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SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (V) USING N-HYDROXY-N-m-TOLYL-N'-PHENYLBENZAMIDINE

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ABSTRACT

A method has been devised for extractive separation and simultaneous spectrophotometric determination of vanadium (V) employing N-hydroxy-N-m-tolyl-N'-phenylbenzamidine (HTPB). The method is based on the formation of a water insoluble blue-violet vanadium (V) complex in 1.0 to 10.0 M acetic acid, which can be extracted with chloroform. The complex shows a broad absorption maxima at 560–580 nm, when measured against chloroform blank. The λ_{\max} (570 nm) of the complex and that of the reagent (313 nm) are well separated, hence the excess of the reagent does not interfere in the photometric determination. The method is rapid, sensitive and highly selective. The separation and determination of vanadium (V) can be carried out in the presence of a large number of foreign ions including Fe(III), Mo(VI), Cr(III), Mn(II) and Ni(II). The method has been successfully applied to determine the vanadium content of BCS steels accurately.

INTRODUCTION

N-BENZOYL-N-phenylhydroxylamine (BPHA) and its analogues¹⁻⁴ have been recommended for determination of vanadium (V) but lack selectivity. Some investigators^{5,6} have pointed out that in this method the extraction is not quantitative because of partial reduction of vanadium in concentrated hydrochloric acid. In the present communication, N-hydroxy-N-m-tolyl-N'-phenylbenzamidine has been found to be a sensitive and highly selective reagent for the extractive separation and photometric determination of trace quantities of vanadium. The drawbacks mentioned above have been successfully overcome by this method. No partial reduction takes place, hence extraction is quantitative. The method has been applied to determine the vanadium content of BCS alloys.

EXPERIMENTAL

Standard vanadium (V) solution was prepared by dissolving A.R. ammonium metavanadate in double distilled water and standardized titrimetrically⁷. An ECIL spectrophotometer (UV/VIS) model GS-865 was used.

N-Hydroxy-N-m-tolyl-N'-phenylbenzamidine was prepared by the method of Deb and Mishra⁸. The resulting compound was crystallized from benzene. M.P. 138°; yield 52%; Elemental analysis: (Found: C, 79.60%; H, 6.10%; N, 9.35%; Calculated for C₂₀H₁₈N₂O; C, 79.47%; H, 5.95%, N, 9.27%). A, 0.1% solution of the reagent in chloroform was used for extraction purposes.

Recommended procedure

An aliquot of the solution containing 100 μ g of vanadium was taken in 60 ml separatory funnel and to it, 10 ml of glacial acetic acid and sufficient distilled water was added to adjust the volume of aqueous phase to 25 ml, 6 ml of 0.1% solution of the HTPB reagent in chloroform was then introduced. The contents were shaken vigorously for 1 min and the chloroform layer was separated and dried with 2 g of anhydrous sodium sulphate. The aqueous layer was washed twice with 4 ml of chloroform and the combined chloroform extract dried over anhydrous sodium sulphate, and made up the volume to 25 cc and measure the absorbance at 570 nm against chloroform blank.

RESULTS AND DISCUSSION

The V(V)-HTPB complex shows λ_{\max} at 570 nm with ϵ , $4140 \pm 50 \text{ l mole}^{-1} \text{ cm}^{-1}$. The reagent has negligible absorbance in the region 450–700 nm.

Several organic solvents including chloroform, carbon tetrachloride, benzene, toluene and chlorobenzene were found to quantitatively extract the blue-violet vanadium complex from the aqueous phase.

The acidity was maintained with glacial acetic acid and optimum acidity range was found to be 1–10 M acetic acid. A ten-fold molar excess of the reagent was adequate for complete extraction of vanadium (V). Addition of excess reagent had no adverse effect. Order of addition of reagent was not critical. A time of 1 min was sufficient for complete extraction of vanadium (V) at 20–35°.

Beer's law, optimum concentration range, molar absorptivity and precision

The system obeyed Beer's law upto 0.8 to 12.0 ppm. The optimum concentration range on the basis of Ringbom Plot⁹ was found to be 2.0 to 12.0 ppm. The effective molar absorptivity was $4140 \pm 50 \text{ l. mole}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity $0.012 \text{ g metal per cm}^2$. (BPHA method³, ϵ , $4650 \text{ l. mole}^{-1} \text{ cm}^{-1}$ at 510 nm). The mean absorbance value of 10 samples each containing 4 ppm of vanadium (V) was found to be 0.325 at 570 nm. The standard and relative standard deviations were ± 0.002 unit and $\pm 0.61\%$ respectively.

Influence of diverse ions

Chloride, bromide, nitrate, sulphate, ammonium, phthalate, borate, triethanolamine, lanthenoid elements, alkaline and alkali earth elements did not interfere up to 1500 ppm. The tolerance limit of other ions (in ppm) are shown in parenthesis: Fe^{3+} (800); Cu^{2+} (450); Ni^{2+} , Co^{2+} (400); Zn^{2+} , Cd^{2+} (800); Pb^{2+} (1000); Ag^+ (800); Sb^{3+} (400); Zr^{4+} (40); Ce^{4+} (300); Ti^{4+} (25); Mo^{6+} (400); Al^{3+} , Cr^{3+} (400); Ti^{3+} (400).

Composition

In V(V)-HTPB complex, the ratio of vanadium to reagent was determined by molar ratio¹⁰ and Job's method of continuous variation¹¹. The results showed

the formation of 1:2 (metal : reagent) complex in chloroform.

Determination of vanadium in BCS steels

A weighed quantity of sample containing 3 mg of vanadium was dissolved in dilute nitric acid (30%). The hydrated tungstic oxide was filtered and the oxides of nitrogen were boiled off and the vanadium content of the samples were determined by the recommended procedure. The results of samples are shown in table 1.

TABLE 1
Vanadium in BCS steels*

Name of steel	Vanadium found ^a %	Certified value %
64a, alloy steel	1.56	1.57
252, low alloy steel	0.45	0.46
241/1, high speed steel	1.55	1.57

* British Chemical Standard.

^a Average of five determinations.

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