this reagent (HPMPB) was prepared in acetone.

Toluene (RANBAXY) was used as such.

Synthetic samples

Several synthetic (some of them analogous to palau, crocar and permendur) were prepared by mixing solutions of vanadium (V) and other ions in suitable proportions (TABLE 2).

Reverberatory flue dust

Reverberatory flue dust sample (100 mg) from copper manufacture unit containing no vanadium was mixed with a solution of known vanadium content (1 mg) in a silica crucible and dried in an oven at 110-120 °C. It was then fused with sodium peroxide (0.8 g). The fused mass was dissolved in 25-30 mL hot water and neutralized with concentrated H_2SO_4. Iron was precipitated as its hydroxide and separated by filtration. The final volume was made to 100 mL and aliquots (1 and 0.5 mL) were analyzed for vanadium (V) by the proposed method in the presence of 50 mg sodium thiocyanate and 4 mg sodium fluoride.

High speed steel super rapid extra 500

Steel sample (0.1 g) was dissolved by boiling with minimum amount of aqua regia.[24b] Iron was precipitated as Fe (OH)$_3$ by adding 1-2 g of ammonium chloride followed by aqueous ammonia. The precipitates were filtered off and washed with 1 % ammonia solution. The filtrate along with washings was heated to remove excess of ammonia, cooled and adjusted to 100 mL final volume. Aliquot (1 mL) was taken for the determination of vanadium (V) by the proposed method in the presence of 50 mg sodium thiocyanate and 4 mg sodium fluoride.

Procedure

To the sample solution containing up to 12 µg V^V in a 100 mL separatory funnel were added 0.2 mL of 2 mol L^{-1} acetic acid, 1 mL of 0.1% HPMPB in acetone and enough deionized water to make the aqueous volume 10 mL. It was then equilibrated once with an equal volume (10 mL) of toluene for 30 s taking care to release the pressure occasionally through the stopcock. After phase separation the organic extract was passed through Whatman no. 41 filter paper (pretreated with toluene) to remove water droplets if any. The absorbance of the green extract was measured at 415 nm against a reagent blank prepared under identical conditions. Finally, vanadium contents in various samples were computed from the calibration curve prepared under optimum conditions of the procedure.

RESULTS AND DISCUSSION

Absorption spectra

Vanadium (V) formed a green coloured complex with HPMPB in acetic acid medium, which was quantitatively extractable into toluene. It showed absorption maximum in the range 407-417 nm, where the reagent blank had also some absorbance (Figure 1).

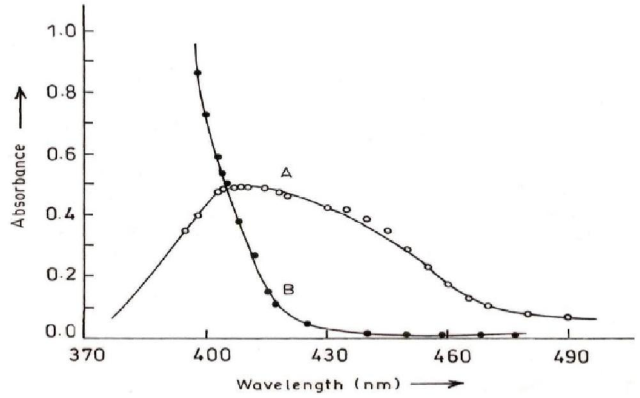


Figure 1 : Absorption spectrum of V (V)-HPMPB complex in toluene. Curve A = 1 µg V (V) ml^{-1} measured against reagent blank; Curve B = Reagent blank measured against pure solvent; HPMPB (0.1 % in acetone) = 1 ml

Standardization of experimental conditions

The extraction showed a decreased trend in CH_3COOH, $HClO_4$, H_3PO_4, HCl and H_2SO_4 media. The decrease in extraction in the presence of strong acids may be due to the formation of oxonium salts of the reagent whereas in H_3PO_4 it may be due to the masking effect of excess phosphate ion concentration over the tolerance level. Therefore, CH_3COOH medium was preferred for further studies. Vanadium (V) complex had been extracted into a large number of water immiscible organic solvents. The absorbance decreased in the order: toluene > carbon tetrachloride = benzene > 1,1-dichloromethane > isobutylmethyl ketone > 1, 2 – dichloroethane > cyclohexane > amyl alcohol = amyl acetate > ethyl acetate > chloroform. As toluene gave stable absorbance with a rapid and clear phase separation, it was selected as the most suitable extractant. The coloured complex of vanadium (V) with HPMPB formed under optimum conditions was stable for more than 10 h in toluene at 415 nm. A maximum and constant absorbance was observed in 0.02 - 0.07 mol L^{-1} acetic acid in presence of 0.9-2.5 mL^{-1} of 0.1% (w/v) acetonic solution of HPMPB at room temperature when the aqueous phase was shaken with 10 cm^{-3} of toluene for 20 - 80 s (TABLE 1).

Stoichiometry of the complex

Equimolar solutions of vanadium and HPMPB reagent at concentration (1.963×10^{-3} M) was to determine the metal-to-ligand ratio by Job's method of continuous variations[27] as modified by Vosburgh and Cooper[28]. The absorbance values are measured at two different wavelengths (415 and 450 nm). The obtained

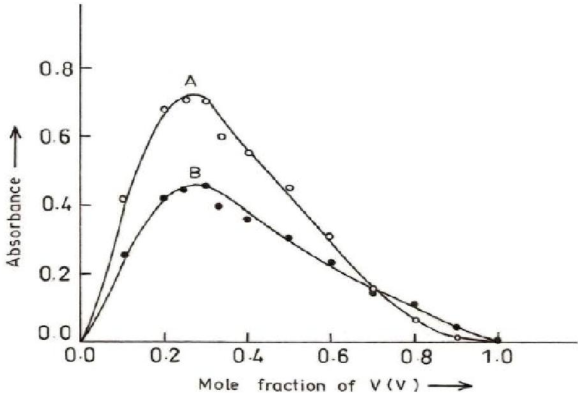
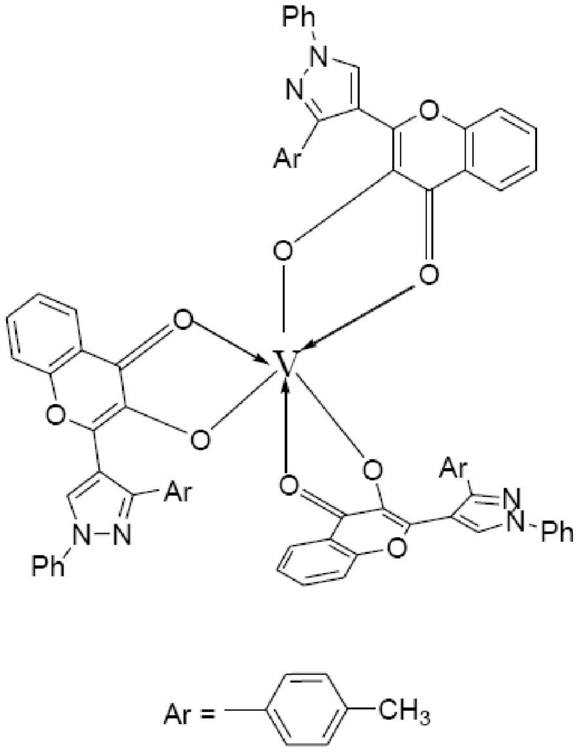


Figure 2 : Job's method of continuous variations. Total concentration [V] & [HPMPB] = 1.963×10^{-3} M; Curve A = 415 nm; Curve B = 450 nm.

curves (Figure 2) are indicative of 1:3 stoichiometry in the extracted species. This is further confirmed using the mole ratio method[29] by taking (1.963× 10^{-3} M) concentration of vanadium, varying the reagent concentration and measuring the absorbance in each case at two different wavelengths, 415 and 450 nm (Figure 3). The composition of the complex is further verified by the equilibrium-shift method[30].

The probable structure of the green-coloured vanadium (V)–HPMPB complex is as given:-



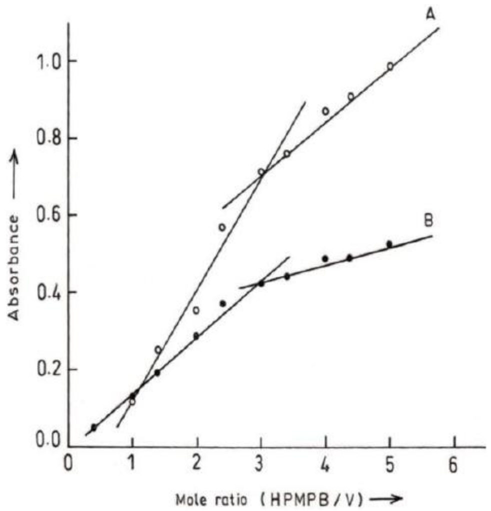


Figure 3 : Mole ratio method. Total concentration of metal fixed = 1.963 × 10^{-3} M; Curve A = 415 nm; Curve B = 450 nm.

Analytical features

The metal complex obeyed Beer's law in the range 0-1.2 μg V^V mL^{-1} and after that concentration it deviated from linearity. The Ringbom plot[26] between log ppm of vanadium concentration and percentage transmittance showed that the optimum concentration of the metal ion, which could be measured most accurately, lied in the range 0.25-1.17 ppm V^V. The molar absorptivity and Sandell's sensitivity were: 2.496×10^4 L^{-1} mol^{-1} cm^{-1} and 0.0020 μg V^V cm^{-2}, respectively at 415 nm. The linear regression equation was, $Y = 0.468X + 0.017$ (Y = absorbance, X = microgram V^V mL^{-1}) and the correlation coefficient, r = 0.9967. The detection limit of the method is 7.628×10^{-5} g L^{-1}.

TABLE 1 : Effect of various parameters on the absorbance of the V – complex

CH_3COOH (M)[a]	0.00	0.01	0.02-0.07	0.08	0.10	0.14	0.20		
Absorbance	0.300	0.430	0.490	0.460	0.450	0.430	0.400		
0.1% HPMPB (mL)[b]	0.2	0.4	0.6	0.8	0.9-2.5	2.6	2.7	3.0	
Absorbance	0.080	0.200	0.320	0.450	0.490	0.480	0.460	0.430	
Equilibration time (s)[c]	0	5	10	15	20-80	90	120		
Absorbance	0.050	0.380	0.420	0.460	0.490	0.450	0.430		
Vanadium (V) (μg mL^{-1})[d]	0.2	0.4	0.6	0.8	1.0	1.1	1.2	1.4	1.6
Absorbance	0.100	0.210	0.310	0.380	0.490	0.520	0.590	0.620	0.670

[a]Vanadium (V) = 10 μg, CH_3COOH = variable, 0.1% HPMPB = 1 mL, equilibration time = 30 s, solvent = toluene, aqueous phase = organic phase = 10 mL, number of extractions = 1; [b]CH_3COOH = 0.2 *M*, other conditions as in (a) except for the variation in HPMPB concentration; [c]0.1% HPMPB in acetone = 1 mL, other conditions same as in (b) except for the variation in equilibration time; [d]equilibration time = 30 s, other conditions same as in (c) except for the variation in vanadium concentration.

Effect of diverse ions

In order to assess the analytical potential of the proposed method, effects of some diverse ions, which often accompany vanadium, were examined by carrying out the determination of 1 μg mL^{-1} of vanadium (V) in the presence of a number of other ions. Chloride, thiourea and nitrate (80 mg each); bromide, iodide, sulphate and sulfosalicylic acid (50 mg each); sulphite and carbonate (15 mg each); acetate (10 mg); phosphate (8 mg); fluoride (4 mg); sodium potassium tartrate (3 mg); glycerol (0.5 mL); citrate (1 mg); disodium EDTA, hydrazine sulphate and sodium dithionite (0.1 mg each) did not affect the determination. However ascorbic acid, hydrogen peroxide and oxalate interfered. The cations Al^{III}, Co^{II}, Ni^{II}, Hg^{II}, Zn^{II}, Ba^{II}, Mn^{II}, Mg^{II}, Cd^{II}, Se^{IV}, Ce^{IV} and Sr^{II} (10 mg each); Ca^{II}, Pb^{II} and Ag^{I} (9 mg each); As^{III}, Cr^{III} and Sb^{III} (5 mg each); Be^{II} (3 mg); U^{VI}, Os^{VIII}, Rh^{III} and Cr^{VI} (1 mg each); Au^{III}, Pd^{II}, Cu^{II} and Fe^{II} (0.8 mg each); Ir^{III} (0.08 mg); Nb^{V} and Ta^{V} (0.05 mg each) caused ≤ 1 % error in the proposed method. The interference due to Fe^{III} (1.5 mg) could be eliminated by adding 5 mg of sodium thiocynate and that of Th^{IV} (0.4 mg), W^{VI} (0.1 mg) and Sn^{II} (0.1 mg) were masked with 0.4 mg sodium fluoride, whereas interference due to Zr^{IV} and Ti^{IV} (0.1 mg each) and Mo^{VI} (0.05 mg) were masked by adding 0.8 mg phosphate and 0.3 mg sodium potassium tartrate prior to the addition of HPMPB, respectively

TABLE 2 : Analysis of vanadium (V) in synthetic and real samples by the proposed method

Comp. of sample, mg	V (V), µg	
	Added	Found*
Ni (0.06), Pt (0.02), Pd (0.01)^{a}	10	10.04±0.68
Fe (0.7), Cr^{VI} (0.01), Co (0.018)^{a,b}	7.5	7.44±1.53
Co (0.3), Fe (0.2), Mn (0.02)^{a,b}	5	5.04±1.16
Sn (0.05), Mg (5), Ba (5)^{c}	4	4.04±2.82
Al (2), Hg (2), W (0.05)^{c}	8	7.96±1.91
Zr (0.01), Cu (0.1), As (1)^{d}	5	5.14±2.32
Mo (0.01), Cd (2), Ag (1)^{e}	10	10.06±1.21
U (0.1),Zr (0.05), Ce (0.5)	7	7.04±0.83
Cr^{III} (2), Ir (0.05), Ca (5)	9	8.86±1.29
Se (5), Rh (0.1), Pb (1)	10	9.94±1.21
Reverberatory flue dust (100)^{b,c}	10	10.15±1.21
	5	4.86±2.32
High speed steel super rapid extra 500^{b,c}	1%^{f}	1.01%±1.04

***Average of triplicate analysis (Mean±%RSD); [a]compositions analogous to palau, crocar and permendur, respectively; [b]In presence of 50 mg sodium thiocynate; [c]In presence of 4 mg sodium flouride; [d]In presence of 8 mg sodium phosphate; [e]In presence of 3 mg sodium potassium tartrate; [f]Certified value.**

TABLE 3 : Comparison of the proposed method with some of the existing ones

Aqueous conditions	Solvent, (λ_{max}, nm)	Sandell's sensitivity (µg cm^{-2}) (Molar absorptivity, L mol^{-1} cm^{-1})	Interfering metal ions	Reference
V (V), acidic medium, benzohydroxamic acid	1-Hexanol (450)	0.012 (4.24×10^{3})	Fe (III), Bi (III), Sb (III), Al (III), Sn (II), Ti (IV), Zr (IV), Mo (VI), W (VI)	16
V (V), pH 3.5-4.5, picolinealdehyde benzothiozolylhydrazone, shaking time 10 min.	Benzene (528)	0.0033 (1.54×10^{4})	Fe (III), Fe (II), Co (II), Pd (II)	17
V (V), 0.7 *M* HCl, sodium sulphite, sodium acetate, 8-hydroxyquinoline	Isobutylmethyl ketone (430)	0.0088 (5.73×10^{3})	Zr (IV), Al (III), Fe (III), Fe (II), Co (II), Cu (II)	18
V (V), 0.0-0.5 *M* CH_3COOH, 0.1% 2$'$-hydroxyacetophenone benzoylhydrazone in acetone	Chloroform (375)	0.0057 (8.93×10^{3})	Fe (III)	31
V (V), pH 6-8, dithionite, 5, 7-dibromo-8-hydroxyquinoline	Chloroform (420)	0.006 (7.27×10^{3})	Mo (VI)	32
V (V), pH 2.0-4.0, 0.05% variamine blue (VB)	- (570)	0.003 (1.65×10^{4})	Cr (VI),Fe (III), Ce (IV), W (VI)	19
V (V), butaperazine dimaleate (BPD), phosphoric acid	- (513)	0.0061 (1.05×10^{5})	Cr (VI), Ce (IV)	20
V(V), 0.02-0.07 *M* CH_3COOH, 0.9-2.5 mL of 0.1% HPMPB	Toluene (415)	0.0020 (2.496×10^{4})	37 metal ions do not interfere	Proposed method

CONCLUSIONS

The proposed method is simple, rapid, sensitive and highly selective as it is free from the interference of a large number (37) of metal ions, including platinum metals. The proposed method is better than the existing methods (TABLE 3) particularly with respect to selectivity and simplicity.

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