

Spectrophotometric determination of Vanadium(V) in traces using solvent extraction technique

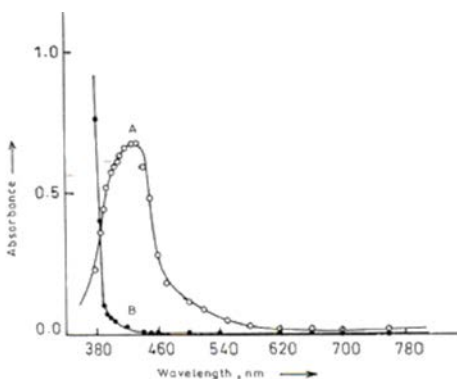
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ABSTRACT



A simple, rapid, sensitive and selective extractive method of spectrophotometric determination of vanadium(V) using 6-chloro-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4H-1-benzopyran (CHMPB) as a new complexing reagent has been developed. A 1:2 yellow V(V) – CHMPB complex is formed at 425 nm in CH₃COOH medium which is extractable into toluene and is stable for more than 6 hrs. The formed complex shows Beer's law validity in the range 0.0-2.4 µg V ml⁻¹ with a molar absorptivity and Sandell's sensitivity of 1.73 x 10⁴ l mol⁻¹ cm⁻¹ and 0.0033 µg V cm⁻², respectively at 425 nm. The method has good reproducibility, is free from the interference of a large numbers of elements and applied successfully to various synthetic and industrial samples including reverberatory flue dust and water samples.

Keywords: Vanadium, 6-chloro-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4H-1-benzopyran, extraction, spectrophotometry, determination

INTRODUCTION

Vanadium is found in combined state in nature in form of different minerals such as patronite, vanadinite, carnotite and bauxite. It also occurs in carbon containing deposits as crude oil, coal and tar sands. As the vanadates are generally very soluble in nature therefore watering is an important way for redistribution of vanadium around environment. It is abundant in most of the soils in variable amounts and is taken up by plants at levels that reflect its

availability. Vanadium atom is also an essential compound of some enzymes particularly vanadium nitrogenase used by some nitrogen fixing micro-organisms. Vanadium is found in environment in algae, plants, invertebrates, fish and many other species.¹ The literature survey reveals that vanadium is associated with various environmental and health effects.²⁻⁴

Thus, it becomes necessary that the food, water or any other material that we use should be free from vanadium contents. The concentration and determination of vanadium has been determined by various techniques. The spectrophotometric determination technique using solvent extraction for the microanalysis of vanadium is simple, rapid, cheap, sensitive and highly selective, so it is used in this study.

In the spectrophotometric determination of vanadium(V), different organic reagents including benzopyran derivatives have been used in the past. Our study in this regard gives a new method

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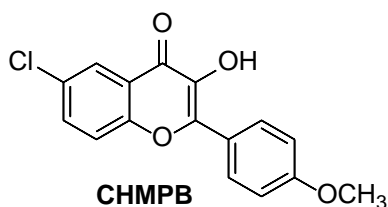
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for the complexation and extractive determination of vanadium(V) using 6-chloro-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (CHMPB) as a new reagent possessing similar chelating tendency yet enhancing sensitivity, selectivity and rapidity of determination as compared to some of the previous methods.⁵⁻¹⁵

EXPERIMENTAL

Apparatus, Reagents and solutions

A Systronics - 166 UV-visible spectrophotometer with 10 mm matched glass cells was used for absorbance measurement and spectral studies, respectively. Solutions of vanadium (V), acetic acid and other metal ions were prepared as reported earlier.¹⁵ 6-Chloro-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4*H*-1-benzopyran (CHMPB) was synthesized by the literature method¹⁶ and its 0.1%(w/v) solution was prepared by dissolving in distilled ethanol. Toluene (Ranbaxy) was used as such.



Samples

Synthetic samples (some of them analogous to technical samples like palau) were prepared by mixing microgram amounts of vanadium(V) and with other metal ions in suitable proportions to give various compositions as shown in Table 1.

Table 1. Analysis of different samples by the proposed method

S. No.	Composition of sample		V found** (µg)
	Matrix*	V added (µg)	
1.	Bi(0.1), Nb(0.5), Co(0.1)	15.0	15.2
2.	Al(1.0), Cu(1.0)	20.0	20.1
3.	Sr(1.0), Pb(0.5)	10.0	10.1
4.	Ir(0.01), Cd(0.1)	16.0	16.1
5.	Hg(1), Ce(0.05), As(0.05)	10.0	10.2
6.	U(0.1), Mn(0.1), Rh(0.1)	18.0	18.4
7.	Zn(0.1), Ag(0.1), Nb(0.02)	06.0	06.1
8.	Bi(0.5), Au(0.005), Th(0.3)	20.0	20.3
9.	Ta(0.02), Zr(0.005) ^a	08.0	08.2
10.	[Ni(0.03), Pt(0.01), Pd(0.003)] ^b	05.0	05.4
11.	Reverberatory flue dust ^c (100)	10.0	10.1
12.	Tap water	10.0	09.8
13.	Well water	10.0	10.2

*Figures in brackets indicate the mg amount of metal ion. ** Average of Duplicate Analyses. ^aIn presence of 10 mg sodium potassium tartrate.

^bComposition analogous to Palau. ^cIn presence of 10 mg sodium fluoride.

Reverberatory flue dust sample (0.1 g, vanadium free) was brought into solution as reported¹⁵ earlier and vanadium determined in aliquots by the proposed method after adding 10 mg sodium fluoride in each case.

A known amount of vanadium (0.01 mg) was mixed with water samples (10 ml each from tap and well) followed by addition of 6% H₂O₂ (1 ml) and aqueous ammonia (2 ml). The mixture solution was boiled, evaporated to dryness, the residue dissolved in 0.24 M CH₃COOH and vanadium was determined by the proposed method.

Procedure

Acetic acid (1.2 ml of 2 M), and CHMPB (2 ml of 0.1% ethanol solution) were added to an aliquot of the sample solution containing vanadium (V) up to 24 µg (in a 125 ml separatory funnel) and appropriate amount of deionized water was added to make the final aqueous volume 10 ml. The mixture was then equilibrated with equal volume of toluene (10 ml) for 30 s. A single extraction was sufficient to give 100% transference of the complex from aqueous to organic phase. The yellow organic phase was filtered through Whatman filter paper (No. 41, pretreated with toluene) to remove water droplets and absorbance of the extract was measured at 425 nm against a similarly prepared reagent blank. Finally vanadium content in various samples was computed from the calibration curve.

Modification in the procedure was required for samples containing other metal cations by involving the addition of appropriate masking agents preceding the addition of reagent : 0.02 mg each of W(VI) and Fe(III), and 0.01 mg each of Mo(VI) and Sn(II) + 10 mg of KF ; 0.01 mg of Zr(IV) + 10 mg of sodium potassium tartrate.

RESULTS AND DISCUSSION

CHMPB gives an extractable yellow coloured complex with V(V) in neutral to weakly acetic acid media. In strong acids like HClO₄, H₃PO₄, H₂SO₄ and HCl, colour of the complex is not stable and absorbance decreases in order, CH₃COOH > HClO₄ > H₃PO₄ > HCl > H₂SO₄. The complex formed is generally not extractable in alkaline medium.

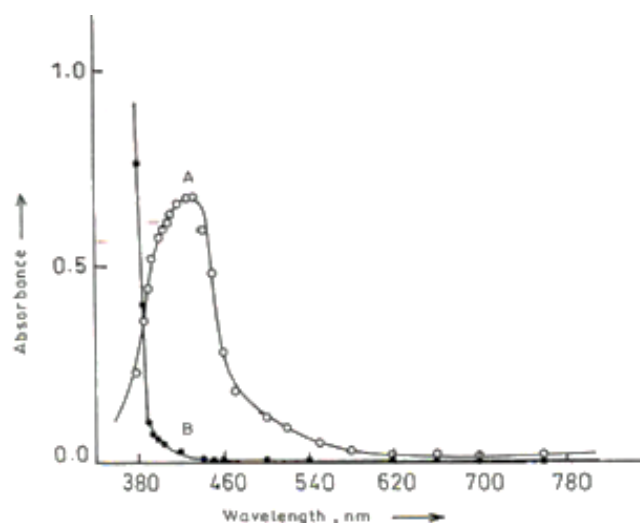


Figure 1. Absorption Spectra of V(V) – CHMPB Complex, a) Complex against reagent blank b) Reagent blank against pure toluene 2.0 µg V ml⁻¹; Other conditions same as given in the procedure

Table 2. Effect of various parameters on the absorbance of V(V)-CHMPB Complex

CH ₃ COOH ^a /M	0	0.04	0.1	0.14	0.2	0.22-0.28	0.3	0.32	0.4
Absorbance	0.1	0.28	0.41	0.48	0.52	0.54	0.51	0.46	0.36
CHMPB ^b /ml	0.2	0.5	0.7	1	1.2	1.5	1.7-2.4	2.5	3
Absorbance	0.11	0.28	0.36	0.46	0.54	0.61	0.68	0.64	0.39
Equilibration time ^c / sec	0	5	10	15-180					
Absorbance	0.07	0.52	0.62	0.68					

Conditions: a) V(V) = 20 µg; CH₃COOH = variable; CHMPB [0.1% (w/v) in ethanol] = 1 ml; aqueous volume = solvent volume = 10 ml; Solvent = toluene; Equilibration Time = 30 sec; λ_{max} = 425 nm b) CH₃COOH = 0.24 M; other conditions being the same as in (a) excepting variation in CHMPB content. c) CHMPB [0.1% (w/v) in ethanol] = 2 ml; other conditions being the same as in (b) excepting variation in equilibration time

Vanadium(V) – CHMPB complex is easily extracted by a large number of water immiscible solvents. The absorbance decreases in order: toluene > benzene > chloroform > dichloromethane > isobutylmethylketone > 1,2-dichloroethane > ethyl acetate > isopentyl acetate > isopentyl alcohol. Hence toluene giving maximum and stable absorbance (> 6 hrs) is found to be most suitable. A single extraction with equal volume (10 ml) of toluene is sufficient to give quantitative extraction and maximum absorbance of the complex.

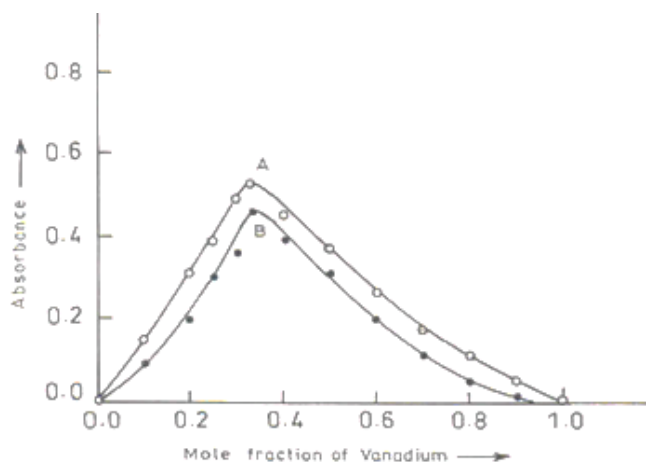


Figure 2. Continuous Variation of Vanadium(V) and CHMPB, [V] and [CHMPB] = 1.96×10^{-3} M, Curve A = 425 nm; Curve B = 450 nm

The optimum values of other parameters found to achieve maximum and constant absorbance for 0-24 µg V(V) in 10 ml aqueous solution are: 0.22 – 0.28 M CH₃COOH, 1.7 -2.4 ml of 0.1 % CHMPB solution in ethanol and equilibrating once between 15-180 s with an equal volume of toluene (Table 2).

The absorbance spectrum of V(V) – CHMPB complex in toluene against reagent blank at optimal conditions shows an absorption maximum at 425 nm where the reagent blank hardly shows any absorbance (Figure 1). Beer's law is obeyed over the analyte's concentration range of 0.0 -2.4 µg V ml⁻¹. The molar absorptivity and Sandell's sensitivity are calculated to be 1.73×10^4 l mol⁻¹ cm⁻¹ and 0.0033 µg V cm⁻², respectively, at 425 nm. The reproducibility of the method is tested by performing ten sets of experiments keeping the same amount (2.0 µg V ml⁻¹) of the metal ion each

time. The standard deviation of the method is ± 0.0021 absorbance units.

Stoichiometry of the Complex

Equimolar (1.96×10^{-3} M) solutions of vanadium(V) and CHMPB are used to determine M:L ratio of the formed complex by Job's continuous variations method¹⁷ as modified by Vosburgh and Cooper.¹⁸ In the extracted species, the absorbance values are noted at two different wavelengths namely 425 and 450 nm with the obtained curves of 1:2 stoichiometry (Figure 2). The ratio is further verified by the mole-ratio method¹⁹ (Figure 3).

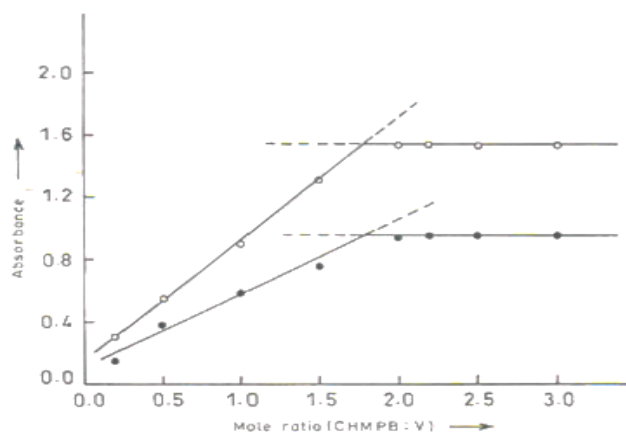


Figure 3. Mole Ratio Method : [V] = 0.98×10^{-3} M, Curve A = 425 nm; Curve B = 450 nm

Effect of diverse ions

Under the optimum condition of the procedure containing 20 µg V(V), the anions/complexing agents added as their sodium or potassium salts in 10 ml aqueous volume (mg amounts in parentheses) such as thiourea, chloride, bromide, iodide, thiocyanate, sulphate, sulphite, nitrate and phosphate (50 each); fluoride, tartrate and acetate (10 each) and citrate (2) have no effect on the absorbance of V(V) – CHMPB complex. However, ascorbic acid, oxalate and EDTA "Disodium salt" even in traces interfere seriously.

Among the cations, Mg(II) and Cd(II) (10 each); Ni(II), Zn(II), Pb(II), Sr(II), Co(II), Ba(II), Mn(II), Hg(II), Ca(II), Be(II), Al(III) and Th(IV) (5 each); Cu(II) and U(VI) (2 each); Rh(III) and

Ce(IV) (1 each); Bi(III), Se(IV), Ti(IV) and As(V) (0.5 each); Ag(I), Au(III), Nb(V) and Sb(V) (0.1 each); Pd(II), Pt(II), Ir(III), Ru(III) and Os(VIII) (0.05 each) do not cause any interference. The influence of Fe(III), Sn(II), Zr(IV), Mo(VI), and W(VI) can be significantly eliminated by the addition of masking agents, which is included in the modified procedure.

CONCLUSION

A simple, rapid and sensitive extractive spectrophotometric method has been developed for trace determination of vanadium which is free from the interference of a large number of metal ions especially platinum metals and many other transition metals, commonly found associated with vanadium in various technical samples and alloys. The wide applicability of the method in relation to environment is tested by analyzing different synthetic, technical and water samples (Table 1). The proposed method is better than the existing methods especially with respect to sensitivity, selectivity and rapidity.

ACKNOWLEDGMENTS

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