

Aromatic carboxylic acids as extraction system for vanadium in the presence of N-hydroxy-N,N'-diarylbenzamidine

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Abstract. The aromatic carboxylic acids have been used as extractants for micro-gram amounts of vanadium in the presence of N-hydroxy-N-*p*-chlorophenyl-N'-(2-methyl-5-chloro) phenyl-*p*-toluamidine hydrochloride (HCPMCPTH). The validity of the method has been tested by accurately analysing the vanadium content of the standard steel samples.

Keywords. Aromatic carboxylic acids; solvent extraction; V(V)-HCPMCPTH chelate.

1. Introduction

N-hydroxy-N,N'-diarylbenzamidines have been used in the gravimetric determination (Patel and Mishra 1978; Satyanarayana and Mishra 1975; Kharsan and Mishra 1979) of copper(II), nickel(II) and molybdenum(VI), and spectrophotometric determination (Patel and Mishra 1978; Satyanarayana and Mishra 1976, 1974) of manganese(II), iron(III) and vanadium(V). In earlier papers, the solvent extraction and spectrophotometric determination of vanadium(V) with hydroxyamidines in the presence of aliphatic carboxylic acids (Patel *et al* 1979), phenols (Kharsan *et al* 1979a; Patel and Mishra 1979), aldehydes (Kharsan *et al* 1979b) thiocyanate and azide (Kharsan *et al* 1979b) have been described. The present investigation clarifies the use of aromatic carboxylic acids as modifier for the determination of vanadium(V) in the presence of N-hydroxy-N-*p*-chlorophenyl-N'-(2-methyl-5-chloro) phenyl-*p*-toluamidine hydrochloride. Carboxylic acids have been found as an adductant in the extraction mechanism of vanadium(V) like other monobasic and bidentate chelating agents (Kojima and Miwa 1976). This method has an advantage over the existing PBHA methods (Goto and Kakita 1961; Majumdar 1972; Priyadarshini and Tandon 1961; Shendrikar 1969; Vita *et al* 1968) that W(VI), Mo(VI), Ti(IV), Zr(IV), Cr(III), and Mn(II) do not interfere and hence there is no possibility of reduction of vanadium(V). Besides, the rate of extraction and molar absorbance is high as compared to aliphatic acid system (Patel *et al* 1979).

The object of this study is the spectrophotometric determination of vanadium (V) with benzoic, chlorobenzoic, salicylic and phthalic acid and their derivatives in which -COOH group is retained. The various optimisation constants and composition of the mixed chelates have been described.

2. Experimental

A Carl-Zeiss specord recording ultraviolet spectrophotometer and an ECIL UV-VIS spectrophotometer model GS-865 with 1 cm matched silica and quartz cuvettes were employed for all photometric measurements. A Systronics pH meter type-322 was employed for the pH determination. A stock solution of vanadium(V) was prepared by dissolving an AnalaR quality of ammonium metavanadate in distilled water. The vanadium content of the solution was determined volumetrically (Charlot and Bezier 1957). N-Hydroxy-N-*p*-chlorophenyl-N'-(2-methyl-5-chloro)-phenyl-*p*-toluamidine hydrochloride was prepared by the condensation of equimolar ratio of N-(2-methyl-5-chloro)phenyl-*p*-toluimidoyl chloride and N-*p*-chloro-phenylhydroylamine in ether medium (Satyanarayana and Mishra 1974). A chloroform solution of reagent and carboxylic acids (0.1 and 1.0% W/V) was employed.

2.1. Procedure

An aliquot of the solution containing 100 μg of vanadium(V) was transferred to a 100 ml separatory funnel. The volume of the solution was adjusted to about 25 ml. The pH range was adjusted to 2.0 with 2M HCl and dilute ammonia. The solution was stirred for 2 min with 10 ml chloroform solution of reagent and aromatic carboxylic acids (5 ml each). The chloroform extracts were then dried over anhydrous sodium sulphate. The aqueous phase was washed twice with 4 ml portions of chloroform and all the extracts combined into the same volumetric flask and made up to 25 ml. The absorbance was read against chloroform as a blank.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of vanadium(V)-hydroxyamidine complex in the presence and absence of carboxylic acids were studied. The hydroxyamidine showed negligible absorption in the region 450–700 nm. The vanadium(V)-hydroxyamidine complex in the absence of carboxylic acids (at pH 3.0) showed a flat λ_{max} in the region 560–580 nm (ϵ : 700 l. mol⁻¹ cm⁻¹). However, in the presence of carboxylic acids, stable blue-violet ternary complexes are formed (ϵ : 4200–5600 l. mol⁻¹ cm⁻¹) at λ_{max} in the region 575–580 nm.

3.2. Effect of experimental variables

Of the various water immiscible organic solvents tried, chloroform was found to be the best solvent for extraction because of its high solubility and extraction properties,

At least 4 and 250-fold molar excess of hydroxyamidine and carboxylic acids respectively was necessary for full colour development. Addition of more reagents (hydroxyamidine upto 100 and carboxylic acid upto 2000-fold molar excess) causes no additional effect. Order of addition of reagents is not critical.

No adverse effect was observed on the absorbance of the coloured system when the ionic strength of the aqueous phase was adjusted between 1 and 3 M either with NaCl or KCl.

Variation in temperature of the aqueous phase from 20–40° and the volume of the aqueous phase from 10–60 ml did not produce any adverse effect in the absorbance of the chloroform extracts. The chloroform extracts were stable for at least 30 hr at 27 ± 2°.

3.3. Effect of structure of carboxylic acids

The effect of carboxylic acids on the extraction of vanadium(V)-hydroxyamidine complex is shown in table 1. A hyper- and bathochromic shift of complex is observed due to adduct formation in chloroform. A high molar absorbance of adduct is seen by the introduction of –COOH, –OH or –Cl group into benzoic acid nucleus, which may be due to the –I effect and high conjugation of adductant. A period of 1–2 min is sufficient for complete extraction of vanadium(V) complexes. The rate of extraction is dependent on the nature of carboxylic acid used and shows a decreasing trend :

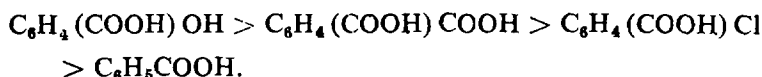


Table 1. Spectral characteristics of vanadium(V)-HCPMCPH-HOOCR coloured system in chloroform.

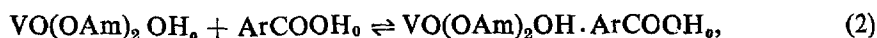
Acid	Approximate pH ranges	Optimum concentration ranges from Beer's law (Ringbom Plot) ppm, V	λ_{max} nm	ϵ	Sandell's sensitivity $\mu\text{g V/cm}^2$	Relative* standard deviation %
				1. mol ⁻¹ cm ⁻¹		
Benzoic	0.8–5.1	1.5–8.8 (1.8–8.4)	575	4200	0.0120	±0.77
<i>o</i> -Chlorobenzoic	1.0–4.8	1.0–8.2 (1.4–8.0)	575	5100	0.0100	±0.72
<i>p</i> -Chlorobenzoic	1.2–5.0	1.0–8.4 (1.6–8.0)	580	4800	0.0105	±0.58
Salicylic	0.8–5.5	1.0–8.8 (1.2–8.4)	575	5500	0.0095	±0.61
Acetylsalicylic	1.0–5.0	1.0–9.0 (1.2–8.4)	580	5600	0.0091	±0.55
Phthalic	1.5–4.2	1.0–8.0 (1.6–7.8)	580	5100	0.0100	±0.82

* 10 measurements are made (each containing 100 $\mu\text{g V/25 ml}$).

3.4. Composition

The ratio of vanadium(V) to hydroxyamidine was determined by Job's method (Job 1928) and the mole ratio method (Yoe and Jones 1944) and vanadium(V) to carboxylic acid by curve fitting method (Sillen 1956). The results obtained indicate the formation of 1 : 2 : 1 [vanadium(V) : hydroxyamidine : carboxylic acid].

Hydroxyamidine reacts with vanadium(V) giving a 1 : 2, VO(OAm)₂OH complex analogous to other monobasic and bidentate chelating extractants (Kojima and Miwa 1976; Kojima and Tanaka 1975). The basic V=O group of complex reacts with carboxylic acid to give a 1 : 1 adduct. The reaction mechanism is illustrated by the following equations :



where, HOAm = hydroxyamidine; ArCOOH = aromatic carboxylic acid and *o* = organic phase.

3.5. Diverse ions

The effect of diverse ions was studied using 100 μg of vanadium(V) in the presence of acetylsalicylic acid. Elements like chloride, bromide, nitrate, sulphate, phosphate, selenate, borate, urea, thiourea, triethanolamine, alkali and alkaline-earth elements and lanthanide did not interfere up to 2000 ppm. The tolerated amount of other ions was considered to be that amount given an error less than 0.3% and shown in parenthesis : Fe(III) (in the presence of trisodium phosphate), Ni(II), Co(II) (800); Zn(II), Pb(II), Tl(III), Al(III), oxalate, citrate, tartrate (600); Th(IV) (800); Mn(II), Hg(II) (500); Cr(III) (300); Cu(II) (100); Ti(IV) (50); Zr(IV) (80); W(VI) (30); Mo(VI) (200); U(VI) (400); arsenate (700).

3.6. Application of the method

The standard steel sample containing approximately 1 mg of vanadium was dissolved using 40% nitric acid. Tungsten was removed in the form of tungstic

Table 2. Determination of vanadium in steel.

Sample	Vanadium* found %	Vanadium certified value %	S
64a Alloy steel	1.554	1.57	±0.0102
241/1 High speed steel	1.562	1.57	±0.0092
252 Low alloy steel	0.448	0.46	±0.0096

* An average of 6 determinations.

oxide. The filtrate was diluted in a 100 ml volumetric flask. The vanadium content was determined as shown in table 2.

4. Conclusion

The proposed method is selective and sensitive, based on the solvent extraction of vanadium(V) as $\text{VO}(\text{OAm})_2\text{OH} \cdot \text{HOOCR}$ adduct in chloroform. The carboxylic acid can be used as modifier to enhance the distribution coefficient of $\text{VO}(\text{OAm})_2\text{OH}$ complex. The optical properties of adduct depend on the nature of carboxylic acids used.

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