Spectrophotometric Determination of Vanadium as V(III) with Dibenzoylmethane

Rakam Singh CHAUHAN and Lajpat Rai KAKKAR*
Department of Chemistry, Kurukshetra University, Kurukshetra 132119 Haryana, India

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Synopsis. A highly sensitive and selective method for the determination of trace amounts of vanadium is developed by effecting complexation of V(III), obtained on reduction of V(V) by dithionite, with dibenzoylmethane in neutral medium. The colored complex is extractable into chloroform, absorption maxima lying at 386 nm. The interfering effect of a large number of elements is eliminated completely, which leads directly to the determination of the metal ion present in traces in samples. The method obeys Beer's law in the range 0—2.4 μg-V cm^{-3} with Sandell's sensitivity of 2.46×10^{-3} μg-V cm^{-2}. Metal to ligand ratio in the extracted species is determined as 1 : 3.

Amongst the chelating extractants, β-diketones occupy an important place so far as the extractive study of various transition elements is concerned.[1)] In case of vanadium which is a multivalent metal ion with a positive valency of 2 to 5, acetylacetone,[2—6)] 2-thenoyltrifluoroacetone,[7,8)] and its thio analog[9)] as also some other reagents like 1-(2-pyridylazo)-2-naphthol,[10)] 4-(2-pyridylazo)resorcinol,[11)] 3,5-dinitrocatechol, and brilliant green,[12)] have been effectively used for analysis particularly in its +4 and +5 states; whereas, the lower valence +3 and +2 have hardly received any attention as their chemistry is relatively much less known for want of stability due to quick oxidation and therefore, there is a lack of sufficient information of their behavior towards different ligands. Since lower valent states of the transition metals are equally important analytically, it is considered of interest to work on V(III) with a view to explore extraction possibilities. Though dibenzoylmethane[13,14)] has already been used for the colorimetric determination of Fe(III) and U(VI), its reaction with V(III) which is produced on reduction with dithionite, is not known and is, therefore, studied in the present case with the following details.

Experimental

Reagents and Solutions. A stock solution of vanadium containing 1 mg-V cm^{-3} is prepared by dissolving an accurately weighed amount of sodium metavanadate (Reachim) in distilled water and standardized by Fe(II) method.[15a)] Lower concentrations at the μg cm^{-3} level are obtained by suitable dilutions.

2.0% (w/v) dibenzoylmethane is prepared in acetone.

Sodium dithionite (Loba Chemie) and chloroform (Qualigens) are used as such.

Solutions of other metal ions are brought in solution by dissolving their commonly available salts in distilled water or dilute acid.

Sample Preparation. a) High Speed Steel Super Rapid Extra 500: The sample (0.2 g) was dissolved by boiling with 15 cm^3 of concentrated hydrochloric acid, 5 cm^3 of concentrated nitric acid and 30 cm^3 of water in a 250 cm^3 conical flask.[15b)] The black residue, if any, is decomposed by boiling further with 20—25 cm^3 of 60% perchloric acid. The solution is carefully evaporated down to about 5 cm^3, cooled, and diluted to 100 cm^3 in a volumetric flask. Suitable aliquots are used for the determination of vanadium.

b) Reverberatory Flue Dust: The flue dust from copper manufacture containing no vanadium is mixed with a known amount of vanadium and dried in an oven. After fusion of the sample with sodium peroxide (8 times the weight of the sample), the leach is neutralized with concd H_2SO_4 and made slightly alkaline. It is boiled and the hydroxide precipitate is filtered off and finally washed well with distilled water. The filtrate along with the washings is made just neutral and vanadium determined as described in the procedure.

Procedure. To a sample solution containing ≤60 μg-V and/or other ions in a 100 cm^3 beaker, add 0.5 cm^3 of dibenzoylmethane reagent and enough distilled water to make the aqueous solution 20 cm^3. It is shaken gently for a while with 0.3 g sodium dithionite and the contents are heated on a water bath at ca. 50 °C for 10 min. The solution is cooled under tap water and then transferred to a 100 cm^3 separatory funnel. The yellow colored complex is extracted by equilibrating once for 30 s with 20 cm^3 of chloroform. The solvent layer is filtered into a 25 cm^3 volumetric flask through Whatman filter paper No. 41 to remove any droplets of water. This is followed by two treatments of the aqueous layer with 2 cm^3 chloroform each time to ensure quantitative transfer of the complex to the organic phase and the volume is then finally made up to the mark with the pure solvent. The absorbance is measured at 386 nm on a UV-visible spectrophotometer (Shimadzu-UV-140-02) against a reagent blank prepared in an analogous manner, and vanadium is determined from the calibration curve.

Modification for samples containing Cu(II), Fe(III), and Ti(IV): thiourea (≤300 mg), ascorbic acid (≤500 mg), and tartrate (≤150 mg) are to be added prior to the addition of dithionite to mask Cu(II), Fe(III), and Ti(IV), respectively.

Results and Discussion

V(III) obtained on reduction of V(V) by sodium dithionite[16)] reacts with dibenzoylmethane (DBM) to form a yellow colored species in neutral or slightly acidic solution. The colored species can be quantitatively extracted into chloroform, and the absorbance of the organic phase is measured at 386 nm.

The reaction of V(III) with DBM is temperature-dependent. The complex formation increases slowly with temperature. Upto 40 °C, it is not complete, and if the temperature of the water bath is maintained in the

Table 1. Analysis of Various Samples by the Proposed Method

Ser.	Composition of sample		
No.	Matrix[a]	V Added	V Found
		µg	µg
1.	W(2), U(2)	20	20, 19.5
2.	W(1), Fe(2), Cr(0.5)	25	25
3.	Mo(0.2)	20	20
4.	Cr(0.2), Mo(0.1)	10	10, 9.5
5.	Co(0.5), Ni(0.5)	35	34.5
6.	Cu(2), Zn(2), Mn(2)	30	29.5
7.	Re(2), Zr(1), Bi(0.5), Mg(1)	25	24
8.	Pd(0.1), Pt(0.1), Os(0.1), Ru(0.1), Rh(0.1)	20	20
9.	Ba(1), Ca(1), Hg(0.5), Ce(1), Se(0.5)	40	39
10.	Pb(1), Ag(0.5), Sb(1)	50	50, 49
11.	[Co(0.052), Fe(0.034)][b]	14	14
12.	[Fe(7.5), Cr(0.6), W(1.75)][b]	30	29.5
13.	[Fe(1), Ni(0.4), Cr(0.5), Mn(0.02)][b]	20	20
14.	[Ni(0.24), Pt(0.08), Pd(0.08)][b]	40	39.5
15.	[Fe(1.7), Cr(0.24), Co(0.015)][b]	15	15
16.	[Co(0.49), Fe(0.489), Mn(0.003)][b]	17	17.5
17.	High speed steel super rapid extra 500	1%[c]	0.96%, 0.97%
18.	Reverberatory flue dust, 150 mg	25	23.5, 24.2

a) Figure in bracket indicates the amount of the metal ion in mg. b) Sample Nos. 11—16 correspond to vicalloy, high speed steel, nichroloy, palau, crocar, and permendur, respectively. c) Reported value.

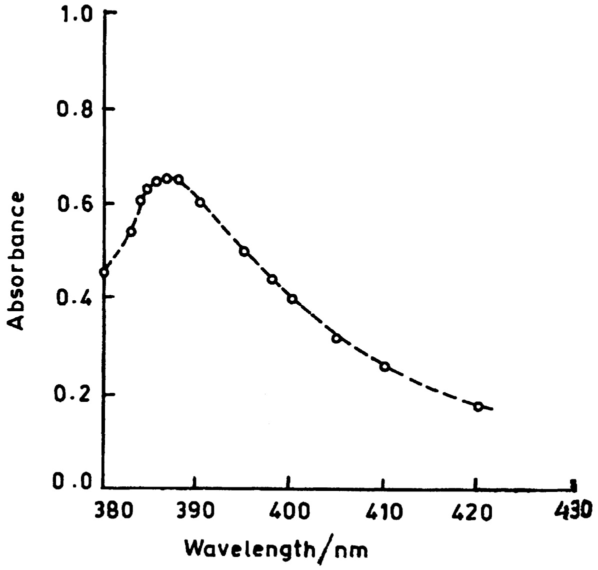

Fig. 1. Absorption spectrum of V(III)-dibenzoylmethane complex in chloroform. Metal Complex (1.6 µg-V ml^{-1}) measured against reagent blank.

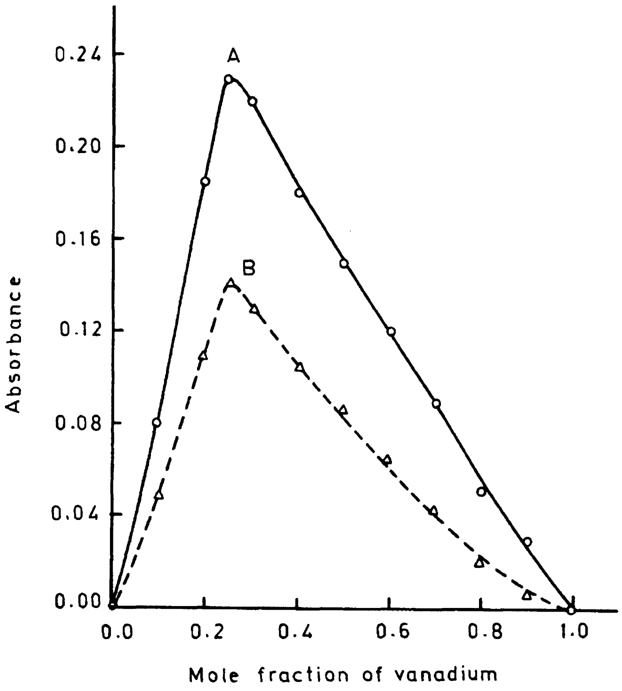

Fig. 2. Job's method of continuous variation. conditions: A – Vanadium = 1.37×10^{-4} M, DBM = 1.37×10^{-4} M. B – Vanadium = 9.8×10^{-5} M, DBM = 9.8×10^{-5} M. λ_{max} 386 nm.

range of 45—55 °C for 8—15 min, full color development of the complex takes place. Therefore, it is considered suitable to carry out the reaction at 50 °C for studying the effect of other parameters on absorbance, namely, heating time, HCl, dithionite, reagent concentration, and equilibration time.

On the basis of the data obtained from the study of various parameters as referred to above, it is concluded that for ≤60 µg-V, 0—0.05 M HCl (M=mol dm^{-3}), 0.4—2.5 cm^3 of 2% (w/v) dibenzoylmethane in acetone, 0.2—0.8 g sodium dithionite, heating on a water bath at 45—55 °C for 8—15 min in 20 cm^3 aqueous volume, equilibrating with 20 cm^3 chloroform for 10 s—10 min, are the optimum conditions for quantitative transfer of the metal complex to the solvent phase with absorption maxima at 386 nm.

V(III)–DBM complex is highly extractable showing maximum absorbance into a number of solvents, such as chloroform, dichloromethane, benzene, and dichloroethane; whereas, in case of isopentyl alcohol, ethyl methyl ketone, isobutyl methyl ketone, toluene, carbon tetrachloride, benzyl alcohol, butyl acetate, and carbon disulfide, a gradual fall in absorbance value is observed in the descending order. For a quick and clear phase separation and also to economise the system, chloroform is chosen.

Under the experimental conditions as mentioned in the procedure, anions like chloride, sulfate, nitrate, 500 mg each; phosphate, acetate, 400 mg each; thiocyanate 300 mg; tartrate 150 mg; fluoride 50 mg; ascorbic acid 500 mg, thiourea 300 mg, and sulfosalicylic acid 50 mg, do not influence the absorbance of the complex; whereas, EDTA and oxalate decrease it considerably.

In 20 cm^3 aqueous volume, the following metal ions do not interfere with the determination: Re(VII), W(VI), U(VI), Mo(VI), Cr(VI,III), Zr(IV), Ce(IV), Fe(II), Zn(II), Ba(II), Ca(II), Mg(II), Mn(II), Sr(II), 0.5 mg cm^{-3}; Os(VIII), Pt(IV), Ru(III), Rh(III), Pd(II), 0.025 $mg\,cm^{-3}$ (higher amounts were not tested). Ag(I), Pb(II), Hg(II), Co(II), Ni(II), Cd(II), Bi(III), Sb(III), and Se(IV) at concentrations of 0.5 $mg\,cm^{-3}$, do not interfere. Cu(II), Fe(III), and Ti(IV) at concentrations of 0.5 $mg\,cm^{-3}$ could be masked with thiourea, ascorbic acid, and tartrate, respectively.

Spectral Characteristics. The absorption spectra of the V(III)–DBM complex in chloroform shows that λ_{max} lies at 386 nm (Fig. 1). Beer's law is obeyed in the range 0—2.4 $\mu g\text{-}V\,cm^{-3}$. The optimum concentration of the metal ion that can be measured accurately, as evaluated from Ringbom plot,[17)] is 0.59—2.14 ppm vanadium. Molar absorptivity, and Sandell's sensitivity of the metal complex are 2.07×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ and $2.46\times10^{-3}\mu g\text{-}V\,cm^{-3}$, respectively.

Stoichiometry of the Complex. The ratio of vanadium to DBM in the extracted species is determined by Job's method of continuous variations by taking equimolar solutions of vanadium and DBM in two different sets of experiments (1.37×10^{-4} M for the first set and 9.8×10^{-5} M for the second). The two curves obtained are indicative of 1 : 3 stoichiometry of the metal and ligand in the extracted species (Fig. 2). This is further confirmed by mole ratio method.

Applications. The proposed method of vanadium determination is simple and at the same time highly selective. It is free from the interference of a large number of transition elements including platinum metals which usually pose problems while effecting spectrophotometric determination of vanadium. The wide applicability of the method is tested by the analysis of several synthetic and technical samples, high-speed steel and reverberatory flue dust, and the results obtained are quite in agreement with the amount of metal ion initially added/reported value (Table 1). The proposed method compares favorably with the existing methods, especially in respect of sensitivity and also has a good reproducibility with a standard deviation of ±0.0025.

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