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Extractive Separation and Photometric Determination of Vanadium with Benzoylacetone

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

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A very simple and rapid method for the extractive separation and photometric determination of vanadium is worked out using benzoylacetone as a complexing reagent for V(III), produced on reduction of V(V) with sodium dithionite in dil acetic acid medium. The colored complex is extractable into benzene. The interfering effect of a large number of elements is eliminated completely leading directly to the determination of the metal ion present in traces in samples. The method is applicable to the analysis of different technical samples and the results obtained are highly reproducible. Metal to ligand ratio in the extracted species is determined as 1 : 3.

Though vanadium in its compounds has established the positive valency of 2 to 5, but the compounds of pentavalent vanadium are most stable in solutions, followed by V(IV), and perhaps for the same reason, most of the methods of analysis of vanadium are based on the ability of V(V) and V(IV) to react with different complexing reagents namely, oxine,[1)] benzoin oxime,[2)] cupferron,[3)] *N*-benzoyl-*N*-phenylhydroxylamine,[4)] dithiocarbamates,[5)] dithiocarbonates,[6)] generally in acidic or alkaline media resulting in the formation of colored complexes whose extractive possibilities into various organic solvents can be investigated. So far as less known states namely, +3 and +2 of the element are concerned, there is still a lack of information on their use in carrying out chemical analysis to separate small quantities of the metal ion, primarily due to their low stability on production. It is, in this context, imperative and gains significance with a view to study their behavior towards different organic compounds, whose nature, otherwise is somewhat obscure.

In the work presented below, V(III) obtained on reduction of V(V) with dithionite, has been found to react with "benzoylacetone" (1-phenyl-1,3-butanedione), a β-diketone, for effecting separation by extraction into benzene with subsequent photometric determination of vanadium.

Experimental

Stock solution of vanadium containing 2 mg ml^{-1} of the metal ion is prepared by dissolving an accurately weighed amount of sodium metavanadate (Reachim) in distilled water and standardized by Fe(II) method.[7a)] Lower concentrations to the µg ml^{-1} level are obtained by suitable dilution therefrom.

Solutions of other metal ions are prepared by dissolving their commonly available salts in distilled water or dilute acids. Benzoylacetone, 1% (w/v), is prepared in acetone. Sodium dithionite (Loba Chemie), acetic acid (SRL, AR) and benzene (E. Merck, AR) are used.

Samples. 1) High Speed Steel Super Rapid Extra 500: The sample is brought into solution by dissolving it in aqua regia.[7b)]

2) Ferrovanadium: The alloy is treated with nitric acid[7c)] to bring it into solution.

3) Reverberatory Flue Dust: Flue dust containing no vanadium is mixed with a known amount of metal ion 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 adjusted to pH ca. 7 and vanadium determined as described below in the procedure.

Procedure. 1) Extractive Separation: To a sample solution containing $\leqslant$ 1 mg V and/or other metal ions in a 100 ml separatory funnel, add 2 ml of 1 M acetic acid (1 M=1 mol dm^{-3}), 2 ml of 1% benzoylacetone reagent in acetone and 500 mg sodium dithionite (solid). The contents are mixed gently and the volume is made up to 20 ml with distilled water. The solution is allowed to stand undisturbed for 20 min and the brownish red complex formed is extracted by equilibrating once with an equal volume of benzene for one min, while taking care to release the pressure occasionally through the stop cock. Allow the two layers to separate and drain off the aqueous phase. The metal ion from the organic layer is stripped off by back extracting it twice with an equal volume of 3 M HCl each time for 3 min. The back extracts are processed for determination of vanadiun.[8)]

Alternatively, the aqueous layer is collected in a beaker and oxidized with H_2O_2 in alkaline medium. The excess peroxide is boiled off in acidic medium. Vanadium left, if any, in the solution so obtained, is determined by phosphotungstate method,[8)] and the metal ion extracted into the solvent is obtained by difference.

2) Photometric Determination: For determination of vanadium in traces, solution containing $\leqslant$70 µg in 20 ml aqueous volume is adjusted to the experimental conditions exactly as described under (1). The colored species on extraction into benzene is filtered into a 25 ml volumetric flask through a Whatman filter paper No. 41 to remove any suspended droplets of water. It is filled up to the mark with pure solvent and the absorbance is measured at 390 nm against the reagent blank prepared in an analogous manner using digital (EC) spectrophotometer in 1 cm cells. The amount of the metal ion is determined from the calibration curve constructed using the data obtained on taking different volumes of vanadium solution (in varying µg amounts) and the corresponding absorbances measured as referred to above.

Results and Discussion

In presence of reductants, vanadium is known to exist in the +3 and +4 states in solutions. Due to the multivalent nature of the metal, several organic compounds have often been found useful for its extraction. Since the extraction of the metal ion in different oxidation states with β-diketones[9] is also considered equally effective, the studies on the analytical applications of benzoylacetone with respect to vanadium in the lower-valent state +3 in particular deserve attention. It is, therefore, thought interesting to look into its various aspects while understanding the behavior of this reagent towards vanadium and the other associated metal ions.

Pentavalent vanadium, on reduction with sodium dithionite[10] in weakly acid solutions, forms V(III) which gives a brownish red complex on reaction with benzoylacetone (in acetone). The colored species is highly extractable into various organic solvents like, benzene, chloroform, carbontetrachloride, dichloromethane, and isobutylmethylketone. To economize the procedure, benzene is preferred as an extractant.

Vanadium (III) forms the complex with benzoylacetone in neutral as well as dilute acid medium, but the extraction is found to be fairly well in case of the latter. At the same acidity (0.05 M), extraction in acetic, sulfuric, hydrochloric, and phosphoric acids decreases in the same order. Acetic acid is, therefore, the suitable acid medium.

Effect of different variables like acid concentration, dithionite, benzoylacetone, color development time, and equilibration time, on the extraction of vanadium is

Table 1. Effect of Various Parameters on the Extraction of V(III)-Benzoylacetone Complex

Acetic acid,[a] (M)	0	0.05	0.08—0.3	0.35	0.4	0.45	
% Extraction	72	82.2	84.5	83	81	77.5	
Dithionite,[b] (g)	0.05	0.1	0.2	0.3	0.4—1.0	1.2	1.5
% Extraction	76.5	80.8	84.5	88	92.5	92	90.5
Benzoylacetone[c] (1.0% w/v soln in acetone), (ml)	0.2	0.3	0.5	1.0	1.5—5.0		
% Extraction	52.5	83.34	92.5	96	97.5		
Color development time,[d] (min)	2	5	10	15—25			
% Extraction	94.5	97.5	99.6	100			
Equilibration time,[e] (min)	0.5	1	2	3	4	5	
% Extraction	100	100	100	100	100	100	

a) Conditions: Vanadium=200 μg, dithionite=200 mg, benzoylacetone=0.5 ml, color development time=5 min, aqueous volume=solvent volume=20 ml, solvent=benzene, equilibration time=1 min, no of extractions=1. b) Conditions: Acetic acid=0.1 M; other conditions are the same as in (a) except dithionite. c) Conditions: Dithionite=500 mg; other conditions are the same as in (b) except benzoylacetone. d) Conditions: Benzoylacetone=2 ml; other conditions are the same as in (c) except color development time. e) Conditions: Color development time=20 min; other conditions are the same as in (d) except equilibration time.

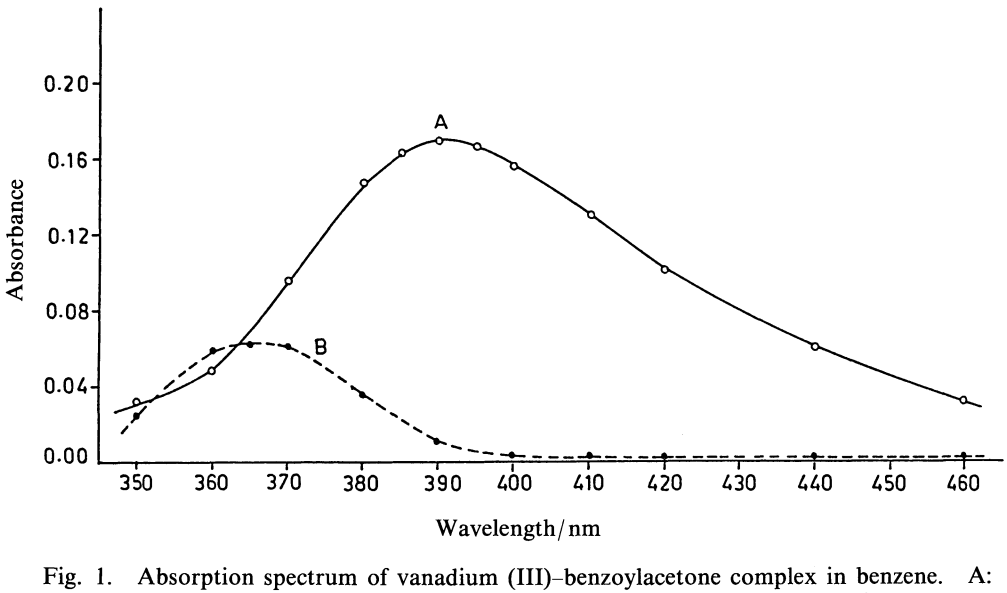

Fig. 1. Absorption spectrum of vanadium (III)-benzoylacetone complex in benzene. A: 1.6 μg V ml^{-1} measured against reagent blank. B: reagent blank measured against benzene.

shown in Table 1. From the consideration of the data obtained, it is evident that the optimum conditions for the system are as already described in the procedure.

Upto 1 mg vanadium, the extraction is quantitative in a single step. If the metal ion concentration exceeds 1 mg, a corresponding raise in dithionite and benzoylacetone is necessitated for obtaining 100% extraction in one operation. It has been seen that for every increase of 5 mg in vanadium content, dithionite and benzoylacetone are to be increased by 300 mg and 6 ml respectively over and above the amounts added initially in the procedure.

Effect of Diverse Ions: Under the conditions of the procedure, several cations namely, Os(VIII), Re(VII), W(VI), Cr(VI, III), U(VI), Ti(IV), Zr(IV), Ce(IV), Pt(IV), Ru(III), Rh(III), Al(III), Fe(III, II), Pd(II), Mn(II), Zn(II), Ba(II), Ca(II), Mg(II), and Be(II) give colorless extracts and are, therefore, noninterfering. Se(IV), Bi(III), As(III), Sb(III), Hg(II), Cu(II), Co(II), Ni(II), Pb(II), and Ag(I) form precipitates without any adsorption of vanadium. The extraction can be effected as such or after filtration of the precipitates. It does not influence the extraction of the metal ion either. Mo(VI) interferes. Chloride, sulfate, nitrate, ascorbic acid, thiocyanate (500 mg each); thiourea (300 mg); sulfosalicylic acid (100 mg); phosphate, tartrate (50 mg each); do not influence the extraction.

Spectral Characteristics: The absorption spectrum of V(III)-benzoylacetone complex in benzene indicates

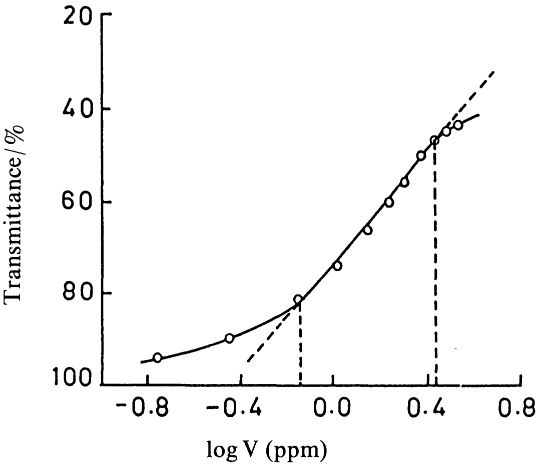

Fig. 2. Ringbom plot for V(III)-benzoylacetone complex.

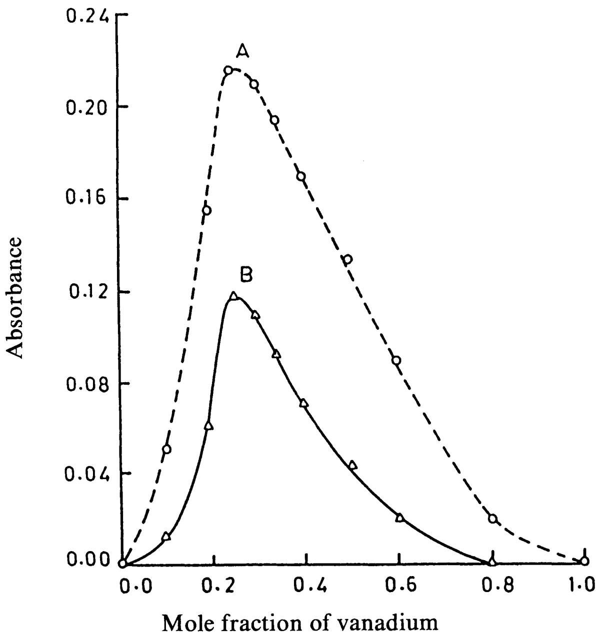

Fig. 3. Continuous variation of vanadium and benzoylacetone.
Conditions: A: Vanadium=1.96×10^{-3} M, Benzoylacetone=1.96×10^{-3} M. B: Vanadium=9.8×10^{-4} M, Benzoylacetone=9.8×10^{-4} M.

Table 2. Analysis of Samples by the Proposed Method

Sr. No.	Sample composition		V found
	Matrix[a]	V added µg	µg
1.	W(1), Cr(2), U(1), Pd(0.2)	20.0	19.95
2.	Fe(1), W(2), Cr(1), Ni(0.2), Rh(0.2)	30.0	29.8
3.	Re(2), Al(2), Zn(2), Mn(2), Bi(0.2)	40.0	39.5
4.	Ag(0.2), Pt(0.2), Ru(0.2), Zr(0.5), Ce(1),Ca(2)	12.0	11.9
5.	Cu(0.2), Se(0.2), As(0.2), Cd(0.2), Mg(2), Be(2)	15.0	14.8
6.	Pb(0.2), Co(0.2), Sb(0.2), Ba(2)	50.0	49.5
7.	[Ni(0.15), Pt(0.05), Pd(0.05)][b]	25.0	25.0
8.	[Fe(1.7), Cr(0.24), Co(0.015)][b]	15.0	15.0
9.	[Fe(2.5), Ni(1), Cr(1), Mn(0.05)][b]	50.0	49.8
10.	High speed steel super rapid extra 500	1.0%[c]	0.95% 0.93%
11.	Ferrovanadium	35%[c]	34.95%
12.	Reverberatory flue dust (250)	18.0	17.8
	Reverberatory flue dust (100)	25.0	24.9

a) Number in brackets indicates the amount of the metal ion in mg. b) Samples Nos. 7, 8, and 9 correspond to palau, crocar, and nichroloy (cast), respectively. c) Reported value.

Table 3. Comparison of the Proposed Method with Some Existing Extractive Separation Procedures Using β-Diketones

Sr. No.	Aqueous conditions	Extractant	Interfering ions	Comments	Reference
1.	V(V), pH 1.1	Acetylacetone: 1-butanol (1 : 1)	W(VI), U(VI), Th(IV), Al(III), Cr(III), Be(II), Cu(II), Mn(II), Ni(II), EDTA, oxalate, tartrate, citrate	Serious interferences, determination not effected	12
2.	V(V), 6 M HCl, Acetylacetone	C_6H_6	Cu(II), Mn(II)	13 metals separated, determination not effected	13
3.	V(V), pH 2.5—4.1	4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione in 1-butanol	W(VI), U(VI), Ti(IV), Fe(III), Sn(II), Cu(II), Mn(II), EDTA	10 metal ions separated, determination effected	14
4.	V(IV), pH 5.0 (adjusted with 0.01 M H_2SO_4 and 0.01 M NH_3 soln)	1,1,1-Trifluoro-4-(2-thienyl)-4-thioxo-2-butanone in CCl_4 -1-butanol mixture	Ce(IV), Zr(IV), Fe(III), Au(III), Al(III), Cd(II), Hg(II), Mn(II), Co(II), Ni(II), Cu(II), Pb(II), Ag(I)	Frequent use of masking agents is necessitated for the removal of several interferences, determination effected	9
5.	V(IV), pH 2.0, Zn metal	Acetylacetone: Chloroform (1 : 1)	Ti(IV), Al(III), Fe(III)	For quantitative extraction, 30 min' equilibration time required, determination not effected	15
6.	V(V), 0.1 M Acetic acid, 1% (w/v) benzoylacetone in acetone, sodium dithionite (solid) (Proposed method)	C_6H_6	Mo(VI)	30 metal ions including Pt-metals separated, simultaneous determination of vanadium effected	Proposed method

that the maxima lies at 390 nm where the absorbance of the reagent blank is negligibly small (Fig. 1). The Bouguer-Lambert-Beer law holds for the vanadium concentration in the range of 0—2.8 $\mu g\ V\ ml.^{-1}$ However, the optimum concentration range with the highest accuracy as evaluated from Ringbom's curve (Fig. 2) is 0.72—2.75 ppm for vanadium. Molar absorptivity, specific absorptivity and Sandell's sensitivity of the system are $5.732\times10^3\ dm^3\,mol^{-1}\,cm^{-1}$, $0.1125\ ml\,g^{-1}\,cm^{-1}$, and $8.88\times10^{-3}\ \mu g\ V\,cm^{-2}$, respectively.

The complex is highly stable whose absorbance remains unchanged for >2.5 h.

Stoichiometry of the Complex: The ratio of the metal ion to benzoylacetone in the extracted species is determined by Job's method[11] of continuous variations by taking their equimolar concentrations (1.96×10^{-3} M, 9.8×10^{-4} M) in two different sets. It is inferred from the curves that the metal to ligand ratio in the complex is 1 : 3 (Fig. 3).

Applications. Benzoylacetone is used for the first time for the analysis of vanadium. The proposed procedure for the extractive separation and determination of vanadium is one of the most selective methods available for vanadium and compares favorably with the existing ones using β-diketones (Table 3) with good sensitivity. The method is quite simple, less time consuming and free from the serious interference of a large number of metal ions generally associated with vanadium in samples including Pt metals, thereby eliminating them altogether before the determination can be had. The usefulness of the method is tested by the satisfactory analysis of a variety of technical samples—high speed steel, ferrovanadium, reverberatory flue dust, and several synthetic samples and the results obtained are quite in agreement with the reported value/amount added initially (Table 2). The method is highly reproducible with a standard deviation of ±0.003.

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References

1) O. Klug and A. Metlenko, *Chem. Anal.,* **10**, 819 (1965); M. Tanaka and I. Kajima, *J. Inorg. Nucl. Chem.,* **29**, 1769 (1967); N. Kurmaiah, D. Satyanarayana, and V.P.R. Rao, *Anal. Chim. Acta,* **35**, 484 (1966).

2) J. Inglot and M. Panz, *Chem. Anal.,* **15**, 965 (1970).

3) M. Ezawa, *Bunseki Kagaku,* **19**, 1026 (1970).

4) D. E. Ryan, *Analyst,* **85**, 569 (1960).

5) H. Bode, *Z. Anal. Chem.,* **144**, 165 (1955).

6) H. Amano, *Sci. Rept. Res. Inst. Tohoku Univ., Ser. A,* **12**, 24 (1960).

7) G. Charlot and D. Bezier, "Quantitative Inorganic Analysis ," London (1957), p. a) 623, b) 305, c) 625.

8) E. B. Sandell, "Colourimetric Determination of Traces of Metals," 3rd ed, Interscience, New York (1959), p. 926.

9) K. R. Solanke and S. M. Khopkar, *Talanta,* **21**, 245 (1974); A. K. De, S. M. Khopkar, and R. A. Chalmers, "Solvent Extraction of Metals," Van Nostrand Reinhold Company, London(1970), p. 64.

10) V. Yatirajam and S.P. Arya, *Talanta,* **23**, 596 (1976).

11) P. Job, *Ann. Chim.,* **9**, 113 (1928).

12) D. Satyanarayana, N. Kurmaiah, and V.P.R. Rao, *Chemist Analyst,* **53**, 78 (1964).

13) D. Satyanarayana and V.P.R. Rao, *Indian J. Technol.,* **2**, 163 (1964).

14) A. K. De and M. S. Rahaman, *Anal. Chem.,* **35**, 1095 (1963); A. Ikehata and T. Shimizu, *Bull. Chem. Soc. Jpn.,* **38**, 1385 (1965).

15) J. P. McKaveney and H. Freiser, *Anal. Chem.,* **30**, 526 (1958).