



Spectrophotometric Determination of Vanadium(V) after Separation by Adsorption of its N-*p*-Bromophenylthiobenzohydroxamic Acid Complex on Microcrystalline Naphthalene

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The method of adsorption of N-*p*-bromophenylthiobenzohydroxamic acid vanadium(V) complex on microcrystalline naphthalene followed by a solid-liquid separation is described for the trace analysis of vanadium. This complex is stable in naphthalene dimethyl formamide solution. The absorbance has showed a linear relationship to the concentration of vanadium in the range 7-150 µg per 10 mL of dimethyl formamide. The molar absorptivity and sensitivity have been found to be $2.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.01346 \text{ µg cm}^{-2}$, respectively for the absorbance of 0.001 with a standard deviation of 0.17 %.

Key Words: Photometric determination, Adsorption, Vanadium, Formamide, Naphthalene.

INTRODUCTION

Vanadium is used mainly in the steel alloys and petrochemicals industries. Vanadium species are most stable and more toxic. Vanadium acts as a growth-promoting factor and participates in fixation and accumulation of nitrogen in plants, whereas high concentration of vanadium reduces the productivity of the plants¹⁻⁴. Therefore, the determination of vanadium in environmental and biological samples is highly desirable.

For the quantitative determination of vanadium in trace amount, there are several frequently adopted methods such as atomic absorption spectrophotometry (AAS), X-ray fluorescence spectroscopy, spectrofluorimetry, spectrophotometry, etc. Among these, spectrophotometric methods are preferred as they are more economical, easy to handle, with a comparable sensitivity and accuracy, good precision⁵⁻¹⁰. It is one of the most commonly used techniques for routine analysis of metals.

Many spectrophotometric methods for the determination of trace amount of vanadium in plant material, synthetic mixtures, water, soil, pharmaceutical, biological and steel samples are based on the methods such as the complex formation, redox reaction, ion-association, catalytic-kinetic reactions and solvent extraction¹¹⁻¹⁵. Some of the applied organic reagents for spectrophotometric determination of vanadium includes thionine¹¹, 1,5-diphenylcarbazine¹⁶, 5,7-dichloroxine-rhodamine¹⁷, N-(1-naphthalene-1-yl)ethane-1,2-diamine-dihydrochloride³, N-benzoyl-N-phenylhydroxylamine¹⁸,

variamine blue¹⁹ and 6-chloro-3-hydroxy-7-methyl-2-(2-thienyl)-4*H*-chromen-4-one²⁰.

Several thiosemicarbazones, diketones and oximes have been explored as analytical reagents for the spectrophotometric determination of metals^{7,17,21-24}. Hydroxamic acid and their thio analogues are found to react with many cations to give colour reaction of analytical importance. The usual liquid-liquid extraction method cannot be used directly for the extraction of metal ions which form complexing reagents at high temperature. This difficulty can be avoided with the method of solid-liquid separation after liquid-liquid extraction developed by many researchers using naphthalene as an extractant^{9,12}. This method has many advantages over the usual liquid-liquid extractant. This method is very convenient and less time consuming.

In the present investigation, N-*p*-bromophenylthiobenzohydroxamic acid vanadium (V) complex has been explored as a new reagent for the separation, extraction and sensitive spectrophotometric determination of vanadium from water samples. The method is based on adsorption of N-*p*-bromophenylthiobenzohydroxamic acid vanadium(V) complex on microcrystalline naphthalene followed by a solid-liquid separation described for the trace analysis of vanadium.

EXPERIMENTAL

Stock solution of vanadium (1000 ppm) was prepared by dissolving requisite amount of ammonium meta vanadate in double distilled water. A 15 ppm vanadium solution was

prepared by diluting 15 mL of stock solution to 1000 mL with double distilled water⁴. 0.2% solution of N-*p*-bromophenylthiobenzohydroxamic acid solution (in ethanol) and 20 % naphthalene solution in acetone has been used for the present investigation. Acetate buffer (pH, 3-6) has applied to adjust the pH of the solution. Chemicals of analytical reagent grade has used for this study. A double beam UV-VIS spectrophotometer (Systronic-2201) was used for all absorbance measurements. An expanded scale pH meter (EC model) equipped with glass and calomel electrode was used for pH measurements.

Procedure: An aliquot of solution containing 120 µg of vanadium was transferred into a 100 mL tightly stopped Erlenmeyer flask. The pH of the solution was adjusted to be near 4.5 adding 3.5 mL buffer solution and then 3.0 mL of 0.2 % N-*p*-bromophenylthiobenzohydroxamic acid solution was added. This solution was mixed well and digested for 1 h. Now 2 mL of 20 % naphthalene solution has mixed and shaken vigorously for 15 min. The complex absorbed on microcrystalline naphthalene has been separated out from aqueous solution through a filter paper (Whatmann No. 42) and then washed with water and dried. Finally, the complex absorbed on microcrystalline naphthalene was dissolved in 10 mL dimethylformamide. The absorbance of the solution has been measured against reagent blank spectrophotometrically.

RESULTS AND DISCUSSION

Absorption spectra: Absorption spectrum of vanadium(V) complex has been taken in the wavelength region of 360 to 625 nm. The complex has a peak at 405 nm where reagent blank has negligible absorbance. Therefore, wavelength at 405 nm has been selected as standard value for all absorbance measurements.

Effect of pH: The effect of pH variation has studied for absorbance of vanadium(V) complex at 405 nm. The results showed that pH 4.5 is suitable for all absorbance measurements.

Effect of N-*p*-bromophenylthiobenzohydroxamic acid concentration: The effect of reagent concentration on absorbance of vanadium(V) complex has been studied by adding various volume of reagent solution to sample solution containing 120 µg of vanadium. The reagent solution 2.5 to 5.0 mL is sufficient for complete extraction of trace amount of vanadium(V).

Effect of naphthalene concentration: The effect of naphthalene concentration on the absorbance of vanadium(V) complex has been studied by adding different volume of 20 % naphthalene solution. The absorbance has increased upto 2 mL and remained constant in the range of 2.0 to 4.5 mL of naphthalene solution. Therefore, 2 mL of 20 % naphthalene solution has taken as most suitable amount for measurement.

Effect of digestion time: The digestion for 58 to 80 min has no effect on the absorbance of complex. Thus, 60 min for digestion of solution has selected.

Effect of diverse ions: The effect of presence of various metal ions with measurable amount has been investigated and results are shown in Table-1.

Calibration curve for vanadium(V): The vanadium complex in naphthalene dimethylformamide solution has

TABLE-1
EFFECT OF DIVERSE METAL IONS

Diverse metal ions	Amount added (µg)	Found (µg)
Co(II)	40	121.0
	120	120.9
Sn(II)	50	120.8
	100	120.7
Zn(II)	70	121.1
	150	120.8
Mn(II)	30	119.2
	90	119.5
Cu(II)	30	120.1
	70	120.3
Mg(II)	50	121.1
	110	120.8
Ni(II)	60	119.3
	100	119.4
Bi(III)	50	119.6
	120	119.5
Fe(III)	60	119.4
	150	119.8
Pd (IV)	40	120.4
	90	120.6
Pt (IV)	30	121.0
	80	121.4

Vanadium = 120 µg pH = 4.5; Naphthalene = 0.4 g

obeyed Beer's law in the range 7-150 µg per 10 mL. The molar absorptivity and sensitivity has determined at 2.6×10^4 L mol⁻¹ cm⁻¹ and 0.01346 µg cm⁻² for absorbance of 0.001, respectively.

Conclusion

The adsorption of N-*p*-bromophenylthiobenzohydroxamic acid vanadium(V) complex on microcrystalline naphthalene followed by a solid-liquid separation method has been successfully applied for the determination of vanadium(V) in water samples. The N-*p*-bromophenylthio-benzohydroxamic acid vanadium(V) complex is stable in naphthalene dimethyl formamide solution. The absorbance has showed a linear relationship to the concentration of vanadium in the range 7-150 µg per 10mL of dimethyl formamide. The molar absorptivity and sensitivity have been found to be 2.46×10^4 L mol⁻¹ cm⁻¹ and 0.01346 µg cm⁻¹, respectively, for the absorbance of 0.001 with a standard deviation of 0.17 %. The method has good sensitivity and accuracy and offers several interesting features such as simplicity, rapidity and low cost.

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