EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM WITH ANTHRANILIC ACID IN PRESENCE OF PYRIDINE

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Abstract

Vanadium (III) gives a greenish- yellow complex with anthranilic acid in presence of pyridine. The complex is extractable with chloroform and is used for photometric determination of vanadium by measuring the absorbance at 390 nm against a reagent blank. Beer's Law holds good in the range of 1-20 μg V/ml. Moderate amounts of Pb (II), Ca (II), Sr (II), Ba (II), Cd (II), Mg (II), Mn (II), Ni (II), Co (II), Cu (II), Zn (II) and limited amounts of W (VI), Al (III), Th (IV), Zr (IV), Sn (II), Sb (III), Ti (IV), Fe (III), and Cr (VI) can be tolerated. U (VI) and Mo (VI) interfere.

Introduction

Vanadium occurs in a variety of natural samples [1-3] and in synthetic alloys [3-5]. A selective and sensitive method will be useful for the analysis of such samples. A large number of methods are available in the literature for the spectrophotometric determination of vanadium but only a few of them are satisfactory as far as their sensitivity and selectivity are concerned. One of the methods for enhancing the selectivity of a reaction is to change the oxidation state either of the element under investigation or of the interfering ions. Accordingly, vanadium (V) is reduced to vanadium (III) by dithionite addition to the neutral or slightly acidic solution and is complexed with anthranilic acid and pyridine that forms the basis for the extractive spectrophotometric determination of vanadium as presented here.

Experimental Section

Reagents and Solutions: A stock solution of vanadium (V) (10 mg ml^{-1}) was prepared from sodium metavandate, standardised by titrating with iron (II) [6]. The stock solution was further diluted to give a solution containing 100 μg V/ml. Anthranilic acid solution was prepared in acetone (4%, w/v). Solutions of other elements were prepared by dissolving their soluble salts in water or hydrochloric acid.

Absorbance was measured with Perkin - Elmer 550S Spectrophotometer using 1 cm glass cells.

Determination procedure: To the sample solution containing $\leqslant$ 500 μg vanadium at pH 5-8 taken in a 150-ml separatory funnel, 0.4- 0.6 g of sodium dithionite was added. The final volume of aqueous phase was made to 20 ml including the volume of pyridine and anthranilic acid to be added after reduction. After stoppering the funnel, the contents were shaken for 1 min. After adding 1 ml of anthranilic acid and 0.5 ml of pyridine, the complex was extracted twice with 10 ml of chloroform each time shaking for 1 min. The combined extract was taken into a 25 ml measuring flask (kept in ice cold water if the temperature exceeds 20°C) and the volume was made up to the mark with chloroform. After adding 0.5- 1.0 g of anhydrous sodium sulphate, the absorbance of the greenish- yellow complex was measured at 390 nm against a similarly treated reagent blank. Vanadium content was determined from a standard calibration curve prepared by taking different quantities of vanadium.

Results and Discussion

Vanadium (V) is reduced to vanadium (III) by dithionite [7] addition to slightly acidic or alkaline solution. Anthranilic acid forms a complex with vanadium (III) which gives a colourless extract on

Key words: Anthranilic acid, Pyridine, Chloroform

shaking with chloroform. However in presence of pyridine, a greenish- yellow extract is obtained whose absorption spectrum is shown in Fig. 1. The complex shows a band at 370 nm where the reagent blank also absorbs strongly. However, the absorbance of the reagent blank drops quickly and becomes very small beyond 390 nm where the absorbance measurements are made.

Effect of variables The effect of various parameters on the absorbance of the complex is shown in Table 1. Unless varied as shown in Table 1, for these studies 20ml of aqueous phase containing 25 μg V/ml at pH 5-8, 0.4 g of dithionite, 0.5 ml of pyridine and 1 ml of anthranilic acid is extracted twice with 10 ml of chloroform. In each case the solution is shaken for 1 min. after adding dithionite. Effect of initial pH [1-11] of the aqueous solution on the extraction of the complex was studied. Extraction increases with the increase in pH up to 5 where it is maximum and remains constant in the range of 5-8, but it is found to decrease with the further increase in pH beyond pH 8. On the basis of these studies, the optimum conditions for maximum absorbance are: initial pH 5-8 of the aqueous phase, reduction with 0.4- 0.6 g of sodium dithionite, 1-6 ml of

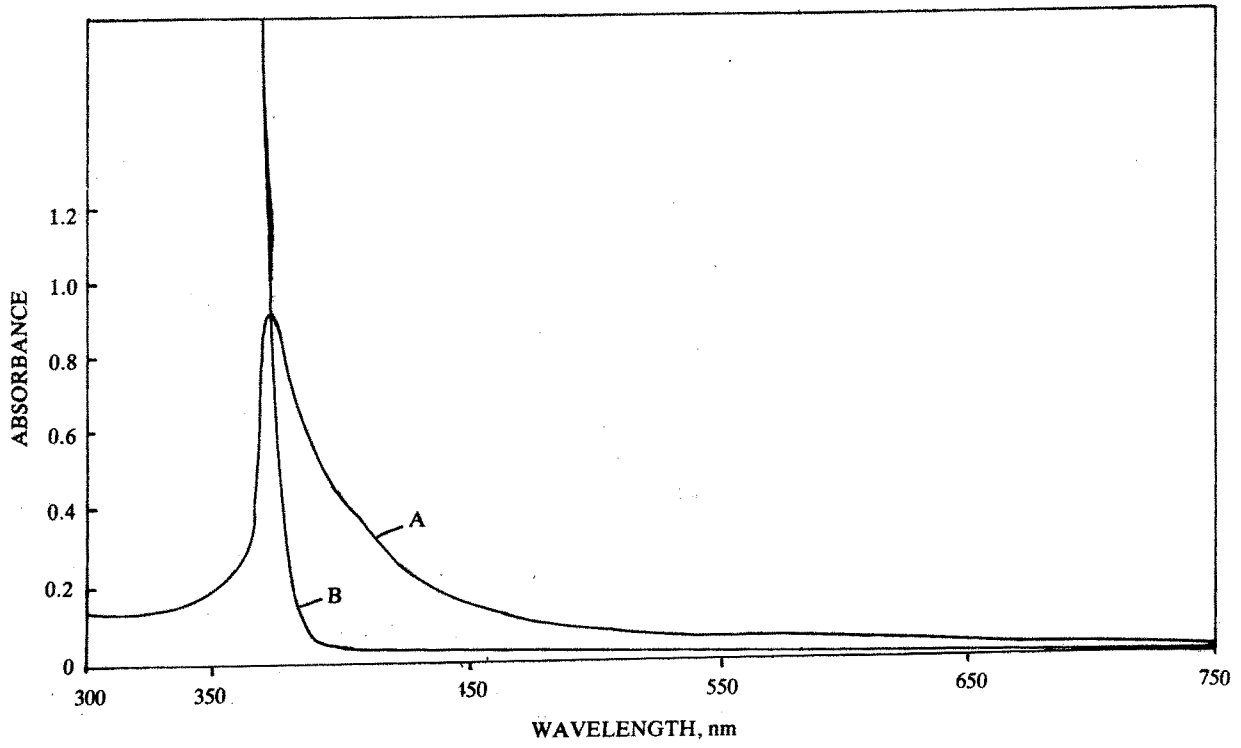

Fig. 1. ABSORPTION SPECTRUM OF V (III)- PYRIDINE-ANTHRANILATE COMPLEX IN CHLOROFORM A-20μg V/ml W.R.T. REAGENT BLANK, B- REAGENT BLANK W.R.T. CHLOROFORM

anthranilic acid (4% in acetone), 0.5- 1.0 ml of pyridine, one min. shaking time after adding dithionite and two extractions with 10 ml of chloroform with equilibraton time 1-5 min.

Extraction into different solvents The complex is extractable into different solvents viz. chloroform, benzene, ethyl acetate, iso- amyl alcohol, methyl isobutyl ketone, butanol and carbon tetrachloride, the absorbance decreases in that order. The absorption spectra of the complex in different solvents is shown in Fig. 2. Among the solvents tested chloroform is found to be the most suitable solvent giving maximum absorbance. Benzene is equally good but with slightly lower absorbance.

The complex is stable for 45 min. up to 20°C but the instability of the complex increases with the increase in temperature. However, the stability of the complex can be maintained if the flask containing the extracted phase is kept in ice- cold water. Beer's law is obeyed in the range 1-20 $\mu g\ ml^{-1}$ with a Sandell sensitivity of 0.038 $\mu g\ V\ cm^{-2}$.

Composition of the complex Job's method of continuous variations [8] was used for determination of nature of the complex. The molar ratio of vanadium to

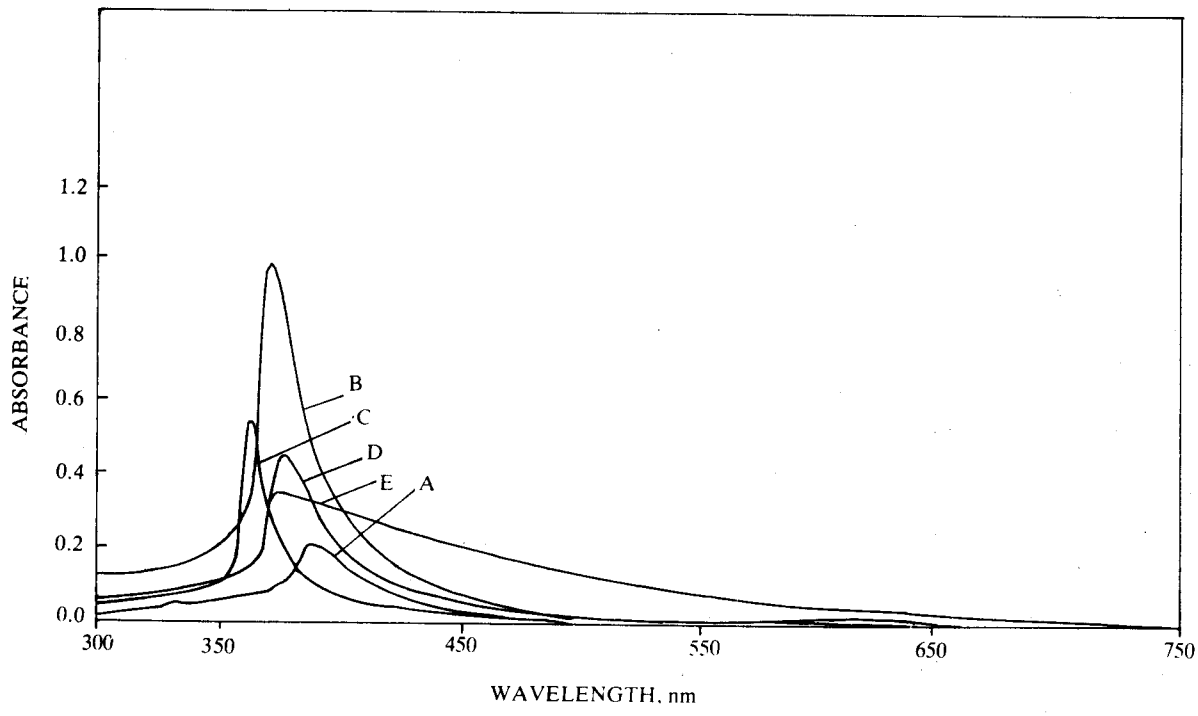

Fig. 2. ABSORPTION SPECTRA OF V (III)- PYRIDINE-ANTHRANILATE IN VARIOUS SOLVENTS W.R.T. REAGENT BLANK V- 20 μg ml: A- iso- AMYL ALCOHOL: B- BENZENE; C- CARBON TETRACHLORIDE: D- ETHYL ACETATE; E- METHYL ISOBUTYL KETONE

Table 1:Effect of various parameters on the absorbance of V(III)- pyridine- anthranilic acid complex.

Dithionite*, g	0.1	0.2	0.3	0.4-0.6	1.0	1.2
Absorbance	0.196	0.425	0.501	0.536	0.510	0.314
Anthranilic acid, ml (4% in acetone)	0.1	0.2	0.5	0.7	1.0-6.0	7.0
Absorbance	0.073	0.241	0.381	0.489	0.536	turbid
Pyridine: ml	0.1	0.2	0.3	0.5-1.0	1.2	
Absorbance	0.318	0.461	0.510	0.536	turbid	
Equilibration time, min	0.15	0.5	1.0-5.0		8.0	
Absorbance	0.425	0.462	0.536		0.510	

25 μg V/ml of aqueous phase.
* Shaken for one min. after adding the reductant

anthranilic acid in the complex was found to be 1:3.

Effect of diverse ions The effect of various anions and complexing agents was studied on the extractive determination of vanadium. There is a slight decrease in absorbance in the presence of chloride and sulphate but no such decrease is observed in the presence of chloride (1 g) if the chloroform is shaken beforehand with 2M sodium chloride solution. 0.1 g each of tartrate and acetate can be tolerated. Thiourea enhances the absorbance. EDTA, sulphosalicylic acid and ascorbic acid considerably decrease the absorbance while triethanolamine, oxalate and phosphate almost completely mask the extraction of vanadium.

On reduction with sodium dithionite at pH 5-8 copper, mercury and lead give coloured precipitates of their sulphides while calcium, strontium and barium give white precipitates which need not be filtered off. The addition of 100 mg of sodium tartrate, before dithionite reduction to the solutions of thorium, zirconium, titanium, tin, antimony, bismuth and aluminium prevent the hydrolysis of these ions which otherwise form precipitates and lead to emulsion formation on shaking with chloroform. Iron (III) gets extracted giving brownish extract. However, iron (II) produced by dithionite reduction gives colourless extract and its reoxidation is prevented by the passage of carbon dioxide for 2-3 min. through the solution and by the addition of sodium tartrate. The extraction behaviour of the various elements under the conditions of procedure was studied and most of the important elements are not extracted. However, presence of iron, tungsten, aluminium, zinc, chromium, nickel, cerium and manganese decrease the extraction of vanadium and thereby their tolerance limits get decreased. This can be improved by adding 3-4 times the amount of anthranilic acid prescribed in the method and in the case of tungsten also sodium tartrate to the just alkaline sample solution. Under these conditions, the tolerance limit of these ions in 20 ml solution are: 10 mg each of Pb (II), Ca (II), Sr (II), Ba (II), Cd (II), Be (II) and Mg (II); 4 mg each of Ni (II), Co (II), Cu (II), Hg (II), Zn (II), Mn (II), Ag (I) and La (III); 2 mg each of W (VI), Pt (IV), Al (III), Th (IV) and Zr (IV); 1 mg each of Sn (II), Sb (III) and Bi (III); 0.5 mg of Ti (IV); 0.2 mg each of Cr (VI) and Fe (III). Mo (VI) and U (VI) interfere.

Comparison with other methods Among all the reagents available for the detection and determination of vanadium, N- benzoyl- N- phenylhydroxyl- amine (BPHA) and its analogues are considered excellent reagents. Many methods have been reported for spectrophotometric determination of vanadium with BPHA and its analogues [9]. But it has been pointed out [10- 11] that the extraction is not quantitative, because of the partial reduction of vanadium (V) in relatively concentrated hydrochloric acid medium, which causes a negative error in the determination of vanadium (V). A comparison of the proposed method with some of the existing methods of vanadium determination using different reagents including N- p-octyloxybenzoyl- N- phenylhydroxylamine is shown in Table 3. As indicated in the table, the proposed method has better selectivity and a wider Beer's Law range apart from other advantages such as simplicity and rapidity of method.

Applications The proposed method using vanadium

(III)- pyridine anthranilic acid complex is quite selective as analytically important metal ions such as Cr (VI, III), Mn (II), Fe (II, III), Co (II), NI (II), Cu (II), Zn (II), Al (III), W (VI), Zr (IV) and Th (IV) do not interfere. It makes use of ordinary and easily available reagents and takes about 15 min. for a single determination. The method can be utilised in the analysis of synthetic as well as natural samples like Palau, Va alloy, Victor bronze, fuel ash, residual oils and biological samples, to mention a few examples. In the absence of real samples, the applicability of the method was tested on some synthetic samples with satisfactory results as shown in Table 2.

Table 2 Analysis of synthetic samples

Sr.No.	Sample Composition		
	Matrix*	V added μg	V found μg
1.	Ni(3) Co(4)	200	201
2.	Zn(4) Cu(2) Mn(3)	150	150.149
3.	Ni(4) Fe(0.2) Zn(3)	400	397
4.	Pb(1.5) Cd(3) Hg(4)	300	300
5.	Al(2) Cu(3)	500	496
6.	W(1.5) Co(2) Zn(3)	400	398, 401

*mg amounts of elements shown within brackets

Table 3. Comparison of the proposed method with some of the existing methods of vanadium determination.

Method	λmax nm	Beer's Law range, μg V/ml	Interference	Ref. No.
V(V)-1-phenylthiosemicarbazide	310	0-11.0	Cr(III),Mn(VII),Pt(IV),Fe(II,III), Ag(I),Hg(II)	[12]
V(IV,V)-Calichrome	634	0-4.0	Cr(II),Al(III),Ti(IV),Zr(IV),Fe(III), Ni(II),Cr(III)	[13]
V(V)-gossipol	600	0-6.0	Mo(VI),W(VI),Fe(III),Zr(IV),Cu(II), Ni(II)	[14]
V(V)-sulfonazo	620	0-2.0	Fe(III),Ti(IV),Zr(IV),PO_4^{3-}	[15]
V(IV)-maleonitrile dithionite	580	0.6-10.0	Ni(II),Cu(II),Co(II),Cd(II),Fe(III)	[16]
V(V)-3,5-dinitrocatechol-brillant green	630	0-0.3	Ti(IV),Mo(VI),W(VI),EDTA	[17]
V(V)-N-p-octyloxybenzoyl-N-phenylhydroxylamine	570	0-4.6	W(VI),Cr(VI)	[18]
V(III)-anthranilic acid-pyridine	390	1-20.0	Mo(VI),U(VI)	

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