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Original Scientific Paper

Spectrophotometric Studies on the Vanadium(V)-Chelates with *N*-Arylhydroxamic Acids. A Superior Method for the Extraction and Spectrophotometric Determination of Vanadium in Steels*

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The reaction of 18 *N*-arylhydroxamic acids with V(V) in different acidities and under varying experimental conditions have been investigated. In concentrated HCl an intensely violet chelate of V(V), which is readily extracted into chloroform, is formed. The substitution in the hydroxamic acid functional grouping affects the hue and spectral characteristics of the V(V)-chelates.

It is inferred that *N*-*p*-Cl-phenyl-*p*-methoxybenzohydroxamic acid retains all the useful features of *N*-phenylbenzohydroxamic acid as a reagent for V(V) but surpasses it in sensitivity and selectivity of the reaction.

With this quick method vanadium has been determined in analysed steels without the recourse of masking agents or prior separations. The excellent results obtained on these samples are taken as a proof of the reliability, precision and accuracy of the method.

In recent years, a large number of *N*-arylhydroxamic acids have been examined as reagents for V(V)¹⁻¹¹. Majumdar (5) has reported that *N*-*p*-Cl-phenylbenzohydroxamic acid is a more selective reagent compared to *N*-phenylbenzohydroxamic acid, PBHA, for the spectrophotometric determination of vanadium. Gupta (10) has reported that *N*-*m*-tolyl-*p*-methoxybenzohydroxamic acid is a more sensitive reagent for vanadium. Guided by these observations 16 new hydroxamic acids derived from *N*-*p*-Cl-phenylhydroxylamine were synthesised¹¹ and their complexes with V(V) are examined for possible analytical applications.

EXPERIMENTAL

Reagents

Approximately 0.005 M solutions of *N*-arylhydroxamic acids were prepared in ethanol free chloroform. Ammonium metavanadate was dissolved in distilled water, acidified with a few drops of 10 M sulphuric acid. It was then heated to about 80 °C and treated with a few drops of very dilute potassium permanganate solution until a faint pink colour persisted. Vanadium contents in the solution was

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determined volumetrically¹². The solutions of foreign ions were prepared from Analar grade salts, following the procedure of West¹³.

Apparatus

An EC India, GS 865 spectrophotometer having 10 mm matched quartz cells and calibrated by standard methods was employed for measuring the spectra of coloured extracts using chloroform as a blank.

Colour Reaction

Procedure I — In Aqueous — ethanol, Weakly Acidic Media (pH 1 to 6.5). In a 25 ml volumetric flask, 10 ml of 0.005 M ethanolic hydroxamic acid solution was mixed with 10 ml of 2.5×10^{-4} M V(V) solution. The volume was made up to the mark with ethanol and hydrochloric acid so as to adjust the pH in the range of 1 and 6.5. A mahogany red solution thus obtained fades gradually.

Procedure II — Solvent Extraction, In Weakly Acidic Media (pH = 1 to 6.5). In a separating funnel, 10 ml of V(V) solution was mixed with 10 ml of chloroform solution of hydroxamic acid (instead of ethanolic solution in the same pH ranges). The mahogany red chloroform layer was transferred to a 25 ml volumetric flask.

Procedure III — Solvent Extraction, In Strongly Acidic Media (2 to 10 M HCl). In a separating funnel, 10 ml of V(V) solution was acidified with hydrochloric acid so as to maintain the acidity between 2 M and 10 M and mixed with 10 ml of ethanol free chloroform solution of hydroxamic acid. The contents were vigorously shaken for 30 sec. The coloured organic layer was collected into a volumetric flask.

Procedure IV — Solvent Extraction. In strongly acidic media (2 M H₂SO₄ — 4 M HF). In a separating funnel, 10 ml of V(V) solution was acidified with 2 ml of each concentrated sulphuric and hydrofluoric acids. 10 ml of the chloroform solution of hydroxamic acid was then added and shaken. The red V(V) complex was extracted after 2 min. The aqueous layer was re-extracted with 5, 3 and 3 ml portions of chloroformic hydroxamic acid to ensure complete extraction of vanadium. These extracts were transferred into a 25 ml volumetric flask. The volume was made up to the mark with chloroform.

Solvents

The extraction can be accomplished by a variety of solvents such as chloroform, carbon tetrachloride and benzene. Chloroform being heavier than water, is convenient to handle and extraction being almost instantaneous, is preferred. Small amounts of ethanol affect the absorption spectrum of the extracts. The absorption band registers a hypsochromic and hypochromic effect. The change in colour, position and intensity of the absorption band continues to vary (depending on the quantity of ethanol) until the extracts finally become red and the absorption band is considerably broadened. Presumably, this gradually destroys the violet V(V)-chelates (14).

Procedure for Analysis of Vanadium and its Application in the Analysis of Steel

A suitable weight of the steel turnings was treated with 3 to 4 ml of 12 M Analar sulphuric acid in a tall 400 ml Corning beaker. It was then gently heated until the metal dissolved and black carbon appeared. A few drops of concentrated nitric acid were added from time to time till all the carbon disappeared. The solution was heated to fumes of sulphur trioxide, then cooled and diluted with 10 ml of water. It was then transferred to a 100 ml volumetric flask and was made up to the mark with water.

A suitable aliquot of steel solution was taken in a separating funnel and the volume of aqueous phase was adjusted to about 25 ml by water and hydrochloric acid so as to maintain the acidity around 4 M. Ten ml 0.005 M chloroform solution of N-p-Cl-phenyl-p-methoxybenzohydroxamic acid, CPMBHA, was then added to the funnel and shaken. The organic layer was collected in a 50 ml beaker containing about 1.5 g of anhydrous sodium sulphate to remove tiny water droplets from extracts and then transferred to a 25 ml volumetric flask. The aqueous layer and sodium sulphate crystals were washed free of colour with small portions of chloro-

form and the washings were also transferred to the volumetric flask. Finally the volume was made up to the mark with chloroform, and the absorbance was measured at 540 μm .

RESULTS AND DISCUSSION

The reaction of V(V) with *N*-arylhydroxamic acids in aqueous-ethanol at low acidities forming a mahogany red complex was unsatisfactory for quantitative work, because the full colour develops gradually and is stable for a short time. The results depend on a rigid control of pH.

The use of a water immiscible solvent viz. chloroform (procedure II) improves the stability of the colour system in weakly acidic media, although the value of absorbances and wavelength of maximum absorption are erratic and depend on time. Zharovskii¹⁵ used 0.23 M PBHA solution in ethanol with V(V) at pH = 3. A reddish brown extract in chloroform was measured at 440 nm; $\epsilon = 3600$. Besides, sodium fluoride and phosphoric acid were used as masking agents for Fe(III) and Ti(IV).

At 0.1 to 2 M hydrochloric acid the complex shows variation in colour and the stability of the colour system increases with increasing acidity. In aqueous media at 2 to 10 M hydrochloric acid a bluish violet complex is formed which decomposes in a few sec.

Among the procedures described (Procedure III) the reaction of V(V) with *N*-arylhydroxamic acids employing solvent extraction for the stability of complexes appeared to be most attractive. The method is simple to operate, the formation of a coloured complex is almost instantaneous and stable, permits flexibility in the adjustment of experimental parameters, it is economical and vanadium is determined without the recourse of masking agents or prior separations. The method is superior to the currently favoured phosphotungstate method.

Earlier, using PBHA, Priyadarshini (1) and Ryan⁴ reported that Ti(IV) interferes with this method. Vita¹⁶ extracted V(V) in uranium minerals using 0.01 M chloroformic PBHA in 4 M hydrochloric acid and observed that an excess of chloride ions keeps the uranium in an anionic form. Further, it aids the extraction of V(V). Patrovsky¹⁷ determined small amounts of vanadium in rocks using sulphosalicylic acid and ammonium fluoride as masking agents. Iwasaki¹⁸ used sodium fluoride as a masking agent. Pilkington¹⁹ observed that owing to the higher stability of the Ti(IV)-PBHA complex, it cannot be masked.

The use of the mixture of sulphuric-hydrochloric acid, procedure IV, for the determination of V(V) did not appear to offer any special practical advantage. Although care and precautions were exercised to remove hydrofluoric acid resistant polypropylene separatory funnels also restrained us gradually turned foggy due to the etching action of trace amounts of hydrofluoric acid present in the extracts. The nonavailability of leak proof hydrofluoric acid resistant polypropylene separatory funnels also restrained us from examining this system in detail.

Effect of Substitution

The effects of attaching various substituent groups to the carbon and nitrogen atoms of the hydroxamic acid functional grouping.



are prominently reflected in the spectral characteristics of V(V) chelates (TABLE — I). CPMBHA, out of the 16 new hydroxamic acids, reflected the promising characteristics of bathochromic and hyperchromic effect in V(V) chelate.

TABLE I

Spectral Characteristics of Vanadium(V)-Chelates of N-Arylhydroxamic Acids in Chloroform (From ≈ 4 M HCl)

No.	Hydroxamic Acid	Colour of Extract	λ_{\max} nm	ϵ l mol ⁻¹ cm ⁻¹ ± 50
1.	<i>N-p</i> -Cl-Phenylbenzo-	V	530	4650*
2.	<i>N-p</i> -Cl-Phenyl- <i>o</i> -methylbenzo-	BV	540	4680
3.	<i>N-p</i> -Cl-Phenyl- <i>m</i> -methylbenzo-	V	530	4750
4.	<i>N-p</i> -Cl-Phenyl- <i>p</i> -methylbenzo-	BV	535	4850
5.	<i>N-p</i> -Cl-Phenyl- <i>o</i> -Cl-benzo-	V	525	4480
6.	<i>N-p</i> -Cl-Phenyl- <i>m</i> -Cl-benzo-	V	530	4220
7.	<i>N-p</i> -Cl-Phenyl- <i>p</i> -Cl-benzo-	V	525	4650
8.	<i>N-p</i> -Cl-Phenyl- <i>m</i> -Br-benzo-	V	530	4500
9.	<i>N-p</i> -Cl-Phenyl- <i>p</i> -F-benzo-	V	530	4550
10.	<i>N-p</i> -Cl-Phenyl- <i>m</i> -nitrobenzo-	V	525	3800
11.	<i>N-p</i> -Cl-Phenyl- <i>p</i> -nitrobenzo-	V	525	4340
12.	<i>N-p</i> -Cl-Phenyl- <i>o</i> -methoxybenzo-	BV	545	4600
13.	<i>N-p</i> -Cl-Phenyl- <i>m</i> -methoxybenzo-	BV	535	4650
14.	<i>N-p</i> -Cl-Phenyl- <i>p</i> -methoxybenzo-	BV	540	5350
15.	<i>N-p</i> -Cl-Phenylphenylaceto-	RV	510	4000
16.	<i>N-p</i> -Cl-Phenylphenoxyaceto-	RV	500	3750
17.	<i>N-p</i> -Cl-Phenyl- <i>n</i> -butyro-	RV	510	4100
18.	<i>N</i> -Phenylbenzo-	V	530	4650**

V = Violet; BV = Bluish Violet; RV = Reddish Violet.

* Reported $\epsilon = 4500$ (5),

** Reported $\epsilon = 4650$; $\lambda_{\max} = 510$ nm (1),
 $\epsilon = 4490$; $\lambda_{\max} = 530$ nm (4).

Acidity

The absorption band of the chloroform extracts remained intact and the maximum colour development took place while the acidity of the aqueous phase was maintained between 2.5 M and 9 M hydrochloric acid. Absorbance measurements revealed that all the chloroform extracts showed a broad band, the sides of band being symmetrical. This evidently suggested that only one complex was formed.

Concentrated nitric acid oxidises the hydroxamic acid imparting brown extracts in chloroform. Dilute nitric acid, however has no deleterious action. Concentrated sulphuric acid yields golden yellow extracts with hydroxamic acids in chloroform, while with dilute sulphuric acid the extraction is both small and slow. The red extracts formed in acetic acid are unstable and turn violet on the addition of hydrochloric acid. The presence of nitric, acetic, phosphoric and sulphuric acids were tolerated if their concentrations in the aqueous phase were kept less than 1 M.

Mole Ratio of Vanadium to Ligand: A 1 : 10 mole ratio of vanadium to ligand ensures the maximum colour development. In practice, for each mg of vanadium nearly 80 mg of ligand was used.

Effect of Variables: Varying the volume of aqueous phase from 5 ml to 75 ml gave concurrent readings. The order in which the reagents were mixed was not critical. The ionic strength of the aqueous phase when varied from 3 to 7 g mole⁻¹ with hydrochloric acid and potassium chloride, caused no difficulty. The temperature of the aqueous phase between 10 and 40 °C did not produce any measurable change.

Beer's Law: A plot of absorbance against vanadium concentration gives a straight line showing that Beer's law is valid between 26 µg and 270 µg in 25 ml of chloroform at 540 nm with CPMBHA. The practical range of vanadium determination by this method is computed to be 1.9 to 6.6 ppm of metal. In a typical measurement, the coefficient of variation was found to be 0.65%.

Divers Ions: In the determination of V(V) with CPMBHA Al(III), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Th(IV), Zn(II), Ca(II), Sr(II), Ba(II), Mg(II), Cd(II), Hg(II), UO₂(II), fluoride, tartrate, oxalate, citrate, borate, acetate, phosphate, nitrate, perchlorate, sulphate and EDTA do not interfere even at the level of 0.1 mg of vanadium and 20 mg of foreign ions. Reducing agents, like Fe(II) which reduces V(V) to its lower oxidation states do interfere. Tungstate ions yield a precipitate on addition of hydrochloric acid and it is removed before the extraction of V(V). Mo(VI) and Zr(IV) interfered with the procedure. Ti(IV) is tolerated up to the weight ratio of 20 times.

The results obtained for the British Chemical Standard samples of steels (TABLE — II) are in an excellent agreement with certificate values. This establishes the reliability, precision and accuracy of this newly developed quick method for vanadium with CPMBHA without the recourse of masking agents or prior separations.

TABLE II
Determination of Vanadium in B. C. S. Steels with CPMBHA

B. C. S. Steels	Vanadium % of Certified	Weight of steel mg*	% of Vanadium found
Cr — V Alloy No. 224	0.24 ₂	402.0	0.24 ₀
Low Alloy No. 252	0.46 ₀	201.0	0.46 ₂
Low Alloy No. 256	0.36 ₀ 0.36 ₀	342.2 342.4	0.36 ₂ 0.35 ₉

* Sample solution was made up to 100 ml and 5 to 10 ml aliquots used for analysis.

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SAŽETAK

Spektrofotometrijsko ispitivanje vanadij(V) helata sa N-arilhidroksam kiselinama. — Poboljšana metoda za spektrofotometrijsko određivanje vanadija u čelicima

D. R. Agrawal i S. G. Tandon

Studirane su reakcije V(V) sa 18 N-arilhidroksam kiselinama uz različite eksperimentalne uvjete. U koncentriranoj HCl stvara se V(V) helat intenzivno ljubičaste boje, koji se brzo ekstrahira sa kloroformom. Zamjena funkcionalnih grupa hidroksam kiselina utječe na spektralne karakteristike V(V) helata.

Ustanovljeno je da je N-p-Cl-fenil-p-metoksibenzohidroksam kiselina, kao reagens za određivanje V(V), selektivnija i osjetljivija od N-fenilbenzohidroksam kiseline.

Ovom brzom metodom određen je vanadij u BCS analiziranim uzorcima čelika bez upotrebe maskirajućih agensa ili prethodnog odjeljivanja. Odlični rezultati dobiveni na tim uzorcima dokaz su pouzdanosti, preciznosti i točnosti predložene metode.

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