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 TECHNOLOGY**
**SELECTIVE EXTRACTION AND SPECTROPHOTOMETRIC
 DETERMINATION OF VANADIUM (V) AS MIXED LIGAND COMPLEX WITH N-
 HYDROXY- N (2-METHYL) PHENYL N' (4-FLUORO) PHENYLEXNZAMIDINE
 HYROCHLORIDE AND THIOCYANNATE**
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ABSTRACT

A novel extraction spectrophotometric method has been proposed for the determination of vanadium (v) using N-Hydroxyl-N-(2-Methyl) N'-(4-flouro) phenyl benza-amidinehydrochloride and thiocyanate HMPFBH reacts with vanadium in acidic medium to form 1:2 (metal ligand) blue-violet complex in chloroform. The absorption spectra consist of a flat peak in the range of 550-590 nm with molar absorbance 700 ± 20 mole⁻¹ cm⁻¹ when thiocyanate is added to this solution a marked increase in wave length of maximum absorbance is observed. On this basis a simple rapid and sensitive method has been developed for the determination of microgram quantities of vanadium in alloy steels. The ternary complex V(v) HMPFBH-SCN-absorbs strongly at 590nm with molar absorbance 6114 mole⁻¹cm⁻¹ and sandell sensitivity 8.34×10^{-3}

The system obeys Beer's law in the range 1.6 pH to 3.2 pH. Ions like Cl⁻, SO₄²⁻, F⁻ etc. Fe²⁺, C₄H₂⁺, CO₂⁺, Ni²⁺ do not interfere in the determination. The method has been applied for the determination of vanadium in steel sample.

KEYWORDS: Solvent Extraction, Mixed ligand Complex, Vanadium, Spectrophotometer, Absorbance, Sandell's sensitivity.

I. INTRODUCTION

The toxic effect of vanadium and its compounds is considered to be similar as that of lead and mercury. These effects are due to industrial exposure to vanadium compounds are followed by different ailments in man such as bronchitis, pneumonia, irritation of mucous membrane, gastro intestinal and nervous disorders¹⁻⁶. Talvite⁷ estimated vanadium in biological sample with 8 hydroxyl quinolone N-benzoylphenyl hydroxylamine and its analogies are ardely used as reagents for vanadium but Donaldson⁸ claims that low and erratic results are obtained by these methods.

Many monobasic and bidentate chelating agents react with vanadium form 1:2 (metal: reagent) complex having a basic V=O group and acidic V=OH group in the same molecule. The basic group reacts with acidic substances to give a hyper and bathochromic effect while the acidic group reacts with basic substances. To give a hyper and Hypsochromic effect coloured mixed and the anion⁹⁻¹⁵

N-hydroxy-N-(2-methyl)phenyl N'(4-flouro) phenyl benzamidine hydrochloride reacts with vanadium to form blue-violet 1:2 (metal: ligand) complex in chloroform. These complexes absorb in the region 550-590 nm having low absorbance value. In presence of complexing agent like thiocyanate, the wave-length of this coloured species shift to longer wave-length with an increase in absorbance value at λ max. on the basis of strong synergism which is attributed to 1:2:2 (metal: reagent : thiocyanate) mixed complex formation, for solvent extraction and spectrophotometric determination of microgram amounts of Vanadium (v) has been developed. This method is suitable for accurate determination of vanadium in standard steel samples.

II. EXPERIMENTAL

Apparatus

A CARL Zeiss Zena spectrometer spekol was used for colorimetric determination of the complex. The pH values were determined with a systronic pH meter type 321.

Standard Vanadium solution

Vanadium (v) stock solution containing approximately 0.05 mg vanadium per ml was prepared by dissolving B.D.H. Analar grade ammonium meta vanadate in doubly distilled water. The vanadium content of this solution was determined volumetrically using potassium permagnet¹⁶ from this stock solutions, a solution containing 20 ug vanadium (v) ml⁻¹ was prepared.

Chloroform

Commercial chloroform was washed five or six times with half its volume of distilled water & dried over fused calcium chloride.

Reagent Solution

A 0.3% solution of HMPFBH in chloroform was employed for extraction work. This was stable for several weeks when kept in amber coloured bottles.

A 2% aqueous solution of ammonium thiocyanate were prepared and used for colour development.

Colour Reaction

The hydroxyamidine synthesised in this investigation react with vanadium (v), in the presence of thiocyanate to form 1:1:2 greenish blue adduct extractable into chloroform over the wide pH range. The colour are stable for over 24 hrs. at room temperature & follow Beer's Law.

Procedure-

Take a solution containing 100 µg of vanadium (v) in 125 ml separatory funnel, add 5 ml of Ammonium thiocyanate solution and bring the total volume of aqueous phase to 15 ml adjusting the pH 1.0 to 3.2 with HCL or ammonia. Introduce 10 ml chloroform solution of the reagent and shake vigorously for 2 min. separate the chloroform layer in a 50 ml beaker. Wash the aqueous phase with 2×4 ml. portion of chloroform and add the washing to the contents of the beaker. Dry the combined extract into a 25 ml standard flask and make up to volume with chloroform. Measure the absorbance at wavelength of maximum absorption (590 nm) against chloroform as a blank

III. RESULT AND DISCUSSION

Choice of solvent for extraction

Various water immiscible organic solvents were tried to accomplish the extraction of vanadium mixed complexes. Benzene, toluene, CCl₄, chlorobenzene. Chloroform were found suitable where alcohols & esters were unsuitable for extraction work as the mixed chelator were unstable & less sensitive.

Chloroform was found to be most satisfactory because HMPFBH is more soluble in it. The vanadium complex are more readily extractable in this solvent more over this solvent also offers various advantages over other such as its cheapness, easy recovery and handling effect of pH

The pH adjustments were done with 2M found unsuitable for extraction work and colour development optimum pH range is 1.0 to 3.2.

Effect of HMPFBH

The effect of amount of HMPFBH was studied by taking fixed amount of vanadium (v) and constant excess of thiocyanate, keeping other variable constant A 8 fold molar ratio of HMPFBH to vanadium was adequate for complete extraction of mixed complexes with thiocyanate. Addition of excess reagent up to 100 fold molar excess caused no adverse effect on the λ max employed for extraction works.

Effect of thiocyanate

The effect of thiocyanate on extraction of fixed amount of vanadium was examined at 0.03 M concentration of HMPFBH in chloroform keeping other variable constant. The thiocyanate for complete extraction of vanadium (v)^{17,18}

Volume and concentration of aqueous phase

The volume of aqueous phase could be varied 10 ml to 50 ml without any change in absorbance values of the coloured systems. In practice the volume of the aqueous phase was always adjusted to 25 ml as it is desirable to work with equal volume. Variation of temperature from 20-40^o in aqueous phase did not affect the absorbance.

Effect of electrolytes

The distribution ratio of the mixed complexes are high hence the rate of extraction and absorbance values were not affected by electrolytes such as NH₄Cl, NaCl&KCl (up to 3.0 m)

Extraction time and stability of colour

The period of shaking was varied from 0.5 to 60 min. The extraction was found to be quantitative within 1-3 min. The coloured system were stable for 24 h at room temp.

Adherence to Beer's law

The vanadium (v) HMPFBH-SCN⁻ complex follows Beer's law in the range 1.6 to 7.0 ppm. Sandell¹⁴ recommends an optimum range of 0.2 to 0.7 units of absorbance measurement.

Molar absorptivity and sensitivity

The optimum concentration range is from 1.6 to 7.0 ppm. The effective molar absorptivity of thiocyanate is 6.114×10^{-3} (0.00834) ug of vanadium (v) per cm²

Precision

The absorbance value of 10 samples, each containing 100 ug of metal in final volume of 25 ml was measured the result indicate that the method is precise and reproducible.

Effect of diverse ions

To study the effect of diverse ions on the procedure a fixed amount of vanadium (4ppm) was mixed with known quantity of ion under study and the pH of the solution was kept 1.0 to 3.2 The interference due Fe³⁺& Cu²⁺ could be eliminated by masking with trisodium phosphate and thiourea respectively. Mo (v) gave chloroform soluble yellow complex with reagent and had no interfering effect.

Application of the method-:The proposed method has been applied accurately and precisely for determining vanadium contents in standard samples of steel.

Name of steel alloy	<i>Table Determination of vanadium in BSC *steel.</i>		certified value
	Vanadium found	Average	
241/1 Alloy steel	1.560, 1.550 1.548, 1.552 1.568	1.555	1.570
64Alloy steel	1.58, 1.56 1.56, 1.55 1.64	1.57	1.570
252 low Alloy steel	0.456, 0.468 0.450, 0.454 0.468	0.459	0.460

Obtained from Bureau of Analysed sample Ltd
Newhan Hall Middlebrough Newyorks.

IV. COMPARISON WITH OTHER METHODS

The reagents and methods employed for spectrophotometric determination of vanadium (v) has been recently reviewed by G. Svehla and G.Tolg¹⁹ Benzohydroxamic and N'Benzoylphenyl hydroxylamine²⁰, 8 hydroxiquinoline etc. have been recommended. It suffers from the interference of iron & other elements such as chromium, manganese. Copper, cobalt, Nickel etc. which are associated with vanadium in its ores & alloys.

V. CONCLUSION

Simple, rapid, sensitive and selective method has been developed for extraction spectrophotometric determination of vanadium (v) with N-hydroxy-N-(2-methyl) phenyl N' (4-fluoro) phenyl benzamidine hydrochloride and thiocyanate. The coloured mixed complexes are extractable into chloroform. This method have been applied to determine the vanadium contents of BCS steel samples Mo(vi), W(vi), Nb(V), Ta(v), Zr(IV), Al(III), Cr(III), Ni(II), Co(II), Mn(II) etc. Associated with vanadium in its ores and alloys.

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